Jim Zoval, Ph.D.

General, Organic, and Biochemistry

Acknowledgements and Author Information

Special thanks to my editors:

Dr. Curt McLendon for his expertise in chemistry, attention to scientific and grammatical detail, and our many conversations about science and education.

Ms. Lee McLendon for her expertise in education, science, and language skills.

Ms. Susan Cook for her eye for format quality and her written language skills.

I would also like to thank Dr. Bill Alston, Dr. Scott Fier, Mr. Monroe Lee, Dr. Marc Madou, Prof. Larry Perez, Dr. Tony Huntley, Dr. Karah Street, and Prof. Steve Teh for their input for this book.

Thanks to some of my chemistry students who provided much input: Ms. Jessica Ellis, Ms. Christine Maalouf, Capt. Anthony Manzo, Ms. Anna Migliorini, Dr. Hayate Ouatah, Ms. Maria Redman, and Ms. Jenna Sherman.

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On the Cover:

Green sea turtle (*Chelonia mydas*, on the endangered species list). Location of photo: Coral reef at the south end of Maluaka Beach in Maui. Area is known locally as Turtle Town. Photo courtesy of Ms. Gretchen Stark Schmidt, RN

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Chapter 1: Stuff and Energy

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Everything in the physical universe can be placed into one of two categories: stuff (matter) or energy. A good definition of chemistry is the study of matter and how it interacts with other matter or energy. The way this is studied often involves measurements. In chapter one, I will give a brief introduction to the "*scientific method,*" and to matter and energy. Then, some of the methods and math tools used to do science will be discussed and practiced.

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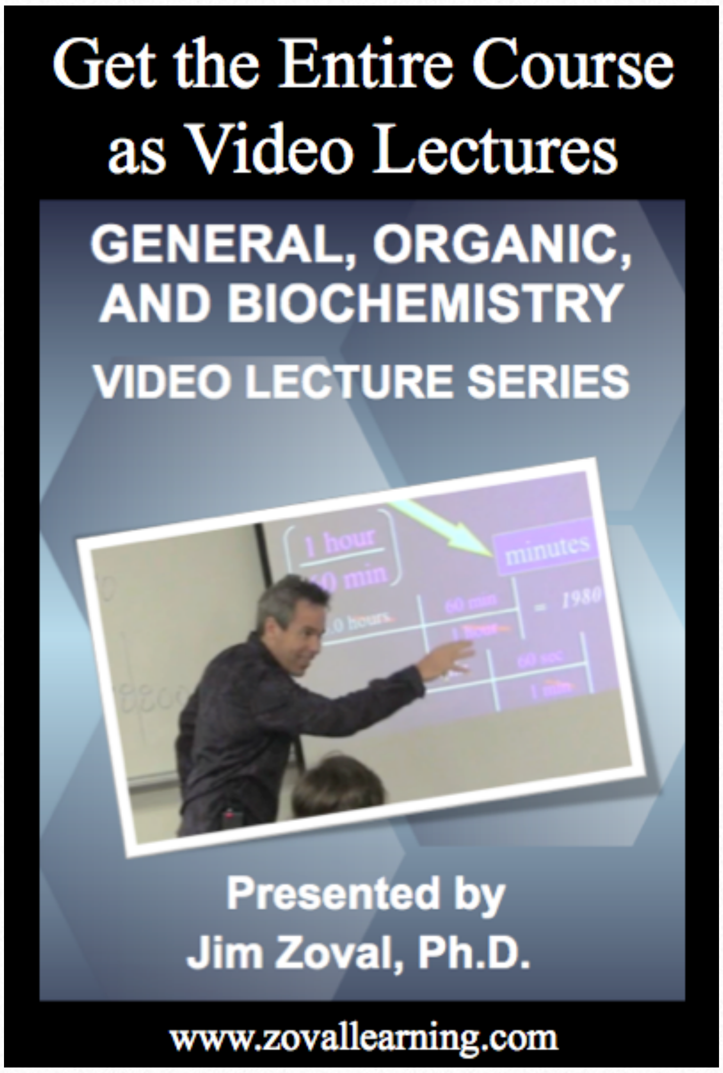


1.1 Chapter 1 Educational Goals

1. Explain, compare, and contrast the terms **scientific method**, **hypothesis**, and **experiment**.
2. Compare and contrast scientific **theory** and **scientific law**.
3. Define the terms **matter** and **energy**. Describe the three phases (states) of matter and the two forms of energy.
4. Describe and give examples of **physical properties** and **physical change.**
5. Perform **unit conversion** calculations.
6. Express and interpret numbers in **scientific (exponential) notation**.
7. Explain the difference between the terms **accurate** and **precise**.
8. Know and use the rules for **significant figures**.
    - Given a value, determine the number of significant figures.
    - Use the correct number of significant figures to report the results of calculations involving measured quantities.

1.2 Scientific Method

Why do science? When this question is contemplated and discussed, two faces of science are often revealed.

1) One face of science was eloquently summarized by Dr. Richard Dawkins when he said: "**Science is the poetry of reality**."

This statement seemed absurd and abstract when I first heard it - so I thought I should google "poetry" - I ask forgiveness from my English professors for not remembering the definition of poetry!

Poetry, though there is not a clear definition even among experts in the field, uses *creativity in literature* to **express states of mind**.

- Examples of the creative tools used in poetry are verse, form, rhyme, symbol, metaphor.

Science uses *creativity in math and reason* to **express state of reality.**

- Examples of creative tools used in science are engineering, mathematics, and scientific method.

This face of science by itself, though intellectually interesting, can be purely aesthetic, possibly tending toward purely academic.

2) The second face of science is that ***science can improve peoples lives***.

For example, consider how the childhood blood cancer (Leukemia) survival rate has improved since 1964. In 1964, the survival rate was 4%; it is close to 95% now. This is because of scientist's and engineer's hard work and implementation of scientific method and technology.

When do you believe something? Psychologists call what we believe our "**world-view.**" Individuals observe their world and try to come up with explanations, to themselves, for what they observe. These explanations to one's self are one's ***world-view***. For example, when people looked at the sun rising and setting, a widely accepted explanation in the past was that *the sun orbits the earth*. This explanation was quite believable and reliable. However, as more observations were made, they could no longer be explained by the model of the sun orbiting the earth. A new model of *the earth rotating on its axis* was used to explain the observations. **This is how science works.** The idea is that ***science can produce generalizations with predictive value***. Science makes no claims of "truth"; it is just a method used to gather and interpret observations (data). The interpretations have **predictive value**. For example, the model of the Earth rotating around the sun (and the moon rotating around the earth) predicts the existence and behavior of tides.

Figure 1.1
Model of the Sun, Earth, Moon, and an Inner Planet

Mechanical model of the Earth, the sun, the moon, and an inner planet; library of Van Vleck Observatory, Wesleyan University, Middletown, Connecticut, USA.

Source: Wikimedia Commons, Author: Joel Mabel, CC-BY-SA, http://creativecommons.org/licenses/by-sa/3.0/legalcode

There are two ways to do science: **scientific theory** and **scientific law**. It is important to note that both methods are used to acquire predictive power and both begin with observation(s).

Scientific Theory

Other words for **theory** are *model* or *explanation*. Scientific theory uses models/explanations to make sense of observables. Often, a first guess at a model is proposed. The first guess is called a ***hypothesis***. The hypothesis can usually be tested by experiment or additional observations. If the hypothesis continues to be validated by experiment or new observations, it becomes ***theory***. If the hypothesis is not consistent with experimental results or new observations, it is rejected and a new model is required. Note that there is sometimes more than one theory that is consistent with (explains or models) reality/observation. In the healthcare field, another word for theory or model is ***diagnosis***.

Another way to "do science" is to use ***scientific law***. A scientific law is simply ***a statement about something that generally occurs***. Note that in using scientific law, no explanation (model) is given. For example, let's consider Isaac Newton's *laws of motion*. By making careful observations/measurements of how objects moved when forces, such as gravity, were applied to them, Newton determined mathematical equations that could **predict** the trajectory (path) and speed of the objects. Newton made no attempt to explain "why" his equations worked. This can be contrasted with scientific theory that involves proposing a model or explanation for what is observed.

Figure 1.2

William Blake's Newton (1795)
color print with pen & ink and watercolor.

Isaac Newton (1642-1727) is best known for his laws of motion, co-founder of calculus, and invention of the reflecting telescope. Source: Wikimedia Commons, PD

Another example of a scientific law will be seen in chapter 5 when we study the gas laws. Charles's Law describes the relationship between the temperature and the pressure of a gas in a container. Jaques Charles (1746-1843) observed that the pressure is proportional to the temperature. This statement is a scientific law, a statement about something that generally occurs. Note that Charles made no attempt to explain why the pressure of a gas is proportional to the temperature.

Many times, a scientific law is found, and then later an explanation is developed and tested. If the explanation survives the tests, the *law* becomes a *theory*. For example, a scientific theory called Kinetic Molecular Theory can explain what was originally known as Charles's Law.

1.3 An Introduction to Matter and Energy

Everything in the physical universe can be placed into one of two categories: stuff (matter) or energy. Earlier, I defined chemistry as the study of matter (stuff) and how matter interacts with other matter or energy. In this section, matter and energy will be defined and discussed.

Matter

Matter is anything that has *mass* and *occupies space*. Matter can be described and categorized in terms of its ***physical properties***; those characteristics that can be determined without changing the chemical composition of matter (i.e. without changing it into a different substance). Let's consider some physical properties of table sugar (sucrose). Table sugar is white, tastes sweet, and is brittle (can be crushed into powder). Crushing sugar does not change it into another substance, but simply breaks larger sugar crystals into many smaller crystals. Tasting sugar does not change it into another substance, however after tasting, sugar is converted into other substances in the digestion process. You will study the chemistry of digestion and metabolism in chapter 15.

Figure 1.3
Magnification of Table Sugar Crystals

A photograph of table sugar. The sugar was placed on a ruler, and the black lines are 1mm apart.
Source: Wikimedia Commons, Author: Lauri Andler, CC-BY-SA, http://creativecommons.org/licenses/by-sa/3.0/legalcode

Matter can also be described in terms of its ***chemical properties***. Chemical properties of substances describe *how substances are converted to new substances* in processes called chemical reactions. You will learn about chemical reactions in chapter 6.

Matter is typically found in one of three different physical ***phases*** (sometimes called ***states***). The three phases of matter are: solid, liquid, and gas, are illustrated in Figure 1.4. Solids have fixed shapes and volumes. Liquids have variable shapes and fixed volumes. Gases have variable shapes and volumes. A fourth, higher energy phase of matter that does not normally occur at temperatures on earth is called the plasma phase.

Changing the phase of matter, converting matter between solid, liquid, and gas is considered a *physical change* because the identity of the substance **does not** change. You will study phase changes in more detail in chapter 5. Examples of phase changes are: freezing water to make ice, boiling water to make steam, and melting an iron rod. Note that in all of these examples, the identity of the substance does not change; is remains H_2O.

Figure 1.4 **Three Phases of Matter**

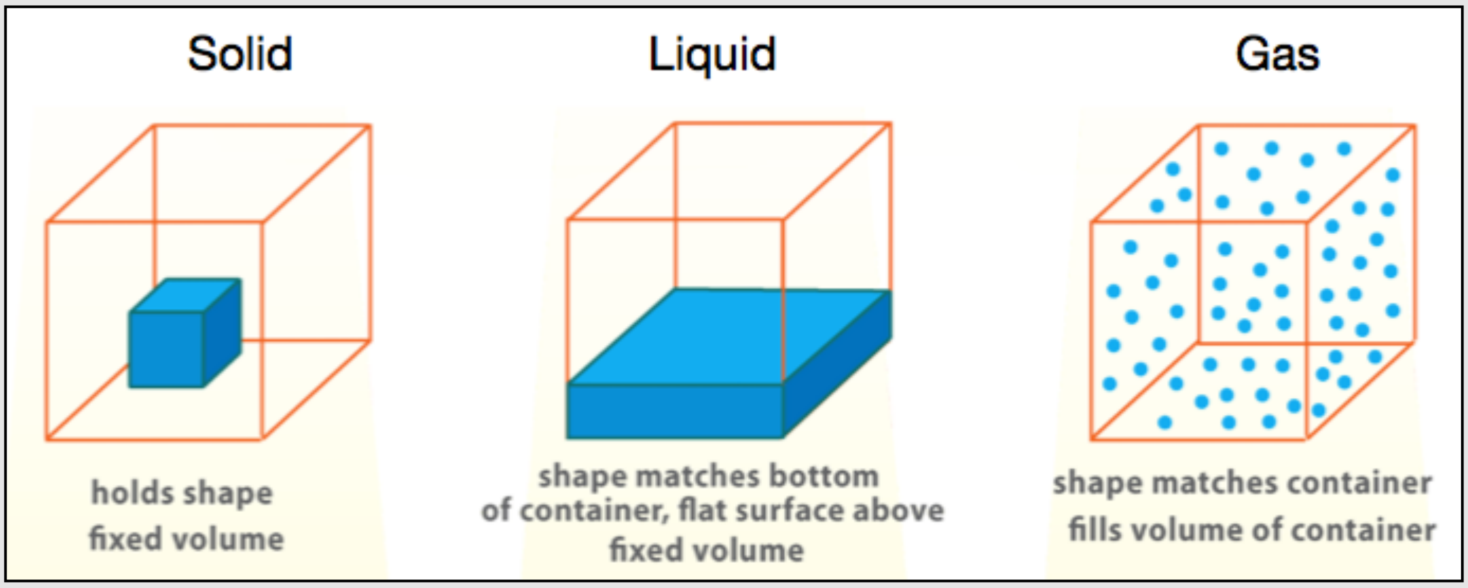


Illustration of the solid, liquid, and gas phases.
Source: Wikimedia Commons, Source: NASA, PD

Energy

Energy is commonly defined as ***the ability to do work***. Any time that matter is changed (physical or chemical change), work has been done. Energy can be found in two forms, **potential energy** and **kinetic energy**. *Potential energy* is stored energy; it has the *potential* to do work. An example of potential energy is water stored in a dam (Figure 1.5). If a valve is opened, the water will flow downhill and turn a paddle connected to a generator to create electricity. In this example, when the valve was opened and the water began to move, potential energy was converted to *kinetic energy*. Kinetic energy is *the energy of motion*. Any time matter is moving, it has kinetic energy.

An important law that is ***central to understanding nature*** is: **matter will exist in the lowest possible energy state.** Another way to say this is "if matter can lose energy, it will ***always*** do so."

Figure 1.5 **Shasta Dam, California, USA**

Water stored in a dam is an example of potential energy. Water moving downward within a dam to turn a turbine and generate electricity is an example of kinetic energy.
Source: Wikimedia Commons, Author: Apaliwal, CC-BY, http://creativecommons.org/licenses/by/2.0/legalcode

Review 1.1: Kinetic Energy vs. Potential Energy

Which are mainly examples of potential energy?

a) A mountain climber sits at the top of a peak.
b) A mountain climber rappels down a cliff.
c) A hamburger sits on a plate.
d) A nurse inflates a blood pressure cuff.

For ***i-books*** versions: **Click here to check answer**

For **hard copies** or **a pdf versions**, use the key in Appendix 1.

1.4 Measurements

Doing science involves collecting and interpreting ***data***. Data consists of *observations* and *measurements*. In this section, you will learn about units of measurement, how to express very large and very small values using scientific notation, and accuracy vs. precision in measurements.

Units of Measurement

One type of observation is a ***measurement***. All observations are not necessarily measurements; noting the aroma of a substance is not a measurement. Measurements consist of two parts, a ***number*** and a **unit**. For example, if you think about your age, the unit most often used is *years*. If you consider your height, the unit most often used is feet (USA, UK) or centimeters (most other countries). There are historical and practical reasons why we see many different units used for the same property. Consider some of the many units used for distance: inch, foot, yard, mile, millimeter, centimeter, meter, kilometer, furlong, league, and fathom. An international effort made by governments and the scientific community to standardize the use of certain units has implemented "The International System of Units" (abbreviated SI from the French "Le Système International D'unités"). Some SI units and their symbols (abbreviations) are shown in Table 1.1.

Making Measurements.
Source: Wikimedia Commons PD

Table 1.1
SI Units and Their Symbols

Quantity	SI Unit Name	Symbol
Length	meter	m
Mass	kilogram	kg
Time	second	s
Temperature	Kelvin	K

When writing measured values, one should always include the unit of measure after the number. Usually the abbreviation/symbol for the unit is used. Other, non-SI units, are frequently used in the sciences. Table 1.2 lists some commonly used unit names and their symbols.

Table 1.2
Commonly Used Units and Their Symbols

Quantity	Unit Name	Symbol
Length	foot inch	ft in
Mass	gram pound	g lb
Volume	Liter	L
Temperature	Fahrenheit Celsius (or Centigrade)	^{0}F ^{0}C

Scientific Notation

When making measurements, particularly in science and in the health sciences, there are many times when we must use very large or very small numbers. One way to simplify writing these very large and small numbers is to use ***scientific notation*** (sometimes called *exponential notation*). For example, a typical red blood cell, as shown in Figure 1.6, has a diameter of about 0.0000075 m. The use of scientific notation allows us to express this number without writing so many zeros. Using scientific notation, this diameter is written as 7.5×10^{-6} m.

- Values expressed in scientific notation are written as a number (greater than or equal to 1 and less than 10) *multiplied* by a **power of 10.**

$$7.5 \times 10^{-6}$$

- The superscripted number to the right of the ten is called an ***exponent***.

An exponent with a ***positive value*** tells you how many times to **multiply** a number by 10.

$$3.5 \times 10^4 = 3.5 \times 10 \times 10 \times 10 \times 10 = 35000$$

An exponent with a ***negative value*** tells you how many times to **divide** a number by 10.

$$3.5 \times 10^{-4} = \frac{3.5}{10 \times 10 \times 10 \times 10} = 0.00035$$

Figure 1.6
Red Blood Cells

An electron microscope image of red blood cells.
Source: Wikimedia Commons, PD. The photos are attributed to Drs. Noguchi, Rodgers, and Schechter of NIDDK.

Converting from Regular Notation to Scientific Notation

It is important to be able to convert from regular (standard) numerical notation to scientific notation as follows.

Step 1: Move the decimal point to the right of the first (left-most) non-zero number.

- Multiply the resulting number by 10 raised to an *exponent*.
- The *exponent* will be equal to the number of decimal places moved.

Step 2: When you move the decimal point to the **left**, the exponent is **positive**.

Step 3: When you move the decimal point to the **right**, the exponent is **negative**.

Let's do an example following the three steps above:

Example: Convert 8600000000 into scientific notation.

Step 1: Move the decimal point to the right of the first (left-most) non-zero number.

- Multiply the resulting number by 10 raised to an exponent.

$$8600000000. \longrightarrow 8.6 \times 10^{?}$$

- The *exponent* will be equal to the number of decimal places moved.
  We moved the decimal point **9** places ***to the left***.

Step 2: When you move the decimal point to the **left**, the exponent is **positive**.

$$8.6 \times 10^{9}$$

Step 3: When you move the decimal point to the **right**, the exponent is **negative**.
This is not the case in our example here, we moved the decimal point to the left.

Example: Convert 0.000000075 into scientific notation.

Step 1: Move the decimal point to the right of the first (left-most) non-zero number.

$$0.000000075 \longrightarrow 7.5$$

- Multiply the resulting number by 10 raised to an exponent

$$7.5 \times 10^{?}$$

- The *exponent* will be equal to the number of decimal places moved.
  We moved the decimal point **8** places (to the right).

Step 2: When you move the decimal point to the **left**, the exponent is **positive**.
This is not the case, we moved the decimal point to the right.

Step 3: When you move the decimal point to the **right**, the exponent is **negative**.

$$7.5 \times 10^{-8}$$

Note that when you begin with a number less than 1, you will end up with a negative exponent. When you begin with a number that is 1 or greater, you will end up with a positive exponent.

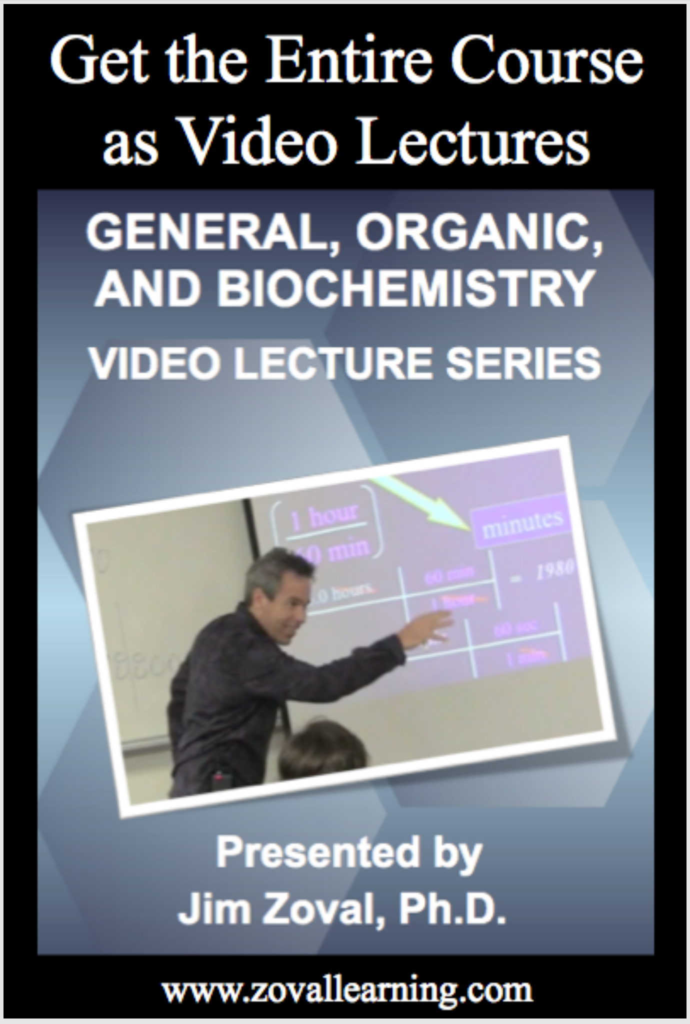
Review 1.2: Scientific Notation

Convert the each of the following numbers into scientific notation.

a) 5839
b) 740000
c) 0.573
d) 0.00000006

i-books users, **Click here to check answer**

For **print or pdf versions**, see the answer key in Appendix 1.



Converting from Scientific Notation to Regular Notation

You just learned how to convert from regular numerical notation to scientific notation. Now let's do the reverse; convert from scientific notation to regular notation.

Step 1: Note the value of the ***exponent***.

Step 2: The value of the exponent will tell you which direction <u>and</u> how many places to move the decimal point.

- If the value of the exponent is **positive**, remove the power of ten and move the decimal point that value of places to the ***right***.
- If the value of the exponent is **negative**, remove the power of ten and move the decimal point that value of places to the ***left***.

Example: Convert 3.7 x 10^5 into regular notation.

Step 1: Note the value of the ***exponent***: The exponent is **positive 5**.

Step 2: The value of the exponent will tell you which direction <u>and</u> how many places to move the decimal point.

- If the value of the exponent is **positive**, remove the power of ten and move the decimal point that value of places to the ***right***.

  We will move the decimal point 5 places to the ***<u>right</u>***.

When the decimal point is not shown explicitly in a number, as in our answer, it is assumed to be ***after the right-most digit***.

- If the value of the exponent is **negative**, remove the power of ten and move the decimal point that value of places to the ***left***.

  This was not the case in our example, the exponent was positive.

Let's do another example: Convert 1.604 x 10^{-3} into regular notation.

Step 1: Note the value of the ***exponent***: The exponent is ***negative* 3**

Step 2: The value of the exponent will tell you which direction <u>and</u> how many places to move the decimal point.

- If the value of the exponent is **positive**, remove the power of ten and move the decimal point that value of places to the ***right***. **This was not the case in our example, the exponent was negative.**
- If the value of the exponent is **negative**, remove the power of ten and move the decimal point that value of places to the ***left***.

  We will move the decimal point 3 places to the ***<u>left</u>***.

Note: .001604 is often written as **0.001604**. This extra zero to the left of the decimal point is commonly used; it is especially important to use it when *there is a non-zero integer immediately to the right of the decimal point*. This is done so the decimal point is *more easily noticed*, for example: **0.6200** instead of **.6200**. The added zero is called the **"safety zero."**

Review 1.3: Scientific Notation

Convert the following numbers into regular numerical notation.

a) 5.2789×10^2
b) 1.78538×10^{-3}
c) 2.34×10^6
d) 9.583×10^{-5}

If using an i-books version of the text, **Click here to check answer**

If using a pdf or hard copy, check your answer using the key in Appendix 1.

Accuracy, Precision, and Significant Figures in Measurements

If I were to ask you your age, you would probably report a whole number. For example, you may say 37. If you wish to practice what we learned earlier in this section, you would also report a unit and say "37 years," although we do not do so in practice because folks would correctly assume you meant years....and not days, months, or seconds! If you did report your age as 37 (or 37 years), would that be exact? Was it your birthday on this day? Was it not only your birthday, but the exact same hour, second....moment that you were born 37 years ago? Almost certainly not. I hope you see my point; very few measurements are exact numbers. The nature of our measurement determines how close we come to the actual value (sometime called the "true" value).
There are three important factors to consider when making measurements:

1. Accuracy
2. Precision
3. Significant Figures

There is a difference between the terms accuracy and precision. **Accuracy** depends on how *close* a measured value is to the *actual value*. **Precision** is related to the *reproducibility* of measurements. The use of significant figures when reporting measured and calculated values allows the reader to understand how close to the *actual value* we can rely on a reported value to be. For example, if you read that a fossil is 120,000 years old, does that mean it is 120,000 years old and not 120,001 or 119,999 years old? Or is the value known to be somewhere between 119,000 and 121,000 years old? The correct use of significant figures enables the reader to know the answer to these questions. These types of questions can be very important within the health science field in diagnostic lab testing for substances that are indicators of disease. How accurate and precise are the reported values? Very often in medical labs and scientific journals, values are reported with a ***confidence interval***. When you receive test results, you may see that your "total cholesterol" level is (193 ± 4 mg/dL). The ± 4 mg/dL is called the *confidence interval*. Reporting a confidence interval is an advanced method used to indicate how well a value is known. In this book we will use a simpler method. *We will use **significant figures** to express how well we know a value.*

Figure 1.7 A Glucometer

A digital glucometer. Accu-Chek Performa, by Roche.
Source: Wikimedia Commons, Author: Penarc, CC-BY-SA, http://creativecommons.org/licenses/by-sa/3.0/legalcode

Accuracy

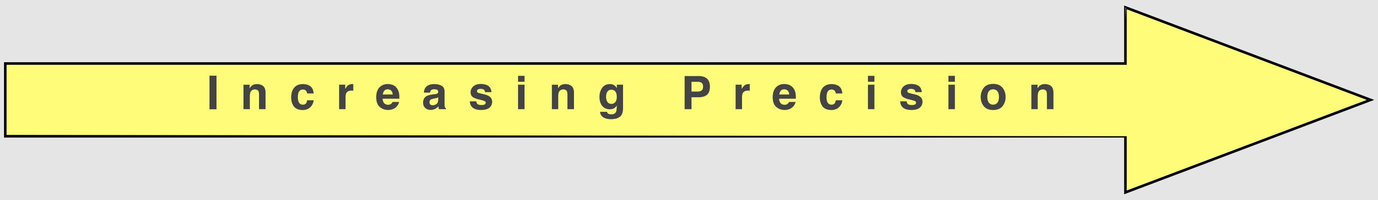
The *accuracy* of a measurement is related to how close a measured value is to its **actual value**. Suppose that a standardized glucose solution is prepared to have a known concentration of 125 mg/dL. Two home glucose measuring devices (glucometer, Figure 1.7) from different manufacturers are compared for accuracy. When testing the standardized glucose solution, the first glucometer gives a reading of 121 mg/dL and the second glucometer gives a reading of 136 mg/dL. Which glucometer, the first or second, is more *accurate*? I hope you thought the first glucometer was more accurate because it measured a concentration closer to the *known* value of 125 mg/dL.

Precision

The precision of a measurement is related to how "*repeatable*" measurements are. Suppose that two home glucose measuring devices from different manufacturers are compared for ***precision***. Each glucometer will measure the blood glucose concentration of a fasting patient three times within a few minute period. The first glucometer gives readings of 83 mg/dL, 86 mg/dL, and 85 mg/dL. The second glucometer gives readings of 84.5 mg/dL, 84.4 mg/dL, and 84.7 mg/dL Which glucometer, first or second, is more *precise*? I hope you thought the second glucometer was more precise because the measured values ***were closer to each other*** (more repeatable). The precision of a measured value ultimately depends on the ***sensitivity*** of the measuring device. The ***precision of a measured value*** can be determined by the *right-most decimal place* reported. In the example of the glucometer precision, the first glucometer readings were precise to the "ones" place and the second glucometer readings were precise to ".1" (also called tenths) decimal place. The names and precision of the decimal places **for the number 869.257** are shown in Table 1.3.

Table 1.3 Decimal Place Names and Precision for the Number 869.257

Digit in Number	8	6	9	2	5	7
Decimal Place Name	Hundreds (100's)	Tens (10's)	Ones (1's)	Tenths (1/10th's)	Hundredths (1/100th's)	Thousandths (1/1000th's)



The quality of the equipment used to make a measurement is one factor in obtaining accurate and precise results. The ability of the human operator to correctly use the measuring device is another factor.

Significant Figures

One way to include information on the precision of a measured value (or a value that is calculated using measured values) is to report the value using the correct number of significant figures. A simple way to understand significant figures is to say that a digit is significant if we are sure of its value. Let's consider an example of an old tree, as seen in Figure 1.8. A botanist reports that a tree is 500 years old. If we actually know that this value is precise to plus or minus one month, that means that all the digits in the number are indeed known and the number has **three** significant figures (the 5, and both zeros). But, what if the reported age of the tree is only precise to *plus or minus ten years*. In this case, the only digit we truly know is the 5, the two zeros are just there to keep the 5 in the "hundreds" decimal place. In this case there is only **one** significant figure. In the next section, we will see how we can write the number "five hundred" using one significant figure or using three significant figures. Then in the following section, we will learn how to report the correct number of significant figures in quantities calculated from measured values.

Figure 1.8 An Old Tree

A Small-leaved Lime tree (tilia cordata) estimated to be between 500 and 800 years old.

Source: Wikimedia Commons, Author: Stefan Wernli, CC-BY-SA, http://creativecommons.org/licenses/by-sa/3.0/legalcode

Method for Counting Significant Figures

Measured and calculated values should be reported using either confidence intervals **or** significant figures. In this book, ***we will use the significant figure method***. We can look at a numerical value and determine the number of significant figures as follows:

- If the decimal point is **present**, starting from the ***left***, count all numbers (including zeros) beginning with the first non zero number.
- If the decimal point is **absent**, starting from the ***right***, count all numbers (including zeros) beginning with the first non zero number.
- When numbers are given in scientific notation, do not consider the power of 10, only the value before (x 10^n).

Let's do a couple of examples using the five hundred year-old tree we discussed in the previous section.

Example: If the botanist reported the age of the tree as **500 years**, how many significant figures are given?

Note that although the decimal point is implied to be after the right-most zero, it is absent (not shown explicitly), therefore we use the decimal point absent rule shown above; if the decimal point is **absent**, starting from the ***right***, count all numbers (including zeros) beginning with the first non zero number. We will start inspecting each digit from right (to left) as shown by the arrow. We will start counting when we get to the first non zero number.

500 ←

We do not count the first two zeros, but start counting at the **5**. Therefore, there is **one** significant figure present.

Example: If the botanist reported the age of the tree as **500. years** (note the decimal point present), how many significant figures are given?

Note that in this case, the decimal point is **present** (shown), therefore we use the decimal point present rule shown above; if the decimal point is **present**, starting from the ***left***, count all numbers (including zeros) beginning with the first non zero number. We will start inspecting each digit from left to right as shown by the arrow. We will start counting when we get to the first non zero number.

→ 500.

We begin with the **5**, then count all numbers ***including zeros***. In this case, the two zeros are also significant. Therefore there are **three** significant figures present.

Outside of the science fields, "**500**" and "**500.**" are generally thought of as equivalent, however, the use of significant figures tells us that when we write "**500.**" (with the decimal point present) we know that number one hundred times more precisely than when we write "**500**" (without the decimal point). We have precision to the "ones" decimal place in "**500.**" vs. precision to the "hundreds" place in "**500**".

Here are some other examples:

Example: How many significant figures are contained in 0.00045?

Note that in this case, the decimal point is **present** (shown), therefore we use the decimal point present rule shown above; if the decimal point is **present**, starting from the ***left***, count all numbers (including zeros) beginning with the first non zero number. We will start inspecting each digit from left to right as shown by the arrow. We will start counting when we get to the first non zero number.

→ 0.00045

We begin with the **4**, then count all numbers ***including zeros***. Therefore there are **two** significant figures present.

Example: How many significant figures are contained in 0.0002600?

If the decimal point is **present**, starting from the ***left***, count all numbers (including zeros) beginning with the first non zero number. We will start inspecting each digit from left to right as shown by the arrow. We will start counting when we get to the first non zero number.

→ 0.0002600

We begin with the **2**, then count all numbers ***including zeros***. Therefore there are **four** significant figures present.

Example: How many significant figures are contained in 7080?

If the decimal point is **absent**, starting from the ***right***, count all numbers (including zeros) beginning with the first non zero number. We will start inspecting each digit from right (to left) as shown by the arrow. We will start counting when we get to the first non zero number.

7080 ←

We do not count the first zero, but start counting at the **8,** and then count ***all*** *numbers* ***(including zeros)***. Therefore, there are **three** significant figures present.

When converting back and forth from standard numerical notation to scientific notation, the number of significant figures used **should not change**. For example, if we wish to write 0.000540 in scientific notation, we would write 5.40×10^{-4}. Note that we began with ***three*** significant figures in standard numerical notation, so we use ***three*** significant figures in scientific notation.

Review 1.4: Understanding Significant Figures

Specify the number of significant figures in each of the values listed below.

a) 23.5
b) 0.0073000
c) 6.70×10^3
d) 48.50
e) 6200
f) 6200.
g) 6200.0
h) 0.6200
i) 0.62
j) 930

i-books users: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

Review 1.5: Understanding Significant Figures

Write each measured value in ***scientific notation***, being sure to use *the correct number of significant figures*.

a) 5047 cal
b) 87629.0 L
c) 0.00008 g
d) 0.07460 lb

i-books users: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

Calculations Involving Significant Figures

In the previous section, you learned how to look at measured values and determine how many significant figures are present. This is important not only to determine how precisely we know a measured value, but it will also be needed in determining the precision (number of significant figures) to report in calculated values. Beginning now, and through the remainder of the book and problem sets, when doing calculations you should assume they are from measured values and report the correct number of significant figures in the answer. You can do so by using one of the following two rules:

- When doing **multiplication and/or division** with measured values, the answer should have the *same number of significant figures* as the measured value with the ***least*** number of significant figures.

- When doing ***addition and/or subtraction*** with measured values, the answer should have the ***same precision*** as the least precise measurement (value) used in the calculation.

Let's learn how (and why) to do this using a couple of examples. We will start with an example that uses the ***multiplication and/or division rule***. Imagine you have a company that provides a service to measure the density of rocks and minerals. Recall that density is a calculated value.

$$\text{density} = \left(\frac{\text{mass}}{\text{volume}}\right)$$

Suppose that a rock sample has a mass of 7.439 grams and a volume of 1.3 mL. You put those numbers into the density equation above and use your calculator to find the density:

$$\text{density} = \left(\frac{7.439\text{ g}}{1.3\text{ mL}}\right) = 5.72230769\text{ g/mL}$$

Is 5.72230769 g/mL the density value that you would report to your customer? Would it seem reasonable to you that if we only know the volume (1.3 mL) precision to two significant figures that you would be able to know the density with a precision to ***nine*** significant figures? You may say, "Why did my calculator give me the wrong answer?" The reason is that calculators, unless they have a significant figure capability, assume all values are exact. In other words, when you enter the number 7.439, your calculator assumes that to be 7.34900000000000000000... with zeros continuing infinitely. The calculator assumes 1.3 to be 1.3000000000000000000000... We must use the "Significant Figures in Calculations" rules shown above to round the calculator value for the density to the correct number of significant figures. Since we are doing a division calculation, we use the appropriate rule:

- When doing **multiplication and/or division** with measured values, the answer should have the *same number of significant figures* as the measured value with the ***least*** number of significant figures.

    - How many significant figures do we have in each of our measured values?
        - Mass = 7.439 g, this value has ***four significant figures***
        - Volume = 1.3 mL, this value has ***two significant figures***

- The answer should have the *same number of significant figures* as the measured value with the ***least*** number of significant figures = 2 significant figures (from the volume measurement).
    - We **round** the answer to **two significant figures**.

- A simple way to round is to either (on paper or in your mind), draw a line where we will round the number. In our example, we are going to round the number to ***two*** significant figures, so we draw a line where a ***two*** significant figure value would end:

$$5.7|2230769$$

There are many "rounding" methods. In this book, we will use the following method for rounding:

Only consider the single digit *immediately* to the right of the line that you drew (or imagined). In our case it is the "2" shown in the box below:

$$5.7|\boxed{2}230769$$

- If this digit is ***less than five***, we leave the value to the left alone. This is the case in our example, so we write the density, rounded to *two significant figures* as **5.7** g/mL.
- If the first digit to the right of the line we drew (or imagined) is ***five or greater***, we round the right-most significant figure "***up***" by one digital increment. **For example,** if we had the following number for the density, we would round ***up***:

$$5.7|\boxed{6}230769$$

The rounded value in this case is **5.8 g/mL**.

In the previous example, we divided one number by another. In multiplication and/or division calculations that use more than two numbers, do the entire calculation then round to the correct number of significant figures. For example:

$$5.993 \times 4.5 \div 2.98 = ?$$

First we use our calculators to get the unrounded value: **9.04983221**

We use our rule: When doing **multiplication and/or division** with measured values, the answer should have the *same number of significant figures* as the measured value with the ***least*** number of significant figures.

- We *round* the answer to **two significant figures**.

$$9.0|4983221 = 9.0$$

Review 1.6: Rounding Practice

Round each value to 3 significant figures.

a) 5067
b) 8762
c) 0.000085493
d) 0.074649
e) five thousand

If you are using i-books, **Click here to check answer**

For pdf or hard copies of the text, check your answer using the key in Appendix 1.

We saw how to use significant figures in multiplication and/or division rule in the previous example for the calculation of the density of an object. Now, let's learn how to use the ***significant figures in addition and/or subtraction*** rule. Let's do so using an example calculation:

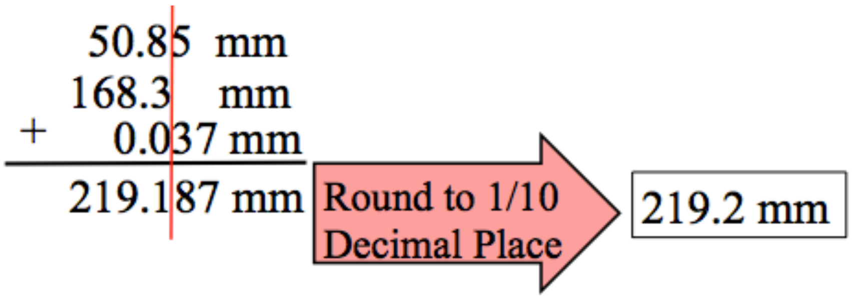
Example: The thickness of a book, a box, and a piece of paper are all measured using different types of measuring devices. The book is 50.85 mm thick, the box 168.3 mm thick and a piece of paper 0.037 mm thick. The three objects are stacked on top of each other. What is the height of the stack?

If you were to do the addition on your calculator, the display would read 219.187, but now we need to round to the correct number of significant figures.

- **RULE:** When doing ***addition and/or subtraction*** with measured values, the answer should have the ***same precision*** as the least precise measurement (value) used in the calculation.
    - Which of the measured values is least precise?
        - 50.85 mm (the book) ....precise to the 1/100 decimal place
        - 168.3 mm (the box) ....precise to the 1/10 decimal place
        - 0.037 mm (the paper).......precise to the 1/1000 decimal place

I hope you agree that the **168.3** is the least precise value. Note that we are looking at *precision* of the values, not the number of significant figures.

- Our rule for addition and/or subtraction demands that the answer should have the ***same precision*** as the least precise measurement (value) used in the calculation.
    - Since the least precise value (168.3) is precise to the 1/10 decimal place, then we round our answer to the 1/10 decimal place.



Note the logic of the rule. Since we do not know the digit that comes after the 3 in 168.3, how could we know the calculated value more precisely than the tenths (1/10) decimal place (the decimal place of the 3).

Before you try a few problems involving significant figures in calculations, I want to warn you about a common error made by chemistry students. The most common **MISTAKE** that I see students make is TO APPLY THE MULTIPLICATION AND/OR DIVISION RULE **TO** ADDITION OR SUBTRACTION CALCULATIONS.

Review 1.7: Use of Significant Figures in Calculations

Assume that the following calculations are for measured values. Report the calculated values to the correct number of significant figures.

a) 0.25 x 4.77
b) 690.4 ÷ 12
c) 2.333 – 0.33
d) 12.7 + 0.214 + 3.66

If you are using i-books, **Click here to check answer**

If using a pdf or hard copy of the text, check your answer using the key in Appendix 1.

1.5 Unit Conversions

Figure 1.9 **A 1948 Tucker Convertible**

This car **converts** from open-roof to closed-roof. In this section you will learn how to **convert** from one unit to another unit. Source: Wikimedia Commons, Author: anonymous,CC-BY-SA, http://creativecommons.org/licenses/by-sa/3.0/legalcode

Conversion Factors and the Factor Label Method

In a previous section of this chapter, we saw that for historical and practical reasons we often see several different units used for a particular property. Recall the many different units used for distance: inch, foot, yard, mile, millimeter, centimeter, meter, kilometer, furlong, league, and fathom. In this section, we will learn how to do a calculation (called the "Factor Label Method") to convert from one type of unit to another unit. This same method of calculation will be important in other problem solving seen in later chapters of this text and throughout the field of science and engineering.

Below are a couple of typical unit conversion problems. We will use these problems as examples in this section:

- A package weighs 3.50 kg (kilograms); what is the weight in lbs. (pounds)?
- A student is 60.0 in (inches) tall; what is the student's height in cm (centimeters)?

Conversion Factors

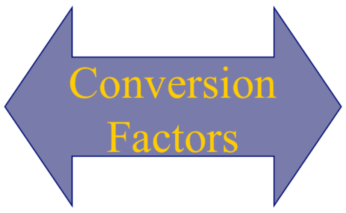
To convert from one unit to another, we must know the ***relationship*** between the two units of measure. Let's consider the relationships needed in our two example problems:

- A package weighs 3.50 kg; what is the weight in lbs. ?
  - The relationship between kilograms and pounds is: one kg is equal to 2.20 lbs.
  - We write this as an ***equivalence statement***: 1 kg = 2.20 lb.
- A student is 60.0 inches tall; what is the student's height in cm?
  - Equivalence statement: 1 in = 2.54 cm (exactly)

To convert from one unit (given unit) to another unit, we multiply the given value by a “**conversion factor.**” Let’s do so with our examples.

- A package weighs 3.50 kg (kilograms); what is the weight in lbs. (pounds)?
    - ***Equivalence statement***: 1 kg = 2.20 lb
    - We can write the equivalence statement as ***conversion factors***:

$$\left(\frac{1\text{ kg}}{2.20\text{ lb}}\right)$$



$$\left(\frac{2.20\text{ lb}}{1\text{ kg}}\right)$$

Begin all conversion factor calculations with the value you are given, then multiply it by the *conversion factor*. But wait a minute, we see above that the conversion factor can be written two ways. One conversion factor puts kg on the top of the fraction and lb on bottom, the other is reversed, with lb on top and kg on bottom. Which one do you think we will use? If you know about cancellation of like values in fractions, then you probably chose the conversion factor on the right so that the *given units* of kg would cancel and we would be left with the *desired units* of pounds. If you do not recall how we cancel “like” values in fractions, consider this fraction:

$$\left(\frac{7 \text{ x } 6 \text{ x } 9}{9 \text{ x } 7}\right) \Rightarrow \left(\frac{\cancel{7} \text{ x } 6 \text{ x } \cancel{9}}{\cancel{9} \text{ x } \cancel{7}}\right) = 6$$

The “like” values, 7 and 9, “cancel” because they appear on both the top and bottom of the calculation. Just as “like” numbers in both numerator (top) and denominator (bottom) of a calculation cancel, so do “like” units. The cancellation of units in a mathematical equation is called *dimensional analysis*.

Let’s now apply this to our calculation:

- We will start by writing the value we are given (3.50 kg), then multiply it by the correct version of the conversion factor.
- The correct version of the conversion factor has the desired units on top and the given units on bottom:

$$3.50\,\cancel{\text{kg}}\left(\frac{2.20\text{ lb.}}{1\,\cancel{\text{kg}}}\right) = 7.70\text{ lb.}$$

- Note that the given units (kg) cancel, and we are left with the desired unit (lb.). Also, we had three significant figures in the given value, three significant figures in the conversion factor, therefore we use three significant figures in the answer.

- Another way to write the equation above is to use the ***line*** method, as shown below:

$$\begin{array}{c|c|} 3.50\,\cancel{\text{kg}} & 2.20\text{ lb.} \\ \hline & 1\,\cancel{\text{kg}} \end{array} = 7.70\text{ lb.}$$

It may be helpful for you to begin using this ***line*** method now because I will be using it in the remainder of the book. Hopefully you see that conversion from one unit to another is a very simple **two-step task**:

- **Step 1:** Write the given value.
- **Step 2:** Multiply it by the correct version of the conversion factor.

A couple tips to help you with conversion problems:

- Always include units with the values.
- Do the dimensional analysis to verify that the given unit cancels and you are left with the desired unit.

Let’s work on our second conversion problem:

A student is 60.0 inches tall; what is the student’s height in cm?

- Equivalence statement: 1 inch = 2.54 cm (exactly)
- We can write the equivalence statement as *conversion factors*:

Begin all unit conversion calculations with the value you are given, as shown below.

$$\begin{array}{l|l|} 60.0\ \text{in} & \qquad \\ \hline & \end{array}$$

Next, multiply the given value by the *conversion factor*. Recall from our previous example that the conversion factor can be written two ways. One conversion factor has inch on the top and cm on the bottom of the fraction, the other is reversed, with cm on the top and inch on the bottom. Which one shall we will use? Hopefully you chose the conversion factor on the right so that the *given units* of inch would cancel and we would be left with the *desired units* of cm. Multiply the given value by the correct version of the conversion factor:

$$\begin{array}{l|c|} 60.0\ \cancel{\text{in}} & 2.54\ \text{cm} \\ \hline & 1\ \cancel{\text{in}} \end{array} = 152\ \text{cm}$$

Note that the given units (in) cancel, and we are left with the desired unit (cm). Also, we had three significant figures in the given value, and an ***infinite number significant figures*** in the conversion factor because it was an **exact** value. Since three is *much less than infinity*, we use three significant figures in the answer.

The relationships between units are called ***equivalence statements***. The equivalence statements for some units are shown in Table 1.4. Some equivalence statements can be **exact**. An equivalence statement is exact if it is a ***defined or agreed*** upon value. Examples of defined equivalence statements with exact values are 60 seconds = one minute, 1 mL = 1 cm^3, and 12 inches = one foot. These are units that were *defined* when the unit system was invented. Some units became exact ***after*** they were invented. This was done by ***agreement*** within the scientific community. Examples of ***“agreed upon”*** exact equivalence statements are 1 in = 2.54 cm, 1lb. = 453.59237 g, and 1 cal = 4.184 J.

Table 1.4 Relationships Between Various Units

Quantity	Unit Name	Symbol	Related Equivalence Statements
Length	foot inch centimeter	ft in cm	1 foot = 12 inches (exactly) 1 inch = 2.54 centimeters (exactly)
Mass	gram kilogram pound ounce	g kg lb. oz.	1g = 0.001 kg (exactly) 1 lb. = 453.59237 g (exactly) 1 lb. = 16 oz. (exactly) 1kg = 2.20 lb.
Volume	liter gallon fluid ounce milliliter cubic centimeter	L gal fl. oz. mL cm^3 *or* cc	1 L = 33.814 US fl. oz. 0.0338 fl. oz. = 1 mL 1 mL = 1 cm^3 (exactly)
Energy	calorie Joule	cal J	1 cal = 4.184 J (exactly)

We use the *equivalence statements* to make *conversion factors*. If the equivalence statement is exact then the conversion factor is also exact. We will be using conversion factors (exact and non-exact) in calculations, so we will need to consider the number of significant figures in conversion factors. There are a few important things to consider:

- **Exact conversion factors** have ***an infinite number*** of significant figures.
  - In our previous example we used an exact equivalence statement: 1 in = 2.54 cm.
  - In the corresponding conversion factors, we treat these numbers as 1.0000000000000... and 2.540000000000000000... (with the zeros continuing infinitely).

- In **non-exact conversion factors**, the "1" is considered exact.
  - Example: 1 kg = 2.20 lb. Here the 1 is exact (has an infinite number of significant figures) and the 2.20 has three significant figures.

What do you do if you are not sure if a unit conversion is exact or not? You should ask your instructor how they wish you to proceed. I tell my students that if they are not sure, treat the conversion factor as if it was *non-exact* - **<u>or</u>** look it up.

Review 1.8: Unit Conversion Problems

a) How many feet in 248.9 inches? 1 ft = 12 inches (exactly)
b) How many eggs in 7.5 dozen eggs? 12 eggs = 1 dozen (exactly)
c) How many calories in 119 joules (J)? see Table 1.4 for the conversion factor

i-books users: **Click here to check answer**

If using a pdf or hard copy of the text, check your answer using the key in Appendix 1.

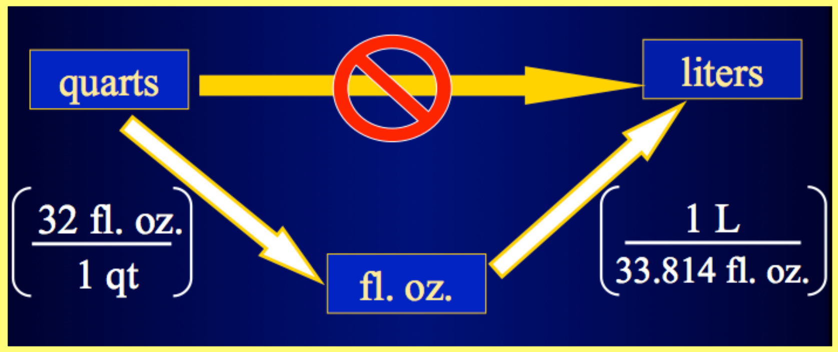
Two Step Unit Conversions

If you are trying to convert between units and do not know the relationship (conversion factor) between the units, you may still be able to solve the problem by using more than one conversion step. For example, let's say that you want to know: **How many liters (L) are contained in 5.75 quarts?** Furthermore, *assume you <u>do not have</u> the relationship between quarts and liters* (nor do you have access to the internet where you can find the relationship). However, you do have a table that gives you the following conversion factors:

- 1 quart = 32 fluid ounces (fl. oz.)
- 1 L = 33.814 fl. oz.

Since you do not have the relationship between L and fl. oz., you ***cannot*** do this problem in one step. Do you see another way to do the problem given the two conversion factors listed above? Perhaps you noticed that you could do this problem in two steps. First, convert quarts to fluid ounces, then fluid ounces to liters, as indicated by the conversion map shown in Figure 1.10.

Figure 1.10
A Conversion Map for a Two Step Conversion of Quarts to Liters



We can do **two** unit conversion calculations:

- **Conversion 1:** Convert 5.75 quarts to fl. oz.

$$\begin{array}{c|c|} 5.75\,\cancel{\text{qt}} & 32\ \text{fl. oz.} \\ \hline & 1\,\cancel{\text{qt}} \end{array} = \mathbf{184\ fl.\ oz.}$$

- **Conversion 2:** Convert fl. oz. to L

$$\begin{array}{c|c|} \mathbf{184}\,\cancel{\mathbf{fl.\ oz.}} & 1\ \text{L} \\ \hline & 33.814\,\cancel{\text{fl. oz.}} \end{array} = \mathbf{5.44\ L}$$

Next, I would like to show you an *advanced move* for doing conversions that require more than one step. Instead of doing ***two*** separate calculations, you can combine ***both*** calculations into ***one*** equation. For the problem that we just did, we would write:

$$\begin{array}{c|c|c|} 5.75\,\cancel{\text{qt}} & 32\,\cancel{\text{fl. oz.}} & 1\ \text{L} \\ \hline & 1\,\cancel{\text{qt}} & 33.814\,\cancel{\text{fl. oz.}} \end{array} = \mathbf{5.44\ L}$$

Both methods, doing two separate equations or combining the conversions in a single equation, are equally correct and give the same answer.

Review 1.9: Two-Step Unit Conversions

Now you try a two step conversion: How many inches are in 5.5 meters given that:

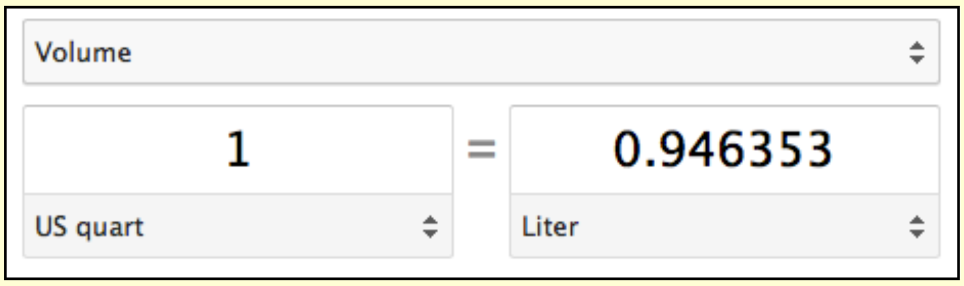
1 inch = 2.54 cm (exactly)
100 cm = 1 m (exactly)

i-book users: **Click here to check answer**

If using a pdf or hard copy of the text, check your answer using the key in Appendix 1.

Unit Conversions from the Internet

Now that you know how to convert from one unit to another, I want to show you a shortcut for unit conversions that you can do when you have access to the internet - as we do most of the time. In our last example problem, we assumed that we did not have the conversion factor needed to do a one-step conversion. You can easily get all your conversion factors from the Google homepage. In our example, we assumed that we did know the relationship between quarts and liters, however it is easily obtained on Google. Simply type “quarts to liters” in the Google search line, the first search result that is displayed will be a “unit converter engine.” If you are connected to the internet now, try it. Here is what you should see on the top of your search result list:



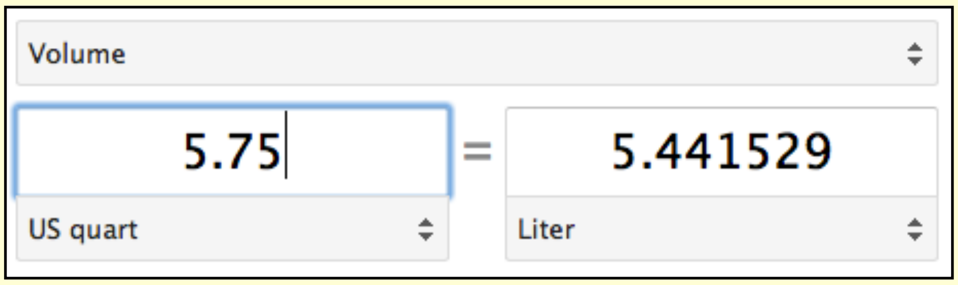
Volume

1 = 0.946353

US quart

Liter

It gets better. This converter engine is *interactive*. You can actually click on the quarts box and enter a number. I entered the number we used in our example (5.75 quarts) and the display gave me the corresponding value in liters.



Volume

5.75 = 5.441529

US quart

Liter

Once you have the converter engine displayed on your screen, you can do additional conversions by first selecting the type of unit (volume is displayed above, but you could change that to length, mass, etc.), then selecting the given unit and the desired unit.

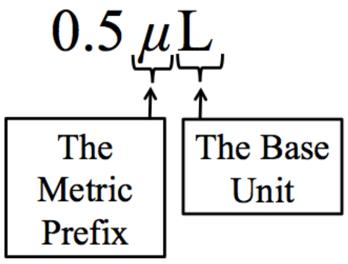
There are also several (free) unit conversion apps available for phones.

A couple of warnings are important here. First, at the time I am writing this edition, the engine does not round to the correct number of significant figures. Second, I suggest that if you are going to use these internet-generated values in a publication, double check them!

Metric Prefixes

Earlier in this chapter, we used *scientific notation* to simplify working with very large or very small numbers. Another way to simplify working with large or small numbers is to use ***metric prefixes***. Let's examine this concept using an example:

The volume of blood required for diabetics to measure blood glucose levels in modern glucometers is about 0.0000005 L. Instead of writing all those zeros, it is much more practical to use a ***metric prefix*** and write:

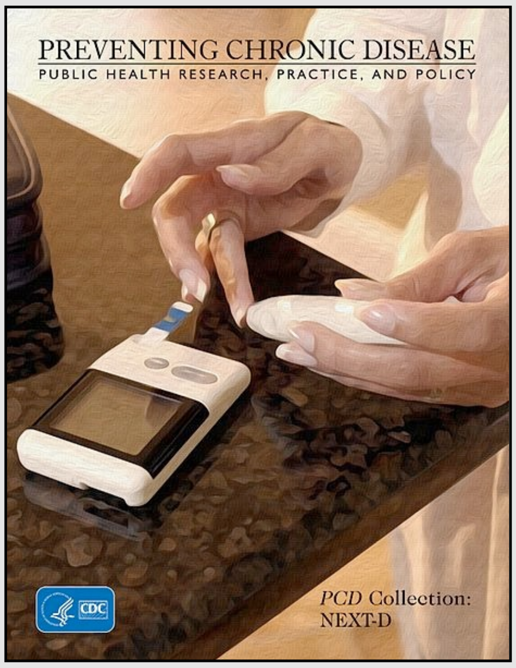


Here we see the micro (μ) prefix. The metric prefix tells the fraction or multiple of the **base unit(s)**. For example:

$$1 \text{ x } 10^{6}\ \mu\text{L} = 1\ \text{L}$$

The **base unit** can be ***any*** metric unit: liter (L), gram (g), meter (m), joule (J), second (s), calorie (cal), etc.

Figure 1.11
A Glucometer and Lancet



Diabetes patients use a ***lancet*** to puncture the skin and release a small amount of blood (about 0.5 μL). The blood is then place on a small test strip that has been preloaded into the glucometer for blood sugar analysis.
Source: Wikimedia Commons. PD, From the US Center for Disease Control and Prevention.

Unit Conversions Within The Metric System

We saw that it was more practical to write 0.5 μL than 0.0000005 L. Note that this is simply a *unit conversion*. It is an important skill to be able to do unit conversions within the metric system. You already know how to do unit conversions if you are given the relationship between the given unit and the desired unit. Table 1.5 provides the relationship between metric units. I call this table the "Equality Table" because all the values within the table are equal. Since all the values in the table are equal, we can make *equivalence statements* and *conversion factors* for conversions ***within the metric system***. For example, if we want to know the relationship between centigram (cg) and gram (g), we can use the table by finding the values to be used in the conversion factor. The base unit is the gram. For centigram (cg), we look up ***centi*** in the table and see that the value is 100. For gram, the ***base unit***, the value is 1 (note, we can tell that this is the ***base unit*** because there is **no metric prefix**). We now have the relationship between grams and centigrams: **1 g = 100 cg**. Since all metric prefix values are <u>*defined*</u> *quantities*, <u>all</u> conversions ***within the metric system*** are <u>exact</u> and have an ***infinite number of significant figures***.

Table 1.5 Equality Table for Conversions within the Metric System

1 base unit (no metric prefix)	
10 d (deci)	0.1 da (deca)
100 c (centi)	0.01 h (hecto)
1000 m (milli)	0.001 k (kilo)
$1 \text{ x } 10^{6}\ \mu$ (micro)	$1 \text{ x } 10^{-6}$ M (mega)
$1 \text{ x } 10^{9}$ n (nano)	$1 \text{ x } 10^{-9}$ G (giga)

Review 1.10: Conversion Factors for Relationships within the Metric System

Use the Equality Table to find the relationships between the following pairs of units:

a) ____________ kg = _____________ mg
b) ____________ L = _____________ mL
c) ____________ nm = _____________ Mm
d) ____________ g = _____________ dg

i-books users: **Click here to check answer** For pdf or hard copy versions, check your answer using Appendix 1.

Now that we know how to get the relationships between various metic units, let's do the unit conversion for our glucometer blood volume example given earlier. The volume of blood required to measure blood glucose levels in modern glucometers is about 0.0000005 L. **Convert this value from liters (L) to microliters (μL).**

Solution: First we find the *relationship* between L and μL to get the conversion factor.

- Use the Equality Table to get the relationship between μL and L.

1 base unit (liters in this problem)	
10 d (deci)	0.1 da (deca)
100 c (centi)	0.01 h (hecto)
1000 m (milli)	0.001 k (kilo)
1 x 10^6 μ (micro)	1 x 10^{-6} M (mega)
1 x 10^9 n (nano)	1 x 10^{-9} G (giga)

- Equivalence statement: **1 L = 1 x 10^6 μL**

Now we can write conversion factors:

$$\left(\frac{1 \times 10^{6}\ \mu L}{1\ L}\right) \xleftrightarrow[\text{Factors}]{\text{Conversion}} \left(\frac{1\ L}{1 \times 10^{6}\ \mu L}\right)$$

Multiply the given value by the form of the conversion factor that has the ***given unit*** on the bottom and ***desired unit*** on top:

$$\begin{array}{c|c|} 0.0000005\ \cancel{L} & 1 \times 10^{6}\ \mu L \\ \hline & 1\ \cancel{L} \end{array} = 0.5\ \mu L$$

Conversion factors within the metric system are ***exact*** and therefore have an *infinite* number of significant figures. The given value had one significant figure, therefore the answer has one significant figure.

Review 1.11: Unit Conversion within the Metric System

a) How many cL (centiliters) in 0.0175 kL (kiloliters)?
b) A vial contains 2681 mg of blood serum. Convert this into grams (g).

i-books users: **Click here to check answer**

If using a pdf or hard copy of the text, check your answer using the key in Appendix 1.

Temperature Units and Conversions

Measuring temperature gives us an idea of how "hot" or "cold" something is. The three commonly used temperature units (sometimes called temperature scales) and their relationship to the other temperature units are shown in Table 1.6. Conversions between the various temperature units are done a bit differently from the conversion calculations we did in previous sections. This is because temperature units are ***not*** *proportional* to each other. Therefore we do not use "*conversion factors.*" To convert from one temperature unit to another, use the equations given in Table 1.6. Note that the 1.8, 32, and 273.15 are ***exact values*** and have an *infinite number of significant figures*.

Figure 1.12
A Mercury Thermometer

A mercury thermometer with °F units on the right and °C units on the left. As mercury in a narrow glass tube expands with increasing temperature, the height of the mercury increases.
Source: Wikimedia Commons,
Author: Nino Barbieri, CC-BY-SA,
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Some of the temperature conversion equations involve mixed operations (addition/subtraction ***and*** multiplication/division). When doing temperature conversion calculations that involve both multiplication or division ***and*** addition or subtraction, ***first*** do a calculation for the operation shown in parenthesis and round that value to the correct number of significant figures, **then** use the rounded number to carry out the **next** operation.

Example: Covert 73 °F to Celsius (°C)

The relationship between °F and °C is given in Table 1.6.

°C = (°F - 32) ÷ 1.8, we use **73** °F in this equation an get:

°C = (**73** - 32) ÷ 1.8

We do the operation shown in parenthesis first (the addition) using the significant figure rule for addition and/or subtraction:

The correctly rounded value for (73 - 32) is **41**.

Next, place the ***rounded value*** into the original equation:

°C = (**41**) ÷ 1.8

Use a calculator to get the *unrounded* value: **22.7777778 °C**

Round this value to the correct number of significant figures using the **multiplication and/or division** in calculations rule.

- **41** has ***2 significant figures***
- 1.8 (exactly 1.8) has ***an infinite number significant figures***

We will **round 22.7777778 °C** to *2 significant figures*: **23 °C**

Table 1.6 Temperature Units and Related Unit Conversions

Temperature Scale	Unit Symbol	Related Unit Conversions
Celsius (also known as centigrade)	°C	°C = K - 273.15 °C = (°F - 32) ÷ 1.8
Fahrenheit	°F	°F = (1.8 x °C) + 32 To convert °F to K, first convert to °C, then to K
Kelvin	K	K = °C + 273.15 To convert K to °F, first convert to °C, then to °F

Two common errors among chemistry students doing temperature unit conversions are:

(1) Not considering 1.8, 32, and 273.15 to be ***exact*** while rounding answers to the correct number of significant figures.

(2) Applying the significant figures in multiplication/division calculations rule to addition and subtraction calculations.

Review 1.12: Temperature Unit Conversion

Convert the following temperatures:

a) 175 °C = _______________ K
b) 36 °C = _______________ °F
c) 98.6 °F = _______________ °C
d) 87 °F = _______________ K

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

For more practice with unit conversions, use these worksheets:

http://www.zovallearning.com/GOBlinks/ch1/wsunitconversions.pdf

The link below is for a unit conversions worksheet that applies unit conversions to dosage calculations:
http://www.zovallearning.com/GOBlinks/ch1/dosageconversionproblemworksheetandkey.pdf

Chapter 2: Atoms

Figure 2.1 Light is Emitted from Atoms in Fireworks

It is the arrangement of subatomic particles and their interactions with each other that make possible fireworks displays.
Source: Wikimedia Commons, Author: Michael Lane,
CC-BY-SA, http://creativecommons.org/licenses/by-sa/3.0/legalcode

Of what is “stuff” made? In the first 4 chapters of this book, I would like to facilitate you in building ***your own understanding of matter*.** To do this, we will take a look at the fundamental particles from which all matter is made. I will discuss how these fundamental particles are arranged in matter and how they interact with one another.

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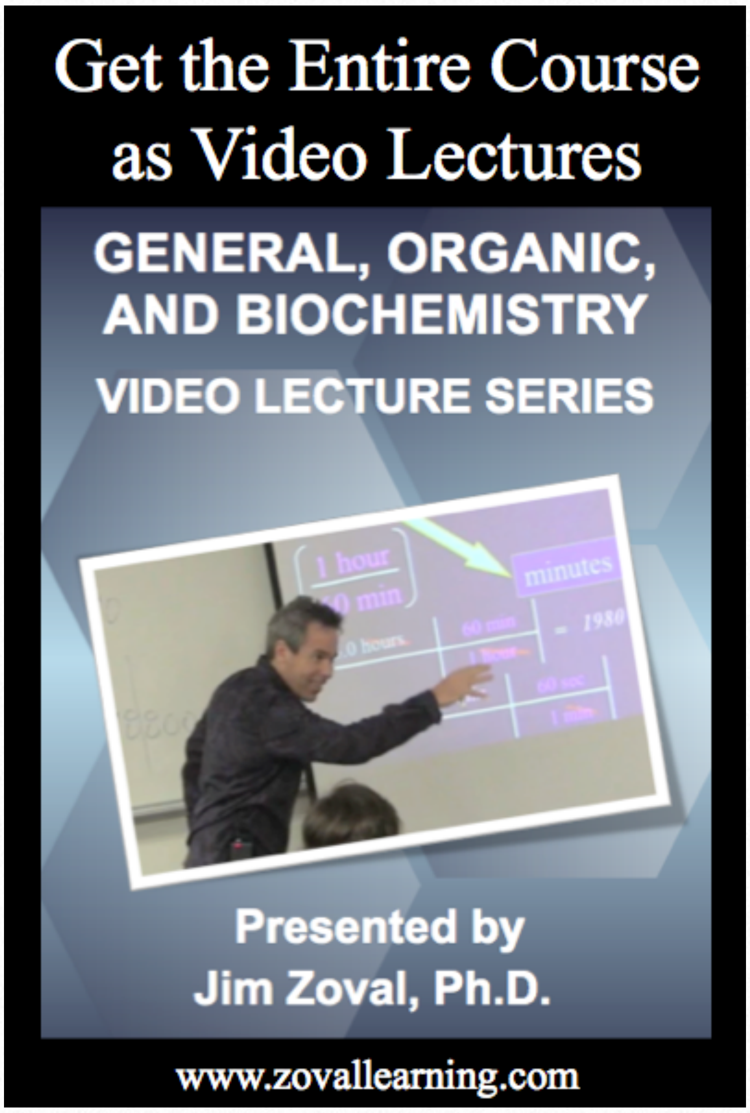

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2.1 Chapter 2 Educational Goals

1. Describe the subatomic structure of an atom.

2. Define the terms **element** and **atomic symbol.**

3. Understand how elements are arranged in the periodic table based on the number of protons they contain.

4. Understand how **atomic number** and **mass number** are used to indicate details of an atom’s nucleus.

5. Know how **isotopes** of an element differ from one another.

6. Define the term **mole** and describe the relationship between **moles** and **molar mass**.

7. Given the **molar mass** of an element, convert between number of atoms, number of moles, and mass (grams).

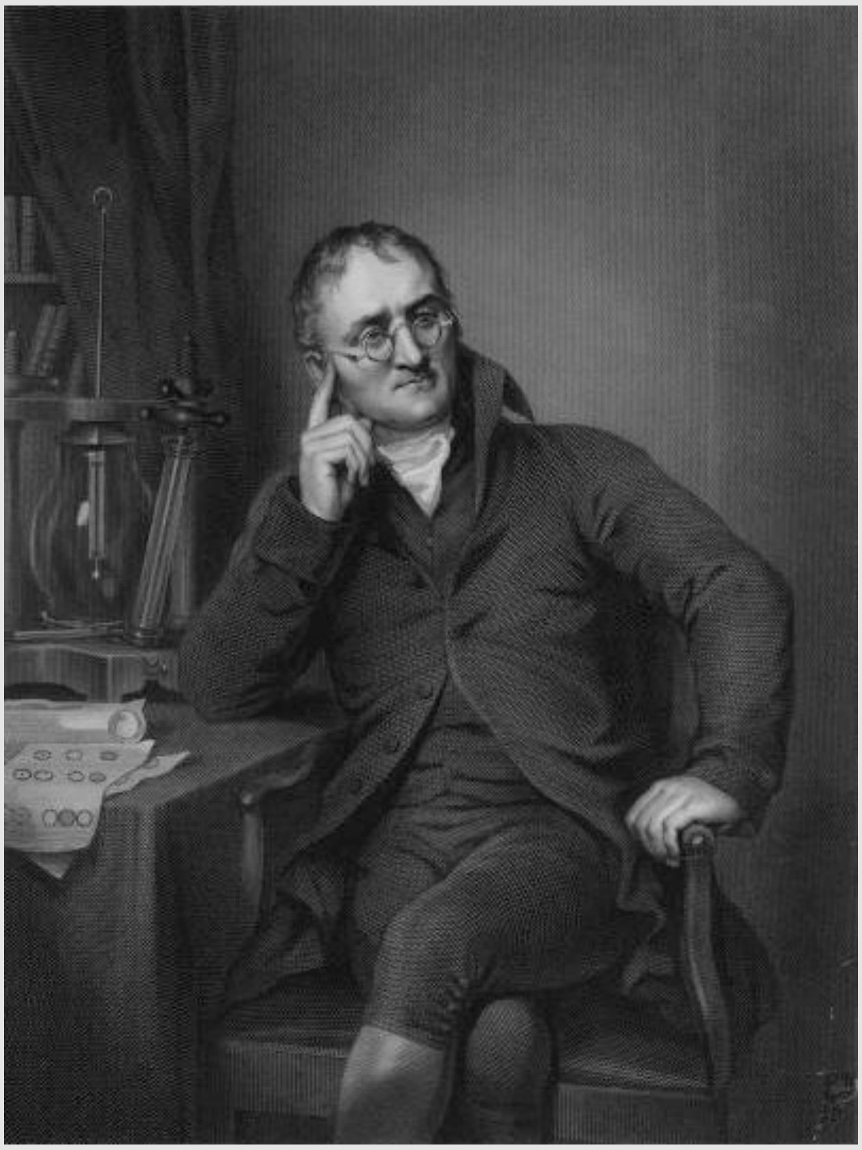
2.2 An Introduction to Atoms

Matter (stuff) is made of atoms. The first scientist to describe matter as being composed of atoms was John Dalton (Figure 2.2). For quite a while, it was thought that atoms were the smallest particles in nature. After much work by the scientific community, it was discovered that atoms are made up of even smaller particles we call **subatomic particles**.

Let us begin developing a model of the atom. It may be a good idea right now to stop and draw a picture of an atom, let's say a carbon atom, to examine your current model of the atom. It will be interesting, later in chapter 3 when we have finished developing our understanding of modern atomic theory, for you to go back and look at what you will draw now. If that model changes, don't worry - that's what we in the educational business call "learning." It is my goal for the remainder of chapter 2 and the first part of chapter 3 to help facilitate you to develop ***your own model*** (understanding) of atoms. Let's see your current atomic model. Stop and draw a carbon atom. If you have no idea - just guess. Save your illustration.

Atoms are made of **subatomic particles**. There are *three* types of subatomic particles that will make up our atomic model: ***protons, neutrons,*** *and* ***electrons***. Protons and neutrons are compacted together in what we call the **nucleus** of atoms. Electrons are distributed in space around the nucleus and can be thought of as moving very fast in a volume surrounding the nucleus. We will go into great detail of exactly how electrons are structured (arranged) relative to the nucleus, but for now let's keep it simple. Think of the nucleus as a beehive, and the electron(s) as bee(s) swarming around the nucleus. This is not quite the complete atomic theory, but for now, we will call it our *beehive* model of the atom.

Figure 2.2 John Dalton



John Dalton (1776-1884) By Henry Roscoe (author), William Henry Worthington (engraver), and Joseph Allen (painter) [Public Domain], via Wikimedia Commons Source: U.S. Library of Congress

Atoms are mostly empty space. To elaborate, I will use an analogy with familiar objects. If the nucleus (protons and neutrons) is represented by a golf ball placed on the pitcher's mound of a baseball field, then the region occupied by electron(s) moving around the nucleus would be about the size of the baseball stadium and its parking lot!

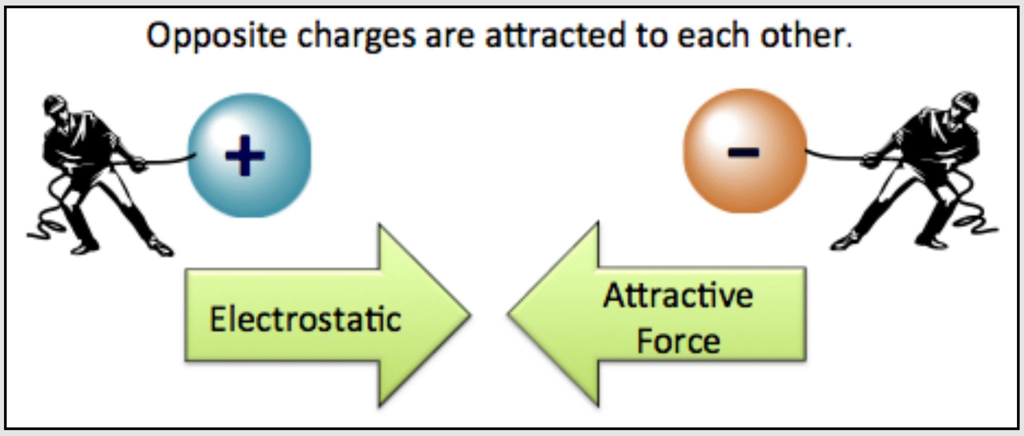
2.3 Subatomic Particles

There are a few fundamental properties of nature. You are likely familiar with some or all of them. Gravity is one of them. Magnetism and mass are others. Another fundamental property in nature is **electrical charge**. You can think of electrical charge a bit in the same way as you do magnetism. If you hold two magnets together, you will notice a force (either attractive or repulsive) and you will feel the magnets either tending to come together or move further away from each other. This is due to magnetism. Particles with electrical charge behave in a similar manner.

Particles ***may or may not*** have electrical charge. There are two types (states) of electrical charge; we arbitrarily call one state **positive** and the other state **negative**. ***Every thing we discuss in this chemistry book ultimately occurs because of the interaction of these two types of charges.***

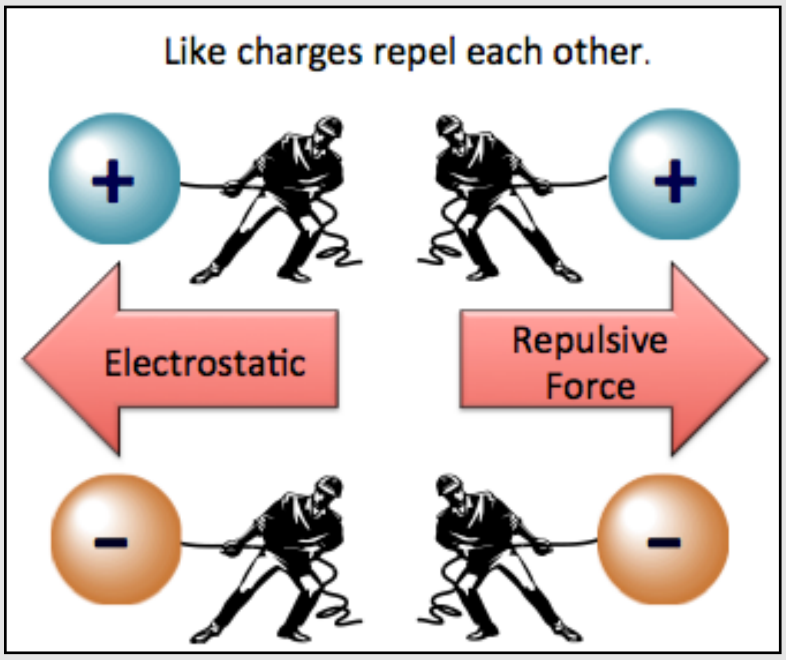
Particles with ***opposite charges attract*** each other. The natural attraction is called **electrostatic attractive force**. Consider the positive and negative charged spheres illustrated in Figure 2.3. Oppositely charged particles will accelerate toward one another if not held apart.

Figure 2.3 Electrostatic Attraction



Particles with the like charges ***repel*** each other. The natural repulsion is called **electrostatic repulsive force**. Consider the two positively charged spheres illustrated in the top of Figure 2.4. Like charged particles will accelerate away from one another if not held together. The same electrostatic repulsion would occur between two negatively charged particles, as shown on the bottom of Figure 2.4.

Figure 2.4 Electrostatic Repulsion



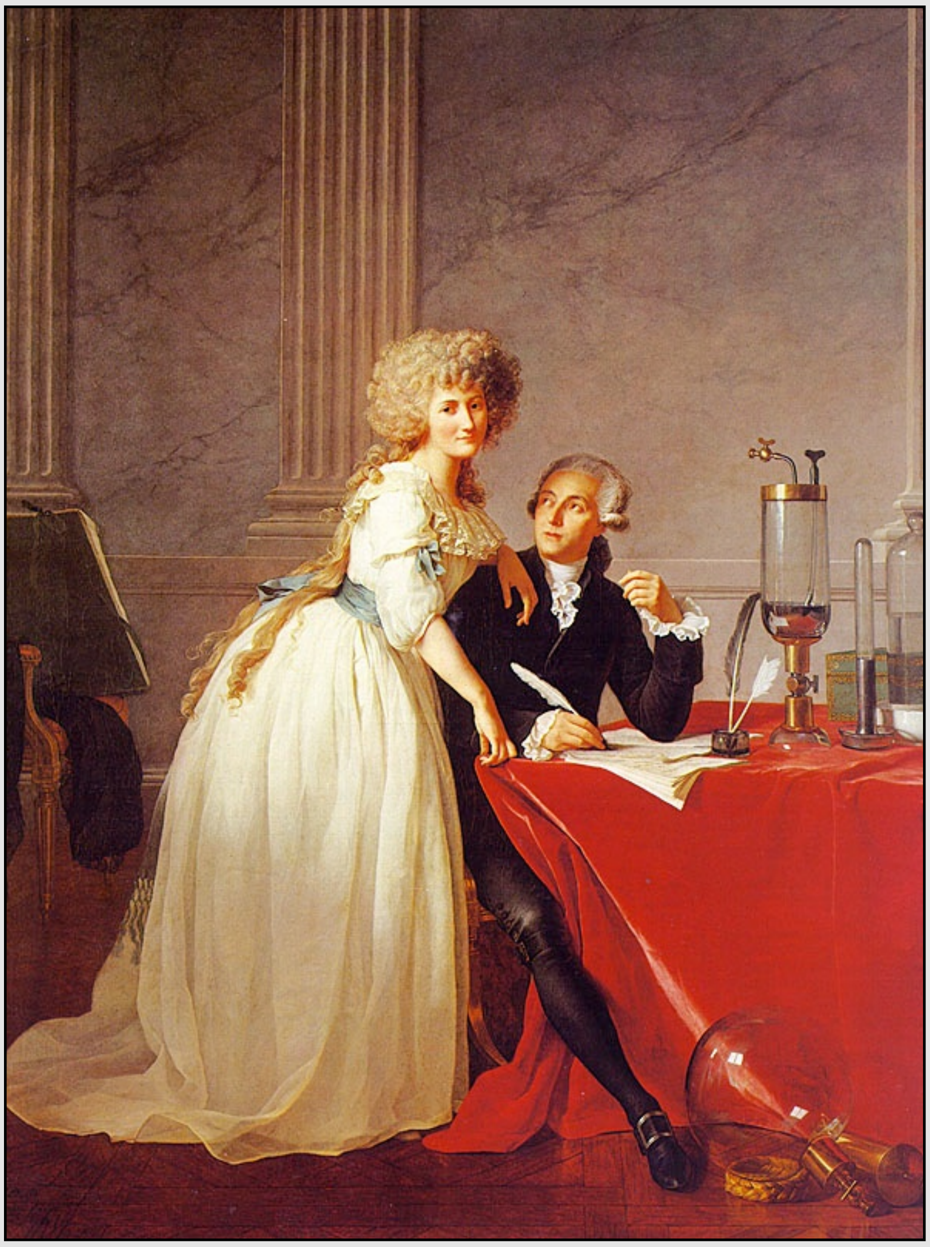
Subatomic Particles

Protons

There are three types of subatomic particles: protons, neutrons, and electrons. **Protons** are ***positively charged*** particles located in the nucleus of an atom. The number of protons a particular atom contains determines that atom's identity. We differentiate atoms with a particular number of protons by their names. For example, any atom that contains just one proton is called hydrogen. An atom with two protons is called helium. An atom with six protons is called carbon.

Historically, matter with different numbers of protons, such as hydrogen, helium, and carbon were called the **elements.** In 1789, Antoine Lavoisier (1743-1794) published the first table of the elements. It contained 32 elements (there were some mistakes). Lavoisier is sometimes called "the father of modern chemistry" and his wife, Marie-Anne Pierette Paulze (1758-1836), been called "the mother of modern chemistry." After Marie-Anne met Antoine, she became an outstanding chemist, learned English in order to publish their work in international journals, and was quite an artist.

Figure 2.5
Antoine Lavoisier and his wife Marie-Anne Pierette Paulze



''PORTRAIT OF MONSIEUR LAVOISIER AND HIS WIFE''
BY JAQUES-LOUIS DAVID. SOURCE: WIKIPEDIA COMMONS, PD

How many of these elements (types of atoms) exist? There are 92 elements that occur in nature. About 25 others have been man-made by slamming two atoms together causing their nuclei to combine, however these new atoms do not last long (fractions of a second up to one year), they break apart into smaller atoms. A modern periodic table of the elements is shown on the next page. You can download a copy of this periodic table at: www.zovallearning.com/GOBlinks/ch2/periodictablezovalbasic.pdf

Elements are ordered in the periodic table in this manner for various logical reasons. As we progress through chapters 2 and 3 we will understand why the elements are arranged as seen in the periodic table.....starting now!

Note that each element is represented by its **atomic symbol** (a one- or two-letter name abbreviation) and occupies a box in the table. Above each element's symbol is the **atomic number**. The atomic number tells us the ***number of protons*** in an atom of that particular element. Elements are ordered by *increasing* atomic number. Look at carbon, symbol C, atomic number 6. Carbon has an atomic number of *six* because an atom with six protons is called carbon. If it had *seven* protons, it would not be carbon - it would be nitrogen and have an atomic number of 7. Atomic number can be abbreviated using "**Z.**" For example, with carbon, **Z** = 6, with hydrogen, **Z** = 1.

Periodic Table of the Elements

I Alkali Metals	II Alkaline Earth Metals											III	IV	V	VI	VII Halogens	VIII Noble Gases
1 **H** Hydrogen 1.0079																	2 **He** Helium 4.003
3 **Li** Lithium 6.941	4 **Be** Beryllium 9.012183											5 **B** Boron 10.811	6 **C** Carbon 12.0107	7 **N** Nitrogen 14.0067	8 **O** Oxygen 15.9994	9 **F** Fluorine 18.998403	10 **Ne** Neon 20.1797
11 **Na** Sodium 22.989770	12 **Mg** Magnesium 24.3050											13 **Al** Aluminum 26.9815	14 **Si** Silicon 28.0855	15 **P** Phosphorus 30.973762	16 **S** Sulfur 32.066	17 **Cl** Chlorine 35.4527	18 **Ar** Argon 39.948
19 **K** Potassium 39.0983	20 **Ca** Calcium 40.078	21 **Sc** Scandium 44.955908	22 **Ti** Titanium 47.867	23 **V** Vanadium 50.9415	24 **Cr** Chromium 51.9961	25 **Mn** Manganese 54.938044	26 **Fe** Iron 55.845	27 **Co** Cobalt 58.933194	28 **Ni** Nickel 58.6934	29 **Cu** Copper 63.546	30 **Zn** Zinc 65.39	31 **Ga** Gallium 69.723	32 **Ge** Germanium 72.61	33 **As** Arsenic 74.92160	34 **Se** Selenium 78.971	35 **Br** Bromine 79.904	36 **Kr** Krypton 83.80
37 **Rb** Rubidium 85.4678	38 **Sr** Strontium 87.62	39 **Y** Yttrium 88.90584	40 **Zr** Zirconium 91.224	41 **Nb** Niobium 92.90637	42 **Mo** Molybdenum 95.95	43 **Tc** Technetium (98)	44 **Ru** Ruthenium 101.07	45 **Rh** Rhodium 102.90550	46 **Pd** Palladium 106.42	47 **Ag** Silver 107.8682	48 **Cd** Cadmium 112.414	49 **In** Indium 114.818	50 **Sn** Tin 118.710	51 **Sb** Antimony 121.760	52 **Te** Tellurium 127.60	53 **I** Iodine 126.90447	54 **Xe** Xenon 131.29
55 **Cs** Cesium 132.90545	56 **Ba** Barium 137.327	57 **La** Lanthanum 138.90545	72 **Hf** Hafnium 178.49	73 **Ta** Tantalum 180.9479	74 **W** Tungsten 183.84	75 **Re** Rhenium 186.207	76 **Os** Osmium 190.23	77 **Ir** Iridium 192.217	78 **Pt** Platinum 195.078	79 **Au** Gold 196.96657	80 **Hg** Mercury 200.59	81 **Tl** Thallium 204.3833	82 **Pb** Lead 207.2	83 **Bi** Bismuth 208.98038	84 **Po** Polonium (209)	85 **At** Astatine (210)	86 **Rn** Radon (222)
87 **Fr** Francium (223)	88 **Ra** Radium (226)	89 **Ac** Actinium (227)	104 **Rf** Rutherfordium (261)	105 **Db** Dubnium (262)	106 **Sg** Seaborgium (263)	107 **Bh** Bohrium (262)	108 **Hs** Hassium (265)	109 **Mt** Meitnerium (266)									

58 **Ce** Cerium 140.116	59 **Pr** Praseodymium 140.90766	60 **Nd** Neodymium 144.24	61 **Pm** Promethium (145)	62 **Sm** Samarium 150.36	63 **Eu** Europium 151.964	64 **Gd** Gadolinium 157.25	65 **Tb** Terbium 158.92534	66 **Dy** Dysprosium 162.50	67 **Ho** Holmium 164.93033	68 **Er** Erbium 167.26	69 **Tm** Thulium 168.93422	70 **Yb** Ytterbium 173.04	71 **Lu** Lutetium 174.967
90 **Th** Thorium 232.0377	91 **Pa** Protactinium 231.03588	92 **U** Uranium 238.0289	93 **Np** Neptunium (237)	94 **Pu** Plutonium (244)	95 **Am** Americium (243)	96 **Cm** Curium (247)	97 **Bk** Berkelium (247)	98 **Cf** Californium (251)	99 **Es** Einsteinium (252)	100 **Fm** Fermium (257)	101 **Md** Mendelevium (258)	102 **No** Nobelium (259)	103 **Lr** Lawrencium (262)

Electrons

Electrons are ***negatively charged*** subatomic particles. They are light-weight particles that move extremely fast. For the remainder of chapter 2 we can visualize the electrons as bees flying around a beehive (the beehive represents the nucleus). In chapter 3 you will learn more details about the regions around the nucleus that the electrons can occupy. Electrons are very light compared to protons and neutrons. Protons and neutrons are about 2000 times **heavier** than electrons and therefore compose most of an atom's mass. I will discuss *how many* electrons are contained in an atom in chapter 3.

Static Electricity

When two different, non-charged objects come in contact and rub against each other, very often we see electrons transferred from one of the object to the other. The object that loses electrons becomes positively charged and the object that received the electrons becomes negatively charged. This effect can be seen in the image where the child transfers electrons to the slide. This leaves the child with a net positive charge. The effect of the positive charge can be easily seen in the child's hair. Note that since all of the hairs are positively charged, the hairs repel one another (electrostatic repulsion). The hairs move as far apart from other hairs as possible to achieve the lowest energy configuration. The lowest energy configuration of hair has positively charged hairs as far apart as possible from other positively charged hairs.

Source: Wikimedia Commons, Author: Ken Bosma, CC-BY-SA, http://creativecommons.org/licenses/by-sa/3.0/legalcode

Neutrons

Let's move on to our next subatomic particle, the **neutron.** Neutrons are located in the nucleus (with the protons). Neutrons do not have electrical charge; we say they are **electrically neutral**. Recall from our discussion of electrostatic repulsion that the protons have positive charge and repel each other. What holds the protons together in the compact nucleus of an atom? It is the neutrons. We can think of neutrons acting as the "glue" to hold the positive protons close to each other in the nucleus. The name of the force involved is called the "*nuclear strong force.*" The names, charges, and symbols for the three types of subatomic particles are shown in Table 2.1.

Table 2.1 Subatomic Particles

SUBATOMIC PARTICLE	SYMBOL	CHARGE
PROTON	p	positive (1+)
NEUTRON	n	none
ELECTRON	e or e^-	negative (1-)

How many neutrons are in an atom?

We ***cannot determine*** the number of neutrons in an atom based on the number of protons. This is because atoms of a particular element ***do not all have the same number of neutrons***. Let's consider the element carbon as an example. Some carbon atoms have 6 neutrons, some have 7, and some have 8 neutrons. If you had a pile of carbon atoms in front of you and you were able to magically reach in and grab a single carbon atom, you would have about a 99% chance of grabbing a carbon with 6 neutrons, about a 1% chance of grabbing a carbon atom with 7 neutrons, and about a 0.1% chance of grabbing a carbon atom with 8 neutrons. These three different forms of carbon are called ***isotopes*** of carbon. **Isotopes** are defined as atoms with the *same* number of protons (same element), but a *different* number of neutrons.

You learned that an atom's ***"atomic number* (Z)*"*** is the number of protons it contains. When considering the number of neutrons in an isotope of a particular atom, it is useful to learn a new term called **"mass number."** The ***mass number*** of an atom is defined as *the number of protons* ***plus*** *the number of neutrons*. Mass number can be abbreviated using "**A.**"

	SYMBOL	DEFINITION
ATOMIC NUMBER	Z	number of protons
MASS NUMBER	A	number of protons + number of neutrons

Let's go back to our example for **carbon**. We saw three isotopes of carbon; about 99% of carbon atoms have 6 neutrons, about 1% have 7 neutrons, and about 0.1% have 8 neutrons. These percentages are called the ***natural abundances***. It tells us how much (percent) of each isotope of particular element exists in nature. The natural abundances of isotopes for each element will vary. They are found by measurement and tabulated for reference. You will often see one of two "shorthand notation" methods used to differentiate the various isotopes:

Method 1: Write the *element symbol*, a dash, then the *mass number* (A)

Let's use our three isotopes of carbon for examples:

NUMBER OF NEUTRONS IN THE CARBON ATOM	SHORTHAND NOTATION
6	C-12
7	C-13
8	C-14

Method 2: Write the *element symbol*, we superscript the *mass number* (A) to the left of the symbol.

NUMBER OF NEUTRONS IN THE CARBON ATOM	SHORTHAND NOTATION
6	^{12}C
7	^{13}C
8	^{14}C

- Although redundant, sometimes the atomic number (Z) is also subscripted to the left of the symbol.
    - For example:

$$^{12}_{6}\text{C}$$

Whenever you are ever given the mass number and the atomic number (or element name), you can determine the number of neutrons.

EXAMPLE: How many neutrons are in ^{23}Na?

SOLUTION: We know the **mass number** is defined as: (number of protons + number of neutrons) = **23.** We also know that sodium has 11 protons (see periodic table, atomic number = 11). Therefore ^{23}Na must have 12 neutrons because 11 + 12 = 23.

Review 2.1: Subatomic Particles

Fill in the blanks for the following isotopes:

a) **^{14}N** number of protons _______ number of neutrons _____ atomic number_______ mass number ____

b) **^{15}N** number of protons _______ number of neutrons _____ atomic number_______ mass number ____

c) **^{42}Ca** number of protons _______ number of neutrons _____ atomic number_______ mass number ____

d) **^{1}H** number of protons _______ number of neutrons _____ atomic number_______ mass number ____

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

2.4 Atoms

Now you have begun to build a model of the atom in your brain. Atoms are composed of subatomic particles. The protons and neutrons are located in the nucleus and the electrons, like bees, are moving very quickly around the nucleus. **Atoms, by definition, are electrically neutral.** This is because they always have the ***same number of protons and electrons***. Note that the nucleus is positive and the electrons are negative, however the total positive charge from protons and the total negative charge from the electrons ***cancel each other*** (add up to zero charge). Let us consider a carbon atom. Carbon is in box #6 (atomic number = 6) of the periodic table because it has 6 protons. Since atoms are *always electrically neutral*, a carbon atom **must** therefore have 6 electrons (total charge = (+6) plus (-6) = ZERO).

The Mole

Atoms are very small. For example, a copper US penny minted between 1962 and 1981 is composed 95% copper and 5% zinc. How many copper atoms are in the coin? It contains about 3 grams of copper made up from 30,000,000,000,000,000,000,000 atoms!!! Since atoms are so small and, in most applications we work with very large quantities of atoms, it is not practical to discuss the amount of matter in terms of atoms. An analogous situation is seen in how bakers purchase eggs. Bakers very rarely buy single eggs. Because they purchase large numbers of eggs, they get them by the *dozen* (1 dozen = 12 items). Chemists use a similar "***counting unit***" for large quantities; we use a "chemist's dozen," which we call a **mole**.

A mole is not 12 items; it is **6.022×10^{23}** items! The mole is defined as the number of carbon atoms in exactly 12 grams of carbon-12 (^{12}C). This value is determined experimentally and was later named ***Avogadro's Number*** to honor a chemist, Amedeo Avogadro (see Figure 2.6). Avogadro is best known for discovering that the volume of a gas is proportional to the number of atoms or molecules in the container. The **mole unit** is sometimes abbreviated as "**mol**," not much of a time saver, but we already used "m" for both *meter* and *milli*, "Mo" is a symbol for a element, so the best we can do is to use **mol**.

Figure 2.6
Amedeo Avogadro

Picture of Amedeo Avogadro (1776-1856), Painting title: The Italian Scientist
Public Domain (US-PD)
Source: Edgar Fahs Smith Collection

A mole, **6.022×10^{23}** items, is so large that it is quite hard to even contemplate. Try to get a feel for the size of this number by considering the following: 1 mole of marshmallows would be enough marshmallows to make a 12 mile-thick layer of marshmallows covering the entire face of the Earth. However, because atoms are so small, 1 mole of carbon atoms could be easily held in one hand! One mole of water molecules could be contained in a volume smaller than that of a shot glass.

We define and use the ***mole*** counting unit as a practical way to discuss how much matter is present. The reason using the *mole* is more practical than referring to the amount of *atoms* is because you would never be required to go into a laboratory and weigh, for example 35 *atoms*. However, the amounts of matter with which we most often work are in the range of about 0.01 to 10 *moles*. If we ever need to convert back from number of moles to the number of particles, we can use the definition of the mole as an equality statement and conversion factor. Let's do a ***moles to atoms*** conversion example problem.

Converting from Moles to Number of Atoms:

Example: How many atoms are contained in 7.32 moles of nitrogen?

Solution: We do this problem just as we did the other unit conversion problems in chapter 1. Here we are converting from *mole units* to *atom units.* We need to know the *relationship* between atoms and moles. We use the definition of the mole as the *equivalence statement*:

- 1 mole = 6.022 x 10^{23} particles (in this case, N atoms)
- Given the equivalence statement, we can write *conversion factors*:

Next, we will set up a unit conversion equation as in chapter 1; we multiply the *given unit* (7.32 moles) by the correct form of the conversion factor:

- We use a form of the conversion factor that has moles on the bottom and atoms on the top:

$$\begin{array}{c|c|} 7.32\ \cancel{\text{moles}} & \mathbf{6.022 \times 10^{23}}\ \text{atoms} \\ \hline & 1\ \cancel{\text{mole}} \end{array} = 4.41 \times 10^{24}\ \text{atoms}$$

Since the given number has three significant figures and we used four significant figures in Avogadro's Number, the answer has three significant figures.

- Note that Avogadro's Number is determined experimentally. At the time of writing this book, it has been determined to be 6.02214129 x 10^{23} (9 sig figs), **however in this text we will use 6.022 x 10^{23} (rounded to four significant figures).**

Converting from Number of Atoms to Moles

If we know the number of atoms present, we can convert to the number of moles. Let's use the copper US cent discussed earlier. I mentioned that a copper US penny minted between 1962 and 1981 contains about 30,000,000,000,000,000,000,000 copper atoms. **How many moles of copper are in one of these pennies?**

Solution: Here we are converting from *atom units* to *mole units.* We need to know the *relationship* between atoms and moles. We use the definition of the mole as the *equivalence statement*:

- 1 mole = 6.022 x 10^{23} particles (in this case, Copper (Cu) atoms)

Next we will set up a unit conversion equation; we multiply the *given unit* (3 x 10^{22} atoms) by the correct form of the conversion factor:

- We use form of the conversion factor that has atoms on the bottom and moles on the top:

$$\begin{array}{c|c|} 3 \times 10^{22}\ \cancel{\text{atoms}} & \mathbf{1\ mole} \\ \hline & \mathbf{6.022 \times 10^{23}}\ \cancel{\text{atoms}} \end{array} = 0.05\ \text{moles}$$

Since the given number has ***one*** significant figure and we used 4 significant figures in Avogadro's Number, the answer has ***one*** significant figure.

Because of increases in the price of copper, if modern US pennies contained this much copper they would be worth much more than one cent. Currently, US pennies are made mostly from zinc and have a thin layer of copper over the surface.

Review 2.2: Conversions Between Number of Atoms and Moles

Do the following conversions:

a) 3.45 moles = _________________ atoms

b) 4.2×10^{24} atoms = _________________ moles

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

The Mole and Mass

Just as bakers use the dozen (12 items) as a counting unit, chemists use the ***mole*** "counting unit" for large quantities. Many chemical observables are determined by how many atoms are present. Because the number of atoms used in most applications is so large, we use the mole concept to discuss the amount of matter present. If we wished to obtain 8.00 moles of carbon for an experiment, how would we do so? When we want to measure the amount of matter we use balances (Figure 2.8).

Figure 2.7 An Antique Balance

Source: Wikimedia Commons, Author: Berthold Werner CC-BY-SA, http://creativecommons.org/licenses/by-sa/3.0/legalcode

Figure 2.8 A Modern Balance

Source: Wikimedia Commons, Author: Karelj, PD

Balances give us the mass (or weight) of the sample. Is there a relationship between the mass of an element and the number of moles? I suppose you correctly guessed (or knew) that there is indeed a relationship between mass and number of moles. The relationship is called the **molar mass** (or **atomic mass**). The *molar masses* of the various elements are determined experimentally and are usually shown under the symbol of the element in the periodic table. The molar mass of an element is defined as **the *mass* (in grams) of *one mole* of the element**. The units of *molar mass* are **grams per mole (g/mole).**

For example: **What is the molar mass of carbon?**

We find carbon (symbol C) in the periodic table, then look for the molar mass. We see that the molar mass of carbon is 12.0107 g/mole. This means if you have one mole of carbon (6.022×10^{23} atoms), it would weigh 12.0107 grams.

Review 2.3: Finding the Molar Mass of an Element

Use the periodic table to find the molar mass of Argon (symbol Ar).

For ***i-book*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

Converting Between Moles and Grams of an Element

I began the discussion of *molar mass* by presenting the question: **If we wished to obtain 8.00 moles of carbon for an experiment, how would we do so?** Let's solve this problem now. Because the molar mass gives us the relationship between the number of moles and the mass of an element, it can be used to convert back and forth between moles and mass (in grams). Note, this is simply a *unit conversion problem*, we wish to convert from units of **moles** to units of **grams**!

Solution: We use our **Factor Label Method** (just like any other unit conversion problem):

- From the molar mass, we can write an *equivalence statement*: 1 mole of carbon = 12.0107 grams.
  - The equivalence statements can be written as conversion factors:

$$\left(\frac{1\ \text{mole C}}{12.0107\ \text{g C}}\right) \qquad \left(\frac{12.0107\ \text{g C}}{1\ \text{mole C}}\right)$$

Next we will set up a unit conversion equation; we multiply the *given unit* (8.00 moles) by the correct form of the conversion factor. Use the form of the conversion factor that has moles on the bottom and grams on the top:

$$8.00\ \cancel{\text{moles}} \times \frac{\textbf{12.0107 grams}}{1\ \cancel{\text{mole}}} = 96.1\ \text{grams}$$

Molar masses are determined *experimentally* and are therefore **<u>not</u> exact values**. Since the given number of moles (8.00) has three significant figures and there are six significant figures in the molar mass, the answer has three significant figures.

Review 2.4: Converting Between Moles and Grams

a) What is the mass of 12.3 moles of argon (symbol Ar)?
b) What is the mass of 4.5 moles of Lead (symbol Pb)?

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

In the previous examples, we were given the number of moles of an element and converted to the mass (grams). Conversely, if we are given the mass (grams) we can convert to the number of moles.

Example: How many moles are contained in 23.67 grams of copper (symbol Cu)?
Solution: We use our **Factor Label Method**:

- From the molar mass, we can write an *equivalence statement*: 1 mole copper = 63.546 grams.
- We use the equivalence statement to get the conversion factor and set up a unit conversion equation. Multiply the *given unit* (23.67 grams) by the correct form of the conversion factor. We use the form of the conversion factor that has grams on the bottom and moles on the top:

$$23.67\ \cancel{\text{grams}} \times \frac{1\ \text{mole}}{63.546\ \cancel{\text{grams}}} = 0.3725\ \text{moles}$$

Since the given number of grams (23.67) has four significant figures and there are five significant figures in the molar mass, the answer has four significant figures.

Review 2.5: Converting From Mass (Grams) to Moles

How many moles are contained in 5.00 grams of hydrogen (symbol H)?

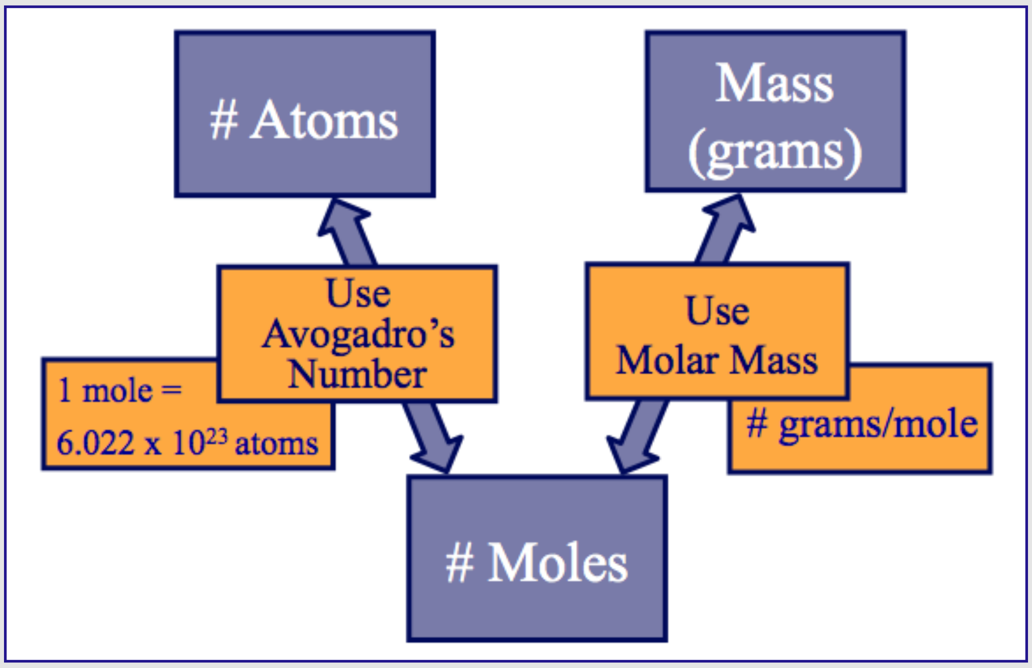
For i-books versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

IMPORTANT NOTE ON ROUNDING MOLAR MASSES: In the previous examples, we did not round the molar masses; we used the values given in the periodic table. However, *to save time*, molar masses are often rounded to fewer significant figures than are given in periodic tables. When rounding molar masses, one should never round to fewer significant figures than are contained in any other values used in the calculation. That is to say, do not round molar masses such that they would be the value that limits the number of significant figures in a calculated value. I will do so in the remainder of this text by rounding molar masses to the *hundredths* place (two places to the right of the decimal point). Although it is not a universally "agreed upon" rule to round molar masses to the hundredths place, it may be convenient for you to do so while solving problems in this text so that your calculated values will exactly match the values in my solutions. The rare and only exception to this will be if the molar mass was unable to be determined experimentally with such precision. For example, because of measurement limitations, the molar mass of lead is only known to the tenths decimal place (207.$\underline{2}$ g/mole).

Converting Between Mass and Number of Atoms

You have just learned how to convert between atoms and moles and between moles and mass. These unit conversions are summarized in the Atom-Mole-Mass Conversion Map shown in Figure 2.9. Students may find it helpful to refer to this conversion map as you are learning how to do atom-mole-mass conversion problems.

Figure 2.9: Atom-Mole-Mass Conversion Map



Suppose you are given the mass of a sample and wish to determine the number of atoms present. Can you think of a way to do so? Hint: look at the conversion map! Perhaps you realized that you would need to use **two steps**:

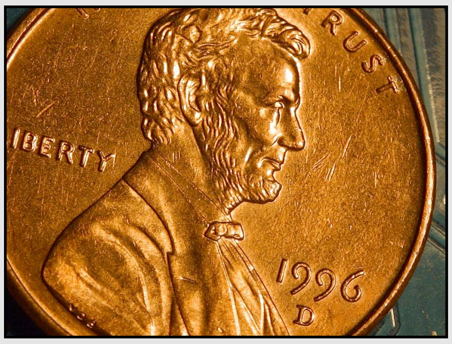
(1) Convert from mass to moles

(2) Convert moles to # of atoms

Conversely, if you were given the number of atoms present and wished to calculate the mass, you would do a two-step conversion in the opposite order than listed above. You learned how to do two-step conversions in chapter 1.

Let’s do an example problem: A 1996 US penny is comprised of 97.5% zinc and a 2.5% copper coating. **The penny contains 2.44 grams of zinc (symbol Zn). How many zinc atoms are present?**

Figure 2.10
1996 US Penny



We will need to do two steps. First we will convert from mass (grams) to moles, then we will convert moles to # of zinc atoms:

- **Conversion 1:** convert mass (2.44 grams Zn) to moles

$$\begin{array}{c|c|} 2.44\ \cancel{\text{g Zn}} & 1\ \text{mole Zn} \\ \hline & 65.39\ \cancel{\text{g Zn}} \end{array} \quad \mathbf{= 0.0373\ moles\ Zn}$$

- **Conversion 2:** convert **0.0373 moles Zn** to # of zinc atoms

$$\begin{array}{c|c|} \mathbf{0.0373\ \cancel{moles\ Zn}} & 6.022 \times 10^{23}\ \text{Zn atoms} \\ \hline & 1\ \cancel{\text{mole Zn}} \end{array} \quad = \quad \mathbf{2.25 \times 10^{22}\ Zn\ atoms}$$

Perhaps you recall the “advanced move” for doing conversions that require more than one step. Instead of doing two separate conversions, *you can combine the equations*:

$$\begin{array}{c|c|c|} 2.44\ \cancel{\text{g Zn}} & 1\ \cancel{\text{mole Zn}} & 6.022 \times 10^{23}\ \text{Zn atoms} \\ \hline & 65.39\ \cancel{\text{g Zn}} & 1\ \cancel{\text{mole Zn}} \end{array} \mathbf{= 2.25 \times 10^{22}\ Zn\ atoms}$$

Now you try one:
Convert in the opposite direction; you will be given the number of atoms in an object and you will calculate the object’s mass. **What would be the mass (grams) of a pure-gold (100% gold) coin that contained 2.00 x 10^{22} atoms?** You should get **6.54 grams** for your answer. **See next page for the complete solution.**

If you ARE a Saddleback College student, see your instructor for details and the password.

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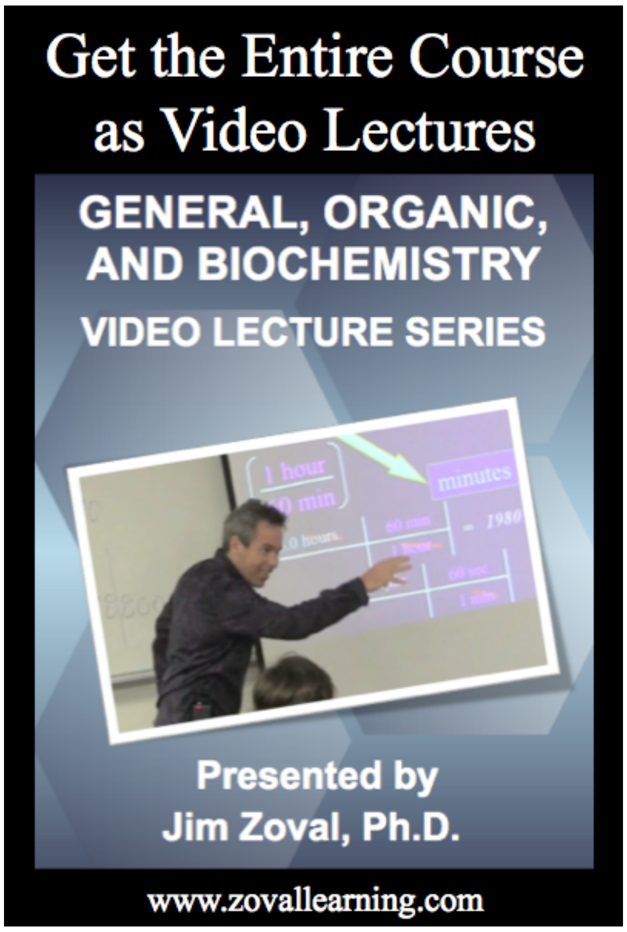


We will need to do two steps. First we will convert from number of atoms to moles, and then we will convert moles to grams:

- **Conversion 1:** convert 2.00×10^{22} Au atoms to moles

$$\begin{array}{r|c|} 2.00 \times 10^{22}\ \cancel{\text{Au atoms}} & 1 \text{ mole Au} \\ \hline & 6.022 \times 10^{23}\ \cancel{\text{Au atoms}} \end{array} = \textbf{0.0332 moles Au}$$

- **Conversion 2:** convert **0.0332 moles Au** to grams

$$\begin{array}{r|c|} \textbf{0.0332}\ \cancel{\textbf{moles Au}} & 196.97 \text{ g Au} \\ \hline & \cancel{1 \text{ mole Au}} \end{array} = \textbf{6.54 grams Au}$$

Or, *you can combine the equations*:

$$\begin{array}{r|c|c|} 2.00 \times 10^{22}\ \cancel{\text{Au atoms}} & \cancel{1 \text{ mole Au}} & 196.97 \text{ g Au} \\ \hline & 6.022 \times 10^{23}\ \cancel{\text{Au atoms}} & 1\ \cancel{\text{mole Au}} \end{array} = \textbf{6.54 grams Au}$$

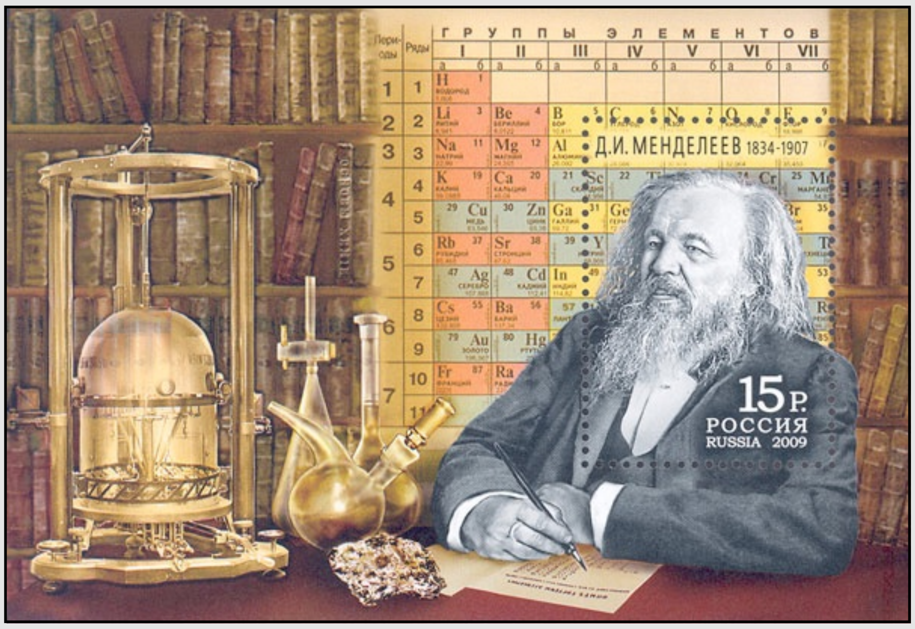
Download this worksheet for more practice with atomic molar mass:
http:www.zovallearning.com/GOBlinks/ch2/atomicmolarmassworksheetandkey.pdf

2.5 The Periodic Table

You were introduced to the periodic table earlier in this chapter. As we continue to build our model of atoms and matter in later chapters, we will gain more understanding of why the elements are arranged as they are in the periodic table and how the periodic table can be very useful in predicting the chemical and physical properties of matter. In the following section, we will learn some of the terminology used when discussing elements and the periodic table. We will also learn of some physical properties of matter that can be predicted using the periodic table.

Although Antoine Lavoisier is credited with publishing the first table of the elements, Dmitry Mendeleyeev (Figure 2.11) is credited with the first published **periodic** table of the elements.

Figure 2.11 Dmitry Mendeleyeev (1834-1907)



Dmitry Mendeleyeev is credited with the first published **periodic** pable of the elements in 1869. He is shown here in a Russian souvenir sheet stamp.
Source: Wikimedia Commons, PD

Recall from earlier in this chapter that the elements are listed in the periodic table according to the number of protons they contain (atomic number). The atomic number is shown above the element's symbol in the periodic table.

The elements can be divided into three categories based on their conductivity of heat and electricity as shown in Table 2.2.

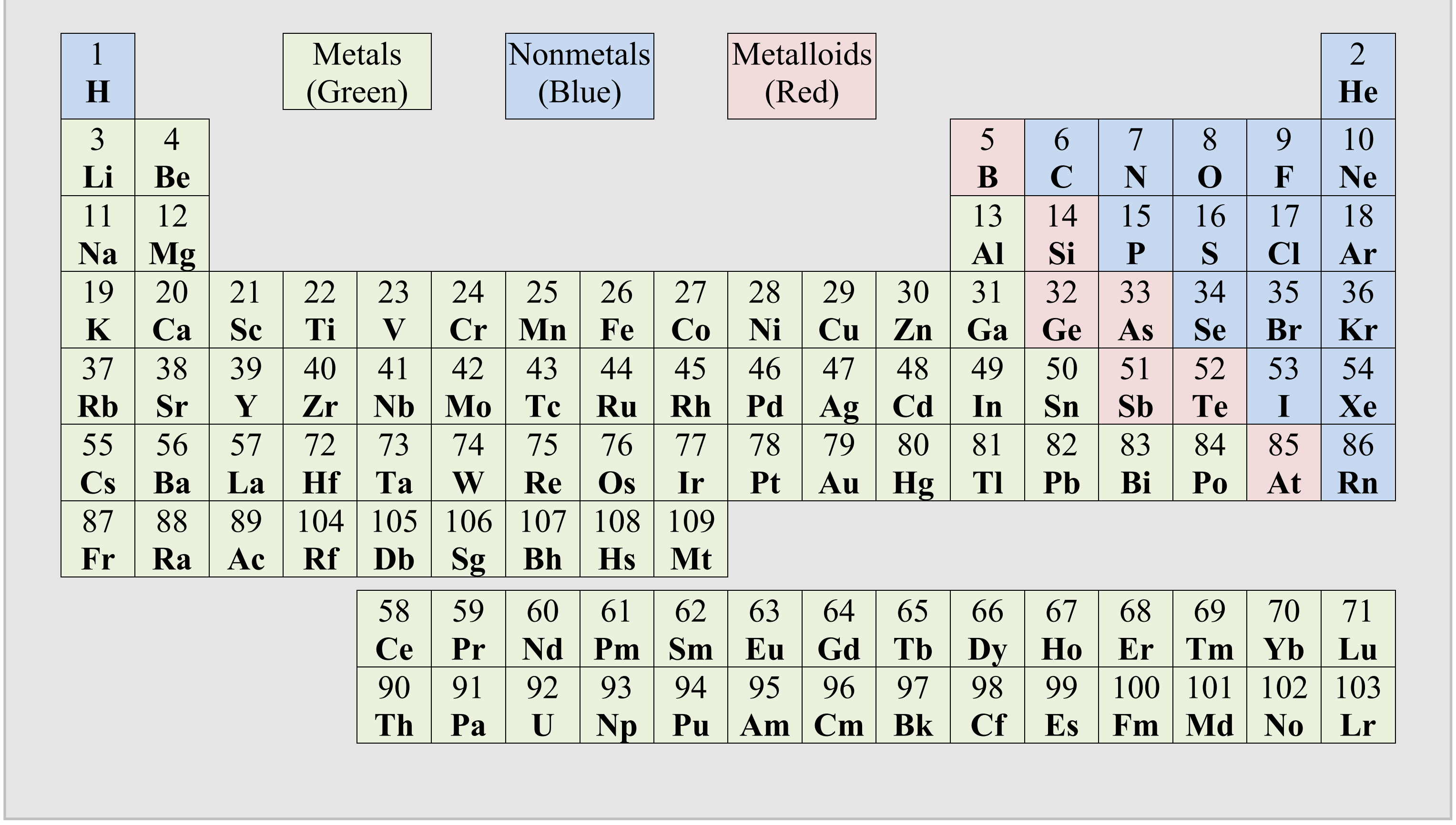
Table 2.2. Classification of Elements Based on Electrical and Heat Conduction

CATEGORY	PROPERTIES
Metals	•Good conductors of heat and electricity •Ductile (can be pulled into wires and pounded flat) •Have a luster
Nonmetals	•Poor conductors of heat and electricity •Brittle (break or shatter if bent or hammered)
Metalloids (sometimes called Semimetals)	Intermediate conductors of heat and electricity

It should be noted that although carbon is considered to be a nonmetal, one of its various crystal forms (graphite), is a good electrical conductor, and in another crystal form (diamond), it is the best-known naturally occurring heat conductor!

Figure 2.12 shows the arrangement of the elements into the three categories (metals, nonmetals, and metalloids) in the periodic table.

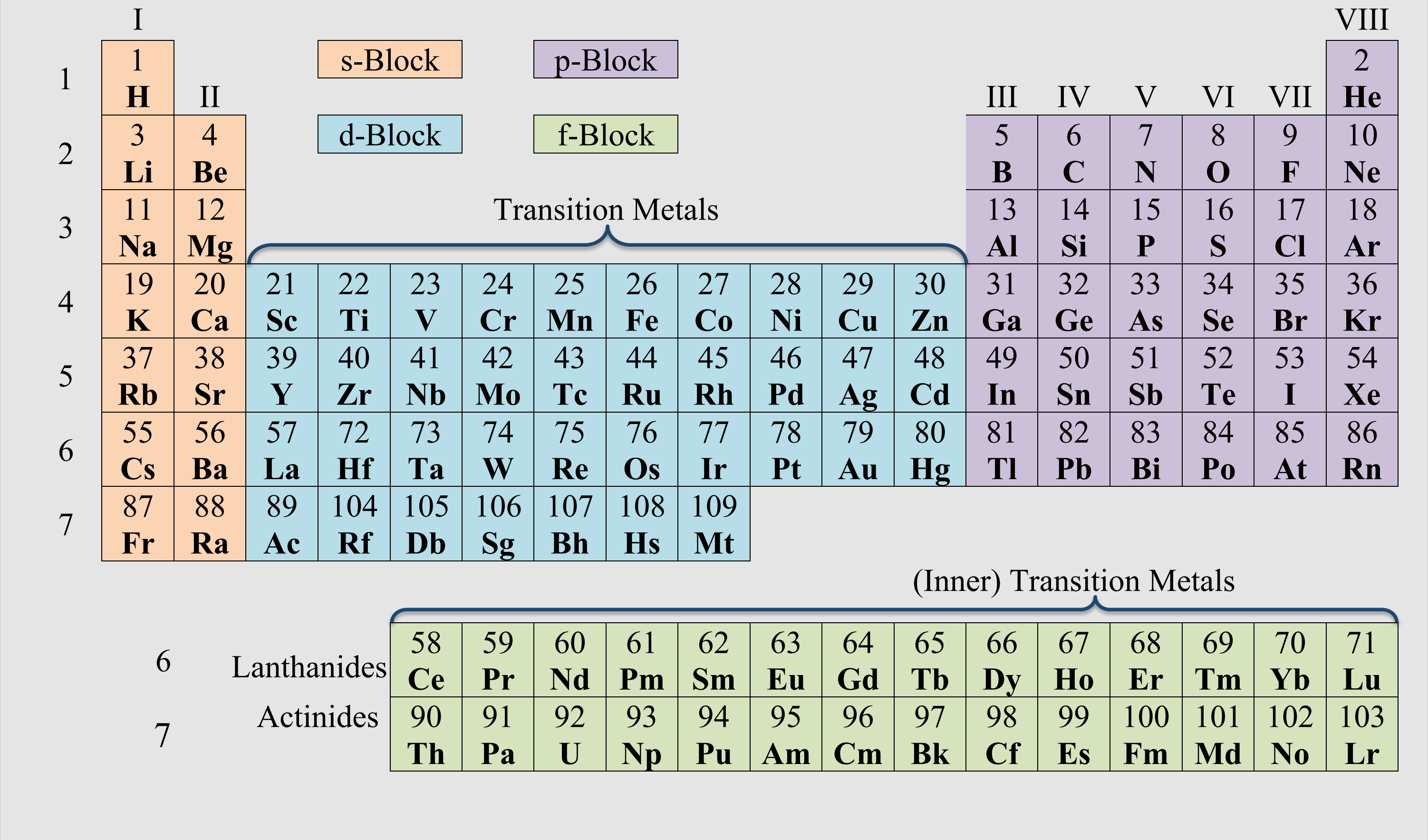
Figure 2.12 Periodic Arrangement of Metals, Nonmetals, and Metalloids



1 H			Metals (Green)			Nonmetals (Blue)			Metalloids (Red)								2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt									
				58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
				90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

Elements in the periodic table are arranged in columns called **Groups** (sometimes, but much less often, called **Families)**. Sometimes these groups are shown with **group numbers** in Roman numerals above the column as given in Figure 2.13. The elements in **Group I** (also called Group 1A) are called the ***alkali metals***. Although it is not a metal, note that hydrogen is in this group *for reasons that I will discuss in chapter 3*. The elements in **Group II** (also called group 2A) are called the ***alkaline earth metals***. The elements in **Group VII** (also called group 7A) are called the ***halogens***. The elements in **Group VIII** (also called group 8A) are called the **noble gases.**

Figure 2.13 Arrangements Blocks, Transition Metals, and Periods



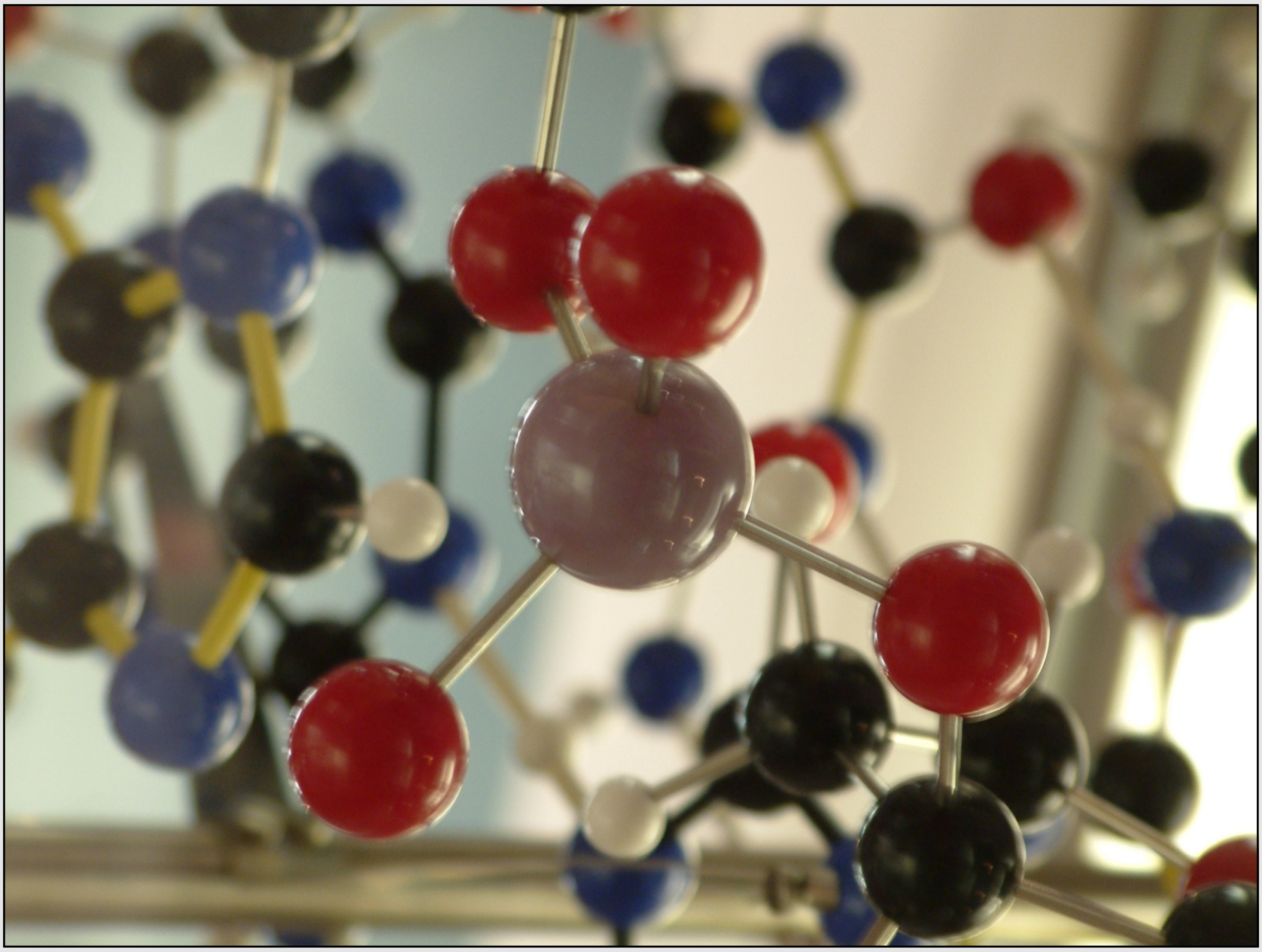
	I																	VIII
1	1 H	II		s-Block			p-Block						III	IV	V	VI	VII	2 He
2	3 Li	4 Be		d-Block			f-Block						5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg					Transition Metals						13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	89 Ac	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt									
											(Inner) Transition Metals							
6			Lanthanides		58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
7			Actinides		90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

The elements in Group I and Group II are in what is called the **s-Block.** The elements in Groups III - VIII are in the **p-Block**. The **transition metals**, *located between the s- and p-Blocks*, are in the **d-Block**. The **Inner Transition Metals**, located in the bottom two rows of the periodic table are in the **f-Block.** They are called ***lanthanides*** (top row of the *f-Block*) and ***actinides*** (bottom row of the *f-Block*). The ***rows*** in the periodic table are called **Periods.** The periods are often numbered to the left of each row. The arrangements of the s-, p-, d-, and f-blocks, transition metals, inner transition metals, and the period numbers are shown in Figure 2.13.

The *s-, p-, d-, and f-block* designations and the *period numbers* are related to the area that an element's electron(s) occupy and will be discussed in chapter 3. Most matter *does not exist as individual atoms*. Atoms will "bind" with other atoms to form compounds such as water (H_2O), carbon dioxide (CO_2), and table salt (sodium chloride). The periodic table is very useful in predicting the compounds that are formed when atoms combine and predicting the properties (behavior) of the compounds.

You can download a copy of this periodic table at:
www.zovallearning.com/GOBlinks/ch2/periodictablezovalbasic.pdf

Chapter 3: Compounds



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Most substances around us do not exist as individual atoms. Atoms will “bond” with other atoms to form compounds such as water (H_2O), carbon dioxide (CO_2), and table salt (sodium chloride). In chapter 3, we will discuss the nature of this “bonding” of atoms to other atoms. However, to understand and predict chemical bonding we will need to develop our model of the atom a bit more. We will do so by learning the details of how electrons are arranged around an atom’s nucleus.

Video Lectures for the General, Organic, and Biochemistry Course

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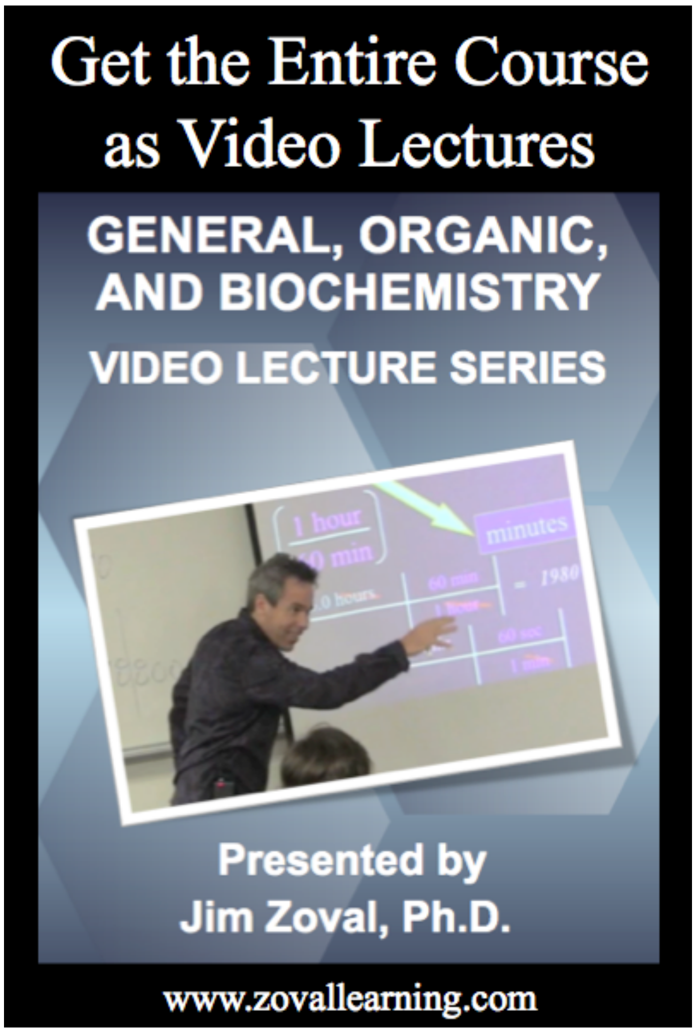


3.1 Chapter 3 Educational Goals

1. Understand where electrons are located in atoms and how the locations of electrons affect the energy of the atom.

2. Define the term **valence electron** and draw the **electron dot structure** of an atom or ion.

3. Define the term **ion** and explain how the electron dot structure of a s- or p-block element can be used to predict the charge of the monoatomic ion.

4. Given the symbol, be able to name monoatomic **cations** and **anions** (and vice versa).

5. Explain the difference between an **ionic bond** and a **covalent bond**.

6. Understand the structural difference between ionic and covalent compounds.

7. Given the name, be able to write the formulas of ionic compounds and binary covalent compounds (and vice versa).

8. Define the terms **molar mass**, **formula mass,** and **molecular mass** and use these values in unit conversions involving moles and mass.

9. Given the formula, draw the **line bond structures** of diatomic molecules.

3.2 The Arrangement of Electrons

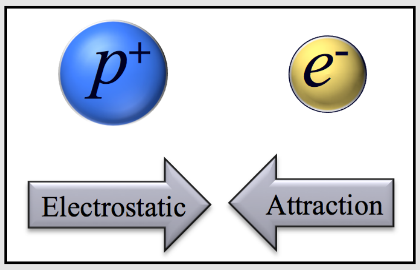
Before we learn about **compounds**, we must build on our understanding of atoms and their electrons. You have been developing your model of the atom. Recall that another word for model is theory, so you are working on **Atomic Theory**. Let's start with a review of what you have learned so far. I want you to draw an illustration of your current model of a carbon-12 atom. Show as much subatomic particle detail as you can. Stop reading now and draw the carbon atom.

Based on what you learned in chapter 2, your model should contain the following components. For the subatomic particles, you should have ***protons, neutrons,*** and ***electrons***. Carbon has *atomic number* 6, so you should have 6 protons. I asked you to draw the carbon-12 *isotope*, 12 is the *mass number* (number of protons + number of neutrons), so you should have drawn 6 neutrons. The protons and neutrons should be together in the nucleus. Since atoms (by definition) are electrically neutral, they have the same number of electrons as protons. Your model should show 6 electrons. The protons and neutrons are densely packed in the center and the electrons are dispersed around the nucleus. We called this ***incomplete*** model, the ***beehive*** model of the atom. The nucleus is represented as the beehive and the bees are represented as electrons flying around the hive. Our model of the ***nucleus*** is complete, however, in order to understand the properties of matter, you will need to learn a bit more about *how the electrons are configured* (arranged) in atoms. Specifically, in the beginning of chapter 3 you will learn:

- **Where electrons are located in atoms.**
- **How the locations of electrons effect the energy of the atom.**

Scientists used light to study how electrons are arranged around the nucleus. Energy, in the form of light or heat, can be absorbed by atoms. ***Energy is absorbed by moving an electron to a new area***. Consider a hydrogen atom. Hydrogen has one proton (+) in the nucleus and one electron (-). Electrostatic attraction works to keep the electron close to the nucleus. Energy, added by the worker in Figure 3.1, must be absorbed by the atom in order to move the electron further away from the nucleus.

Figure 3.1 Hydrogen Atom: Illustration of Energy Absorption



An electron can be moved to a region further away from the nucleus by absorbing energy. The energy in this illustration is represented by the worker's effort.

An example of light (energy) absorbed by matter is paint. Consider the red Ferrari in Figure 3.2. Sunlight, containing all the colors (white light), illuminates the car. The paint in the car ***absorbs*** the violet, blue, green, yellow, and orange light but does not absorb the red light. The car appears red because the **only** color of light reflected to the observer is red.

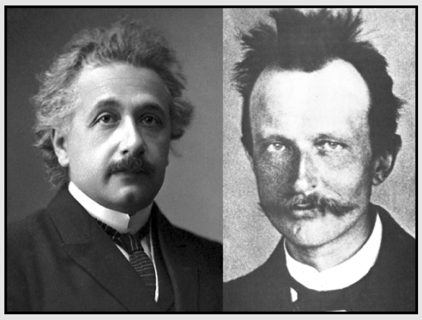
Figure 3.2 Red Ferrari 599 GTB Fiorano

The car appears red because the only color of the sun's white light not absorbed by the paint is red.
Source: Wikipedia Commons, Author: Sovxx, CC-BY-SA, http://creativecommons.org/licenses/by-sa/3.0/legalcode

Earlier in the book, I mentioned an important law that is central to understanding nature: **matter will exist in the lowest possible energy state**. Another way to say this is "if matter can lose energy, it will ***always*** do so." Energy is released when an electron that has been "excited" to a higher energy region moves back to a lower energy area closer to the nucleus. Let's consider the hydrogen atom illustrated in Figure 3.1. The worker creates an "excited state" or "high energy" hydrogen atom by moving the electron away from the nucleus. In nature, the high energy state is achieved by the atom absorbing energy from heat or light. Now imagine what would happen if the worker released the electron. If you imagined that the electron would move back toward the positive nucleus, you are correct. Because of the electrostatic attractive force, the atom is in *a lower energy state* when the electron is closer to the nucleus. To make this transition from high energy back to low energy, as nature dictates, the extra energy **must be released** from the atom. Energy is conserved, that is to say that energy *cannot be created or destroyed, it just changes forms*. One way that an atom can release energy is to collide with another atom and transfer its extra energy by increasing the velocity of the other atom. Another way to release the energy is to **emit light**. An example of light emitted by atoms is fireworks. It was when scientists were able to observe and measure the energy of the light emitted by excited atoms that the modern atomic theory was conceived.

The Modern Model of the Atom

Figure 3.3
Albert Einstein and Max Planck

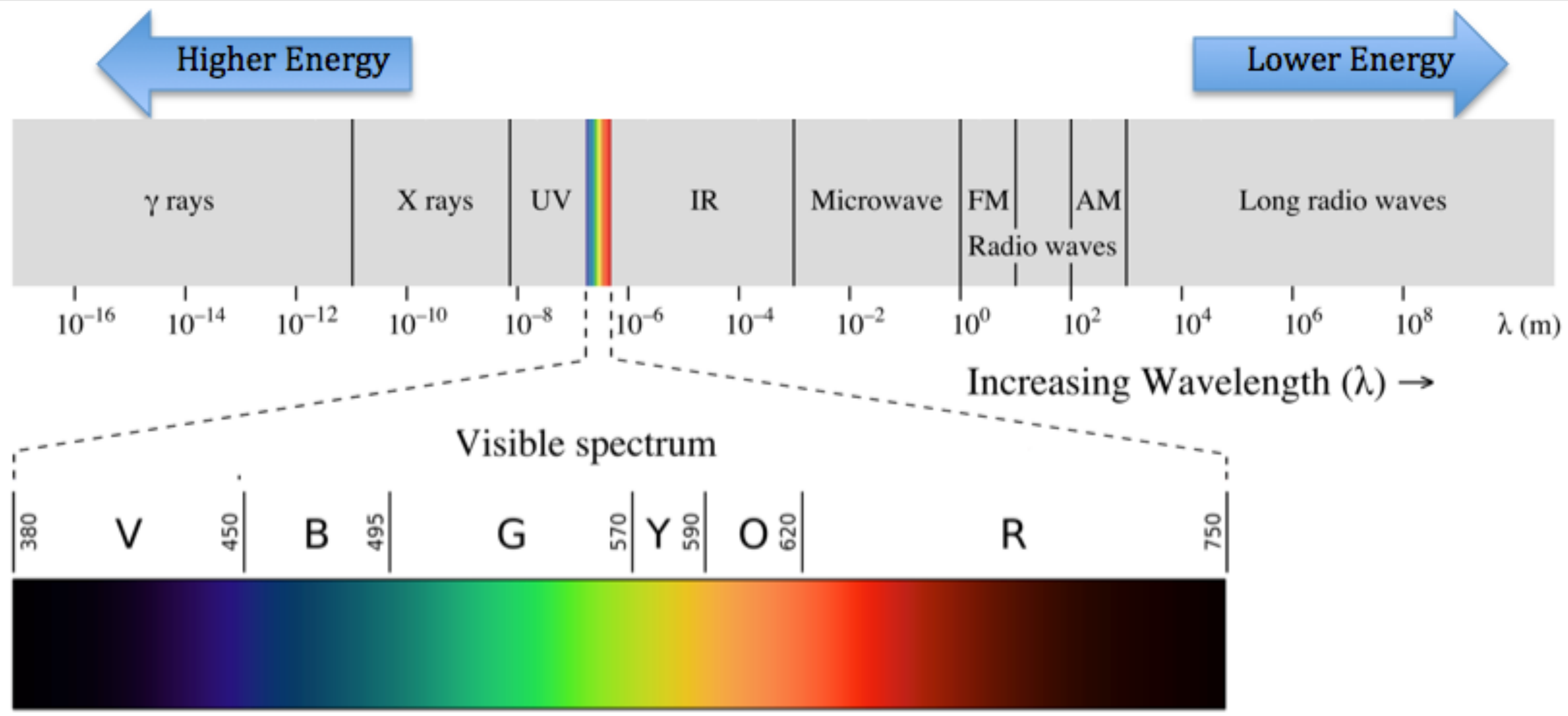


Left: Albert Einstein (1879-1955)
Right: Max Planck (1858-1947)
Source: Wikimedia Commons, US-PD

As instrumentation technology advanced during the late 1800's and the first decade of the 1900's, Dalton's atomic theory that atoms were the smallest units in nature needed to be revised. Subatomic particles were discovered. Other observations were being made at this time that could not be predicted by the "classical mechanics" physics that was pioneered by Isaac Newton. **New** scientific laws and models of nature were needed to explain and predict the latest observations. Our understanding of nature was dramatically changed when Max Planck and Albert Einstein (Figure 3.3) introduced "**quantum mechanics**." They proposed that energy is absorbed and emitted by atoms ***only*** in *discrete* amounts called **quanta**. Another word for "*discrete*" is "*distinct.*"

Classical Mechanics could not explain the pattern of **light** given off by excited (energized) atoms. Another word for ***light*** is ***electromagnetic radiation***. Visible light, the part of the electromagnetic spectrum that can be detected with the human eye, is a small part of the electromagnetic radiation spectrum. Light can be thought of in two ways; as very light particles (photons) **<u>or</u>** as waves. When described as waves, we refer to light's ***wavelength***. The *energy* of light varies (inversely) with the *wavelength* as shown in Figure 3.4. Short wavelengths correspond to higher energy, longer wavelengths correspond to lower energy light.

Figure 3.4 **The Electromagnetic Radiation Spectrum**



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Scientists observed that when light was emitted from hot gases, that the pattern of light, called the emission spectrum, was not continuous. Continuous light would appear as white light containing all the colors (energies) of the rainbow. Instead, only discrete colors/energies of light were observed. The emission spectrum from hot hydrogen atoms is shown in Figure 3.5. Recall that the light emitted from excited atoms is generated by electrons losing energy as they move from areas further from the nucleus (high energy) to areas nearer the nucleus (low energy). To lose the energy in this process, atoms emit light.

Figure 3.5 **Hydrogen Atomic Emission Spectra**

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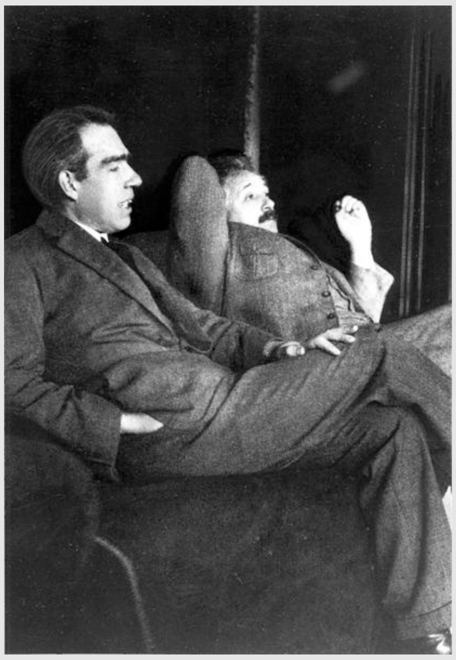
Figure 3.6
Niels Bohr (1882-1962) with Albert Einstein



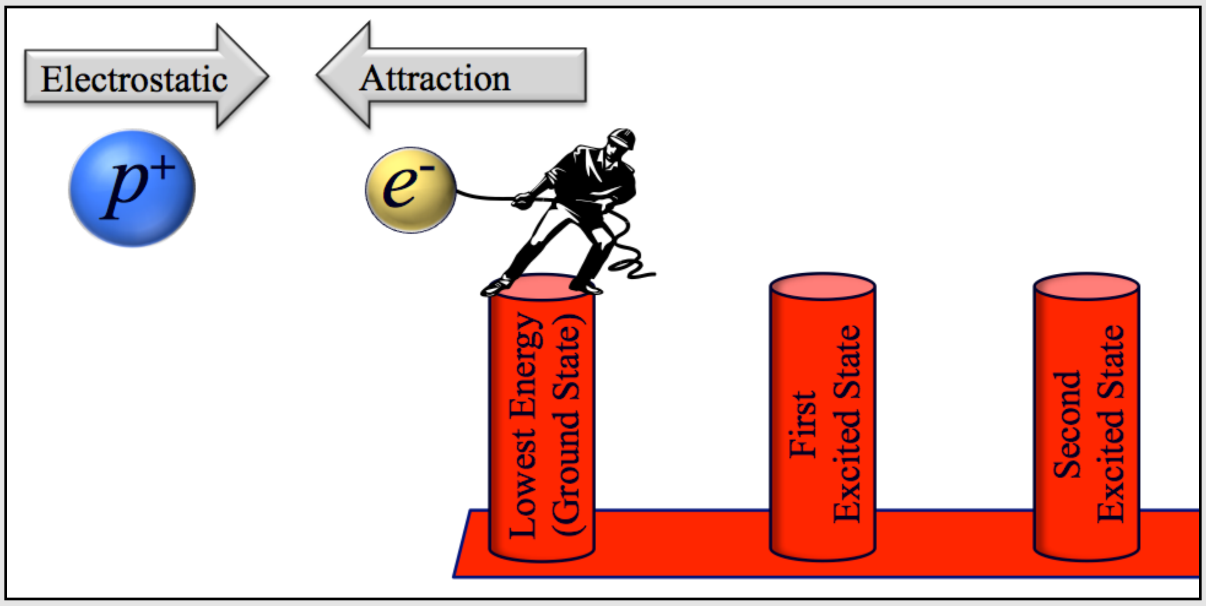
Niels Bohr (left) with Albert Einstein. Source: Wikimedia Commons, Author: Paul Ehrenfest, US-PD

The observation that only discrete energies are emitted from excited atoms is explained using an atomic model that says that the ***electrons can only exist in certain areas and therefore atoms have discrete energies***. We say that the energy of atoms is "**quantized**." You can compare quantization to the experience of buying shoes. Shoes only come in certain, distinct sizes. Just as shoe size is quantized, so are the energies that atoms can have. *Nature is interesting.* The mathematical model called quantum mechanics is used to describe atoms. The first scientist to propose a model of the atom where electrons existed in specific regions that had discrete energies was Niels Bohr. (Figure 3.6).

In the remainder of this section, I will conclude the development of our model of the atom. This will involve using some of the terminology of quantum mechanics. A complete description of quantum mechanics is far beyond the scope of the text, mainly because it requires the use of advanced mathematics.

Let me try to reinforce the concept of atoms having discrete energies. Recall our Illustration of hydrogen atom energy absorption in Figure 3.1. If the worker could pull that electron away from the nucleus and stop at ***any*** distance, then we would expect to observe ***any*** amount of energy (***any color***) to be emitted when the electron moves back to the low energy position close to the nucleus. Since the sample would contain *millions* of atoms all at various high energy positions, we would observe all colors being emitted. The emission spectra would consist of white light and when dispersed through a prism it would look like the visible spectrum "rainbow" shown in the bottom of Figure 3.4. But that ***is not what is observed***; only discrete colors are observed as seen in Figure 3.5. An illustration that can explain discrete energy emission is shown in Figure 3.7. When an atom's electron(s) are in the lowest possible energy area, we call this the **ground state**. At room temperature, all atoms will exist in their ground state unless *temporarily* excited to a higher energy area. A hydrogen atom contains only one electron and is in its ground state when that electron is in the area closest to the nucleus. As proposed by Einstein and Planck, energy is absorbed and emitted by atoms in *discrete* amounts. Absorption of a discrete amount of energy corresponds to the worker **only** being able to move to ***particular areas*** (represented by red posts) in Figure 3.7. When hydrogen's electron is in any other region than the ground state (lowest energy), we call that an **excited state** of hydrogen. We happen to live in a universe where everything tends to exist in the lowest energy state possible. Therefore, the excited atom will soon lose energy as the electron moves back to the ground state position. When the energy lost is in the form of light, that light will be the color (wavelength) corresponding to the energy difference between the initial "excited" region and the final, lower energy region.

Figure 3.7 Illustration of the "Quantized" Energy of Hydrogen



Absorption of a discrete amount of energy corresponds to the worker ***only*** being able to move the electron to *particular areas* (represented by red posts). An excited atom will lose energy as the electron moves back to a lower energy area.

The Modern Model of the Atom: Nature is Strange and Surprising

Bohr's model worked well for the hydrogen atom with *just one electron*, but not for atoms with more than one electron. Bohr's model was not correct and was eventually replaced by our current model, called the Quantum Mechanical Model. As I describe our current understanding of the atom, you will see that nature is strange and surprising. By strange and surprising, I mean that the areas electrons occupy would have been hard to predict based on "common sense." Common sense may have led us to predict that the electrons "orbit" the nucleus in the same way that planets orbit the sun. But this is not the case (though your high school chemistry teacher may have used it to explain some properties of matter). Electrons do not exist/move in two-dimensional circular paths; they exist in three-dimensional areas. Common sense would, perhaps, lead one to believe that the three-dimensional areas electrons occupy would be spherical shapes centered on the nucleus, however this is not always the case. Before I go on to describe the shapes of areas that electrons occupy and the corresponding energies of these areas, I want to restate the two basic principles that tell us why electrons are configured this way.

In Chapter 2, I discussed two key principles that are responsible for ***everything else*** we will learn about chemistry:

1. We live in a universe where everything tends to exist in the lowest energy state possible.
2. All of the chemical and physical properties discussed in this book *ultimately occur because of interaction of the charges (electrostatic attraction and repulsion).*

Let's apply these principles to the arrangement of the negatively-charged particles as they are attracted to the positive nucleus (and repelled by other electrons). The electrons are attracted to the nucleus by the natural laws that govern positive and negative charges, however these natural laws are more complex than the "classical mechanics" laws that worked well to describe large objects such as planets in elliptical orbits around the sun. For light particles moving very fast, such as electrons, electrostatic forces in nature are quite complex; they are not at all consistent with "common sense" and require a complex mathematical description called quantum mechanics. In short, electrons will be in the lowest energy regions possible, and the shapes of these regions are determined by the natural laws of physics that apply to the universe. Since a mathematical treatment of Quantum Mechanics is far beyond the scope of this book, I ask you to accept, on ***faith alone,*** my description of its features. I think you will agree that nature is indeed strange and surprising.

As you finalize your understanding of the atom, some of the details can be a bit abstract (as you may have already noticed). You can avoid getting lost in the detail (and wonder) of nature by focusing on the following two educational goals:

1. **Understand where electrons are located in atoms.**
2. **Understand how the location of electrons affect the energy of the atom.**

The Hydrogen Atomic Model

I will begin by describing a hydrogen atom. Hydrogen is unique because it has only **one** electron. After discussing the hydrogen atom, we will make a minor change to the model in order to describe all of the other atoms that contain more than one electron.

We begin with the nucleus. We do not need to add to our current understanding of the nucleus. Hydrogen contains one proton. The most abundant isotope of hydrogen is ^{1}H, mass number =1 (contains one proton and zero neutrons), however other isotopes of hydrogen contain neutron(s). The number of neutrons in an atom will not effect the arrangement of electrons in our atomic models because there are no electrostatic interactions between electrons and neutrons.

Electrons exist in certain three-dimensional regions called ***orbitals***. **NOTE**: ***orbitals*** are not the same as ***orbits***. *Orbitals* are **three-dimensional** shapes and can be contrasted to *orbits* that are **two-dimensional** circular or elliptical paths.

Orbitals can be described by these properties:

1. **The *average* distance an electron in a particular orbital is from the nucleus.**
   Since orbitals are three-dimensional and the electrons move (very quickly) within the orbitals, the distance an electron is from the nucleus is not constant (as it would be in a circular two-dimensional path). Therefore, we talk about the electron's ***average distance*** from the nucleus. Recall that the closer an electron is to the nucleus, the lower the energy because of electrostatic attraction. As orbitals get larger, the average distance of an electron from the nucleus increases, therefore the ***larger the orbital*** occupied by an electron, the ***greater the energy***. We can relate this concept to the illustration of the "quantized" energy of hydrogen shown in Figure 3.7. Moving an electron from the low energy (ground state) red post to one of the higher energy "excited state" red posts corresponds to moving the electron from the smallest orbital (electron on average closest to the nucleus) to a larger orbital.
2. **The three-dimensional shape of the orbital.**
   Not only do the sizes of orbitals vary, the shapes of orbitals vary as well. When the shapes of orbitals are shown as three-dimensional representations, the shapes represent the region that would contain the electron 90% of the time. The remaining 10% of the time, the electron would be outside of the shape that is shown in the graphic representation.

The orbitals are *centered on the nucleus,* and are labeled by a **number**. We use the symbol (**n**). In a hydrogen atom, this number is related to the orbital size and the energy of an electron in the orbital. The orbitals are numbered from lowest energy (smallest size) to higher energy (larger size). The origin of these numbers are from the mathematics of quantum mechanics and they are referred to as "energy level," or "quantum number," or "quantum level," or "shell." We will use the term "shell" or "quantum level" in this book. Now let's add the electron to the hydrogen atom. In the lowest energy state of a hydrogen atom (the *ground state*), the electron occupies the **n**=1 quantum level.

Figure 3.8
The shape of an **s** orbital

- The **n**=1 quantum level has **one** orbital.
- It is called an **s** orbital (**s** represents the ***shape* of the orbital**, we use 1**s** because **n**=1).
- **s** orbitals are **spherical** in shape. The shape of an **s** orbital is shown in Figure 3.8.
- The nucleus (not shown in the figure) is in the center of the orbital.

The electron always occupies the lowest energy state (quantum level) unless it gains extra energy. Although hydrogen has only one electron, there are many other possible higher energy orbitals that an electron can temporarily occupy if it absorbs energy. For example, the electron in hydrogen can move from the **n**=1 level to the **n**=2 quantum level (or any other quantum level) if it absorbs the amount of energy corresponding to the difference in energy between the two levels.

Let's consider the **n**=2 quantum level. Things are a bit different in this level compared to the **n**=1 level.

- The **n**=2 quantum level has **four** orbitals, as illustrated in Figure 3.9.
- There is **one s** orbital (all **s** orbitals are spherically shaped, we use 2**s** because **n**=2)
- There are **three p** orbitals (**p** represents the shape, see the three **p** orbitals in Figure 3.9, we use 2**p** because **n**=2)
  - I mentioned that the quantum mechanical nature of the universe is strange and surprising. The shape of **p** orbitals is one of the reasons I say this. The spherical shape of the s orbital may have been predictable by common sense, but who would have guessed this **p** shape?
- The **p** orbitals all have the same shape and only differ in how they are arranged around the nucleus.
- Often the *x*, *y*, and *z* subscripts ($2\mathbf{p}_x$,$2\mathbf{p}_y$,$2\mathbf{p}_z$) are used to indicate that the relative orientations of the **p** orbitals are along on the *x*, *y*, and *z* axis. The orbitals are all centered on the nucleus and the nucleus is at the origin of the *xyz* axis coordinate system.

The shape of the 2**s** orbital is spherical, very much like the 1**s** orbital, but ***larger***. Since it is larger, the average distance of an electron to the nucleus would be greater. It is for this reason that an electron in the 2**s** orbital is higher energy than an electron in the 1**s** orbital.

Figure 3.9 The Shapes of the 2s and 2p Orbitals

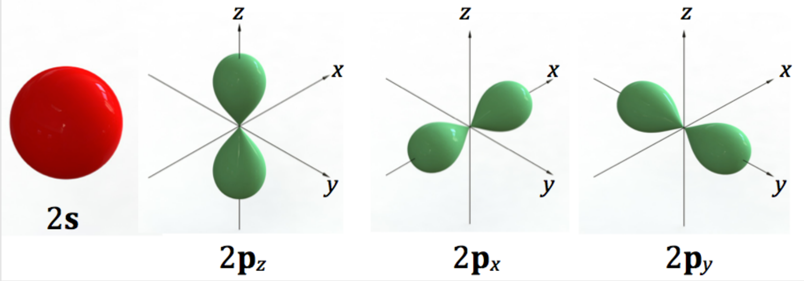
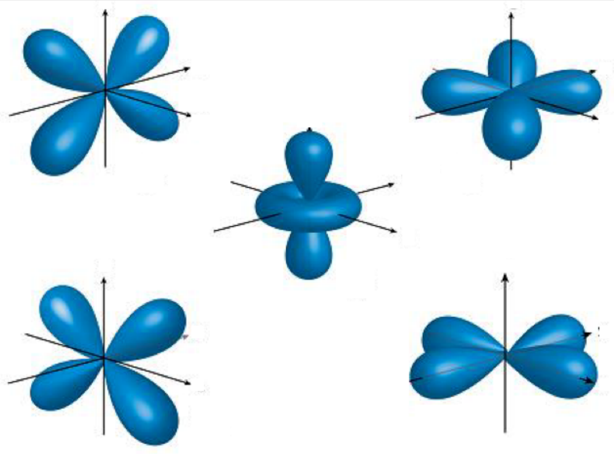


Figure 3.10
The Shapes of the **d** Orbitals



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The next quantum level is the **n**=3 level.

- The **n**=3 level has **nine** orbitals.
- There is **one s** orbital, **three p** orbitals, and **five d** orbitals.
    - The shapes of the 3**s** and 3**p** orbitals are similar to those of the 2**s** and 2**p** orbitals, respectively, but they are ***larger***.
- The **d** orbitals are illustrated in Figure 3.10.
    - *As is the case for all orbitals*, the **d** orbitals are centered on the nucleus.
    - As in the case of **p** orbital shapes, nature is again a bit strange and is not predicted by common sense! Who would have predicted any of these **d** orbital shapes, especially the one in the middle of Figure 3.10?

The next quantum level is the **n**=4 level.

- The **n**=4 level has **sixteen** orbitals.
- There is one **s** orbital, three **p** orbitals, five **d** orbitals, and **seven f** orbitals.
- The shape of the 4**s**, 4**p**, and 4**d** orbitals are similar to the 3**s**, 3**p**, and 3**d** orbitals, respectively, but they are ***larger***.
- The **f** orbitals have shapes that are even more complicated then the **d** orbitals.

The next quantum level is the **n**=5 level. The **n**=5 level has **twenty-five** orbitals. This just keeps going, **n**= 6, 7, 8, etc. Although quantum levels with **n** > 4 contain orbitals other than **s**, **p**, **d**, and **f**, these other orbitals are *never occupied by electrons of any element in its ground state*. The only time an electron can occupy any of those orbitals will be if the atom absorbs energy. In that case, the electron will momentarily occupy the excited state orbital, then lose the extra energy and move back to the ground state orbital.

Energy Level Diagram for Hydrogen

As a hydrogen atom's orbitals get larger with increasing quantum numbers (**n**), the average distance from the electron to the nucleus increases, therefore the e*nergy of the orbital increases*. We can organize the various atomic orbitals according to their energy in an illustration called an **energy level diagram**. Figure 3.11 shows the energy Level diagram for the first five quantum levels (**n** = 1-5).

In an **energy level diagram,** we draw a short horizontal line that is labeled for each orbital. The orbitals are arranged, from bottom to top, in order of increasing energy. Each electron is depicted as an ***arrow*** above the line that represents the orbital occupied by it. Since an electron occupies the lowest possible energy orbital, we place an arrow in the 1**s** orbital as seen in Figure 3.11.

Figure 3.11 **Energy Level Diagram for Hydrogen**

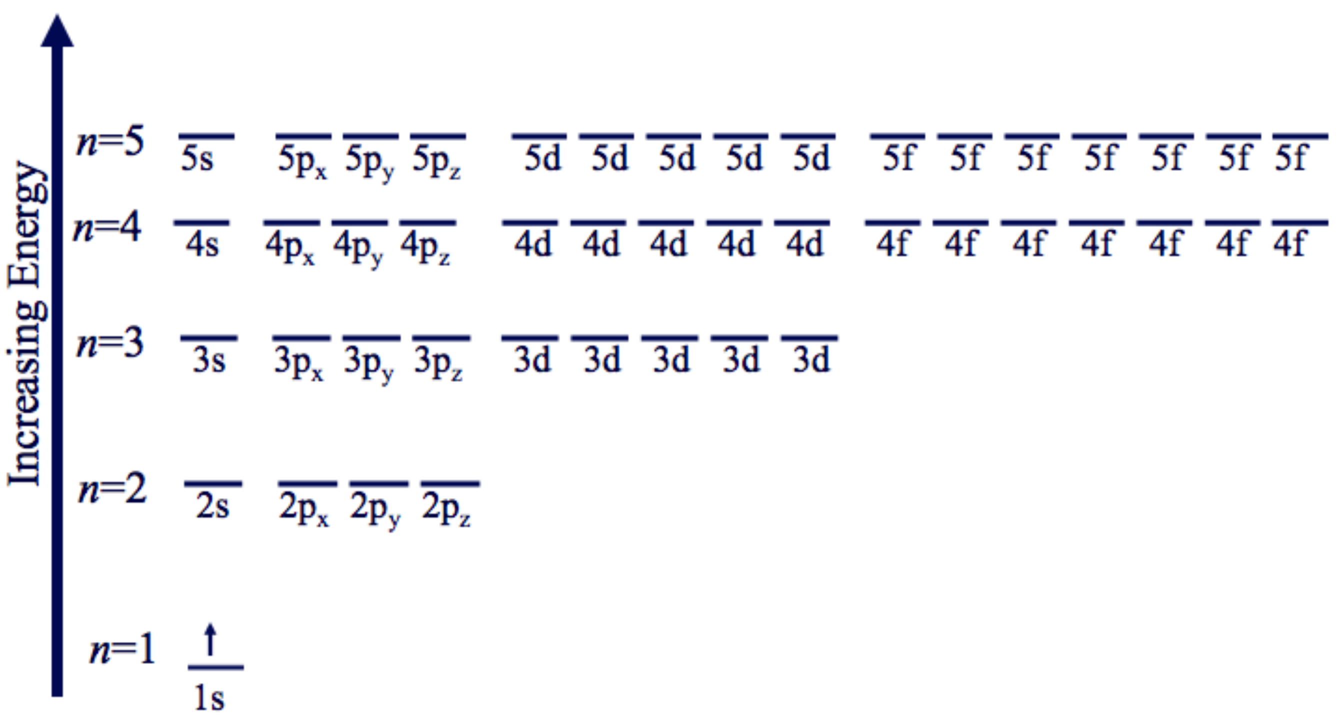
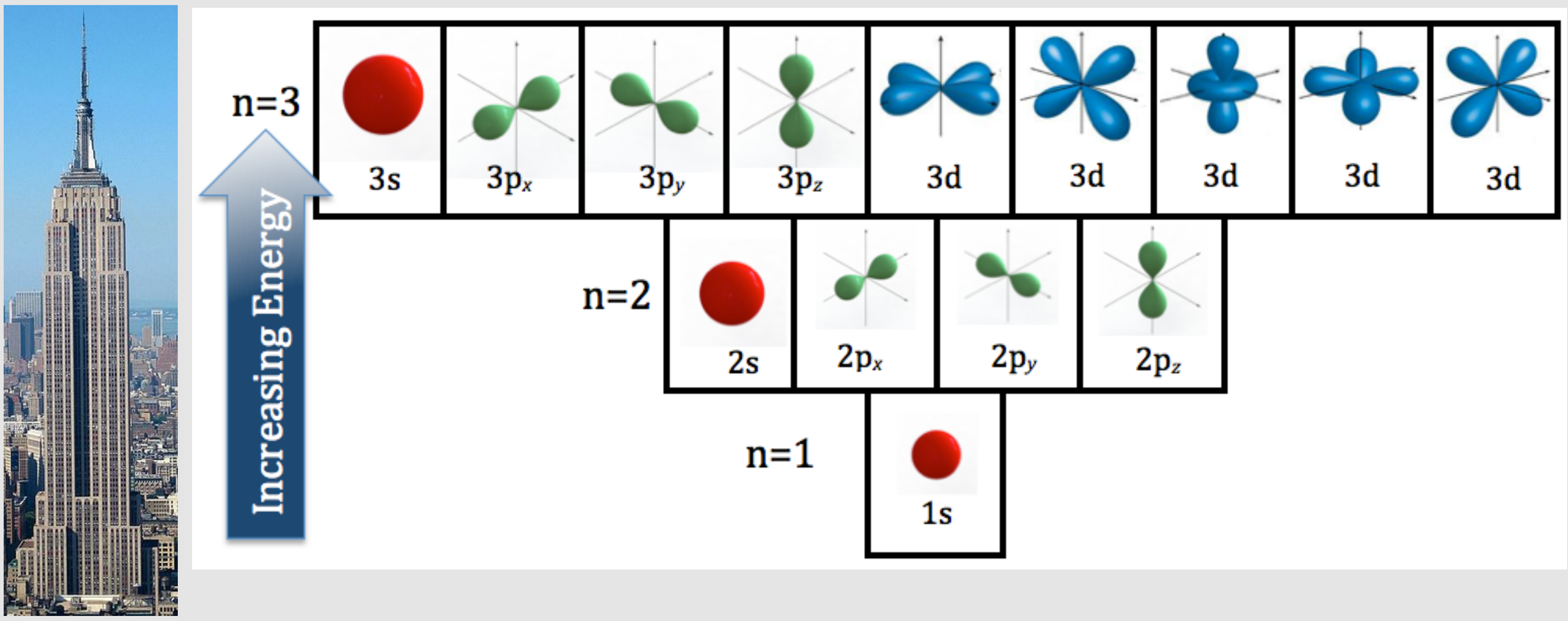


Figure 3.12

Skyscraper Model of the Hydrogen Atomic Quantum Levels and Orbital Shapes



In the skyscraper model of atomic quantum levels and orbitals, the quantum (**n**) levels represent floors/levels in a skyscraper. The various orbitals in each quantum level represent rooms on that floor/level.
Skyscraper image source: Wikimedia Commons, Author: Avala CC-BY-SA, http://creativecommons.org/licenses/by-sa/3.0/legalcode

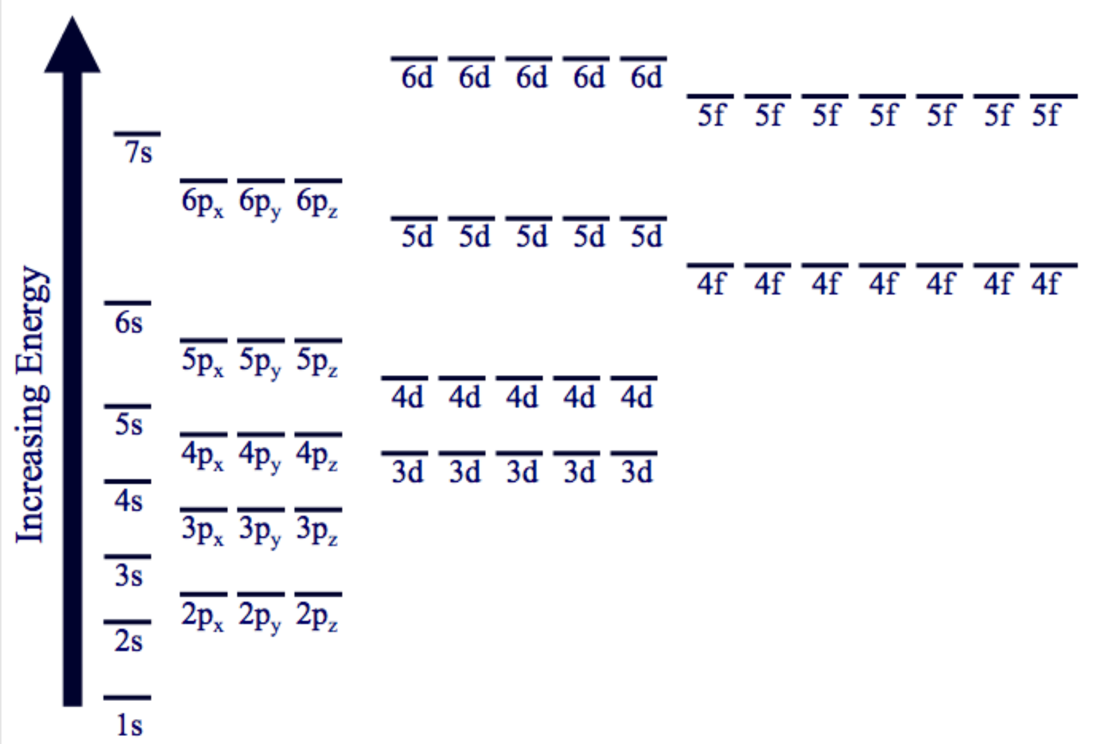
Since all of this can seem abstract and confusing, I want you to consider an analogy to help you understand atomic orbitals and their energies. Let's compare the energy level diagram to a *skyscraper*, we will call this our **skyscraper model**. The different floors of the skyscraper represent the quantum levels (**n**) as illustrated in Figure 3.12. The first floor is the lowest energy floor so it would correlate with **n**=1, the ground state. The second floor is higher in energy than the first floor. If you wanted to go from the first floor to the second floor, you would need to use some energy climbing up the stairs. The second floor represents the **n**=2 orbitals. The higher the floor, the more energy - just like the hydrogen atom, the larger the value of **n**, the greater the energy. In a particular floor, you could have one or more rooms. Rooms on a particular floor are analogous to the various orbitals in a particular *quantum level*. In our skyscraper model, the *first floor* has just **one room** representing the only orbital in the **n**=1 level (the 1**s** orbital). Our skyscraper has ***four*** rooms on the *second floor*, representing the ***four*** orbitals in the **n**=2 quantum level (the 2**s**, 2**p**$_x$, 2**p**$_y$, and 2**p**$_z$ orbitals). Our skyscraper has ***nine*** rooms on the *third floor*, representing the ***nine*** orbitals in the **n**=3 quantum level (the 3**s**, 3**p**$_x$, 3**p**$_y$, 3**p**$_z$, and the *five* 3**d** orbitals). This just keeps going; the *fourth floor* has sixteen rooms, etc. The *energy level diagram* in Figure 3.11 and the *skyscraper model* are useful in achieving two important educational goals:

1. **Understand where electrons are located in atoms.**
    - Electrons occupy three-dimensional regions called orbitals, the orbitals are labeled 1**s**, 2**s**, 2**p**, etc. in *energy level diagrams* (Figure 3.11) and are drawn *and* labeled in our *skyscraper model* (Figure 3.12).
2. **Understand how the location of electrons effect the energy of the atom.**
    - The relative energies of the various atomic orbitals are shown in both the energy level diagram and the skyscraper model.

Atomic Model for Multi-Electron Atoms

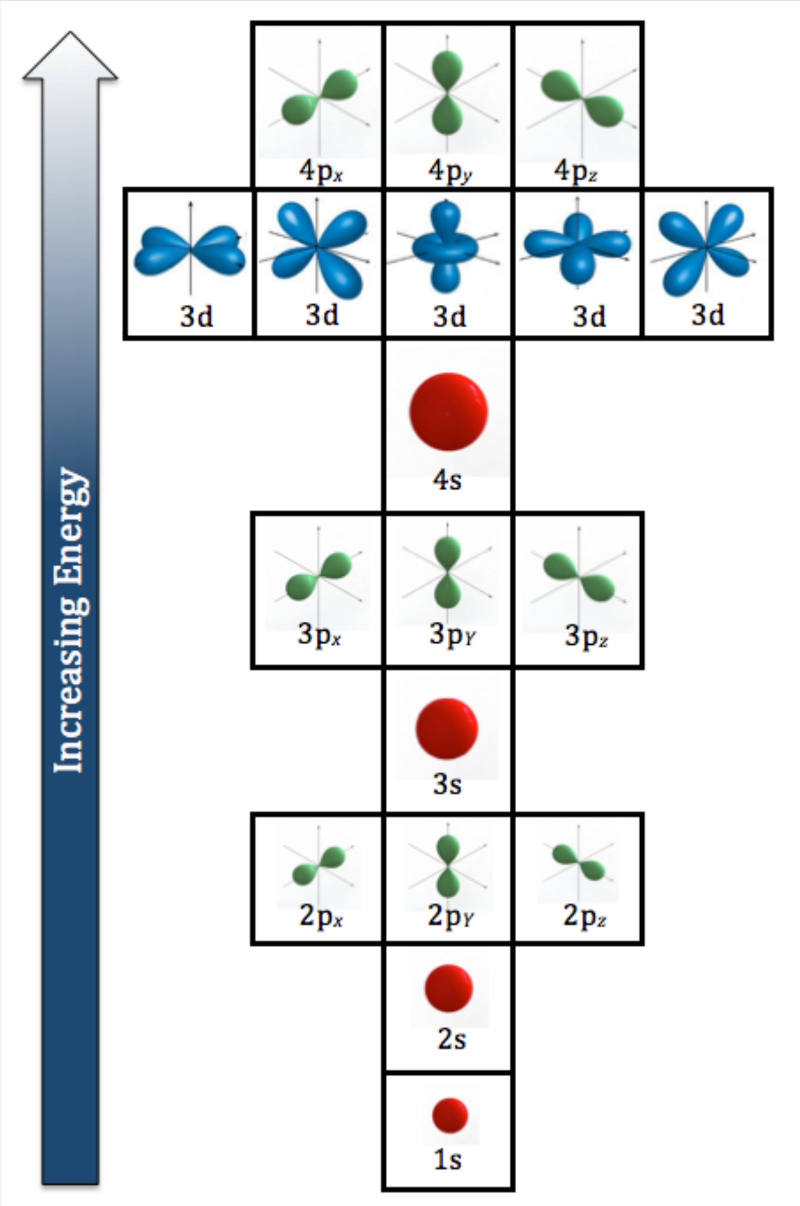
You just learned about the orbitals and their energies for the *hydrogen atom*. The hydrogen atom is a special case because it involves only **two** charged particles, the nucleus and one electron. When there is *more than one electron present*, as is the case for all atoms other than hydrogen, in addition to the **electrostatic attraction** between the nucleus and the electrons, there also exists **electrostatic repulsion** between the electrons. This causes some changes to the relative energies of the various atomic orbitals. The results of the nature of the added electron-electron electrostatic repulsion can be seen in the energy level diagram for multi-electron atoms in Figure 3.13. The important difference between the hydrogen energy level diagram and the multi-electron energy level diagram is that orbitals in the same quantum level (**n**) are no longer all at the same energy level. For example, in the hydrogen atom, the 2**s**, $2\mathbf{p}_x$, $2\mathbf{p}_y$, and $2\mathbf{p}_z$ orbitals all have the same energy, however in multi-electron atoms the 2**s** and 2**p** orbitals have different energies. The 2**p** orbitals are higher in energy than the 2**s** orbital in multi-electron atoms. The same is true for the other quantum levels. Look at the **n**=3 level for multi-electron atoms in Figure 3.13. You see that the *five* 3**d** orbitals are higher energy than the three 3**p** orbitals, and that the 3**p** orbitals are higher energy than the 3**s** orbital. We can adapt our skyscraper model to visualize the relative energies and the shapes of the various atomic orbitals in multi-electron atoms, as shown in Figure 3.14.

Figure 3.13 Energy Level Diagram for Multi-Electron Atoms



The important difference between the hydrogen energy level diagram and this multi-electron energy level diagram is that the **s**, **p**, **d**, and **f** orbitals in the same quantum level (**n**) are no longer all at the same energy level.

Figure 3.14 Skyscraper Model of the Orbital Energies for Multi-Electron Atoms



Arrangement of the Electrons in Multi-Electron Atoms

We live in a universe where matter exists in the lowest possible energy state. Electrons are arranged (configured) into the orbitals of multi-electron atoms in the way that results in the lowest possible energy. Nature does this by obeying the following principles:

1) The Aufbau Principle

"Aufbau" (German) means *build-up* or *construct*. The aufbau principle states that an electron occupies the ***lowest energy orbital that can receive it***.

2) The Pauli Exclusion Principle

An orbital can hold a maximum of **two** electrons. Electrons have a quantum mechanical property called **spin**. Similar to an electrical charge being either **+** or **-**, spin has just two possible states. We call the spin states "**up**" or "**down.**" *When two electrons occupy the same orbital, one electron has spin "**up**" the other has spin "**down.**"* Having two electrons in the same orbital with opposite spin states is lower in energy than when both spins are the same. **This is all that you need to know about spin** to understand all of the concepts covered in this textbook. You may find it interesting that spin is responsible for magnetic properties of matter. In fact, spin is the reason that electrons behave as tiny magnets!

3) Hund's Rules

i) When electrons are configured into orbitals that all have the same energy, for example the 2**p**$_x$, 2**p**$_y$, and 2**p**$_z$, a ***single electron*** is placed into **each** of the equal-energy orbitals before a second electron is added to an occupied orbital.

ii) When electrons are configured into a *set of orbitals* that all have the same energy, the spins of the first electrons to be placed into each orbital are all in the same state (for example all "up"). I will elaborate in an upcoming example of a carbon atom.

Both of Hund's Rules are caused from nature's tendency to minimize the energy. **You will have a chance to gain more understanding of Hund's Rules, the Pauli Exclusion Principle, and the Aufbau Principle in some of the examples that follow.**

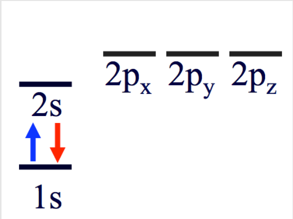
The quantum mechanical nature of the atom is quite abstract (strange). This can be especially true for a first year chemistry student. I do have some good news for you now! The atomic theory that you just read about is the most abstract concept that is discussed in this book. In order to help you solidify the model of the atom that you are constructing, let's apply the model to some specific atoms.

Example: How are the electrons configured in a helium atom?
Solution: A good way to understand the electron configuration is to draw an energy level diagram.

Energy level Diagram for Helium:

- A helium atom has two electrons. We use the multi-electron energy level diagram on all atoms other than hydrogen! An electron is *represented* by an ***arrow*** in an Energy Level Diagram. We will use an *upward*-pointing arrow to represent the spin "**up**" state and *downward*-pointing arrow to represent the spin "**down**" state.
- *The first electron* occupies the 1**s** orbital according to the ***Aufbau Principle***. This electron is represented by the **blue arrow** in Figure 3.15. We will put the spin in the "up" position.

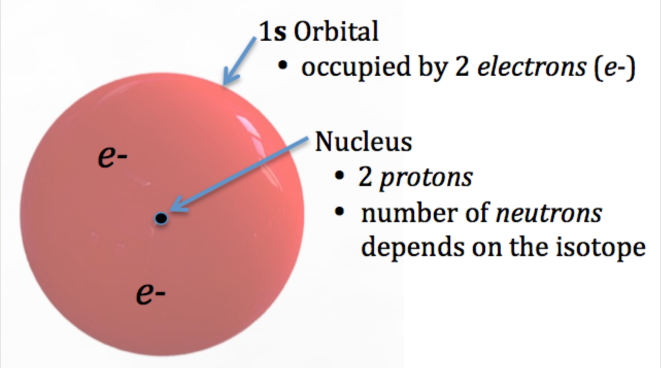
Figure 3.15 Energy Level Diagram for Helium



- Note that the Helium energy level diagram in Figure 3.15 does not include as many high energy orbitals (**n** >2) as were shown in Figure 3.13. There are an infinite number of quantum levels possible for all atoms, however, since helium *only has two electrons* and we are only concerned with the ***ground state*** (lowest energy state), we do not need to include so many high energy orbitals since they will not be occupied by electrons.
- Where do we put *the second electron*? Do we put it in the 1**s** or in the 2**s** orbital? According to the **Aufbau Principle**, an electron occupies the ***lowest energy orbital that can receive it***. The **Pauli Exclusion Principle** tells us that an orbital can hold (a maximum of) two electrons. The lowest energy orbitals must be filled with electrons before electrons can occupy higher energy orbitals!Therefore, the *second electron* will occupy the 1**s** orbital. Note that although I chose to show the 2**s** and 2**p** orbitals in the helium energy level diagram, they are not occupied by electrons in helium's ground state.
- Finally, we need to determine the spin state of the second electron. According to the **Pauli Exclusion Principle**, the spin's of electrons that occupy the same orbital must be in opposite directions. Since we arbitrarily put the first electron into the 1**s** orbital with its spin "up," we put the second electron into the 1**s** orbital with its spin "down." The *second electron* is represented by the **red arrow** in Figure 3.15.
    - Although ***we will not need to use information on spin "up" or "down"*** to master the concepts of this textbook, we will use spin states in our energy level diagrams because that is a convention (practice) used by chemists.

The information from the energy level diagram can be combined with our understanding of the nucleus to draw an illustration of a helium atom (Figure 3.16). Note that the nucleus is not drawn to scale with the orbital. If drawn to scale in the figure, the nucleus would be too small to see even if you used a light microscope!

Figure 3.16 Model of a Helium Atom



Note that the nucleus is not drawn to scale with the orbital. The number of neutrons in the nucleus depends on the isotope. For example, if this atom was ^{4}He, there would be 2 neutrons.

Do you recall when I asked you to draw a carbon atom in the beginning of this chapter? **Try it again now.** You can start by making an multi-electron energy level diagram (see Figure 3.13) for carbon. Next, draw the electron-occupied orbital shapes, centered on the nucleus. Finish your drawing of the carbon atom by adding the electrons to the appropriate orbitals. It may help to look at the multi-electron skyscraper model (Figure 3.14) while making your drawing.

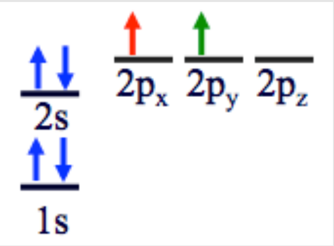
If you saved your original carbon atom drawing from Chapter 2, compare it to the drawing that you just made. If your drawing has changed since the first time you made it, that is because your mental model of the atom has changed. In the education business, we call that *learning*. Let's check your model.

Example: Draw a carbon atom.
Solution: We will begin by constructing an energy level diagram.

Energy level Diagram for Carbon:

- A carbon atom has 6 electrons. We use the multi-electron energy level diagram.

Figure 3.17 Energy level Diagram for Carbon



- *The **first and second electrons*** occupy the 1**s** orbital according to the ***Aufbau Principle***.
- Note that the carbon energy level diagram in Figure 3.17 does not include as many high energy orbitals (**n** >2) since carbon *only has six electrons*.
- Since the 1**s** orbital is now full (orbitals hold a maximum of two electrons), *the **third and fourth electrons*** occupy the 2**s** orbital.
- The ***fifth electron*** goes into any one of the three 2**p** orbitals. The three 2**p** orbitals all are equivalent in energy. They are identical and indistinguishable; they only differ in their *x,y,z*-axis orientation. We will arbitrarily choose to put the ***fifth electron*** into the $2\mathbf{p}_x$ orbital (represented by the red arrow in Figure 3.17).
- The ***sixth electron*** goes into one of the other *unoccupied* 2**p** orbitals. Recall **Hund's Rule (i)**: when electrons are configured into orbitals that all have the same energy, a ***single electron*** is placed into **each** of the equal-energy orbitals before the second electron(s) is added to an occupied orbital. We can put the sixth electron into either the $2\mathbf{p}_y$ or $2\mathbf{p}_z$ orbital. I arbitrarily chose to put the ***sixth electron*** into the $2\mathbf{p}_y$ orbital (represented by the green arrow in Figure 3.17).
- How did we know to put the spin state of the sixth electron in the "up" state? **Hund's Rule (ii)** explains that when electrons are configured into a *set of orbitals* that have the same energy, the spins of the first electrons to be placed into each orbital are all in the same state (for example all "up").

Another useful method for determining how electrons are configured in atoms is to represent the electrons as arrows in the skyscraper energy level model as shown for our carbon atom in Figure 3.18.

The information from the energy level diagram can be combined with our understanding of the nucleus to draw an illustration of a carbon atom (Figure 3.19). The nucleus contains **six** protons. The 1**s** orbital and the 2**s** orbital each contain two electrons. Two of the 2**p** orbitals contain one electron each and the third 2**p** orbital is unoccupied. The number of neutrons in the nucleus depends on the isotope. For example, if this atom was ^{12}C, there would be **six** neutrons.

Figure 3.18
Skyscraper Model for the Orbital Energies of Carbon

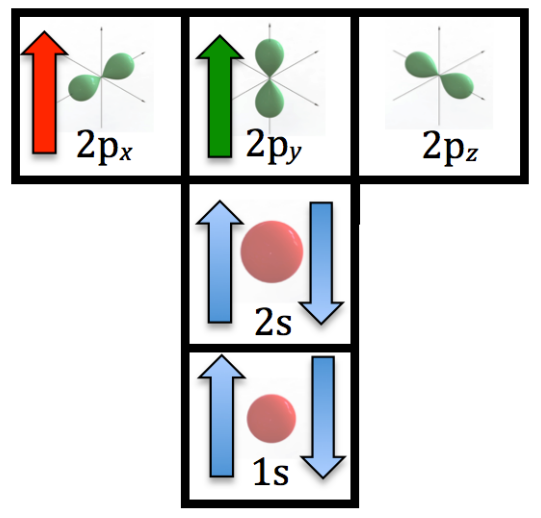
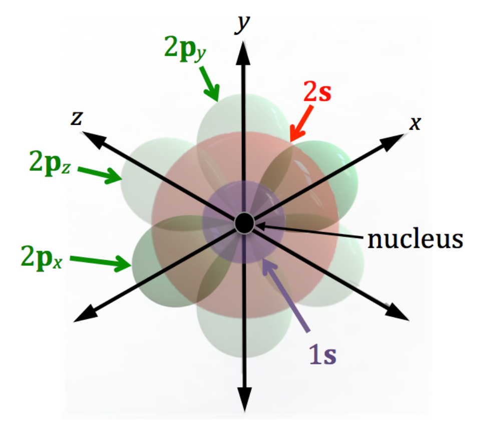


Figure 3.19
Model of the Carbon Atom Illustration



Note that the nucleus is not drawn to scale with the orbitals. If the nucleus was drawn to scale, it would be smaller than the size of a single bacteria cell.

You now know the modern theory of the atom!

- You know about the nucleus (protons and neutrons).
- You know about the electrons (energies, orbitals, and how the electrons are arranged in orbitals).

Review 3.1: Drawing Energy Level Diagrams

Draw an energy level diagram for the oxygen (O) atom.

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

Review 3.2 Drawing Energy Level Diagrams

Draw an energy level diagram for the krypton (Kr) atom.

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

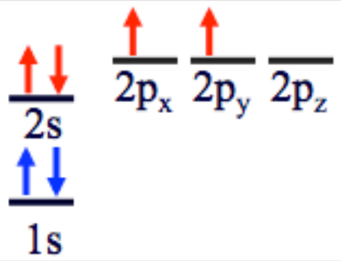
3.3 Valence Electrons

Valence electrons are the electrons held in the quantum level with the greatest value of **n**. In s- and p- block elements (recall Figure 2.13), these are the electrons that are *furthest* from the nucleus and therefore the least "*tightly*" held to the nucleus. They are the least "tightly" held because electrostatic attractive force decreases as the distance between the negative electron and the positive nucleus increases. It is important to know how many valence electrons are in an atom for two reasons:

1. These are the electrons that are involved in **chemical bonding** to other elements to form **compounds**.
2. These are the electrons that some elements lose to become **ions**.

I realize that I have not defined some of the above terms! Please be patient, the following sections of chapter 3 will focus on building your understanding of the terms **chemical bonding**, **compounds**, and **ions**.

Figure 3.20
Energy Level
Diagram for Carbon



Example: How many valence electrons does a carbon atom have?

Solution: Start with our definition of **valence electrons**: the electrons held in the quantum level with the ***greatest value*** of **n.** We can easily visualize this by constructing an *energy level diagram* for carbon as shown in Figure 3.20. Carbon has electrons in the **n**=1 (1**s**) and the **n**=2 levels (2**s**, 2p_x, and 2p_y). The electrons held in the quantum level with the greatest value of **n** are obviously the electrons in the **n**=2 level. Carbon has two electrons in the 2**s** orbital and two electrons in the 2**p** orbitals, therefore ***carbon has four valence electrons***. The valence electrons are represented by the red arrows in Figure 3.20. These are the electrons that are furthest from the nucleus, least "tightly" held by the nucleus, and will be involved in bonding to other atoms when carbon compounds, such as carbon dioxide (CO_2), are formed. The two electrons in the 1**s** orbital (represented by blue arrows in Figure 3.20) are called ***core electrons*** and are not involved in chemical bonding.

Review 3.3: Determining the Number of Valence Electrons in Oxygen

How many valence electrons do oxygen (O) atoms have?

For ***i-book*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

Review 3.4 Determining the Number of Valence Electrons in Krypton

a) Look at the energy level diagram that you drew for **krypton (Kr)** in Review Problem 3.2 in the previous section. If you have not drawn the energy level diagram yet, do so now and check your answer before proceeding with this problem.
b) **Circle the orbital(s)** that contain the **valence electrons**.
c) How many valence electrons do krypton atoms have?

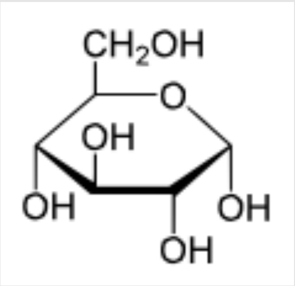
For ***i-book*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

Now that you understand how to determine the number of valence electrons from the electron configuration of an atom, I would like to show you a short cut. ***Elements are arranged in the periodic table according to the number of valence electrons.*** Therefore, it is possible to determine the number of valence electrons from an atom's location in the periodic table. For s- and p-block elements, all elements in the same periodic column (group) have the same number of valence electrons as all others in that column. When two atoms have the same number of valence electrons, we call that **isoelectric**. *Isoelectric* atoms often behave in similar ways. For example, oxygen atoms often chemically "bond" to two hydrogen atoms to form water (H_2O); sulfur atoms, which are ***isoelectric*** with oxygen (same column on the periodic table and also has six valence electrons), often "bond" with two hydrogen atoms to form hydrogen sulfide (H_2S). Recall that the columns in periodic table for the s- and p-block elements are labeled with **group numbers** above the column (often in Roman numerals). The group numbers for the columns *represent* the number of valence electrons contained in those atoms. For this reason, the s- and p-block elements are sometimes called the "**representative elements**"; their group number ***represents*** the number of valence electrons. When you did an earlier review exercise, you found that oxygen had six valence electrons. That is why oxygen is in Group VI. You found that krypton had eight valence electrons. That is why krypton is in Group VIII.

Electron Dot Structures

You may have seen drawings of compounds such as glucose shown in Figure 3.21. The lines in these drawings indicate that the valence electrons that were present in the atoms have formed "bonds" to other atoms. In order for you to understand this type of bonding pattern, I will ask you to first participate in the academic exercise of drawing ***electron dot structures*** of atoms. *Electron dot structures* show the number of *valence electrons* that an atom carries. In these structures, *valence electrons are represented by* ***dots***.

Figure 3.21 Glucose

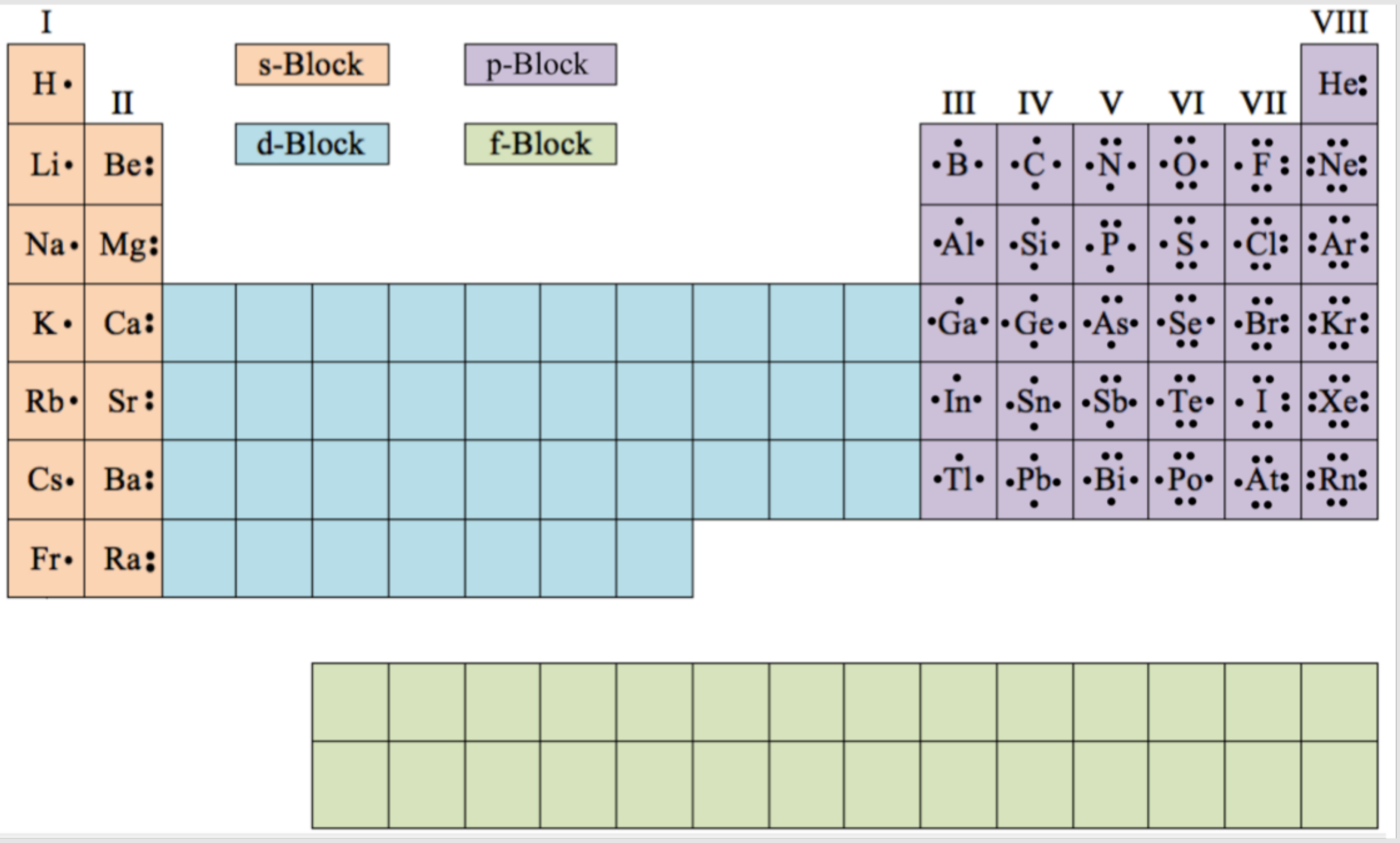


Consider the **s**-block elements. We know that the elements in the Group I column are **isoelectric** and have <u>one</u> valence electron. **Electron Dot Structures** of Group I elements show one dot next to the element's symbol as seen in Figure 3.22. The elements in the Group II column are **isoelectric** and have <u>two</u> valence electrons. We draw two dots next to the element's symbol (2 dots = 2 electrons).

Next, consider the **p**-block elements. Draw single dots around the element's symbol until the fifth dot, then pair the dots as shown in Figure 3.22 . Note that helium (He) is an exception, it is in Group VIII, however it has only two valence electrons! The reason for this will be given in the discussion the **noble gases** (our next topic).

Figure 3.22

Periodic Table with Electron Dot Structures



Noble Gases and The Octet Rule

The Group VIII elements (He, Ne, Ar, Kr, Xe, and Rn) belong to the **noble gas family**, which gets its name from the fact that these elements are resistant to change and, with few exceptions, do not lose or gain electrons. This observation is related to the ***scientific law*** that I have been stating often; we happen to live in a universe where matter will exist in the lowest possible energy state. So if matter is in the lowest energy state possible, it will never spontaneously change into a higher energy without energy being added from an external source! When you hear the term stable, un-reactive, or resistant to change, you should think of that as a l*ow energy state*. When you hear the term unstable, reactive, or explosive, it indicates a high energy state. The resistance to change (stability) of the noble gases is related to having their outermost quantum level (*also called* ***outermost shell***) completely filled with electrons. You can verify this by constructing energy level diagrams of any noble gas element. Helium's outermost shell (the n=1 quantum level) is completely filled with its two electrons. ***All of the other noble gas elements*** have completely filled outermost shells with ***eight*** electrons. This stability of those noble gas elements that have ***eight*** electrons in their outermost shell led to what chemists call the **Octet Rule.**

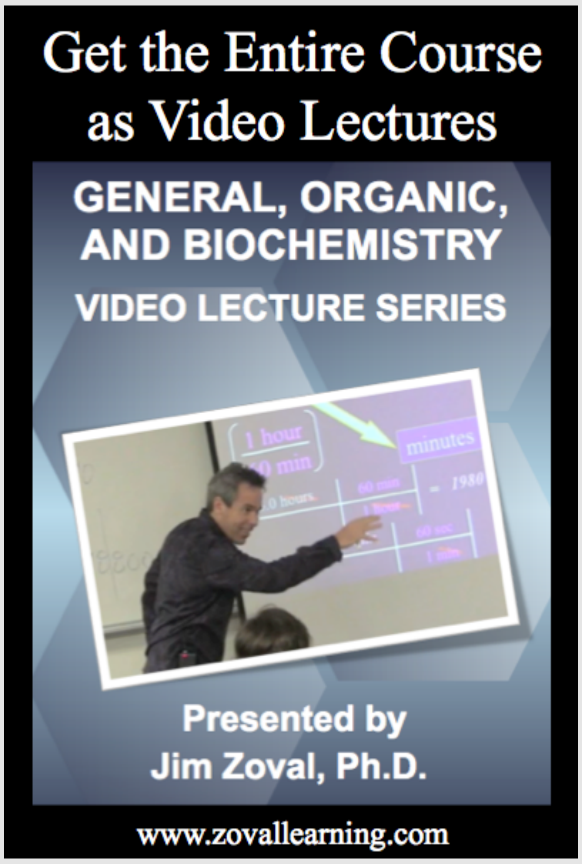
Most substances around us do not exist as individual atoms. Atoms will "bond" with other atoms to form compounds such as water (H_2O), carbon dioxide (CO_2), and table salt (sodium chloride). In the remainder of chapter 3, we will discuss the nature of this "bonding" of atoms to other atoms. **The Octet Rule is quite useful in predicting and understanding bonding patterns in chemical compounds.**

The Octet Rule

Chemical compounds tend to form so that each atom, by gaining, losing, or sharing electrons, has an ***octet*** (eight) of electrons in its outermost shell.

There are exceptions to the octet rule. An important exception that we will always use is for ***hydrogen*** and ***helium***.

- Hydrogen and helium have filled outer shells (are stable) with just ***two*** electrons because their outermost level (**n**=1) has only one orbital.

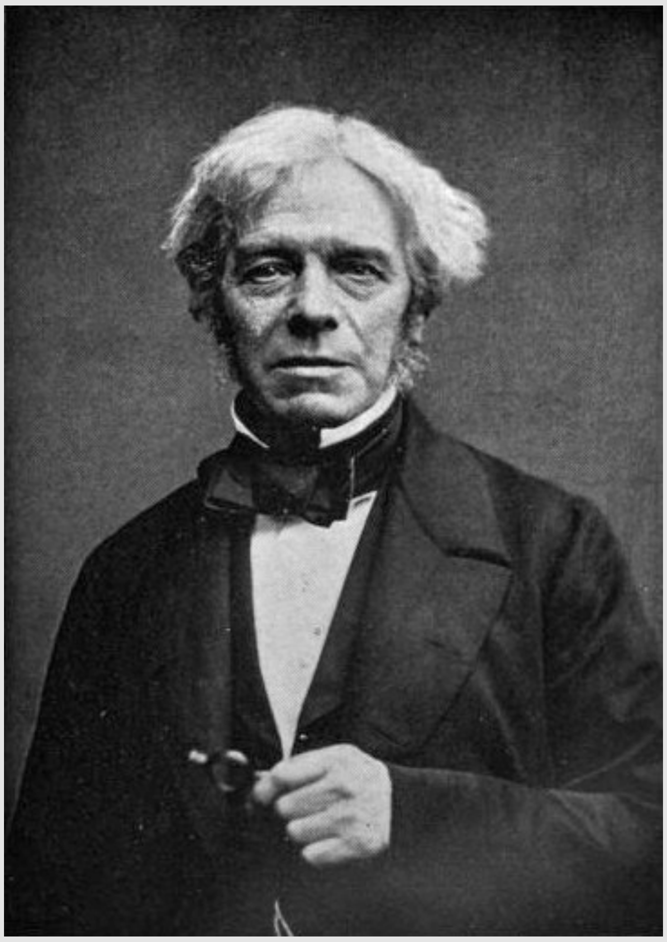


3.4 Ions

Atoms have the same number of electrons as protons and are therefore ***electrically neutral***. The nucleus of an atom is positive and the electrons are negative, however the total positive charge from protons and the total negative charge from the electrons cancel each other (add up to zero charge). Consider a **sodium** atom. Sodium is in box number 11 (atomic number = 11) of the periodic table because it has eleven protons. Since atoms are ***always electrically neutral***, a sodium atom must therefore have eleven electrons [total charge = (positive 11) plus (negative 11) = ZERO].

An **ion** is a small particle that has an ***electrical charge***. The word "ion" is Greek for "going." Michael Faraday (Figure 3.23) introduced the term "ion" in 1834 to describe the unknown particles that went from one electrode to another in water that contained dissolved matter. Atoms can ***gain <u>or</u> lose electrons*** to become **ions**. Ions can have a *positive charge* if they have more protons than electrons. Likewise, ions can have a *negative charge* if they have more electrons than protons. Many substances that you are familiar with exist as ions. For example, table salt (sodium chloride) is composed of sodium ions and chloride ions.

Figure 3.23 **Michael Faraday**



Michael Faraday (1791-1867) introduced the term "ion" in 1834.
Source: Wikimedia Commons, US-PD, Author: John Watkins

Metal atoms can ***lose*** electron(s) to form ***positive ions***.

- If an atom *loses* one or more electrons, it will then have more protons than electrons and have an overall *positive charge*.
- *Positive ions* are called **cations**.
    - **Cation** is a Greek word meaning "down" and was related to the direction of charge flow in Michael Faraday's experimental work.

Nonmetal atoms can ***gain*** electron(s) to form ***negative ions***.

- If an atom *gains* one or more electrons, it will then have more electrons than protons and have an overall *negative charge*.
- *Negative ions* are called **anions**.
    - **Anion** is a Greek word meaning "up."

Recall the relative placement of metal vs. nonmetal atoms on the periodic table (Figure 2.12) shown in chapter 2.

The Octet Rule in the Formation of Ions

The ***Octet Rule*** can be used to predict the formation of ions. Recall the ***Octet Rule***: Chemical compounds tend to form so that each atom, by gaining, losing, or sharing electrons, has an ***octet*** of electrons in its outermost shell. In the last section, you learned that the noble gases are resistant to change and, with few exceptions, do not lose or gain electrons because of the stability (low energy) that results from their outer shell being completely filled with electrons. For other atoms, it would be energetically favorable (lower energy) to gain or lose electrons in order to achieve the stability that comes with having *eight* electrons in the outermost shell. Very often, ions are formed such that the ***ion*** has an octet in its outermost shell. This tendency will allow us to predict the charge of the ion that is formed for particular elements. I will elaborate on concept by discussing some examples.

The Formation of Cations From Metal Atoms

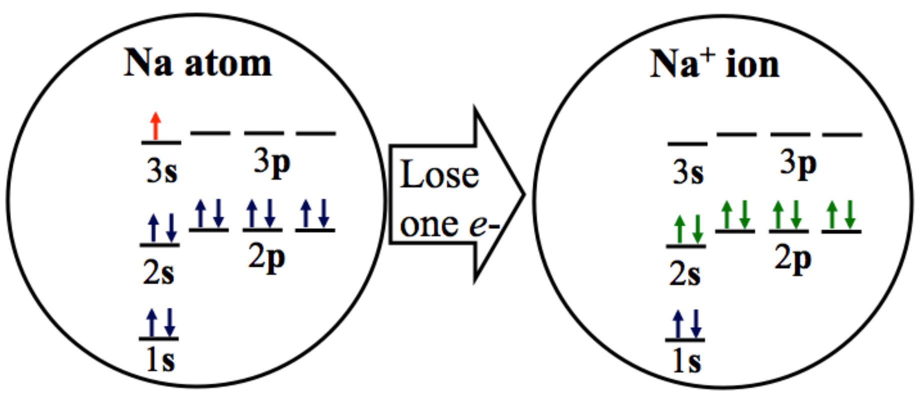
Let's consider the formation of a **sodium cation**:
We will begin with a *neutral* sodium ***atom***. A sodium atom has eleven protons and eleven electrons. I have drawn an illustration of a *sodium* **atom** with an insert of its energy level diagram on the left side of Figure 3.24. Note that a sodium **atom** has one valence electron (in the 3**s** orbital, colored red on the left in Figure 3.24). It would be lower energy for sodium to have eight valence electrons as stated by the octet rule.

There are ***two*** scenarios in which sodium can achieve an octet of electrons in its outermost shell:

> **Scenario #1:** The sodium atom could ***gain seven electrons*** to completely fill the 3**s** and three 3**p** orbitals. This scenario would result in a sodium ion with a *negative 7 charge* because the ion would still have eleven protons, but would have eighteen electrons! The *total charge* is equal to positive 11 plus negative 18, which is equal to **negative 7**.
>
> **Scenario #2:** The sodium atom could ***lose the valence electron in the 3s orbital*** as shown on the **right** in Figure 3.24. In this scenario, the valence electrons would be the *octet of electrons* in the **n**=2 shell (colored green on the right in Figure 3.24). The **n**=2 shell would be the *outermost* (valence) shell because there are no longer electrons in the **n**=3 shell. This scenario would result in a sodium ion with a positive 1 charge. The *total charge* is equal to positive 11 plus negative 10, which is equal to **positive 1**.

When considering the two scenarios discussed above, it is energetically favorable (lower energy) to form the ion **with the least amount of total charge** (only consider the *magnitude* of the charge, whether the charge is positive or negative *does not matter*). A sodium ion with a *positive 1* is lower in energy than a sodium ion with a *negative 7* charge. Therefore, a sodium **atom** will lose one electron when a sodium **ion** is formed (as discussed in scenario #2 and shown in Figure 3.24).

Figure 3.24
Formation of a Sodium Ion



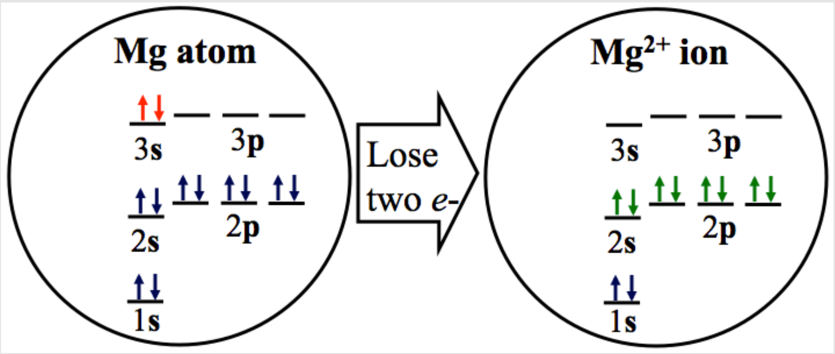
When a sodium atom (left) loses it's one electron in the **n**=3 shell, the outermost shell occupied by electrons in the sodium ion (right) becomes the **n**=2 shell. The sodium ion that is formed has eight valence electrons in its outmost shell. This corresponds to the low energy state described by the octet rule.

When writing electrical charge, it is the practice of chemists to write the *value of the charge* followed by the positive (+) or negative (-) sign. For example, we would write "1+" for "positive one" charge; for a charge of "positive two," we write "2+"; for a charge of "negative two," we write "2-." When the charge is positive one or negative one, the number "1" is often omitted and only the + or - is shown. When abbreviating the ions using symbols, the charge is *superscripted* to the right of the element's symbol. This allows the reader to differentiate between the *atom* and the *ion* of a particular element. For example, we write "Na" for a ***sodium atom***, however for a ***sodium ion*** we write Na^{1+} or Na^{+}.

Let's consider another cation; **the formation of a magnesium cation:**

A magnesium atom has twelve protons and twelve electrons. I have drawn an illustration of a *magnesium* **atom** with an insert of its energy level diagram on the left in Figure 3.25. Note that a magnesium **atom** has two valence electrons (in the 3**s** orbital, shaded red in on the left in Figure 3.25). It would be lower energy for magnesium to have eight valence electrons as stated by the octet rule. There are ***two*** ways that magnesium can achieve an octet of electrons in its outermost shell:

Figure 3.25 Formation of a Magnesium Ion



When a magnesium atom (left) loses its two electrons in the **n**=3 shell, the outermost shell in the magnesium ion (right) is the **n**=2 shell. The magnesium ion that is formed has eight valence electrons in its outmost shell. This corresponds to the low energy state described by the octet rule.

Scenario #1: The magnesium atom could ***gain six electrons*** to completely fill the 3**s** and three 3**p** orbitals and therefore have an *octet of electrons* in its outermost shell. This scenario would result in a magnesium ion with a *negative 6 charge*.

Scenario #2: The magnesium atom could ***lose the two valence electrons in the 3s orbital*** as shown on the *right* in Figure 3.25. In this scenario, the valence electrons would be the *octet of electrons* in the **n**=2 shell (shaded green in the right in Figure 3.25).

Since the ion with the least amount of total charge will have lower energy, it is easier to lose two electrons than to gain six! A magnesium **atom** loses two electrons when a magnesium **ion** (Mg^{2+}) is formed.

Review 3.5: Predicting the Charge of s- and p-Block Ions

Based on the octet rule, what would be the charge of an aluminum ion?

(HINT: Begin with the energy level diagram (or the number of valence electrons) for an aluminum atom)

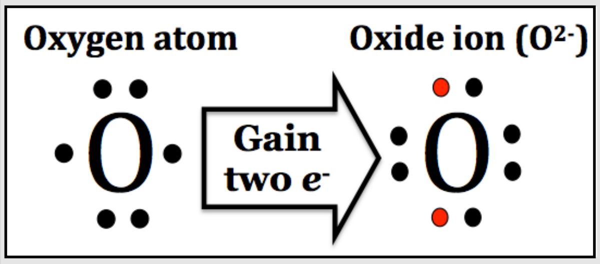
For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

The Formation of Anions From Nonmetal Atoms

Let's consider the anion formed from an oxygen atom.

We will begin with a *neutral* oxygen ***atom***. An oxygen atom has eight protons and eight electrons. You may have noticed from our previous examples that the octet rule and the number of valence electrons ultimately determines the charge for an ion of a particular element. So instead of considering the energy level diagram, in this example we use the alternative method of starting with the **electron dot structure** of an *oxygen atom*. Oxygen is in **Group VI** on the periodic table because an oxygen atom has ***six*** valence electrons. I have drawn the electron dot structure of an oxygen atom on the left side of Figure 3.26. It would be lower energy for oxygen to have eight valence electrons as proclaimed by the octet rule.

Figure 3.26
Formation of an Oxide Ion



When an oxygen atom (left) gains two electrons, oxide ion (right) that is formed has eight valence electrons in its outmost shell. This correspond to the low energy state described by the octet rule.

There are ***two*** ways that oxygen can achieve an octet of electrons in it's outermost shell:

1) The oxygen atom could ***lose the six valence electrons.*** This scenario would result in an oxide ion with a positive 6 charge.

2) The oxygen atom could ***gain two electrons*** as shown on the right in Figure 3.26. This scenario would result in a oxide ion with a *negative 2 charge.*

Since the ion with the least amount of total charge will have lower energy, it is easier to gain two electrons than to lose six! An oxygen **atom** *gains* two electrons, as shown on the right in Figure 3.26, when an **oxide ion** (O^{2-}) is formed.

Review 3.6: Predicting the Charge of s- and p-Block Ions

What would be the charge of an **ion** formed from a **chlorine** atom?
(HINT: Begin with the number of valence electrons in a chlorine atom)

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

Determining the Charge of Ions Summary

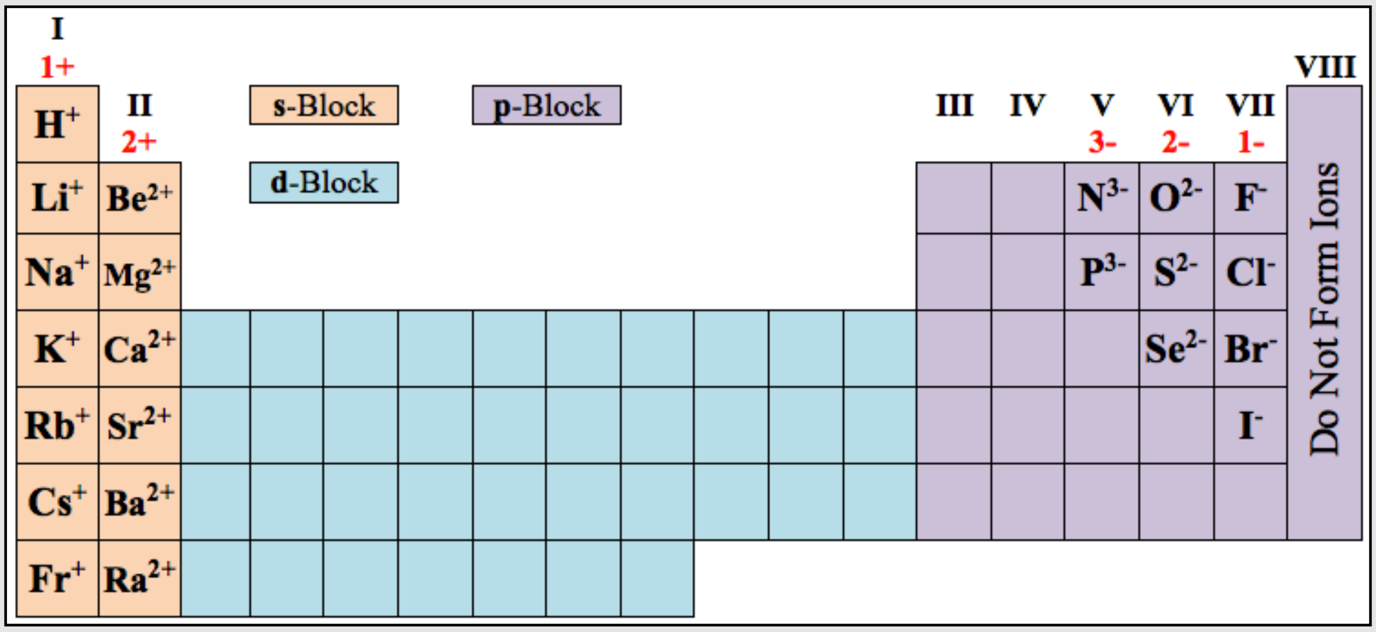
We can determine the charge of an ion formed from ***s-block metals*** and ***p-block nonmetals*** from the number of valence electrons in those elements. This information is summarized in Table 3.1.

Table 3.1 Charge for s-Block Cations and p-Block Nonmetal Anions

Periodic Group	Number of Valence Electrons of the Element	Number of Electrons Gained or Lost in Ion Formation	Charge of Ion Formed
s-Block Elements			
Group I	1	Lose 1 electron	1+
Group II	2	Lose 2 electrons	2+
p-Block Nonmetal Elements			
Group III	There are no Group III non-metals (only metals and metalloids)		
Group IV	4	Do not form ions, high energy to gain **<u>or</u>** lose 4 electrons!	
Group V	5	Gain 3 electrons	3-
Group VI	6	Gain 2 electrons	2-
Group VII	7	Gain 1 electron	1-
Group VIII	8	Do not form ions, noble gas atoms have filled outer shells.	

The number of valence electrons for **s**-block elements and **p**-block *nonmetal* elements is determined from their positions (Group) on the periodic table. When we know the number of valence electrons one of these elements contains, the octet rule allows us to predict the charge of its ion, as shown in Figure 3.27.

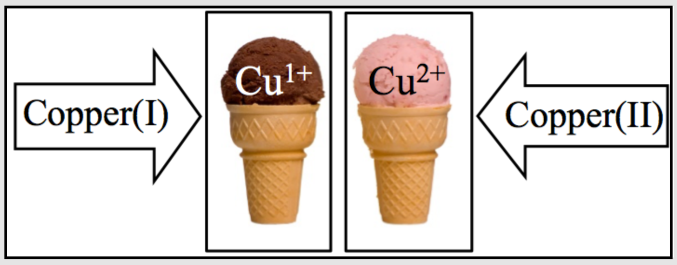
Figure 3.27 Periodic Table with Charges for s-Block Cations and p-Block Nonmetal Anions



Note that the Group VIII rare gas elements do not form ions. This is because the atoms, with electron-filled outer shells, are the low energy state. It would be higher in energy for them to exist as ions. The noble gas atoms, except for helium, have an octet of electrons in their outermost shell. The Group IV nonmetal, carbon, is not shown because carbon does not form ions. Carbon would need to gain or lose four electrons to satisfy the octet rule; gaining or losing four electrons is energetically unfavorable.

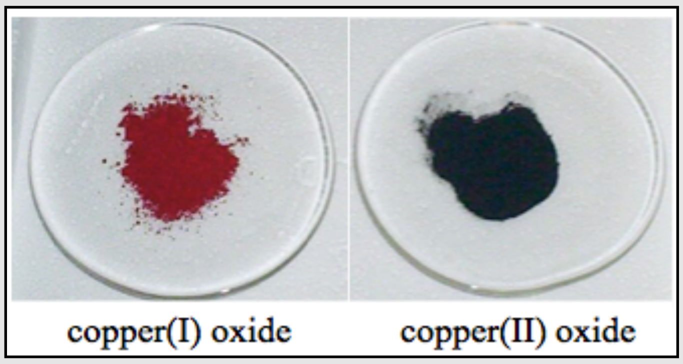
You may be wondering how to determine the charge of the ions formed from the transition metals and p-block *metals*. Unfortunately, the charges for the ions from many of those elements ***cannot*** be determined by on their position in the periodic table. Furthermore, many of the transition metals and **p**-block metals can form more than one type (charge) of ion. For example, we find that copper ion can exits in the Cu^{1+} or Cu^{2+} ionic states. I will use an ***ice cream analogy***: copper ions come in two flavors. To differentiate the various charge states of these ions when reading or writing their names, we use Roman numerals corresponding to the charge after the element name as shown in Figure 3.28. We ***only*** use the Roman numeral for ions that can exist in more than one charge state. When saying the ion's name, one would say "copper one" for Cu^{1+} and "copper two" for Cu^{2+}. When copper ions chemically combine with oxide ions, we find that two different compounds exist: copper(I) oxide and copper(II) oxide. These two compounds have different physical properties such as color and melting temperature. Images of these two oxides of copper are shown in Figure 3.29. Some transition metal ions only exist with one charge (they only come in one flavor). For example, cadmium ions only exist as Cd^{2+}. Roman numerals ***are not used*** when the metal cations *have just one charge state.*

Figure 3.28
Ice Cream Analogy for Copper Ions



In nature, copper ions can exist as Cu^{1+} ***or*** Cu^{2+}. To differentiate the various charge states of these ions, we use Roman numerals corresponding to the charge after the element name.

Figure 3.29
Copper Ions in Compounds



Source: Wikimedia (US-PD), Author: Walkerma

Since the charges of many of the transition metal and p-block metal ions ***cannot*** be easily predicted from their positions on the periodic table, we must refer to tabulated values. Table 3.2 lists the charges for some transition metals and p-block ions. This table does not contain data for the ions formed by *all* **p**-, **d**-, and **f**-block metal elements, however it includes the ions that you will need in order to solve and understand any of the examples and problems in this textbook. If you find it necessary for some future career or academic need, to know the charge(s) of ions not listed in Table 3.2, that information can be readily found on the internet.

Table 3.2
Charges for Some Transition Metal and p-Block Metal Ions

Ions that occur with only one charge			
Name	Charge	Name	Charge
aluminum ion	Al^{3+}	cadmium ion	Cd^{2+}
silver ion	Ag^{+}	zinc ion	Zn^{2+}
Ions that occur with multiple charges			
Name	Charge	Name	Charge
copper(I) ion	Cu^{+}	tin(II) ion	Sn^{2+}
copper(II) ion	Cu^{2+}	tin(IV) ion	Sn^{4+}
iron(II) ion	Fe^{2+}	lead(II) ion	Pb^{2+}
iron(III) ion	Fe^{3+}	lead(IV) ion	Pb^{4+}
cobalt(II) ion	Co^{2+}	mercury(I) ion	Hg^{+}
cobalt(III) ion	Co^{3+}	mercury(II) ion	Hg^{2+}

The use of Roman numerals to indicate the charge for metals *with varying charge* is now the accepted standard used by chemists. I want to mention the historical or "classic" method that was previously used, just in case you happen to see it somewhere. The charge-state with the greater charge was indicated by adding the "-ic" suffix to the metal element's Latin name. The lesser charge-state was indicated by the "-ous" suffix. For example, "cupric" was used for copper(II) and "cuprous" for copper(I). Similarly, "ferric" was used for iron(III) and "ferrous" for iron(II).

Naming Monoatomic Ions

In the preceding text, I have used some names of ***monatomic ions***. The word *monatomic* comes from “mono” meaning *one* or *single*, and “atomic” as in *atom*. A ***monatomic ion*** is an ion that is made when a **single atom** gains or loses electron(s). Monatomic ions can be contrasted to **polyatomic ions**. *Polyatomic ions* are electrically-charged particles formed from a small number of atoms that are “bonded” together. I will discuss polyatomic ions very soon, but for now, I will introduce you to the rules for naming *monatomic ions*.

Naming Monatomic *Cations*

Cations use the name of the element, followed by the word “ion.”

- Examples:
  - **Na^{+}** is referred to as a **sodium ion**.
  - **Mg^{2+}** is referred to as a **magnesium ion.**

For monatomic cations that can occur with multiple charges, indicate the charge using Roman numerals after the element’s name.

- Examples
  - **Fe^{2+}** is referred to as an **iron(II) ion**
  - **Fe^{3+}** is referred to as an **iron(III) ion**

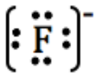
Naming monatomic *Anions*

Anions are named by changing the *suffix* (ending) of the name to “**-ide.**”

- Examples:
  - **F^{-}** is referred to as a **fluoride ion**.
  - **O^{2-}** is referred to as an **oxide ion**.

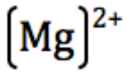
Electron Dot Structures of Ions

We can draw electron dot structures for ions. For **anions**, we draw the element’s symbol and the dots representing the valence electrons contained by the anion in ***brackets***. The charge of the anion is *superscripted* to the right.
Example**:** The electron dot structure of the fluoride ion is:



For **cations**, since metal elements *lose electrons*, the **dots are omitted**. We draw the element’s symbol in *brackets* with the charge of the cation *superscripted* to the right.

- Example: The electron dot structure of the magnesium ion is:



Review 3.7: Names and Electron Dot Structures of Ions

a) Write the name of the K^{+} ion.
b) Write the name of the N^{3-} ion.
c) Write the name of the Co^{3+} ion.
d) Draw the electron dot structure for a sulfide ion.
e) Draw the electron dot structure for a calcium ion.

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

Polyatomic Ions

Several atoms often "*stick*" (bond) together to form a small particle. If the resulting particle has the s*ame number of protons as electrons*, then it will be ***electrically neutral***, and we call the particle a **molecule**. If, on the other hand, there is an *excess of protons or an excess of electrons* in the particle, then it will have an ***overall electrical charge***, and we call the particle a **polyatomic ion**. I will discuss the nature of the forces (bonds) that hold atoms together in molecules and in polyatomic ions in the next section of this chapter. An *example* of a polyatomic ion is the *nitrate ion*. In the formation of a nitrate ion, one nitrogen atom, three oxygen atoms, and ***one extra electron*** are *bonded* together to form a particle with a (1-) electrical charge. The nitrate ion has this (1-) charge because it has one more electron than protons. The nitrogen atom and the three oxygen atoms all contained equal amounts of protons and neutrons, however the extra electron is responsible for the (1-) charge. Because the nitrate ion contains one nitrogen atom, three oxygen atoms, and has a (1-) charge, we abbreviate the name by writing NO_3^-.

Table 3.3 lists the names and charges for some polyatomic ions. This table does not contain data for all of the known polyatomic ions, however it includes the polyatomic ions that you will need in order to solve and understand any of the examples and problems in this textbook. If you find it necessary, for some future career or academic need, to know the names and charge(s) of polyatomic ions not listed in Table 3.3, that information can be found on the internet.

Table 3.3
Some Polyatomic Ion Names and Charges

POLYATOMIC CATIONS	
H_3O^+ hydronium ion	NH_4^+ ammonium ion
POLYATOMIC ANIONS	
OH^- hydroxide ion	HSO_4^- hydrogen sulfate (or bisulfate) ion
CO_3^{2-} carbonate ion	PO_4^{3-} phosphate ion
HCO_3^- bicarbonate (also called hydrogen carbonate) ion	HPO_4^{2-} hydrogen phosphate ion
NO_2^- nitrite ion	$H_2PO_4^-$ dihydrogen phosphate ion
NO_3^- nitrate ion	CrO_4^{2-} chromate ion
SO_3^{2-} sulfite ion	$Cr_2O_7^{2-}$ dichromate ion
SO_4^{2-} sulfate ion	$C_2H_3O_2^-$ acetate ion (sometimes written as $CH_3CO_2^-$)
	CN^- cyanide ion

3.5 An Introduction to Compounds

Most substances around us do not exist as individual atoms. Atoms can ***bond*** with other atoms, and ions can ***bond*** with other ions to form ***compounds*** such as water (H_2O), carbon dioxide (CO_2), and table salt (sodium chloride). In the remainder of chapter 3, I will discuss the nature of the chemical bonding process. You will learn about the forces that hold the atoms or ions together and learn how to name compounds. **Compounds** are defined as matter that is constructed of two or more *chemically bonded* elements.

Chemical bonds are the ***electrical attractive forces*** that hold atoms or ions together in a compound. Each compound has the same *proportion* of the *same* elements. For example, water will ***always*** have two hydrogen atoms for every one oxygen atom. It is for this reason that we use the notation "H_2O" to represent water. Likewise, sodium chloride will ***always*** have one sodium ion for every one chlorine ion. This is known as the ***law of constant proportions*** (sometimes called the ***law of constant composition***) and is also sometimes referred to as **Proust's Law** because it was first observed and reported by the French chemist Joseph Proust (shown in Figure 3.30)

There are *three types* of **chemical bonding**:

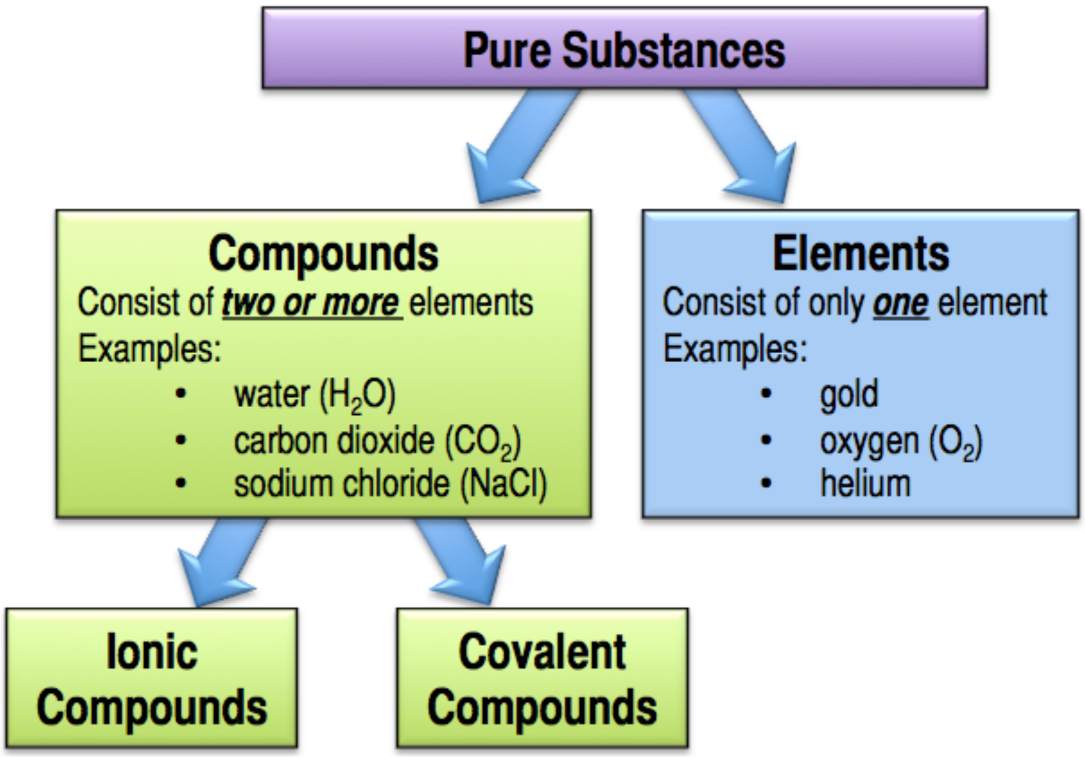
1) **Ionic Bonding**
2) **Covalent Bonding**
3) **Metallic Bonding**

In this chapter, we will discuss the first two types, *ionic bonding* and *covalent bonding*. We will learn about *metallic bonding* in chapter 5.

Figure 3.30
Joseph Proust
(1754–1826)

Source: PD-US

Chemistry is the study of matter (stuff) and the changes it undergoes. ***Physical changes***, such as *melting* or *boiling*, result in changes in *physical properties* and do not involve the formation of new *pure substances*. For example, the melting of ice is simply H_2O being changed from the *solid* phase to the *liquid* phase. The chemical bonds between the oxygen and hydrogen atoms do not change in that process. **Chemical changes**, on the other hand, result in the formation of **new** *pure substances*. To make a new pure substance, ***chemical bonds must be broken and/or new chemical bonds are made***. This happens in a process called a **chemical reaction**, which we will study in chapter 6.



A *major principle* of chemistry is that the observed (macroscopic) properties of a substance are related to its "microscopic" structure. The *microscopic* structure entails details such as the kind of atoms/ions and the pattern in which they are ***bonded*** to each other.

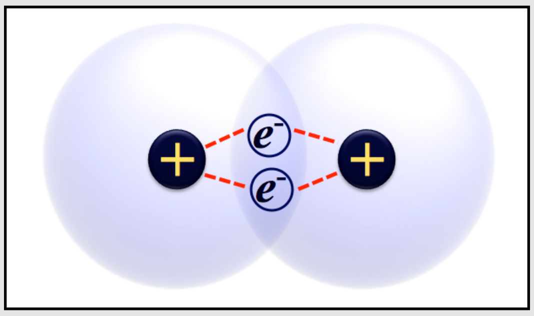
3.6 Covalent Chemical Bonding

Atoms or ions come together to form compounds simply because there are forces that hold them together. Both ionic and covalent bonding occur because of electrostatic attractive forces between *all of the subatomic particles* that make up the compound. In this section, I will discuss the nature of covalent bonding.

Covalent bonding is defined as the chemical bonding *force* that results from the ***sharing of electron pair(s)*** between two atoms. The resulting collection of atoms results in the formation of either molecules or polyatomic ions. **A molecule is an electrically neutral group of atoms held together by covalent bonds.** Electrically neutral means that there is no overall charge. The total number of protons and electrons from *all the atoms* in the molecule are equal, therefore the positive and negative charges cancel. **Polyatomic ions**, as discussed earlier in this chapter, are similar to molecules in that they consist of atoms held together by covalent bonds, however they contain extra electrons or extra protons and therefore have an overall electrical charge.

Figure 3.31

Covalent Bonding in an Hydrogen Molecule (H_2)



Electrostatic forces (dashed red lines) caused by negatively charged electrons between the positively charged nuclei hold two atoms together in a covalent bonding.

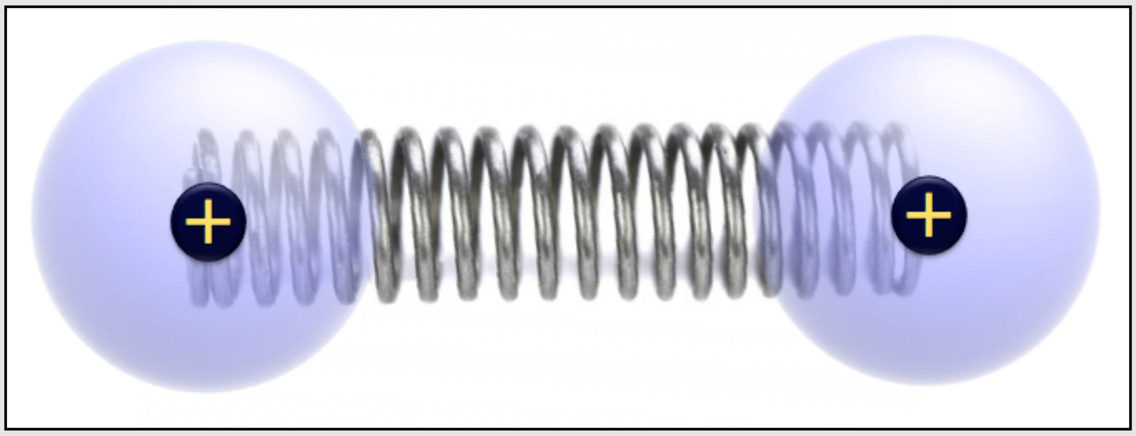
Why does sharing of electron pairs result in an attractive electrostatic force capable of holding atoms together? To begin to answer this question, consider the two hydrogen atoms coming together to form a covalent bond as shown in Figure 3.31. Note that each hydrogen atom has one proton and one electron. In covalent bonding, the atoms ***share*** *electron pairs*. Each hydrogen atom provides one electron in the shared pair. The shared electron pair spends significantly more time in the area between the positive nuclei of the hydrogen atoms than in other regions. The electron pair between the nuclei create a positive-negative-positive electrostatic attractive "sandwich" and this force holds the atoms together. The dashed red lines in Figure 3.31 indicate the electrostatic attractive interactions.

If you could magically shrink yourself and grab a single H_2 molecule, you could push and pull on the the hydrogen atoms. When you would do so, the covalent bond would behave like a spring between the atoms as illustrated in Figure 3.32. If you pulled the atoms apart, the electrostatic force would resist as if you were pulling on each end of a spring. If you pushed the atoms closer together, the positive nuclei would repel each other and it would feel like you were compressing a spring. This is not only true for the covalent bonding that is discussed in this section, it is also the case in ionic bonding that will be discussed in the next section.

Although common sense may suggest that this is the end of the explanation of covalent bonding, we must consider ***quantum mechanical effects (the octet rule)*** to fully describe the nature of covalent bonding. For example, if the positive-negative-positive electrostatic sandwich model is all that is needed to account for covalent bonding, then we would see two helium atoms held together. However, this does not occur for He; the He_2 molecule does not exist.

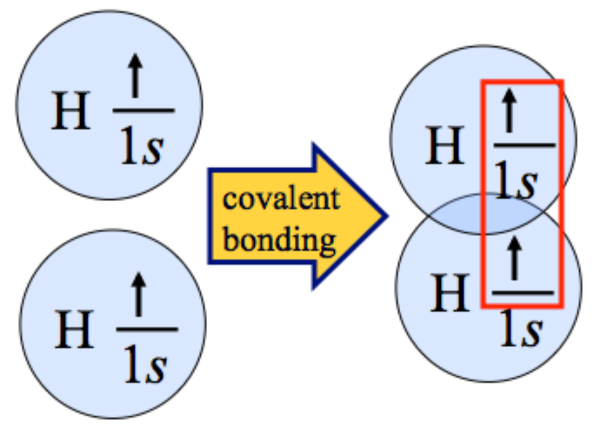
Figure 3.32

The Forces in Chemical Bonding Behave Very Much Like Tiny Springs Between the Nuclei of Atoms



Recall the octet rule: Chemical compounds tend to form so that each atom, by gaining, losing, or **sharing electrons**, has an octet of electrons in its outermost shell (**n**). The stability is related to atoms having their outermost shell completely filled with electrons. The major exception to the octet rule is for hydrogen and helium because they have filled outer shells with just two electrons since the **n**=1 shell only has one orbital. **Therefore the octet rule for hydrogen and helium is satisfied with two valence electrons**. Keeping this in mind, let's consider the ability for the formation of a covalent bond; first between two hydrogen atoms and then between two helium atoms. On the left side of Figure 3.33, two isolated (non-bonded) hydrogen atoms are illustrated with inserts of their valence electrons in an energy level diagram. Since hydrogen atoms only have one electron, we do not expect this to be a low energy (stable) situation and, in nature, isolated hydrogen atoms do not exist for any significant amount of time. If two hydrogen atoms get close to each other, they can share the valence electrons as illustrated on the right side of Figure 3.33. When this occurs, <u>each</u> hydrogen has two electrons in it outermost shell. This is a stable, low energy situation as predicted by the octet rule! We find H_2 molecules existing in nature; you can buy a gas cylinder filled with H_2. Shared electron pairs spend significantly more time in the area between the bonded atoms than in other regions. **The octet rule in the formation of molecules is: *molecules tend to form such that the atoms are surrounded by an octet (eight) of valence electrons (except for hydrogen and helium that have two electrons).***

Figure 3.33 The Octet Rule in the Formation of a Hydrogen Molecule



Left: Illustration of two isolated (non-bonded) hydrogen atoms with inserts of their valence electrons in an energy level diagram. **Right:** If two hydrogen atoms get close to each other, they can share the valence electrons. When this occurs, <u>each</u> hydrogen has two electrons in it outermost shell, resulting in a stable, low energy situation as predicted by the octet rule.

Next, let's consider why He_2 molecules do not exist. Each helium atom contains two electrons in its 1**s** orbital, so if the atoms come together to share electrons, the stable situation of having each helium atom surrounded by two electrons cannot be achieved. Furthermore, each individual (isolated) helium atom ***already*** satisfies the octet rule; they have two electrons in their 1**s** orbitals. It is for this reason that helium is placed in group VIII with the noble gases in the periodic table. Any additional shared electrons that would be gained by forming covalent bonds would lead to a higher energy, less stable situation that violates the octet rule. And indeed, helium, like all the noble gases, exists as single, unbound atoms. When you fill a balloon with helium from a tank, you are filling it with *helium* ***atoms***.

We can come to the same conclusion as to the formation of hydrogen *molecules* using electron dot structures. Let's start with two isolated hydrogen atoms. We draw the symbols for hydrogen (H) each with one dot representing the valence electron as shown in the top of Figure 3.34. When the two hydrogen atoms come together, the shared electrons are drawn as a pair of dots in between the H's as shown in the middle of Figure 3.34. Note that we now have an ***electron dot structure*** of the **H_2 molecule**. Very soon we will stop drawing electron dot structures of molecules, instead we will draw **line bond structures**. In line bond structures, the shared electron pairs that form the covalent bond(s) are drawn as a line. When considering a line bond structure, it is important to remember that <u>**each**</u> line represents ***two electrons***. The line bond structure for the H_2 molecule is shown on the bottom of Figure 3.34.

Figure 3.34 **H_2 Covalent Bond Formation**

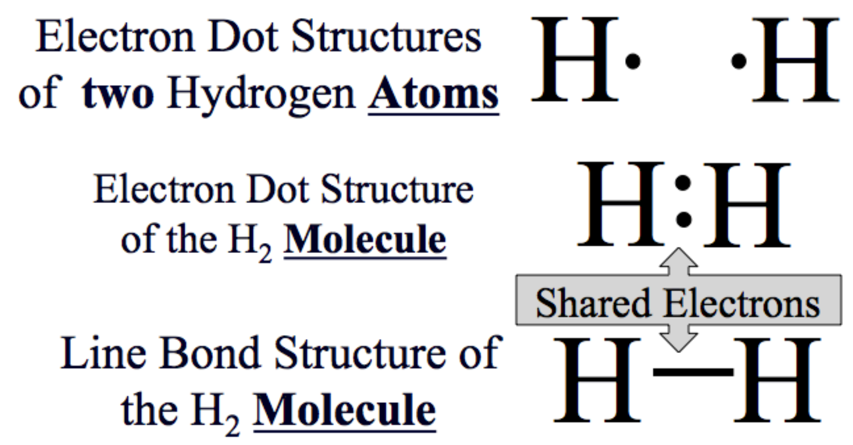
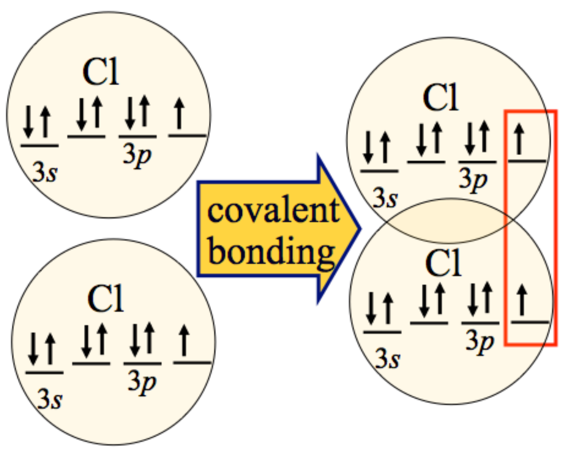


Illustration of the covalent bond formation using electron dot structures and line bond structures. Pairs of shared electrons (covalent bonds) are shown as two dots between atoms in electron dot structure. Shared electron pairs are represented by lines in line bond structures.

Figure 3.35
The Octet Rule in the Formation of a Chlorine (Cl_2) Molecule

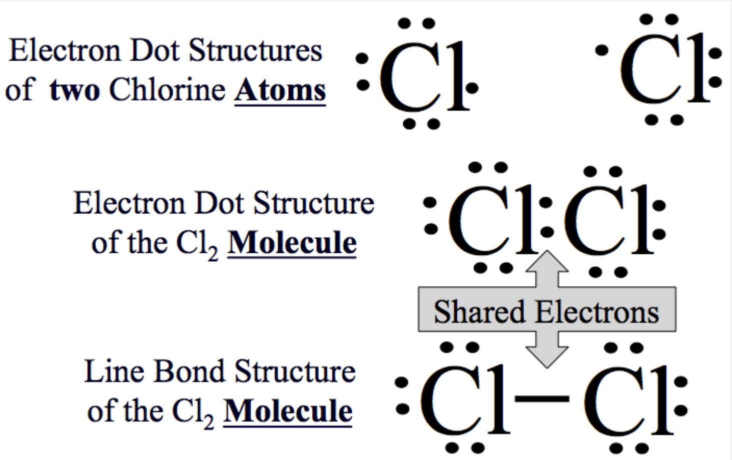


Two chlorine atoms (left) can share the valence electrons to form a chlorine (Cl_2) molecule (right). The shared electrons are shown in the red box.

Let's consider some other molecules formed from covalent bonds. Chlorine gas exists as a diatomic (two atom) molecule (Cl_2). A single chlorine atom has seven valence electrons and therefore would not be stable. The stability of the filled outer shell described by the octet rule requires eight electrons. On the left side of Figure 3.35, two isolated (non-bonded) chlorine atoms are illustrated with inserts of their *valence electrons* in an energy level diagram. The core electrons (non-valence) are not shown because they are not involved in covalent bonding. The "*co-*" in *covalent* stands for *partner* or *shared*, the "*valent*" stands for *valence electrons,* so put together, "*co-valent*" means *shared valence electrons*. If two chlorine atoms get close to each other, they can share the valence electrons as illustrated on the right side of Figure 3.35. The shared electrons are shown in the red box. Now each chlorine has ***eight electrons*** in it outermost shell. This is a stable, low energy situation as predicted by the octet rule; ***molecules tend to form such that the atoms are surrounded by an octet (eight) of valence electrons.***

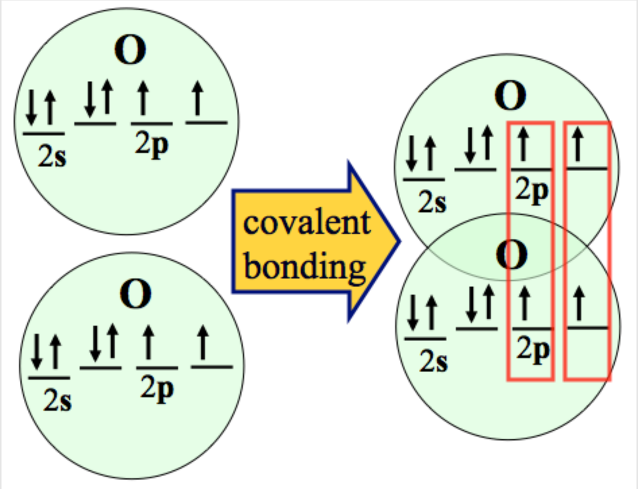
Bond formation can also be modeled using electron dot structures. We start with two isolated chlorine atoms. Draw the symbols for both chlorine (Cl) atoms, each with seven dots representing the valence electrons as shown in the top of Figure 3.36. When the two chlorine atoms come together, the shared electrons are drawn as a pair of dots in between the Cl's as shown in the *electron dot structure* of the Cl_2 molecule (middle of Figure 3.36), or as a **line** in the *line bond structure* (bottom of Figure 3.36). Notice that when drawing electron dot structures or line bond structures of molecules that not all of the atoms' valence electrons are shared. For example, look at the line bond structure of the Cl_2 molecule in the bottom of Figure 3.36; each Cl has *three pairs of electrons* that are not shared. We call these pairs of unshared electrons "**lone pairs.**" The presence of ***lone pairs*** can be quite important in later chapters when we consider the *shapes of molecules* and how molecules *interact with other molecules*.

Figure 3.36
Cl_2 Covalent Bond Formation



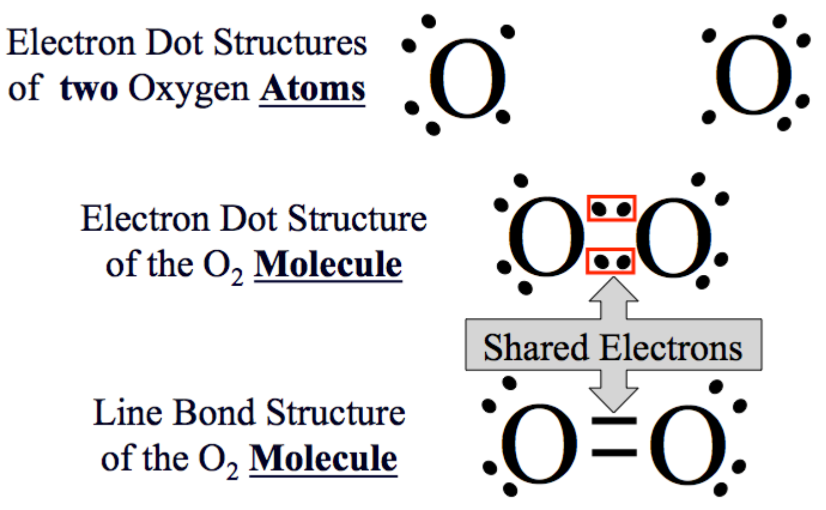
Sometimes, the stable, low energy state predicted by the octet rule is achieved by sharing ***more than one pair of electrons***. For example, in an oxygen molecule (O_2), **two pairs** of electrons are shared. Oxygen gas exists as a diatomic (two atom) molecule. A single oxygen atom has six valence electrons and therefore would not be stable; the stability of the filled outer shell requires eight electrons. On the left side of Figure 3.37, two isolated (non-bonded) oxygen atoms are illustrated with inserts of their *valence electrons* in an energy level diagram. If two oxygen atoms get close to each other, they can share **two pairs** of valence electrons as illustrated on the right side of Figure 3.37. The shared electrons are shown in the **red boxes**. Now each oxygen atom has ***eight electrons*** in its outermost shell. This is a stable, low energy situation as predicted by the octet rule. **When two pairs of electrons are shared, we call that a *double bond.*** Double bonds are "*stronger*" than single bonds. For a given pair of bonded atoms, it would take more energy to break an oxygen-oxygen double bond than an oxygen-oxygen single bond.

Figure 3.37
The Octet Rule in the Formation of an Oxygen (O_2) Molecule



Two oxygen atoms (left) can share the valence electrons to form an oxygen (O_2) molecule (right). The ***two pairs*** of shared electrons are shown in the red boxes.

Figure 3.38
O_2 Covalent Bond Formation

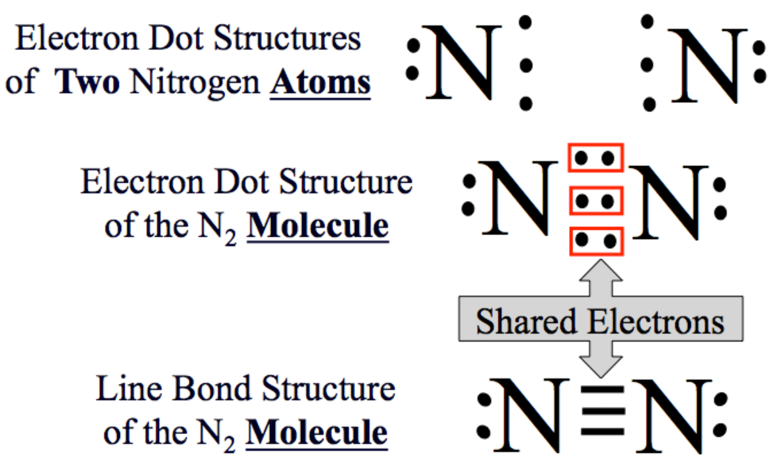


A **double bond** is formed when **two** pairs of electrons are shared. Double bonds are indicated by **two lines** between bonded atoms in line bond structures.

The double bond formation of an oxygen molecule can also be modeled using electron dot structures. We start with two isolated oxygen atoms. Draw dot structures of each oxygen atom with six dots representing the valence electrons as shown in the top of Figure 3.38. I have rotated the electrons in the dot structures by 45° so that when the oxygen atoms come together, the shared electrons will line up with each other. When the two oxygen atoms come together, the ***two pairs*** of shared electrons are drawn as pairs of dots in between the oxygens in the *electron dot structure* of the O_2 molecule (middle of Figure 3.38). In this figure, the two pairs of shared electrons are shown in red boxes. **We can check for *octets*; note that upon bond formation each oxygen nucleus is surrounded by an octet of valence electrons.** The shared electron pairs are shown as **lines** (*one line per pair*) in the *line bond structure* (bottom of Figure 3.38). A **double bond** is indicated by ***two*** lines between bonded atoms.

Some molecules have **three pairs** of shared electrons. An example of this is the nitrogen molecule (N_2). Nitrogen molecules are the major component of air. Let's use the electron dot structures of two ***nitrogen atoms*** to get the *line bond structure* of an N_2 molecule. We begin with two isolated nitrogen atoms. Draw dot structures of each nitrogen atom with five dots representing the valence electrons as shown in the top of Figure 3.39. I have rotated the ***unpaired electrons*** in the dot structures so that when the nitrogen atoms come together, the shared electrons will line up with each other. When the two nitrogen atoms come together, ***three pairs*** of electrons are shared. Note that by sharing the electrons, each nitrogen atom is surround by an octet of electrons. The shared electrons are drawn as pairs of dots between the nitrogens in the electron dot structure of the N_2 molecule (middle of Figure 3.39). **We can check for *octets*; note that upon bond formation each nitrogen nucleus is surrounded by an octet of valence electrons.** The three pairs of shared electrons are drawn as **lines** in the line bond structure (bottom of Figure 3.39). **When three pairs of electrons are shared, we call that a *triple bond.*** Triple bonds are "*stronger*" than double and single bonds. For a given pair of bonded atoms, it would take more energy to break a nitrogen-nitrogen triple bond than a nitrogen-nitrogen double or single bond.

Figure 3.39
N_2 Covalent Bond Formation



A **triple bond** is formed when **three** pairs of electrons are shared. Triple bonds are indicated by **three lines** between bonded atoms in line bond structures.

In our covalent bonding examples, you have seen **diatomic** (two atom) molecules only. However, most molecules contain more than two atoms. You will learn a method for predicting the bonding pattern and drawing line bond structures for molecules containing more than two atoms in the beginning of chapter 4.

Naming Covalent Compounds

Atoms that are covalently bonded together are called **covalent compounds.** The covalent bonding that we will see in this book will *always* involve ***nonmetal elements* only**. The nonmetal atoms can share electrons to form molecules (molecular compounds) or polyatomic ions. When discussing molecules we use a ***molecular formula*** that shows the *types (elements)* and *numbers of atoms* that make up a single molecule. The number of atoms of each element contained in the molecule is written as a ***subscript*** after the element's symbol. For example, we saw that two *hydrogen atoms* form a *hydrogen molecule*; we write the *molecular formula* of the hydrogen molecule as "H_2." When there is only one atom of a particular element present in a molecule the subscripted "1" is omitted for that element. For example, a water molecule contains two hydrogen atoms and one oxygen atom; we write the molecular formula as H_2O, **not** H_2O_1. Glucose is a molecule that is very important in biochemistry; it is the molecule that plants make in a process called photosynthesis and, not coincidentally, it is the primary source of energy in human metabolism. A glucose molecule contains six carbon atoms, twelve hydrogen atoms, and six oxygen atoms. The *molecular formula* for glucose is $C_6H_{12}O_6$.

Some molecules ***only*** contain ***one*** element, for example H_2, Cl_2, and O_2. These molecules often take the name of the elements they contain. For example, O_2 is simply called "oxygen."

Binary covalent (molecular) compounds contain only **two** elements (the "**bi-**" prefix indicates "**two**"). Examples of binary covalent molecules are HCl, H_2O, and CO_2. Be aware that an H_2O molecule, like many other binary molecular compounds, contains more than two atoms, however, since it contains only **two** elements (oxygen and hydrogen) it is classified as a *binary covalent molecule*. The same is true for CO_2.

Educational Goals:

- Given the **name** of a ***binary covalent molecule***, be able to write the **molecular formula**.
- Given the **molecular formula** of a ***binary covalent molecule***, be able to write the **name** of the molecule.

Method for Naming a Binary Covalent (Molecular) Compound

Goal: Given the **molecular formula** of a ***binary covalent molecule***, be able to write the **name** of the molecule.

1. List the name of the first element in the formula.
2. List the second element and add the –ide suffix.
3. Use Greek prefixes (Table 3.4) to indicate the number of each atom in the formula.
   - ✦Exception: If there is just one atom of the ***first*** element in the formula, do not use **mono-** for the ***first element in the name***.
   - ✦The **o** or **a** at the ***end of the Greek prefix*** is omitted when the element's name begins with a vowel.

Table 3.4

Greek Prefix	Number
mono	1
di	2
tri	3
tetra	4
penta	5
hexa	6
hepta	7
octa	8
nona	9
deca	10

Example: Write the name for N_2S_4

1. List the name of the first element in the formula.

   nitrogen

2. List the second element and add the –ide suffix.

   nitrogen **sulfide**

3. Use Greek prefixes (Table 3.4) to indicate the number of each atom in the formula.
   - ✦Exception: If there is just one atom of the ***first*** element in the formula, do not use **mono-** for the ***first element in the name***.

     Not applicable in this example; there are two nitrogens so we use "di-."
   - ✦The **o** or **a** at the ***end*** of the **Greek prefix** is omitted when the element's name begins with a vowel.

     Not applicable in this example

___nitrogen _____sulfide

ANSWER: dinitrogen tetrasulfide

Example: Write the name for SO_3

1. List the name of the first element in the formula.

   sulfur

2. List the second element and add the –ide suffix.

   sulfur **oxide**

3. Use Greek prefixes to indicate the number of each atom in the formula.

   ✦Exception: do not use **mono-** for the ***first element in the name***.

   NOTE, we did not write "monosulfur" because of this rule!

   ✦The **o** or **a** at the ***end*** of the **Greek prefix** is omitted when the element's name begins with a vowel.

   Not applicable in this example.

   ____ sulfur _____ oxide

ANSWER: sulfur trioxide

Example: Write the name for CO.

1. List the name of the first element in the formula.

   carbon

2. List the second element and add the –ide suffix.

   carbon **oxide**

3. Use Greek prefixes to indicate the number of each atom in the formula.

   ✦Exception: do not use **mono-** for the ***first element in the name***.

   NOTE, we do not write "monocarbon" because of this rule!

   ✦The **o** or **a** at the ***end*** of the **Greek prefix** is omitted when the element's name begins with a vowel.

   NOTE, we do not write monooxide because of this rule!

   ____ carbon _____ oxide

ANSWER: carbon monoxide

Review 3.8: Naming Binary Covalent (Molecular) Compounds

Write the names of the following compounds:

a) S_2I_4
b) P_5F_8
c) N_2O_4 (Keep in mind the exceptions in rule #3)
d) NBr_3
e) N_2O_5
f) PCl_3
g) H_2S
h) N_2O

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

Some binary covalent compounds are most often referred to using their **common names**. A few common names that are used in the healthcare field are water (H_2O), ammonia (NH_3), hydrogen peroxide (H_2O_2), nitrous oxide (NO), and hydrogen sulfide (HS).

For covalent compounds containing **more than two types of elements**, we use **common names** or **systemic names**. We will use *systemic names* in later chapters to name organic (carbon containing) molecules.

Examples of molecules with *more than two* elements and their common names:

- acetone (C_3H_6O)
- glucose ($C_6H_{12}O_6$)

Method for Writing the Molecular Formula of a Binary Covalent (Molecular) Compound

Goal: Given the **name** of a ***binary covalent molecule***, be able to write the **molecular formula** of the molecule.

1. Write the symbol of the first element in the compound's name, then the symbol of the second element in the compound's name.

2. Indicate how many atoms of each element the molecule contains using subscripts after the atomic symbol.
   ✦The numbers of atoms are given in the Greek prefixes in the molecule's name.
   ✦NOTE: If there is no Greek prefix in front of the first element in the name, that means the number is 1.

Example: Write the formula of **dinitrogen tetrafluoride.**

1. Write the symbol of the first element in the compound's name, then the symbol of the second element in the compound's name:

   N F

2. Indicate how many atoms of each element the molecule contains using subscripts after the atomic symbol.
   ✦The numbers of atoms are given in the Greek Prefixes in the molecule's name.
   - **di**nitrogen **tetra**fluoride

ANSWER: N_2F_4

Example: Write the formula of **carbon disulfide.**

1. Write the symbol of the first element in the compound's name, then the symbol of the second element in the compound's name:

   C S

2. Indicate how many atoms of each element the molecule contains using subscripts after the atomic symbol.
   ✦The numbers of atoms are given in the molecule's name in Greek prefixes.
   ✦NOTE: If there is no Greek prefix in front of the first element in the name, that means the number is 1.
   - carbon **di**sulfide
     - Since there is ***no Greek prefix*** for carbon, we know there is ***one*** *carbon atom* the molecule.

ANSWER: CS_2

- NOTE: When there is only one atom of a particular element present in a molecule the subscripted "1" is omitted for that element; we write "CS_2," **not** "C_1S_2."

Review 3.9: Writing the Molecular Formula for Binary Covalent Compounds

Write the molecular formulas of the following compounds:

a. disulfur tetrafluoride
b. carbon trioxide
c. nitrogen pentoxide
d. nitrogen tribromide
e. dinitrogen heptachloride
f. carbon tetrachloride
g. hydrogen monochloride
h. trihydrogen monophosphide
i. dihydrogen monoxide

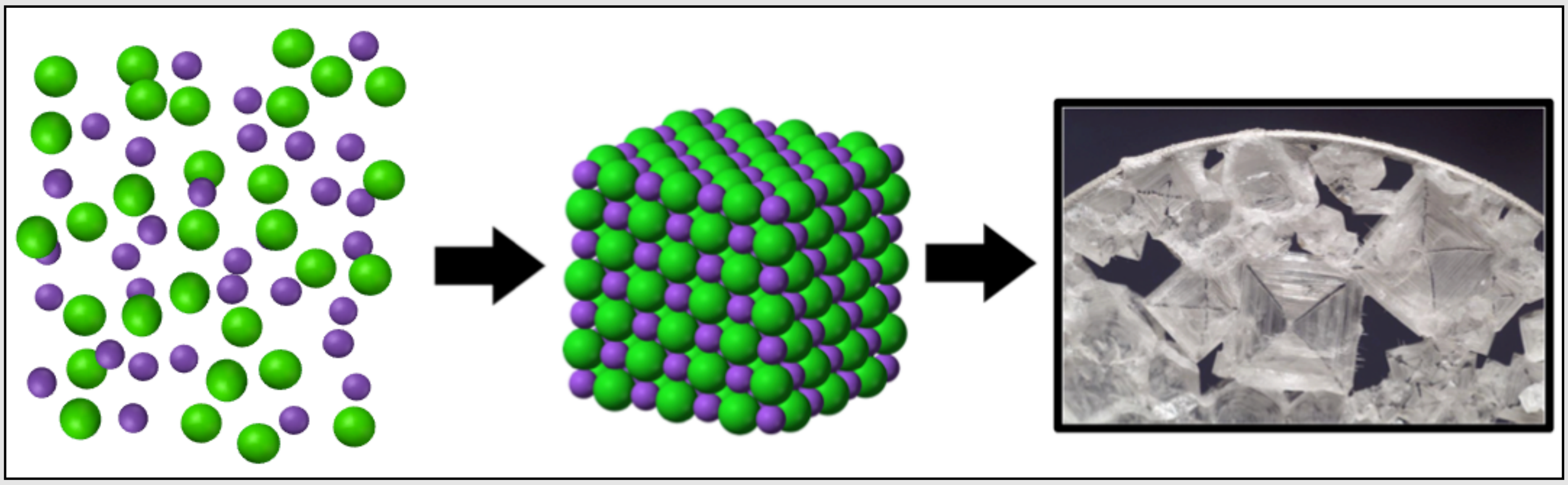
For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

3.7 Ionic Chemical Bonding

When atoms or ions come together to form compounds, they do so because there are forces that hold the atoms together. In both ionic and covalent bonding, the forces arise from electrostatic attractive forces between all of the subatomic particles that make up the atoms or ions in the compound. In this section, I will discuss the nature of **ionic bonding and how to name ionic compounds**.

We begin with a definition of **ionic bonding**: Chemical bonding that results from the electrostatic attraction between **large numbers** of ***cations*** and ***anions***. It is the electrostatic attractive force between the positive cations and the negative anions that hold the compound together. Let's consider the ionic compound sodium chloride ($NaCl$). In this compound, many sodium ions combine with many chloride ions in a three-dimensional pattern that minimizes the distance between the oppositely charged cations and anions and maximizes the distance between the like-charged particles (anion-anion and cation-cation). This process is illustrated in Figure 3.40. Notice the regular, repeating pattern in the middle of Figure 3.40 that results from ionic bonding. We call this structure a **crystal** or **crystal lattice**. It is this regular, repeating structure on the scale of the individual ions that give crystals the interesting geometrical shapes that we see on the macro-scale when we look at them with our eyes or with a microscope (on right in Figure 3.40).

Figure 3.40 **Ionic Bonding in the Formation of a Sodium Chloride Crystal**



Ionic bonding occurs when **many** Na^+ ions (represented as purple spheres) combine with **many** Cl^- ions (green spheres) in a geometric pattern that minimizes the Na^+ to Cl^- distance and maximizes the Na^+ to Na^+ and Cl^- to Cl^- distance. This results in the formation of a sodium chloride crystal (illustrated in middle) and shown in a microscope image (right).
Source: Wikimedia Commons, PD

Ionic bonding (ionic compounds) results from:

1. Combining **metal ions** with **nonmetal ions**.
2. Combining **polyatomic ions** with ***other*** **ions**.

Now is a good time for you to consider the fundamental difference between **covalent compounds** and **ionic compounds**. **Covalent compounds** exist as very small particles (***called molecules***) composed of a relatively *small number of atoms*. **Ionic compounds** are composed of *very large numbers* of cations and anions (usually many millions) arranged in a ***crystal lattice***. For example, consider the difference between a water molecule (covalent) and an ionic compound such as sodium chloride. A water molecule contains *three* atoms; contrast that with a typical grain (crystal) of table salt (sodium chloride) that contains on the order of 3,000,000,000,000,000,000 sodium ions and 3,000,000,000,000,000,000 chloride ions. The forces holding the atoms together in covalent compound arise from sharing of electron pairs; the forces holding the ions together in ionic compounds arise from electrostatic attractive forces between anions and cations. As you build your mental model of how matter exists, keep in mind this important difference between covalent (molecular) compounds and ionic compounds.

The Structure of Ionic Compounds

Highly positive or highly negative charged objects are high in energy and therefore not stable and unlikely to exist. For this reason, cations and anions will combine in a ratio such that the total charge of the crystal is **ZERO**. The total positive charge from cations will be equal to the total negative charge from anions, therefore the overall charge of the crystal will equal *zero*. This lack of total charge is why you do not get electrocuted (shocked) when you take hold of the salt shaker at dinner!

Let's consider a **sodium chloride** crystal. Millions of sodium ions combine with millions of chloride ions in such a way that the total charge of the crystal is equal to zero. A sodium ion has a charge of 1^{+}. A chloride ion has a charge of 1^{-}. To have a total charge of zero, the sodium and chloride ions ***must*** combine in a one-to-one ratio in the crystal. For every sodium ion, there is one chloride ion! If this did not happen, the result would be a high energy, unstable configuration and, as I have been emphasizing throughout this book, that is not what happens in nature! The low energy state for a crystalline substance is one that has **ZERO total charge**.

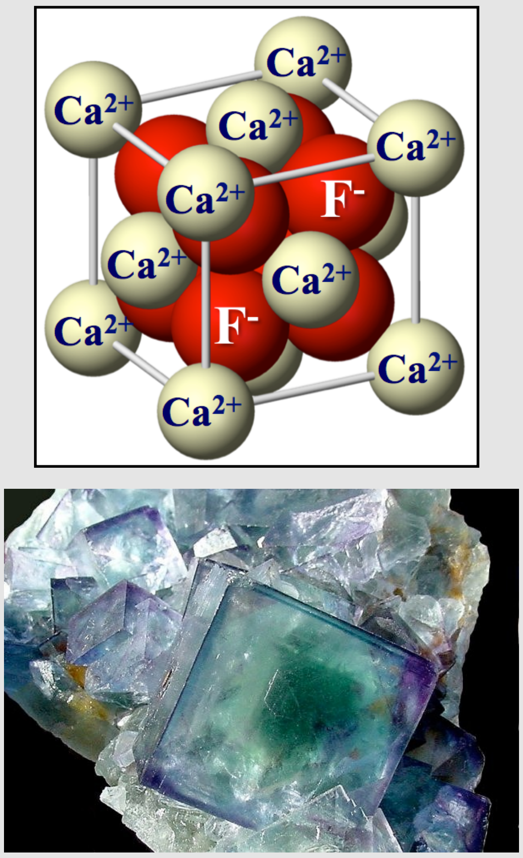
Formula Units

We described *molecules* using ***molecular formulas*** in the previous section when we studied *covalent compounds*. The use of *molecular formulas* would not make sense for ionic compounds; they do not form molecules, instead they form crystals. We write a different type of ***formula*** for ionic compounds. We write the **formula unit** for the compound. The *formula unit* looks like the molecular formula used for covalent compounds, however it means something ***entirely*** different. The *formula unit* uses ***subscripted numbers*** after the ion's symbol that indicate the ***ratio*** that the cations and anions combine in the ionic crystal. As in the case of molecular formula, when a subscript would have a value of "1," the subscript is omitted. We write the cation symbol first followed by a numerical subscript (if needed), then we write the anion symbol followed by a numerical subscript (if needed). For sodium chloride, since sodium ions and chloride ions combine in a **one-to-one ratio**, we write the formula unit of sodium chloride as:

$$\mathbf{NaCl}$$

Let's consider *another* **ionic** crystal. **Calcium fluoride** crystals exist in nature and go by the mineral name *fluorite* or *fluorspar*. It is the world's major industrial source of fluoride ions. Millions of calcium ions combine with millions of fluoride ions in such a way that the total charge of the crystal is equal to zero. Calcium ions have a charge of 2^{+}. Fluoride ions have a charge of 1^{-}. In order for the crystal to have a *total charge of zero*, there must be two F^- ions for every one Ca^{2+} ion such that the positive and negative charges cancel each other. An illustration of the crystal structure of calcium fluoride is shown in Figure 3.41. Note that the repeating unit of the crystal lattice (called a *unit cell*) is contained **inside** the cube shown in white bars in the figure. Within the cube are eight F^- ions (red spheres) and a **total** of four Ca^{2+} ions (yellow spheres). It may not be immediately apparent why I say a **total** of only four Ca^{2+} ions. Let me clarify. We are concerned with the number Ca^{2+} ions ***inside the cube***. None of the Ca^{2+} ions are ***entirely*** contained *inside the cube*. Let's add up the *fractions* of calcium ions *inside* the cube. There is 1/8th of a Ca^{2+} ion on *each* of the eight corners of the cube, so 8 corners x (1/8) = 1 Ca^{2+} ion. There is 1/2 of a Ca^{2+} ion on *each* of the six faces of the cube, so 6 faces x (1/2) = 3 Ca^{2+} ions. That gives us a **total** of four Ca^{2+} ions **inside** the cube. Four Ca^{2+} cations with eight F^- anions with give us the Ca^{2+}:F^- ratio of 1:2. **We always use the lowest integer values for ratios**; we use 1:2, **not** 4:8. Some scientists spend their careers determining and studying crystalline structures. If you have ever studied mineralogy in geology, you may have some knowledge of crystalline structures.

Figure 3.41 Crystal Structure of Calcium Fluoride



Top: An illustration of of the crystal structure of calcium fluoride.

Source: Wikimedia Commons. Author: Benjah PD

Bottom: Photograph of a calcium fluoride crystal.

Source: Wikimedia Commons, PD-US

We write the **formula unit** for calcium fluoride as:

$$\mathbf{CaF_2}$$

Naming and Writing the Formula Unit for an Ionic Compound

Educational Goals:

- Given the **name** of an ***ionic compound***, be able to write the **formula unit**.
- Given the **formula unit** of an ***ionic compound***, be able to write the **name**.

Method for Writing Formula Units for Ionic Compounds

Goal: Given the **name** of an ***ionic compound***, be able to write the **formula unit**.

1. Write the symbol of the first ion (the cation) in the compound's name, then the symbol of the second ion (the anion) in the compound's name.

2. Indicate the **ratio** of the ions in the compound using ***subscripts*** after each ion.

    - The ratio of the ions is deduced by *balancing the charges* of the ions so that the total charge in the crystal is equal to **zero**.
        - We find the ion's charge from its position on the periodic table or, for polyatomic ions, we look it up in a table.
        - You will know the charge for the metals t*hat occur with various charges* because the charge will be written in the compound's name in Roman numerals.
        - When a subscript would have a value of "1," the subscripted is omitted.

    - For ***polyatomic ions***:
        - When the subscript for a polyatomic ion is ***greater than 1***, the polyatomic ion formula is written in parenthesis and the subscript is written after/outside of the parenthesis. You will see this rule in one of the examples that follow.

Mastering the educational goals involved in naming compounds is done by ***working on many problems***. Let's get to know and understand the naming rules by doing some examples. Then, be sure to do the review problems.

Example: Write the formula for **calcium bromide**.

1. Write the symbol of the first ion in the compound's name, then the symbol of the second ion in the compound's name.

$$\mathrm{Ca} \quad \mathrm{Br}$$

2. Indicate the ratio of the ions in the compound using subscripts after each ion.
    - This step involves filling in the subscripts boxes:

$$\mathrm{Ca}_{\boxed{?}}\,\mathrm{Br}_{\boxed{?}}$$

- The ratio of the ions is deduced by balancing the charges of the ions such that the total charge of the crystal is **zero**.
    - We find the ion's charge from its position on the periodic table
    - First, temporarily write the charge of each ion above the ion's symbol.

$$\mathrm{Ca}^{2+}_{\boxed{?}}\ \mathrm{Br}^{1-}_{\boxed{?}}$$

- Next, place numbers in the subscripted boxes such that the total charge of the compound is zero.
    - Note that in this example, we need two bromide ions, each has a charge of (1-), to cancel the (2+) charge of the calcium ion.
        - $[2 \times (-1)_{\text{from bromide}}] + [1 \times (+2)_{\text{from calcium}}] = 0$ zero total charge.

$$\mathrm{Ca}^{2+}_{\boxed{1}}\ \mathrm{Br}^{1-}_{\boxed{2}} = \mathrm{CaBr_2}$$

Now that I showed you the rigorous, theoretical way to get the ratio that the ions combine such that the total charge is equal to zero, I can show you a shortcut called the ***Criss-Cross Method***. **Use the cation's charge for the anion's subscript and anion's charge for the cation's subscript (omit the negative and positive signs) to get that ratio.** The Criss-Cross Method has a mathematical basis and is related to "*cross-multiplying*" used in simplifying fractions in arithmetic and algebra.

$$\mathrm{Ca}^{2+}_{\boxed{1}}\ \mathrm{Br}^{1-}_{\boxed{2}} = \mathrm{CaBr_2}$$

Note, we ***do not*** *leave the charges* written above the symbols in the completed formula.

Let's do an example that contains a *polyatomic ion*.

Example: Write the formula for **magnesium nitrate**.

1. Write the symbol of the first ion in the compound's name, then the symbol of the second ion in the compound's name.
    - When you see the "-ate" or "-ite" suffix as in *nitrate*, let that be a hint that the compound contains a polyatomic ion.

$$\mathrm{Mg}\quad \mathrm{NO_3}$$

2. Indicate the ratio of the ions in the compound using subscripts after each ion.
    - This step involves filling in the subscripts boxes:

$$\mathrm{Mg}_{\boxed{?}}\ \mathrm{NO_3}_{\boxed{?}}$$

- The ratio of the ions is deduced by balancing the charges of the ions.
    - We find the ion's charge from its position on the periodic table or, for polyatomic ions, we look it up in a table.
        - See the polyatomic ion table.
    - First, temporarily write the charge of each ion above the ion's symbol.

$$\mathrm{Mg}^{2+}_{\boxed{?}}\ \mathrm{NO_3}^{1-}_{\boxed{?}}$$

- Next, place numbers in the subscripted boxes such that the total charge of the compound is zero.
    - Note that in this example, we need two nitrate ions, each has a charge of (1-), to cancel the (2+) charge of the magnesium ion.
        - $[2 \times (-1)_{\text{from nitrate}}] + [1 \times (+2)_{\text{from magnesium}}] = 0$ zero total charge.

$$\mathrm{Mg}^{2+}_{\boxed{1}}\ \mathrm{NO_3}^{1-}_{\boxed{2}} = \mathrm{Mg(NO_3)_2}$$

- When the subscript for a polyatomic ion is ***greater than 1***, the polyatomic ion formula is written in parenthesis and the subscript is written after/outside of the parenthesis.

•Alternatively....use the *Criss-Cross Method* shortcut:

$$\mathrm{Mg}^{2+}_{\boxed{1}}\ \mathrm{NO_3}^{1-}_{\boxed{2}} = \mathrm{Mg(NO_3)_2}$$

Example: Write the formula for **iron(II) phosphate.**

1. Write the symbol of the first ion in the compound's name, then the symbol of the second ion in the compound's name.
    - An "-ate" or "-ite" suffix as in *phosph<u>ate</u>* indicates that it is a polyatomic ion.

$$\mathrm{Fe}\quad \mathrm{PO_4}$$

2. Indicate the ratio of the ions in the compound using subscripts after each ion.
    - This step involves filling in the subscripts boxes:

$$\mathrm{Fe}_{\boxed{?}}\,\mathrm{PO_4}_{\boxed{?}}$$

- The ratio of the ions is deduced by balancing the charges of the ions.
    - We find the ion's charge from its position on the periodic table or, for polyatomic ions, we look it up in a table.
        - See the polyatomic ion table. From the table, note that phosphate has a charge of 3-.
    - You will know the charge for a metal t*hat occurs with various charges* because the ***charge will be written in the compound's name in Roman numerals***.
        - **iron(II)** phosphate: The charge on the Fe ion is 2+ because of the **(II)** in the name.
        - First, temporarily write the charge of each ion above the ion's symbol.

$$\overset{2+}{\mathrm{Fe}}_{\boxed{?}}\quad \overset{3-}{\mathrm{PO_4}}_{\boxed{?}}$$

- Next, place numbers in the subscripted boxes such that the total charge of the compound is zero.
    - We will use the ***Criss-Cross Method*** shortcut in this example.
        - Use the cation's charge for the anion's subscript and anion's charge for the cation's subscript (omit the negative and positive signs) to get that ratio.

$$\overset{2+}{\mathrm{Fe}}_{\boxed{3}}\quad \overset{3-}{\mathrm{PO_4}}_{\boxed{2}} = \mathrm{Fe_3(PO_4)_2}$$

- When the subscript for a polyatomic ion is ***greater than 1***, the polyatomic ion formula is written in parenthesis and the subscript is written after/outside of the parenthesis.

Example: Write the formula for **barium sulfide**.

1. Write the symbol of the first ion in the compound's name, then the symbol of the second ion in the compound's name.

$$\mathrm{Ba}\quad \mathrm{S}$$

2. Indicate the ratio of the ions in the compound using subscripts after each ion.
    - The ratio of the ions is deduced by balancing the charges of the ions.
        - We find the ion's charge from its position on the periodic table.
        - First, temporarily write the charge of each ion above the ion's symbol.

$$\overset{2+}{\mathrm{Ba}}_{\boxed{?}}\,\overset{2-}{\mathrm{S}}_{\boxed{?}}$$

- Next, place numbers in the subscripted boxes such that the total charge of the compound is zero.
    - We will use the ***Criss-Cross Method*** shortcut in this example.
        - Use the cation's charge for the anion's subscript and anion's charge for the cation's subscript (omit the negative and positive signs) to get that ratio.

$$\mathrm{Ba}^{2+}_{\boxed{2}}\mathrm{S}^{2-}_{\boxed{2}} = \mathrm{BaS} \qquad \textbf{\underline{DO NOT} WRITE:}\ \mathrm{Ba_2S_2}$$

    - NOTE: The subscripts in ionic compounds represent the *ratio in which large numbers of anions and cations combine to form crystals*. **When writing ratios, we use smallest integer values**. We do not use 2:2 since 2:2 = 1:1. As *another* example, if, after you apply Criss Cross Method, you end up with 2:4, you would use 1:2.

Reducing the ratio to the lowest integer value in *formula units* is done for **ionic compounds only**; we **do not** do so for *molecular formulas* of **covalent compounds**! This makes sense when we consider the fundamental difference between ionic compounds and molecules. The *molecular formula* represents the *number atoms of each element contained in a single molecule*. The **formula unit** used for *ionic compounds* represents ***ratios*** of large numbers of cations to large numbers of anions contained in a crystal. For example; a molecule called hydrogen peroxide contains two hydrogen and two oxygen atoms, therefore it has the **molecular formula** H_2O_2. The barium sulfide compound in our example has millions of barium ions and millions of sulfide ions that combine in a one-to-one ratio, therefore its **formula unit** is BaS.

Review 3.10: Writing the Formula Unit for Ionic Compounds

Write the formula for the following ionic compounds:

a) sodium bicarbonate
(Note: bicarbonate is a polyatomic ion, see the polyatomic ion table for its formula and charge)
b) sodium fluoride
c) iron(III) chloride
d) sodium carbonate
e) copper(II) sulfate
f) magnesium hydroxide
g) barium nitrate
h) lithium sulfate
i) magnesium chloride
j) silver nitrate
k) aluminum sulfate
l) calcium hydroxide

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

Method for Writing the Names of Ionic Compounds

Goal: Given the **formula unit** of an ***ionic compound***, be able to write the **name**.

1) Write the **cation** name first, then the **anion** name.
    - Monoatomic ***anions*** (anions composed of one element) use the "ide" suffix.
    - We get the names of *polyatomic ions* from the polyatomic ion table.

2) If the cation is one of the metals with various charges, write the charge using parenthesis and Roman numerals after the metal name.

Let's learn and practice these naming rules by doing some examples. Then, be sure to do the review problems on your own; you will become proficient at naming compounds by ***working on many problems***.

Example: Write the name for **$CaBr_2$**

1) Write the **cation** name first, then the **anion** name.
    - These are both monoatomic ions (composed of one element, calcium for the cation and bromine for the anion)
    - Monotonic ***anions*** use the "ide" suffix. We write "bromide" for the anion name.

calcium brom*ide*

2) If the cation is one of the metals that can occur with various charges, write the charge using parenthesis and Roman numerals after the metal name.
    - Not necessary in this example, there is ***not*** a metal that can occur with various charges.

ANSWER: calcium bromide

You may have noticed that the rules for naming ionic compounds are different from those used when naming covalent (molecular) compounds. In covalent compounds, we needed to use Greek prefixes to indicate the numbers of each atom in the molecule. This is not necessary for ionic compounds because the ratio of ions used in the *formula units* can be deduced from the charges of the ions (such that the total charge is equal to zero). It is for this reason that **we do not use, see, or need Greek prefixes when naming ionic compounds**.

Example: Write the name for **$Mg(NO_3)_2$**

1) Write the **cation** name first, then the **anion** name.
    - Since the anion (NO_3) is composed of more than one type of element, we conclude that it must be a *polyatomic ion*.
        - We get the names and charges for *polyatomic ions* from the polyatomic ion table.
            - The name for NO_3^- is nitrate and it has a (1-) charge.

magnesium nitrate

2) If the cation is one of the metals with various charges, write the charge using parenthesis and Roman numerals after the metal name.
    - Not necessary in this example, there is not a metal that can occur with various charges.

ANSWER: magnesium nitrate

Next, let's name an ionic compound that contains one of the metals that occurs in nature with varying charge.

Example: Write the name for **CuF_2**

1) Write the **cation** name first, then the **anion** name.
   - Monoatomic anions (composed of one element) use the "ide" suffix.

copper fluoride

2) If the cation is one of the metals with various charges, write the charge using parenthesis and Roman numerals after the metal name.
   - Copper is one of the metals that occur with varying charge (see Table 3.2).

copper(?) fluoride

   - We must figure out what the charge of the copper ion in this compound is; we can **deduce** the charge on transition metal cations ***from the charge on the anions.***
     - Recall that the ***total charge*** for any compound must equal **zero**.
       - Since there are **two fluorides**, each with a charge of (1-), and there is **only one copper** in the formula, we can conclude that the charge on the copper must be (2+). The total charge from the cation(s) must cancel with the total charge from the anion(s).
         - $[2 \times (1-)]_{\text{from fluorides}} + [1 \times (2+)]_{\text{from copper(II)}} = 0$

ANSWER: copper(II) fluoride

Review 3.11: Writing the Names for Ionic Compounds

Write the names for the following ionic compounds:

a. NaCl

b. $Fe_2(CO_3)_3$

Fe is one of the metals that can occur with varying charge, you will need to **deduce** the charge on the iron cation based on the three carbonates and their charge. See Table 3.2: transition metal charges.

c. $Cu(OH)_2$ (Note: Cu is one of the metals that can occur with varying charge)

d. $(NH_4)_2SO_4$ (Note: NH_4^+ is a polyatomic ***cation***)

e. $LiNO_3$

f. $BaSO_4$

g. $Mg(NO_3)_2$

h. AgCl

Silver (Ag) is a transition metal, however **it is not one that can occur with varying charge**, therefore you ***do not need to indicate the charge*** in parenthesis after the cation name. See Table 3.2: Transition Metal Charges.

i. $Al(OH)_3$

j. $CaSO_4$

k. FeS

l. $PbCl_2$ (Note: Pb is one of the metals that can occur with varying charge)

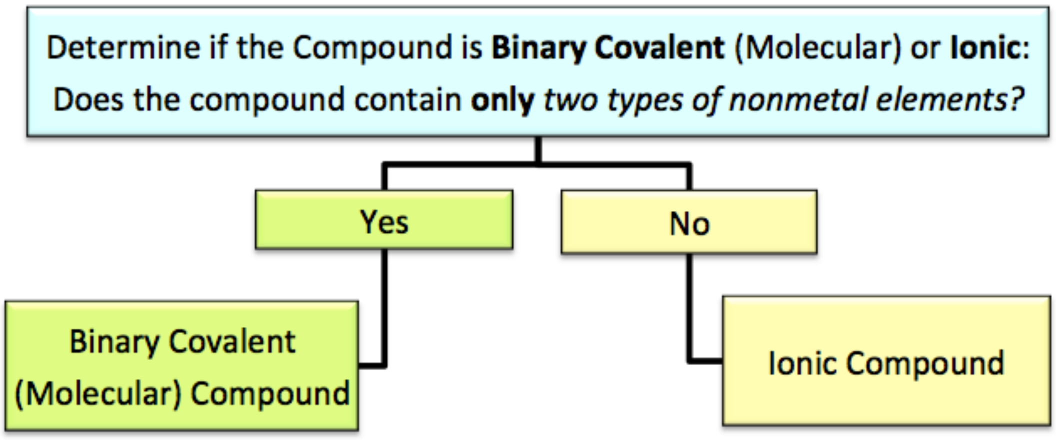
m. NaI

n. $MgCO_3$

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

3.8 Naming Compounds Summary

Since we use different methods in **naming binary covalent (molecular) compounds** and i**onic compounds**, the first step in naming or writing the formula of a compound is to determine to which of those two compound classes it belongs. This can be done as follows:

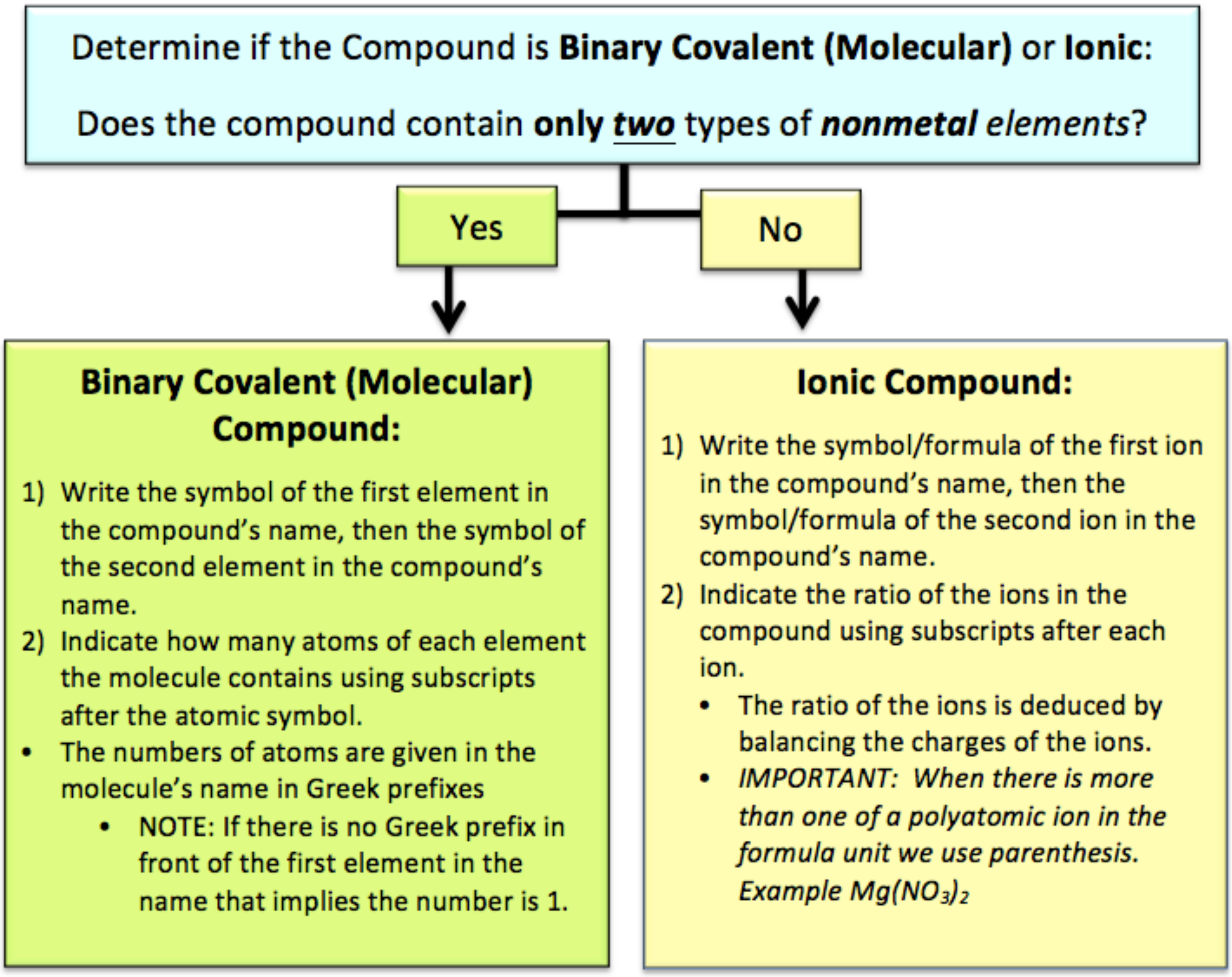


Binary covalent (molecular) compounds will contain only **two** types of **<u>nonmetal</u> elements**; however, there may be more than one atom of each element in a molecule. For example, CO_2 contains a total of three *atoms*, however, it is classified as a binary covalent compound because it contains just **two *types of elements***, carbon and oxygen. We will discuss naming covalent compounds that contain *more than two types of elements*, like glucose $C_6H_{12}O_6$, in later chapters.

Once it is determined that a compound is **ionic** or **binary covalent**, you will be expected to do the following:

1) Given the **name** of a ***compound***, be able to write the **formula**.
2) Given the **formula** of a ***compound***, be able to write the **name**.

1). Given the **name** of a ***compound***, be able to write the **formula**.



Binary Covalent (Molecular) Compound:

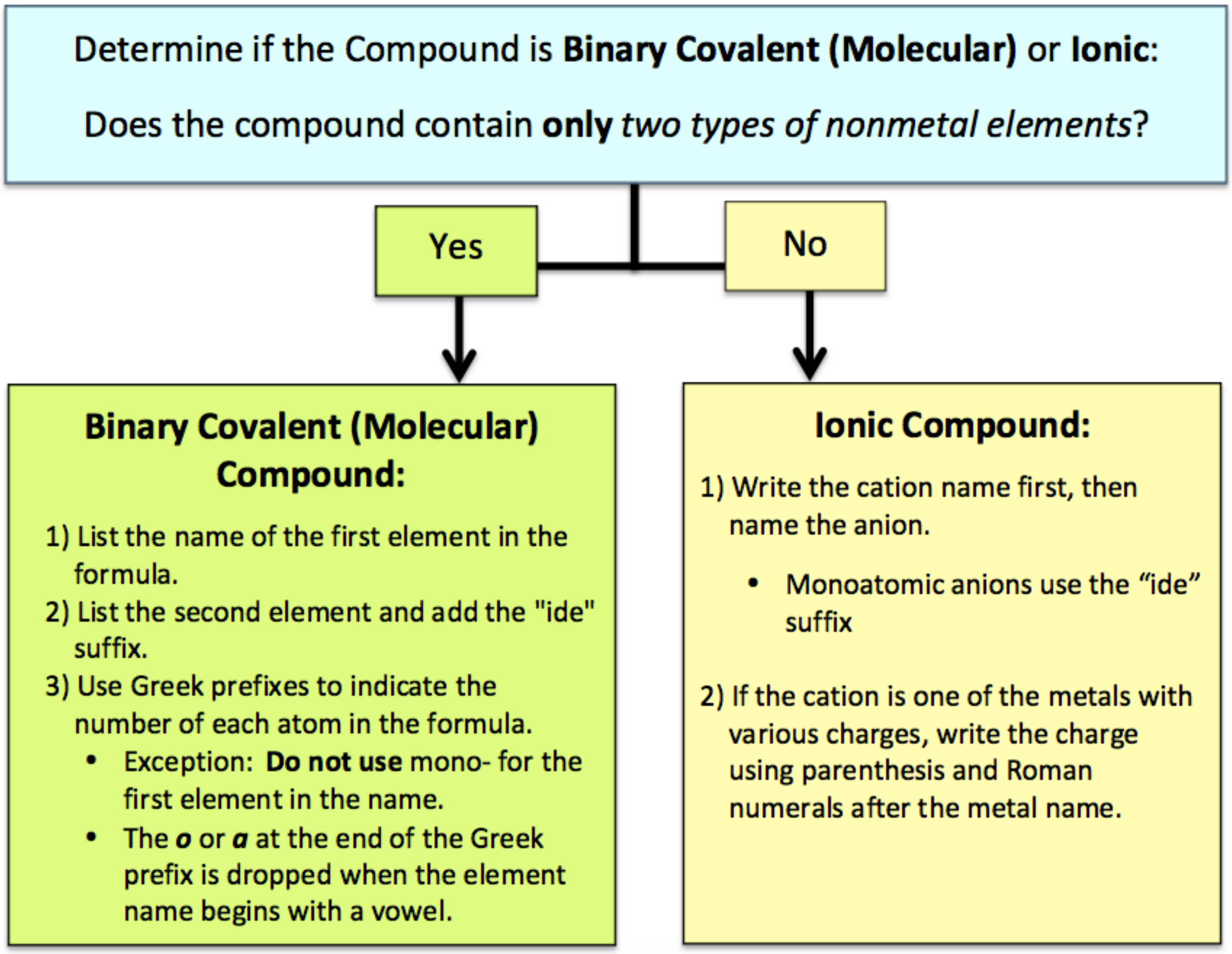
1) Write the symbol of the first element in the compound's name, then the symbol of the second element in the compound's name.
2) Indicate how many atoms of each element the molecule contains using subscripts after the atomic symbol.

- The numbers of atoms are given in the molecule's name in Greek prefixes
  - NOTE: If there is no Greek prefix in front of the first element in the name that implies the number is 1.

Ionic Compound:

1) Write the symbol/formula of the first ion in the compound's name, then the symbol/formula of the second ion in the compound's name.
2) Indicate the ratio of the ions in the compound using subscripts after each ion.
   - The ratio of the ions is deduced by balancing the charges of the ions.
   - *IMPORTANT: When there is more than one of a polyatomic ion in the formula unit we use parenthesis. Example* $Mg(NO_3)_2$

2) Given the **formula** of a ***compound***, be able to write the **name.**



Determine if the Compound is **Binary Covalent (Molecular)** or **Ionic**:

Does the compound contain **only** *two types of nonmetal elements*?

Binary Covalent (Molecular) Compound:

1) List the name of the first element in the formula.
2) List the second element and add the "ide" suffix.
3) Use Greek prefixes to indicate the number of each atom in the formula.
   - Exception: **Do not use** mono- for the first element in the name.
   - The ***o*** or ***a*** at the end of the Greek prefix is dropped when the element name begins with a vowel.

Ionic Compound:

1) Write the cation name first, then name the anion.
   - Monoatomic anions use the "ide" suffix
2) If the cation is one of the metals with various charges, write the charge using parenthesis and Roman numerals after the metal name.

3.9 Molar Mass of Compounds

In chapter 2, you learned how to *convert* between the ***mass of a sample of a particular atom*** and the number of ***moles***. We did this by using the **molar mass** of the element as the *conversion factor*. The ***molar masses*** that we find in the *periodic table* are the mass (in grams) of one mole of atoms of the element. The ***molar mass*** gives us the *relationship* between the mass (grams) and the number of moles for a particular element.

How can we convert from mass to moles (and vice versa) for compounds? We will need the molar mass of the compound to do so. We cannot get the molar mass of a compound *directly* from the periodic table as we did for atomic molar masses. We do not have a "*periodic table of the compounds*"; it would be huge because there are thousands of known compounds and there are new ones being discovered in nature or synthesized in labs! **This section will discuss how we can calculate the molar mass of a compound and how we use the molar mass of a compound to do mole-mass conversions.**

To calculate the molar mass of a **molecule** we **add up** the ***atomic molar masses*** of **all** atoms in the molecule. The *molar mass* of a molecule is also called the **molecular mass**. Let's calculate the molar mass of H_2O.

There are ***two*** hydrogen atoms and ***one*** oxygen atom in an H_2O molecule. To calculate the molar mass of H_2O, add up the atomic molar mass of two hydrogen atoms and one oxygen atom as shown in Table 3.5. The molar mass of H_2O is 18.02 grams/mole. This means that one mole of water molecules (6.022 x 10^{23} molecules) has a mass of 18.02 grams.

Table 3.5 Calculation of the Molar Mass for H_2O

Atom	# of Atoms	Atomic Molar Mass	Total
oxygen	1	x 16.00 g/mole	= 16.00 g/mole
hydrogen	2	x 1.01 g/mole	= 2.02 g/mole
Molar Mass of H_2O			**= 18.02 g/mole**

Review 3.12: Calculating the Molar Mass of Compounds

Calculate the molar mass of the following compounds:

(**NOTE:** If you wish your calculated values to *exactly* match the solutions in this text, round the ***atomic molar masses*** to ***two*** *places after the decimal point when possible*.)

a) Methane (CH_4, methane is the major ingredient of natural gas)

b) Glucose ($C_6H_{12}O_6$, glucose is the final product of photosynthesis)

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

Note that, as in the case of atoms, the molar mass of a compound is the ***relationship*** between *moles* and *mass (grams)*, therefore we can **convert** between moles and grams of compounds.

Example: ***How many grams of H_2O is contained in 4.76 moles?***

Solution: We use our Factor Label Method (just like any other unit conversion problem):

- Use the molar mass of H_2O (18.02 g/mole) from Table 3.5.
- Use the molar mass to write an *equivalence statement*: **1 mole H_2O = 18.02 grams.**
- The equivalence statements can be written as conversion factors:

$$\left(\frac{1\text{ mole }H_2O}{18.02\text{ g }H_2O}\right) \xleftrightarrow{\text{Conversion Factors}} \left(\frac{18.02\text{ g }H_2O}{1\text{ mole }H_2O}\right)$$

Next, we will set up a unit conversion equation; we multiply the *given unit* (4.67 moles) by the correct form of the conversion factor:

- Use the form of the conversion factor that has moles on the bottom and grams on the top:

$$\frac{4.76\ \cancel{\text{moles } H_2O}}{} \left|\ \frac{\textbf{18.02 grams}\ H_2O}{1\ \cancel{\text{mole } H_2O}}\right| = 85.8 \text{ grams } H_2O$$

- Since the given number of moles (4.76) has three significant figures and we used four significant figures in the molar mass, the answer has three significant figures.

Review 3.13: Converting Between Moles and Grams of Compounds

a) What is the mass of 15.3 moles of carbon dioxide?
b) What is the mass of 0.57 moles of hydrogen monochloride?

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

In the previous example and problems, we were given the number of moles of a compound and then converted to the mass (grams). Conversely, if we are given the mass we can convert to the number of moles.

Example: How many moles are contained in 23.67 grams of methane (CH_4)?

Solution: We use our **Factor Label Method**:

- Use the molar mass of methane (CH_4, 16.05 g/mole). You calculated this in Review Problem 3.11.
- From the molar mass, we can write an *equivalence statement*: **1 mole CH_4 = 16.05 grams.**
- Use the equivalence statement to get the conversion factor.

- Next, we will set up a unit conversion equation; multiply the *given unit* (23.67 grams) by the correct form of the conversion factor:
  - We use form of the conversion factor that has grams on the bottom and moles on the top:

$$\frac{23.67\ \cancel{\text{grams } CH_4}}{} \left|\ \frac{1 \text{ mole } CH_4}{16.05\ \cancel{\text{grams } CH_4}}\right| = 1.475 \text{ moles } CH_4$$

- Since the given number of grams (23.67) has four significant figures and we used four significant figures in the molar mass, the answer has four significant figures.

Review 3.14: Converting From Mass (Grams) to Moles of Compounds

How many moles are contained in 2.93 grams of H_2O?

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

Converting Between Mass and Number of Molecules

You have just learned how to convert between moles and mass of a compound and vice versa. How would you convert between mass and number of molecules? In chapter 2 you used **Avogadro's Number** to convert between number of moles and number of atoms (1 mole = 6.022×10^{23} atoms). Since the mole is simply a *counting unit*, like "dozen," we can also use it to discuss the number of molecules present (1 mole = 6.022×10^{23} molecules). Furthermore, we could ***also** convert between molecules and moles* since **Avogadro's Number applies to molecules**; one mole of a molecular compound contains 6.022×10^{23} molecules. These unit conversions are summarized in the Molecules-Mole-Mass Conversion Map shown in Figure 3.42. You may find it helpful to refer to this conversion map as you are working on molecules-mole-mass conversion problems.

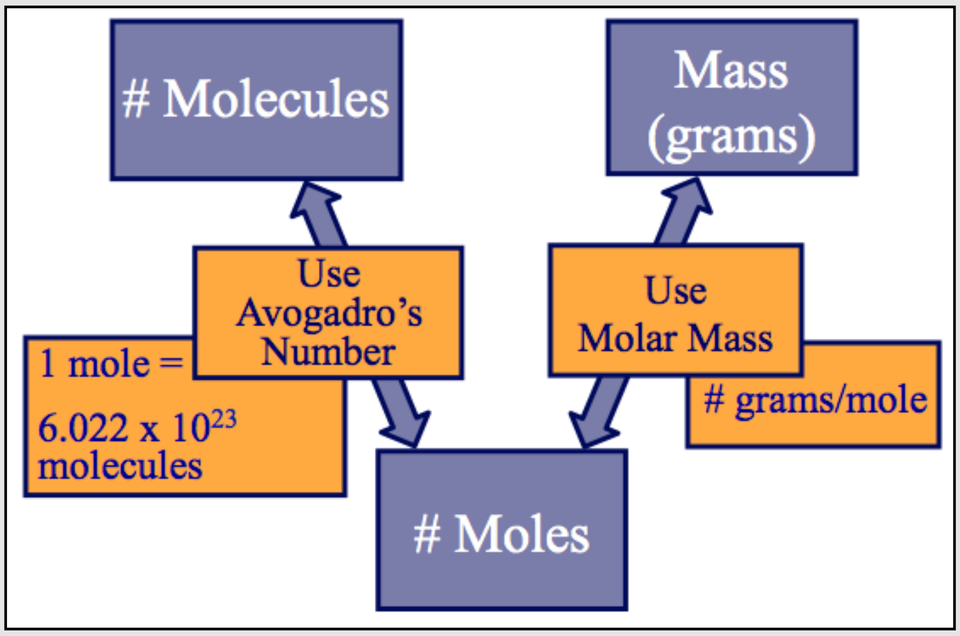
Suppose you are given the mass of a compound and wish to determine the number of molecules present. You may recall we did this same type of problem for converting from mass of atoms to the number of atoms. Look at the conversion map in Figure 3.42!

We will use **two steps**:

(1) Convert from mass to moles
(2) Convert moles to # of molecules

Conversely, if you were given the number of molecules present and wished to calculate the mass, you would do a two-step conversion in the opposite order than listed above. You learned how to do two-step conversions in chapter 1.

Figure 3.42 Molecules-Mole-Mass Conversion Map



Let's do an example problem: A cup of water contains about 237 grams of water.

How many H_2O molecules are contained in 237 grams?

We will need to do 2 steps. First we will convert from mass (grams) to moles, then we will convert moles to number of H_2O molecules:

- **Conversion 1:** convert mass (237 grams) to moles
- **Conversion 2:** convert **moles H_2O** to number of H_2O molecules

Perhaps you recall the "advanced move" for doing conversions that require more than one step. Instead of doing two separate conversions, *we combine the equations*:

$237\ \cancel{g\ H_2O}$	$1\ \cancel{mole\ H_2O}$	6.022×10^{23} H_2O molecules	**= 7.92×10^{24}** H_2O molecules
	$18.02\ \cancel{g\ H_2O}$	$1\ \cancel{mole\ H_2O}$	

Now you try one. Convert in the *opposite direction*; given the number of ***molecules*** of a substance, you calculate its ***mass***.

Review 3.15: Converting Between Number of Molecules and Grams of Compounds

What is the mass (grams) of 2.25×10^{24} H_2O molecules?

For i-books versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

Formula Mass (Molar Mass of Ionic Compounds)

When using the molar mass of ionic compounds, we calculate the mass of a compound based on the number of each ion as it appears in the formula unit. For this reason, the *molar mass of an ionic compound* is also called **formula mass**. For example, the formula unit for sodium chloride is $NaCl$ (because there is a 1:1 ratio of sodium ions to chloride ions in the crystal). One mole of sodium chloride contains one mole of sodium ions and one mole of chloride ions. The molar mass (or formula mass) is calculated by adding the molar masses of the ions, as shown in Table 3.6. Although ions have extra or missing elections, their molar masses are calculated by adding the atomic molar masses of the elements they contain. The reason we can do this is because the mass of electrons is negligible compared to the mass of protons and neutrons. Note that this is exactly how we calculated the molar mass of molecular compounds, however, you should keep in mind that pure ionic compounds exist as large numbers of anions and cations held together in a crystal. You would **never** be asked how many molecules are in an ionic compound.

Table 3.6 Calculation of the Formula Mass for Sodium Chloride

Ion	# of ions in the Formula Unit	Molar Mass of ion	Total
Sodium	1	x 22.99 g/mole	= 22.99 g/mole
Chloride	1	x 35.45 g/mole	= 35.45 g/mole
Molar Mass (Formula Mass) of NaCl			**= 58.44 g/mole**

Let's calculate the molar mass (formula mass) for an ionic compound that contains a polyatomic ion.

Example: What is the molar mass of iron(II) phosphate, $Fe_3(PO_4)_2$?

Solution: The formula unit for iron(II) phosphate is $Fe_3(PO_4)_2$ (because there is a 3:2 ratio of iron ions to phosphate ions in the crystal). One mole of iron(II) phosphate contains three moles of iron ions and two moles of phosphate ions. The molar mass is calculated by adding the molar masses of the ions as shown in Table 3.7.

Table 3.7 Calculation of the Formula Mass for Iron(II) Phosphate

Ion	# of Ions in the Formula Unit	Molar Mass of ion	Total
Iron(II)	3	x 55.85 g/mole	= 167.55 g/mole
Phosphate	2	x 94.97 g/mole based on: one phosphorus **and** four oxygens ***per ion***	= 189.94 g/mole
Molar Mass (Formula Mass) of $Fe_3(PO_4)_2$			**= 357.49 g/mole**

Mass - Mole Conversions for Ionic Compounds

Given the definition of molar mass/formula mass for ionic compounds and the ability to calculate it from the formula unit, we can now convert between moles of an ionic compound and mass.

Example: What is the mass of 0.23 moles of $Fe_3(PO_4)_2$?

Solution: We use our **Factor Label Method** (just like any other unit conversion problem):

- Use the molar mass (formula mass) of $Fe_3(PO_4)_2$ (357.49 g/mole). We calculated this in the previous example.
- From the molar mass, write an *equivalence statement*: 1 mole $Fe_3(PO_4)_2$ = 357.49 grams.
- The equivalence statement is used as a conversion factor.

$$\begin{array}{c|c} 0.23\ \cancel{\text{moles } Fe_3(PO_4)_2} & 357.49\ \textbf{grams}\ Fe_3(PO_4)_2 \\ \hline & 1\ \cancel{\text{mole } Fe_3(PO_4)_2} \end{array} = 82 \text{ grams } Fe_3(PO_4)_2$$

Since the given number of moles (0.23) has two significant figures and we used four significant figures in the molar mass, the answer has two significant figures.

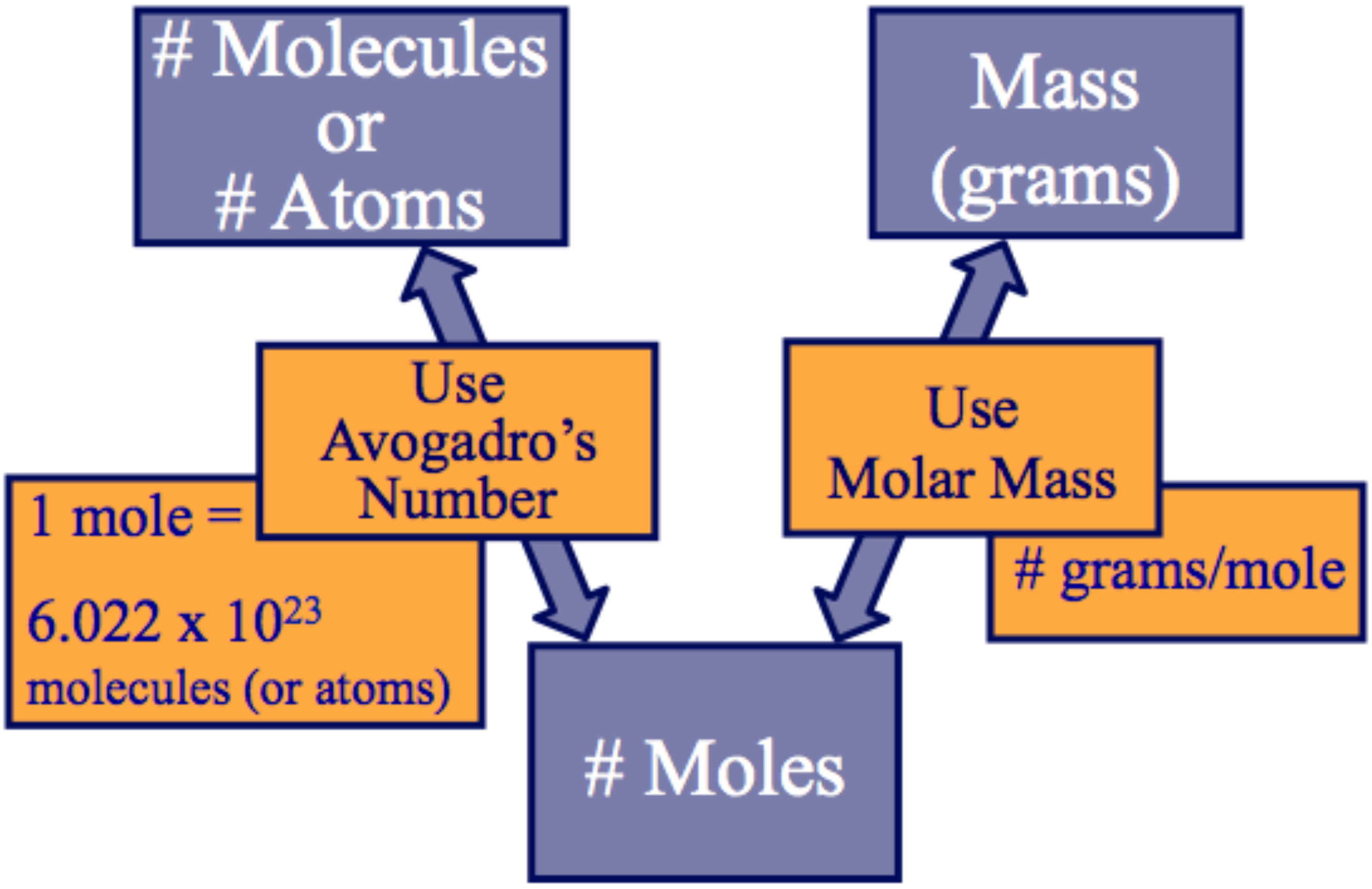
Now you try one. Convert in the *opposite direction*; given the ***mass***, you calculate the number of ***moles.***

Review 3.16: Converting Between Moles and Grams of Ionic Compounds

How many moles of $NaCl$ are contained in 95.2 grams?

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

3.10 Additional Mass-Moles-Molecules Problems



How many moles are contained in 24.0 grams of FeF_3?	ANSWER: **.213 moles**
How many moles are contained in 458 grams of Na_2SO_4?	ANSWER: **3.22 moles**
What is the mass (grams) of 7.40 moles of $AgNO_3$?	ANSWER: **1260 grams (note: 3 significant figures)**
What is the mass of 7.50×10^{23} molecules of H_2SO_4?	ANSWER: **122 grams**
How many molecules are contained in 122 grams of NO_2?	ANSWER: **1.60×10^{24} molecules**
What is the mass of 9.40×10^{25} molecules of H_2?	ANSWER: **315 grams**
How many molecules are contained in 237 grams of CCl_4?	ANSWER: **9.28×10^{23} molecules**
How many molecules are contained in 2.30 grams of NH_3?	ANSWER: **8.13×10^{22} molecules**
What is the mass of 3.30×10^{23} molecules of N_2I_6?	ANSWER: **433 grams**
How many moles are contained in 2.00×10^{19} molecules of CCl_4?	ANSWER: **3.32×10^{-5}moles**
What is the mass of 1.00×10^{24} molecules of BCl_3?	ANSWER: **195 grams**
What is the mass of 4.50 moles of $Ba(NO_2)_2$?	ANSWER: **1030 grams (note: 3 significant figures)**
How many molecules are contained in 9.34 grams of water?	ANSWER: **3.12×10^{23} molecules**

Chapter 4: Organic Chemistry

Organic chemistry is the chemistry of carbon-containing compounds.

Autumn by Giuseppe Arcimboldo (1527-1593) Louvre Museum.
Source: Wikimedia, US-PD

In chapters 2 and 3, I have helped you build your own understanding of matter, in particular, the structure of matter. In chapter 2, you learned how subatomic particles (protons, neutrons, and electrons) combine to form atoms. In chapter 3, you learned about how electrons are arranged around the nucleus of an atom and also about *valence electrons* in order to use the octet rule to predict the bonding patterns in *diatomic* molecules and *ionic* crystals.

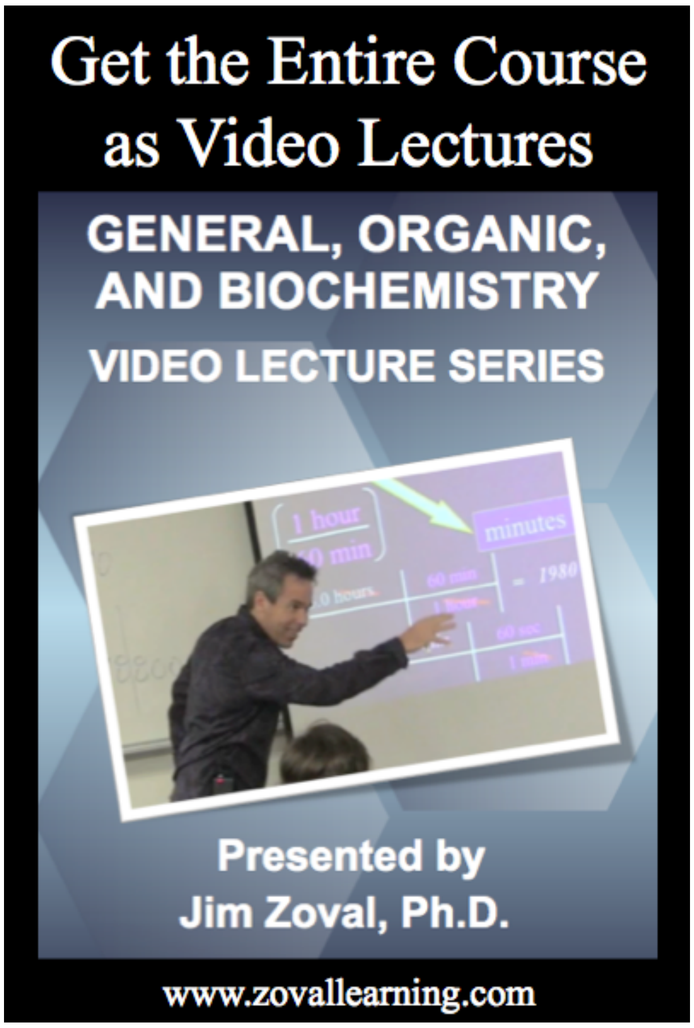
In chapter 4 you will continue to learn about bonding patterns in larger molecules with a focus on organic compounds. Bonding patterns are quite important because the observed “macroscopic” properties of a substance are related to its “nanoscopic” structure. The *nanoscopic* structure of molecules is on the nanometer size scale and includes details such as the type of atoms, the pattern in which they are *bonded* to each other, the *three-dimensional shape*, and how the electrons are distributed within the molecule. Nanoscopic properties determine the ability of a molecule to interact with other molecules and therefore control biological effects; for example, how antibodies bind to antigens (non-self), how some diseases work, how enzymes in our body work, the shape and function of DNA and RNA, etc. Throughout the remainder of this book, you will see how these nanoscopic details of a molecule will affect observed, macroscopic properties such as melting and boiling temperatures, rates of evaporation, ability of one substance to dissolve another substance, and biochemical interactions.

Chapter 4 will conclude with an introduction to organic compounds. You will learn about a family of organic compounds called hydrocarbons and be introduced to some other important classes of organic molecules.

Video Lectures for the General, Organic, and Biochemistry Course

If you **ARE** a **Saddleback College student**, the video lectures for this chapter and all others are available through your class website for ***FREE***. See your instructor for details and the password.

If you **ARE NOT** a **Saddleback College student,** the video lectures can be accessed at: www.zovallearning.com

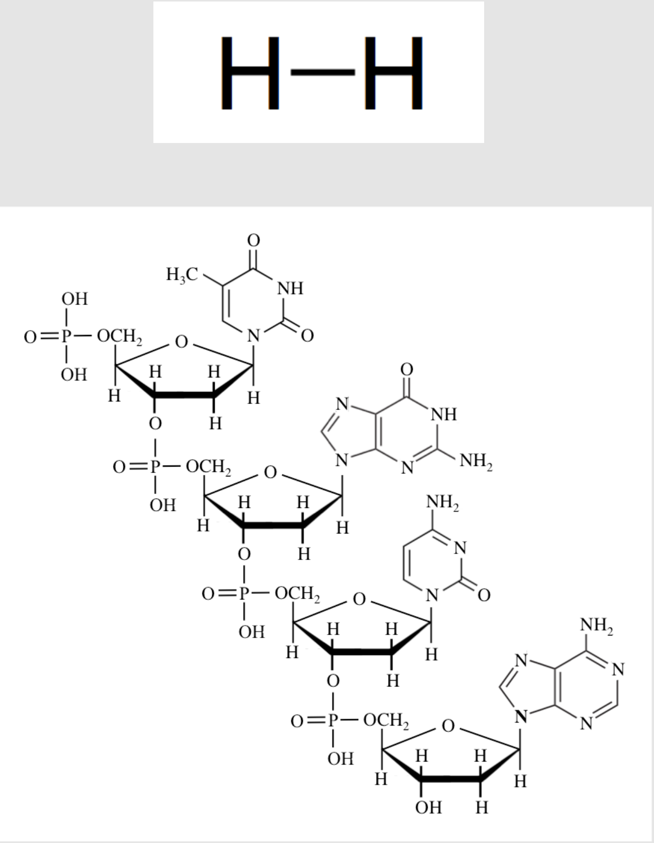


4.1 Chapter 4 Educational Goals

1. Given the formula of a diatomic or small molecule, draw the **line bond structure.**
2. Understand and construct **condensed** and **skeletal structural formulas** given the line bond structures and vice versa.
3. Given the structural formula, determine the **formal charge** of **O** *and* **N** *atoms*.
4. Given the line bond structure of a ***small molecule***, predict the **molecular shape** and **bond angle(s)**.
5. Given the structure of a ***large molecule***, predict the **bond angle(s)** around any atom.
6. Define **electronegativity** and explain its relationship to *polar covalent bonds*.
7. Give a simple rule that can be used to predict whether or not a ***covalent bond*** is **polar**.
8. Classify diatomic, small, and large *molecules* as **polar** or **nonpolar**.
9. Describe, compare, and contrast the five **noncovalent interactions**.
10. Describe, compare, and contrast the four classes of **hydrocarbons**.
11. Given the structural formula of an alkane, alkene, or alkyne, be able to give the name and vice versa.
12. Explain the difference between **constitutional isomers**, **conformations**, and the **stereoisomers** known as **geometric isomers**. Give examples of two different classes of hydrocarbons that can exist as geometric isomers.
13. Define the term **functional group** and describe the structural features that distinguish hydrocarbons, alcohols, carboxylic acids, and esters from one another.

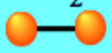
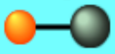
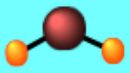
4.2 Line Bond Structures of Molecules

Figure 4.1
Structures of H_2 and DNA



Line bond structure of H_2 (**top**) and the structure of a *small section* of a DNA molecule (**bottom**)
Source: Wikimedia
Author: Vojtech.dostal/Boumphreyfr

We draw **line bond structures** to show how atoms are bonded together in ***molecules***. The structures of molecules can be very simple, as in the case of H_2, or very complex, as in the case of large molecules such as DNA (Figure 4.1). Perhaps you think the DNA molecule in Figure 4.1 is quite hard or impossible to understand. At this point it may be; however as you get to the end of this book and your course, I think you will agree that it is actually quite easy to understand. In chapter 3, you used the concept of valence electrons and the octet rule in order to draw line bond structures of *diatomic* molecules (H_2, HCl, Cl_2, O_2, and N_2). In this section, I will show you a method for drawing line bond structures of small molecules. The educational goal for this section is: *given the formula for a diatomic or small molecule, be able to draw its line bond structure.* In this book, we will often categorize molecules by their *size*. The three size categories are defined as follows:

Molecular Size Category	Description	Example(s)	
Diatomic Molecule	Molecule contains **only two atoms**	H_2 	HCl 
Small Molecule	Molecule has **<u>one</u> central atom** with ***<u>all</u> other*** atoms bonded to the central atom	CH_4 	H_2O 
Large Molecule	Larger than *Small Molecule*; there **is <u>not</u> just one single, central atom** with **<u>all</u>** the other atoms bonded to it	C_3H_8 	

A Method for Drawing Line Bond Structures of Diatomic or Small Molecules

You can begin to learn how to use this method by considering a few examples. If you follow these steps in order, you will be able to draw correct line bond structures. There are six steps. We will start with a molecule with which you are familiar, dihydrogen monoxide, better know in its liquid state as water (H_2O).

Example: Draw the line bond structure for H_2O.

Step 1: Count the total number of **valence electrons** from all the atoms in the molecule.

This step allows us to determine how many *electrons* that we will see in the completed line bond structure. Recall that only the atoms' *valance electrons* are drawn in line bond structures. *Core electrons* are <u>not</u> shown because they do not need to be considered in order to draw correct line bond structures. The *valence electrons* ultimately determine the ***bonding pattern***, and as you will learn in later sections of this chapter, and the ***shape*** of a molecule. The *valence electrons* from all of the atoms contained in a molecule appear in its line bond structure as *either* **lines** representing electron pairs shared between two atoms, <u>*or*</u> **lone pairs.**

- For H_2O (two hydrogen atoms and one oxygen atom)

2 H atoms $2 \times 1e^- = \mathbf{2e^-}$
1 O atom $1 \times 6e^- = \underline{\mathbf{6e^-}}$
Total number of *valence electrons* = $\mathbf{8e^-}$

- The line bond structure of H_2O will show ***eight electrons***

Step 2: Draw the "**Skeleton Structure**": Attach the atoms together with ***single bonds*** in the most *symmetric* way possible.

This step will give you the connectivity of the atoms, the pattern of how the atoms are bonded together. I use the term ***skeleton structure*** because it is the "bare bones" (the absolute minimum number of bonds) needed to hold the atoms together in the molecule. A good way to build a mental picture of this step is to think of the atoms as styrofoam spheres and think of the single bonds as toothpicks. You are connecting the spheres to each other using the toothpicks.

- In nature, the atoms in small molecules tend to be arranged in symmetric patterns. The reason for this goes back to matter existing in the lowest possible energy state. We will not discuss a rigorous proof in this text, however, symmetric bonding patterns are lower in energy than non-symmetric patterns.
- Let's consider which of the following H_2O bonding pattern choices is the most *symmetric*:

(a) **H-H-O** or (b) **H-O-H** or (c) **O-H-H**

  - Did you think that the choice (b), **H-O-H**, is the most symmetric? If so, you are correct, notice that if you rotate that structure by 180° around a vertical axis that goes through the oxygen atom, you end up with the same pattern, **H-O-H**. That is <u>not true</u> for the other two choices. For example, if you use the same rotation for the pattern in choice (a) **H-H-O**, horizontally, you get a *different* pattern **O-H-H**.

- The ***skeleton structure*** for H_2O is: **H-O-H**

Step 3: Subtract the number of electrons used to make the ***skeleton structure*** from the *total number of valence electrons*.

This step will tell us how many electrons will need to be added to our skeleton structure. We will add additional electrons (if needed) in Step 4, but ***not now***.

- We calculated the total number of electrons that our line bond structure will contain back in Step 1.
  - For the line bond structure of H_2O we calculated a **total of eight electrons.**
  - The skeleton structure (from Step 2) is: **H-O-H** How many electrons are in the *skeleton structure*?
  - Each line represents the *two shared electrons*.
  - You can determine the number of electrons used to make the skeleton structure by *multiplying the number of lines/bonds by* ***2***:
    - (2 bonds) x (2 electrons per single bond) = **4 electrons were used to make the skeleton structure.**
- **Number of** electrons that need to be added to our skeleton structure:

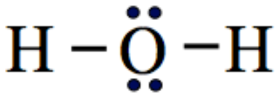
Total number of electrons in line bond structure (from Step 1) =	$8e^-$
Number of electrons used in skeleton (from Step 2) =	$-\ 4e^-$
Remaining number electrons to be added =	$\mathbf{4e^-}$

Step 4: Add the remaining electrons as **lone pairs** as *evenly* as possible on all atoms except hydrogen.

In this step, we add the remaining electrons (calculated in Step 3) to our skeleton structure. These electrons are added as ***lone pairs*** to atoms in the molecule. I used the term "*evenly*"; this means that we distribute the electrons fairly uniformly around the molecule in order to minimize the electrostatic repulsion between the negatively charged lone pairs. Note that there may be several acceptable ways to do this and *all of them* will lead to the correct line bond structure. There are a few other things to keep in mind while *adding the lone pairs*:

- Avoid placing more than eight electrons (this includes shared electrons and lone pairs) around any atom as stated in the octet rule.
- ***Hydrogens*** within molecules *will* ***<u>never</u>*** *have a lone pair*; hydrogen is an exception to the octet rule. Therefore, hydrogen atoms will always be attached with *just one single bond*, which results in its two-electron filled outer shell.
- Add the electrons in this step as **lone *pairs* only** (two dots next to each other) never draw single, unpaired electrons.
  - Note that arrangement of the lone pairs in Step 4 *may <u>not</u> be symmetric*, **that is ok**; the symmetry rule discussed in Step 2 only applies to the atoms, not the lone pairs.

- Begin the implementation of Step 4 with the skeleton structure from ***Step 2***: **H-O-H**
  - Add the remaining electrons as **lone pairs** as evenly as possible on all atoms *except hydrogen*.

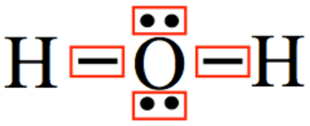


  - As we calculated in Step 3, we need to add four electrons to our skeleton structure.
  - We must add them as **lone pairs** to the oxygen atom (hydrogen can only have one single bond and never has lone pairs). Remember that each **lone pair = two electrons**!

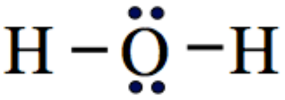
We do not stop at Step 4 even though we now have the correct number of electrons in our line bond structure.

Step 5: Check for **octets**.

In this step, we check our structure from Step 4 to make sure that the **octet rule** is satisfied ***for all atoms*** in the molecule. This is done by inspecting each atom to see if it is *surrounded* by a total of eight electrons. Be sure to include shared electrons in bond(s) and lone pairs. Look above, to the right, below, and to the left and count the electrons. I have done this for the oxygen in H_2O (below); the electrons that *surround* oxygen are in red boxes.



- Note that the oxygen is surrounded by ***eight electrons***. There are two single bonds (each bond contains two electrons) and there are two lone pairs, for a total of eight electrons. The hydrogens are each surrounded by two electrons (one single bond) which satisfies the octet rule for hydrogen.
- When the octet rule is satisfied ***for all atoms*** in the molecule as it is in this example, STOP, **YOU ARE FINISHED**!
- The line bond structure for H_2O is:



Many students make the mistake of going on to Step 6 when the molecule, as drawn in Step 5, already satisfies the octet rule. Do not do that; the next step in our method, Step 6, ***is only done when the octet rule is not satisfied*** for one or more atoms in the molecule!

Step 6 (if needed): Use **lone pairs** to make *double* or *triple bonds* **until** the octet rule is satisfied *for all atoms* in the molecule.

In this step, we ***change*** *lone pairs* into bonds to make double, or if needed, triple bonds in order to satisfy the octet rule.

- The key here is not to just draw new lone pairs; use **existing** lone pairs to make double or triple bonds. If you add a *new* lone pair of electrons, then the molecule will contain too many electrons. It would have more electrons than calculated in Step 1; adding two extra electrons will change it from a molecule to a polyatomic ion with a 2^- charge.
- I suggest that you work on line bond structure problems using a pencil so that you can erase lone pair(s) and then use the two electrons to change a single bond into a double bond or to change a double bond into a triple bond. We did not need to do so in our H_2O molecule example; next we will do a couple of examples where we need to use Step 6.

Do you recall from the last chapter when we brought *two* oxygen ***atom*** electron dot structures together to form an O_2 molecule? When combined in the O_2 molecule, the oxygen atoms *shared* ***two pairs*** *of electrons* and we called that a **double bond.** We used the same treatment of two nitrogen atoms to form an N_2 molecule where the N atoms *shared three pairs of electrons* and we called that a **triple bond.** Our new method for drawing line bond structures should also predict the double bond in O_2 and the triple bond in N_2. Let's see if it works!

Example: Draw the line bond structure of the diatomic molecule O_2.

Step 1: Count the total number of **valence electrons** from all the atoms in the molecule.

- For O_2 (two oxygen atoms)

2 O atoms 2 x 6e^- = 12e^-
Total number of *valence electrons* = 12e^-

- The line bond structure of O_2 will show ***twelve electrons***

Step 2: Draw the "**Skeleton Structure**": Attach the atoms together with ***single bonds*** in the most symmetric way possible.

For a diatomic molecule, this step is a simple, there is only one way to connect two atoms together with a bond. Think about connecting two styrofoam balls, you would use just one toothpick in between the spheres to hold them together!

- The skeleton structure for O_2 is: **O-O**

Step 3: Subtract the number of electrons used to make the ***skeleton structure*** from the *total number of valence electrons*.

This step will tell us how many electrons need to be added to the skeleton structure. We will add additional electrons (if needed) in Step 4, but *not now*.

- We calculated the total number of electrons that the line bond structure will contain back in Step 1.
    - The line bond structure of O_2 will show a **total of twelve electrons.**
    - The skeleton structure (from step 2) is: **O-O** How many electrons are in the *skeleton structure*?
        - (1 bond) x (2 electrons per single bond) = **two electrons used in the skeleton structure.**
- **Number of** electrons that need to be added to our skeleton structure:

Total number of electrons in line bond structure (from Step 1) = 12e^-
Number of electrons used in skeleton (from Step 2) = $\underline{-\ 2e^-}$
Remaining number electrons to be added = 10e^-

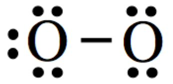
Step 4: Add the remaining electrons as **lone pairs** as *evenly* as possible on all atoms except hydrogen.

In this step, we add the remaining electrons (calculated in Step 3) to our skeleton structure. These electrons are added as ***lone pairs*** to atoms in the molecule.

- Add the electrons as **lone *pairs* only** (two dots next to each other); never draw single, unpaired electrons.
- Begin the implementation of Step 4 with the skeleton structure from ***Step 2***:

O-O

- Add the remaining electrons.
    - As we calculated in Step 3, we need to add ***ten electrons*** to our skeleton structure.
    - We must add them as **lone pairs** to the oxygen atoms (remember that each **lone pair = two electrons**).
    - To add the lone pairs "evenly," we try to distribute the electrons fairly uniformly around the molecule, however the last lone pair to be added must either go on the left oxygen or the right oxygen. Either way you do this will lead to the correct line bond structure. I ***arbitrarily*** chose to add the fifth lone pair to the oxygen on the left.

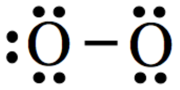


- If I had chosen to add the last lone pair to the oxygen on the *right*, then the resulting structure would be identical; it would appear as if you were looking at the structure that I drew above, but from behind the page!

The arrangement of the lone pairs in Step 4 *is <u>not</u> always symmetric* - **that is ok** - the symmetry rule discussed in Step 2 only applies to the *arrangement of the atoms*, not to the *lone pairs*.

Step 5: Check for **octets**.

In this step, we check our structure from Step 4 to make sure that the **octet rule** is satisfied ***for all atoms*** in the molecule. We do so by inspecting each atom to see if it is *surrounded* by a total of eight electrons. This will include electrons in bonds *and* lone pairs. Look above, to the right, below, and to the left of each atom and count the electrons.



- Note that the oxygen *on the left* is surrounded by ***eight electrons***. There is one single bond and three lone pairs, for a total of eight electrons. However, the oxygen on the right is only surrounded by ***six electrons***, one single bond and two lone pairs, for a total of six electrons.

- The octet rule is **not satisfied *for all atoms*** in the molecule since the oxygen on the right only has six electrons in its outermost shell. In this example, we need to go to **Step 6**!

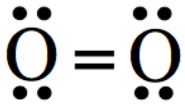
Step 6: Use **lone pairs** to make *double* or *triple bonds* **until** the octet rule is satisfied *for all atoms* in the molecule.

In this step, we ***change*** *lone pairs* into bonds to make double, or if needed, triple bonds in order to satisfy the octet rule.

- The key here is not to just draw new lone pairs; use **existing** lone pairs to make double or triple bonds. If we add a new lone pair of electrons, then the molecule will contain too many electrons.
- It would not make sense to change one of the lone pairs on the ***right-most oxygen*** into a bond; that oxygen would still only be surrounded by six electrons. Furthermore, the oxygen on the left would then be surrounded by ten electrons.
- So, let's change one of the lone pairs on the ***left-most oxygen*** into a bond. It does not matter which lone pair on the left-most oxygen that you change into a bond; they are all equivalent. I will arbitrarily choose to share the lone pair that is **shaded blue** in the illustration below:

- Each time you **change** a lone pair to bond, making a double bond, check to see if the octet rule is satisfied for *all atoms* in the molecule.

The octet rule is now satisfied. The line bond structure for O_2 is:



- Each oxygen is surrounded by an *octet* of electrons. The oxygen on the *left* is surrounded by ***eight electrons***. There is one double bond (***two pairs*** of shared electrons = four electrons) and there are two lone pairs (two electrons per lone pair), for a total of ***eight electrons.*** The oxygen on the right is, identically, surrounded by ***eight electrons***.

- When the octet rule is satisfied ***for all atoms*** in the molecule as it is in this example, STOP, **YOU ARE FINISHED**!

Our new method for drawing line bond structures worked as advertised in the O_2 example; we ended up with a double bond as predicted in chapter 3 by joining two oxygen atom electron dot structures. Next, let's see if the *Method* predicts the triple bond for N_2!

Example: Draw the line bond structure of the diatomic molecule N_2.

Step 1: Count the total number of **valence electrons** from all the atoms in the molecule.

- For N_2 (two nitrogen atoms):

2 N atoms 2 x $5e^-$ = $10e^-$
Total number of *valence electrons* = $10e^-$

- The line bond structure of N_2 will show ***10 electrons***

Step 2: Draw the "**Skeleton Structure**": Attach the atoms together with ***single bonds*** in the most symmetric way possible.

For a diatomic molecule, this step is simple since there is *only one way* to connect two atoms together with a bond.

  - The skeleton structure for N_2 is: **N-N**

Step 3: Subtract the number of electrons used to make the ***skeleton structure*** from the *total number of valence electrons*.

This step will tell us how many electrons need to be added to the skeleton structure.

- We calculated the total number of electrons that our line bond structure will contain back in Step 1.
    - The line bond structure of N_2 will show a **total of ten electrons.**
    - The skeleton structure (from step 2) is: **N-N** How many electrons are in the *skeleton structure*?
    - 1 bond x (2 electrons per single bond) = **two electrons are used in the skeleton structure.**
- **Number of** electrons that need to be added to the skeleton structure:

Total number of electrons in line bond structure (from Step 1) = 10*e*-
Number of electrons used in skeleton (from Step 2) = - 2*e*-
Remaining number electrons to be added = 8*e*-

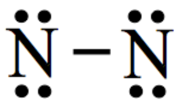
Step 4: Add the remaining electrons as **lone pairs** as *evenly* as possible on all atoms except hydrogen.

In this step, we add the remaining electrons (calculated in Step 3) to our skeleton structure. These electrons are added as ***lone pairs*** to atoms in the molecule.

  - Begin the implementation of Step 4 with the skeleton structure from ***Step 2***:

N-N

  - Add the remaining electrons as **lone pairs** as evenly as possible on all atoms *except hydrogen*.
    - As we calculated in Step 3, we need to add ***eight electrons*** to our skeleton structure.
    - Distribute the electrons uniformly around the molecule as shown below:



$$\underset{\cdot\cdot}{\ddot{N}}-\underset{\cdot\cdot}{\ddot{N}}$$

Step 5: Check for **octets**.

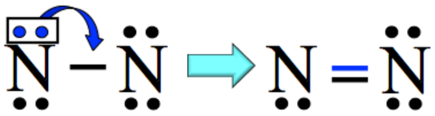
In this step, we check our structure from Step 4 to make sure that the **octet rule** is satisfied ***for all atoms*** in the molecule. We do so by inspecting each atom to see if it is *surrounded* by a total of eight electrons. Note that the nitrogen on the left is surrounded by ***six electrons***. There is one single bond and two lone pairs, for a total of six electrons. Likewise, the nitrogen on the right is only surrounded by ***six electrons***.

  - The octet rule is **not satisfied;** we need to go to **Step 6**!

Step 6: Use **lone pairs** to make *double* or *triple bonds* **until** the octet rule is satisfied *for all atoms* in the molecule.

In this step, we ***use*** *lone pairs* to make double, or if needed, triple bonds in order to satisfy the octet rule.

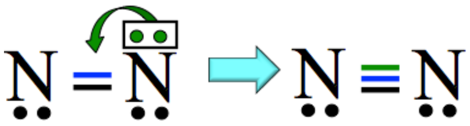
- Do not just draw new lone pairs, use **existing** lone pairs to make double or triple bonds.
- Let's change one of the lone pairs on either one of the nitrogens into a bond. It does not matter which lone pair you change into a double bond; they are all equivalent. I will arbitrarily choose to share the lone pair that is **shaded blue** in the illustration below:



- Each time you **use** a lone pair to make a double bond, check to see if the octet rule is satisfied for all atoms in the molecule.
    - After the change (to the right of the arrow), the right-most nitrogen is now surrounded by ***eight electrons***; there is one double bond (***two pairs*** of shared electrons = four electrons) and two lone pairs (two electrons per lone pair). However, the left-most nitrogen is only surrounded by *six electrons*.

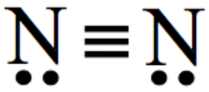
The octet rule is not yet satisfied. We must continue to change lone pairs into shared electrons!

- It would not make sense to change one of the lone pairs on the left-most nitrogen into a bond; that nitrogen would still only be surrounded by six electrons. Furthermore, the right-most nitrogen would then be surrounded by ten electrons.
- Let's change one of the lone pairs on the right-most nitrogen into a bond. It does not matter which lone pair from the right-most oxygen you change into a bond; they are all equivalent. I will arbitrarily choose to share the lone pair that is **shaded green** in the illustration below:



- The two nitrogen atoms now share three pairs of electrons.

The octet rule is now satisfied. The line bond structure for N_2 is:



- Each nitrogen is surrounded by an octet of electrons. The left-most nitrogen is surrounded by ***eight electrons***; there is one triple bond (***three pairs*** of shared electrons = six electrons) and one lone pair. The right-most nitrogen is, identically, surrounded by ***eight electrons***.
- When the octet rule is satisfied ***for all atoms*** in the molecule as it is in this example, **YOU ARE FINISHED**!

In this example, we ended up with a *triple bond* as predicted in chapter 3 by joining two nitrogen atom electron dot structures. You will become proficient at using this method by doing many problems. I have made a guide for you to use while practicing problems. You can view a template of the guide and a couple of examples of how to use the template in **Appendix 2.**

The method for drawing line bond structures that I introduced in this section will indeed work every time for all of the line bond structures in this book that you are asked to draw. A quick "disclaimer" here: the method is only intended for use with molecules that obey the octet rule, and that includes most molecules. In this book, you will only be asked to draw line bond structures for molecules that obey the octet rule, though in a later chapter I will point out a few molecules of biological importance that violate the rule.

Review 4.1: Drawing Line Bond Structures

Use the template in the Appendix to draw line bond structures of the following molecules:

a. Br_2
b. NF_3
c. H_2S
d. SO_3
e. CO_2
f. SO_2

See the following pages for the solutions

Guide for Drawing Line Bond Structures
Example: Draw the Line Bond Structure for Br_2

Step 1: Count the total number of valence electrons from all the atoms in the molecule.

Atom	Number of atoms		Number of valence electrons per atom		Totals
Br	2	x	7	=	14
		x		=	
Total number of electrons to appear in the line bond structure =					14

Step 2: Draw the "Skeleton" Structure
Attach the atoms together with *single bonds* in the most symmetric way possible.

Br — Br

\# of electrons used in skeleton = ___2___

(Multiply the number of bonds in skeleton by two)

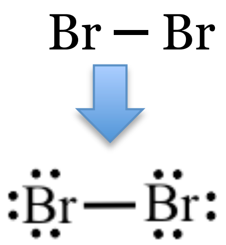
Step 3: Subtract the number of electrons used to make the skeleton structure from the total number of valence electrons.

Total # of valence electrons (from Step 1) _14__

\# of electrons used in skeleton (from Step 2) - __2__

Remaining # electrons to be added = _12__

Step 4: **First:** Re-draw skeleton (from Step 2):

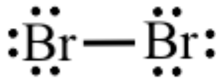


Next, add the remaining electrons to the above structure as lone pairs as evenly as possible on all atoms *except hydrogen*.

- Add remaining electrons to the skeleton as ***lone pairs.***

Step 5: Check for Octets

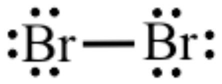
Check the structure in **Step 4** for octets of electrons around each atom (except hydrogen).



If octet rule is satisfied, you are done.
In this case, the octet rule is satisfied.

If octet rule is not satisfied, go to **Step 6.**

Step 6: Use **lone pairs** to make *double* or *triple bonds* **until** the octet rule is satisfied *for all atoms* in the molecule.
The octet rule was satisfied in Step 5, therefore Step 6 is not needed in this case.



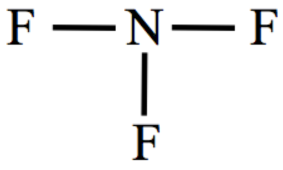
Guide for Drawing Line Bond Structures
Example: Draw the Line Bond Structure for NF_3

Step 1: Count the total number of valence electrons from all the atoms in the molecule.

Atom	Number of atoms		Number of valence electrons per atom	Totals
N	1	x	5 =	5
F	3	x	7 =	21
Total number of electrons to appear in the line bond structure =				26

Step 2: Draw the "Skeleton" Structure

Attach the atoms together with *single bonds* in the most symmetric way possible.



# of electrons used in skeleton = ___6___

(Multiply the number of bonds in skeleton by two)

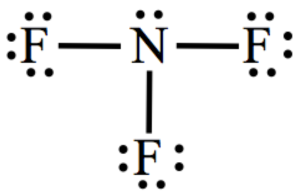
Step 3: Subtract the number of electrons used to make the skeleton structure from the total number of valence electrons.

Total # of valence electrons (from Step 1) _26__

# of electrons used in skeleton (from Step 2) - __6__

Remaining # electrons to be added = _20__

Step 4: **First:** Re-draw skeleton (from Step 2):

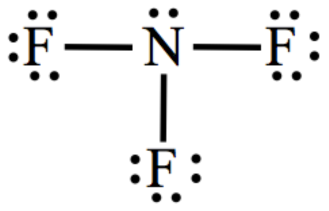


Next, add the remaining electrons to the above structure as lone pairs as evenly as possible on all atoms *except hydrogen*.

- Add remaining electrons to the skeleton as ***lone pairs.***

Step 5: Check for Octets

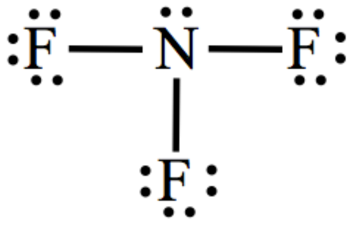
Check the structure in **Step 4** for octets of electrons around each atom (except hydrogen).



If octet rule is satisfied, you are done.
In this case, the octet rule is satisfied.

If octet rule is not satisfied, go to **Step 6.**

Step 6: Use **lone pairs** to make *double* or *triple bonds* **until** the octet rule is satisfied *for all atoms* in the molecule.
The octet rule was satisfied in Step 5, therefore Step 6 is not needed in this case.



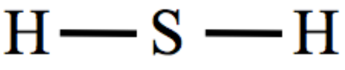
Guide for Drawing Line Bond Structures
Example: Draw the Line Bond Structure for H_2S

Step 1: Count the total number of valence electrons from all the atoms in the molecule.

Atom	Number of atoms		Number of valence electrons per atom		Totals
S	1	x	6	=	6
H	2	x	1	=	2
Total number of electrons to appear in the line bond structure =					8

Step 2: Draw the "Skeleton" Structure

Attach the atoms together with *single bonds* in the most symmetric way possible.



# of electrons used in skeleton = ___4___

(Multiply the number of bonds in skeleton by 2)

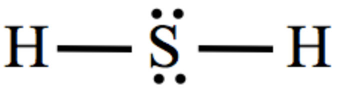
Step 3: Subtract the number of electrons used to make the skeleton structure from the total number of valence electrons.

Total # of valence electrons (from Step 1) __8__

# of electrons used in skeleton (from Step 2) - __4__

Remaining # electrons to be added = __4__

Step 4: **First:** Re-draw skeleton (from Step 2):

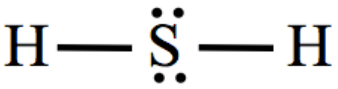


Next, add the remaining electrons to the above structure as lone pairs as evenly as possible on all atoms *except hydrogen*.

- Add remaining electrons to the skeleton as ***lone pairs.***

Step 5: Check for Octets

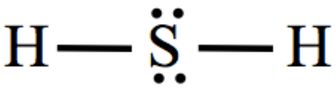
Check the structure in **Step 4** for octets of electrons around each atom (except hydrogen).



If octet rule is satisfied, you are done.
In this case, the octet rule is satisfied.
If octet rule is not satisfied, go to **Step 6.**

Step 6: Use **lone pairs** to make *double* or *triple bonds* **until** the octet rule is satisfied *for all atoms* in the molecule.

The octet rule was satisfied in Step 5, therefore Step 6 is not needed in this case.



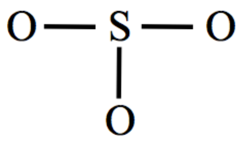
Guide for Drawing Line Bond Structures
Example: Draw the Line Bond Structure for SO_3

Step 1: Count the total number of valence electrons from all the atoms in the molecule.

Atom	Number of atoms		Number of valence electrons per atom	Totals
S	1	x	6 =	6
O	3	x	6 =	18
Total number of electrons to appear in the line bond structure =				24

Step 2: Draw the "Skeleton" Structure

Attach the atoms together with *single bonds* in the most symmetric way possible.



# of electrons used in skeleton = ___6___

(Multiply the number of bonds in skeleton by two)

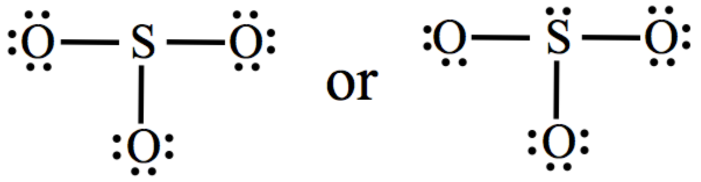
Step 3: Subtract the number of electrons used to make the skeleton structure from the total number of valence electrons.

Total # of valence electrons (from Step 1) __24__

# of electrons used in skeleton (from Step 2) - __6__

Remaining # electrons to be added = _18__

Step 4: **<u>First:</u>** Re-draw skeleton (from Step 2):



Next, add the remaining electrons to the above structure as <u>lone pairs</u> as evenly as possible on all atoms *except hydrogen*.

- Add remaining electrons to the skeleton as ***lone pairs.***

Step 5: Check for Octets

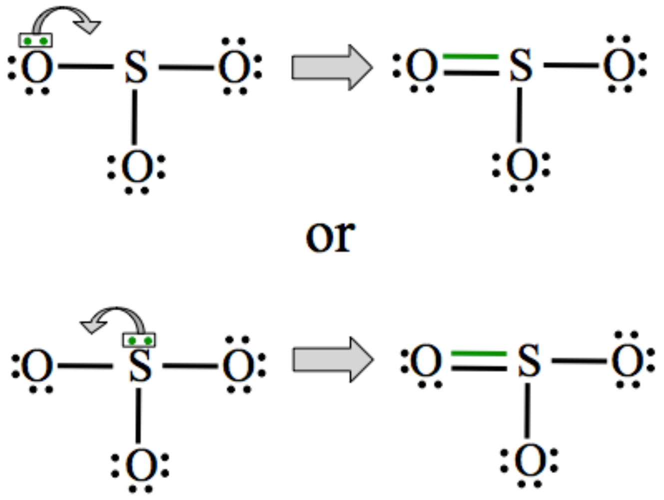
Check the structure in **Step 4** for octets of electrons around each atom (except hydrogen).

If octet rule is satisfied, you are done.
If octet rule is not satisfied, go to **Step 6.**

In this case, the octet rule **<u>is not</u>** satisfied, go to Step 6.

Step 6: Use **lone pairs** to make *double* or *triple bonds* **<u>until</u>** the octet rule is satisfied *for all atoms* in the molecule.

- ***Change*** *lone pairs* into double, or if needed, triple bonds in order to satisfy the octet rule.



Guide for Drawing Line Bond Structures
Example: Draw the Line Bond Structure for CO_2

Step 1: Count the total number of valence electrons from all the atoms in the molecule.

Atom	Number of atoms		Number of valence electrons per atom	Totals
C	1	x	4 =	4
O	2	x	6 =	12
Total number of electrons to appear in the line bond structure =				16

Step 2: Draw the “Skeleton" Structure
Attach the atoms together with *single bonds* in the most symmetric way possible.

O — C — O

# of electrons used in skeleton = ___4___

(Multiply the number of bonds in skeleton by two)

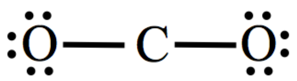
Step 3: Subtract the number of electrons used to make the skeleton structure from the total number of valence electrons.

Total # of valence electrons (from Step 1) _16__

# of electrons used in skeleton (from Step 2) - __4__

Remaining # electrons to be added = _12__

Step 4: <u>First:</u> Re-draw skeleton (from Step 2):



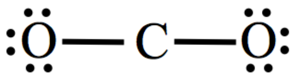
Note: there are other ways to add the lone pairs. No matter which way you use, if you do Steps 5 & 6 correctly, you will end up with the same correct line bond structure.

Next, add the remaining electrons to the above structure as <u>lone pairs</u> as evenly as possible on all atoms *except hydrogen*.

- Add remaining electrons to the skeleton as ***lone pairs.***

Step 5: Check for Octets

Check the structure in **Step 4** for octets of electrons around each atom (except hydrogen).

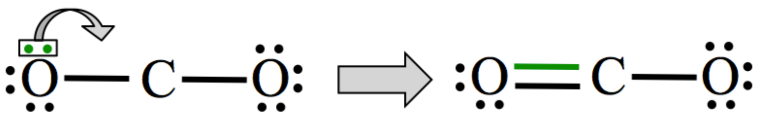


If octet rule is satisfied, you are done.
If octet rule is not satisfied go to **Step 6.**

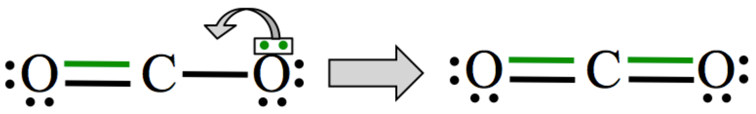
In this case, the octet rule **<u>is not</u>** satisfied, go to Step 6.

Step 6: Use **lone pairs** to make *double* or *triple bonds* **<u>until</u>** the octet rule is satisfied *for all atoms* in the molecule.

- ***Change*** *lone pairs* into double, or if needed, triple bonds in order to satisfy the octet rule.



Now the octet rule is satisfied for the left-most oxygen, but not for the carbon or the right-most oxygen. So you must repeat Step 6 until the octet rule is satisfied for all atoms in the molecule.



Guide for Drawing Line Bond Structures
Example: Draw the Line Bond Structure for SO_2

Step 1: Count the total number of valence electrons from all the atoms in the molecule.

Atom	Number of atoms		Number of valence electrons per atom	Totals
S	1	x	6 =	6
O	2	x	6 =	12
Total number of electrons to appear in the line bond structure =				18

Step 2: Draw the "Skeleton" Structure
Attach the atoms together with *single bonds* in the most symmetric way possible.

O — S — O

# of electrons used in skeleton = 4

(Multiply the number of bonds in skeleton by two)

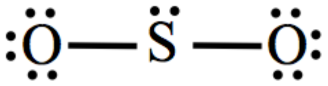
Step 3: Subtract the number of electrons used to make the skeleton structure from the total number of valence electrons.

Total # of valence electrons (from Step 1) 14

# of electrons used in skeleton (from Step 2) - 4

Remaining # electrons to be added = 14

Step 4: First: Re-draw skeleton (from Step 2):



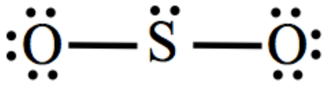
Note: there are other ways to add the lone pairs. No matter which way you use, if you do Steps 5 & 6 correctly, you will end up with the same correct line bond structure.

Next, add the remaining electrons to the above structure as lone pairs as evenly as possible on all atoms *except hydrogen*.

- Add remaining electrons to the skeleton as ***lone pairs.***

Step 5: Check for Octets

Check the structure in **Step 4** for octets of electrons around each atom (except hydrogen).

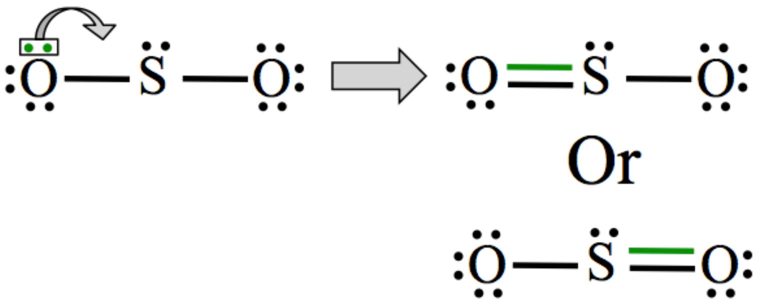


If octet rule is satisfied, you are done.
If octet rule, is not satisfied go to **Step 6.**

In this case, the octet rule **is not** satisfied, go to Step 6.

Step 6: Use **lone pairs** to make *double* or *triple bonds* **until** the octet rule is satisfied *for all atoms* in the molecule.

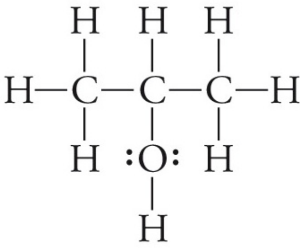
- ***Change*** *lone pairs* into double, or if needed, triple bonds in order to satisfy the octet rule.



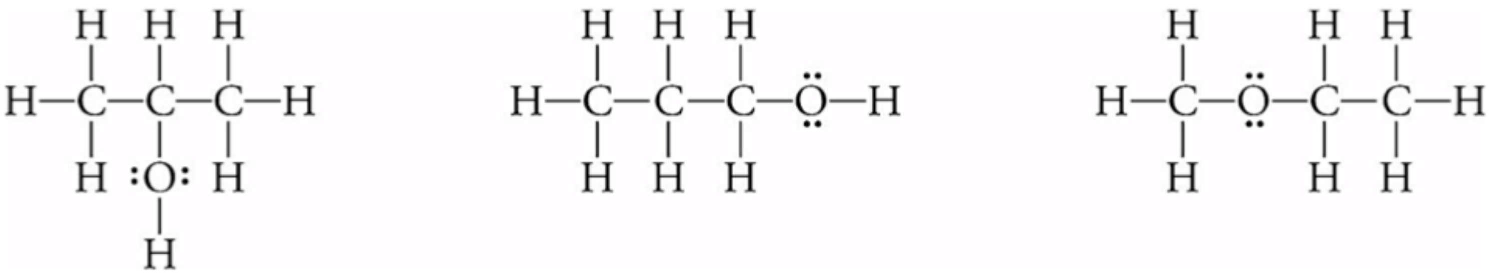
4.3 Structural Formulas

A **molecular formula** shows us the number and types of atoms contained in a molecule. In the last section, we used *line bond structures* to indicate the pattern in which atoms are *connected* by covalent bonds *within* molecules. Drawings, such as line bond structures, that show the connectivity of atoms within molecules are called **structural formulas.** Let's take a moment to compare and contrast ***molecular formulas*** vs. ***structural formulas***.

The **molecular formula** of isopropyl alcohol (often called rubbing alcohol) is C_3H_8O.
The **structural formula** of isopropyl alcohol is:



Which of these two types of formulas, the ***molecular formula*** or the ***structural formula***, do you think is more informative?
If you think the structural formula is more informative, you are correct; it shows the number and types of atoms as well as the *pattern in which atoms are connected!* There are actually three ***completely different molecules*** that have this same molecular formula of C_3H_8O:



These three molecules each have *different* physical properties such as their density, evaporation rates, and the temperature at which they boil (boiling point). They also have different chemical properties such as the amount of energy they release when burned. The bonding pattern that is shown in the structural formula of a molecule will allow us to determine the three-dimensional arrangement of a molecule's atoms and how the electrons are distributed within the molecule. The three-dimensional arrangement of a molecule's atoms and the electron distribution within a molecule determine the molecule's physical and chemical properties.

Line bond structural formulas explicitly show all the information about how the atoms are connected and the presence of all single bonds, double bonds, triple bonds and lone pairs. In practice, chemists often use one of two short-cut forms of structural formulas. These are called **condensed structural formulas** and **skeletal formulas**. These short-cuts are only informative and valuable if none of the information contained in the line bond structure is lost. As I discuss these structural formulas, they may seem to have lost some of the bonding pattern information because the information is ***implied*** instead of ***explicitly*** drawn. It may seem difficult to follow at first, but as you practice and use these throughout the next couple of chapters, they will become easier.

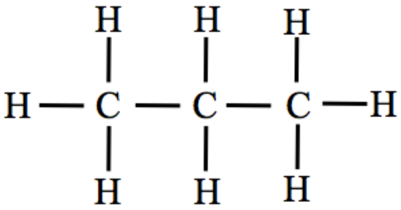
Condensed Structural Formulas (Condensed Structures)

Organic chemistry is the chemistry of carbon-containing compounds. You will begin to learn about organic molecules later in this chapter. Most organic molecules in biological systems are large molecules consisting mostly, if not entirely, of carbon, hydrogen, nitrogen, and oxygen. It is very useful to use condensed structural formulas when drawing large molecules in order ***to save time***. In condensed structures, not all bonds are shown. For example, a carbon bonded to three hydrogen atoms is drawn as "CH_3"; likewise, an oxygen bonded to one hydrogen atom is drawn as "OH."

When drawing condensed structures:

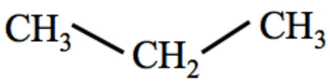
- Single bonds between carbon and hydrogen ***are omitted***.
- Single bonds between carbons (C-C) ***can be*** omitted.
- Single bonds between oxygen or nitrogen ***and*** hydrogen ***can be*** omitted.
- Bonds between all *other* pairs of atoms must be drawn.
- Lone pairs ***can be*** omitted.
- Double and triple bonds ***are always drawn***.

It may seem counterintuitive that bonding pattern information is not lost while using the above method. Let's unpack and practice the *condensed structure* concept by doing a few examples together. The first type of organic molecules that you will learn about in this chapter are called *hydrocarbons*. Can you guess which two types of atoms hydrocarbons contain? If you said carbon and hydrogen, you are correct. A molecule called *propane* has the ***molecular formula*** of C_3H_8. Propane can be compressed from gas to liquid and stored in transportable containers for use in barbecues, portable stoves, lanterns, and home central heating. The connectivity of these carbon and hydrogen atoms can be seen *explicitly* in propane's ***line bond structure***:



In ***condensed structures***, single bonds between carbon and hydrogen atoms ***are omitted***. We can draw the condensed structure of propane as:

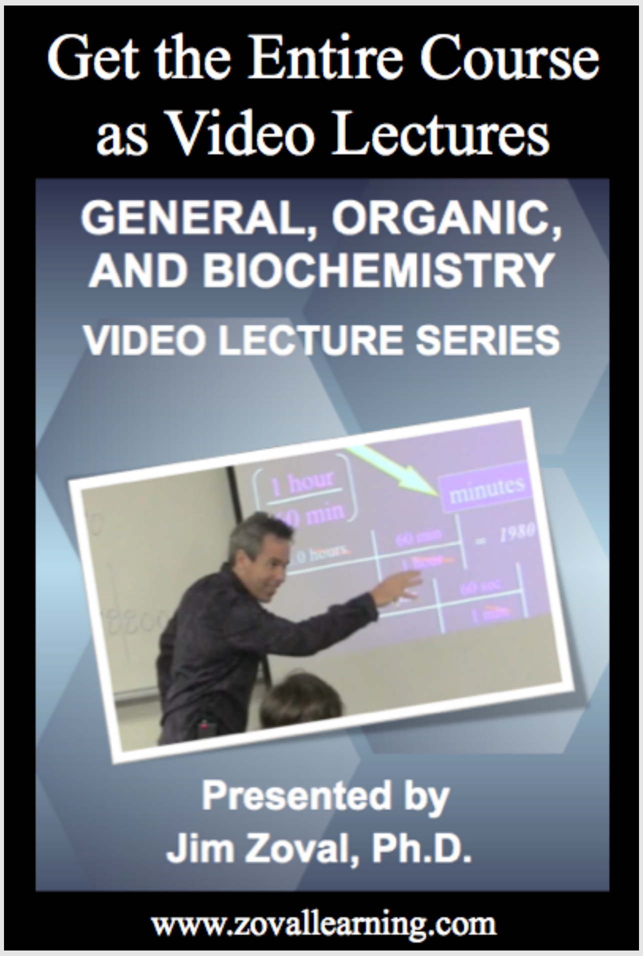
$CH_3—CH_2—CH_3$ or



For those of you who use auto-graded, online problems sets, as my students do, the online system will probably require that you draw condensed structures **as shown above** in order for the auto-grader to determine if you have the carbon-carbon atom connectivity correct. When drawing condensed structures, for ***non***-auto-graded use, further condensation is possible. Carbon-carbon single bonds can be omitted when the carbon atoms are in a linear sequence such as the three carbons in propane. In this case, the condensed structure can also be drawn as:

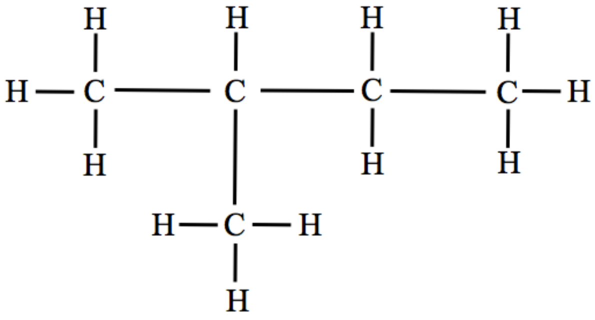
$$CH_3CH_2CH_3$$

Do you see how the connectivity pattern information is retained even though all of the bonds are not shown explicitly? Note that the left-most carbon is bonded to three hydrogens and to the middle carbon. We know that there could not be hydrogen(s) bonded between the left-most carbon and the middle carbon because hydrogen ***will never have more than one bond*** (recall the octet rule for hydrogen, no more than two electrons). The right-most carbon is bonded to three hydrogens and the middle carbon. The middle carbon is bonded to two hydrogens, the left-most carbon, and the right-most carbon. So, even though not all of the bonds are drawn in condensed structures, they are ***implied*** and can be *unequivocally* known.

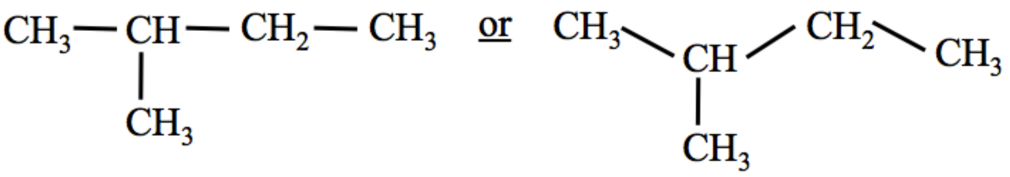


Let's do another example. Isopentane is a molecule that is used in Aquafresh® toothpaste to enable the gel-to-foam change when the toothpaste is applied to teeth. The ***line bond structure*** for isopentane is:

In isopentane, there are four carbons bonded in a ***linear sequence*** (drawn horizontally in the line bond structure). There is one carbon that "***branches***" from the linear sequence at the second carbon from the left.

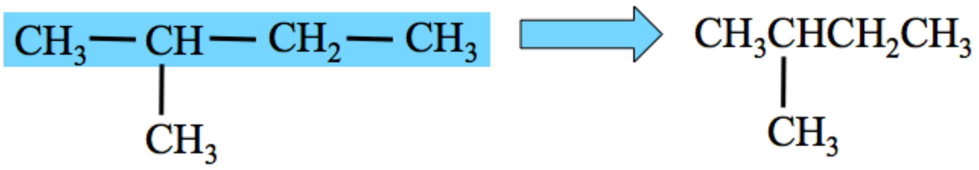


In ***condensed structures***, single bonds between carbon and hydrogen atoms ***are omitted***. We can draw the condensed structure as:



$$\underset{\textstyle CH_3}{CH_3{-}\underset{|}{CH}{-}CH_2{-}CH_3}$$

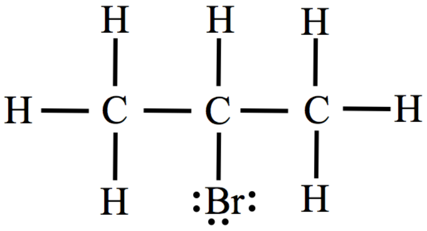
When you are asked to draw *condensed structures* for auto-graded, online problem sets, you should draw all of the carbon-carbon bonds *as shown above*. If one wishes, for non auto-graded use, further condensation is possible. Single bonds between carbon atoms ***in a linear sequence*** can be omitted as in the case of the four carbons in a linear sequence in isopentane. In the illustration below, the four carbons in a *linear sequence* are shown in the blue shaded region (left) and then further condensed (right):



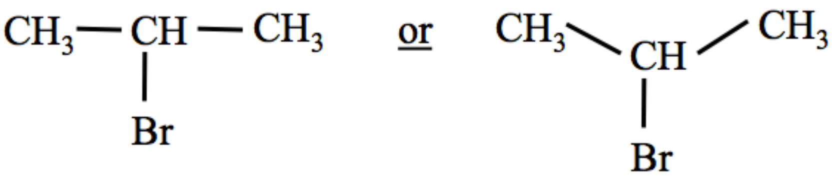
$$\underset{\textstyle CH_3}{CH_3{-}\underset{|}{CH}{-}CH_2{-}CH_3} \Rightarrow \underset{\textstyle CH_3}{CH_3\underset{|}{CH}CH_2CH_3}$$

You may be wondering which of the condensed structures shown above is the "*correct*" answer. ***They are <u>both</u> acceptable forms of condensed structures.*** As mentioned earlier, many online, auto-graded applications require that the condensed structures be entered as drawn above on the *left*. On exams in my class, if I ask students to draw a condensed structure of isopentane, I would give full credit to either of the structures shown above. However, you should check with your instructor as to which form of condensed structures she/he wishes you to use.

Let's continue unpacking the drawing of condensed structures with another example. Isopropyl bromide is commercially available and is used as a starting compound in the synthesis of other compounds. The ***line bond structure*** of isopropyl bromide is:

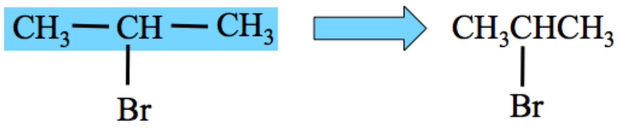


In ***condensed structures***, single bonds between atom pairs ***other than*** C-C, C-H, O-H, and N-H are ***always drawn***. Therefore the C-Br bond is drawn as shown below in the condensed structures:



$$\underset{\textstyle Br}{CH_3{-}\underset{|}{CH}{-}CH_3}$$

Single bonds between carbon atoms in a linear sequence can be omitted as in the case of the three carbons in a *linear sequence* in isopropyl bromide. In the two (equivalent) forms of condensed structures below, the three carbons in a linear sequence are shown in the blue shaded region (left) and then further condensed (right):



$$\underset{\displaystyle Br}{CH_3-\overset{}{CH}-CH_3} \Rightarrow CH_3\underset{\displaystyle Br}{CH}CH_3$$

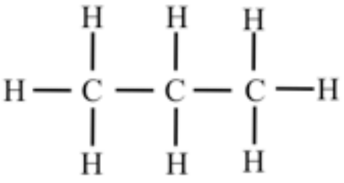
Skeletal Structural Formulas (Skeletal Structures)

Another *structural formula* that chemists use in order to more easily and quickly draw molecules is called the **skeletal structure**. Do not confuse "skelet**al**" structures with the "skelet**on**" structure used in Step 2 of our method for drawing line bond structures.

When drawing *skeletal structures*:

- Carbons are not drawn; they are implied to exist where lines (bonds) meet or at the end of a line (bond).
- Hydrogens are omitted if they are bonded to carbon.
- Bonds between oxygen or nitrogen ***and*** hydrogen may be omitted.
- Atoms other than carbon and hydrogen are ***always*** drawn.
- Lone pairs ***can be*** omitted.

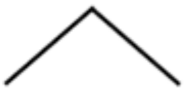
It may seem hard to believe that information about atom connectivity in the molecule is not lost when omitting the atoms and/or bonds as just described. But it is true. Let's consider the skeletal structures for the three examples that I discussed for condensed structures. We will begin with propane; the line bond, condensed, and skeletal structure are shown below:



Line Bond Structure

$CH_3-CH_2-CH_3$

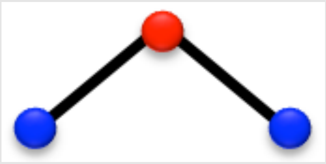
Condensed Structure



Skeletal Structure

In ***skeletal structures***, carbons are not drawn; they are implied to exist where lines (bonds) meet or at the end of a line (bond). Figure 4.2 shows the skeletal structure of propane with blue or red spheres overlaid at the location of the carbon atoms. There are two carbon atoms indicated by blue spheres at the end of lines (bonds) and there is a third carbon atom, indicated by a red sphere, where lines meet. Note that the lines (bonds) in a linear sequence of carbons are *not drawn flat* (horizontally); they must be drawn at angles so the viewer can see where the lines meet. Some of the auto-graded, online problem graphics show spheres, as in Figure 4.2, at the carbon positions.

Figure 4.2
Skeletal Structure of Propane with Spheres Added to Indicate the Location of the Carbons



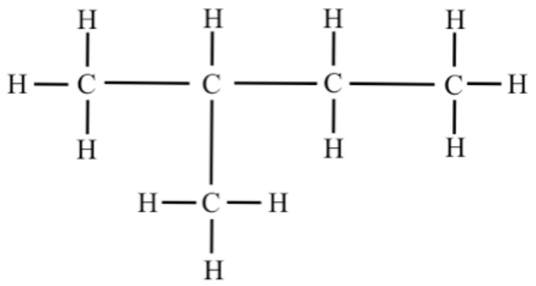
Blue or red spheres indicate the location of the carbons. Carbons are located at the end of lines (blue spheres) or where lines meet (red spheres).

If the hydrogens bonded to carbon are omitted from skeletal structures, how does one determine how many hydrogens are bonded to each carbon? The answer to this is quite simple and is related to the octet rule. In ***line bond structures***, where all bonds (lines) and lone pairs are shown explicitly:

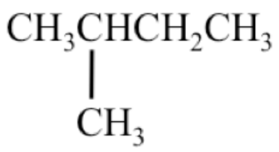
- Carbon atoms will **always** have ***four*** *lines going to them*.
    - Each line represents two shared electrons, therefore each carbon is surrounded by an octet of electrons.
- We will ***never*** see ***lone pairs*** on carbon in any molecule that contains more than one carbon atom.

Let's apply this understanding to each of the carbon atoms in the propane skeletal structure shown in Figure 4.2 in order to deduce the number of hydrogens bonded to each carbon. We will begin with the ***left-most*** carbon. Only one line/bond is shown *explicitly* going to the left-most carbon. We know that carbons will **always** have ***four pairs of shared electrons around them***, therefore we can deduce that there must ***also*** be *three hydrogens* bonded to that carbon. We can use the same argument to deduce that the right-most carbon has three hydrogens bonded to it. Can you deduce how many hydrogens are bonded to the ***middle carbon*** (represented by the red sphere) in Figure 4.2? We see that two lines/bonds are shown explicitly. Since carbons will **always** have ***four pairs of shared electrons around them***, we can deduce that there must be *two hydrogens* bonded to the middle carbon.

Three types of structural formulas for isopentane are shown below:



Line Bond Structure



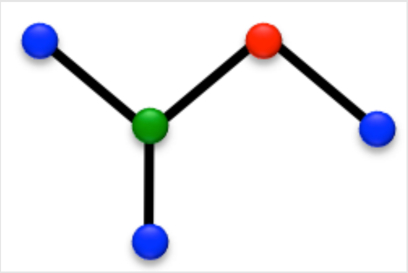
$$\mathrm{CH_3\underset{\underset{\displaystyle CH_3}{|}}{C}HCH_2CH_3}$$

Condensed Structure

Skeletal Structure

In ***skeletal structures***, carbons are not drawn; they are implied to exist where lines (bonds) meet or at the end of a line (bond). Figure 4.3 shows colored spheres at the location of the carbons in the skeletal structure of isopentane. There are three carbons indicated by blue spheres at the end of lines (bonds) one carbon indicated by a red sphere where two lines meet, and a fourth carbon indicated by a green sphere where three lines meet. Can you tell how many hydrogens are bonded to each carbon by looking ***only*** at the ***skeletal structure*** of isopentane?

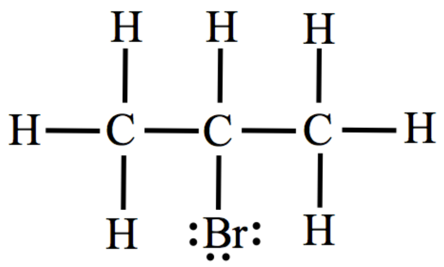
Figure 4.3
Skeletal Structure of Isopentane with Spheres Added to Indicate the Location of the Carbons



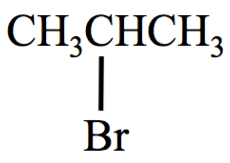
Blue, green, or red spheres indicate the location of the carbons. Carbons are located at the ends of lines (blue spheres) or where lines meet (green and red spheres).

Consider the three carbons represented by the ***blue*** spheres. Only one line/bond is shown *explicitly* going to each of these carbons. We know that carbons will **always** have ***four pairs of shared electrons around them***, therefore we can deduce that there must ***also*** be *three hydrogens* bonded each of these carbons. We see that two lines/ bonds are shown explicitly going to the carbon represented by the ***red*** sphere. We can deduce that there must be *two hydrogens* bonded to this carbon. Finally, we see that three lines/bonds are shown going to the carbon represented by the ***green*** sphere. We can deduce that there must be *one hydrogen* bonded to this carbon.

Three types of structural formulas for isopropyl bromide are shown below:

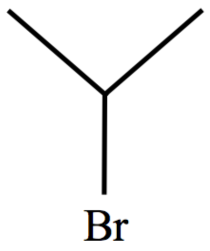


Line Bond Structure



$$\mathrm{CH_3\underset{\underset{\displaystyle Br}{|}}{C}HCH_3}$$

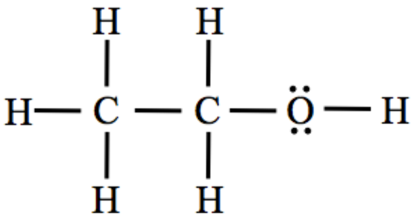
Condensed Structure



Skeletal Structure

In ***skeletal structures***, carbons are not drawn; atoms other than carbon and hydrogen are always drawn. In the skeletal structure for isopropyl bromide, the bromine atom is therefore shown. There are ***three carbons*** in isopropyl bromide and the bromine is bonded to the *middle carbon*. Note that *since there is a bromine atom at the end of the line/bond* coming downward from the middle carbon, there is not a carbon at the end of that line!

Let's do one more example. Ethanol (also called ethyl alcohol) is the narcotic component of adult beverages. The ***line bond structure*** of ethanol is:



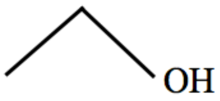
Line bond structures show all atoms, bonds, and lone pairs. There are several acceptable ways to draw the condensed structure of ethanol. Most *auto-graded,* online problems, would require you to draw this ***condensed structure***:

$$CH_3—CH_2—OH$$

Further condensation is allowable for ***non*** *auto-graded* use. Single bonds between carbon atoms in a linear sequence can be omitted as in the case of the two carbons in a linear sequence in ethanol (as shown below). Carbon-oxygen bonds are often omitted in condensed structures (below right). *Both structures shown below and the structure shown above are acceptable condensed structures for ethanol*:

$$CH_3CH_2—OH \quad \textbf{or} \quad CH_3CH_2OH$$

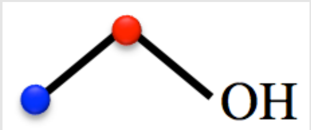
The ***skeletal structure*** for ethanol is:



In ***skeletal structures***, hydrogens are omitted if they are bonded to carbon. All other atoms are drawn. Therefore, in the skeletal structure for ethanol, the oxygen atom and the hydrogen, *which is bonded to oxygen,* are shown. Bonds between oxygen or nitrogen ***and*** hydrogen may be omitted from skeletal structures.

Figure 4.4 shows the skeletal structure of ethanol with spheres overlaid at the location of the carbons. There are ***two carbons*** in ethanol. One carbon, represented by a **blue** sphere, is at the end of a line (bond) and the second carbon, represented by a **red** sphere, is where lines meet. The carbon represented by the **red** sphere is bonded to a carbon (on it's left) and oxygen (on it's right). Note that *since there is an oxygen atom at the end of the line/bond* coming downward from the red carbon, there is not a carbon at the end of that line!

Figure 4.4 Skeletal Structure of Ethanol with Spheres Added to Indicate the Location of the Carbons

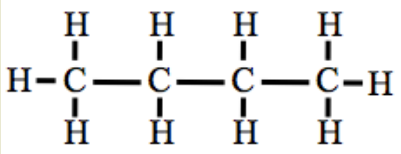


Blue or red spheres indicate the location of the carbons. Carbons are located at the end of a line (blue sphere) or where lines meet (red sphere).

The larger the molecule, the more time that is saved by drawing structural formulas using the condensed and skeletal formula short-cut methods. Chemists who frequently draw large molecules use skeletal structures most often. As a chemistry student, it may seem difficult to completely and quickly know the bonding pattern connectivity from looking at a condensed or skeletal structure, however it becomes much easier with practice. Before going on to the next section of this chapter, I suggest that you work on the practice problems on the next page. You will also have a chance to practice more structural formulas later in this chapter when I discuss organic molecules.

Review 4.2: Drawing Condensed and Skeletal Formulas

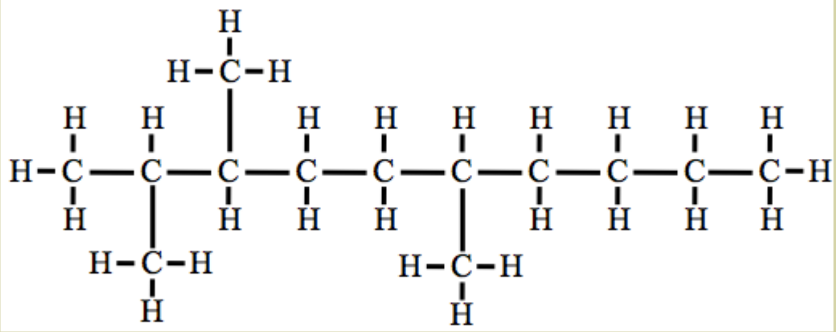
Butane is used as a propellent in aerosol sprays such as deodorants. When blended with propane and other hydrocarbons, it is used as a fuel that is called LPG (liquified petroleum gas). The line bond structure of butane is shown below. Draw the condensed structure and the skeletal structure of this molecule.



For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

Review 4.3: Drawing Condensed and Skeletal Formulas

The line bond structure of a large hydrocarbon molecule is shown below. Draw the condensed structure and the skeletal structure of this molecule.



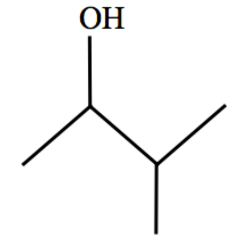
For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

Review 4.4: Drawing Line Bond and Condensed Formulas

Sec-isoamyl alcohol is used as a solvent and starting material for the synthesis of other compounds The ***skeletal structure*** of sec-isoamyl alcohol is shown on the right. Draw the **line bond structure** and the **condensed structure** of this molecule.

For ***i-book*** versions: **Click here to check answer**

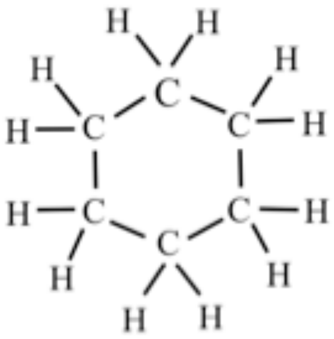
For **print or pdf versions**, see the answer key in Appendix 1.



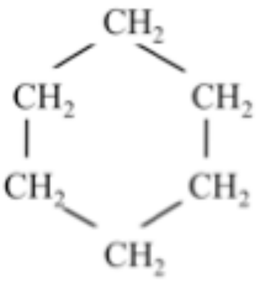
sec-isoamyl alcohol

Structural Formulas of Cyclic Compounds

In our prior examples, we have seen atoms bonded in a ***linear sequence***. In some cases, we saw atoms or groups of atoms "***branching***" from a *linear sequence*. Many compounds contain atoms bonded, not in a linear sequence, but in a "**ring**" pattern. Molecules that contain rings of atoms are called **cyclic compounds**. An example of a *cyclic compound* is a molecule called cyclohexane. The three structural formulas for cyclohexane are:



Line Bond Structure

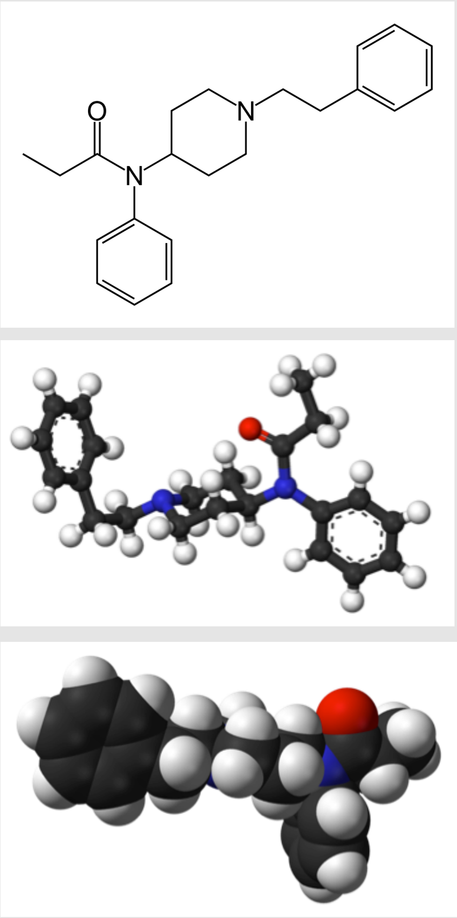


Condensed Structure

Skeletal Structure

4.4 Molecular Geometry

Figure 4.5 Fentanyl



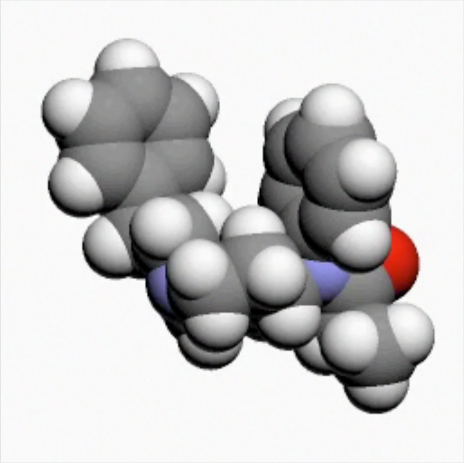
Skeletal structural formula (**top**), ball-and-stick model (**middle**), and space-filling model (**bottom**) of fentanyl. In both the ball-and-stick model and the space-filling model, carbon atoms are shaded black, oxygen atoms are shaded red, nitrogen atoms are shaped blue, and hydrogen atoms are shaded white.
Source: Wikimedia Commons, PD
Author: Ben Mills

Let's define **molecular geometry** as the *spacial arrangement* of a molecule's atoms. Molecules very rarely take the shapes that are drawn in their structural formulas. Structural formulas, whether line bond, condensed, or skeletal, are either one- or two-dimensional. Most molecules are ***three-dimensional***. Line bond structures are commonly drawn with the lines/bonds at 90º angles, but the **bond angles** in molecules (the angle between covalent bonds), with rare exceptions, are not at 90º. Skeletal and condensed structures often use bond angles of 90º or approximately 120º only for convenience in depicting the bonding pattern connectivity, not necessarily to represent the actual bond angles/geometry of the molecule.

Let me clarify using an example. Fentanyl is a therapeutic drug used for pain relief and is combined with other compounds to be administered as an anesthetic. It is about 100 times more potent than morphine! The ***skeletal structure*** of fentanyl is shown in the ***top*** insert of Figure 4.5. The "***geometry***" of the molecule can be depicted in two types of views in the middle and lower inserts of Figure 4.5. A "**ball-and-stick model**" is shown in the middle insert. Ball-and-stick models are images that are intended to show *molecular geometry* using perspective graphics. A **"space-filling model"** of fentanyl is shown in the the bottom insert of Figure 4.5. Space-filling models are images that, like ball-and-stick models, are intended to show *molecular geometry*, but also depict the scaled atom sizes (atomic radii). In both the ball-and-stick model and the space-filling model, carbon atoms are shaded black, oxygen atoms are shaded red, nitrogen atoms are shaded blue, and hydrogen atoms are shaded white. Images of ball-and-stick or space-filling molecules are best viewed when they can be rotated in 3D graphics (movies). If you are using the ***i-book*** format, you can watch the movie by clicking the play icon in Movie 4.1. For **print or pdf versions** of the book, the movie can be seen at:
http://www.zovallearning.com/streamvid/fentanyl.html

The important concept I would like you to understand is that the structural formulas, whether line bond, condensed, or skeletal, *do not **explicitly** show the actual bond angles within molecules*. However, **the bond angles can be *predicted* from a molecule's structural formula**; that is the main educational goal of this section.

Movie 4.1 Rotating Fentanyl Model



Click the play icon to rotate the space-filling model of fentanyl.
Source: Wikimedia Commons, Author: fuse809
CC-BY-SA, http://creativecommons.org/licenses/by-sa/3.0/legalcode

Predicting the Molecular Geometry

Molecular geometry was defined as the *spacial arrangement* of a molecule's atoms. To know the exact molecular geometry, we must know all of the bond angles and bond lengths (distance between bonded atoms) within a molecule. In this book, we will ignore variations in bond lengths since these relatively minor deviations in length do not directly affect the concepts presented. Therefore, for our discussions, *predicting molecular geometry will be equivalent to predicting the bond angles within a molecule.* **Bond angles can be predicted from the structural formula using a model called Valence Shell Electron Pair Repulsion (VSEPR) Theory**. The name may sound complicated, however the method is quite simple. For ***diatomic molecules***, the geometry of the molecule is always **linear**; the two atoms that make up the molecule exist on the same line. Since there is only one bond (whether single, double, or triple), it does not make sense to talk about a bond angle. To discuss a bond angle, there must be two bonds originating from the same atom. Think about lines - you could not measure an angle with just one line, you would need a second line!

Recall our three size categories for molecules; *diatomic*, *small*, and *large*. When considering ***small molecules***, molecules with *one central atom* and *all* other atoms bonded to the central atom, you will learn how to use the VSEPR Theory to predict the angles between the bonds (molecular geometry) then determine the molecule's "**molecular shape"** category. You will also use the VSEPR Theory to predict bond angles around any particular atom in a large molecule.

Valence Shell Electron Pair Repulsion (VSEPR) Theory

The bond angles around *any particular atom of interest* in a molecule can be predicted because the ***groups of electrons*** surrounding this atom ***will repel each other***. These **electron groups** (abbreviated as EG) consist of, as the name implies, groups of electrons that are localized to a certain area. You can easily recognize an EG by looking for one of the following:

(1) **A bonded atom** (an atom bonded to the *atom of interest*).

- Each bonded atom counts as **one** electron group (EG). Whether the bonded atom is connected to the atom of interest with a single, double, or triple bond, *all of these shared electrons are localized within a particular region and therefore count as* ***one EG***. In order to determine the bond angles, we will be counting electron groups. ***A common error that students make*** is to count double bonds as two EGs or count triple bonds as 3 EGs - be careful not to do so.

(2) **A lone pair** (on the *atom of interest*).

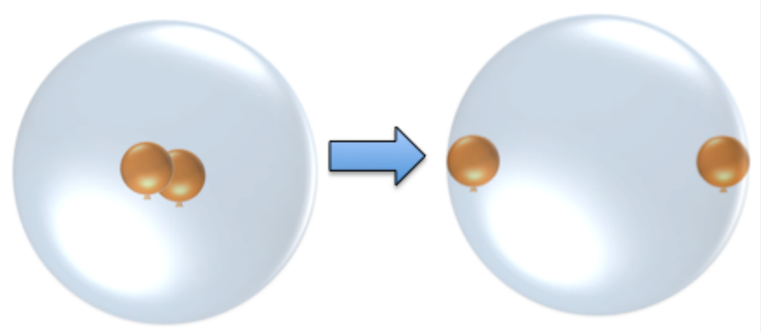
- Each lone pair counts as ***one electron group*** (EG). Even though lone pairs are not attached to other atoms, they do occupy a localized area around the atom of interest and therefore repel other electron groups.

The central concept in the VSEPR Theory is that the electron groups (bonded atoms and lone pairs) on an atom of interest will repel each other because they are composed of electrons and electrostatic repulsion forces occur. ***The lowest energy arrangement of the electron groups around the atom of interest is the one in which the groups are as far apart from each other as possible (that is, with the largest angles between them).*** It is therefore possible to predict the **bond angles** around an atom of interest by getting the **Electron Group Arrangement**.

Electron Group Arrangement: Predicting the Arrangement of Electron Groups

Before I discuss the arrangement of electron groups, I would like you to consider the arrangement of electrically-charged objects with which you may be more familiar, then transfer that understanding to the EGs. Have you ever rubbed an air-filled balloon with a natural fiber such as cotton or wool? If you do this, some of the electrons on the fiber are transferred to the balloon and the balloon gets a negative charge. If you do this to two balloons and then try to place them close to each other, they will move apart from each other because of the electrostatic repulsive force. What do you think would happen if ***two*** negatively charged balloons are placed into a hollow, clear sphere? Try to visualize your prediction of how the electrically-charged balloons would arrange themselves in the sphere. Electrostatic repulsion will cause the balloons to move as far apart from each other as possible as illustrated in Figure 4.6. The same thing happens with ***electron groups***.

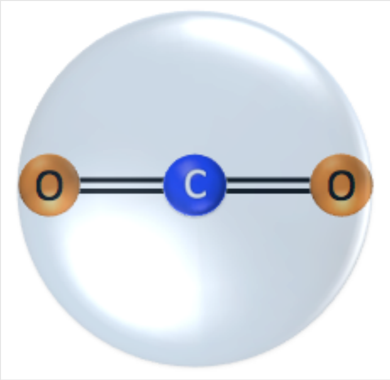
Figure 4.6
Electrostatic Repulsion Between Two Balloons in a Hollow Sphere



If two negatively-charged balloons are placed in a hollow sphere, they will move apart from each other because of the electrostatic repulsive force.

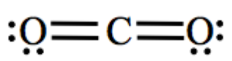
I will use carbon dioxide as an example of a molecule with two electron groups. You drew the line bond structure for CO_2 in Review Problem 4.1 of this chapter. You may wish to redraw it now as a review.

Figure 4.7
The Arrangement of Two Electron Groups



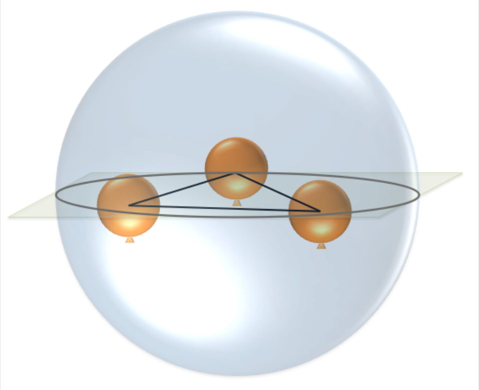
Two electron groups are arranged around a central atom (or other atom of interest in a large molecule) at angles of 180º. All of the electron groups, as well as the central atom, are on the same line.

The line bond structure for carbon dioxide (CO_2) is:



Carbon is the central atom and we are interested in how the electron groups are arranged around the central atom. Note that there are two ***electron groups*** around the central atom. Each bonded atom counts as **one** electron group; there are two oxygen atoms bonded to the central atom. A common mistake made by students is to count *each* double bond as two electron groups. Even though there are four electrons in each double bond, the double bond comprises one electron group; all four electrons are grouped together in a small area and will repel **other** electron groups. The two electron groups, the bonded oxygen atoms, will move as far apart from each other as possible. I will construct the CO_2 molecule in an imaginary, clear, hollow plastic sphere. The central atom goes in the center of the sphere. The two electron groups (bonded oxygen atoms) are placed as far apart from each other as possible as shown in Figure 4.7. This is how two electron groups arrange themselves around a central atom (or other atom of interest in a large molecule). In CO_2, this arrangement results in a **bond angle** (the angle between the C-O bonds) of 180º. Note that the lone pairs *on the oxygen atoms* do not affect the angles between the electron groups on the carbon. In the balloon analogy, it is the hollow sphere that keeps the balloons from continuing to move further apart from each other; covalent bonding and electrostatic attraction (for lone pairs) prevents the electron groups from moving further apart.

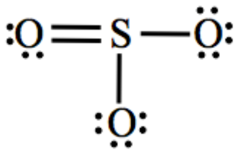
Figure 4.8
Electrostatic Repulsion Between Three Balloons in a Hollow Sphere



If three negatively-charged balloons are placed in a hollow sphere, they will move as far away from each other as possible. The balloons arrange themselves all on a plane that bisects the sphere and at the vertices (corners) of an equilateral triangle upon the bisecting plane.

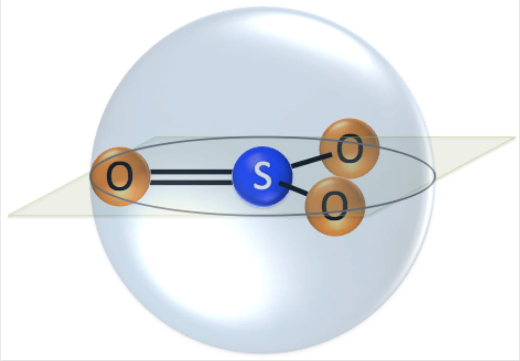
Next, let's consider the arrangement of ***three*** electron groups. We will begin by predicting how three negatively-charged balloons will arrange themselves in a hollow sphere. Electrostatic repulsion causes the balloons to move as far apart from each other as possible. In this case, the balloons arrange themselves all on a plane that bisects the sphere and at the vertices (corners) of an equilateral triangle upon the bisecting plane as shown in Figure 4.8. The same thing happens to three electron groups! I will use sulfur trioxide as an example of a molecule with three electron groups. You drew the line bond structure for SO_3 in Review Problem 4.1 of this chapter.

The line bond structure for sulfur trioxide (SO_3) is:



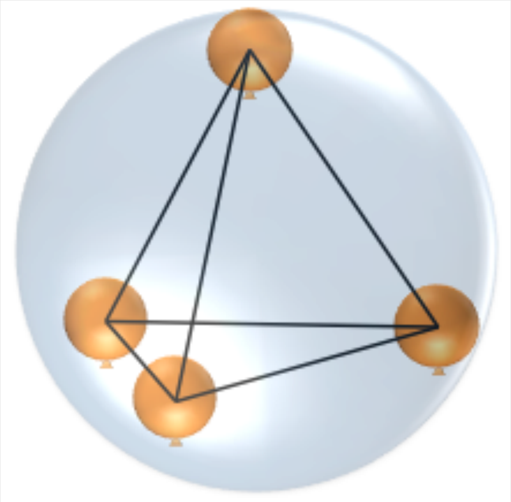
Sulfur is the central atom, and we are interested in how the electron groups are arranged around the central atom in order to determine the bond angles. There are three ***electron groups*** around the central atom. Each bonded atom counts as **one** electron group; the three electron groups, the bonded oxygen atoms, will move as far apart from each other as possible. To construct the SO_3 molecule in an imaginary, clear, hollow sphere, the sulfur atom is placed in the center of the sphere and the three electron groups (bonded oxygen atoms) are placed as far apart from each other as possible. Figure 4.9 shows how ***three*** electron groups are arranged around a central atom (or other atom of interest in a large molecule). In SO_3, this arrangement results in **bond angles** (the angles between the S-O bonds) of 120º. All of the electron groups, as *well as the central atom,* are on the same plane.

Figure 4.9
The Arrangement of Three Electron Groups



Three electron groups are arranged around a central atom (or other atom of interest in a large molecule) at angles of 120º to each other. All of the electron groups, *as well as the central atom,* are on the same plane.

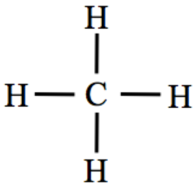
Figure 4.10
Electrostatic Repulsion Between Four Balloons in a Hollow Sphere



Four negatively-charged balloons arrange themselves at the corners of a isosceles triangular pyramid within the sphere.

Let's consider the arrangement of ***four*** electron groups. We will begin by visualizing how four negatively-charged balloons arrange themselves in a hollow sphere. You may have been able to predict the arrangements of two or three balloons because they are arranged in one- and two-dimensions respectively. The arrangement that results from *four* negatively-charged balloons contained in a sphere is *three*-dimensional. In this case, the balloons arrange themselves at the corners of an equilateral triangular pyramid within the sphere as shown in Figure 4.10. The same thing happens to four electron groups! I will use methane (CH_4) as an example of a molecule with four electron groups.

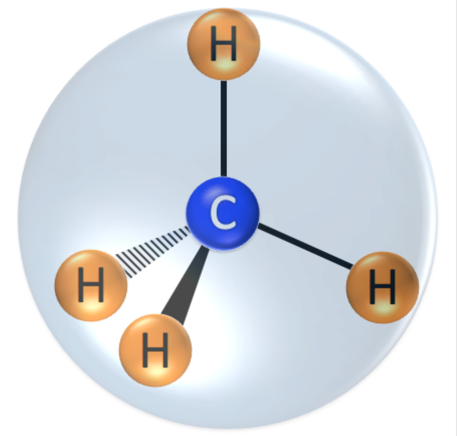
The line bond structure for methane (CH_4) is:



$$\begin{array}{ccccc} & & \mathrm{H} & & \\ & & | & & \\ \mathrm{H} & - & \mathrm{C} & - & \mathrm{H} \\ & & | & & \\ & & \mathrm{H} & & \end{array}$$

We are interested in how the electron groups are arranged around the central atom in order to determine the angles between them. There are four ***electron groups*** around the central atom. Each bonded atom counts as **one** electron group; the four electron groups, the bonded hydrogen atoms, will move as far apart from each other as possible. To construct the CH_4 molecule in an imaginary, clear, plastic sphere, the carbon atom is placed in the center of the sphere and the four electron groups (bonded hydrogen atoms) are placed as far apart from each other as possible. Figure 4.11 shows how ***four*** electron groups are arranged around a central atom (or other atom of interest in a large molecule). **All** of the angles between *four* electron groups are110° (some books use 109.5°).

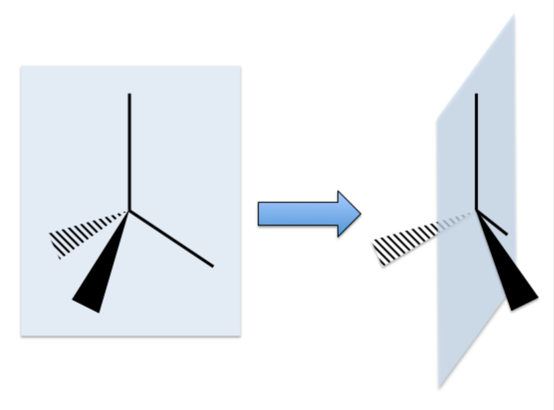
Figure 4.11
The Arrangement of Four Electron Groups



Four electron groups are arranged around a central atom (or other atom of interest in a large molecule) with bond angles of approximately 110°.

Illustrating three-dimensional objects on a flat surface, such as a page, requires special techniques. Artists use a technique called "perspective," where angles are drawn as they *appear* when viewing an object from a particular position. One technique used by chemists to illustrate the three-dimensional details of the arrangement of atoms in molecules is to use the "**wedge and dash**" technique as I have done in Figure 4.11. It is important for you to understand this technique because of its use throughout this book and other scientific literature and also because it is often required in both written and online homework problems. In *wedge and dash* illustrations, ***solid wedges*** indicate bonds that would be coming *out and above* the page (toward the viewer) in the three-dimensional object. ***Dashed shapes*** indicate bonds that would be coming *out and behind* the page (away from the viewer) in the three-dimensional object. Regular lines (neither wedge nor dash) indicate bonds that exist on the plane of the page in the three-dimensional object. I have tried to make these last three statements easier to understand by illustrating them in Figure 4.12.

Figure 4.12
Wedge and Dash Representations

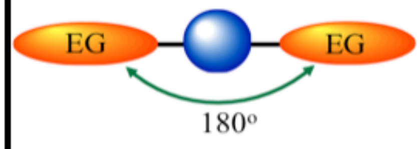
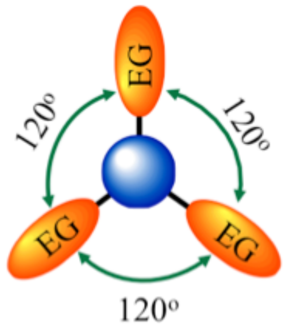
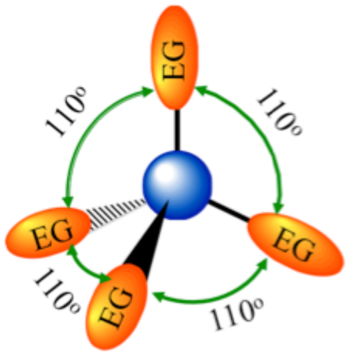


Left: Illustration of a page with a wedge and dash representation.
Right: Illustration of the three-dimensional information meant to be implied in ***wedge and dash*** representations.

Note that if you look at the ***line bond structure*** of CH_4, the bond angles are drawn at 90°. *Line bond structures* do not *explicitly* show the bond angles, only the atomic connectivity. However, combining the connectivity information contained in line bond structures with VSEPR Theory, we can ***predict the bond angles*** around any atom of interest in any molecule as we have done for CO_2, SO_3, and CH_4.

Most molecules obey the ***octet rule*** and therefore will have *no more than four electron groups*. Although this textbook does not include discussions of bond angles for molecules or polyatomic ions that contain atoms surrounded by more than four electron groups, VSEPR can indeed be used to predict bond angles for these molecules that do not obey the octet rule.

Let's review angles and the arrangement of electrons groups around an atom of interest:

2 Electron Groups	3 Electron Groups	4 Electron Groups
		

Two electron groups are arranged around an atom at 180° angles. Three electron groups are arranged around an atom at 120° angles and the electron groups exist on the same plane as the atom to which they are all connected. Four electron groups are arranged around an atom at 110° angles to each.

NOTE: For two or three electron groups, the angles will deviate *slightly* from 120° and 110° when one (or more) of the electron groups is a *lone pair*. The reason for this is that electron groups repel (push away) other electron groups more strongly than do bonded atoms. In this course, these *slight* deviations in angles ***can be ignored*** because their effects are ***not significant*** in the chemistry that will be discussed.

Molecular Shape: Categorizing the Shape of Small Molecules

VSEPR Theory is applicable to small and large molecules. When applying the Theory to either small or large molecules, one can determine the angle between the electron groups around any particular atom of interest. I have used the term "atoms of interest" in the preceding text in order that VSEPR Theory can be applied to any atom in any molecule. When electron groups on an atom of interest are *bonded atoms* (as opposed to *lone pairs*), we refer to the angles between the bonded atoms as **bond angles**. For ***small molecules***, there exists one central atom with all other atoms bonded to the central atom, therefore the only bond angles that exist are between bonds originating from the central atom. This simplified geometry allows us to categorize (name) particular ***molecular shapes*** seen in small molecules.

Given the line bond structure, small molecules can be categorized by their **molecular shape** as follows:

Step 1. Get the Electron Group Arrangement

Find the angle between the electron groups and their arrangement around the central atom. You already learned how to do this:

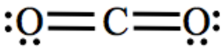
- **Two electron groups:** 180° angle, both electron groups are on the same line as the central atom.
- **Three electron groups:** 120° angles, all electron groups are on the same plane as the central atom. Angles will deviate slightly from 120° if one of the electron groups is a lone pair.
- **Four electron groups:** 110° angles, occupies three dimensions in space. Angles will deviate slightly from 110° if one or more of the electron groups is a lone pair.

Step 2. Determine the Molecular Shape Category Based on the Arrangement of Atoms.

Small molecules are categorized according to the arrangement of the atoms **only**. Although lone pairs are also electron groups and are therefore important in determining the electron group arrangement in Step 1, they are treated as being "invisible" when assigning molecular shape category names. I am sure most readers do not understand what is meant by *"treating lone pairs as invisible"* at this point, however it will become much clearer as we do some examples. We will unpack this concept of Molecular Shape Categorization now by doing an example for each small molecule shape category.

Example: What is the name of the **molecular shape** of carbon dioxide (CO_2)?

In Section 2 of this chapter, you learned how to draw the line bond structure of small molecules if you are given the molecular formula. The line bond structure for carbon dioxide (CO_2) is:



Step 1. Get the electron group arrangement.

Find the angle between the electron groups and their arrangement around the central atom.

- Carbon is the central atom and we are interested in how the electron groups are arranged around the central atom. There are <u>two</u> ***electron groups*** around the central atom. Each bonded atom counts as **one** electron group; there are no lone pairs on the central atom. The lone pairs on the oxygen atoms ***do not affect*** the arrangement of electron groups around the central atom!
- **Two electron groups: 180º angles, all electron groups are on the same line as the central atom.**

Step 2. Determine the molecular shape category based on the arrangement of atoms.

Small molecules are categorized according to the arrangement of the atoms **only**. Lone pairs are treated as being "invisible" when assigning molecular shape category names.

- Consider a *ball and stick model* of CO_2 using the electron group arrangement determined in Step 1:

Because all atoms are on the same line (co-linear), this ***molecular shape*** is called **linear**. *All* small molecules with two atoms and no lone pairs *on the central atom* are categorized as **linear.**

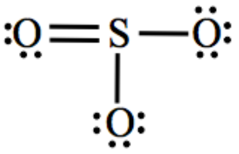
A very helpful tool for determining molecular shape is called the "**ABE Method.**"

- "**A**" represents the central atom (carbon in our CO_2 example).
- "**B**" represents atom(s) bonded to the central atom (each oxygen in our CO_2 example).
- "**E**" represents lone pair(s) on the central atom (none seen in CO_2 since there are no lone pairs *on the central atom*).

The **ABE** Method uses a "general notation" that indicates the type and number of electron groups (**B** or **E**) that surround the central atom (**A**). We write the **ABE** Method notation for CO_2 and ***all*** other small molecules that have *<u>two</u>* bonded atoms and *<u>no</u>* lone pairs *on the central atom* as "**AB_2**." There are two oxygens bonded to the central atom therefore we write "B_2." **<u>All</u>** AB_2 molecules have **180º bond angles** and are in the **linear** molecular shape category. The ball and stick model of **AB_2** molecules is:

Example: What is the name of the molecular shape of sulfur trioxide (SO_3)?

The line bond structure for sulfur trioxide (SO_3) is:



Step 1. Get the electron group arrangement.

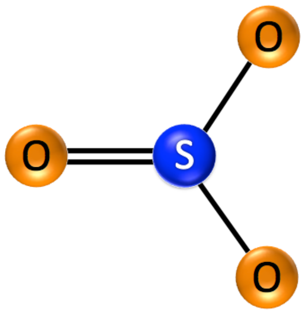
Find the angle between the electron groups and their arrangement around the central atom.

- Sulfur is the central atom and we are interested in how the electron groups are arranged around the central atom. There are <u>three</u> ***electron groups*** around the central atom. Each bonded atom counts as **one** electron group; there are *no lone pairs* on the central atom. The lone pairs on the oxygen atoms ***do not affect*** the arrangement of electron groups around the central sulfur atom!

- **Three electron groups: 120º angles, all electron groups are on the same plane as the central atom.**

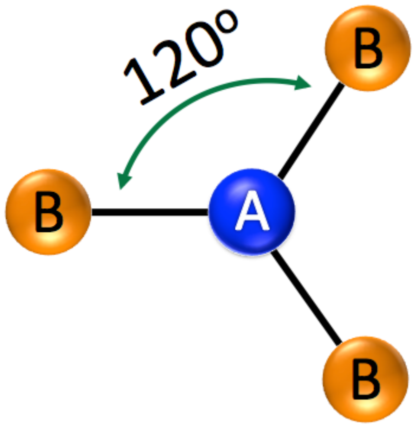
Step 2. Determine the molecular shape category based on the arrangement of atoms.

Consider a ball and stick model of SO_3 using the electron group arrangement determined in Step 1:



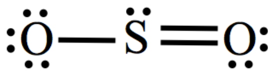
Because all atoms are on the same plane and the bonded atoms are at the vertices (corners) of a triangle, this *molecular shape* is called **trigonal planar**. *All* small molecules with three atoms and no lone pairs *on the central atom* are categorized as **trigonal planar.**

We write the ABE Method notation for SO_3 and ***all*** other small molecules that have *<u>three</u>* bonded atoms and *<u>no</u>* lone pairs *on the central atom* as "**AB_3**." There are three oxygens bonded to the central atom, therefore we write "**B_3**." **<u>All</u>** **AB_3** molecules have **120º bond angles** and are in the **trigonal planar** molecular shape category. The model of **AB_3** molecules is:



Example: What is the name of the molecular shape of sulfur dioxide (SO_2)?

Note that we are now considering sulfur dioxide, not sulfur trioxide that we used in our last example. The line bond structure for sulfur dioxide (SO_2) is:



Step 1. Get the electron group arrangement.

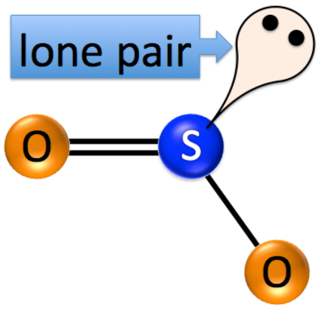
Find the angle between the electron groups and their arrangement around the central atom.

- Sulfur is the central atom and we are interested in how the electron groups are arranged around the central atom. There are three ***electron groups*** around the central atom. There are **two** bonded atoms and **one** *lone pair* on the central sulfur atom.
- **Three electron groups: approximately 120° angles, all electron groups are on the same plane as the central atom.**

    Note that I wrote *"approximately* **120°**" for the bond angles (the "≈ 120°" used in the illustration above means "about equal to 120° " or "approximately 120°"). Earlier in this section, I mentioned that the angles can deviate slightly from 120° if one of the electron groups is a lone pair. I also told you that for the purposes of this course, these slight deviations in electron group angles ***can be ignored***.

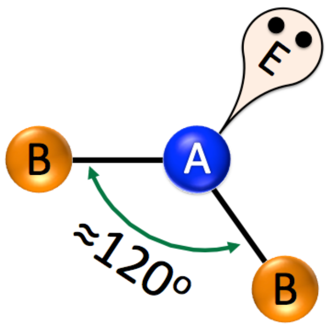
Step 2. Determine the molecular shape category based on the arrangement of atoms.

Consider a ball and stick model of SO_2 using the electron group arrangement determined in Step 1:



Small molecules are categorized according to the arrangement of the atoms **only**. Lone pairs are treated as being "invisible" when assigning molecular shape category names. In SO_2, all ***atoms*** are on the same plane but not on the same line, therefore this ***molecular shape*** is called **bent**. *All* small molecules with two atoms and one lone pair *on the central atom* are categorized as **bent.**

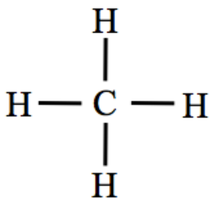
We write the ABE Method notation for SO_2 and ***all*** other small molecules that have *two* bonded atoms and *one* lone pair *on the central atom* as "**AB_2E**." There are two oxygen atoms bonded to the central atom therefore we write "**B_2**." Recall that the "**E**" in ABE notation represents lone pair(s). There is *one* lone pair on the central atom therefore we write "**E.**" **All AB_2E** molecules have **bond angles** that are *approximately* **120°** and are in the **bent** *molecular shape* category. The model of **AB_2E** molecules is:



Lone pairs repel (push away) other electron groups more strongly than do bonded atoms. Therefore in **AB_2E** molecules, the bond angles are bit less than 120°, so we write "≈ 120°" or "approximately 120°."

Example: What is the name of the molecular shape of methane (CH_4)?

Get the electron group Arrangement. The line bond structure for methane (CH_4) is:



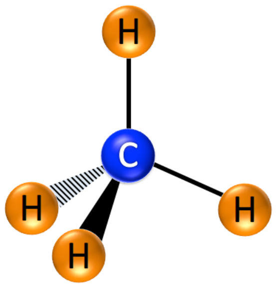
Step 1. Get the electron group arrangement.

Find the angle between the electron groups and their arrangement around the central atom.

- Carbon is the central atom and we are interested in how the electron groups are arranged around the central atom. There are four ***electron groups*** around the central atom. Each bonded atom counts as **one** electron group; there are *no lone pairs* on the central carbon atom.
- **Four electron groups: 110° angles.**

Step 2. Determine the molecular shape category based on the arrangement of atoms.

Consider a ball and stick model of CH_4 using the electron group arrangement determined in Step 1:



When four electron groups are present they arrange themselves in three dimensions, we therefore use the ***wedge and dash*** representation in order to illustrate the three dimensional molecule on a two dimensional surface such as this page. Figure 4.13 shows the significance of lines, wedges, and dashes implied in the *wedge and dash* representation of the methane molecule.

In this molecular shape, the bonded atoms are at the corners of a *regular triangular pyramid* as shown previously in Figure 4.10. A regular triangular pyramid has its base and all three sides composed of identical, equilateral triangles and is called a regular tetrahedron. This ***molecular shape*** is therefore called **tetrahedral**. *All* small molecules with four atoms and no lone pairs *on the central atom* are categorized as **tetrahedral.**

We write the ABE Method notation for CH_4 and ***all*** other small molecules that have *four* bonded atoms and *no* lone pairs *on the central atom* as "**AB_4.**" There are four atoms bonded to the central atom, therefore we write "**B_4.**" **All** **AB_4** molecules have **110° bond angles** and are in the **tetrahedral** molecular shape category. The model of **AB_4** molecules is:

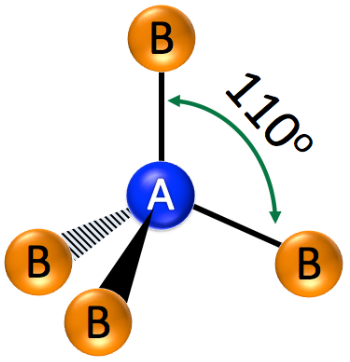
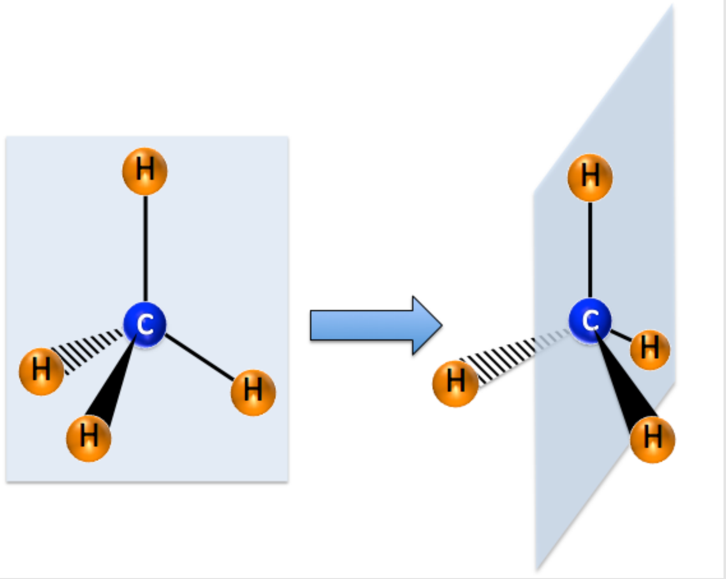
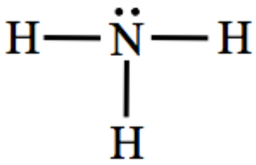


Figure 4.13
Significance of lines, wedges, and dashes implied in the wedge and dash representation of the methane molecule.



Example: What is the name of the molecular shape of ammonia (NH_3)?

The line bond structure for ammonia (NH_3) is:



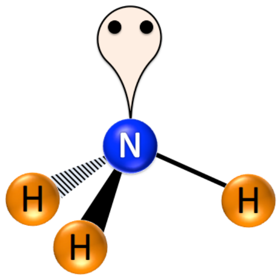
Step 1. Get the electron group arrangement.

Find the angle between the electron groups and their arrangement around the central atom.

- There are <u>four</u> ***electron groups*** around the central atom. There are **three** bonded atoms and **one** *lone pair* on the central atom.
- **Four electron groups (with one lone pair):** approximately **110º angles.** Angles deviate slightly from 110º because one of the electron groups is a lone pair.

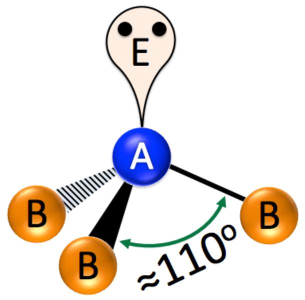
Step 2. Determine the molecular shape category based on the arrangement of atoms.

- Consider a ball and stick model of NH_3 using the electron group arrangement determined in Step 1:



Small molecules are categorized according to the arrangement of the atoms **only**. Lone pairs are treated as being "invisible." In NH_3, the atoms form a triangular pyramid with the nitrogen on the top of the pyramid and the three hydrogens at the corners of the triangular base of the pyramid. This ***molecular shape*** is therefore called **pyramidal** (some texts refer to this shape as *trigonal pyramid*). *All* small molecules with three atoms and one lone pair *on the central atom* are categorized as **pyramidal.**

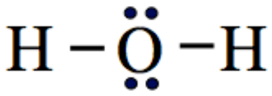
We write the ABE Method notation for NH_3 and ***all*** other small molecules that have *<u>three</u>* bonded atoms and *<u>one</u>* lone pair *on the central atom* as "**AB_3E**." There are three atoms bonded to the central atom, therefore we write "**B_3.**" There is *one* lone pair on the central atom, therefore we write "**E**." **<u>All</u>** **AB_3E** molecules have **bond angles** that are *approximately* **110º** and are in the **pyramidal** molecular shape category. The model of **AB_3E** molecules is:



Lone pairs repel other electron groups more strongly than do bonded atoms. Therefore in **AB_3E** molecules, the bond angles are bit less than 110º, so we write "≈ 110º" or "approximately 110º."

Example: What is the name of the molecular shape of water (H_2O)?

The line bond structure for water (H_2O) is:



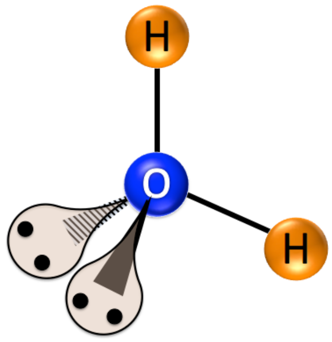
Step 1. Get the electron group arrangement.

Find the angle between the electron groups and their arrangement around the central atom.

- There are four ***electron groups*** around the central atom. There are **two** bonded atoms and **two** *lone pairs* on the central oxygen atom.
- **four electron groups:** approximately **110º angles.** Angles deviate slightly from 110º because two of the electron groups are lone pairs.

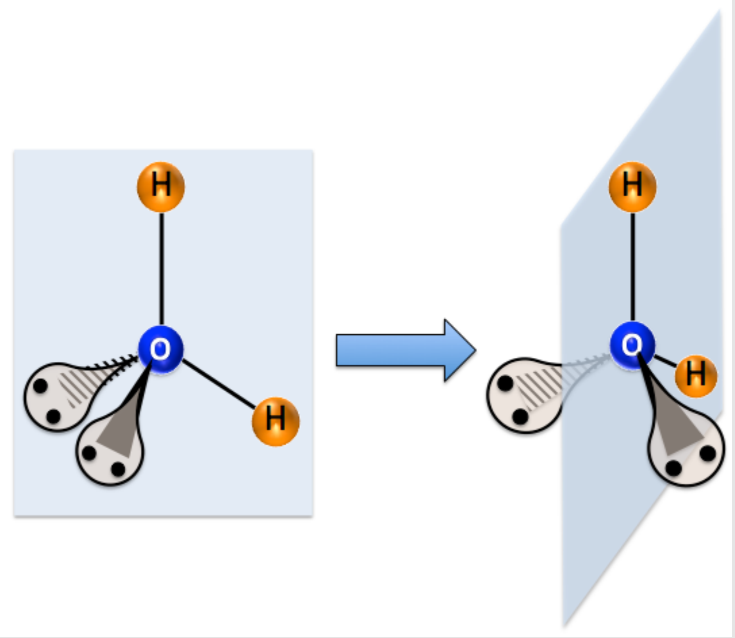
Step 2. Determine the molecular shape category based on the arrangement of atoms.

Draw a ball and stick model of H_2O using the electron group arrangement determined in Step 1:

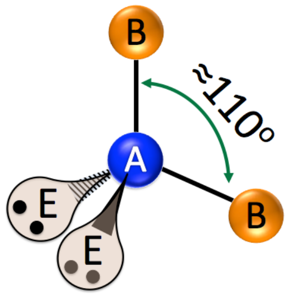


Small molecules are categorized according to the arrangement of the atoms **only**. Lone pairs are treated as being "invisible" when assigning molecular shape category names. Figure 4.14 shows the significance of lines, wedges, and dashes implied in the wedge and dash representation of the water molecule. In H_2O, the hydrogen atoms and oxygen atom are on the same plane but not on the same line, therefore this *molecular shape* is called **bent**. *All* small molecules with two atoms and two lone pairs *on the central atom* are categorized as **bent.**

Figure 4.14
Significance of lines, wedges, and dashes implied in the wedge and dash representation of the water molecule.



We write the ABE Method notation for H_2O and ***all*** other small molecules that have two bonded atoms and two lone pairs *on the central atom* as "**AB_2E_2**." There are two atoms bonded to the central atom, therefore we write "**B_2**." There are *two* lone pairs on the central atom, therefore we write "**E_2**." **All** **AB_2E_2** molecules have **bond angles** that are *approximately* **110º** and are in the **bent** molecular shape category. The model of **AB_2E_2** molecules is:



Because **AB_2E_2** molecules have two lone pairs on the central atom, the bond angles are bit less than 110º, so we write "≈ 110."

You may recall that you have seen the "**bent"** molecular shape category previously for SO_2. However, there is a difference in the molecular geometry between H_2O and SO_2; can you think of how they are different? Although both molecules have the **bent** shape, H_2O has a *bond angle* of ≈ 110º (four electron groups) and SO_2 has a bond angle of ≈ 120º (three electron groups).

Review of Molecular Shape Categories for Small Molecules

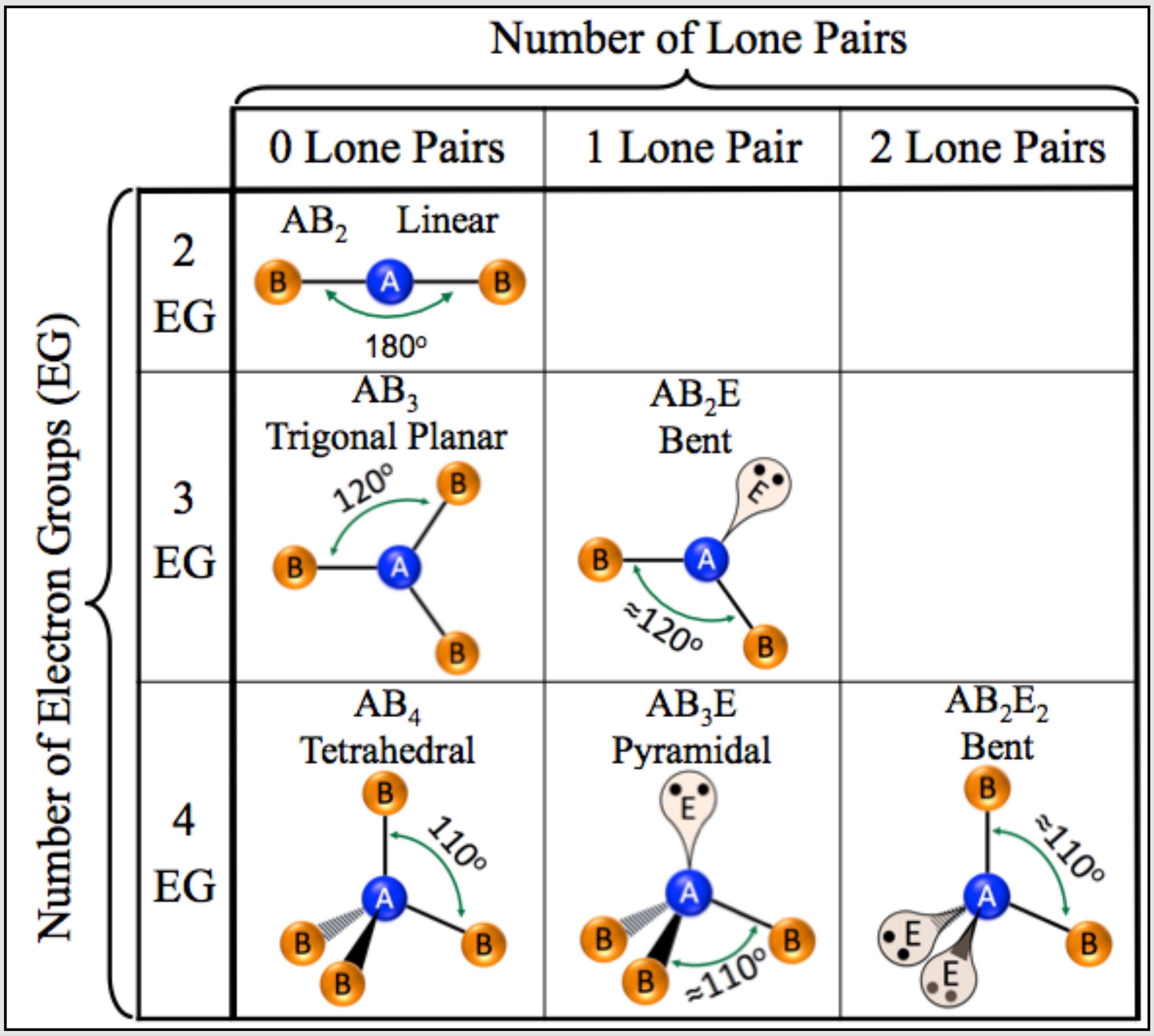
Table 4.1
Molecular Shape and Bond Angles for ABE Classes

ABE Class	Bond Angles	Molecular Shape
AB_2	180°	Linear
AB_3	120°	Trigonal Planar
AB_2E	≈ 120°	Bent
AB_4	110°	Tetrahedral
AB_3E	≈ 110°	Pyramidal (or Trigonal Pyramid)
AB_2E_2	≈ 110°	Bent

Bond angles and **molecular shape categories** can be predicted using the **ABE Method.** Table 4.1 lists the bond angles and molecular shape names for the various ABE classes.

Table 4.2 arranges the various **ABE** classes according to the number of electron groups (EG) and lone pairs on the central atom.

Table 4.2 Molecular Shape Table



Review 4.5: Predicting Bond Angles and Molecular Shapes for Small Molecules

Predict the **bond angles** (or approximate bond angles) and the **molecular shape** category for each of the following *small molecules*. (**Hint**: start by drawing the line bond structures, then refer to Table 4.1 or Table 4.2)

a) NF_3

b) H_2S

c) ozone (O_3), ozone has an oxygen as the central atom with the other two oxygen atoms bonded to it.

d) CS_2

e) carbon tetrachloride

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

Molecular Geometry of Large Molecules

The bond angles around any *atom of interest* in a large molecule can be predicted in the same manner that we used for small molecules. Simply use the **ABE** method, but in this case let "**A**" represent the *atom of interest* in the large molecule instead of the central atom of a small molecule. "**B"** and "**E**" represent the electron groups; "**B**" for atoms bonded ***to the atom of interest*** and "**E**" for lone pairs ***on the atom of interest***. The bond angles for the various **ABE** classes are the same angles that we used for small molecules and are listed in Table 4.3.

Table 4.3
The Geometry of Large Molecules: ABE Method

ABE Class	Bond Angles
AB_2	180°
AB_3	120°
AB_2E	≈ 120°
AB_4	110°
AB_3E	≈ 110°
AB_2E_2	≈ 110°

Example: The line bond structure of an ethane molecule is shown to the right:

What are the ***bond angles*** around **each** of the carbon atoms in an ethane molecule?

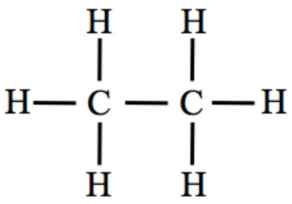
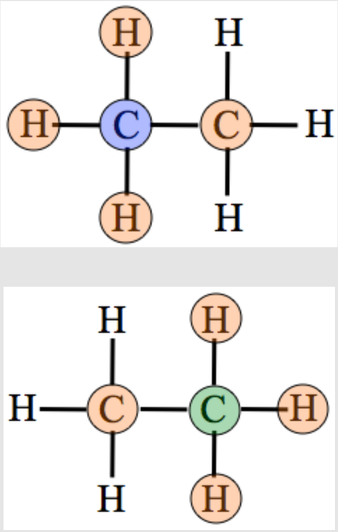


Figure 4.15
Determination of the Bond Angles in Ethane

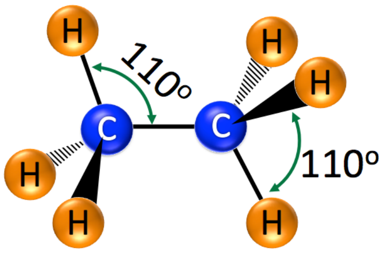


Top: The *left-most* carbon (shaded blue) is surrounded by four electron groups (shaded orange)
Bottom: The *right-most* carbon (shaded green) is also surrounded by four electron groups (shaded orange).

Let's consider the left-most carbon first. The ***left-most*** carbon is shaded blue in Figure 4.15 (**top**). Note that this carbon is surrounded by four electron groups (shaded orange); all are bonded atoms, three hydrogens and the *other* carbon atom. Since the left-most carbon is surrounded by four electron groups and all of the electron groups are bonded atoms, it is in the **AB_4** class and therefore ***all*** bond angles around this carbon are 110° (see Table 4.3). The non-highlighted hydrogen atoms on the right-most carbon *do not significantly affect the bond angles around the left-most carbon*.

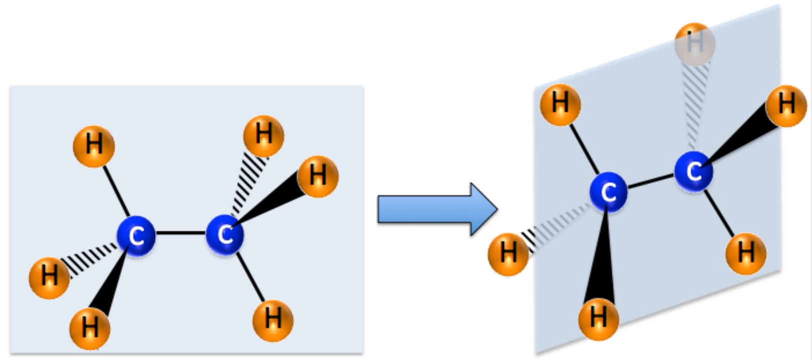
Next, let's consider the ***right-most*** carbon in ethane. The *right-most* carbon is shaded green in Figure 4.15 (**bottom**). Note that this carbon is also surrounded by four electron groups, all are bonded atoms; three hydrogens and the *other* carbon atom. Since the right-most carbon is surrounded by four electron groups and all of the electron groups are bonded atoms, it is in the **AB_4** class and therefore ***all*** bond angles around this carbon are 110°. Do you recognize that the two carbons in ethane are *identical and indistinguishable*? If you view the right-most carbon f*rom behind the page*, it becomes the left-most carbon from that perspective!

A wedge and dash representation of ethane is shown to the right.



Although not all bond angles are explicitly listed in the wedge and dash drawing, note that **all** bond angles around ***each carbon atom*** are 110°. Figure 4.16 shows the significance of lines, wedges, and dashes implied in the wedge and dash representation of the ethane molecule.

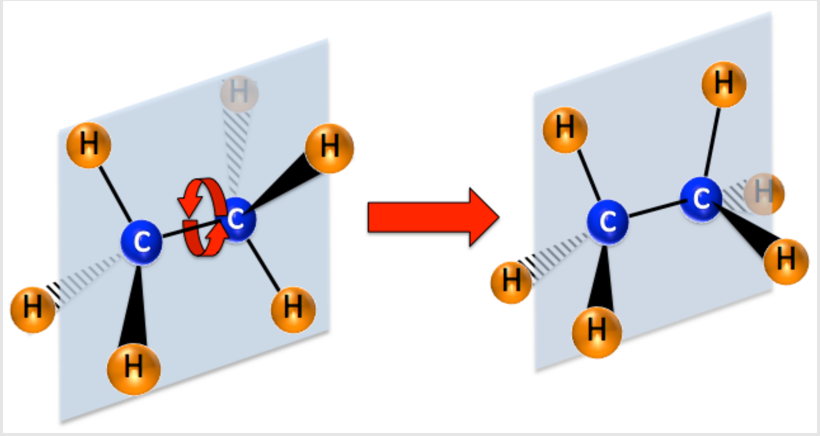
Figure 4.16
Significance of lines, wedges, and dashes implied in the wedge and dash representation of the ethane molecule.



Ethane is a molecule that we categorize as a “*large molecule*”; there is not a single, central atom with *all the other atoms* bonded to it as is the case for the “*small molecule*” category. In ***small molecules***, all bonds *originate from the central atom* and this simplified *molecular geometry* allowed us to use ***molecular shapes*** categories. You may have noticed that we only discussed **molecular geometry (*bond angles*)** for ***large molecules***; we do not categorize large molecules by “*molecular shape*” as we did for small molecules. The reason for this is that, with few exceptions, single bonds can “***rotate***” and therefore large molecules are **always *changing their shape***. Figure 4.17 and Movie 4.2 illustrate rotation of single bonds using an ethane molecule as an example. It is important to understand that although single bonds are capable of rotation, ***the bond angles around any particular atom do not change upon rotation***. Only single bonds freely rotate; because of the nature of ***double*** and ***triple bonds***, they *do not* rotate. For **print or pdf versions** of the book, the movie can be seen at: http://www.zovallearning.com/streamvid/ethane-conformations.html.

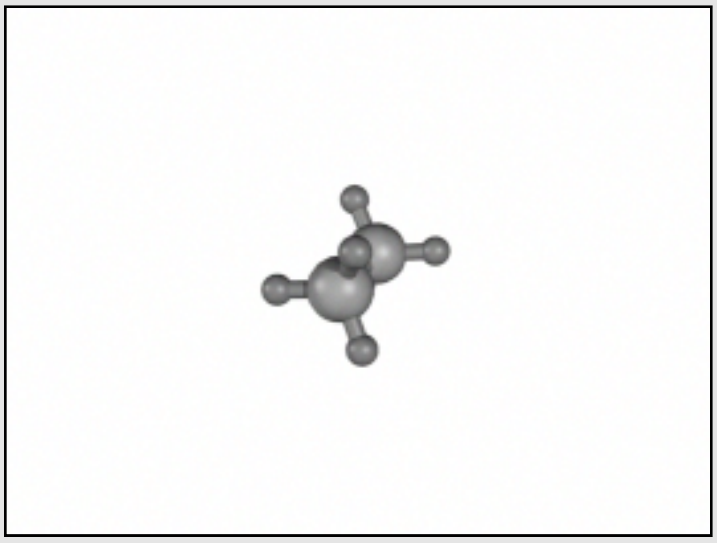
I will discuss one more example of bond angle determination in a large molecule, then I will ask you to try a few on your own.

Figure 4.17 Rotation Around a Single Bond in Ethane



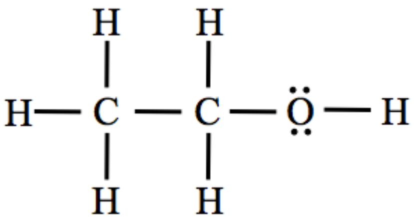
Free rotation occurs around single bonds, therefore most large molecules are always *changing their shapes.* In this figure, one of the *infinite number of shape changes* of which ethane is capable of is shown by the rotation of one of the methyl groups by 60º around the carbon-carbon bond axis.

Movie 4.2 Ethane Bond Rotation



Source: Wikimedia Commons, Author: Ralf, CC-BY-SA, https://creativecommons.org/licenses/by/2.5/deed.en

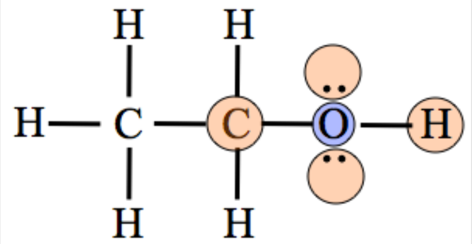
Example: The line bond structure of an ethanol molecule is shown on the right. What is the bond angle for the bonds coming from ***the oxygen atom*** in an ethanol molecule?



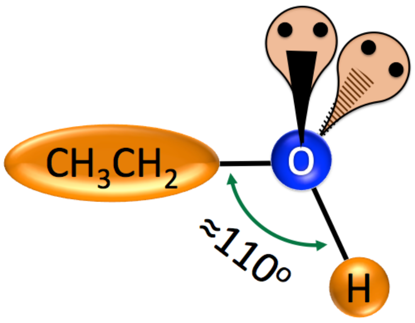
$$\begin{array}{ccccccccc} & & H & & H & & & & \\ & & | & & | & & & & \\ H & - & C & - & C & - & \ddot{\underset{..}{O}} & - & H \\ & & | & & | & & & & \\ & & H & & H & & & & \end{array}$$

We could determine the bond angles around each carbon atom or the oxygen atom, however in this example we are asked specifically about the bond angles around the oxygen atom (shaded blue in Figure 4.18). Note that the oxygen is surrounded by **four electron groups**, two bonded atoms (a carbon and a hydrogen) and two lone pairs. The electron groups are shaded orange in the figure. Since the oxygen atom is surrounded by two bonded atoms and two lone pairs, it is in the **AB_2E_2** class and the bond angle is approximately 110º (see Table 4.3). The non-highlighted atoms in Figure 4.18 *do not significantly affect the bond angles **around the oxygen***.

Figure 4.18 Determination of the Bond Angles in Ethanol

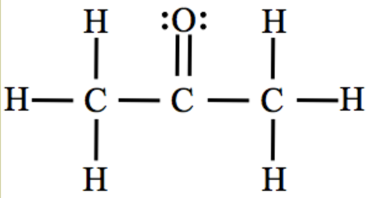


The *oxygen* (shaded blue) is surrounded by four electron groups; two bonded atoms and two lone pairs (shaded orange).



Review 4.6: Predicting Bond Angles in Large Molecules

The line bond structure of an acetone molecule is shown on the right.



a. What are the bond angles around the **left-most carbon** atom?
b. What are the bond angles around the **carbon atom in the middle** of the molecule?
c. What are the bond angles around the **right-most** carbon atom?

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

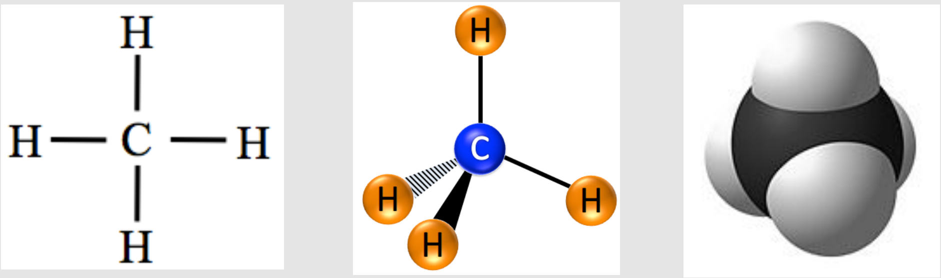
In this section of chapter 4, you have seen how the connectivity of atoms shown in structural formulas, such as line bond structures, can be used to determine molecular geometries (bond angles). The molecular geometries are quite important because the observed (macroscopic) properties of a molecular compound are related to its ***nanoscopic*** structure. The *nanoscopic* structure of molecules includes details such as the kind of atoms, the pattern in which they are ***bonded*** to each other, the molecular geometry, and how the electrons are distributed within the molecule. In the next section, I will discuss how the distribution of electrons within a molecule is determined by its molecular geometry. Throughout the remainder of this book, you will see how the nanoscopic details of a molecule will affect observed, macroscopic properties such as biological effects, melting and boiling temperatures, rates of evaporation, and the ability of one substance to dissolve another substance.

4.5 The Distribution of Electrons in Molecules

In the preceding sections of this chapter, I have been helping you build your own understanding of matter. In this chapter, we have been focusing on molecular compounds. At this point, if you are given the molecular formula of a *small molecule*, I would expect you to be able to draw its line bond structure, predict the bond angles, and know its molecular shape name. Also, if you were given the line bond, condensed, or skeletal formula for a *large molecule*, I would expect you to predict the bond angles around any particular atom in the molecule. It is quite important to understand these molecular geometry aspects in order to understand how the electrons are distributed in molecules. The electron distribution is a major factor that determines the properties of molecular compounds. For example, consider two molecules that are quite similar in size - CO_2 and H_2O. Both molecules contain three atoms, however at room temperature they are in different phases; CO_2 exists as a gas, whereas H_2O exists as a liquid (water). Combining your new understanding of molecular geometry with the information you will learn in this section about the distribution of electrons in molecules will provide you with enough insight to understand why molecular compounds (such as CO_2 and H_2O) have different properties.

To begin our discussion, let's revisit our various representations of the methane molecule that appear in Figure 4.19. A line bond structure is shown on the **left**. The ***molecular geometry*** is depicted in the **middle** and **right** inserts. A "***wedge-dash, ball-and-stick*** **model**" is shown in the **middle** insert. A **"space-filling model"** of methane is shown in the **right** insert. Space-filling models are images that show *molecular geometry* and also indicate the approximate *area that electrons occupy.* Here is a new concept: ***the electrons are not always evenly distributed within molecules.*** Sometimes electrons spend more time in one particular region of the molecule giving that region *additional negative charge*. Sometimes a particular region of a molecule is electron deficient, giving that region of the molecule *additional positive charge*. The existence of this uneven charge within a molecule is a major factor that makes the properties of molecules such as CO_2 and H_2O quite different.

Figure 4.19 Representations of Methane (CH_4)

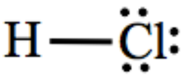


Left: The line bond structure of methane.
Middle: A wedge-dash, ball-and-stick representation.
Right: A "space-filling model." Space-filling models show *molecular geometry* and also indicate the approximate *area that electrons occupy.*

You can begin to understand the distribution of electrons in molecules by considering diatomic molecules (molecules composed of just two atoms). Let's first consider the H_2 molecule: $H—H$

The two electrons in the ***covalent bond*** are "*shared evenly*" by the hydrogens. Here I use the term "*shared evenly*" to mean that the electrons do not spend more time, *on average*, closer to any one of the two hydrogen atoms. This is because the bond is between ***like atoms***; the electrons are equally attracted to each of the positively-charged hydrogen nuclei (the *plural* of **nucleus** is **nuclei**). Whenever thinking about electrons, think of them as constantly moving. Electrons in covalent bonds exist primarily in the *region between the two bonded atoms* that share them, however they ***are not stationary***. When electrons are shared between like atoms, such as in H_2, they are, on average, evenly or equally distributed between the atoms.

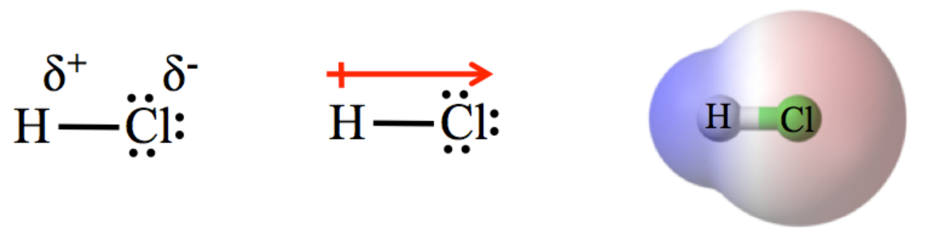
Next, let's consider the HCl molecule:



$H—\ddot{\underset{..}{Cl}}:$

The two electrons in the **H-Cl** ***bond*** are ***not*** shared ***equally*** by the chlorine and hydrogen atoms. The shared electrons spend, on average, a bit more time nearer the chlorine than the hydrogen. This is because the bond is between ***un-like*** atoms (chlorine vs. hydrogen); the shared electrons happen to be more strongly attracted to the chlorine than they are to the hydrogen. When electrons in bonds are *not equally* shared, as is the case for *un-like atoms*, we call the bond a **polar bond**. When electrons in bonds are *evenly* (equally) shared, as is the case for *like atoms* such as we saw in the **H-H** ***bond***, we call the bond a **nonpolar bond**. ***Polarization*** is a general term used to indicate difference, dichotomy, separation, opposition, contradiction, etc. In this case, there is a polarization (separation/difference) of the electrical charge distribution. Scientists and engineers use the term **electric dipole** to describe this physical state that results when there is a separation of charge over a short distance such as the length of a chemical bond. Since the electrons spend a bit more time nearer to the chlorine, the chlorine end of the bond acquires a ***partial negative charge***. I say "*partial"* because it does not get a full **1$^-$** charge. Although the electrons are *unevenly* shared, they are still shared, therefore the charge is not a full 1^- charge as would result from chlorine having an extra electron *that was not shared* as does a *chloride ion*. Since the electrons in the H-Cl covalent bond spend more time nearer the chlorine, then the hydrogen end of the bond acquires a ***partial positive charge***. Figure 4.20 shows three equivalent methods used to indicate ***bond polarity*** using the HCl molecule as an example. The line bond structure on the ***left side of*** Figure 4.20 uses the Greek lowercase letter delta (**δ**) to indicate a *partial positive charge* (**δ^+**) or a *partial negative charge* (**δ^-**) near the appropriate atoms. An alternative way to indicate bond polarity and partial charge is to use the **dipole arrow** shown in red above the line bond structure in the ***middle*** of Figure 4.20. When using *dipole arrows*, the arrow points to the partial negative charged region and a crossed line (looks like + on the end of the arrow) is used to indicate the partial positive charged region. The space filling model on the ***right side*** of Figure 4.20 not only shows the region that the molecule's electrons occupy, but is also shaded to indicate the *electron distribution*. The area where electrons spend more time and therefore has a partial negative charge is shaded red. The area that is electron deficient has a partial positive charge and is shaded blue.

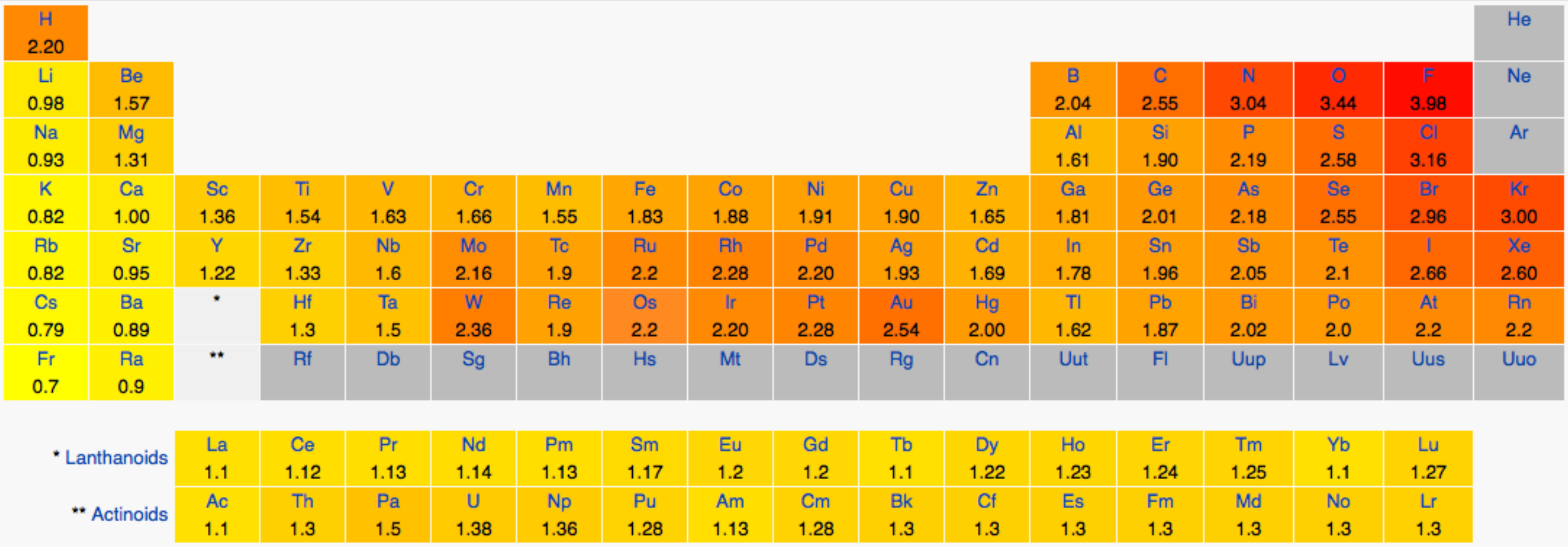
Figure 4.20 **Representations of Bond Polarity in HCl**



This figure shows three equivalent methods used to indicate bond polarity using the HCl molecule as an example. **Left:** The Greek lowercase letter, delta (**δ**), is used to indicate *partial positive charge* (**δ^+**) or *partial negative charge* (**δ^-**) on the appropriate atoms.
Middle: *A dipole arrow* (shown in red) can also be used to show polarity. The arrow points to the partial negative charged region and a crossed line (looks like + on the end of the arrow) is used to indicate the partial positive charged region. **Right:** A *shaded* space-filling model can be used to indicate polarity. The area that has a partial negative charge is shaded red and the area that has a partial positive charge and is shaded blue.
Source: Wikimedia Commons, Author: B. Mills, PD

While discussing the polarity of the **H-Cl** bond, I mentioned that "the shared electrons happen to be more strongly attracted to the chlorine than they are to the hydrogen." The reason for this is based on the electrostatic attractive forces between the shared electrons and the nuclei and core electrons of the bonded atoms. The relative ability of an atom in a bond to attract electrons is called its **electronegativity**. The *more* electronegative atom in the bonded pair will have a stronger attraction to the shared electrons, the electrons will spend a bit more time in the vicinity of that atom, therefore the atom will have a partial negative charge. The *less* electronegative atom in the bond will have a partial positive charge. Electronegativities of elements are calculated from experimental measurement. The electronegativities of the elements are shown in Table 4.4. Electronegativity values are among the few quantities in science literature that have ***no units***. Note that there is a **periodic trend** in electronegativity values of the **s-** and **p-**block elements; electronegativity increases going from left to right (in a row) and bottom to top (in a column).

Table 4.4 **Electronegativity Values**



H 2.20																	He
Li 0.98	Be 1.57											B 2.04	C 2.55	N 3.04	O 3.44	F 3.98	Ne
Na 0.93	Mg 1.31											Al 1.61	Si 1.90	P 2.19	S 2.58	Cl 3.16	Ar
K 0.82	Ca 1.00	Sc 1.36	Ti 1.54	V 1.63	Cr 1.66	Mn 1.55	Fe 1.83	Co 1.88	Ni 1.91	Cu 1.90	Zn 1.65	Ga 1.81	Ge 2.01	As 2.18	Se 2.55	Br 2.96	Kr 3.00
Rb 0.82	Sr 0.95	Y 1.22	Zr 1.33	Nb 1.6	Mo 2.16	Tc 1.9	Ru 2.2	Rh 2.28	Pd 2.20	Ag 1.93	Cd 1.69	In 1.78	Sn 1.96	Sb 2.05	Te 2.1	I 2.66	Xe 2.60
Cs 0.79	Ba 0.89	*	Hf 1.3	Ta 1.5	W 2.36	Re 1.9	Os 2.2	Ir 2.20	Pt 2.28	Au 2.54	Hg 2.00	Tl 1.62	Pb 1.87	Bi 2.02	Po 2.0	At 2.2	Rn 2.2
Fr 0.7	Ra 0.9	**	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Uut	Fl	Uup	Lv	Uus	Uuo
* Lanthanoids		La 1.1	Ce 1.12	Pr 1.13	Nd 1.14	Pm 1.13	Sm 1.17	Eu 1.2	Gd 1.2	Tb 1.1	Dy 1.22	Ho 1.23	Er 1.24	Tm 1.25	Yb 1.1	Lu 1.27	
** Actinoids		Ac 1.1	Th 1.3	Pa 1.5	U 1.38	Np 1.36	Pu 1.28	Am 1.13	Cm 1.28	Bk 1.3	Cf 1.3	Es 1.3	Fm 1.3	Md 1.3	No 1.3	Lr 1.3	

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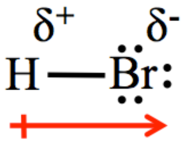
One can determine which atom in a polar bond is partially positive and which is partially negative by comparing the electronegativity values of the two atoms. I will elaborate on this statement and some of the concepts associated with bond polarity by doing an example problem.

Example: Draw a line bond structure of hydrogen monobromide (HBr). Predict which atom is partially positive and which atom is partially negative. Add the **δ^+** or **δ^-** symbols to the appropriate atom (as seen on the left-most structure in Figure 4.20). Add a dipole arrow above or below the line bond structure to indicate the polarity (as seen on the middle structure in Figure 4.20).

Solution: Bromine is more electronegative than hydrogen. The electrons that are shared in the covalent bond spend more time nearer the bromine atom, therefore the bromine has a partial negative charge (**δ^-**) and the hydrogen has a partial positive charge (**δ^+**). The dipole can be indicated using a dipole arrow with the arrow pointing toward the partial negative charge.



Review 4.7: Bond Polarity

Bromine monofluoride (BrF) exists as a brown gas and is used as an algaecide, fungicide, and disinfectant in some industrial applications. Draw the line bond structure of bromine monofluoride. Predict which atom is partially positive and which atom is partially negative. Add the **δ^+** or **δ^-** symbols to the appropriate atom (as seen on the left-most structure in Figure 4.20). Add a dipole arrow above or below the line bond structure to indicate the polarity (as seen on the middle structure in Figure 4.20).

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

The degree of bond polarization depends on the ***difference*** in electronegativities between the two bonded atoms. Greater differences in the abilities of the bonded atoms to attract the shared electrons (greater electronegativity) results in ***more polarized bonds***. What does it mean to have a "more polarized bond"? A physicist would say that there is a "stronger dipole." If a particular bond is "more polarized" than another, this indicates that the partial positive charge (**δ^+**) and the partial negative (**δ^-**) charge are greater in the more polarized bond.

Example: Which bond is ***more polarized***, the H-F or H-Br bond?

Solution: To determine which bond is more polarized, we must compare the difference in electronegativities of the bonded atoms in H-F and H-Br. We refer to the tabulated electronegativity values in Table 4.4. The electronegativity of hydrogen, fluorine, and bromine are 2.20, 3.98, 2.96, respectively.

- First, we calculate the ***difference*** in electronegativity between F and H: 3.98 - 2.20 = **1.78**
- Next, we calculate the ***difference*** in electronegativity between Br and H: 2.96 - 2.20 = **0.76**

Since there is a greater difference in electronegativity between F and H vs. Br and H, **the H-F bond is more polarized than the H-Br bond.** We say that the H-F dipole is greater than the H-Br dipole.

Summary of Bond Polarity

We can classify covalent bonds as being *either* **polar** or **nonpolar**. ***Polar bonds*** occur because of *unequal sharing* of electrons in covalent bonds when two *unlike*-atoms (such as H-Br or H-Cl) are bonded together. ***Nonpolar bonds*** occur when the electrons are shared evenly between two like-atoms (such as H-H or F-F).

The Polarity of Molecules

Now that you have an understanding of ***bond polarity***, you are ready to learn how to determine if a ***molecule*** is polar or nonpolar. Similar to the concept of *bond polarity*, when electrons are not symmetrically distributed **in a molecule**, it results in a **polar molecule**; a molecule with one end that has a partial negative charge and one end that has a partial positive charge. The existence and degree of polarity (strength of the dipole) in molecules is quite important in the physical and chemical properties of molecular compounds and has implications in many of the chemistry concepts that you will learn throughout this book (and your career). For example, one type of force responsible for attracting molecules ***to other molecules*** that is, in part, responsible for whether the molecules exist close to each other in the liquid or solid phase instead of the gas phase is called the **dipole-dipole force**. The partially positive (**δ^+**) end of one molecule's dipole is attracted to the partially negative (**δ^-**) end of another molecule's dipole (and vice versa) by an electrostatic attraction as illustrated in Figure 4.21.

Figure 4.21
Illustration of Dipole-Dipole Forces

Polar molecules are attracted to other polar molecules by electrostatic forces called dipole-dipole forces. The partially positive (**δ^+**) end of one molecule's dipole is attracted to the partially negative (**δ^-**) end of another molecule's dipole (and vice versa).

Dipole-dipole forces are similar to ionic bonding, however they are *not nearly as strong* because the charge on dipoles is ***partial*** (**δ^+** and **δ^-**) not ***full*** (1^+ or 1^-) or ***multiple*** (2^+, 2^- etc.) as is the case for ***ions***.

Just because a molecule contains polar bonds does not necessarily mean that it is a polar molecule. This statement may sound counterintuitive, but it is indeed true. In the remainder of this section, you will learn how to determine if a **molecule** is polar or nonpolar based on ***both*** the existence (or not) of polar bonds **and** its molecular geometry. It is very important to be careful in differentiating, in your thoughts and statements, whether you are referring to ***polar bonds*** or ***polar molecules***! I will show you a method for determining the polarity of a molecules for each of our *molecular size categories* (diatomic, small, and large molecules). As a reminder, our three size categories are shown in Table 4.5.

Table 4.5 Molecular Size Category Table

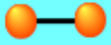
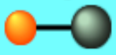
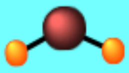
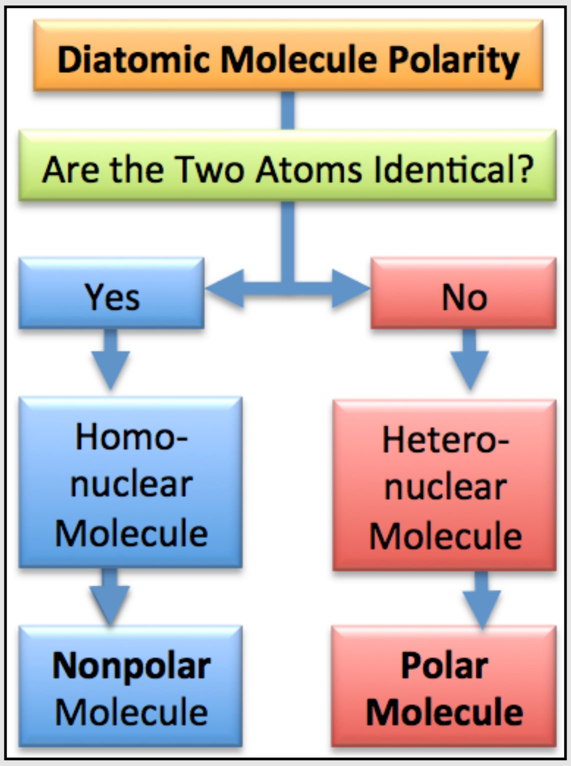
Molecular Size Category	Description	Example(s)	
Diatomic Molecule	Molecule contains **only two atoms**	H_2 	HCl 
Small Molecule	Molecule has **one central atom** with ***all other*** atoms bonded to the central atom	CH_4 	H_2O 
Large Molecule	Larger than *Small Molecule*; there **is not just one single, central atom** with **all** the other atoms bonded to it	C_3H_8 	

Figure 4.22
Polarity of Diatomic Molecules



The Polarity of Diatomic Molecules

Since diatomic molecules contain *only one bond*, the polarity of the molecule depends only on the polarity of that bond. A **homonuclear diatomic molecule** such as H_2 or O_2 contains like-atoms (homo) and a nonpolar bond, therefore the molecule is ***nonpolar***. A **heteronuclear diatomic molecule** such as HBr or HF contains two *un-like* atoms (hetero) and a polar bond, therefore the molecule is **polar**. A thought flow-chart for the determination of the polarity of diatomic molecules is shown in Figure 4.22.

Review 4.8: Determining the Polarity of Diatomic Molecules

Categorize each of the diatomic molecules listed below as polar or nonpolar.

a) H_2
b) carbon monoxide (CO)
c) N_2
d) nitrogen monoxide (NO)

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The Polarity of Small Molecules

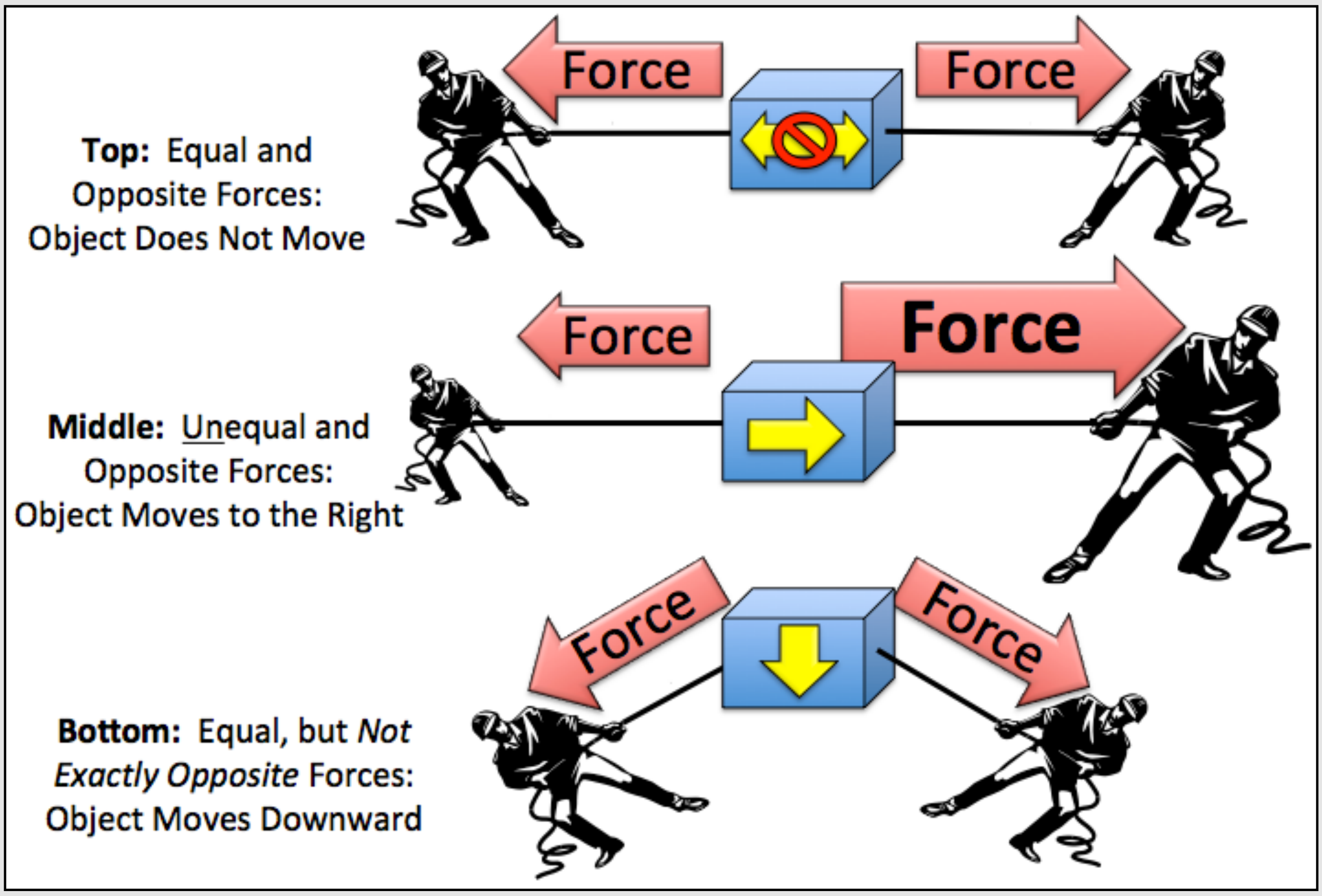
Small molecules contain more than one bond. The *individual bonds within a molecule* can be polar and/or nonpolar. Even if a small molecule has polar bonds, this fact alone does not guarantee that the molecule is polar. In order to determine if a small molecule is polar, we must "***add up***" all of the individual dipoles from each bond. Let's begin our discussion of *small molecule polarity* by contemplating what is meant by "***adding up***" dipoles.

Dipoles are physical quantities that not only have a magnitude (amount of charge), but also have a direction. An analogous physical quantity that you are familiar with is *velocity*. When you drive your car, to completely describe your path you would use both the *speed* (miles per hour) and the *direction* you are traveling. Another physical quantity with both magnitude and direction is a force. When you pull on an object, how fast and where the object moves depends on how hard you pull ***and*** in what *direction* you pull. Quantities with both magnitude and direction are called **vector quantities**. Covalent bond electric dipoles are vector quantities; they have both *magnitude* (based on differences in electronegativity of the bonded atoms) and *direction* (based on bond angles). Recall that we used an arrow to indicate the direction of bond dipoles.

Before we discuss "*adding up*" dipole vectors, let's *add up* some vector quantities of which you have prior knowledge. We will consider adding a couple of force vectors. If you pull on a rope that is connected to an object, you cause a tension force and the object will move in the direction you are pulling it. If *multiple* ropes with tension are acting on the object, then it will move at a rate and direction that depend on the ***sum of all the tension forces***. In other words, if you wish to predict the overall force on an object, "***add up***" all the individual forces acting upon it. Consider the three cases illustrated in Figure 4.23. The scenario on **top** illustrates a case where two equal tensions (represented by vector arrows with the same length) are exerted in *opposite directions*. In this case, the object is pulled with equal force in opposite directions. The object does not move because the forces are "balanced" or "cancel." Mathematically, we say that the *forces add up to zero*. In the scenario illustrated in the **middle** of Figure 4.23, the two tension forces are in opposite directions, however the force pulling to the right is larger (represented by a larger vector arrow). In this scenario, the object would move to the right; the forces are not "balanced" and do not "cancel" - the forces ***do not*** *add up to zero*. In the scenario illustrated on the **bottom** of Figure 4.23, the two tension forces are equal (represented by vector arrows with the same length), *however* they are not oriented in *exactly* opposite directions. In this scenario, the object would move ***downward***; the forces are not "balanced" and do not "cancel" - the forces ***do not*** *add up to zero*.

Figure 4.23

Illustration of "Adding Up" Force Vectors

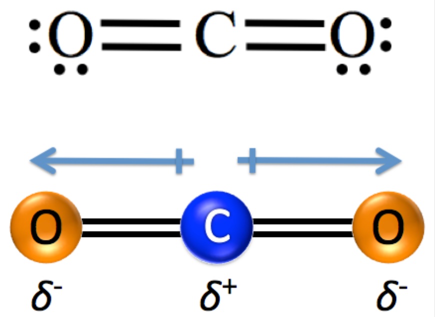


Top: Two equal tensions (represented by the red vector arrows of the same length) are exerted in opposite directions. The blue box does not move because the forces are "balanced" or "cancel"; they *add up to zero*.
Middle: The two tension forces are in opposite directions, however the force pulling to the right is larger (represented by a larger vector arrow). The blue box moves to the right because the forces are not "balanced" and do not "cancel" - they ***do not*** *add up to zero*.
Bottom: The two tension forces are equal but they are *not oriented in exactly opposite directions.* The blue box moves downward because the forces are not "balanced" and do not "cancel" - they ***do not*** *add up to zero*.

Now that you have a qualitative understanding of “adding up” vector quantities, I would like you to consider the polarity of these two molecules: carbon dioxide (CO_2) and water (H_2O). We will add up the individual bond dipoles within each of the two molecules in order to determine the polarity of each molecule.

Let’s first consider CO_2. The line bond structure for CO_2 is shown at the ***top*** of Figure 4.24. In the previous section of this chapter, we determined that a CO_2 molecule has a *linear* shape with 180° bond angles. CO_2 contains **two** polar bonds; the bond dipole vectors are drawn above the bonds in the ball-and-stick model shown at the ***bottom*** of Figure 4.24. Oxygen is more electronegative than carbon, therefore the oxygens have a partial negative charge and carbon has a partial positive charge.

Figure 4.24
Polarity of CO_2

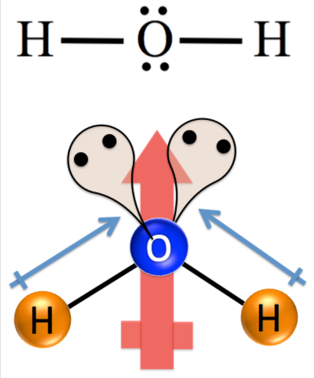


Top: Line bond structure of CO_2.
Bottom: Ball-and-stick model of CO_2 with the C-O bond dipole arrows. The bond dipole *directions* are ***exactly opposite of each other*** and the dipoles “***add up”*** to zero (cancel), therefore CO_2 is a nonpolar molecule.

Note that both dipoles are *equal in strength* (magnitude) because they are both carbon-oxygen bonds. Furthermore, since the shape of CO_2 is *linear*, the bond dipole directions are ***exactly opposite of each other*** and the dipoles “***add up”*** to zero (cancel) and result in a **nonpolar molecule**. When the dipoles in a molecule have the *same magnitude* **and** are *pointing in exactly opposite directions*, we say that the molecule is **symmetric.** The bond dipoles of symmetric molecules **always** add up to zero (cancel), therefore CO_2 and all other symmetric molecules are **nonpolar molecules**. A nonpolar *molecule* does not have a dipole since the individual bond dipoles add up to zero! This is much like the two equal forces in the top illustration of Figure 4.23; the analogy of the object *not moving* because the forces on it cancel can be related to this molecule being nonpolar because its dipoles cancel.

Next, lets consider the H_2O molecule. The line bond structure for H_2O is shown on the ***top*** of Figure 4.25. In the previous section of this chapter, we determined that the H_2O molecule has a *bent* shape with 110° bond angles. Like CO_2, H_2O also contains **two** polar bonds; the individual bond dipole vectors are shown (in blue) above the bonds in the ball and stick model of H_2O in the ***bottom*** of Figure 4.25. Oxygen is more electronegative than hydrogen, therefore the oxygen has a partial negative charge and the hydrogens have a partial positive charge.

Figure 4.25
Polarity of H_2O



Top: Line bond structure of H_2O
Bottom: Ball-and-stick model of H_2O with the O-H bond dipole shown as the two thin blue arrows. Since H_2O is not symmetric the bond dipoles *directions* ***are not*** *exactly opposite of each other* and the dipoles *do not* cancel each other. H_2O is a polar molecule because the two bond dipoles (blue arrows) add up to the molecular dipole (thick red arrow).

Both dipoles are *equal in strength* (magnitude) because they are both oxygen-hydrogen bonds. Because the shape of H_2O is *bent*, the bond dipole directions **are not *exactly opposite of each other*** and the two bond dipoles do not cancel each other. The two bond dipoles (blue arrows) “*add up”* to the molecular dipole (thick red arrow) and result in a **polar molecule**. This is analogous to adding up the two forces in the **bottom** illustration of Figure 4.23; the object moves when the two equal forces acting upon it are *not* pointing in exactly opposite directions. Polar molecules, such as H_2O, have one region with a partial positive charge and another region with partial negative charge as indicated by the thick red arrow in Figure 4.25.

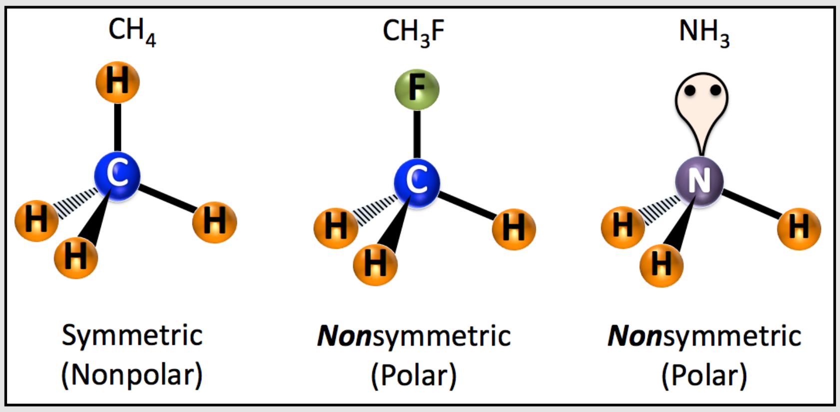
When the dipoles in a molecule **are not** of equal magnitude ***or*** are ***not*** pointing in *exactly opposite directions*, we say that the molecule is ***nonsymmetric.*** The bond dipoles of ***nonsymmetric*** molecules **do not** add up to zero (cancel), therefore H_2O and all other non-symmetric molecules are **polar molecules**.

So far, you have seen that symmetric small molecules are nonpolar and that non-symmetric small molecules are polar. It was fairly straight forward to visualize whether the dipoles were oriented in such a manner that they cancel each other (or not) in our examples of CO_2 and H_2O; in these cases the molecular geometry was either one-dimensional (CO_2, linear) or two-dimensional (H_2O, bent). It is a bit more difficult to visualize the addition of bond dipoles in the case of three-dimensional molecules. There is a mathematical method of vector addition that is taught in calculus classes and therefore is not something that most readers of this text have studied. Would it not be nice to have an easy way to determine if a small molecule was symmetric (and therefore nonpolar) or non-symmetric (and therefore polar)? I have very good news for you; there is indeed an easy, short-cut way to determine if a small molecule is symmetric. **A small molecule is *symmetric* if the <u>central atom</u> is surrounded by *identical electron groups*.** Recall that electron groups (EG) are ***bonded atoms*** and ***lone pairs***. When looking at a molecule's line bond structure, if there are *no lone pairs* on the central atom **<u>and</u>** *all of the atoms* bonded to the central atom are identical to each other, then the molecule is ***symmetric and nonpolar***. If this is not the case, then the molecule is ***nonsymmetric and therefore polar***.

This shortcut method for symmetry determination and molecular polarity works for *all small molecules* regardless of whether the shape is one-, two-, or three-dimensional. Figure 4.26 has a few examples of how we can apply this method. In CH_4 (Figure 4.26, **left**), the central carbon atom is surrounded by four identical electron groups; four bonded atoms, all of which are hydrogen. CH_4 is therefore symmetric and ***symmetric molecules are nonpolar*** because their bond dipoles add up to zero (cancel).

In fluoromethane (CH_3F, Figure 4.26 **middle,** used in the production of semiconductor electronic materials), the central carbon atom is **<u>not</u>** surrounded by identical electron groups. All four electron groups are bonded atoms, three of them are hydrogen atoms, however, the fourth electron group is a fluorine atom. The non-identical electron groups eliminate the symmetry. CH_3F is therefore ***non***symmetric and ***non-symmetric molecules are polar*** since their bond dipoles <u>*do not*</u> cancel each other. In CH_3F, since the ***magnitudes*** of all four bond dipoles are *not the same* (the C-F bond dipole is greater than C-H bond dipoles), the bond dipoles <u>*do not*</u> add up to zero.

Figure 4.26
Symmetry of Small Molecules

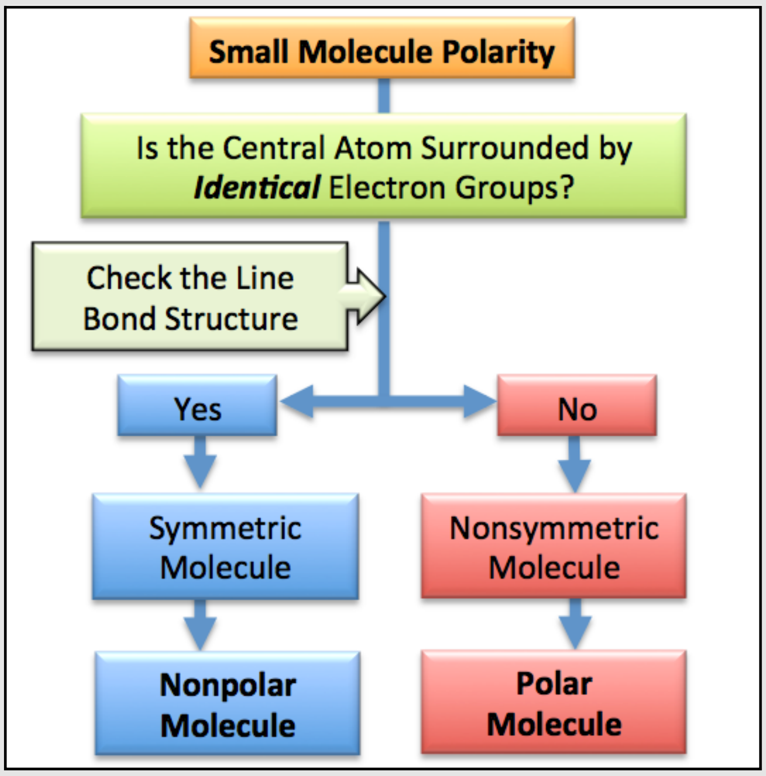


In CH_4 (**left**), the central carbon atom is surrounded by four identical electron groups; four bonded atoms all of which are hydrogen. CH_4 is therefore **symmetric and *nonpolar***. In CH_3F (**middle**), the central carbon atom is **<u>not</u>** surrounded by identical electron groups, three of them are hydrogen atoms, however, the fourth electron group is a fluorine atom. CH_3F is therefore **nonsymmetric and *polar*.** In NH_3 (**right**), the central nitrogen atom is **<u>not</u>** surrounded by identical electron groups; three of the electron groups are hydrogen atoms however, the fourth electron group is *a lone pair*. CH_3F is therefore **nonsymmetric and *polar***.

In ammonia (NH_3, Figure 4.26, **right**), the central nitrogen atom is **<u>not</u>** surrounded by identical electron groups; three of the electron groups are hydrogen atoms, but the fourth electron group is *a lone pair*. NH_3 is therefore nonsymmetric and nonsymmetric molecules are polar. Lone pair(s) on a central atom will always eliminate the symmetry. This leads to another short-cut that will work for all of the molecules considered in the book; ***when the central atom has one or more lone pairs, the molecule will be nonsymmetric and therefore polar***.

In discussing the polarity of *small molecules*, you have seen two molecules (CO_2 and H_2O); both contain ***polar bonds***. However, *only one* of the molecules (H_2O) is a ***polar molecule***. It is important to differentiate, in your thoughts and language, between polar *bonds* and polar *molecules*. **Even if a small molecule has polar bonds, this fact alone does not guarantee that the molecule is polar.** A thought flow-chart for the determination of the polarity of small molecules is shown in Figure 4.27.

Figure 4.27
Thought Flow-Chart for the Polarity of Small Molecules



Review 4.9: Determining the Polarity of Small Molecules

Categorize each of the diatomic molecules listed below as **polar or nonpolar**. Note that you will need to begin with the line bond structure of a molecule in order to determine its polarity.

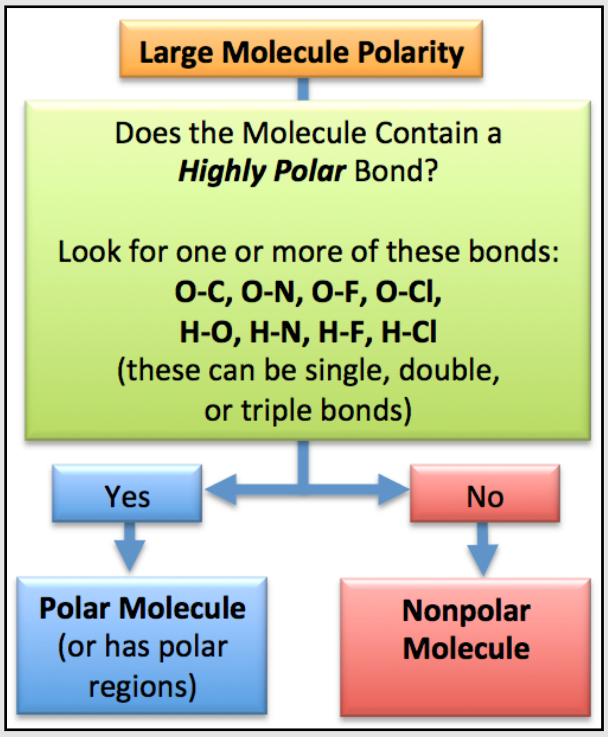
a. NF_3
b. H_2S
c. O_3
d. CS_2
e. CCl_4

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

The Polarity of Large Molecules

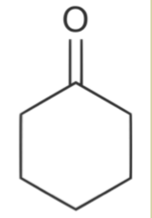
Large molecules will be considered polar (or have polar regions) if they contain **one or more "*highly polar*" bonds**. A ***highly polar*** bond is a bond with a large magnitude dipole. Bonds between atoms that have relatively *large differences in their electronegativity* values have large magnitude dipoles. For our purposes, the bonds that we will deem to be "highly polar" are bonds **between** a carbon or hydrogen atom **and** an oxygen, nitrogen, fluorine, or chlorine atom. These can be single, double, or triple bonds. There are a few exceptions to this rule that you will learn about in later chapters; however, until that time we will consider any large molecule to be polar if it contains one of the highly polar bonds that were listed above. A thought flow-chart for the determination of the polarity of *large molecules* is shown in Figure 4.28.

Figure 4.28
Thought Flow-Chart for the Polarity of Large Molecules



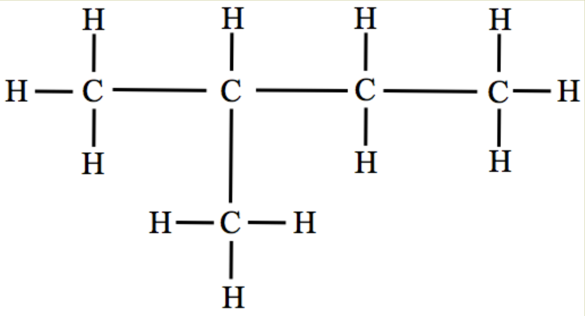
Review 4.10: The Polarity of Large Molecules

a) Cyclohexanone (skeletal structure shown below) is used as a starting material in the synthesis of Nylon.



Is cyclohexanone a **polar** or **nonpolar** molecule?

b) The line bond structure of 2-methylbutane is shown below.



Is 2-methylbutane a **polar** or **nonpolar** molecule?

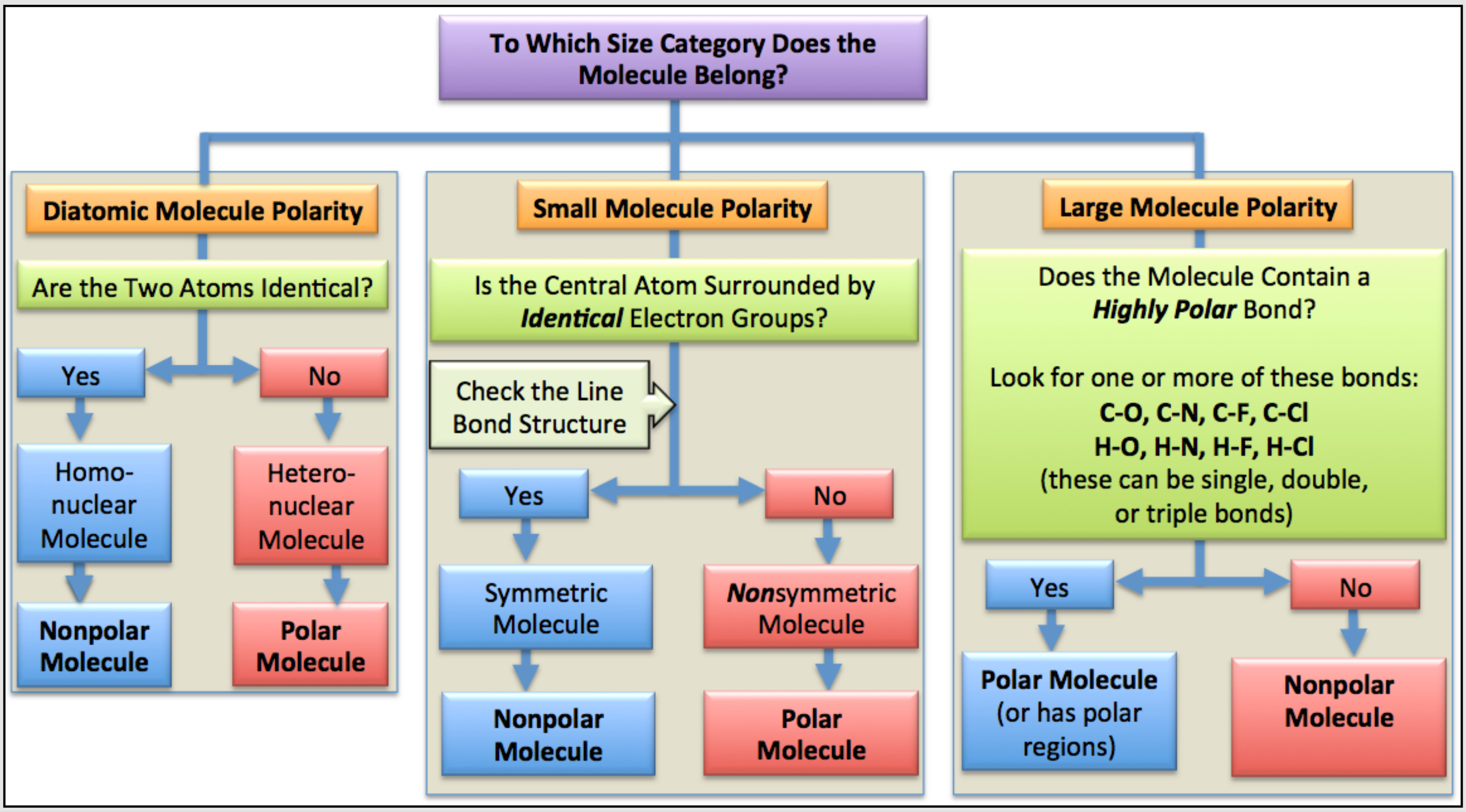
For ***i-books*** versions: **Click here to check answer**
For **print or pdf versions**, see the answer key in Appendix 1.

Summary of the Polarity of Molecules

The existence and degree of polarity (strength of the dipole) in molecules is quite important in the physical and chemical properties of molecular compounds. You may recall that I discussed how one of the forces responsible for attracting molecules ***to other molecules*** can result in the substance existing as a liquid or solid instead of a gas, and now you can understand why this attraction is called the **dipole-dipole force**. Later in this chapter, you will learn about other molecule-to-molecule attractive forces that vary depending on whether or not the molecules involved are polar. Therefore, it is an important educational outcome that you are able to categorize molecules as being either polar or nonpolar based on their structural formula. The complete thought map flow-chart for polarity determination is given in Figure 4.29.

Figure 4.29

Thought Map Flow-Chart for Polarity Determination



Formal Charge

In this section of chapter 4, we are considering the ***distribution of charge*** in covalent compounds. You have just learned that because of unequal sharing of electrons, regions of a molecule can be **partially charged**. One of the charged regions can have a *partial positive charge* (δ^+) with another region having *partial negative charge* (δ^-). We used the term "partial" when discussing polarity because partial charge ***does not*** have a full 1+ or 1- magnitude as would result from having an extra entire electron or lacking an entire electron such as ions do.

There is ***one more*** phenomenon that results in the *uneven distribution of charge*. We will use the concept of **"formal charge"** to account for electrically-charged regions within molecules and polyatomic ions. The *formal charge* concept involves identifying ***atoms*** in molecules (or in polyatomic ions) that have an *excess or deficiency* of electrons. An excess of electrons on a particular atom means that there are more electrons in the vicinity of an atom than there are protons in the atom. If there is one extra electron in the vicinity of a particular atom, the *formal charge* of the atom would be 1-. If there are two extra electrons in the vicinity of an atom the formal charge of that atom would be 2-. Conversely, when we say that an atom is electron deficient, this means that there are **fewer** electrons in the vicinity of a particular atom than there are protons in the atom. If an atom has a deficiency of one electron (one more proton than electrons), the formal charge of the atom would be 1^+. If there is a deficiency of two electrons on an atom, the formal charge on that atom would be 2+.

What Do You Need to Know About Formal Charge?

For the remainder of this textbook, I will only need you to be able to determine the formal charge on two elements - **nitrogen** and **oxygen.** We will soon be focusing on organic biomolecules. Biomolecules consist primarily of **C**, **H**, **O**, and **N**. In the molecules that you will come across in this book, *carbon* and *hydrogen* atoms ***will never*** have a formal charge. *Oxygen* and *nitrogen* ***may or may not*** have a formal charge. The formal charge on oxygen and nitrogen atoms in compounds is based on the covalent bonding pattern as described below.

1) The Formal Charge on Oxygen:

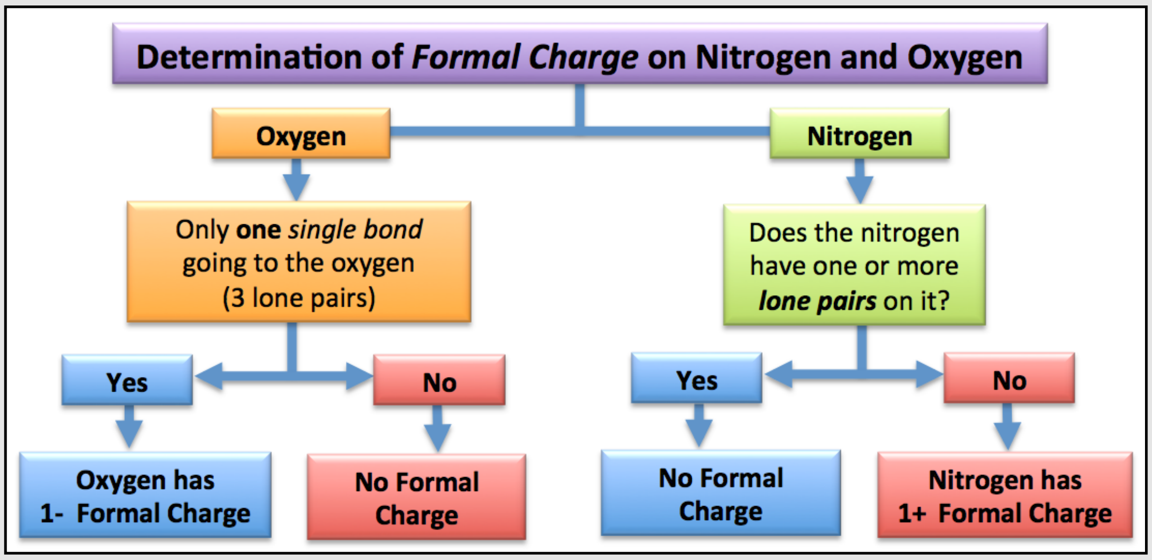
- Oxygen has a formal charge of 1- when it has ***just one single bond*** (three lone pairs).
- In ***all other cases that we discuss in this text***, oxygen will not have a formal charge (formal charge = zero).

2) The Formal Charge on Nitrogen:

- Nitrogen will have *no formal charge* when it has ***one or more lone pairs on it***.
- In ***all other cases***, nitrogen has a 1+ formal charge.

Determination of the formal charge of oxygen and nitrogen is summarized in the thought-map flowchart in Figure 4.30.

Figure 4.30
Thought-Map Flowchart for Determining Formal Charge on Oxygen and Nitrogen

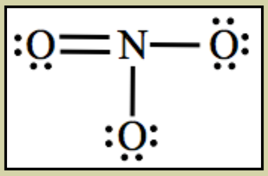


It will be important to determine the presence or absence of *formal charge* in compounds because these negative or positive formally charged regions in compounds will be attracted to other complimentary (oppositely-charged) regions. For example, one of the forces that is responsible for the large molecules called proteins to "fold" into compacted shapes that enable them to perform their biological role is the electrostatic attraction of positive formal charge in the vicinity of nitrogen to the negative formal charge in the vicinity of oxygen. Disruption of these interactions by concentrated salt solutions can diminish or destroy the protein's biological activity.

OPTIONAL: If you are interested in learning the details of how formal charges are assigned to oxygen, nitrogen, and other atoms based on their bonding patterns, you can find that information in Appendix 3.

Review 4.11: Determining the Formal Charge on Oxygen and/or Nitrogen

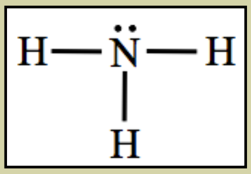
The line bond structure of the nitrate ion (NO_3^-) is shown below. Add the formal charge (superscript) to the line bond structure next to any oxygen or nitrogen atom that has a non zero formal charge.



For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

Review 4.12: Determining the Formal Charge on Oxygen and/or Nitrogen

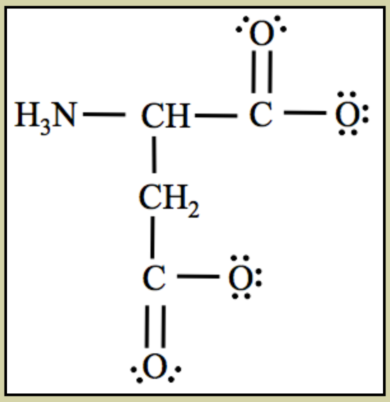
The line bond structure of ammonia (NH_3) is shown below. Does nitrogen have a formal charge in this molecule?



For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

Review 4.13: Determining the Formal Charge on Oxygen and/or Nitrogen

Aspartic acid is one of the 20 common amino acids that make up the proteins in our bodies. Aspartic acid was discovered in 1827 when it was derived from a compound found in asparagus. The condensed structure of the aspartic acid is shown below. Add the formal charge (superscript) next to any ***oxygen or nitrogen atom*** in the condensed structure that has a non zero formal charge.



For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

Summary of the Distribution of Electrons in Molecules

In this section, you learned *two ways* to predict the ***distribution of charge*** in compounds.

1) **Molecular Polarity:** Because of the unequal sharing of electrons, regions of a molecule can have **partial charge**. These charged regions have a *partial positive charge* ($\boldsymbol{\delta^+}$) or *partial negative charge* ($\boldsymbol{\delta^-}$).

2) **Formal Charge:** A region in the vicinity of a particular atom in a molecule or polyatomic ion can have ***formal charge*** *because of an excess or deficiency* of electron(s) at that atom.

Both the polarity and presence of formal charges are important in understanding how compounds interact with each other, and also in understanding the forces within large biological compounds (such as DNA, RNA, proteins, and carbohydrates) that are crucial for maintaining their shape and biological function. You will learn about these forces in the next section of this chapter.

4.6 Noncovalent Interactions

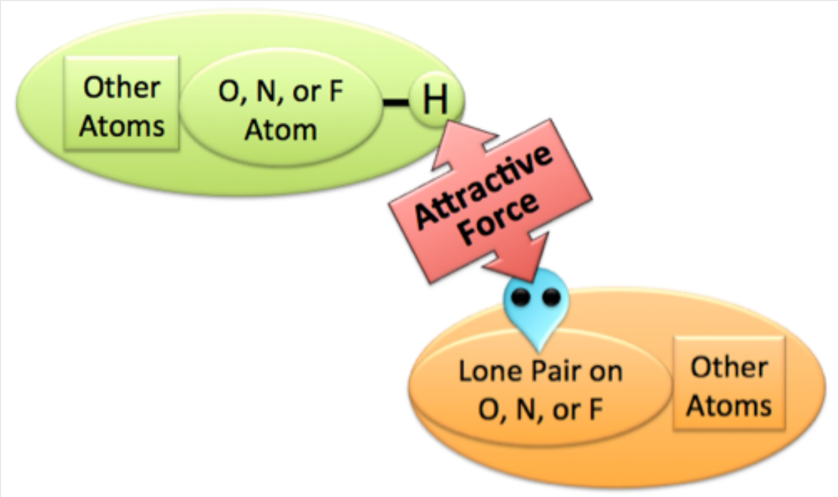
In chapter 3 you learned about ionic compounds; you saw how large numbers of cations and anions arrange themselves into a three-dimensional, regular repeating pattern called a crystal lattice. *Ionic compounds* exist as crystalline solids at room temperature because the ions are held together by relatively strong electrostatic forces called ionic chemical bonds. *Molecular compounds* can also exist as crystalline solids. For example, at or below 0 °C, H_2O will form the crystalline solid that we refer to as ice. H_2O molecules are not ions, so *what forces are responsible for holding H_2O molecules, or other molecules, together in their solid states?* The answer is that there are *electrostatic attractive forces* called **noncovalent interactions** that attract molecules to other molecules. In this section, you will learn about **five** types of ***noncovalent interactions***. These *noncovalent interactions* not only occur between individual molecules, but are also responsible for the way single, large biomolecules such as proteins and RNA "fold" into the compact three-dimensional shapes that are crucial for their bioactivity. *Noncovalent interactions* are quite different from the *covalent bonding forces* that are present within molecules and polyatomic ions. Covalent forces result from shared electrons. *Noncovalent interactions*, as the name implies, do not involve the sharing of electrons; they are strictly electrostatic attractions.

I will now introduce you to each of the **5 noncovalent interactions**.

1) Hydrogen Bonding

Hydrogen bonding is the result of the electrostatic attraction *between* the partial positive charged end of a ***particularly strong polar bond*** and the negative charge of a lone pair of electrons on a very electronegative atom. The "particularly strong polar bond" is limited to an O-H, N-H, or F-H covalent bond. The partially positive (hydrogen) end of any one of these three *particularly strong polar bonds* ***on one molecule (or polyatomic ion)*** will be strongly attracted to a lone pair that is present on an O, N, or F ***(very electronegative atoms)***. Hydrogen bonding attraction can occur between two or more individual molecules, or, in the case of large molecules that have conformations that fold back upon themselves, this attraction can occur between regions within an individual molecule. For those of you who like visualizations, an illustration of the hydrogen bonding concept is shown in Figure 4.31.

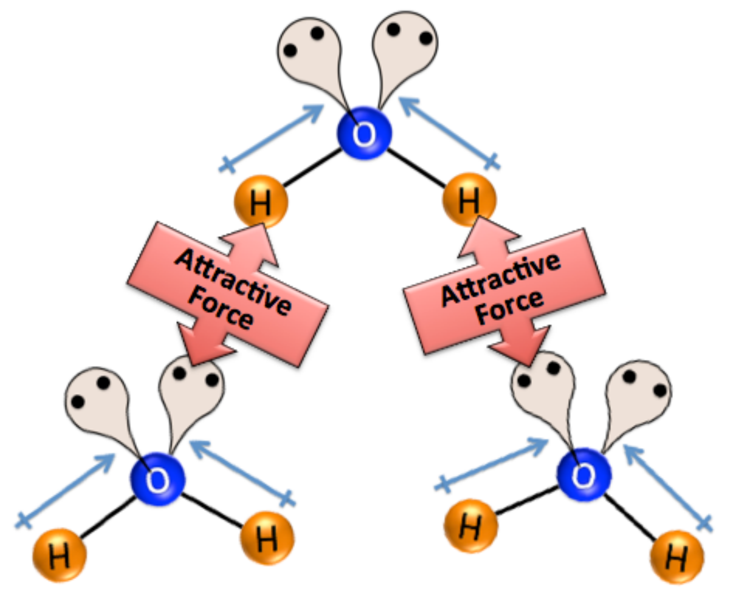
Figure 4.31 Hydrogen Bonding



Hydrogen bonding is the result of the electrostatic attraction *between* the partial positive charged end of a ***particularly strong polar bond*** (O-H, N-H, or F-H) and the negative charge of a lone pair of electrons on a very electronegative atom (O, N, or F).

Hydrogen bonding is the major force responsible for H_2O, a relatively small and light molecule, existing in the liquid phase instead of the gaseous phase at room temperature. Figure 4.32 illustrates hydrogen bonding between H_2O molecules. The partially positive (hydrogen) end of the highly polar O-H bond on one water molecule is attracted to a lone pair of electrons present on an oxygen in ***another*** H_2O molecule. IMPORTANT: Hydrogen bonding is an attractive force between two molecules or polyatomic ions, it ***is not*** a covalent bond to a hydrogen atom *within* a single covalent molecule or polyatomic ion.

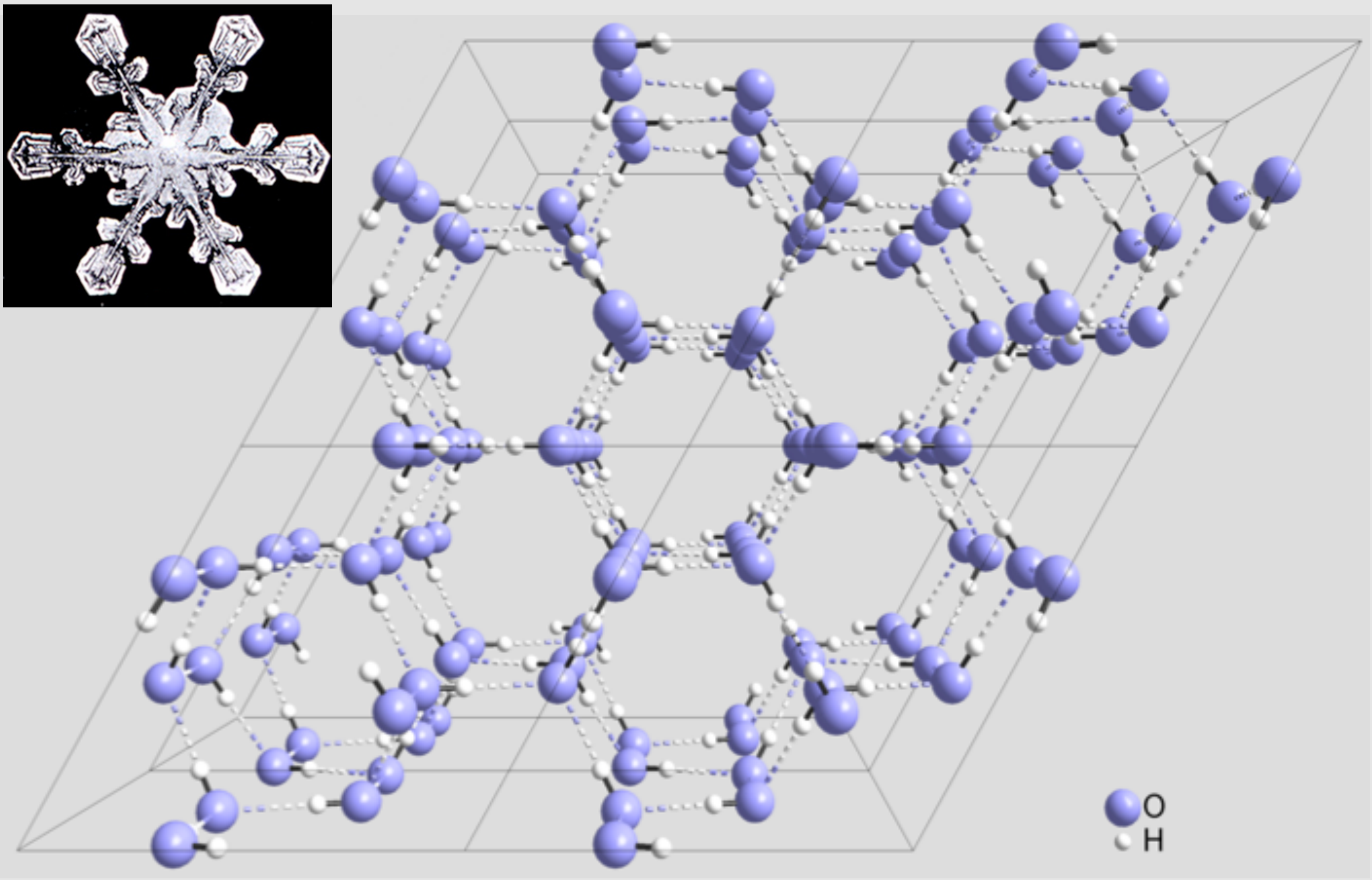
Figure 4.32
Hydrogen Bonding in H_2O



Hydrogen bonding between H_2O molecules. The partially positive (hydrogen) end the highly polar O-H bond on one water molecule is attracted to the lone pair of electrons present on an oxygen of ***another*** molecule.

Note that in ice, the individual H_2O molecules arrange themselves in a pattern that maximizes the number of hydrogen bonds. Figure 4.33 shows hydrogen bonds (as dashed lines) in a ball and stick model of an ice crystal. The individual H_2O molecules arrange themselves in a pattern that maximizes the number of hydrogen bonds. It is because of this crystal lattice order on the nanoscopic scale that snow flakes have geometric order and, in my opinion, natural beauty on the microscopic scale.

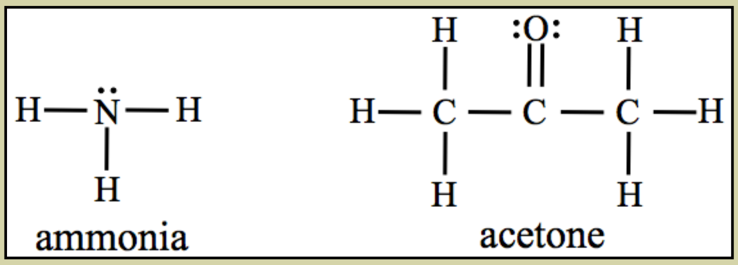
Figure 4.33 **A Ball and Stick Model of Ice**



Main image: A ball and stick model showing the crystal structure of ice. Hydrogen bonds are represented by dotted lines. The H_2O molecules arrange themselves in a pattern that maximizes the number of hydrogen bonds. It is because of this nano-scale order of molecules that snow flakes have the order and natural beauty on the macro-scale.
Author: Anonymous, Source: Wikimedia
Top-left insert: A microscopic image of a snowflake.
Author: Wilson Bentley, Source: USPD

Review 4.14: Understanding Hydrogen Bonding

The line bond structures of ammonia and acetone are shown below:



a. Can hydrogen bonding occur between two ammonia molecules?
b. Can hydrogen bonding occur between two acetone molecules?
c. Can hydrogen bonding occur between an ammonia molecule and an acetone molecule?

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

2) Dipole-Dipole Forces

Polar molecules are attracted to other polar molecules by a type of noncovalent interaction called the **dipole-dipole force.** The partially positive (**δ^+**) end of one molecule's dipole is attracted to the partially negative (**δ^-**) end of another molecule's dipole (and vice versa) by electrostatic attraction as illustrated below.

Dipole-dipole forces are similar to ionic bonding, however they are *not nearly as strong* because the charge on molecular dipoles is ***partial*** (**δ^+** and **δ^-**) not ***full*** (1^+ or 1^-) or ***multiple*** (2^+, 2^- etc.) as is the case for *ions*.

Review 4.15: Understanding Dipole-Dipole Forces

Which of the following substances are capable of interacting through dipole-dipole forces:

a) Can a dipole-dipole force occur between two H_2O molecules?
b) Can a dipole-dipole force occur between two methane (CH_4) molecules?
c) Can a dipole-dipole force occur between two acetone molecules? (see review problem 4.14 for acetone's structure)

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

3) London Dispersion Forces

It is *noncovalent interactions* that hold molecules together such that they exist in the solid or liquid phases instead of the gaseous phase. Whether a substance exists in the gas, liquid, or solid phase is determined by a competition between *noncovalent interactions* (working to keep the particles close to one another) and *temperature* (kinetic energy working to distribute the particles randomly in their container). If the noncovalent interactions are dominant, then the substance will exist in the solid or liquid phase; if the temperature/kinetic energy can overcome the noncovalent interactions, then the substance will exist in the gaseous phase.

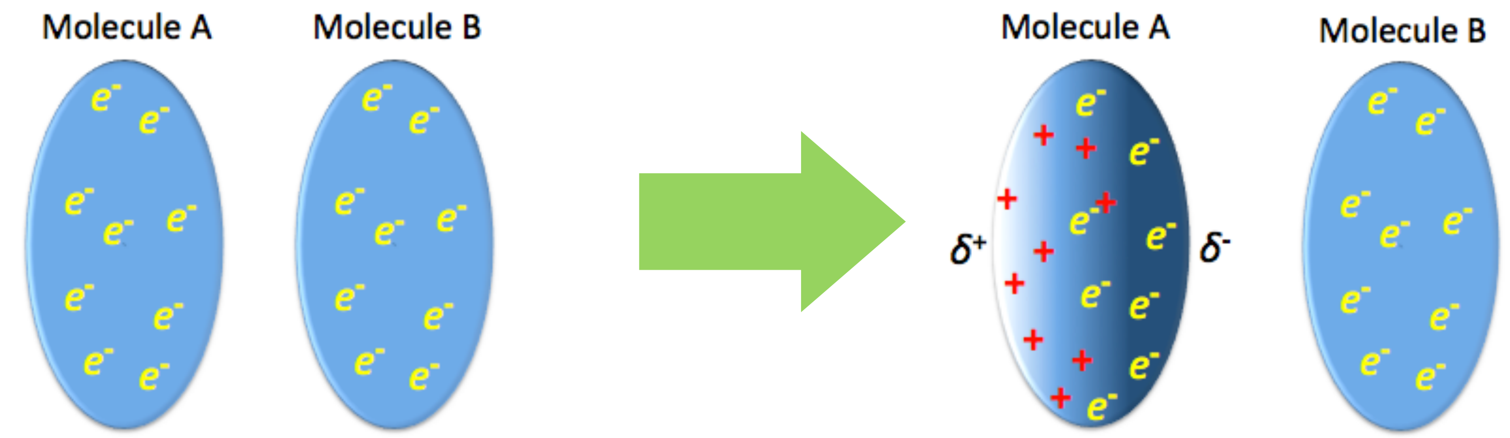
So far, you have seen how molecules that are capable of hydrogen bonding can be attracted to each other and how polar molecules can be attracted to each other. With a knowledge of the presence of noncovalent interactions, we can understand why molecular compounds may exist in the liquid or solid phases. It was observed that nonpolar molecules such as CO_2, O_2, and N_2, which are ***not capable*** of interacting through dipole-dipole forces or hydrogen bonding, can be cooled to temperatures at which they exist in the liquid and solid phases. In 1930, Fritz London (Figure 4.34), along with R. Eisenschitz, came up with a model to explain this observation.

Figure 4.34
Fritz London

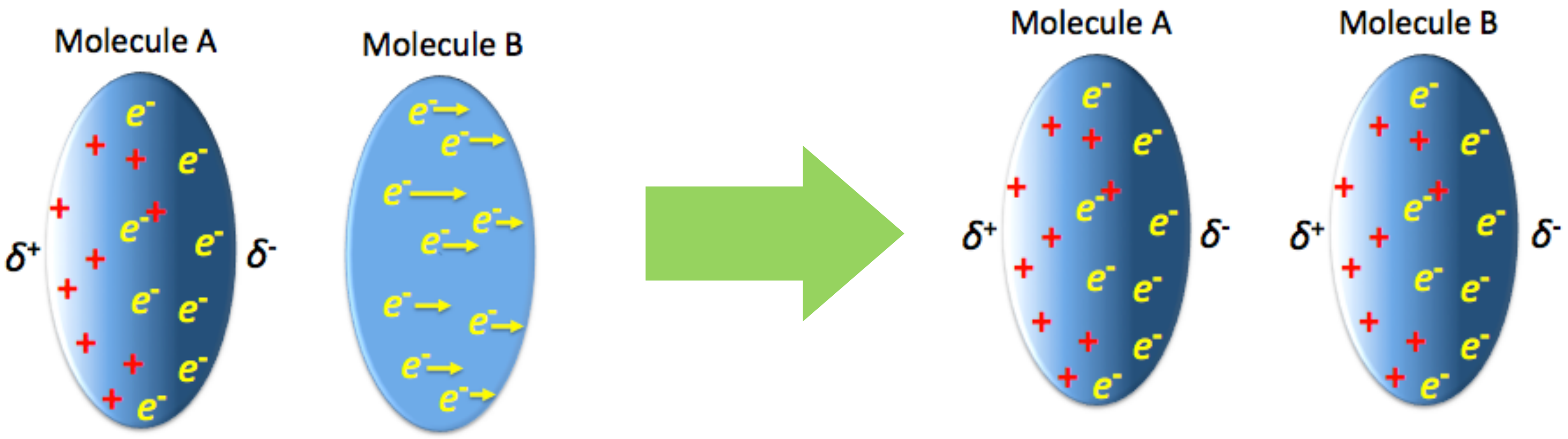
German-American scientist Fritz London (1900-1954)
Source: Wikimedia, PD
Author: G. F. Hund

London dispersion forces, named in honor of Fritz London, are sometimes referred to as London forces, dispersion forces, induced-dipole forces, or induction forces. They are caused by an "instantaneous" dipole in one molecule inducing the formation of a "temporary" dipole in another molecule. How does this occur? Let's consider two nonpolar molecules - Molecule A and Molecule B. They can be identical or different molecules. Since they are both nonpolar molecules, neither molecule has a permanent dipole; on average, the electrons are evenly distributed within each molecule. Note that I said "on average" that the electrons are evenly distributed. We think of the electrons as being in motion, and although *on average* they are evenly distributed, there are moments when there happens to be a few more electrons on one side of the molecule than the other side. In this case, we say that the molecule has a temporary, ***instantaneous dipole***. It is not a permanent dipole. An analogous situation that you would be more familiar with is to suppose that a group of people were blindfolded and asked to randomly walk around a room; **on average**, the people would be evenly distributed in the room (nonpolarized). However, there would be moments when there happened to be a bit more people on one side of the room (temporarily/instantaneously polarized).

Okay, back to our two molecules. First, consider the two molecules having their electrons evenly distributed and therefore not temporarily polarized as shown below **(left)**. While molecules A and B happen to be close together, consider a moment in time when molecule A develops a *temporary instantaneous dipole* (below, **right**).



The electrons that are initially evenly distributed (un-polarized) in Molecule B are repelled by the negative side (**δ^-**) of the instantaneous dipole of Molecule A. In this case, the electrons in molecule B move away from the negative side of Molecule A as illustrated below.



Now, both Molecule A and Molecule B have temporary dipoles and are attracted to each other because of the electrostatic interaction between the positive and negative ends of the dipoles. Note that in this process, the temporary dipole of Molecule A *dispersed* the electrons in molecule B such that a dipole was *induced* in Molecule B. That is why this noncovalent interaction is referred to as London *dispersion* forces or *induced*-dipole forces. There exists a significant difference between the *dipole-dipole forces* that were described previously and *London dispersion forces*. Dipole-dipole forces result from the interactions of ***permanent dipoles*** in polar molecules, whereas London dispersion forces result from the interaction of instantaneous and induced dipoles.

All molecules, polar and nonpolar, contain electrons and will therefore be attracted to each other through London dispersion forces. Although polar molecules have *permanent dipoles* that are oriented in a fixed direction, momentary, instantaneous dipoles will randomly form with their orientation in any random direction.

The larger a molecule is, the easier (lower in energy) it is to polarize its electrons. **Therefore, the larger a molecule, the stronger is its London dispersion force interactions.** This trend can be observed by noting the boiling points of the molecules in Table 4.6. I chose these particular molecules for this table because the ***only*** noncovalent interactions in which these molecules can interact are London dispersion forces. They do not have what is needed for hydrogen bonding; nor do they interact through dipole-dipole forces because they are all nonpolar molecules. If this is not apparent to you now, I suggest that you take a moment to review hydrogen bonding and dipole-dipole forces. The larger the molecule, the stronger the London dispersion forces, therefore larger molecules have higher boiling points. Higher boiling points mean that the substance must be heated to a higher temperature in order to overcome the London dispersion forces holding the molecules together to change the phase from liquid to gas (boil). Notice that the largest molecule in the table, pentane, is a liquid at room temperature (about $22^{o}C$) because it has stronger London dispersion forces relative to the other molecules in the table.

Table 4.6
Effect of Molecular Size on London Dispersion Forces

Molecule Name	Condensed Structure	Boiling Point (^{o}C)	Phase at Room Temperature
methane	CH_4	-164	gas
ethane	CH_3CH_3	-89	gas
propane	$CH_3CH_2CH_3$	-42	gas
butane	$CH_3CH_2CH_2CH_3$	0	gas
pentane	$CH_3CH_2CH_2CH_2CH_3$	36	liquid

Review 4.16: Understanding London Dispersion Forces

a. Can London dispersion forces occur between two CBr_4 molecules?
b. Can London dispersion forces occur between two H_2O molecules?

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

Review 4.17: Understanding London Dispersion Forces

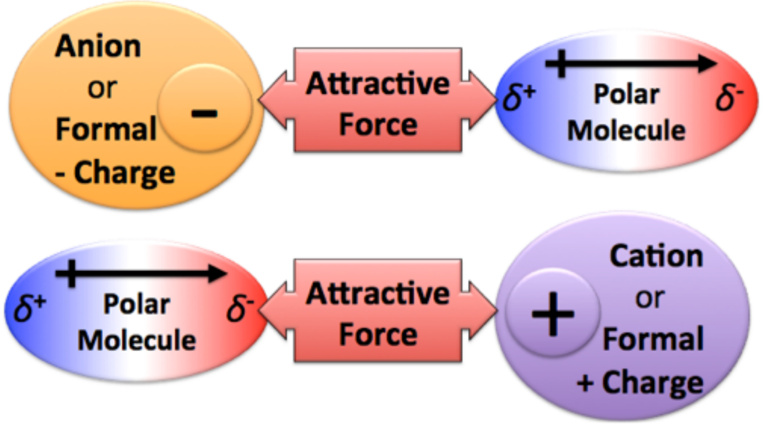
Which of the following substances is predicted to have the higher boiling point:

decane ($CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$) **<u>or</u>** nonane ($CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$)

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

4) Ion-dipole Interactions

The fourth type of noncovalent interaction is the **ion-dipole interaction**. An ion-dipole interaction, as the name implies, is the electrostatic attractive interaction ***between*** an ion (or formal charge) ***<u>and</u>*** the dipole of a polar molecule. The attraction could be ***between*** an anion (or negative formal charge) ***<u>and</u>*** the partially positive end **(δ^+)** of a dipole, or vice versa, ***between*** a cation (or positive formal charge) ***<u>and</u>*** the partially negative end **(δ^-)** of a dipole. Both of these cases are illustrated below.



Many ionic crystals can be “dissolved” in water as a result of ion-dipole forces that attract water molecules to ions. For example, when sodium chloride crystals are placed in water, the strong sodium-chloride ionic bonds are broken. The individual sodium cations and chloride anions are each surrounded by ***many*** water molecules as a result of ion-dipole interactions. You will learn more details of the dissolving process in chapter 7.

Review 4.18: Understanding Ion-Dipole Interactions

Can an ion-dipole interaction occur between ammonium (NH_4^+) and H_2O?

Click here to check answer If using a pdf or hard copy, check your answer using the key in Appendix 1.

Review 4.19: Understanding Ion-Dipole Interactions

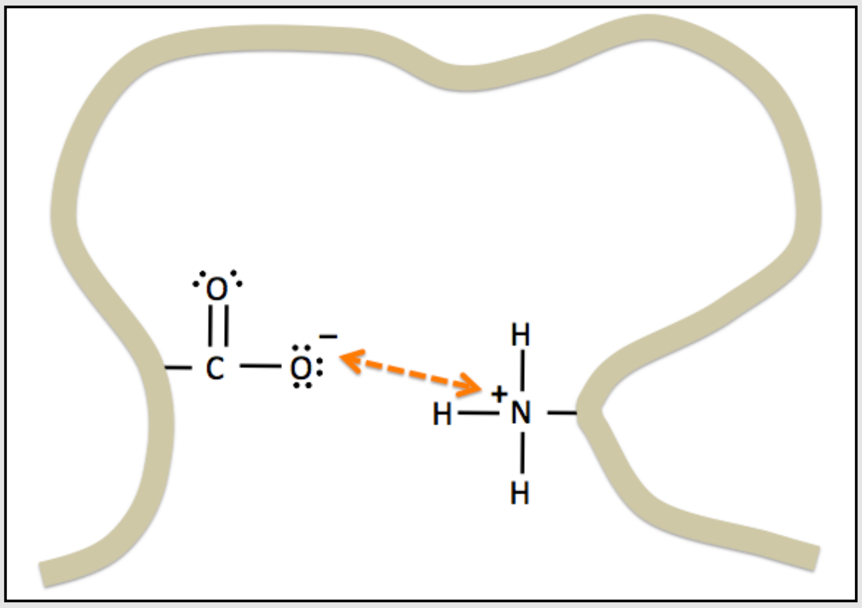
Can an ion-dipole interaction occur between bromide (Br^-) and I_2?

Click here to check answer If using a pdf or hard copy, check your answer using the key in Appendix 1.

5) Salt Bridges

The fifth type of noncovalent interaction is the **salt bridge**. A salt bridge is the electrostatic attractive interaction ***between*** a negative formal charge ***<u>and</u>*** a positive formal charge in protein. Salt bridges are one of the noncovalent interactions that are responsible for the way a protein folds up onto itself to give it the shape that is necessary for it to perform its biological function. Protein contains atoms with a positive formal charge and atoms with a negative formal charge. The positive and negative formally charged atoms are attracted to each other through salt bridge interactions. An illustration of a salt bridge interaction in protein is shown in Figure 4.35. In the figure, a large protein molecule (represented by the brown ribbon) contains atoms with positive formal charge and atoms with negative formal charge that are attracted to each other through a salt bridge interaction (indicated by the dashed double arrow).

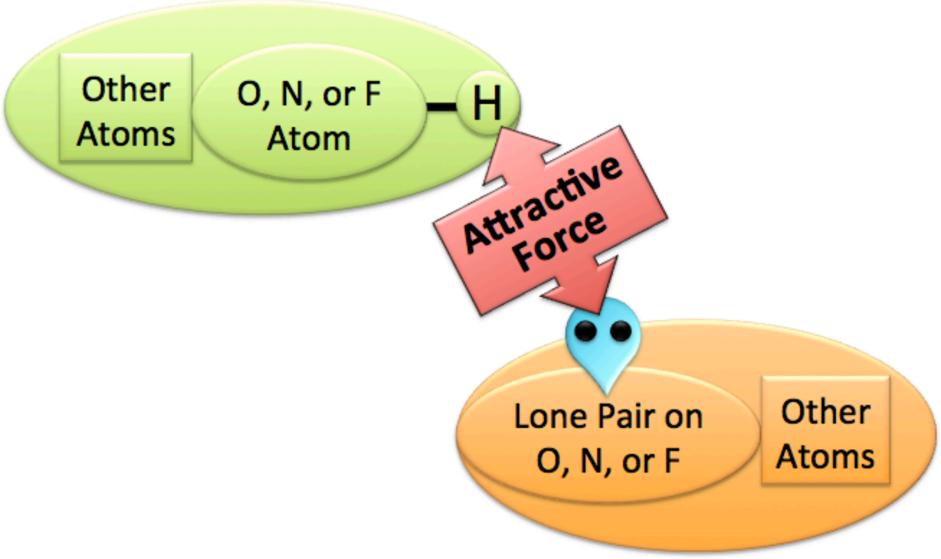
Figure 4.35
Illustration of a Salt Bridge Interaction in a Protein Molecule



A protein molecule (represented by the brown ribbon) contains positive and negative formal charges. The charges are attracted to each other through salt bridge interactions (indicated by the dashed double arrow).

Summary and Review of Noncovalent Interactions

In this section, you learned five types of **noncovalent interactions**. When these interactions occur between molecules (as opposed to monatomic or polyatomic ions), they are sometimes also referred to as **intermolecular forces.** Noncovalent interactions cause molecules to be attracted to each other and can result in molecular compounds existing in the liquid or solid phases. In the case of large molecules and polyatomic ions that can *fold back upon themselves*, noncovalent attractive interactions can occur between two regions *within an individual particle*. The five noncovalent interactions are described and illustrated below.

Noncovalent Interaction	Interaction Between:
Hydrogen Bonding Electrostatic attractive force between the partially positive charged hydrogen end of an O-H, N-H, or F-H bond and the negative charge of a lone pair on an O, F, or N.	
Dipole-Dipole Electrostatic attractive force between *two* ***polar*** *molecules.*	
London Dispersion Forces Electrostatic attractive force between ***any*** *two molecules.*	
Ion-Dipole Electrostatic attractive force between a *dipole* and *an ion or formal charge.* The partially positive charge of a dipole is attracted to a negatively charged ion *or* a negative formal charge. The partially negative charge of a dipole is attracted to a positively charged ion *or* positive formal charge.	 
Salt Bridge Electrostatic attractive force between a negative formal charge and a positive formal charge in protein.	

Download this worksheet for more practice with noncovalent interactions:
http://www.zovallearning.com/GOBlinks/ch4/noncovalent-interactions-worksheet-and-key.pdf

4.7 Introduction to Hydrocarbons

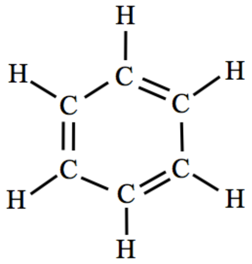
Organic chemistry is often defined as the study of carbon-containing compounds. Carbon-containing compounds are of immense importance in understanding biochemistry. Organic compounds are categorized on the basis of the atoms they contain and on their bonding patterns. The first class of organic compounds that you will learn about are called **hydrocarbons**. Can you guess which two elements are contained in hydrocarbons? As the name implies, hydrocarbons are *molecules that contain only carbon and hydrogen*. Hydrocarbons are the main source of energy used by humans. Hydrocarbons are burned in a chemical process called combustion in order to do various types of work or to generate heat. The majority of the hydrocarbons on earth exists as *crude oil (or petroleum)*, a mixture of various hydrocarbon molecules and small amounts of other substances. Crude oil is considered a "fossil fuel" because it is formed from huge amounts of dead organisms, primarily zooplankton and algae, that have been buried under sedimentary rock and exposed to high temperature and pressure. Under those conditions and in the absence of oxygen, the molecules from the dead organisms are converted to petroleum through a series of chemical reactions. You will learn about chemical reactions in chapter 6. Fossil fuel is called a *non-renewable* energy source since its process of formation occurs over millions of years. The hydrocarbon molecules in crude oil are further separated (refined) into various materials such as gasoline, petroleum jelly, paraffin wax, diesel fuel, asphalt, and baby oil.

Figure 4.36
A Crude Oil Drilling Platform

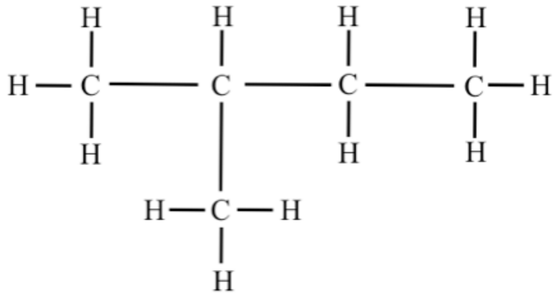
An oil drilling platform located in the Baltic Sea. The majority of the world's hydrocarbons exist as crude oil.
Source: Wikimedia Commons PD, Author: Mirafiori

Hydrocarbons can be categorized into four subcategories, listed in Table 4.7, based on their chemical bonding patterns. Hydrocarbons are also classified as being either **saturated** (all single bonds) or **unsaturated** (contains one or more carbon-carbon double or triple bonds).

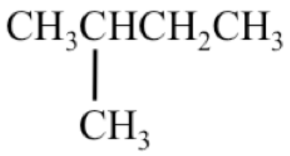
Table 4.7 Subcategories and Saturation of Hydrocarbons

Category	Defining Feature	Saturation	Example
alkane	all single bonds	saturated	ethane $CH_3{-}CH_3$
alkene	at least one carbon-carbon ***double*** bond	unsaturated	ethene $CH_2{=}CH_2$
alkyne	at least one carbon-carbon ***triple*** bond	unsaturated	ethyne $CH{\equiv}CH$
aromatic	alternating double and single bonds in a ***cyclic*** hydrocarbon	unsaturated	benzene 

Another way that hydrocarbons are classified by their bonding pattern is either as **normal, branched**, or **cyclic**. You may recall my discussion of these molecular geometries in a previous section of this chapter; let's review them now. The ***line bond, condensed, and skeletal structures*** for isopentane are drawn below.



Line Bond Structure

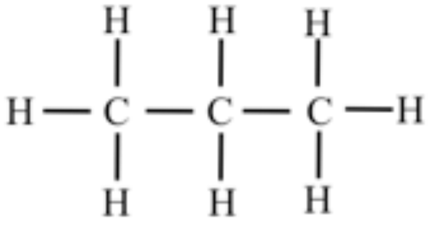


$$\underset{\displaystyle CH_3}{CH_3CHCH_2CH_3}$$

Condensed Structure

Skeletal Structure

In isopentane, there are four carbons bonded in a ***linear sequence*** (drawn horizontally in the line bond structure). There is one carbon that "***branches***" from the linear sequence at the second carbon from the left. Alternatively, when the carbons in a hydrocarbon molecule are bonded in a linear sequence (no branching), we call it a **normal** hydrocarbon. For both *normal and branched alkanes*, if "***n***" is the number of carbon atoms in the molecule, then the alkane will have the molecular formula of $C_nH_{(2n+2)}$. An example of a normal hydrocarbon is propane. The ***line bond, condensed, and skeletal structures*** for propane are drawn below.



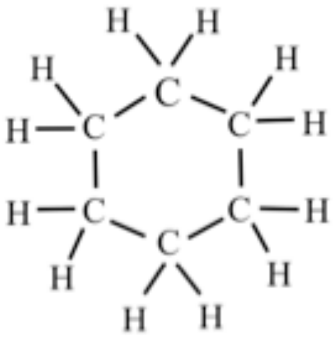
Line Bond Structure

$CH_3—CH_2—CH_3$

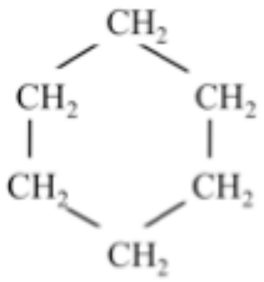
Condensed Structure

Skeletal Structure

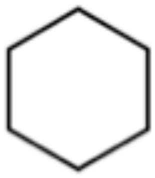
When the carbons in a hydrocarbon molecule are bonded together such that they form a ring, we call it a **cyclic** hydrocarbon. An example of a cyclic hydrocarbon is cyclohexane. The ***line bond, condensed, and skeletal structures*** for cyclohexane are drawn below.



Line Bond Structure



Condensed Structure



Skeletal Structure

In the remaining sections of this chapter, you will learn more about each of the four classes of hydrocarbons: alkanes, alkenes, alkynes, and aromatic. You will learn how to name them and learn details of their bonding patterns. I will discuss how the bonding patterns in hydrocarbons influences physical properties, such as their boiling point, melting point, and interactions with water. Learning about hydrocarbons provides a good foundation for understanding other organic compounds such as alcohols, amines, and esters. After learning about such organic compounds, you will be well-suited to understand biomolecules, such as carbohydrates, proteins, triglycerides, phospholipids, cholesterol, DNA, and RNA. Combining your understanding of general, organic, and biological molecules will allow you to master biological concepts that involve chemistry, such as metabolism, cellular processes, diseases, medications, medical diagnostic testing, how muscles work, immunology, etc. I hope that sounds exciting to you; it sure is fascinating for me!

4.8 Alkanes

Gas stations. **Left**: Hiroshima, Japan, **Right**: East Timor (Southeast Asia). Alkanes are the major component of gasoline.
Source: Wikimedia Commons, PD, Authors: Fg2(left) ,Tony Forster (right)

Alkanes are molecules that consist *only of carbon and hydrogen* and contain ***only single bonds***. The primary source of alkanes is *crude oil* and *natural gas*. Natural gas is formed in the same way as crude oil, except that the original source of organics is from buried plants and animals. It is composed primarily of methane (CH_4) and ethane (C_2H_6), but also has significant amounts of propane (C_3H_8), butane (C_4H_{10}), pentane (C_5H_{12}), other hydrocarbons, and some non hydrocarbon gases. Alkanes with 4-12 carbons are the major component of gasoline. Gasoline that is high in branched alkanes is preferred because the branched molecules reduce engine "knocking." The "octane rating" of gasoline is related to the amounts and types of branched alkanes. Gasoline also contains small amounts of alkenes. Currently in the US, refineries are required to add alcohol (a renewable fuel source) to gasoline at a concentration of 10%. Diesel fuel is composed of alkane molecules with 9-16 carbons (75%) and aromatic hydrocarbons (25%). Alkane molecules with more than sixteen carbon atoms are used for fuel oil (kerosene) and lubricating oil. Alkanes have historically been referred to as paraffins; this terminology should not be confused with "paraffin wax." Paraffin wax is composed primarily of alkane molecules with 20-40 carbon atoms. Paraffin wax is used for candles, electrical insulation, and lubrication.

Alkanes are **saturated hydrocarbons**; they contain no double or triple bonds. The term *saturated* indicates that the hydrogen-to-carbon ratio is maximized, therefore the molecule is "*saturated*" with hydrogens. When double or triple bonds are present, as is the case with *unsaturated hydrocarbons*, there must be fewer hydrogens attached in order for the octet rule to be satisfied.

Naming Alkanes

The systemic method devised by the International Union of Pure and Applied Chemistry (IUPAC) is a widely-used method of naming alkanes and other classes of organic compounds. An educational goal for this subsection is: given the structural formula of an alkane, you will be able to name the molecule (and vice versa). Using the IUPAC systemic rules for naming alkanes involves identifying an alkane's **"parent chain"** and its **"substituents"** (atoms or groups of atoms attached to the parent chain). In alkanes, the *substituents*, called **alkyl groups**, are constructed *solely of carbon and hydrogen atoms*. I will introduce you to a step-by-step method for naming alkanes in which the terms "parent chain," "substituents," and "alkyl groups" will be further developed. Later in this chapter, you will learn how to name the other classes of hydrocarbons (alkenes, alkynes, and aromatic hydrocarbons), and in upcoming chapters, other families of organic molecules. Naming those compounds is based on the method you will learn for alkanes. We will do some example problems together, then you will have the chance to try some on your own. The way to master naming organic compounds is to ***do many practice problems***.

i) Method for Naming Normal and Branched Alkanes

WARNING: As you read through these steps for the first time, naming alkanes will seem quite complicated; however, it will become much easier later when I use these steps to do some example problems. **Do not expect yourself to master naming alkanes as you read these steps for the first time.**

Table 4.8
Prefixes for Naming Parent Chains

Number of Carbons in Parent Chain	Prefix
1	meth
2	eth
3	prop
4	but
5	pent
6	hex
7	hept
8	oct
9	non
10	dec

Step 1. Name the *parent chain*.

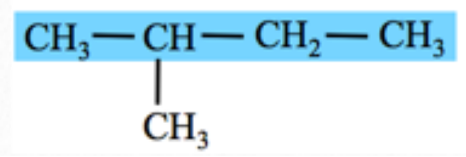
For normal and branched alkanes, the ***parent chain is the longest, continuous chain of carbons atoms***.

- The parent chain is named by combining a prefix, which specifies the number of carbon atoms in the parent chain, with the “-ane” suffix. The parent chain numbering prefixes and parent chain names for chains with up to ten carbon atoms are shown in Table 4.8.
    - Note that the top four prefixes in the table are unique to organic chemistry; then, the remaining prefixes are the traditional Greek-Latin numbering prefixes.
- The prefixes in Table 4.8 will not only be used for alkanes, but will be used in naming parent chains for all organic molecules.
- Example: If a linear or branched alkane has three carbon atoms in the parent chain, the parent chain name is ***prop****ane*.

Step 2. Name any alkyl group substituents.

Alkyl group substituents are comprised of the carbons and hydrogens that “branch” from the parent chain.

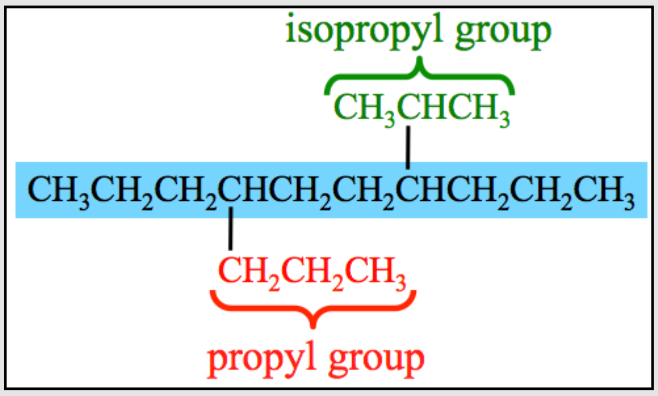
- In the molecule drawn below (a branched alkane), the parent chain has four carbons (shaded blue) and one **alkyl group substituent** (the CH_3 branching downward from the parent chain).



$$\underset{\displaystyle CH_3}{CH_3-\underset{|}{CH}}-CH_2-CH_3$$

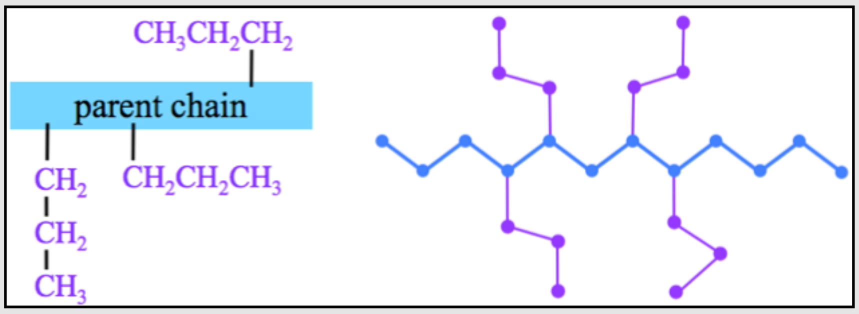
Alkyl group substituents are named based on the number of carbons in the substituent. For example, in the molecule shown above there is *one carbon* in the substituent. If there is *one carbon* in a substituent, we call it a ***methyl*** group. If there are *two carbons* in the substituent, we call it an ***ethyl*** group.

Figure 4.37
Propyl vs. Isopropyl



When *three carbons* are contained in a substituent, then there are ***two*** distinct bonding patterns that are possible. These two substituents need to have different names. I have drawn a molecule that contains the two types of three-carbon alkyl groups in Figure 4.37. The parent chain is shaded blue. If a carbon on the *end of the substituent* is bonded to the parent chain, we call the substituent a **propyl** group (shaded red) in Figure 4.37). On the other hand, if the carbon *in the center of the substituent* is bonded to the parent chain, we call the substituent an **isopropyl** group (shaded green in Figure 4.37).

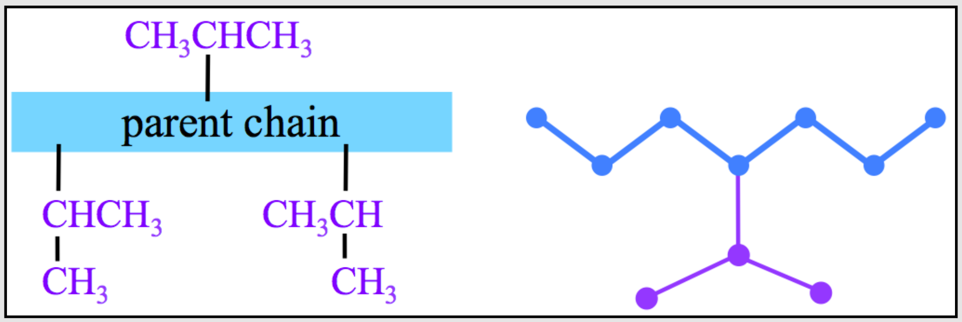
Figure 4.38
Different Ways to Draw Propyl Groups



There are multiple, correct ways to draw propyl and isopropyl groups in structural formulas. Take a few moments to convince yourself that all of the **propyl groups** in the condensed and skeletal structures in Figure 4.38 are indeed identical. I have represented the parent chain in blue and the propyl groups in purple. In the skeletal structure, in order for you to more easily identify the carbons in the parent chain vs. those in substituents, I have added large, shaded dots at the carbon positions.

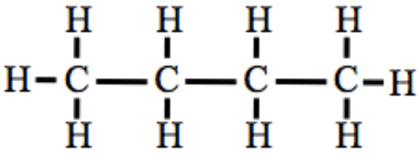
Figure 4.39 shows several correct ways to draw **isopropyl groups** (shaded purple) in condensed structures (left) and how to draw an isopropyl group in a skeletal structure (right).

Figure 4.39
Different Ways to Draw Isopropyl Groups



If there are *four carbons* contained in a substituent, there are four distinct bonding patterns that are possible and therefore the four substituents need to have different names. The condensed structures of alkyl group substituents with 1-4 carbon atoms are shown in Table 4.9. There are larger alkyl groups substituents, however you will not see any of them in this book. I ask my students to memorize the top four on the list (*methyl* through *butyl*); you should check with your instructor to see which ones you need to memorize.

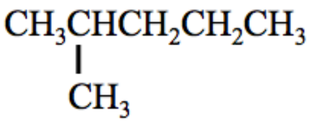
In a normal (unbranched) alkane, there are no substituents, and therefore the molecule's name is identical to the parent chain name. For example: The name for the normal alkane with four carbons is butane (drawn below).



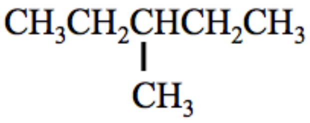
$$H-\overset{\substack{H\\ \vert}}{\underset{\substack{\vert\\ H}}{C}}-\overset{\substack{H\\ \vert}}{\underset{\substack{\vert\\ H}}{C}}-\overset{\substack{H\\ \vert}}{\underset{\substack{\vert\\ H}}{C}}-\overset{\substack{H\\ \vert}}{\underset{\substack{\vert\\ H}}{C}}-H$$

Step 3. Determine the *point of attachment* of alkyl group(s) to the parent chain.

In order to uniquely name molecules, the name must indicate to which *parent chain-carbon* a substituent is attached. For example, there are ***two different molecules*** that both have a 5-carbon parent chain <u>and</u> one methyl group substituent (below).



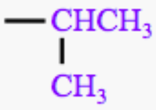
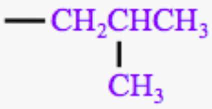
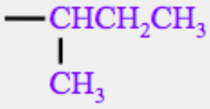
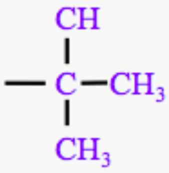
$$CH_3\underset{\substack{\vert\\ CH_3}}{CH}CH_2CH_2CH_3$$



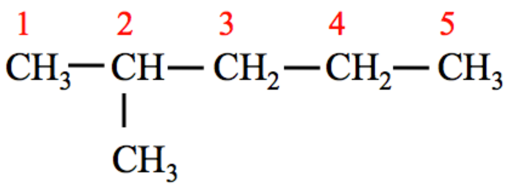
$$CH_3CH_2\underset{\substack{\vert\\ CH_3}}{CH}CH_2CH_3$$

Notice the difference in the two molecules above, the molecule *on the left* has the methyl group attached to the parent chain's *second carbon* from the left; the molecule *on the right* has the methyl group attached to the parent's *third* carbon from the left. These two molecules are not equivalent; they have slightly different boiling points and melting points.

Table 4.9
Alkyl Groups

Number of Carbon Atoms	Alkyl Group Name	Condensed Structure
1	methyl	$-CH_3$
2	ethyl	$-CH_2CH_3$
3	propyl	$-CH_2CH_2CH_3$
3	isopropyl	 $-\underset{\substack{\vert\\ CH_3}}{CH}CH_3$
4	butyl	$-CH_2CH_2CH_2CH_3$
4	isobutyl	 $-CH_2\underset{\substack{\vert\\ CH_3}}{CH}CH_3$
4	*sec*-butyl	 $-\underset{\substack{\vert\\ CH_3}}{CH}CH_2CH_3$
4	*tert*-butyl (or *t*-butyl)	 $-\overset{\substack{CH\\ \vert}}{\underset{\substack{\vert\\ CH_3}}{C}}-CH_3$

- In order to assign “position numbers” to the substituents, the carbons ***in the parent chain*** are numbered. Since there are two ends of the parent chain, we ***begin numbering from the end of the parent chain that is nearest to a substituent***. For example, the parent chain carbons are assigned position numbers (in red) for alkane shown below.



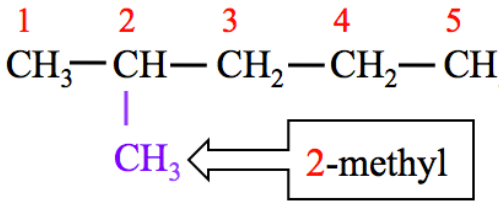
$$\overset{1}{CH_3}-\underset{\underset{\displaystyle CH_3}{|}}{\overset{2}{CH}}-\overset{3}{CH_2}-\overset{4}{CH_2}-\overset{5}{CH_3}$$

In the alkane shown above, note that the *point of attachment* of the methyl group substituent is to the carbon at position number “2” on the parent chain.

Step 4. Construct the name of the alkane by placing the alkyl groups in alphabetical order and specifying their position numbers, followed by the name of the parent chain.

Let’s unpack Step 4 using the molecule from the previous step.

- **Step 4A:** List the alkyl groups along with their position numbers, ***in alphabetical order***.
  - Write the position number(s) in front of the substituent(s).
    - In our example molecule, we write: **2-methyl**.



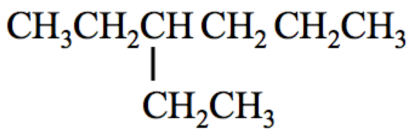
$$\overset{1}{CH_3}-\underset{\underset{\displaystyle CH_3}{|}}{\overset{2}{CH}}-\overset{3}{CH_2}-\overset{4}{CH_2}-\overset{5}{CH_3}$$

  - Add the labels di, tri, or tetra in front of the alkyl group name <u>**if**</u> two, three, or four (respectively) identical substituents are present.
    - We did not need to do so in our example; we had no multiple, identical substituents.
    - I will elaborate on this step in a later example.

- **Step 4B:** Write the parent chain name ***behind*** the list of alkyl groups.
  - In our example, we have only one substituent: **2-methyl**.
  - The parent chain is **pentane**.
  - We write the IUPAC name of this molecule as: **2-methylpentane**.
    - Do not include a space between the last substituent listed and the parent chain name.

Let’s do a few naming alkane problems together.

Example: Give the IUPAC name for the alkane shown below.

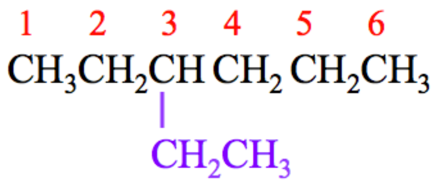


$$CH_3CH_2\underset{\underset{\displaystyle CH_2CH_3}{|}}{CH}CH_2CH_2CH_3$$

Step 1. Name the *parent chain*.

For normal and branched alkanes, the ***parent chain is the longest, continuous chain of carbons atoms***.

- The parent chain numbering prefixes and parent chain names are shown in <u>Table 4.8</u>.
- In this example, the parent chain is **hexane**; it contains six carbons.



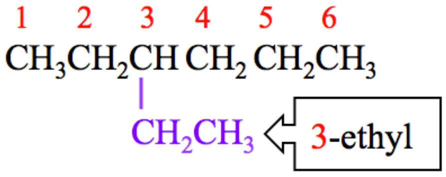
$$\overset{1}{CH_3}\overset{2}{CH_2}\underset{\underset{\displaystyle CH_2CH_3}{|}}{\overset{3}{CH}}\overset{4}{CH_2}\overset{5}{CH_2}\overset{6}{CH_3}$$

Step 2. Name any alkyl group substituents.

- In the molecule, there is one **alkyl group substituent** (the $-CH_2CH_3$ branching downward from the parent chain).
- The alkyl group has two carbons. Use Table 4.9 to find the alkyl group name: **ethyl**

Step 3. Determine the *point of attachment* of alkyl group(s) to the parent chain.

- In order to assign "position numbers" to the substituents, the carbons ***in the parent chain*** are numbered. Since there are two ends of the parent chain, we ***begin numbering from the end of the parent chain that is nearest to a substituent****.*
  - The parent chain carbons are assigned position numbers (in red).
  - The point of attachment of the ethyl group is to the parent chain's carbon number 3.



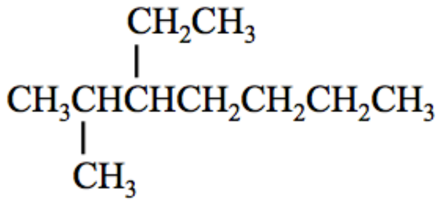
$$CH_3CH_2\underset{\displaystyle CH_2CH_3}{\underset{|}{CH}}CH_2CH_2CH_3$$

Step 4. Construct the name of the alkane by placing the alkyl groups in alphabetical order and specifying their position numbers, followed by the name of the parent chain.

- **Step 4A:** List the alkyl groups along with their position numbers, ***in alphabetical order****.*
  - Write the position number(s) in front of the substituent(s).
    - Use a ***dash*** between position *numbers* and *letters*.
      - In our example molecule, we write: **3-ethyl**.
    - Add the labels di, tri, or tetra in front of the alkyl group name **if** two, three, or four (respectively) identical substituents are present.
      - We did not need to do so in our example; we had no multiple, identical substituents.

- **Step 4B:** Write the parent chain name ***behind*** the list of alkyl groups.
  - The parent chain is **hexane**, we have only one substituent: **3-ethyl**.
  - We write the name of this molecule as: **3-ethylhexane**.

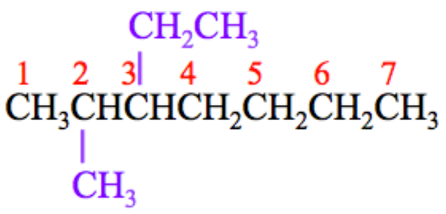
Example: Give the IUPAC name for the alkane shown below.



$$CH_3\underset{\displaystyle CH_3}{\underset{|}{CH}}\overset{\displaystyle CH_2CH_3}{\overset{|}{CH}}CH_2CH_2CH_2CH_3$$

Step 1. Name the *parent chain*.

- For normal and branched alkanes, the ***parent chain is the longest, continuous chain of carbons atoms***.
  - The parent chain is **heptane**; it contains seven carbons.



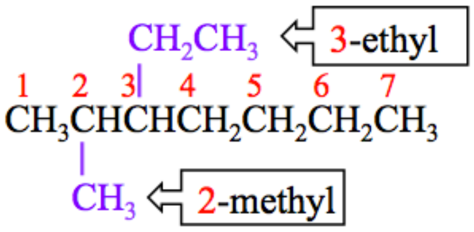
$$CH_3\underset{\displaystyle CH_3}{\underset{|}{CH}}\overset{\displaystyle CH_2CH_3}{\overset{|}{CH}}CH_2CH_2CH_2CH_3$$

Step 2. Name any alkyl group substituents.

- There are two **alkyl group substituents**. There is an **ethyl** group and a **methyl** group.

Step 3. Determine the *point of attachment* of alkyl group(s) to the parent chain.

- The point of attachment of the methyl group is carbon number 2.
- The point of attachment of the ethyl group is carbon number 3.



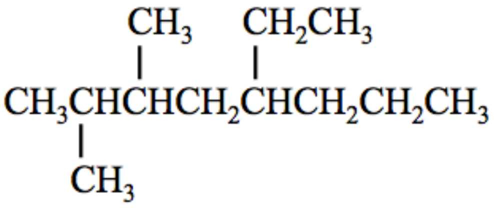
$$CH_3\underset{CH_3}{\underset{|}{CH}}\overset{CH_2CH_3}{\overset{|}{CH}}CH_2CH_2CH_2CH_3$$

Step 4. Construct the name of the alkane by placing the alkyl groups in alphabetical order and specifying their position numbers, followed by the name of the parent chain.

- **Step 4A:** List the alkyl groups along with their position numbers, ***in alphabetical order****.*
  - Write the position number(s) in front of the substituent(s).
    - We list **ethyl *before*** **methyl** because of alphabetical order.
  - We write: **3-ethyl-2-methyl**.
    - Always use a ***dash*** between position *numbers* and *letters*.
  - Add the labels di, tri, or tetra in front of the alkyl group name **if** two, three, or four (respectively) identical substituents are present.
    - We had no multiple, ***identical*** substituents (one is **methyl**, the other **ethyl**).
- **Step 4B:** Write the parent chain name ***behind*** the list of alkyl groups.
  - We write the name of this molecule as: **3-ethyl-2-methylheptane**
    - **Always** place a ***dash*** between position *numbers* and *letters*

Lets do one more problem together before you try some on your own. In this example, we will name a molecule with more than one of the ***same*** alkyl group substituents so that I can elaborate on the use of the *prefix labels* for ***identical substituents***.

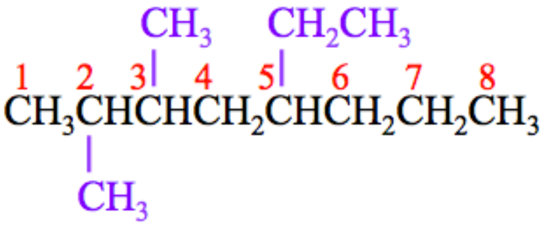
Example: Give the IUPAC name for the alkane shown below.



$$CH_3\underset{CH_3}{\underset{|}{CH}}\overset{CH_3}{\overset{|}{CH}}CH_2\overset{CH_2CH_3}{\overset{|}{CH}}CH_2CH_2CH_3$$

Step 1. Name the *parent chain*.

- For normal and branched alkanes, the ***parent chain is the longest, continuous chain of carbons atoms***.
  - The parent chain is **octane**; it contains eight carbons.



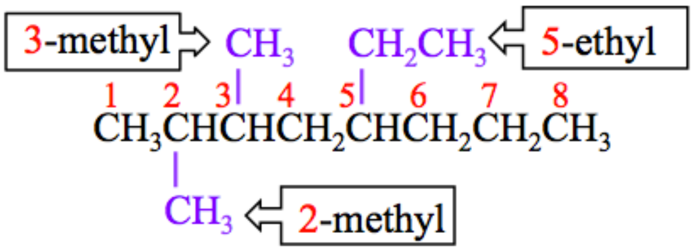
$$CH_3\underset{CH_3}{\underset{|}{CH}}\overset{CH_3}{\overset{|}{CH}}CH_2\overset{CH_2CH_3}{\overset{|}{CH}}CH_2CH_2CH_3$$

Step 2. Name any alkyl group substituents.

- There are three **alkyl group substituents**. There is an **ethyl** group and ***two*** **methyl** groups.

Step 3. Determine the *point of attachment* of alkyl group(s) to the parent chain.

- The point of attachment of the methyl groups are carbon number 2 ***and*** carbon number 3.
- The point of attachment of the ethyl group is carbon number 5.



$CH_3CHCHCH_2CHCH_2CH_2CH_3$

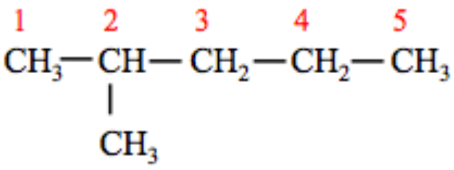
Step 4. Construct the name of the alkane by placing the alkyl groups in alphabetical order and specifying their position numbers, followed by the name of the parent chain.

- **Step 4A:** List the alkyl groups along with their position numbers, ***in alphabetical order.***
  - Add the labels di, tri, or tetra in front of the alkyl group name **if** two, three, or four (respectively) identical substituents are present.
    - Here we have two ***identical*** substituents (the **methyl** groups).
      - We will use the **"di" prefix** for the *methyl groups* (**dimethyl**)
  - Write the position number(s) in front of the substituent(s)
    - Since one of the methyl groups is on carbon number 2 and the other is on carbon number 3, we write **2,3-dimethyl**.
      - Place a ***comma*** *between position numbers*, note that we used "2,3-"
      - Place a ***dash*** between position *numbers* and *letters.*
    - The ethyl group is on carbon number 5, so we write **5-ethyl**.
  - We list the alkyl groups along with their position numbers, ***in alphabetical order.***
    - *IMPORTANT:* DO NOT CONSIDER THE PREFIXES (di-, tri-, tetra-) WHEN LISTING THE ALKYL GROUPS IN ALPHABETICAL ORDER; ALPHABETIZE BASED ON THE ALKYL GROUP NAME ONLY (methyl, ethyl, propyl, isopropyl, etc).
    - Because of this rule list **ethyl *before* dimethyl** because **e** comes before **m**.
  - We write: **5-ethyl-2,3-dimethyl**
- **Step 4B:** Write the parent chain name ***behind*** the list of alkyl groups.
  - We write the name of this molecule as: **5-ethyl-2,3-dimethyloctane**.

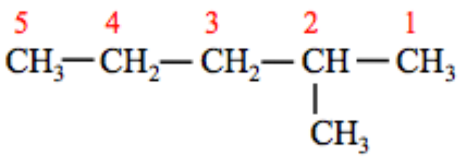
Before I ask you to work on some naming alkane problems, I want to warn you about a couple of things to be aware of while naming organic compounds.

1) Do not assume that the parent chain position numbers always start with carbon number 1 as the left-most parent carbon.

There is often many different ways to draw the same molecule. For example, 2-methylpentane can be correctly drawn as either of the structures shown below.



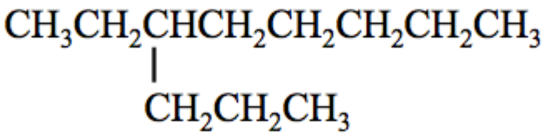
$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-CH_2-CH_3$



$CH_3-CH_2-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3$

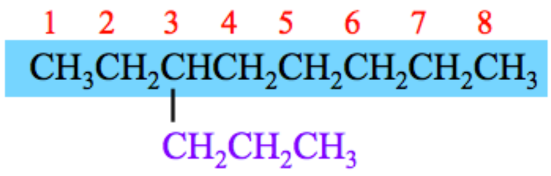
The position numbers ***in the parent chains*** are shown in red. We ***begin numbering from the end of the parent chain that is nearest to a substituent.*** Note that the use of this IUPAC systemic numbering method is important, or else the same molecule could have two different names. For example, if parent chain carbons were always simply numbered from left-to-right, then the *right-most* molecule above would be named *4-methylpentane*. Using the IUPAC method for numbering carbons, *4-methylpentane* does not exist, only 2-methylpentane. Hence the practicality of the IUPAC numbering system; there may be *many correct ways to draw a molecule*, but for each molecule ***there exists only one unique name***!

2) Do not assume that the parent chain is always drawn horizontally in a single line.
For normal and branched alkanes, the ***parent chain is the longest, continuous chain of carbons atoms***. In order to help first-semester organic chemistry students understand this point in naming alkanes, students are often given structures where the longest continuous chain of carbons is a bit tricky to recognize. For example, name the molecule shown below.



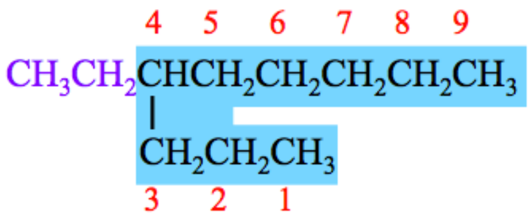
$$CH_3CH_2\underset{\underset{CH_2CH_2CH_3}{|}}{C}HCH_2CH_2CH_2CH_2CH_3$$

You may be temped to use octane for the parent chain (shaded blue), and then name the molecule **3-propyloctane**.



$$CH_3CH_2\underset{\underset{CH_2CH_2CH_3}{|}}{C}HCH_2CH_2CH_2CH_2CH_3$$

THAT IS INCORRECT! The ***parent chain is the longest, continuous chain of carbons atoms, NOT necessarily*** the carbon chain that is drawn horizontally in a single line. The correct way to think about naming this molecule is shown below.

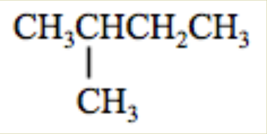


$$CH_3CH_2\underset{\underset{CH_2CH_2CH_3}{|}}{C}HCH_2CH_2CH_2CH_2CH_3$$

The parent chain is nonane and there is an *ethyl* substituent on carbon number 4. The parent chain is *numbered from the end of the chain that is nearest to a substituent.* The name of this molecule is **4-ethylnonane**. You have been warned...DON'T BE FOOLED BY TEXTBOOK AND EXAM AUTHORS! Now it is time for you to try a few naming problems on your own.

Review 4.20: Given the Formula, Write the Molecule's Name

Back in chapter 3, I referred to the molecule below using its "common name," which is isopentane. What is the IUPAC system name for isopentane?

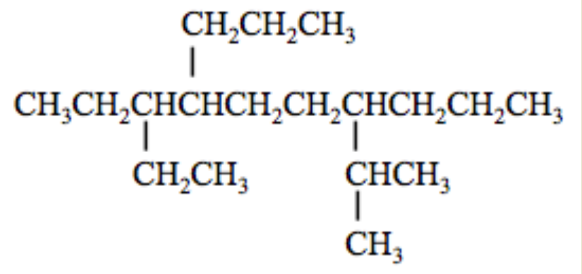


$$CH_3\underset{\underset{CH_3}{|}}{C}HCH_2CH_3$$

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

Review 4.21: Given the Formula, Write the Molecule's Name

What is the IUPAC system name for the alkane shown below?

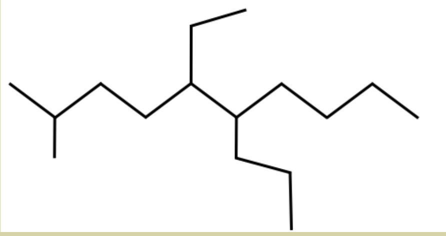


$$CH_3CH_2\underset{\underset{CH_2CH_3}{|}}{C}H\overset{\overset{CH_2CH_2CH_3}{|}}{C}HCH_2CH_2\underset{\underset{\underset{\underset{CH_3}{|}}{CHCH_3}}{|}}{C}HCH_2CH_2CH_3$$

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

Review 4.22: Given the Formula, Write the Molecule’s Name

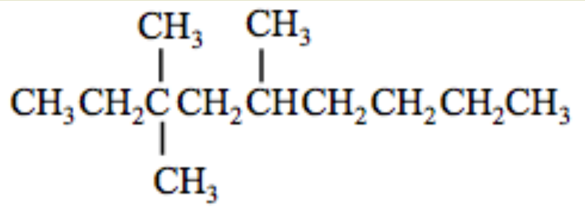
What is the IUPAC system name for the alkane shown below? HINT: If this seems tricky, it is because you are given the skeletal structure. Try drawing the line bond or condensed structure before naming.



For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

Review 4.23: Given the Formula, Write the Molecule’s Name

What is the IUPAC system name for the alkane shown below?



$$CH_3CH_2\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}CH_2\overset{\overset{\displaystyle CH_3}{|}}{C}HCH_2CH_2CH_2CH_3$$

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

Review 4.24: Given the Name, Draw the Molecule

Draw the ***condensed*** ***and*** ***skeletal*** structure for 3-methylheptane.

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

Review 4.25: Given the Name, Draw the Molecule

Draw the ***condensed*** ***and*** ***skeletal*** structure for 6-isopropyl-2,2-dimethyl-4-propylnonane.

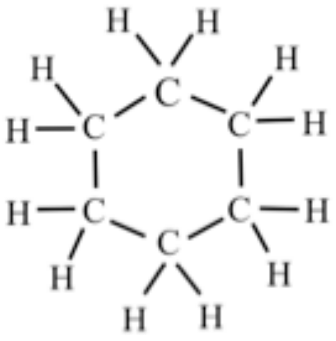
For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

Download this worksheet for more practice Drawing and Naming Alkanes:

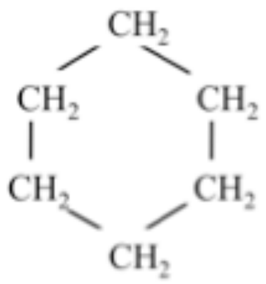
www.zovallearning.com/GOBlinks/ch4/alkanes-worksheet-and-key.pdf

ii) Method for Naming Cyclic Alkanes

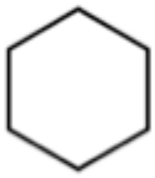
So far, you have learned how to name normal and branched alkanes. Some alkanes contain carbon atoms bonded, not in a linear sequence, but in a "**ring**" pattern. These alkanes are called **cycloalkanes**. An example of a cycloalkane is *cyclohexane*. The structural formulas for *cyclohexane* are shown below



Line Bond Structure



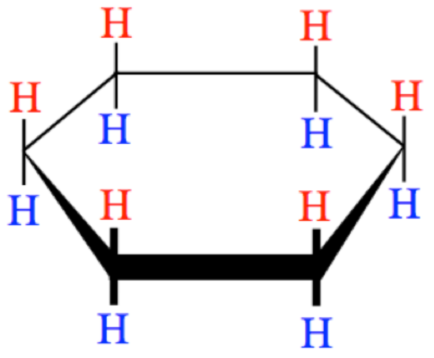
Condensed Structure



Skeletal Structure

In this sub-section, you will learn how to name cycloalkanes. We will use slightly different rules for naming cycloalkanes than we used for linear and branched alkanes. It is very common to see five- and six-carbon rings that occur in nature. The reason for this is that the bond angles in 5- and 6-carbon rings is fairly close to the 110° bond angles expected in molecules with AB_4 geometry. Although less frequent, three-, four-, seven-, and eight-carbon rings also occur. Before discussing the rules and some examples for naming cycloalkanes, I would like to point out some details of ring structure geometry and the types of structural representations that are used for cycloalkanes. In addition to the line bond, condensed, skeletal, and ball-and-stick representations, another structural representation called a "**side-view**" is also used for cycloalkanes. Side-view structures contain information about the three-dimensional arrangement of the atoms. The ball-and-stick model and a side-view structure for cyclohexane are shown below.

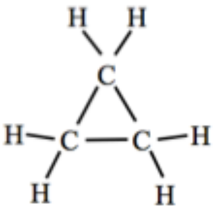
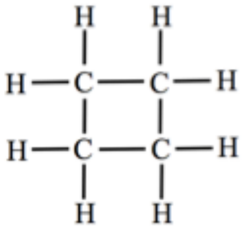
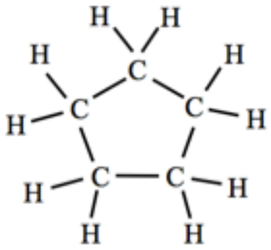
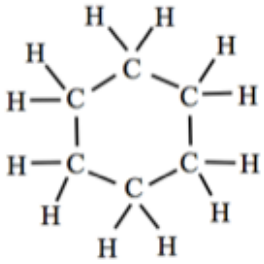
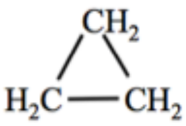
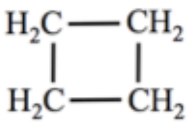
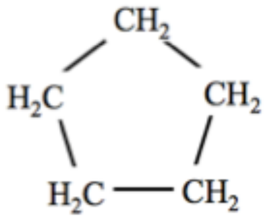
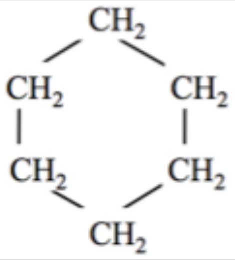
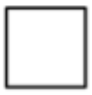
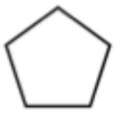
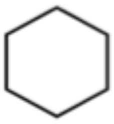
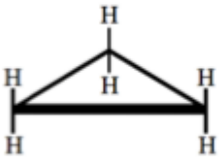
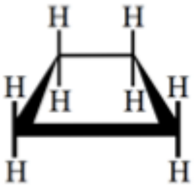
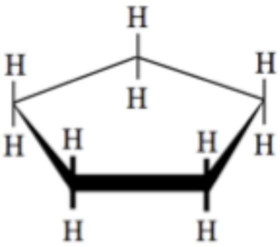
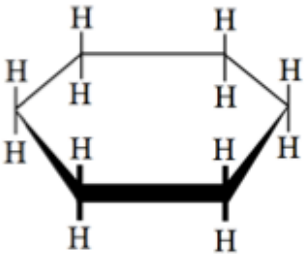
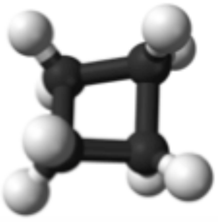
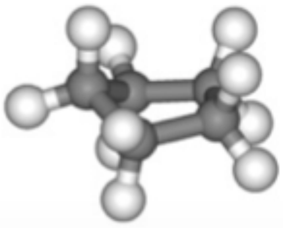
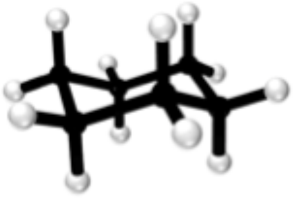
Ball-and-Stick Model



Side-View Structure

Note that in the ball-and-stick model (**left**), the ring of carbons (carbon atoms shaded black) is oriented horizontally. Each carbon is bonded to ***two hydrogen atoms***. From each ring-carbon, one of these two bonds is oriented in a direction *pointing* ***above*** the ring structure (bonds to the red-shaded hydrogens), and the other bond is oriented in a direction *pointing* ***below*** the ring structure (bonds to the blue-shaded hydrogens). Another way to state this is: each carbon in the ring of a cycloalkane will have one bond *pointing* ***above*** the ring structure and one *pointing* ***below*** the ring structure. It is convenient to express this three-dimensional information in the **side-view structural formula**. The actual bond angles are shown in the *ball-and-stick models* and are ***implied*** in the *side-view* representation. In ***side-view*** structures, bold lines are used to indicate the perspective when viewing the ring. The ring is depicted as being oriented horizontally with the **bold edges** toward the viewer. The two bonds that are oriented upwards or downwards from the ring-carbons are drawn vertically. The hydrogen atoms in red font correspond to the hydrogens shown as red spheres in the ball and stick model; likewise the hydrogen atoms in the blue font correspond to the hydrogens shown as blue spheres in the ball-and-stick model. You will learn why this three-dimensional information is important later in this chapter and in some of the biochemistry chapters. Table 4.10 shows the line bond, condensed, skeletal, side-view, and ball-and-stick representations for some cycloalkanes.

Table 4.10 Structural Representations of Cycloalkane Rings

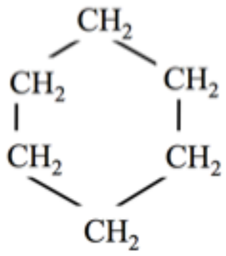
	Cyclopropane	Cyclobutane	Cyclopentane	Cyclohexane
Line Bond Structure				
Condensed Structure				
Skeletal Structure				
Side-View Structure				
Ball-and-Stick Model				

The naming rules for cycloalkanes are very similar to the rules that you saw for normal and branched alkanes. Just like branched alkanes, cycloalkanes can have substituents. I will introduce you to the steps for naming cycloalkanes using examples, and then I will ask you to practice naming some cycloalkanes on your own.

Step 1. Name the *parent chain*.

For cycloalkanes, the ***parent chain is the ring of carbon atoms***.

- The parent chain is named based on the number of carbon atoms in the ring. The parent chain names for ring structures with 3 to 8 carbon atoms are shown in Table 4.11.
- Note that these names are based on the names used for the parent chains of branched alkanes, ***however* the term "cyclo" is used as a prefix.**
  - A common mistake made by first-semester students is the failure to differentiate *cyclic* and *noncyclic* structures. For example, see the difference between hexane and cyclohexane below:



Cyclohexane

$CH_3—CH_2—CH_2—CH_2—CH_2—CH_3$

Hexane

Table 4.11 Parent Chain Names for Cycloalkanes

Number of Carbon Atoms in Ring	Parent Chain Name
3	cyclopropane
4	cyclobutane
5	cyclopentane
6	cyclohexane
7	cycloheptane
8	cyclooctane

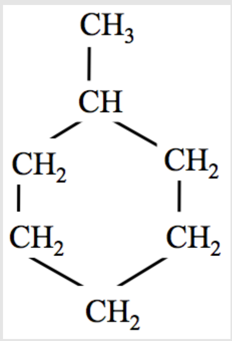
Step 2. Name any alkyl groups substituents.

The alkyl groups are named in the same way as we did for branched alkanes (methyl, ethyl, propyl, isopropyl, etc.). See Table 4.9 to review alkyl group names and structures.

Step 3. Determine the *point of attachment* of alkyl group(s) to the parent chain.

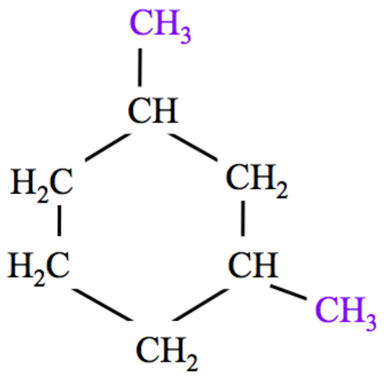
In order to uniquely name molecules, the name must indicate to which *parent chain-carbon* a substituent is attached. For cycloalkanes, the parent chain is a *ring structure,* therefore we ***use the following rules for assigning position numbers to the ring-carbons.***

- If there is ***only one substituent***, a position number is not used. This is because *all* carbons in the ring are equivalent and identical.
    - Name the molecule by placing the alkyl group substituent name in front of the parent chain name; ***no further steps are needed***.
    - For example, consider the molecule drawn ***to the right*** with a single, methyl group substituent attached to a 6-carbon ring. We name this molecule methylcyclohexane. Be sure to write methyl**cyclo**hexane and not methylhexane!



methylcyclohexane

- If there is ***more than one substituent***, assign position numbers to the alkyl groups.

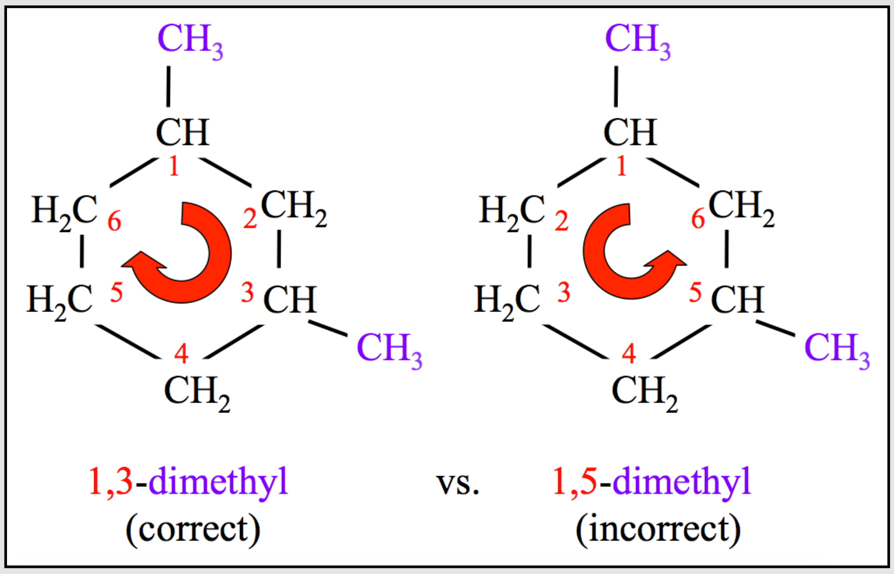


- For ***identical substituents***, arbitrarily assign one of them to position number one. Then, beginning with carbon number one, number the other carbons in the direction (clockwise or counterclockwise) that gives the smallest sum of position numbers.

- For example, the molecule drawn **to the left** has identical substituents (both are methyl groups).

- In the illustrations ***below***, I have shown the two choices, *one correct and one incorrect*, for assigning position numbers.

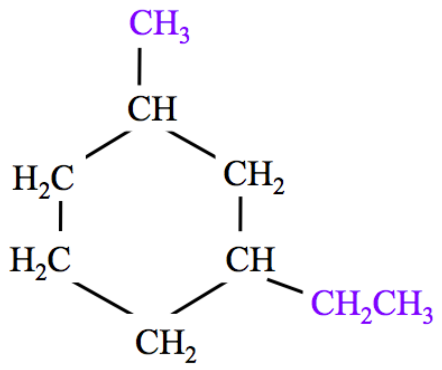
Assigning Position Numbers for Cycloalkanes



We number in the direction (clockwise vs. counter-clockwise) that gives the smallest sum of position numbers; in this case the correct choice is the clockwise direction as in the left-most molecule.

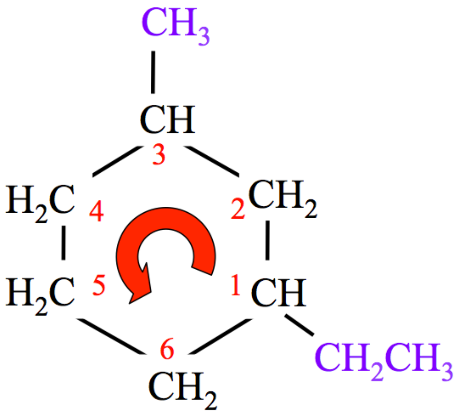
- There are <u>two</u> methyl groups, I ***arbitrarily*** chose the carbon at the top of the ring to be carbon number **1**.
- If the carbons are then numbered in the ***clockwise direction*** (as on the *left-most molecule* in the illustration), the methyl groups are at **positions number 1 and 3.**
- Alternatively, if the carbons are numbered in the ***counter-clockwise direction*** (as on the *right-most molecule* in the illustration), the methyl groups are at **positions number 1 and 5.**
- Our rule demands that we number in the direction that gives the *smallest sum of position numbers*; in this case it is the ***clockwise*** direction, as in the *left-most* molecule.
    - (1+3) is less than (1+5)

- When substituents are ***non identical***, the ring-carbon attached to the substituent that comes **first in alphabetical order is assigned position number 1.**



  - For example, the molecule drawn *to the **right*** has ***non identical*** substituents (one is *methyl* and the other *ethyl*).

    - We assign the position **number 1** to the ring-carbon that is bonded to the ***ethyl group*** (as shown below) because <u>e</u>thyl comes before <u>m</u>ethyl alphabetically.

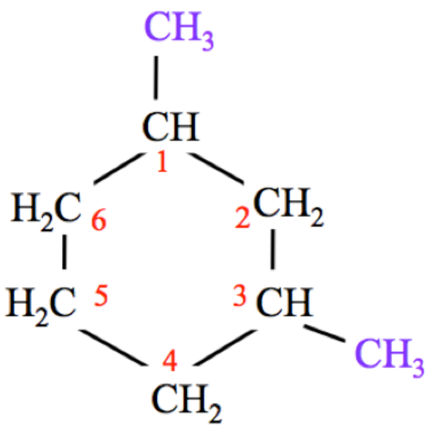


1-ethyl-3-methyl

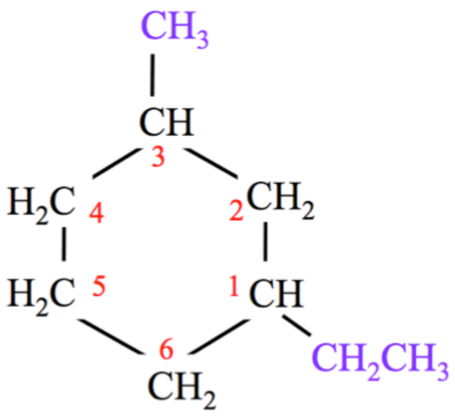
    - We number the ring-carbons in the **counter-clockwise direction** in order to result in the *smallest sum of position numbers.*

Step 4. Construct the name of the alkane by placing the alkyl groups in alphabetical order and specifying their position numbers, followed by the name of the parent chain.

- Step 4 is used in the exact same way for *cycloalkanes* as for *branched alkanes.*
- Let's name the cycloalkanes from our last two examples:

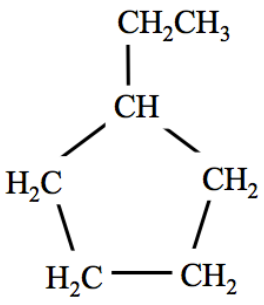


1,3-dimethylcyclohexane



1-ethyl-3-methylcyclohexane

Let's do a couple more naming cycloalkane problems together.



Example: Give the IUPAC name for the cycloalkane shown to the right:

Step 1. Name the *parent chain*.

For cycloalkanes, the ***parent chain is the ring of carbons atoms***.

- This parent chain names for ring structures with three to eight carbon atoms are shown in Table 4.11.
  - The parent chain name is **cyclopentane**

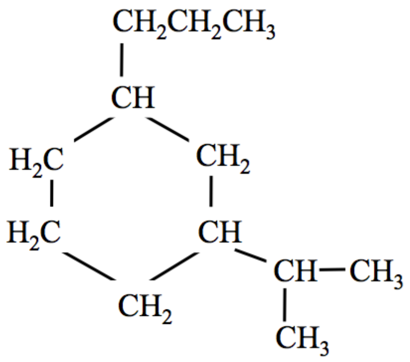
Step 2. Name any alkyl groups substituents.

- The alkyl group has two carbons. Use Table 4.9 to find the alkyl group name: **ethyl**

Step 3. Determine the *point of attachment* of alkyl group(s) to the parent chain.

- If there is ***only one substituent***, a position number *is not needed*.
- Name the molecule by placing the alkyl group substituent name in front of the parent chain name; ***no further steps are needed***.

The name of the molecule is **ethylcyclopentane**.



Example: Give the IUPAC name for the cycloalkane shown to the right:

Step 1. Name the *parent chain*.

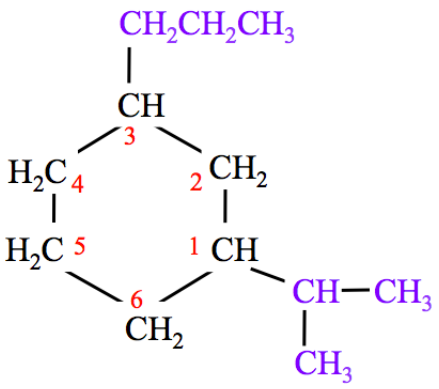
- The parent chain name is **cyclohexane**

Step 2. Name any alkyl groups substituents.

- There are two alkyl groups: **isopropyl** and **propyl**

Step 3. Determine the *point of attachment* of alkyl group(s) to the parent chain.

- If there is more than one substituent, assign position numbers to the alkyl groups.



- When substituents are ***non identical***, the ring-carbon attached to substituent that comes **first in alphabetical order is assigned position number one.**
- We assign the position **#1** to the ring-carbon that is bonded to the ***isopropyl group*** (as shown to the ***left***) because isopropyl comes before propyl alphabetically.
- Note that in this example, we number the ring-carbons in the **counter-clockwise position** in order to result in the *smallest sum of position numbers.*

Step 4. Construct the name of the alkane by placing the alkyl groups in alphabetical order and specifying their position numbers, followed by the name of the parent chain.

Step 4A: List the alkyl groups along with their position numbers (when applicable), *in alphabetical order.*

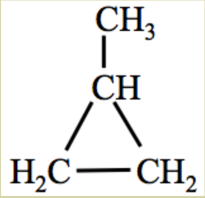
- **1-isopropyl-3-propyl**

- **Step 4B:** Write the parent chain name ***behind*** the list of alkyl groups.

The name of the molecule is **1-isopropyl-3-propylcyclohexane**.

Review 4.26: Given the Structural Formula, Name the Cycloalkane

The cycloalkane molecule shown below exists as a colorless gas at room temperature. What is the IUPAC system name for this molecule?



Click here to check answer For **print or pdf versions**, see the answer key in Appendix 1

Review 4.27: Given the Name, Draw the Structural Representations of Cycloalkanes

Draw the line bond, condensed, **and** skeletal structures of the following cycloalkanes:

a. 1,1-dimethylcyclobutane

b. 1-methyl-3-propylcyclopentane

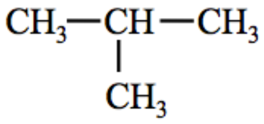
c. 1,4-diethylcyclohexane

Click here to check answer For **print or pdf versions**, see the answer key in Appendix 1

Constitutional Isomers

Isomers are molecules that have the same molecular formula, but differ in the way the atoms are arranged. The word isomer, like so many other words used in science, is derived from the Greek language, "***isos***" meaning *equal* and "***merós***" meaning *part*. I will discuss two types of isomers in this chapter. The first type of isomers that we will consider is called **constitutional isomers**. Molecules that have the same *molecular formula*, but ***different*** *atomic connections* are called constitutional isomers. Consider the two constitutional isomers for C_4H_{10} shown below.

$CH_3—CH_2—CH_2—CH_3$

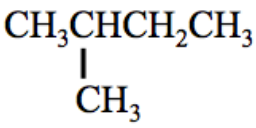


$$\underset{\displaystyle CH_3}{CH_3—\underset{|}{CH}—CH_3}$$

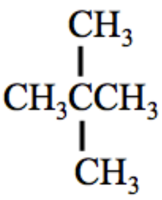
Both molecules have the same molecular formula (C_4H_{10}); however the bonding pattern (atomic connections) differ. Although constitutional isomers have the same molar mass and atoms, they have different physical and chemical properties. For example, the butane (above, left) has a boiling point of 0 °C and 2-methylpropane (above, right) has a boiling point of -11.7 °C.

Example: Draw the three constitutional isomers of C_5H_{12}.

$CH_3CH_2CH_2CH_2CH_3$



$$CH_3\underset{\underset{\displaystyle CH_3}{|}}{CH}CH_2CH_3$$



$$CH_3\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}CH_3$$

Note that the *middle* structure is 2-methylbutane. I did not draw another structure with the methyl group attached to the third carbon from the left because that would still be 2-methylbutane; if the methyl group was placed in that position, carbon number 1 would be the right-most carbon.

You try one:

Review 4.28: Constitutional Isomers

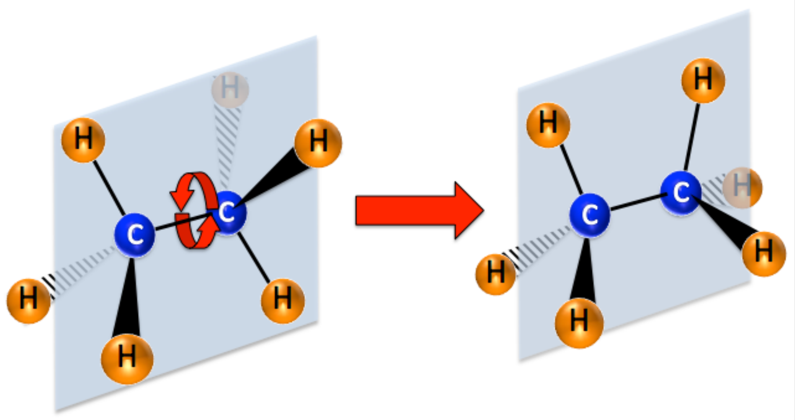
There are ***five*** constitutional isomers of C_6H_{14}, **draw** (condensed structures) **and name** each of them.

Click here to check answer For **print or pdf versions**, see the answer key in Appendix 1

Conformations

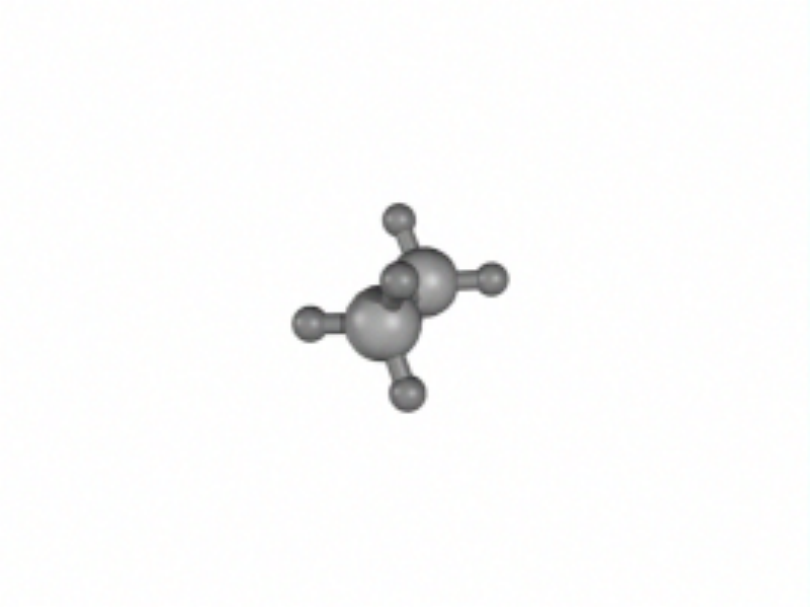
Earlier in this chapter you learned that **rotation** around ***single bonds*** allows most large molecules to assume an infinite number of three-dimensional shapes. The infinite number of shapes that a molecule can take, because of the rotation around bonds, are called ***conformations***. Figure 4.40 and Movie 4.3 illustrate the rotation around single bonds using an ethane molecule as an example.
For **print or pdf versions** of the book, the movie can be seen at: http://www.zovallearning.com/streamvid/ethane-conformations.html.

Figure 4.40 Rotation Around Single Bonds



Free rotation occurs around single bonds, therefore most large molecules are always *changing their shapes.* In this figure, one of the *infinite number of shape changes* of which ethane is capable of is shown by the rotation of one of the methyl groups by 60º around the carbon-carbon bond axis.

Movie 4.3 Ethane Conformations



Do not confuse ***conformations*** with ***constitutional isomers***! The different **conformations** of a molecule have the *same molecular formula* and have the ***same atomic connections***; whereas **constitutional isomers** have the *same molecular formula* yet ***different atomic connections***.

Example of Conformations: Butane

Rotation about the bond between carbon number 2 and carbon number 3 in butane gives rise to an infinite number of different conformations (three-dimensional shapes) for the molecule. Figure 4.41 shows a few of the possible conformations.

Figure 4.41
A few of the infinite conformations of butane resulting from rotation about the single bond between carbon number 2 and carbon number 3.

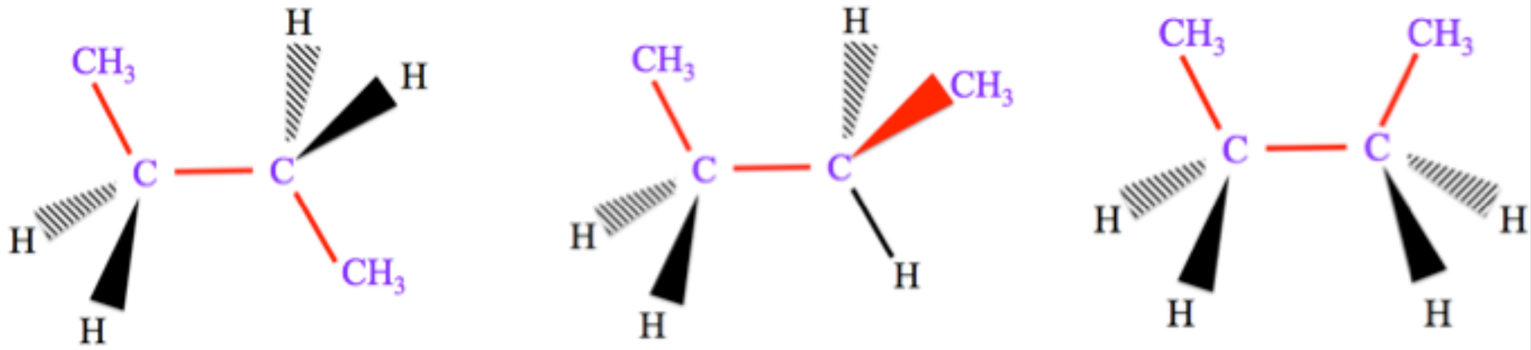


Figure 4.41 only shows some conformations that result from rotation around the bond between carbon numbers 2 and 3; although not illustrated in the figure, there is also rotation around the bond between carbons number 1 and 2 and around the bond between carbons number 3 and 4.

The higher the temperature, the faster the rotation. Because of the nature of ***double*** and ***triple bonds***, rotations around them are not possible.

Stereoisomers

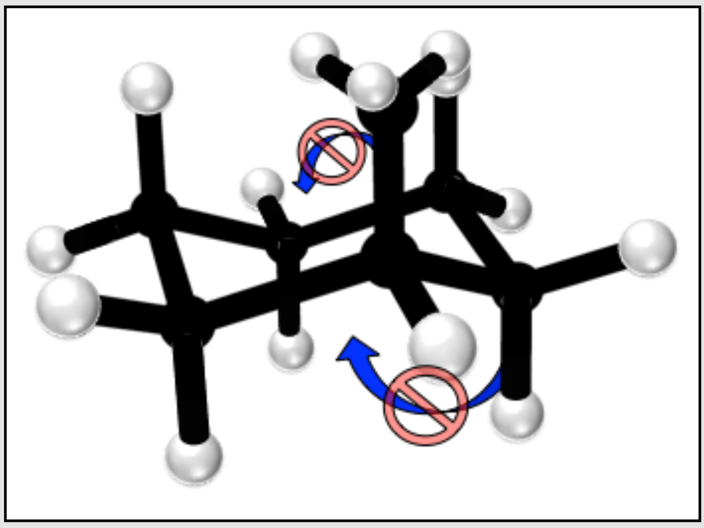
In ***cycloalkanes***, the free rotation around the carbon-carbon single bonds is ***restricted*** because hydrogens and/or substituents bonded to ring-carbons are too large to rotate through the center of the ring structure. The restricted rotation results in the existence of a special type of **stereoisomers**. You will learn about a *few types* of *stereoisomers* while reading this book. Before I discuss the special type of stereoisomer that results from restricted bond rotation, I want to give you a definition of ***stereoisomers***.

Stereoisomers are molecules that:

1) have the *same* molecular formula
2) have the *same* atomic connections
3) have a *different* 3-dimensional shape
   - ***So far the definition of stereoisomers is the same as conformations - but the next item makes them quite different.***
4) **cannot** be converted from one to another without ***breaking and reforming bonds*** (it is ***not*** possible for one stereoisomer to take the shape of another stereoisomer by rotation around a bond).

The first type of *stereoisomers* that I will introduce you to are called **geometric isomers**. When *stereoisomers* exist because of ***limited bond rotation***, the stereoisomers are called **geometric isomers.**

Figure 4.42
Restricted Bond Rotation in Cycloalkanes



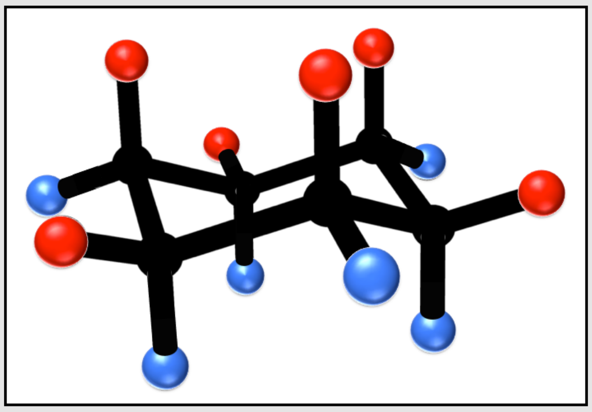
Ball and stick model of methylcylohexane as an example of restricted rotation. In cycloalkanes, the hydrogens and substituents that are bonded to ring-carbons cannotcannotcannotcannotcannotcannot rotate through the center of the ring because there is not enough space to do so. Their rotation is hindered by the ring.

Geometric Isomers

Geometric isomers are *stereoisomer*s that exist because of *restricted* rotation around carbon-carbon bonds. Before discussing geometric isomers, I want to elaborate on why rotation around single bonds can be "restricted." This occurs in *ring structures of cycloalkanes*. Each carbon atom in the ring has a total of four bonds; two of the bonds are to its neighboring ring-carbons, and the other two bonds are to hydrogen atoms or substituents. In order for there to be free rotation around the carbon-carbon single bonds *of the ring structure*, the hydrogens or substituents would need to rotate through the center (hole) of the ring. This is not possible, there is not enough room for the hydrogens or any other substituents to pass through the center of the ring. This concept is illustrated for methylcyclohexane in Figure 4.42. Although I only used two arrows (blue) to indicated limited rotation, it is important to note that neither the -CH_3 substituent nor any of the hydrogens can rotate through the ring structure. This is true for all hydrogens and all substituents bonded to any cycloalkane ring. The implications of this are important in understanding geometric isomers of cycloalkanes.

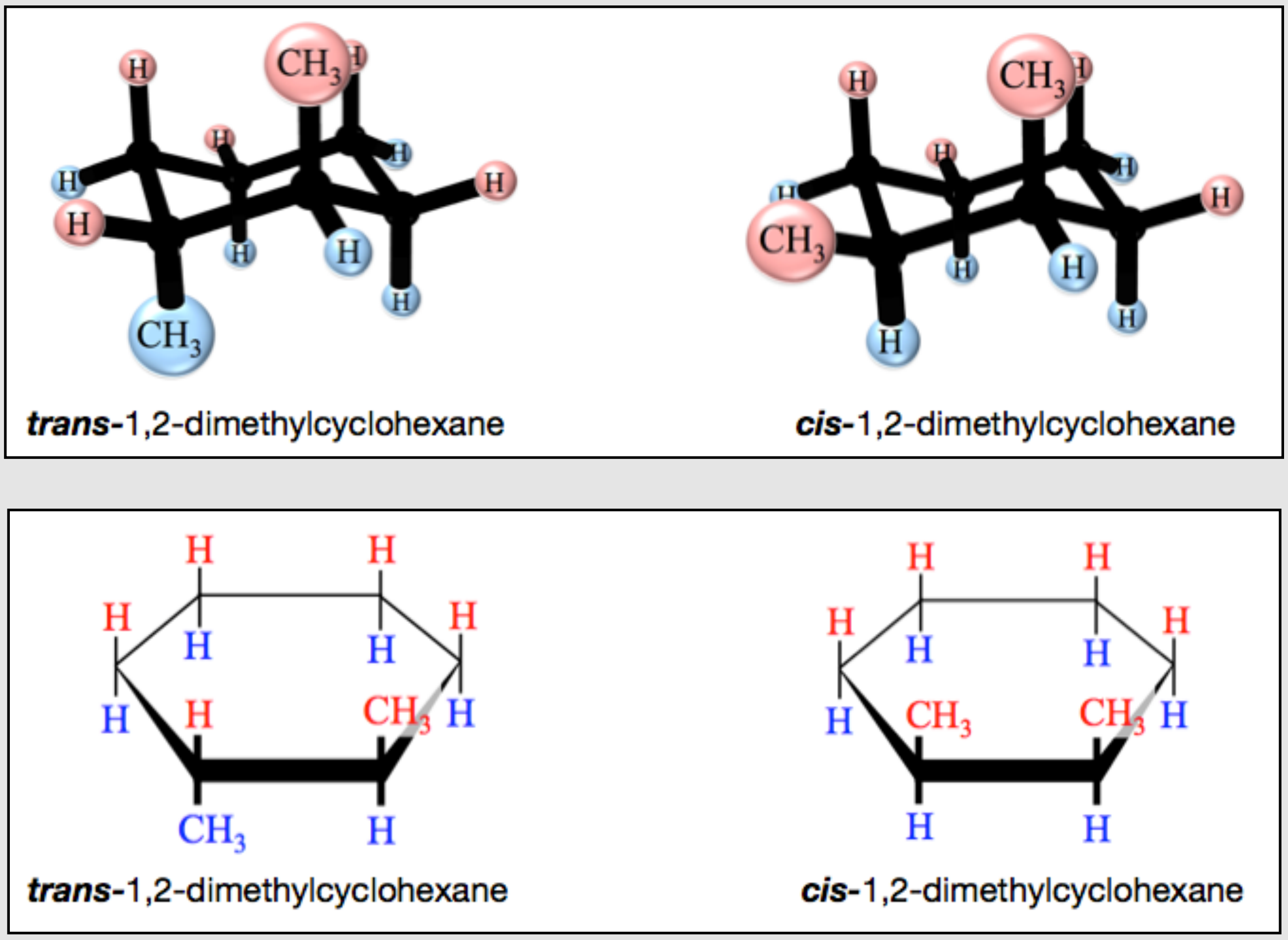
Consider the six-carbon ring shown in Figure 4.43. ***Each*** ring-carbon in cycloalkanes will have two bonds going to hydrogens and/or substituents; one of these two bonds is oriented in a direction *pointing* ***above*** the ring structure (bonds to the red-shaded spheres), and the other bond is oriented in a direction *pointing* ***below*** the ring structure (bonds to the blue-shaded spheres). In this illustration, the spheres (blue or red) represent either hydrogens or any other substituents. Since the hydrogens or substituents of cycloalkanes are unable to rotate, they are "***locked***" in a particular orientation, either *pointing* ***above*** the ring structure or *pointing* ***below*** the ring structure. Now, let's see how this *restricted rotation* results in the existence of ***geometric isomers***.

Figure 4.43
Geometry of a Six-Carbon Ring Structure



Geometric isomers come in ***pairs*** – one is the "**cis-**" and one is the "**trans-**" isomer. When cycloalkanes have ***two*** substituents, ***each on a different ring-carbon***, then there are two geometric isomers possible. For *cycloalkanes*, a ***cis*** geometric isomer has ***both substituents*** oriented in the same direction (either **both** *pointing* ***above*** the ring structure or **both** *pointing* ***below*** the ring structure). Conversely, a ***trans*** geometric isomer has the two ***substituents*** oriented in opposite directions (**one** *pointing* ***above*** the ring structure and the **other** *pointing* ***below*** the ring structure). The two geometric isomers for 1,2-dimethylcyclohexane are shown in Figure 4.44. In the top insert of Figure 4.44, the ball-and-stick representation is shown. The hydrogens and/or substituents that are oriented in the upward direction are shaded red and those oriented in the downward direction are shaded blue. Notice the ***trans*** isomer (***top, left***) has **one** methyl group pointing ***above*** the ring structure and the **other** *pointing* ***below*** the ring structure. The ***cis*** isomer (***top, right***) has ***both methyl groups*** oriented in the same direction (**both** *pointing* ***above*** the ring structure). To visualize the cycloalkane geometric isomers, we must use *ball-and-stick representations* ***or*** draw **side view** *structures*; **cis** vs. **trans** cannot be seen using our standard line bond, condensed, or skeletal structures. The *side view*s of the two geometric isomers for 1,2-dimethylcyclohexane are shown in the bottom insert of Figure 4.44.

Figure 4.44 Structural Representations of the *cis* and *trans* Isomers of 1,2-dimethylcyclohexane

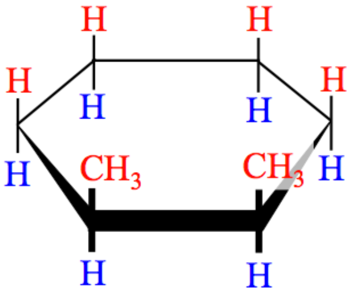


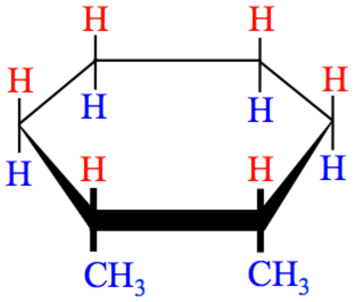
Top: ***Ball-and-stick representation*** of the two geometric isomers for 1,2-dimethylcyclohexane. The hydrogens and/or substituents that are oriented in the upward direction are shaded red and those oriented in the downward direction are shaded blue. Notice the ***trans*** isomer (***top, left***) has **one** methyl group pointing ***above*** the ring structure and the **other** *pointing* ***below*** the ring structure. The ***cis*** isomer (***top, right***) has ***both methyl groups*** oriented in the same direction (**both** *pointing* ***above*** the ring structure).

Bottom: ***Side view structure*** of the two geometric isomers for 1,2-dimethylcyclohexane.

Because alkyl group substituents cannot rotate through the center of the ring, the ***trans*** and ***cis*** isomers of cycloalkanes are ***two different molecules***; they have slightly different physical properties (density, melting points, vapor pressure, etc.) and different chemical properties. There are only slight differences in many properties because the isomers are very similar (but not identical). One important difference in the properties of some geometric isomers is the way they interact with enzymes in the body. For example, some enzymes will only work to produce one of the isomers.

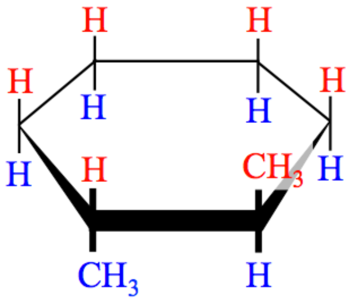
It was arbitrary that I chose to number the ring carbons so that carbon number 1 and carbon number 2 are on the edge of the ring that is depicted as being closest to the viewer in the representations of 1,2-dimethylcyclohexane in Figure 4.44. Although that numbering convention is most common, I could have chosen any two neighboring carbons as carbon numbers 1 and 2 and the resulting drawings would be equally correct representations of the isomers. There are often many equivalent, correct ways to draw structural formulas of large molecules. In addition to the arbitrary choice in numbering ring carbons, more than one equivalent structural representation can be drawn for the same geometric isomer. For example, when drawing ***cis*** isomers of cycloalkanes, the two substituents can be drawn with either **both** substituents ***above*** the ring structure ***or*** **both** ***below*** the ring structure. Both representations are equivalent. The two equivalent, and equally correct, ways to draw ***cis-***1,2-dimethylcyclohexane are shown below.

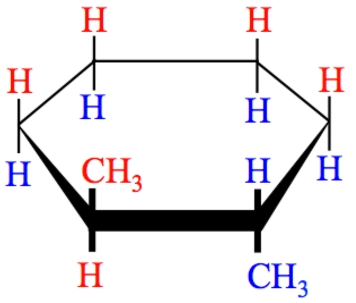




One way to understand that the pair of molecules shown above are identical is to imagine that you take a photo of the left-most molecule, then ***turn the photo upside down***, you would see that both methyl groups in photo are now oriented in the downward direction - just like the right-most molecule. Therefore, they are the same molecule, ***cis-***1,2-dimethylcyclohexane!

Likewise, when drawing ***trans*** isomers of cycloalkanes, it can be drawn using two equivalent representations. For example, two equivalent ways of drawing ***trans***-1,2-dimethylcyclohexane are shown below.





Review 4.29 Drawing Side View Structures for Geometric Isomers

Draw the side view structures of the ***cis*** and ***trans*** isomers for 1,2-dimethylcyclopentane.

Click here to check answer For **print or pdf versions**, see the answer key in Appendix 1

Review 4.30 Identifying Geometric Isomers

Which of the following molecules have cis and trans isomers? There may be more that one correct selection.

a) 1,2-dimethylcyclopentane
b) 1-ethyl-2-propylcyclobutane
c) 1-methylcyclohexane
d) 1,1-dimethylcylcohexane

Click here to check answer For **print or pdf versions**, see the answer key in Appendix 1

4.9 Alkenes, Alkynes, and Aromatic Hydrocarbons

Alkenes

Alkenes are molecules that consist *only of carbon and hydrogen atoms* and contain ***at least one carbon-carbon double bond***. They are unsaturated hydrocarbons. Alkenes are also referred to as **olefins**.

Naming Alkenes

Naming alkenes involves identifying an alkene's "**parent chain"** and its **substituents** (atoms or groups of atoms attached to the parent chain). The systemic method we will use for naming alkenes is very similar to the method you used for naming alkanes, however there are some significant differences.

Systemic Method for Naming Alkenes:

Step 1. Find and name the *parent chain*.

The *parent chain is the longest, continuous chain of carbon atoms that **contains the double bond**.*

- The parent chain is named by combining a numbering prefix that specifies the number of carbon atoms in the parent chain, with the "**-ene**" suffix, which identifies the molecule as an **alkene**. This parent chain numbering prefixes are the same as were used for *alkanes*, however we use the "ene" suffix.
    - Example: If an alkene has three carbon atoms in the parent chain, the parent chain name is *prop**ene***.
- For alkenes with ***more than three carbons***, the position of the double bond must be indicated by adding a number to the parent chain name as described below.
    - Assign *position numbers* to the carbons in the parent chain.
        - Position number **1** is assigned to the carbon at the end of the parent chain that is **closest to the double bond.**
            - If the double bond is between carbons number **1** and **2**, the number "1" is used as a prefix to the parent chain name. For example, in the molecule below, the parent chain is called **1**-pentene.

$$\overset{1}{\mathrm{CH_2}}{=}\overset{2}{\mathrm{CH}}{-}\overset{3}{\mathrm{CH_2}}{-}\overset{4}{\mathrm{CH_2}}{-}\overset{5}{\mathrm{CH_3}}$$

            - If the double bond is between carbons number **2** and **3**, the number "2" is used as a prefix to the parent chain name. For example, in the molecule below, the parent chain is called **2-**pentene.

$$\overset{1}{\mathrm{CH_3}}{-}\overset{2}{\mathrm{CH}}{=}\overset{3}{\mathrm{CH}}{-}\overset{4}{\mathrm{CH_2}}{-}\overset{5}{\mathrm{CH_3}}$$

            - If the double bond is between carbons number 3 and 4, the number "3" is used as a prefix to the parent chain name...etc.
    - **Note** that this is different from the method we used for numbering *alkanes*; for alkanes we assigned position number 1 to the carbon on the end of the parent chain that was closest *to a substituent*.

Step 2. Name any alkyl group substituents.

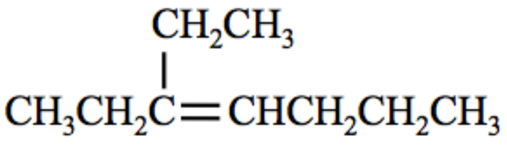
Alkyl group substituents are named in the same way as you did for alkanes.

Step 3. Construct the name of the alkene by placing the alkyl groups in alphabetical order and specifying their position numbers, followed by the name of the parent chain.

- This is done the same way as you did with alkanes.
- Remember to use a dash between position numbers and letters.

Let's do a couple of naming alkene problems together.

Example: What is the name of the alkene shown to the right:

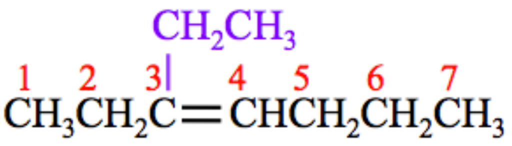


$\mathrm{CH_3CH_2\overset{\overset{CH_2CH_3}{|}}{C}{=}CHCH_2CH_2CH_3}$

Step 1. Find and name the *parent chain*.

The *parent chain is the longest, continuous chain of carbon atoms that* ***contains the double bond****.*

- The parent chain is named by combining a numbering prefix which specifies the number of carbon atoms in the parent chain, with the "**-ene**" suffix, which identifies the molecule as an **alk<u>ene</u>**.
    - There are seven carbons in the parent chain
- For alkenes with ***more than three carbons***, the position of the double bond must be indicated by adding a number to the parent chain name.
    - Assign ***position numbers*** to the carbons in the parent chain.
        - Position number **1** is assigned to the carbon *at the end* of the parent chain that is **closest to the double bond.**
            - Since the double bond is between carbons number **3** and **4**, the number "3" is used as a prefix in the parent chain name.
                - Parent chain name: **3-heptene**



$\mathrm{\overset{1}{CH_3}\overset{2}{CH_2}\overset{\overset{CH_2CH_3}{3|}}{C}{=}\overset{4}{CH}\overset{5}{CH_2}\overset{6}{CH_2}\overset{7}{CH_3}}$

Step 2. Name any alkyl group substituents.

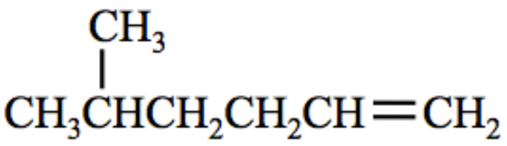
Alkyl group substituents are named in the same way as we did for alkanes.

- There is one substituent in this example: **ethyl**

Step 3. Construct the name of the alkene by placing the alkyl groups in alphabetical order and specifying their position numbers, followed by the name of the parent chain.

- Remember to use a dash between position numbers and letters.
- The ethyl substituent is attached to carbon number **3**, use **3-ethyl.**
- The name of this molecule is **3-ethyl-3-heptene**.

Example: What is the name of the alkene shown to the right:

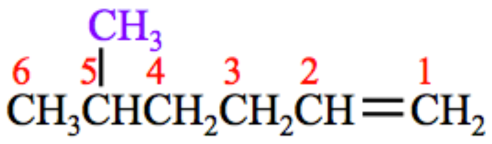


$\mathrm{CH_3\overset{\overset{CH_3}{|}}{C}HCH_2CH_2CH{=}CH_2}$

Step 1. Find and name the *parent chain*.

The *parent chain is the longest, continuous chain of carbon atoms that* ***contains the double bond****.*

- The parent chain is named by combining a numbering prefix that specifies the number of carbon atoms in the parent chain, with the "**-ene**" suffix, which identifies the molecule as an **alk<u>ene</u>**.
    - There are six carbons in the parent chain
- For alkenes with ***more than three carbons***, the position of the double bond must be indicated by adding a number to the parent chain name.
    - Assign ***position numbers*** to the carbons in the parent chain.
        - Position number **1** is assigned to the carbon *at the end* of the parent chain that is **closest to the double bond.**
            - Note that I have numbered the parent chain beginning with the *right-most* carbon since it is closest to the double bond.

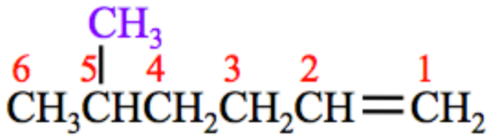


$\mathrm{\overset{6}{CH_3}\overset{\overset{CH_3}{5|}}{C}H\overset{4}{CH_2}\overset{3}{CH_2}\overset{2}{CH}{=}\overset{1}{CH_2}}$

- The double bond is between carbons number **1** and **2**, the number "1" is used as a prefix to the parent chain name.
    - Parent chain name: **1-hexene**

Step 2. Name any alkyl group substituents.

- There is one substituent in this example: **methyl**



$$\mathrm{\overset{6}{C}H_3\overset{\overset{CH_3}{|}}{\overset{5}{C}}H\overset{4}{C}H_2\overset{3}{C}H_2\overset{2}{C}H{=}\overset{1}{C}H_2}$$

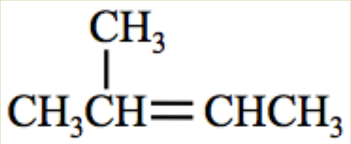
Step 3. Construct the name of the alkene by placing the alkyl groups in alphabetical order and specifying their position numbers, followed by the name of the parent chain.

- The methyl substituent is attached to carbon number 5, use **5-methyl.**
- The name of this molecule is **5-methyl-1-hexene**.

You try a few naming alkenes problems.

Review 4.31: Naming Alkenes

Write the name of this alkene.

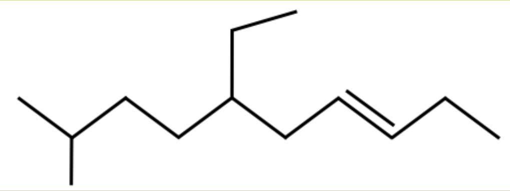


$$\mathrm{CH_3\overset{\overset{CH_3}{|}}{C}H{=}CHCH_3}$$

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

Review 4.32: Naming Alkenes

Write the name of this alkene.



For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

Review 4.33: Given the Name, Draw the Alkenes

Draw the line bond, condensed, and skeletal structure for each of the following alkenes.

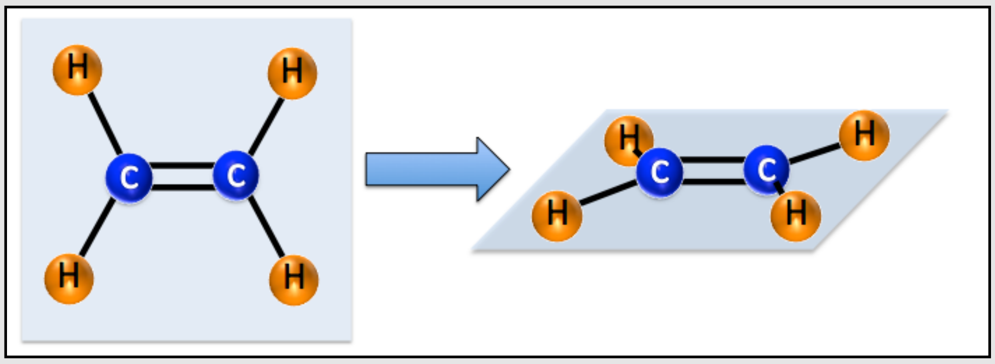
a. 2-methyl-1-butene
b. 3-ethyl-4-methyl-3-hexene

For i-books versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

Geometric Isomers of Alkenes

The bonding pattern around a carbon with a double bond is quite different from that of a carbon with all single bonds. *Unlike the case for single bonds*, ***there is no rotation around double bonds***. Furthermore, all other bonds to both double-bonded carbon atoms ***are on the same plane as the double bond***. This molecular geometry is shown in the ball-and-stick model of the alkene shown in Figure 4.45. Each of the double-bonded carbons (blue) is surrounded by *three electron groups* (three bonded atoms, no lone pairs, AB_3), therefore the bond angles around the carbons are 120º. For simplicity, the alkene used in the figure is the smallest alkene (ethene), however this geometry is the same whether there are hydrogens, other atoms, alkyl groups, or any other groups of atoms bonded to double-bonded carbons. Since there is no rotation around double bonds, all of the ***atoms*** bonded to the double-bonded carbons in alkenes ***always remain on the same plane as the <u>double</u> bond***.

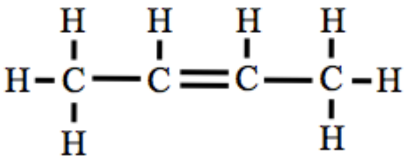
Figure 4.45
Geometry Around Double-Bonded Carbons in Ethene.



Two different perspectives for viewing the geometry around double-bonded carbons. An ethene molecule is viewed on a plane oriented vertically (left) and then rotated 90º backwards and viewed on a horizontal plane (right).

In the previous section, you learned that that geometric isomers can exist because of limited rotation. I showed you how this can occur for single bonds in ring structures of cycloalkanes because there is not enough room for the hydrogens or any other substituent to pass through the center of the ring. Because of the *geometry and lack of rotation around double bonded carbons*, **some alkenes can exist as geometric isomers (*cis* and *trans*).**

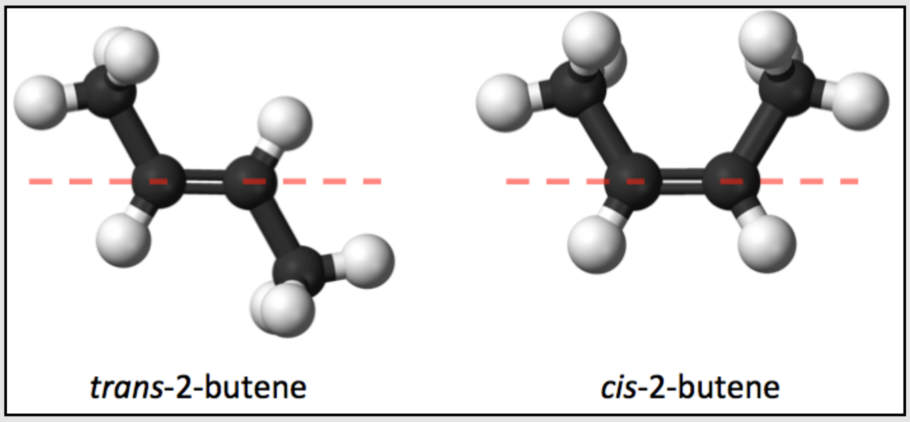
I will elaborate on isomerism in alkenes using an example. Consider the line bond structure of 2-butene below:



$$H{-}\overset{H}{\underset{H}{C}}{-}\overset{H}{C}{=}\overset{H}{C}{-}\overset{H}{\underset{H}{C}}{-}H$$

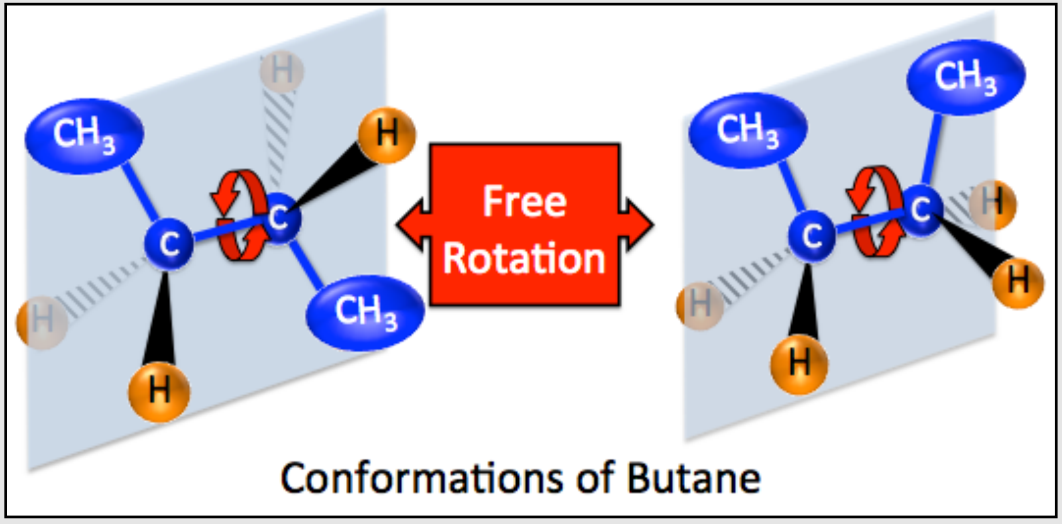
There are two possible geometric arrangements of the two methyl groups attached to the double bonded carbons. A ball-and-stick representation of both of the possible geometries is illustrated in Figure 4.46. In this figure, carbon atoms are shaded black and hydrogen atoms are shaded white. We identify the ***cis*** and ***trans*** isomers by noting the positions of alkyl groups on each of the double-bonded carbons relative to an imaginary line passing *along the double bond* (shown as a red dashed line in Figure 4.46). When ***<u>both</u>*** of the alkyl groups are on ***opposite sides*** of the imaginary line, we have the ***trans*** geometric isomer. Note that the alkyl groups in 2-butene are both methyl groups (CH_3). In the left-most structure shown in Figure 4.46, the methyl groups are on *opposite sides* of the red dashed line and this isomer is named ***trans***-2-butene. The term ***trans*** is a Latin noun or prefix that means "*across*" or "*opposite side*"; this is appropriate for geometric isomers because, relative to the line along the double bond (or ring-carbons in cycloalkanes), the alkyl groups are *across* from each other. When the alkyl groups are ***<u>both</u> on the same side*** of the imaginary line along the double bond, we have the ***cis*** geometric isomer. This is the case in the right-most structure shown in Figure 4.46; the methyl groups are on *the same side* of the red dashed line and this isomer is named ***cis***-2-butene. The term ***cis*** is a Latin prefix meaning "on the *same side.*"

Figure 4.46 Geometric Isomerism in Alkenes

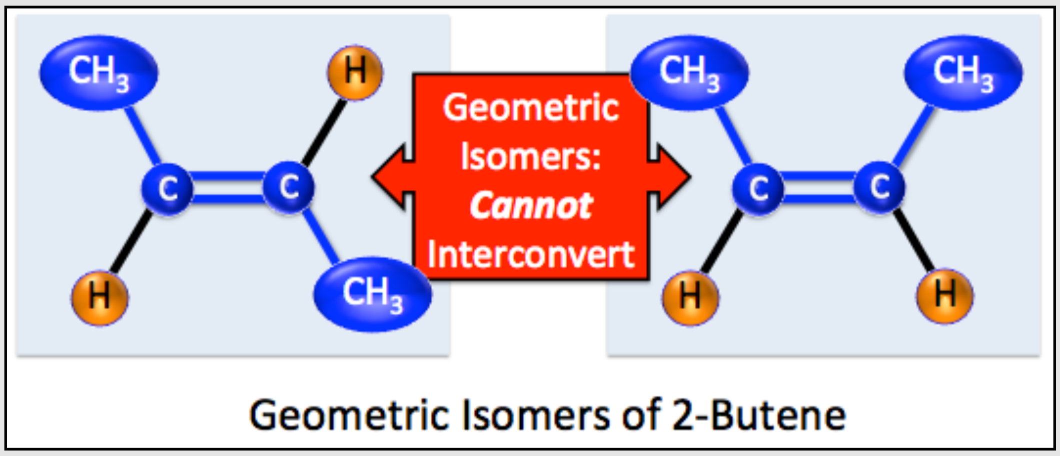


Ball and stick representations of the two geometric isomers of 2-butene. Carbon atoms are shaded black and hydrogen atoms are shaded white. **Left**: the methyl groups are on *opposite sides* of the red dashed line and this isomer is named ***trans***-2-butene. **Right**: the methyl groups are on *the same side* of the red dashed line and this isomer is named ***cis***-2-butene.

Figure 4.47
Geometric Isomerism vs. Conformations



Conformations of Butane



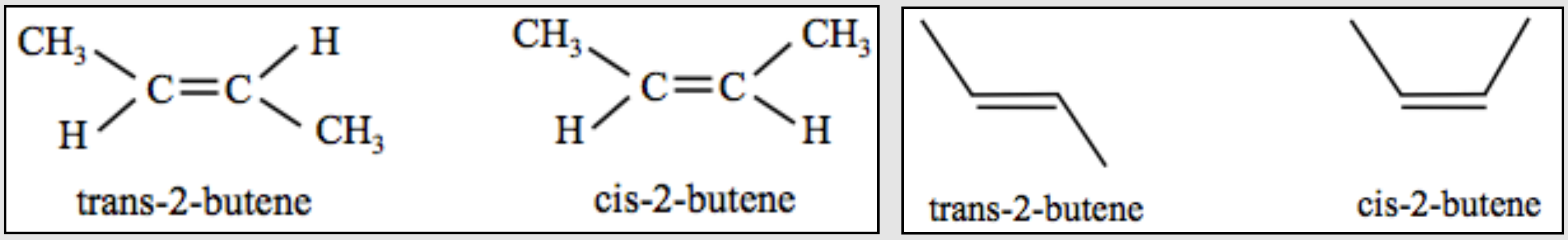
Geometric Isomers of 2-Butene

Top: Rotation around the single bonds in butane results in an infinite number of conformations of a single molecule. **Bottom:** Restricted rotation around the double bond in 2-butene allows for the existence of two noninterconvertible isomers: ***trans*** (bottom left) and ***cis*** (bottom right).

Since the nature of double bonds does not allow free rotation, it is not possible for a ***trans*** isomer to rotate and thereby convert to the ***cis*** isomer; they are two distinct, noninterconvertible molecules with different physical and chemical properties. For example, because of their different geometries, the melting point of cis-2-butene is 4 °C and the the melting point of trans-2-butene is 1 °C. I want to elaborate on the *inability for cis and trans isomers to interconvert* by contrasting ***geometric isomers*** and ***conformations***. *Conformations* of a molecule arise from rotation around single bonds. An infinite number of conformations are possible for an ***individual*** molecule. In contrast, *geometric isomers* are two, distinct molecules that cannot interconvert by rotation around bonds. Figure 4.47 illustrates the difference between conformations of but**ane** and geometric isomerism of 2-but**ene**. The illustration in the **top insert** of Figure 4.47 shows how a 180° rotation around a single bond results in two of the infinite number of conformations for a but**ane** molecule. The illustration in the bottom insert of Figure 4.47 shows the two distinct geometric isomers for 2-but**ene**; these are two different molecules. Just like ***conformations***, they have the *same* molecular formula (C_4H_8), the *same* atomic connectivity, and *different* spacial arrangements of atoms. However, *geometric isomers* are different from *conformations* in that they cannot be interconverted by rotation around a bond (because rotation is restricted around a double bond).

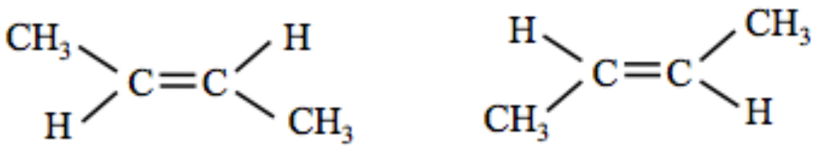
Before asking you to work on some problems that involve the concept of alkene geometric isomerism, I want to discuss some concepts related to drawing structural representations of alkene isomers. Perhaps you recall that, in order to differentiate *cis* vs. *trans* isomers in ***cycloalkanes***, you needed to draw "*side views.*" In order to differentiate *cis* vs. *trans* when using ***condensed structures*** for alkenes, the 120° bond angles around the double-bonded carbons are drawn as shown in the *left insert* of Figure 4.48. In ***skeletal structures***, the bonds to the alkyl groups that emanate from the double-bonded carbons are oriented as shown in the *right insert* of Figure 4.48.

Figure 4.48 **Condensed and Skeletal Representations of Alkene Geometric Isomers**



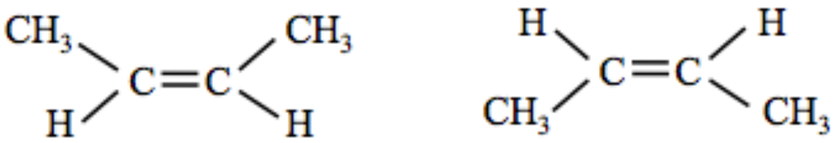
In order to differentiate trans vs. cis alkene isomers, the 120° bond angles must be shown around the double-bonded carbons.
Left: Condensed structure formula of *trans*- and cis-2-butene.
Right: Skeletal structural formula of *trans*- and *cis*-2-butene.

It is important to know that there will be *two correct ways* to draw **each** *cis* and **each** *trans* isomer. For example, the two condensed structures of ***trans***-2-butene shown below are equivalent and equally correct representations of the isomer.



Both are *trans*-2-butene

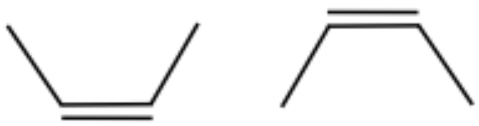
If you turn either one of the above structures upside down, it would be identical to the other. Note that in both structures, the alkyl substituents are on opposite sides of an imaginary line drawn along the double bond. Using the same argument, the two condensed structures of ***cis***-2-butene shown below are equivalent.



Both are *cis*-2-butene

This duality for drawing equivalent structural formulas also applies to ***skeletal structures***. The two equivalent methods for drawing both *trans*- and *cis*-2-butene skeletal structures are shown below.

Both are *trans*-2-butene



Both are *cis*-2-butene

Keep this point in mind when checking your answers to problems; you may have the correct structure/answer, but drawn upside down from how it is shown in the key.

Review 4.34: Geometric Isomerism in Alkenes

Draw the condensed **and** skeletal structures for each of the following molecules.

a) *trans*-2-pentene

b) *cis*-2-pentene

c) *trans*-3-hexene

d) *cis*-3-hexene

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

Alkynes

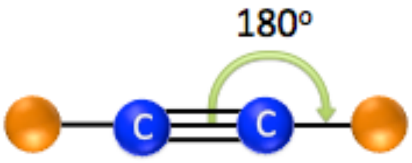
Alkynes are hydrocarbon molecules that contain ***at least one carbon-carbon triple bond***. Like the alk*enes*, they are unsaturated hydrocarbons. Alkenes are also referred to as **olefins**.

Naming Alkynes

Alkynes are named in the same way as you did for alkenes; the only difference is that we use the "**yne**" suffix instead of the"**ene**" suffix.

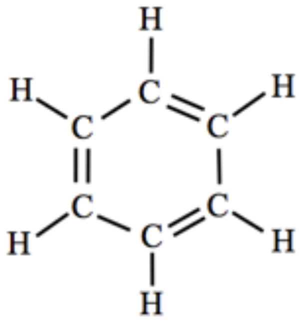
Alkyne Molecular Geometry

Alkynes involve a triple bond and the bond angles around the triple-bonded carbons are 180° as illustrated below. Each of the triple-bonded carbons can have only one other group single bonded to it (octet rule) and **this AB_2 geometry <u>cannot</u> result in geometric (*cis/trans*) isomers.**

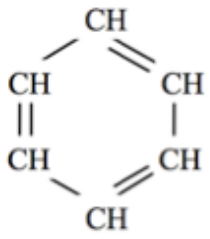


Aromatic Hydrocarbons

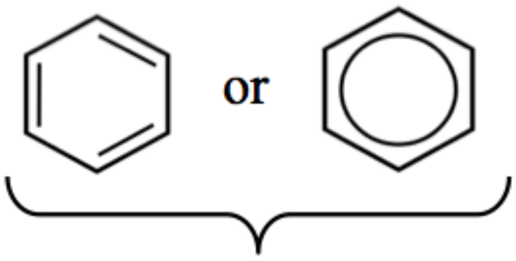
The fourth and final class of hydrocarbons are the ***aromatic hydrocarbons***. Aromatic hydrocarbons can be identified based on their structural formulas; they have alternating single and double bonds between the carbons that form the ring. Aromatic hydrocarbons are found in oil, coal, and tar deposits. The smallest and simplest aromatic hydrocarbon that occurs is called benzene. The line bond, condensed, and skeletal formulas of benzene are shown below.



Line Bond Structure



Condensed Structure

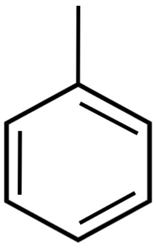


Skeletal Structures

Notice that there are ***two ways*** to draw the *skeletal formulas* for aromatic ring formulas; drawing a circle inside the ring is a shortcut used to indicate alternating single and double bonds in the ring-carbons.

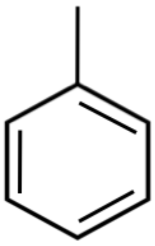
Naming Aromatic Hydrocarbons

Aromatic hydrocarbons are named using the same method that you used for cycloalkanes; the ring structure is the parent chain. In this text, we will limit our naming of aromatic hydrocarbons to benzene and benzene rings with substituents. For example, the *common name* for the molecule on the right is toluene, the systemic name is ***methylbenzene***. As was the case for cycloalkanes, we do not need to use a position number when there is only one substituent bonded to a ring structure.

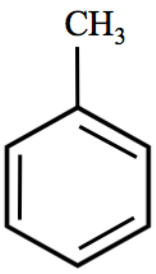


Methylbenzene

Note that sometimes book and journal authors combine (*hybridize*) skeletal and condensed structures when drawing cyclic compounds. Compare the skeletal and the skeletal/condensed hybrid structures shown below.



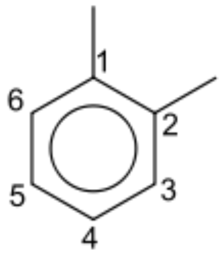
Skeletal



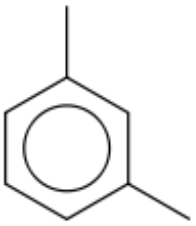
Skeletal/Condensed Hybrid

If you are using an online problem system and the question specifies a particular structure (i.e. line bond, condensed, skeletal), the auto-grader may not accept the hybrid as a correct response.

When cyclic compounds have *more than one substituent,* position numbers are included (you did so for cycloalkanes) as shown in the three dimethylbenzene *constitutional* isomers below:



1,2-dimethylbenzene
(*ortho*-xylene)



1,3-dimethylbenzene
(*meta*-xylene)

1,4-dimethylbenzene
(*para*-xylene)

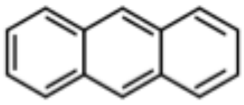
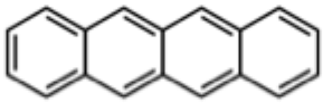
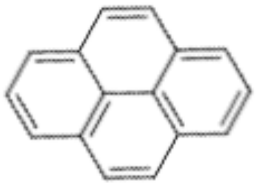
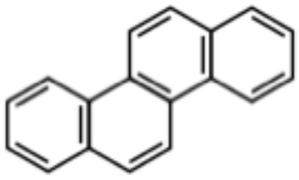
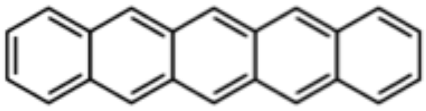
The common names are shown in parenthesis under the systemic names. Note that when substituents are at positions number 1 and 2, then "***ortho-***" is used as a *prefix* in the common names; when substituents are at positions number 1 and 3, then "***meta-***" is used; "***para-***" is used for substituents at positions number 1 and 4.

Some cyclic compounds have **fused rings**. Fused rings occur when neighboring rings *share carbon atoms*. For example, naphthalene, *shown below*, is an aromatic hydrocarbon that consists of ***two fused rings***. The shared carbon atoms are highlighted red.

Naphthalene

Aromatic hydrocarbons that contain fused rings are called **polycyclic aromatic hydrocarbons (PAHs)**. Some of the other PAHs are shown in Table 4.12.

Table 4.12 PAH Structures

Number of fused rings	Skeletal Structure	Name
3		Anthracene
4		Tetracene
4		Pyrene
4		Chrysene
5		Pentacene

Download this worksheet for more practice naming unsaturated hydrocarbons and drawing and identifying *cis* and *trans* compounds: http://www.zovallearning.com/GOBlinks/ch4/NamingandDrawingAlkenes.pdf

Physical Properties of Hydrocarbons

Hydrocarbons contain only nonpolar covalent bonds, therefore they are *nonpolar molecule*s. The ***only*** *noncovalent interaction* through which hydrocarbons can interact with each other is the *London dispersion force*. Recall that the larger the molecule, the greater the strength of attraction from London dispersion forces. For this reason, the boiling points of hydrocarbons increase as the length of the hydrocarbon increases. This trend in boiling point can be seen for some alkanes in Table 4.13.

Table 4.13 Boiling Points of Some Alkanes

Molecule Name	Condensed Structure	Boiling Point (°C)
methane	CH_4	-164
ethane	CH_3CH_3	-89
propane	$CH_3CH_2CH_3$	-42
butane	$CH_3CH_2CH_2CH_3$	0
pentane	$CH_3CH_2CH_2CH_2CH_3$	36

Since hydrocarbons are *nonpolar* molecules, they are not attracted to water through any of the noncovalent interactions other than London dispersion forces. Furthermore, since water is a small molecule, it can only interact *weakly* through London dispersion forces. For these reasons, hydrocarbons do not significantly mix (dissolve) in water. Another way to say this is that it is lower in energy for water molecules to be surrounded by water molecules than by hydrocarbons (and vice versa).

4.10 Functional Groups

A **functional group** is an ***atom*****,** ***group of atoms*****, or** ***bond*** that gives a compound a particular set of physical and chemical properties. Organic compounds are categorized into various **families** by the functional group(s) that they contain. You have already seen a couple examples of organic molecule ***families*** defined by the *type of carbon-carbon* ***bond present***. When a carbon-carbon double bond (*functional group*) is present, the molecule is assigned to the *alkene* family. In the case of a carbon-carbon triple bond, we assigned the molecule to the *alkyne* family. There are several families of organic compounds that you will encounter in this book. As an introduction to functional groups and families of organic compounds, in this section, I will introduce you to three organic families: alcohols, carboxylic acids, and esters. Each of these *families* is characterized by the presence of a distinct *functional group*.

1) The Alcohol Family

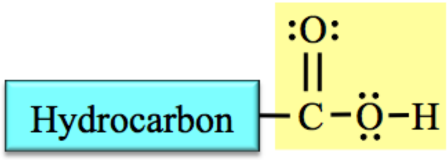
Alcohols contains one or more **hydroxyl (-OH)** functional groups attached to a ***hydrocarbon*** part. The general form of an alcohol is shown below with the hydroxyl group highlighted in yellow.

A specific example of an alcohol is ethanol. Ethanol is quite well known for being produced when carbohydrates, with the help of enzymes present in yeast, are used to make to beer, wine, and distilled adult beverages. You will learn more about alcohols, carbohydrates, and enzymes in later chapters. The condensed structural formula for ethanol is shown below.

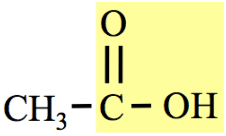
$$CH_3CH_2-OH$$

2) The Carboxylic Acid Family

Carboxylic acids contain a ***carboxyl functional*** group attached to a hydrocarbon part. Carboxyl groups contain <u>both</u> a ***carbonyl group***, which is a carbon double bonded to an oxygen **(C=O)**, ***<u>and</u>*** a hydroxyl group **(-OH)** that are connected to each other and to the hydrocarbon part as shown below. The carboxyl group is highlighted in yellow.



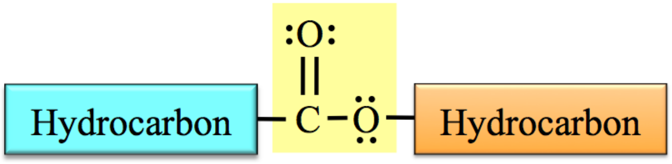
A specific example of a carboxylic acid is *acetic acid*. White vinegar is a mixture composed of 95% water and 5% acetic acid. You will learn about acids in chapters 8 and 9. The condensed structural formula for *acetic acid* is shown below.



$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-OH$$

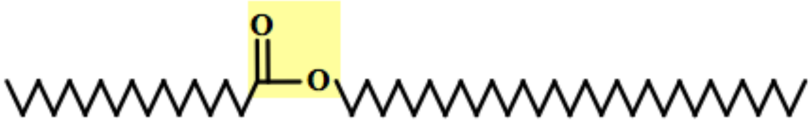
3) The Ester Family

Esters contain a ***carboxylate functional*** group that is bonded <u>between</u> ***two*** hydrocarbon parts. ***Carboxylate groups*** contain both a ***carbonyl group*** **(C=O)**, ***<u>and</u>*** an ***oxygen atom*** that are connected to each other as shown below in the yellow highlighted box.

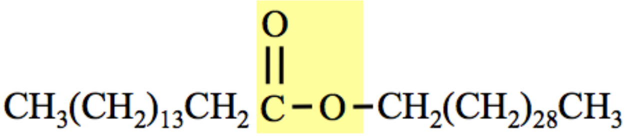


The boxes that represent each hydrocarbon part are shaded with different colors because the two hydrocarbon parts *are not always identical*.

Waxes are examples of esters. Waxes are produced in plants and animals; they are esters with relatively large hydrocarbon parts. The *skeletal* structural formula for one of the esters found in beeswax is shown below.



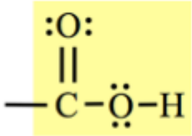
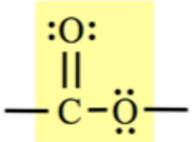
A shortcut can be used when drawing *condensed structures* of large molecules such as the ester shown above. Neighboring -CH_2- groups can be further condensed in parenthesis as shown below:



$$CH_3(CH_2)_{13}CH_2\overset{\overset{O}{||}}{C}-O-CH_2(CH_2)_{28}CH_3$$

A summary of the organic families and functional groups is given in Table 4.14.

Table 4.14
Some Organic Families and their Functional Groups

Organic Family	Functional Group	Description
Alkene	$C{=}C$ carbon-carbon double bond	Hydrocarbon with one or more ***carbon-carbon double bonds***.
Alkyne	$C{\equiv}C$ carbon-carbon triple bond	Hydrocarbon with one or more ***carbon-carbon triple bonds.***
Alcohol	-OH hydroxyl group	One or more hydroxyl groups bonded to a hydrocarbon
Carboxylic Acid	 $-\overset{\overset{:O:}{\|\|}}{C}-\ddot{\underset{..}{O}}-H$ carboxyl group	Carboxyl group bonded to a hydrocarbon
Ester	 $-\overset{\overset{:O:}{\|\|}}{C}-\ddot{\underset{..}{O}}-$ carboxylate group	Carboxylate group bonded ***between*** two hydrocarbons

Chapter 5

Solids, Liquids, and Gases

Icebergs in Antarctica.
Source: Wikimedia Commons US-PD, Author: Dave Moble

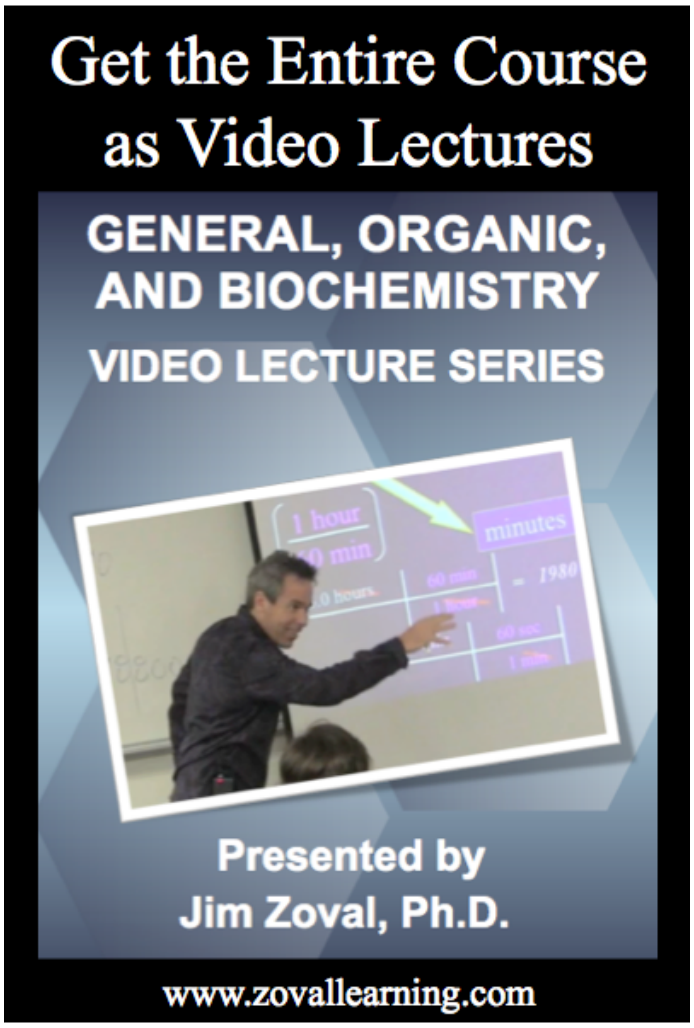
So far, you have learned about the underlying, nanometer scale, structure of matter. In chapter 5, you will use your new understanding of matter's nano-scale structure to better understand the macro-scale properties of the world that you can observe directly.

We defined chemistry as ***the study of matter and how it interacts with energy and with other matter***. In the previous chapters, you developed a model of matter. You learned that atoms consist of protons, neutrons, and electrons. You learned how these subatomic particles arrange themselves when they form atoms. Then you saw how atoms can combine to form ionic or covalent compounds. You learned how molecules and ions interact with each other through noncovalent interactions (hydrogen bonding, dipole-dipole forces, London forces, ion-dipole interactions, and salt bridges). In chapter 5 you will learn about *how matter interacts with energy*. I will begin this chapter by discussing three phases of matter: solid, liquid, and gas. Throughout this chapter, I will elaborate on the characteristics and properties of the three phases of matter.

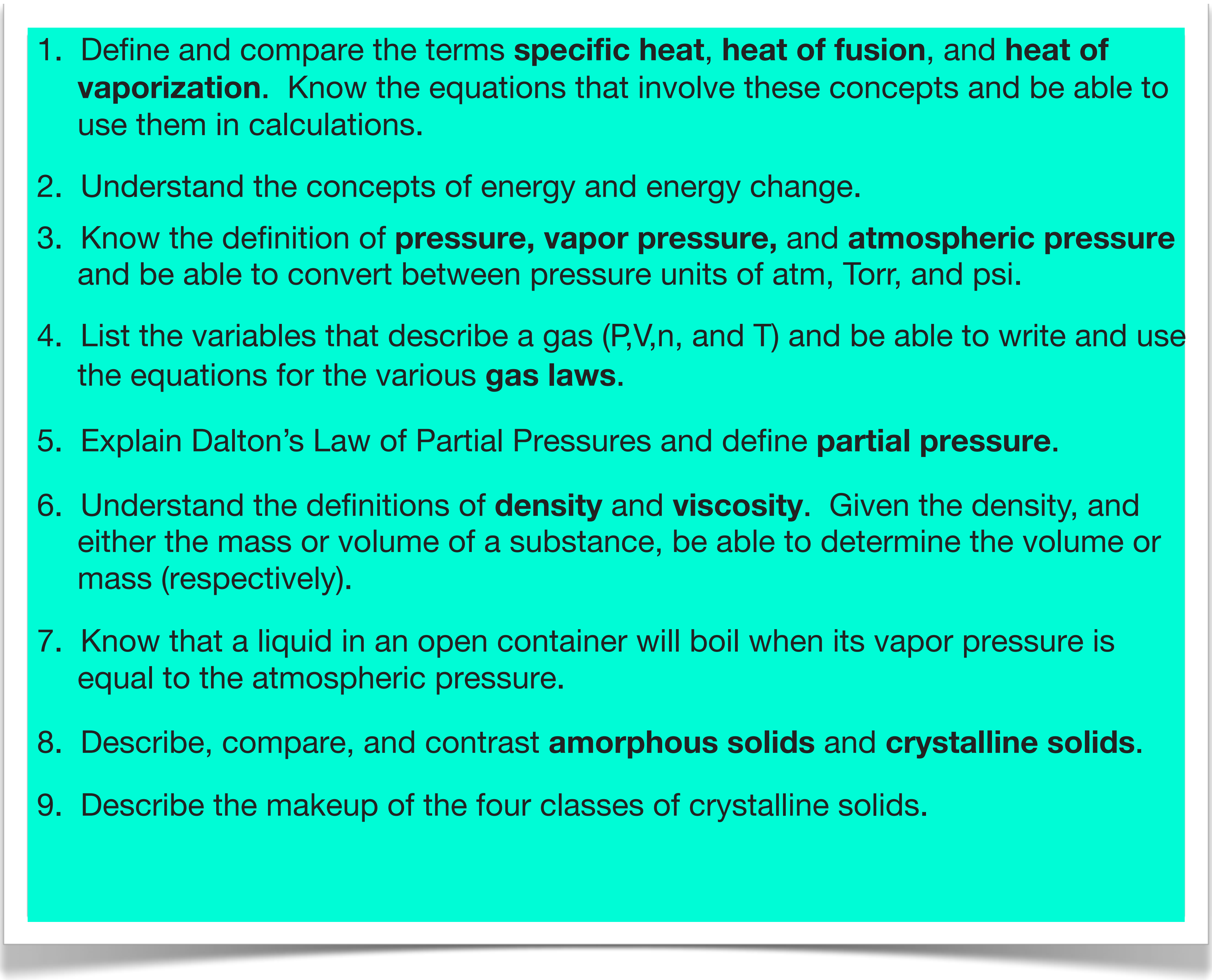
Video Lectures for the General, Organic, and Biochemistry Course

If you **ARE** a **Saddleback College student**, the video lectures for this chapter and all others are available through your class website for ***FREE***. See your instructor for details and the password.

If you **ARE NOT** a **Saddleback College student,** the video lectures can be accessed at: www.zovallearning.com



5.1 Chapter 5 Educational Goals



1. Define and compare the terms **specific heat**, **heat of fusion**, and **heat of vaporization**. Know the equations that involve these concepts and be able to use them in calculations.
2. Understand the concepts of energy and energy change.
3. Know the definition of **pressure, vapor pressure,** and **atmospheric pressure** and be able to convert between pressure units of atm, Torr, and psi.
4. List the variables that describe a gas (P,V,n, and T) and be able to write and use the equations for the various **gas laws**.
5. Explain Dalton's Law of Partial Pressures and define **partial pressure.**
6. Understand the definitions of **density** and **viscosity**. Given the density, and either the mass or volume of a substance, be able to determine the volume or mass (respectively).
7. Know that a liquid in an open container will boil when its vapor pressure is equal to the atmospheric pressure.
8. Describe, compare, and contrast **amorphous solids** and **crystalline solids.**
9. Describe the makeup of the four classes of crystalline solids.

5.2 Matter and Energy

Matter is typically found in one of three different physical ***phases***. These three phases of matter are: solid, liquid, and gas. At a given temperature, ***solids*** have fixed shapes and volumes, ***liquids*** have variable shapes and fixed volumes, and ***gases*** have variable shapes and volumes. A fourth, higher energy phase of matter that does not naturally occur at temperatures on earth is called the plasma phase. A plasma is similar to a gas, however it is composed of ions and unbound electrons. The solid, liquid, and gas phases are illustrated in Figure 5.1.

Figure 5.1 Three Phases of Matter

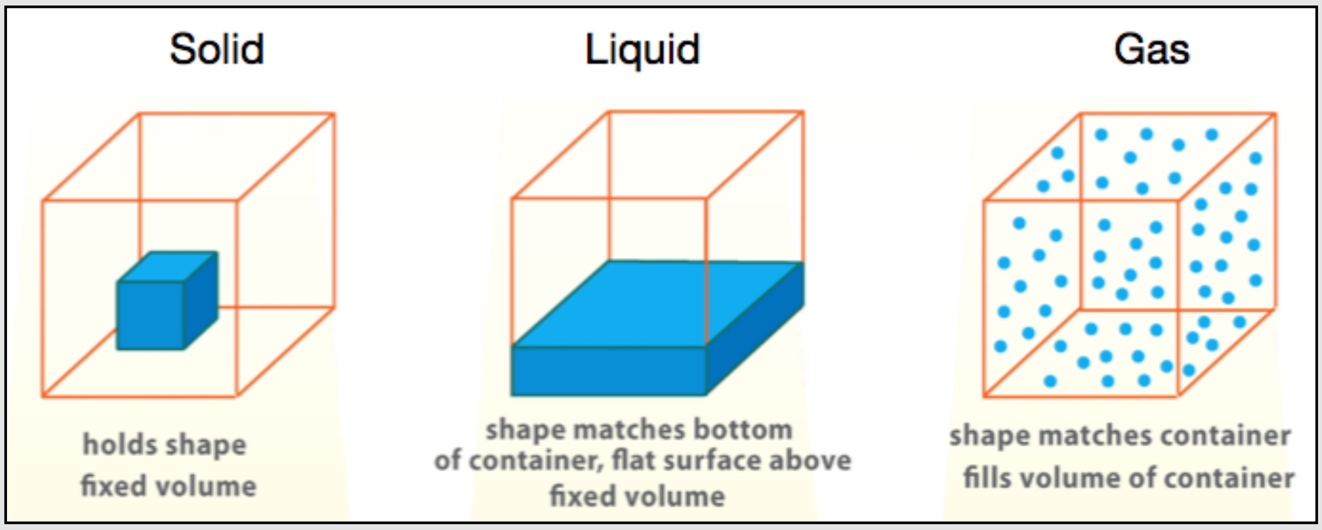


Illustration of the solid, liquid, and gas phases and the description of the various phases.
Source: Wikimedia Commons PD-USGOV-NASA

Changing the phase of matter, that is, converting matter between solid, liquid, and gas phases is considered a ***physical change*** because the chemical composition **does not** change. Examples of phase changes are: freezing water to make ice, boiling water to make steam, and melting an iron rod. In order for a substance to change phases and/or temperature, energy must be added or removed from the substance. Before we discuss the energetics of temperature and phase changes, let's consider what energy is and how chemical compounds can gain, lose, or store energy.

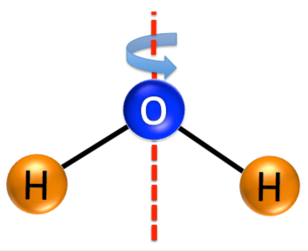
Energy

Energy is most often defined as *the ability to do work*. Any time that matter is changed (physical or chemical change), work has been done. Energy can be found in two forms, **potential energy** and **kinetic energy**. ***Potential energy*** is stored energy; it has the *potential* to do work. An example of potential energy is the energy that is stored in the chemical bonds of propane. Consider propane fueled barbecues. If propane is mixed with the oxygen molecules in air and a spark is applied, a process called combustion uses the energy that was stored in propane molecules to generate heat. In this example, some of the potential energy in the propane and oxygen molecules is converted to the *kinetic energy* (motion) of the CO_2 (g) and H_2O (g) that are produced in the combustion process. ***Kinetic energy*** is *the energy of motion*. Whenever matter is moving, it has kinetic energy. Kinetic energy can be thought of as the energy of the **motion of atoms or ions.** Furthermore, you can think of **temperature** as being a measure of how fast the atoms, ions, or molecules in a substance are moving.

More Kinetic Energy = More Atomic Motion = Higher Temperature

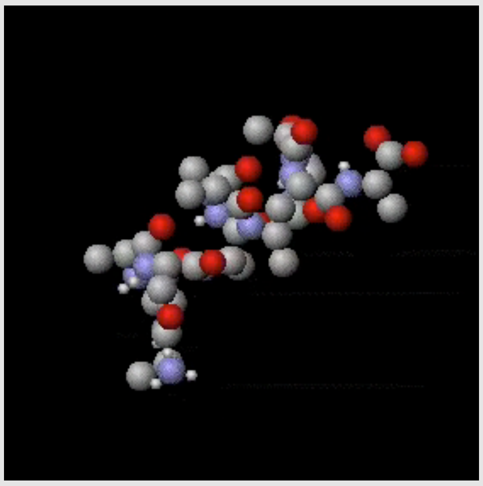
Keep in mind that although a substance is in the liquid or solid phase, the atoms within are moving. In the gas phase, it is easy to imagine the moving particles. Gas particles will move in almost perfectly straight lines until they collide with other particles or with the container walls. In liquids, the particles are much closer to each other than in gases, therefore the particles are colliding with other particles much more often than the particles in a gas. In chapter 3, I mentioned that a chemical bond between two atoms behaves like a spring connecting the atoms as illustrated to the right. Imagine hitting the molecular model on the right with a hammer and seeing the atoms and spring vibrate. Since the atoms are vibrating, they are moving, the higher the temperature, the faster the atoms move. So, unless a chemical compound has *zero energy* (which is impossible in this universe) the compound will always have some energy in atomic vibrations. If a solid compound is at a *high temperature*, the atoms are

Figure 5.2 Molecular Rotation



vibrating at *high speeds*. If you touch this hot solid, the vibrating atoms will collide with the atoms that make up the compounds in your skin, causing the atoms in your skin to start vibrating at higher speeds, and you experience this as feeling "hot" or "getting burned." If the vibrating atoms in the solid transfer enough energy to the skin, chemical bonds can be broken and a burn injury occurs. When chemical bonds are broken, you can think of that as breaking the tiny springs holding the atoms together. We call this a chemical reaction; you will learn about chemical reactions in chapter 6. Another way that molecular substances contain kinetic energy in the motion of atoms is by spinning (rotating). For example, water molecules can spin/rotate around an axis as shown in Figure 5.2. The higher the temperature, the faster the spinning motion. Microwave ovens heat food because microwave electromagnetic radiation interacts with the electric dipole of water molecules causing the water molecules to spin faster. In the case of large molecules, in addition to the entire molecule spinning around an axis, kinetic energy can be present in the rotation of groups of atoms around single bonds (conformational changes). For those of you who are using an ***i-books*** version of this book, the combined motion from vibration and rotation around single bonds is shown in Movie 5.1 for a large (protein) molecule. You will learn about protein molecules in chapter 13. For **print or pdf versions** of the book, the movie can be seen at: http://www.zovallearning.com/streamvid/bond-vibration-and-rotation.html.

Movie 5.1 Vibration and Rotations Around Single Bonds in a Large Molecule



In large molecules, kinetic energy is also present in the vibration of bonds and the rotation of groups of atoms around single bonds (conformational changes).
Source: Wikimedia Commons, Author: Greg L. CC-BY-SA, http://creativecommons.org/licenses/by-sa/3.0/legalcode

Energy Changes

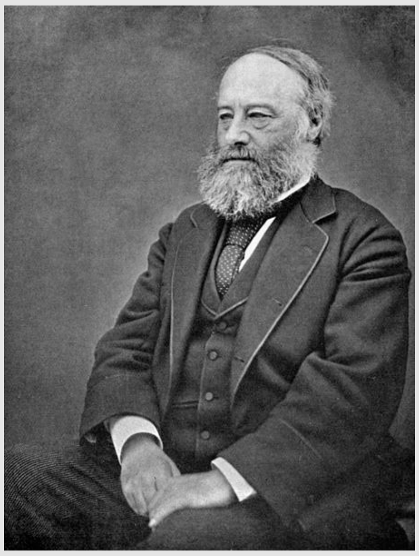
As you know, if you take an ice-cube out of your freezer and put it on your kitchen counter, the ice will warm up. As the ice sits on the counter, it will slowly get warmer (change temperature) because the kitchen is warmer than the freezer. How does this happen? The air molecules in the room and the molecules on the kitchen counter surface are at a higher temperature than the ice. This means that the atoms in the air and counter are *moving faster* than the atoms in the water molecules. As the air molecules collide with the ice molecules, they transfer kinetic energy to the atoms in the ice. Likewise, the atoms in the counter surface collide with and transfer kinetic energy to the atoms in the ice. As kinetic energy is transferred to the ice through collisions, the atoms in ice vibrate faster, therefore the temperature of the ice is increasing. The ice is getting warmer. At some point, the ice will change phase from solid to liquid; we call this melting. Melting occurs when the *noncovalent interactions* holding the molecules in place are overcome by the kinetic energy. If the water (melted ice) is taken from the counter and placed in a pot and then heated above a gas burner, some of the kinetic energy (motion) of the CO_2 gas and H_2O gas that are produced in the combustion process would be transferred to the atoms of the pot, then from the atoms of the pot to the atoms in the water molecules. As the atoms in the water increase their speed/temperature, at some point, the water molecules will overcome the noncovalent interactions that are holding them together in the liquid phase. The liquid would change to gas; we call this boiling.

It is the ***noncovalent interactions*** that hold molecules together such that they exist in the solid or liquid phase instead of the gaseous phase. Whether a molecular compound exists in the gas, liquid, or solid phase is determined by a competition between noncovalent interactions (working to keep the molecules close to one another) and temperature (kinetic energy working to distribute the molecules evenly in the container). If the noncovalent interactions are dominant, then the substance will exist in the solid or liquid phase; if the temperature/kinetic energy can overcome the noncovalent interactions, then the substance will exist in the gaseous phase.

Units of Energy

Energy is ***not*** something that can be directly measured. For example, we calculate the energy of a moving object *by measuring its velocity*. We have thermometers to measure temperature, but there is no such thing as an "energometer." Classic, non-electronic thermometers work because the liquid (often mercury or colored-alcohol) in the bulb and the tube expands or contracts as the temperature increases or decreases. Upon an increase in temperature, expansion of liquid in the bulb causes an observable increase in the liquid level of the tube. The opposite process and observation happens for a decrease in temperature. In electronic (thermocouple, RTD, and thermistor) thermometers, the electrical current passing through the materials that compose their probe depends on temperature. These devices are calibrated so that the displayed temperature is related to the measured electrical current (amperes). Optical (infrared) thermometers operate by measuring the amount of infrared (IR) light that is emitted from an object. The amount of IR light that an object emits depends on the object's temperature.

Figure 5.3
James Joule



James Prescott Joule (1818-1889) was a physicist and brewer. He worked with Lord Kelvin to discover the absolute scale of temperature. The SI energy unit was named in his honor.

Source: PD

The *two energy units that you will use in this textbook* are the **calorie (cal)** and the **Joule (J)**. The word "*calorie*" is derived from the Latin word "*calor,*" which means *heat*. The Joule was named in honor of the English physicist and brewer, James Prescott Joule (Figure 5.3) who, along with Lord Kelvin, developed the Kelvin absolute temperature scale.

Since energy is measured indirectly, energy units are defined based on measurements of quantities, such as temperature and electricity. For example, the ***calorie*** energy unit is defined as the amount of energy required to raise the temperature of *one gram* of water by 1 °C. The ***Joule*** energy unit is defined as the amount of energy required to pass a certain amount of current through a material with a certain resistance for a period of one second. The scientific community standardized these two measurements using the agreed upon conversion factor that **1 cal is equal to *exactly* 4.184 J.** Recall that "exactly" or agreed upon conversion factors have an infinite number of significant figures. Now that you know the conversion factor, you should be able to convert between calorie and Joule energy units.

Example: Convert 60.1 calories to Joules

We do this conversion just like we did all the other conversions in earlier chapters.

- Since we know the relationship between calories and Joules (1 cal = 4.184 J), we can use this equivalence statement as a conversion factor.

$$\begin{array}{c|c|} 60.1\,\cancel{\text{cal}} & 4.184\text{ J} \\ \hline & 1\,\cancel{\text{cal}} \end{array} = 251\text{ J}$$

- We have 3 significant figures in the given amount of calories and since the relationship between Joules and calories is exact, there are an infinite number of significant figures in the conversion factor. Therefore the answer has 3 significant figures.

Review 5.1: Convert between Joules and calories.

Convert 78 Joules to calories.

For ***i-book*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

Food "Calories" vs. "calories"

One more note on energy units. We are all familiar with nutritional labeling of food. Note that nutritionists use the "food **C**alorie" notation with capital "C" in the spelling and unit. A food "**C**alorie" is equal to 1000 calories (1 Cal = 1000 cal). Another way to say this is: a food Calorie is equal to a kilocalorie (1 Cal = 1 kcal). An apple contains about 120 Cal (120,000 cal). This is about equal to the amount of energy required to bring six cups of water from room temperature to boiling.

Nutrition Facts
Serving Size 1 cup (228g)
Servings Per Container 2

Amount Per Serving

Calories 250 Calories from Fat 110

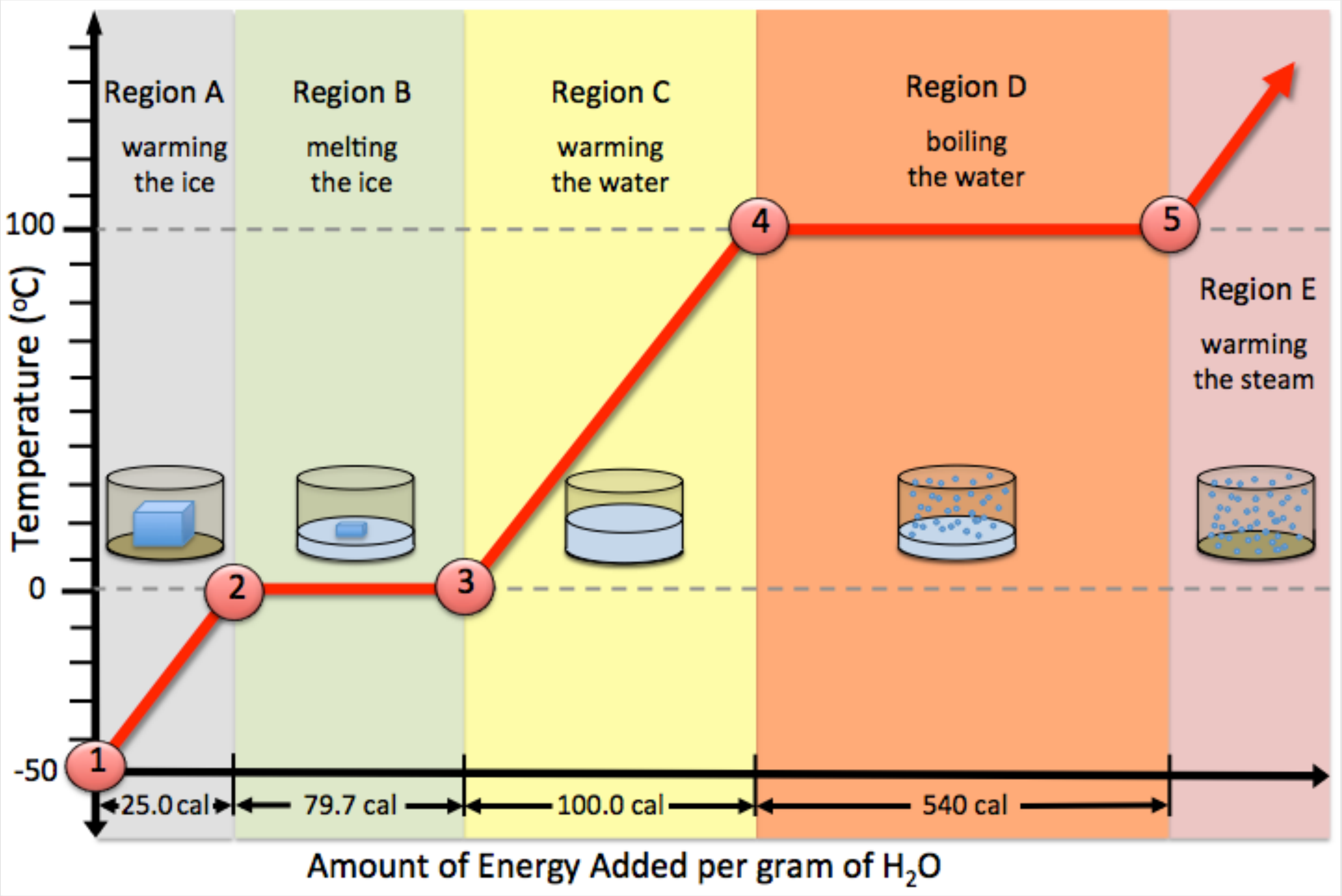
Temperature Changes and Phase Changes

Heat can be defined as the amount of energy that is ***transferred to or from*** matter in order to change its temperature and/or phase. When energy is added to, or removed from matter, one of these two *physical changes* may occur:

1) A change of **temperature**.
2) A change of **phase.**

Consider what happens when energy is added to ice that is originally at -50 °C. In this hypothetical situation, the ice is placed in a *closed container* and the container is put into a hot oven. Figure 5.4 is a graph that plots the temperature of a substance as energy is transferred to the substance. The temperature dependence on the amount of energy added is plotted as red lines.

Figure 5.4 **Temperature of H_2O in a Closed Container as Energy is Added**



Graph of temperature of H_2O in a closed container vs. the amount of energy added. The energy (cal) values shown below the horizontal axis are the amount of energy added per gram of H_2O. The H_2O begins as ice that is originally at -50 °C. In this hypothetical situation, the ice and container are put into a hot oven. The temperature vs. energy added is plotted as red lines.

Note that the red line(s) begin at ***Point #1*** at a temperature of -50 °C. Next, as energy is transferred from the warm air in the oven to the ice, the ice begins to change temperature (warm). This process occurs in ***Region A*** in the figure. The ice continues to warm until it reaches 0 °C, its melting point, at ***Point #2*** in the figure. After this point, although energy is still being transferred to the melting ice, *the temperature no longer changes*! The added energy is going into *breaking the intermolecular forces* that are holding the H_2O molecules in their crystal lattice positions. This process occurs in ***Region B*** of the figure. After some time passes, the last bit of the ice crystal melts (***Point #3*** in the figure). There is now only water in the container and the energy from the oven begins to change the temperature of the water. This warming of the water occurs in ***Region C*** of the figure. The temperature of the water continues to rise until the water reaches its boiling point (100°C, ***Point #4*** in the figure). Beginning at this point in time, the energy transferred from the oven goes into breaking the intermolecular forces that are holding the water molecules near each other, thereby changing the phase of H_2O from liquid to gas (***boiling***). The temperature remains at 100 °C until the last bit of water is evaporated. This occurs in ***Region D*** of the figure. After the last bit of water is converted to gas, the energy transferred from the oven will increase the H_2O vapor (gas). This occurs in ***Region E*** of the figure. Since the container is closed and gas does not escape, the gas continues to get warmer until it reaches the temperature of the oven. Notice that H_2O vapor can become extremely hot, much hotter than the boiling point of water. It is for this reason that you must be careful when opening sealed containers that were heated in microwave ovens; you can get severely burned by the extremely hot vapor. It would require much more energy than can be supplied by an oven to *break the **covalent bonds*** holding the hydrogen atoms to the oxygen atom. It is possible to break those covalent bonds with high energy lasers.

I will discuss calculations that involve either ***temperature changes*** or ***phase changes***. Let's begin with ***temperature changes***.

Calculations Involving Temperature Changes

In the purest sense, **energy** is a quantity that can only be zero or have ***positive*** values. Consider light; there can be either no light, or some light; ***the idea of a negative amount of light makes no sense***. The same is true for energy, however the scientific community agreed that energy added to a substance is assigned ***positive values***, and that energy removed from a substance is assigned ***negative values***.

The amount of heat that needs to be added or removed to cause a specific temperature change varies from substance to substance and is ***determined experimentally*** for each substance. The amount of energy that must be added (or removed) from ***one gram*** of a substance to result in a temperature change of **one °C** is called the substance's **specific heat**. We use the symbol "**S**" to represent specific heat. Since specific heat is the amount of ***energy*** transferred per ***one gram*** and ***per 1 °C*** temperature change, its units will be either **cal/(g•°C)** or **J/(g•°C)**. Another term used for ***specific heat*** is *heat capacity*. Specific heats (**S**) for various substances are listed in Table 5.1.

Table 5.1 Specific Heats for Various Substances

Substance	Specific Heat (S)
Water (H_2O liquid)	1.000 cal/(g°C)
Ice (H_2O solid)	0.500 cal/(g°C)
Steam (H_2O gas)	0.480 cal/(g°C)
Ethanol (liquid)	0.586 cal/(g°C)
Copper (solid)	0.0925 cal/(g°C)
Aluminum (solid)	0.0215 cal/(g°C)
Gold (solid)	0.0310 cal/(g°C)

There exists a mathematical relationship between the amount of energy transferred (heat) ***to <u>or</u> from*** a substance and the resulting temperature change. The relationship between the energy added or removed from a substance and how much its temperature changes is:

$$\mathbf{Q = S \cdot m \cdot (\Delta T)} \qquad \textit{Equation 5.1}$$

In this equation, the symbol "**Q**" is used to represent the energy transferred (or heat); ***note that heat is energy, not temperature***! "**S**" is the specific heat of the substance and "**m**" is the mass of the substance. We will use the term "**(ΔT)**" for the amount of the ***change in temperature*** (in °C units), that occurs when the energy is added or removed from the substance. In science, the Greek letter "**Δ**" is very often used as the phrase "*change in*."

To be consistent with the convention of assigning positive energy values for energy added to a substance and negative energy values for energy removed from a substance, (**ΔT**) is always defined as the final temperature minus the initial temperature ($\Delta T = T_{final} - T_{initial}$). Note that if energy is ***added to a substance*** and a temperature change occurs, the final temperature will always be ***greater than*** the initial temperature and therefore **ΔT** ($= T_{final} - T_{initial}$) would be ***positive***. In *Equation 5.1*, the mass (**m**) and specific heat (**S**) are both *always* positive, therefore when **ΔT** is also positive, the calculated energy (**Q**) will be ***positive***. On the other hand, if energy is ***removed from a substance*** and a temperature change occurs, the final temperature will always be ***less than*** the initial temperature and **ΔT** ($= T_{final} - T_{initial}$) will be ***negative***; in this case the energy (**Q**) calculated using *Equation 5.1* will be ***negative***.

- **Positive energy values** indicate that energy was ***transferred to a substance***.
- **Negative energy values** indicate that energy was ***removed from a substance***.

I will show you a couple of examples of ***calculations that involve temperature changes***, then ask you to try a few on your own.

Example: How much energy (calories) is required to be added to 7.00 grams of water that is initially at 37.0°C in order to raise the temperature to 65.0 °C?

Solution: The relationship between the temperature change, mass of an object, and transferred energy is given by *Equation 5.1*:

$$\mathbf{Q = S \cdot m \cdot (\Delta T)}$$

- We wish to solve for **Q** (amount of energy transferred to the water). In order to do so, we must know the values of the specific heat (**S**), the mass of water (**m**), and (**ΔT**).
  - Specific heat values (**S**) are determined experimentally and tabulated for reference. Table 5.1 lists the specific heat of water as (1.000 cal/g°C).
  - Note that it is not a coincidence that the specific heat of water has the value of 1.000 cal/g°C because that is how the calorie unit was ***defined***; the amount of energy needed to raise the temperature of ***one gram*** of water by ***1°C***.
  - The mass of water in this problem is **7.00 grams**.
  - The ***change in temperature*** of the water ($\Delta T = T_{final} - T_{initial}$) = (65.0 °C - 37.0 °C) = **28.0 °C**.
- These values (S, m, and ΔT) are used in Equation 5.1 to calculate the energy (Q).

$$\mathbf{Q = S \cdot m \cdot (\Delta T)}$$

$$\mathbf{Q} = \left(\frac{1.000\text{ cal}}{\cancel{\text{g}}\ \cancel{^\circ\text{C}}}\right)(7.00\ \cancel{\text{g}})\ (28.0\ \cancel{^\circ\text{C}}) = \mathbf{196\ cal}$$

  - Notice that grams and °C units *cancel*. Since the specific heat unit is (**cal/g°C)**, the calculated energy therefore has the unit of ***calorie***. Sometimes specific heats are tabulated with units of **(J/g°C)**; when this is the case, the calculated energy would have the unit of Joule (J).
  - There are four significant figures in the specific heat (**S**), and three significant figures in the mass and **ΔT**, so the answer has three significant figures.
  - The calculated energy value (196 cal) is consistent with the convention of assigning positive energy values when energy is transferred to a substance.

Example: Suppose that 3625 calories of energy is transferred to 245 grams of water that is originally at 22.4 °C:

a) What is the change in temperature (**ΔT**) of the water?
b) What is the final temperature (**T_{final}**) of the water?

Solution: The relationship between the temperature change, mass of an object, and transferred energy is given by *Equation 5.1*:

$$\mathbf{Q = S \cdot m \cdot (\Delta T)}$$

- In this problem, *we are not solving for the amount of energy transferred* (**Q**) to the water; we are given that quantity (3625 cal).
- We wish to solve for **ΔT** (the change in the temperature of the water).
  - We need to re-arrange *Equation 5.1* to solve for **ΔT**.
  - We do this by dividing both sides of the equation by (**S • m**):

$$\mathbf{\frac{Q}{S \cdot m} = \frac{\cancel{S} \cdot \cancel{m} \cdot (\Delta T)}{\cancel{S} \cdot \cancel{m}}}$$

- The specific heat (S) and mass (m) on the *right side* of the equation ***cancel*** to give the form of Equation 5.1 that is used to solve for **ΔT**:

$$\mathbf{(\Delta T) = \frac{Q}{S \cdot m}}$$

- In order to solve this equation, we must know the values of **Q**, **S**, and **m**.
  - Table 5.1 lists the specific heat (**S**) of water as (1.000 cal/g °C).
  - We were given *the amount of energy transferred* (**Q**) to the water (3625 cal) and the mass of the water (245 g).
  - The change in temperature is then calculated:

$$(\Delta T) = \frac{Q}{S \cdot m} = \frac{3625\ \cancel{\text{cal}}}{\left(\frac{1.000\ \cancel{\text{cal}}}{\cancel{\text{g}}\ ^{\circ}\text{C}}\right) 245\ \cancel{\text{g}}} = 14.8\ ^{\circ}\text{C}$$

Answer part (a): The ***change in*** temperature of the water (**ΔT**) = **14.8 °C**.

Answer part (b): Since the ***initial temperature*** of the water was 22.4 °C, and the water temperature ***changed by*** 14.8°C, we can get the ***final temperature*** of the water by adding 14.8 °C to 22.4 °C = **37.2 °C**.

Review 5.2: Calculations Involving Temperature Changes

a. How much energy (calories) is required to be added to 12.00 grams of ethanol that is initially at 24.0 °C in order to raise the temperature to 42.0 °C? (**NOTE:** You are warming *ethanol*, not water; see Table 5.1 for the specific heat of ethanol.)

b. How much energy must be added to 128 grams of ice that is initially at -54.0 °C in order to raise the temperature of the ice to its *melting point* (0.00 °C)? (**NOTE:** You are warming ***ice***, not water. The specific heat of ice is ***not** the same* as the specific heat of water. See Table 5.1 for the specific heat of ***ice.***)

c. How much energy must be removed from 584 grams of water that is initially at 22.0 °C in order to lower the temperature of the water to its *freezing point* (0.00 °C)?

d. Suppose that 1250 calories of energy transferred to water that was originally at 22.4 °C, raises the temperature of the water to 34.8°C. What is the ***mass*** (**m**) of the water that was heated? (HINT: Solve Equation 5.1 for mass (**m**).)

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

Phase Changes

Adding a sufficient amount of energy to liquids will overcome the noncovalent interactions holding the particles together to produce a gas; this phase change is called **boiling**. The reverse of this process, changing from gas to liquid, will occur if enough energy is removed from the gas; we call this **condensation**. *Adding* a sufficient amount of energy to solids will overcome the forces holding the molecules in place to form a liquid; this phase change is called **melting**. The reverse of this process, changing from liquid to solid, will occur if enough energy is removed from the liquid; we call this **freezing**. Under certain conditions, substances can be converted ***directly*** from the solid phase to the gas phase; we call this **sublimation**. You may have seen this with “dry ice” (solid CO_2 converting to gaseous CO_2 without forming liquid CO_2). Until now, I have discussed phase changes *qualitatively*, now I will discuss this concept *quantitatively.* **Qualitative** treatments involve ***non-numeric*** descriptions of concepts or systems. **Quantitative** treatments involve measuring and/or calculating ***numerical*** values.

Calculations Involving Phase Changes

The amount of energy required to ***melt* one gram** of a substance is called its **heat of fusion** (abbreviated as $\mathbf{H}_{fus}$). Heats of fusion for substances are determined *experimentally*. Each substance has a unique heat of fusion. For example, the heat of fusion for ice is 79.7 cal/g and the heat of fusion for gold is 15 cal/g. Since these values are the energy that is required to melt one gram of the substance, the units will be either cal/g or J/g. To do the opposite process, change from one gram of liquid to solid (freezing), the same amount of energy must be ***removed** from the substance*, and therefore the ***sign*** of the *heat of fusion value* must be changed from *positive* to *negative*. For example, the amount of energy needed to be *removed* from water in order to convert it to ice is: (**-H**$_{fus}$) = -79.7 cal/g.

The energy required to *convert* **one gram** of a substance from liquid to gas (by boiling) is called its **heat of vaporization** (abbreviated as **H**$_{vap}$). Like heats of fusion, heats of vaporization for substances are determined experimentally, vary from substance to substance, and are tabulated using energy units per gram. The heats of fusion and heats of vaporization for a few substances are listed in Table 5.2.

Table 5.2 Heats of Fusion and Heats of Vaporization of Some Substances

Substance	**heat of fusion** (**H**$_{fus}$)	**heat of vaporization** (**H**$_{vap}$)
H_2O	79.7 cal/g	540 cal/g
ethanol (ethyl alcohol)	26.05 cal/g	230 cal/g
2-propanol (rubbing alcohol)	21.37 cal/g	159 cal/g

The values listed in Table 5.2 are the amounts of energy needed to melt or vaporize ***one gram*** of a substance. We can use these values to calculate the energy needed to melt or vaporize any amount (mass) of the substance using *Equation 5.2,* below.

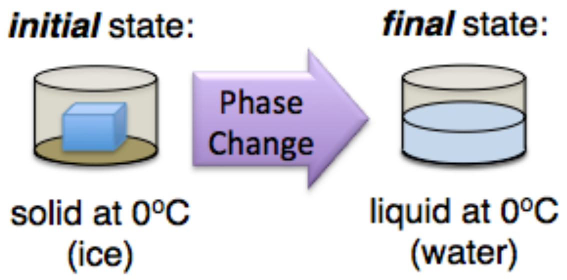
$$\mathbf{\Delta E} = (\text{mass}) \cdot (\mathbf{H}_{fus} \text{ or } \mathbf{H}_{vap})$$

Equation 5.2

In this equation, "**ΔE**" is the symbol for "**change in energy**." This is the amount of energy that was added to, or removed from the substance ***in order to change the phase***. **ΔE** is defined as the final energy of the substance (after phase change) ***minus*** its energy before the phase was changed ($\mathbf{\Delta E} = E_{final} - E_{initial}$). When using this equation, the unit for mass will be the gram (g) since the units for heats of fusion and vaporization in Table 5.2 are calories *per* ***gram***. I will elaborate on calculations involving phase changes by showing you some example problems.

Example: How much energy is required to melt 46.7 grams of ice that is originally at its melting point (0 °C)?

Solution: It is often useful to make a drawing of the process to be considered in a problem. For this problem, the drawing could look something like this:



- The energy required or released in a ***phase change*** can be calculated using *Equation 5.2*:

$$\mathbf{\Delta E} = (\textbf{mass}) \cdot (\mathbf{H}_{fus} \text{ or } \mathbf{H}_{vap})$$

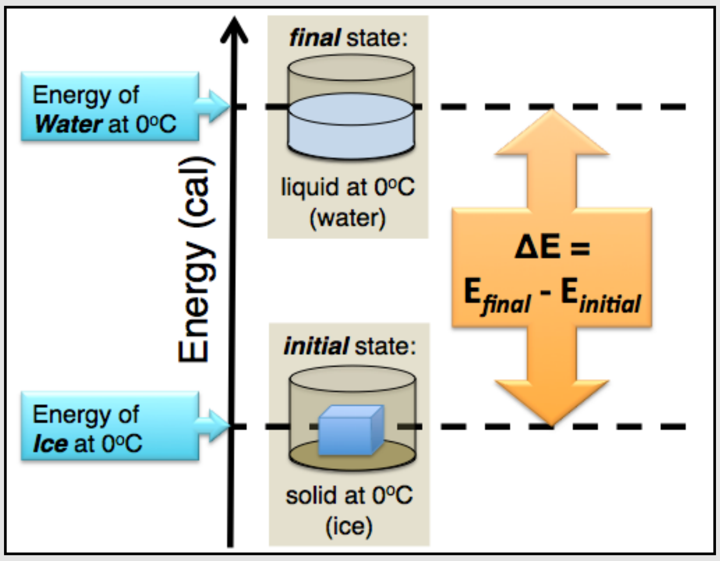
- Since we are interested in the phase change from *solid to liquid*, we use Table 5.2 to find the **heat of fusion** (abbreviated as **H**$_{fus}$) for H_2O. The heat of fusion for H_2O is **79.7 cal/g**. The **mass** of H_2O, **46.7 g**, was given in the question. Inserting these values into *Equation 5.2* gives:

$$\mathbf{\Delta E} = (46.7\ \cancel{\text{g}})\left(\frac{79.7\ \text{cal}}{\cancel{\text{g}}}\right) = \textbf{3720 cal} \quad \underline{\textbf{\textit{or}}}\ \ \mathbf{3.72 \times 10^3\ cal}$$

- There are three significant figures in the ***heat of fusion*** value. Since heats of fusion are determined *by experiment*, they ***are not exact values***. There are three significant figures in the mass. The answer, ΔE, must be rounded to three significant figures.
- It is important to understand that there was ***no change in temperature*** involved in *this* example problem. We began with ice at its melting point (0 °C), added 3720 cal of energy in order to convert it to water at 0 °C. If more energy were to be added at this point, the energy would begin to warm the water.

- Figure 5.5 illustrates the energy change involved in melting ice. Note that the calculated energy change (ΔE) is positive.
- In order to convert ice to water, energy must be added such that the noncovalent interactions holding the H_2O molecules in their ice crystalline lattice positions are overcome. That is why the energy of water at 0°C is at a higher level than the energy of ice in Figure 5.5.
- The definition of **ΔE** as being equal to the ***final*** energy ***minus*** the ***initial*** energy, for example in this problem $\Delta E = E_{final}\text{ (water)} - E_{initial}\text{ (ice)}$, is consistent with the convention of assigning *positive energy* values when energy is added to a substance and *negative energy* values when energy is removed from a substance.

Figure 5.5
Energy Levels of the Phase Change for Melting Ice



Example: Determine the amount of energy needed to be removed from 50.0 g of water that is originally at its freezing point (0 °C) in order to freeze it.

Solution: The energy required or released in a ***phase change*** can be calculated using *Equation 5.2*:

$$\mathbf{\Delta E} = \textbf{(mass)} \cdot (\mathbf{H}_{fus} \text{ or } \mathbf{H}_{vap})$$

- In this example, we are interested in the phase change from ***liquid to solid***. We use Table 5.2 to find the **heat of fusion** (abbreviated as $\mathbf{H}_{fus}$) for H_2O, **HOWEVER**, we must ***change the sign*** of $\mathbf{H}_{fus}$.
  - Since we are ***freezing*** (*liquid to solid)* as opposed to *melting,* as done in the last example problem, we are *removing energy* from water in order to solidify it into ice.
    - We use a *negative sign* with the heat of fusion ($-\mathbf{H}_{fus}$ = **-79.7 cal/g**).
  - The **mass** of H_2O, **50.0 g**, was given in the question.
- Inserting these values into *Equation 5.2* gives:

$$\Delta E = (\ 50.0\ \cancel{g}\ )\left(\frac{-79.7\text{ cal}}{\cancel{g}}\right) \;=\; \mathbf{-3990\ cal} \quad \underline{\textbf{\textit{or}}}\ \mathbf{-3.99 \times 10^3\ cal}$$

- There are three significant figures in the ***heat of fusion*** value. Since heats of fusion are determined *by experiment*, they ***are not exact values***. There are three significant figures in the mass. The answer, ΔE, must be rounded to three significant figures.
- The *negative value* of **ΔE** that was calculated in *this* example is consistent with the convention of assigning *negative energy* values when energy is removed from a substance.

Review 5.3: Calculations Involving Phase Changes

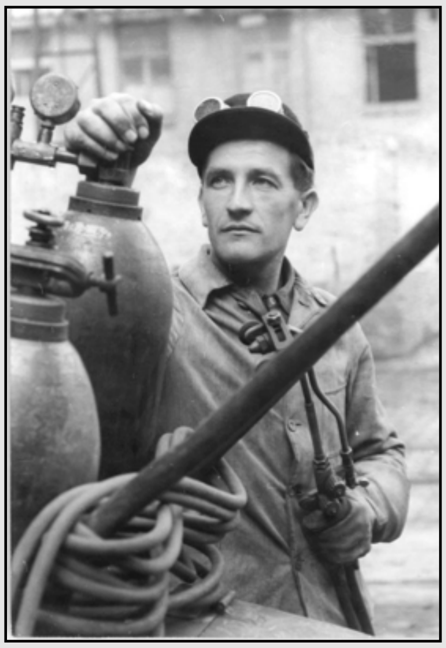
a. How much energy (calories) is required to convert 35 grams of water (originally at its boiling point, 100 °C) into steam?
   - **NOTE:** You are converting from liquid to gas, use the heat of vaporization ($\mathbf{H}_{vap}$) for H_2O. See Table 5.2 for heats of vaporization.

b. How much energy must be removed from 224 grams of liquid ethanol (originally at its freezing point) in order to solidify it? (Hint: you will need information from Table 5.2)

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

TO PRACTICE MORE TEMPERATURE AND PHASE CHANGE PROBLEMS SEE:
http://www.zovallearning.com/GOBlinks/ch5/wstempphasechangeworksheet.pdf

Figure 5.6 An Oxy-Fuel Welder



Oxy-Fuel welding is done by the combustion of two gases, 0_2 and a fuel gas (often acetylene). Source: Wikimedia Commons, Author: Bundesarchiv, Bild 183-26798-0003 / CC-BY-SA, http://creativecommons.org/licenses/by-sa/3.0/legalcode

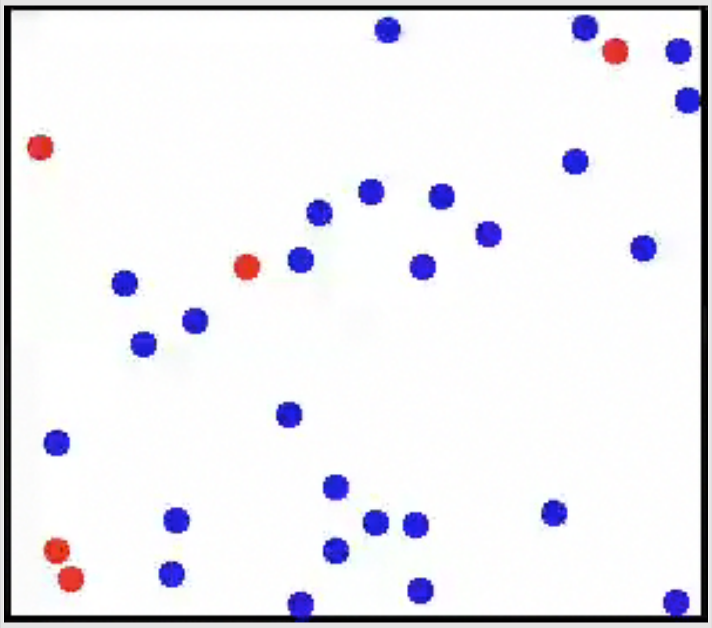
5.3 Gases and Gas Laws

Properties of Gases

Except for the noble gases (He, Ne, Ar, Kr, Xe, and Ra), gases are composed of molecules. Compared to liquids and solids, particles in the gas phase are *very far apart from one another*. It is for this reason that gases have *low densities*. Because of the relatively large distances between gas particles, most of the volume occupied by a gas is *empty space*. Another word used for empty space is ***vacuum***. Since a gas is mostly empty space, uncolored gases are invisible and colored gases are translucent (we can see light through them). Gases completely fill their container. In mixtures of gases (two or more types of gas particles), each gas is distributed evenly throughout the container (except for a few heavy, higher molecular weight gas molecules such as SF_6). Gaseous particles travel at high speeds in all directions and will mix with other types of gas particles in a process called **diffusion**. *Diffusion* is the movement of one substance within another substance until it is evenly distributed. Gases are easily *compressed*. **Compressibility** is the ability to make the space a substance occupies become smaller.

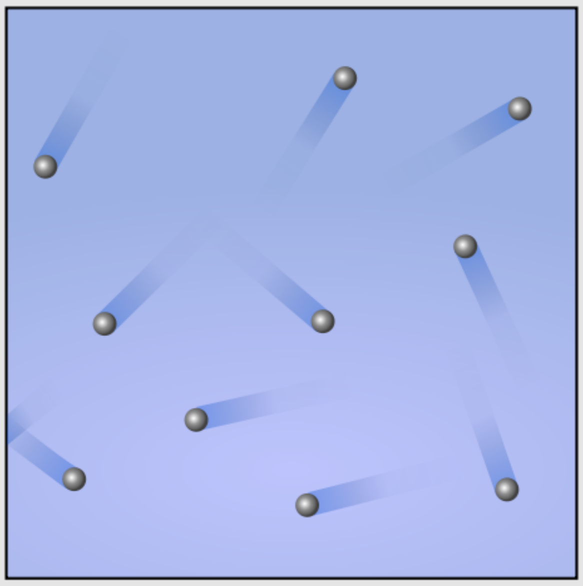
Under most conditions, the behavior of atoms or molecules in the gas phase is quite simple to predict. At the temperatures and pressures normally encountered on the surface of the earth, we can model gas phase particles as moving along straight lines until they collide with other particles or with the container walls. The ***average speed*** of the particles increases as the temperature increases. Figure 5.7 illustrates our model of gas particles. For those of you who are using an ***i-books*** version of this book, this model of gases can be seen in Movie 5.2. For **print or pdf versions** of the book, the movie can be seen at: http://www.zovallearning.com/streamvid/gas-molecule-movement.html

Movie 5.2
Model of the Gas Phase



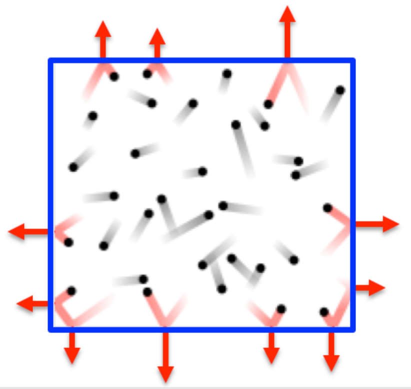
This movie depicts the behavior of gases. Gas particles are represented by spheres in this movie, and there are two types of gas particles represented by red and blue spheres.
Source: Wikimedia Commons, Author: Greg L CC-BY-SA, http://creativecommons.org/licenses/by-sa/3.0/legalcode

Figure 5.7
Model Illustration of the Gas Phase



At the temperatures and pressures normally encountered on the surface of the earth, we can model gas phase particles as moving along straight lines until they collide with other particles or with the container walls. The average speed of the particles increases as the temperature increases.
Source: Wikimedia Commons, Author: Sharayanan, CC-BY-SA, http://creativecommons.org/licenses/by-sa/3.0/legalcode

Figure 5.8 Gas Pressure



Gas pressure is caused by collisions of gaseous particles with the container walls (or other surfaces). Each collision of a gas particle (shown as a black sphere) with the wall of the container (blue square) produces a force upon the wall (shown as a red arrow). The sum of the forces from all of the collisions divided by the container's inner surface area is the pressure.
Source: Wikimedia Commons, Author: Becarlson CC-BY-SA, http://creativecommons.org/licenses/by-sa/3.0/legalcode

Gas Pressure

One parameter that is used to describe gases is **pressure**. In general, *pressure* is defined as the amount of ***force*** that acts upon a unit ***surface area***. Mathematically, this is the ratio of the force to the surface area. You may be familiar with the pressure unit of *pounds per square inch* (psi), often measured when filling car or bicycle tires with compressed air. **Gas pressure** is caused by collisions of gaseous particles with the container walls or other surfaces. This concept is illustrated in Figure 5.8 where each collision of a gas particle (shown as black spheres) with the wall of the container (blue square) produces a force upon the wall (shown as a red arrow). The sum of the forces from all of the collisions divided by the container's inner surface area is the *pressure*.

Source: Wikimedia Commons, PD

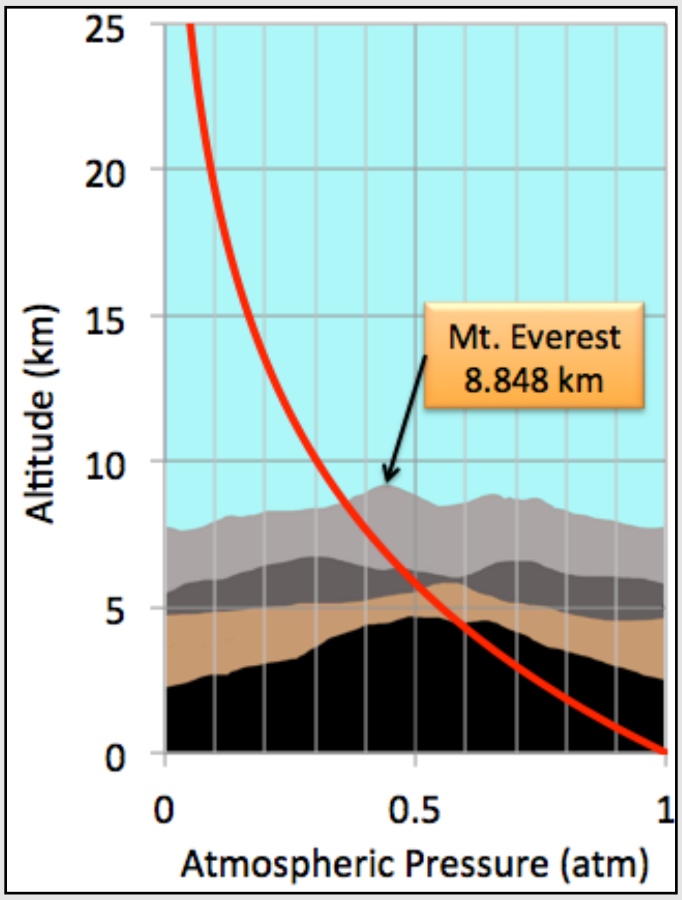
The gas particles that surround the earth form the **earth's atmosphere** and are commonly referred to as **air.** Air is a *mixture* of gases. The dry air (H_2O vapor excluded) nearest to the surface of the earth contains about 78% nitrogen, 21% oxygen, 1% argon, 0.04% carbon dioxide, and trace amounts of some other gases. The percentage of H_2O vapor varies between 0.001% and 5% depending on local weather conditions. You have likely heard the term ***atmospheric pressure*** when listening to weather reports. Atmospheric pressure, sometimes referred to as "air pressure," is simply the pressure exerted by the air at a particular location. Figure 5.9 shows the the Earth's atmosphere when viewed from space. The gases in the atmosphere reflect (scatter) more blue light than other colors and this gives the atmosphere a blue "glow."

Figure 5.9
The Earth's Atmosphere

View of the crescent moon through the top of the earth's atmosphere. Photographed above 21.5°N, 113.3°E by International Space Station crew Expedition 13.
Source: Wikimedia Commons, US-PD

Wherever there is air, atmospheric pressure exists. Since the earth's gravity acts on the gas particles, air at lower elevations is denser (more concentrated) than at higher elevations. Since there are less gas particles present and therefore less collisions occurring at higher altitudes, atmospheric pressure decreases as the altitude increases. A plot of the relationship between the altitude and atmospheric pressure is shown in Figure 5.10. Note that the pressure on top of Mt. Everest is equal to about half of the pressure that we experience near sea level. This means that there are about half as many molecules in a liter of air on top of Mt. Everest as there are at sea level; you would inhale half of the amount of oxygen in one breath as you would at sea level. Most mountaineers who climb above 8 km use oxygen tanks/masks so they can maintain safe blood oxygen levels.

Figure 5.10
Plot of Pressure vs. Altitude



Graph of pressure vs. altitude overlaid on an illustration of proportional mountain peak heights. The peaks represented in order of highest to lowest are Everest, McKinley, Sharp, and Rainier.
Source: Wikimedia, NASA US-PD

Figure 5.11
Evangelista Torricelli
(1608–1647)

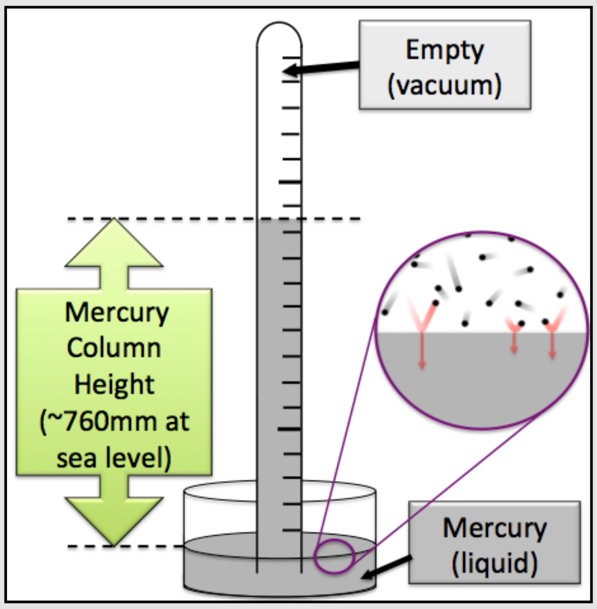
Source: Wikimedia Commons, Painter, Lorenzo Lippi (circa 1647, Galleria Silvano Lodi & Due) PD

Measuring Pressure

The term "**manometer**" is used for a device that measures pressure. Devices used to measure atmospheric pressure are called **barometers**. Italian physicist and mathematician Evangelista Torricelli (Figure 5.11) is credited with the invention of the barometer in 1643.

Historically, the most common types of barometers involved a column of liquid "*supported*" by air. In order to minimize the size of the device, mercury - a very high-density liquid - is commonly used. An illustration of a *mercury barometer* is shown in Figure 5.12. The collisions of gas particles in the air with the surface of the mercury force mercury ***upward*** in the column. This is balanced by the ***downward*** pull of gravity on the mercury in the column. Gravity is relatively constant; however, the pressure of the air varies with elevation and local weather conditions, therefore the height of mercury in the column will change as the air pressure changes. The height of a column of mercury at sea level is about 760 mm; this value will vary slightly depending on the weather.

Figure 5.12
Mercury Barometer



An illustration of a mercury barometer. The collisions of gaseous air particles with the surface of the mercury force mercury upward in the column. This is balanced by the downward pull of gravity on the mercury. Gravity is relatively constant, however the pressure from the air varies with local weather conditions, therefore the height of mercury in the column will vary with air pressure. The height of a column of mercury at sea level is about 760 mm.

Modern manometers include *mechanical* and *electronic* instruments. Microfabrication manufacturing technologies have enabled the use of miniaturized manometers in devices such as wristwatches and mobile phones. When microprocessors in these devices combine the measured pressure data with the information in the pressure vs. altitude relationship (as you saw in Figure 5.10), the altitude can be extrapolated, then displayed.

Units of Pressure

I mentioned earlier that *pressure* is defined as *the amount of force that acts upon a unit of surface area*; the ratio of the force over the surface area. The SI unit for pressure is the **pascal (Pa)** and is equal to one Newton (unit of force) per square meter. The pascal unit is named in honor of the French mathematician, physicist, inventor, writer, and philosopher Blaise Pascal (1623-1660), who, among other significant inventions and mathematical work, is known for his contributions in the field of liquid pressures (hydrodynamics and hydrostatics). By following up on the work of Torricelli, Pascal is credited with the invention of the syringe and the hydraulic press. Another pressure unit that is based on force per unit area is **pounds per square inch (psi)**. The **atmosphere (atm)** pressure unit has a magnitude that is approximately equal to the atmospheric pressure at sea level. The **millimeters of mercury (mm Hg)** pressure unit is based on the height of a column of mercury at one atmosphere pressure; over time this value has been defined as exactly 1/760 of an **atmosphere (atm)** unit. In honor of Evangelista Torricelli, a pressure unit called the "**Torr**" was established and is equivalent to *almost exactly* one **mm Hg**. There is a technical, numerical difference between the **Torr** unit and **mmHg** that is so small that it is often neglected. When doing calculations, we will treat the **Torr**-to-**mm Hg** relationship as ***exactly one-to-one*** in this book.

The *pressure units that we will use in this textbook* are **atm, psi, mm Hg,** and **Torr**. The relationships between these factors are given below.

- 1 atm = 760 mm Hg (exact, infinite significant figures)
- 1 mm Hg = 1 Torr (considered exact, infinite significant figures)
- 1 atm = 760 Torr (considered exact, infinite significant figures)
- 1 atm = 14.7 psi (three significant figures shown here)

You can use these relationships as *conversion factors* in order to convert from one pressure unit to another. I will demonstrate with an example, then ask you to try a few pressure unit conversion problems.

Example: As I am writing this example problem, the atmospheric pressure in Aliso Viejo, California, where I live, is currently 757 mm Hg. What is the pressure in atmosphere units (atm)?

We do this conversion just like we did for the unit conversions in earlier chapters.

- Since we know the relationship between atmospheres and millimeters of mercury (1 atm = ***exactly*** 760 mm Hg), we can use this equivalence statement as a conversion factor:

$$\begin{array}{c|c|} 757\ \cancel{\text{mm Hg}} & 1\ \text{atm} \\ \hline & 760\ \cancel{\text{mm Hg}} \end{array} = 0.996\ \text{atm}$$

- We have three significant figures in the given pressure. Since the relationship between atmospheres and millimeters of mercury is exact, there are infinite number of significant figures in the conversion factor. Therefore the answer has three significant figures.

Review 5.5: Pressure Unit Conversions

a. Convert 698 Torr to atm.
b. Convert 757 mmHg to atm.
c. Convert 35.0 psi to atm.
d. Convert 596 mm Hg to Torr.

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

The Gas Laws

In chapter 1, I told you that there are two methods used to do science: **Scientific Theory** and **Scientific Law**. Both methods are used to acquire predictive power and both begin with observations. *Scientific Theory* uses models/ explanations to make sense of observables. Another word for theory is *model* or *explanation*. A ***Scientific Law*** is a statement about something that generally occurs. Note that when using *scientific law*, no explanation (models) is given. In the following subsection I will discuss the **gas laws**. We call these "gas laws" because they are mathematical statements about observed properties of gases; no model was originally proposed to explain why these mathematical relationship exist.

In all but extremely high pressure or very low temperature conditions, gases are very accurately and precisely described using only four parameters: the temperature (**T**), the volume of the container (**V**), the pressure (**P**) , and the amount of gas particles present (**moles**). The ***gas laws*** are the mathematical relationships between the pressure, volume, temperature, and the number of moles of gas particles that are present in a closed container.

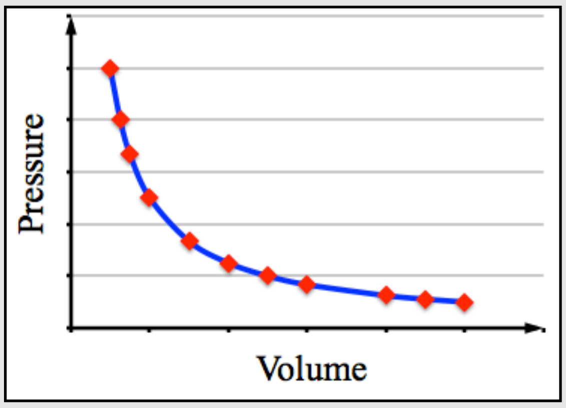
1) Boyle's Law

Robert Boyle, a 17th-century Irish natural philosopher, chemist, physicist, and inventor, studied the relationship between the pressure and volume of a gas. Boyle noticed that the pressure of a gas in a closed container is ***inversely proportional*** to the volume of the container. If two parameters are "inversely proportional," when one parameter (volume in this case) decreases, the other parameter (pressure in this case) increases. Furthermore, the increase and decrease (inverse relationship) follows a mathematical equation. Graphs were not yet in use at the time of Boyle's work, however if the pressure is measured at several different volumes and the data points are plotted, the data points would fall upon the blue curve as illustrated in Figure 5.14. The mathematical equation of the blue curve in this figure is shown in *Equation 5.3* below:

Robert Boyle (1627–1691)

Source: Wikimedia Commons, US-PD, Artist: Johann Kerseboom

Figure 5.14
Gas Pressure vs. Container Volume



If the pressure of a gas is measured at several different volumes and the data points are plotted, the data points fall upon the curve (blue line) described by Equation 5.3

$$P = (\text{Constant}) \times \left(\frac{1}{V}\right)$$

Equation 5.3

A gas's pressure (**P**) is equal to a "**constant**" number times the *inverse* of the container's volume (**1/V**). Can you see ***from this equation*** that if the volume of the container (**V**) is decreased, then **(1/V)** increases, and therefore the pressure (**P**) will increase. Conversely, if the volume of the container (**V**) is increased, then **(1/V)** decreases, and therefore the pressure (**P**) will decrease. The "**constant**" in this equation is just a number, its value is a consequence of nature and depends on temperature and the amount of gas present. As you will see in the discussion that follows, the exact value of this constant is not important to know because it is not used in the practical application of Boyle's Law.

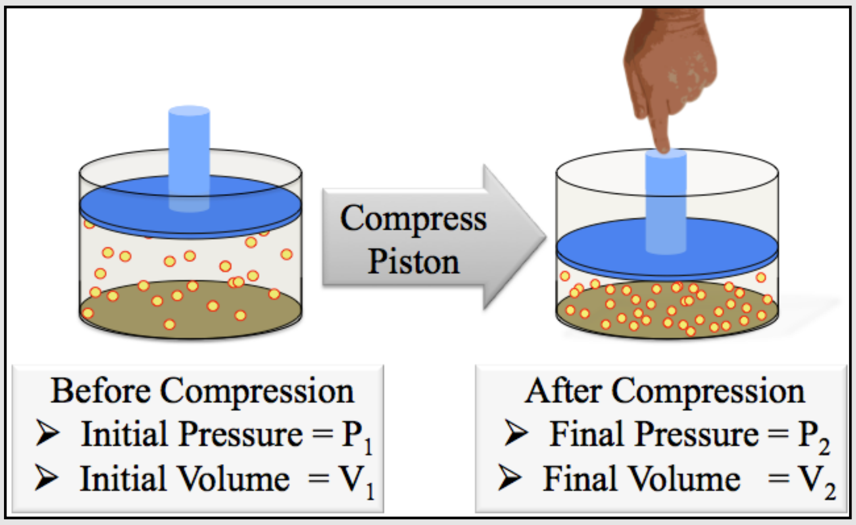
In order for me to introduce you to the practical application and form of *Boyle's Law*, I need to discuss a bit more math. When observables such as pressure and volume are ***inversely proportional***, a unique situation exists. In order to illustrate this important and useful situation, I will multiply both sides of *Equation 5.3* by (**V**) so that (**V**) cancels on the right-hand side of the equation to give:

$$P \times V = (\text{Constant})$$

Equation 5.4

This form of the Equation tells us that no matter how the pressure and volume of a gas may be changed, the **product of the pressure and volume never changes** (is *constant*). The implication of this is very useful in order to predict pressure and volume *changes* to a gas. For example, consider the compression of a gas contained in the cylinder with a piston that is illustrated in Figure 5.13. Before the piston (shaded blue) is compressed, the gas in the cylinder has an ***initial*** pressure (**P_1**) and an ***initial*** volume (**V_1**). Then the gas is compressed by applying a force (pressing) downward on the piston. After compression, the gas has a ***final*** pressure (**P_2**) and ***final*** volume (**V_2**). Since the product of the pressure and volume of a gaseous system is always constant, *so long as the temperature and amount of gas do not change*, the initial and final pressures and volumes are related to each other in what is referred to as **Boyle's Law**.

Figure 5.13
Compression of a Gas in a Cylinder with a Piston.

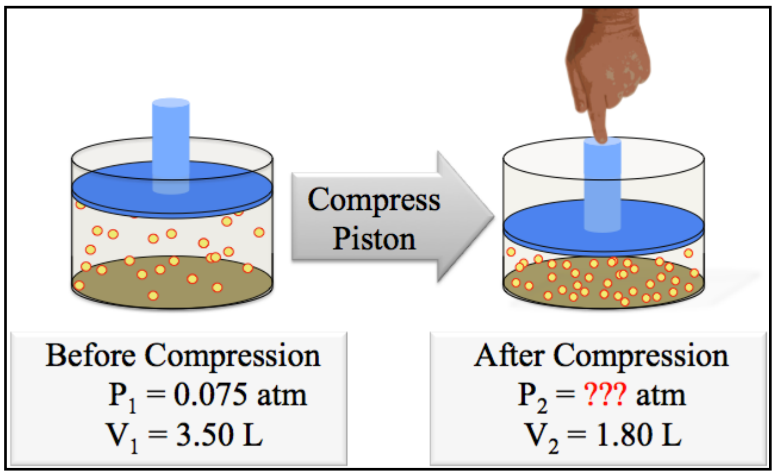


Boyle's Law

$$P_1 \cdot V_1 = P_2 \cdot V_2$$

The example problems that follow will illustrate how *Boyle's Law* is used to predict the final pressure of a gas when its volume is changed in containers such as pistons.

Example: Consider the compression of a gas at constant temperature as shown in the illustration *on the right*. The initial volume (V_1) is 3.50 L and the initial pressure (P_1) is 0.075 atm, then the piston is compressed to give a final volume (V_2) of 1.80 L. What is the value of the final pressure (P_2)?



Solution: Use ***Boyle's Law***: $P_1 \cdot V_1 = P_2 \cdot V_2$

Boyle's Law contains four variables: P_1, V_1, P_2, and V_2. When any three of these variables are known, the fourth variable can be found using algebra.

- In this example, we know P_1, V_1, and V_2, and we wish to find the final pressure (P_2):

$$P_1 \cdot V_1 = P_2 \cdot V_2$$

- To solve for P_2, we divide ***both sides*** of the equation by V_2:

$$\frac{P_1 \cdot V_1}{V_2} = \frac{P_2 \cdot \cancel{V_2}}{\cancel{V_2}}$$

- V_2 cancels on the right-hand side; we have isolated the unknown variable (P_2):

$$\frac{P_1 \cdot V_1}{V_2} = P_2$$

- Insert the known values of P_1, V_1, and V_2, then solve for the final pressure (P_2):

$$P_2 = \frac{(0.075\text{ atm}) \cdot (3.50\,\cancel{\text{L}})}{(1.80\,\cancel{\text{L}})} = 0.15\text{ atm}$$

  - Our answer has two significant figures.

There are a couple of *important things to keep in mind* when using ***Boyle's Law***:

1) Boyle's Law is only applicable *when the temperature does not change in the process*.

2) You can use any volume (or pressure) units, however the initial and final volume (or pressure) units *must be the same* so that they will cancel. Note that liter units (L) cancelled in the last step of the example problem.

Review 5.6: Using Boyle's Law

If 123 mL of gas that has a pressure of 782 Torr is compressed to a final volume of 63 mL, what would be the final pressure of the gas?

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

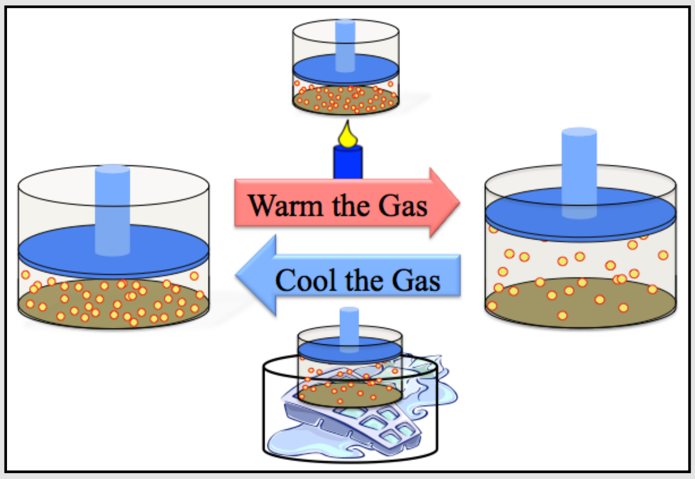
2) Charles' Law

You probably knew, even before you took a chemistry course, that when a gas is warmed, its volume will increase, and cooling a gas will have the opposite effect. This process is illustrated in Figure 5.15. Jacques Charles, a French inventor, scientist, mathematician, and balloonist, studied the mathematical relationship between the volume and temperature of a gas. Charles noticed that the volume of a gas in a closed container is ***directly proportional*** to the temperature (at constant pressure). If two parameters are "*directly proportional*," this means that when one parameter increases, the other parameter increases *by the same factor*. Charles found that if the volume is measured at several different temperatures and the data points are plotted, the data points would fall upon a straight line as illustrated in Figure 5.16. This is true for any two variables that are directly proportional. The equation for the relationship between a gas's volume and temperature is given in *Equation 5.5*:

Jacques Charles (1746 – 1823)

Source: Wikimedia Commons, US-PD

Figure 5.15 Warming and Cooling a Gas

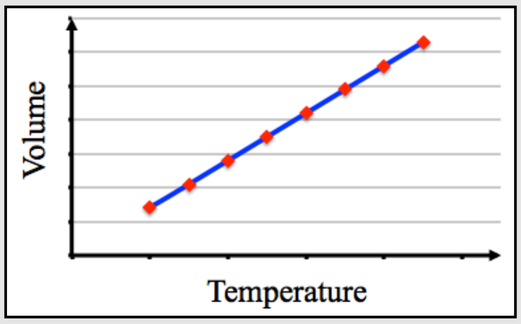


When a gas is warmed, its volume will increase, and cooling a gas will have the opposite effect. Charles noticed that the volume of a gas in closed but shape container is ***directly proportional*** to its temperature (at constant pressure).

$$V = (\text{Constant}) \times T \qquad \textit{Equation 5.5}$$

A gas' volume (V) is equal to a "**constant**" number times the *temperature* (**T, in kelvin units**). We must use the *absolute temperature scale*, kelvin units, whenever we are using the gas laws. The Kelvin scale starts at zero (corresponding to zero kinetic energy) and includes only *positive values*. Celsius (°C) or Fahrenheit (°F) scales cannot be used because they can have *negative* values. If a negative temperature value was used in *Equation 5.5,* then a *negative volume* would be calculated; this is problematic because a negative volume makes no sense.

Figure 5.16
Gas Volume vs. Temperature



If the volume of a gas is measured at several different temperatures and the data points are plotted, the data points would fall upon a straight line.

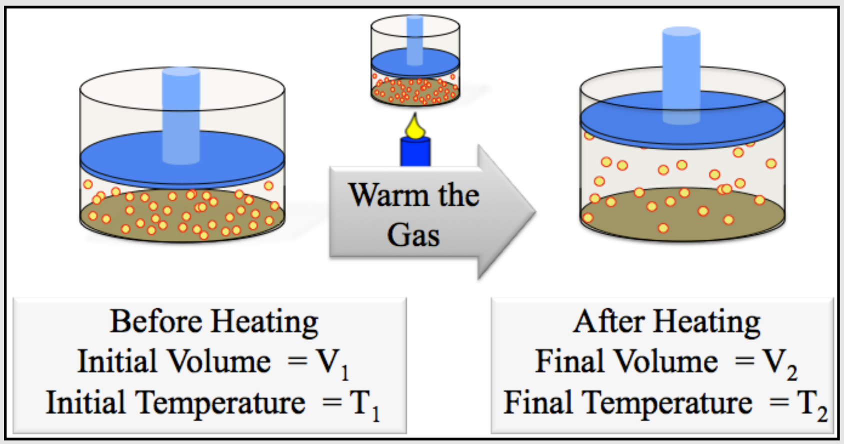
Can you tell ***from Equation 5.5*** that if the temperature of the gas (T) is increased, then the volume (V) will increase by the same factor? The opposite is true for a decrease in temperature. This is why the term "*directly*" proportional is used. "**Constant**" in this equation is just a number; its value is a consequence of nature and depends on the pressure and the amount of gas present.

When observables such as volume and temperature are ***directly proportional***, a unique situation exists. In order to illustrate this, I will divide both sides of *Equation 5.5* by (T) so that (T) *cancels* on the right-hand side of the equation to give:

$$\frac{V}{T} = (\text{Constant}) \qquad \textit{Equation 5.6}$$

This form of the equation tells us that no matter how the volume and temperature of a gas may be changed, the ***ratio of the volume to temperature never changes*** (is *constant*). This fact is useful in order to predict volume and temperature changes to a gas. For example, consider the warming of a gas contained in the cylinder that is illustrated in Figure 5.17. Since the piston is *free to move*, and the mass of the piston (and the external room pressure) exerts a ***constant downward force*** on the gas, the pressure inside the cylinder does not change in this process. Before heating, the gas in the cylinder has an initial volume (V_1) and an initial temperature (T_1). Then, the gas is warmed to a final temperature (T_2) and final volume (V_2). Since the ***ratio*** of the volume to temperature never changes, the initial and final volumes and temperatures are related to each other in what is referred to as **Charles' Law**.

Figure 5.17 Warming a Gas under a Piston



Charles' Law

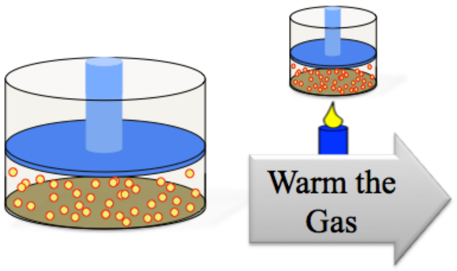
$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

Example: The initial volume of gas in a cylinder with a piston is 7.20 liters. The gas is heated from 265 K to 428 K (at constant pressure). What is the final volume?

Solution: Use ***Charles' Law***: $\frac{V_1}{T_1} = \frac{V_2}{T_2}$

Charles' Law contains four variables, V_1, T_1, V_2, and T_2. When any three of these variables are known, the fourth variable can be found using algebra.

- It can be very helpful to make a *drawing and a table* such as the ones shown below when doing gas law problems.



Before Heating	After Heating
Initial Volume = 7.20 L	Final Volume = ???
Initial Temperature = 265 K	Final Temperature = 428 K

- In this example, we know V_1, T_1, and T_2; we wish to find V_2: $\frac{V_1}{T_1} = \frac{V_2}{T_2}$

- To solve for V_2, we multiply both sides of the equation by T_2: $\frac{T_2 \cdot V_1}{T_1} = \frac{V_2 \cdot \cancel{T_2}}{\cancel{T_2}}$

- T_2 cancels on the right-hand side; we have isolated the unknown variable (V_2): $\frac{T_2 \cdot V_1}{T_1} = V_2$

- Insert the known values of V_1, T_1, and T_2 then solve for the final volume (V_2):

$$V_2 = \frac{(428\ \cancel{K}) \cdot (7.20\ L)}{(265\ \cancel{K})} = 11.6\ L$$

  - Our answer has three significant figures.

There are a couple of *important things to keep in mind* when using ***Charles' Law***:

1) Charles' Law is only applicable *when the pressure does not change in the process*.
2) Temperature must be entered into the Charles' Law equation in kelvins.
   - If you are given the initial and/or final temperature in °C or °F, **convert to K** *before* using Charles' Law.

Review 5.7: Using Charles' Law

The initial volume of gas in a cylinder with a piston is 1.80 liters. The gas is ***cooled*** from 125 °C to 22 °C (at constant pressure). What is the final volume? CAUTION: Which temperature units must be used in gas law calculations?

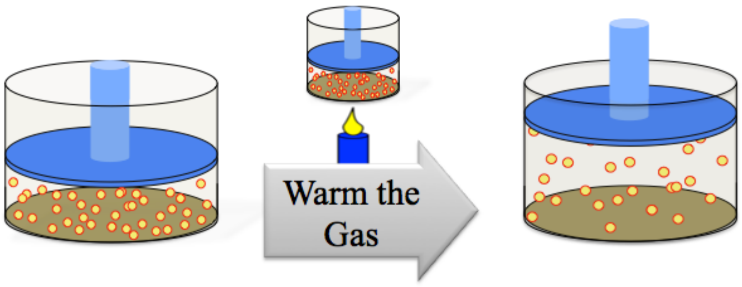
For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

I want to show you one more example for Charles' Law in order to point out an algebraic step that is needed in some gas law problems.

Example: The initial volume of a gas in a cylinder with a piston is 4.50 L and the initial temperature is 295 K. When the gas is heated, its volume increases to 8.80 L (at constant pressure), what is the final temperature?

Solution: Because the volume and temperature are changing (at constant pressure) we use ***Charles' Law***: $\frac{V_1}{T_1} = \frac{V_2}{T_2}$

- The *illustration and a table* below show the process and list the variables to be considered when using Charles' Law.



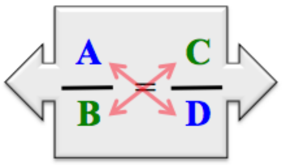
Before Heating
Initial Volume = 4.50 L
Initial Temperature = 295 K

After Heating
Final Volume = 8.80 L
Final Temperature = ??? K

- In this example, we know V_1, T_1, and V_2; we wish to find T_2: $\frac{V_1}{T_1} = \frac{V_2}{T_2}$

The variable that we wish to solve for, T_2, is in the *denominator* of the fraction. There is a mathematical shortcut called "cross-multiplication" that allows us to simplify the equation:

$$\text{If } \frac{A}{B} = \frac{C}{D}$$



, then $A \cdot D = B \cdot C$

- We apply this to our equation for Charles' law:
  - The variable we wish to solve for, T_2, is ***no longer in the denominator*** of the equation.

$$\text{Since } \frac{V_1}{T_1} = \frac{V_2}{T_2} \text{, then } V_1 \cdot T_2 = T_1 \cdot V_2$$

  - To solve for T_2, we divide both sides of the equation by V_1:

$$\frac{\cancel{V_1} \cdot T_2}{\cancel{V_1}} = \frac{T_1 \cdot V_2}{V_1}$$

- V_1 cancels on the left side; we have isolated the unknown variable (T_2). Insert the known values of V_1, T_1, and V_2, then solve for the final temperature:

$$T_2 = \frac{T_1 \cdot V_2}{V_1} = \frac{(295\ \text{K}) \cdot (8.80\ \cancel{\text{L}})}{(4.50\ \cancel{\text{L}})} = 577\ \text{K}$$

3) Gay-Lussac’s Law

Imagine a gas in a container with a ***fixed-volume*** such as the propane tanks used for barbecues, lanterns, or outdoor heaters. What do you think would happen to the pressure if the gas was warmed? If you thought that the pressure would increase, you are correct. Pressure is caused by the total force exerted on a surface. When the temperature increases, the average speed of the gas particles increases. This results in a greater pressure because both the frequency of collisions of gas particles with the container’s inner surface ***and*** the average force per collision increase.

Top: Gay-Lussac (1778 –1850)
Bottom: Amonton (1663 – 1705)

Source: Wikimedia Commons, US-PD

Joseph Luis Gay-Lussac (French chemist and balloonist) and Guillaume Amonton (French scientific instrument inventor and physicist) studied the relationship between the temperature and pressure of a gas. They noticed that the pressure of a gas in a fixed-volume container is ***directly proportional*** to the temperature. You learned about the mathematical relationship between *directly proportional* quantities in the discussion of Charles’ Law; the same principles apply here. Because the pressure and temperature of a gas are directly proportional, the ***ratio of the pressure to temperature never changes*** (is *constant*).

$$\frac{P}{T} = (\text{Constant}) \qquad \textit{Equation 5.8}$$

“**Constant**” in this equation is just a number; its value is a consequence of nature and depends on the volume and the amount of gas present.

Since the ***ratio*** of pressure to temperature never changes *when a gas undergoes a change (at constant volume),* the initial and final pressures and temperatures are related to each other in what is referred to as **Gay-Lussac’s Law**.

Gay-Lussac’s Law

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$

There are a couple of *important things to keep in mind* when using ***Gay-Lussac’s Law***:

1) It is only applicable *when the volume does not change in the process*.

2) Temperature must be entered in kelvins.

- If you are given the initial and/or final temperature in ^{o}C or ^{o}F, **convert to K**.

The math and concepts involved in solving Gay-Lussac’s Law problems are identical to those of Charles’ Law, so instead of showing you an example, I will have you go directly to a review problem.

Review 5.8: Using Gay-Lussac’s Law

The initial pressure of gas in a container is 15.7 atmospheres (atm). The gas is ***heated*** from 292 K to 525 K . The container’s volume does not change. What is the final pressure?

For ***i-book*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

4) The Combined Gas Law

We have seen laws that predict changes in gaseous systems when *only* the pressure and volume change (Boyle's Law), or when *only the* volume and temperature change (Charles' Law), or when *only* the temperature and pressure change (Gay-Lussac's Law). But how do we predict the behavior of a gas if ***all three parameters***, temperature, volume, and pressure, ***undergo changes***? By mathematically combining the three previous gas laws, we get *Equation 5.9* showing that the ratio of the pressure-volume product to the temperature is constant:

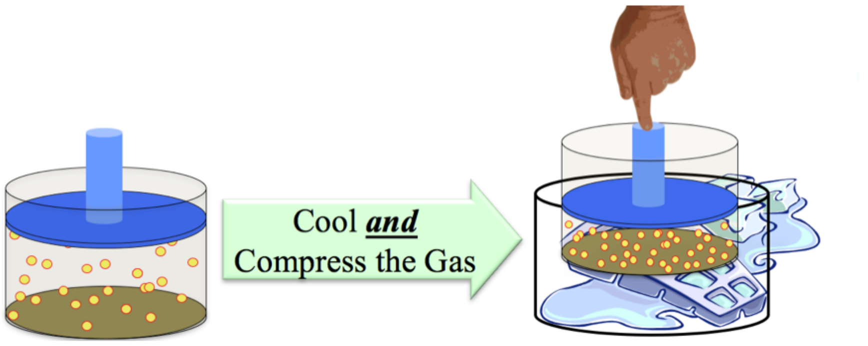
$$\frac{\mathbf{P} \cdot \mathbf{V}}{\mathbf{T}} = \text{(Constant)} \qquad \textit{Equation 5.9}$$

"**Constant**" in this equation is just a number; its value is a consequence of nature and depends only on the amount of gas present. Since the quantity on the left-hand side of *Equation 5.9* never changes*, when a gas undergoes a pressure, volume,* ***and*** *temperature change,* the initial and final pressures, volumes, and temperatures are related to each other in what is referred to as the **combined gas law**.

Combined Gas Law

$$\frac{\mathbf{P_1} \cdot \mathbf{V_1}}{\mathbf{T_1}} = \frac{\mathbf{P_2} \cdot \mathbf{V_2}}{\mathbf{T_2}}$$

Example: A gas in a cylinder with a piston has an initial pressure of 1.00 atm and an initial volume of 10.0 liters. The gas is cooled from 298 K to 265 K ***and*** the piston is compressed to give a final volume of 7.0 L (as illustrated below). What is the ***final pressure***?



Initial State
Initial Pressure = 1.00 atm
Initial Volume = 10.0 L
Initial Temperature = 298 K

Final State
Final Pressure = ???
Final Volume = 7.0 L
Final Temperature = 265 K

Solution: We will use ***the combined gas law*** because the pressure, volume, and temperature ***are all changing***. The combined gas law contains six variables, P_1, V_1, T_1, P_2, V_2, and T_2. When any five of these variables are known, the sixth variable can be found using algebra.

- In this example, we know P_1, V_1, T_1, V_2, and T_2; we wish to find $\mathbf{P_2}$: $$\frac{\mathbf{P_1} \cdot \mathbf{V_1}}{\mathbf{T_1}} = \frac{\mathbf{P_2} \cdot \mathbf{V_2}}{\mathbf{T_2}}$$
- To solve for $\mathbf{P_2}$, we divide both sides of the equation by $\mathbf{V_2}$ **and** multiply both sides by $\mathbf{T_2}$: $$\frac{\mathbf{T_2} \cdot \mathbf{P_1} \cdot \mathbf{V_1}}{\mathbf{V_2} \cdot \mathbf{T_1}} = \frac{\mathbf{P_2} \cdot \cancel{\mathbf{V_2}} \cdot \cancel{\mathbf{T_2}}}{\cancel{\mathbf{T_2}} \cdot \cancel{\mathbf{V_2}}}$$
- $\mathbf{T_2}$ and $\mathbf{V_2}$ cancel on the right-hand side; we have isolated the unknown variable ($\mathbf{P_2}$): $$\frac{\mathbf{T_2} \cdot \mathbf{P_1} \cdot \mathbf{V_1}}{\mathbf{V_2} \cdot \mathbf{T_1}} = \mathbf{P_2}$$
- Insert the known values of P_1, V_1, T_1, V_2, and T_2, then solve for the final pressure ($\mathbf{P_2}$):
  - Temperature must be entered into the combined gas law (and all gas law equations) in kelvin. $$\mathbf{P_2} = \frac{(265\ \cancel{\mathrm{K}}) \cdot (1.00\ \mathrm{atm}) \cdot (10.0\ \cancel{\mathrm{L}})}{(7.0\ \cancel{\mathrm{L}}) \cdot (298\ \cancel{\mathrm{K}})} = \mathbf{1.3\ atm}$$
  - Our answer has two significant figures since the final volume has only two significant figures.

Review 5.9: Using the Combined Gas Law

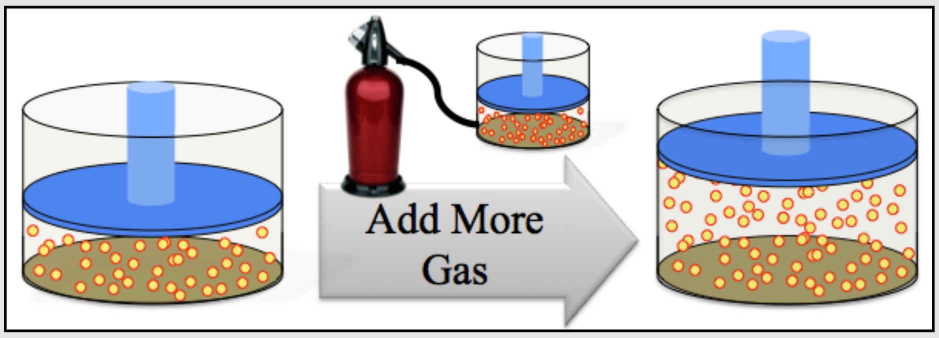
At an ocean depth where the pressure is 2.00 atm and the temperature is 282 K, a scuba diver releases a bubble of exhaled gas with a volume of 10.0 mL. What is the volume of the exhaled gas bubble *when it reaches the surface*, where the pressure is 1.00 atm and the temperature is 295K ?

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

5) Avogadro's Law

If you were to add more gas to a cylinder below a piston, the volume would increase as illustrated in Figure 5.18. The presence of additional gas particles in the cylinder results in more collisions of the particles with the piston. The piston is then displaced upward until the force/pressure of the gas within the cylinder is once again balanced by the external pressure and gravity acting on the piston. By allowing the piston to move freely in this process, the initial and final pressure of the gas does not change.

Figure 5.18
Illustration of the Process Described by Avogadro's Law



Avogadro noticed that the volume of a gas is directly proportional to the number of moles of gas particles (at constant pressure and temperature).

Amadeo Avogadro, to whom you were introduced in chapter 2, studied the mathematical relationship between the amount of gas particles present and the volume of the gas. This work, in large part, is why the number of particles in a mole, Avogadro's Number, was named in his honor. Avogadro noticed that the volume of a gas is ***directly proportional*** to the number of moles of gas particles (at constant pressure and temperature). Because the volume and number of moles of a gas are *directly proportional*, the ***ratio of the volume to the number of moles never changes***. The initial and final number of moles present and volumes are related to each other in what is referred to as **Avogadro's Law**.

Avogadro's Law

$$\frac{V_1}{n_1} = \frac{V_2}{n_2}$$

"n_1" and "n_2" in Avogadro's Law are used to represent the initial and final *number of moles of gas particles*, respectively.

The math steps involved in solving Avogadro's Law problems are identical to those used to solve Charles' Law and Guy-Lussac's Law problems, therefore, instead of showing you an example, I will have you go directly to a review problem.

Review 5.10: Using Avogadro's Law

0.56 moles of gas are contained in a cylinder with a piston and the volume of gas is 4.0 L. If 2.00 moles of gas are ***added*** to this cylinder (at constant pressure and temperature), what is the final volume? CAUTION: The final number of moles (n_2) is not 2.00 moles; 2.00 moles of gas were *added* to the existing gas!

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

6) The Ideal Gas Law

At *extremely low temperatures, since* the gas particles are moving slowly, they spend a significant amount of time close to other particles, and at extremely high pressures the gas particles very often collide with other particles. Under either of these conditions, *noncovalent interactions* and *particle size* become important and cause deviations in the behavior of gases such that their properties can no longer be precisely predicted by the gas laws. In order for a gas to obey the gas laws perfectly, it could not experience *any* noncovalent interactions *and* have an infinitely small volume; this ***hypothetical gas*** is called an "**ideal gas.**" No ***real gas*** perfectly obeys these laws, **HOWEVER**, the gas laws are ***very reliable*** in predicting the properties (P,V,T, and n) of gaseous systems at all ***<u>but</u>*** extremely high pressure **or** extremely low temperature conditions.

By mathematically combining *Avogadro's Law* and the *Combined Gas Law*, we get an equation that shows the relationship between pressure, volume, temperature, and the amount of a gas present (moles). We call this relationship the **ideal gas law**.

Ideal Gas Law

$$\mathbf{P \cdot V = n \cdot R \cdot T}$$

In the ***ideal gas law*** equation, **n** represents the *number of moles* of gas particles that are present, and R is called the **gas constant**. The ***gas constant*** (**R**) is just a number that does not change; its value is a consequence of nature. The value of **R** was determined experimentally. In this book, we will use the value of **R** rounded to *three significant figures*:

$$\mathbf{R} = 0.0821\left(\frac{\mathbf{L \cdot atm}}{\mathbf{K \cdot mole}}\right)$$

It may seem unusual that the units of the gas constant contain liters, atmospheres, kelvins, and moles, however the existence and necessity of these units will become clear in the example and problems that follow this discussion.

We applied the previous five gas laws to systems where ***a change occurred***. For example, when a gas was at an initial state (with $\mathbf{P_1}$ and $\mathbf{V_1}$), and then the pressure and volume were changed (at constant temperature), we used *Boyle's Law* to predict either $\mathbf{P_2}$ or $\mathbf{V_2}$ of the final state. Unlike the previous gas laws, the **ideal gas law** is used to predict a property (**P**, **V**, **T**, or **n**) of a gaseous system at any time; ***no change*** *in the system will be involved*. The *ideal gas law* involves ***four variable parameters***: **P**, **V**, **T**, and **n**; when three of these four variables are known, we can use the *ideal gas law* to predict the value of the fourth, unknown variable.

Example: What is the volume of 1.00 moles of a gas at a pressure of 1.00 atm and a "comfortable" room temperature of 295 K?

Solution: When you see a problem like this, where a gaseous system ***is not undergoing a change***, be aware that you will be using the **ideal gas law.** The ideal gas law contains four variables, **P**, **V**, **T**, and **n.** The gas *constant* (**R**) is not a variable; it is **constant**! One more thing to note, we do not need the "1" and "2" subscripts for initial and final states because the gas is not undergoing a change.

- It is helpful to make *a table* such as the one below when doing an ideal gas law problem.

Variables:
$P = 1.00$ atm
$V =$???
$n = 1.00$ mole
$T = 295$ K

- In this example, we know P, T, and n; we wish to solve the ideal gas law equation for the volume (V):

$$P{\bullet}V = n{\bullet}R{\bullet}T$$

- To solve for V, we divide both sides of the equation by P:

$$\frac{\cancel{P}{\bullet}V}{\cancel{P}} = \frac{n{\bullet}R{\bullet}T}{P}$$

- P cancels on the left side of the equation; we have isolated the unknown variable (V):

$$V = \frac{n{\bullet}R{\bullet}T}{P}$$

- Insert the known values of P, T, n, and R, and then solve for the volume (V):

$$V = \frac{(1.00\ \cancel{\text{mole}}) \bullet \left(\frac{0.0821\ \text{L} \bullet \cancel{\text{atm}}}{\cancel{\text{K}} \bullet \cancel{\text{mole}}}\right) \bullet (295\ \cancel{\text{K}})}{(1.00\ \cancel{\text{atm}})} = 24.2\ \text{L}$$

I have shaded the *gas constant* (**R**) and its units *green* so that you can see how to insert them into the equation.

Since the gas constant has units of **(L•atm/K•mole)**, when using the ideal gas law, the pressure must have **atm** units, the temperature must have **K** units, and the volume must have **L** units. Note that in this example liters, moles, and kelvin units cancelled with the units in the gas constant. The only unit that does not cancel is liters (**L**) because we are solving for the volume and its units will be liters. CAUTION: If you are given **P**, **V**, or **T** in any other units, you must first convert them to units that match the gas constant's units.

Review 5.11: Using the Ideal Gas Law

A gas in a 3.80 L container has a pressure of 8.63 atm and a temperature of 295 K. How many moles of gas are present?

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

Review 5.12: Using the Ideal Gas Law

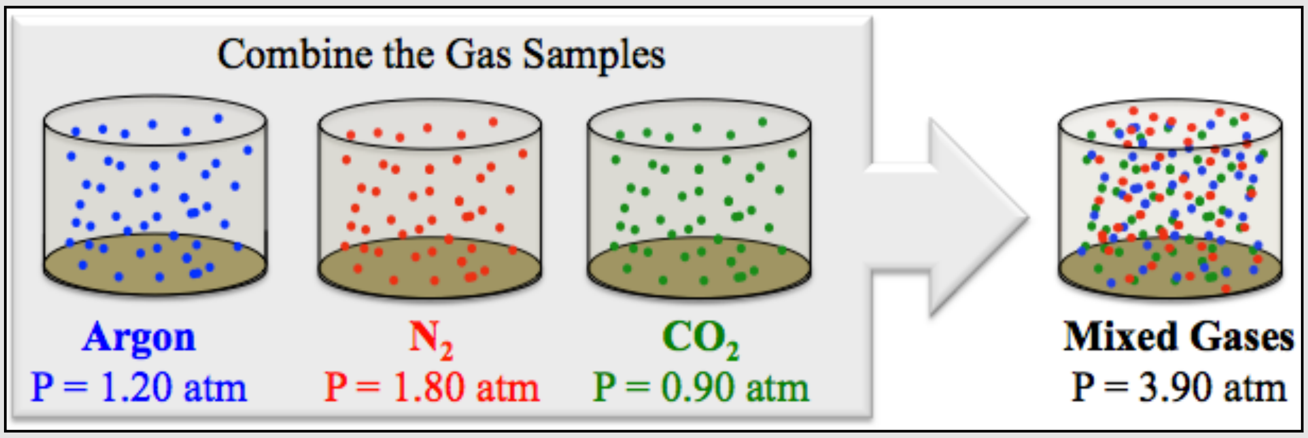
What is the volume of 17.0 grams of carbon dioxide gas if its pressure is 568 Torr and its temperature is 25 °C? **HINT:** You will need to do some *unit conversions* **before** entering values into the ideal gas law. Also, you were not given the number of moles of gas ***directly***, but perhaps you can figure out how many moles of gas are present based on the given information.

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

7) Dalton's Law

The identity of a gas does not need to be known when using the gas laws. The gas laws work quite well whether the gas is CO_2, N_2, argon, or any other gas. The reason for this is related to the gas laws' ability to precisely predict the behavior of gases in all but extremely high pressure or low temperature conditions. Under most conditions, ***real gases*** behave very similar to ***ideal gases.*** This is true because gas particles are far apart from other particles most of the time, and they are moving so fast that when they approach each other and/or collide, they do not experience noncovalent interactions for significant amounts of time. ***Another simplification in describing gases results from this situation; not only are the gas laws applicable to any single type of gas, they work just as well for mixtures of gases***. John Dalton, whom I discussed in chapter 2 for his work on atomic theory, was the first person to report that the gas laws applied equally well to gas mixtures. ***Dalton's Law*** states that the *total pressure of a mixture of gases* in a container is equal to the sum of the pressures that each gas in the mixture would exert *if that gas were alone in the container*. For example, a sample of argon in a one-liter container has a pressure of 1.20 atm, a sample of N_2 in a one-liter container has a pressure of 1.80 atm, and a sample of CO_2 in a one-liter container has a pressure of 0.90 atm as illustrated in Figure 5.19. If these three samples, the Ar, N_2, and CO_2, were combined in a one-liter container, the total pressure would be the sum of the pressures that *each gas exerted* when it was alone in the container (total pressure of the mixture = 1.20 atm + 1.80 atm + 0.90 atm = 3.90 atm).

Figure 5.19 **Dalton's Law**



A sample of argon in a one-liter container has a pressure of 1.20 atm, a sample of N_2 in a one-liter container has a pressure of 1.80 atm, and a sample of CO_2 in a one-liter container has a pressure of 0.90 atm. If these three samples, the Ar, N_2, and CO_2, were combined in a one-liter container, the total pressure would be the sum of the pressures that *each gas exerted* when it was alone in the container (total pressure of the mixture = 1.20 atm + 1.80 atm + 0.90 atm = 3.90 atm).

The amount of pressure exerted by an individual gas in a mixture is called that gas's **partial pressure**. You will likely hear the term "*partial pressure*" in some of your biology books and in other health applications. ***Dalton's Law*** is also referred to as **Dalton's Law of Partial Pressures**. For Dalton's Law to be applicable, the temperature and volume of the gases must not change.

Review 5.13: Understanding Dalton's Law of Partial Pressures

A sample of O_2 gas in 20.0 liter container has a pressure of 625 Torr. In another 20.0 L container, a sample of neon gas has a pressure of 127 Torr. If the two gas samples are combined in a 20.0 L container, what would be the pressure of the gas mixture?

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

One Final Note on Gases

The difference between ***scientific law*** and ***scientific theory*** is that a *scientific law* is a statement (mathematical or literal) about something that is repeatedly observed; a *scientific theory* is a model/explanation of observations. Both methods - scientific theory and scientific law - are useful in predicting future events and are central to discovering and implementing technologies. Sometimes a *scientific law* is found, and then later a *scientific theory* (explanation/model) is established. This is the case for the gas laws. A scientific theory, called ***Kinetic Molecular Theory*** is used to explain what were originally known as the *gas laws*. A detailed discussion of Kinetic Molecular Theory is far beyond the scope of this book. I did use aspects of the theory when discussing the reasons that the gas laws work well in most conditions, why they are not applicable to gaseous systems at extremely high pressure or low temperature conditions, why they are independent of the gas's identity, and why they are applicable to gas mixtures.

Gas Law Summary

Gas Law Name	Equation
Boyle's Law	$P_1 \cdot V_1 = P_2 \cdot V_2$
Charles' Law	$\frac{V_1}{T_1} = \frac{V_2}{T_2}$
Gay-Lussac's Law	$\frac{P_1}{T_1} = \frac{P_2}{T_2}$
Combined Gas Law	$\frac{P_1 \cdot V_1}{T_1} = \frac{P_2 \cdot V_2}{T_2}$
Avogadro's Law	$\frac{V_1}{n_1} = \frac{V_2}{n_2}$
Ideal Gas Law	$P \cdot V = n \cdot R \cdot T$

TO PRACTICE MORE GAS LAW PROBLEMS SEE:

http://www.zovallearning.com/GOBlinks/ch5/wsgaslawsworksheetkey.pdf

5.4 Liquids

Figure 5.20
Maltose Syrup

Source: Wikimedia Commons
Author: Scott Bauer, US-PD

The major difference between liquids and gases is that the particles are much closer to each other in liquids than they are in gases. Noncovalent interactions therefore play a very important role in determining the properties of liquids. Consider how much closer H_2O molecules are to each other in the liquid phase vs. the gas phase. At its normal boiling point (100 °C and 1 atm pressure), one mole of liquid H_2O occupies a volume of about **19 mL**, however one mole of H_2O gas occupies a volume of about **31,000 mL**.

Properties of Liquids

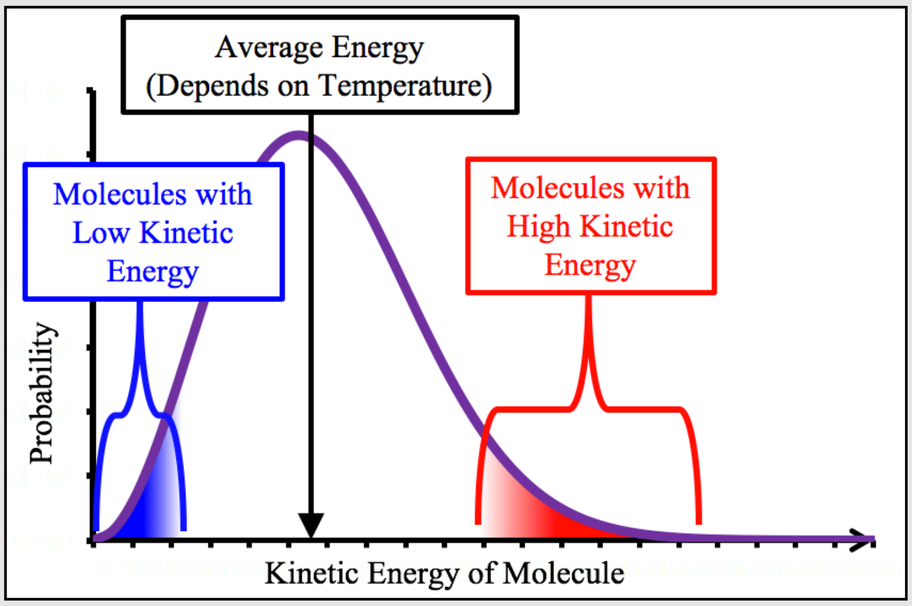
Viscosity

You have probably noticed a difference in the way syrup and water behave when you pour them. We often say that syrup is "thicker" than water because it flows more slowly than water. The technical way to make this statement is, "syrup is more ***viscous*** than water." **Viscosity** is a measure of a substance's *resistance to flow*. The nanometer scale explanation for the existence of viscosity is that molecules in a liquid need to "slide" past the molecules that surround them in order for the liquid to flow. Noncovalent interactions attract the molecules to each other and impede their ability to slide past each other. The stronger the noncovalent interactions, the ***more viscous*** a liquid is. Temperature (kinetic energy) aids molecules in overcoming the noncovalent interactions in order to more easily slide past each other, therefore a liquid's viscosity is temperature dependent. With very few exceptions, the ***higher*** the temperature, the ***lower*** a substance's viscosity. You may have observed this if you compared hot and cold syrup's ability to flow (viscosity). Figure 5.20 shows maltose syrup, which is a high-viscosity liquid.

Vapor Pressure

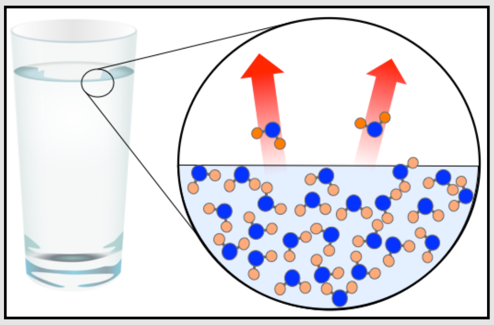
Consider a glass of water that is at a "comfortable" room temperature of 22 °C. As you know, water slowly **evaporates** even though it is at a temperature less than its boiling point (100°C). If you left an unsealed glass of water alone for a year, you would not find any water remaining in the glass. We need a model to explain how the water molecules changed from liquid to gas phase at a temperature that is lower than its boiling point. Earlier in this chapter, I told you that you can think of temperature as a measure of the ***average*** kinetic energy of a substance. I use the word "***average***" because not every molecule in a sample has the *exact same amount* of kinetic energy. Think of the glass of water that we are considering; because of random collisions between the water molecules, individual molecules in the glass are *constantly gaining and losing energy*. The *total* energy and the *average* energy of the water do not change; the water molecules simply ***exchange*** energy with each other. There are about 1 x 10^{25} H_2O molecules in a glass of water. We certainly ***do not*** expect every molecule to have *exactly the same* amount of kinetic energy. Let's do some statistics. In random events such as collisions of molecules, there is a ***probability distribution*** of molecular kinetic energies as shown in Figure 5.21. Statisticians refer to *probability distributions* as **histograms**. The horizontal axis shows the molecular kinetic energies. The vertical axis is the probability of a molecule having a particular kinetic energy. The probability distribution (shown as a purple curve) has a *maximum height* at the *most probable kinetic energy.* Except at extremely low temperatures, the ***average kinetic energy*** of the molecules is *very close to the center (peak) of the distribution* (indicated by the black arrow). ***The average energy depends on the temperature.*** Because of the shape of the histogram, ***a relatively small number of molecules*** have *very low kinetic energy* (as indicated by the blue shaded area under the curve) or *very high kinetic energy* (as indicated by the red shaded area under the curve). These low-probability ends of histogram curves are called "tails." When thinking about the system on the nanometer scale, it is as if each molecule is at its own temperature. Since thermometers are on the macro-scale size, they interact with many millions of molecules and therefore measure the average energy/temperature.

Figure 5.21 Kinetic Energy Histogram



A ***probability distribution*** of molecular kinetic energies. The horizontal axis shows kinetic energy. The vertical axis is the probability of a molecule having a particular energy. This probability distribution (shown as a purple curve) has a maximum height at the most probable kinetic energy that is very close to the average kinetic energy (indicated by the black arrow), except in the case of extremely low temperatures.

Figure 5.22 Evaporation Illustration

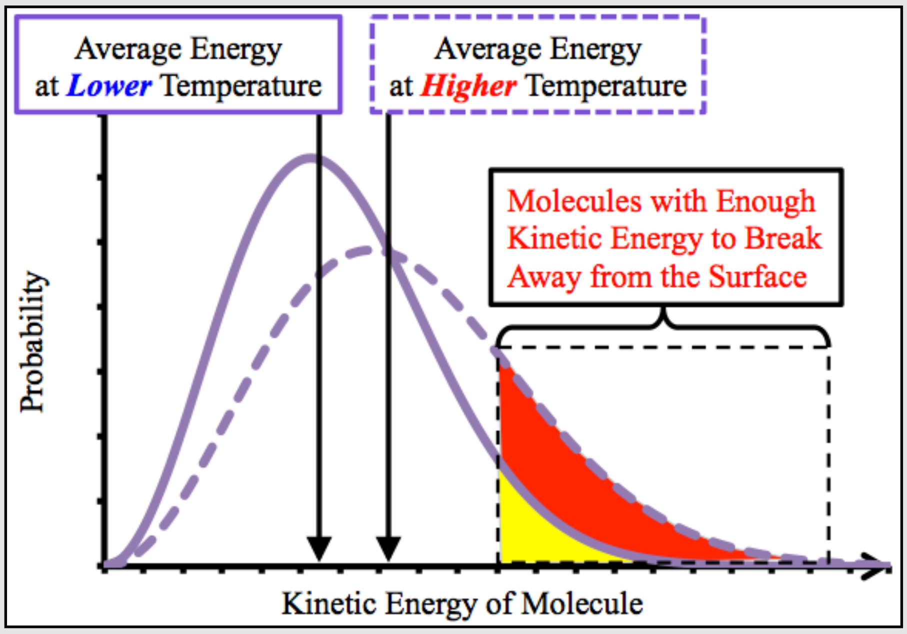


If molecules in the high energy tail (shaded red) of the histogram in Figure 5.21 happen to be on the surface of the water, they have enough kinetic energy to “break free” from the noncovalent interactions holding them to their neighboring molecules.

Consider the molecules in the ***high energy tail*** (shaded red) of the histogram in Figure 5.21. When some of these molecules happen to be on the surface of the water, they have enough kinetic energy to “break free” from the noncovalent interactions holding them to their neighboring molecules as illustrated in Figure 5.22. We call this process **evaporation**.

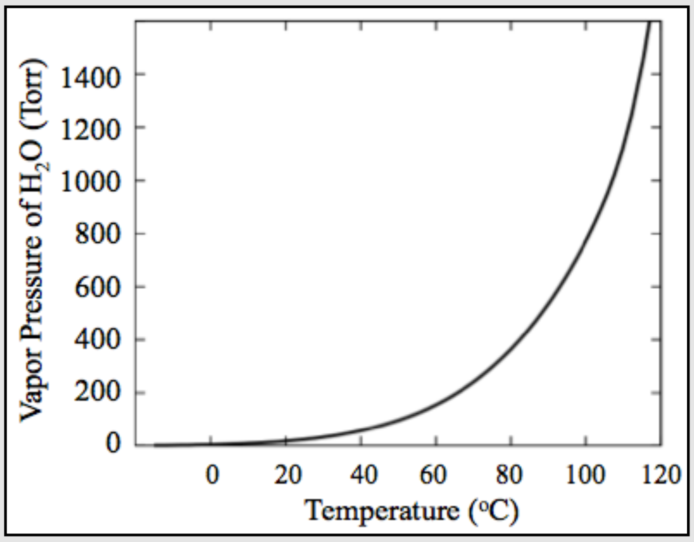
If a piston were brought into contact with the surface of the liquid, the molecules that are escaping the liquid’s surface would exert an upward force on the piston. The total force from the molecules breaking free from the liquid (per surface area unit) is referred to as the **vapor pressure** of a substance. The vapor pressure of a substance is related to its evaporation rate; the greater the vapor pressure, the faster the evaporation rate. You may be familiar with how quickly rubbing alcohol evaporates as compared to water. The vapor pressure of rubbing alcohol at 25 °C is 31 Torr and the vapor pressure of water, at the same temperature, is only 24 Torr. Ultimately this trend can be explained by water’s stronger noncovalent interactions; water is capable of more hydrogen bonding and is more polar than rubbing alcohol.

Figure 5.23
Kinetic Energy Histogram Temperature Dependence



The solid purple curve is the kinetic energy histogram at a lower temperature, and the dashed curve is the histogram for the higher temperature. When the temperature increases, the histogram (and the average kinetic energy) will shift to the right and more molecules will be able to break free from the surface (vaporize).

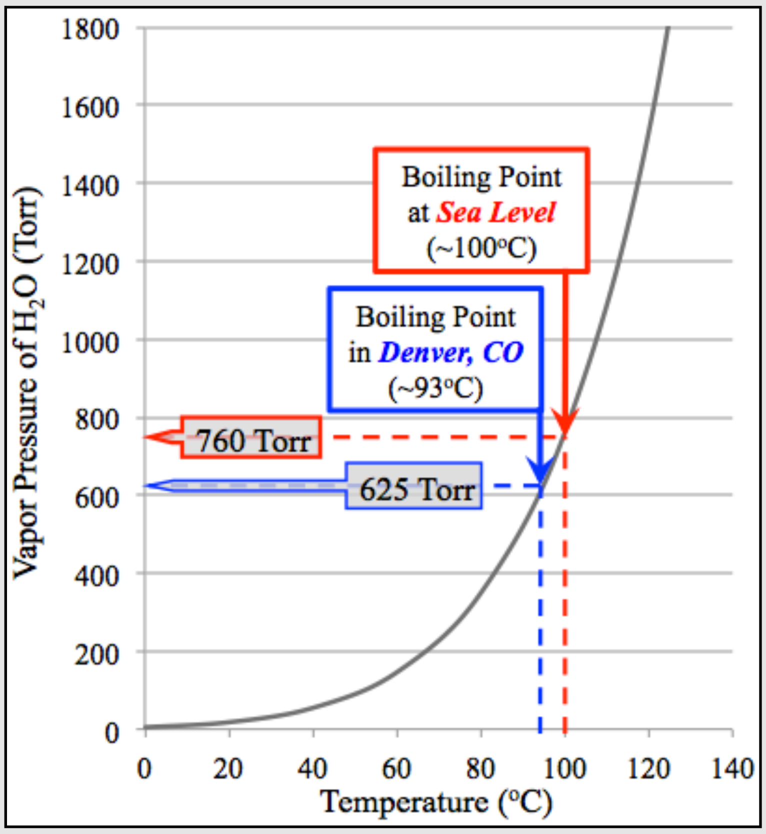
Figure 5.24
Vapor Pressure of Water vs. Temperature



The Temperature Dependence of the Vapor Pressure

How do you think a kinetic energy histogram would change if the temperature were increased? If you thought that the entire curve would shift to the right (higher energy), you are correct. Since temperature is a measure of the average kinetic energy, if the temperature increases, the average kinetic energy must shift to the right as shown in Figure 5.23. In addition to the histogram shifting to the right, it also gets a bit wider as the temperature increases. The solid curve is the histogram at the original (lower) temperature and the dashed curve is for the histogram at the higher temperature. When particles have enough kinetic energy, they can break free into the gas phase. The amount of area that is shaded yellow under the lower temperature histogram in Figure 5.23 (solid curve) represents the molecules that have enough energy to break free of the surface at the lower temperature. This can be compared to the significantly greater number of molecules that have enough energy to break free of the surface at the higher temperature, represented by the amount of area shaded red (and yellow) under the higher temperature histogram (dashed curve). The vapor pressure of a substance ***increases with temperature***. The temperature dependence of the vapor pressure of water is shown in Figure 5.24.

Figure 5.25 Vapor Pressure of Water vs. Temperature



The boiling point of a liquid in an open container is the temperature at which its vapor pressure equals the atmospheric pressure. The dashed red line indicates that the vapor pressure of water at 100 °C is equal to 760 Torr (1 atm). This is why water in an open container at sea-level, where the pressure is 760 Torr (1 atm), boils at 100°C.

Boiling Points of Liquids

The boiling point of a liquid in an open container is the temperature at which its vapor pressure equals the atmospheric pressure. In closed containers, liquids boil when their vapor pressure equals the pressure of the gas above them. Consider the graph of the vapor pressure of water vs. temperature in Figure 5.25. The dashed red line indicates that the vapor pressure of water at 100 °C is equal to 760 Torr (1 atm). This is why water will boil at 100 °C in an open container at sea-level where the atmospheric pressure is 760 Torr (1 atm). The temperature at which a liquid boils at 1 atm pressure is called its ***normal boiling point***. It is no coincidence that the *normal boiling point of water* is exactly 100 °C; the Celsius scale is based on the *normal boiling point* and *freezing point* (0 °C) of water. You may have heard that it takes more time to cook food (in boiling water) at higher elevations. This is true because water will boil at a lower temperature as the elevation increases (because the atmospheric pressure decreases). For example, if you were to cook food in boiling water while in Denver, Colorado (elevation 5280 ft) where the air/atmospheric pressure is about 625 Torr, water boils at about 93°C, as indicated by the blue dashed lines in Figure 5.25. Therefore, it would take longer to cook food in boiling water at this elevation than it would at sea level.

You may be familiar with ***pressure cookers***. The gas pressure above the water in a pressure cooker is significantly greater than 1 atm, therefore water boils at a temperature greater than 100 °C. Work on *Review Problem 5.14* to find the cooking temperature in a pressure cooker.

Review 5.14: Understanding Boiling Point

In pressure cookers, the water is boiled at a pressure of about 1500 Torr. Use the graph in Figure 5.25 to **estimate** the temperature at which food is cooked in a pressure cooker.

For ***i-books*** versions: **Click here to check answer**

For **print or pdf versions**, see the answer key in Appendix 1.

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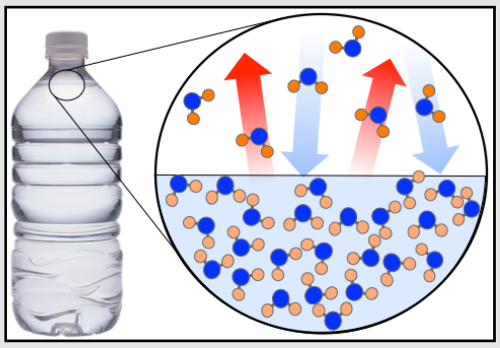
Now that you understand the details of ***evaporation***, let's conclude this subsection on liquids by considering what happens in a capped water bottle. In ***closed containers***, liquid phase molecules are not only evaporating, gaseous H_2O molecules are also colliding with the liquid's surface, losing energy, and re-entering the liquid phase (**condensation**). These processes are illustrated in Figure 5.26. The red arrows represent ***evaporation*** and the blue arrows represent ***condensation***. When the bottle is ***open***, the H_2O vapor that leaves the bottle does not return to the liquid phase in the bottle. Once the bottle is ***capped***, the amount of vapor increases until there are so many H_2O molecules in the gas phase that they are colliding with the surface and re-entering the liquid (**condensing**) at the ***same rate*** that they are evaporating.

Figure 5.26
Evaporation and Condensation in a Closed Bottle



5.5 Solids

Figure 5.27
Diamonds

Diamonds are an example of a crystalline solid.
Source: Wikimedia Commons, Author: Mario Sarto CC-BY-SA, http://creativecommons.org/licenses/by-sa/3.0/legalcode

The major difference between solids and liquids is that the atoms, ions, or molecules that make up a solid ***cannot move away from their neighboring particles***, whereas the particles that make up liquids are able to do so. It is for this reason that you are not able to pour solids. Although solid phase particles are not able to overcome the noncovalent interactions holding them next to neighboring particles, they do contain *kinetic energy* in the form of *vibrations* and, in some cases, *conformational* changes.

Classification of Solids

Solids can be classified based on whether or not the arrangement of particles is ***ordered***. In ***crystalline solids***, the atoms, ions, or molecules are arranged in an *ordered*, three-dimensional pattern called a crystal lattice. In **amorphous solids**, the particles ***are not*** arranged in an *ordered* pattern.

1) Crystalline Solids

The four types of **crystalline solids**, along with their descriptions and some examples, are listed in Table 5.3. I have discussed the first two types of crystalline solids listed in Table 5.3 in previous chapters: ***ionic solids*** and ***molecular solids***. I will now introduce you to two *other types* of crystalline solids: **covalent network solids** and **metallic solids**.

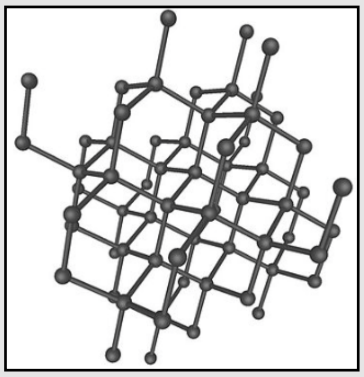
Table 5.3 **Types of Crystalline Solids**

Type	Description	Examples
Ionic Solids	Composed of cations and anions that are arranged in a lattice pattern such that the attraction of unlike charge is maximized and the repulsion of like charge is minimized (ionic bonding).	Table Salt (NaCl) Baking Soda ($NaHCO_3$)
Molecular Solids	Composed of molecules that are arranged in a lattice pattern such that the attraction of intermolecular forces are maximized.	Ice Table Sugar (Sucrose)
Covalent Network Solids	The entire bulk of the solid is composed of atoms that **are all** *covalently bonded to their neighbors.*	Diamond Silica
Metallic Solids	The nuclei and their core electrons are in lattice positions, and the valence electrons are dispersed *throughout the entire crystal.*	Gold Aluminum

Covalent Network Solids

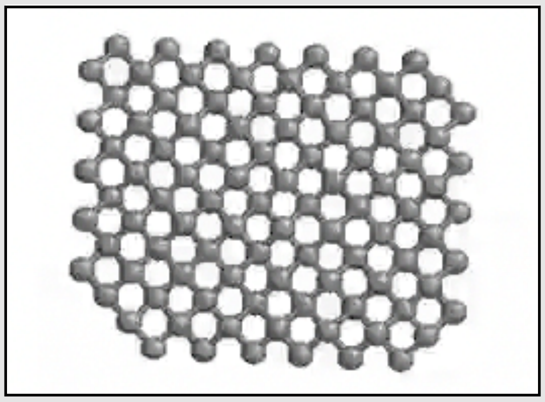
In **covalent network solids**, the entire bulk of the solid is composed of atoms that **are all** *covalently bonded to their neighbors*. The covalent bonding pattern ***extends throughout the entire crystal***. Very few substances exist as covalent networks. *Diamond* is a material that exists as a covalent network. Pure diamond is composed of carbon atoms that are each covalently bonded to ***four*** other carbon atoms. This bonding pattern (AB_4 geometry class, 110° bond angles) is illustrated in Figure 5.28 and in Movie 5.3. If you are using an ***i-books*** version of this book, click on the movie thumbnail. For **print or pdf versions** of the book, the movie can be seen at: http://www.zovallearning.com/streamvid/diamond.html

Figure 5.28
Covalent Networks:
The Crystal Structure of Diamond.



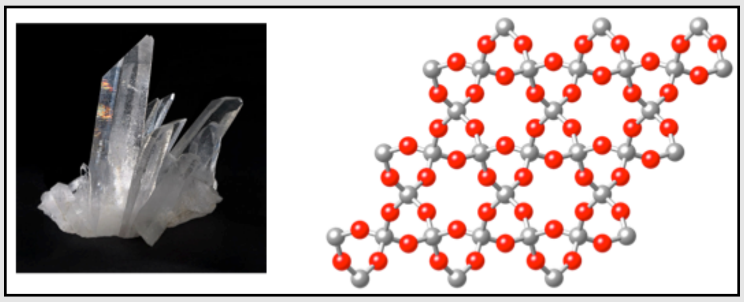
Diamond is composed of carbon atoms that are each covalently bonded to ***four*** other carbon atoms.
Source: Wikimedia Commons, Author: Itub CC-BY-SA, http://creativecommons.org/licenses/by-sa/3.0/legalcode

Movie 5.3
Covalent Networks:
The Crystal Structure of Diamond.



Source: Wikimedia Commons
Author: Brian, PD

Figure 5.29 **Covalent Network Example: Quartz**



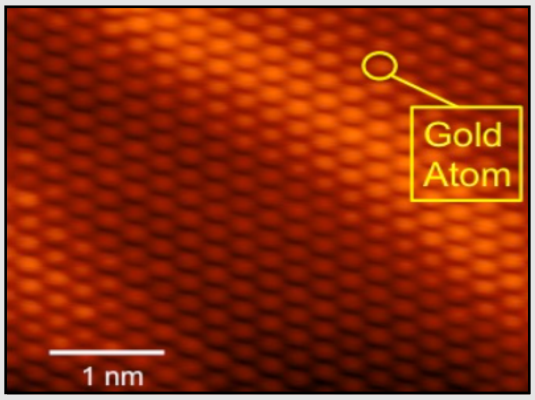
Left: A quartz crystal.
Right: The covalent network bonding pattern of quartz. Quartz is composed of silicon (Si, shaded grey) and oxygen (shaded red).
Source: Wikimedia Commons, Authors: JJ Harrison (left) and Ben Mills (right) CC-BY-SA, http://creativecommons.org/licenses/by-sa/3.0/legalcode

Another example of a *covalent network solid* is quartz. Quartz is composed of silicon (Si) and oxygen atoms. The covalent network bonding pattern of quartz is illustrated in Figure 5.29 (with the silica atoms shaded grey and the oxygen atoms shaded red).

Metallic Solids

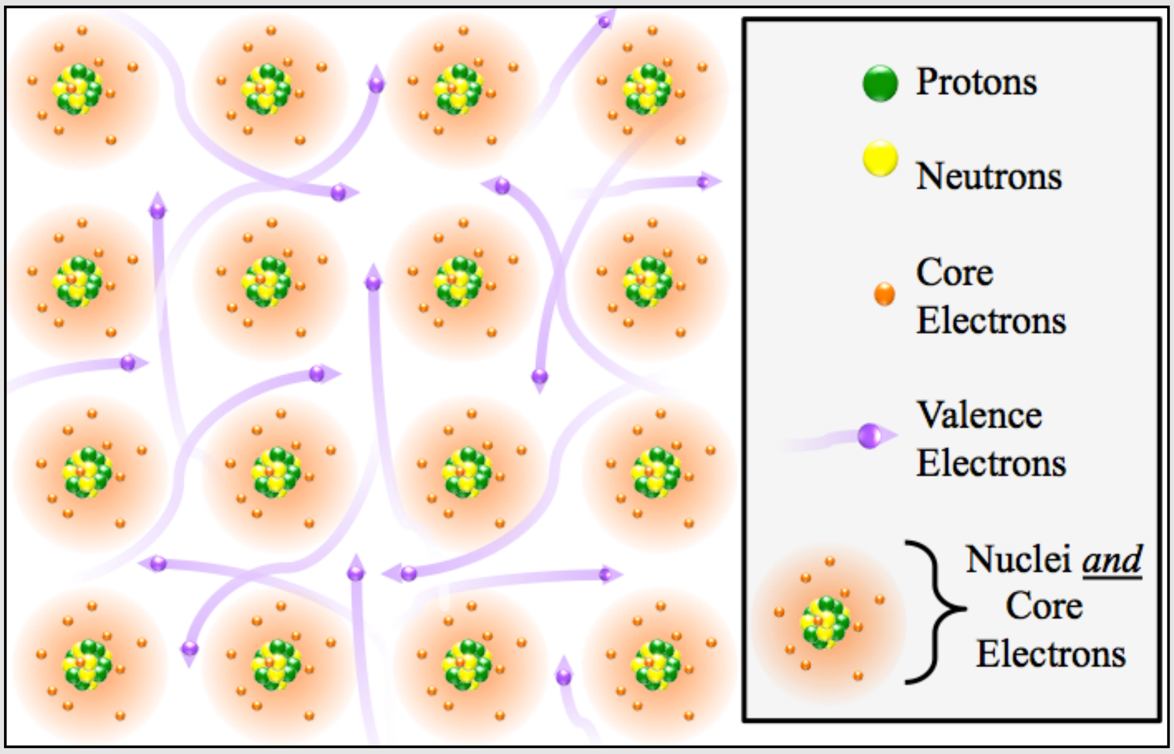
You have learned about two types of *chemical bonds*: ***ionic bonds*** and ***covalent bonds***. I have not yet presented a model of how metal atoms are held together in the solid state. There is *one other type of **chemical bonding*** called **metallic bonding**. Metal atoms form crystals. Figure 5.30 is an atomic force microscope image of the surface of solid gold. Atomic force microscopes are capable of resolving (imaging) individual atoms. Each bright spot in Figure 5.30 is a gold atom. The gold atoms are held together by *metallic bonding*. In metallic bonding, the nuclei and their core electrons are arranged in a lattice pattern, and the valence electrons are dispersed ***throughout the entire crystal***. Figure 5.31 is a two-dimensional model that illustrates how the nuclei, core electrons, and valence electrons are arranged in metals. The mobile valence electrons in metallic bonding are sometimes referred to as a "***sea of electrons***." ***Each metal nucleus*** with its ***core electrons*** has an overall *positive charge and is called a "**cationic center**."* The *electrostatic attraction* between the **negative charge of the *sea of electrons*** and the ***positive cationic centers*** is responsible for holding the particles together in metals. A model of the positive "cationic" centers and the sea of electrons (purple shaded area) is shown in Figure 5.32.

Figure 5.30 **Surface of Solid Gold**



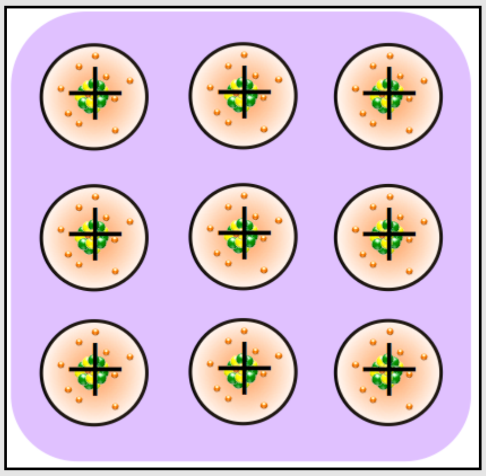
An atomic force microscope image of the surface of solid gold. Each bright spot is a gold atom. Source: Virginia Technical Institute, Physics Dept. Showcase, (with permission) Author: Prof. Chenggang Tao

Figure 5.31 **Model for Metallic Bonding**



Arrangement of the nuclei, core electrons, and valence electrons in metallic solids. The valence electrons are dispersed ***throughout the entire crystal***. Each of the nuclei with its core electrons have an overall positive charge.

Figure 5.32
Cationic Centers and Sea of Electrons

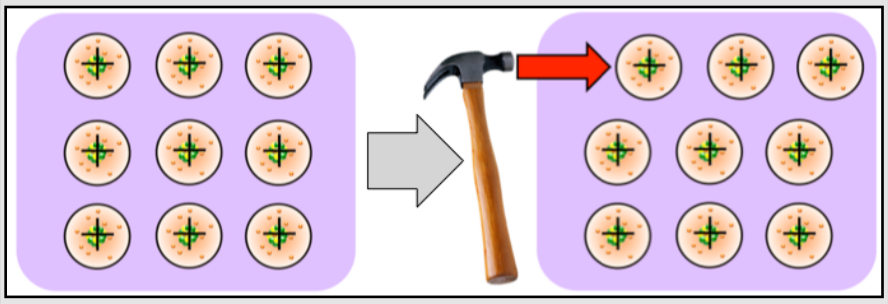


A model of the positive "cationic" centers and the sea of electrons. The *electrostatic attraction* between the **negative charge of the *sea of electrons*** and the ***positive cationic centers*** is responsible for holding the particles together in metals.

Properties of Metallic Substances

Metallic substances are solid at room temperature with one exception; mercury exists as a liquid. Metallic solids are **malleable.** ***Malleable*** substances can be hammered or beaten into thin sheets. For example, a single gram of gold can be hammered into a sheet with an area of one square meter. The reason metals can be flattened without breaking (shattering), can be visualized in the cationic centers/sea of electrons model as shown in Figure 5.33. When a layer of *cationic centers* is shifted by hammering, the *sea of electrons* is still present to hold the solid together. Figure 5.33 shows a row of metal nuclei being shifted as would occur during hammering. The opposite of "***malleable***" is "***brittle***." *Brittle* substances shatter when hammered or crushed. *Ionic compounds* are brittle because shifting the ion positions would put cations next to other cations and anions next to other anions and result in a strong electrostatic repulsion. Covalent networks are brittle because the covalent bonds can be broken when hammered or crushed.

Figure 5.33 Malleability of Metals

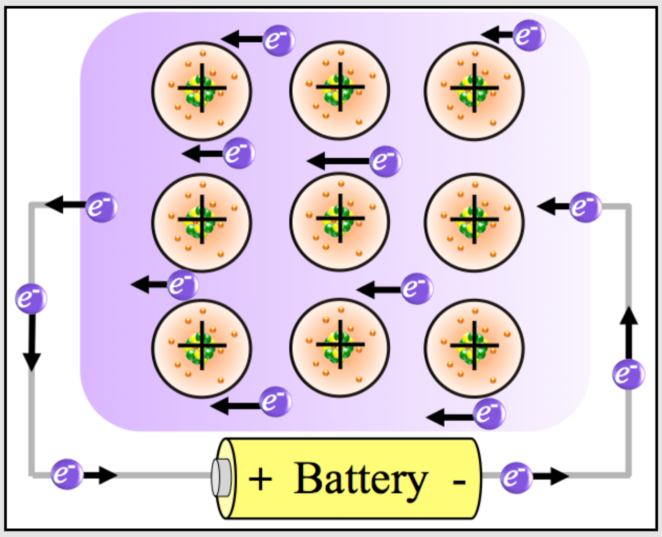


Metallic solids are **malleable.** A row of metal nuclei being shifted as would occur during hammering. If a layer of cationic nuclei is shifted by hammering, the sea of electrons is still present to hold the solid together.

Metallic solids are **ductile.** *Ductile* substances can be drawn or pulled through a series of increasingly smaller holes to produce wire. The ductile property of metals can be explained by the same reasoning that was used to understand their malleability.

Metallic substances are good **conductors of electricity.** The relative ability for electrons to move through a substance is called its electrical conductivity. The opposite of electrical conductivity is electrical resistance. The reason metals are good conductors of electricity can be visualized in the cationic centers/sea of electrons model as shown in Figure 5.34. When the positive and negative terminals of a battery (or other power source) are connected to opposite sides of a metal, the ***mobile valence electrons*** will be attracted (and move) to the positive terminal of the battery. The negative terminal will supply new electrons that will also move through the metal toward the positive terminal of the battery. This is called an electrical circuit. The rate of electron flow depends on the resistance of the material in the circuit and the voltage of the battery or power source.

Figure 5.34 Electrical Conductivity of Metals



Metallic substances are good **conductors of electricity.** When the positive and negative terminals of a battery (or other power source) are connected to opposite sides of a metal, the ***mobile valence electrons*** will be attracted (and move) to the positive terminal of the battery. The negative terminal will supply new electrons which will also move through the metal toward the positive terminal of the battery.

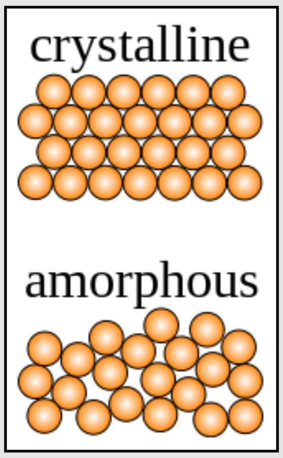
One Last Note on Crystalline Solids

It is also possible for the ***noble gas atoms*** (He, Ne, Kr, Xe, and Ra) to exist as crystalline solids by cooling them to temperatures that only exist (on earth) in cryogenic refrigerated systems [-71°C, (for Ra) to -272 °C (for He)]. At these extremely low temperatures, London induced forces become significant even between ***atoms*** and the noble gases crystallize.

2) Amorphous Solids

In **amorphous solids**, the particles ***are not*** arranged in a regular pattern. The word amorphous is from the Greek "a," *without*, and "morphé," *form*. Examples of amorphous solids include natural and synthetic rubbers. Two-dimensional models of amorphous solids and of crystalline solids are shown in Figure 5.35. In *crystalline solids*, the particles are arranged in an ordered lattice, however no such order exists in *amorphous material*. The molecules in amorphous solids are held together by noncovalent interactions.

Figure 5.35
Two-Dimensional Models of Crystalline and Amorphous Solids



In crystalline solids, the particles are arranged in an ordered lattice, however no such long-range order exists in amorphous material.

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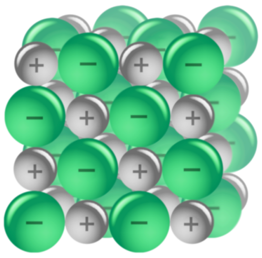
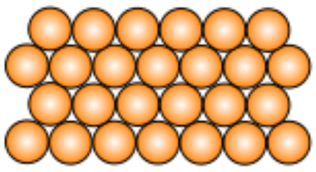
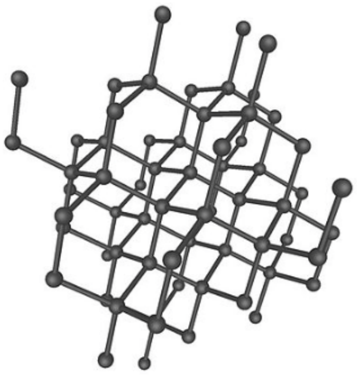
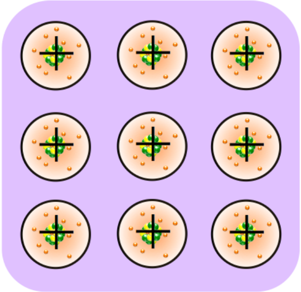
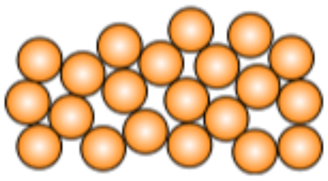
http://creativecommons.org/licenses/by-sa/3.0/legalcode

Summary of Solids

Type	Description	Example(s)	Structural Model
Ionic Solids (Crystalline)	Composed of cations and anions that are arranged in a lattice pattern such that the attraction of unlike charges is maximized and the repulsion of like charges is minimized (ionic bonding).	Table Salt (NaCl)	
Molecular Solids (Crystalline)	Composed of molecules that are arranged in a lattice pattern such that the noncovalent interactions are maximized.	Ice Table Sugar (Sucrose)	
Covalent Network Solids (Crystalline)	The entire bulk of the crystalline solid is composed of atoms that **are all** *covalently bonded to their neighbors.*	Diamond	
Metallic Solids (Crystalline)	The nuclei and their core electrons are in lattice positions and the valence electrons are mobile and dispersed throughout the entire crystal.	Gold, Aluminum	
Amorphous Solids	The particles **are not** arranged in an ordered pattern.	Natural and Synthetic Rubbers	

Chapter 6: Chemical Reactions

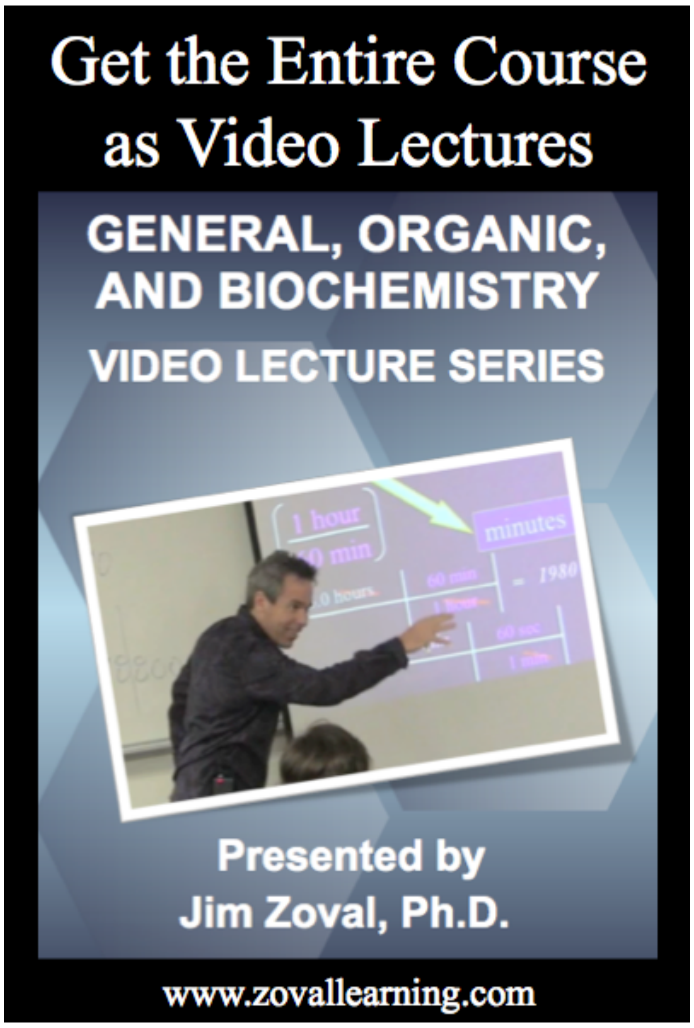
Space Shuttle Atlantis takes flight on the STS-27 mission on December 2, 1988. The Shuttle takes about 8.5 minutes to accelerate to a speed of over 17,000 mph and go into orbit. Atlantis uses two types of rocket engines that each use a chemical reaction for propulsion. Source: Wikimedia Commons, Author: NASA, PD

In chapter 5 you learned about ***physical changes***. In chapter 6 you will learn about **chemical changes** that occur in processes called ***chemical reactions***. Chemical reactions occur in nature and in man-made events. A series of chemical reactions occurs in plants as they convert carbon dioxide and water molecules into the carbohydrate molecules that we eat and oxygen molecules that we breathe. Chemical reactions are used for propulsion in automobile engines and rocket thrusters. Some chemical reactions occur very quickly, as in explosions, and some reactions very slowly, as in the rusting of a nail. Chemistry is the study of how matter interacts with energy and/or other matter; one way this happens is in chemical reactions.

Video Lectures for the General, Organic, and Biochemistry Course

If you **ARE** a **Saddleback College student**, the video lectures for this chapter and all others are available through your class website for ***FREE***. See your instructor for details and the password.

If you **ARE NOT** a **Saddleback College student,** the video lectures can be accessed at: www.zovallearning.com



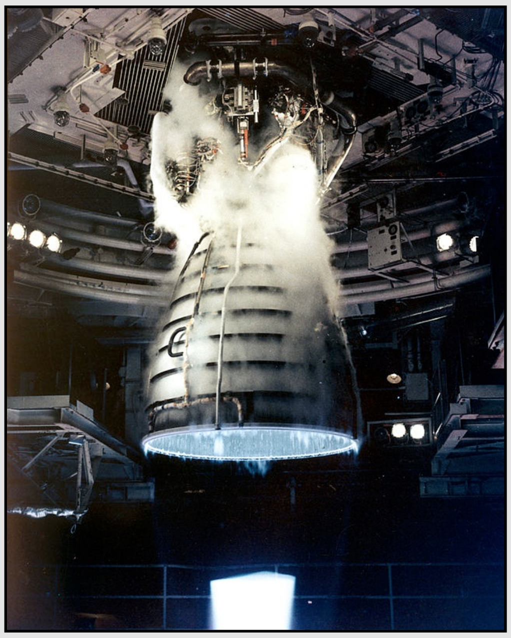
6.1 Chapter 6 Educational Goals

1. Define the term “**chemical reaction.**”
2. Given the **reactants** and **products** in a chemical reaction, *write* and *balance* chemical equations.
3. Be able to do **stoichiometry calculations**.
4. Identify **redox reactions** and determine which species is oxidized and which is reduced.
5. Understand and identify the four ***general types*** of reactions.
6. Identify combustion, hydrogenation of alkenes, hydrolysis of esters, hydration of alkenes, and dehydration of alcohol reactions.
7. Given the reactants for **combustion, hydrogenation of alkenes, hydrolysis of esters, hydration of alkenes,** or **dehydration of alcohol reactions**, be able to *predict* and *draw* structural formulas of the products.
8. Describe the difference in energy changes (ΔG) for **spontaneous** and non-spontaneous reactions, and list the factors that affect the rate of a chemical reaction.

6.2 Introduction to Chemical Reactions

A **chemical reaction** is a process in which chemical bond(s) are *broken* ***and/or*** new bonds are *made,* such that one or more *new substances* are formed. One of the rocket engines in the space shuttle uses a chemical reaction in which oxygen gas and hydrogen gas are ***changed*** into gaseous H_2O molecules. In this reaction of rocket fuel, the H_2O vapor molecules that are produced are moving extremely fast. Propulsion is achieved when the fast-moving H_2O gas molecules collide with the rocket's *thruster*, and thereby apply force to the rocket. A space shuttle thruster is shown in Figure 6.1. To describe the chemical reaction, we say, "oxygen gas ***reacts*** with hydrogen gas to ***produce*** gaseous H_2O." Scientists often write a **chemical equation** to describe a ***chemical reaction***. Chemical equations are similar to mathematical addition equations, except in chemical equations an arrow (→) is used *instead of* an equal (=) sign. For example, the **"*unbalanced*" *chemical equation*** for the reaction of oxygen and hydrogen to produce H_2O vapor is:

Figure 6.1 Rocket Thruster



A close-up view of a Space Shuttle Main Engine during a test firing. Propulsion is achieved when the fast-moving H_2O gas molecules that are produced in a chemical reaction collide and thereby apply force to the rocket's thruster.
Source: Wikimedia Commons, Author: NASA, PD

$$H_2 + O_2 \longrightarrow H_2O \qquad \textit{Equation 6.1}$$

When writing chemical equations, we often indicate the state of each reactant and product in parenthesis after its chemical formula. One of the following states is used: gas (g), liquid (l), solid (s), or aqueous (aq). Aqueous (aq) indicates that the substance is dissolved in water. For our rocket fuel example, we write:

$$H_2\,(g) + O_2\,(g) \longrightarrow H_2O\,(g) \qquad \textit{Equation 6.2}$$

The substances on the ***left-hand side*** of the reaction arrow (→) are referred to as the **reactants**. The substances on the ***right-hand side*** of the reaction arrow are referred to as the **products**.

In the rocket fuel chemical reaction, we began with two *reactants* (O_2 and H_2), and ended with one *product* (H_2O). In our "*unbalanced*" equation, there are two oxygen atoms on the left-hand side of the arrow (in O_2) and only one oxygen atom on the right-hand side (in H_2O). This is why the term "*unbalanced*" was used. Antoine Lavoisier and his wife, Marie-Anne Pierette Paulze, and Mikhail Lomonosov are credited for proposing and verifying the **law of conservation of mass**. This law states that ***matter is neither created nor destroyed in a chemical reaction, only the chemical bonding changes.*** The mass of the products formed in a chemical reaction is always equal to the sum of the masses of the reactants that were used. The *law of conservation of mass* requires that the same number of atoms of each element appear ***on both sides of the chemical equation***; when this is applied to a chemical equation, we say that the equation is "***balanced***." In our rocket fuel chemical equation, we need to have at least *two* H_2O molecules on the right-hand side to "balance" the two oxygen atoms on the left-hand side (in O_2). We use a **coefficient** (shown in red) and re-write the equation as:

$$H_2\,(g) + O_2\,(g) \longrightarrow \mathbf{2}\,H_2O\,(g) \qquad \textit{Equation 6.3}$$

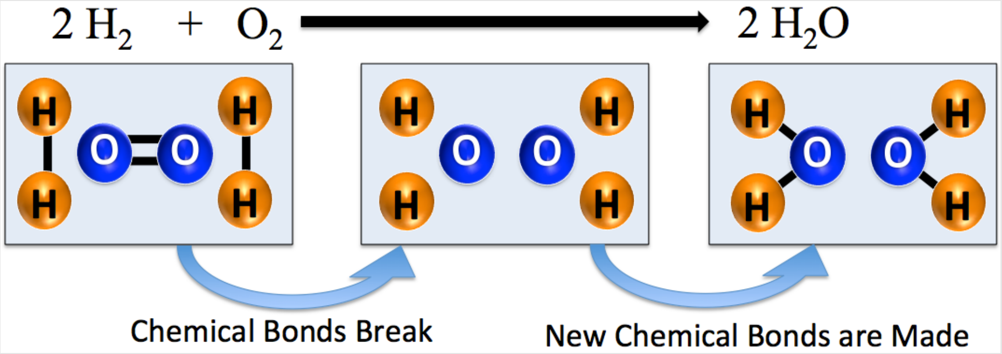
The coefficients indicate the multiples of each reactant and each product needed in order to have a *balanced equation*. If no coefficient appears for a substance, this implies that the coefficient is "1." Since I added a coefficient of "**2**" to H_2O as shown in *Equation 6.3*, the *oxygen atoms* are now *balanced*; there are *two oxygen* atoms ***on each side*** of the equation. Is this equation completely balanced now? No, the hydrogen is not yet balanced. There are two hydrogen atoms on the reactant side (on the left) of the equation and the two H_2O molecules on the product side (right-hand side) contain a total of four hydrogen atoms (two hydrogens for *each* H_2O). We need to use *another coefficient* to balance the equation. We need two H_2 molecules on the *reactant side* in order to balance the chemical equation:

$$\mathbf{2}\,H_2\,(g) + O_2\,(g) \longrightarrow \mathbf{2}\,H_2O\,(g) \qquad \textit{Equation 6.4}$$

Now, in *Equation 6.4*, the law of conservation of mass is satisfied. In this reaction, it takes two H_2 molecules to react with one O_2 molecule to produce two H_2O molecules. One of the educational goals for this chapter is for you to be able to balance chemical equations. Later in this section, I will provide you with a methodical approach for balancing equations, along with several practice problems.

I told you that a chemical reaction is a process in which ***chemical bond(s)*** are *broken* ***and/or*** new bonds are made such that one or more *new substances* are formed. Consider how this occurred in our reaction of rocket fuel. In order to produce two H_2O molecules, ***two*** H-H bonds and the O-O double bond must break and ***four*** new O-H bonds must be made, as illustrated in Figure 6.2.

Figure 6.2 **Breaking and Making Chemical Bonds in a Chemical Reaction**



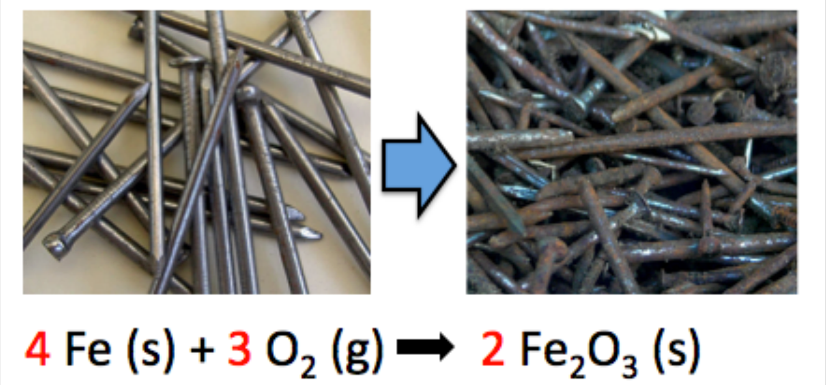
A chemical reaction (or chemical change) is a process in which chemical bond(s) are broken and/or made such that one or more new substances are formed. In order to produce two H_2O molecules, ***two*** H-H bonds and the O-O double bond must break and ***four*** new O-H bonds must be made.

The exact order of bond breaking and making in chemical reactions is called the **reaction mechanism.** The details of the particular reaction mechanism for our reaction of rocket fuel and many other chemical reactions are not completely known and remain an active area of research in academia and industry.

Observational Evidence of Chemical Reactions

When reactants are converted into new substances, several macro-scale observations may present evidence that a chemical reaction has occurred.   A ***color change*** is evidence of a chemical reaction. Many substances absorb visible light and therefore appear with a particular color. As a colored reactant is converted to product(s), the color of the reactant disappears. Chemical reactions ***always*** involve the formation of *one or more* ***new substances*** called ***product(s).*** If a product absorbs visible light, a new color will appear. This is the basis of the color change seen in the chemical reaction that occurs when a nail "rusts." The reactants are iron metal and O_2 gas. Although iron metal does not absorb visible light, it does reflect it, and therefore has a "silver" appearance. The iron metal nail reacts with O_2 in the air to form Fe_2O_3 (rust). Fe_2O_3 absorbs all colors of visible light, a bit more strongly in the blue region, and therefore has a dark brown/red color as shown in Figure 6.3.

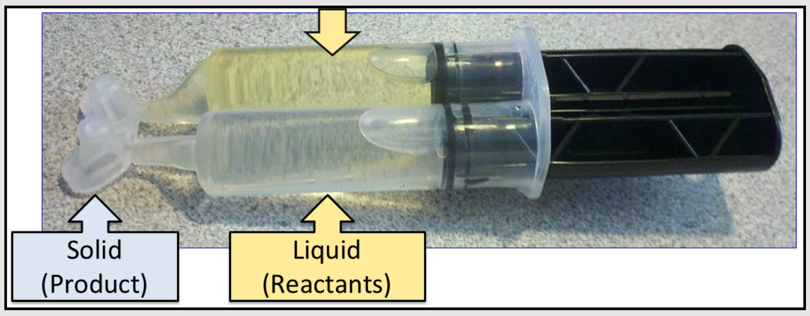
Figure 6.3 Rusting of Nails



The rusting of nails is a chemical reaction that is evidenced by a color change. The iron metal nail reacts with O_2 in the air to form Fe_2O_3 (rust). The reactant, iron, has a "silvery" luster color; the product Fe_2O_3 has a dark brown/red color.
Source: Wikimedia Commons, Authors: Walter J. Pilsak (left, CC-BY-SA, http://creativecommons.org/licenses/by-sa/3.0/legalcode) and Andreas Praefcke (right, PD)

The ***formation of a new phase*** is evidence of a chemical reaction. For example, epoxy adhesives involve a chemical reaction of two liquid reactants that form a new, solid product substance, as shown in Figure 6.4.

Figure 6.4 Formation of a Solid in a Reaction



In the reaction that forms epoxy adhesive, two liquids are converted to a new, solid material.
Source: Wikimedia Commons, Author: Taktoa, CC-BY-SA, http://creativecommons.org/licenses/by-sa/3.0/legalcode), boxes with arrows added.

Another example of a reaction in which a ***new phase is formed*** is the reaction of aqueous acetic acid (white vinegar) with sodium bicarbonate (baking soda).

$$C_3H_4O_2\,(aq) \;+\; Na_2HCO_3\,(s) \;\longrightarrow\; H_2O\,(l) \;+\; Na_2C_3H_3O_2\,(aq) \;+\; CO_2\,(g)$$

acetic acid **sodium bicarbonate** **water** **sodium acetate** **carbon dioxide**

Figure 6.5 Gas Formation in a Chemical Reaction

The reaction of aqueous acetic acid (white vinegar) with sodium bicarbonate (baking soda) produces water, dissolved sodium acetate, and carbon dioxide ***gas***. The formation of carbon dioxide gas is clearly evident as bubble formation.

Source: Wikimedia Commons, Author: Katerha CC-BY, http://creativecommons.org/licenses/by/2.0/legalcode

This reaction produces water, dissolved sodium acetate, and carbon dioxide ***gas***. There is no direct observational evidence of the formation of water or dissolved sodium acetate, however, the formation of carbon dioxide gas is clearly evident as the bubble formation seen in Figure 6.5.

Figure 6.6 Temperature Change in a Chemical Reaction

A photograph of a thermite reaction. The temperature of the iron metal that is produced is so high that it melts and can be seen as sparks with trails of light.

Source: Wikimedia Commons
Author: Nikthestunned, CC-BY-SA, http://creativecommons.org/licenses/by-sa/3.0/legalcode

Observation of a ***temperature change*** is evidence of a chemical reaction. An example of a chemical reaction in which the temperature ***increases*** is a thermite reaction. In a thermite reaction, a metal powder reacts with a metal oxide powder. The thermite reaction shown in Figure 6.6 is the reaction between aluminum powder and iron(III) oxide powder:

$$2\,Al\,(s) + Fe_2O_3\,(s) \longrightarrow Al_2O_3\,(s) + 2\,Fe\,(l)$$

The temperature of the products is so high - up to 2500 ^{o}C - that the iron metal melts and can be seen as sparks with trails of light.

Observation of the ***emission of light*** is evidence of a chemical reaction. Examples of this are the thermite reaction (above) and a chemical reaction that occurs in fireflies. In a series of two reactions, a molecule called firefly luciferin is converted to oxyluciferin. Other reactants (O_2 and ATP) and products (AMP, diphosphate, and CO_2) are involved in the reactions but are not shown below. The oxyluciferin is produced with electrons that are in excited states (not the ground state). This high-energy oxyluciferin product emits light as the electrons relax to their ground state in a process called **bioluminescence**.

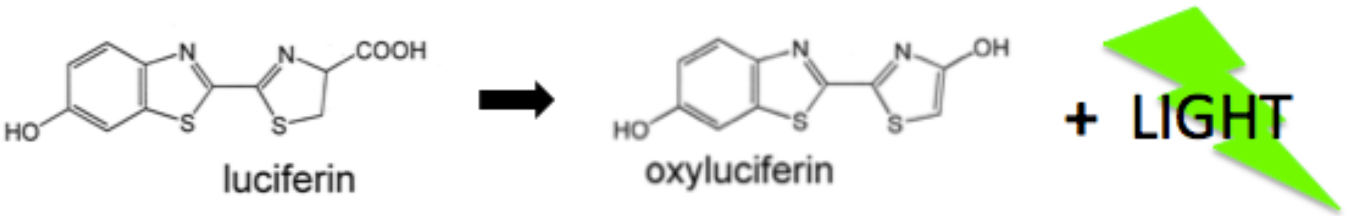


Figure 6.7 Emission of Light in a Reaction

In a series of two reactions that occur in fireflies, a molecule called firefly luciferin is converted to oxyluciferin. The oxyluciferin is produced with electrons that are in excited states (not the ground state). This high-energy oxyluciferin product emits light.

Source: Wikimedia Commons, Author: Emmanuelm at en.wikipedia, CC-BY, http://creativecommons.org/licenses/by/2.0/legalcode

Observation of ***a new odor*** is evidence of a chemical reaction. Chemical reactions ***always*** involve the production of one or more new *substances*. If a new odor is detected, then a new substance must have been produced. An example of the detection of a new odor from a chemical reaction is "rotting." Rotting is a process in which organic compounds are broken down into smaller molecules and in most cases distinctive, unpleasant odors are observed. Rotting involves many different chemical reactions and it varies for each type of organic material. Some of these decomposition reactions involve reactants and enzymes from other organisms such as bacteria and fungi. Although it was tempting, in order to keep this book pleasant, and in taking first-class advice from my wife, I have not included an image of a decomposed animal.

The ***appearance of a flame*** is evidence of a chemical reaction. Flames appear in some reactions that involve an increase in temperature. For example, the burning (combustion) of hydrocarbons are almost always accompanied by flames. Natural gas is composed primarily of methane (CH_4). When methane combusts, it reacts with oxygen gas to produce carbon dioxide gas and H_2O vapor and flames are observed.

$$CH_4\,(g) \quad + \quad 2\,O_2\,(g) \quad \longrightarrow \quad CO_2\,(g) \;+\; 2\,H_2O\,(g)$$

6.3 Balancing Chemical Equations

Source: Wikimedia Commons, US PD

Matter is neither created nor destroyed in a chemical reaction. Therefore, the same number of atoms of each element appear on both sides of a ***balanced chemical equation***. I introduced you to the ***law of conservation of mass*** and the need to balance chemical equations in the previous section. ***Some students*** are able to balance chemical equations "*in their heads*" by inspection of the unbalanced equation. This approach often involves trial and error placement of coefficients. ***Other students*** prefer a systematic, methodical approach. In this section, I will provide you with a systematic method for balancing equations. **Whether you use the inspection (trial and error) approach *or* the systematic method, the end result is the *same* *balanced equation*.**

There are ***three steps*** involved in the *systematic balancing method*:

Step 1: Make a table that lists the elements that are present and count all atoms on each side of the *unbalanced* equation.

- If **H_2 or O_2** is present, list these elements last.
- A polyatomic ion may be counted as one "element" ***if it appears on both sides of the equation.***

Step 2: Balance an element in the table by adding ***coefficient(s)*** to the equation (start with the first element on the list).

Step 3: Recount each atom and update the table, then repeat **Steps 2 and 3** for all elements as needed until the equation is balanced.

In order for you to learn how to use this balancing method, I will use it to do some example problems. We will begin by applying our method to the reaction of rocket fuel.

Example: Balance the equation for the following reaction:

$$\underline{\qquad\qquad} H_2\,(g) + \underline{\qquad\qquad} O_2\,(g) \rightarrow \underline{\qquad\qquad} H_2O\,(g)$$

Step 1: Make a table that lists the elements that are present and count all atoms on each side of the *unbalanced* equation.

- If **H_2 or O_2** is present, list these elements last.
  - **H_2** and/or **O_2** are often present in chemical reactions. When **H_2** and/or **O_2** are present, we list hydrogen and oxygen last because **H_2** and **O_2** *consist of only one type of element*, and therefore when a coefficient is added to these molecules, it will not change the number of atoms of other elements that have already been balanced.
- A polyatomic ion may be counted as one "element" ***if it appears on both sides of the equation.***
  - This is not necessary in this example. There are no polyatomic ions.
- There are ***two*** oxygen atoms on the *reactant side* of the *unbalanced* equation (in O_2) and **one** oxygen atom present on the product side (in H_2O). There are ***two*** hydrogen atoms on the *reactant side* of the equation (in H_2) and **two** hydrogen atoms present on the product side (in H_2O).

Amount on Reactant Side	Element	Amount on Product Side
2	**O**	1
2	**H**	2

Step 2: Balance an element in the table by adding coefficients to the equation (start with the first element on the list).

- The oxygen atoms are not balanced; there are two on the reactant side and only one on the product side. Find a factor to multiply the number of oxygen atoms by in order to balance them. We need to multiply the number of oxygen atoms on the product side of the equation by a factor of **2**.

Amount on Reactant Side	Element	Amount on Product Side
2	**O**	1 x 2 = 2
2	**H**	2

- Use this factor as a ***coefficient for the substance that contains the element*** on the appropriate side of the chemical equation. Since we multiplied the oxygen ***on the product side*** of the equation by a factor of **2**, we place a coefficient of **2** in front of the H_2O.

$$\underline{\qquad\qquad}H_2(g) + \underline{\qquad\qquad}O_2(g) \rightarrow \mathbf{2}\ H_2O(g)$$

Step 3: Recount each atom and update the table, then repeat **Steps 2 and 3** for all elements, until the equation is balanced.

- We placed a coefficient of **2** in front of the H_2O in order to balance the oxygen. This indicates that ***two*** water molecules are formed. By adding the coefficient of **2**, we ***also*** changed the number of hydrogen atoms that are on the product side. There are now ***two*** water molecules and each water molecule contains *two* hydrogens, therefore we now have a total of ***4 hydrogen atoms*** on the product side.
- After recounting each atom, update the table:

Amount on Reactant Side	Element	Amount on Product Side
2	**O**	1 x 2 = 2
2	**H**	~~2~~ → 4

- **Repeat Steps 2 and 3** for all elements, ***until the equation is balanced***.

  Moving from the *top to the bottom* of the list of elements in the table, repeat Steps 2 and 3 until the equation is balanced. Oxygen is now balanced, so we move down the list to hydrogen.

  - **Step 2 (again):** Balance an element in the table by adding coefficients to the equation.
  - There are ***two*** hydrogen atoms on the reactant side and ***four*** on the product side. Find the factor to multiply the number of hydrogen atoms by in order to balance them. We need to multiply the number of hydrogen atoms on the reactant side of the equation by a factor of **2**.

Amount on Reactant Side	Element	Amount on Product Side
2	**O**	1 x 2 = 2
2 x 2 = 4	**H**	~~2~~ → 4

  - Use the factor as a ***coefficient for the substance that contains the element*** on the appropriate side of the chemical equation. Since we multiplied the hydrogens on the reactant side of the equation by a factor of **2**, we place a coefficient of **2** in front of the H_2.

$$\mathbf{2}\ H_2(g) + O_2(g) \rightarrow \mathbf{2}\ H_2O(g)$$

  Step 3 (again): Recount each atom and update the table, then repeat **Steps 2 and 3** for all elements as needed until the equation is balanced.

  When we placed a coefficient of **2** in front of the H_2, it did not change the number of any other atoms in the equation (oxygen in this example). ***The equation is now balanced.***

    - Note that the coefficient for O_2 is absent. We never write a coefficient of "1"; the absence of a coefficient for a substance implies a value of 1 for that substance.

You try one now. **Balance the following equation:** (The solution and commentary for each step is given on the next page.)

$$\underline{\qquad\quad}Mg\ (s) + \underline{\qquad\quad}O_2\ (g) \rightarrow \underline{\qquad\qquad}MgO\ (s)$$

Solution:

Step 1: Make a table that lists the elements that are present and count all atoms on each side of the *unbalanced* equation.

$$\_\_\_\_\_\text{Mg}\,(s) + \_\_\_\_\_\_\text{O}_2\,(g) \rightarrow \_\_\_\_\_\_\_\text{MgO}\,(s)$$

- If **H_2 or O_2** is present, list these elements last.
- A polyatomic ion may be counted as one "element" if it appears on both sides of the equation.

  There are no polyatomic ions in this example.

There is ***one*** magnesium on the *reactant side* and ***one*** magnesium on the product side (in MgO). There are ***two*** oxygens on the *reactant side* (in O_2) and **one** oxygen present on the product side (in MgO).

Amount on Reactant Side	Element	Amount on Product Side
1	**Mg**	1
2	**O**	1

Step 2: Balance an element in the table by adding coefficients to the equation (start with the first element on the list).

- Magnesium is balanced; there is one magnesium on each side.
- The oxygens are not balanced; there are two on the reactant side and only one on the product side. Find the factor to multiply the number of oxygen atoms by in order to balance them.

  We need to multiply the oxygens on the product side of the equation by a factor of 2.

Amount on Reactant Side	Element	Amount on Product Side
1	**Mg**	1
2	**O**	1 x 2 = 2

- Use the factor as a ***coefficient for the substance that contains the element*** on the appropriate side of the chemical equation. Since we multiplied the oxygen ***on the product side*** of the equation by a factor of **2**, we place a coefficient of **2** in front of the MgO.

$$\_\_\_\_\_\text{Mg}\,(s) + \_\_\_\_\_\_\text{O}_2\,(g) \rightarrow \mathbf{2}\ \text{MgO}\,(s)$$

Step 3: Recount each atom and update the table, then repeat **Steps 2 and 3** for all elements, until the equation is balanced.

- We placed a coefficient of **2** in front of the MgO in order to balance the oxygens. This indicates that ***two*** formula units of MgO are formed. By adding the coefficient of **2**, we also change the number of magnesiums that are on the product side. There are now **two** formula units of MgO and each formula unit contains *one* magnesium, therefore we now have a total of ***two magnesiums*** on the product side.
  - The term "***formula unit***" was used for magnesium oxide (MgO) because it is an ionic compound and therefore does not exist as an individual *molecule*.
- After recounting each atom, update the table:

Amount on Reactant Side	Element	Amount on Product Side
1	**Mg**	~~1~~ → 2
2	**O**	1 x 2 = 2

- **Repeat Steps 2 and 3** for all elements as needed ***until the equation is balanced***.

  Moving from the *top to the bottom* of the list of atoms in the table, repeat **Steps 2 and 3** until the equation is balanced. **Mg *is no longer balanced*.**

  - **Step 2 (again):** Balance an element in the table by adding coefficients to the equation.

$$\_\_\_\_\_\text{Mg}\,(s) + \_\_\_\_\_\_\text{O}_2\,(g) \rightarrow \mathbf{2}\ \text{MgO}\,(s)$$

  - There are ***two*** magnesiums on the product side and only ***one*** on the reactant side. Find the factor to multiply the number of magnesium atoms by in order to balance them. We need to multiply the magnesiums on the reactant side of the equation by a factor of **2**. Use the factor as a coefficient in the equation.

Amount on Reactant Side	Element	Amount on Product Side
1 x 2 = 2	**Mg**	~~1~~ → 2
2	**O**	1 x 2 = 2

  - Since we multiplied the magnesium on the reactant side of the equation by a factor of **2**, we place a coefficient of **2** in front of the Mg.

$$\mathbf{2}\ \text{Mg}\,(s) + \text{O}_2\,(g) \rightarrow \mathbf{2}\ \text{MgO}\,(s)$$

The equation is now balanced.

I gave you a couple of instructions for performing **Step 1** that will save time and make balancing a bit simpler**.** The *first* was: ***If H_2 or O_2 is present, list them last.*** You saw the utility of this suggestion in the first example problem. We list them last because they *consist of only one type of element*, and therefore when a coefficient is added it will not change the number of any other atoms that have already been balanced. The *second instruction* was, ***a polyatomic ion may be counted as one "element" if it appears on both sides of the equation.*** I will now show you an example of a problem that involves the same polyatomic ion *on each side of the equation*.

Example: Balance the following chemical equation:

$$\_\_\_\_\_\_\ \mathrm{Al}\ (s)\ +\ \_\_\_\_\_\_\ \mathrm{FeSO_4}\ (aq)\ \rightarrow\ \_\_\_\_\_\_\ \mathrm{Al_2(SO_4)_3}\ (aq)\ +\ \_\_\_\_\_\_\ \mathrm{Fe}\ (s)$$

Step 1: Make a table that lists the elements that are present and count all atoms on each side of the *unbalanced* equation.

- If H_2 **or** O_2 is present, list these elements last.

  Neither are present in this example.

- **A polyatomic ion may be counted as one "element" if it appears *on both sides* of the equation.**

  In this reaction, there was no chemical change *in the sulfate* (SO_4^{2-}) *polyatomic ion*; it appears ***on both sides*** of the equation. When this occurs, balance the polyatomic ion as if it was an element in your table's list:

Amount on Reactant Side	Element	Amount on Product Side
1	**(SO_4)**	3
1	**Al**	2
1	**Fe**	1

This is a shortcut that makes balancing much easier since you no longer need to balance sulfate's sulfur and oxygen atoms *individually*.

Step 2: Balance an element in the table by adding coefficients to the equation (start with the first element on the list.)

- The sulfate ions *are not balanced*; there is ***one*** on the reactant side and ***three*** on the product side. We need to multiply the sulfates on the reactant side of the equation by a factor of **3**.

Amount on Reactant Side	Element	Amount on Product Side
1 x 3 = 3	**(SO_4)**	3
1	**Al**	2
1	**Fe**	1

Use the factor as a ***coefficient for the substance that contains the sulfate*** on the appropriate side of the chemical equation. Since we multiplied the sulfates ***on the reactant side*** of the equation by a factor of **3**, we place a coefficient of **3** in front of the $FeSO_4$.

$$\_\_\_\_\_\_\ \mathrm{Al}\ (s)\ +\ \mathbf{3}\ \mathrm{FeSO_4}\ (aq)\ \rightarrow\ \_\_\_\_\_\_\ \mathrm{Al_2(SO_4)_3}\ (aq)\ +\ \_\_\_\_\_\_\ \mathrm{Fe}\ (s)$$

Step 3: Recount each atom and update the table, then repeat **Steps 2 and 3** for all elements, until the equation is balanced.

- We placed a coefficient of **3** in front of the $FeSO_4$ in order to balance the sulfates. This indicates that **three** formula units of $FeSO_4$ are formed. By adding the coefficient of **3**, we also change the number of irons that are on the *reactant side*.
- We now have a total of ***3 irons*** on the reactant side.
- After recounting each atom, update the table:

Amount on Reactant Side	Element	Amount on Product Side
1 x 3 = 3	**(SO_4)**	3
1	**Al**	2
~~1~~ → 3	**Fe**	1

-

- **Repeat Steps 2 and 3** for all elements as needed ***until the equation is balanced***.

  Moving from the *top to the bottom* of the list of atoms in the table, repeat **Steps 2 and 3** until the equation is balanced.

  - **Step 2 (again):** Balance an element in the table by adding coefficients to the equation.

    There are ***two*** aluminums on the product side and only ***one*** on the reactant side. We need to multiply the aluminums on the reactant side of the equation by a factor of **2**.

Amount on Reactant Side	Element	Amount on Product Side
1 x 3 = 3	(SO_4)	3
1 x 2 = 2	**Al**	2
~~1~~ → 3	**Fe**	1

  - Since we multiplied the aluminums on the reactant side of the equation by a factor of **2**, we place a coefficient of **2** in front of the Al.

$$\mathbf{2}\ \mathrm{Al}\ (s) \ + \ \mathbf{3}\ \mathrm{FeSO_4}\ (aq) \ \rightarrow \ \_\_\_\_\_\_\ \mathrm{Al_2(SO_4)_3}\ (aq) \ + \ \_\_\_\_\_\_\ \mathrm{Fe}\ (s)$$

  - **Step 3 (again):** Recount each atom and update the table, then repeat **Steps 2 and 3** for all elements, until the equation is balanced.
    - Since aluminum is not combined with any other types of atoms as a ***reactant***, we did not change the amount of any other elements or sulfates by adding the coefficient.

  - **Step 2 (again):** Balance an element in the table by adding coefficients to the equation.

    There are ***three*** irons on the reactant side and only ***one*** on the product side. We need to multiply the irons on the product side of the equation by a factor of **3**.

Amount on Reactant Side	Element	Amount on Product Side
1 x 3 = 3	(SO_4)	3
1 x 2 = 2	**Al**	2
~~1~~ → 3	**Fe**	1 x 3 = 3

  - Since we multiplied the irons on the product side of the equation by a factor of **3**, we place a coefficient of **3** in front of the Fe.

$$\mathbf{2}\ \mathrm{Al}\ (s) \ + \ \mathbf{3}\ \mathrm{FeSO_4}\ (aq) \ \rightarrow \ \mathrm{Al_2(SO_4)_3}\ (aq) \ + \ \mathbf{3}\ \mathrm{Fe}\ (s)$$

  - **Step 3 (again):** Recount each atom and update the table, then repeat **Steps 2 and 3** for all elements, until the equation is balanced.
    - Since iron is not combined with any other types of atoms as a ***product***, we did not change the amount of any other elements or sulfates by adding the coefficient.

The equation is now balanced.

I want to show you an example in which the same element appears in two different substances ***on the same side of a chemical equation***. In the following example, oxygen appears in ***both*** of the reaction ***products***.

Example: Balance the following reaction for the combustion of propane:

$$\_\_\_\_\_\ C_3H_8\,(g) + \_\_\_\_\_\ O_2\,(g) \rightarrow \_\_\_\_\_\ CO_2\,(g) + \_\_\_\_\_\ H_2O\,(g)$$

Step 1: Make a table that lists the elements that are present and count all atoms on each side of the *unbalanced* equation.

- If **H_2 or O_2** is present, list these elements last.
- We list oxygen last:

Amount on Reactant Side	Element	Amount on Product Side
3	**C**	1
8	**H**	2
2	**O**	2 (in CO_2) + 1 (in H_2O) = 3

Step 2: Balance an element in the table by adding coefficients to the equation (start with the first element on the list.)

- The carbon atoms *are not balanced*; there are ***three*** on the reactant side and only ***one*** on the product side. We need to multiply the carbon on the product side of the equation by a factor of **3**.

Amount on Reactant Side	Element	Amount on Product Side
3	**C**	1 x 3 = 3
8	**H**	2
2	**O**	2 (in CO_2) + 1 (in H_2O) = 3

- Use the factor as a ***coefficient for the substance that contains the element*** on the appropriate side of the chemical equation. Since we multiplied the carbon atoms ***on the product side*** of the equation by a factor of **3**, we place a coefficient of **3** in front of the CO_2.

$$\_\_\_\_\_\ C_3H_8\,(g) + \_\_\_\_\_\ O_2\,(g) \rightarrow \mathbf{3}\ CO_2\,(g) + \_\_\_\_\_\ H_2O\,(g)$$

Step 3: Recount each atom and update the table, then repeat **Steps 2 and 3** for all elements, until the equation is balanced.

- We placed a coefficient of **3** in front of the CO_2 in order to balance the carbon atoms. By adding the coefficient of **3**, we also change the number of oxygen atoms that are on the product side. We now have a total of ***7 oxygen atoms*** on the reactant side (6 from CO_2 and 1 from H_2O).
- After recounting each atom, update the table:

Amount on Reactant Side	Element	Amount on Product Side
3	**C**	1 x 3 = 3
8	**H**	2
2	**O**	6 (in 3 CO_2) + 1 (in H_2O) = 7

- **Repeat Steps 2 and 3** for all elements as needed ***until the equation is balanced***.
  - Moving from the *top to the bottom* of the list of atoms in the table, repeat **Steps 2 and 3** until the equation is balanced.

  - **Step 2 (again):** Balance an element in the table by adding coefficients to the equation. There are ***8*** hydrogen atoms on the reactant side and only ***2*** on the product side. We need to multiply the hydrogen atoms on the product side of the equation by a factor of **4**.

Amount on Reactant Side	Element	Amount on Product Side
3	**C**	1 x 3 = 3
8	**H**	2 x 4 = 8
2	**O**	6 (in 3 CO_2) + 1 (in H_2O) = 7

- Since we multiplied the hydrogen atoms on the product side of the equation by a factor of **4**, we place a coefficient of **4** in front of the H_2O.

$$\_\_\_\_\_ \ C_3H_8\,(g) + \_\_\_\_\_ \ O_2\,(g) \rightarrow \mathbf{3}\ CO_2\,(g) + \mathbf{4}\ H_2O\,(g)$$

- **Step 3 (again):** Recount each atom and update the table, then repeat **Steps 2 and 3** for all elements, until the equation is balanced.

  By placing **4** in front of the H_2O, we also change the number of oxygen atoms that are on the product side. We now have a total of ***10 oxygen atoms*** on the product side (**6** from the **3** CO_2 and **4** from the **4** H_2O).

Amount on Reactant Side	Element	Amount on Product Side
3	**C**	1 x 3 = 3
8	**H**	2 x 4 = 8
2	**O**	6 (in 3 CO_2) + 4 (in 4 H_2O) = 10

- **Step 2 (again):** Balance an element in the table by adding coefficients to the equation. There are ***ten*** oxygen atoms on the product side and only ***two*** on the reactant side. We need to multiply the oxygens on the reactant side of the equation by a factor of **5**.

Amount on Reactant Side	Element	Amount on Product Side
3	**C**	1 x 3 = 3
8	**H**	2 x 4 = 8
2 x 5 = 10	**O**	6 (in 3 CO_2) + 4 (in 4 H_2O) = 10

- Since we multiplied the oxygen atoms on the reactant side of the equation by a factor of **5**, we place a coefficient of **5** in front of the O_2.

$$C_3H_8\,(g) + \mathbf{5}\ O_2\,(g) \rightarrow \mathbf{3}\ CO_2\,(g) + \mathbf{4}\ H_2O\,(g)$$

- **Step 3 (again):** Recount each atom and update the table, then repeat **Steps 2 and 3** for all elements as needed until the equation is balanced.

  The equation is now balanced. I hope you see the utility of listing oxygen ***last*** in the table when O_2 is present; because the oxygen in O_2 is not combined with any other elements, we did not change the amount of the other elements by adding a coefficient to O_2. The same is true for hydrogen; list hydrogen ***last*** in the table when H_2 is present.

Sometimes two coefficients must be *simultaneously* applied in order to balance an element. The example that follows will show you when and how this is done.

Example: Balance the following chemical equation: $\_\_\_\_\_\_ \ Al\,(s) + \_\_\_\_\_\_ \ O_2\,(g) \rightarrow \_\_\_\_\_\_ \ Al_2O_3\,(s)$

Step 1: Make a table that lists the elements that are present and count all atoms on each side of the *unbalanced* equation.

Amount on Reactant Side	Element	Amount on Product Side
1	**Al**	2
2	**O**	3

Step 2: Balance an element in the table by adding coefficients to the equation (start with the first element on the list.)

- Aluminum *is not balanced*; there is ***one*** on the reactant side and ***two*** on the product side. We need to multiply the aluminum on the reactant side of the equation by a factor of **2**.

Amount on Reactant Side	Element	Amount on Product Side
1 x 2 = 2	**Al**	2
2	**O**	3

- Since we multiplied the aluminum ***on the reactant side*** of the equation by a factor of **2**, we place a coefficient of **2** in front of the Al (s).

$$\mathbf{2}\ \mathrm{Al}\ (s) + \underline{\qquad}\ \mathrm{O_2}(g) \rightarrow \underline{\qquad}\ \mathrm{Al_2O_3}\ (s)$$

Step 3: Recount each atom and update the table, then repeat **Steps 2 and 3** for all elements, until the equation is balanced.

- Since aluminum metal is not combined with oxygen as a ***reactant***, we did not change the amount of oxygen.

- **Repeat Steps 2 and 3** for all elements as needed ***until the equation is balanced***.
  Moving from the *top to the bottom* of the list of atoms in the table, repeat Steps 2 and 3 until the equation is balanced.

  - **Step 2 (again):** Balance an element in the table by adding coefficients to the equation.
    There are ***two*** oxygens on the reactant side and ***three*** on the product side. ***This is a situation that you have not yet seen in our examples***. We need to add coefficients to the **both sides of the equation** to balance the oxygens.
    - Since there are 2 oxygens on one side of the equation and 3 oxygens on the other, we must find the ***least common multiple*** of 2 and 3. The least common multiple of these two numbers is 6.
      - 2 x 3 = 6 and 3 x 2 =6
    - There are ***2*** oxygens on the ***reactant side*** of the equation, so we need to multiply the oxygens on the reactant side by a factor of **3**.
    - There are ***3*** oxygens on the ***product side*** of the equation, so we need to multiply the oxygens on the product side by a factor of **2**.

Amount on Reactant Side	Element	Amount on Product Side
1 x 2 = 2	**Al**	2
2 x 3 = 6	**O**	3 x 2 = 6

  - Since we multiplied the oxygens on the ***reactant side*** of the equation by a factor of **3**, we place a coefficient of **3** in front of the $\mathbf{O_2}(g)$.

$$\mathbf{2}\ \mathrm{Al}\ (s) + \mathbf{3}\ \mathrm{O_2}(g) \rightarrow \underline{\qquad}\ \mathrm{Al_2O_3}\ (s)$$

  - Since we multiplied the oxygens on the ***product side*** of the equation by a factor of **2**, we place a coefficient of **2** in front of the $\mathbf{Al_2O_3}$ (s).

$$\mathbf{2}\ \mathrm{Al}\ (s) + \mathbf{3}\ \mathrm{O_2}(g) \rightarrow \mathbf{2}\ \mathrm{Al_2O_3}\ (s)$$

  - **Step 3 (again):** Recount each atom and update the table, then repeat **Steps 2 and 3** for all elements, until the equation is balanced.
    - By placing **2** in front of the $\mathrm{Al_2O_3}$ (s), we changed the number of aluminums that are on the product side. We now have a total of ***4 aluminums*** on the product side.

Amount on Reactant Side	Element	Amount on Product Side
1 x 2 = 2	**Al**	2 → 4
2 x 3 = 6	**O**	3 x 2 = 6

  - **Step 2 (again):** Balance an element in the table by adding coefficients to the equation.
    - Since there are ***four aluminums*** on the product side and only ***two*** on the reactant side, multiply the aluminum on the reactant side of the equation by a factor of **2**.

- We have already multiplied the aluminums on the reactant side by a factor of **2**. Since we now are multiplying the aluminums on the product side of the equation by a factor of **2** ***for a second time***, we multiply the existing $Al(s)$ coefficient of **2** by the second factor of **2** to give a new total of **4**.

Amount on Reactant Side	Element	Amount on Product Side
(1 x 2) x 2 = 4	**Al**	2
2 x 3 = 6	**O**	3 x 2 = 6

$$(\mathbf{2} \times \mathbf{2})\ Al\,(s) + \mathbf{3}\ O_2(g) \rightarrow \mathbf{2}\ Al_2O_3\,(s)$$

$$\mathbf{4}\ Al\,(s) + \mathbf{3}\ O_2(g) \rightarrow \mathbf{2}\ Al_2O_3\,(s)$$

The equation is now balanced.

Review 6.1: Balancing Equations: General Concepts

Answer the following questions about the chemical equation shown below:

$$2\ H_2 + O_2 \rightarrow 2\ H_2O$$

a. What are the reactants?
b. What is the product?
c. What do we call the number "2" in front of the H_2 (and H_2O)?
d. Is the reaction balanced?
e. Why is there not a coefficient for O_2?
f. How many hydrogen **atoms** are needed to produce **two** H_2O molecules?
g. How many oxygen **atoms** are needed to produce **two** H_2O molecules?
h. How many hydrogen **molecules** are needed to produce **two** H_2O molecules?
i. How many oxygen **molecules** are needed to produce **two** H_2O molecules?
j. Write the "word equation" that you would use to describe this reaction.
   - Use words in a sentence, not formulas or an arrow. ***Ignore the coefficients***.

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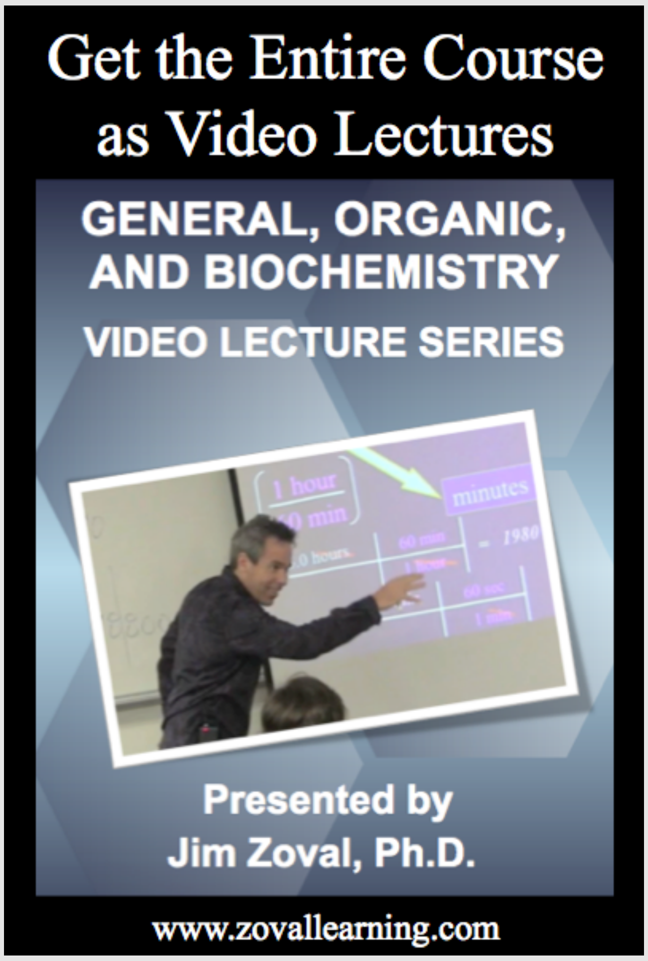

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Common Errors to Avoid When Balancing Chemical Equations

When you are asked to balance an equation, for example, _____ N_2 + _____ $O_2 \rightarrow$ _____ N_2O, *be mindful of the following*:

1) **Do not** change the ***formula*** of a reactant or product.

$$N_2 + O_2 \rightarrow N_2O_2$$

By ***changing*** the product from N_2O to N_2O_2, you are not balancing the equation *for the given reaction*. The formation of N_2O_2 may or may not occur, however *it is not the reaction whose equation you were asked to balance*.

2) **Do not** add ***new*** reactants or products.

$$N_2 + O_2 \rightarrow N_2O + O$$

By adding a new product (O), you are not balancing the equation for *the reaction that you were asked to balance*.

3) **Do not** use ***multiples of the coefficients*** when writing the balanced equation.

We ***would not*** write: $4\ N_2 + 2\ O_2 \rightarrow 4\ N_2O$

Although the equation above is balanced, the convention for balancing equations is to use the ***lowest set*** of coefficients. To get this set, we divide each coefficient by the greatest common factor of all coefficients. The greatest common factor of the coefficients in our equation is **2**, so the correct balanced equation is written as:

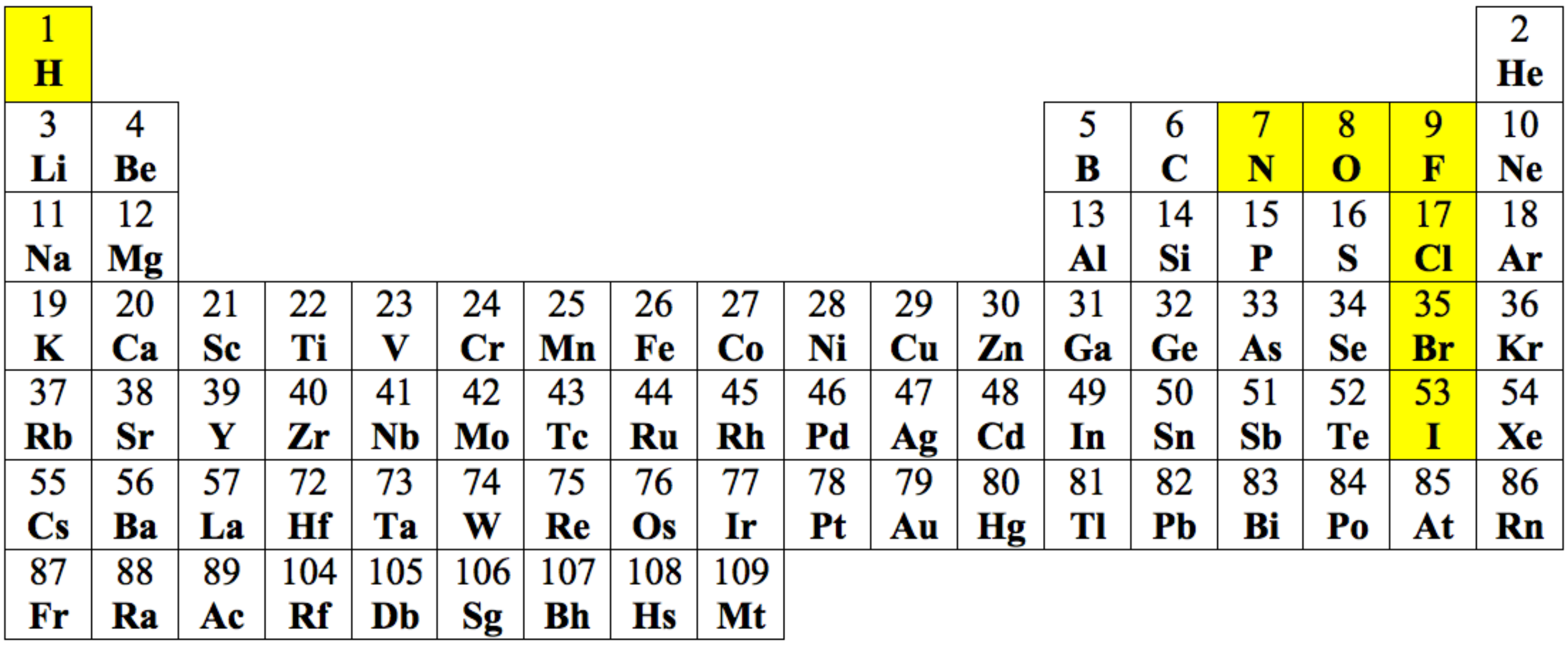
$$2\ N_2 + O_2 \rightarrow 2\ N_2O$$

4) When chemical reactions are described in ***words***, the following ***diatomic molecules*** are referred to by ***their element's names***:

$$H_2,\ N_2,\ O_2,\ F_2,\ Cl_2,\ Br_2,\ \text{and}\ I_2$$

When uncombined with other elements in compounds, these elements exist as *diatomic molecules*. These elements are highlighted in the periodic table shown in Figure 6.8. Except for H_2, these substances can be remembered by the upside-down "**L**" pattern seen in their periodic table positions.

Figure 6.8 **Elements that Exist as Diatomic Molecules**



1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt									

The highlighted elements, when *uncombined* with other elements in compounds, exist as ***diatomic molecules*** that are referred to by their element's names.

When describing our example reaction, $2\ N_2 + O_2 \rightarrow 2\ N_2O$, ***in spoken words***, we would say, "***nitrogen*** reacts with ***oxygen*** to produce (or form) dinitrogen monoxide."

Note that oxygen ***also*** exists as O_3, however O_3 is called "ozone."

Review 6.2: Balancing Equations

Balance the following chemical equations:

a. $Fe + O_2 \rightarrow Fe_2O_3$
b. $H_2 + Cl_2 \rightarrow HCl$
c. $Ag + H_2S \rightarrow Ag_2S + H_2$
d. $CH_4 + O_2 \rightarrow CO_2 + H_2O$
e. $HgO \rightarrow Hg + O_2$
f. $Co + H_2O \rightarrow Co_2O_3 + H_2$

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

Review 6.3: Writing Balanced Equations from Reaction Descriptions

Write ***balanced chemical equations*** for each of the following descriptions of a chemical reaction.

- You **do not** need to include the *states* of the reactants or products.
- **IMPORTANT NOTE:** Before attempting to balance the equations, you must first convert the ***compound names*** into the correct ***chemical formulas***. If you begin to struggle with that, you may wish to go back to chapter 3 and re-work the naming problems.

a. Aluminum metal ***reacts with*** copper(II) chloride ***to produce*** aluminum chloride and copper metal.
b. Lead(II) nitrate reacts with sodium bromide to produce lead(II) bromide and sodium nitrate.
    - HINT: Since you have the same polyatomic ion (nitrate) on both sides of the equation you can use the shortcut that was listed in Step #1 of our balancing method.
c. Zinc metal reacts with oxygen gas to produce zinc oxide.
    - Oxygen is one of the diatomic molecules that are referred to by their element's name.
d. Aluminum sulfate reacts with barium iodide to produce aluminum iodide and barium sulfate.
e. At temperatures reached during baking, sodium bicarbonate (baking soda) decomposes (reacts) to produce sodium carbonate, carbon dioxide, and dihydrogen monoxide.
    - Bicarbonate is a *polyatomic ion* (**not** the same as the carbonate polyatomic ion).
f. Sodium metal reacts with water to produce sodium hydroxide and hydrogen gas.
g. Lead(IV) sulfide reacts with oxygen gas to produce lead(IV) oxide and sulfur dioxide.
h. Zinc metal reacts with phosphoric acid to produce zinc phosphate and hydrogen gas.
    - NOTE: the formula of phosphoric acid is H_3PO_4

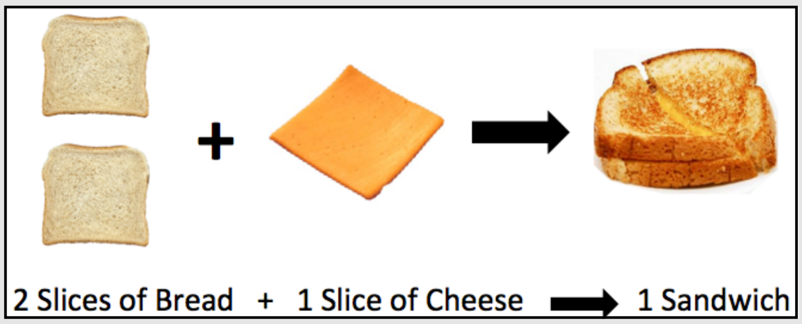
For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

6.4 Stoichiometric Calculations for Chemical Reactions

Stoichiometry (Pronounced: STOY-KEE-AHM-EH-TREE) is the calculation of the amounts of reactants and/or products in a chemical reaction. The term comes from the Greek words *stoicheion* "element" and *metron* "measure." The calculated values allow us to predict how much product(s) will be produced from a given amount of reactant(s), or conversely, how much reactant(s) will be needed in order to produce a desired amount of product. Stoichiometric calculations are based on **the law of conservation of mass**.

Before we do ***stoichiometric calculations*** with chemicals, let's do a similar problem with something with which we are all familiar - ***food***!!! I will use the formation of a grilled cheese sandwich as an analogy to a chemical reaction. Consider the production of a simple grilled cheese sandwich made by combining two slices of bread and one slice of cheese as shown in Figure 6.9. If this was an actual chemical reaction we would say, "two slices of bread ***react with*** one slice of cheese ***to produce*** one cheese sandwich." I believe that you already understand the central concept in stoichiometric calculations, and this will be shown to be true by your ability to answer the following two questions:

Figure 6.9 Cheese Sandwich Formation Analogy to a Chemical Reaction



***Question #1**:* Suppose you want to make as many cheese sandwiches as possible for lunch. If you have 20 slices of bread, how many slices of cheese do you need?

***Question #2**:* If you have an *unlimited* supply of cheese slices, how may sandwiches can you make from the 20 slices of bread?

I am fairly sure that you already knew enough about the ratios involved in preparing food to have figured out that you would need 10 slices of cheese to go with the 20 slices of bread (*Question #1 above*) and that if you have an *unlimited* supply of cheese and only 20 slices of bread that you could make 10 sandwiches (*Question #2 above*). Doing stoichiometric calculations are no more difficult than solving these sandwich questions. You did the same math, perhaps subconsciously, that you would use in real chemical reaction calculations. When we do stoichiometry calculations for real reactions, the first thing that we need to have is a balanced chemical equation. For the sandwich analogy, the balanced equation is:

$$2\ \mathrm{B} + \mathrm{C} \rightarrow \mathrm{B_2C}$$

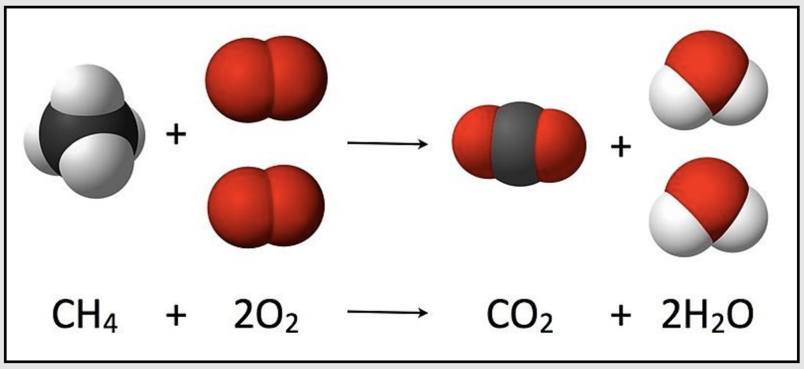
Where **B** represents slices of bread, **C** represents slices of cheese, and a sandwich "compound" is therefore a "$\mathrm{B_2C}$." Notice that the ***law of conservation of mass*** is obeyed; there are the same total number of **B**'s and **C**'s on ***each side*** of the equation. In the case of the sandwich, you knew the balanced equation and you did the calculation "*in your head.*" Perhaps you did the calculation so fast that you were not even aware of it! In question #1, you ***converted*** from slices of *bread* to slices of *cheese*. To do so, you needed to know the relationship between slices of bread and slices of cheese (just like you have done in previous unit conversion problems). The relationship between the amounts of reactants used and/or products formed can be found from the ***coefficients*** in the balanced chemical equations. It is for this reason that coefficients are sometimes referred to as "**stoichiometric coefficients.**" In question #1, you converted from ***units*** of "slices of bread" to ***units*** of "slices of cheese" as shown below.

$$\begin{array}{c|c|}20\ \cancel{\text{slices of bread}} & 1\ \text{slice of cheese}\\ \hline & 2\ \cancel{\text{slices of bread}}\end{array} = 10\ \text{slices of cheese}$$

In question #2, you converted from **units** of "slices of bread" to ***units*** of "sandwiches" as shown below.

$$\begin{array}{c|c|}20\ \cancel{\text{slices of bread}} & 1\ \text{sandwich}\\ \hline & 2\ \cancel{\text{slices of bread}}\end{array} = 10\ \text{sandwiches}$$

Figure 6.10
Illustration and Balanced Equation for the Combustion Reaction of Methane



Top: The black spheres represent carbon atoms, the red spheres represent oxygen atoms and the white spheres represent hydrogen atoms.
Bottom: The balanced chemical equation. All reactants and products for this reaction are in the gas phase.
Source: Wikimedia Commons, Author: Robert A. Rohde, CC-BY-SA, http://creativecommons.org/licenses/by-sa/3.0/legalcode

I used the formation of a cheese sandwich analogy because you are quite familiar with making sandwiches; now we will move on to work on real chemical reactions. The coefficients in the balanced equation represent the ratios in which reactants are consumed and products are made in a chemical reaction. For example, consider the reaction for the combustion of methane shown in Figure 6.10. Use the balanced chemical equation shown in the figure to answer the following questions:

1) How many H_2O molecules are produced from 1 CH_4 molecule? ________

2) How many O_2 molecules are needed to produce 2 H_2O molecules? ________

3) How many CH_4 molecules are needed to react with 2 O_2 molecules?________

Inspection of the coefficients gives us the answers 2, 2, 1 (in that order) to these three questions. In practice, scientists and technicians usually work with very large numbers of particles, not just a few molecules or ions. It is more practical to consider the coefficients to represent the ratios in which ***moles of substances*** are used and produced in a chemical reaction. Therefore, when I reword the three questions above to inquire about the ***number of moles*** used or produced, the answers would be the same as they were when I asked about the *number of molecules:*

How many ***moles*** of H_2O are produced from 1 ***mole*** of CH_4? *Answer: 2*
How many ***moles*** of O_2 are needed to produce 2 ***moles*** of H_2O? *Answer: 2*
How many ***moles*** of CH_4 are needed to react with 2 ***moles*** of O_2? *Answer: 1*

Your understanding of the coefficients in chemical equations will help you to construct conversion factors and use them in stoichiometric calculations. I will do a few examples, then ask you to do some problems on your own.

Example: For the combustion of methane reaction in Figure 6.10, how many moles of H_2O can be produced from 2.84 moles of methane (CH_4)? Assume you have an unlimited supply of O_2.

Solution: We always begin with the balanced chemical equation:

$$CH_4\,(g) + 2\,O_2\,(g) \rightarrow CO_2\,(g) + 2\,H_2O\,(g)$$

We will approach stoichiometry problems ***just as we did with unit conversion problems using our factor-label method***. Set up the calculation by first writing the ***given quantity*** with its units:

$$\begin{array}{l|c|} 2.84 \text{ moles } CH_4 & \qquad\qquad \\ \hline & \end{array} \quad =$$

Next, *use the appropriate conversion factor*:

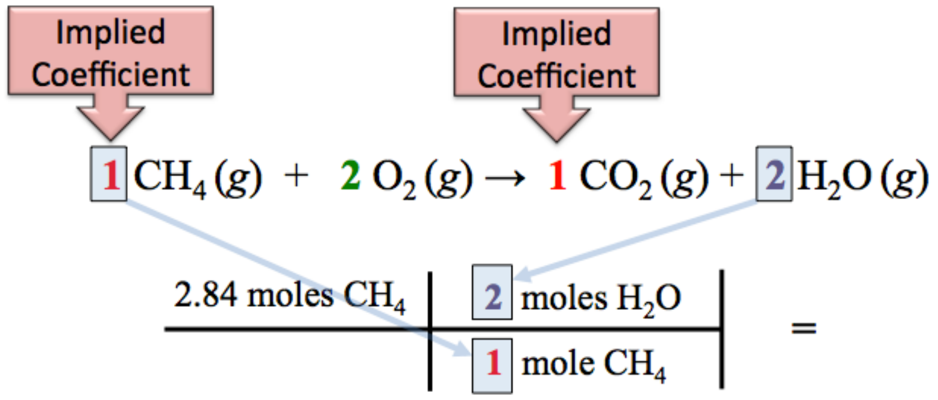
- In this problem, we are converting from units of "**moles of CH_4**" to units of "**moles of H_2O.**"
- Write the conversion factor's ***units (only)***. As with all unit conversions, we put the ***given units*** in the denominator (so they will cancel) and the ***desired units*** in the numerator.

$$\begin{array}{l|c|} 2.84 \text{ moles } CH_4 & \text{moles } H_2O \\ \hline & \text{moles } CH_4 \end{array} \quad =$$

Next, find the relationship between **moles of CH_4** and **moles of H_2O** ***from the coefficients in the chemical equation***:

$$CH_4\,(g) \;+\; 2\,O_2\,(g) \rightarrow CO_2\,(g) + 2\,H_2O\,(g)$$

- If a substance's coefficient is *absent*, as is the cases of CH_4 and CO_2 in the chemical equation for this example, a value of "**1**" is implied.
- The balanced equation tells us that **2 moles of H_2O** are produced for every **1 mole of CH_4** that reacts; we use this ratio as the conversion factor:



The given units of **moles of CH_4** cancel and we end up with the desired units of **moles of H_2O.**

$$\begin{array}{l|l|}
2.84\ \cancel{\text{moles } CH_4} & 2\ \text{moles } H_2O \\
\hline
 & 1\ \cancel{\text{mole } CH_4}
\end{array} \;=\; 5.68\ \text{moles } H_2O$$

The given value (2.84 moles of CH_4) has *three* significant figures. The conversion factor has *an **infinite** number of significant figures* because ***the coefficients are exact numbers***. Therefore our answer has 3 significant figures.

In some stoichiometry problems, like the example problem just completed, you will be given a certain amount of one reactant and an *unlimited supply* of the other reactant(s), and then asked to calculate how much *product* could be made. In other stoichiometry problems, you may need to calculate how much of one reactant *would be needed* to react with a given amount of ***another reactant*** as in the example that follows.

Example: For the combustion of methane reaction, how many moles of O_2 will be needed to react with 6.93 moles of CH_4?

Solution: In stoichiometry problems, begin with the balanced chemical equation:

$$CH_4\,(g) \;+\; 2\,O_2\,(g) \rightarrow CO_2\,(g) + 2\,H_2O\,(g)$$

Set up the calculation by first writing the ***given quantity*** with its units:

$$\begin{array}{l|l|}
6.93\ \text{moles } CH_4 & \\
\hline
 &
\end{array} \;=$$

Next, *use the appropriate conversion factor*:

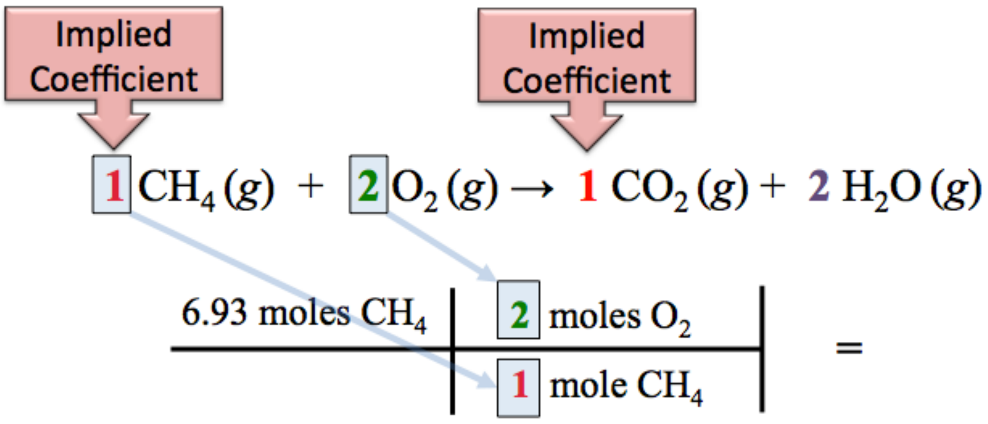
- In this problem, we are converting from units of "**moles of CH_4**" to units of "**moles of O_2**."
- Enter the conversion factor's ***units (only)***. Write the ***given units*** in the denominator (so they will cancel) and the ***desired units*** in the numerator.

$$\begin{array}{l|l|}
6.93\ \text{moles } CH_4 & \text{moles } O_2 \\
\hline
 & \text{moles } CH_4
\end{array} \;=$$

Next, find the relationship between **moles of CH_4** and **moles of O_2** ***from the coefficients in the chemical equation***:

$$CH_4\,(g) \;+\; 2\,O_2\,(g) \rightarrow CO_2\,(g) + 2\,H_2O\,(g)$$

- The balanced equation tells us that 2 **moles of O_2** are ***needed to react with*** every 1 **mole of CH_4** present; we use this ratio as the conversion factor:



The given units of **moles of CH_4** cancel and we end up with the desired units of **moles of O_2.**

$$\begin{array}{l|l|} 6.93\ \cancel{\text{moles } CH_4} & 2\ \text{moles } O_2 \\ \hline & 1\ \cancel{\text{mole } CH_4} \end{array} \;=\; 13.9 \text{ moles } O_2$$

Sometimes stoichiometry problems involve the calculation of how much of **one reactant** *would be needed* to ***produce*** a specified amount of ***product*** as in the example that follows.

Example: For the combustion of methane reaction, how many moles of O_2 will be needed to ***produce*** 1.74 moles of H_2O? Assume there is an unlimited supply of CH_4.

Solution: Begin with the balanced chemical equation:

$$CH_4\,(g) \;+\; 2\,O_2\,(g) \rightarrow CO_2\,(g) + 2\,H_2O\,(g)$$

$$\begin{array}{l|l|} 1.74 \text{ moles } H_2O & \qquad\qquad \\ \hline & \end{array} \;=$$

Set up the calculation by first writing the ***given quantity*** with its units:

Next, *use the appropriate conversion factor*:

- In this problem, we are converting from units of "**moles of H_2O**" to units of "**moles of O_2**".

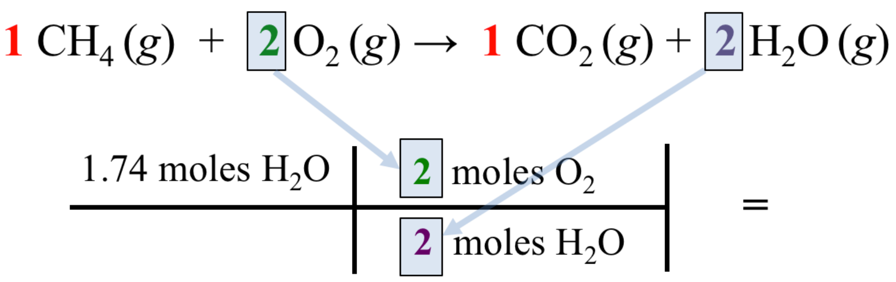
$$\begin{array}{l|l|} 1.74 \text{ moles } H_2O & \text{moles } O_2 \\ \hline & \text{moles } H_2O \end{array} \;=$$

- Enter the conversion factor's ***units.***

Next, find the relationship between **moles of H_2O** and **moles of O_2** ***from the coefficients in the chemical equation***:

$$CH_4\,(g) \;+\; 2\,O_2\,(g) \rightarrow CO_2\,(g) + 2\,H_2O\,(g)$$

- The balanced equation tells us that 2 **moles of O_2** are needed in order ***to produce*** 2 **moles of H_2O**; we use this ratio as the conversion factor:



The given units of **moles of H_2O** cancel and we end up with the desired units of **moles of O_2.**

$$\begin{array}{l|l|} 1.74\ \cancel{\text{moles } H_2O} & 2\ \text{moles } O_2 \\ \hline & 2\ \cancel{\text{moles } H_2O} \end{array} \;=\; 1.74 \text{ moles } O_2$$

Now you try a couple of stoichiometry calculation problems.

Review 6.4: Understanding Stoichiometry Calculations

In a combustion reaction, propane (C_3H_8) reacts with oxygen to produce CO_2 and H_2O as shown in the balanced chemical equation below.

$$C_3H_8\,(g) + 5\,O_2\,(g) \rightarrow 3\,CO_2\,(g) + 4\,H_2O\,(g)$$

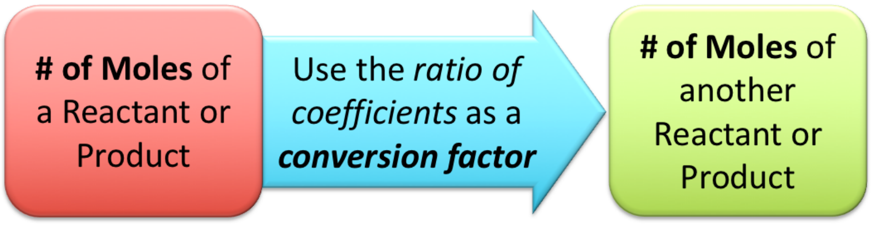
a) How many moles of H_2O can be produced from 1.32 moles of propane (C_3H_8)? Assume there is an unlimited supply of O_2.

b) How many moles of O_2 will be needed to react with 12.6 moles of C_3H_8?

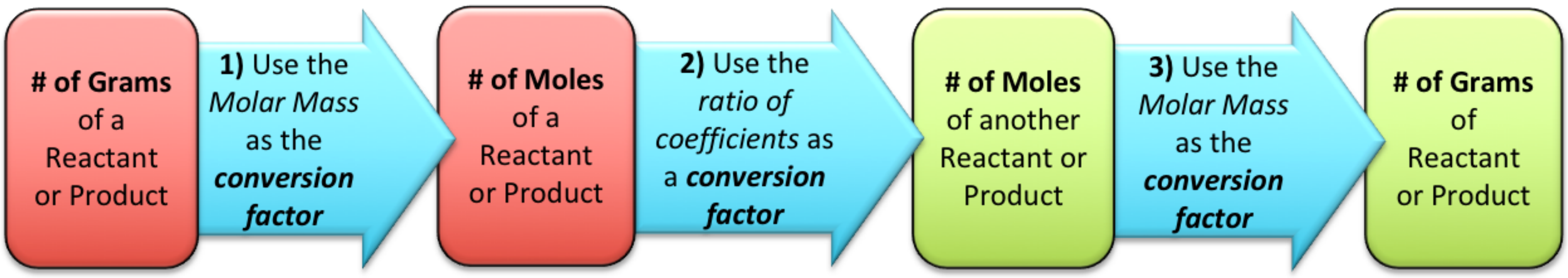
c) How many moles of O_2 will be needed to ***produce*** 0.843 moles of H_2O (assume that you have an unlimited supply of C_3H_8)?

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

In the previous stoichiometry problems, we were given the number of moles of a particular product or reactant and asked to calculate the number of moles of another product or reactant involved in the reaction. We did so by using the ratios of the substances' coefficients as conversion factors. This process is shown in the schematic diagram below.



We cannot *directly* measure the number of moles on a balance in the lab. In practice, we usually know the ***number of grams*** of a reactant or product and wish to determine the ***number of grams*** of another reactant needed ***<u>or</u>*** the ***number of grams*** of a product in a reaction. Because the coefficients that we use as conversion factors in stoichiometric calculations are the ***ratios of moles***, we must **first convert all masses (grams) to moles,** do the stoichiometric calculations, and then convert the calculated number of moles for the substance of interest into grams. This ***three-step process*** is shown in the schematic diagram below.



Take a look at the following examples of ***grams*** → ***moles*** → ***moles*** → ***grams*** stoichiometry problems, then try a few on your own.

Example: For the combustion of propane:

$$C_3H_8\,(g) \; + \; 5\,O_2\,(g) \rightarrow 3\,CO_2\,(g) + 4\,H_2O\,(g)$$

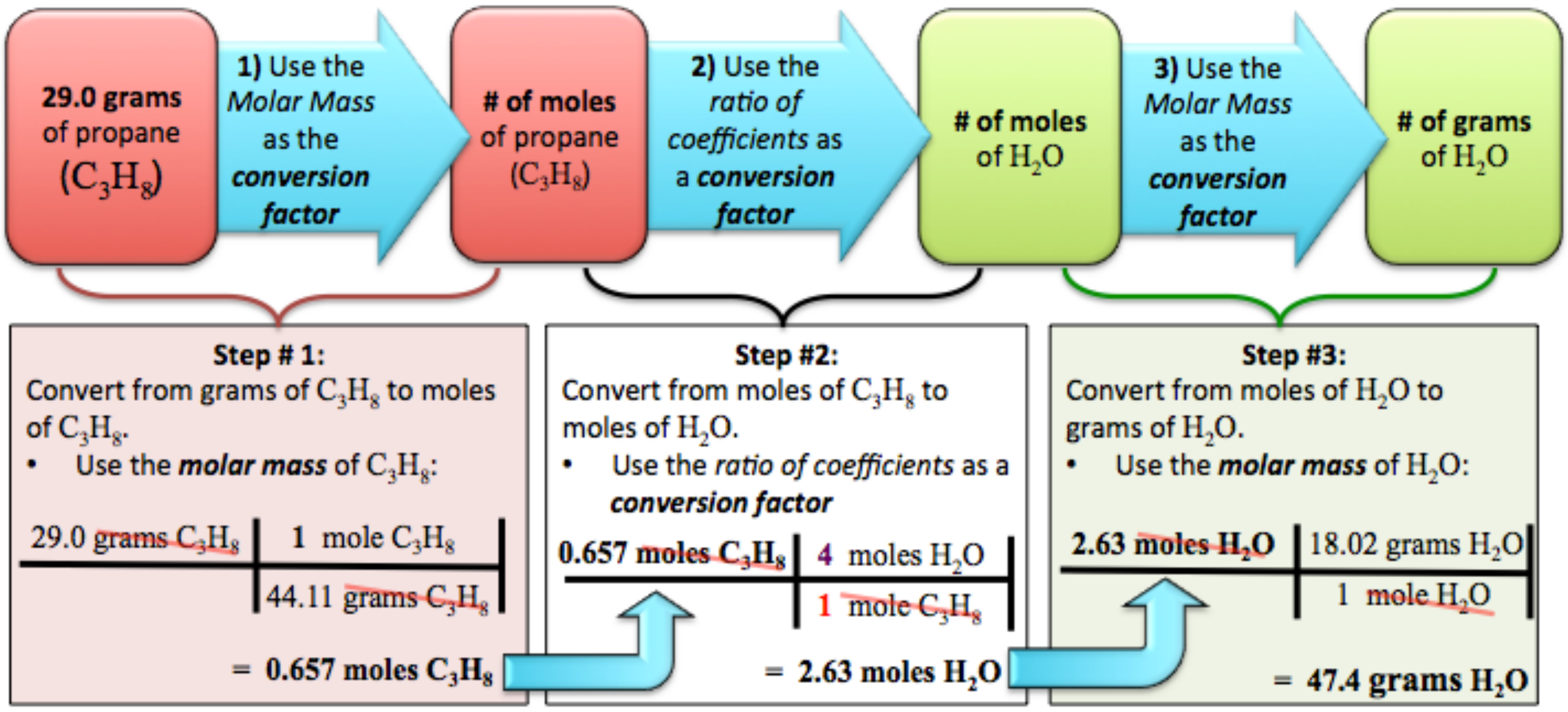
How many **grams** of H_2O can be produced from 29.0 **grams** of propane (C_3H_8)? Assume you have an unlimited supply of O_2.

Solution: We will use **three steps** to solve this problem:

Step 1: Convert ***grams of propane*** (C_3H_8) to ***moles of propane*** (using the molar mass of propane).

Step 2: Convert *moles of **propane*** to *moles of* $\mathbf{H_2O}$.

Step 3: Convert ***moles of*** $\mathbf{H_2O}$ to ***grams of*** $\mathbf{H_2O}$ (using the molar mass of $\mathbf{H_2O}$).



Step # 1:
Convert from grams of C_3H_8 to moles of C_3H_8.
- Use the ***molar mass*** of C_3H_8:

$$\frac{29.0\ \cancel{\text{grams } C_3H_8}}{} \left| \frac{1\ \text{mole } C_3H_8}{44.11\ \cancel{\text{grams } C_3H_8}} \right| = \mathbf{0.657\ moles\ C_3H_8}$$

Step #2:
Convert from moles of C_3H_8 to moles of H_2O.
- Use the *ratio of coefficients* as a ***conversion factor***

$$\frac{\mathbf{0.657}\ \cancel{\mathbf{moles\ C_3H_8}}}{} \left| \frac{4\ \text{moles } H_2O}{1\ \cancel{\text{mole } C_3H_8}} \right| = \mathbf{2.63\ moles\ H_2O}$$

Step #3:
Convert from moles of H_2O to grams of H_2O.
- Use the ***molar mass*** of H_2O:

$$\frac{\mathbf{2.63}\ \cancel{\mathbf{moles\ H_2O}}}{} \left| \frac{18.02\ \text{grams } H_2O}{1\ \cancel{\text{mole } H_2O}} \right| = \mathbf{47.4\ grams\ H_2O}$$

Alternative Solution: You may feel comfortable enough to use the short cut where all three of the conversions above are combined into one equation:

$$\frac{29.0\ \cancel{\text{grams } C_3H_8}}{} \left| \frac{1\ \cancel{\text{mole } C_3H_8}}{44.11\ \cancel{\text{grams } C_3H_8}} \right| \frac{4\ \cancel{\text{moles } H_2O}}{1\ \cancel{\text{mole } C_3H_8}} \left| \frac{18.02\ \text{grams } H_2O}{1\ \cancel{\text{mole } H_2O}} \right| = \mathbf{47.4\ grams\ H_2O}$$

Example: For the combustion of propane:

$$C_3H_8\,(g) \;+\; 5\,O_2\,(g) \rightarrow 3\,CO_2\,(g) + 4\,H_2O\,(g)$$

How many ***grams*** of O_2 will be needed to ***produce*** 50.0 grams of H_2O (assume that you have an unlimited supply of C_3H_8)?

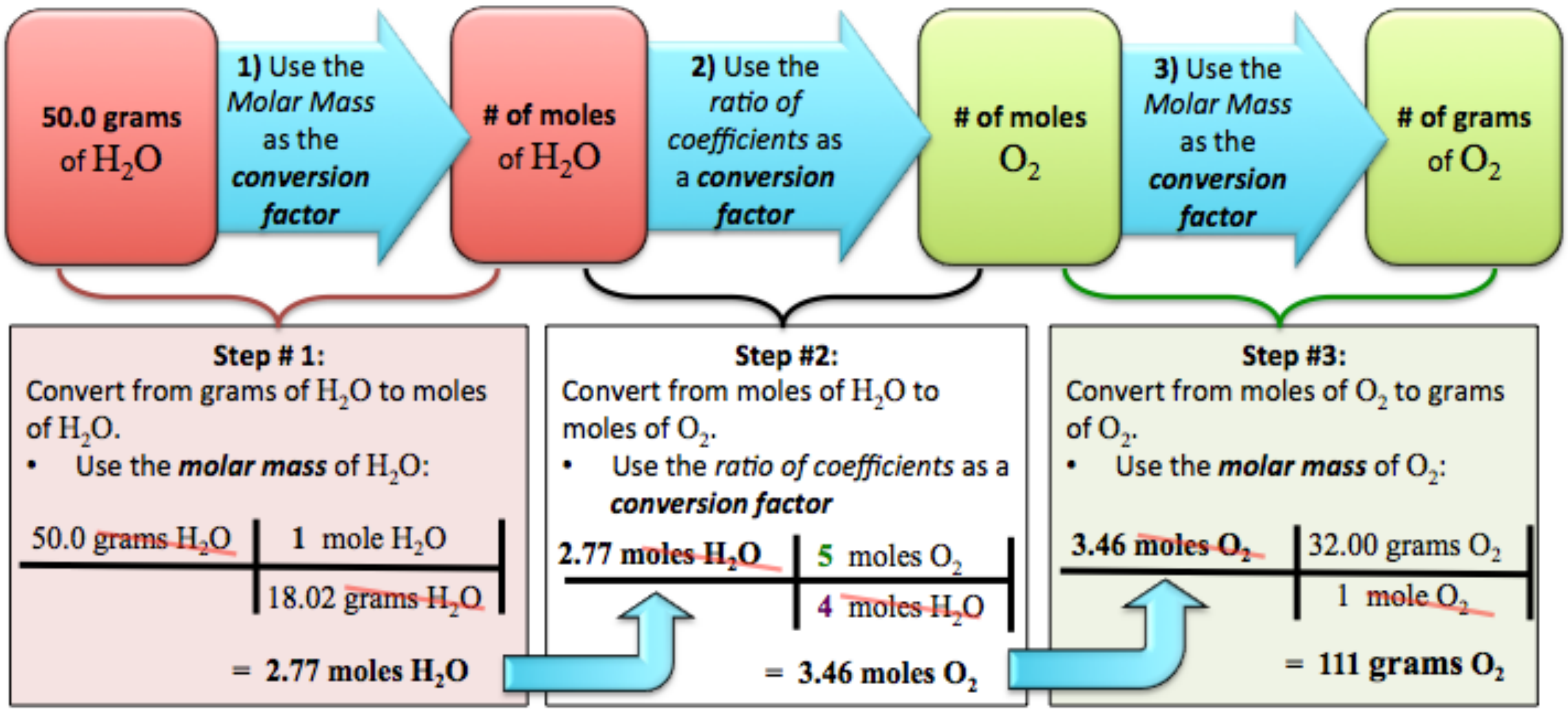
Solution: In this example, we are given the *desired* amount (***grams)*** of ***product*** (H_2O) and asked to calculate how many ***grams of a reactant*** (O_2) will be needed. We are told to assume that we have an unlimited supply of the other reactant (C_3H_8), therefore the amount of H_2O produced depends only on the amount of O_2 used in the reaction. We call the reactant that limits that amount of product, O_2 in this example, the "**limiting reagent**".

We will use **three steps** to solve this problem:

Step 1: Convert the desired number of ***grams of*** H_2O to ***moles of*** H_2O.

Step 2: Convert ***moles of*** H_2O to ***moles of*** O_2.

Step 3: Convert ***moles of*** O_2 to ***grams of*** O_2.



Step # 1:
Convert from grams of H_2O to moles of H_2O.

- Use the ***molar mass*** of H_2O:

$$\frac{50.0\ \cancel{\text{grams H}_2\text{O}}}{} \times \frac{1\ \text{mole H}_2\text{O}}{18.02\ \cancel{\text{grams H}_2\text{O}}} = \mathbf{2.77\ moles\ H_2O}$$

Step #2:
Convert from moles of H_2O to moles of O_2.

- Use the *ratio of coefficients* as a ***conversion factor***

$$\frac{2.77\ \cancel{\text{moles H}_2\text{O}}}{} \times \frac{5\ \text{moles O}_2}{4\ \cancel{\text{moles H}_2\text{O}}} = \mathbf{3.46\ moles\ O_2}$$

Step #3:
Convert from moles of O_2 to grams of O_2.

- Use the ***molar mass*** of O_2:

$$\frac{3.46\ \cancel{\text{moles O}_2}}{} \times \frac{32.00\ \text{grams O}_2}{1\ \cancel{\text{mole O}_2}} = \mathbf{111\ grams\ O_2}$$

Alternative Solution: Combine all three of the conversions above into one equation:

$$\frac{50.0\ \cancel{\text{grams H}_2\text{O}}}{} \times \frac{1\ \cancel{\text{mole H}_2\text{O}}}{18.02\ \cancel{\text{grams H}_2\text{O}}} \times \frac{5\ \cancel{\text{moles O}_2}}{4\ \cancel{\text{moles H}_2\text{O}}} \times \frac{32.00\ \text{grams O}_2}{1\ \cancel{\text{mole O}_2}} = \mathbf{111\ grams\ O_2}$$

Now you try one:

When you are finished, you can check your answer with the solution on the next page.

Example: For the combustion of propane: $C_3H_8\,(g) \;+\; 5\,O_2\,(g) \rightarrow 3\,CO_2\,(g) + 4\,H_2O\,(g)$

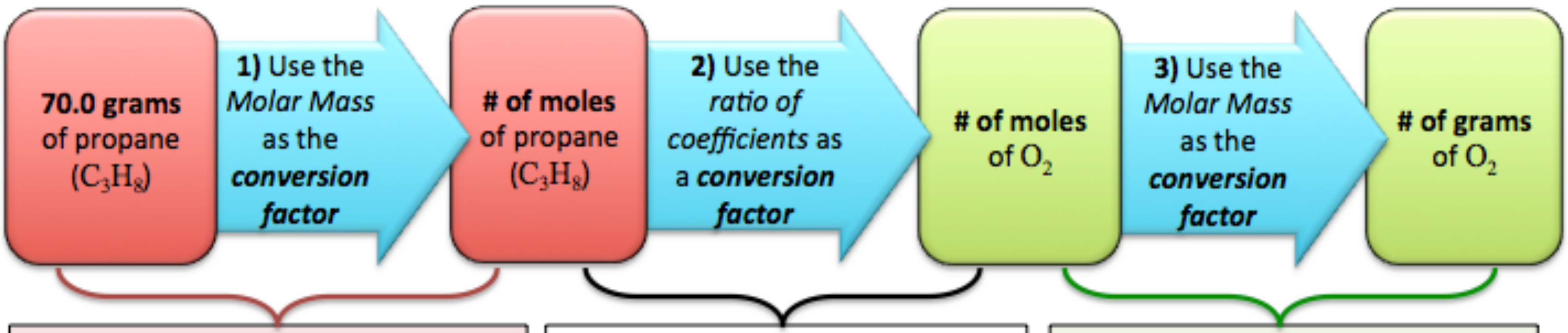
How many ***grams*** of O_2 will be needed to react with 70.0 ***grams*** of C_3H_8?

Solution: Use **three steps** to solve this problem:

Step 1: Convert the given number of ***grams of*** C_3H_8 to ***moles of*** C_3H_8.

Step 2: Convert ***moles of*** C_3H_8 to ***moles of*** O_2.

Step 3: Convert ***moles of*** O_2 to ***grams of*** O_2.



70.0 grams of propane (C_3H_8)

1) Use the *Molar Mass* as the ***conversion factor***

# of moles of propane (C_3H_8)

2) Use the *ratio of coefficients* as a ***conversion factor***

# of moles of O_2

3) Use the *Molar Mass* as the ***conversion factor***

# of grams of O_2

Step # 1:

Convert from grams of C_3H_8 to moles of C_3H_8.

- Use the ***molar mass*** of C_3H_8:

$$\frac{70.0\ \cancel{\text{grams } C_3H_8}}{} \;\Bigg|\; \frac{1 \text{ mole } C_3H_8}{44.11\ \cancel{\text{grams } C_3H_8}}$$

$$= \mathbf{1.59 \text{ moles } C_3H_8}$$

Step #2:

Convert from moles of C_3H_8 to moles of O_2.

- Use the *ratio of coefficients* as a ***conversion factor***

$$\frac{\mathbf{1.59}\ \cancel{\textbf{moles } C_3H_8}}{} \;\Bigg|\; \frac{5 \text{ moles } O_2}{1\ \cancel{\text{mole } C_3H_8}}$$

$$= \mathbf{7.95 \text{ moles } O_2}$$

Step #3:

Convert from moles of O_2 to grams of O_2.

- Use the ***molar mass*** of O_2:

$$\frac{\mathbf{7.95}\ \cancel{\textbf{moles } O_2}}{} \;\Bigg|\; \frac{32.00 \text{ grams } O_2}{1\ \cancel{\text{mole } O_2}}$$

$$= \mathbf{254 \text{ grams } O_2}$$

Alternative Solution: Combine all three of the conversions above into one equation:

$$\frac{70.0\ \cancel{\text{grams } C_3H_8}}{} \;\Bigg|\; \frac{1\ \cancel{\text{mole } C_3H_8}}{44.11\ \cancel{\text{grams } C_3H_8}} \;\Bigg|\; \frac{5\ \cancel{\text{moles } O_2}}{1\ \cancel{\text{mole } C_3H_8}} \;\Bigg|\; \frac{32.00 \text{ grams } O_2}{1\ \cancel{\text{mole } O_2}} \;\Bigg| = \mathbf{254 \text{ grams } O_2}$$

Review: More Stoichiometry Problems

Use the link below to download a worksheet (and key).

http://www.zovallearning.com/GOBlinks/ch6/stoichiometry.pdf

The Percent Yield of a Chemical Reaction

In some of the stoichiometry problems that you have encountered, you were asked to calculate the amount of product formed. In those cases, you were given a certain amount of one reactant, which is referred to as the ***limiting reagent***, and an unlimited supply of the other reactant. The ***limiting reagent*** is the reactant that would be depleted first as reactants are converted to products. You based your stoichiometric calculations of the amount of product made on the amount of the *limiting reagent*.

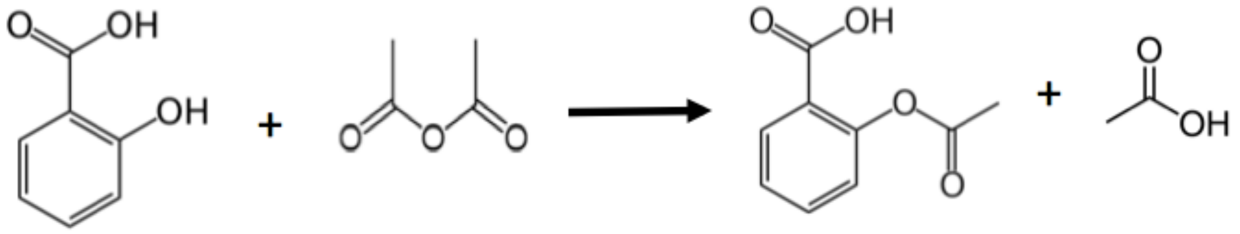
The calculated amount of product that can be made is called the "**theoretical yield.**" This is the *maximum amount* of product that could be made in a reaction (based on the amount of the *limiting reagent)*. In a laboratory or a chemical manufacturing facility, the ***actual amount*** *of product* that is collected can be less than the *theoretical yield*. There are three possible reasons for this: not all of the limiting reactant gets converted to product; "side- reactions" occur that convert reactants to different products than the desired one; and some product is lost in separating it from remaining reactants, other products, and/or side-reaction products. The amount of product purified and collected in the field (laboratory or other facility) is referred to as the "**actual yield**" (sometimes called "**experimental yield**"). The ratio of the ***actual yield*** to the ***theoretical yield*** is a measure of the *efficiency* of the chemical production process. The ratio of the actual yield to the theoretical yield is often multiplied by a factor of 100 in order to get the "**percent yield**" as shown in *Equation 6.1* below:

$$\text{Percent Yield} = \left(\frac{\text{Actual Yield}}{\text{Theoretical Yield}}\right) \times 100\%$$

Equation 6.1

Percent means "***for every 100***." The percent yield is the number of product units actually purified and collected ***for every 100*** product units that could have "theoretically" been made ***if*** **all** of the *limiting reagent* was converted to product ***and*** **all** of the product was purified and collected. The actual yield and theoretical yield values can be entered into *Equation 6.1* in **either moles *or* mass**, so long as you use the ***same units*** for **both** values. Let's do an example problem in order for you to further understand the *percent yield* concept.

Example: ***Aspirin*** is manufactured using the reaction of *salicylic acid* and *acetic anhydride* as shown below.



salicylic acid + acetic anhydride → aspirin + acetic acid

$$C_7H_6O_3 + C_4H_6O_3 \rightarrow C_9H_8O_4 + C_2H_4O_2$$

If a drug company purifies and collects 6874 grams of ***aspirin*** that was made from 7539 grams of ***salicylic acid***, what was the **percent yield** of their reaction? Assume that they began with an *excess* of acetic anhydride, therefore *salicylic acid was the **limiting reagent***.

Solution: We are asked to calculate the **percent yield**. To calculate the **percent yield** as defined in *Equation 6.1***,** we must know the ***actual yield and*** the ***theoretical yield***.

- **Actual yield** is the amount of product purified and collected. We were given the *actual yield* (6874 grams of aspirin) in this problem. In percent yield problems, ***unless you are in the lab to collect and purify the product, you will always be given the actual yield.***

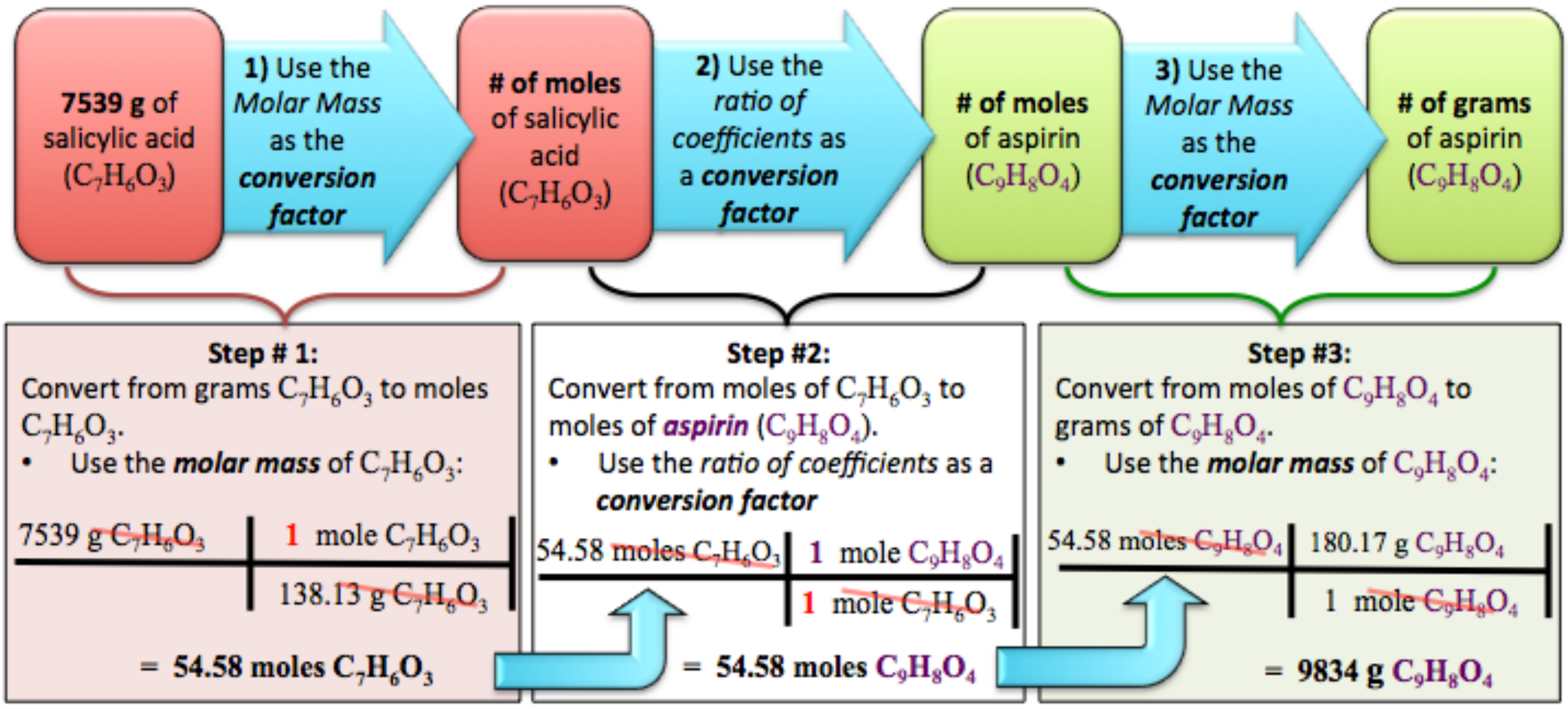
- **Theoretical yield** is the calculated amount of product that could be made in a reaction based on the amount of the *limiting reagent*. ***We get the theoretical yield by doing the stoichiometry calculation***.

Use **three steps** to get the ***theoretical yield*** of aspirin :

Step 1: Convert the given number of ***grams*** *of salicylic acid* **($C_7H_6O_3$)** to ***moles*** *of salicylic acid*.

Step 2: Convert ***moles of salicylic acid*** **($C_7H_6O_3$)** to ***moles of aspirin*** **($C_9H_8O_4$).**

Step 3: Convert ***moles of aspirin*** **($C_9H_8O_4$)** to ***grams of aspirin***.



Step # 1:
Convert from grams $C_7H_6O_3$ to moles $C_7H_6O_3$.

- Use the ***molar mass*** of $C_7H_6O_3$:

$$\frac{7539\ \cancel{\mathrm{g\ C_7H_6O_3}}}{} \times \frac{1\ \mathrm{mole\ C_7H_6O_3}}{138.13\ \cancel{\mathrm{g\ C_7H_6O_3}}}$$

$$= \mathbf{54.58\ moles\ C_7H_6O_3}$$

Step #2:
Convert from moles of $C_7H_6O_3$ to moles of ***aspirin*** ($C_9H_8O_4$).

- Use the *ratio of coefficients* as a ***conversion factor***

$$\frac{54.58\ \cancel{\mathrm{moles\ C_7H_6O_3}}}{} \times \frac{1\ \mathrm{mole\ C_9H_8O_4}}{1\ \cancel{\mathrm{mole\ C_7H_6O_3}}}$$

$$= \mathbf{54.58\ moles\ C_9H_8O_4}$$

Step #3:
Convert from moles of $C_9H_8O_4$ to grams of $C_9H_8O_4$.

- Use the ***molar mass*** of $C_9H_8O_4$:

$$\frac{54.58\ \cancel{\mathrm{moles\ C_9H_8O_4}}}{} \times \frac{180.17\ \mathrm{g\ C_9H_8O_4}}{1\ \cancel{\mathrm{mole\ C_9H_8O_4}}}$$

$$= \mathbf{9834\ g\ C_9H_8O_4}$$

Alternatively, combine all three of the conversions above into one equation:

$$\frac{7539\ \cancel{\mathrm{grams\ C_7H_6O_3}}}{} \times \frac{1\ \cancel{\mathrm{mole\ C_7H_6O_3}}}{138.13\ \cancel{\mathrm{grams\ C_7H_6O_3}}} \times \frac{1\ \cancel{\mathrm{mole\ C_9H_8O_4}}}{1\ \cancel{\mathrm{mole\ C_7H_6O_3}}} \times \frac{180.17\ \mathrm{g\ C_9H_8O_4}}{1\ \cancel{\mathrm{mole\ C_9H_8O_4}}} = \mathbf{9834\ g}\ \mathrm{C_9H_8O_4}$$

Now that we know the ***actual yield <u>and</u>*** the ***theoretical yield***, we calculate the **percent yield**:

$$\textbf{Percent Yield} = \left(\frac{\text{Actual Yield}}{\text{Theoretical Yield}}\right) \times 100\,\% = \left(\frac{6874\ \cancel{\mathrm{g}}}{9834\ \cancel{\mathrm{g}}}\right) \times 100\,\% = \mathbf{69.90\,\%}$$

- The **"100%"** in the percent yield equation is **exact** (has an infinite number or significant figures), therefore our answer has 4 significant figures.

Review 6.5: Understanding Percent Yield

A drug company runs a large scale reaction to prepare the pain reliever acetaminophen. The chemists at the company calculate a ***theoretical yield*** of 42 kg of acetaminophen for the reaction. If 33 kg of acetaminophen are purified and collected, what is the ***percent yield*** of the reaction?

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

6.5 Energy Changes in Chemical Reactions

All chemical reactions involve changes in energy. Some reactions ***release energy*** as heat, light, electricity, and/or mechanical energy (work). The energy that is released in a chemical reaction comes from ***potential energy*** contained in the ***reactant(s)***. Examples of reactions that produce heat and light are combustion reactions (burning). We call reactions that release energy, in the form of heat, **exothermic reactions**. Combustion reactions can also produce *mechanical energy; another way to state this is, "combustion reactions can do work."* For example, when combustion occurs in the cylinder/piston system of an internal combustion engine, a sudden increase in the number of moles of gas present (produced in the reaction) causes a large increase in pressure within the cylinder, which then moves the piston. The piston is coupled to a shaft that rotates and ultimately rotates the wheels. Examples of reactions that release electrical energy are the reactions that occur in various types of batteries.

Source: Wikimedia Commons, Author: Sebastian Ritter, CC-BY-SA, http://creativecommons.org/licenses/by-sa/3.0/legalcode

Figure 6.11 **Electrolysis of Water**

A battery submerged in water. Oxygen and hydrogen gas bubbles are generated at the battery terminals. $H_2O\ (l)$ is converted to $O_2\ (g)$ at the (+) terminal (right-most terminal) and $H_2\ (g)$ at the (-) terminal (left-most terminal).

Some reactions must continuously absorb energy in order to occur. An example of this is the *formation* of hydrogen and oxygen gas (at room temperature) from water.

$$2\ H_2O\ (l) \longrightarrow 2\ H_2\ (g) + O_2\ (g)$$

Note that this is the ***reverse*** of the rocket fuel reaction that I discussed earlier. The conversion of hydrogen and oxygen to H_2O releases energy; so it makes sense that the ***reverse reaction***, converting H_2O to hydrogen and oxygen would require energy. The conversion of water to hydrogen and oxygen gas can be done by adding electrical energy to water in a process called **electrolysis**. Figure 6.11 shows the formation of hydrogen and oxygen gas bubbles that are generated at the terminals of the battery submerged in water.

Spontaneity of Chemical Reactions

Recall the important law that is central to understanding nature: **matter tends to exist in the lowest possible energy state**. We applied this law to understand why light is emitted from atoms and why most substances exist as molecules or ions instead of as isolated atoms. This is a *universal law,* therefore it also applies to chemical reactions; **chemical reactions can occur when the total energy of the products is less than the total energy of the reactants**. When a chemical reaction can continue to occur *without an external input of energy*, we say the reaction is ***spontaneous***. Let's examine the concepts of reaction energy and spontaneity by examining a reaction that we are familiar with - the combustion of propane gas. Propane gas is the major component of liquified petroleum gas (LPG). It is used throughout the world as a source of heat in gas ranges, ovens, climate control, outdoor cooking, and hot water tanks. During combustion, propane reacts with oxygen gas to produce carbon dioxide gas and H_2O vapor.

$$C_3H_8\ (g) + 5\ O_2\ (g) \longrightarrow 3\ CO_2\ (g) + 4\ H_2O\ (g)$$

Many of us have used propane gas in outdoor lanterns and barbecues. We know that once we use a spark or match to start the reaction, that the combustion reaction continues to occur *without an external input of energy*. It is therefore a ***spontaneous reaction***.

Let's think about the change in energy (ΔE) in the combustion of propane. The total energy (E) is the sum of kinetic energy (E_k) and potential energy (E_p).

$$\mathbf{E = E_k + E_p}$$

In chapter 5, you learned that a particle's *kinetic energy* comes from its motion. Potential energy is stored in a substance's chemical bonds (and noncovalent interactions). *Breaking* chemical bonds ***requires*** energy. *Making* new chemical bonds ***releases*** energy.

For our combustion of propane example reaction:

$$C_3H_8\,(g) \quad + \quad 5\,O_2\,(g) \quad \longrightarrow \quad 3\,CO_2\,(g) \quad + \quad 4\,H_2O\,(g)$$

In the ***reactants***, *potential energy* is stored in C-C bonds, C-H bonds, and the O-O bonds. During the reaction, chemical bonds in the reactants are broken and new chemical bonds (C-O and O-H) are formed in the products. In the ***products***, *potential energy* is stored in C-O bonds, and O-H bonds. We all know, from our familiarity with the combustion of propane gas, that energy is ***released*** in this reaction. The *amount* of energy released in the reaction is equal to the difference in potential energy ($\Delta\mathbf{E_p}$) between the potential energy of the products ($\mathbf{E_{p\ products}}$) and potential energy of the reactants ($\mathbf{E_{p\ reactants}}$):

$$\mathbf{Energy\ Released = (\Delta E_p) = (E_{p\ products}) - (E_{p\ reactants})}$$

This ***released energy*** does not just vanish into a hole in the universe! Energy is never created or destroyed, it only changes its form. The energy released in the reaction is converted to ***kinetic energy in the products***, and then is eventually transferred to surrounding matter such as air (or the items cooking on the barbecue). In the case of similar reactions that happen in *internal combustion engines*, some of the energy that is released goes into mechanical work (moving the car), and the remainder goes into warming of the engine, and then finally into warming of the air that contacts the car's engine and radiator. The ratio of energy that goes into *moving the car* to the total energy released by the reaction is called the **engine efficiency**. In the case of reactions that occur in batteries, most of the energy released in the reaction goes into kinetic energy of electrons moving through an electrical circuit; the remainder of the energy goes into warming the battery and surroundings.

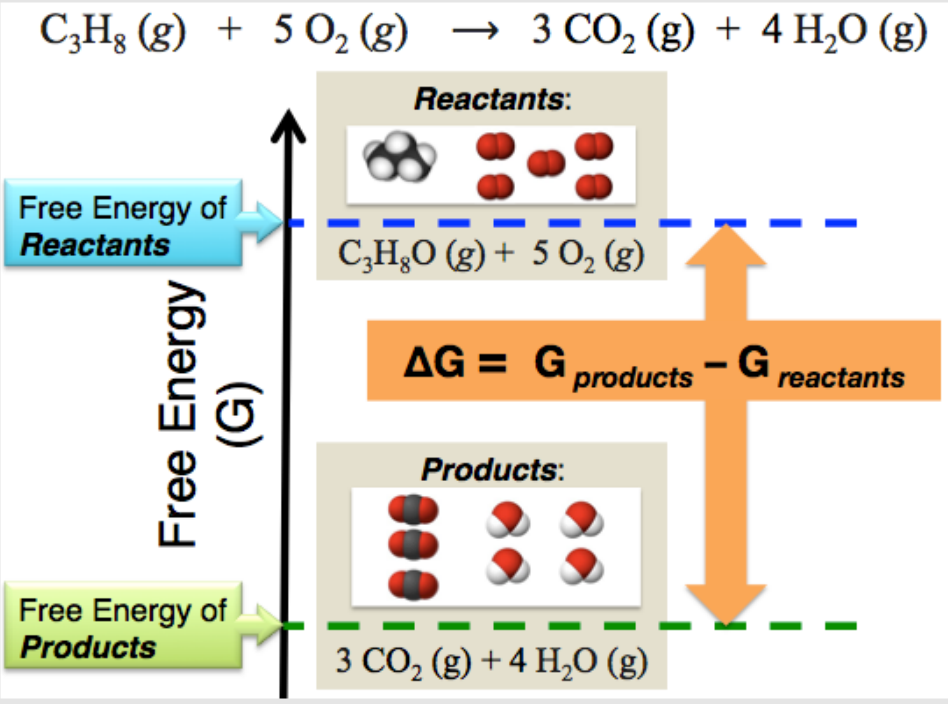
The field of study called **thermodynamics** often deals with calculating the energy changes in chemical reactions. These energetic calculations are useful for predicting how chemical systems will behave under various conditions because matter tends to exist in the lowest possible energy state. For example, the combustion of propane reaction occurs ***because the bonding arrangement of atoms in the products is at a lower energy than that of the reactants.*** Energy calculations are only useful when they involve properties (variables) that can be directly measured (such as temperature, moles of each substance, volume, and pressure). When using the temperature and pressure as variables in energy calculations, we refer to the calculated energy as "**free energy**" abbreviated with the symbol "**G.**" The details of the difference between total energy (**E**) and free energy (**G**) are beyond the scope of this textbook. For our purposes, you can consider the free energy (**G**) and total energy (**E**) to be ***equivalent***. An important point that I would like you to know, and what makes the use of the free energy of value to scientists, is that the law of nature that applies to total energy (**E**), ***also*** *applies to free energy* (**G**); **matter tends to exist in the lowest possible *free energy* state, therefore chemical reactions will occur when the total *free energy* of the products is less than the total *free* energy of the reactants.**

Let's consider the combustion of propane in terms of ***free energy*** **(G)**. Figure 6.12 illustrates the difference in ***free energy*** between the products and the reactants for this reaction. This figure is an *energy level diagram*, similar to the energy level diagrams that you saw in chapter 3, with higher energy toward the top. The amount of free energy present in the reactants *alone* ($G_{reactants}$) is indicated by the blue dashed line. The amount of free energy contained in products *alone* ($G_{products}$) is indicated by the green dashed line. The ***change in free energy*** (ΔG) for reaction is equal to the difference in free energy between the products ($G_{products}$) and the reactants ($G_{reactants}$):

$$\Delta G = (G_{products}) - (G_{reactants}) \qquad \textit{Equation 6.4}$$

The *change* in free energy is indicated in the figure by the orange double-arrow. Note the use of our convention of defining **change (Δ)** as the final state (products only) ***minus*** the initial state (reactants only). The free energy of the products for the combustion of propane is less than the free energy of the reactants as indicated by their positions in the energy level diagram in Figure 6.12. When the *free energy* of the ***products*** of a reaction is ***less than*** the free energy of the ***reactants***, we say that the reaction is **exergonic**.

Figure 6.12 Free Energy (G) Level Diagram



Free energy level diagram for the products vs. the reactants for the combustion of propane reaction. The amount of free energy present in the reactants *alone* ($G_{reactants}$) is indicated by the blue dashed line. The amount of free energy contained in products *alone* ($G_{products}$) is indicated by the green dashed line. The ***change in free energy*** (ΔG) for reaction is equal to the difference in free energy between the products ($G_{products}$) and the reactants ($G_{reactants}$).

Chemical reactions will occur spontaneously when the *free energy* of the product(s) is less than the *free energy* of the reactant(s).

- When the free energy of the *products* of a reaction is ***less than*** the free energy of the *reactants*, the ***change in free energy*** (**ΔG**) will have a **negative value**. You should be able to convince yourself of this by examining *Equation 6.4*.

Summary of Spontaneity of Reactions:

When a chemical reaction can continue to occur *without an external input of energy*, we say the reaction is ***spontaneous***.

- The following statements are true for ***spontaneous reactions***:
  - The free energy of the ***products*** of the reaction is less than the free energy of the ***reactants***.
  - The sign of **ΔG** is ***negative***.

Rates of Chemical Reactions

Review 6.6: Identifying Spontaneous Reactions

Determine if the following reactions are **spontaneous** or **non-spontaneous**.

a) $2\,H_2\,(g) + O_2\,(g) \longrightarrow 2\,H_2O\,(g)$, ΔG = -54,640 calories (per mole of product formed)

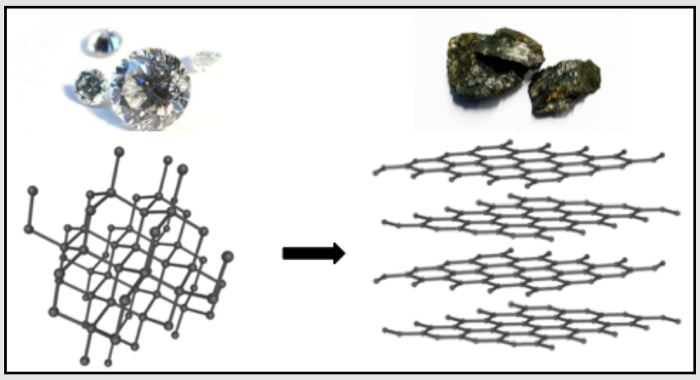
b) $2\,H_2O\,(l) \longrightarrow 2\,H_2\,(g) + O_2\,(g)$, ΔG = 56,670 calories (per mole of products formed)

c) The rusting of an iron nail: $4\,Fe + 3\,O_2 \rightarrow 2\,Fe_2O_3$ (HINT: Have you ever observed a rusty nail?)

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

Knowing if the value of **ΔG** is negative or positive allows us to predict whether or not a reaction is spontaneous, however it does not give us any information about ***how quickly a reaction happens***. Some reactions happen very quickly, for example, the explosions of fireworks. Some reactions happen so slowly that you cannot tell that the reaction is occurring even when viewed for a few hours, for example the rusting of a nail. An extreme example of a slow reaction is the conversion of diamonds into graphite. In this reaction, the carbon bonding pattern changes from AB_2E to AB_3 as shown in the figure on the right. **ΔG** for the reaction is -693 calories/mole of carbon and ***this reaction is spontaneous***. However, have you ever seen diamonds in jewelry turn into graphite? I think not. The reason you do not see this is that the reaction is happening at such a ***slow rate*** that it is not directly observable or even measurable in your lifetime.

C (*s, diamond*) ⟶ C (*s, graphite*)



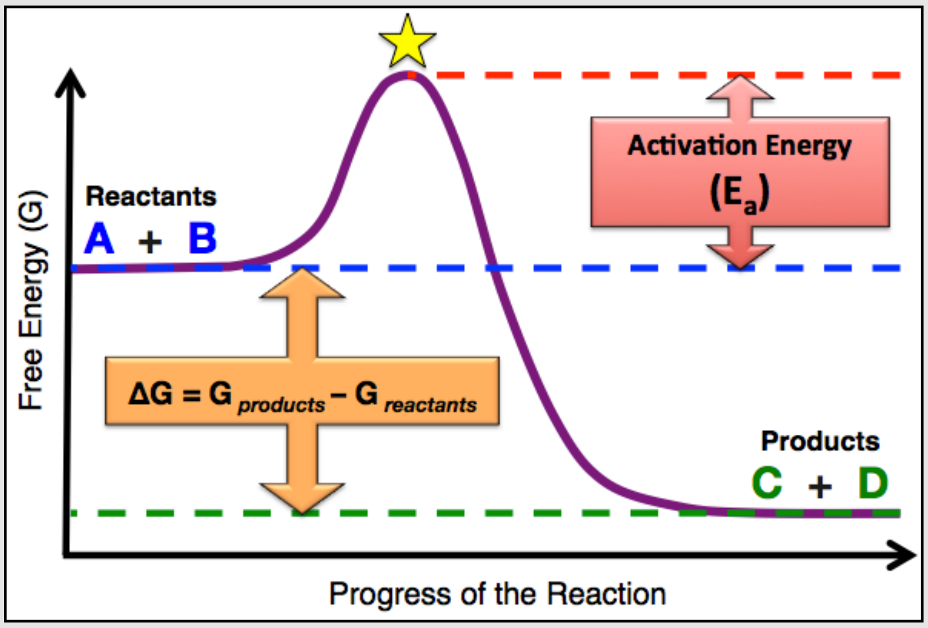
Source: Wikimedia Commons, Authors: Diamond (top left), Mario Sarto; Graphite (top right) Daniel Schwen; Models: Michael Ströck. All images under: CC-BY-SA, http://creativecommons.org/licenses/by-sa/3.0/legalcode

To understand the factors that determine and influence how quickly chemical reactions happen, we must consider the energy during ***the process*** of converting reactants to products. We will do so using an energy level diagram similar to the one that you saw on the previous page, however, we graph the free energy ***as the reaction progresses***. Let's consider a generalized chemical reaction where **molecule A** *reacts* with **molecule B** to *produce* **molecule C** and **molecule D**:

$$A + B \rightarrow C + D$$

An energy level diagram for this generalized reaction is illustrated in Figure 6.13. The horizontal axis indicates the *progress of the reaction* (process of converting reactants to products). The **purple curve** represents the free energy during the reaction process. We begin on the ***left*** where we have the *reactants only*. The free energy of the reactants ($G_{reactants}$) is indicated by the horizontal blue dashed line. As the reaction progresses, we move from *left to right*. In order for **A** to react with **B**, they must collide. As **A** and **B** approach each other, ***the free energy increases*** because of factors such as electrostatic repulsion between the electrons on the reactants, changes in molecular geometry, and disruption of noncovalent interactions. This increase in energy can be seen in the free energy curve (purple curve) as the reaction progresses. At some point, the free energy reaches a maximum value (peak) as indicated by the yellow star in the figure. At this point, the matter no longer exists as individual reactant molecules (**A** and **B**), nor has it been converted to product molecules (**C** and **D**). The matter exists in what we call a **transition state**, where the bonds in the reactants have not all been completely broken and/or the new bonds in the products have not been completely formed. The *free energy* of the *transition state* is indicated by the red dashed line. As the reaction progresses past the transition state, new bonds are formed in the product molecules **C** and **D**, and bond angles and bond distances relax to their low energy geometries, and the product molecules move apart from each other. All of these processes result in ***lowering the free energy*** as can be seen in the figure as the reaction progresses from the transition state to the products. The free energy of the products is indicated by the green dashed line. In this example, the free energy of the products is less than the free energy of the reactants, therefore **ΔG** is *negative* and the reaction is *spontaneous*. The amount of free energy needed to progress ***from reactants to the transition state*** is called the **activation energy** (E_a). The **rates of chemical reactions** (how quickly the reactions happen) depend on the *activation energy*. **The lower the activation energy, the faster the reaction rate.**

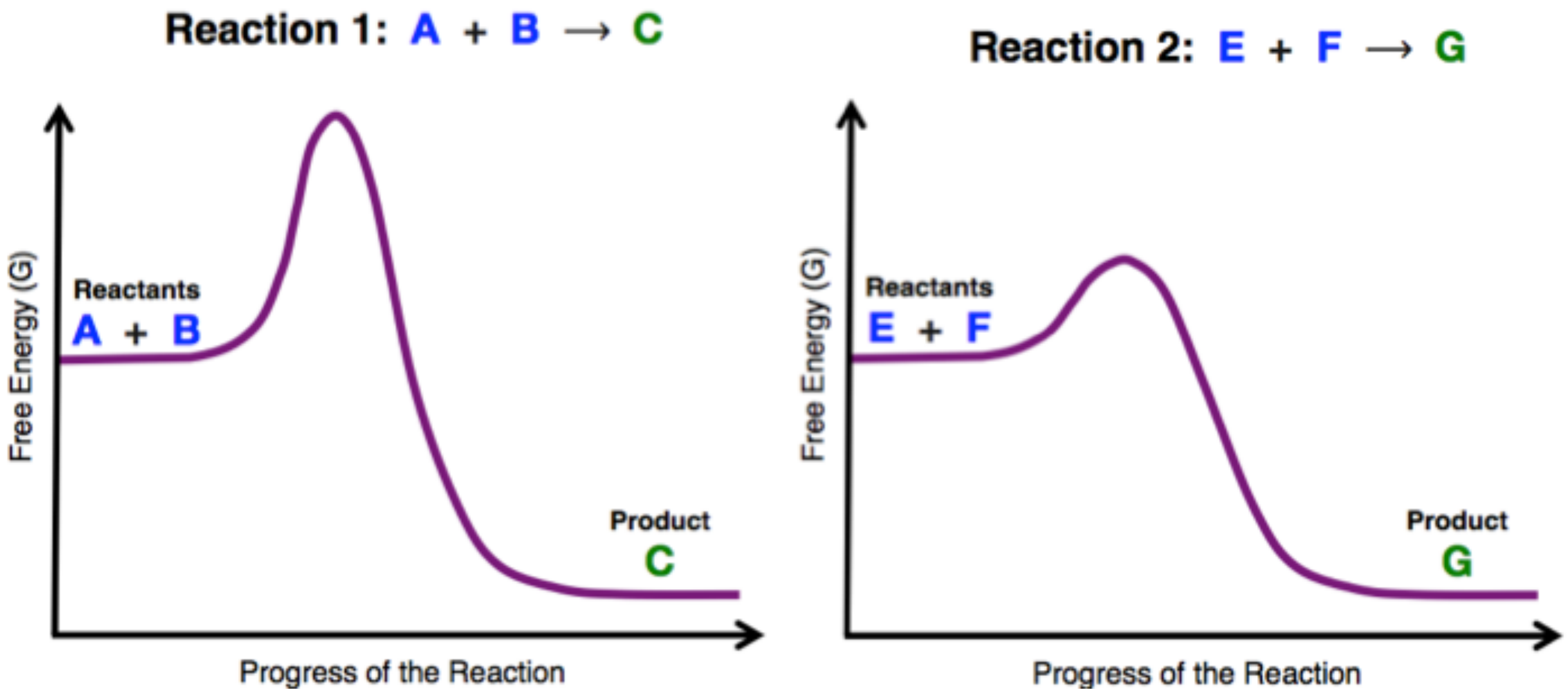
Figure 6.13 Energy Level Diagram for the Generalized Reaction: A + B → C + D



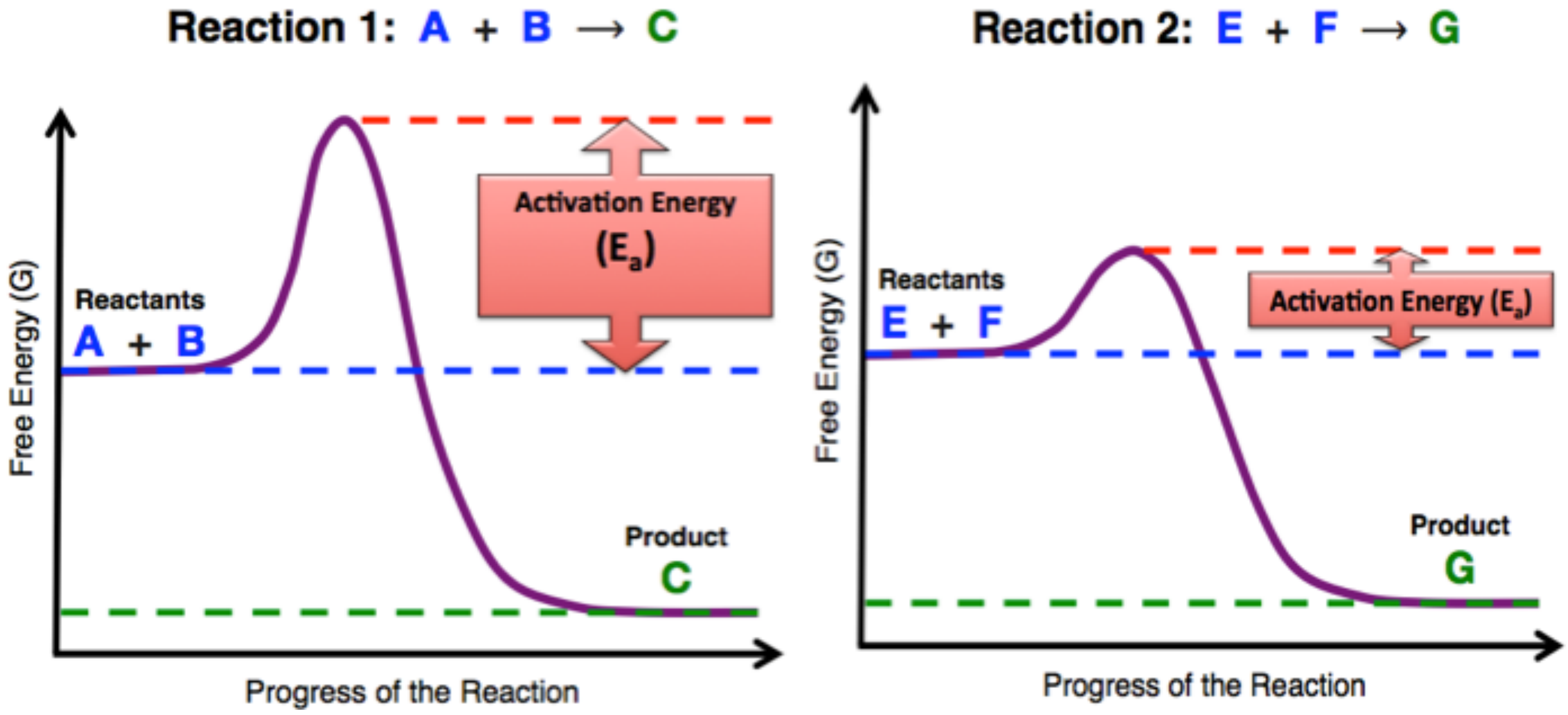
The amount of free energy needed to progress from reactants to the transition state (indicated by the yellow star) is called the activation energy (E_a). The rates of chemical reactions depend on the activation energy. The greater the activation energy, the slower the rate.

The following example problem involves the relationship between the rate of a reaction and the activation energy.

Example: The energy level diagrams for two spontaneous reactions are shown below. Which reaction has a ***faster rate***?



Solution: Compare the ***activation energies***. The ***lower*** the activation energy, the ***faster*** the reaction rate.

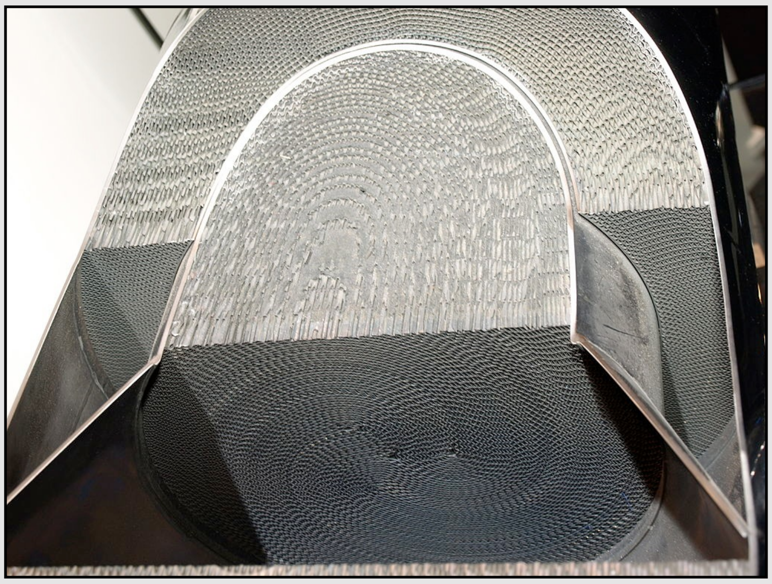


Because **Reaction 2** has a *lower* activation energy, it has the *faster reaction rate*.

The Temperature Dependence of Reaction Rates

The reaction energy level diagram shows an increase in free energy as the reaction progresses from reactants to the maximum energy peak at the *transition state*. This increase is called the *activation energy*. If the temperature of the reactants is increased, the reactants can more readily overcome the *activation energy* and therefore more readily be converted to product(s). For this reason, the reaction rate depends on the temperature. ***As the temperature increases, the reaction rate increases.*** In general, for every 10° C increase in temperature, the reaction rate doubles. Conversely, for every 10 °C decrease in temperature, the reaction rate decreases by a factor of one-half. This is one of the reasons that we keep food refrigerated; the lower temperature slows the reactions that are involved in the decomposition of food and bacterial growth.

Figure 6.14 The Inside of a Catalytic Converter



A catalytic converter was cut open to show the large amount of surface area that is coated with the metal catalyst. The surfaces of catalytic converters are usually coated with platinum or rhodium.
Source: Wikimedia Commons, PD

Catalysis

Another way to change the rate of a chemical reaction is to use a **catalyst**. A ***catalyst*** can be any *substance that increases the rate of a chemical reaction*. Unlike reactants, catalysts are not changed in a reaction. Living organisms produce catalysts consisting of large molecules, usually proteins, that are called **enzymes**. Humans have thousands of chemical reactions that must occur in order to sustain life. Many of these reactions would happen too slowly to be useful if not catalyzed by enzymes. For example, an enzyme called amylase, present in our saliva, catalyzes the digestion reaction of starch. Industrial processes often use surfaces of substances such as metals to catalyze reactions. For example, ***catalytic converters*** use platinum or rhodium surfaces as catalysts to remove poisonous by-products (carbon monoxide, nitrogen oxides, and unreacted hydrocarbons) produced in the *incomplete* combustion of fossil fuels. Figure 6.14 shows the inside of a catalytic converter.

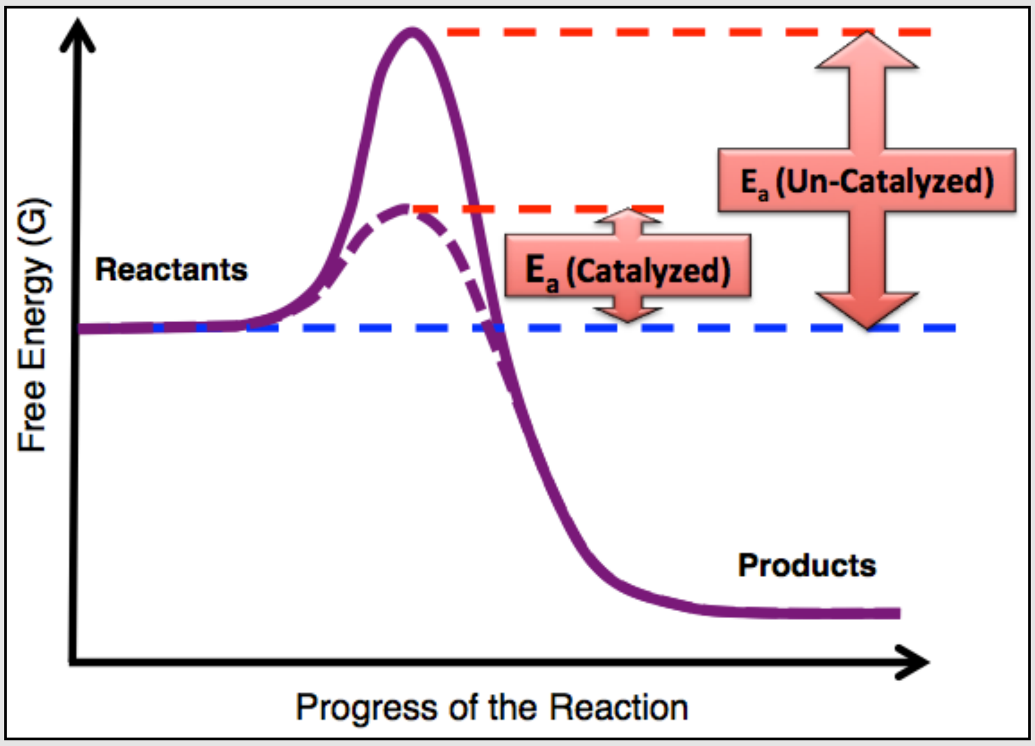
The platinum or rhodium in catalytic converters catalyzes these reactions:

- Reduction of nitrogen oxides to nitrogen and oxygen, for example: $2\ NO \rightarrow O_2 + N_2$
- Oxidation of carbon monoxide to carbon dioxide: $2\ CO + O_2 \rightarrow 2\ CO_2$
- Oxidation of unburnt hydrocarbons to carbon dioxide and water, for example: $C_9H_{20} + 14\ O_2 \rightarrow 9\ CO_2 + 10\ H_2O$

How do Catalysts Increase the Rates of Reactions?

Catalysts increase the rates of reactions by ***decreasing the activation energy (E_a)***. An energy level diagram illustrating the free energy of a reaction with and without a catalyst is shown in Figure 6.15. The solid purple curve represents the un-catalyzed reaction and a dashed purple curve is used for the catalyzed reaction. In the catalyzed reaction, the reactants require less energy to overcome the *activation energy* and are therefore converted to products at a ***faster*** rate. You will learn more details of how catalysts lower the activation energy when I discuss enzymes in chapter 13.

Figure 6.15 Energy Level Diagram for a Catalyzed and an Un-Catalyzed Reaction



The free energy for an un-catalyzed reaction (solid purple curve) and a catalyzed reaction (dashed purple curve). The catalyzed reaction has a ***lower activation energy*** (E_a) and therefore a ***faster*** reaction rate.

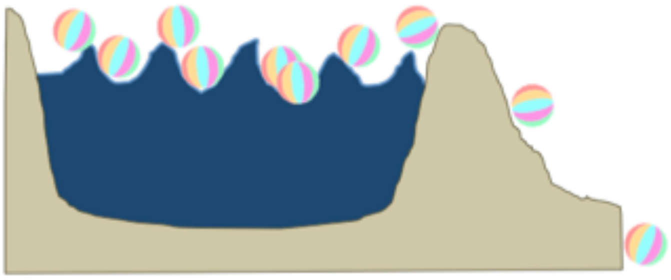
Beach Balls in a Lake Analogy for Rates of Reactions

I want to end this section by giving you an analogous model to help you understand how temperature and catalysts effect the rate of chemical reactions. The process that I will use to model chemical reactions is beach balls being removed from a lake.

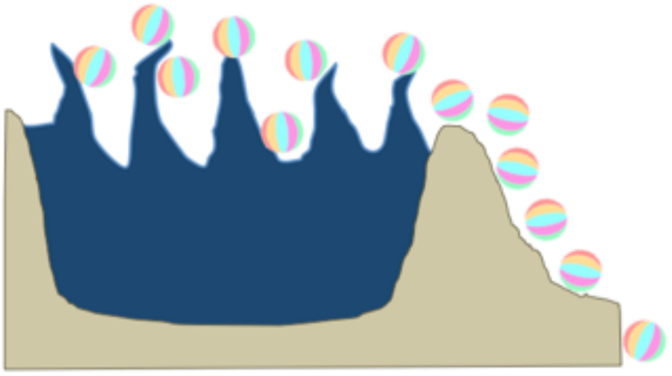
Beach balls (in the lake)   →   Beach-balls (out of the lake)

The Temperature Dependence of the Reaction Rate

In this model, the *height of the lake's shoreline* represents the **activation energy**. Increasing the size of the waves in the lake is analogous to raising the temperature of a chemical reaction. Larger waves cause the beach-balls to leave the lake ***at a faster rate*** as shown in the illustration below:



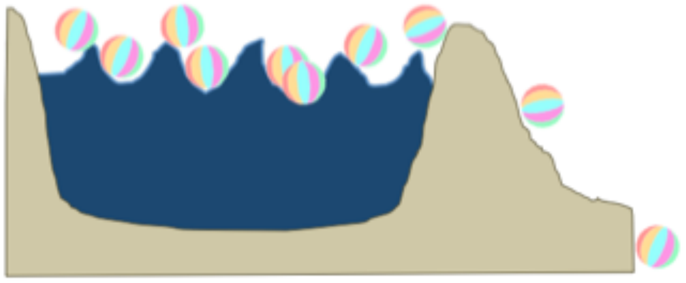
Lower Temperature



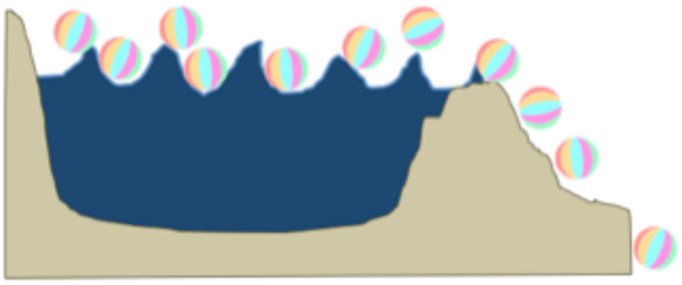
Higher Temperature

The Effect of Catalysts on the Reaction Rate

Again, the *height of the lake's shoreline* represents the **activation energy**. The *presence of a catalyst* is analogous to ***lowering the shoreline***, and results in the beach-balls leaving the lake *at **faster rate*** as shown in the illustration below:



Un-Catalyzed Reaction



Catalyzed Reaction

Summary of Rates of Chemical Reactions

- The **reaction rate** is a measure of *how quickly a reaction occurs*.
- The **rates** of chemical reactions depend on the ***activation energy*** and the ***temperature***.
- The ***lower*** the **activation energy**, the ***faster*** the reaction ***rate***.
- As the ***temperature increases***, the reaction rate ***increases***.
    In general, the reaction rate doubles for every 10° C increase in temperature.
- **Catalysts** increase the rate of a reaction by ***decreasing*** the **activation energy (E_a)**.

You will learn more about catalysis in some of the biochemical applications that I discuss in chapter 13.

6.6 General Types of Chemical Reactions

Many reactions can be categorized into one of ***four general types*** based solely on *changes in the bonding pattern* (not the identity of the reactants or products). These four general reaction types are listed and described below. The educational goal for this section is that, given one of these four types of reactions, you will be able to name the category in which it belongs.

1) SYNTHESIS REACTIONS

A **synthesis reaction** is one in which a single compound is formed from two or more substances. The general form of a synthesis reaction is:

$$\mathbf{A} + \mathbf{B} \rightarrow \mathbf{AB}$$

Where **A** represents an element or compound, **B** represents another element or compound, and **AB** is the compound formed from **A** and **B**. An example of a synthesis reaction is the reaction that occurs between sodium metal and oxygen gas (O_2):

$$4\ Na\ (s) + O_2\ (g) \rightarrow 2\ Na_2O\ (s)$$

2) DECOMPOSITION REACTIONS

A **decomposition reaction** is a reaction in which a single reactant breaks down into two or more substances. It is simply the reverse of a synthesis reaction. The general form of a decomposition reaction is:

$$\mathbf{AB} \rightarrow \mathbf{A} + \mathbf{B}$$

An example of a decomposition reaction is the thermal (heat induced) decomposition of mercury(II) oxide:

$$2\ HgO\ (s) \rightarrow 2\ Hg\ (l) + O_2\ (g)$$

Note that the key to identifying a decomposition reaction is that one reactant species is converted to two or more product species. In our example, we start the reaction with just one reactant present, $HgO\ (s)$; after the reaction occurs, there are two different substances, $Hg\ (l)$ and $O_2\ (g)$.

3) SINGLE-REPLACEMENT REACTIONS

In a **single-replacement reaction**, an element *replaces* another element from a compound. The general form of a single-replacement reaction, where **A** replaces **B**, is:

$$\mathbf{A} + \mathbf{BX} \rightarrow \mathbf{AX} + \mathbf{B}$$

A and **B** represent different *elements*, **BX** represents a compound made from **B** and **X**, and **AX** is the compound made of **A** and **X**. *Before reacting*, element **A** is alone and element **B** is in compound **BX**. *After the reaction,* element **B** is alone and element **A** is in compound **AX**. An example of a single-replacement reaction is:

$$Cu\ (s) + AgNO_3\ (aq) \rightarrow Cu(NO_3)_2\ (aq) + Ag\ (s)$$

In this reaction, copper metal ($Cu\ (s)$) *replaces* the silver ion (Ag^+) in silver nitrate.

4) DOUBLE-REPLACEMENT REACTIONS

In a **double-replacement reaction**, two substances "***switch partners***." The general form of a double-replacement reaction, where **AX** and **BY** *switch partners*, is:

$$\mathbf{AX} + \mathbf{BY} \rightarrow \mathbf{AY} + \mathbf{BX}$$

Double replacement reactions occur in *aqueous* solutions. You will learn more about double-replacement reactions when I discuss solutions in chapter 7. An example of a double-replacement reaction is the reaction of sodium chloride and silver nitrate:

$$NaCl\ (aq) + AgNO_3\ (aq) \rightarrow NaNO_3\ (aq) + AgCl\ (s)$$

Review 6.7: Categorizing or Reactions by Type

Categorize each of the following reactions as either: synthesis, decomposition, single-replacement, or double-replacement.

a. $2\ H_2O\ (l) \rightarrow 2\ H_2\ (g) + O_2\ (g)$
b. $KBr\ (aq) + AgNO_3\ (aq) \rightarrow KNO_3\ (aq) + AgBr\ (s)$
c. $2\ Mg\ (s) + O_2\ (g) \rightarrow 2\ MgO\ (s)$
d. $Mg\ (s) + 2\ HCl\ (aq) \rightarrow MgCl_2\ (aq) + H_2\ (g)$

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

6.7 Redox Reactions

The term "***redox***" is an abbreviated combination (*portmanteau*) of the words "***reduction***" and "***oxidation***." In a ***redox*** chemical reaction, an ***oxidation*** and a ***reduction*** occur *simultaneously*. Many of the reactions that I have used as examples in previous sections are redox reactions. Redox reactions often occur in biological systems. For example, the series of chemical reactions in which we *metabolize food* and the series of chemical reactions called *photosynthesis* both contain many redox reactions.

Oxidation is the ***loss of electron(s)*** by an atom, ion, or molecule. **Reduction** is the ***gain of electron(s)*** by an atom, ion, or molecule. These two processes always occur *simultaneously* in ***redox*** reactions; **electrons are *transferred* from one atom, ion, or molecule *<u>to another</u>* atom, ion, or molecule.** The electron(s) that are "lost" by the *oxidized species* are "gained" by the *reduced species*. A useful mnemonic to differentiate oxidation and reduction is the term "**OIL RIG**" (**<u>O</u>**xidation **<u>i</u>**s the **<u>L</u>**oss of electrons; **<u>R</u>**eduction **<u>i</u>**s the **<u>G</u>**ain of electrons).

A **battery** is a system in which both oxidation and reduction occur; the electrons that are lost by the reactant that is oxidized in one of the battery's "cells" move through a wire (or other electrical circuit) to another "cell" where they are accepted by the reactant that is reduced.

In redox reactions, the ***reactant that was oxidized*** (lost electron(s)) is sometimes referred to as the "**reducing agent**" because it *transferred its electron(s)* to the reactant that was reduced. Conversely, the ***reactant that was reduced*** (gained electron(s)) is sometimes referred to as the "**oxidizing agent**" because it *accepted electron(s)* from the reactant that was ***oxidized***.

Redox Reactions of *Inorganic* Compounds

It is possible to identify redox reactions for *inorganic compounds* by inspecting the chemical equation and determining if electrons are transferred from one species to another. One atom or ion in a reactant will lose electron(s) and therefore its charge will increase (in the positive direction) by one charge unit for every electron that is lost. The electron(s) that are lost are transferred to another reactant. The charge of the atom or ion in the reactant that gains the electron(s) will decrease (toward zero or negative values) by one charge unit for every electron that is gained. I will elaborate on this using an example. Let's consider the reaction of sodium metal and oxygen:

$$4\ \mathrm{Na}\ (s) + \mathrm{O_2}\ (g) \rightarrow\ 2\ \mathrm{Na_2O}\ (s)$$

How did the transfer of electrons occur in this reaction? To answer this question, you must understand that ***the total charge of any pure element or compound is always ZERO!*** This fact will help you to determine the charge of each atom or ion in the reactants and products, and then to know if the charge of the species ***changed*** during the reaction. This change in the charge of an atom or ion is an indication that a redox reaction occurred. $\mathrm{Na}\ (s)$ and $\mathrm{O_2}\ (g)$ are pure elements. Since the ***total charge of any pure element or compound is always ZERO***, and these two substances are each composed of *only one type of element*, the charge of each of the atoms in a piece of pure sodium metal or a sample of pure oxygen gas ***is equal to ZERO***. Next, let's consider the charges on the Na and O in the $\mathbf{Na_2O}$ (s) ***product***. We once again must understand that the **total charge of any pure element or compound is always ZERO**. Since sodium oxide ($\mathrm{Na_2O}$) is a ***compound***, it has a total charge = ZERO. We ***also*** must recognize that sodium oxide is an ***ionic compound*** (we know this because there is a metal in the compound). Although the *total charge* of $\mathrm{Na_2O}$ is ZERO, the sodium cations and oxygen anions are charged particles; the charge of a sodium ***ion*** is always 1+, the charge of an oxide ion is always 2-. Note that ions combine in a ratio such that the total charge of a compound = ZERO; that is why sodium oxide has the formula $\mathrm{Na_2O}$.

Now let's examine how electrons are transferred from one reactant to the other in the reaction. We will do so by considering what happens to the charge of sodium and oxygen as they are converted from reactants to products. Let's consider sodium first. As a reactant, sodium exists as a pure element and has a charge of ZERO (a zero is sometimes shown as a superscript to indicate zero charge: $\mathrm{Na^o}$). In the product ($\mathrm{Na_2O}$), ***each*** sodium has a charge of 1+. Because the charge of sodium increased by <u>one</u> charge unit in the reaction, we can conclude that each sodium must have ***lost <u>one</u> electron***:

$$\mathrm{Na^o}\ \rightarrow\ \mathrm{Na^+}\ +\ e^-$$

When a species loses electron(s), we call that *oxidation*. ***Sodium was oxidized in this reaction***. An oxidation cannot occur without a reduction; the electron(s) will be transferred to another atom or ion. Where did the electron that sodium lost go? Since oxygen is the only other reactant, it must have been transferred to the oxygen! Let's verify this by looking for a change in the charge of oxygen in the reaction process. In the reactant, oxygen exists as O_2 and has a charge of ZERO. In the product (Na_2O), oxygen has a charge of 2-. Since the charge of oxygen decreased, by <u>two</u>, (toward negative) in the reaction, we can conclude that ***each*** oxygen (in O_2) must have ***gained <u>two</u> electrons***:

$$O^{o} + 2\,e^{-} \rightarrow O^{2-}$$

When a species ***gains*** electron(s), we call that *reduction*. ***Oxygen was reduced in this reaction***.

	Reactant	**Charge in Reactant**	**Element**	**Product**	**Charge in Product**
Oxidation	Na^{o}	ZERO	Sodium	Na^{+}	1+
Reduction	O_2	ZERO	Oxygen	O^{2-}	2-

The fact that ***each*** oxygen gains 2 electrons and ***each*** sodium only loses 1 electron is accounted for in the balanced chemical equation:

$$4\ Na\ (s) + O_2\ (g) \rightarrow 2\ Na_2O\ (s)$$

The ratio of sodium atoms to oxygen atoms is 2:1. ***Four sodium atoms*** react with ***two oxygen atoms*** (in O_2). Two sodium atoms are required to reduce ***each*** oxygen atom.

Let's do an example problem where we are prompted to answer several questions that are given as hints in order to determine which reactant was oxidized and which was reduced.

EXAMPLE: Answer the questions that follow for the reaction:

$$Mg\ (s) + Cl_2\ (g) \rightarrow MgCl_2\ (s)$$

a) What is the charge of each of the magnesium atoms in the reactant [Mg (*s*)]? **Answer: 0 (ZERO)**

Mg (*s*) is a pure element. Since the ***total charge of any pure element or compound is always ZERO***, and Mg (*s*) is composed of *only one type of element*, the charge of each of the atoms in a piece of pure magnesium metal ***is equal to ZERO***.

b) What is the charge of each of the magnesium ions in the product? **Answer: 2+**

Since magnesium chloride ($MgCl_2$) is a ***compound***, it has a total charge = ZERO. We ***also*** know that magnesium chloride is an ***ionic compound***, and that although the compound's total charge is ZERO, the magnesium cations (and chloride anions) are charged particles; the charge of magnesium ***ions*** is always **2+,**

c) Did each magnesium atom ***gain*** or ***lose*** electron(s) in this reaction? If so, how many? **Answer: magnesium lost two electrons.**

As a reactant, magnesium exists as Mg (*s*) and has a charge of ZERO. In the product, the magnesium ion has a charge of 2+. Since the charge of magnesium ***increased by <u>two</u> charge units*** in the reaction, we can conclude that each magnesium must have ***lost <u>two</u> electrons***:

$$Mg^{o} \rightarrow Mg^{2+} + 2e^{-}$$

d) Was magnesium oxidized or reduced? **Answer: oxidized**

When a species loses electron(s), we call that *oxidation*.

e) What is the charge of each of the chlorine atoms in the ***reactant*** Cl_2? **Answer: 0 (ZERO)**

Cl_2 (g) is a pure element. Since the ***total charge of any pure element or compound is always ZERO***, and Cl_2 is composed of *only one type of element*, the charge of each of the atoms in a Cl_2 molecule ***is equal to ZERO***.

f) What is the charge of the ***each*** of the chloride ions in the product? **Answer: 1-**

See the discussion of magnesium ions in the product for question (b). The charge of a chloride ***ion*** is always **1-**,

g) Did each chlorine atom gain or lose electron(s) in this reaction? If so, how many?
Answer : each chlorine gained one electron.

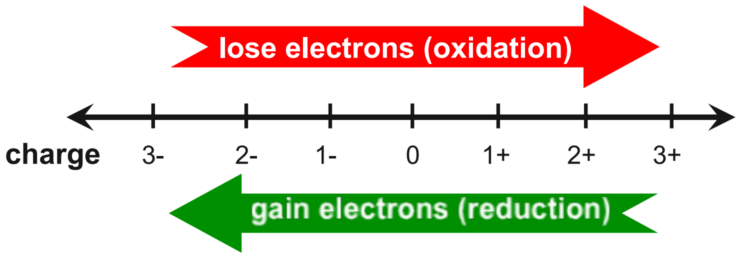
As a reactant, chlorine exists as Cl_2 (g) and has a charge of ZERO. In the product, each chloride ion has a charge of 1-. Because the charge of chlorine ***decreased by one charge unit*** in the reaction, we can conclude that each chlorine must have ***gained one electron***:

$$Cl^{o} + e^{-} \rightarrow Cl^{-}$$

h) Was chlorine oxidized or reduced? **Answer: reduced**
When a species gains electron(s), we call that *reduction*.

Summary and Practice Problem for Redox Reactions of *Inorganic* Compounds

It is possible to identify redox reactions for inorganic compounds by inspecting the chemical equation and determining if electron(s) are transferred from one species to another. If the charge was ***increased*** (toward positive) in the conversion of reactants to products, ***an oxidation occurred***. If the charge was ***decreased*** (toward negative) in the conversion of reactants to products, ***a reduction occurred***.



Review 6.8: Identifying Redox Reactions for *Inorganic* Compounds

Answer the questions that follow for the reaction:

$$2\ Li\ (s) + Br_2\ (g) \rightarrow 2\ LiBr\ (s)$$

a. What is the charge of each of the lithium atoms in the reactant [Li (s)]?
b. What is the charge of each of the lithium ions in the product?
c. Did each lithium atom ***gain*** or ***lose*** electron(s) in this reaction? if so, how many?
d. Was lithium oxidized or reduced?
e. What is the charge of each of the bromine atoms in the ***reactant*** [Br_2 (g)]?
f. What is the charge of ***each*** of the bromide ions in the product?
g. Did each bromine atom gain or lose electron(s) in this reaction? If so, how many?
h. Was bromine oxidized or reduced?

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

Redox Reactions of *Covalent* Compounds

We identified redox reactions for *inorganic compounds* by inspecting the chemical equation and determining if there was a change in the charge of atoms or ions. The transfer of electrons to or from covalent compounds is *not as easily recognized* as was the case for elements and ionic compounds in inorganic redox reactions. For ***covalent compounds***, such as organic and biological compounds, the gaining and losing of electrons is the result of a gain or loss of bond(s) to oxygen atoms or hydrogen atoms. For our purposes, oxidation and reduction for covalent compounds can be identified as follows:

- An atom in a covalent compound is **oxidized** if it ***gains*** *bond(s)* to ***oxygen*** and/or ***loses*** *bond(s)* to ***hydrogen***.
- An atom in a covalent compound is **reduced** if it ***loses*** *bond(s)* to ***oxygen*** and/or ***gains*** *bond(s)* to ***hydrogen.***

An example of redox reaction for covalent *compounds* is the **combustion of hydrocarbons.** In the "complete combustion" of hydrocarbons, the hydrocarbon molecules react with oxygen gas (O_2) to form carbon dioxide and H_2O vapor. When there is an insufficient supply of O_2, "incomplete combustion" occurs and other products, such as carbon monoxide, are formed. In this book, when the term "combustion" is used, we will consider that to mean "complete combustion." A specific example of the combustion of a hydrocarbon is the reaction of methane and oxygen gas to form carbon dioxide and H_2O vapor:

$$CH_4\,(g) + \mathbf{2}\,O_2\,(g) \rightarrow CO_2\,(g) + \mathbf{2}\,H_2O\,(g)$$

Let's use our criteria for oxidation and reduction of covalent compounds to determine which species was oxidized and which was reduced in this reaction. Carbon is bonded to four hydrogen atoms and to zero oxygen atoms as a reactant (in CH_4). After reacting, carbon is bonded to zero hydrogens and two oxygens. This change in carbon's bonding matches our criteria for the ***oxidation*** of a covalent compound; an atom is **oxidized** if it ***gains*** *bond(s)* to ***oxygen*** and/or ***loses*** *bond(s)* to ***hydrogen***. **The carbon in methane was oxidized in this reaction.** Let's consider *oxygen* next. *Each* oxygen atom in O_2 is bonded to ***one*** other *oxygen atom* and **zero** *hydrogen atoms* before reacting. After the reaction, oxygen appears in *both* products. The oxygen in CO_2 is bonded to zero *other* oxygen atoms (it lost a bond to oxygen in the reaction). The oxygen in H_2O is bonded to zero *other* oxygen atoms and to two hydrogen atoms (it ***lost*** a bond to oxygen and ***gained*** two bonds to hydrogen). All of these changes in oxygen's bonding match our criteria for the ***reduction*** of a covalent compound; an atom is **reduced** if it ***loses*** *bond(s)* to ***oxygen*** and/or ***gains*** *bond(s)* to ***hydrogen.*** **The oxygens in $O_2\,(g)$ were reduced in this reaction.**

An example of a redox reaction that is involved in biological systems is the reduction of NAD$^+$/oxidation of lactate.

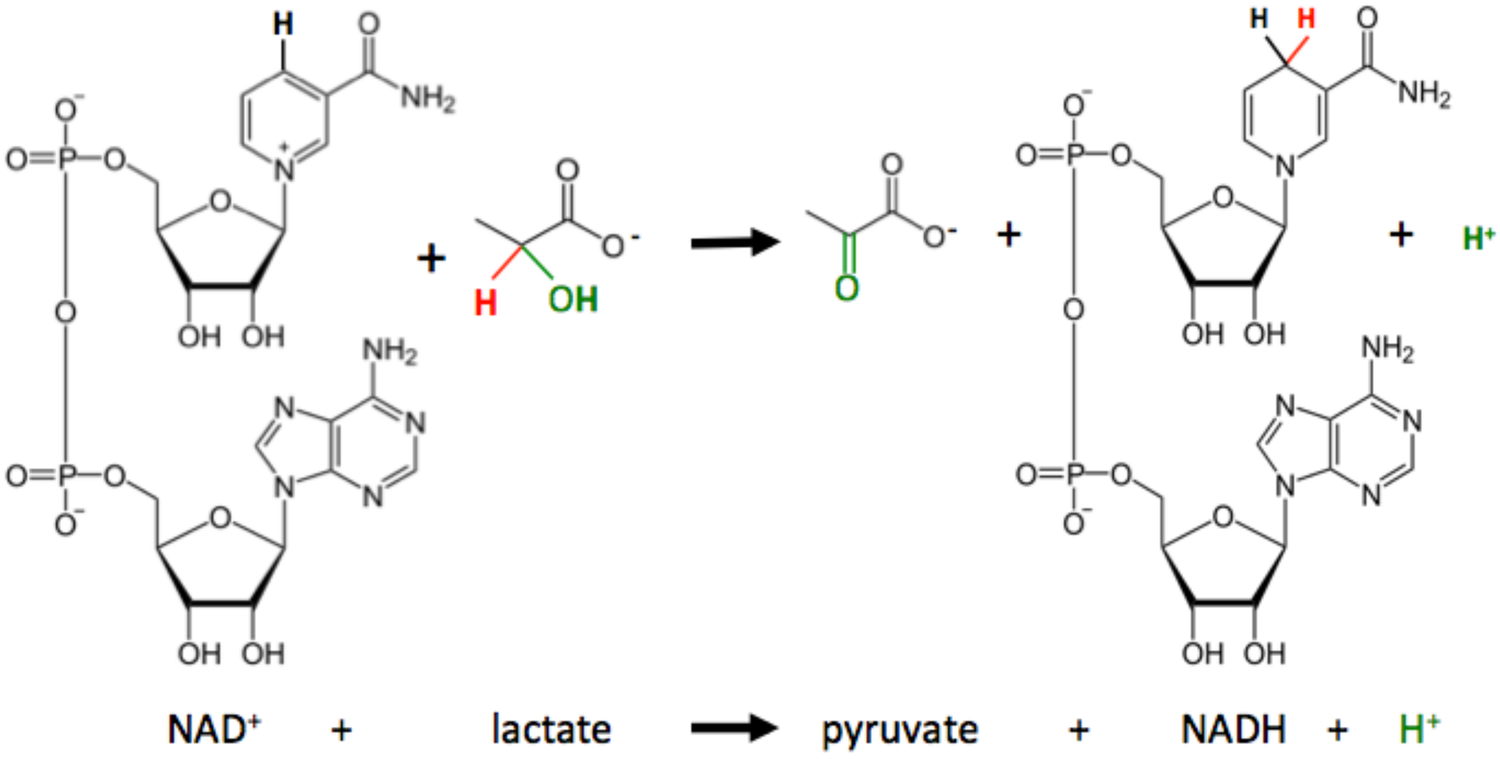
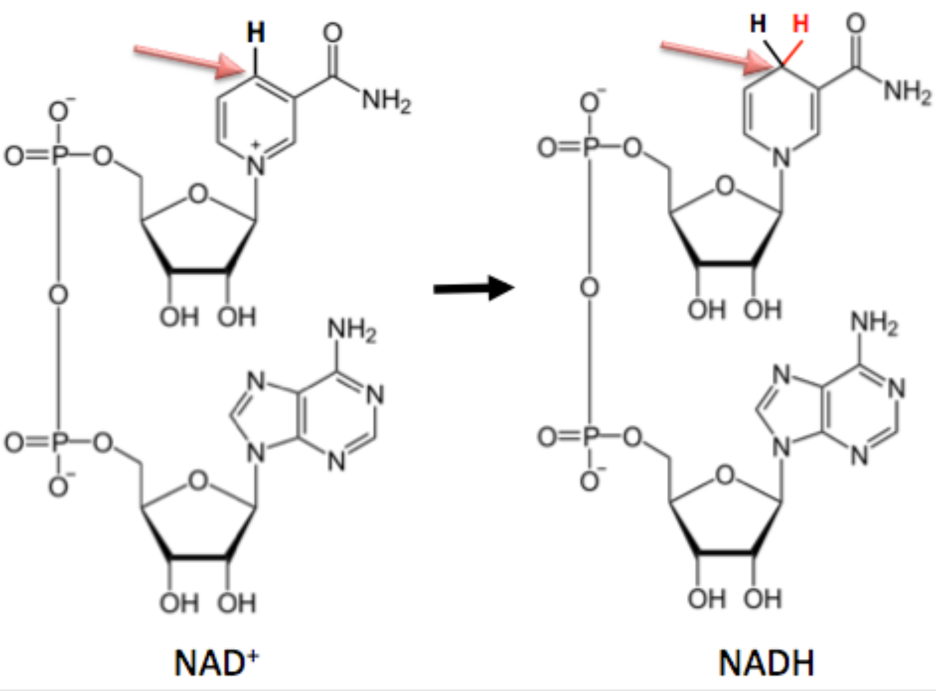


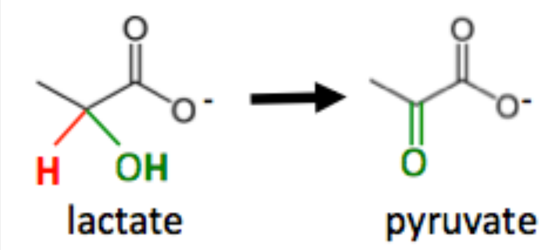
Figure 6.16 Reduction of NAD$^+$



In animals, this reaction is used to convert lactate to pyruvate. This is an important reaction that's involved in the metabolism of food. We can use our criteria for oxidation and reduction of covalent compounds to determine which species was oxidized and which was reduced in this reaction. Let's begin by considering the change that occurred for NAD$^+$. Look at the carbon *indicated by the red arrow* at the very top of the six membered ring of the NAD$^+$ shown in Figure 6.16. This carbon is bonded to ***one*** hydrogen atom as a reactant (in NAD$^+$). After reacting, this same carbon is bonded to ***two*** hydrogens. This change in that carbon's bonding matches our criteria for the ***reduction*** of a covalent compound; an atom is **reduced** if it ***loses*** *bond(s)* to ***oxygen*** and/or ***gains*** *bond(s)* to ***hydrogen***. **The carbon in NAD$^+$ was reduced in this reaction.** ***We often alternatively state this as "NAD$^+$ was reduced."***

Now, let's consider the change that occurred for *lactate*. The lactate reactant and pyruvate product are shown in Figure 6.17. ***Both*** a carbon *<u>and</u>* an oxygen in lactate ***lost bonds*** to hydrogen. Both of these changes match our criteria for the ***oxidation*** of a covalent compound; an atom is **oxidized** if it ***gains*** *bond(s)* to ***oxygen*** and/or ***loses*** *bond(s)* to ***hydrogen***. **A carbon *<u>and</u>* an oxygen in lactate were oxidized in this reaction.** ***We can also state this as: "lactate was oxidized."***

Figure 6.17
Oxidation of Lactic Acid



Review 6.9: Identifying Redox Reactions for *Covalent* Compounds

Indicate which atoms in the reactants in each of the following reactions were *oxidized* **<u>and</u>** which were *reduced*.

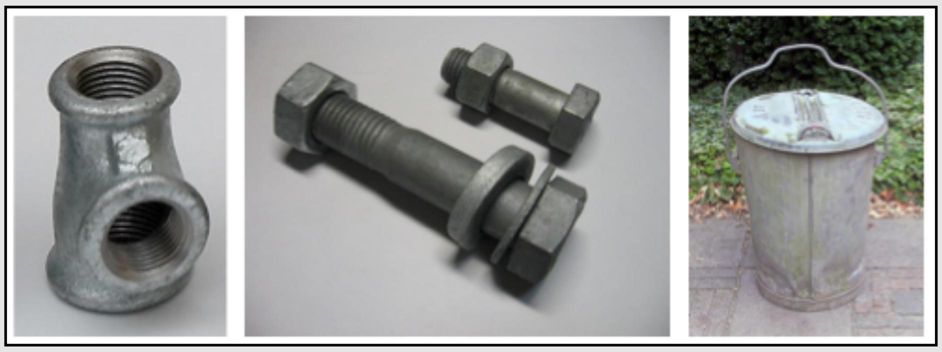
a) $\mathbf{2}\ H_2(g) + O_2(g) \rightarrow \mathbf{2}\ H_2O(g)$
b) ethene + $H_2(g) \rightarrow$ ethane

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

Some Industrial Uses of Redox Reactions

Many metals are mined as cations in ionic compounds (metal oxides, metal sulfides, metal carbonates, or metals combined with other anions) and then the metal cations are ***reduced*** to pure metals in an industrial process called **smelting**. For example, iron(II) oxide, copper nitrate, and lead sulfide, are converted to pure iron, copper, and lead, respectively. The reducing agent is usually carbon monoxide.

Figure 6.18 **Galvanized Steel Products**



Left: A galvanized iron/steel pipe fitting. **Middle:** Galvanized nuts, bolts, and washers. **Right**: A galvanized trash can. All of these metal products are galvanized to protect them from corrosion.
Source: Wikimedia Commons, Authors: Torsten Bätge (left), PD (middle), Rasbak (right), left and right images under CC-BY-SA, http://creativecommons.org/licenses/by-sa/3.0/legalcode

Cathodic corrosion protection is a process that combines a small quantity of a more easily oxidized metal (called the sacrificial metal) with the metal that is to be *protected* from oxidation. Metal oxidation is also called **corrosion**. In cathodic protection, the sacrificial metal corrodes before the protected metal. An example of cathodic protection is ***galvanized*** steel. In the galvanization process, a thin layer of zinc is applied to steel (iron) as a sacrificial metal. Several galvanized steel products are shown in Figure 6.18.

The process called "**bleaching**" uses fairly strong oxidizing agents. Oxidizing agents accept electrons from the species that is being oxidized. The substance that is commonly referred to as liquid bleach uses the hypochlorite ion (ClO^-) as an oxidizing agent.

$$ClO^- + H_2O + \mathbf{2}\boldsymbol{e-} \rightarrow Cl^- + 2OH^-$$

Bleach removes electrons from the molecules that make up "stains" or infectious agents. In the case of stains, when oxidized by bleach, they no longer absorb visible light and therefore can no longer be seen. Other bleaching methods use oxidizing agents such as hydrogen peroxide (H_2O_2) instead of hypochlorite.

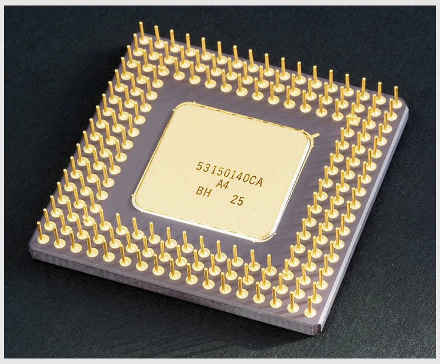
It is estimated that 50% of the world's population eat food that is grown using ***nitrogen fertilizers***[1]. The fertilizer industry employs the *reduction* of N_2 (from air) and the *oxidation* of H_2 in order to make ammonia in a process called **nitrogen fixation**.

$$N_2 + 3\ H_2 \rightarrow 2\ NH_3$$

Ammonia is either used directly or as a starting material for the synthesis of other nitrogenous fertilizers.

Electroplating processes use redox reactions to apply a thin coat of metal on another metal or conductive material. You may have heard the term "gold plated" or "silver plated." In these processes, the base metal is submerged into water that contains dissolved cations of the metal to be plated. Aided by a power source and an oxidation elsewhere, the metal cations are ***reduced*** to ***pure metal*** on the surface of the base metal. In *gold plating*, silver or copper are often used as the *base metal*. The base metal is submerged in water containing dissolved gold cyanide (AuCN). As electrons are supplied to the base metal from the power source, they are transferred to the gold ions (reduction) and pure gold metal is deposited/plated on the base metal's surface. This process is used in the jewelry business and is also an important step in the manufacture of electronic devices such the electrical connectors on microchips as seen in Figure 6.19.

Figure 6.19 Gold Plated Electrical Connectors



Gold is plated onto electronic devices such as this microprocessor chip made by Intel.
Source: Wikimedia Commons, Author: Andrew Dunn, CC-BY-SA, http://creativecommons.org/licenses/by-sa/3.0/legalcode

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[1] *Erisman, Jan Willem; MA Sutton, J Galloway, Z Klimont, W Winiwarter (October 2008). "How a century of ammonia synthesis changed the world", Nature Geoscience* ***1*** *(10): 636.*

Biochemical Redox Reactions

You will learn about the chemistry of biological systems (biochemistry) in the later chapters of this textbook. *You will see many redox reactions occurring in biology.* Biological systems employ a series of chemical reactions in order to get energy from food molecules in the ***cellular respiration*** process. Many of these reactions are redox reactions. The energy in food molecules originates from the sun. Sunlight is converted to chemical energy (in the form of carbohydrate molecules) in a series of chemical reactions called photosynthesis. Many of the reactions of ***photosynthesis*** are redox reactions.

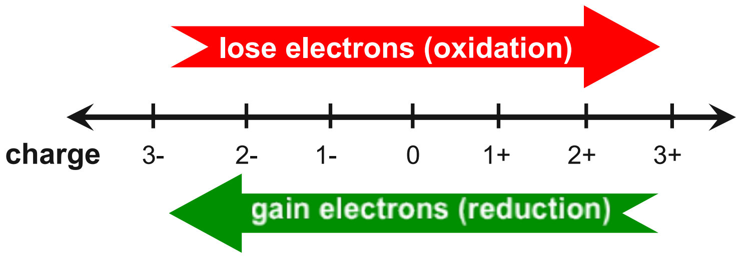
Summary of Redox Reactions

Oxidation is the ***loss of electron(s)*** by an atom, ion, or molecule in a chemical reaction.

Reduction is the ***gain of electrons*** by an atom, ion, or molecule in a chemical reaction.

It is possible to identify ***redox reactions*** for **inorganic compounds** by inspecting the chemical equation and determining if electrons are transferred from one species to another.

- One atom or ion in a **reactant** will **lose electrons** and therefore its ***charge*** will **increase** (in the positive direction) by one charge unit for every electron that is lost.
- The ***charge*** of the atom or ion in the **reactant** that **gains** the electron(s) will **decrease** (toward negative values) by one charge unit for every electron that is gained.

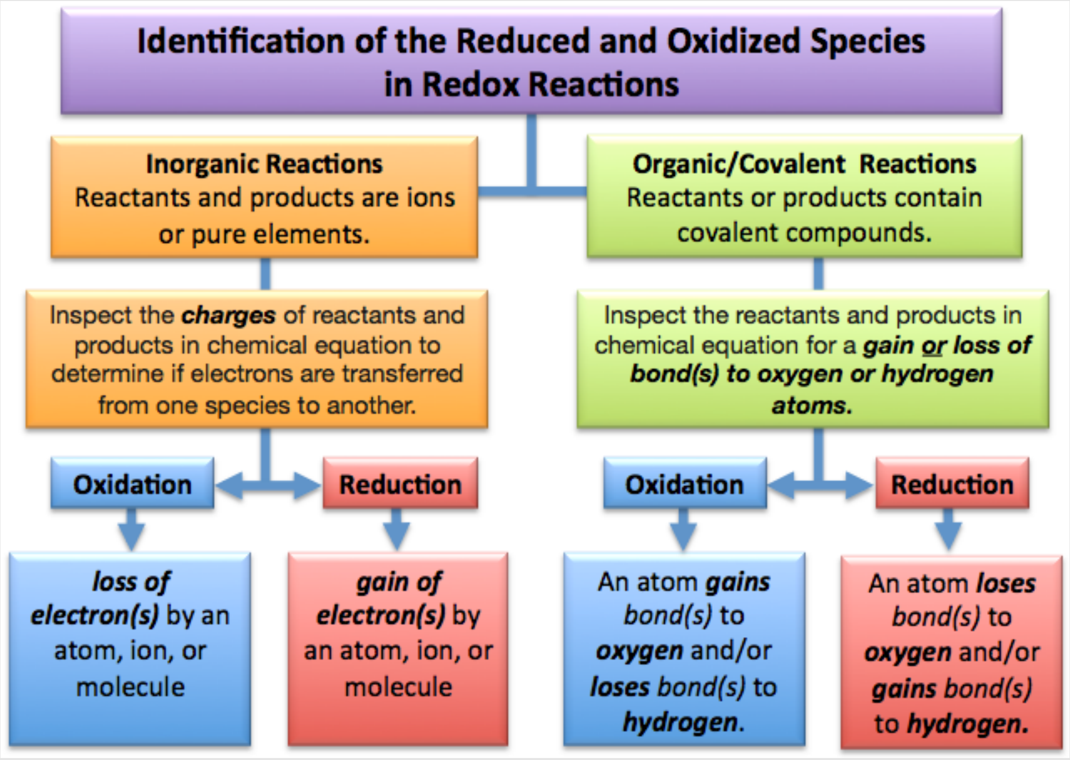


For **covalent compounds** such as organic molecules:

- An atom in a covalent compound is **oxidized** if it ***gains*** *bond(s)* to ***oxygen*** and/or ***loses*** *bond(s)* to ***hydrogen***.
- An atom in a covalent compound is **reduced** if it ***loses*** *bond(s)* to ***oxygen*** and/or ***gains*** *bond(s)* to ***hydrogen.***

A thought-map for identifying the oxidation and reduction species in redox reactions is given below in Table 6.1.

Table 6.1 Oxidation and Reduction Thought-Map



Identification of the Reduced and Oxidized Species in Redox Reactions

Inorganic Reactions
Reactants and products are ions or pure elements.

Inspect the ***charges*** of reactants and products in chemical equation to determine if electrons are transferred from one species to another.

Oxidation

loss of electron(s) by an atom, ion, or molecule

Reduction

gain of electron(s) by an atom, ion, or molecule

Organic/Covalent Reactions
Reactants or products contain covalent compounds.

Inspect the reactants and products in chemical equation for a ***gain or loss of bond(s) to oxygen or hydrogen atoms.***

Oxidation

An atom ***gains*** *bond(s)* to ***oxygen*** and/or ***loses*** *bond(s)* to ***hydrogen.***

Reduction

An atom ***loses*** *bond(s)* to ***oxygen*** and/or ***gains*** *bond(s)* to ***hydrogen.***

6.8 Reactions of Organic Molecules

You will learn about many reactions of organic molecules in this book. In this chapter, I will discuss ***four classes of organic reactions*** that involve the ***families*** of organic molecules that you were introduced to in chapter 4: hydrocarbons, alcohols, carboxylic acids, and esters. The four classes of organic reactions are seen very often in biological systems as you will discover in the biochemistry chapters of this book. Before we begin, let's review the structure of alcohols, carboxylic acids, and esters.

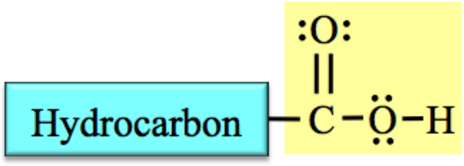
Proctor and Gamble's Soap Making Facility

One of the reactions that you will learn about in this section is the hydrolysis of esters. This is the reaction that is used to make soaps.
Source: geograph.org.uk, Author: Nigel Chadwick
CC-BY-SA, http://creativecommons.org/licenses/by-sa/3.0/legalcode

Alcohols contain one or more **hydroxyl (-OH)** functional groups attached to a ***hydrocarbon***. The hydroxyl group is also referred to as a **hydroxy** group. The general form of an alcohol is shown below with the hydroxyl group highlighted in yellow.

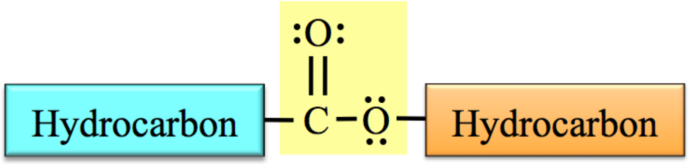
$$\text{Hydrocarbon}-\underset{\cdot\cdot}{\ddot{O}}-H$$

Carboxylic acids contain a ***carboxyl functional*** group attached to a hydrocarbon. Carboxyl groups contain a carbon atom, two oxygen atoms, and a hydrogen atom that are connected to each other and the hydrocarbon part as shown below. The carboxyl group is highlighted in yellow.



$$\text{Hydrocarbon}-\overset{\overset{:O:}{||}}{C}-\underset{\cdot\cdot}{\ddot{O}}-H$$

Esters contain a ***carboxylate functional*** group that is bonded *between* **two** hydrocarbon parts. Carboxylate groups contain a carbon atom and two oxygen atoms that are attached *between* two hydrocarbon parts as shown below. The carboxylate group is highlighted in yellow.



$$\text{Hydrocarbon}-\overset{\overset{:O:}{||}}{C}-\underset{\cdot\cdot}{\ddot{O}}-\text{Hydrocarbon}$$

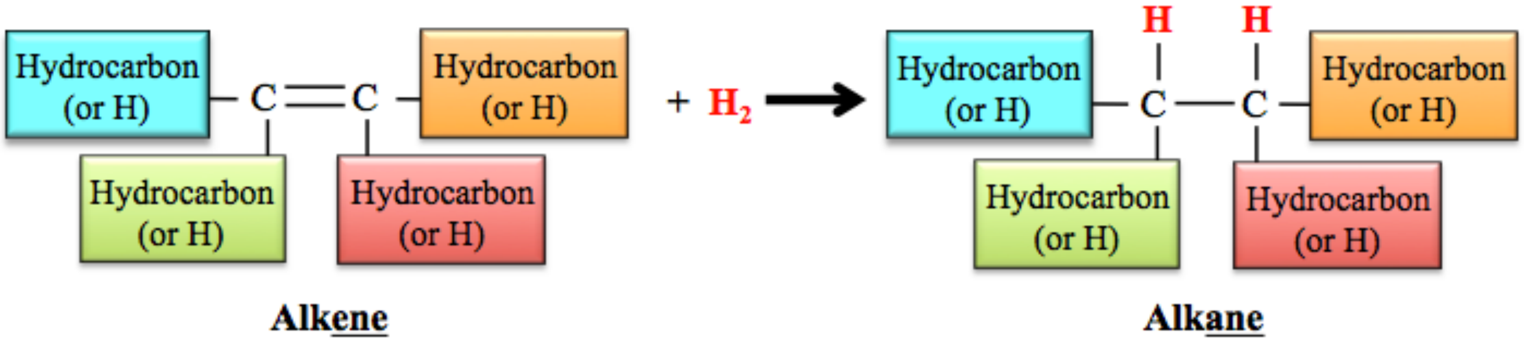
The ***four classes of organic reactions*** to be studied in this section are:

1) **Hydrogenation: Reduction of Alkenes**
2) **Hydrolysis of Esters**
3) **Hydration of Alkenes**
4) **Dehydration of Alcohols**

The **educational goal** for this section is, ***if you are given the specific reactant(s) for any of these four classes of reactions, you should be able to predict (draw) the product(s).*** A good way to do this is to know the "**general form**" of the organic reaction. I will elaborate on what is meant by the "***general form"*** of an organic reaction in the discussion of the reaction that follows.

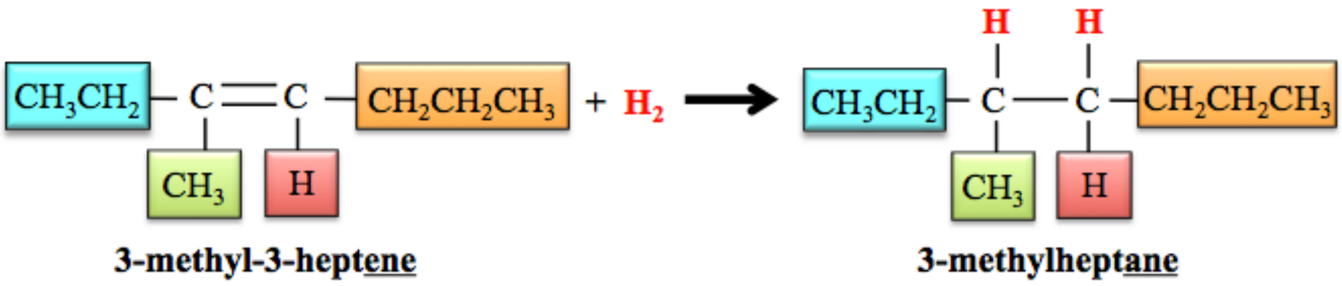
1) Hydrogenation: Reduction of Alkenes

Alkenes react with hydrogen gas (H_2) in a reaction called **hydrogenation**. In the presence of a *catalyst*, such as platinum, a hydrogen atom from H_2 is added to each of the double bonded carbon atoms in the ***alkene*** to produce the corresponding ***alkane***. Hydrogen gas acts as a *reducing agent*; the carbon atoms in an alkene are ***reduced*** (*they gain hydrogen atoms)*. The ***general form*** for the hydrogenation of alkenes reaction is shown below:

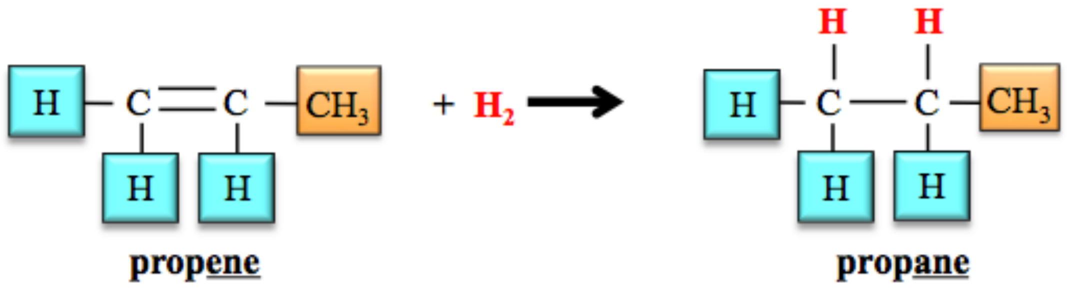


The ***general form*** of an equation contains the generic structures of products and reactants. For example, in the general form for the hydrogenation equation above, a *generic structure* representing ***any alkene*** is drawn as the *reactant* and a *generic structure* representing ***any alkane*** is drawn for the *product*. The boxes represent any hydrocarbon (alkyl group) or a hydrogen atom, and are shaded with different colors to indicate that ***the hydrocarbon parts may or may not be identical***. For example, consider the ***specific*** alkene hydrogenations in the following example reactions:

Example: Hydrogenation of 3-methyl-3-heptene



Example: Hydrogenation of propene



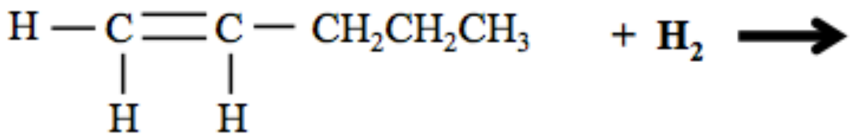
Knowing the "*general form*" of an organic reaction allows you to predict and draw the product(s) when given specific reactant(s).

Example: Draw and name the ***product*** of the following reaction:

$$CH_2{=}CHCH_2CH_2CH_3 \quad + H_2 \longrightarrow$$

Solution: First, we must identify the organic reaction to be the *hydrogenation of an alkene* based on the given reactants. So far, you have ***only*** seen hydrogenation of alkene reactions, but as you learn the other classes of organic reactions, the identification of the reaction class will require a bit of thought.

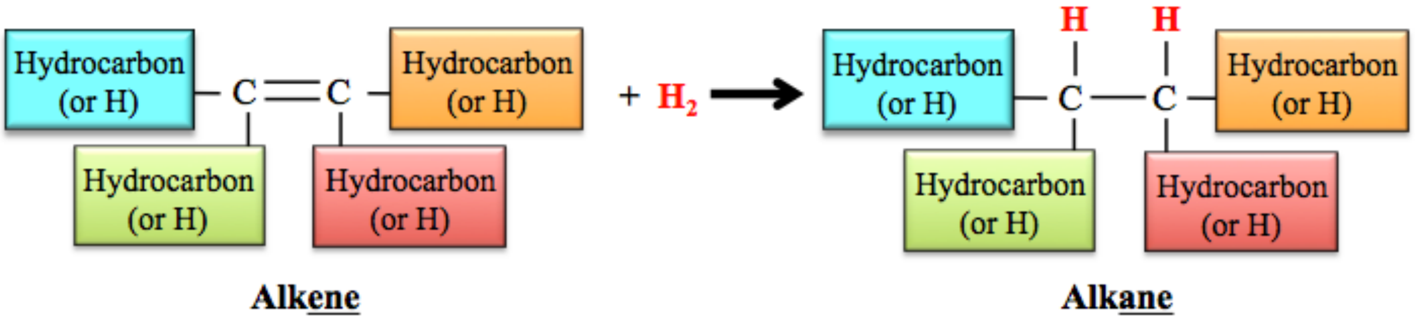
Next, refer to the general form of the reaction and determine what specific groups compose the boxes used for hydrocarbon parts or hydrogens. It may be easier for you to draw all the bonds that are connected to the double bonded carbons:



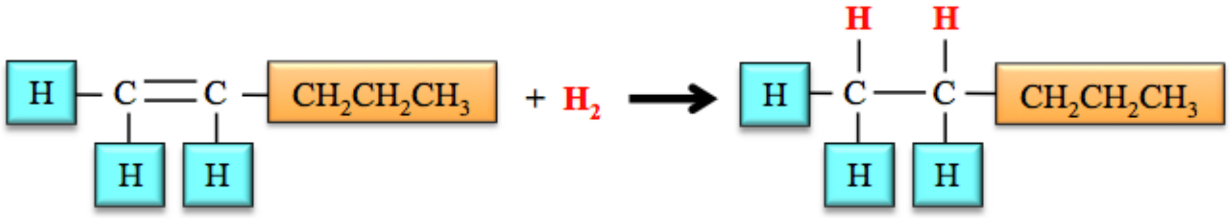
$$H-\underset{H}{\overset{}{C}}=\underset{H}{C}-CH_2CH_2CH_3 \quad + H_2 \longrightarrow$$

Replace the ***generic groups*** (in boxes) from the ***general form*** of the reaction with the ***specific groups*** for the given alkene and the corresponding alkane product:

General form for the hydration of alkenes:



Specific equation for the hydrogenation of 1-pentene:



Draw the structure of the product and reactants:

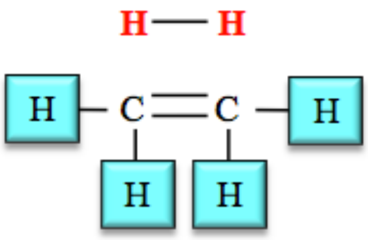
$$CH_2{=}CHCH_2CH_2CH_3 \quad + \; H_2 \longrightarrow CH_3CH_2CH_2CH_2CH_3$$

1-pentene **pentane**

Before I ask you to try a couple of problems on your own, I want to show you another way to predict the product for hydrogenation of alkene reactions. This method will be useful in several other types of reactions that you will learn. In the hydrogenation reaction, we made *new bonds* to ***both of the atoms (carbons)*** that were connected to each other with a double bond. Chemical reactions where new bonds are formed to atoms at each end of a double bond occur so frequently that organic chemist have a special name for it: "***addition across a double bond***." Products for reactions where *addition across a double bond* occurs can be easily predicted by learning the following method of "***flipping***" bonds.

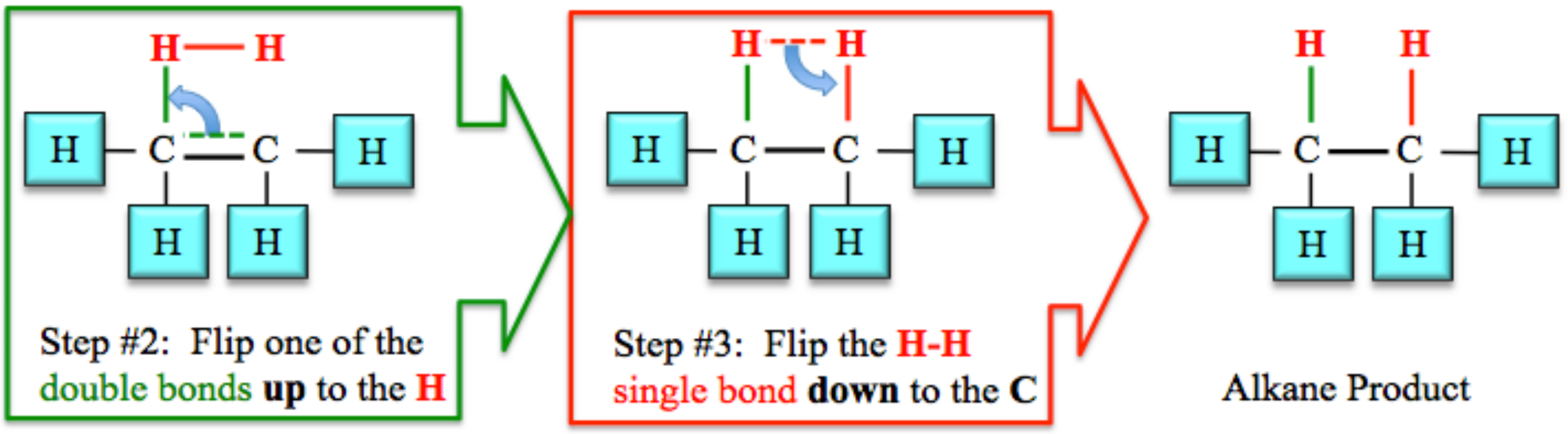
EXAMPLE of ***addition across a double bond***: Add H_2 across the double bond of **ethene** (hydrogenation of ethene).

Step 1: Draw the molecule to be added across the double bond and the molecule with the double bond as shown to the right.



Step #1:
Draw the H-H directly above the double bond.

Steps 2 and 3: ***Flip*** the bonds as shown below to get the product of the reaction.



Watch this video to see an animation of adding across a double bond:
http://www.zovallearning.com/streamvid/hydrogenation-of-alkenes.html

Review 6.10: Predicting the Product for Hydrogenation of Alkenes Reactions

Predict and name the product for the hydrogenation of **3-hexene** using the addition across a double bond method.

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

Review 6.11: Predicting the Product for Hydrogenation: Reduction of Alkenes Reactions

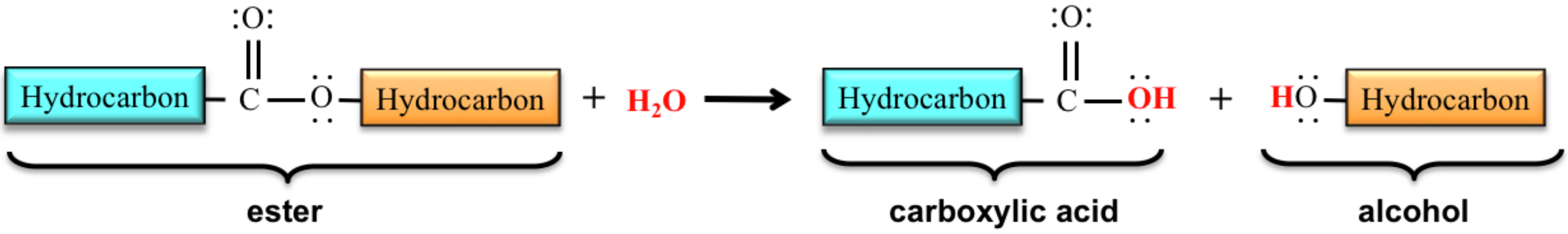
Predict and name the product for the hydrogenation of **3,4-dimethyl-3-heptene** using the addition across a double bond method.

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

Water is a reactant or product in a number of reactions important to organic and biochemistry. The next three classes of organic reactions involve a water molecule as either a reactant or product.

2) Hydrolysis of Esters

In a **hydrolysis** reaction, water (hydro) is used to break (lyse) a bond in a molecule. The **hydrolysis of esters** reaction occurs in nature and has industrial uses. For example, triglycerides (fats) are esters and undergo hydrolysis reactions in the digestion process. In the hydrolysis of an ester, a water molecule breaks a bond in the ester to form a **carboxylic acid** and an **alcohol**. The general form of the hydrolysis of esters equation is:



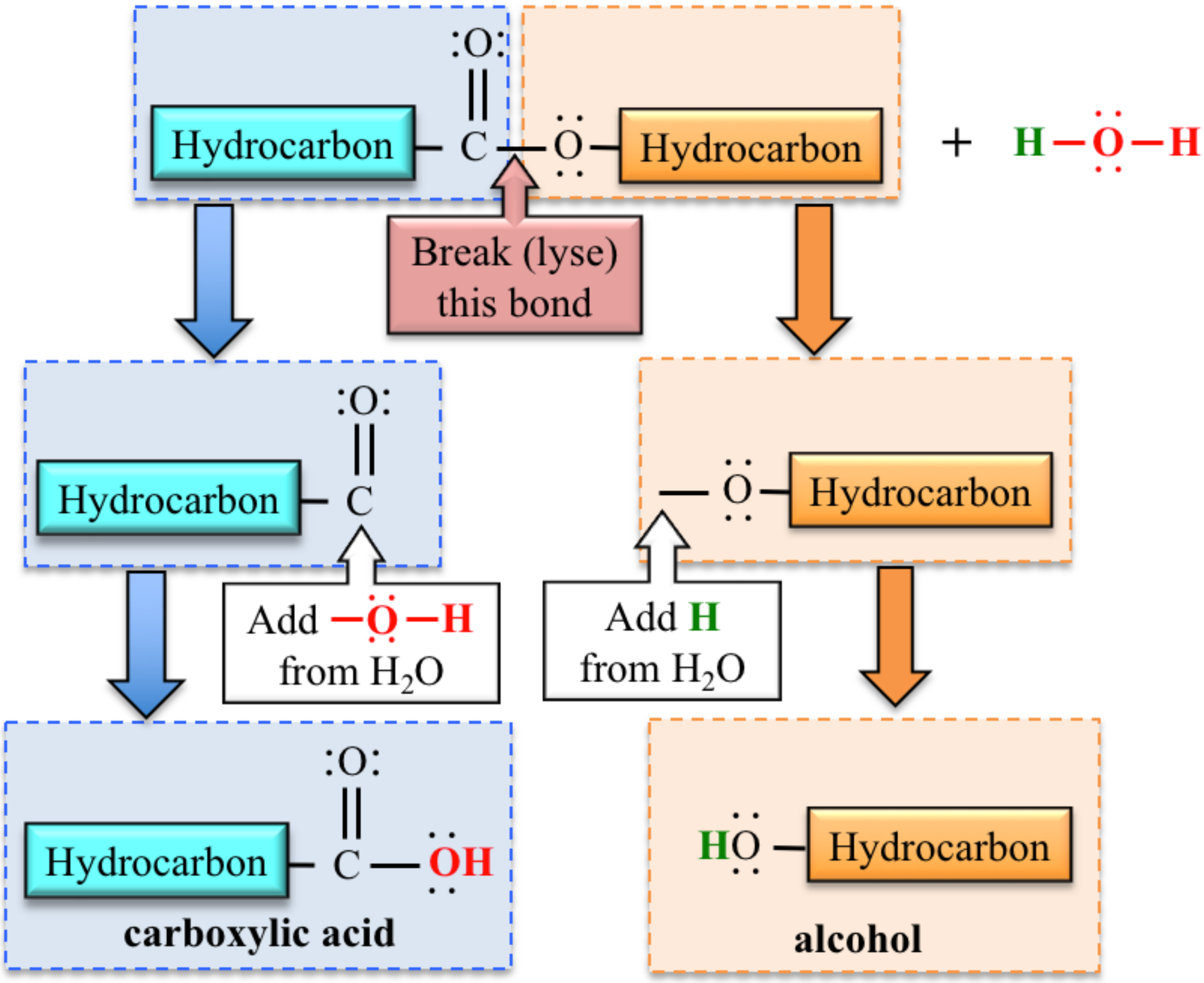
Knowing the "*general form"* of the hydrolysis of esters equation, and then identifying the hydrocarbon parts will allow you to predict and draw the carboxylic acid and alcohol products when given a specific *ester* reactant.

I want to show you *another way* to predict the products for hydrolysis of ester reactions.

Step 1: Draw the structural formula of the ester and identify the hydrocarbon parts.

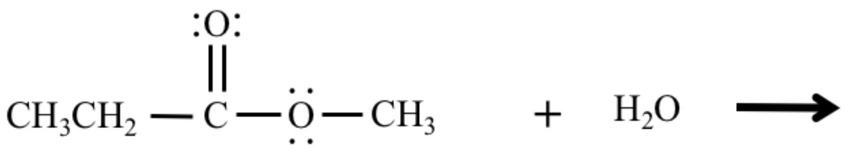
Step 2: Break (lyse) the carbon-oxygen ***single bond*** <u>between</u> the *carbonyl* carbon and the oxygen. The *carbonyl* carbon is the carbon that is double bonded to an oxygen. See the red box and arrow in the illustration on the right.

Step 3: Add the **-OH** from the water to the *carbonyl* carbon ***and*** then add the **H** from the water to the oxygen on the ***other fragment***.



When you use these three steps, it will result in the correct ***carboxylic acid*** <u>*and*</u> ***alcohol***.

Hydrolysis of Esters Example Problem: Many esters are naturally occurring flavor and fragrance molecules. An ester named *methyl propanoate* has a fruity rum-like fragrance. Draw the structural formulas of **both products** in the hydrolysis of methyl propanoate:



$$CH_3CH_2-\overset{\overset{\Large :O:}{||}}{C}-\ddot{\underset{..}{O}}-CH_3 + H_2O \longrightarrow$$

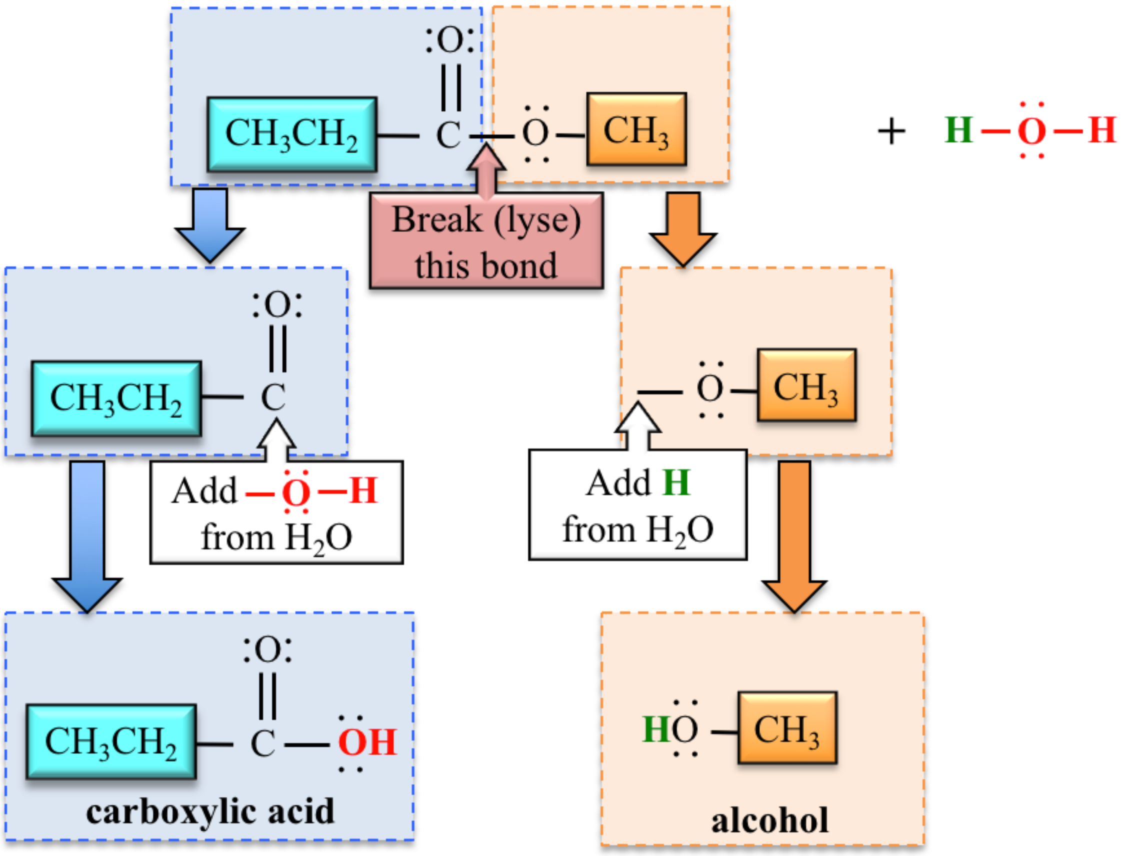
methyl butanoate

Solution:

Step 1: Draw the structural formula of the ester and identify the hydrocarbon parts.

Step 2: Break (lyse) the carbon-oxygen ***single bond*** <u>between</u> the *carbonyl* carbon and the oxygen. The *carbonyl* carbon is the carbon that is double bonded to an oxygen.

Step 3: Add the **-OH** from the water to the *carbonyl* carbon ***and*** then add the **H** from the water to the oxygen on the ***other fragment.***

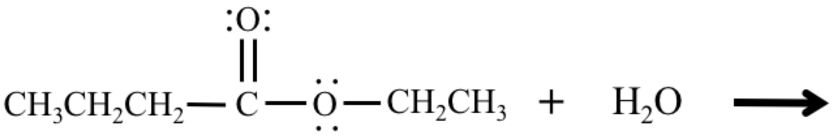


When you use these three steps, it will result in the correct carboxylic acid and alcohol. The chemical equation for this reaction is:

$$CH_3CH_2-\overset{\overset{\Large :O:}{||}}{C}-\ddot{\underset{..}{O}}-CH_3 + H-\ddot{\underset{..}{O}}-H \longrightarrow CH_3CH_2-\overset{\overset{\Large :O:}{||}}{C}-\ddot{\underset{..}{O}}H + H\ddot{\underset{..}{O}}-CH_3$$

Now you try one:

PROBLEM: An ester named *ethyl butanoate* is one of the most frequently used additive flavor ingredients in the food and beverage industry. It is used mostly for orange flavoring and is also used for pineapple, cherry, guava, bubblegum, peach, apricot, fig, and plum. Draw the structural formulas of both products in the hydrolysis of ethyl butanoate:



$$CH_3CH_2CH_2-\overset{\overset{\Large :O:}{||}}{C}-\ddot{\underset{..}{O}}-CH_2CH_3 + H_2O \longrightarrow$$

ethyl butanoate

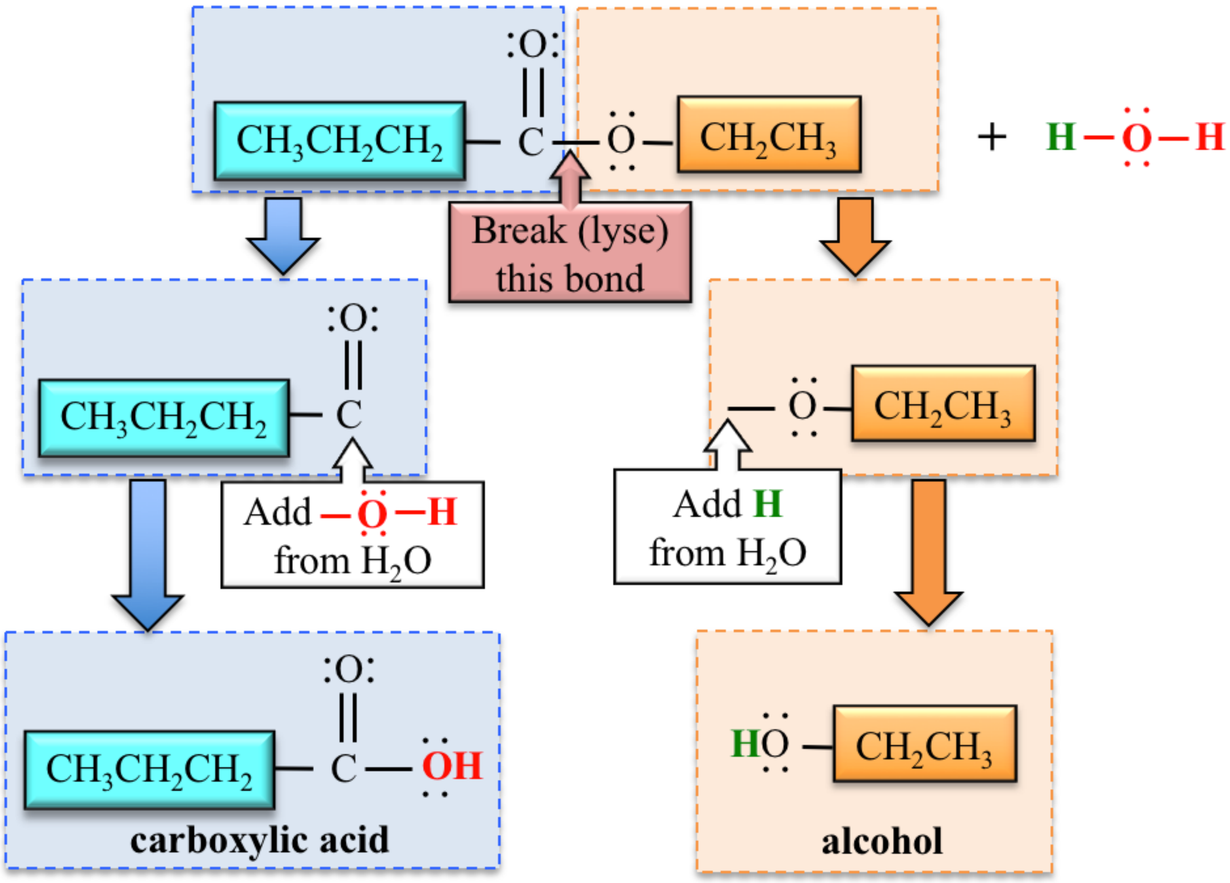
See the next page to *check your answer*.

Solution:

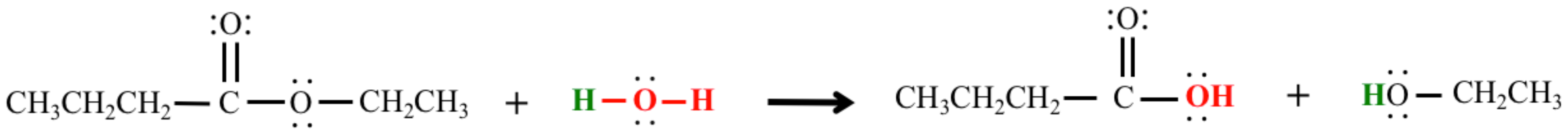
Step 1: Draw the structural formula of the ester and identify the hydrocarbon parts.

Step 2: Break (lyse) the carbon-oxygen ***single bond*** between the *carbonyl* carbon and the oxygen. The *carbonyl* carbon is the carbon that is double bonded to an oxygen.

Step 3: Add the **-OH** from the water to the *carbonyl* carbon ***and*** then add the **H** from the water to the oxygen on the ***other fragment.***



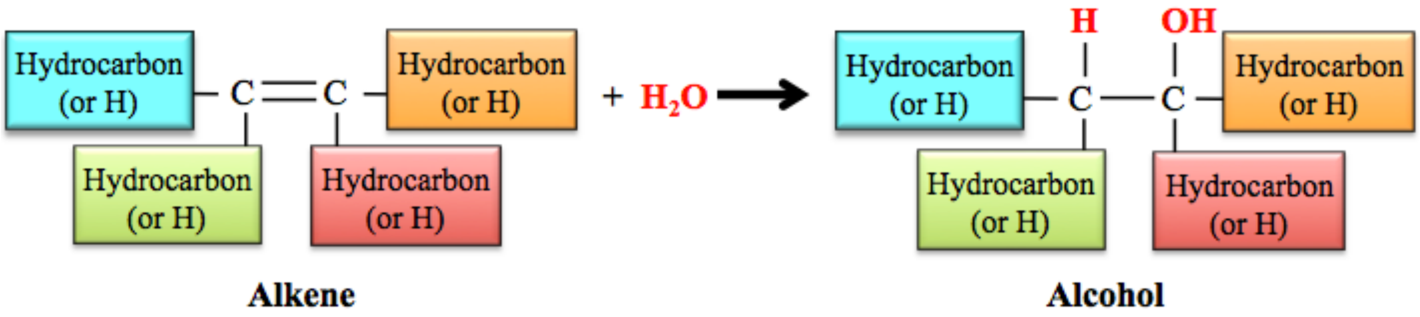
The chemical equation for this reaction is:



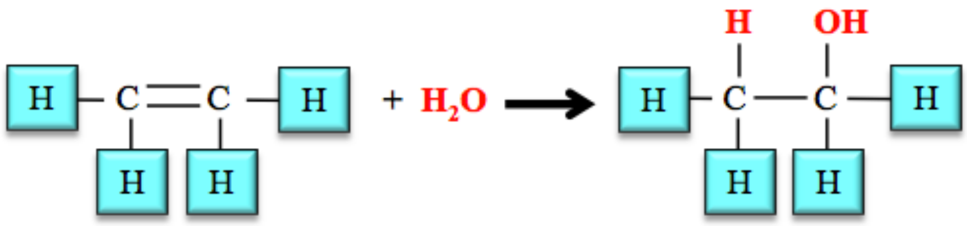
$$CH_3CH_2CH_2-\overset{\overset{:O:}{\|}}{C}-\ddot{\underset{\cdot\cdot}{O}}-CH_2CH_3 + H-\ddot{\underset{\cdot\cdot}{O}}-H \longrightarrow CH_3CH_2CH_2-\overset{\overset{:O:}{\|}}{C}-\ddot{\underset{\cdot\cdot}{O}}H + H\ddot{\underset{\cdot\cdot}{O}}-CH_2CH_3$$

3) Hydration of Alkenes

Alkenes react with water molecules to produce alcohols. A hydrogen atom from **H_2O** is added to one of the double bonded carbon atoms, and the **-OH** from the **H_2O** is added to the ***other*** double bonded carbon atom in the ***alkene*** to produce the corresponding ***alcohol.*** The ***double bond*** in the alkene is converted to a ***single bond*** in the alcohol. The ***general form*** for the hydration of an alkene reaction is shown below:



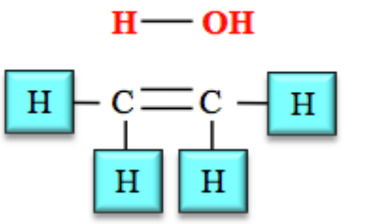
A specific example of the hydration of alkenes reaction is the reaction of ***ethene*** and **H_2O**:



You may have noticed the similarity of this *hydration reaction* to the *hydrogenation of alkenes*. Hydration reactions are another example of reactions in which a molecule is ***added across a double bond***. In the *hydration of alkenes reaction*, water is added ***across the double bond of an alkene,*** therefore we can use the *bond flipping method* to predict the structure of the alcohol that is produced. I will show you an example of the bond flipping method using the **hydration of *ethene*** reaction:

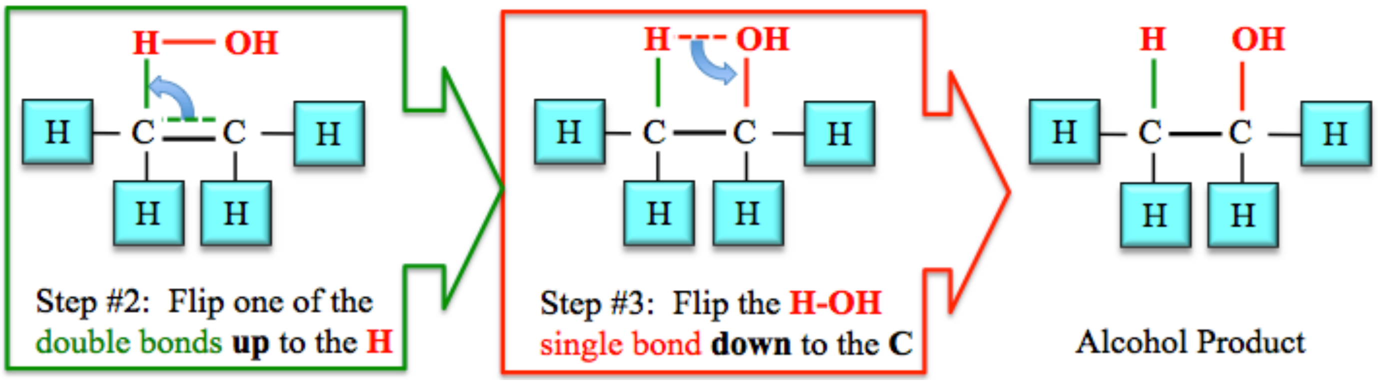
EXAMPLE: ***Addition of H_2O across a double bond***. Add **H_2O** across the double bond of **ethene** (hydration of ethene).

Step 1: Draw the molecule to be added across the double bond and the molecule with the double bond as shown to the right.



Step #1:
Draw the H - OH directly
above the double bond.

Steps 2 and 3: *Flip* the bonds as shown below to get the product of the reaction.



Review 6.12: Predicting the Product for Hydration Alkenes Reactions

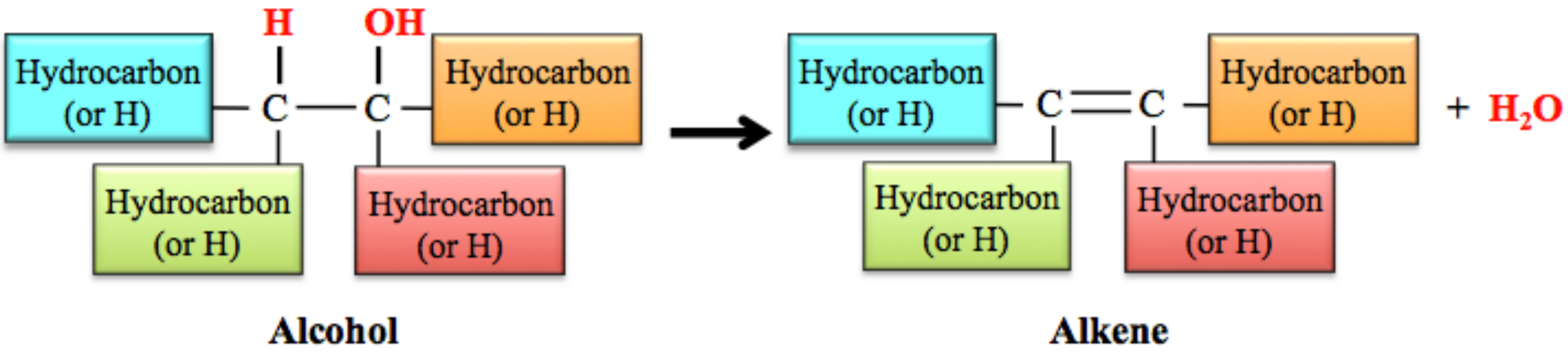
Draw the alcohol that is produced when 2-butene undergoes a hydration reaction:

$$CH_3CH = CHCH_3 \quad + \; H_2O \longrightarrow$$

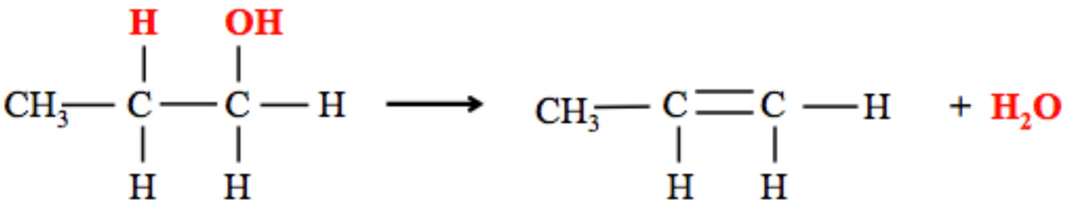
For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

4) Dehydration of Alcohols

Dehydration of alcohols is the ***reverse*** of hydration of alkenes. H_2O is removed from an alcohol to form an alkene. A hydroxyl group (**-OH**) is removed from a carbon atom and a **H** is removed from a carbon that is *adjacent* to the carbon that was bonded to the hydroxyl group. A double bond forms between these two carbons. The ***general form*** for the *hydration of an alcohol reaction* is shown below:

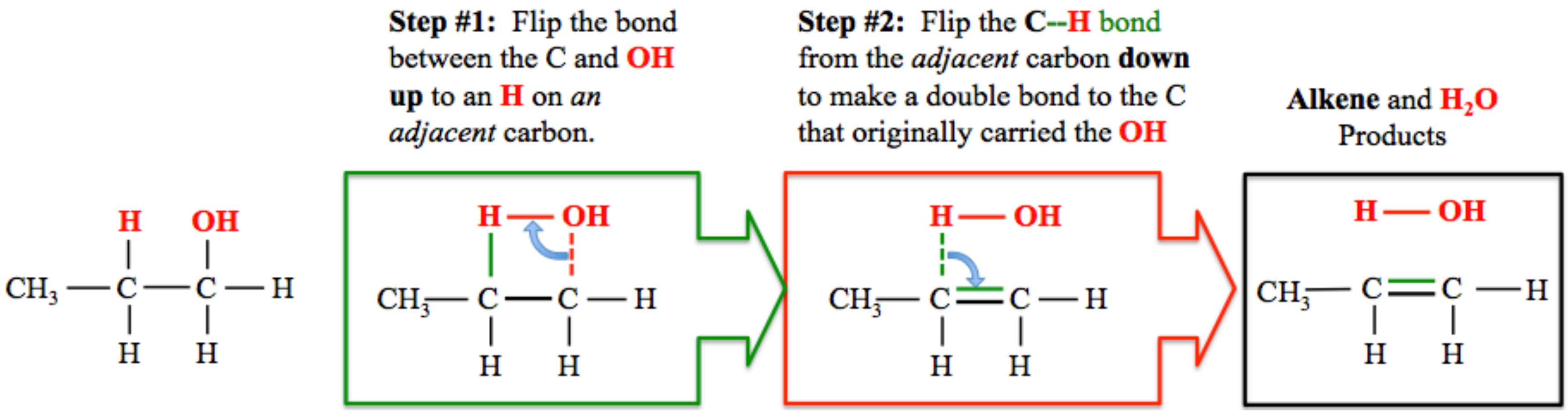


A specific example is the dehydration of propyl alcohol:



$$CH_3-CH(H)-CH(OH)-H \longrightarrow CH_3-CH=CH-H + H_2O$$

Since this reaction is the ***reverse** of the hydration of alkenes* reaction, we can ***flip*** the bonds in the ***opposite order*** to that which we used when we added water *across the alkene double bond*. Doing so can be very helpful in determining the alkene product of dehydration of alcohol reactions. I will use the dehydration of propyl alcohol as an example. Beginning with the structure of the alcohol, perform the following two steps:



Step #1: Flip the bond between the C and **OH** **up** to an **H** on *an adjacent* carbon.

Step #2: Flip the **C--H bond** from the *adjacent* carbon **down** to make a double bond to the C that originally carried the **OH**

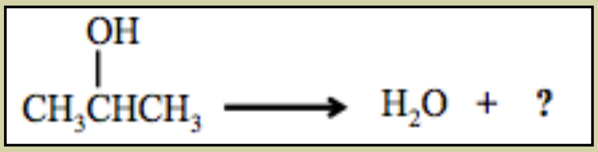
Alkene and **H_2O** Products

propyl alcohol

Now you try a dehydration problem:

Review 6.13: Predicting the Product for Dehydration of Alcohol Reactions

Name and draw the condensed structural formula for the alkene that is produced when isopropyl alcohol undergoes a dehydration reaction:



$$CH_3CH(OH)CH_3 \longrightarrow H_2O + ?$$

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

Summary of Classes of Organic Reactions

Organic Reaction Class	Reactant(s)	Product(s)
Hydrogenation of Alkenes	Alkene + H_2	Alkane
Hydrolysis of Esters	Ester + H_2O	Carboxylate ion + Alcohol
Dehydration of Alcohols	Alcohol	Alkene + H_2O
Hydration of Alkenes	Alkene + H_2O	Alcohol

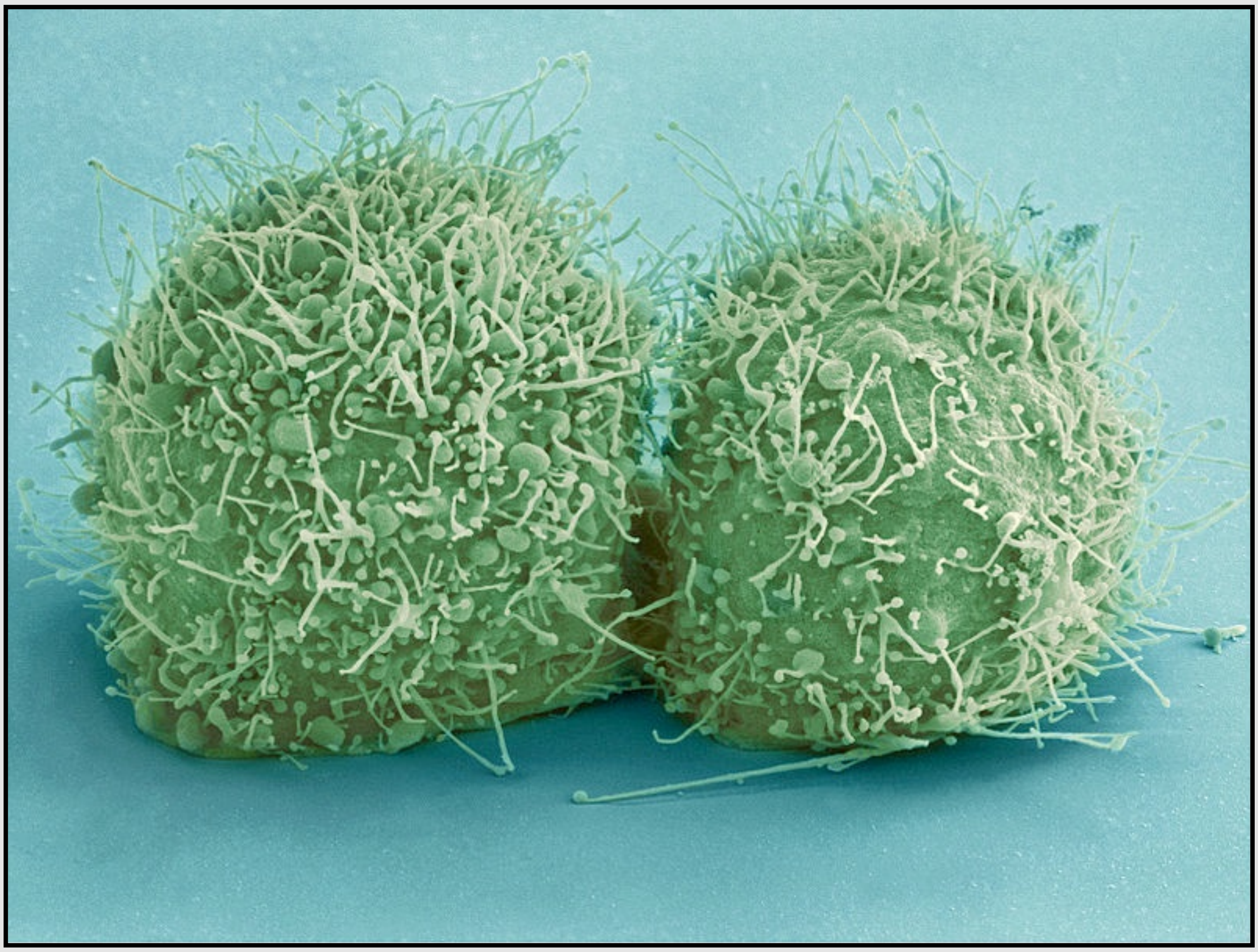
Recommendation:

Work on the "***Chapter 6 Reactions Worksheet"*** as soon as you can. This worksheet is provided in the lecture notes package and on the website.

Get the entire course as a series of video lectures at: www.zovallearning.com

Chapter 7:

Solutions, Colloids, and Suspensions



Biological cells are small containers filled will various solids, as well as ions and molecules that are dissolved in water. This image is a colorized, scanning electron micrograph of just-divided HeLa cells.

Source: Wikimedia Commons, Author: National Institutes of Health (NIH), PD

Most matter on earth is not composed of just one pure substance. For example, saltwater, soil, milk, plants, animals, and air, are all mixtures of pure substances. In this chapter, you will learn about three types of mixtures: solutions, colloids, and suspensions. Many medications are administered as solutions (some as colloids and suspensions). In the healthcare field, an understanding of mixtures is very important in order to know how much and at what rate medicines should be administered.

7.1 Chapter 7 Educational Goals

1. Compare and contrast **mixtures** and **pure substances.**
2. Understand, compare, and contrast the terms **homogeneous mixture** and **heterogeneous mixture.** For a homogeneous mixture, explain the difference between **solute(s)** and **solvent**.
3. Predict the effect of temperature and pressure on the **solubility** of gases in water and the effect of temperature on the solubility of solids in water.
4. Be able to use the **Solubility Rules Table** to determine if an ionic compound will significantly dissolve in water.
5. Predict whether a **precipitation reaction** will occur when two specified aqueous solutions of ionic compounds are mixed; if a precipitation reaction will occur, write a balanced chemical equation for the reaction.
6. Compare the relative solubilities of organic molecules based on the functional groups or the relative sizes of the hydrocarbon (nonpolar) regions.
7. Explain, compare, and contrast the terms **hydrophilic**, **hydrophobic**, and **amphipathic**, and give examples of compounds that belong to each category.
8. Be able to calculate the **concentration** of a solution using various concentration units of measurements (%, parts per thousand, ppm, ppb, molarity, molality, osmolality, osmolarity, and Eq/L).
9. Given the concentration, be able to convert from the volume of solution to the amount of solute (and vice versa).
10. Given a solution's initial concentration, be able to use the **dilution equation** to determine the concentration of the solution after dilution.
11. Compare and contrast **solutions**, **suspensions**, and **colloids**.
12. Describe the processes of **diffusion** and **osmosis**. Define **osmotic pressure** and predict the effect of solute concentration on the osmotic pressure.

7.2 Mixtures

In chapters 2-5, you learned about **pure substances**: *elements*, *ionic compounds,* and *covalent (molecular) compounds*. Most of the objects around us in nature ***are not composed of just one pure substance***. When two or more pure substances are combined, we refer to the combination as a **mixture.** Figure 7.1 is meant as a guide to help you know and understand the differences between the various ways in which matter occurs.

Source: Wikimedia Commons, Author: Chris 73
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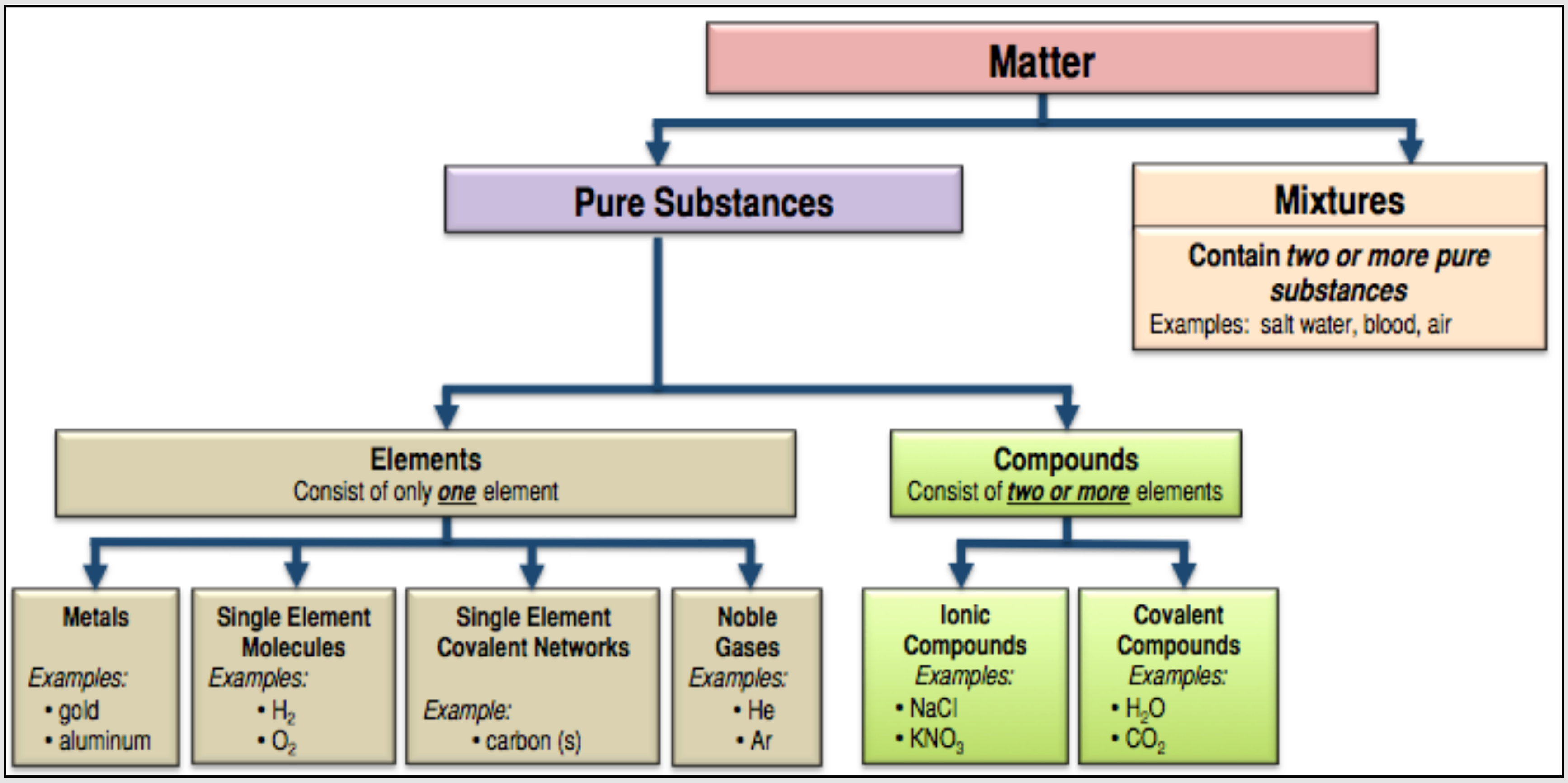
Figure 7.1 **Classification of Matter**



Macro-Scale Classification of Mixtures: Homogeneous vs. Heterogeneous

One way in which mixtures are classified is by their macro-scale, visually observed ***homogeneity***. A **homogeneous mixture** appears to be the same throughout the entire sample/object. A **heterogeneous mixture** has visible regions of varying composition. For example, if you dissolve a spoon of sugar in water, the resulting mixture would be ***homogenous***. If you were to repeatedly withdraw one drop of the sugar-water from various random regions in the glass, each of the drops would be identical. This can be contrasted with a ***heterogeneous*** mixture. An example of a *heterogeneous* mixture is a chocolate chip cookie. In some small regions of the chocolate chip cookie, a chocolate chip can be seen; in other small regions a chocolate chip is not seen. If you were to use tweezers/forceps to repeatedly withdraw a small sample of the cookie form various random regions of the cookie, the samples that you withdrew may not all appear to be identical. The amount of chocolate in each sample could vary. You may see that a few of the samples are 100% chocolate, some may contain both chocolate *and* non-chocolate parts, and in other samples you may not observe any chocolate parts at all.

7.3

Introduction to Solutions

Solutions are mixtures of pure substances in which the pure substance particles (molecules, ions, or noble gas atoms) are evenly distributed throughout the entire volume of the mixture. The pure substance that is in the *greatest abundance* is referred to as the **solvent**. Typically, especially in biological systems, *the solvent is water*. The other pure substance components of a solution are called **solutes**. With very few exceptions, the solution takes the same *physical phase* (gas, liquid, or solid) as the *solvent*. The ***solutes*** are said to be "**dissolved**" in the ***solvent***.

Various Solutions. Source: Wikimedia Commons, Author: Chemrose CC-BY-SA, http://creativecommons.org/licenses/by-sa/3.0/legalcode

Solutions can be gaseous, liquid, or solid. An example of a **gas-phase solution** is air. Air is a mixture of several gases, mostly nitrogen, oxygen, and carbon dioxide. An example of a **solid-phase solution** is brass. Brass is a mixture of copper and zinc. When one solid (such as zinc) is evenly dispersed in another solid (such as copper), the solid solution is called an **alloy**.

Figure 7.2 A Whale Shark's Gills

Fish, such as this whale shark, extract the dissolved O_2 gas from water using their gills. Source: Wikimedia Commons, Author: Jaontiveros CC-BY-SA, http://creativecommons.org/licenses/by-sa/3.0/legalcode

We will focus on **liquid-phase solutions** for the remainder of the chapter and book. There are 3 types of *liquid-phase solutions:*

1) ***Gas*** *dissolved in a liquid* solvent
2) ***Liquid*** *dissolved in a liquid* solvent
3) ***Solid*** *dissolved in a liquid* solvent

An example of a gaseous solute dissolved in a liquid solvent is CO_2 dissolved in water; this is how beverages are carbonated. Another example of a gaseous solute dissolved in a liquid solvent is O_2 dissolved in water; fish extract the O_2 from water using their gills (Figure 7.2). Whenever a gas is present above a liquid, some of the gas will dissolve in the liquid. An example of a liquid *solute* dissolved in a liquid *solvent* is ethyl alcohol dissolved in water; this is the basis of adult beverages. An example of a solid solute dissolved in a liquid solvent is table salt ($NaCl$) or table sugar (sucrose molecules) dissolved in water. Most solutions used in biological applications, such as in biomedical analytical labs and research labs, are *liquid-phase solutions*. For the remainder of this book, I will use the term **solution** to mean **liquid-phase solution.**

Review 7.1: Understanding the Concepts and Terminology of Solutions

If the following pairs of pure substances are mixed in the ratios given to form solutions, identify each substance as either **solvent *or* solute**:

a. 5 grams of sodium chloride and 100 grams of water
b. 10 mL of ethyl alcohol and 250 mL of water
c. 100 mL of acetone and 10 mL of water

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

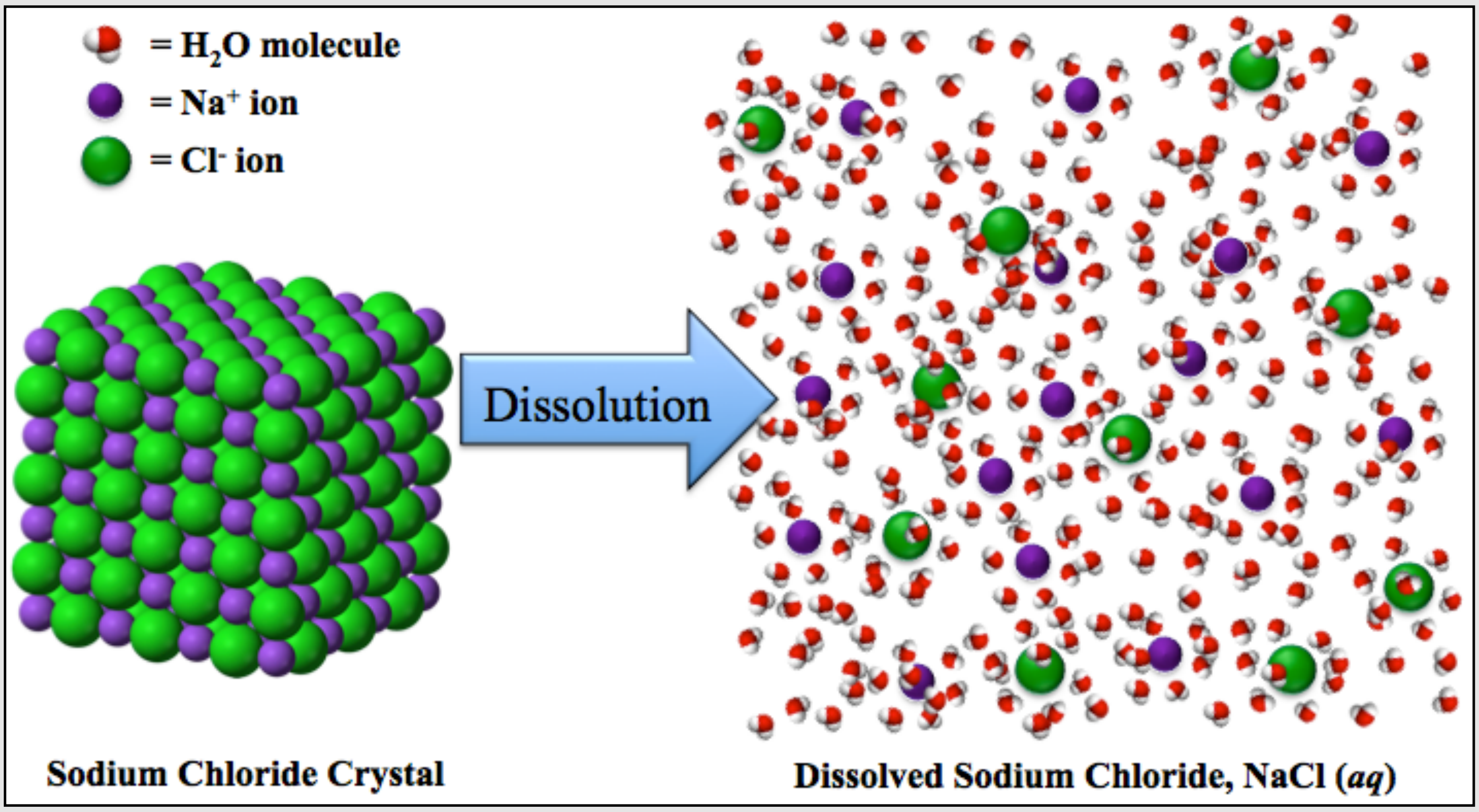
The Dissolution Process: Solvation

Another term for "*dissolving*" is **dissolution**. In liquid and solid phase solutions, the solute and solvent particles are attracted to each other by one or more of the five types of *noncovalent interactions*. The stronger the **solute-solvent** interactions, the more solute that can be dissolved. I will show you a couple of examples and illustrations to help you understand the concepts of dissolution and solvation.

The Dissolution of Ionic Compounds

Example: The dissolution of sodium chloride. Some ionic compounds dissolve in water. Consider a crystal of sodium chloride that is placed in water. When ionic compounds dissolve, the ions **dissociate** (become separated from each other) and enter the liquid phase solution as illustrated in Figure 7.3.

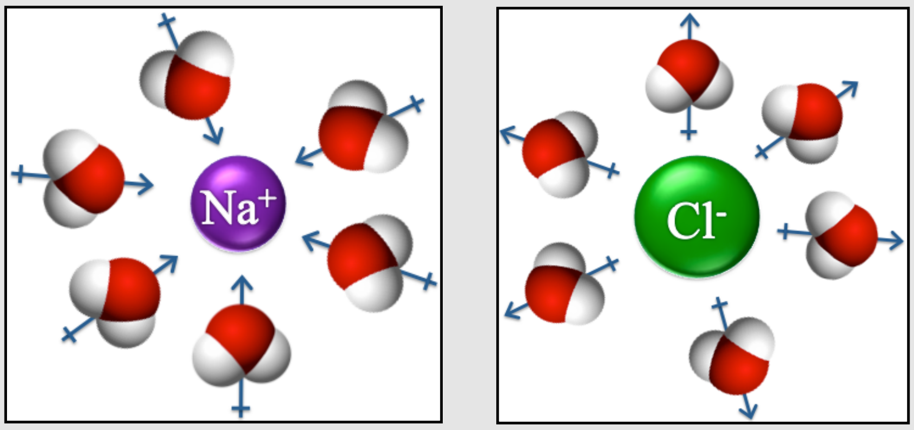
Figure 7.3 **The Dissolution of a Sodium Chloride Crystal in Water**



When sodium chloride or other soluble ionic compounds are placed in water, the ionic bonds in the solid are broken and the ions **dissociate** (become separated from each other).

In a sodium chloride crystal, the sodium ions and chloride ions are held together with ionic bonds, as shown on the left-hand side of Figure 7.3. When the crystal is placed in water, these ionic bonds are replaced with *noncovalent interactions* between the ions and water molecules. The water molecules surround the sodium cations and chloride anions on the surface of the crystal and displace the ions into the liquid phase. The water molecules and ions are attracted to each other through ***ion-dipole forces***. The ***partially negatively-charged ends*** of several water molecule dipoles are attracted to the ***positive charge*** of each sodium ion as illustrated in Figure 7.4. Likewise, the ***partially positively-charged ends*** of several water molecule dipoles are attracted to the ***negative charge*** of each chloride ion. We use the term **solvation** to describe a *solute* particle becoming surrounded by *solvent* molecules. **Solvation causes dissolution of the solute.**

Figure 7.4 **Solvated Ions**



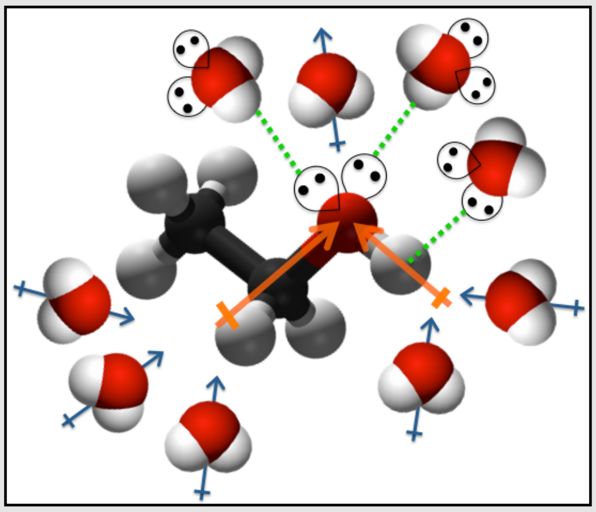
Left: *A solvated sodium ion.* The partial negatively-charged ends of several water molecule dipoles (indicated by blue dipole arrows) are attracted to the positive charge of a sodium ion. **Right:** *A solvated chloride ion.* The partially positively-charged ends of several water molecule dipoles are attracted to the negative charge of a chloride ion.

The Dissolution of Molecules

Molecules will dissolve in a particular solvent when the **solute-solvent** noncovalent interactions are strong enough to overcome the solute-solute interactions. This is true whether the solute molecules existed as a liquid or a solid before being placed in the solvent. *Unlike ionic compounds* that ***dissociate***, when molecules dissolve, the *individual* molecules become *solvated*.

Example: The dissolution of ethyl alcohol (CH_3CH_2-OH) in water. Ethyl alcohol dissolves in water because it has significantly strong noncovalent interactions with water. These **solute-solvent** noncovalent interactions enable the solvation of ethyl alcohol molecules by water molecules as illustrated in Figure 7.5. Hydrogen bonding, dipole-dipole forces, and London forces occur between ethyl alcohol and water. Since water molecules are relatively small, the London forces between water and ethyl alcohol are not very strong; if they were the only noncovalent interactions present, ethyl alcohol would not dissolve in water. Ethyl alcohol's lone pairs can form hydrogen bonds with a *hydrogen bonded to oxygen* in water (and vice versa), as indicated by the green dashed lines in Figure 7.5. Since ethyl alcohol *and* water are *polar molecules*, they can also interact through dipole-dipole forces. The dipoles of ethyl alcohol's **highly-polar bonds** are indicated by orange dipole arrows and water's molecular dipoles are indicated by blue dipole arrows.

Figure 7.5 Solvation of a Molecule



A solvated ethyl alcohol molecule. ***Hydrogen bonding*** attraction (indicated by the green dashed lines) occurs between ethanol and water. ***Dipole-dipole*** interactions occur between the partial negative charged ends of several water molecule dipoles (blue arrows) and the positive ends of ethanol molecule dipoles (orange arrows).

Solutes that are ***polar*** are capable of dissolving in ***polar solvents***. Solutes that are ***nonpolar*** are capable of dissolving in ***nonpolar solvents***. This phenomenon is summarized in the easily-remembered phrase, "**like dissolves like.**"

Figure 7.4 and Figure 7.5 are two-dimensional illustrations of solvation; in reality, water molecules completely surround solvated ions and molecules to create what is called a **hydration shell** or **hydration sphere**. Because of the relatively small size of solvated molecules and ions, the forces imparted upon them from collisions with solvent molecules are much greater than the force of gravity. It is for this reason that solvated ions and molecules do not settle to the bottom of a mixture, but instead, move in random directions in-between collisions. This type of random, chaotic movement is called **Brownian motion** and results in the solute being evenly dispersed within the solvent. Since ions and molecules are evenly dispersed within the solvent, ***solutions are homogeneous***.

Review 7.2: Dissolution and Solvation

If you dissolved ***one mole*** of the following substances in water, how many moles of solvated ions would be present (include both cations and anions in the number of moles of solvated ions)?

a. NaCl
b. $BaCl_2$

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

Review 7.3: Dissolution and Solvation

List **all** of the noncovalent interactions that can occur *between solute and solvent* for the following solutions:

a. oxygen gas dissolved in water
b. carbon dioxide gas dissolved in water
c. potassium iodide dissolved in water
d. pentane dissolved in octane

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

Figure 7.6 **An Oil Spill**

Since oil does not dissolve in water and is less dense than water, the brown oil can be seen floating (and burning) on the ocean surface. Source: PD

Solubility

Solubility is a term that refers to the *amount of solute that can be dissolved.* Some *liquid-in-liquid* solutions can be made at any ratio of the liquids. For example, water and ethyl alcohol will mix no matter what the ratio is of water to ethyl alcohol. When two liquids mix with each other in any ratio, we say that the substances are "**miscible.**" Some pairs of liquids will not mix with each other at all. For example, oil will not significantly dissolve in water, this is why we see oil floating on the top of water when oil spills occur (Figure 7.6). When two liquids will not mix with each other we say that the substances are "**immiscible.**" For most solute/solvent pairs, there is a limit on how much solute can dissolve in a particular solvent. For example, you can only dissolve so much salt or sugar in water. At some point, the solution becomes **saturated** and the amount of dissolved solute cannot increase. If you continue to add a solid solute to a **saturated solution**, the excess solute will exist as a solid in the container. On the nano-scale, the solid is actually still dissolving in a saturated solution, however there are so many solute molecules or ions in the solution that they are re-crystalizing on the solid's surface at the same rate at which the solid is dissolving. This is analogous to water molecules evaporating and re-condensing at the same rate in a capped water bottle.

The Solubility of *Gases* in Water

The solubility of a ***dissolved gas*** depends on <u>both</u> *temperature* and *pressure*. Whenever a gas is present above a liquid, some of the gas will dissolve in the liquid. The higher the partial pressure of a particular gas above a liquid, the more of that gas will dissolve in the liquid. William Henry (Figure 7.7) was first to report that the amount of gas dissolved in a liquid is directly proportional to the *partial pressure* of the gas. This relationship between the amount of gas dissolved and pressure is known as "Henry's Law." The physical explanation for this is simply that when there are more gas molecules above the liquid, more of the molecules collide with the surface of the liquid and therefore more enter the liquid phase. I like to brew my own beer. I need to be careful not to have the CO_2 pressure to my 5 gallon keg too high or else the beer will become over-carbonated. This leads to a bad "mouth-feel" of the beer. Perhaps some readers are more familiar with carbonated soda. When a carbonated beverage is opened, the CO_2 gas above the liquid that was at high pressure in the sealed bottle or can is released. When this happens, the partial pressure of CO_2 in the opened container is now much less, and the CO_2 gas slowly comes out of the solution. You observe this as small bubbles being formed. When you see bubbles, this means that the individual molecules that were solvated, have come out of the liquid-phase solution. After enough time passes, almost all of the dissolved CO_2 escapes into the air and we say the the drink has gone "flat." Scuba divers must be very careful not to go from deep water (high pressure) to shallow water (low pressure) too quickly because the dissolved gases in their blood (N_2, O_2, and CO_2) will come out of solution (as bubbles). This can be fatal and is referred to as decompression sickness or the "bends." Infants that are born with insufficient lung capacity are often placed in environments with high oxygen partial pressure in order to increase their blood oxygenation. This is very typical in cases of premature births. Several medical conditions require measuring and monitoring the amount of oxygen and/or carbon dioxide dissolved in blood.

Figure 7.7
William Henry
(1774 – 1836)

An engraving of William Henry by Henry Cousins. Source: PD

The solubility of gases in water also depends on *temperature*. The **lower** the temperature of the aqueous solutions, the greater the solubility of gases. For example, cold water can dissolve more oxygen than warm water. The physical reason for this temperature dependence of gas solubility is related to the temperature dependence of vapor pressure, which I discussed in chapter 5. At higher temperatures, the dissolved gas molecules have more kinetic energy and are more able to overcome solute-solvent attraction in order to escape from the surface of the liquid-phase.

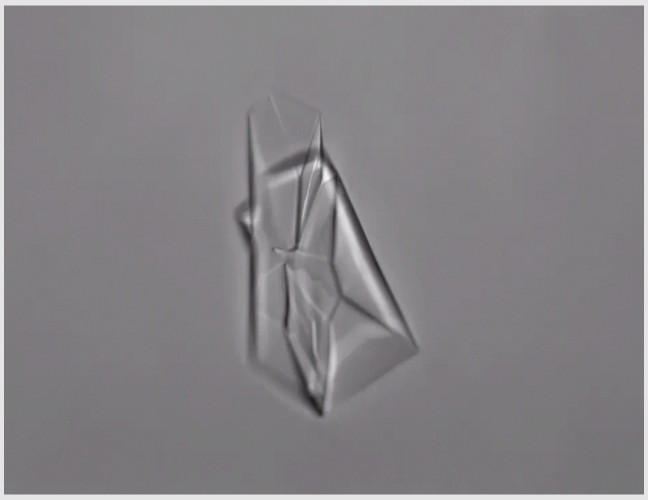
The Solubility of *Solids* in Water

The solubility of a ***solid solute*** depends on *temperature*. As the temperature of water increases to its normal boiling point (100ºC), the solubility of most *solid solutes* increases. Notice that this is the opposite of the behavior of *gaseous solutes*. You may have taken advantage of this physical property of a solute if you have ever done a "crystal growing" activity. If so, you heated water and then dissolved a solid in the hot water to the point of saturation; no more solid could dissolve. Since the water was hot, the solubility of the solid was quite high. You probably placed a suspended object, such as a stick or string, into the liquid and then allowed the liquid to cool to room temperature. As the solution cooled, the solubility of the solid decreased. At this point, you had a **supersaturated solution**, therefore the dissolved particles ***had to*** recrystallize. A ***supersaturated solution*** is an unstable (high energy) solution that will reach a stable (saturated) state by the *recrystallization* of the solute. This can happen quickly or over a period of days, depending on the identity of the solid. The suspended string or stick provides a surface where the recrystallization can more readily occur. "Rock candy" is made in this way by the recrystallization of table sugar. Figure 7.8 shows some rock candy crystals that were recrystallized onto suspended wooden sticks. A bit of food coloring was added to each of the solutions to produce various colors. A time lapse video of citric acid crystal growth from a supersaturated solution is shown in Movie 7.1. For **print or pdf versions** of the book, the video can be seen at: http://www.zovallearning.com/streamvid/recrystallization-of-citric.html.

Figure 7.8 Rock Candy

"Rock candy" made by the recrystallization of table sugar on to suspended wooden sticks. Food coloring was added to the solutions to produce various colors.
Source: Wikimedia Commons, Author: Evan Amos, CC-BY-SA, http://creativecommons.org/licenses/by-sa/3.0/legalcode

Movie 7.1
Re-Crystallization of Citric Acid from Saturated Solution



Recrystallization of citric acid crystals from a supersaturated solution.
Source: Wikimedia Commons, Author: Zephyris CC-BY-SA, http://creativecommons.org/licenses/by-sa/3.0/legalcode

Sometimes certain compounds in urine will reach supersaturation levels and crystallize. For example, urinary stones (renal calculus) can form in the kidney (kidney stones or nephrolithiasis), ureter (ureterolithiasis), or bladder (cystolithiasis) from the crystallization of calcium-containing compounds, uric acid, or struvite. Kidney stones are typically about 3-5 mm in diameter, however they can grow to larger sizes such as the 8 mm kidney stone shown in Figure 7.9.

Figure 7.9 A Kidney Stone

An 8 mm kidney stone. A cm ruler (1 mm increments) is shown in the background.
Source: Wikimedia Commons, Author: Robert R Wal, PD

The Solubility of Ionic Compounds in Water

Some ionic compounds dissolve to a significant extent in water; some do not. It is difficult to use theoretical methods to predict the extent to which an ionic compound will dissolve. It is therefore convenient to use "**solubility rules"** in order to know which ionic compounds will significantly dissolve in water. I use the term "*significantly*" because all ionic solids will produce at least a trace of dissolved ions when placed in water. In many cases, the amount of dissolved ions is so small that, for most purposes, it is negligible. Such ionic compounds that do not significantly dissolve are categorized as "*water insoluble*" in solubility rules tables. Insoluble compounds exist in their crystal/solid form when placed in water. Ionic compounds that dissolve to a significant extent, such as the $NaCl$ that I used as an example, are classified as "*water soluble.*" A solubility rules table is shown below (Table 7.1). In this table, ionic compounds are first classified as ***water soluble*** or ***water insoluble*** based on their ***anions***, and then exceptions are listed.

Table 7.1 Solubility Rules Table

Water Soluble			
Compound	**Example**	**Exceptions**	**Exception Example**
Nitrates	$NaNO_3$	None	None
Chlorides, Bromides, and Iodides	$NaCl$	Compounds containing Ag^+, Pb^{2+}, or Hg^+, and HgI_2	$AgCl$
Sulfates	K_2SO_4	Compounds containing Pb^{2+}, Sr^{2+}, Ba^{2+}, or Hg^+	$PbSO_4$
Water Insoluble			
Compound	**Example**	**Exceptions**	**Exception Example(s)**
Hydroxides	$Mg(OH)_2$	Compounds containing alkali (Group I) metals *or* Ca^{2+}, Sr^{2+}, Ba^{2+}, NH_4^+	$NaOH$
Phosphates, Carbonates, and Chromates	$FePO_4$	Compounds containing alkali (Group I) metals *or* NH_4^+	K_2CO_3, Li_3PO_4, Na_2CrO_4

Let's do a couple of example problems to help you learn how to use this table in order to determine if a particular ionic compound is *water soluble* *or* *water insoluble*.

Example: Is KNO_3 water soluble?

Solution:

STEP 1: Find the solubility classification in Table 7.1 based on ***the identity of the anion***.

- We see that ***nitrates*** are in the **water soluble class.**

STEP 2: Check to see if the compound's ***cation*** causes the compound to be an **exception** for the solubility class.

- There are *no exceptions* for ***nitrates***. This means that ***all nitrates are water soluble***, therefore KNO_3 is ***water soluble***.

Example: Is $Cu(OH)_2$ water soluble?

Solution:

STEP 1: Find the solubility classification in Table 7.1 based on ***the identity of the anion***.

- We see that ***hydroxides*** are in the **water insoluble class.**

STEP 2: Check to see if the ***cation*** causes the compound to be an **exception** for the solubility class.

- There are exceptions for hydroxides, however Cu^{2+} ***is not* one of them.** Therefore $Cu(OH)_2$ is **not** ***water soluble***. If $Cu(OH)_2$ were mixed with water, it would exist as solid crystals submerged in water.

Example: Is $BaSO_4$ water soluble?

Solution:

STEP 1: Find the solubility classification in Table 7.1 based on ***the identity of the anion***.

- We see that ***sulfates*** are in the **water soluble class**.

STEP 2: Check to see if the ***cation*** causes the compound to be an **exception** for the solubility class.

- There are some exceptions for sulfates and Ba^{2+} ***is one of them***. Therefore $BaSO_4$ is **not** ***water soluble***.

Example: Is KOH water soluble?

Solution:

STEP 1: Find the solubility classification in Table 7.1 based on ***the identity of the anion***.

- We see that ***hydroxides*** are in the **water insoluble class**.

STEP 2: Check to see if the ***cation*** causes the compound to be an **exception** for the solubility class.

- There are exceptions for hydroxides, and K^+ ***is one of them***; it is an alkali (Group I) metal. Therefore KOH is ***water soluble***.

Now you try some water solubility determination problems:

Review 7.4: Solubility of Ionic Compounds

Use Table 7.1 to determine which of the following compounds are water soluble.

a. potassium iodide
b. iron(II) nitrate
c. copper(II) hydroxide
d. silver bromide
e. sodium sulfate
f. potassium hydroxide
g. lead(II) chromate
h. ammonium hydroxide

For i-books versions: **Click here to check answer** For print or pdf versions, see the answer key in Appendix 1.

Electrolytes

Only solutions that contain dissolved ***ions*** are capable of conducting electricity. Solutions that are capable of conducting electricity are sometimes referred to as **electrolyte solutions**. Water soluble ionic compounds can produce dissolved ions and are called **electrolytes**. *Electrolyte solutions* are required in biological functions such as the transmission of nerve impulse signals and muscle actuation. Our bodies obtain electrolytes from food and drink. In physiology, the electrolyte ions of major importance are: sodium (Na^+), potassium (K^+), calcium (Ca^{2+}), magnesium (Mg^{2+}), chloride (Cl^-), hydrogen phosphate (HPO_4^{2-}), and hydrogen carbonate (HCO^{3-}, also known as bicarbonate).

Review 7.5: Electrolytes

Which of the compounds from the ***previous review question*** (**7.4**) are electrolytes?

For i-books versions: **Click here to check answer** For print or pdf versions, see the answer key in Appendix 1.

Review of Solubility Trends

Solids Solutes Dissolved in Water

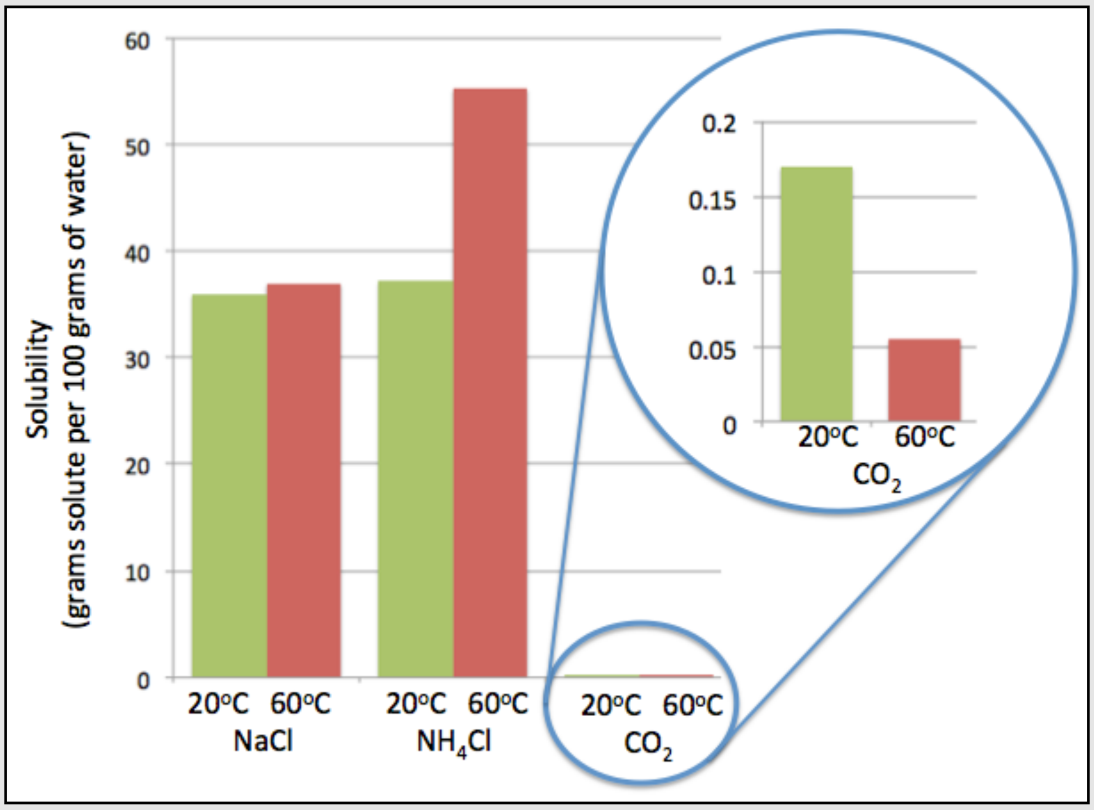
- The solubilities of most ***solids*** in water increase as the temperature increases.
- It is difficult to predict, from theory, whether ionic compounds will significantly dissolve, so we use "*solubility rules.*"

Gaseous Solutes Dissolved in Water

- The solubilities of ***gases*** in water decrease as the temperature increases.
- The solubility of a gas increases as the *partial pressure* of that gas above the solution increases.

Figure 7.10 shows the solubility of two solid solutes (sodium chloride and ammonium chloride) and a gaseous solute (carbon dioxide) in water at 20°C and 60°C. The solubility values used in this table are the maximum number of grams of solute that can be dissolved in 100 grams of water. Note that the solubilities of the solids ($NaCl$ and NH_4Cl) increase as the temperature increases, however, the solubility of the gaseous solute (CO_2) decreases as the temperature increases.

Figure 7.10 **The Solubility of Sodium Chloride, Ammonium Chloride, and Carbon Dioxide at 20°C and 60°C**



The solubility values are the maximum number of grams of solid that can be dissolved in 100 grams of water.

Review 7.6

Solubility of Solids vs. Gases

Which of the following substances would you expect to show an increase in solubility as the temperature of water increased from room temperature to its boiling point?

a. O_2
b. $NaNO_3$
c. H_2
d. table sugar (sucrose)
e. N_2
f. $CuCl_2$

For ***i-books*** versions:

Click here to check answer

For **print or pdf versions**, see the answer key in Appendix 1.

Review 7.7: Solubility of Solids Dissolved in Water

Use Figure 7.10 to answer the following questions:

a. Would a mixture of 30.0 grams of $NaCl$ and 100.0 grams of water at 20°C be homogeneous or heterogeneous?
b. If you mixed 50.0 grams of NH_4Cl with 100.0 grams of water at 20°C, would it completely dissolve?
c. If you mixed 50.0 grams of NH_4Cl with 100.0 grams of water at 60°C, would it completely dissolve?
d. If you mixed 60.0 grams of $NaCl$ with 100.0 grams of water at 20°C, would the mixture be homogenous or heterogenous?
e. If you mixed 60.0 grams of $NaCl$ with 100.0 grams of water at 20°C, approximately how many grams would be dissolved?
f. If you mixed 60.0 grams of $NaCl$ with 100.0 grams of water at 20°C, approximately how many grams of solid $NaCl$ would be present?

For i-books versions: **Click here to check answer** For print or pdf versions, see the answer key in Appendix 1.

7.4 Reactions of Ions in Solution

In chapter 6, you learned about **double replacement reactions**. In a **double replacement reaction**, two substances "***switch partners.***" The general form of a double replacement reaction, where **AX** and **BY** *switch partners*, is:

$$AX + BY \rightarrow AY + BX$$

There are two types of double replacement reactions:

1) Precipitation Reactions

2) Gas Producing Double Replacement Reactions

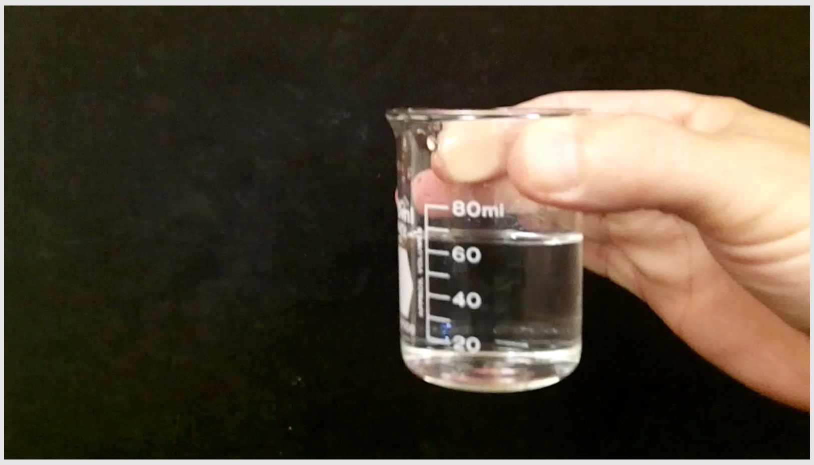
The ***educational goals*** for this section are:

- Recognize precipitation reactions and gas producing double replacement reactions.
- Given the reactants of a precipitation reaction, determine the identity of the products and write a balanced chemical equation for the reaction.

1) Precipitation Reactions

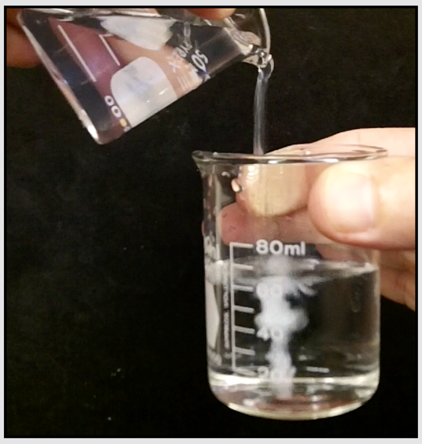
Precipitation reactions may occur when ***two*** solutions that contain dissolved ions are mixed. A ***solid*** is *always* formed in a precipitation reaction. Often, many *tiny* crystals are formed and this gives the mixture a cloudy appearance. The cloudy appearance may be white, black, or some other color, depending on the identity of the particular solid that is formed. We say the solid "***precipitated***" from the solution. An example of a double replacement reaction is the reaction of sodium chloride and silver nitrate. When a clear and colorless sodium chloride solution is poured into a clear and colorless silver nitrate solution, tiny white silver chloride crystals are formed as seen in Figure 7.11 and Movie 7.2. For **print or pdf versions** of the book, the video can be seen at: http://www.zovallearning.com/streamvid/precipitation-reaction1.html. The small, white crystals give the mixture a cloudy, white appearance.

Movie 7.2 Precipitation of Silver Chloride



Video of the reaction that occurs when a sodium chloride solution is poured into a silver nitrate solution. For **print or pdf versions** of the book, the video can be seen at: http://www.zovallearning.com/streamvid/precipitation-reaction1.html

Figure 7.11
Precipitation of Silver Chloride



When a sodium chloride solution is poured into a silver nitrate solution, tiny, white silver chloride crystals are formed. These crystals give the cloudy, white appearance seen in this figure.

The balanced chemical equation for this precipitation reactions is:

$$NaCl\,(aq) + AgNO_3\,(aq) \rightarrow NaNO_3\,(aq) + AgCl\,(s)$$

Before the reaction occurs, one glass beaker contains aqueous $NaCl$ (water, solvated sodium ions, and solvated chloride ions); a second glass beaker contains aqueous $AgNO_3$ (water, solvated silver ions, and solvated nitrate ions). If $NaNO_3$ ***or*** $AgCl$ is not water soluble, it will crystallize (precipitate) when the contents of the two beakers are mixed. The appearance of the solid precipitate indicates the formation of new ionic bonds and that a precipitation chemical reaction has occurred. Whenever two aqueous solutions of ions are mixed, if a cation from one of the original solutions and an anion from the other original solution forms a ***water insoluble ionic compound***, then a precipitation reaction will occur and a precipitate (solid) will form. We can use the Solubility Rules Table (Table 7.1) to predict whether a precipitation reaction will occur for any given pair of aqueous ionic reactants. I will show you a method to do this and a couple of examples.

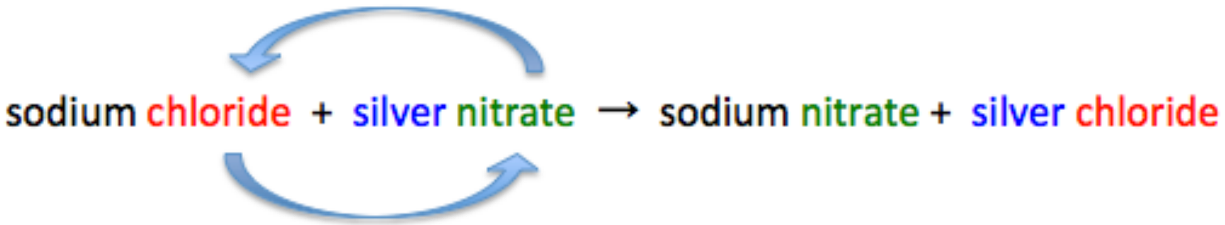
Method for Predicting if a Precipitation Reaction will Occur and Writing the Balanced Chemical Equation for Precipitation Reactions.

I will show you what I think is the easiest method for writing a balanced chemical equation for a precipitation reaction if you are given a pair of reactants. For the first example, we will use the reaction of sodium chloride and silver nitrate (shown in Figure 7.11 and Movie 7.2)

Step 1: Write ***reactants' names*** and arrow for the chemical equation using ***word form*** (not the chemical formula).

sodium chloride + silver nitrate →

Step 2: Add the "*possible*" **products** to the word equation by switching ***anions***.



sodium chloride + silver nitrate → sodium nitrate + silver chloride

Step 3: Convert the ***word*** equation to a ***formula*** equation.

- Write the formulas instead of the compound names. You learned how to do this in chapter 3.

$$\mathrm{NaCl} + \mathrm{AgNO_3} \rightarrow \mathrm{NaNO_3} + \mathrm{AgCl}$$

Step 4: ***Balance*** the equation:

- You learned how to do this in chapter 6.
- In this example, the equation is already balanced; each of the coefficients is "1."

$$\mathrm{NaCl} + \mathrm{AgNO_3} \rightarrow \mathrm{NaNO_3} + \mathrm{AgCl}$$

Step 5: Add the ***phase*** of each of the reactants and "possible" products to the chemical equation.

- In *all precipitation reactions*, ***the reactants are always aqueous***.
- Use the Solubility Rules Table (Table 7.1) to determine the phase of each "possible" product.
  - If a compound is ***water soluble***, it remains dissolved and we write "(aq)."
  - If a compound is ***water insoluble***, it precipitates as a solid and we write "(s)."

$$\mathrm{NaCl}\,(aq) + \mathrm{AgNO_3}\,(aq) \rightarrow \mathrm{NaNO_3}\,(aq) + \mathrm{AgCl}\,(s)$$

In this example, the silver chloride precipitated. New chemical bonds were made and a precipitation chemical reaction occurred.

Example: Determine if a precipitation reaction would occur when a lead(II) nitrate solution is mixed with a potassium chromate solution and, if a reaction does occur, write the balanced chemical equation.

Step 1: Write ***reactants' names*** and arrow for the chemical equation using ***word form*** (not formulas):

lead(II) nitrate + potassium chromate →

Step 2: Add the "*possible*" **products** to the word equation by switching ***anions***:

lead(II) nitrate + potassium chromate → lead(II) chromate + potassium nitrate

Step 3: Convert the ***word*** equation to a ***formula*** equation:

- You learned how to do this in chapter 3.

$$\mathbf{Pb(NO_3)_2 + K_2CrO_4 \rightarrow PbCrO_4 + KNO_3}$$

Step 4: ***Balance*** the equation:

$$\mathbf{Pb(NO_3)_2 + K_2CrO_4 \rightarrow PbCrO_4 + 2\ KNO_3}$$

Step 5: Add the ***phase*** of each of the reactants and "possible" products to the chemical equation.

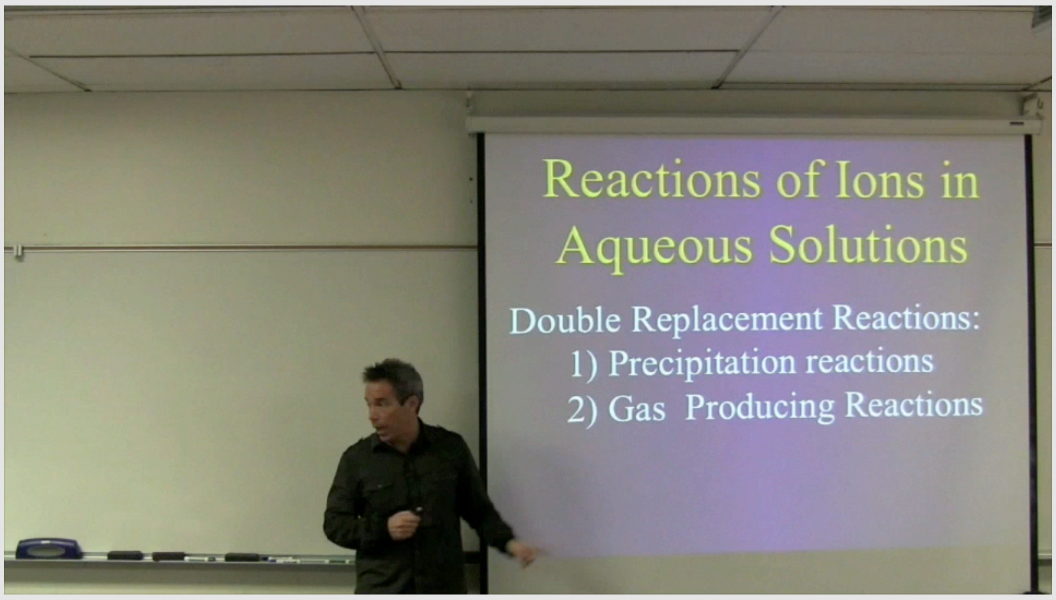
- In all *precipitation reactions*, ***the reactants are always aqueous***.
- Use the Solubility Rules Table (Table 7.1) to determine the phase of the "possible" products.
  - If a compound is water ***soluble***, it remains dissolved and we write "(aq)."
  - If a compound is water ***insoluble***, it precipitates as a solid and we write "(s)."

$$\mathbf{Pb(NO_3)_2}\,(aq) + \mathbf{K_2CrO_4}\,(aq) \rightarrow \mathbf{PbCrO_4}\,(s) + \mathbf{2\ KNO_3}\,(aq)$$

In this example problem, we predicted that a precipitation reaction would occur and that solid lead(II) chromate ($PbCrO_4$) would be formed. Lead(II) chromate is a yellow solid and can be seen forming in Movie 7.3 as this reaction occurs. The small, yellow crystals give the mixture a cloudy, yellow appearance.

For **print or pdf versions** of the book, the video can be seen at: http://www.zovallearning.com/streamvid/precipitation-reaction2.html.

Movie 7.3 Precipitation of Lead(II) Chromate



Reactions of Ions in Aqueous Solutions

Double Replacement Reactions:
1) Precipitation reactions
2) Gas Producing Reactions

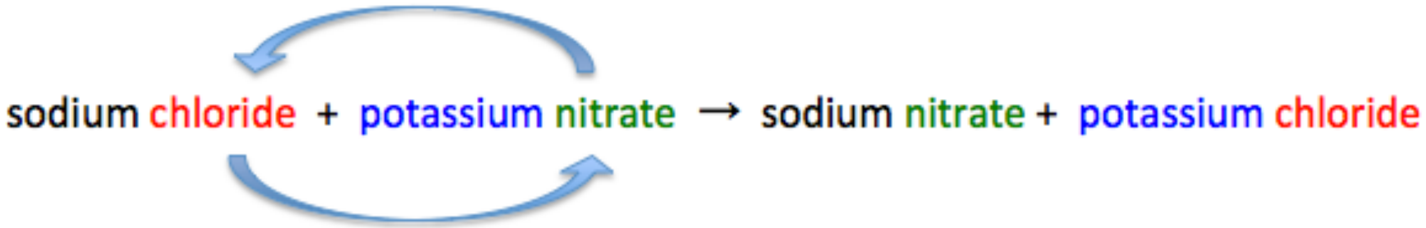
Video of the reaction that occurs when a potassium chromate solution is poured into a lead(II) nitrate solution. For print or pdf versions of the book, the video can be seen at: http://www.zovallearning.com/streamvid/precipitation-reaction2.html

Example: Determine if a precipitation reaction would occur when a sodium chloride solution is mixed with a potassium nitrate solution and, if a reaction does occur, write the balanced chemical equation.

Step 1: Write ***reactants' names*** and arrow for the chemical equation using ***word form*** (not formula):

sodium chloride + potassium nitrate →

Step 2: Add the "*possible*" **products** to the word equation by switching ***anions***:



Step 3: Convert the ***word*** equation to a ***formula*** equation:

$$NaCl + KNO_3 \rightarrow NaNO_3 + KCl$$

Step 4: ***Balance*** the equation:

- In this example, the equation is already balanced; each of the coefficients is "1".

$$NaCl + KNO_3 \rightarrow NaNO_3 + KCl$$

Step 5: Add the ***phase*** of each of the reactants and "possible" products to the chemical equation.

- In all *precipitation reactions*, ***the reactants are always aqueous***.
- Use the Solubility Rules Table (Table 7.1) to determine the phase of the "possible" products.

$$NaCl\,(aq) + KNO_3\,(aq) \rightarrow NaNO_3\,(aq) + KCl\,(aq)$$

IMPORTANT: If **both** of the "possible" products ***are water soluble***, then **no reaction occurred**. There were solvated cations and anions in each the two solutions before mixing, then the solutions were mixed and the cations and anions remained solvated in the mixture. No new chemical bonds were made, therefore no chemical reaction occurred. It is for this reason that I say "possible" products in the wording of this method. When no reaction occurs in precipitation reaction problems such as this example, you can write "No Reaction" instead of the "possible" products:

$$NaCl\,(aq) + KNO_3\,(aq) \rightarrow \textbf{No Reaction}$$

Now you try a couple of problems:

Review 7.8: Predicting the Products of Precipitation Reactions

Determine if a precipitation reaction would occur when a silver nitrate solution is mixed with a barium chloride solution ***and***, if a reaction does occur, write the balanced chemical equation.

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

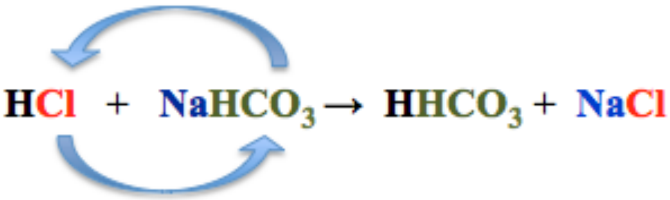
Review 7.9: Predicting the Products of Precipitation Reactions

Determine if a precipitation reaction would occur when a iron (III) bromide solution is mixed with a potassium phosphate solution ***and***, if a reaction does occur, write the balanced chemical equation.

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

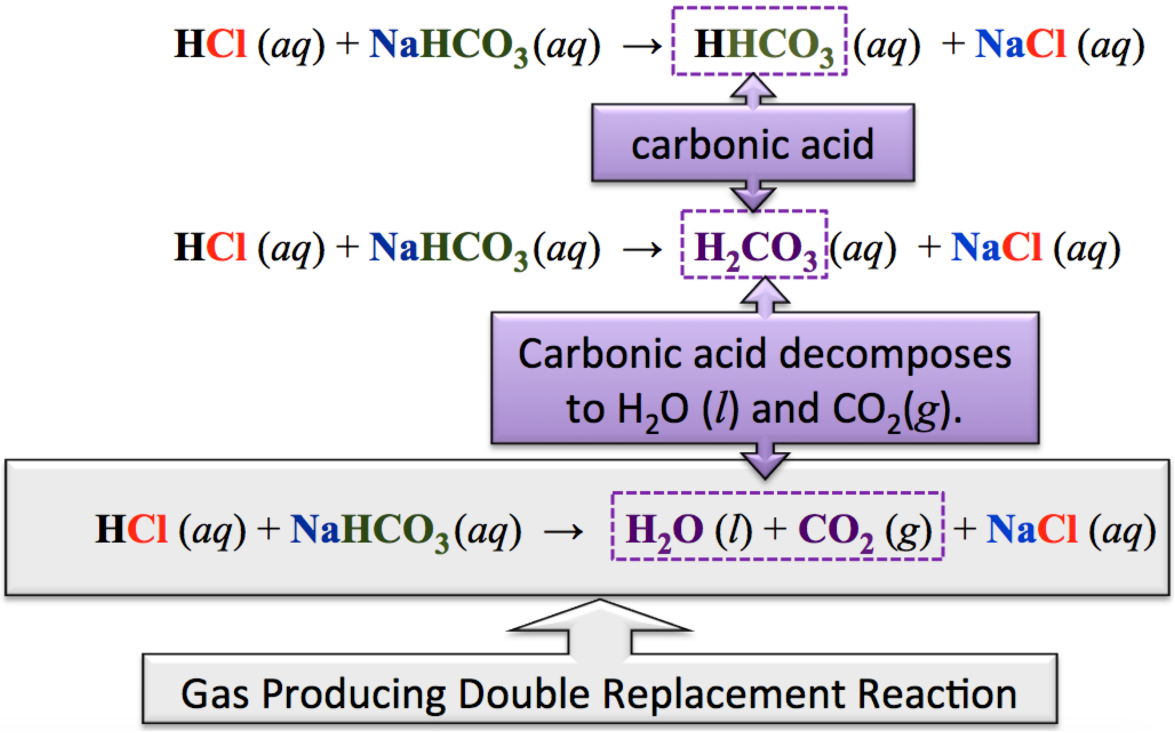
2) **Gas Producing Double Replacement Reactions**

A **gas producing double replacement reaction** is a special type of double replacement in which a gas is produced. The gas producing double replacement reaction that is typically encountered in the health sciences field and, therefore the only gas producing reaction with which I would like you to be familiar, is the reaction of aqueous hydrogen monochloride (**HCl**, also know as hydrochloric acid) and aqueous sodium bicarbonate (**$NaHCO_3$**).



$$\mathbf{HCl + NaHCO_3 \rightarrow HHCO_3 + NaCl}$$

In this reaction, the ***bicarbonate*** and **chloride** anions switch partners to form aqueous ***carbonic acid*** (**$HHCO_3$**) and ***sodium chloride***. In the chemical equation ***above***, I wrote the formula of carbonic acid as **$HHCO_3$** in order to help you see how **Cl^-** and **HCO_3^-** "*switched partners*"; however the correct way to write the formula for carbonic acid is **H_2CO_3**, as shown on the right.



$$HCl\ (aq) + NaHCO_3 (aq) \rightarrow \boxed{HHCO_3} (aq) + NaCl\ (aq)$$

carbonic acid

$$HCl\ (aq) + NaHCO_3 (aq) \rightarrow \boxed{H_2CO_3} (aq) + NaCl\ (aq)$$

Carbonic acid decomposes to H_2O (*l*) and CO_2(*g*).

$$HCl\ (aq) + NaHCO_3 (aq) \rightarrow \boxed{H_2O\ (l) + CO_2\ (g)} + NaCl\ (aq)$$

Gas Producing Double Replacement Reaction

Carbonic acid is *unstable* and quickly undergoes a *decomposition reaction* in which it is converted to **CO_2 (*g*)** and **H_2O (*l*)**.

The overall gas producing double replacement reaction equation is written in the grey box on the right.

This particular gas producing reaction is important in medicine because sodium bicarbonate is used as an over-the-counter therapeutic agent to treat acid indigestion (heartburn). Sodium bicarbonate is the primary active ingredient in many antacids, such as alka-seltzer. Sodium bicarbonate "neutralizes" acid in the stomach to produce water, carbon dioxide gas, and salt. You will learn much more about acids in later chapters.

Worksheet and Key: Reactions of Ions in Solution

For more practice problems writing the chemical equations for double replacement reactions see:
www.zovallearning.com/GOBlinks/ch7/reactions-of-ions-in-solutions.pdf

7.5 The Solubility of Organic Molecules

You are probably familiar with "lava lamps" such as the one shown in Figure 7.12. Lava lamps contain two *immiscible* (will not mix) liquids that have approximately the same density. There is a light source in the bottom of the lamp that not only projects light up into the liquids, but also warms the liquid that is on the bottom of the container. As the liquid on the bottom warms, it expands and its *density decreases*. At some point, the liquid on the bottom becomes less dense than the liquid above it and the less dense liquid rises - much like a hot air balloon rises. The liquid that went to the top now cools and the liquid on the bottom warms, causing the process to repeat. The liquids will continue to displace each other whenever the lamp is on.

Figure 7.12
A Lava Lamp

Source: Wikimedia Commons,
Author: Benutzer Wollschaf,
CC-BY-SA,
http://creativecommons.org/licenses/by-sa/3.0/legalcode

Molecules will dissolve in a particular solvent when the **solute-solvent** noncovalent interactions are strong enough to overcome the solute-solute interactions. The ***more*** **solute-solvent** noncovalent attractive interactions that can occur, the more solute that can be dissolved. It is for this reason that ***polar solutes*** are capable of dissolving in ***polar solvents***, and ***nonpolar*** solutes are capable of dissolving in ***nonpolar solvents***, as summarized by the phrase "*like dissolves like.*"

The reason that the two liquids in lava lamps do not mix is because they do not solvate each other. In lava lamps, one liquid, water, is capable of *dipole-dipole interactions* ***and*** *hydrogen bonding interactions*. Although London forces can occur between *any* two molecules, the attraction is not particularly strong for water because water is a small molecule. The other liquid in lava lamps is a mixture of nonpolar molecules. This *nonpolar* liquid is not capable of participating in hydrogen bonding because it does not contain highly-polar O-H, N-H, or F-H bonds or lone pairs on O, N, or F, nor is it capable of dipole-dipole interactions (it is nonpolar); it is only capable of interacting through London forces. Since the water and the nonpolar liquid do not share significant noncovalent interactions, they remain in separate liquid phases (i.e.,they are immiscible). Another solubility related phenomenon occurs in lava lamps. Dye molecules (molecules capable of absorbing light and thereby giving solutions color) are dissolved in the water and the organic liquid. *Two different dye molecules must be used.* ***Only*** polar dye molecule(s) will dissolve in water, and, ***only*** nonpolar dye molecules will dissolve in the nonpolar liquid. This phenomenon also enables a desirable color contrast between the immiscible liquid phases when two differently-colored dyes are used.

We can use the general rule of "like dissolves like" to predict the *relative* water solubilities of various organic solute molecules. For an organic molecule to have significant water solubility, it must be polar and/or capable of hydrogen bonding with water. Let's consider the water solubility of the organic molecule families that I introduced you to in chapter 4: *hydrocarbons*, *alcohols*, *carboxylic acids*, and *esters*.

Water Solubility of Hydrocarbons

Hydrocarbons are *nonpolar* molecules. They are not capable of hydrogen bonding or dipole-dipole interactions, therefore they are not significantly soluble in water.

Water Solubility of Alcohols, Carboxylic Acids, and Esters

Water molecules are attracted to ***alcohols and many other families of organic molecules*** through hydrogen bonding and/or dipole-dipole interactions. The *general form* of an ***alcohol*** molecule is:

As the ***hydrocarbon part*** of various alcohol molecules gets ***larger***, *the water solubility decreases*. This trend of decreasing solubility as the hydrocarbon part of organic molecules gets larger is also seen in carboxylic acids, esters, and all of the other types of organic molecules that you will be introduced to in later chapters. As the hydrocarbon part of a molecule gets larger, London forces become more important (stronger), the molecule becomes less polar, and the organic molecules are *more attracted to each other* than they are to water molecules. When this occurs, it is *lower in energy* for the organic molecules to be surrounded by other organic molecules and therefore the water solubility drastically decreases. Table 7.2 shows the trend in decreasing water solubility for some alcohol molecules as their hydrocarbon part gets larger.

Table 7.2 Water Solubility of Various Alcohols

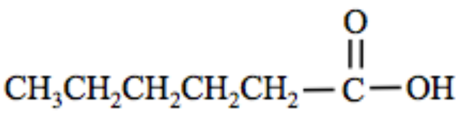
Molecule Name	Condensed Structure	Solubility in Water
methanol	CH_3OH	miscible in any ratio with water
ethanol	CH_3CH_2OH	miscible in any ratio with water
1-propanol	$CH_3CH_2CH_2OH$	miscible in any ratio with water
1-butanol	$CH_3CH_2CH_2CH_2OH$	slightly soluble
1-pentanol	$CH_3CH_2CH_2CH_2CH_2OH$	insoluble

The Solubility of Organic Molecules in *Non Aqueous* Solutions

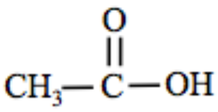
Not all solutions involve water as the solvent. Non water ***polar solvents*** behave quite like water in regard to their ability to dissolve polar solutes better than nonpolar solutes. On the other hand, ***nonpolar solvents*** dissolve nonpolar solutes more readily than polar solutes; ***like dissolves like***. For example, pentane cannot be significantly dissolved in water, however it can be dissolved in hexane.

Review 7.10: Relative Water Solubility of Organic Molecules

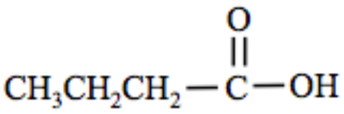
a) List the following carboxylic acids in order of ***increasing solubility in <u>water</u>*** (least soluble to most soluble).


$CH_3CH_2CH_2CH_2CH_2-\overset{\overset{O}{||}}{C}-OH$

hexanoic acid

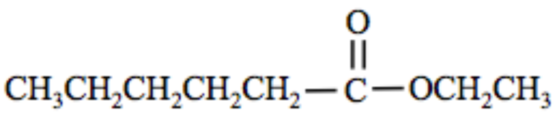

$CH_3-\overset{\overset{O}{||}}{C}-OH$

ethanoic acid

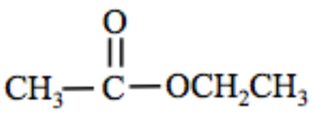

$CH_3CH_2CH_2-\overset{\overset{O}{||}}{C}-OH$

butanoic acid

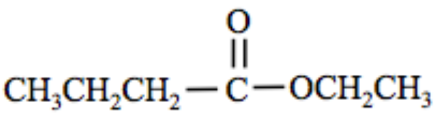
b) List the following esters in order of ***increasing solubility in <u>water</u>***.


$CH_3CH_2CH_2CH_2CH_2-\overset{\overset{O}{||}}{C}-OCH_2CH_3$

ethyl hexanoate


$CH_3-\overset{\overset{O}{||}}{C}-OCH_2CH_3$

ethyl ethanoate


$CH_3CH_2CH_2-\overset{\overset{O}{||}}{C}-OCH_2CH_3$

ethyl butanoate

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

7.6 Concentration of Solutions

The term "**concentration**" refers to the ***amount of a solute in a solution***. Other qualitative (non numeric) descriptions of the amount of solute are sometimes used; a solution with a relatively large amount of solute is said to be "***concentrated***," and a solution with a relatively small amount of solute is said to be "***dilute.***" In this section you will see how to ***quantitatively*** (with numeric values) describe the amount of solute that is present in a solution. The ***concentration*** of a solution is the *numeric quantity* of solute that is dissolved in a particular quantity of solution (or solvent). There are several *units of measure* that are commonly used to report concentration. For example, we could use the number of moles of solute per liter of solution, or we could use the number of grams of solute per liter of solution. In this section, I will introduce you to the most commonly used concentration units and, for each type of concentration unit, I will show you how to calculate the concentration of solutions when you are given the amount of solute and the amount of solution (or solvent).

Various Units Used for Concentration

1) Percent (%) Concentration

Percent means "*parts per hundred*" and is calculated from the ratio of the part to the whole, times 100.

$$\% = \left(\frac{\text{Part}}{\text{Whole}}\right) \times 100$$

There are 3 different percent (%) concentration units that are commonly used:

- **percent weight to weight: % (w/w)**
- **percent volume to volume: % (v/v)**
- **percent weight to volume: % (w/v)**

Percent *weight to weight* - % (w/w) - is defined as the ratio of the mass of the ***solute*** to the mass of the ***entire solution***, multiplied by 100:

$$\%\ (\text{w/w}) = \left(\frac{\text{mass of } \textit{solute}}{\text{mass of } \textit{solution}}\right) \times 100$$

Example: A 10% (w/w) sodium chloride solution contains 10 grams of dissolved sodium chloride in every 100 grams of solution.

Percent weight to weight is sometimes referred to as "*mass percent*" or "*gram percent*."

Percent *volume to volume* - % (v/v) - is often used for liquid-in-liquid solutions. It is defined as the ratio of the volume of the ***solute*** to the volume of the ***entire solution***, multiplied by 100:

$$\%\ (\text{v/v}) = \left(\frac{\text{volume of } \textit{solute}}{\text{volume of } \textit{solution}}\right) \times 100$$

Percent volume to volume is commonly used to indicate the concentration of alcohol in adult beverages. Most beers are between 4 and 11% (v/v), wines range from about 9 to 16% (v/v), and most distilled alcoholic beverages range from about 30 to 80% (v/v). Sometimes the % (v/v) alcohol concentration in adult beverages is referred to as "*alcohol by volume* (ABV)" or "*alcohol percent by volume*." The concentration of alcohol in the beer shown in Figure 7.13 is given in "*alcohol percent by volume*."

Figure 7.13

Percent Volume to Volume Concentration of Alcohol in Beer

The concentration of alcohol in the beer shown in this figure (Sierra Nevada Brewing Company's Torpedo IPA) is given in *alcohol percent by volume*. In 7.2% (v/v) beer, there are 7.2 mL of alcohol for every 100 mL of beer.

Percent *weight to volume* - % (w/v) - is defined as the number of grams of ***solute*** contained in 100 mL of ***solution.*** % (w/v) is calculated by multiplying the ratio of the grams of the ***solute*** to the volume (mL) of the ***entire solution***, by 100.

$$\%\ (\text{w/v}) = \left(\frac{\text{grams of } solute}{\text{mL of } solution}\right) \times 100$$

Before discussing the other types of concentration units, I will show you examples of how to calculate percent concentrations and then ask you to try a few problems on your own.

Percent Weight to Weight Example: What is the % (w/w) concentration of a sodium chloride solution prepared by adding 5.0 grams of sodium chloride to 130.0 g of water?

Solution: Calculate the concentration using the equation/definition of % (w/w):

$$\%\ (\text{w/w}) = \left(\frac{\text{mass of } solute}{\text{mass of } solution}\right) \times 100$$

To calculate the % (w/w), we need to know two quantities: the mass of the ***solute*** **<u>AND</u>** the mass of the ***solution.***

- The mass of the ***solute*** (sodium chloride in this example) was given: **5.0 g**
- The mass of the ***solution:***
  - ***BE CAREFUL HERE: WE USE THE MASS OF THE SOLUTION <u>NOT</u> THE MASS OF THE SOLVENT. The solution is a mixture composed of water <u>and</u> sodium chloride!***
  - The mass of the solution is equal to the mass of the ***solute*** ($NaCl$, 5.0 g) ***plus*** the mass of the ***solvent*** (water, 130.0 g):

5.0 g + 130.0 g = **135.0 g**

Insert the mass of the solute and the mass of the solution into the equation for % (w/w):

$$\%\ (\text{w/w}) = \left(\frac{5.0\ \text{g}}{135.0\ \text{g}}\right) \times 100 = 3.7\ \%\ (\text{w/w})$$

The solution's concentration is **3.7 % (w/w)**. In a 3.7 % (w/w) solution, there are 3.7 g of solute contained in every 100 g of solution.

Note that in this % (w/w) problem, the mass units cancel, therefore we can use any mass units as long as we use the same unit for the mass of solute **<u>and</u>** mass of solution. For example, you can use **kg** for the mass of the solute so long as you use **kg** for the mass of the solution.

Percent Volume to Volume Example: What is the % (v/v) concentration of a solution prepared by adding 27 mL of alcohol to enough water to make 552 mL of solution?

Solution: Calculate the concentration using the equation/definition of % (v/v):

$$\%\ (\text{v/v}) = \left(\frac{\text{volume of } solute}{\text{volume of } solution}\right) \times 100$$

To calculate the %(v/v), we need to know two quantities: the volume of the ***solute*** **<u>AND</u>** the volume of the ***solution.***

- Volume of the ***solute*** (alcohol in this example) was given: **27 mL**
- Volume of the ***solution*** is was given: **552 mL**

Insert the volume of the solute and the volume of the solution into the equation for % (v/v):

$$\%\ (\text{v/v}) = \left(\frac{27\ \text{mL}}{552\ \text{mL}}\right) \times 100 = 4.9\ \%\ (\text{v/v})$$

The solution's concentration is **4.9 % (v/v).** In a 4.9 % (v/v) solution, there are 4.9 mL of solute contained in every 100 mL of solution.

As in the previous % (w/w) example, in this % (v/v) problem, the volume units cancel, therefore we can use any volume units as long as we use the same unit for the volume of solute **and** the volume of solution.

Percent Weight to Volume Example: What is the % (w/v) concentration of a solution prepared by adding 12.0 g of table sugar to enough water to make 125.0 mL of solution?

Solution: Calculate the concentration using the equation/definition of % (w/v):

$$\% \text{ (w/v)} = \left(\frac{\text{grams of } solute}{\text{mL of } solution}\right) \times 100$$

To calculate the % (w/v), we need to know two quantities: the mass **(g)** of the ***solute*** **AND** the volume **(mL)** of the ***solution.***

- mass of the ***solute*** (table sugar in this example) was given: **12.0 g**
- mL of ***solution*** was given: **125.0 mL**

Insert the mass (g) of the solute and mL of the solution into the equation for % (w/v):

$$\% \text{ (w/v)} = \left(\frac{12.0 \text{ g}}{125 \text{ mL}}\right) \times 100 = 9.6 \ \% \text{ (w/v)}$$

The solution's concentration is **9.6 % (w/v)**. In a 9.6 % (w/v) solution, there are 9.6 g of solute contained in every 100 mL of solution.

NOTE: Percent **weight to volume (% w/v)** is sometimes referred to as percent **mass to volume (% m/v)**

Now you try some percent concentration problems:

Review 7.11: Calculating Percent Weight to Weight Concentration

What is the **% (w/w)** concentration of a magnesium chloride solution prepared by adding 1.3 g of magnesium chloride to 43.0 g of water?

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

Review 7.12: Calculating Percent Volume to Volume Concentration

What is the **% (v/v)** concentration of a solution prepared by adding 145 mL of acetone to enough water to make 1914 mL of solution?

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

Review 7.13: Calculating Percent Weight to Volume Concentration

What is the **% (w/v)** concentration of a solution prepared by adding 3.2 g of sodium hydroxide to enough water to make 735 mL of solution?

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

2) Concentration in Parts per Thousand, Parts per Million, Parts per Billion, Parts per Trillion

You learned that percent means *parts per hundred.* Parts per thousand, parts per million (ppm), parts per billion (ppb), and parts per trillion (ppt) are defined in a similar way as percent concentration however, instead of multiplying the ratios of solute to solution by 100, they are multiplied by a thousand, million, billion, or trillion, respectively. Just like percent concentration (parts per hundred), parts per thousand, ppm, ppb, and ppt units can be (w/w), (v/v), or (w/v). For example, the definitions or percent, parts per thousand, ppm, ppb, and ppt, ***in (w/w)***, are:

$$\%\ (\text{w/w}) = \left(\frac{\text{mass of } \textit{solute}}{\text{mass of } \textit{solution}}\right) \times 100$$

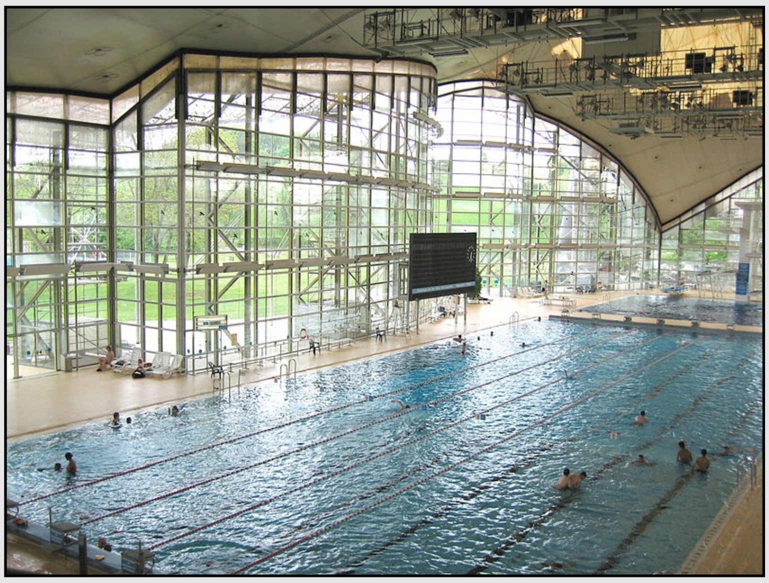
$$\text{parts per thousand (w/w)} = \left(\frac{\text{mass of } \textit{solute}}{\text{mass of } \textit{solution}}\right) \times 1000$$

$$\text{ppm (w/w)} = \left(\frac{\text{mass of } \textit{solute}}{\text{mass of } \textit{solution}}\right) \times \left(1 \times 10^{6}\right)$$

$$\text{ppb (w/w)} = \left(\frac{\text{mass of } \textit{solute}}{\text{mass of } \textit{solution}}\right) \times \left(1 \times 10^{9}\right)$$

$$\text{ppt (w/w)} = \left(\frac{\text{mass of } \textit{solute}}{\text{mass of } \textit{solution}}\right) \times \left(1 \times 10^{12}\right)$$

Figure 7.14 An Olympic Size Pool



One drop of alcohol dissolved in this Olympic-size pool would result in an alcohol concentration of about 20 parts per trillion (ppt).
Source: Wikimedia Commons, Author: Jeff Wilcox, CC-BY
http://creativecommons.org/licenses/by/2.0/legalcode

The ppm, ppb, and ppt units are often used for very dilute solutions. If you were to mix one drop of alcohol into an Olympic size pool such as the one shown in Figure 7.14, the alcohol concentration would be about 20 part per trillion (v/v). Let's take a look at the calculation in the example problem that follows.

Parts per Trillion (ppt) Volume to Volume Example: The volume of an Olympic-size swimming pool is about 2.5×10^9 mL. The volume of one drop of ethyl alcohol is about 0.050 mL. What is the ppt (v/v) concentration of alcohol if 0.050 mL (~1 drop) is mixed into a pool with a volume of 2.5×10^9 mL?

Solution: Calculate the concentration using the equation/definition of ppt (v/v):

$$\text{ppt (v/v)} = \left(\frac{\text{volume of } \textit{solute}}{\text{volume of } \textit{solution}}\right) \times \left(1 \times 10^{12}\right)$$

To calculate the ppt (v/v), we need to know two quantities: the volume of the ***solute*** AND the volume of the ***solution.***

- Volume of the ***solute*** (alcohol in this example) was given: **0.050 mL**
- Volume of the ***solution:***
  - The volume of the solution is equal to the volume of the ***solute*** (alcohol, 0.050 mL) ***plus*** the volume of the ***solvent*** (water, 2.5×10^9 mL). *In this problem*, the volume of the solute is *negligible* compared to the volume of water. This is shown to be true in the application of our significant figures rule for addition/subtraction:

$$0.050 \text{ mL} + 2.5 \times 10^9 \text{ mL} = \mathbf{2.5 \times 10^9 \text{ mL}}$$

Insert the volume of the solute and the volume of the solution into the equation for ppt (v/v):

$$\text{ppt (v/v)} = \left(\frac{0.050 \text{ mL}}{2.5 \times 10^{9} \text{mL}}\right) \times \left(1 \times 10^{12}\right) = 20.\ \text{ppt (v/v)}$$

The solution's concentration is **20. ppt (v/v).** In a 20. ppt (v/v) solution, there are 20. mL of solute contained in every trillion (1×10^{12}) mL of solution. This alcohol concentration is much less than can be detected using current analytical instrumentation. The *lower limit of detection* of ethyl alcohol in blood is currently about 0.1 parts per thousand.

Review 7.14: Calculating Parts per Thousand Weight to Weight Concentration

The legal limit of blood alcohol concentration in most states corresponds to about 0.080 grams of alcohol per 100.0 grams of blood (solution). What is the **parts per thousand (w/w)** blood alcohol concentration at this legal limit?

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

3) Concentration in Molarity

Chemists often use a concentration unit of measure called **Molarity**. ***Molarity*** is defined as the number of ***moles of solute*** per ***liter of solution***. It can be calculated by taking the ratio of moles of solute to the volume (in liters) of solution:

$$\text{Molarity} = \left(\frac{\text{moles of } solute}{\text{liters (L) of } solution} \right)$$

Calculating a solution's molarity using this equation/definition results in units of **moles/L**. The mole/L unit is often referred to as **molar** and abbreviated as "**M**." Keep in mind, the "**M**" *can be interchanged with* "**mole/L**." For example, if a solution is made by dissolving 0.030 *moles of solute* with enough solvent to make 1.00 *liter (L) of solution*, you could say the concentration is 0.030 moles/L ***or*** 0.030 molar (**M**).

Calculation of Molarity Example: What is the molarity of a solution that is prepared by dissolving 0.015 moles of sugar in enough water to make 2.1 liters of solution?

Solution: Calculate the concentration using the equation/definition of molarity:

$$\text{Molarity} = \left(\frac{\text{moles of } solute}{\text{liters (L) of } solution} \right)$$

To calculate the ***molarity***, we need to know two quantities: **moles** of the ***solute*** **AND** the volume **(in L)** of the ***solution.***

- moles of the ***solute*** (sugar in this example) was given: **0.015 moles**
- liters of ***solution*** was given: **2.1 L**

Insert the moles of the *solute* and liters (L) of *solution* into the equation for molarity:

$$\text{Molarity} = \left(\frac{0.015 \text{ moles}}{2.1 \text{ L}} \right) = 0.0071 \text{ moles/L} \quad \text{or} \quad 0.0071 \text{ M}$$

The solution's concentration is **0.0071 moles/L.** Alternatively, you can write **0.0071 M** and say "**0.0071 molar**."
In a 0.0071 molar (M) solution, there are 0.0071 ***moles of solute*** contained in every ***liter of solution***.

In some molarity calculations, since mass (grams) is the parameter that is directly measurable, you will begin with the *number of* ***grams*** *of solute*. When this is the case, use the solute's molar mass to convert from grams to moles. I will have you do such a molarity calculation in the following review problem:

Review 7.15: Calculating Concentration in Molarity

What is the molarity of a solution that is prepared by dissolving 3.83 grams of glucose ($C_6H_{12}O_6$) in enough water to make 5.00 L of solution?

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

4) Concentration in Osmolarity

Some properties of solutions depend on the number of dissolved particles (ions or molecules) that the solution contains. For example, the rate of diffusion of ions or molecules through biological membranes depends on the number of dissolved particles. The **osmole** (Osm or osmol) unit is used to indicate *the number of moles of dissolved particles*. The concentration unit of measure called **osmolarity** is commonly defined as the number of ***moles of dissolved particles (osmoles)*** per ***liter of solution***. Osmolarity can be calculated by taking the ratio of osmoles of solute to the volume (in liters) of solution:

$$\text{Osmolarity} = \left(\frac{\text{osmoles of } solute}{\text{liter (L) of } solution}\right)$$

Calculating a solution's osmolarity using this equation/definition results in units of **osmoles/L**. The osmoles/L unit is often referred to as **osmolar** and abbreviated as "**osM**." You may be wondering, "What is the difference between a solution's osmolarity and molarity?" Sometimes it's the same; and sometimes it's different. **Ionic compound** solutes dissociate (break apart into *individual ions*) when solvated. For every mole of an *ionic compound* that is dissolved, the solution contains ***two or more moles*** of dissolved particles (osmoles), therefore the solution's molarity and osmolarity ***have different values***. **Molecular compound** solutes do not dissociate when solvated. For every one mole of a dissolved *molecular compound*, the solution contains one mole of dissolved particles (one osmole), therefore the solution's molarity and osmolarity ***have the same value***. I will elaborate on this concept by calculating the of osmolarity for a molecular compound solute and for an ionic compound solute.

Osmolarity calculation for a molecular compound example: If 0.50 moles of glucose (a molecular compound) is dissolved in enough water to make 2.00 L of solution, what is the ***osmolarity*** of the solution?

Solution: Calculate the concentration using the equation/definition of osmolarity:

$$\text{Osmolarity} = \left(\frac{\text{osmoles of } solute}{\text{liter (L) of } solution}\right)$$

To calculate the **os*molarity***, we need to know two quantities: the number of **osmoles** of the ***solute*** **<u>AND</u>** the volume **(L)** of the ***solution.***

- **osmoles** of the ***solute*** (glucose):
  - You were not given the number of osmoles ***directly***, however, you were given the *number of moles* of glucose (0.50 moles). Since glucose is a molecular compound, it does not dissociate *into ions* when dissolved. For every mole of a molecular compound that is dissolved, the solution will contain one mole of dissolved particles (one osmole). In this problem, 0.50 moles of glucose were dissolved, therefore the solution contains **0.50 osmoles** of glucose.

- liters (L) of ***solution*** was given: **2.00 L**

Insert the **osmoles** of the *solute* and liters (L) of *solution* into the equation for osmolarity:

$$\text{Osmolarity} = \left(\frac{0.50 \text{ osmoles}}{2.00 \text{ L}}\right) = 0.25 \text{ osmoles/L} \text{ or } 0.25 \text{ osmolar}$$

The solution's concentration is **0.25 osmoles/L.** Alternatively, you can write **0.25 osmolar**.

Note that in this example, since glucose is a molecular (non dissociating) compound, the molarity and the osmolarity ***have the same value***.

Next, I will show you an example for the calculation of osmolarity for an *ionic compound.* We will begin with the same number of moles and same solution volume as we did in the previous example for glucose. You will see that for the dissolution of ***ionic compounds,*** the *molarity* and *osmolarity* ***are <u>not</u> equal***.

Osmolarity calculation for an ionic compound example: If 0.50 moles of sodium chloride are dissolved in enough water to make 2.00 L of solution, what is the ***osmolarity*** of the solution?

Solution: Calculate the concentration using the equation/definition of osmolarity:

$$\text{Osmolarity} = \left(\frac{\text{osmoles of } solute}{\text{liter (L) of } solution}\right)$$

To calculate the **osmolarity**, we need to know two quantities: the number of **osmoles** of the ***solute*** **AND** the volume (in L) of the ***solution.***

- **osmoles** of the ***solute*** (NaCl)
  - You were not given the number of osmoles ***directly***, however, you were given the *number of moles* of sodium chloride (0.50 moles). Sodium chloride dissociates when dissolved, so for every ***mole*** of sodium chloride, the solution will contain ***two osmoles***: *one osmole* of sodium ions ***plus*** *one osmole* of chloride ions.

$$\mathbf{NaCl}(s) \rightarrow \underbrace{\mathbf{Na^+}(aq)}_{\boxed{\begin{array}{c}\textbf{one osmole}\\ \textbf{of Na}^+\end{array}}} + \underbrace{\mathbf{Cl^-}(aq)}_{\boxed{\begin{array}{c}\textbf{one osmole}\\ \textbf{of Cl}^-\end{array}}} = \textbf{2 osmoles}$$

  - Multiply the number of moles of sodium chloride that are in the solution (0.50 moles) by a factor of **2** to convert ***moles*** of sodium chloride to ***osmoles***:

$$0.50 \text{ moles } \mathbf{NaCl}\left(\frac{\mathbf{2}\text{ osmoles}}{\text{mole }\mathbf{NaCl}}\right) = \textbf{1.0 osmoles}$$

  - 0.50 moles of sodium chloride were dissolved, therefore the solution contains **1.0 osmoles**.

- liters (L) of ***solution*** was given: **2.00 L**

Insert the **osmoles** of the *solute* and liters (L) of *solution* into the equation for osmolarity:

$$\text{Osmolarity} = \left(\frac{1.0 \text{ osmoles}}{2.00 \text{ L}}\right) = 0.50 \text{ osmoles/L} \;\text{ or }\; 0.50 \text{ osmolar}$$

The solution's concentration is **0.50 osmoles/L.** Alternatively, you can write **0.050 osm/L** ***or*** **0.050 osmolar**. Even though we started with the *same number of moles of solute* and the *same volume of solution* in this example as we did in the previous example for a glucose solution, the osmolarity values are different ***because of the difference in the number of particles (osmoles) that are formed upon dissolution of molecular vs. ionic solutes.***

In the review problem that follows, I will ask you to do an osmolarity calculation for a $BaCl_2$ solution. You will begin with the same number of moles and same volume as we used in the previous examples for glucose and sodium chloride. Keep in mind that for every *one* mole of $BaCl_2$ that dissolves, *three* osmoles are formed (one osmole of Ba^{2+} and two osmoles of Cl^-).

$$\mathbf{BaCl_2}(s) \rightarrow \underbrace{\mathbf{Ba^{2+}}(aq)}_{\boxed{\begin{array}{c}\textbf{One Osmole}\\ \textbf{of Ba}^{2+}\end{array}}} + \underbrace{\mathbf{2\ Cl^-}(aq)}_{\boxed{\begin{array}{c}\textbf{Two Osmoles}\\ \textbf{of Cl}^-\end{array}}} = \textbf{3 Osmoles}$$

Review 7.16: Calculating Concentration in Osmolarity

If 0.50 moles of $BaCl_2$ (***an ionic compound***) is dissolved in enough water to make 2.00 L of solution, what is the ***osmolarity*** of the solution?

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

Converting between Molarity and Osmolarity

Knowing the number of particles (osmoles) that are formed upon dissolution of a solute will enable you to easily convert between molarity and osmolarity. The number of osmoles formed per mole of solute dissolved can be used as a ***conversion factor***.

Converting between Molarity and Osmolarity for an Ionic Compound:

Example : If the ***molarity*** of a sodium chloride solution is 1.2 M, what is the ***osmolarity***?

Solution: Begin by noting that the molar (M) means moles/L. You can think of this as a unit conversion problem; 1.2 moles/L is the ***given quantity*** and we wish to convert to osmoles/L (osmolarity). Always begin unit conversions with the **given quantity** and its units:

$$\underbrace{\frac{1.2\ \text{moles NaCl}}{\text{L}}}_{\boxed{\text{Molarity (moles/L)}}}\left|\frac{\qquad\qquad}{\qquad\qquad}\right| = ?\left(\frac{\text{osmoles}}{\text{L}}\right)$$

In order to convert to osmoles/L, we need to convert moles of NaCl to osmoles. We know the relationship between moles of NaCl and osmoles; for every *one* mole of NaCl that is dissolved, we get *two* osmoles (**1** mole NaCl = **2** osmoles).

- Use this relationship as the conversion factor:

$$\underbrace{\frac{1.2\ \cancel{\text{moles NaCl}}}{\text{L}}}_{\boxed{\text{Molarity (moles/L)}}}\left|\underbrace{\frac{\mathbf{2}\ \text{osmoles}}{\mathbf{1}\ \cancel{\text{mole NaCl}}}}_{\boxed{\text{Conversion Factor (osmoles/mole NaCl)}}}\right| = \mathbf{2.4}\underbrace{\left(\frac{\text{osmoles}}{\text{L}}\right)}_{\boxed{\text{Osmolarity (osmoles/L)}}}$$

If the ***molarity*** of a sodium chloride solution is 1.2 M, the ***osmolarity*** is 2.4 osmoles/L.

Converting between Molarity and Osmolarity for a Molecular Compound:

Converting between molarity and osmolarity for molecular solutes is simple. The molarity is equal to osmolarity for molecular solutes because they do not dissociate.

Example: if the molarity of a molecular compound is 1.2 M, then the osmolarity is 1.2 osmoles/L.

You try one:

Review 7.17: Converting between Molarity and Osmolarity

If the ***molarity*** of an $FeCl_3$ (***an ionic compound***) solution is 0.010 M, what is the ***osmolarity***?

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

5) Concentration in Molality

Another frequently used unit of measure for concentration is **molality**. Note the spelling of **molality** differs *by only one letter* from **molarity. Molality** is defined as the number of ***moles of solute*** per ***kg of solvent***. The difference between molality and molarity is that molality refers to the amount of solute dissolved per kg of *solvent* (not solution), whereas molarity refers to the amount of solute dissolved per *liter of solution*. ***Molality*** can be calculated by taking the ratio of moles of solute to the mass (in kilograms) of the solvent:

$$\text{Molality} = \left(\frac{\text{moles of } \textit{solute}}{\text{kg of } \textit{solvent}} \right)$$

Calculating a solution's molality using this equation/definition results in units of **moles/kg**. The moles/kg unit is often referred to as **molal** and abbreviated as "***m***." The "***m***" unit *can be interchanged with* "**moles/kg**." For example, if a solution is made by dissolving 0.020 *moles of solute* in 1.00 kg *of solvent*, you could say the concentration is 0.020 moles/kg ***or*** 0.020 molal (***m***). Be sure to use italic "***m"*** so it is not confused with meter (**m**) distance unit.

Calculation of Molality Example: What is the molality of a solution that is prepared by dissolving 0.125 moles of sodium chloride in 1.60 kg of water?

Solution: Calculate the solution's molality using the equation/definition of molality:

$$\text{Molality} = \left(\frac{\text{moles of } \textit{solute}}{\text{kg of } \textit{solvent}} \right)$$

To calculate the ***molality,*** we need to know two quantities: the **moles** of the ***solute*** **AND** the mass (in kg) of the ***solvent.***

- The moles of the ***solute*** ($NaCl$) was given: **0.125 moles**
- The mass of the ***solvent*** (water) was given: **1.60 kg**

Insert the moles of the *solute* and kg of *solvent* into the equation for molality:

$$\text{Molality} = \left(\frac{0.125 \text{ moles}}{1.60 \text{ kg}} \right) = 0.0781 \text{ moles/kg} \;\text{ or }\; 0.0781\ m$$

The solution's concentration is **0.0781 moles/kg.** Alternatively, you can write **0.0781 *m*** and say "**0.0781 molal**." In a 0.0781 molal (***m***) solution, there are 0.0781 ***moles of solute*** contained in every ***kg of solvent***.

You try one:

Review 7.18: Calculating Concentration in Molality

What is the molality of a solution that is prepared by dissolving 1.34 moles of ethyl alcohol in 0.75 kg of water?

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

IMPORTANT NOTE: One kilogram (kg) of water has a volume of 1 liter (L). **Molarity** and **molality** are often taken to be ***approximately equal*** in cases of *dilute aqueous solutions*. This is a reasonable approximation because in a "*dilute*" solution, the *solution* is almost entirely *solvent* (water).

5) Concentration in Osmolality

Osmolality is to molality as osmolarity is to molarity. ***Osmolality*** is defined as the number of ***osmoles*** per ***kilogram of solvent***. It can be calculated taking the ratio of ***osmoles*** (moles of dissolved particles) to the mass (in kilograms) of the solvent:

$$\text{Osmolality} = \left(\frac{\text{osmoles of } \textit{solute}}{\text{kg of } \textit{solvent}}\right)$$

Calculating a solution's osmolality using this equation/definition results in units of **osmoles/kg**. The osmoles/kg unit is often referred to as **osmolal**.

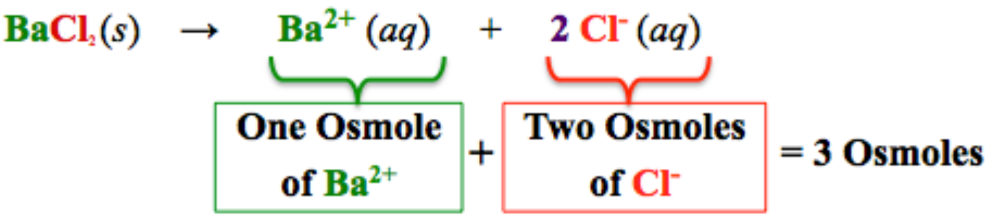
6) Concentration in Equivalents per Liter (Eq/L)

Some properties of solutions depend on the ***total charge*** of the ions in solution. For example, the ability of a solution to conduct electricity depends on the total charge of the ions in solution. In cells, membrane potentials that generated nerve signals depend on the total charge of ions in solution. An **equivalent** (**Eq**) is defined as a ***mole of charge***. The concentration unit of measure called **equivalents per liter (Eq/L)** is defined as the number of ***equivalents*** (*moles of charge*) per ***liter of solution***:

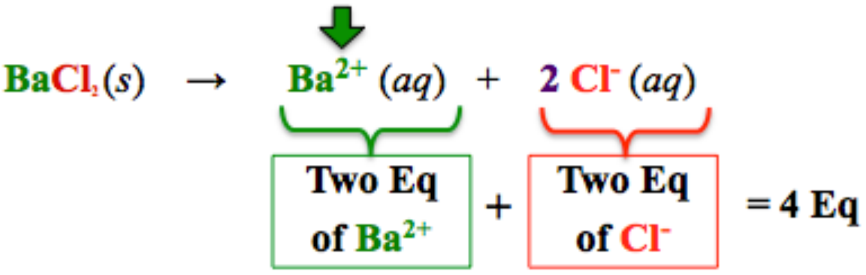
$$\text{Eq/L} = \left(\frac{\text{Eq of } \textit{solute}}{\text{liter (L) of } \textit{solution}}\right)$$

At first glance, an equivalent (Eq) may appear to be the same as an osmole, however this is not always the case. An equivalent is a mole of charge; an osmole is a mole of dissolved particles. I will elaborate by comparing the number of osmoles vs. the number of equivalents present when one mole of $BaCl_2$ is dissolved:

- When **one mole** of $BaCl_2$ is dissolved, ***3 osmoles*** are formed (one osmole of Ba^{2+} and two osmoles of Cl^-).



- When **one mole** of $BaCl_2$ is dissolved, ***4 equivalents*** **(Eq)** are formed. Since barium ions have a **2+ charge**, one mole of barium ions contains ***two*** *moles of charge* (***two*** equivalents). The ***two*** moles of chloride ions contain ***two*** *equivalents* (***two*** moles of "1-" charge).



Review 7.19: Understanding Equivalents

When one mole of $Fe_2(SO_4)_3$ is dissolved in water:

a. How many equivalents are present?
b. How many equivalents of sulfate are present (equivalents from sulfate only)?
c. How many equivalents of iron(III) are present (equivalents from Fe^{3+} only)?

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

Example for Calculating Eq/L: If 0.50 moles of $BaCl_2$ is dissolved in enough water to make 2.00 L of solution, what is the **Eq/L *concentration*** of the solution?

Solution: Calculate the concentration using the equation/definition of Eq/L:

$$\text{Eq/L} = \left(\frac{\text{Eq of } solute}{\text{liter (L) of } solution}\right)$$

To calculate the **Eq/L** concentration, we need to know two quantities: the number of **equivalents (Eq)** present **AND** the volume (in L) of the ***solution.***

- **Eq** present:
  - For every ***one mole*** of $BaCl_2$ dissolved, **4 Eq** are formed (two Eq of **Ba^{2+}** and two Eq of **Cl^-**).

$$\mathbf{BaCl_2}\,(s) \rightarrow \mathbf{Ba^{2+}}\,(aq) + \mathbf{2\ Cl^-}\,(aq)$$

  - Multiply the number of moles of $BaCl_2$ by a factor of **4** to convert ***moles*** of $BaCl_2$ to **Eq**:

$$0.50 \text{ moles } BaCl_2 \left(\frac{\mathbf{4\ Eq}}{\text{mole } BaCl_2}\right) = \mathbf{2.0\ Eq}$$

  - 0.50 moles of barium chloride were dissolved, therefore the solution contains **2.0 Eq**.

- liters (L) of ***solution*** was given: **2.00 L**

Insert the **Eq** present and liters (L) of *solution* into the equation for **Eq/L** concentration:

$$\text{Eq/L} = \left(\frac{2.0 \text{ Eq}}{2.00 \text{ L}}\right) = 1.0 \text{ Eq/L}$$

You try one:

Review 7.20: Calculating Concentration in Eq/L

If 0.015 moles of $Fe_2(SO_4)_3$ is dissolved in enough water to make 2.5 L of solution, what is the **Eq/L *concentration*** of the solution?

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

7.7 Calculations for Solutions

A glucose-in-water solution (sometimes called a dextrose solution) is frequently used as an intravenous (IV) therapy to reestablish or maintain hydration and/or nutrition. Most glucose-in-water IV solutions have a glucose concentration of 0.278 moles/L (or 0.0278 M). Suppose you know that a patient received 3.50 L of a 0.278 M glucose IV solution, how many moles (or grams) of glucose were administered in that volume? Or, suppose you wished to administer 0.200 moles of glucose to a patient, what volume of the IV solution would need to be dispensed? In this section, you will learn how do calculations to find how much solute is contained in a specified amount of solution *and* how much solution contains a specified amount of solute.

The key to mastering this section is to be aware of the following two statements:

- *The relationship between the amount of solute and the amount of solution is the* ***concentration***.

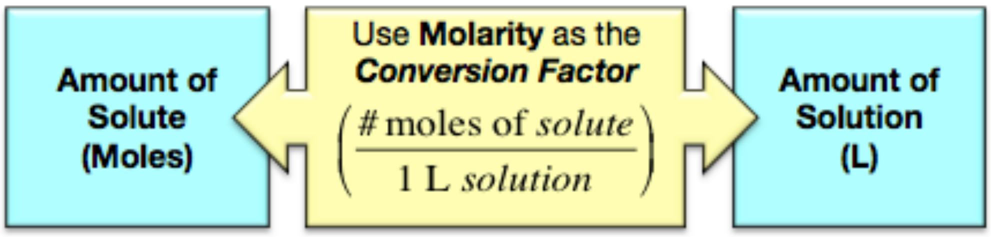
- You can convert between the *amount of solute* and the *amount of solution* by ***using the concentration as a conversion factor***.

A Healthcare Professional Administering an Intravenous (IV) Solution

U.S. Air Force Senior Airman Megan Stanton, a medic with the 366th Medical Operations Squadron, hangs a bag of IV fluid for a patient in the urgent care center at Mountain Home Air Force Base, Idaho.
Source: Wikimedia Commons, PD
Author: TSgt Samuel Morse

Molarity Concentration Calculations for Solutions

The ***molarity*** (moles/L) of a solution gives us the relationship between the amount (moles) of solute and the volume (L) of solution. We can therefore use the molarity as a ***conversion factor*** when converting between the moles of solute in a given volume (L) of solution, ***or*** the volume (L) of solution that will contain a given amount (moles) of solute.

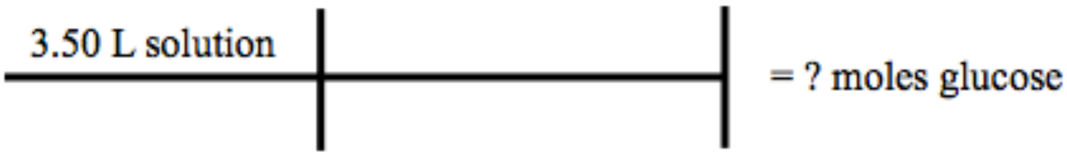


I will elaborate on this concept by using molarity as a conversion factor in order to answer the two questions about the glucose IV solution that were posed in the first paragraph of this page.

Volume of Solution to Amount of Solute Example: Suppose you know that a patient received 3.50 **L** of a 0.278 **M** glucose IV solution, how many moles of glucose were administered to the patient?

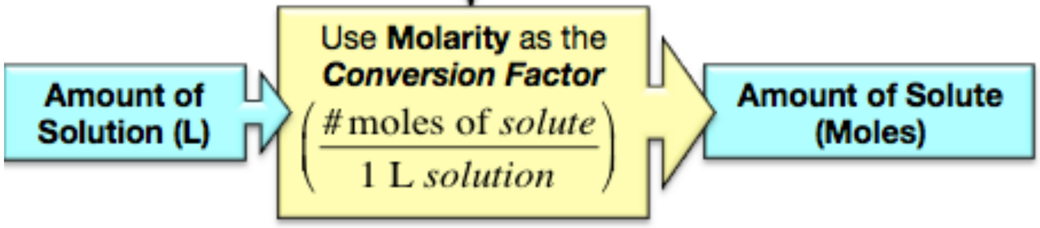
Solution: We are asked to determine the ***amount of solute*** (moles of glucose) that would be contained in the given ***amount of solution*** (3.50 L). ***IMPORTANT:*** *The relationship between the amount of solute and the amount of solution is the* ***concentration***. In this problem, we are given the molarity (**M**); recall that molarity is the number of **moles of solute per liter of solution (mole/L)**. Since *molarity concentration* is the ***relationship*** between *moles of solute* and *liters of solution*, we use it as a ***conversion factor*** to convert between *liters of solution* and *moles of solute (glucose).* Do these types of problems using our factor-label method as you did for other unit conversion problems:

STEP 1) Set up the equation using the given quantity:



STEP 2) We need to convert from liters of solution to moles of solute (glucose). We can write the molarity as an equivalence statement (0.278 moles of solution = 1 liter of solution). To use the concentration as a conversion factor, we put the given units (L of solution) in the denominator so that the given units will cancel, and then put the desired units (moles of glucose) in the numerator:

$$3.50\ \cancel{\text{L solution}} \times \frac{0.278\ \text{moles glucose}}{1\ \cancel{\text{L solution}}} = 0.973\ \text{moles glucose}$$



3.50 L of a 0.278 M glucose solution will contain 0.973 moles of glucose.

In this example problem, we were given the amount of solution (L) and the concentration of the solution, and asked to find the amount of solute present. Next, I will show you how to solve the second glucose IV solution problem in which we are asked to determine what volume of the solution contains a given amount of solute. Our approach is the same; ***we will use the concentration as the conversion factor***.

Moles of Solute to Volume (L) of Solution Example:

Suppose you wished to administer 0.200 moles of glucose from a 0.278 M glucose IV solution to a patient, what ***volume*** (in liters) of the solution would need to be dispensed?

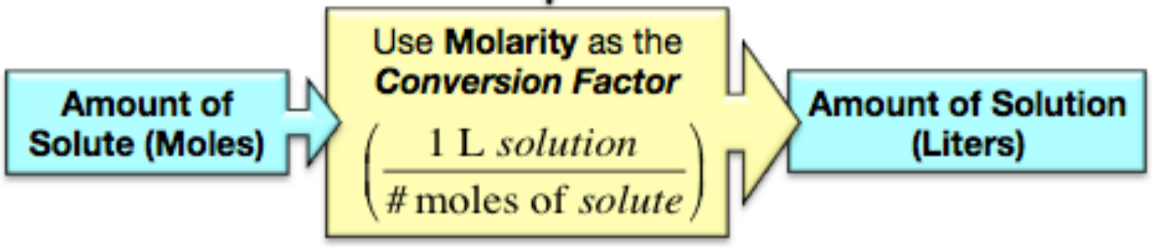
Solution: We are asked to determine the ***amount of solution (L)*** that would contain a given ***amount of solute*** (0.200 moles of glucose). *Molarity concentration* is the ***relationship*** between *moles of solute* and *liters of solution*; we use it as a ***conversion factor*** to convert between moles of solute (glucose) and liters of solution.

STEP 1) Set up the equation using the given quantity:

$$0.200\ \text{moles glucose} \times \frac{\quad}{\quad} = ?\ \text{L solution}$$

STEP 2) We need to convert moles of solute (glucose) to liters of solution. To use the concentration as a conversion factor, we put the given units (moles glucose) in the denominator so that the given units will cancel, and then put the desired units (L of solution) in the numerator:

$$0.200\ \cancel{\text{moles glucose}} \times \frac{1\ \text{L solution}}{0.278\ \cancel{\text{moles glucose}}} = 0.719\ \text{L solution}$$



0.719 L of a 0.278 M glucose solution would be given to the patient in order to provide 0.200 moles of glucose.

Next, I want to show you an example problem that combines the concepts of the ***previous section*** (calculating a solution's concentration) *and* the concepts of this section (calculations of how much solute is contained in a certain amount of solution *or* how much solution contains a certain amount of solute).

Example: If 1.25 g of acetone (C_3H_6O) is dissolved in enough water to make 0.550 L of solution;

- **a)** What is the **molarity (M)** of the solution?
- **b)** How many ***moles*** of acetone are contained in 0.0679 L of this acetone ***solution***?
- **c)** What **volume (L)** of this acetone solution would contain 0.0079 ***moles*** of acetone?

Solutions:

a) What is the **molarity (M)** of the solution?

Calculate the concentration using the equation/definition of molarity:

$$\text{Molarity} = \left(\frac{\text{moles of } solute}{\text{liters (L) of } solution}\right)$$

To calculate the ***molarity***, we need to know two quantities: the **moles** of ***solute*** **AND** the volume (in L) of ***solution.***

- moles of the ***solute*** (acetone in this example)
  - We were not given the number of moles ***directly***, however, we were given the *grams* of acetone (1.25 g).

    Calculate the *molar mass* of acetone (C_3H_6O), and then convert from grams to moles:
    - The molar mass of acetone is **58.09 g/mole**.

$$\begin{array}{l|l|} 1.25\ \cancel{\text{grams } C_3H_6O} & 1 \text{ mole } C_3H_6O \\ \hline & 58.09\ \cancel{\text{grams } C_3H_6O} \end{array} = 0.0215 \text{ moles } C_3H_6O$$

- L of ***solution*** was given: **0.550 L**

Insert the moles of the *solute* and liters (L) of *solution* into the equation for molarity:

$$\text{Molarity} = \left(\frac{0.0215 \text{ moles}}{0.550 \text{ L}}\right) = 0.0391 \text{ moles/L} \text{ or } 0.0391 \text{ M}$$

b) How many ***moles*** of acetone are contained in 0.0679 L of this acetone ***solution***?

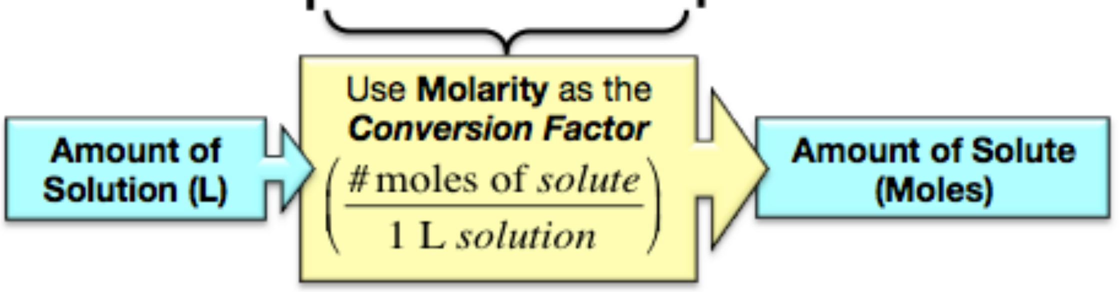
Molarity concentration is the ***relationship*** between *moles of solute* and *liters of solution*; we use it as a ***conversion factor*** to convert between *liters of solution* and *moles of solute (acetone).*

STEP 1) Set up the equation using the given quantity:

$$\begin{array}{l|l|} 0.0679 \text{ L solution} & \qquad\qquad \\ \hline & \end{array} = \text{? moles acetone}$$

STEP 2) To use the concentration as a conversion factor, we put the given units (L of solution) in the denominator so that the given units will cancel, and then put the desired units (moles of acetone) in the numerator:

$$\begin{array}{l|l|} 0.0679\ \cancel{\text{L solution}} & 0.0391 \text{ moles acetone} \\ \hline & 1\ \cancel{\text{L solution}} \end{array} = 0.00265 \text{ moles acetone}$$

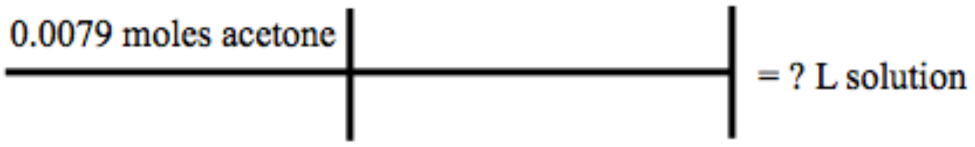


0.0679 L of the 0.0391 M solution will contain 0.00265 moles of acetone.

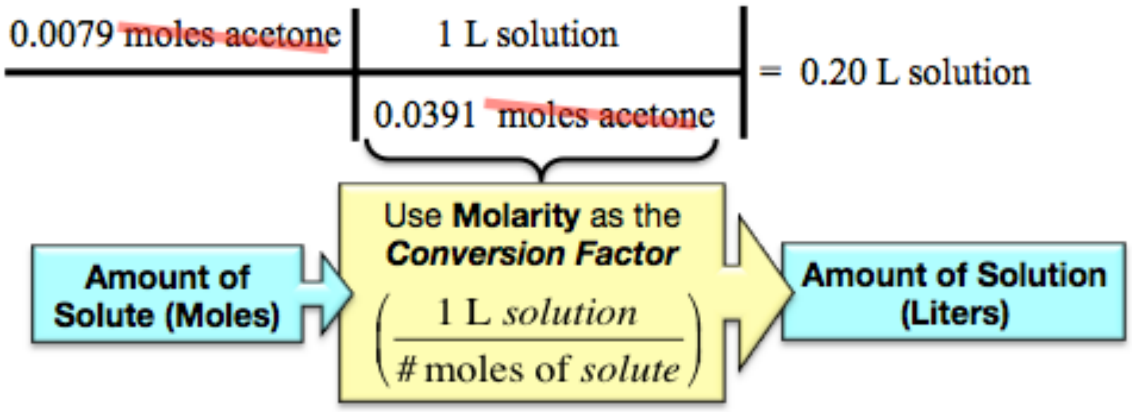
c) What **volume (L)** of this acetone solution would contain 0.0079 ***moles*** of acetone?

Use the molarity as a ***conversion factor*** to convert between moles of solute (acetone) and liters of solution.

STEP 1) Set up the equation using the given quantity:



STEP 2) We need to convert moles of solute (acetone) to liters of solution. Use the concentration as a conversion factor.



0.0079 moles of acetone would be contained in 0.20 L of this 0.0391 M acetone solution.

You try some:

Review 7.21: Molarity Calculations for Solutions:

The "LD50" or lethal dosage 50 (the ingested quantity that results in a 50% chance of death) of ethyl alcohol for a 150 pound individual is 10.4 moles. If a particular wine has an ethyl alcohol molarity concentration of 2.8 M, what volume (in liters) of wine contains 10.4 moles of ethyl alcohol (the lethal dosage)?

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

Review 7.22: Follow-up Calculation from the Previous Review Problem (7.18)

If 1 liter = 5.0 glasses, how many glasses of wine from the previous review problem would be in the lethal dosage that was calculated?

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

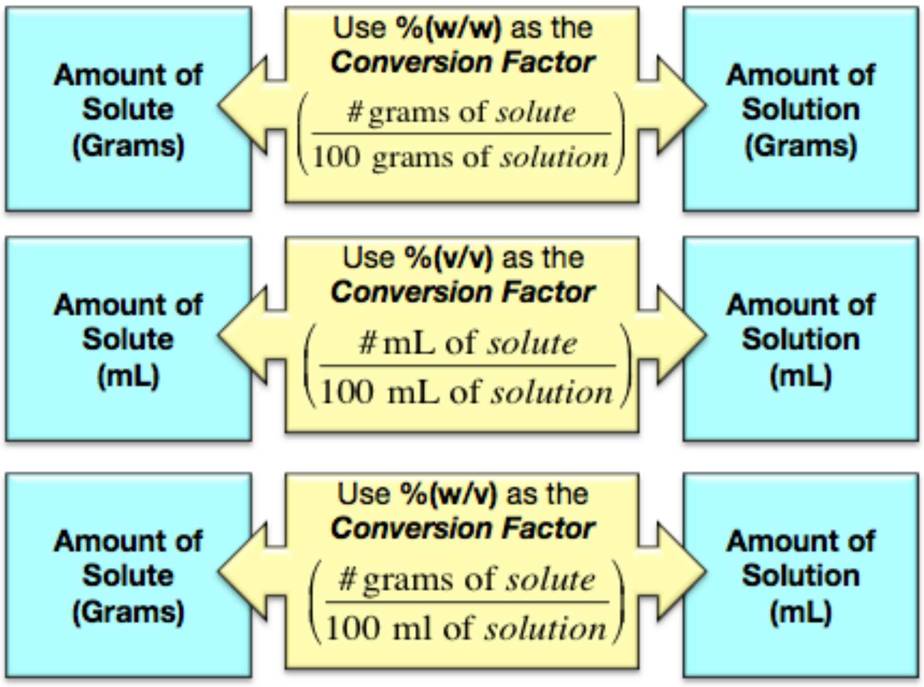
Review 7.23: Molarity Calculations for Solutions:

How many ***grams*** of silver nitrate ($AgNO_3$) are contained in 0.384 L of a 0.200 M silver nitrate solution?

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

Percent (%) Concentration Calculations for Solutions

Percent (%) concentration gives the relationship between the amount of solute and the amount of solution:



For example, the **%(w/v)** of a solution gives us the number of ***grams of solute*** contained in ***100 ml of solution***, and can therefore be used to convert between *grams of solute* and *mL of solution*. I will elaborate on this by doing a couple of examples.

Example: Using % (w/v) to Convert From Volume (mL) of Solution to Grams of Solute

Normal saline intravenous drips such as the solution shown in Figure 7.15 are composed of sterile, 0.90 %(w/v) aqueous sodium chloride (NaCl) solutions. They are used to treat or prevent dehydration and hypovolemia. If a patient received 2475 mL of a normal saline solution, how many grams of sodium chloride were delivered?

Figure 7.15
A Normal Saline IV Drip Bag

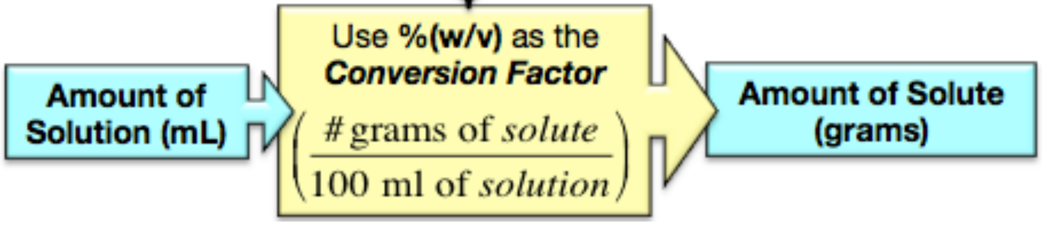
Solution: Use % (m/v) as a conversion factor to convert from volume (mL) of solution to grams of solute.

STEP 1) Set up the equation using the given quantity:

$$\begin{array}{l|l|l} 2475\text{ mL solution} & & = \text{ ? grams NaCl} \\ \hline & & \end{array}$$

STEP 2) We need to convert mL of solution to grams of solute (NaCl). **0.90 % (w/v)** means that there are **0.90 grams** of NaCl in every **100 mL** of solution. To use this concentration as a conversion factor, we put the given units (mL of solution) in the denominator so the given units will cancel, and then put the desired units (grams of NaCl) in the numerator:

$$\begin{array}{l|l|l} 2475\ \cancel{\text{mL solution}} & 0.90\text{ grams NaCl} & = 22\text{ grams NaCl} \\ \hline & \underbrace{100\ \cancel{\text{mL solution}}} & \end{array}$$



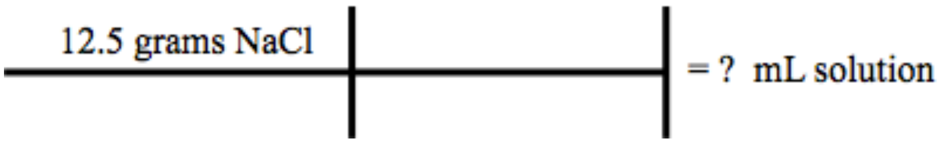
If a patient received 2475 mL of a normal saline solution, then 22 grams of sodium chloride were delivered.

Example: Using % (w/v) to Convert From Grams of Solute to Volume (mL) of Solution

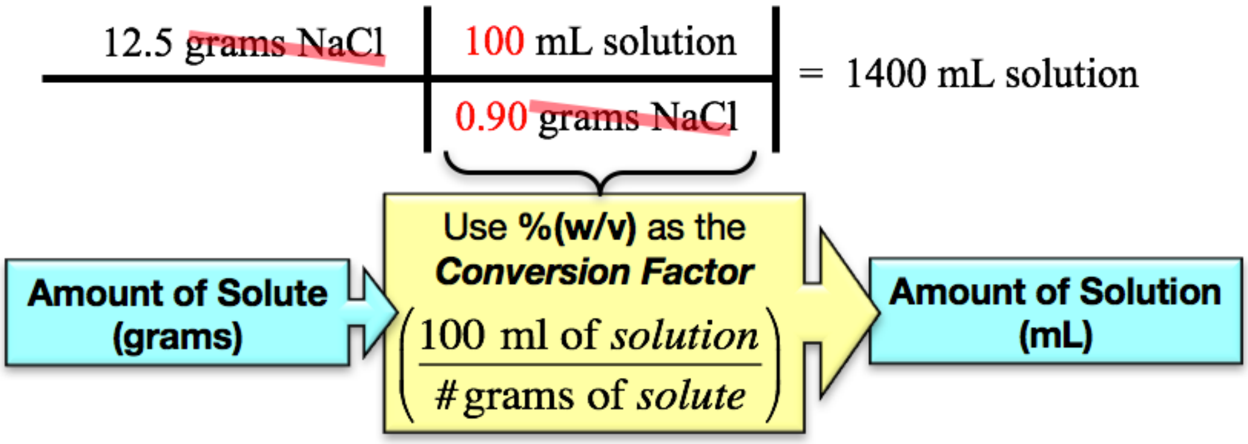
What volume (mL) of a normal saline solution [0.90 % (w/v)] contains 12.5 grams of sodium chloride?

Solution: Use % (w/v) as a conversion factor to convert from grams of solute to volume (mL) of solution.

STEP 1) Set up the equation using the given quantity:



STEP 2) We need to convert grams of solute (NaCl) to mL of solution. To use the concentration as a conversion factor, we put the given units (grams of NaCl) in the denominator so that the given units will cancel, and then put the desired units (mL of solution) in the numerator:



1400 mL of a normal saline solution contain 12.5 grams of sodium chloride.

You try one:

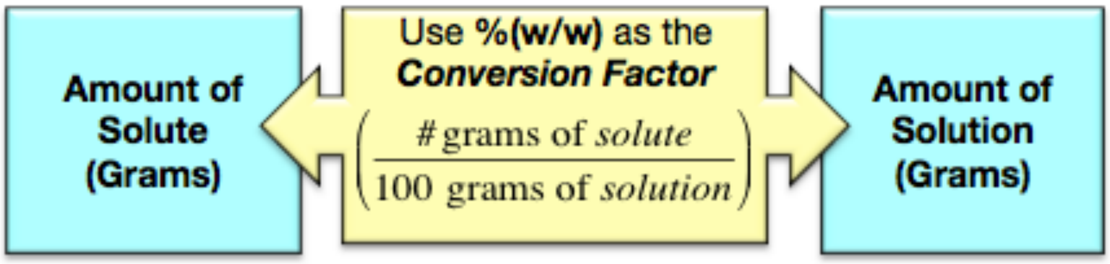
Review 7.24: Percent (%) Calculations for Solutions

The label of the medication vial tells you that the concentration of morphine sulfate for an intravenous injection is 1.0% (w/v). If you wish to administer 0.0025 g of morphine sulfate, what volume (mL) would you inject?

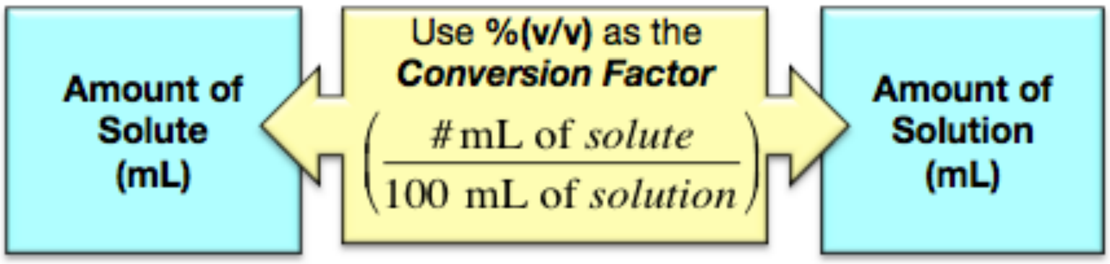
For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

The method for converting between the ***amount of solute*** and the ***amount of solution*** can also be used for % (w/w) and % (v/v).

% (w/w) is used to convert between the ***mass*** of solute *and* the **mass** of solution:

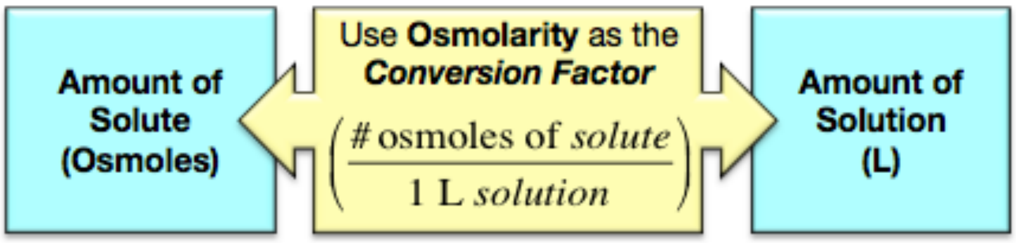


% (v/v) is be used to convert between the **volume** of a liquid solute and the **volume** of the solution:



Osmolarity Concentration Calculations for Solutions

Osmolarity concentration is a relationship between the amount of solute and the amount of solution:



The **osmolarity (osmoles/L)** of a solution gives us the number of ***osmoles of solute*** contained in ***1 L of solution***. It can therefore be used to convert between *osmoles of solute* and *L of solution*.

Example: Using Osmolarity to convert between L of Solution and Osmoles of Solute

How many ***osmoles*** are contained in 2.75 L of a solution that has a concentration of 0.0750 ***osmole/L***?

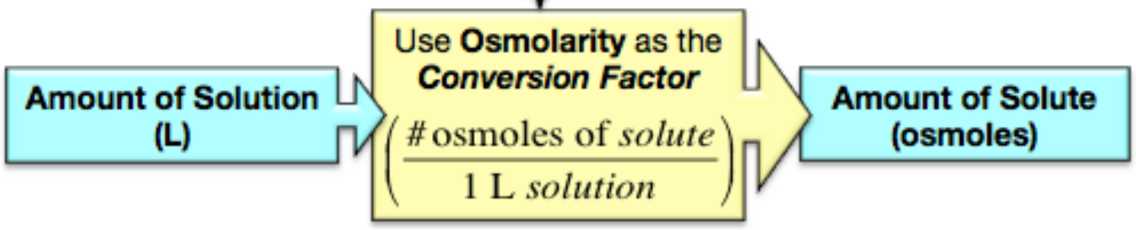
Solution: Use the osmolarity concentration as a conversion factor to convert from liters of solution to osmoles of solute.

STEP 1) Set up the equation using the given quantity:

$$\begin{array}{l|l|} 2.75\text{ L solution} & \\ \hline & \end{array} = ?\text{ osmoles}$$

STEP 2) We need to convert L of solution to osmoles. To use the concentration as a conversion factor, we put the given units (L of solution) in the denominator so that the given units will cancel, and then put the desired units (osmoles) in the numerator:

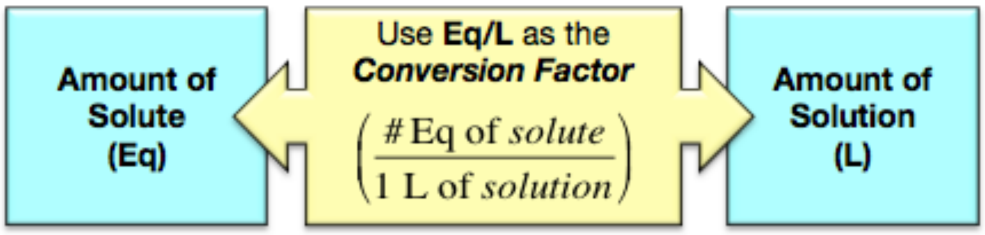
$$\begin{array}{l|l|} 2.75\ \cancel{\text{L solution}} & 0.0750\text{ osmoles} \\ \hline & \underbrace{1\ \cancel{\text{L solution}}} \end{array} = 0.206\text{ osmoles}$$



0.206 *osmoles* are contained in 2.75 L of a 0.0750 *osmole/L solution*.

Equivalents per Liter (Eq/L) Concentration Calculations for Solutions

Eq/L concentration is a relationship between the amount of solute and the amount of solution:



The **Eq/L** of a solution gives us the number of ***equivalents of solute*** contained in ***1 L of solution***. It can therefore be used to convert between *equivalents of solute* and *L of solution*.

Example: Using Eq/L to convert between L of Solution and Equivalents of Solute

How many equivalents of solute are contained in 0.830 L of a 0.0100 M $Fe_2(SO_4)_3$ solution?

Solution: We are given the solution concentration in molarity (M = mole/L), but we need to get (Eq/L) in order to solve the problem. First we will convert molarity (mole/L) to (Eq/L), and then we will use the Eq/L concentration as a conversion factor to convert from liters of solution to equivalents of solute.

1) Convert (mole/L) to (Eq/L):

We wish to convert the concentration from 0.0100 mole/L to Eq/L. This is a unit conversion problem; always begin unit conversions with the given quantity and its units:

$$\begin{array}{c|c|}0.0100\text{ moles }Fe_2(SO_4)_3 & \\ \hline \text{L} & \end{array} = ?\left(\frac{\text{Eq of }SO_4^{2-}}{\text{L of Solution}}\right)$$

In order to convert to Eq/L, we need to convert moles of $Fe_2(SO_4)_3$ to equivalents (Eq). For every ***one mole*** of $Fe_2(SO_4)_3$ dissolved, **12 Eq** are formed.

$$Fe_2(SO_4)_3\,(s) \rightarrow \underbrace{\underbrace{2\,Fe^{3+}\,(aq)}_{\boxed{\begin{array}{c}\text{6 Eq}\\ \text{of }Fe^{3+}\end{array}}} + \underbrace{3\,SO_4^{2-}\,(aq)}_{\boxed{\begin{array}{c}\text{6 Eq}\\ \text{of }SO_4^{2-}\end{array}}}}_{\boxed{\text{12 total Eq}}}$$

- Use this relationship as the conversion factor:

$$\underbrace{\frac{0.0100\ \cancel{\text{moles }Fe_2(SO_4)_3}}{\text{L}}}_{\boxed{\begin{array}{c}\text{Molarity}\\ \text{(moles/L)}\end{array}}}\ \underbrace{\frac{12\text{ Eq}}{1\ \cancel{\text{mole }Fe_2(SO_4)_3}}}_{\boxed{\begin{array}{c}\text{Conversion Factor}\\ (\text{Eq/mole }Fe_2(SO_4)_3)\end{array}}} = 0.120\underbrace{\left(\frac{\text{Eq}}{\text{L}}\right)}_{\boxed{\begin{array}{c}\text{Equivalents per}\\ \text{Liter (Eq/L)}\end{array}}}$$

If the ***molarity*** of a $Fe_2(SO_4)_3$ solution is 0.0100 M, then the ***Eq/L concentration*** is **0.120 Eq/L**.

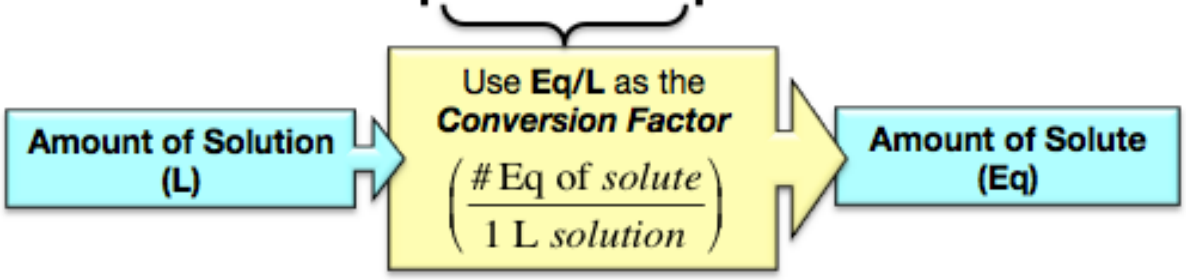
2) Use the Eq/L concentration as a conversion factor to convert from liters of solution to equivalents of solute:

a) Set up the equation using the given amount of solution:

$$\begin{array}{c|c|}0.830\text{ L solution} & \\ \hline & \end{array} = ?\text{ Eq}$$

b) We need to convert L of solution to equivalents. To use the concentration as a conversion factor, we put the given units (L of solution) in the denominator so that the given units will cancel, and then put the desired units (Eq) in the numerator:

$$\begin{array}{c|c|}0.830\ \cancel{\text{L solution}} & 0.120\text{ Eq}\\ \hline & 1\ \cancel{\text{L solution}}\end{array} = 0.0996\text{ Eq}$$



0.0996 equivalents of solute are contained in 0.830 L of a 0.0100 M $Fe_2(SO_4)_3$ solution.

For some applications used in medical diagnostic testing, we are concerned with the number of equivalents of ***a particular ion*** in solution. Let's do an example calculating the equivalents of a particular ion present in a solution.

Example: How many equivalents of sulfate (*not total equivalents*) are contained in 0.830 L of a 0.0100 M $Fe_2(SO_4)_3$ solution?

Solution:

1) Convert molarity (mole/L) to Eq of SO_4^{2-}/L:

We will do this problem in the same way as we did for the previous example problem, ***with one exception***: we will convert the given molarity (0.0100 mole/L) to **Eq** of **SO_4^{2-} /L**

Always begin unit conversions with the given quantity and its units.

$$\frac{0.0100 \text{ moles } Fe_2(SO_4)_3}{\text{L}} \Bigg| \qquad \Bigg| = \textbf{?} \left(\frac{\text{Eq}}{\text{L}}\right)$$

In order to convert to Eq of SO_4^{2-} /L, we need to convert moles of $Fe_2(SO_4)_3$ to equivalents (Eq of SO_4^{2-})

For every ***one mole*** of $Fe_2(SO_4)_3$ that is dissolved, **6** Eq of SO_4^{2-} are formed.

$$\mathbf{Fe_2(SO_4)_3}\,(s) \rightarrow \mathbf{2\ Fe^{3+}}\,(aq) + \underbrace{\mathbf{3\ SO_4^{2-}}\,(aq)}_{\boxed{\textbf{6 Eq of } \mathbf{SO_4^{2-}}}}$$

- Use this relationship as the conversion factor:

$$\underbrace{\frac{0.0100 \cancel{\text{moles } Fe_2(SO_4)_3}}{\text{L}}}_{\boxed{\text{Molarity (moles/L)}}} \Bigg| \underbrace{\frac{\mathbf{6} \text{ Eq of } SO_4^{2-}}{1 \cancel{\text{mole } Fe_2(SO_4)_3}}}_{\boxed{\text{Conversion Factor (Eq } SO_4^{2-}\text{/mole } Fe_2(SO_4)_3\text{)}}} \Bigg| = 0.0600 \underbrace{\left(\frac{\text{Eq of } SO_4^{2-}}{\text{L of Solution}}\right)}_{\boxed{\text{Equivalents of } SO_4^{2-} \text{ per Liter}}}$$

If the ***molarity*** of a $Fe_2(SO_4)_3$ solution is 0.0100 M, then the **Eq SO_4^{2-} *concentration*** is **0.0600 Eq of SO_4^{2-}/L**.

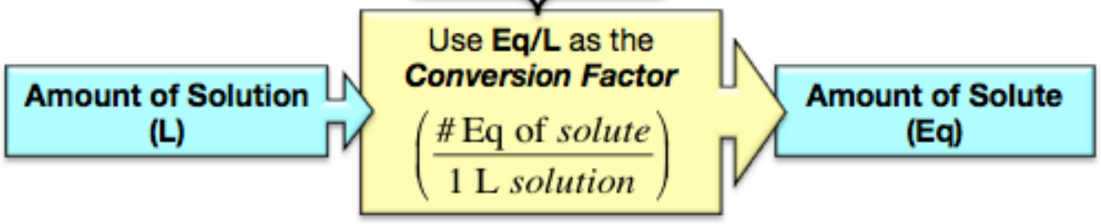
2) Use the Eq of SO_4^{2-}/L concentration as a conversion factor to convert from liters of solution to Eq of SO_4^{2-}:

a) Set up the equation using the given amount of solution:

$$\frac{0.830 \text{ L solution}}{} \Bigg| \qquad \Bigg| = \text{? Eq of } SO_4^{2-}$$

b) We need to convert **L** of solution to equivalents of SO_4^{2-}. To use the concentration as a conversion factor, we put the given units (**L** of solution) in the denominator so the given units will cancel, and then put the desired units (Eq of SO_4^{2-}) in the numerator:

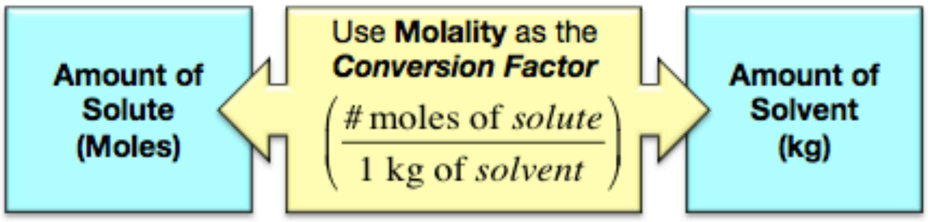
$$\frac{0.830 \cancel{\text{L solution}}}{} \Bigg| \frac{0.0600 \text{ Eq of } SO_4^{2-}}{1 \cancel{\text{L solution}}} \Bigg| = 0.0498 \text{ Eq of } SO_4^{2-}$$



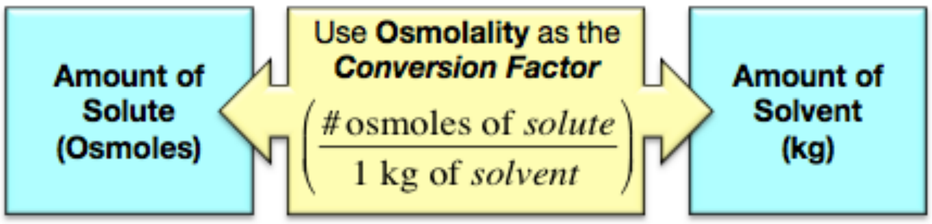
0.0498 Eq of SO_4^{2-} are contained in 0.830 L of a 0.0100 M $Fe_2(SO_4)_3$ solution.

Molality and Osmolality Concentration Calculations for Solutions

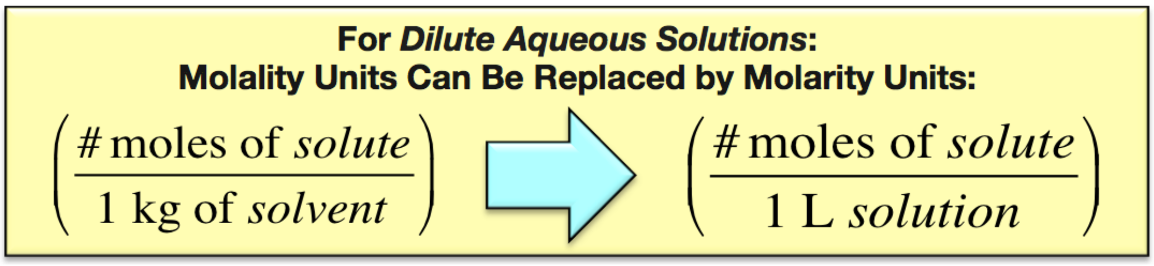
Molality is used to covert between ***moles of solute*** and **kg of solvent**:



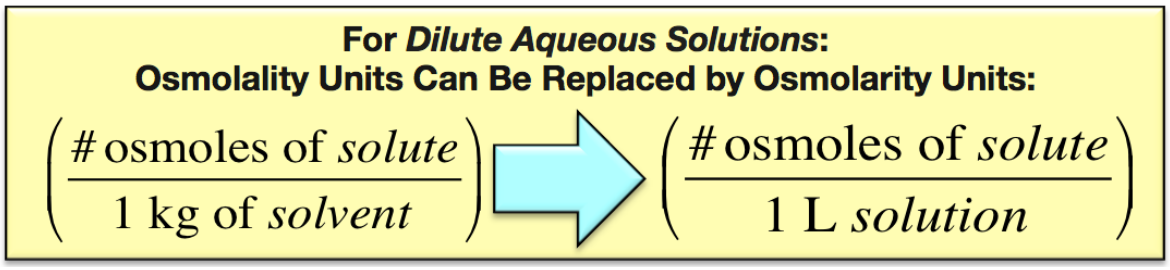
Osmolality is used to covert between osmoles of solute and kg of **solvent**:



In practice, it is more useful to know how much solute is contained in a particular **amount of solution *(not solvent)*** or how much **solution (*not solvent*)** contains a particular amount of solute. In order to work with the *amount of solution instead of the amount of solvent*, a very useful approximation can be made ***for dilute aqueous solutions***. In the case of dilute aqueous solutions, *the solution is almost entirely solvent*. Since 1 kg of water has a volume of 1 L, it is a reasonable approximation to equate ***the amount of solution*** to ***the amount of solvent;*** 1 kg of solvent is ***assumed*** to be the same as 1 L of solution. Using this approximation, the molality is equal to the molarity; we can ***replace*** molality units with molarity units:



For the same reason, using this approximation, the osmolality is equal to the osmolarity; we can ***replace*** osmolality units with osmolarity units.



After switching these concentration units, calculations that involve converting between *amount of solute* and *amount of **solution*** can be done using ***molarity*** or ***osmolarity*** as conversion factors.

Summary of Conversion Factors for Solution Calculations

Amount of Solute	When converting Between Use One of the Following Concentrations as the Conversion Factor:	Amount of Solution
moles of solute	**molarity** (moles/L)	liters (L) of solution
osmoles of solute	**osmolarity** (osmoles/L)	liters (L) of solution
equivalents (Eq) of solute	**equivalents/L** (Eq/L)	liters (L) of solution
mass of solute (typically grams)	**% (w/w)** typically (g solute/100 g solution)	mass of solution (typically grams)
volume of solute (typically mL)	**% (v/v)** typically (mL solute/100 mL solution)	volume of solution (typically mL)
grams of solute	**% (w/v)** (g solute/100 mL solution)	mL of solution

It is very likely that many of you who are reading this book will be taking physiology, medical technology, pharmacology, clinical chemistry, and/or other courses that require you to be able to do calculations for solutions. My colleagues who teach physiology, for example, would expect you to be able to do these calculations ***upon arrival in their class***. The way to become proficient at calculations for solutions is to ***do many problems***, therefore **I strongly suggest that you download and work on the following worksheet.** The worksheet contains a key in the form of a step-by-step solution manual (not just numerical answers).

Worksheet and Key: Calculations for Solutions Problems

www.zovallearning.com/GOBlinks/ch7/calculations-for-solutions.pdf

7.8 The Solubility of Biological Compounds

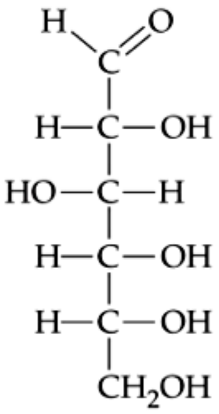
Biological compounds are the organic compounds that occur in biological organisms. Examples of biological compounds that you will learn about in this book are: steroids, fatty acids, bile salts, phospholipids, glycolipids, cholesterol, triglycerides (animal fat and vegetable oil), proteins, carbohydrates, RNA, and DNA. Biological compounds can be put into one of three categories based on their water solubility:

1) Hydrophilic
2) Hydrophobic
3) Amphipathic

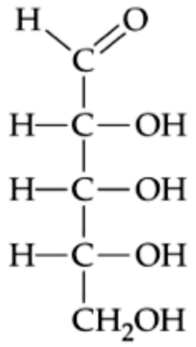
Let's take a look at each of these solubility classes and some examples of the biological compounds that they contain.

1) Hydrophilic Compounds

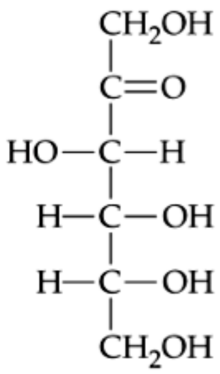
Hydrophilic compounds dissolve in water. The word *hydrophilic* is derived from an ancient Greek word that is translated as "loving water." Compounds that are significantly polar and/or can hydrogen bond with water tend to be water soluble. As a general rule, molecules that have at least ***one polar functional group*** for every ***five carbon atoms*** are water soluble, and therefore classified as **hydrophilic.** You saw *four* ***polar functional groups*** in chapter 4 (section 10): the hydroxyl group (-OH), the carbonyl group (C=O), the carboxyl group (-COOH), and the carboxylate group (COO). There are a few other polar functional groups that you will see in later chapters. The presence of ***formal charge*** will also help a biological compound to dissolve in water because of the attraction of water molecules' dipoles to the charged region of the compound (ion-dipole interactions). *Monosaccharides* are examples of ***hydrophilic compounds***. Monosaccharides are the smallest types of carbohydrate molecules. The structural formulas of three monosaccharides are shown below:



D-Glucose
(makes up starch and
cellulose; source of energy)



D-Ribose
(occurs in ATP, RNA,
and coenzymes)

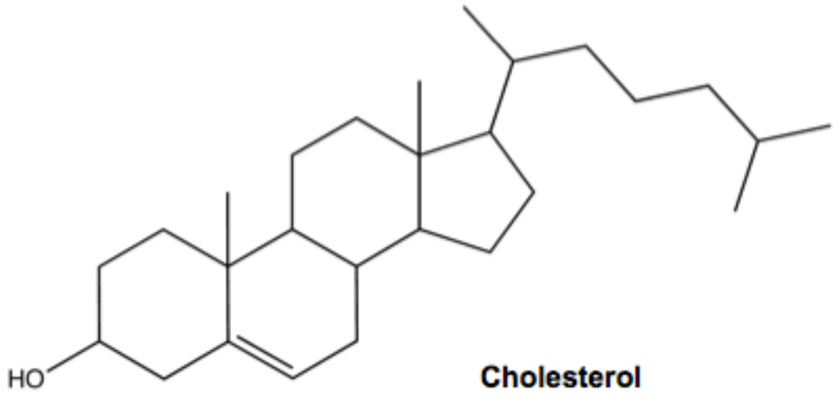


D-Fructose
(sweeter than table sugar,
a component of corn
syrup, occurs in fruit)

The relatively high ratios of polar functional groups (carbonyl groups and hydroxyl groups) to carbon atoms make these and other monosaccharides ***hydrophilic***.

2) Hydrophobic Compounds

Hydrophobic compounds ***do not dissolve*** in water. The word *hydrophobic* is derived from the ancient Greek word that is translated as "having a horror/fear of water." As a general rule, molecules that have ***<u>less than</u> one polar functional group*** for every ***five carbon atoms*** do not dissolve in water and are therefore *hydrophobic*. An example of a hydrophobic compound is the cholesterol molecule:

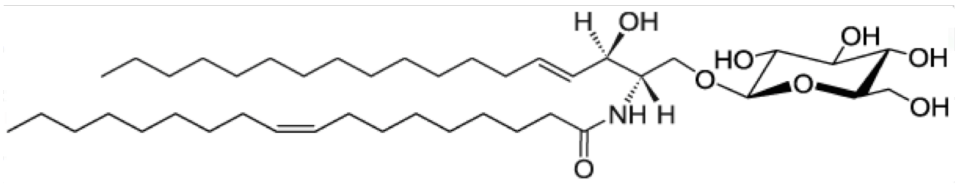


Cholesterol

Note that cholesterol does have *one* polar hydroxyl (-OH) functional group, however the nonpolar part of the molecule is so large that the ratio of polar functional group to total carbons is ***much less*** than **1:5** and therefore cholesterol does not dissolve in water.

Amphipathic Compounds

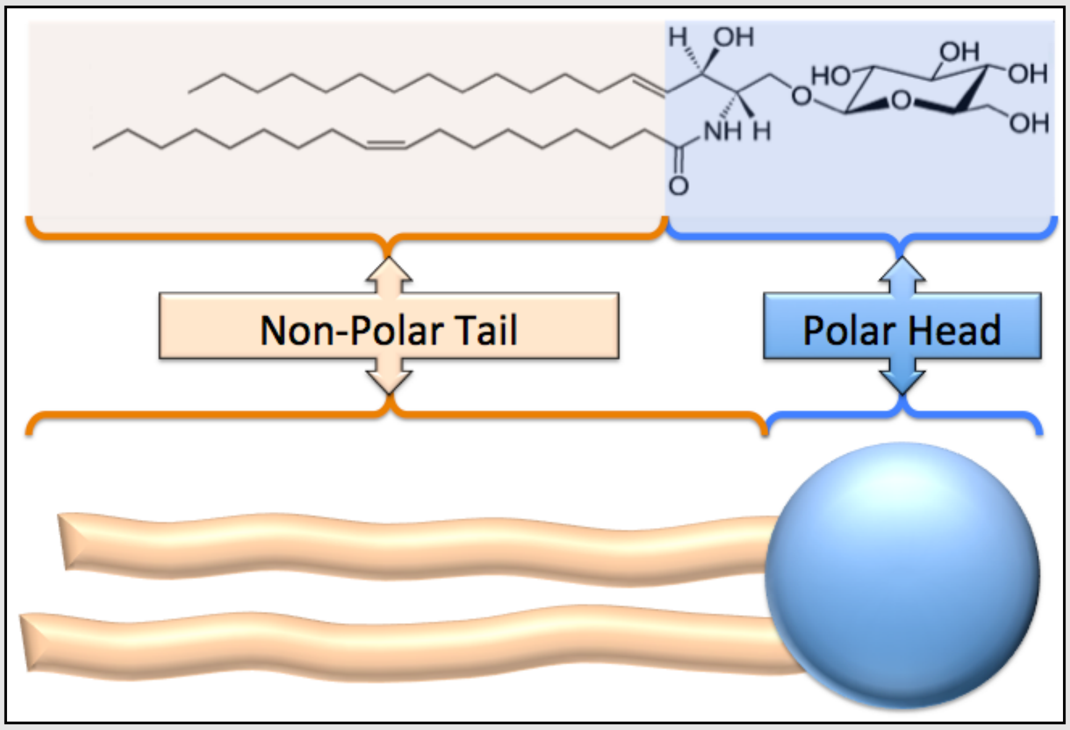
Amphipathic compounds have **both** a large ***nonpolar*** region, which is *not* strongly attracted to water, ***and*** an extremely polar and/or formally-charged region, which is quite strongly attracted to water. *Glycolipids* are examples of amphipathic biological compounds. The particular glycolipid shown in the structure below is one of the most prevalent of the glycolipids that make up cell membranes within the brain.



Which end of the glycolipid shown above (left-hand side or right-hand side) do you think is attracted to water? I hope you recognized that the polar hydroxyl groups and the carbonyl group on the right-hand end of the molecule are strongly attracted to water. The left-hand end of the molecule is a nonpolar region that *does not* have significant attractive interactions with water, however this nonpolar region is strongly attracted to large nonpolar regions of other particles. The large, nonpolar part of the molecule is called the nonpolar "tail." The region of an amphipathic compound that is attracted to water is called the polar "head." The polar head and nonpolar tail regions of our glycolipid example molecule are indicated in Figure 7.16. The polar head region is shaded light blue and the nonpolar tail region is shaded light orange. Amphipathic compounds are often illustrated using a sphere for the polar *head* that is attached to one or more long tubular structures that represent the carbon chains in the nonpolar tail*,* as shown on the bottom of Figure 7.16.

Figure 7.16

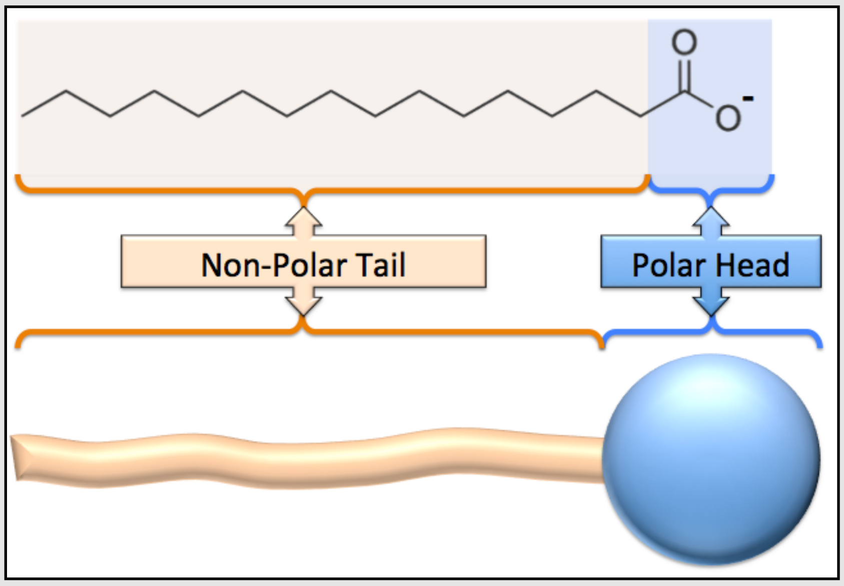
Head and Tail Representation of Amphipathic Compounds



The polar head and nonpolar tail regions of a glycolipid molecule are indicated by the shaded regions. The polar head region is shaded light blue and the nonpolar tail region is shaded light orange. Amphipathic compounds are often illustrated using a sphere for the polar head that is attached to one or more long tubular structures that represent the carbon chains in the nonpolar tail.

Figure 7.17

Head and Tail Representation of Palmitate



In some amphipathic compounds, the tail is composed of only *one* carbon chain. An example of an amphipathic compound that has a single carbon chain tail is palmitate.

In some amphipathic compounds, such as our glycolipid example above, there are *two* carbon chains that make up the nonpolar tail; in other amphipathic compounds, the tail is composed of only one carbon chain. An example of an amphipathic compound that has a single carbon chain tail is palmitate (Figure 7.17). Palmitate is abundant in animals and in some plants. It is a part of animal fat and vegetable oil and is especially highly concentrated in palm oil, hence the name ***palm***itate.

Figure 7.18 Illustration of a Monolayer

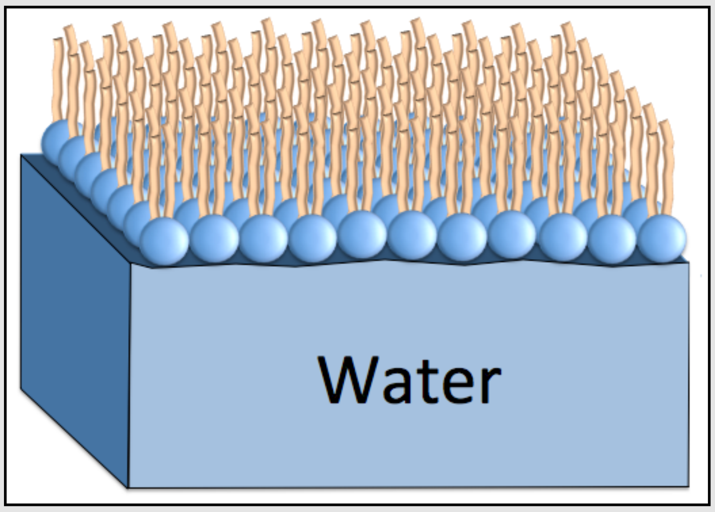
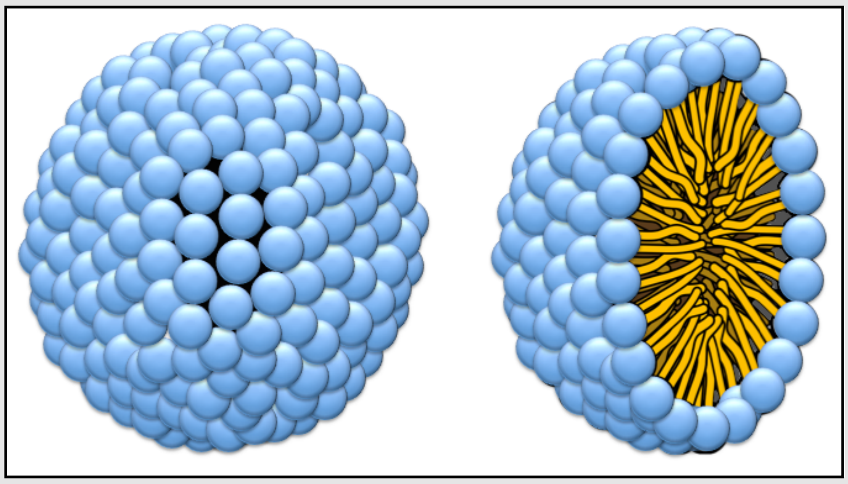


Illustration of a monolayer. Amphipathic compounds form a single (mono) layer of individual particles oriented with their polar heads toward the water and their nonpolar tails pointing upward.

When amphipathic molecules are put into water, they exist as **monolayers** and/or **micelles.** As ***monolayers***, amphipathic compounds form a single (mono) layer of individual particles oriented with their polar heads toward the water and their nonpolar tails pointing upward as illustrated in Figure 7.18.

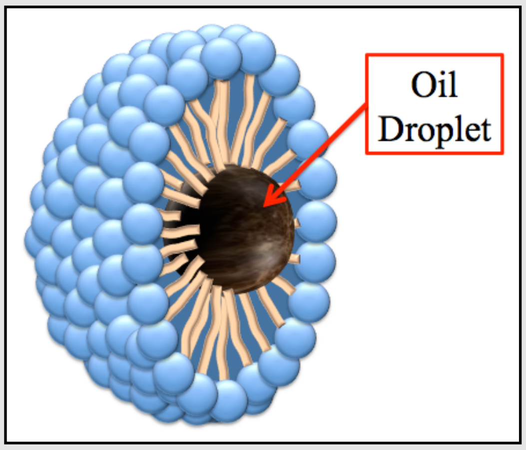
Figure 7.19 Micelle and Micelle Cross Section



Amphipathic compounds making up micelles are oriented with their polar heads outward, toward the water and their nonpolar tails inward, away from the water. **Left:** An illustration of an entire micelle. **Right:** A cross section illustration of the micelle is shown in order for you to visualize the orientation of the nonpolar tails.

Amphipathic compounds can also exist in water as *spherica*l arrangements called ***micelles***. The amphipathic compounds making up micelles are oriented with their polar heads outward, toward the water, and their nonpolar tails inward, away from the water. An illustration of a micelle is shown on the left hand side of Figure 7.19. A cross-sectional illustration of the micelle is shown on the right hand side of Figure 7.19 in order for you to visualize the orientation of the nonpolar tails. Notice that micelles can exist ***within*** the water because of the attraction between the polar heads and the surrounding water molecules.

Figure 7.20 An Oil Droplet Encapsulated within a Micelle



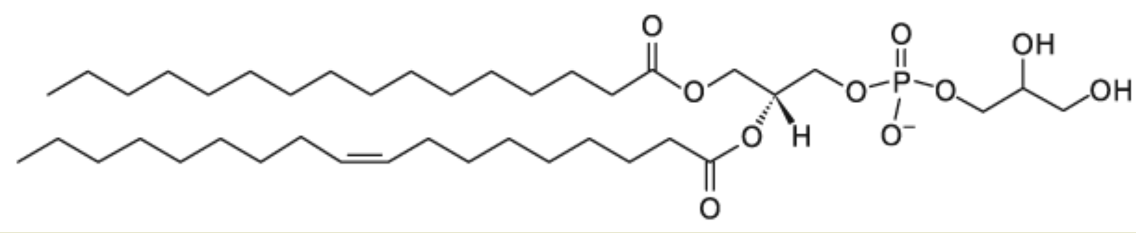
A cross sectional illustration of a soap micelle containing an oil droplet. Soap consists of amphipathic compounds that form micelles capable of encapsulating oil within the their nonpolar tail interiors.

Soap consists of palmitate and/or similar amphipathic compounds. As you know, soap *and* water are much more effective at removing oil from skin than is just water alone. This is because there is no strong attraction between the nonpolar oil molecules and water; however soap forms micelles that *encapsulate* the oil within their nonpolar tail interiors. Micelles containing the oil can move into the rinse water and away from the skin. An illustration of an oil droplet that is encapsulated in a micelle is shown in Figure 7.20. When a liquid contains compounds that are encapsulated by amphipathic compounds in micelles, the mixture is called an **emulsion**. Other emulsions that you are familiar with are hand lotion and mayonnaise.

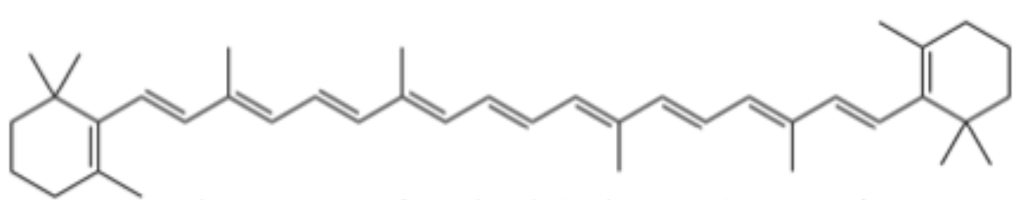
Review 7.25: Classification of Biological Compounds

Predict whether each of the following biological compounds is **hydrophobic** or **amphipathic**?

a.



b.



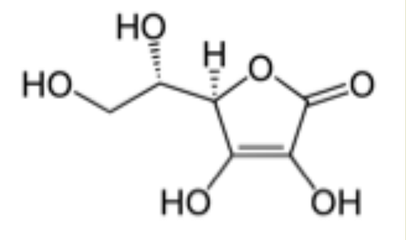
beta-carotene (a molecule in the vitamin A group)

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

Review 7.26: Classification of Biological Compounds

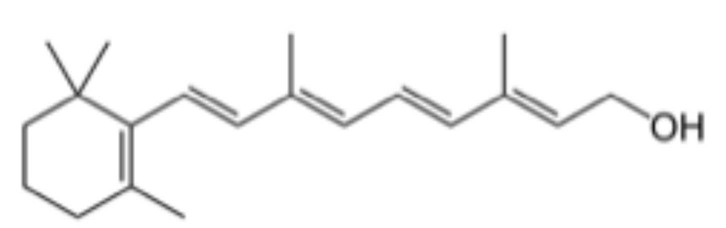
Predict whether each of the following biological compounds is **hydrophilic** or **hydrophobic**?

a.



vitamin C

b.

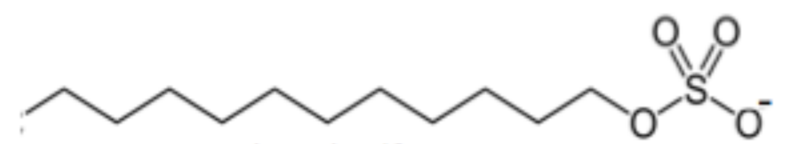


retinol (a molecule in the vitamin A group)

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

Review 7.27: Classification of Biological Compounds

The ion shown below is called laurel sulfate. Laurel sulfate is amphipathic and is often used in shampoo. Is the ***polar head*** located on the *right-hand* ***or*** *left-hand* end of the molecule as it is illustrated below?



laurel sulfate

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

7.9 Dilutions

Dilution is the process of adding more ***solvent*** to a solution. Of course when this occurs, the solution's concentration is decreased. Figure 7.21 shows a series of dilutions (left to right) of a solution containing a red-colored solute. When considering dilutions, the concentration of the solution is ***inversely proportional*** to the volume of the solution. For example, if enough solvent is added to ***double*** the volume, then the concentration is ***decreased by a factor of 1/2***. As you saw in chapter 5 with Boyle's gas law, when properties are inversely proportional, the *product* of the initial and final properties are equal. In the case of dilution, the product of the initial (un-diluted) concentration (C_1) and the volume before dilution (V_1) ***is equal to*** the product of the final (diluted) concentration (C_2) and the final volume (V_2):

Figure 7.21 A Series of Dilutions

A series of dilutions (left to right) of an aqueous solution containing a colored solute.
Source: Wikimedia Commons
Author: A. Markov, CC-BY,
http://creativecommons.org/licenses/by/2.0/legalcode

$$C_1 \bullet V_1 = C_2 \bullet V_2$$

This equation is called the "***dilution equation***" and it can be used with any of the concentration units of measure that include the *volume of solution* (molarity, osmolarity, % (w/v), % (v/v), or Eq/L). For example, the dilution equation can be written using molarity concentration:

$$M_1 \bullet V_1 = M_2 \bullet V_2$$

Take a look at a couple of example dilution problems:

Example: If 25 mL of a 1.5 M solution is diluted to a final volume of 235 mL, what is the final concentration?

The *dilution equation* contains four variables; M_1, V_1, M_2, and V_2. When any three of these variables are known, the forth variable can be found using algebra.

- In this example, we know M_1, V_1, and V_2, and we wish to find the final concentration (**M_2**):

$$M_1 \bullet V_1 = M_2 \bullet V_2$$

$$M_1 = 1.5 \text{ M} \qquad M_2 = ??? \text{ M}$$

$$V_1 = 25 \text{ mL} \qquad V_2 = 235 \text{ mL}$$

- To solve for **M_2**, we divide ***both sides*** of the equation by **V_2**. After doing so, **V_2** cancels on the right-hand side, and we have isolated the unknown variable (**M_2**):

$$M_2 = \frac{M_1 \bullet V_1}{V_2}$$

- Insert the known values of M_1, V_1, and V_2, and then solve for the final concentration (**M_2**):

$$M_2 = \frac{(1.5 \text{ M}) \bullet (25 \cancel{\text{mL}})}{(235 \cancel{\text{mL}})} = 0.16 \text{ M}$$

The final concentration of the diluted solution is 0.16 M. It is always a good idea to check to see **if your answer makes sense**; the value of the calculated final concentration should be ***less than*** the initial concentration!

Example: What final volume would be needed in order to dilute 0.25 L of a 1.0 M solution to a final concentration of 0.070 M?

- In this example, we know M_1, V_1, and M_2, and we wish to find the final volume (**V_2**):

$$M_1 \bullet V_1 = M_2 \bullet V_2$$

$$M_1 = 1.0 \text{ M} \qquad M_2 = 0.070 \text{ M}$$

$$V_1 = 0.25 \text{ L} \qquad V_2 = ??? \text{ L}$$

- To solve for **V_2**, we divide ***both sides*** of the *dilution equation* by **M_2**. After doing so, **M_2** cancels, and we have isolated the unknown variable (**V_2**):

$$V_2 = \frac{M_1 \bullet V_1}{M_2}$$

- Insert the known values of M_1, V_1, and M_2, and then solve for the final concentration (**V_2**):

$$V_2 = \frac{(1.0\ \cancel{\text{M}}) \bullet (0.25 \text{ L})}{(0.070\ \cancel{\text{M}})} = 3.6 \text{ L}$$

To obtain a final concentration of 0.070 M, 0.25 L of a 1.0 M solution must be diluted to a final volume of 3.6 L. Check to **see if your answer makes sense**; the value of the calculated final volume should be ***greater than*** the initial volume!

Now you try a couple of dilution problems:

Review 7.28: Using the Dilution Equation

If 1.70 L of a 1.50 M solution is diluted to a final volume of 3.50 L, what is the final concentration?

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

Review 7.29: Using the Dilution Equation

If 2.00 L is ***added*** to 0.50 L of a 0.200 M solution, what is the final concentration?

HINT: Be careful, think about what the final volume (V_2) would be; ***it is not*** 2.00. The question says "...2.00 L is ***added*** ...."

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

7.10 Colloids and Suspensions

When particles that are larger than typical molecules or ions are put into another medium, typically water, the resulting mixture is classified as either a **colloid** or a **suspension** depending on the particle size. In ***colloids***, the dispersed particles (***colloidal particles***) are small enough that they *do not settle to the bottom of their container*. Conversely, in ***suspensions***, the solid particles are large enough that gravity causes them to settle to the bottom of their container unless the mixture is repeatedly or constantly stirred or shaken.

Colloids

Colloidal particles are typically in the size range of ***1 nanometer up to 1 micrometer***. Because of their relatively small size, the kinetic energy from collisions with the particles making up the medium, typically water molecules, overcomes the force of gravity and the particles remain evenly dispersed in the medium. If the particles are very small, the colloid will not "scatter" light and it will therefore appear clear or colored (but not cloudy). As the particle size gets larger, a colloid mixture will appear cloudy since the light entering the medium is scattered in many different directions by particles. Particles will scatter visible light when they are approximately 0.3 micrometers or larger.

The ***micelles*** that you learned about in Section 6 of this chapter are examples of colloids. Another example of a colloid is milk. Milk contains small agglomerations of many individual protein molecules (these particles are called "casein") as well as particles composed of emulsified fat (triglyceride) molecules. It is these fat particles that are separated from milk to make butter. Milk is classified as a *colloid* rather than a *suspension* because the colloidal particles do not settle to the bottom. Note that milk containers do not say "*shake well before using*" because the particles are small enough to remain evenly dispersed. Other examples of colloids are mayonnaise and hand lotion.

Milk

Milk is a colloid that contains small protein and fat particles.

Suspensions

The solid particles contained in **suspensions** are typically larger than 1 micrometer. Because of their relatively large size compared to colloidal particles, the force of gravity causes the particles to settle to the bottom of the container. The settling process may take seconds or several hours. When stirred or shaken, the suspension will appear cloudy since the particles are large enough to scatter light. An example of a suspension is muddy water. If muddy water is constantly stirred, the clay/dirt particles are evenly distributed throughout the container; however if the stirring is discontinued, the particles will settle to the bottom of the container. Other examples of suspensions are orange juice and pepto-bismol medication. If a liquid contains solid particles and is labeled "shake well before using," then ***it is a suspension***. Orange juice containers are labeled "shake well before using" because the solid particles settle to the bottom. You have likely witnessed this yourself in a glass of orange juice that has been left alone for a few hours.

Orange Juice

Orange juice is a suspension because the solid particles eventually settle to the bottom the container. Source: US-PD

Review 7.30: Understanding Colloids and Suspensions

If sand is added to a glass of water, is the resulting mixture a colloid or suspension?

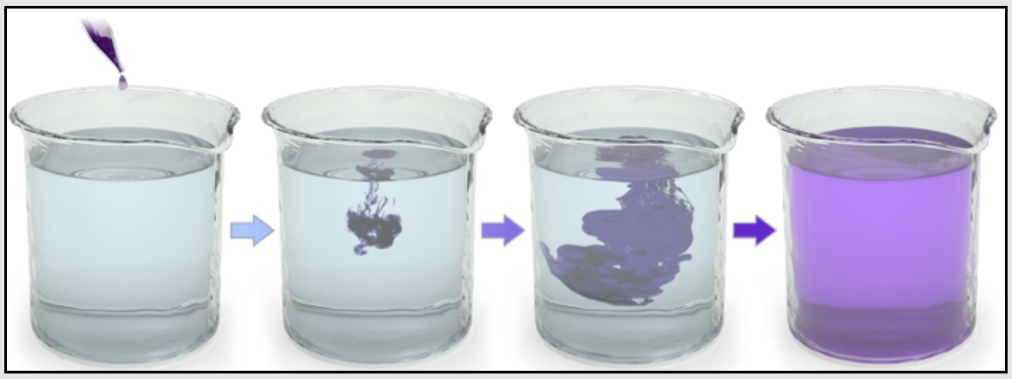
For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

7.11 Diffusion and Osmosis

Diffusion

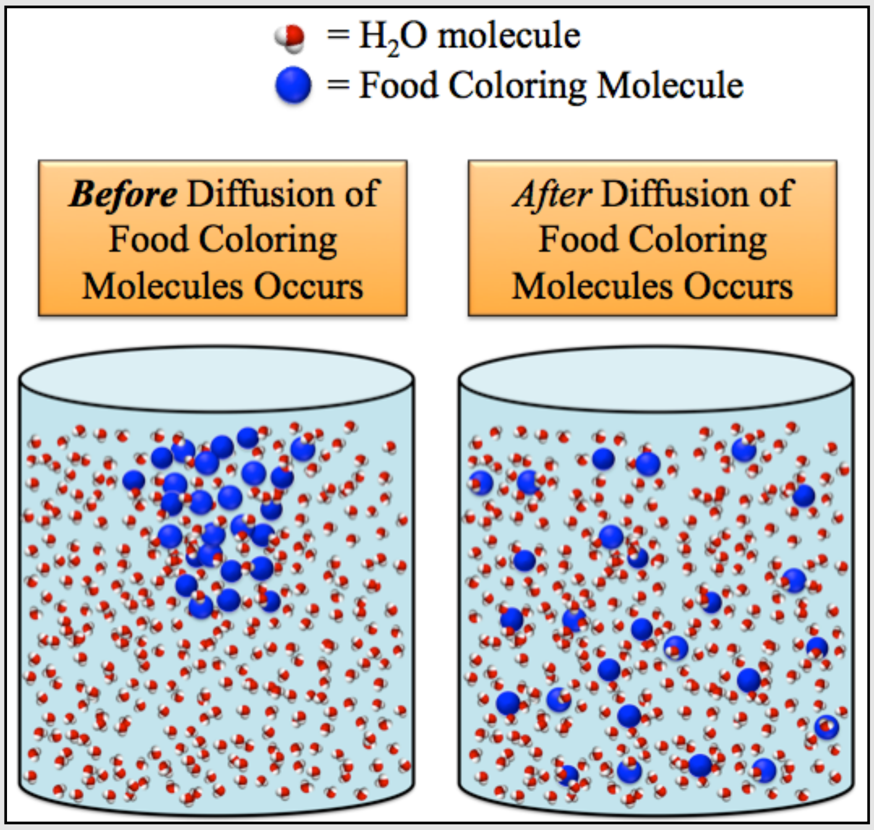
Just like gases, solute and solvent particles in a liquid phase solution travel in random directions until they collide with other particles or the container wall. This type of random movement is called ***Brownian motion*** and results in a process called **diffusion**. ***Diffusion*** is defined as the net transport of a substance, due to *Brownian motion,* from a region of greater concentration of the substance to a region of lesser concentration of the substance. It is the random movement of particles that causes them to be evenly mixed. Diffusion can be macroscopically observed when a few drops of food coloring are placed in a glass of water as shown in the time lapse images of Figure 7.23.

Figure 7.23
Diffusion of Food Coloring Molecules in Water



Time lapse images (left to right) of purple food coloring dropped into water.
Source: Wikimedia Commons, Author: Bruce Blaus
CC-BY: http://creativecommons.org/licenses/by/2.0/legalcode

Figure 7.22 Illustration of Diffusion



Left: Food coloring solute molecules (blue spheres) the moment they are place in water. **Right:** After some time, the diffusion process results in the even distribution of the food coloring molecules throughout the mixture.

Let's consider diffusion *on the nanoscale* as illustrated in Figure 7.22. The container on the left of the figure represents the mixture at the moment the food color molecules are placed in water. At that moment, there is a greater concentration of food coloring molecules (represented by blue spheres) in one region and zero concentration elsewhere. Brownian motion causes the dye molecules to eventually distribute themselves evenly throughout the mixture as shown in the container on the right-hand side of Figure 7.22.

In the diffusion process, substances will ***spontaneously*** move from an area of greater concentration (of the particular substance) to lesser concentration until it is evenly distributed. It is important to note that *water molecules* also diffuse in the example. At the moment the food coloring is added, it displaces some water molecules and, as seen in the container on the left of Figure 7.22, there is a lesser concentration of water molecules in the region of the food coloring molecules and greater concentration of water everywhere else. Brownian motion causes a net transport (diffusion) of water molecules into the region where the food coloring was placed. Both water and food coloring molecules diffused; however, they diffused in opposite directions. When a substance is not evenly distributed and has a greater concentration in one region and a lesser concentration in another region, we say that there is a "**concentration gradient**." Whenever a ***concentration gradient*** is present, and there is not a physical barrier preventing transport, diffusion will occur. In diffusion, we say that the diffusing species move "*with* the concentration gradient." There can only be a net movement of dissolved particles from areas of *lesser* concentration to areas of *greater* concentration (***against*** the concentration gradient) ***when external energy is supplied***. You will learn more about that in later chapters.

Osmosis

A **semipermeable membrane** is any type of physical barrier through which only certain substances can pass. For example, many membranes, both natural and synthetic, are ***permeable*** to water (allow water to pass) but are ***impermeable*** to ions (do not allow ions to pass). As a general rule, *biological membranes* in cells, are permeable to nonpolar molecules and small polar molecules, and are impermeable to ions and large polar molecules. Water molecules pass through holes (pores) in biological membranes called ***aquaporins***.

Osmosis *is the net transport of* ***solvent*** *from a* solution with a *lesser* **solute** particle concentration *through a semipermeable membrane* to a solution with a *greater* **solute** particle concentration. Note that a semipermeable membrane allows ***solvent*** to *continuously* move *back and forth* ***between both sides of a membrane***; however in ***osmosis***, there is a greater amount of solvent transported in the direction from the side of the membrane with ***lesser*** solute particle concentration to the side of the membrane with greater solute particle concentration, resulting in a ***net transport of solvent*** in that direction. Osmosis is difficult to explain in terms of simple physical models and it is beyond the scope of this book to discuss theses models. We will only discuss osmosis for ***aqueous solutions***, therefore for our purposes, **osmosis** *is the net transport of* **water molecules** *from a* solution with a *lesser solute* particle concentration *through a semipermeable membrane* to a solution with a *greater solute* particle concentration.

Osmosis is very important in biology because cell membranes are semipermeable. The difference in solute particle concentration (osmolarity) between the inside of the cell and the surrounding solution has important implications in maintaining the viability of the cell. Consider the three different cases for the solution that surrounds a cell:

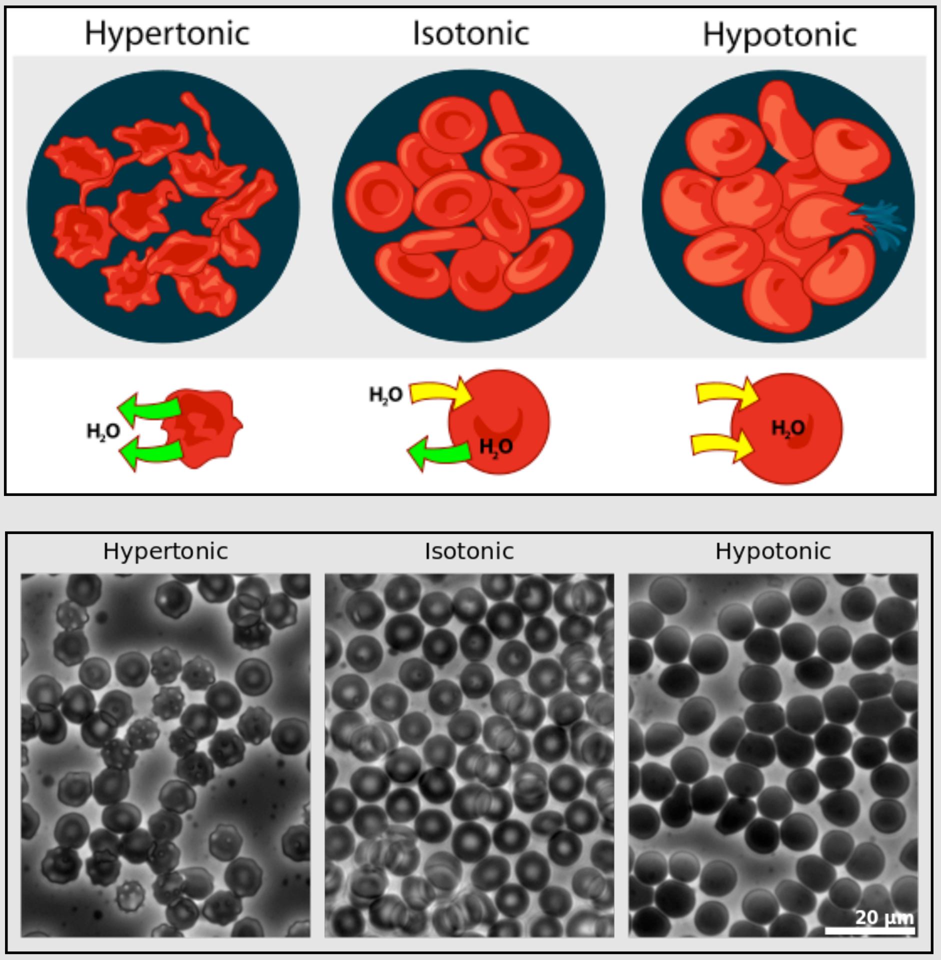
1) In a **hypertonic solution**, there is a greater solute particle concentration outside the cell than inside of the cell, so there is a net flow of water from the inside to the outside of the cell. This results in the shrinking of the cell.

2) In an **isotonic solution**, the concentration of solute particles is the same on the inside and outside of the cell, therefore the flow of water in and out of the cell *are equal* and the cell maintains it natural and healthy (viable) shape.

3) In a **hypotonic solution**, there is a lesser solute particle concentration outside the cell than inside the cell, and there is a net flow of water from the outside to the inside of the cell. This results in the swelling and possible bursting of the cell.

Figure 7.24 shows an illustration of the effect of each of these three types of solutions on red blood cells (top) and microscope images of human red blood cells in each type of solution (bottom).

Figure 7.24 Red Blood Cells in Hypertonic, Isotonic, and Hypotonic Solutions



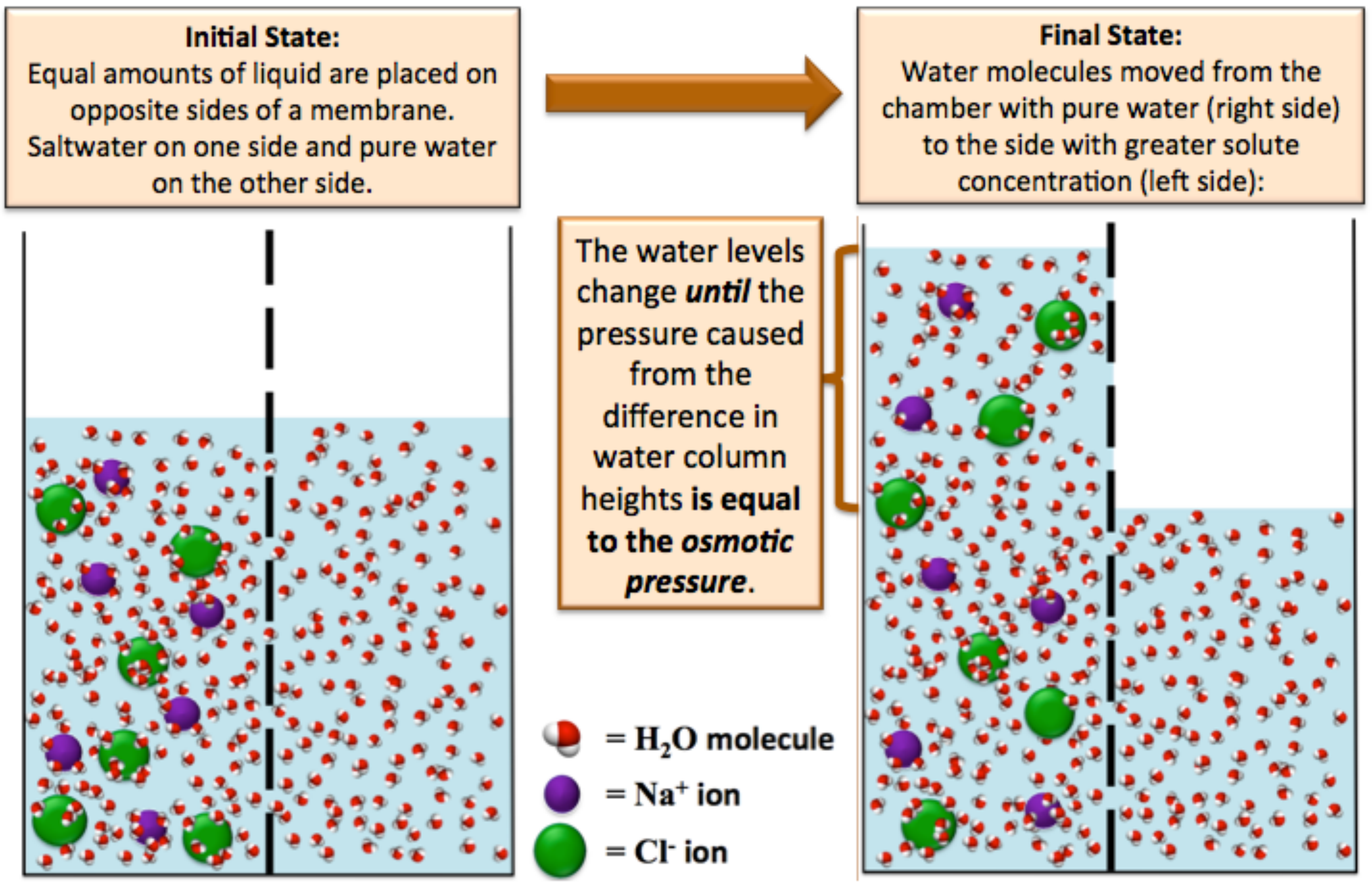
Top: Illustration of red blood cells in hypertonic, isotonic, and hypotonic solutions. The yellow and green arrows represent the net flow of water out of and into the cell. In a hypertonic solution, there is a greater solute concentration outside of the cell than inside of the cell, and there is a net flow of water from the inside to the outside of the cell. This results in the shrinking of the cell. In an isotonic solution, the concentration of solute is the same on the inside and outside of the cell, therefore the flow of water in and out of the cell are equal and the cell maintains its natural and healthy (viable) shape. In a hypotonic solution, there is a lesser solute concentration outside the cell than inside of the cell, and there is a net flow of water from the outside to the inside of the cell. This results in the swelling and possible bursting of the cell. Source: Wikimedia Commons, Author: ladyofhats, PD

Bottom: Human red blood cells viewed by phase contrast light microscopy. Source: Wikimedia Commons, Author: Zephryis CC-BY-SA, http://creativecommons.org/licenses/by-sa/3.0/legalcode

Osmotic Pressure

Osmosis will occur until the *pressure* on the side of the membrane with the greater solute particle concentration increases to a point at which the water molecules move *back and forth* between opposite sides of the membrane *at the same rate*. Consider a container that is divided by a semipermeable membrane. A saltwater solution is placed in the chamber on left-hand side of the membrane and an *equal volume* of pure water is placed in the chamber on the right-hand side of the membrane (as illustrated in Figure 7.25, labeled "Initial State"). At this point, ***osmosis begins***.

Figure 7.25 Illustration of the Osmotic Pressure Concept



A saltwater solution is placed in a chamber on the left-hand side of the semipermeable membrane and an equal volume of pure water is placed in a chamber on the right-hand side of the membrane (Initial State). At this point, osmosis begins. The water column levels on each side of the membrane will change until the pressure caused from the difference in the water column heights equalizes the transport of water molecules between both sides of the membrane (Final State). This excess pressure (applied to the side of the membrane with the greater solute concentration) that is required in order to stop the net flow of water and thereby stop osmosis is equal to the **osmotic pressure.**

There is a net transport of water molecules **from the solution with a *lesser solute particle* concentration (pure water in this scenario), through the membrane, and into the solution with a *greater solute particle* concentration.** As osmosis is occurring, water molecules move through the membrane ***in both directions,*** left *and* right, however, there are more water molecules moving from the pure water side of the membrane (right-hand side) to the greater solute particle concentration side (left-hand side). This results in the level of the water column rising on the left-hand side of the membrane and falling on the right-hand side. The water levels will continue to change until the pressure caused from the ***difference*** *in water column heights* on each side of the membrane ***equalizes*** the transport of water molecules between each side of the membrane (as illustrated and labeled "Final State" in Figure 7.25). **Osmotic pressure** is defined as the pressure associated with **osmosis**. The amount of excess pressure (applied to the side of the membrane with the greater solute particle concentration) that is required in order to stop the net flow of water, and thereby stop osmosis, is equal to the **osmotic pressure**. The greater the difference in ***osmolarity*** between each side of the semipermeable membrane, the greater the *osmotic pressure*.

For membranes that form a continuous enclosure around a solution, such as those of biological cells, the *osmotic pressure* is the pressure required to stop the net transport of water into *or* out of cells. When the solution around a cell becomes ***hypotonic***, there is a lesser solute particle concentration outside the cell than inside the cell, and therefore there is a net flow of water from the outside to the inside of the cell. As water flows into the cell, the pressure on the inside of the cell increases (imagine inflating a ballon). The pressure in the cell will continue to increase until either (1) the ***osmotic pressure*** is reached and osmosis stops, **or** (2) the cell bursts. The bursting of red blood cells is called *hemolysis* and is evidenced by the appearance of red color in the blood *plasma*.

Review 7.31: Understanding Osmotic Pressure

Which of the following systems (#1 or #2) would have a ***greater* osmotic pressure**:

System #1: 1.00 M sodium chloride on one side of a semipermeable membrane and pure water on the other side.

or

System #2: 0.500 M sodium chloride on one side of a semipermeable membrane and pure water on the other side.

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

Review 7.32: Understanding Osmotic Pressure

Which of the following systems (#1 or #2) would have a ***greater* osmotic pressure**:

System #1: 1.00 M $NaCl$ on one side of a semipermeable membrane and pure water on the other side.

or

System #2: 1.00 M $Fe_2(SO_4)_3$ on one side of a semipermeable membrane and pure water on the other side.

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

Chapter 8:
Acids, Bases, and pH

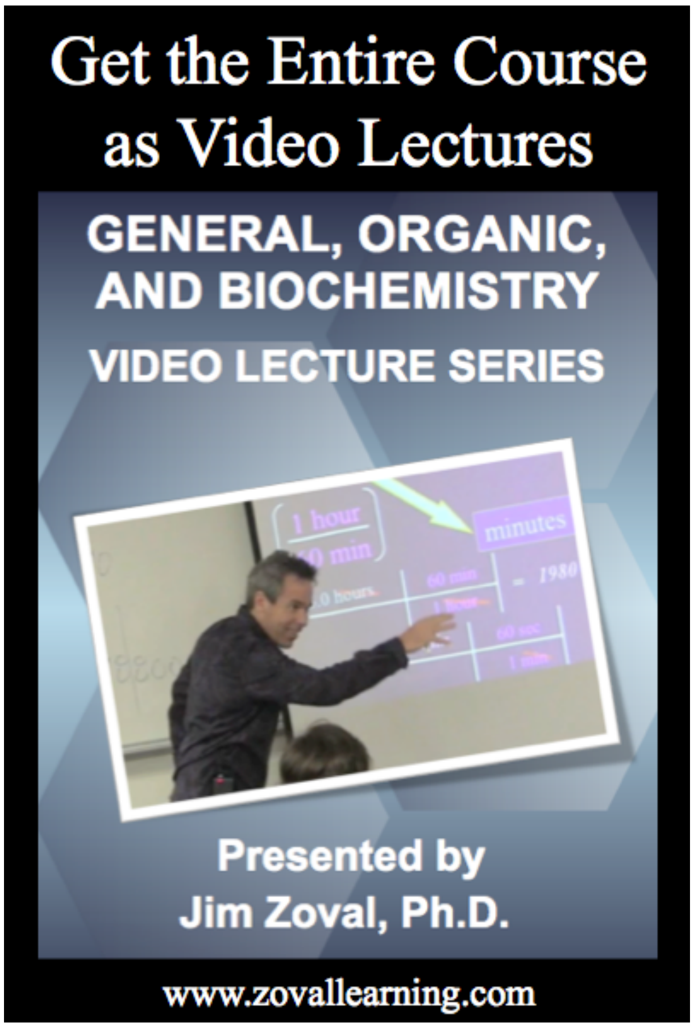
Hydrangea macrophylla

The color of the flowers on some species of Hydrangea, such as the *Hydrangea macrophylla* shown above, is determined by the acidity/basicity of the soil. Soils that are ***acidic*** cause *H. macrophylla* flowers to be blue (as seen in the photograph above), and soils that are ***basic*** cause the flower to be pink. In this chapter, you will learn what is meant by the terms **acid, base, acidic, basic, and pH.** For those of you are who are going into the healthcare field, it is quite likely that you will need to explain to a patient or co-worker what the normal blood pH range is, and what are the causes and effects of abnormal blood pH. You will learn about the chemical system called a "***buffer***" that is used in nature to control the pH in plants and animals. In order for you to adequately understand acids, bases, pH, and buffers, I must begin this chapter by discussing a concept called **chemical equilibrium**.

Video Lectures for the General, Organic, and Biochemistry Course

If you **ARE** a **Saddleback College student**, the video lectures for this chapter and all others are available through your class website for ***FREE***. See your instructor for details and the password.

If you **ARE NOT** a **Saddleback College student,** the video lectures can be accessed at: www.zovallearning.com



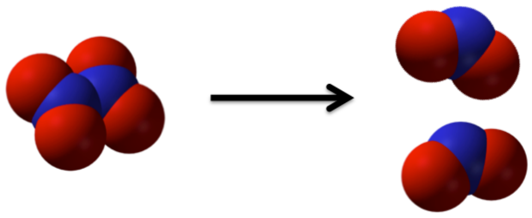
8.1 Chapter 8 Educational Goals

1. Given a chemical equation, write the **law of mass action**.
2. Given the **equilibrium constant** (K_{eq}) for a reaction, predict whether the reactants or products are predominant.
3. Use **Le Châtelier's Principle** to explain how a chemical reaction at equilibrium responds when a change is made to the concentration of reactant or product.
4. Know the definitions of Bronsted-Lowry acids and bases.
5. Given the ***acid form*** or the ***base form*** of a **conjugate pair**, identify its conjugate.
6. List the properties of **acidic** and **basic solutions**.
7. Understand the term "**acid strength**," and know how acid strength is related to the **acidity constant** (K_a) value.
8. Given the $[H_3O^+]$, be able to calculate the $[OH^-]$ (and vice versa).
9. Given the $[H_3O^+]$, be able to calculate the pH (and vice versa).
10. Given the $[H_3O^+]$, $[OH^-]$, or pH, be able to characterize a solution as being **acidic**, **basic**, or **neutral**.
11. Given the reactants, predict the products of a **neutralization reaction**.
12. Given the pH of a solution and the pK_a for a particular acid, determine whether the acid form or the base form of the conjugate pair is predominant.
13. Define a **buffer**, and describe how a buffer solution is made.

8.2 Chemical Equilibrium

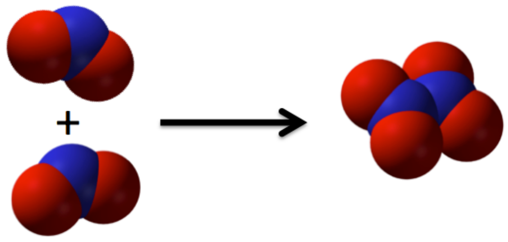
In chapter 6, you learned about **chemical reactions.** You learned that in chemical reactions, new chemical bonds are made and/or existing chemical bonds are broken, and in doing so, ***reactants*** are converted to new substances that we called ***products***. You learned to represent chemical reactions with ***chemical equations*** by writing the formulas of the reactants, then an arrow, followed by the formulas of the products. *What I did not tell you* in chapter 6 is that the products can be converted back into reactants! This is especially important if the reaction occurs in a closed system such as a liquid or gas in a container, or a biological system such as a cell. I will elaborate on the reversibility of chemical reactions using an example.

Dinitrogen tetroxide (N_2O_4) can undergo a *decomposition reaction* to produce two nitrogen dioxide (NO_2) molecules:



$$N_2O_4\,(g) \longrightarrow 2\,NO_2\,(g)$$ *Reaction 8.1*

The ***reaction is reversible***; two NO_2 molecules can collide and then bond with each other to form N_2O_4:



$$2\,NO_2\,(g) \longrightarrow N_2O_4\,(g)$$ *Reaction 8.2*

Figure 8.1
NO_2 (*g*) and N_2O_4 (*g*) in a glass bottle.

At room temperature, significant amounts of ***both*** **NO_2** and **N_2O_4** are present in the bottle. The brown color is from **NO_2**.

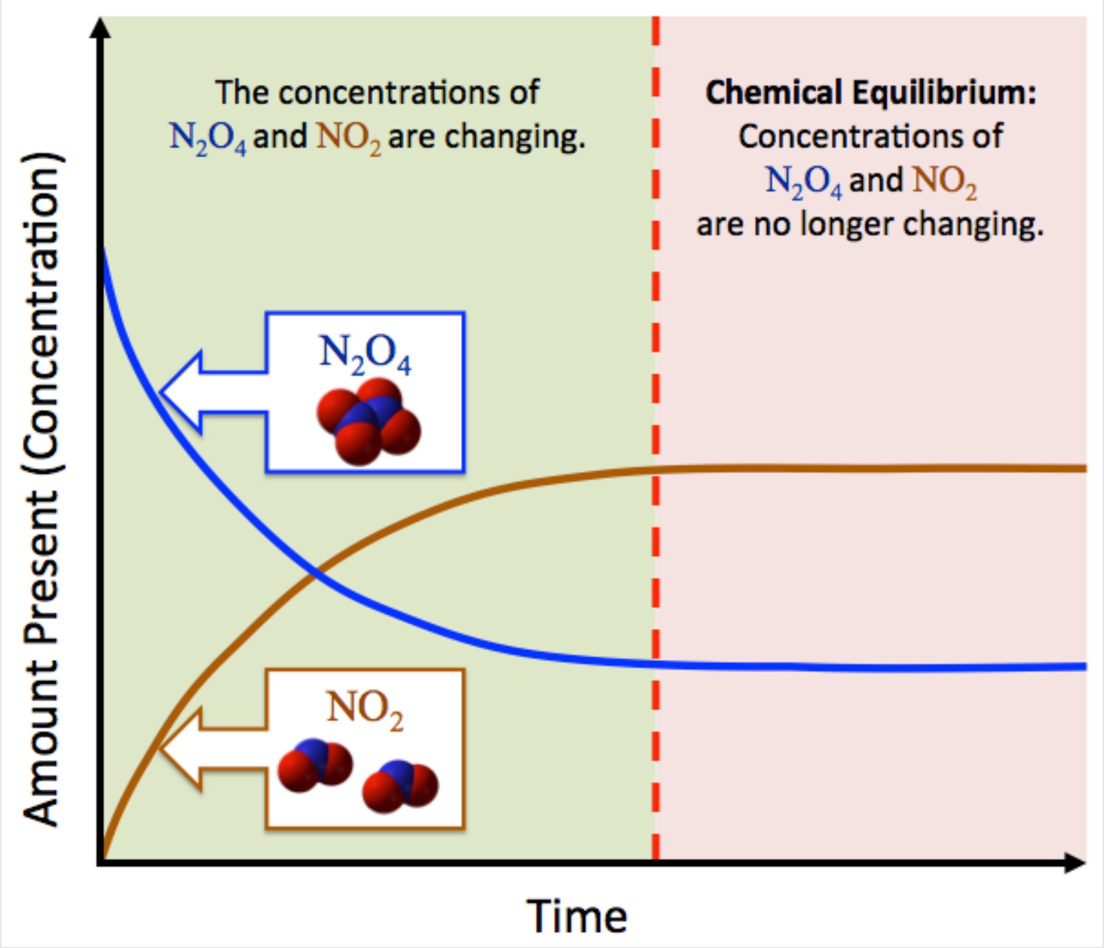
N_2O_4 is colorless, therefore invisible.
Source: PD

N_2O_4 can be isolated in a closed container by lowering the temperature. At low temperatures, N_2O_4 does not have enough energy to decompose (break the N-N bond) to two NO_2 molecules at a significant reaction rate. At low temperatures, *Reaction 8.1* proceeds extremely slowly; however the ***reverse reaction*** (*Reaction 8.2*, which converts NO_2 to N_2O_4) is not as sensitive to temperature and proceeds at a much faster rate. Therefore at low temperatures, N_2O_4 is abundant, and only a trace (very small amount) of NO_2 is present.

Suppose we have a sealed glass container of N_2O_4 at a vey low temperature, and then quickly warm the container to 100°C. As the temperature increases, the rate of *Reaction 8.1* increases and therefore the amount/concentration of NO_2 in the container will increase. N_2O_4 is a *colorless gas* (looks like air) and NO_2 is a *brown gas*. When the container reaches 100°C, the increased amount of NO_2 is easily observed by the appearance of its brown color, as shown in Figure 8.1. As the amount of NO_2 increases, *so does the rate of Reaction 8.2*; the more NO_2 that is present, the greater the chances of two NO_2 molecules colliding with each other and reacting to form N_2O_4. The concentration of NO_2 will increase until the rate of *Reaction 8.2* reaches a point that NO_2 is being converted back into N_2O_4 at the same rate that N_2O_4 is decomposing (*Reaction 8.1*). At this point, *Reactions 8.1* and *8.2* ***are still occurring***; however, they are occurring ***at the same rate*** and therefore the amounts of N_2O_4 and NO_2 are not changing.

It is helpful to consider the process that I have just described by viewing a graph that shows the concentration of N_2O_4 and NO_2 vs. time. The concentrations of N_2O_4 and NO_2 are plotted as blue and brown curves, respectively, in Figure 8.2.

Figure 8.2 Concentrations of NO_2 and N_2O_4 vs. Time



At time = 0 on the *horizontal axis*, the concentration of N_2O_4 is relatively high compared to the concentration of NO_2 which is almost zero. Initially, N_2O_4 is converted to NO_2 at a faster rate than the reverse because there is much N_2O_4 present and very little NO_2 present. We see the concentration of N_2O_4 decreasing fairly quickly and the concentration of NO_2 rising fairly rapidly, as shown during the initial times in the left-most side of the region that is shaded green in Figure 8.2. This will continue to occur for a while, however as the concentration of NO_2 increases, *so does the rate of Reaction 8.2*. The concentration of NO_2 will increase and the concentration of N_2O_4 will decrease until the rate of *Reaction 8.2* reaches a point where NO_2 is being converted back into N_2O_4 at the same rate the N_2O_4 is decomposing (*Reaction 8.1*). This point in time is indicated by the red dashed vertical line in Figure 8.2. At this time, since *Reactions 8.1* and *8.2* are occurring ***at the same rate***, the concentrations of N_2O_4 and NO_2 are not changing, as indicate by the flattened blue and brown lines in the red-shaded region of Figure 8.2. At times to the right of the red dashed line, where the amounts of N_2O_4 and NO_2 are not changing, we say the reaction has reached **chemical equilibrium**.

We use "double arrows" in ***reversible*** chemical reaction equations. For our example reaction, we write:

$$N_2O_4\,(g) \;\rightleftarrows\; 2\ NO_2\,(g)$$

Even though reversible reactions proceed in both *forward* ***and*** *reverse* directions, we use the convention of calling the substances on the left-hand side of the reaction arrows "reactants," and those on the right-hand side "products." We call the process that occurs in the left-to-right direction (reactants to products) the "***forward reaction***,**"** and the process that occurs in the right-to-left direction (products to reactants) the "***reverse reaction***." **Chemical equilibrium is defined as the state in which the rate of the forward reaction *is equal to* the rate of the reverse reaction and concentrations of the reactants and products do not change.**

Some chemical reactions reach equilibrium in a few seconds or less, others can take days (or longer). Once chemical equilibrium has been reached, the concentrations of reactants and products remain constant unless a change is made, such as adding or removing some products or reactants or changing the temperature.

The **law of mass action** can be used to determine the concentrations of reactants and products for a reaction that is at chemical equilibrium. For a general (any) reaction at chemical equilibrium:

$$aA + bB \rightleftarrows cC + dD$$

where a, b, c, and d are the *stoichiometric coefficients* for substances A, B, C, and D respectively. The concentrations of reactants and products at equilibrium must satisfy the ***law of mass action***:

$$K_{eq} = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

The square brackets, **[ ]**, indicate concentration ***in molarity***, for example, "**[A]**" means "**molarity of substance A**". $\mathbf{K}_{eq}$ is called the **equilibrium constant**. Note the word "*constant*" is used because at equilibrium, the concentrations of reactants and products are not changing (*are constant*), therefore $\mathbf{K}_{eq}$ is a constant. Each chemical reaction has its own equilibrium constant value. $\mathbf{K}_{eq}$ values for particular reactions are determined *experimentally* and are often tabulated in reference books or online. The ***law of mass action*** is also referred to as the ***equilibrium expression,*** *as will I for the remainder of this book*. In the *general form* of the *equilibrium expression* shown above, I arbitrarily chose to use *two* reactants (A and B) and *two* products (C and D), however there can be more or fewer than two products and/or reactants. No matter how many products or reactants are involved in a reaction, the equilibrium expression is written by multiplying the concentration of the ***products*** (raised to their stoichiometric coefficient powers) in the ***numerator***, and multiplying the concentration of the ***reactants*** (raised to their stoichiometric coefficient powers) in the ***denominator***. The $\mathbf{K}_{eq}$ value for a particular reaction ultimately depends on the combination of reactant and product concentrations that would cause the mixture to be at the *lowest possible energy*.

Next, I will show you how to write the equilibrium expression for any specific reaction using a couple of examples.

EXAMPLE: Write the *equilibrium expression* for our example reaction: $N_2O_4\,(g) \rightleftarrows 2\ NO_2\,(g)$

SOLUTION: The equilibrium expression is written with the concentration of the *products* (raised to their stoichiometric coefficient powers) in the numerator, and the concentration of the *reactants* (raised to their stoichiometric coefficient powers) in the denominator.

$$K_{eq} = \frac{[NO_2]^2}{[N_2O_4]}$$

Although it may seem unusual to use the molarity *concentration of gases*, it is not inconsistent with the definition of molarity. For gases, this is equal to the number of moles of a particular gas divided by the volume (L) of the container.

Review 8.1: Writing the Equilibrium Expression for a Reaction

Write the equilibrium expression for the following reaction: $ClNO_2\,(g) + NO\,(g) \rightleftarrows NO_2\,(g) + ClNO\,(g)$

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

IMPORTANT NOTE FOR EQUILIBRIUM EXPRESSIONS:

- When solids (*s*) or liquids (*l*) are present as reactants and/or products, they are ***omitted from the equilibrium expression***. The only substances that appear in the equilibrium expression are gases (*g*), aqueous (*aq*) solutes, or solutes dissolved in non-aqueous solutions.

EXAMPLE: Write the equilibrium expression for the reaction of dissolved carbon dioxide and water:

$$CO_2\,(aq) + \mathbf{H_2O\,(\mathit{l})} \rightleftarrows H_2CO_3\,(aq)$$

SOLUTION: Since $\mathbf{H_2O\,(\mathit{l})}$ is a liquid, it is omitted from the equilibrium expression.

$$K_{eq} = \frac{[H_2CO_3]}{[CO_2]}$$

Review 8.2: Writing the Equilibrium Expression for a Reaction

Write the equilibrium expression for the following reaction: $HCl\,(aq) + H_2O\,(l) \rightleftarrows H_3O^+\,(aq) + Cl^-\,(aq)$

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

Equilibrium constants have been measured experimentally for many reactions. For example, in the reaction of boric acid (H_3BO_3) and water,

$$H_3BO_3\,(aq) + H_2O\,(l) \rightleftarrows H_2BO_3^-\,(aq) + H_3O^+\,(aq)$$

the equilibrium expression and the measured value of the equilibrium constant (K_{eq}) is:

$$K_{eq} = \frac{[H_2BO_3^-][H_3O^+]}{[H_3BO_3]} = 5.75 \times 10^{-10}\,M$$

The value of the equilibrium constant allows us to know the relative amounts of products vs. reactants that are present at equilibrium for a particular reaction. The equilibrium expression for K_{eq} is a fraction consisting of the ***products* in the numerator** and the ***reactants* in the denominator.** If K_{eq} is *much greater* than 1, then there are many more product species than reactant species present at equilibrium. In this case, we say that *the products are **predominant** at equilibrium*. Conversely, if K_{eq} is *much less* than 1, then there are many more reactant species than product species present at equilibrium. In this case, we say that *the reactants are **predominant** at equilibrium*. If we consider the reaction of boric acid and water shown above, we see that the value of K_{eq} is *much less* than 1. This tells us that *at equilibrium*, the ***reactants are predominant***; there are many more boric acid molecules (H_3BO_3) present than dihydrogen borate ($H_2BO_3^-$) or hydronium (H_3O^+) ions.

Value of K_{eq}	**Predominant Species**
K_{eq} >> 1	Products
K_{eq} << 1	Reactants

The equilibrium constant for the reaction of sulfuric acid and water is *much greater* than 1:

$$H_2SO_4\,(aq) + H_2O\,(l) \rightleftarrows HSO_4^-\,(aq) + H_3O^+\,(aq), \qquad K_{eq} = 1.0 \times 10^3\ M$$

This tells us that, the ***products are predominant***; there are many more hydrogen sulfate (HSO_4^-) and hydronium (H_3O^+) ions present than sulfuric acid molecules (H_2SO_4) *at equilibrium*.

The value of the equilibrium constant for any particular reaction depends on temperature. Tabulated equilibrium constants usually indicate the temperature at which they were measured. For our purposes, we will ignore the temperature dependence of equilibrium constants. The equilibrium constants used in the remainder of this book are for reactions at (or close to) room temperature (25°C).

Le Châtelier's Principle

Henry Le Châtelier (1850-1936)

Source: US-PD

If a reaction is at equilibrium, and then ***more*** of one of the reactants is added, the system is *no longer in equilibrium*. Consider the general reaction:

$$\mathrm{A + B \rightleftarrows C + D}$$

When a reaction is at equilibrium, the forward rate is equal to the reverse rate, and the concentrations of reactants and products are not changing. If the concentration of reactant **A** or **B** is increased by ***adding*** more of substance **A** or **B,** this causes an increase in the rate of the *forward reaction* because there is now a greater probability of **A** colliding with **B** and then reacting. Upon the addition of substance **A** or **B**, substances **A** and **B** are converted to **C** and **D** at a faster forward rate than the reverse rate. This will continue to occur until enough of **C** and **D** are produced so that the reverse rate is once again equal to the forward rate and equilibrium is reestablished. A similar situation occurs if the concentration of one of the products (**C** or **D**) is increased; the reaction will then proceed faster in the reverse direction until enough **A** and **B** are formed so that the forward rate once again equals the reverse rate.

The opposite situation occurs if some of the reactants or products are ***removed*** from the system. Reactants (or products) can be removed from the system if they are consumed by another chemical reaction, form a solid, or form a gas that is bubbled or evaporated from a liquid-phase reaction. Consider our general reaction, $\mathbf{A + B \rightleftarrows C + D}$, at equilibrium. If some of substance **A** or **B** is ***removed***, this causes a significant decrease in the rate of the forward reaction relative to the reverse reaction simply because there is now a lower probability of **A** colliding with **B** and reacting. Substances **C** and **D** continue to be converted to **A** and **B** at a faster rate than the rate of the forward direction until enough of **A** and **B** are produced so that the forward rate is once again equal to the reverse rate and equilibrium is reestablished. An equivalent situation occurs if ***products are removed***; the reaction will proceed faster in the forward direction until enough products are formed so that the reverse rate is equal to the forward rate and equilibrium is reestablished.

What I have just described is part of a law known as either the "Equilibrium Law" or, more commonly, Le Châtelier's Principle. This law can be used to describe how a reaction at equilibrium responds to a change in concentration of one of the reactants or products as follows: ***the relative rates of the forward and reverse reactions change to counteract the concentration change until equilibrium is re-established***. Predictions based on Le Châtelier's Principle of responses to changes in concentration of reactants or products for a reaction at equilibrium are summarized in Table 8.1.

Table 8.1 Summary of Le Châtelier's Principle for Concentration Changes

Change Made to a Reaction that was at Equilibrium:	Response:
Increase the concentration of a ***reactant.***	Rate of the **forward** reaction becomes **greater** than the rate of the reverse reaction until equilibrium is reestablished.
Increase the concentration of a ***product.***	Rate of the **reverse** reaction becomes **greater** than the rate of the forward reaction until equilibrium is reestablished.
Decrease the concentration of a ***reactant.***	Rate of the **forward** reaction becomes **less** than the rate of the reverse reaction until equilibrium is reestablished.
Decrease the concentration of a ***product.***	Rate of the **reverse** reaction becomes **less** than the rate of the forward reaction until equilibrium is reestablished.

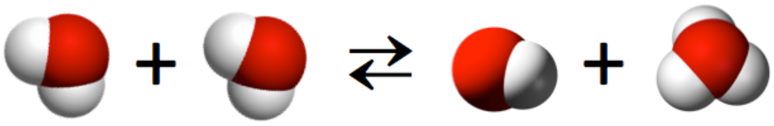
Le Châtelier's Principle Review Problems

Download the Worksheet and Key: www.zovallearning.com/GOBlinks/ch8/equilibrium-worksheet-and-key.pdf

8.3 The Ionization of Water

A reversible reaction that is very important in understanding the chemical behavior of biological solutions is the ionization of water. The reactants are ***two*** water molecules; one water molecule transfers a hydrogen ion (H^+) to the other water molecule to produce a hydroxide ion (OH^-) and a hydronium ion (H_3O^+):

Source: Wikimedia Commons, Author Sergiu Bacioiu, CC-BY http://creativecommons.org/licenses/by/2.0/legalcode



$$\mathbf{2}\,H_2O\,(l) \rightleftarrows OH^-\,(aq) + H_3O^+\,(aq)$$

The reason that this reaction is important in biological systems is that: (1) cells are filled with and surrounded by water, (2) hydronium and hydroxide ions are involved in many biological reactions and effect many biological processes. You may be wondering if this reaction was occurring in the last glass of water that you drank; the answer is yes. This reaction occurs wherever water is present, regardless of what other substance(s) may be present. Can you guess whether the products or the reactant for this reaction is predominant at equilibrium? If you think that the reactant (water) is predominant, you are correct. At equilibrium there are many more water molecules present than hydroxide and hydronium ions.

The equilibrium expression applies to the ionization of water reaction, as it does to all other chemical reactions. The equilibrium expression for K_{eq} in this reaction is:

$$K_{eq} = [OH^-][H_3O^+]$$

Water does not appear in the equilibrium expression because it is a liquid. This equilibrium expression is so commonly used, that the symbol "K_w" is used for equilibrium constant (instead of K_{eq}). The value of the equilibrium constant has been measured experimentally for this reaction:

$$K_w = [OH^-][H_3O^+] = 1.0 \times 10^{-14}\,M^2$$

The unit for K_w is M^2 because we are multiplying two molarity concentrations ($M \cdot M = M^2$).

I want to draw your attention to a few things about this equilibrium expression:

1) The **mathematical product** of the hydroxide ion concentration $[OH^-]$ and hydronium ion concentration $[H_3O^+]$ is always equal to $1.0 \times 10^{-14}\,M^2$; this is true whether the system is pure water *or* an aqueous solution containing one or more solutes.

2) The value of K_w is much less than 1. There is always much ***more water molecules present*** than hydroxide ions and hydronium ions.

3) In solutions (not pure water), there may be *other sources of hydroxide ions and hydronium ions*; therefore the hydroxide ion concentration ***is not necessarily equal to*** the hydronium ion concentration. In aqueous solutions, K_w does not give us enough information to determine the hydroxide ion (OH^-) and hydronium ion (H_3O^+) concentrations ***individually***; we only know that their product, $[OH^-]\cdot[H_3O^+]$, is *always* equal to $1.0 \times 10^{-14}\,M^2$.

The concentration of hydroxide and hydronium ions in *pure water*.

In pure water, the ***only*** *source of hydroxide ions and hydronium ions* is from the ionization of water reaction:

$$\mathbf{2}\ H_2O\ (l) \ \rightleftarrows\ OH^-\ (aq)\ +\ H_3O^+\ (aq)$$

Every time this reaction proceeds in the forward direction ***exactly*** one hydroxide and one hydronium ion are formed. Therefore, in pure water the hydroxide ion concentration is always equal to the hydronium ion concentration. If we solve the equilibrium expression to find which number multiplied by itself is equal to K_w ($1.0 \times 10^{-14}\ M^2$), we can find the concentration of the hydroxide and hydronium ions in *pure water*:

$$K_w = [OH^-][H_3O^+] = 1.0 \times 10^{-14} M^2$$

$$(1.0 \times 10^{-7} M) \times (1.0 \times 10^{-7} M) = 1.0 \times 10^{-14} M^2$$

In ***pure water***, the **hydroxide ion** concentration *and* the ***hydronium ion*** concentration are both equal to 1.0×10^{-7} M.

The concentration of hydroxide and hydronium in aqueous solutions containing *other* solutes.

In aqueous *solutions* (not pure water), there may be *other sources of hydroxide ions and hydronium ions*, therefore the hydroxide ion concentration ***is not necessarily equal to*** the hydronium ion concentration. For example, a sodium hydroxide (NaOH) solution contains more hydroxide ions than does pure water.

If we know the hydronium ion concentration in an aqueous solution, then we can calculate the hydroxide ion concentration. This is very often the case because, as you will learn later in this chapter, there are several technologies that can be used to measure the hydronium ion concentration of a solution. Given the concentration of the hydronium ion, we can calculate the concentration of the hydroxide ion because we know that the product of the hydroxide and the hydronium ion is equal to K_w ($1.0 \times 10^{-14}\ M^2$).

$$[OH^-][H_3O^+] = 1.0 \times 10^{-14} M^2$$

Equation 8.3

Dividing both sides of *Equation 8.3* by $[H_3O^+]$ allows us to solve for the hydroxide ion concentration:

$$[OH^-] = \frac{1.0 \times 10^{-14} M^2}{[H_3O^+]}$$

Equation 8.4

The hydroxide ion concentration ($[OH^-]$) is calculated by inserting the value for the hydronium ion ($[H_3O^+]$) into *Equation 8.4.*

EXAMPLE: If the $[H_3O^+]$ in an aqueous solution is 5.9×10^{-3} M, what is the $[OH^-]$?

SOLUTION: When we know the $[H_3O^+]$, we can solve the equilibrium expression (Equation 8.3) for $[OH^-]$:

$$[OH^-] = \frac{1.0 \times 10^{-14} M^2}{[H_3O^+]}$$

Inserting the known value for the hydronium ion concentration (5.9×10^{-3} M) allows us to solve for the hydroxide ion concentration:

$$[OH^-] = \frac{1.0 \times 10^{-14} M^2}{5.9\ \times\ 10^{-3} M} = 1.7\ \times\ 10^{-12} M$$

If the $[H_3O^+]$ in an aqueous solution is 5.9×10^{-3} M, then the $[OH^-] = 1.7 \times 10^{-12}$ M. Note that one of the molarity units in the numerator cancels with the molarity unit in the denominator:

$$\frac{M^2}{M} = \frac{M \times \cancel{M}}{\cancel{M}} = M$$

Review 8.3: Calculations Involving K_w

If the $[H_3O^+]$ in an aqueous solution is 3.6×10^{-11} M, what is the $[OH^-]$?

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

In the previous problem, we knew the concentration of hydronium and we solved the equilibrium expression for the concentration of hydroxide. If, on the other hand, we know the concentration of hydroxide, then we can calculate the concentration of hydronium. Dividing both sides of Equation 8.3 by $[OH^-]$ allows us to solve for the hydronium concentration:

$$[H_3O^+] = \frac{1.0 \times 10^{-14}\,M^2}{[OH^-]}$$

Inserting the known value for the hydroxide ion concentration allows us to solve for the hydronium ion concentration.

Review 8.4: Calculations Involving K_w

If the $[OH^-]$ in an aqueous solution is 2.4×10^{-9} M, what is the $[H_3O^+]$?

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

Review 8.5: Calculations Involving K_w

In pure water, the $[H_3O^+] = 1.0 \times 10^{-7}$ M, use *Equation 8.4* to solve for the hydroxide ion concentration.

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

Summary of the Ionization of Water

The ionization of water reaction is constantly occurring in any system in which liquid water is present. When the concentration of the hydronium ion is known, then the concentration of hydroxide may be calculated (or vice versa) using *Equation 8.4*.

The ionization of water is a very important reaction in the chemical behavior of biological organisms and environments because hydronium and hydroxide ions are products or reactants in many biological reactions. As described by Le Châtelier's Principle, changes in the hydronium or hydroxide ions can therefore affect the amounts of other products and/or reactants present in biological reactions such as the citric acid cycle and photosynthesis.

8.4 Acids and Bases

A compound can be classified as an "**acid**" or a "**base**" depending on its ability to gain or lose a hydrogen ion (H^+) ***in a chemical reaction***. Note that an H^+ ion is simply a proton; the terms "hydrogen ion" and "proton" can be used interchangeably. A hydrogen atom (^1H) has one proton, one electron, and no neutrons. Only the proton remains when a hydrogen atom loses an electron to become H^+. We will use the definitions of acids and bases popularized and published by Johannes Nicolaus Brønsted and Thomas Martin Lowry.

An **acid *donates*** an H^+ *in a chemical reaction*.

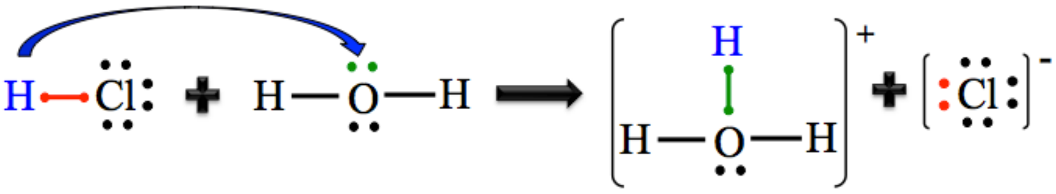
A **base *accepts*** an H^+ *in a chemical reaction*.

Reactions in which an H^+ is transferred are called **acid-base reactions**. If you are given a specific acid-base reaction, you can ***only*** determine which reactant is the *acid* and which reactant is the *base* by inspection of the products *and* reactants. I will elaborate with an example.

Let's consider the chemical reaction of aqueous hydrogen chloride and water. When hydrogen chloride is added to water, it dissociates as shown in the chemical equation below:

$$HCl\ (aq) + H_2O\ (l) \rightleftarrows Cl^-\ (aq) + H_3O^+\ (aq)$$

When discussing which reactant is the ***acid*** and which reactant is the ***base***, we consider the reaction in the ***forward direction***. In the forward direction of this reaction, HCl is the ***acid*** because it *donates* an H^+.



The covalent bond (shaded red) between the hydrogen atom and the chlorine atom is broken in the reaction. The electrons (shaded red) from that broken covalent bond remain with the chlorine to form the chloride ion product. The water molecule is the ***base*** in this reaction because it *accepts* an H^+. One of the lone pairs (shaded green) on H_2O forms a *new covalent bond* with the H^+ in the hydronium ion product.

When a reactant species donates an H^+, its charge ***decreases*** by one charge unit. For example, the HCl in the reaction above had zero charge as a reactant, however after *donating* the H^+, it is converted to Cl^-; the charge *decreased* by one charge unit. Conversely, when a reactant species *accepts* an H^+ in a reaction, its charge *increases* by one charge unit. For example, the H_2O in the reaction above had zero charge as a reactant, however after accepting the H^+ and becoming H_3O^+, its charge *increased* by one charge unit.

You try a couple of problems:

Review 8.6: Identification of the Acid and Base in an Acid-Base Reaction

Determine which reactant is the acid and which reactant is the base in each of the following reactions.

a. $H_3BO_3\ (aq) + H_2O\ (l) \rightleftarrows H_2BO_3^-\ (aq) + H_3O^+\ (aq)$

b. $HSO_4^-\ (aq) + HNO_3\ (aq) \rightleftarrows H_2SO_4\ (aq) + NO_3^-\ (aq)$

c. $CN^-\ (aq) + H_2O\ (l) \rightleftarrows HCN\ (aq) + OH^-\ (aq)$

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

Amphoteric Compounds

You may have noticed that water acted as an *acid* in one of the previous review problems and it acted as a *base* in another one of the problems. In review problem 8.6 (a) water acted as a **base**; it *accepted* an H^+.

$$H_3BO_3\ (aq) + H_2O\ (l) \rightleftarrows H_2BO_3^-\ (aq) + H_3O^+\ (aq)$$

In the review problem 8.6 (c) water reacted as an acid; it *donated* an H^+.

$$CN^-\ (aq) + H_2O\ (l) \rightleftarrows HCN\ (aq) + OH^-\ (aq)$$

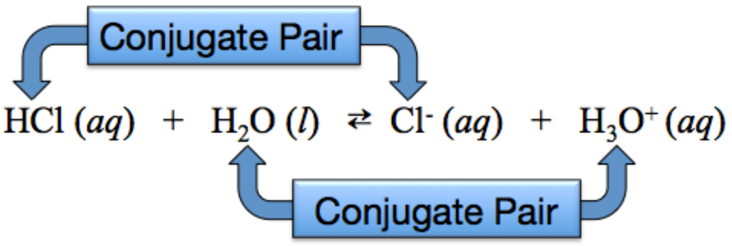
Compounds that can act as acids ***or*** as bases are called **amphoteric compounds**. An example of another amphoteric compound is the bicarbonate ion (HCO_3^-). Bicarbonate acts as an *acid* in one of the following reactions and as a *base* in the other reaction.

$$HCO_3^- + CN^- \rightleftarrows CO_3^{2-} + HCN \quad (HCO_3^- \text{ as an acid})$$

$$HCO_3^- + HCl \rightleftarrows H_2CO_3 + Cl^- \quad (HCO_3^- \text{ as a base})$$

Conjugates

Pairs of chemical species, such as HCN and CN^- *or* H_3BO_3 and $H_2BO_3^-$, which differ only in the presence or absence of an H^+ are called **conjugate pairs**. For each conjugate pair, the species that *contains the extra hydrogen* is called the "***acid form***" or the "*conjugate acid*," and the species with one fewer hydrogen is called the "***base form***" or the "*conjugate base*." Consider the chemical reaction of aqueous hydrogen chloride and water:



There are _two_ conjugate pairs in every acid-base reaction. In the reaction above, one of the conjugate pairs is HCl and Cl^-, and the other conjugate pair is H_2O and H_3O^+. For the HCl/Cl^- pair, HCl is the ***acid form*** and Cl^- is the ***base form***. In the following review problems, I would like you to identify the ***acid form*** and the ***base form*** in each of several conjugate pairs.

Review 8.7: Identification of the Acid Form and Base Form of a Conjugate Pair

Identify the ***acid form*** and the ***base form*** in each of the conjugate pairs:

a. H_3BO_3 and $H_2BO_3^-$
b. H_2O and H_3O^+
c. HSO_4^- and H_2SO_4
d. HNO_3 and NO_3^-
e. CN^- and HCN

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

8.5 pH

There are many applications, in both nature and laboratory settings, when it is important to measure and know the hydronium ion concentration. Since hydronium is a product or reactant in many chemical reactions, its concentration affects the amounts of other products and/or reactants involved in these reactions. An excess or deficiency of hydronium ions will hinder the ability of biological enzymes to catalyze crucial chemical reactions. The concentration of hydronium ions both affects, and is affected by, cellular metabolic activity. If the concentration of hydronium ions is too large or too small, irreversible damage to cells will occur. For these and many other reasons, much work has gone into enabling the experimental measurement of hydronium ion concentration.

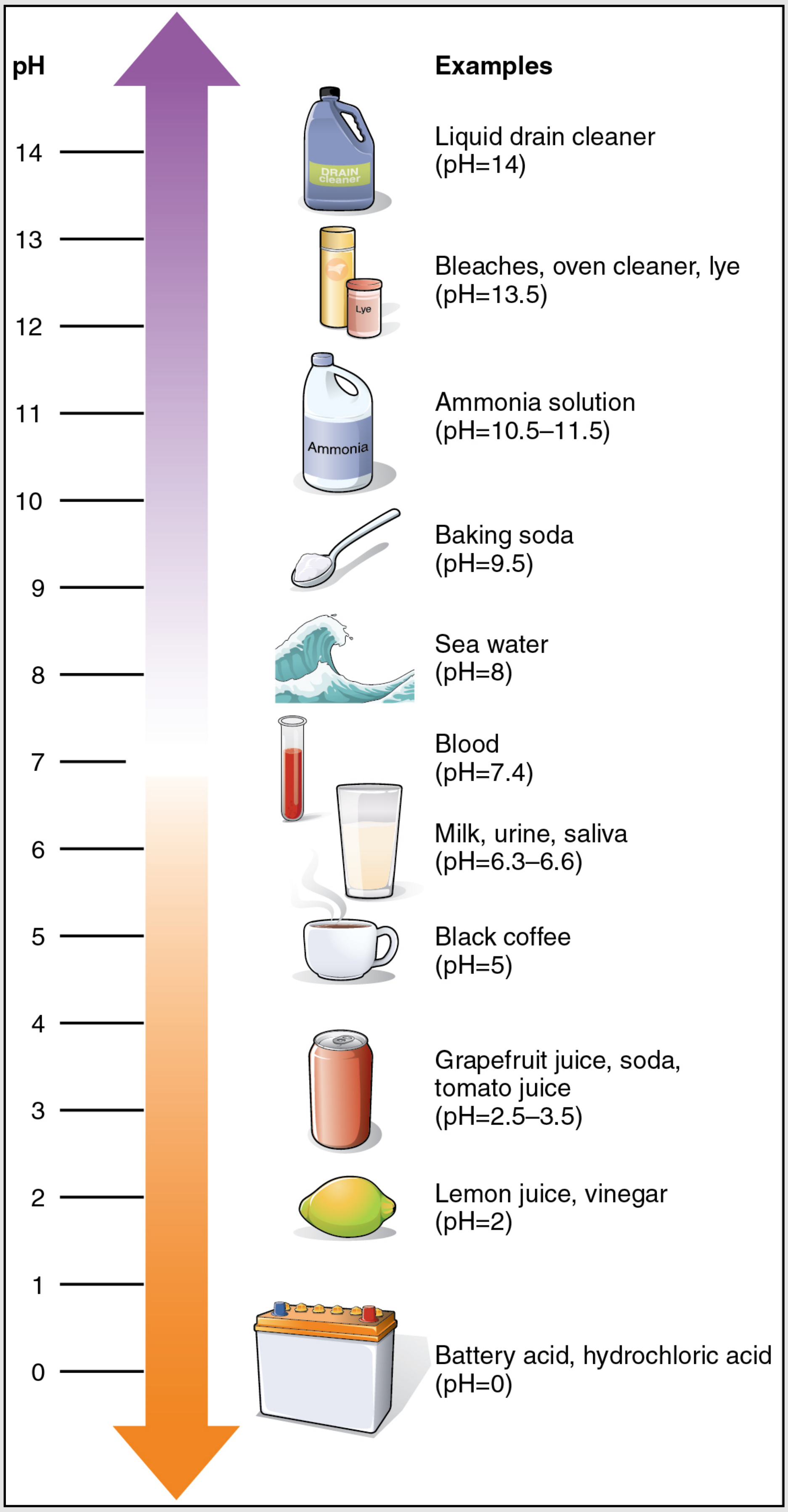
The concentration of hydronium ions is determined experimentally and assigned a numeric value using the **pH scale**. The pH values of some common substances are shown in Figure 8.3.

pH is most commonly defined as the "**negative logarithm of the hydronium ion concentration.**" This definition can be written as a mathematical equation:

$$\mathbf{pH = -\log[H_3O^+]} \qquad \textit{Equation 8.5}$$

If you know very little, or nothing at all, about logarithms, *do not worry*. I will introduce you to everything you need to know about logarithms as they relate to pH. The reason that logarithm values are used has to do with the details of the experimental measurements and a discussion of those details is beyond the scope of this text. For our purposes, the primary thing to understand is that ***pH is simply another way to express the concentration of hydronium ions in a solution***.

Figure 8.3
The pH of Some Common Substances



The pH scale and the pH of some common substances.
Source: Wikimedia Commons, Author: OpenStax College. CC-BY http://creativecommons.org/licenses/by/2.0/legalcode

Calculating the pH of a Solution from the $[H_3O^+]$

If a value (number) changes by a factor of 10, then its logarithm changes by 1. You may be familiar with the Richter scale used in describing the magnitude of earthquakes. The Richter scale is a logarithm scale. An earthquake that has a magnitude of 7 on the Richter scale is *ten times stronger* than an earthquake with a Richter scale value of 6. An earthquake with a Richter scale value of 8 is *one hundred times stronger* than a quake with a Richter scale value of 6. ***Because of the negative sign in our definition of pH, the greater the hydronium ion concentration, the lower the pH value.***

Equation 8.5 gives the relationship between the hydronium ion concentration and the pH. If we know the hydronium ion concentration, we can calculate the pH. I will elaborate using an example problem.

EXAMPLE: If the $[H_3O^+]$ in an aqueous solution is 8.1 x 10^{-3} M, what is the pH?

SOLUTION: Insert the $[H_3O^+]$ into *Equation 8.5* and then use your calculator to solve for the pH.

$$pH = -\log[H_3O^+] = -\log(8.1 \times 10^{-3})$$

In many calculators, to get the log(8.1 x 10^{-3}), you press the "log" key, and then enter 8.1 x 10^{-3}, and then press the equals (=) key. Other calculators require you to reverse the order; enter 8.1 x 10^{-3}, and then press the "log" key. You may have a calculator that requires some other sequence of key strokes. Check your calculator's instruction manual or see your instructor if needed. No matter which calculator you have, when it is used correctly, the displayed value for the logarithm of 8.1 x 10^{-3} can be rounded to -2.09. Do not forget the negative sign in Equation 8.5, which will make the calculated pH positive:

$$pH = -\log[H_3O^+] = -\log(8.1 \times 10^{-3}) = -(-2.09) = \mathbf{2.09}$$

An aqueous solution with a $[H_3O^+]$ of 8.1 x 10^{-3} M has a **pH of 2.09**

TWO IMPORTANT POINTS ABOUT pH:

1) **We do not use units in pH values.** pH is one of the few quantities that are unitless**.**
2) I have been holding you accountable for *significant figures* for so long that you may have thought that I made a significant figure error in this calculation. The given hydronium ion concentration had only two significant figures, however the pH ***appears*** to have three significant figures. I need to give you the rule for significant figures in pH values: **Numbers to the left of the decimal point are *not* significant in pH values.** The mathematical reason for this is that the numbers to the left of the decimal point are not counted as significant - just as the *powers of ten* in scientific notation are not significant. ***Be careful***, **only** apply this rule to the **pH** value and not to $[H_3O^+]$ or $[OH^-]$.

You try a problem:

Review 8.8: Given the $[H_3O^+]$, Calculate the pH

If the $[H_3O^+]$ in an aqueous solution is 3.8 x 10^{-9} M, what is the pH?

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

Could you calculate the pH of a solution if you were given the the $[OH^-]$ instead of the $[H_3O^+]$?
Recall from the previous section of this chapter that if we know the $[OH^-]$, then we can calculate the $[H_3O^+]$ using the equilibrium expression for K_w.

$$[OH^-][H_3O^+] = 1.0 \times 10^{-14} M^2$$

Once the $[H_3O^+]$ is calculated, it can be inserted into Equation 8.5 in order to calculate the pH:

$$pH = -\log[H_3O^+] \qquad \textit{Equation 8.5}$$

I will have you do this calculation in the following review problem:

Review 8.9: Given the $[OH^-]$, Calculate the pH

If the $\mathbf{[OH^-]}$ in an aqueous solution is 2.4 x 10^{-9} M, what is the **pH**?

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

Calculating the [H_3O^+] of a Solution from the pH

We calculated the pH from the [H_3O^+] in the previous example and review problems. Since there are many devices that are used to experimentally measure pH, many applications require that the [H_3O^+] be calculated from the measured pH value. In this case we must employ a mathematical operation called the antilog. I will elaborate using an example.

EXAMPLE: If the pH of an aqueous solution is **3.25**, what is the [H_3O^+]?

SOLUTION: Insert the pH into *Equation 8.5* and use your calculator to solve for the [H_3O^+].

$$\text{pH} = -\log[H_3O^+]$$

$$\mathbf{3.25} = -\log[H_3O^+]$$

Many students may not know (or recall) how to solve this type of problem. We wish to solve for the [H_3O^+], therefore we must isolate it on one side of the equation. First, let's get rid of the negative sign on the right-hand side of the equation by multiplying both sides by (-1). When doing so we get:

-

$$\mathbf{-3.25} = \log[H_3O^+]$$

The next step is to get rid of the "log" on the right-hand side. We do so by taking the "anti-log" of each side of the equation. Taking the anti-log of (log[H_3O^+]) gives [H_3O^+]. Taking the anti-log of a ***numeric value*** means raising 10 to the power of that number, however we will simplify to a numerical value u*sing a calculator*.

$$\text{antilog}(\mathbf{-3.25}) = [H_3O^+]$$

You can use your calculator to get the antilog of (-3.25). For some calculators, you will press the "10^x" key, and then enter -3.25, and then press the equals (=) key. Other calculators require you to reverse the order; enter -3.25, and then press the "10^x" key. The "10^x" is often printed above the calculator's "log" key, and requires the keystroke of "shift" or "2nd" before pressing the key. Check your calculator's instruction manual or see your instructor if needed. The displayed value for the antilog of -3.25 is 5.623413 x 10^{-4}. This value is rounded to 5.6 x 10^{-4}.

$$\text{antilog}(-3.25) = [H_3O^+]$$

$$5.6 \times 10^{-4}\ \text{M} = [H_3O^+]$$

An aqueous solution with a **pH** of **3.25** has a **[H_3O^+]** of **5.6 x 10^{-4} M.**

IMPORTANT NOTES:

1) The molarity in the answer to this problem has two significant figures because the given pH (3.<u>25</u>) had *two* significant figures. Numbers to the *left of the decimal point* are <u>not</u> significant in pH values.

2) Since we are calculating a *molarity* concentration, [H_3O^+], we add the **M** unit.

You try a couple of problems:

Review 8.10: Given the pH, Calculate the [H_3O^+]

If the pH of an aqueous solution is **12.65**, what is the [H_3O^+]?

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Review 8.11: Given the pH, Calculate the [H_3O^+]

If the pH of an aqueous solution is **0.25**, what is the [H_3O^+]?

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

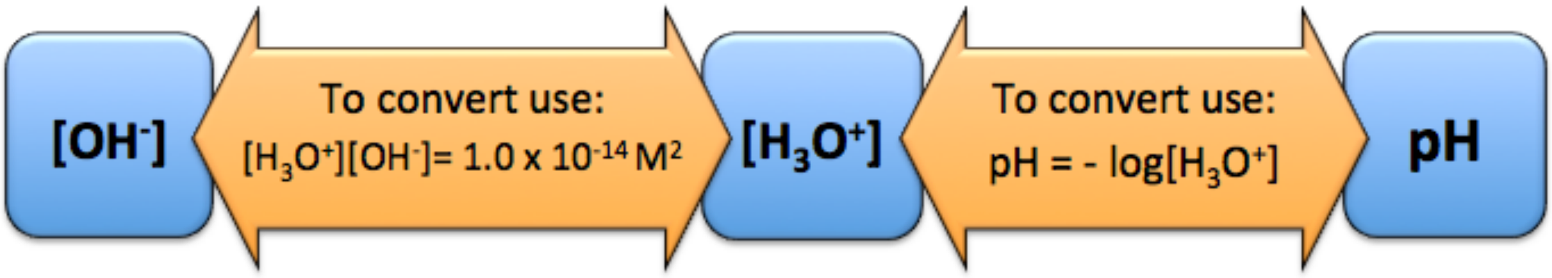
Now that you know how to convert between the hydronium ion concentration and the hydroxide ion concentration using the equilibrium expression for K_w,

$$[OH^-][H_3O^+] = 1.0 \times 10^{-14} M^2$$

and convert between the $[H_3O^+]$ and the pH using the definition of pH given in Equation 9.3,

$$pH = -\log[H_3O^+]$$

if you are given *any* ***one*** *of these three quantities,* $[H_3O^+]$, $[OH^-]$, or pH, you should be able to *calculate* ***the other two***.



Get more practice problems for these conversions at: www.zovallearning.com/GOBlinks/ch8/pH-worksheet-and-key.pdf

8.6 Acidic and Basic Solutions

Compounds are characterized as acids or bases depending on whether they donate or accept H^+ in *a **particular** acid-base reaction*. ***Solutions*** are characterized as **acidic**, **basic**, or **neutral** by the relative amounts of H_3O^+ and OH^- that are present. Solutions that contain more H_3O^+ than OH^- are called **acidic** solutions. Solutions that contain more OH^- than H_3O^+ are called **basic** solutions. Solutions that contain equal concentrations of H_3O^+ and OH^- are called **neutral** solutions. Let's do an example problem to find the **pH** of a ***neutral solution***:

EXAMPLE: What is the pH of a neutral solution?

SOLUTION: By definition, in neutral solutions, the $[H_3O^+] = [OH^-]$. We use the equilibrium expression for the ionization of water to find which number multiplied by itself is equal to K_w (1.0×10^{-14} M^2). We did a similar calculation to determine the hydronium and hydroxide ion concentration in ***pure water***, the equilibrium expression *also* applies to ***any*** aqueous solution.

$$K_w = [OH^-][H_3O^+] = 1.0 \times 10^{-14} M^2$$

$$(1.0 \times 10^{-7} M) \times (1.0 \times 10^{-7} M) = 1.0 \times 10^{-14} M^2$$

In neutral solutions, the $[H_3O^+] = [OH^-]$, therefore they are both equal to 1.0×10^{-7} M.

Once the $[H_3O^+]$ is calculated, it can be inserted into Equation 9.3 in order to calculate the pH:

$$pH = -\log[H_3O^+] \qquad \textit{Equation 8.5}$$

Insert the $[H_3O^+] = 1.0 \times 10^{-7}$ M into *Equation 9.3* and use your calculator to solve for the pH.

$$pH = -\log[H_3O^+] = -\log(1.0 \times 10^{-7} M) = -(-7.00) = \mathbf{7.00}$$

The pH of a neutral solution equals 7.00.

Next, let's think about the pH range of acidic or basic solutions. In ***acidic solutions,*** $[H_3O^+] > [OH^-]$, therefore $[H_3O^+] > 1.0 \times 10^{-7}$ M. When the hydronium ion concentration is ***greater*** than 1.0×10^{-7} M, then the pH is ***less than*** 7.00. Note that as the *hydronium ion* concentration ***increases***, the pH ***decreases***; this is because of the *negative sign* in the definition of pH.

In ***basic solutions,*** $[OH^-] > [H_3O^+]$, therefore $[H_3O^+] < 1.0 \times 10^{-7}$ M. When the hydronium ion concentration is ***less*** than 1.0×10^{-7} M, then the pH is ***greater than*** 7.00. Note that as the *hydronium ion* concentration ***decreases***, the pH ***increases***.

Solution Characterization	pH	$[H_3O^+]$	$[OH^-]$
Acidic	less than 7.00	greater than 1.0×10^{-7} M	less than 1.0×10^{-7} M
Neutral	7.00	1.0×10^{-7} M	1.0×10^{-7} M
Basic	greater than 7.00	less than 1.0×10^{-7} M	greater than 1.0×10^{-7} M

Review 8.12: Neutral, Acidic, and Basic Solutions

For each of the following, write whether it describes an acidic, basic, or neutral solution.

a) pH = 8.9
b) $[H_3O^+] = 1 \times 10^{-9}$ M
c) $[H_3O^+] = 1 \times 10^{-7}$ M
d) $[OH^-] > [H_3O^+]$
e) $[H_3O^+] > [OH^-]$
f) pH = 1.7
g) pH = 12.0
h) $[OH^-] = 6.8 \times 10^{-2}$ M
i) pH = 0.06
j) $[H_3O^+] = [OH^-]$
k) pH = 7.00
l) $[OH^-] = 1.0 \times 10^{-7}$ M

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

Properties of Acidic Solutions

Acidic solutions can oxidize some metals. This often appears as if the metal is dissolving in the solution because the metal cation that is formed in the oxidation reaction is soluble.

Acidic solutions will turn a plant pigment molecule (in blue litmus) from blue to red. Molecules such as litmus are often used as pH indicators. The pH indicator molecules can be fixed to a small strip of paper that can be immersed in the sample; or a drop of the sample can be placed on the indicator paper. Sometimes the pH indicator molecules are dissolved in an "indicator solution" that is added drop-wise to the sample. The color of the pH indicator, after being placed in contact with the test solution, indicates that the solution is in a certain pH range. A pH paper test strip is shown in Figure 8.4.

Figure 8.4
pH Indicator Strips

When pH indicators come in contact with the test solution, the observed color is determined by the pH of the test solution. In the pH test strip shown, there are 4 different pH indicator molecules, each immobilized on a different spot. The various indicator molecules are sensitive to a particular range of pH values.
Source: Wikimedia Commons, Author: Michael Krahe, CC-BY-SA
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A more precise way to measure the pH of a solution is to use a pH meter. A pH meter is an electronic device with an electrode that is sensitive to the hydronium ion concentration. A pH meter is shown in Figure 8.5.

Acidic solutions taste *sour*. The juice from lemons has a relatively high concentration of citric acid - about 5%(w/v) - which gives lemons their sour taste. Citric acid is commercially produced by a strain of mold called *Aspergillus niger.* One of its uses is as a souring additive in foods and beverages. Many solutions are so acidic (pH much less than 7.00) that they will damage your mouth and digestive tract, and can result in death if enough is ingested.

Figure 8.5
A pH Meter

A pH meter being used to measure the pH of a solution.
Source: Wikimedia Commons, Author: Ildar Sagdejev, CC-BY-SA
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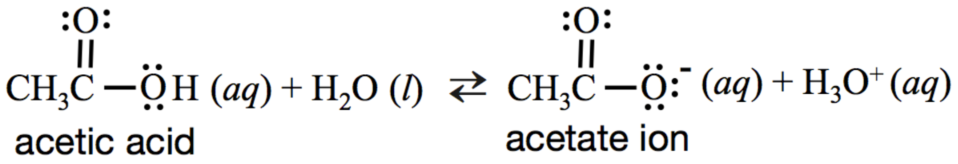
Some molecules contain the word "*acid*" in their name based on the fact that they act as acids when they react with water. Carboxylic *acids* are examples of this. An acidic solution can be prepared by the addition into water of a compound that acts as an acid when reacting with the water. For example, when acetic acid (a carboxylic *acid*) is added to pure water, a reaction occurs and an equilibrium is established:



$$CH_3C(=O)-OH\ (aq) + H_2O\ (l) \rightleftarrows CH_3C(=O)-O^-\ (aq) + H_3O^+\ (aq)$$

Before the acetic acid was added, the pH of the pure water was 7.00; the $[H_3O^+]$ was equal to the $[OH^-]$. When the acetic acid was added, ***more*** H_3O^+ was produced and the $[H_3O^+]$ increased. If the $[H_3O^+]$ increases, then the $[OH^-]$ must decrease since the product of the hydronium ion and hydroxide ion is constant ($[H_3O^+][OH^-] = K_w = 1.0 \times 10^{-14}\ M^2$). The resulting acetic acid solution is ***acidic*** because $[H_3O^+] > [OH^-]$.

The pH of a solution that is prepared by adding an acidic compound into pure water is determined by two factors:

1) The amount of the compound that was added.
2) The extent to which the compound *dissociates* (donates H^+ and thereby produces its *base form* and H_3O^+).

The extent to which an acid dissociates when reacting with water is referred to as "acid strength." When a "**strong acid**" is placed in water and reacts with it, there is very little of the *acid form* present and much more of the *base form* present at equilibrium. An example of a ***strong acid*** is HCl (often referred to as hydrochloric acid). When hydrogen chloride is added to water, it dissociates as shown in the chemical equation below:

$$HCl\ (aq) + H_2O\ (l) \rightleftarrows Cl^-\ (aq) + H_3O^+\ (aq)$$

Recall that the value of the equilibrium constant (K_{eq}) for a reaction indicates the relative amounts of products and reactants that exist at equilibrium. If K_{eq} is much greater than 1, then, at equilibrium, the concentrations of the products are much greater than those of the reactants. In this case we say *the products are predominant at equilibrium*. Conversely, if K_{eq} is much less than 1, at equilibrium, the concentrations of the reactants are much greater than those of the products. When writing the equilibrium constant for the reaction of an acid with water, we use the symbol K_a instead of K_w. K_a is referred to as the **acidity constant** or the **acid dissociation constant**; but keep in mind that it is just the ***equilibrium constant*** for the reaction of the acid with water. There are experimental technical limitations for measuring acidity constants for values greater than 1×10^2, however K_a for the reaction of HCl and water is estimated to be on the order of 1×10^7 M.

$$HCl\ (aq) + H_2O\ (l) \rightleftarrows Cl^-\ (aq) + H_3O^+\ (aq) \qquad K_a \approx 1 \times 10^7\ M$$

The equilibrium expression (equilibrium expression) for this reaction is:

$$K_a = \frac{[Cl^-][H_3O^+]}{[HCl]} \approx 1 \times 10^7\,M$$

K_a is approximately equal to 1×10^7 M, therefore at equilibrium there are about about ***ten million*** Cl^- ions and ***ten million*** H_3O^+ ions for every ***one*** HCl molecule. Almost all of the HCl that is added to pure water is converted to Cl^- and H_3O^+.

When a "**weak acid**" is placed in water and reacts with it, at equilibrium, there is very little of its base form and much more of the acid form present. An example of a ***weak acid*** is boric acid (H_3BO_3). When boric acid is added to water, it dissociates as shown in the chemical equation below:

$$H_3BO_3\ (aq) + H_2O\ (l) \rightleftarrows H_2BO_3^-\ (aq) + H_3O^+\ (aq)$$

K_a for the reaction of H_3BO_3 and water is 5.75 x 10^{-10} M. The equilibrium expression for this reaction is:

$$K_{eq} = \frac{[H_2BO_3^-][H_3O^+]}{[H_3BO_3]} = 5.75\times10^{-10}\,M$$

K_a for this reaction is much less than 1, and *the reactant* (H_3BO_3) *is predominant at equilibrium*. At equilibrium, the concentration of the reactant is much greater than those of the products. K_a is equal to 5.75 x 10^{-10} M, therefore at equilibrium there are about about 25000 H_3BO_3 molecules for every *one* $H_2BO_3^-$ or H_3O^+ ion present.

Summary of Acid Strength:

- ***Strong acids*** have K_a values *much greater* than 1. When ***strong acids*** are placed in pure water, they react with water and an equilibrium is establish in which there is much more of the ***base form*** and H_3O^+ than the ***acid form*** present.

- ***Weak acids*** have K_a values *much less* than 1. When ***weak acids*** are placed in pure water, they react with water and an equilibrium is establish in which there is much more of the ***acid form*** than the ***base form*** and H_3O^+ present.

- The greater the K_a, the stronger the acid. Table 8.2 shows the the K_a values of various acids.

Table 8.2   Various Acids and Their Acidity Constants

Acid Name	Acid Formula	K_a
Perchloric acid	$HClO_4$	1 x 10^9 M (estimated)
Hydrochloric acid	HCl	1 x 10^7 M (estimated)
Chloric acid	$HClO_3$	1 x 10^3 M (estimated)
Phosphoric acid	H_3PO_4	7.5 x 10^{-3} M
Hydrofluoric acid	HF	6.6 x 10^{-4} M
Acetic acid	CH_3CO_2H	1.8 x 10^{-5} M
Carbonic acid	H_2CO_3	4.4 x 10^{-7} M
Dihydrogen phosphate ion	$H_2PO_4^-$	6.2 x 10^{-8} M
Boric acid	H_3BO_3	5.7 x 10^{-10} M
Ammonium ion	NH_4^+	5.6 x 10^{-10} M
Hydrocyanic acid	HCN	4.9 x 10^{-10} M
Bicarbonate ion	HCO_3^-	5.6 x 10^{-11} M
Methylammonium ion	$CH_3NH_3^+$	2.4 x 10^{-11} M
Hydrogen phosphate ion	HPO_4^-	4.2 x 10^{-13} M

Review 8.13: Acid Strength

Use Table 8.2 to determine which is a stronger acid, phosphoric acid or acetic acid.

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

Properties of Basic Solutions

Basic solutions ***feel slippery***. The reason for this is that the hydroxide ions catalyze the hydrolysis of the esters that compose cell membranes in skin. Basic solutions have a ***bitter*** taste and they will turn red litmus pH indicator from red to blue.

Basic solutions can be prepared by dissolving an ionic compound that contains hydroxide in water. For example, the addition of sodium hydroxide to pure water will result in dissociation of the sodium hydroxide crystals to produce sodium ions and hydroxide ions:

$$\mathrm{NaOH}\ (s) \rightleftarrows \mathrm{Na^+}\ (aq) + \mathrm{OH^-}\ (aq)$$

Before $NaOH$ was added, the pH of the pure water was 7.00; the $[OH^-]$ was equal to the $[H_3O^+]$. When the $NaOH$ was added, the $[OH^-]$ increased. If the $[OH^-]$ increases, then the $[H_3O^+]$ must decrease. The resulting $NaOH$ solution is ***basic*** because $[OH^-] > [H_3O^+]$.

Neutralization Reactions

An ***acidic solution*** will react with a ***hydroxide-containing base*** compound to produce a *water* and *an ionic compound* in a reaction called **neutralization**. An example of a ***neutralization reaction*** is the reaction of perchloric acid solution and sodium hydroxide solution:

$$\mathrm{HClO_4}\ (aq) + \mathrm{NaOH}\ (aq) \rightleftarrows \mathrm{H_2O}\ (l) + \mathrm{NaClO_4}\ (aq)$$

In neutralization reactions, the H^+ from the acid bonds to the OH^- to produce water. The (anionic) *base form* of the acid combines with the cationic part of the base to make an *ionic compound* called a **salt**. Although sodium chloride is commonly called "salt," the chemical definition states that a ***salt*** is an ionic compound *formed in a neutralization reaction*.

Review 8.14: Understanding Neutralization Reactions

Predict the products of the following neutralization reactions:

a) $\mathrm{HCl}\ (aq) + \mathrm{NaOH}\ (aq) \rightleftarrows\ ? + ?$

b) $\mathrm{HCl}\ (aq) + \mathrm{KOH}\ (aq) \rightleftarrows\ ? + ?$

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

8.7 The Henderson-Hasselbalch Relationship and Buffer Solutions

Predicting, measuring, and controlling the pH of a solution or biological environment are important. For example, an excess or deficiency of hydronium ions will hinder the ability of enzymes to catalyze crucial chemical reactions; therefore a narrow pH range must be maintained when enzymes are present. We have about 2000 chemical reactions that occur in our bodies, but many of them occur too slowly to be useful without the aid of protein catalysts called enzymes. Nature and certain laboratory applications employ a chemical system, called a **buffer**, that helps to maintain a narrow pH range in bodily fluids or other aqueous solutions.

Before I discuss buffer solutions, it will be helpful to introduce you to the **Henderson-Hasselbalch Equation**. This equation describes the unique relationship that exists between the pH of a solution and the relative amounts of the acid and base forms of a conjugate pair.

The general form of a chemical equation for an acid reacting with water to produce its base form and hydronium can be written as:

$$\mathrm{HA}\ (aq) + \mathrm{H_2O}\ (l) \rightleftarrows \mathrm{A^-}\ (aq) + \mathrm{H_3O^+}\ (aq)$$

HA represents the ***acid form***, and **A^-** represents the ***base form*** of any conjugate pair. The equilibrium expression for this general reaction is:

$$\mathrm{K}_a = \frac{[\mathrm{A}^-][\mathrm{H_3O^+}]}{[\mathrm{HA}]}$$

This expression describes the equilibrium concentration of the acid form, base form, and hydronium ***no matter what other species are dissolved in the aqueous solution***. We can rearrange this equation to get the ratio of the equilibrium concentration of the acid and base form of a conjugate pair. Dividing both sides of the equation above by $[\mathrm{H_3O^+}]$ gives:

$$\frac{[\mathrm{A}^-]}{[\mathrm{HA}]} = \frac{\mathrm{K}_a}{[\mathrm{H_3O^+}]}$$

Equation 8.6

The important thing to see here is that the relative amounts (ratio) of the *base form* and *acid form* of a conjugate pair at equilibrium depends on the K_a value for the particular acid ***and*** $[\mathrm{H_3O^+}]$. Since pH is used as a measure of $[\mathrm{H_3O^+}]$, it is more practical to write *Equation 8.6* in terms of pH instead of $[\mathrm{H_3O^+}]$. The **$[\mathrm{H_3O^+}]$** in *Equation 8.6* can be replaced with **pH** by taking the negative logarithm of both sides of the equation and doing some other algebraic steps:

$$\mathrm{pH} = -\log(\mathrm{K}_a) + \log\left(\frac{[\mathrm{A}^-]}{[\mathrm{HA}]}\right)$$

The "-log(K_a)" term in this equation above is written as "pK_a." Doing so yields what is known as the **Henderson-Hasselbalch Equation**. For a particular conjugate pair, the Henderson-Hasselbalch Equation gives the relationship between the relative amounts of the ***acid and base forms*** present at equilibrium and the **pH** of the solution:

$$\mathrm{pH} = \mathrm{pK}_a + \log\left(\frac{[\mathrm{A}^-]}{[\mathrm{HA}]}\right)$$

The Henderson-Hasselbalch Equation is used so often that K_a values for acids are sometimes tabulated as pK_as. Table 8.3 lists K_a and pK_a values for various acids. Do not be confused by the use of pK_a; it is simply the -log(K_a); pK_a is to K_a as pH is to $[\mathrm{H_3O^+}]$.

Table 8.3 K_a and pK_a Values for Various Acids

Acid Name	Acid Formula	K_a	pK_a $pK_a = -\log(K_a)$
Perchloric acid	$HClO_4$	1×10^{9} M (estimated)	-9.0 (estimated)
Hydrochloric acid	HCl	1×10^{7} M (estimated)	-7.0 (estimated)
Chloric acid	$HClO_3$	1×10^{3} M (estimated)	-3.0 (estimated)
Phosphoric acid	H_3PO_4	7.5×10^{-3} M	2.12
Hydrofluoric acid	HF	6.6×10^{-4} M	3.18
Acetic acid	CH_3CO_2H	1.8×10^{-5} M	4.74
Carbonic acid	H_2CO_3	4.4×10^{-7} M	6.36
Dihydrogen phosphate ion	$H_2PO_4^-$	6.2×10^{-8} M	7.21
Boric acid	H_3BO_3	5.7×10^{-10} M	9.24
Ammonium ion	NH_4^+	5.6×10^{-10} M	9.25
Hydrocyanic acid	HCN	4.9×10^{-10} M	9.31
Bicarbonate ion	HCO_3^-	5.6×10^{-11} M	10.25
Methylammonium ion	$CH_3NH_3^+$	2.4×10^{-11} M	10.62
Hydrogen phosphate ion	HPO_4^{2-}	4.2×10^{-13} M	12.38

We will not use the Henderson-Hasselbalch Equation to do calculations; but we will take advantage of its *implications* in order to predict whether the ***acid form*** or the ***base form*** of a particular conjugate pair is ***predominant*** at equilibrium. A solution containing a conjugate pair can be at ***any*** pH; other species that are in the solution (or might be added) can affect the pH. However, the K_a, and therefore pK_a, for a particular conjugate pair *does not change*. In order to solve problems in this book, you should know and understand the following three statements that are *implied* by the Henderson-Hasselbalch Equation:

- When the **pH** of a solution is ***less than*** the $\mathbf{pK_a}$ of an acid, then the concentration of the *acid form*, [HA], is ***greater than*** the concentration of the *base form*, $[A^-]$. In this case, we say that ***the acid form is predominant***.
- When the **pH** of a solution is ***greater than*** the $\mathbf{pK_a}$ of an acid, then the concentration of the base form, $[A^-]$, is ***greater than*** the concentration of the *acid form*, [HA]. In this case, we say that ***the base form is predominant***.
- When the **pH** of a solution is ***equal to*** the $\mathbf{pK_a}$ of an acid, then the concentration of the *acid form*, [HA], is ***equal to*** the concentration of the *base form*, $[A^-]$.

Table 8.4
Implications of the Henderson-Hasselbalch Equation

Solution Condition	Relative Amounts of Acid and Base Forms
$pH < pK_a$	$[HA] > [A^-]$
$pH > pK_a$	$[A^-] > [HA]$
$pH = pK_a$	$[HA] = [A^-]$

When you are asked whether the *acid form* or the *base form* of a conjugate pair is predominant, you must compare the pH with the pK_a as described in the three statements above, and as summarized in Table 8.4. I will elaborate using an example.

EXAMPLE: If acetic acid and its base form (acetate ion) are present in a solution that has a pH of 7.0, which is predominant, acetic acid or acetate ion?

SOLUTION: We must compare the pH of the solution and the pK_a of acetic acid, and then use the implications of the Henderson-Hasselbalch Equation (from Table 8.4) to predict the predominant species of the acetic acid/acetate ion conjugate pair.

The pH was given (7.0) and the pK_a for acetic acid (from Table 8.3) is 4.74. In this case, the **pH** of the solution is ***greater than*** the **pK_a** of the acetic acid. When the pH > pK_a, the ***base form (acetate ion)*** is predominant.

The general notation "**HA**" for the ***acid form*** and "**A^-**" for the ***base form*** is used to represent any conjugate pair. The superscripted negative sign in "**A^-**" is meant to indicate that the charge of *base form* is one charge-unit less than the charge of the *acid form;* the ***actual charge*** of the base form is *not always* 1-. Likewise, the acid form (**HA**) is not always neutral. You will see examples of this in parts (b) and (c) of the following review problem.

You try a few problems:

Review 8.15: Given the pH and the pKa, Predict the Predominant Species of a Conjugate Pair

For each of the following conjugate pairs, predict whether the acid form or the base form is predominant at the given pH.

a. HF/F^- at pH = 2.7
b. $H_2PO_4^-/HPO_4^{2-}$ at pH = 8.5
c. NH_4^+/NH_3 at pH = 7.0

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

Buffer Solutions

A **buffer** solution is a solution that resists changes in pH when a small amount of acid or base is added. Since hydronium and hydroxide are products or reactants of many reactions in biological organisms and environments, the pH of cells and their surroundings would experience large and damaging pH changes if not for buffers. When a person is dieting, a series of chemical reactions occur in which body fat is metabolized to produce energy. This results in *ketosis*: the production of acetone and two types of acid molecules. If not for the body's buffer solution, the production of the two acid molecules would significantly change the pH of the blood and could result in illness or death.

Research in biochemistry and bioengineering often involves working with pH-sensitive molecules such a proteins or antibodies *in vitro* (outside of their biological environment). The students that do work in my research group are working on technologies to enable artificial, wearable, automated kidneys. One aspect of this work involves immobilizing an enzyme called urease in porous micro-particles. Whenever the students are working with urease, they must use it in a buffer solution because urease's ability to catalyze a reaction is pH-dependent. Furthermore, if the pH gets too high or too low, then urease becomes irreversibly unusable. Urease works best at a pH of about 7.5. The water that comes from the public water systems is not *pure water* and therefore its pH can vary from location to location. The US Environmental Protection Agency recommends, as a standard for public water systems, a pH in the range of 6.5 to 8.5. To work with urease, we wish to adjust the pH to 7.5. One way that we could do so would be to measure the pH of the tap water, then adjust the pH to 7.5 by either adding a small amount of H_3O^+ (from an HCl solution) or OH^-.(from a NaOH solution). The problem with this approach is that, although the pH of the resulting urease solution would be 7.5, small changes in the [H_3O^+] or the [OH^-] brought about by our experimental processes would cause a significant pH change. For example, simply removing the water from the plumbing system allows it to dissolve CO_2 from the air, and this will slowly lower the pH down to about 5.2 because of the **H_3O^+** produced in the following reaction equilibria:

$$CO_2\ (aq) + H_2O\ (l) \rightleftarrows H_2CO_3\ (aq)$$

$$H_2CO_3\ (aq) + H_2O\ (l) \rightleftarrows HCO_3^-\ (aq) + \mathbf{H_3O^+}\ (aq)$$

A better way to stabilize the urease solution at pH to 7.5 is to use a ***buffer***. A buffer is a solution that is made with fairly high concentrations of the ***acid <u>and</u> base forms of a conjugate pair***. This is done using a conjugate pair in which the acid has a pK_a close to the desired pH (within about one pH unit). We choose an acid with a pK_a close to the desired pH because we desire a high concentration of ***<u>both</u>*** the *acid and base form* of the conjugate pair, and according to the Henderson-Hasselbalch Equation, this occurs when the pH is very close to the pK_a. Recall that when the pH = pK_a, there are equal amounts of the acid and the base forms present. At pH values ***far*** from the pK_a, there is a high concentration of *one of the conjugates* and low concentration of *the other*.

Can you guess which of the acids listed in Table 8.3 (and its base form) my research students use in order to buffer their urease solutions very close to pH = 7.5? HINT: Look at the pK_a values for the various acids. They use $H_2PO_4^-$ (and its base form, HPO_4^{2-}) since it has a pK_a = 7.21, which is closest to the desired pH value of 7.5. They make the buffer solution by using a ratio of *base form* to the *acid form* ($[A^-]/[HA]$) so that the pH = 7.5, as described by the Henderson-Hasselbalch Equation:

$$\mathrm{pH} = \mathrm{pK}_a + \log\left(\frac{[\mathrm{A}^-]}{[\mathrm{HA}]}\right)$$

For our purposes, it is not critical, nor do I expect you to be able to do the math and find the ratio of the *base form* to *acid form* of a conjugate pair in order to achieve a desired buffer solution pH. I just want you to *understand* that **the desired pH of a buffer can be obtained by dissolving a certain ratio of the conjugate pair into the solution.**

My research students do use the Henderson-Hasselbalch Equation to find the ratio of the *base form* to *acid form* that is needed to make their pH = 7.5 buffer solution. They add the *base form* as sodium hydrogen phosphate (Na_2HPO_4) and the *acid form* as potassium dihydrogen phosphate (KH_2PO_4) to achieve fairly high concentrations of each (at the calculated ratio). Having high concentrations of ***<u>both</u>*** the *acid form <u>and</u> the base* form is the key to a buffer solution's ability to resist changes in pH when *small* amounts of acid or base are added. I will use Le Chatalier's principle to explain a buffer solution's ability to resist pH change upon the addition of acid or base.

Addition of Acid to a Buffer Solution

If a small amount of acid is added to a ***non buffered solution***, it will cause the pH to decrease since the hydronium ion concentration would increase. However, if a small amount of acid is added to a ***buffered solution***, the excess hydronium ions will cause an *increase in the reverse reaction rate of the buffer conjugate pair equilibrium*, shown below, as predicted by Le Chatalier's Principle.

$$\mathrm{HA}\,(aq) + \mathrm{H_2O}\,(l) \rightleftarrows \mathrm{A^-}\,(aq) + \mathrm{H_3O^+}\,(aq)$$

Movie 8.1 Animation of the Buffering Concept

A video animation showing how a buffer resists pH change when an acid is added. For **print or pdf versions** of the book, the video can be seen at: http://www.zovallearning.com/streamvid/buffering.html

The excess hydronium ions that are added and the *base form* (A^-) of the buffer conjugate pair are converted to $\mathrm{HA}\,(aq) + \mathrm{H_2O}\,(l)$ in the reverse direction of the reaction, and therefore there is not a significant change in the pH of the buffered solution. The removal of the excess hydronium will continue until most of the *base form* of the conjugate pair is depleted. It is for this reason that buffers are made of relatively ***high concentrations*** of the buffering conjugate pairs, and that we say "a buffer is a solution that will resist pH changes when ***small*** amounts of acid or base are added." A video animation showing how a buffer resists pH change when an acid is added is shown in Movie 8.1. For **print or pdf versions** of the book, the video can be seen at: http://www.zovallearning.com/streamvid/buffering.html.

I told you that dieting causes the addition of acid molecules to blood (in **ketosis**) and that the blood's buffering system maintains the pH in the normal range (7.35 - 7.45). When *dieting*, a ***small amount*** of acid is added to the blood; however, during severe *starvation*, *much more* acid is added to the blood. In the case of *starvation*, the *base form* of the blood buffer can be depleted, in a condition called **ketoacidosis**, resulting in illness or death.

Addition of Base to a Buffer Solution

If a small amount of base is added to a ***non buffered solution***, it would increase the pH. The pH would increase because the hydroxide ion concentration would increase, and therefore the concentration of hydronium ions will decrease. However, if a small amount of base is added to a ***buffered solution***, ***the hydronium ion concentration would be maintained because of a decrease in the reverse reaction rate*** of the *buffer conjugate pair equilibrium*, as predicted by Le Châtelier's Principle.

$$\mathrm{HA}\,(aq) + \mathrm{H_2O}\,(l) \rightleftarrows \mathrm{A^-}\,(aq) + \mathrm{H_3O^+}\,(aq)$$

Review 8.16: Buffers

Write the formula of the acid and base form of the conjugate pair that you would use as a buffer solution for each of one of the desired pH values listed below. Use Table 8.3 to select the appropriate acid.

a. pH = 5.0 b. pH = 10.0 c. pH = 7.0

For *i-books* versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

Biological Buffers

An important *intracellular* (within cells) buffer is the dihydrogen phosphate/hydrogen phosphate conjugate pair:

$$\mathrm{H_2PO_4^-}\,(aq) + \mathrm{H_2O}\,(l) \rightleftarrows \mathrm{HPO_4^{2-}}\,(aq) + \mathrm{H_3O^+}\,(aq)$$

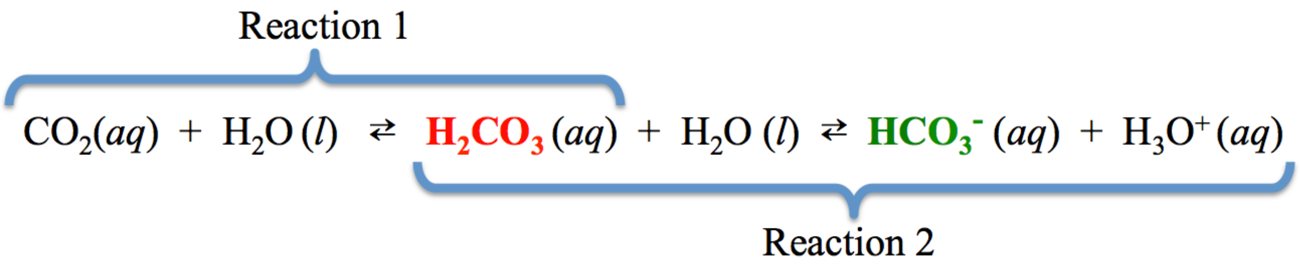
Proteins also act as intracellular buffers. In chapter 13 you will learn how proteins can donate or accept H^+.

Important *extracellular* (outside of cells) buffers, in solutions such as blood or interstitial fluids, are the carbonic acid (**H_2CO_3**)/bicarbonate (**HCO_3^-**) and the ammonium (**NH_4^+**)/ammonia (**NH_3**) conjugate pairs. The "normal" range for the pH of blood plasma is 7.35 to 7.45. In blood, the carbonic acid (**H_2CO_3**)/bicarbonate (**HCO_3^-**) buffering pair is especially useful because the buffer conjugate pair concentrations ([**H_2CO_3**] *and* [**HCO_3^-**]) are replenished through cellular respiration and can be controlled through breathing. To understand how this happens, we must consider these two reactions:

$$\overbrace{\mathrm{CO_2}(aq) + \mathrm{H_2O}\,(l) \rightleftarrows \rlap{$\underbrace{\phantom{\mathrm{H_2CO_3}(aq) + \mathrm{H_2O}\,(l) \rightleftarrows \mathrm{HCO_3^-}(aq) + \mathrm{H_3O^+}(aq)}}_{\text{Reaction 2}}$}\mathbf{H_2CO_3}(aq)}^{\text{Reaction 1}} + \mathrm{H_2O}\,(l) \rightleftarrows \mathbf{HCO_3^-}(aq) + \mathrm{H_3O^+}(aq)$$

The CO_2 in **Reaction 1** is constantly produced in the body during cellular respiration. Most of the CO_2 produced is exhaled; however there is always some CO_2 dissolved in the blood. **Reaction 2** is the carbonic acid/bicarbonate equilibrium, which acts as a **buffer**.

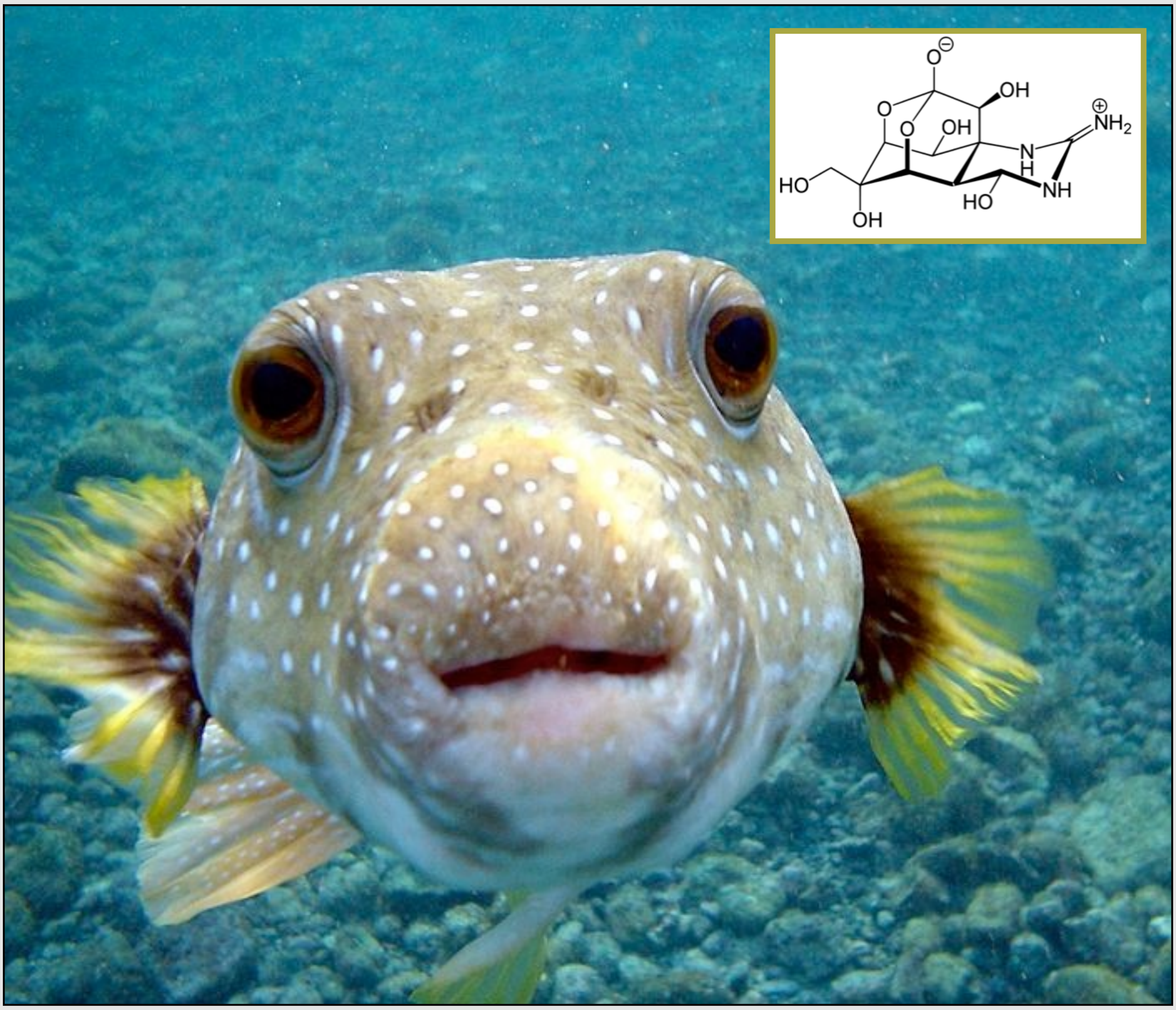
Let's consider what happens when a ***base*** is added to blood. Addition of a ***small amount of base*** to blood would cause a *decrease* in the hydronium ion concentration (and an increase in pH) if it were not replenished by the conversion of **H_2CO_3** into H_3O^+ and **HCO_3^-** in the *forward direction of Reaction 2*. If ***more* base** is added, and the concentration of **H_2CO_3** becomes dangerously low, the blood pH will begin to rise (**alkalosis**). The body has a chemical sensing mechanism that detects the rise in pH and chemical signals are sent to the respiratory system that slow the breathing rate. When this occurs, less CO_2 is exhaled, therefore the blood CO_2 concentration will increase. Think about what Le Châtelier's Principle predicts will happen to the *forward rates of Reactions 1 and 2* when the blood CO_2 concentration increases. Increasing the CO_2 concentration will cause an increase in the *forward rate Reaction 1*, which will increase the concentration of $\mathbf{H_2CO_3}$. This increase in the concentration of $\mathbf{H_2CO_3}$ causes the *forward rate of Reaction 2* to increase, and therefore ***increases*** the hydronium ion concentration. Decreased breathing rates and the subsequent production of hydronium ions will continue until the body's chemical sensing system detects that the pH has been reduced back to the normal range.



$$CO_2(aq) + H_2O(l) \rightleftarrows \mathbf{H_2CO_3}(aq) + H_2O(l) \rightleftarrows \mathbf{HCO_3^-}(aq) + H_3O^+(aq)$$

Next, let's consider what happens when ***acid*** is added to blood. Addition of a ***small amount of acid*** to blood would cause an *increase* in the hydronium ion concentration (and a decrease in pH) if it were not replenished by the conversion H_3O^+ and $\mathbf{HCO_3^-}$ into $\mathbf{H_2CO_3}$ in the *reverse direction of Reaction 2*. If ***<u>more</u> acid*** were added, and the concentration of $\mathbf{HCO_3^-}$ would become dangerously low, and the blood pH would begin to drop (**acidosis**). The body's chemical sensing mechanism detects the drop in pH and chemical signals are sent to the respiratory system that cause an ***increase*** the breathing rate. When this occurs, *more* CO_2 is exhaled therefore the blood CO_2 concentration will decrease. As predicted by Le Châtelier's Principle, decreasing the CO_2 concentration causes the *reverse rates of both Reactions 1 <u>and</u> 2* to be greater than the forward rates, and therefore ***decreases*** the hydronium ion concentration. Increased breathing rates and the subsequent drop in the hydronium ion concentration will continue until the body's chemical sensing system detects that the pH has been increased back to the normal range.

Chapter 9:
Carboxylic Acids, Amines, and Amides



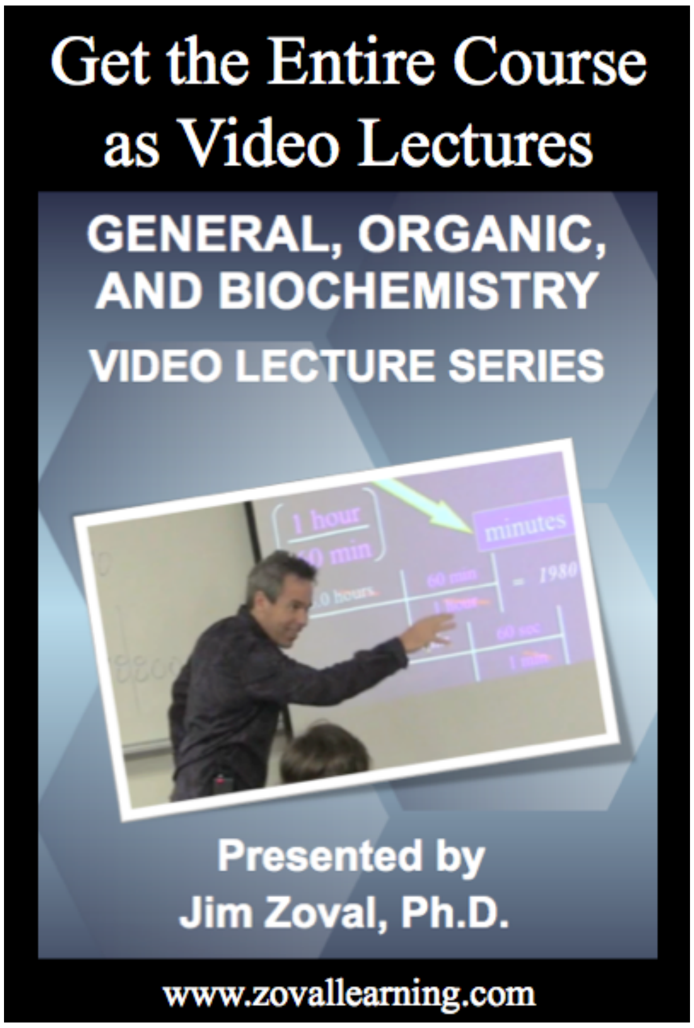
The pufferfish (*Arothron hispidus*) is one of the most poisonous animals on earth because of an amine called tetrodotoxin that is present primarily in its liver and ovaries. The structure of the tetrodotoxin molecule is shown in the insert.
Source: Wikimedia Commons, Author: Brocken Inaglory, CC-BY-SA http://creativecommons.org/licenses/by-sa/3.0/deed.en

In chapter 4, we began our study of organic chemistry (the chemistry of carbon-containing molecules). You learned many of the details about alkanes, alkenes, alkynes, and aromatic hydrocarbons, and were introduced to three other families of organic compounds: alcohols, carboxylic acids, and esters. In this chapter and the next chapter, you will develop further knowledge and understanding of those and organic molecules, with emphasis on their structures, properties, reactions, and their significance in biological systems.

Video Lectures for the General, Organic, and Biochemistry Course

If you **ARE** a **Saddleback College student**, the video lectures for this chapter and all others are available through your class website for ***FREE***. See your instructor for details and the password.

If you **ARE NOT** a **Saddleback College student,** the video lectures can be accessed at: www.zovallearning.com



9.1 Chapter 9 Educational Goals

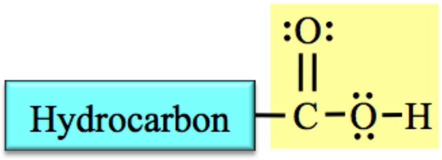
1. Given the structure of a **carboxylic acid**, **carboxylate ion**, **ester**, **amide**, **or amine molecule**, be able to give the systematic names and vice versa.
2. Know and understand the intermolecular forces that attract carboxylic acid, amine, or amide molecules to one another, and how these forces affect boiling points and melting points.
3. Identify **amines** as primary (1^o), secondary (2^o), or tertiary (3^o). Compare and contrast **amines** and **quaternary ammonium ions**.
4. Predict the products for the reactions of carboxylic acids with water, alcohols, amines, ammonia, or with strong bases.
5. Predict the products for the reactions of amines with water or with strong acids.
6. Predict the products for the acid-catalyzed **hydrolysis of an amide**.
7. Identify **chiral carbon** atoms in structural formulas. Given the number of chiral carbons in a molecule, determine the number of **stereoisomers**.
8. Define the term **enantiomer**. Compare and contrast **enantiomers** and **diastereomers**.

9.2 Carboxylic Acids

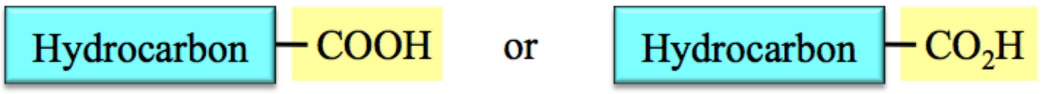
Organic compounds are categorized into various **families** by the presence of distinct *functional groups*. A **functional group** is an ***atom, group of atoms*, or *bond*** that gives a compound a particular set of physical and chemical properties.

The Structure of Carboxylic Acids

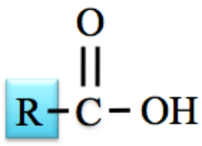
Carboxylic acids contain a ***carboxyl functional*** group attached to a hydrocarbon (alkyl group) part. Carboxyl groups contain both a ***carbonyl group***, which is a carbon double bonded to an oxygen (**C=O)**, ***and*** a hydroxyl group **(-OH)** that are connected to each other and the hydrocarbon part as shown below. The *carboxyl group* is highlighted in yellow.



The carboxyl group is sometimes drawn as "COOH" or "CO_2H" in condensed structures:

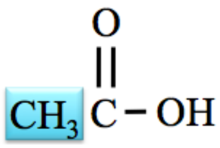


Chemists use the letter "**R**" in the general structures to represent either a hydrocarbon/alkyl group part ***or*** any other organic group of atoms. We write the ***general form*** of a carboxylic acid molecule as:

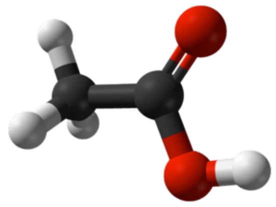


$$R-\overset{\overset{\displaystyle O}{\|}}{C}-OH$$

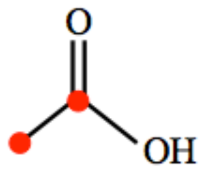
A specific example of a carboxylic acid is *acetic acid*. White vinegar is a mixture composed of 95% water and 5% acetic acid. The hydrocarbon part (**R**) in acetic acid is a methyl group (CH_3). The condensed structural formula and a ball-and-stick model for *acetic acid* are shown below (black sphere = carbon, red sphere = oxygen, and white sphere = hydrogen).



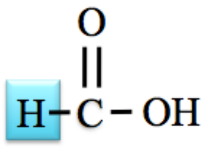
$$CH_3\overset{\overset{\displaystyle O}{\|}}{C}-OH$$



The skeletal structure of acetic acid is shown below. I have added red dots to indicate the carbon atom positions.



In the case of the smallest carboxylic acid, methanoic acid, **R** represents a hydrogen atom.



$$H-\overset{\overset{\displaystyle O}{\|}}{C}-OH$$

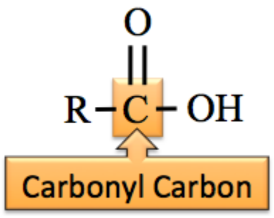
Methanoic acid, also known as formic acid, is the molecule that is responsible for the stinging sensation caused by some ant bites.

Naming Carboxylic Acids

We will use the IUPAC system for naming carboxylic acid molecules. The systematic naming of carboxylic acids is based on the hydrocarbon naming method.

Step 1: Find and name the parent chain.

The parent chain of a carboxylic acid is the longest continuous chain of carbon atoms that includes the ***carbonyl carbon***. The ***carbonyl carbon*** is the carbon in the carbonyl group (**C=O)**.


$$R-\overset{\overset{O}{\|}}{C}-OH$$

Count the number of carbon atoms in the parent chain (include the carbonyl carbon). Starting with the alkane name that corresponds to the number of carbon atoms in the parent chain, replace the "**e**" at the end of the alkane name with "**oic acid.**" For example, if the parent chain of a carboxylic acid contains three carbons, it is called propan***oic acid***.

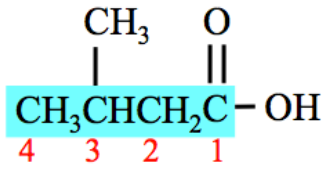
propan***e*** ⟶ propan***oic acid***

Step 2: Name any alkyl group substituents.

Alkyl groups are named in the same way as we did for hydrocarbons. Use Table 4.9 from chapter 4 to find the alkyl group name.

Step 3: Determine the *point of attachment* of alkyl group(s) to the parent chain.

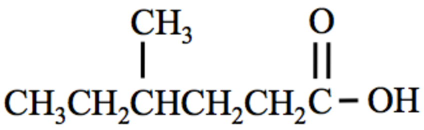
In order to assign "position numbers" to the substituents, the carbons ***in the parent chain*** are numbered. ***Begin numbering at the carbonyl carbon***. For example, the carbons in the parent chain of the molecule shown below are assigned position numbers (in red):


$$\underset{4}{CH_3}\overset{\overset{CH_3}{|}}{\underset{3}{CH}}\underset{2}{CH_2}\overset{\overset{O}{\|}}{\underset{1}{C}}-OH$$

Step 4: Construct the name of the carboxylic acid by placing the alkyl groups in alphabetical order and specifying their position numbers, followed by the name of the parent chain.

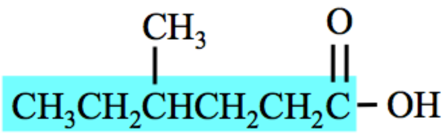
- Use a ***dash*** between position *numbers* and *letters*.
- Add the labels di, tri, or tetra in front of the alkyl group name **if** two, three, or four (respectively) *identical* substituents are present.

Example: Name the molecule that is shown below.


$$CH_3CH_2\overset{\overset{CH_3}{|}}{CH}CH_2CH_2\overset{\overset{O}{\|}}{C}-OH$$

Step 1: Find and name the parent chain.

The parent chain of a carboxylic acid is the longest continuous chain of carbon atoms that includes the ***carbonyl carbon***. The parent chain of the molecule in this example is highlighted blue:


$$CH_3CH_2\overset{\overset{CH_3}{|}}{CH}CH_2CH_2\overset{\overset{O}{\|}}{C}-OH$$

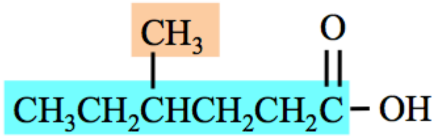
Count the number of carbon atoms in the parent chain (include the carbonyl carbon). Starting with the alkane name that corresponds to the number of carbon atoms in the parent chain, replace the "**e**" at the end of the alkane name with "**oic acid**."

hexan***e*** → hexan***oic acid***

There are six carbon atoms in the parent chain. The name of the parent chain is hexanoic acid.

Step 2: Name any alkyl group substituents.

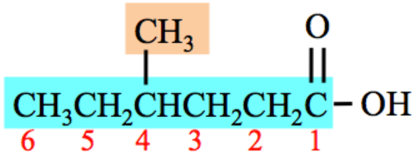
There is one alkyl group substituent: **methyl**. The methyl group substituent in this example is shaded orange:



$$CH_3CH_2\overset{\overset{CH_3}{|}}{C}HCH_2CH_2\overset{\overset{O}{||}}{C}-OH$$

Step 3: Determine the *point of attachment* of any alkyl groups to the parent chain.

Begin numbering the parent chains of carboxylic acids at the carbonyl carbon. The carbons in the parent chain are assigned position numbers (in red):



$$\underset{6}{CH_3}\underset{5}{CH_2}\underset{4}{\overset{\overset{CH_3}{|}}{C}H}\underset{3}{CH_2}\underset{2}{CH_2}\underset{1}{\overset{\overset{O}{||}}{C}}-OH$$

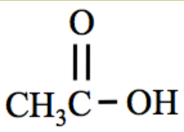
Step 4: Construct the name of the carboxylic acid by placing the alkyl groups in alphabetical order and specifying their position numbers, followed by the name of the parent chain. Use a ***dash*** between position *numbers* and *letters*.

- The methyl substituent is attached to carbon number 4 of the parent chain: **4-methyl**.
- The parent chain name is **hexanoic acid**.
- The name of the molecule is **4-methylhexanoic acid**.

You try a couple of problems:

Review 9.1: Naming Carboxylic Acids

The *common name* of the molecule shown below is acetic acid. What is the IUPAC systematic name for acetic acid?

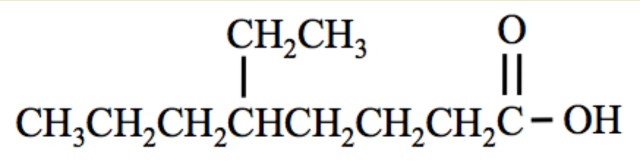


$$CH_3\overset{\overset{O}{||}}{C}-OH$$

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

Review 9.2: Naming Carboxylic Acids

Name the molecule that is shown below.



$$CH_3CH_2CH_2\overset{\overset{CH_2CH_3}{|}}{C}HCH_2CH_2CH_2\overset{\overset{O}{||}}{C}-OH$$

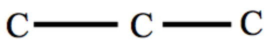
For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

Let’s do a problem in which we are given the name of a carboxylic acid and wish to draw its structural formula.

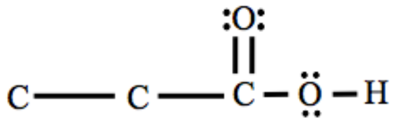
Example: Draw the ***line bond structure*** of 2-methylpropanoic acid.

Solution: First draw the carbons of the *parent chain*.

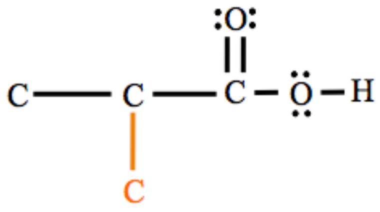
- The parent chain is propanoic acid, therefore it contains three carbons.



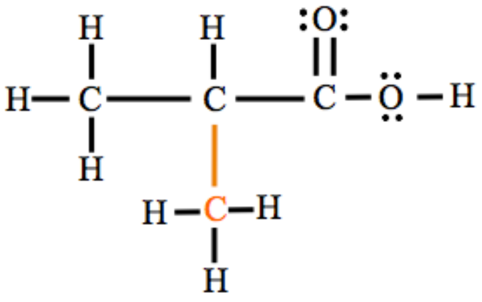
Next, complete the *carboxyl group* by adding a double-bonded oxygen and a hydroxy group to a carbon at the end of the parent chain. It does not matter which end of the parent chain that you use as the carboxyl group, however it is *usually* drawn on the right-hand end of the parent chain. Since we are drawing the *line bond structure*, we must include the lone pairs on oxygens. Add enough lone pairs to the ***oxygens*** so that the octet rule is satisfied.



Next, add the ***carbon*** of the *methyl substituent*. For **2-methyl**propanoic acid, the methyl group’s carbon (shaded orange) is attached to carbon number 2 of the parent chain. Note that the *carbonyl carbon* is assigned position number 1.



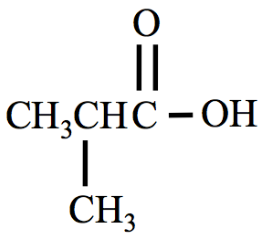
To finish, add enough hydrogens to each carbon in order to satisfy the octet rule:



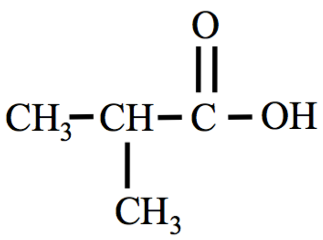
You may find it helpful to used line bond structures when drawing or considering the reactions of organic molecules. The reason for this is that the line bond structures show all the atoms and all the bonds. Once you have the correct line bond structure, it is easier to draw the condensed and skeletal formulas. The condensed and skeletal structures for 2-methylpropanoic acid are shown below.

Condensed Structure

Online problem sets may require you to draw the ***carbon-carbon*** *bonds in condensed structures as shown below:*

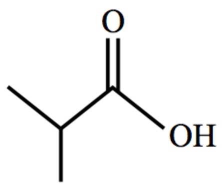


$\mathrm{CH_3\underset{\underset{CH_3}{|}}{CH}\overset{\overset{O}{||}}{C}-OH}$



$\mathrm{CH_3-\underset{\underset{CH_3}{|}}{CH}-\overset{\overset{O}{||}}{C}-OH}$

Skeletal Structure



You try one:

Review 9.3: Naming Carboxylic Acids

Draw the line bond, condensed, and skeletal structural formulas of decanoic acid.

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

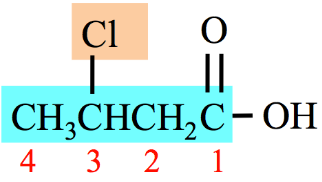
Hydroxyl, Fluorine, Chlorine, and Bromine Substituents

So far, you have only seen alkyl group substituents. It is not uncommon to see carboxylic acids that contain other atoms or groups of atoms that are named as substituents. A hydroxyl group (-OH), fluorine atom, chlorine atom, or bromine atom that is bonded to *the parent chain of a carboxylic acid* is named as a substituent. Table 9.1 lists the names used for each of these substituents. Use position numbers and alphabetize these substituents, along with any alkyl group substituents, when naming carboxylic acids.

Table 9.1
Names of Non-Alkyl Substituents

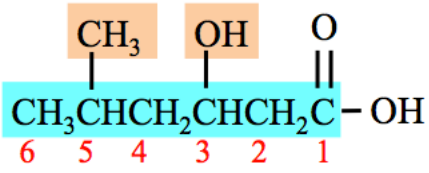
Substituent	Name
OH	hydroxy
F	fluoro
Cl	chloro
Br	bromo

Examples:



$$\underset{4}{CH_3}\underset{3}{\overset{Cl}{\overset{|}{C}}H}\underset{2}{CH_2}\underset{1}{\overset{O}{\overset{\|}{C}}}-OH$$

3-chlorobutanoic acid

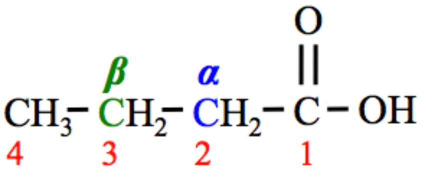


$$\underset{6}{CH_3}\underset{5}{\overset{CH_3}{\overset{|}{C}}H}\underset{4}{CH_2}\underset{3}{\overset{OH}{\overset{|}{C}}H}\underset{2}{CH_2}\underset{1}{\overset{O}{\overset{\|}{C}}}-OH$$

3-hydroxy-5-methylhexanoic acid

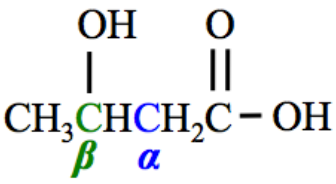
Alpha (*α*) and Beta (*β*) Carbons

Two of the carbon positions in the parent chain of carboxylic acids are designated as "***α***" or "***β***." The ***α*** and ***β*** designations are not part of the IUPAC naming system, however they are commonly used. The carbons that are designated as carbon number 2 and 3 in the IUPAC system are often referred to as the ***α*** carbon and ***β*** carbon, respectively. The ***α*** carbon (shaded blue) and ***β*** carbon (shaded green) are labeled in the structure of butanoic acid shown below.



$$\underset{4}{CH_3}-\underset{3}{\overset{\beta}{CH_2}}-\underset{2}{\overset{\alpha}{CH_2}}-\underset{1}{\overset{O}{\overset{\|}{C}}}-OH$$

The IUPAC systematic name of the molecule shown below is **3**-hydroxybutanoic acid. It is named ***β***-hydroxybutanoic acid when using the ***α***/***β*** designation.



$$CH_3\underset{\beta}{\overset{OH}{\overset{|}{C}}H}\underset{\alpha}{CH_2}\overset{O}{\overset{\|}{C}}-OH$$

Review 9.4: Alpha (*α*) and Beta (*β*) Carbons

Lactic acid is another name for ***α***-hydroxypropanoic acid.

a. Draw the condensed structure of **lactic acid**.
b. What is the IUPAC systematic name for lactic acid?

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

For future reference (not to memorize), the systematic name, common name, structural formula, and natural source(s) for several carboxylic acids are listed in Table 9.2.

Table 9.2 **Names, Structural Formulas, and Natural Sources of Various Carboxylic Acids**

Number of Carbons	IUPAC Name	Common Name	Condensed Structure	Source(s)
1	methanoic acid	formic acid	$HCOOH$	insect stings
2	ethanoic acid	acetic acid	CH_3COOH	bacterial fermentation
3	propanoic acid	propionic acid	CH_3CH_2COOH	bacterial production
4	butanoic acid	butyric acid	$CH_3(CH_2)_2COOH$	butter
5	pentanoic acid	valeric acid	$CH_3(CH_2)_3COOH$	valerian (an herb)
6	hexanoic acid	caproic acid	$CH_3(CH_2)_4COOH$	goat fat
7	heptanoic acid	enanthic acid	$CH_3(CH_2)_5COOH$	rancid oils
8	octanoic acid	caprylic acid	$CH_3(CH_2)_6COOH$	coconuts and breast milk
9	nonanoic acid	pelargonic acid	$CH_3(CH_2)_7COOH$	pelargonium (a genus of flowering plants)
10	decanoic acid	capric acid	$CH_3(CH_2)_8COOH$	coconuts and palm kernel oil
12	dodecanoic acid	lauric acid	$CH_3(CH_2)_{10}COOH$	coconut oil
16	hexadecanoic acid	palmitic acid	$CH_3(CH_2)_{14}COOH$	palm oil
18	octadecanoic acid	stearic acid	$CH_3(CH_2)_{16}COOH$	chocolate
20	icosanoic acid	arachidic acid	$CH_3(CH_2)_{18}COOH$	peanut oil

Water Solubility of Carboxylic Acids

The water solubility of an organic compound depends on the compound's ability to interact with water. You can review section 5 of chapter 7 for a detailed discussion of the solubility of organic compounds in water. All carboxylic acid molecules have a significantly strong attraction to water through hydrogen bonding and dipole-dipole interactions. ***Small*** carboxylic acid molecules have significant water solubility. As the nonpolar (hydrocarbon part) of carboxylic acids gets larger, their water solubility decreases; this is true not only for carboxylic acids, but for all organic molecules. The trend of decreasing water solubility with increasing molecular size can be seen in the solubilities of the carboxylic acid molecules that are listed in Table 9.3.

Table 9.3 **Water Solubility of Carboxylic Acids**

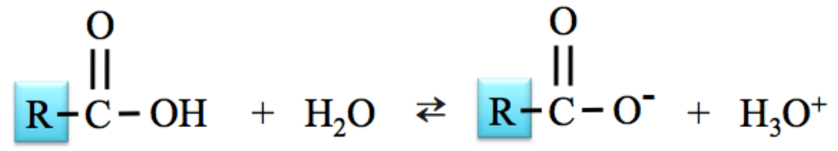
Molecule Name	Condensed Structure	Water Solubility (g/100 mL)
methanoic acid	$HCOOH$	miscible*
ethanoic acid	CH_3COOH	miscible
propanoic acid	CH_3CH_2COOH	miscible
butanoic acid	$CH_3CH_2CH_2COOH$	miscible
pentanoic acid	$CH_3CH_2CH_2CH_2COOH$	3.7
hexanoic acid	$CH_3CH_2CH_2CH_2CH_2COOH$	1.0

*miscible indicates that the substance will mix/dissolve at any carboxylic acid to water ratio.

Chemical Reactions of Carboxylic Acids

1) Reaction of Carboxylic Acids with Water

Carboxylic acids have the word "*acid*" in their names because they readily donate an H^+ in acid-base reactions. When placed in water, a carboxylic acid molecule acts as an acid and water acts as a base. An H^+ from the hydroxyl group (OH) of the carboxylic acid is donated to H_2O. The general form of the reaction of a carboxylic acids and water is shown below.



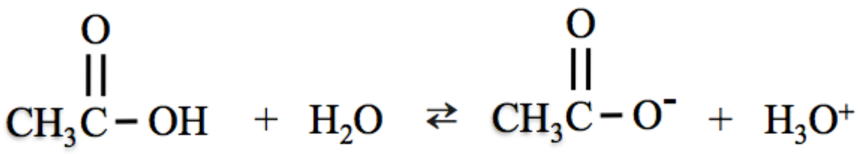
$$R-\overset{\overset{\displaystyle O}{\|}}{C}-OH + H_2O \rightleftarrows R-\overset{\overset{\displaystyle O}{\|}}{C}-O^- + H_3O^+$$

carboxylic acid
(*acid form*)

carboxylate ion
(*base form*)

The *base form* of a carboxylic acid is called a **carboxylate ion**. A carboxylate ion has a charge of (1-) because of the formal charge on the single-bonded oxygen. Recall that an oxygen atom with just one single bond has a (1-) formal charge.

A specific example of the reaction of a carboxylic acid and water is the reaction ethanoic acid and water.



$$CH_3\overset{\overset{\displaystyle O}{\|}}{C}-OH + H_2O \rightleftarrows CH_3\overset{\overset{\displaystyle O}{\|}}{C}-O^- + H_3O^+$$

ethanoic acid
(*acid form*)

ethanoate ion
(*base form*)

The *base form* of ethanoic acid is named **ethanoate ion**. Carboxylate ions are named by replacing the "-ic acid" suffix of their ***acid form*** name with "-ate ion." A few examples are shown below.

ethano**ic acid** → ethano**ate ion**
acet**ic acid** → acet**ate ion**
3-methylpentano**ic acid** → 3-methylpentano**ate ion**

When a carboxylic acid is placed in water, a reaction occurs between the acid and the water, and an equilibrium is established. There is some of the *acid form* present and some of the *base form* present at equilibrium. Carboxylic acids are considered to be "***weak acids***" because their K_a values are much less than 1. When they are placed in pure water, there is *much more* of the acid form of the conjugate pair (carboxylic acid) than the base form (carboxylate ion). The K_a values for a few carboxylic acids are listed in Table 9.4.

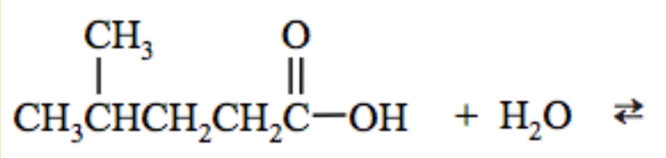
When carboxylic acid/carboxylate ion conjugate pairs are in a solution, even if the solution contains other dissolved species, the relative amounts of the acid form and base form can be predicted by the Henderson-Hasselbalch Equation (see chapter 8, section 7).

Table 9.4 K_a Values for a Few Carboxylic Acids

Acid Name	Acid Formula	K_a	pK_a $pK_a = -\log(K_a)$
Acetic acid	CH_3COOH	1.8×10^{-5} M	4.74
2-hydroxypropanoic acid (lactic acid)	$CH_3CH(OH)COOH$	1.4×10^{-4} M	3.86
propanoic acid	CH_3CH_2COOH	1.3×10^{-5} M	4.88

Review 9.5: Reactions of Carboxylic Acids and Water

Add the products for the following reaction:



$$CH_3\overset{\overset{CH_3}{|}}{C}HCH_2CH_2\overset{\overset{O}{||}}{C}-OH + H_2O \rightleftarrows$$

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

Review 9.6: Drawing and Naming Carboxylate Ions

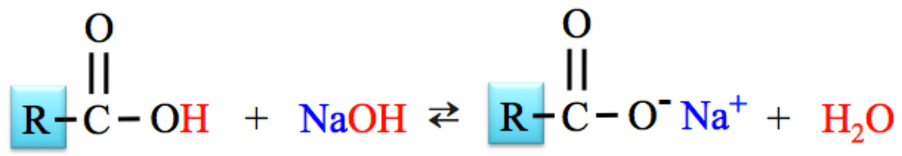
Draw the **condensed structure** *and* write the ***name of the base form*** (carboxylate ion) for each of the following carboxylic acids

a. octanoic acid
b. 3-methylbutanoic acid
c. 5-methylhexanoic acid

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

2) Neutralization: Reaction of a Carboxylic Acid and a Hydroxide Ion

In a **neutralization reaction**, a carboxylic acid will react with a ***hydroxide-containing*** *base* compound to produce *water* and *a* ***carboxylic acid salt***. The general form of the neutralization of a carboxylic acid reaction is shown below.

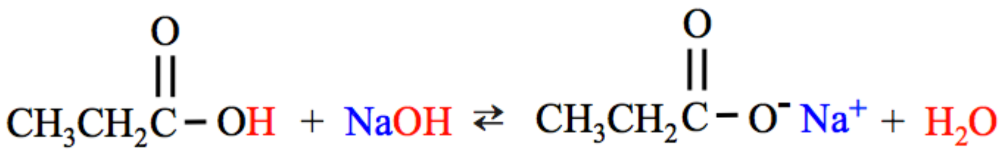


$$R-\overset{\overset{O}{||}}{C}-OH + NaOH \rightleftarrows R-\overset{\overset{O}{||}}{C}-O^- Na^+ + H_2O$$

carboxylic acid

carboxylic acid ***salt***
(an ionic compound)

This is the same neutralization reaction that you learned in the previous chapter; the H^+ from the acid bonds to the OH^- to produce H_2O. The *carboxylate ion* and the *cation* from the base make an *ionic compound* called a **carboxylic acid salt.** A specific example of the neutralization of a carboxylic acid is the reaction of propanoic acid and sodium hydroxide:



$$CH_3CH_2\overset{\overset{O}{||}}{C}-OH + NaOH \rightleftarrows CH_3CH_2\overset{\overset{O}{||}}{C}-O^- Na^+ + H_2O$$

propanoic acid

carboxylic acid ***salt***
(sodium propanoate)

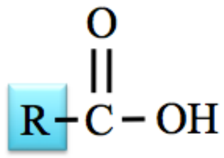
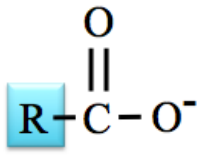
Water Solubility of Carboxylate Ions

A carboxylic acid salt formed from a carboxylate anion and a Na^+ or K^+ cation is water **soluble** if its "R" group contains less than twelve carbon atoms. If its "R" group contains twelve or more carbons, then it is ***amphipathic***. The attraction of water to the formal charge of the carboxylate ion makes the salts more water soluble than their carboxylic acid conjugates. A summary of the solubilities of carboxylic acids and Na^+ or K^+ salts of carboxylate ions is given in Table 9.5.

A carboxylic acid salt formed from a carboxylate anion and a Ca^{2+} or Mg^{2+} cation is water **insoluble**. It is the Ca^{2+} and Mg^{2+} ions that are responsible for the build up of **soap scum** in bathtubs and showers. Water with significant amounts of Ca^{2+} and/or Mg^{2+} ions is called **hard water**. The long-chain carboxylate ions in soap combine with Ca^{2+} or Mg^{2+} to form *insoluble solids* (precipitates) called ***soap scum***. In order to prevent the formation of soap scum and other Ca^{2+} and Mg^{2+} precipitates, Ca^{2+} and Mg^{2+} can be removed from water, in a device called a **water softener**, before the water is distributed throughout a home's plumbing system. Water softeners operate by exchanging Na^+ ions for Ca^{2+} and Mg^{2+} ions.

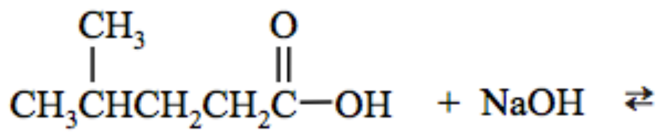
Table 9.5

The Water Solubility of Carboxylic Acids and the Carboxylate Ions of Their Na^+ or K^+ Salts

Carboxylic Acid	Carboxylate Ion
 $R-\overset{\overset{\Large O}{\|\|}}{C}-OH$ Acid Form	 $R-\overset{\overset{\Large O}{\|\|}}{C}-O^-$ Base Form
When **R** gets to **five** carbons, the water solubility decreases dramatically.	If **R** < 12: water soluble If **R** ≥ 12: amphipathic (forms monolayers or micelles)

Review 9.7: Neutralization of Carboxylic Acids

Add the products for the following neutralization reaction:

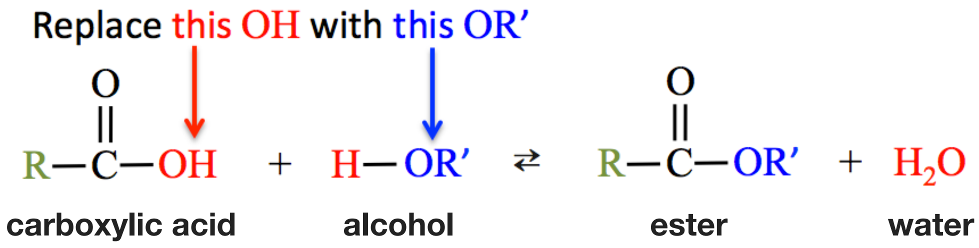


$$CH_3\underset{}{\overset{\overset{CH_3}{|}}{C}}HCH_2CH_2\overset{\overset{O}{\|}}{C}-OH \quad + \ NaOH \ \rightleftarrows$$

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

3) Esterification: The Reaction of a Carboxylic Acid and an Alcohol

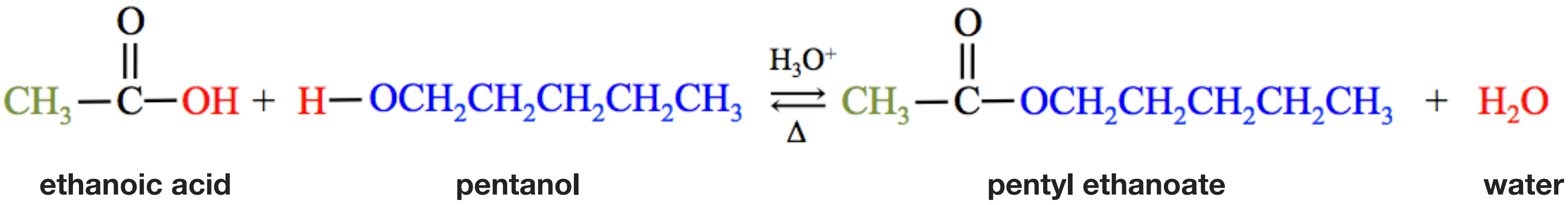
In an ***esterification reaction,*** a carboxylic acid reacts with an alcohol to produce an ester and water. This reaction is very important in the storage and metabolism of fat (triglycerides) and in other biological processes. The general form for the esterification reaction is:



$$R-\overset{\overset{O}{\|}}{C}-OH \ + \ H-OR' \ \rightleftarrows \ R-\overset{\overset{O}{\|}}{C}-OR' \ + \ H_2O$$

There are two R-groups involved in this reaction, one of them is originally part of the carboxylic acid and the other one is originally part of the alcohol. In order to keep track of them in the general reaction, we use "**R**" for the hydrocarbon part of the carboxylic acid, and "**R'**" for the hydrocarbon part of the alcohol. **R** and **R'** may, or may not, be identical. In an esterification reaction, the **OH** from the carboxylic acid is replaced with the **OR'** from the alcohol. The **OH** from the carboxylic acid combines with the **H** from the alcohol to produce water. The formation of water from an **OH** from one reactant and an **H** from another reactant is very common in many biological reactions; you will see this throughout the remainder of this book. You were first introduced to the *alcohol family* of organic molecules in chapter 4. The general form of an alcohol is usually drawn as "**R-OH,**" however, I draw it as "**H-OR**" in esterification reactions so that you can more easily visualize which bonds are broken and formed.

Esterification reactions can be done in the lab by heating a carboxylic acid and alcohol mixture in the presence of a strong acid catalyst. A specific example of an esterification reaction is the reaction of ethanoic acid and pentanol (an alcohol):



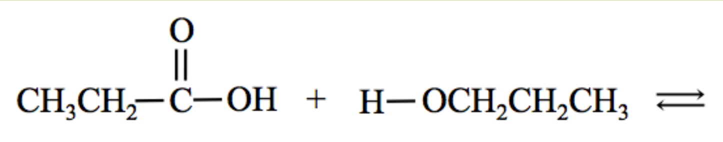
$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-OH + H-OCH_2CH_2CH_2CH_2CH_3 \underset{\Delta}{\overset{H_3O^+}{\rightleftharpoons}} CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-OCH_2CH_2CH_2CH_2CH_3 + H_2O$$

The Greek delta symbol (**Δ**) is often written below the arrows in the chemical equation when heat is used to increase the rate of a reaction, as shown in the equation above. Likewise, when catalysts, such as H_3O^+, are used, the formula or name of the catalyst is often written above the arrows. The ester formed in the reaction above, pentyl ethanoate, has the distinct aroma of bananas. Many esters have pleasant aromas and flavors, and occur naturally in foods. Esters are often added to foods as artificial flavors. They are also used in perfumes.

Review 9.8: Predicting the Products of Esterification Reactions

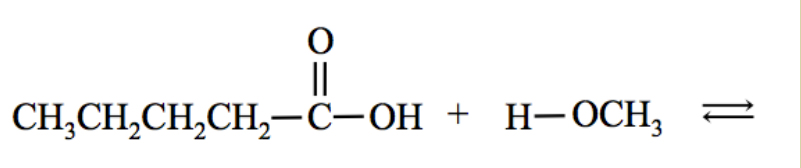
Add the products for the following esterification reactions:

a.



$$CH_3CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-OH + H-OCH_2CH_2CH_3 \rightleftharpoons$$

b.

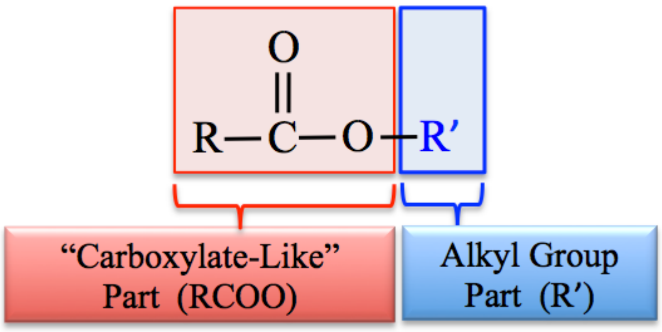


$$CH_3CH_2CH_2CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-OH + H-OCH_3 \rightleftharpoons$$

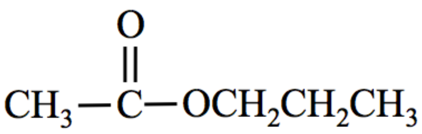
For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

Naming Esters

The IUPAC method for naming esters involves naming the **R'** alkyl group part first, followed by the "*carboxylate-like*" part. These two parts of an ester molecule can be identified as shown in the illustration below.



I will elaborate by using an example. **Name the ester shown below:**

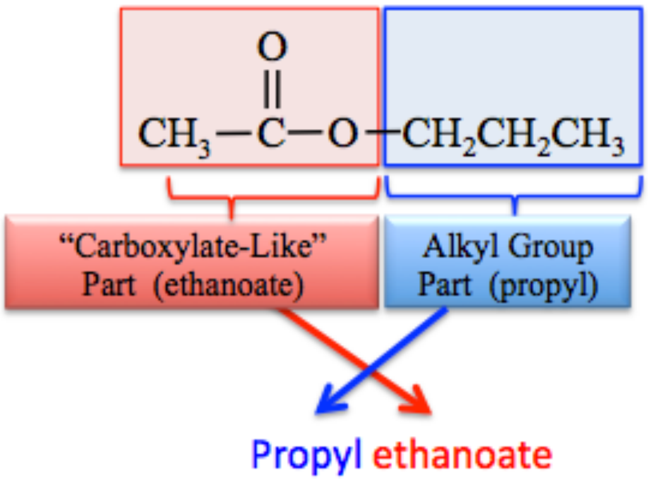


$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-OCH_2CH_2CH_3$$

SOLUTION:

1) Identify the alkyl group (**R'**) part and the carboxylate-like part.

2) The ester is named by writing the alkyl group (**R'**) part name first, then a space, followed by the name that the "carboxylate-like" part would have ***if it were an actual carboxylate ion***. In this example, the "carboxylate-like" part contains two carbons, therefore its name would be ***ethanoate*** if it were an actual carboxylate ion. The alkyl group (**R'**) is a **propyl** group. The name of this ester is **propyl ethanoate**.



Many naturally-occurring esters contain alkyl groups composed of more than four carbons. In chapter 4, you learned the names of alkyl groups with less than five carbons (i.e. methyl, ethyl, propyl, butyl). Table 9.6 lists the names and structures of nonbranched alkyl groups composed of 5-10 carbons.

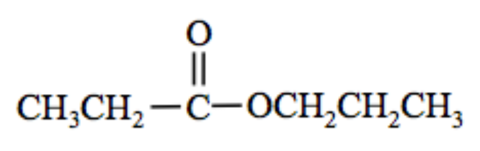
Table 9.6 Names and Structures of Some Alkyl Groups

Number of Carbons	Alkyl Group Name	Condensed Structure
5	pentyl	$-CH_2CH_2CH_2CH_2CH_3$
6	hexyl	$-CH_2CH_2CH_2CH_2CH_2CH_3$
7	heptyl	$-CH_2CH_2CH_2CH_2CH_2CH_2CH_3$
8	octyl	$-CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$
9	nonyl	$-CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$
10	decyl	$-CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$

Review 9.9: Naming Esters

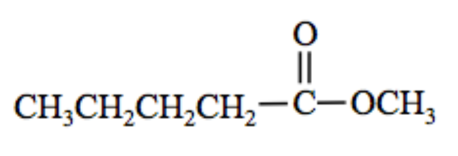
Write the name of each of the esters shown below:

a.



$CH_3CH_2-\overset{\overset{O}{\|}}{C}-OCH_2CH_2CH_3$

b.



$CH_3CH_2CH_2CH_2-\overset{\overset{O}{\|}}{C}-OCH_3$

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

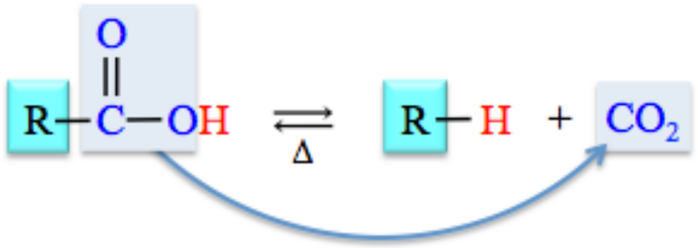
Review 9.10: Drawing Ester Structures

Draw the condensed structure of **octyl butanoate**.

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

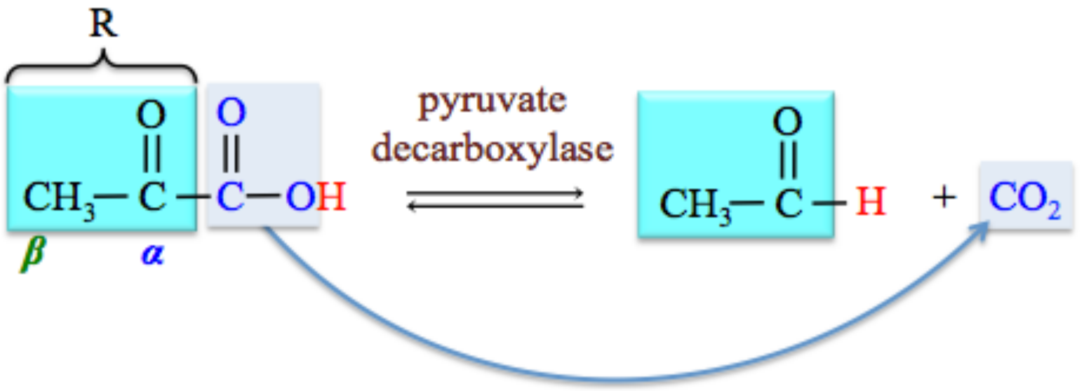
4) Decarboxylation of Carboxylic Acids

Carboxylic acids undergo a decomposition reaction called **decarboxylation.** This reaction is very important in the citric acid cycle and other biological processes. The carbon dioxide that we exhale is produced by decarboxylation reactions in two of the reactions of the citric acid cycle. In decarboxylation reactions, a carboxyl group (COOH) is removed and replaced by a hydrogen atom. The general form for the decarboxylation reaction is:



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-OH \underset{\Delta}{\rightleftharpoons} R-H + CO_2$$

Decarboxylation reactions require heat and/or a catalyst. The enzymes in biological systems that catalyze decarboxylation reactions are called ***decarboxylases***. Carboxylic acids with an **R** group composed of an alkyl group ***only*** do not readily undergo decarboxylation reactions. However when the alpha (***α***) or beta carbon (***β***) of the **R** group is double bonded to an oxygen, then decarboxylation reactions readily occur. For example, the decarboxylation of pyruvic acid is an important reaction in yeast:

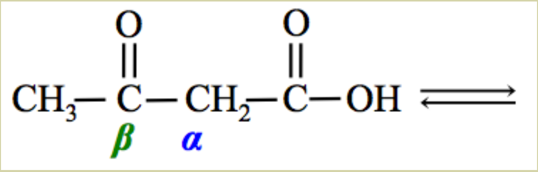


$$\underbrace{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}}_{R}-\overset{\overset{\displaystyle O}{\|}}{C}-OH \xrightarrow{\text{pyruvate decarboxylase}} CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-H + CO_2$$

Note that we have expanded our definition of the "**R**" group to be ***any organic group*** that is unchanged in a reaction. The carbonyl group at pyruvate's ***α***-carbon is unchanged in this decarboxylation reaction. Decarboxylation is not only an important reaction in yeast, it also take place in cellular respiration in other animals. You will see this reaction again when I discuss metabolism in chapter 15.

Review 9.11: Decarboxylation Reactions

The production of molecules called ***ketone bodies*** occurs in humans when large amounts of stored fat are used to produce energy. This can occur during dieting, starvation conditions, or other conditions in a process called **ketosis**. The production of ketone bodies is useful since cells in the brain ***cannot*** get energy from molecules other than sugars or ketone bodies. When *acetoacetic acid* (one of the three ketone body molecules) is produced in ketosis, it is subsequently converted to another ketone body molecule in a decarboxylation reaction. Predict (draw) the products of this decarboxylation reaction of acetoacetic acid (shown below). **NOTE: The *carbonyl* (C=O) *group* at the *β*-carbon of *acetoacetic* acid is not affected by the reaction; it is considered to be part of the R group.** The ***carboxyl group*** **(COOH)** is removed and replaced with a hydrogen.



$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-OH \rightleftharpoons$$

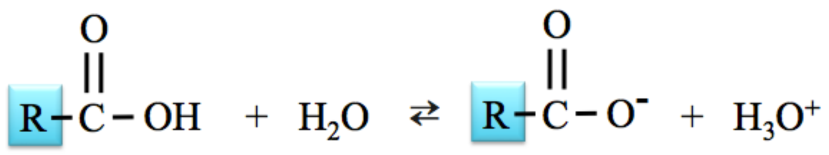
acetoacetic acid

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

Summary of the Reactions of Carboxylic Acids

1) Reactions of Carboxylic Acids with Water

When placed in water, a carboxylic acid acts as an acid and water acts as a base. An H^+ from the hydroxyl group (**OH**) of the carboxylic acid is donated to H_2O.



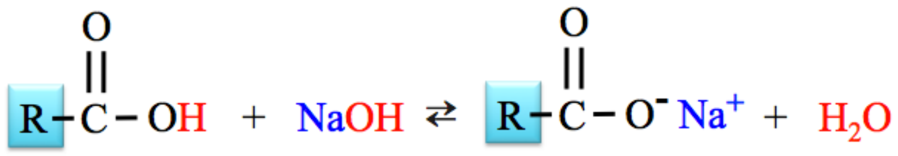
$$R-\overset{O}{\overset{\|}{C}}-OH + H_2O \rightleftarrows R-\overset{O}{\overset{\|}{C}}-O^- + H_3O^+$$

carboxylic acid
(*acid form*)

carboxylate ion
(*base form*)

2) Neutralization: Reaction of a Carboxylic Acid with a Hydroxide Ion

In a **neutralization reaction**, a carboxylic acid will react with a ***hydroxide-containing*** *base* compound to produce *water* and *a* ***carboxylic acid salt***.



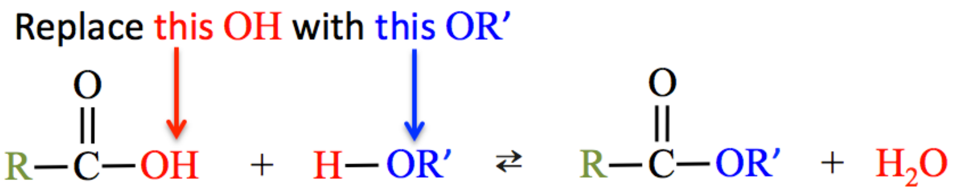
$$R-\overset{O}{\overset{\|}{C}}-OH + NaOH \rightleftarrows R-\overset{O}{\overset{\|}{C}}-O^-Na^+ + H_2O$$

carboxylic acid

carboxylic acid ***salt***
(an ionic compound)

3) Esterification: The Reaction of a Carboxylic Acids with an Alcohol

In an ***esterification reaction,*** a carboxylic acid reacts with an alcohol to produce an ester and water.



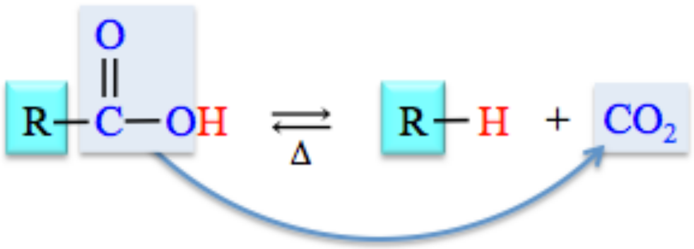
Replace this OH with this OR'

$$R-\overset{O}{\overset{\|}{C}}-OH + H-OR' \rightleftarrows R-\overset{O}{\overset{\|}{C}}-OR' + H_2O$$

Carboxylic Acid Alcohol Ester Water

4) Decarboxylation of Carboxylic Acids

In decarboxylation reactions, a carboxylate group (COOH) is removed and replaced by a hydrogen atom.

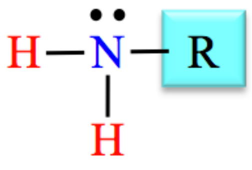


$$R-\overset{O}{\overset{\|}{C}}-OH \underset{\Delta}{\rightleftarrows} R-H + CO_2$$

9.3 Amines

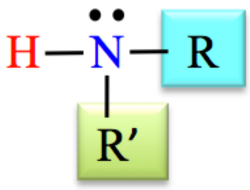
The Structure of Amines

Amines contain a ***nitrogen atom*** with *one* lone pair and *three* single bonds to **R** groups or hydrogen(s). Amines are classified as primary (1º), secondary (2º), or tertiary (3º) based on the number of **R** groups that they contain. The general forms of the three categories of amines are:



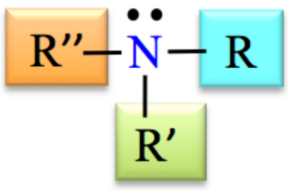
primary (1º) amine

NH_2R



secondary (2º) amine

NHR_2



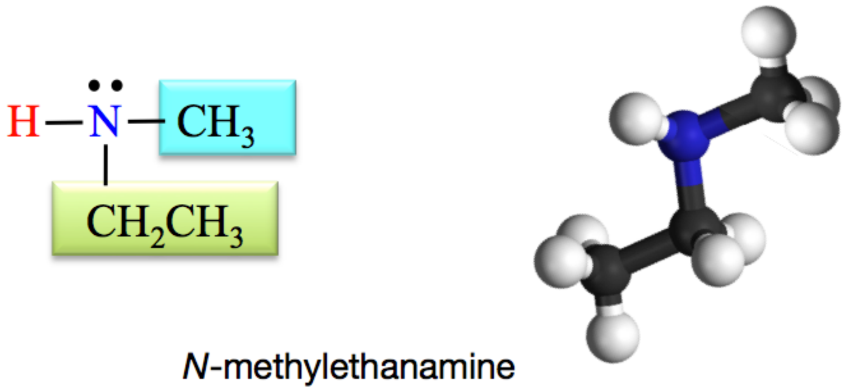
tertiary (3º) amine

NR_3

In **primary (1º) amines**, a nitrogen is bonded to ***one*** **R** group and ***two*** hydrogen atoms. An example of a primary amine is methanamine. The structural formula and ball-and-stick model for methanamine are shown below (blue sphere = nitrogen, black sphere = carbon, and white sphere = hydrogen).

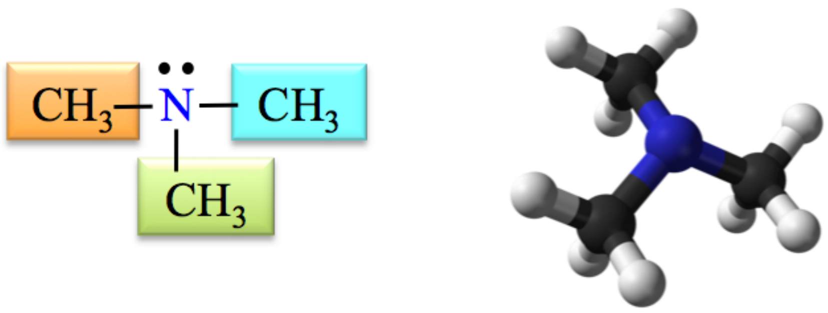
methanamine

In **secondary (2º) amines**, a nitrogen is bonded to ***two*** **R** groups and ***one*** hydrogen atom. One **R** group is written as **R**, and the other as **R'**, to indicate that *they are not necessarily the same alkyl group*. An example of a secondary amine is *N*-methylethanamine:



N-methylethanamine

In **tertiary (3º) amines**, a nitrogen is bonded to ***three*** **R** groups. An example of a tertiary amine is *N,N*-dimethylmethanamine:

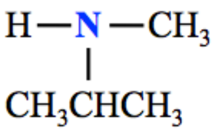


N,N-dimethylmethanamine

Review 9.12: The Structure of Amines

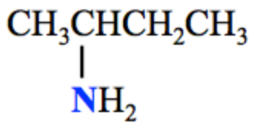
Identify each of the amines shown below as either primary (1º), secondary (2º), or tertiary (3º).

a.



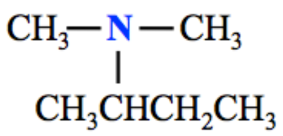
$$\begin{array}{ccc} H - & N & - CH_3 \\ & | & \\ & CH_3CHCH_3 & \end{array}$$

b.



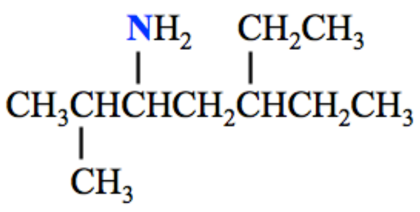
$$\begin{array}{cccc} CH_3 & CH & CH_2 & CH_3 \\ & | & & \\ & NH_2 & & \end{array}$$

c.



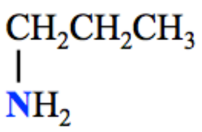
$$\begin{array}{ccc} CH_3 - & N & - CH_3 \\ & | & \\ & CH_3CHCH_2CH_3 & \end{array}$$

d.



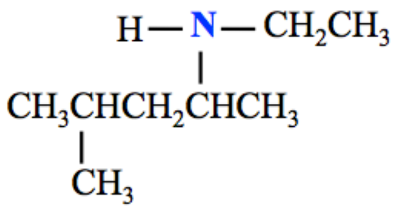
$$\begin{array}{cccccc} & & NH_2 & & CH_2CH_3 & \\ & & | & & | & \\ CH_3 & CH & CH & CH_2 & CH & CH_2CH_3 \\ & | & & & & \\ & CH_3 & & & & \end{array}$$

e.



$$\begin{array}{cc} CH_2 & CH_2CH_3 \\ | & \\ NH_2 & \end{array}$$

f.



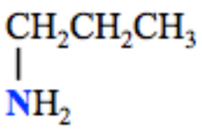
$$\begin{array}{ccccc} & & & H - N - CH_2CH_3 & \\ & & & | & \\ CH_3 & CH & CH_2 & CH & CH_3 \\ & | & & & \\ & CH_3 & & & \end{array}$$

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

Review 9.13: The Structure of Amines

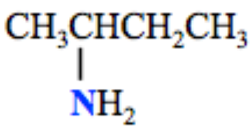
Draw the skeletal structure of each of the molecules shown below:

a.



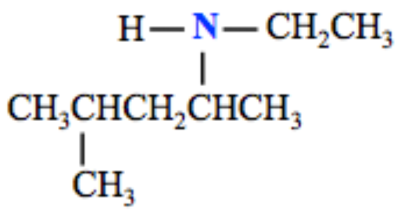
$$\begin{array}{cc} CH_2 & CH_2CH_3 \\ | & \\ NH_2 & \end{array}$$

b.



$$\begin{array}{cccc} CH_3 & CH & CH_2 & CH_3 \\ & | & & \\ & NH_2 & & \end{array}$$

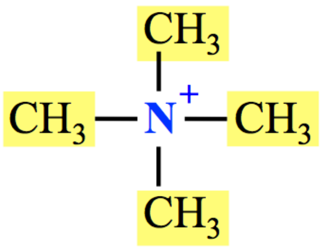
c.



$$\begin{array}{ccccc} & & & H - N - CH_2CH_3 & \\ & & & | & \\ CH_3 & CH & CH_2 & CH & CH_3 \\ & | & & & \\ & CH_3 & & & \end{array}$$

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

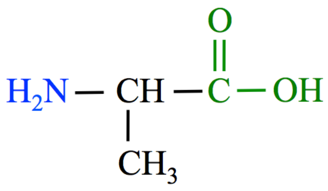
A **quaternary ammonium ion** is formed when *an additional* hydrogen *or* alkyl group (**R**) is added to an amine. The nitrogen in a quaternary ammonium ion *does not have a lone pair* and, therefore has a formal charge of 1+. An example of a ***quaternary ammonium ion*** is the tetramethylammonium ion, which occurs naturally in some animals. This ion is present in especially high concentrations in some species of *Neptunea* (commonly called whelks) that are eaten by humans.



$$\begin{array}{ccc} & CH_3 & \\ & | & \\ CH_3 - & N^+ & - CH_3 \\ & | & \\ & CH_3 & \end{array}$$

tetramethylammonium ion

Some molecules contain *more than one* type of functional group. For example, molecules called **amino acids** contain both an **amino group** (**-NH_2**) *and* a carboxyl group (**-COOH**). An example of an ***amino acid*** is alanine:



$$H_2N-\underset{\underset{CH_3}{|}}{CH}-\overset{\overset{O}{\|}}{C}-OH$$

alanine

Amino acids are the precursors to proteins; you will learn more about amino acids and proteins in chapter 13.

Naming Amines

The *systematic method* that we will use for naming amines is based on the hydrocarbon naming method.

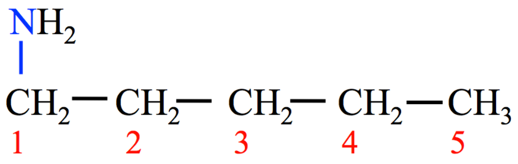
Step 1. Find and name the *parent chain*.

The *parent chain is the longest, continuous chain of carbon atoms that* ***contains the point of attachment to the nitrogen****.*

- Count the number of carbon atoms in the parent chain. Starting with the alkane name that corresponds to the number of carbon atoms in the parent chain, replace the "**e**" at the end of the alkane name with "**amine.**" For example, if the parent chain of an amine contains two carbons, it would be called *ethanamine*.

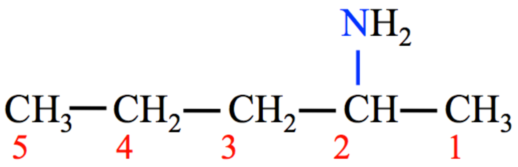
ethan***e*** ⟶ ethan***amine***

- For amines with ***more than two carbons***, the position of *the point of attachment to the* ***nitrogen*** must be indicated by adding a number before the parent chain name, as described below.
    - Assign *position numbers* to the carbons in the parent chain. Position number **1** is assigned to the carbon at the *end of the parent chain* that is **nearest to the point of attachment to the nitrogen.**
        - If the nitrogen is bonded to carbon number **1** of the parent chain, then "1-" is used as a prefix to the parent chain name. For example, in the molecule below, the parent chain is called **1-**pentanamine.



$$\underset{1}{\overset{\overset{NH_2}{|}}{CH_2}}-\underset{2}{CH_2}-\underset{3}{CH_2}-\underset{4}{CH_2}-\underset{5}{CH_3}$$

        - If the nitrogen is bonded to carbon number **2** of the parent chain, then "2-" is used as a prefix to the parent chain name. For example, in the molecule below, the parent chain is called **2-**pentanamine.



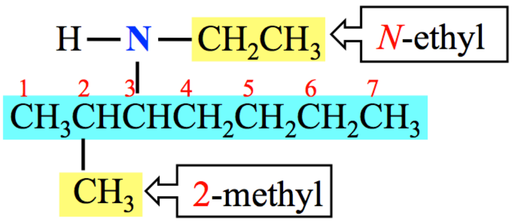
$$\underset{5}{CH_3}-\underset{4}{CH_2}-\underset{3}{CH_2}-\underset{2}{\overset{\overset{NH_2}{|}}{CH}}-\underset{1}{CH_3}$$

    - This is analogous to the numbers that you used as prefixes for the parent chain names of alkenes to indicate the position of the double bond.

Step 2. Name any alkyl group substituents.

Alkyl group substituents that are attached to the parent chain are named in the same way as you did for alkanes.

- For secondary and tertiary amines, the *nonparent chain* **R** group(s) *attached to the nitrogen* are named as substituents. "*N*-" is written in front of the **R** group substituent name, instead of a position *number*, in order to indicate that the **R** group is *attached to the nitrogen*. For example, the amine shown below has a *methyl* substituent attached to the ***parent chain*** and an *ethyl* substituent attached to the **nitrogen**.



The parent chain is highlighted blue. The substituents are are highlighted yellow.

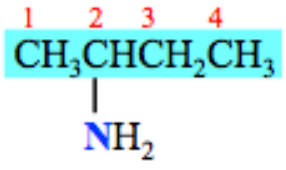
Step 3. Construct the name of the amine by placing the alkyl groups in alphabetical order and specifying their position, followed by the name of the parent chain.

- This is done the same way as you did for hydrocarbons and carboxylic acids.
- Remember to use a dash between position numbers (or "*N*") and letters.

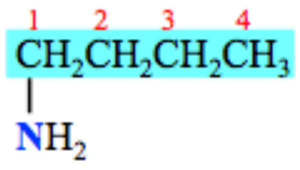
The name of the amine **shown above** in **Step 2** is ***N*-ethyl-2-methyl-3-heptanamine**.

Other examples:

Primary (1°) Amine Examples:

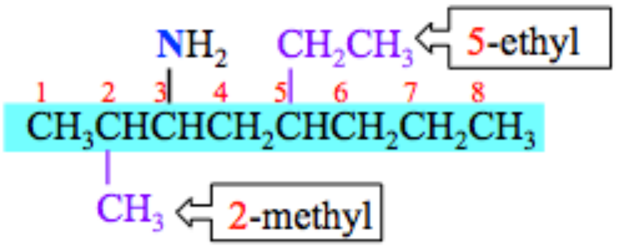


2-butanamine



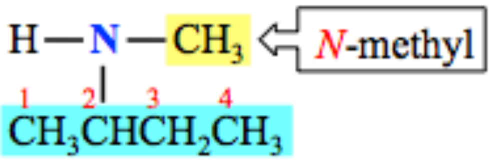
1-butanamine

(also drawn as $CH_3CH_2CH_2CH_2NH_2$)

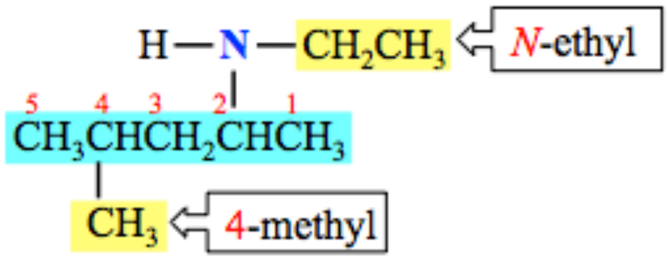


5-ethyl-2-methyl-3-octanamine

Secondary (2°) Amine Examples:

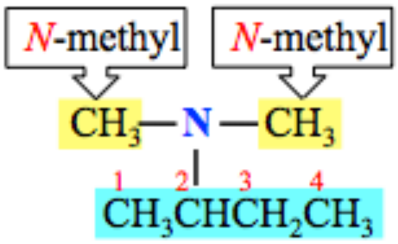


N-methyl-2-butanamine

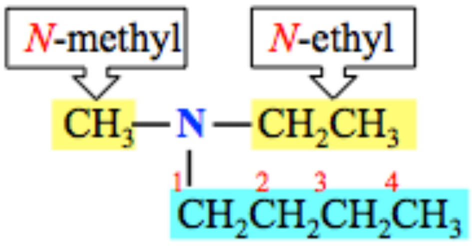


N-ethyl-4-methyl-2-pentanamine

Tertiary (3°) Amine Examples:



N,N-dimethyl-2-butanamine



N-ethyl-*N*-methyl-1-butanamine

Common Names for Amines

Simple amines, those with a relatively few number of carbon atoms, are often identified by ***common names*** by placing “amine” after the names of the alkyl group(s) that are attached to the nitrogen.

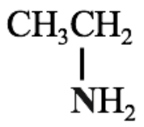
Examples:

CH_3NH_2	$CH_3CH_2NH_2$	$NH(CH_3)_2$	$N(CH_3)_3$
methylamine	**ethylamine**	**dimethylamine**	**trimethylamine**

Review 9.14: Naming Amines

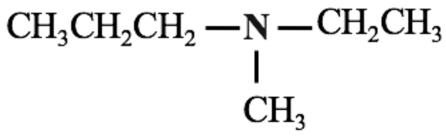
Write the **systematic names** for each of the amines shown below:

a.



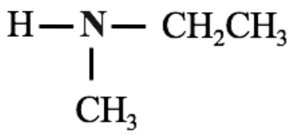
$CH_3\underset{NH_2}{\underset{|}{CH_2}}$

b.



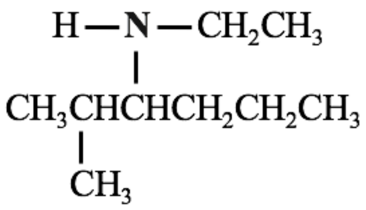
$CH_3CH_2CH_2-\underset{CH_3}{\underset{|}{N}}-CH_2CH_3$

c.



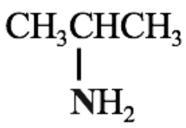
$H-\underset{CH_3}{\underset{|}{N}}-CH_2CH_3$

d.



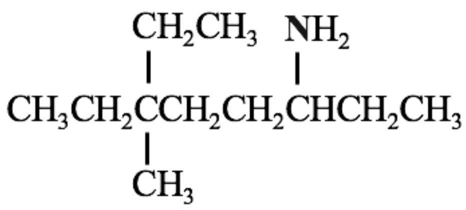
$CH_3\underset{CH_3}{\underset{|}{CH}}\overset{H-N-CH_2CH_3}{\overset{|}{CH}}CH_2CH_2CH_3$

e.



$CH_3\underset{NH_2}{\underset{|}{CH}}CH_3$

f.



$CH_3CH_2\overset{CH_2CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}CH_2CH_2\overset{NH_2}{\overset{|}{CH}}CH_2CH_3$

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

Review 9.15: Drawing the Structural Formulas of Amines

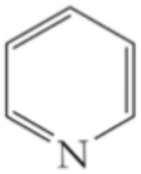
Draw the condensed and skeletal structure of each of the amines listed below.

a. 2-methyl-3-hexanamine
b. *N*-methyl-2-propanamine
c. *N*,*N*-diethylethanamine

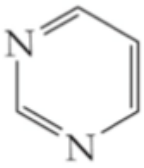
For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

Heterocyclic Compounds

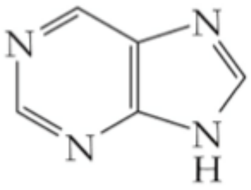
You have seen cyclic compounds such as cyclohexane and cyclopentane. The rings of the cyclic compounds that you have seen so far have contained *only carbon atoms*. Cyclic compounds that contain atoms other than carbon are known as **heterocyclic compounds.** Examples of heterocyclic compounds are:



pyridine

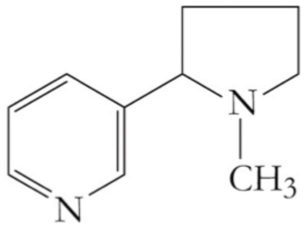


pyrimidine



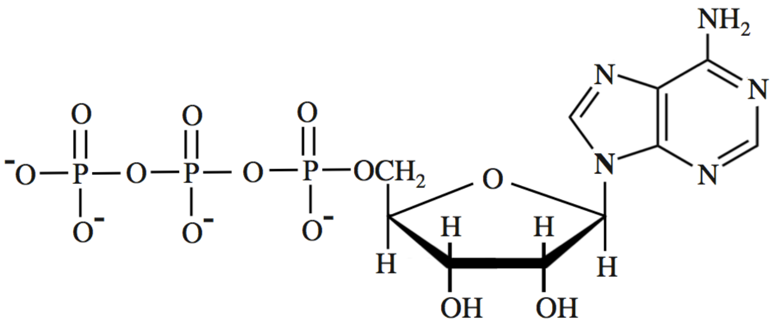
purine

Heterocyclic, nitrogen-containing rings are very common in plants and animals. Nicotine is a naturally occurring, nitrogen-containing heterocyclic molecule from the tobacco plant.

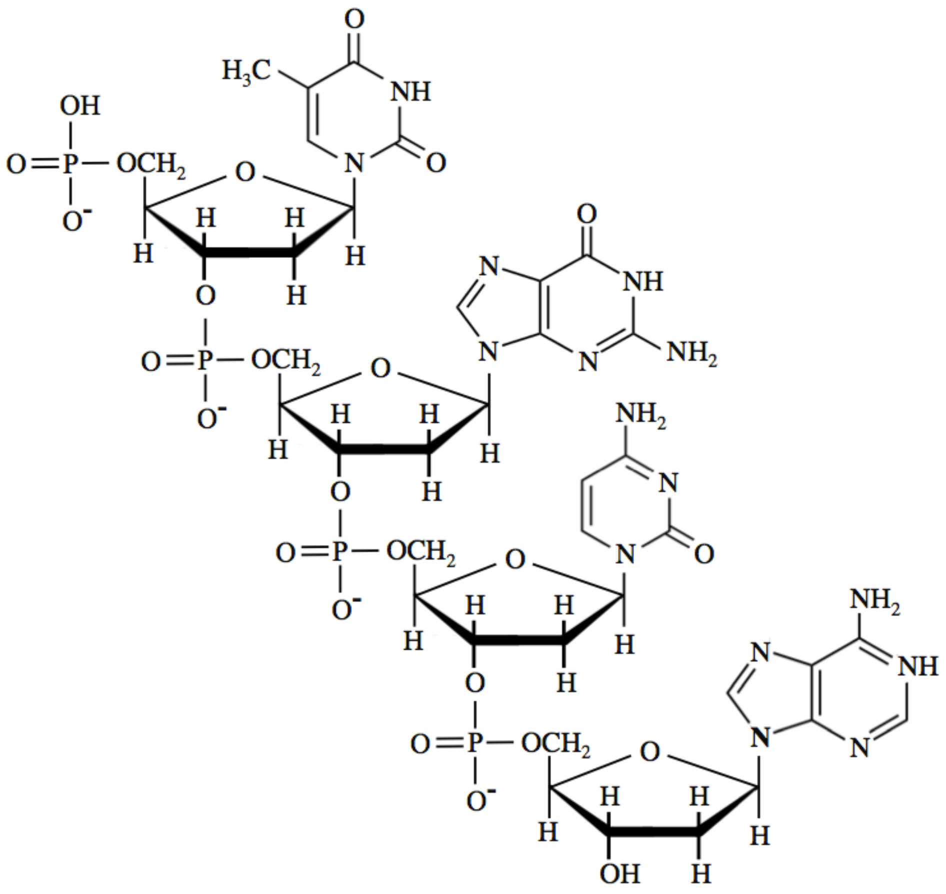


nicotine

Adenosine triphosphate (ATP), used by nature in both plants and animals, is an important compound for energy storage. ATP, shown below (left), has *nitrogen-containing* rings heterocyclic rings and an *oxygen-containing* heterocyclic ring. DNA and RNA contain both *nitrogen-containing* and an oxygen-*containing* heterocyclic ring structures. A structural formula for a small portion of DNA is shown below (right).



adenosine triphosphate (ATP)

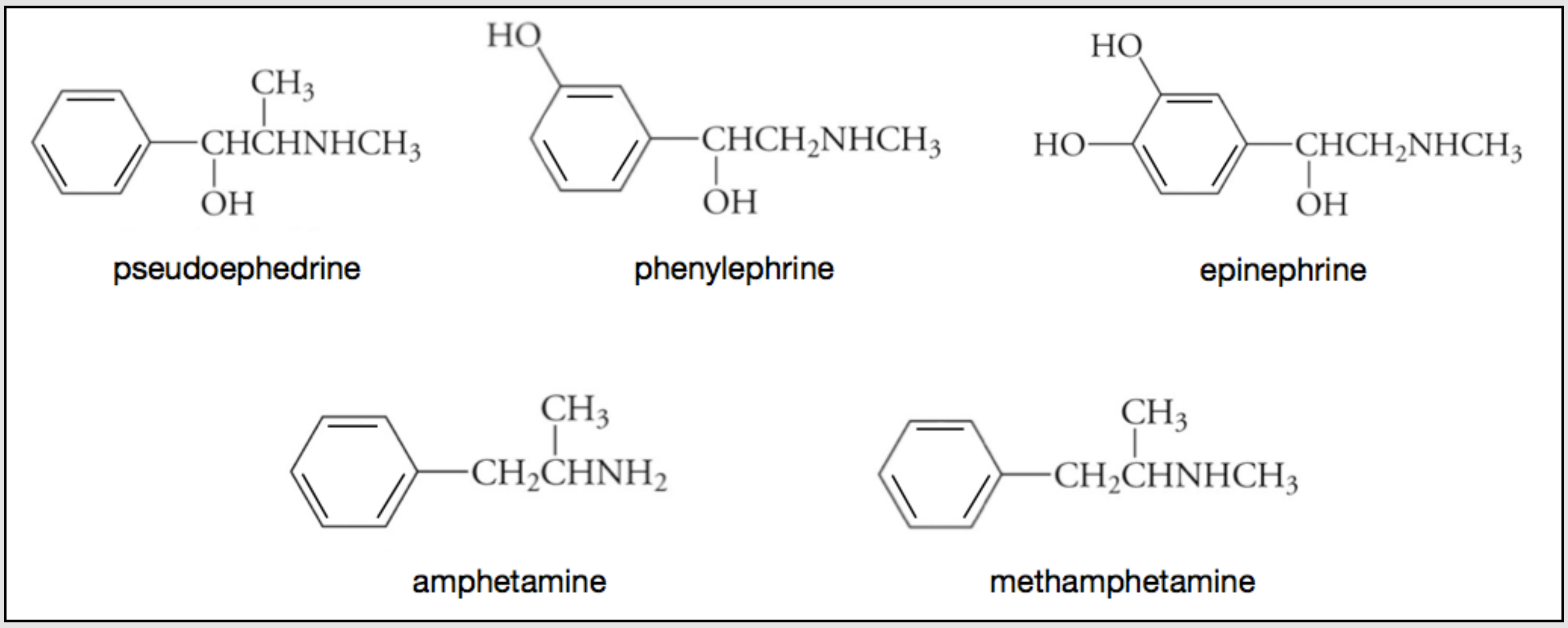


deoxyribonucleic acid (DNA)

Properties of Amines

Many amines have the foul odor of decomposing fish. Amines frequently occur in plants and animals. Smaller amines can irritate skin, eyes, and mucous membrane and are toxic when ingested. Many synthetic and naturally occurring amines are physiologically active. Some examples of physiologically active amines are shown in Figure 9.1.

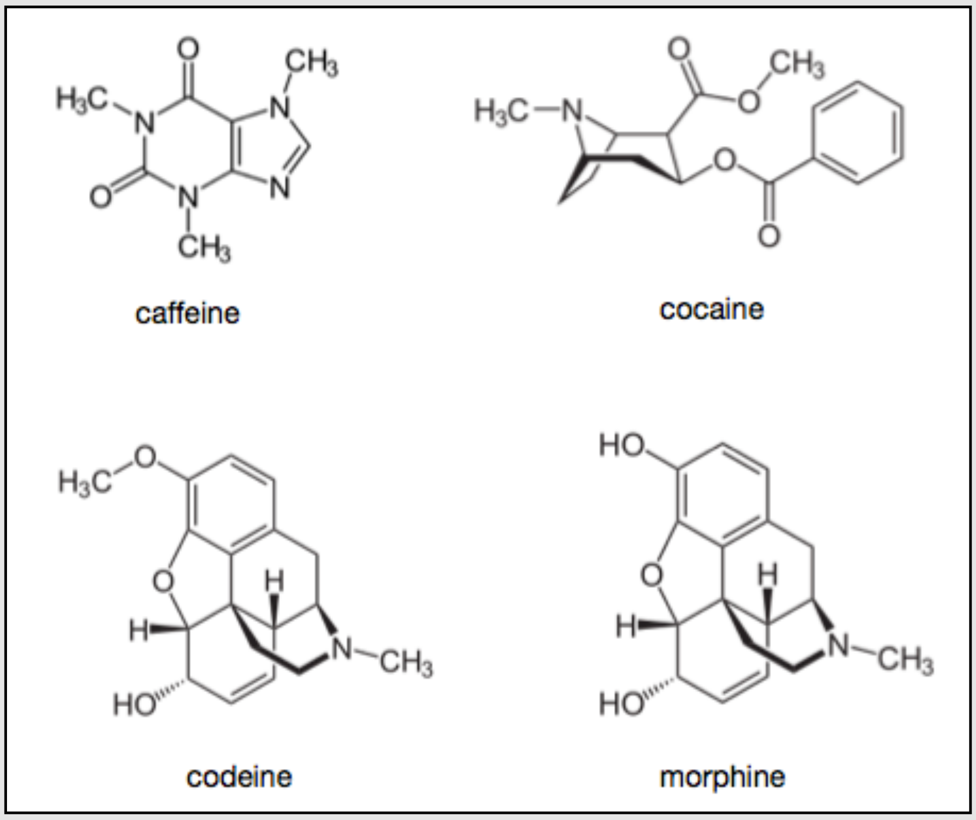
Figure 9.1 Some Physiologically Active Amines



Pseudoephedrine and **phenylephrine** cause vasoconstriction and are used as a nasal decongestant. **Epinephrine** (also called ***adrenaline***) is a naturally occurring hormone and neurotransmitter that is associated with the stimulation of the fight-or-flight response. **Amphetamine** and **methamphetamine** are strong stimulators of the central nervous system. Amphetamine is used as a treatment for attention deficit hyperactivity disorder (ADHD), obesity, and narcolepsy. Methamphetamine has widespread use as an illegal "recreational" psychostimulant and was the focus of the popular TV drama "Breaking Bad." Methamphetamine is rarely prescribed as a therapeutic drug because of its many undesirable side effects.

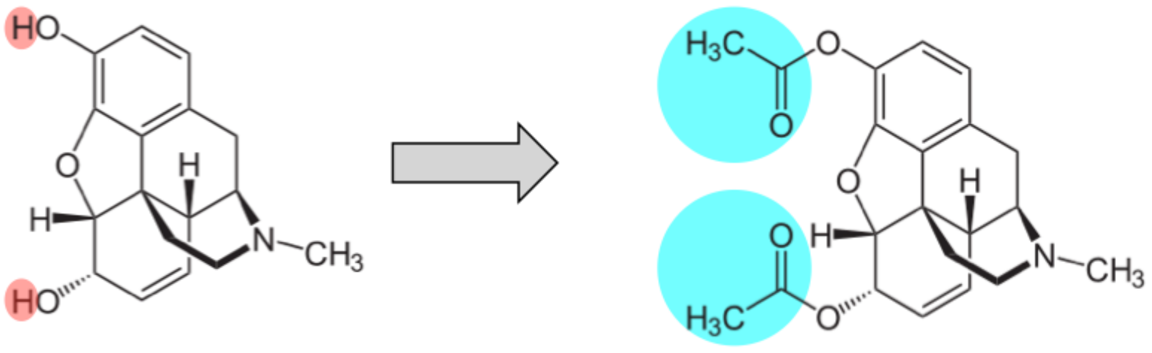
The term "**alkaloid**" is used for physiologically active amines that occur in nature (i.e. bacteria, fungi, plants, and animals). Some examples of alkaloids are shown in Figure 9.2.

Figure 9.2 Examples of Alkaloids



Caffeine is a stimulant that is produced in high concentration by coffee plants and is also found in seeds, leaves, nuts, and berries of other plants. It serves as a natural insecticide. **Cocaine** is a very strong, central nervous system stimulant that is produced in the leaves of the coca plant. **Codeine** and **morphine** are the two most abundant psychoactive components of opium, the dried extract of opium poppy seeds. **Codeine** is used as a pain reliever and to treat coughs. **Morphine** is used to treat severe pain. It is highly addictive.

Heroin is not a “true alkaloid” because it does not occur naturally. It is produced ***from morphine*** by a chemical reaction that replaces the hydrogens of the hydroxyl (**-OH**) groups with acetyl groups ($CH_3C{=}O$, highlighted in blue).



morphine heroin

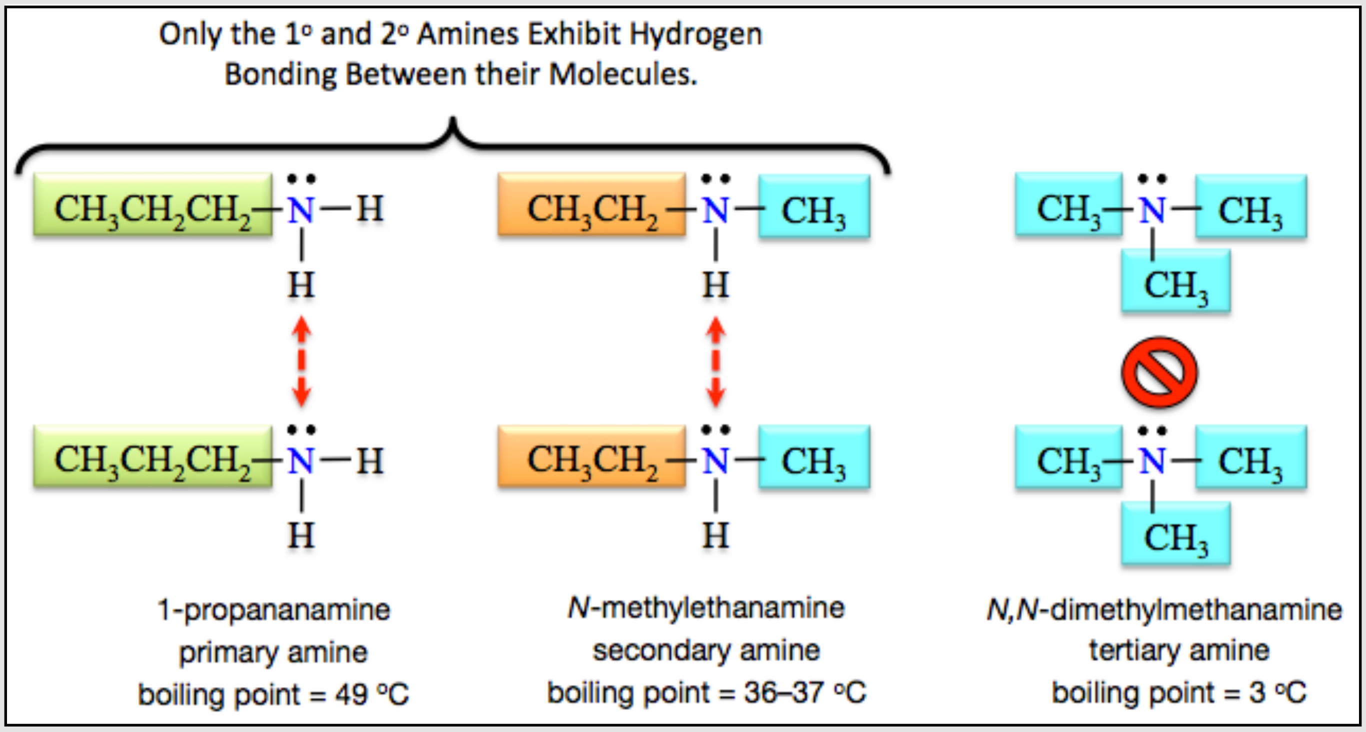
Water Solubility of Amines

All amine molecules have the ability to interact with water through hydrogen bonding and dipole-dipole interactions. ***Small*** amines have significant water solubility. As the hydrocarbon parts of amines get larger, their water solubility decreases; as is the case for all organic molecules.

Boiling and Melting Points of Amines

Amines are polar and can interact with each other through dipole-dipole forces, therefore they have higher boiling and melting points than hydrocarbon molecules of similar size. As pure substances, *primary* and *secondary* amines are capable of hydrogen bonding. Tertiary amines do not have **N-H** bonds, and are therefore incapable of hydrogen bonding with each other. For this reason, primary and secondary amines have higher boiling points than tertiary amines of similar size. Figure 9.3 shows primary, secondary, and tertiary amines that all have the same number of atoms and approximately the same size. Intramolecular hydrogen bonding of the primary amine (1-propanamine) and the secondary amine (N-methylethanamine) - indicated by red dashed arrows - results in significantly higher boiling points when compared to the tertiary amine (N,N-dimethylmethanamine).

Figure 9.3 **Boiling Points of Amines**

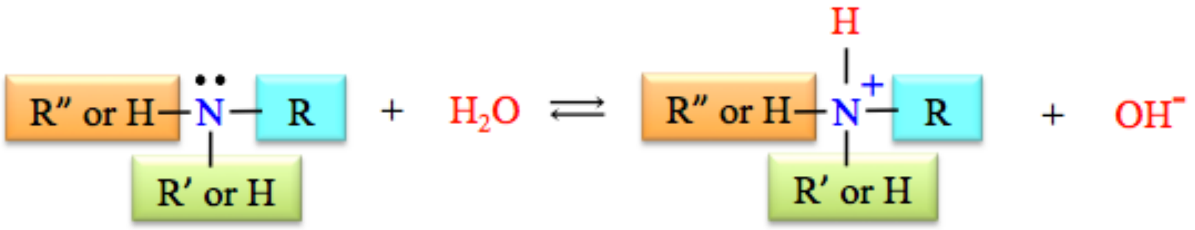


Primary and secondary amines are capable of hydrogen bonding with each other, as indicated by the dashed red lines. Tertiary amines do not have an N-H bond, and are therefore *not* capable of hydrogen bonding with each other. The ability of the primary amine (1-propanamine) and the secondary amine (N-methylethanamine) to interact by hydrogen bonding results in them having significantly higher boiling points than that of the tertiary amine (N,N-dimethylmethanamine).

Chemical Reactions of Amines

1) Reactions of Amines with Water

An amine acts as a ***base*** when it reacts with ***water*** to produce a ***quaternary ammonium ion*** *and a* ***hydroxide ion.*** The general form of the reaction of an amine with water is shown below.



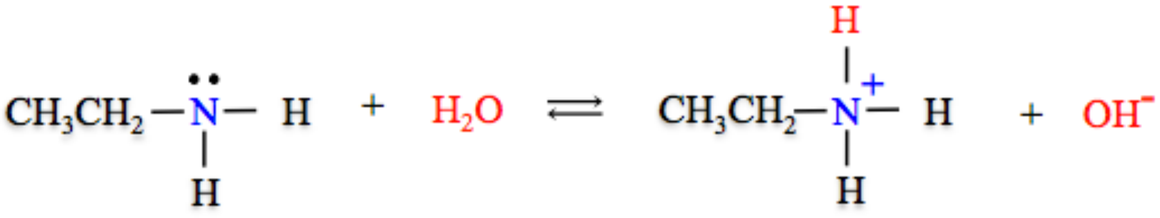
$$R''N(R')R + H_2O \rightleftharpoons R''N^{+}(H)(R')R + OH^-$$

1°, 2°, or 3° amine
(NH_2R or NHR_2 or NR_3)

quaternary ammonium ion + hydroxide

The lone pair on the amine **nitrogen** forms a bond to the H^+ from water. When amines are put into *pure water*, the pH is increased since hydroxide ions are produced in this reaction. The ***amine*** and the ***quaternary ammonium ion*** are a **conjugate pair**. The *amine* is the ***base form*** and the *quaternary ammonium ion* is the ***acid form***. When an amine/quaternary ammonium ion conjugate pair is in a mixture that contains other dissolved species, the relative amounts of the acid form and base form can be predicted by the implications of the Henderson-Hasselbalch Equation.

A specific example of the reaction of an amine with water is the reaction of ethanamine with water:



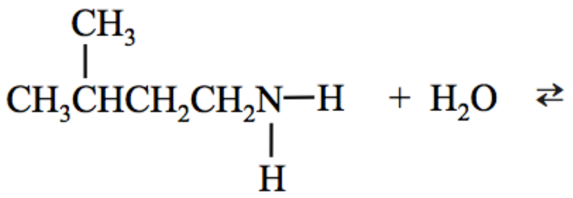
$$CH_3CH_2-\ddot{N}H-H + H_2O \rightleftharpoons CH_3CH_2-N^{+}H_2-H + OH^-$$

ethanamine
(*base form*)

ethylammonium ion
(*acid form*)

Review 9.16: Reactions of Amines and Water

Add the products for the following reaction:

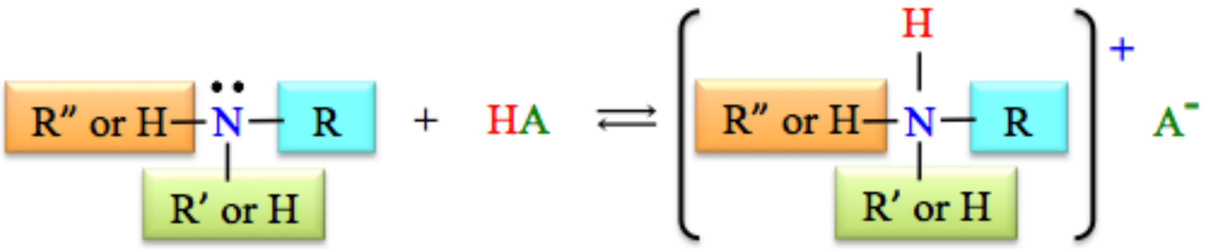


$$CH_3CH(CH_3)CH_2CH_2N(H)-H + H_2O \rightleftharpoons$$

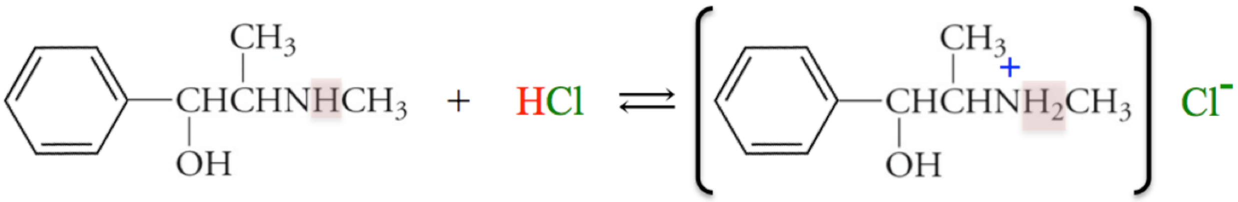
For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

2) Reaction of Amines with Acids

An amine will react with an ***acid*** to produce *a* ***quaternary ammonium compound*** in a **neutralization reaction**. The general form of the equation for the reaction of an amine with an acid is shown below:

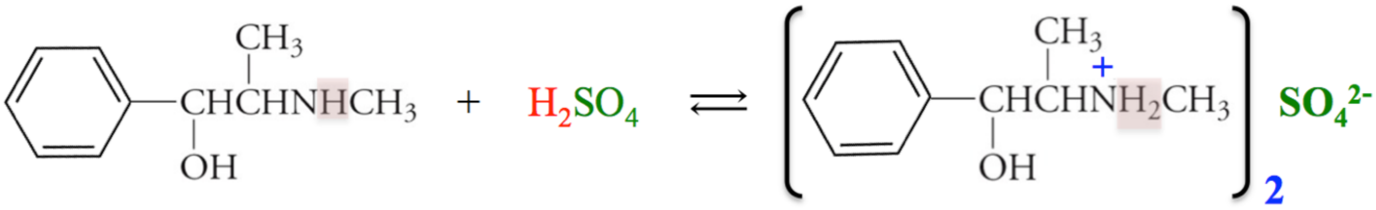


The lone pair on the amine **nitrogen** forms a bond to the H^+ from the acid. Amines that are used as medications, both legal and illegal, are often administered as quaternary ammonium ions in order to increase their water-solubility. The water solubility of the a quaternary ammonium compound is greater than that of its conjugate amine because of the presence of the positive charge of the ion, which gives it a greater attraction to water. The anions of such quaternary ammonium compound medications are often chloride or sulfate since they are prepared by reaction of the amine - sometimes called the "free base" - with hydrochloric acid (HCl) or sulfuric acid (H_2SO_4). For example, pseudoephedrine hydrochloride, used in the decongestant sold as ***Allegra D*** by Bayer Healthcare, and as ***Benadryl*** by Johnson and Johnson, can be prepared by the reaction of pseudoephedrine and HCl.



pseudoephedrine pseudoephedrine hydrochloride

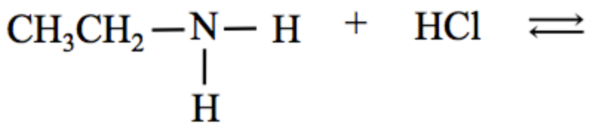
Pseudoephedrine sulfate, used in ***Claritin D*** from MSD Consumer Care, can be prepared by the reaction of pseudoephedrine and H_2SO_4.



pseudoephedrine pseudoephedrine sulfate

Review 9.17: Reactions of Amines and Acids

Add the product for the following reaction:



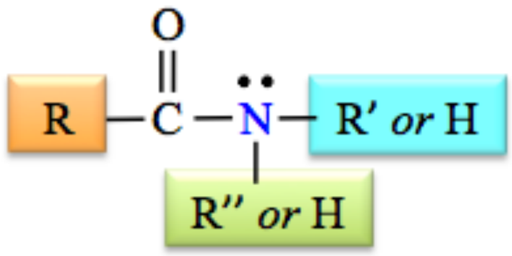
$$CH_3CH_2-\underset{\displaystyle H}{\underset{|}{N}}-H \quad + \quad HCl \quad \rightleftharpoons$$

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

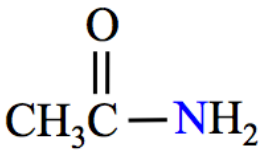
9.4 Amides

The Structure of Amides

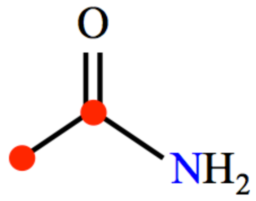
Amides contain both a ***carbonyl group*** **(C=O)**, ***and*** a nitrogen **(N)**, with the nitrogen bonded to the *carbonyl* carbon. The general form of an amide is shown below.

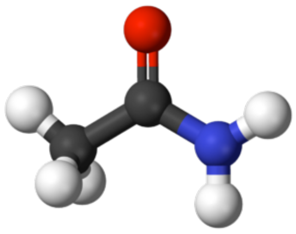


A specific example of an amide is *ethanamide*. Ethanamide is used as a plasticizer (a substance that increases the ability of a material to bend without breaking). The condensed structural formula, skeletal formula, and a ball-and-stick model for *ethanamide* are shown below (black sphere = carbon, red sphere = oxygen, blue sphere = nitrogen, and white sphere = hydrogen).



$CH_3\overset{O}{\overset{\|}{C}}-NH_2$





The amide bonding pattern occurs in nature in the structure of proteins. You will learn about protein structure in chapter 13.

Naming Amides

We will use the IUPAC system for naming amide molecules. The systematic method for naming amides is based on the hydrocarbon naming method.

Step 1: Find and name the parent chain.

The parent chain of an amide is the longest continuous chain of carbon atoms that includes the ***carbonyl carbon*** - *just as we did with carboxylic acids.* Starting with the alkane name that corresponds to the number of carbon atoms in the parent chain, replace the "**e**" at the end of the alkane name with "**amide**." For example, if the parent chain of an amide contains *three* carbons, it is called propan**amide**.

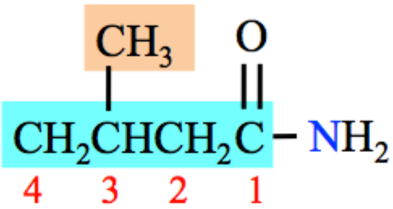
propan**e** ⟶ propan**amide**

Step 2: Name any alkyl group substituents.

Alkyl groups are named in the same way as was done for hydrocarbons.

Step 3: Determine the *point of attachment* of any alkyl groups.

Substituents are assigned positions based on their point of attachment to the parent chain or to the nitrogen. Begin numbering the parent chain at the *carbonyl carbon*. For example, the amide shown below has a "**3-methyl**" substituent.

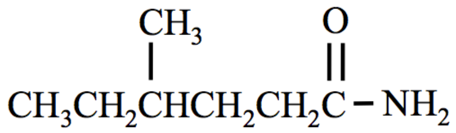


$\underset{4}{CH_3}\underset{3}{\overset{CH_3}{\overset{|}{C}H}}\underset{2}{CH_2}\underset{1}{\overset{O}{\overset{\|}{C}}}-NH_2$

Step 4: Construct the name of the amide by placing the alkyl groups in alphabetical order and specifying their positions, followed by the name of the parent chain.

- Use a ***dash*** between positions and *letters*.
- Add the labels di, tri, or tetra in front of the alkyl group name **if** two, three, or four (respectively) identical substituents are present.

Example: Name the molecule that is shown below.

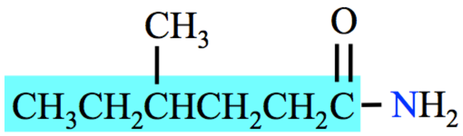


$$CH_3CH_2\overset{\overset{CH_3}{|}}{C}HCH_2CH_2\overset{\overset{O}{\|}}{C}-NH_2$$

Solution:

Step 1: Find and name the parent chain.

The parent chain of an amine is the longest continuous chain of carbon atoms that includes the ***carbonyl carbon***. The parent chain of the molecule in this example is highlighted blue:



$$CH_3CH_2\overset{\overset{CH_3}{|}}{C}HCH_2CH_2\overset{\overset{O}{\|}}{C}-NH_2$$

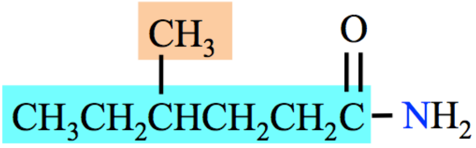
Count the number of carbon atoms in the parent chain (include the carbonyl carbon). Starting with the alkane name that corresponds to the number of carbon atoms in the parent chain, replace the "**e**" at the end of the alkane name with "**amide**."

hexan***e*** ⟶ hexan***amide***

There are six carbon atoms in the parent chain. The name of the parent chain is hexanamide.

Step 2: Name any alkyl group substituents.

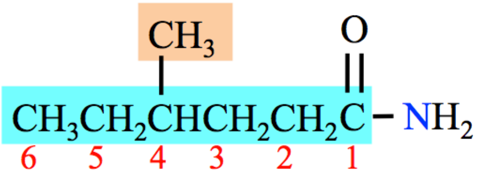
There is one alkyl group substituent: **methyl**. The methyl group substituent in this example is shaded orange:



$$CH_3CH_2\overset{\overset{CH_3}{|}}{C}HCH_2CH_2\overset{\overset{O}{\|}}{C}-NH_2$$

Step 3: Determine the *point of attachment* of any alkyl groups.

Begin numbering the parent chains of amides at the carbonyl carbon. The carbons in the parent chain are assigned position numbers (in red):



$$\underset{6}{CH_3}\underset{5}{CH_2}\overset{\overset{CH_3}{|}}{\underset{4}{C}}H\underset{3}{CH_2}\underset{2}{CH_2}\overset{\overset{O}{\|}}{\underset{1}{C}}-NH_2$$

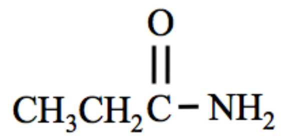
Step 4: Construct the name of the amide by placing the alkyl groups in alphabetical order and specifying their positions, followed by the name of the parent chain. Use a ***dash*** between position *numbers* and *letters*.

- The methyl substituent is attached to carbon number 4 of the parent chain: **4-methyl.**
- The parent chain name is **hexanamide.**
- The name of the molecule is **4-methylhexanamide.**

You try a couple of practice problems:

Review 9.18: Naming Amides

Name the molecule that is shown below.

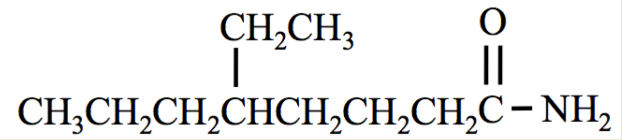


$CH_3CH_2\overset{O}{\overset{\|}{C}}-NH_2$

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

Review 9.19: Naming Amides

Name the molecule that is shown below.



$CH_3CH_2CH_2\overset{CH_2CH_3}{\overset{|}{C}}HCH_2CH_2CH_2\overset{O}{\overset{\|}{C}}-NH_2$

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

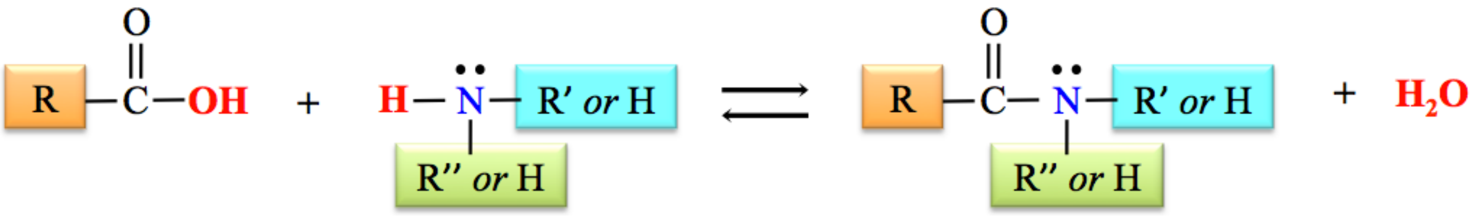
Review 9.20: Drawing Amide Structures

Draw the line bond, condensed, and the skeletal structural formula of pentanamide.

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

Formation of Amides: The Reaction of Carboxylic Acids with Amines.

An amide is produced when a carboxylic acid reacts with an amine or ammonia (NH_3). In this reaction, the hydroxyl group is removed from the carboxylic acid, a hydrogen is removed from the amine, and a water molecule and an amide are produced. The general form of this reaction is shown below.

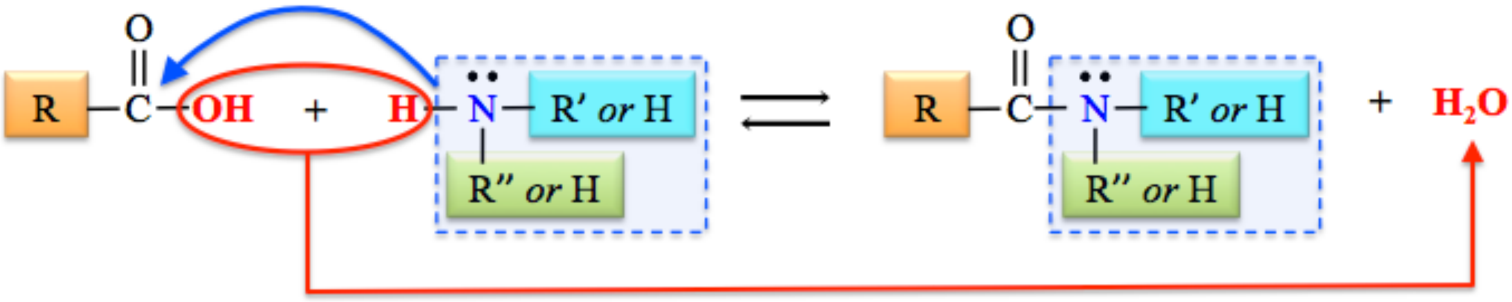


An easy way to predict and draw the products of this reaction is to:

1) Draw the structures of the carboxylic acid and the amine (or ammonia) with the (**OH**) from the carboxylic acid and an **H** from the amine (or ammonia) adjacent to each other, as shown below.

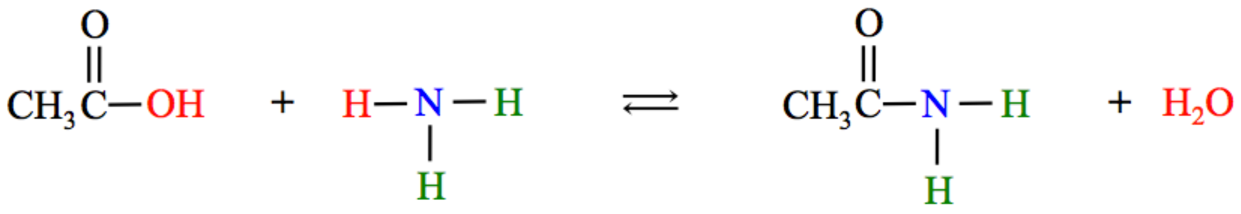
2) Remove the (**OH**) from the carboxylic acid and an H from the amine (or ammonia), and then combine the **H** and **OH** to make H_2O.

3) Bond the ***nitrogen*** and its remaining groups to the ***carbonyl carbon*** of the carboxylic acid.



An amide can form when a carboxylic acid reacts with ammonia, with a primary, or with a secondary amine. For example, ethanoic acid can react with ammonia, methanamine (a 1° amine), ***or*** *N*-methylmethanamine (a 2° amine) as shown below.

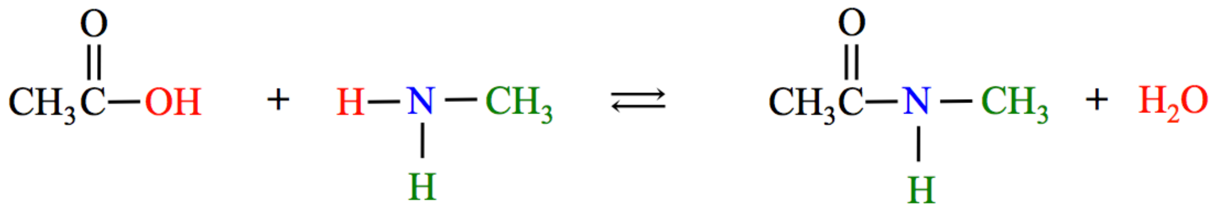
a) Formation of an amide by the reaction of a carboxylic acid and ammonia.



$$CH_3\overset{\overset{O}{\|}}{C}-OH + H-\underset{\underset{H}{|}}{N}-H \rightleftharpoons CH_3\overset{\overset{O}{\|}}{C}-\underset{\underset{H}{|}}{N}-H + H_2O$$

ethanoic acid ammonia ethanamide water

b) Formation of an amide by the reaction of a carboxylic acid and a 1° amine.

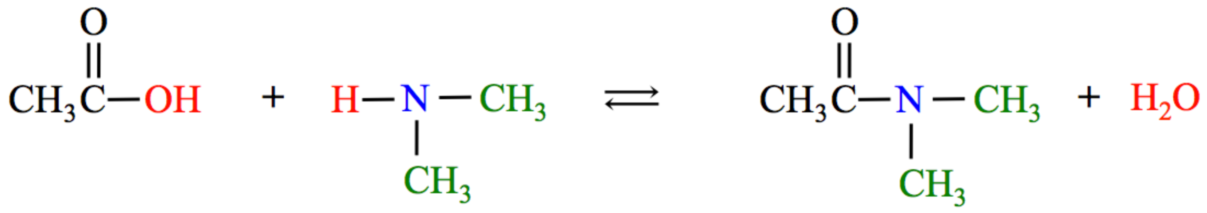


$$CH_3\overset{\overset{O}{\|}}{C}-OH + H-\underset{\underset{H}{|}}{N}-CH_3 \rightleftharpoons CH_3\overset{\overset{O}{\|}}{C}-\underset{\underset{H}{|}}{N}-CH_3 + H_2O$$

ethanoic acid methanamine *N*-methylethanamide water

The "*N*-methyl" in "*N*-methylethanamide" indicates that there is a *methyl* substituent bonded to the nitrogen.

c) Formation of an amide by the reaction of a carboxylic acid and a 2° amine.



$$CH_3\overset{\overset{O}{\|}}{C}-OH + H-\underset{\underset{CH_3}{|}}{N}-CH_3 \rightleftharpoons CH_3\overset{\overset{O}{\|}}{C}-\underset{\underset{CH_3}{|}}{N}-CH_3 + H_2O$$

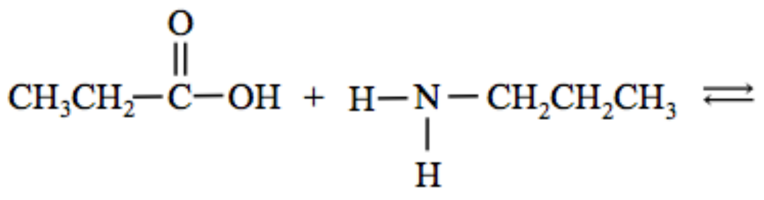
ethanoic acid *N*-methylmethanamine *N,N*-dimethylethanamide water

The "*N,N*-dimethyl" in "*N,N*-dimethylethanamide" indicates that there are two *methyl* substituents bonded to the nitrogen.

Amides are not formed from 3° amines because 3° amines do not have a hydrogen attached to the nitrogen.

Review 9.21: Amide Formation

Add the products for the following reaction <u>and</u> name the *amide* that is produced:



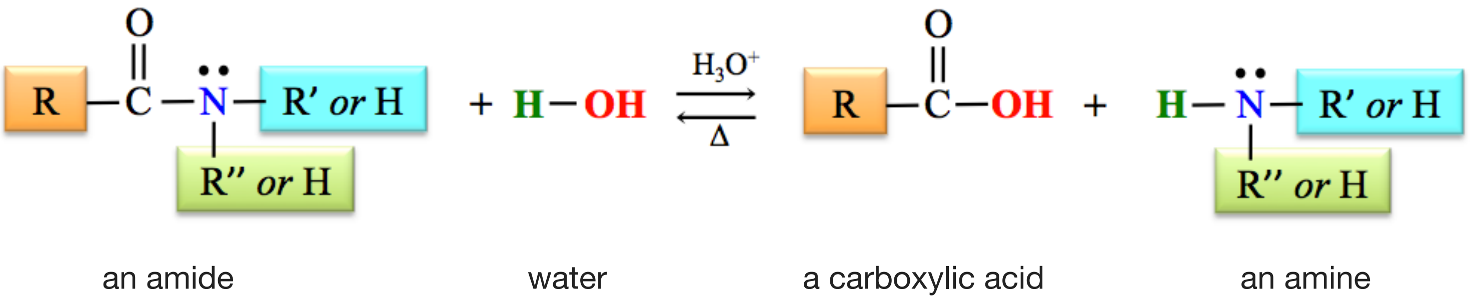
$$CH_3CH_2-\overset{\overset{O}{\|}}{C}-OH + H-\underset{\underset{H}{|}}{N}-CH_2CH_2CH_3 \rightleftharpoons$$

Naming Hint: There will be a substituent attached to the nitrogen (not the parent chain). You will use "*N*-" in the name to indicate that the substituent is bonded to the nitrogen.

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

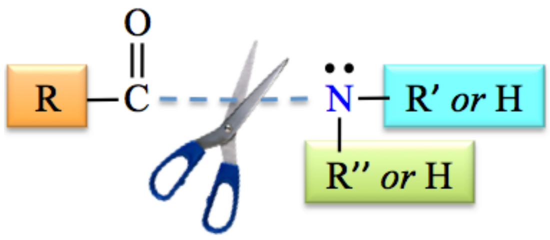
Hydrolysis of Amides

The ***reverse*** of the *amide formation* reaction is the **hydrolysis of amides**. With heat and an acid catalyst, an amide can be hydrolyzed to produce a carboxylic acid and an amine (or ammonia). The general form of the hydrolysis of amides reaction is shown below.

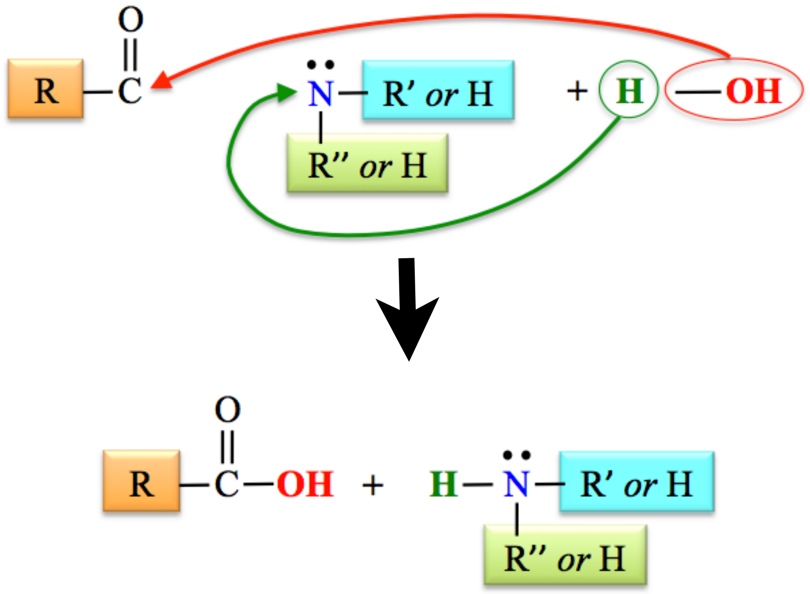


This reaction is very similar to the hydrolysis of esters. An easy way to predict and draw the products of this reaction is to:

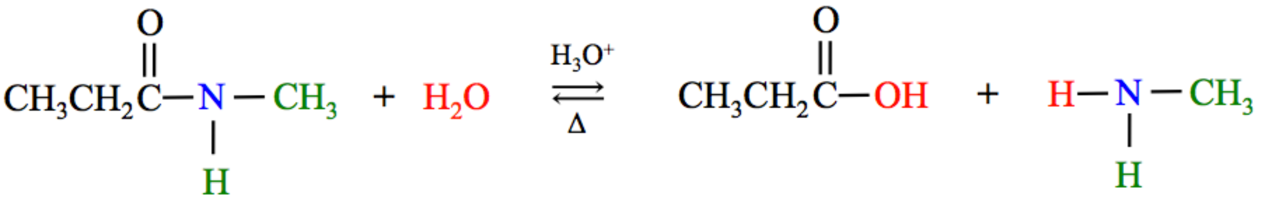
1) Break the bond between the **carbonyl group** and the **nitrogen**.



2) Bond the **OH** from water to the **carbonyl carbon**, and bond the **H** from water to the **nitrogen**.



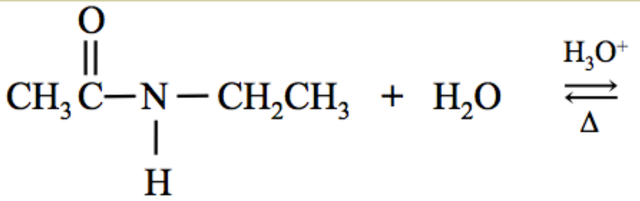
A specific example of this reaction is the hydrolysis of *N*-methylpropanamide.



$$CH_3CH_2\overset{\overset{\large O}{\|}}{C}-\underset{\underset{\large H}{|}}{N}-CH_3 + H_2O \underset{\Delta}{\overset{H_3O^+}{\rightleftarrows}} CH_3CH_2\overset{\overset{\large O}{\|}}{C}-OH + H-\underset{\underset{\large H}{|}}{N}-CH_3$$

Review 9.22: Hydrolysis of Amides

Add the products for the following amide hydrolysis reaction <u>and</u> name ***both*** of the products:



$$CH_3\overset{\overset{\large O}{\|}}{C}-\underset{\underset{\large H}{|}}{N}-CH_2CH_3 + H_2O \underset{\Delta}{\overset{H_3O^+}{\rightleftarrows}}$$

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

9.5 Enantiomers and Diastereomers

Enantiomers

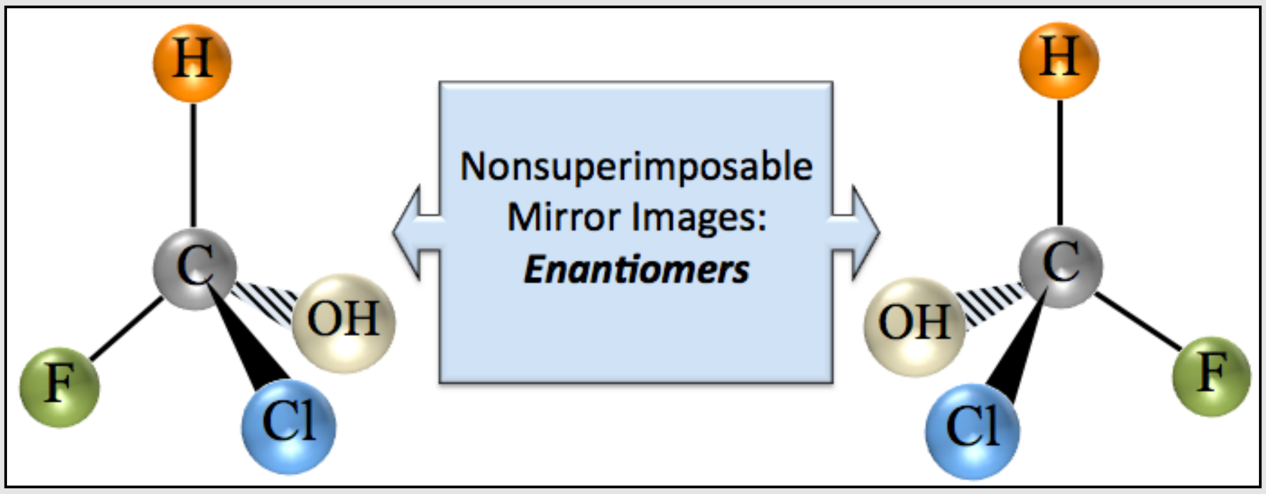
Stereoisomers are molecules that have the *same* molecular formula, have the *same* atomic connections, but have *different* three-dimensional arrangements of the atoms. *Stereoisomers* **cannot** be converted from one to another without ***breaking and reforming bonds*** (it is ***not*** possible for one stereoisomer to take the shape of another stereoisomer by rotation around a bond).

The first type of *stereoisomers* that I introduced you to - in chapter 4 - were **geometric isomers**. When *stereoisomers* exist because of ***limited bond rotation***, they are called **geometric isomers.** You saw that geometric isomers could occur for certain cycloalkanes and alkenes. We designated the geometric isomers as either ***cis*** or ***trans***.

Another type of stereoisomers occurs when ***four different groups are bonded to the same atom***. In these cases, there are two distinct, three-dimensional arrangements of the atoms. For our purposes, we will be concerned with the pairs of stereoisomers that result whenever four different groups are bonded to the same ***carbon atom***. A carbon atom that carries four different groups is called a "**chiral carbon**." The two distinct, three-dimensional arrangements of the atoms around the chiral carbon are ***mirror images*** of each other. When four different groups are arranged in the tetrahedral geometry (we called it AB_4), the mirror images *are not* identical. Another way to describe nonidentical mirror images is with the term "*nonsuperimposable mirror images*." An example of nonsuperimposable mirror images, that is familiar to you, is your pair of hands. Although they are similar, and are mirror images, they are not identical. If they were identical, we would not need ***both*** left **and** right gloves! The term "chiral" comes from the Greek word for hand.

An example of a pair of stereoisomers that results from the presence of a *chiral carbon* is shown in Figure 9.4. Stereoisomers such as these, which are nonsuperimposable mirror images of each other, are called **enantiomers.**

Figure 9.4
Enantiomers

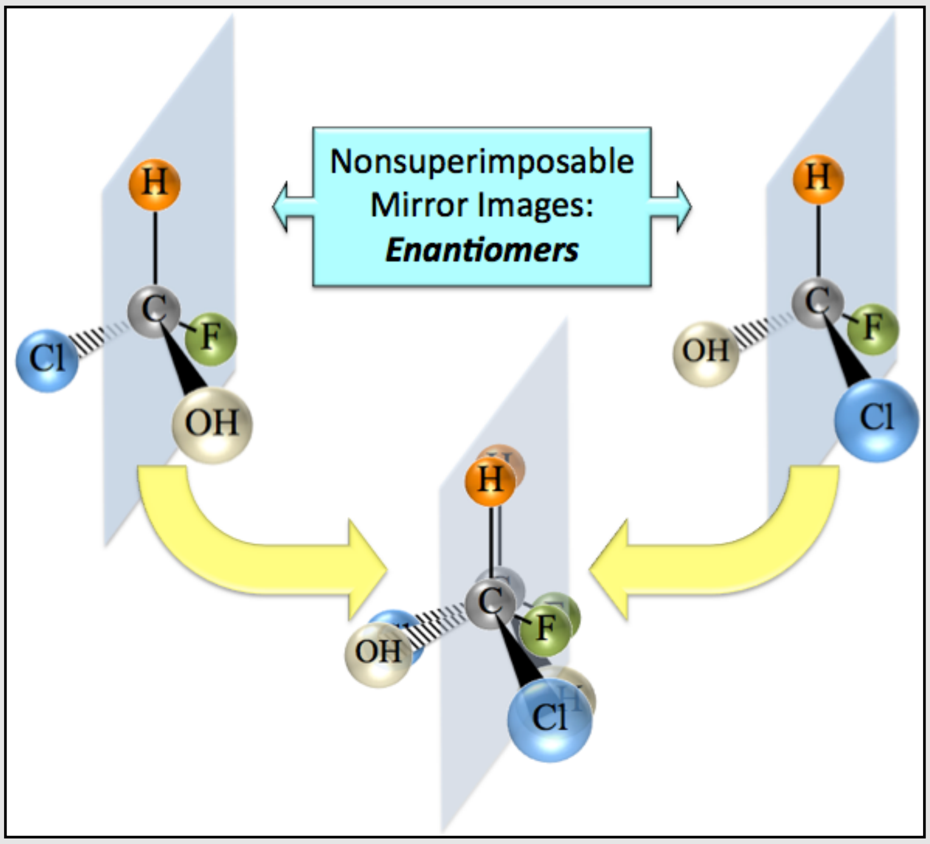


An example of a pair of stereoisomers that occurs because of the presence of a *chiral carbon. The carbon is chiral because it is bonded to four different groups:* **OH, Cl, H,** *and* **F.** The resulting molecules are nonsuperimposable mirror images called **enantiomers.**

Recall that in *wedge and dash* illustrations of three-dimensional objects, ***solid wedges*** indicate bonds that would be coming *out and above* the page (toward the viewer). ***Dashed shapes*** indicate bonds that would be coming *out and behind* the page (away from the viewer). Regular lines (neither wedge nor dash) indicate bonds that would exist on the plane of the page.

Figure 9.5 may help you to visualize and understand that the two molecules shown in Figure 9.4 are not identical. I have graphically depicted the failed attempt to superimpose the pair of enantiomers.

Figure 9.5 Nonsuperimposable Mirror Images

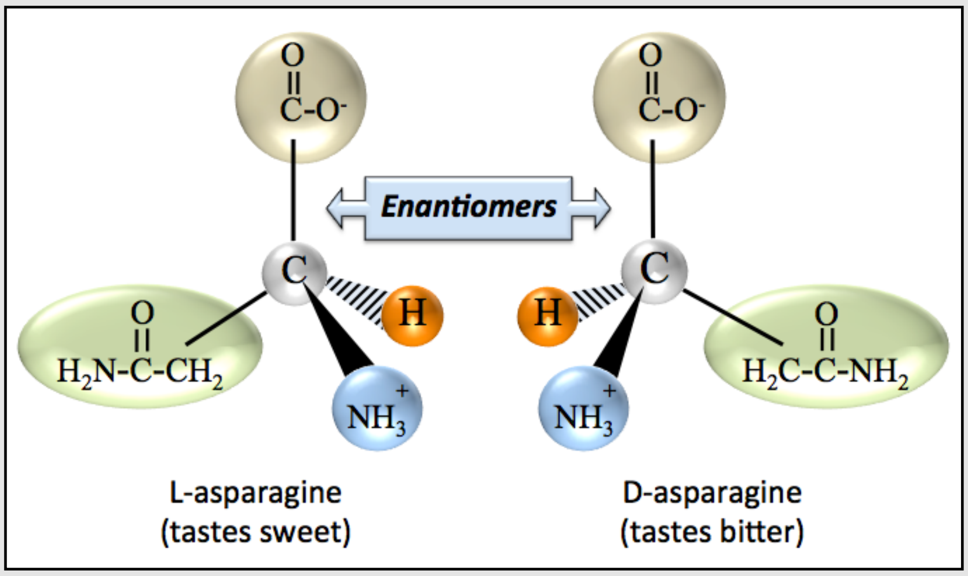


A graphical depiction of the failed attempt to superimpose the pair of enantiomers from Figure 10.4. It is not possible to superimpose a pair of enantiomers. If any two groups that are attached to the chiral carbon are aligned with each other, then the other two groups will be misaligned. In this figure, the hydrogen and fluorine are aligned, however the hydroxide and chloride are not aligned.

To "superimpose," in this context, means to hypothetically put the molecules in the same place and have all like-groups aligned. This is not possible for a pair of enantiomers. If any two groups that are attached to the chiral carbon are aligned with each other, then the other two groups will be misaligned. For example, when I aligned the hydrogen and fluorine in Figure 9.5, then the hydroxide and chloride were not aligned (superimposed).

Pairs of enantiomers have very similar physical properties. For this reason, they are very difficult to separate (purify) from each other. For example, their boiling points are so similar that separation by distillation is not possible. They do differ in a couple of important ways. Since enantiomers' arrangements of electrons are mirror images of each other, they interact with light in different ways. It is for this reason that enantiomers are sometimes called "optical isomers." Another important difference in enantiomers is the way they behave in biological systems. Since enantiomers do not have identical three-dimensional shapes, they do not behave identically when interacting with biomolecules such as enzymes or the receptors that are responsible for taste. The pair of enantiomers of the amino acid named asparagine are shown in Figure 9.6. One of the enantiomers (L-asparagine) has a sweet taste. The other enantiomer (D-asparagine) has a bitter taste. L-asparagine is produced in high concentration in the asparagus plant, where it was first discovered and got its name. You will learn details of the L- and D- designations for enantiomers in chapter 11.

Figure 9.6 Asparagine Enantiomers

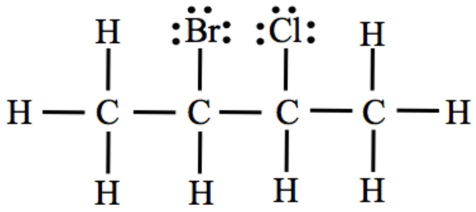


Enantiomers of the amino acid named asparagine. One of the enantiomers (L-asparagine) has a sweet taste. The other enantiomer (D-asparagine) has a bitter taste.

Many enzymes are “**stereospecific.**” This means that they will catalyze a reaction for only ***one*** particular enantiomeric reactant and/or will catalyze the formation of only one enantiomeric product. For example, when the antibiotic that we call penicillin is made by enzymatic reactions by mold, only one enantiomer (penicillin) of a particular molecule is produced. Plants produce only one enantiomer of the glucose molecule (D-glucose). It is therefore understandable that all organisms - with only one known exception of particular bacterium - will only metabolize the D-glucose enantiomer. The biological production and metabolism of glucose coevolved, so it makes sense that nature selected the same enantiomer upon which to rely. The most accepted evolutionary model, at this time, is that nature arbitrarily chose the D-glucose over the L-glucose isomer, however there are other theories that have been postulated.

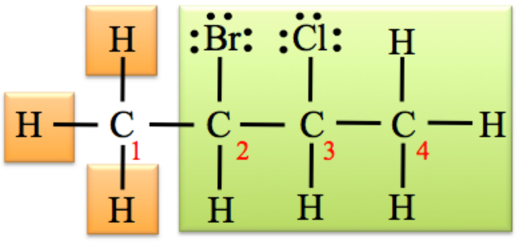
Let’s do an example problem in order to help you identify chiral carbons.

Example: The line bond structure of 2-bromo-3-chlorobutane is shown below. How many **chiral carbons** are in this molecule?

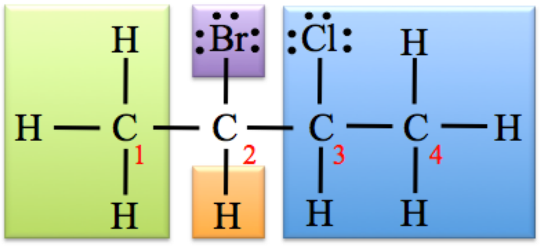


Solution: Consider each carbon individually. A carbon is **chiral** if it is bonded to ***four different groups***.

- **Carbon number 1** is <u>not</u> chiral. It is bonded to four groups, however, the four groups are not all ***different*** from each other. I have highlighted the four groups that are bonded to carbon number **1** in the structure shown below. Three of the groups are hydrogens.

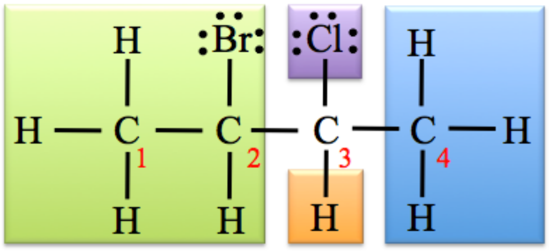


- **Carbon number 2** is chiral; it is bonded to ***four different groups***. I have highlighted the four groups that are bonded to carbon number **2** in the structure shown below.



  - **IMPORTANT:** A mistake that chemistry students sometimes make is to consider only the four ***atoms*** to which a carbon is bonded. If you were to do that with this molecule, you might think that **carbon number 2** is ***not*** chiral since it is bonded to ***two other carbons*** (carbon number **1** and **3**). Be careful; you must consider the entire ***group of atoms to which a carbon is bonded in order to determine if that carbon is chiral***. It is for this reason that I highlighted the *entire groups* that are bonded to carbon number **2** in the structure shown above.

- **Carbon number 3** is chiral; it is bonded to ***four different groups***. I have highlighted the four groups that are bonded to carbon number **3** in the structure shown below.

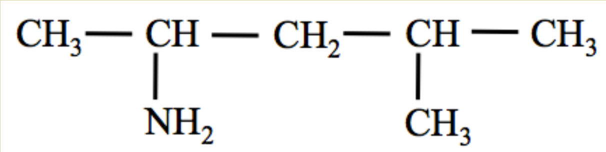


- **Carbon number 4** is not chiral. Three of the groups are the same - three hydrogens.

There are <u>two chiral carbons</u> in 2-bromo-3-chlorobutane - carbons number 2 and 3.

Review 9.23: Identification of Chiral Carbons

The condensed structure of 4-methyl-2-pentanamine is shown below. Circle any chiral carbons in this molecule.



$$CH_3-\underset{\displaystyle NH_2}{\underset{|}{CH}}-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3$$

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

Diastereomers

When ***more than one chiral carbon*** is present in a molecule, then more than one pair of enantiomers will exist. The number of stereoisomers that can exist depends on the *number of chiral carbons*. If we let "**n**" represent *the number of chiral carbons* in a molecule, then the maximum number of stereoisomers is calculated as follows:

$$\textbf{Maximum Number of Stereoisomers} = 2^n \qquad \textit{Equation 10.1}$$

In our example problem from the previous page, we determined that 2-bromo-3-chlorobutane contained two chiral carbons. Therefore we can determine the maximum number of stereoisomers that 2-bromo-3-chlorobutane has by using *Equation 10.1*:

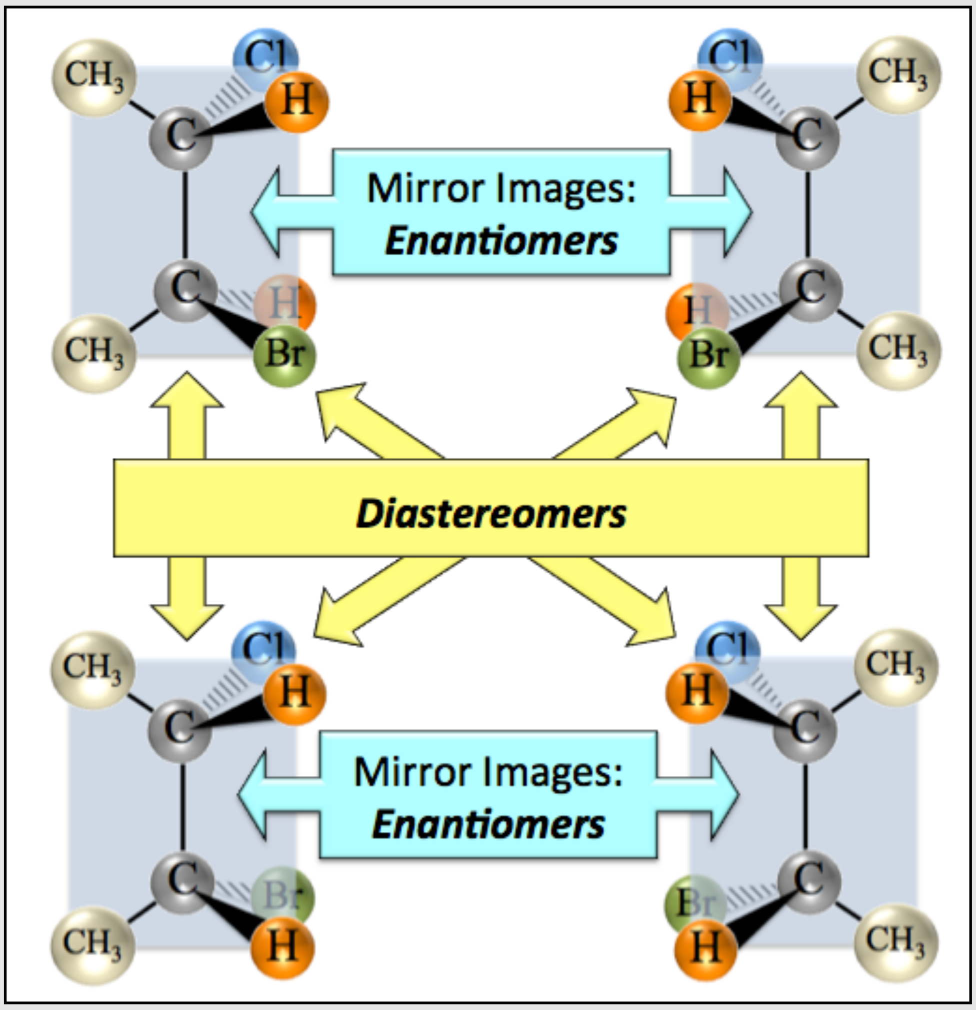
$$\textbf{Maximum Number of Stereoisomers} = 2^n = 2^2 = 4$$

There are *four* stereoisomers of 2-bromo-3-chlorobutane - ***two pairs*** of mirror images. You learned about the relationship between nonsuperimposable mirror image molecules, called ***enantiomers***. Nonsuperimposable molecules ***that are not mirror images of each other,*** *but are* in the group of 2^n stereoisomers, are called **diastereomers**. Figure 9.7 shows the four stereoisomers of 2-bromo-3-chlorobutane. The *enantiomer* relationships are indicated with blue arrows. The *diastereomer* relationships are indicated with yellow arrows.

It may be helpful for you to compare and contrast *enantiomers* and *diastereomers* by using a "family relationship" analogy of *siblings* (for enantiomers) and *cousins* (for diastereomers).

You will see more enantiomers, diastereomers, and geometric isomers in the biochemistry chapters of this book.

Figure 9.7 Enantiomers vs. Diastereomers

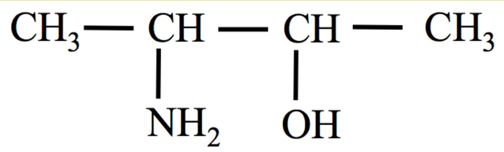


The four stereoisomers of 2-bromo-3-chlorobutane. The *enantiomer* (mirror image) relationships are indicated with blue arrows. The *diastereomer* relationships are indicated with yellow arrows.

Review 9.24: Determining the Number of Stereoisomers

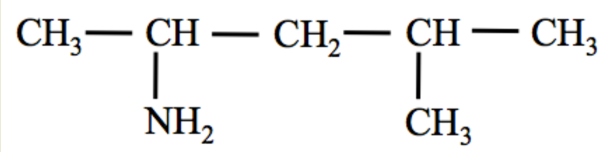
What is the maximum number of stereoisomers that can exist for each of the molecules shown below?

a.



$CH_3-\underset{NH_2}{\underset{|}{CH}}-\underset{OH}{\underset{|}{CH}}-CH_3$

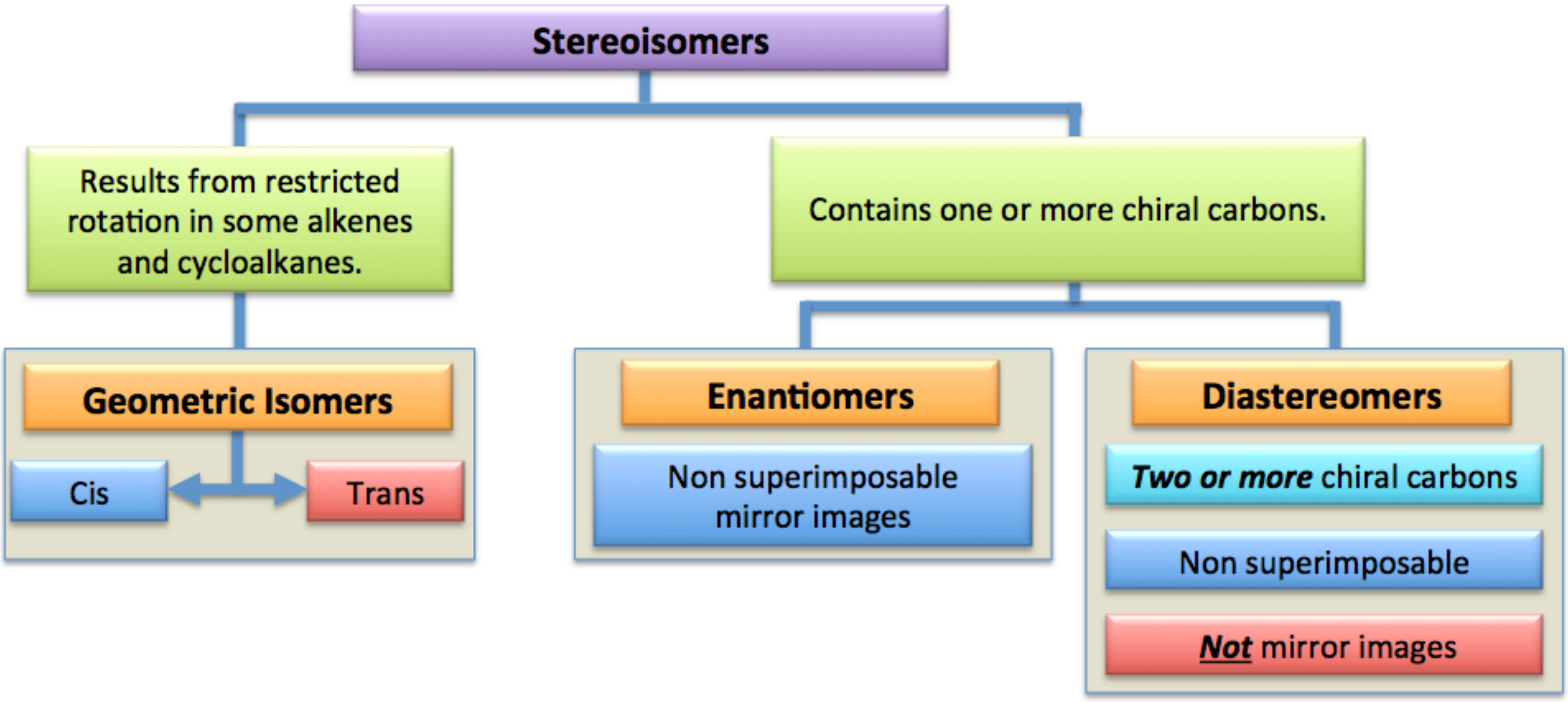
b.



$CH_3-\underset{NH_2}{\underset{|}{CH}}-CH_2-\underset{CH_3}{\underset{|}{CH}}-CH_3$

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

Thought Flow Chart for Stereoisomer Classification



Use the link below for more practice ***naming the compounds*** of chapter 9:

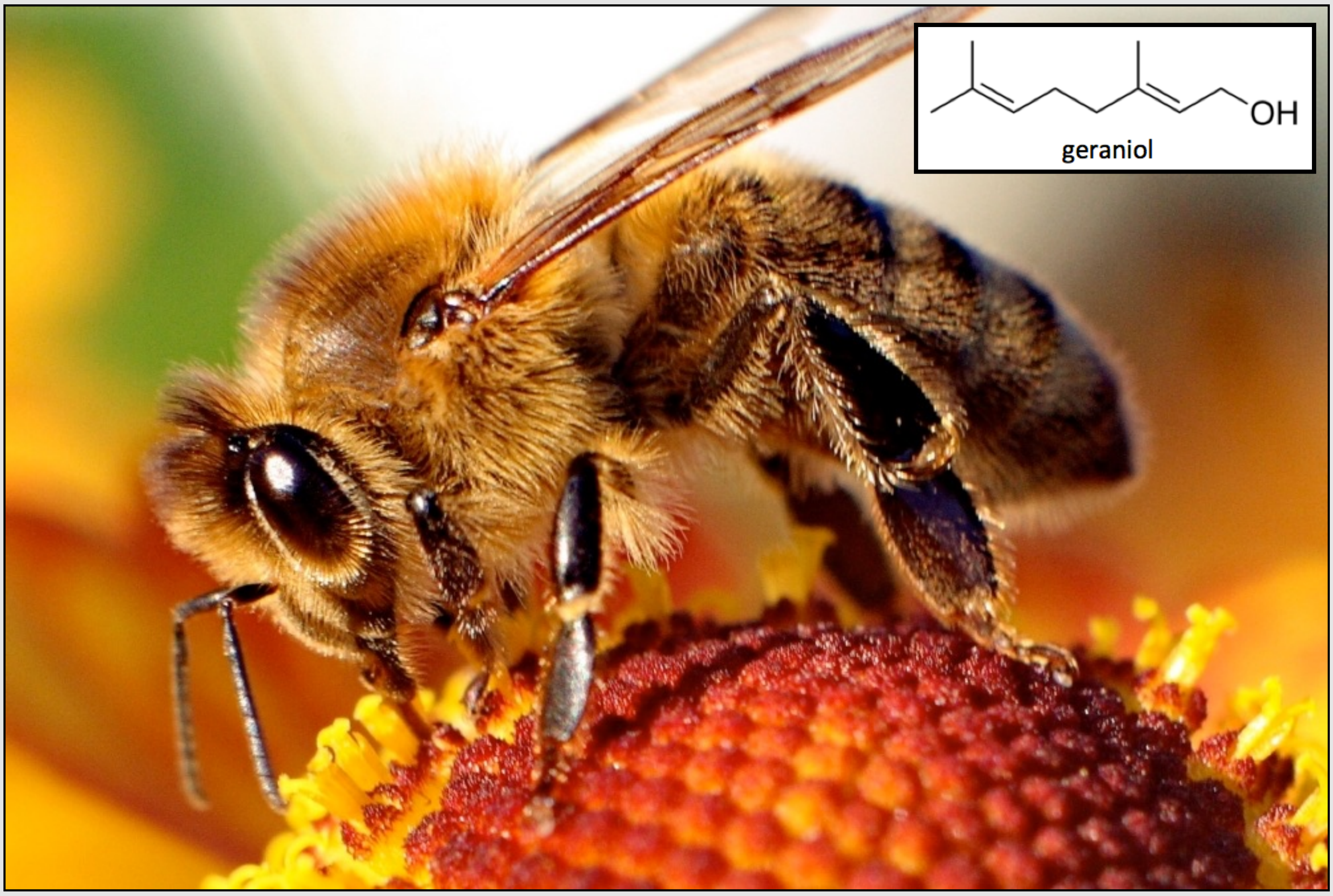
http://www.zovallearning.com/GOBlinks/ch9/naming-ch9-compounds-worksheet-and-key.pdf

Use the link below for more practice ***predicting the products of the reactions*** of chapter 9:

http://www.zovallearning.com/GOBlinks/ch9/ch9-reactions-worksheet-and-key-GOB.pdf

Get the entire course as a series of video lectures at: www.zovallearning.com

Chapter 10:
Alcohols, Ethers, Aldehydes, and Ketones



Honey bees (*genus apis*) produce an ***alcohol*** molecule called *geraniol* that acts as a ***pheromone*** and is used to mark and find entrances to their hives and nectar-bearing flowers. A *pheromone* is a chemical that triggers a social response in members of the same species. The structure of the geraniol alcohol molecule is shown in the insert.
Source: Wikimedia Commons, Author: Maciej A. Czyzewski CC-BY-SA http://creativecommons.org/licenses/by-sa/3.0/deed.en

In this chapter, you will be introduced to some more families of organic compounds and learn about their structures, physical properties, how to name them, some important chemical reactions in which they are involved, and their biological roles.

10.1 Chapter 10 Educational Goals

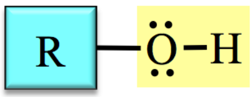
1. Given the structure of an **alcohol**, **ether**, **thiol**, **sulfide**, **aldehyde**, **or ketone molecule**, be able to give its systematic name and vice versa.
2. Know and understand the intermolecular forces that attract alcohol, ether, thiol, sulfide, disulfide, aldehyde, and ketone molecules to one another, and how these forces affect boiling points, melting points, and solubilities.
3. Identify **alcohols** as primary (1°), secondary (2°), or tertiary (3°).
4. Given the reactants, be able to predict the products of the following reactions:
    - oxidation of thiols to produce disulfides
    - nucleophilic substitution reaction of alkyl halides with hydroxide
    - hydration of alkenes
    - dehydration of alcohols
    - oxidation of alcohols
    - oxidation of aldehydes
    - reduction of aldehydes and ketones
    - hemiacetal and acetal formation
5. Predict the **major** and **minor products** for the **hydration of an alkene**.
6. Predict the **major** and **minor products** for the **dehydration of an alcohol**.

10.2 Alcohols

One of the most widely-known alcohol molecules is ethanol, also referred to as ethyl alcohol, because of its use in adult beverages. There are many other molecules in the alcohol family. Alcohol molecules commonly occur in plants and animals. For example, cholesterol is an alcohol. In this section, you will learn about the structure of alcohols, how to name them, their properties, and how they can be produced in chemical reactions. I will introduce you to some compounds that are related to alcohols (thiols, sulfides, and disulfides). You will learn about the reactions of alcohols in a later section, which discusses aldehydes and ketones, because these organic molecules are often reactants or products in reactions involving alcohols.

The Structure of Alcohols

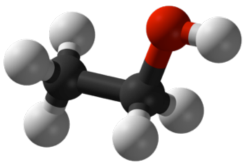
Alcohols contain one or more ***hydroxyl functional*** groups **(-OH)** attached to a hydrocarbon part (alkyl group), as shown below. The *hydroxyl group* is highlighted in yellow.



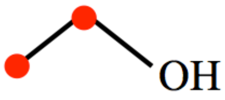
$R-\ddot{\underset{\cdot\cdot}{O}}-H$

A specific example of an alcohol is *ethanol*. The hydrocarbon part (**R**) in *ethanol* is an ethyl group (CH_3CH_2). Condensed structural formulas and a ball-and-stick model for *ethanol* are shown below (black sphere = carbon, red sphere = oxygen, and white sphere = hydrogen).

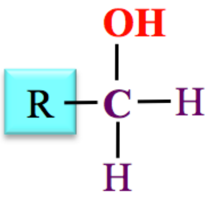
CH_3CH_2-OH *or* CH_3CH_2OH



The skeletal structure of *ethanol* is shown below. I have added red dots to indicate the carbon atom positions.

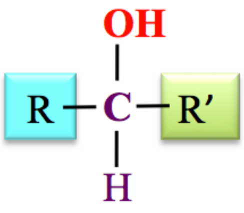


Alcohols are classified as primary (1°), secondary (2°), or tertiary (3°) based on the number of **R** groups ***attached to the carbon that is "carrying" (bonded to) the hydroxyl group***. The general forms of these three categories of alcohols are:



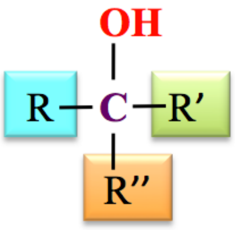
$$R-\overset{\displaystyle OH}{\underset{\displaystyle H}{C}}-H$$

primary (1°) alcohol



$$R-\overset{\displaystyle OH}{\underset{\displaystyle H}{C}}-R'$$

secondary (2°) alcohol



$$R-\overset{\displaystyle OH}{\underset{\displaystyle R''}{C}}-R'$$

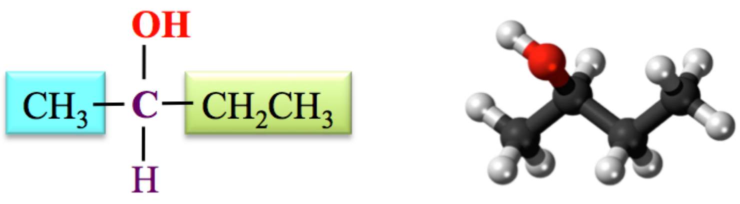
tertiary (3°) alcohol

In **primary (1°) alcohols**, *the carbon that is "carrying" the hydroxyl group* is bonded to ***<u>one</u>*** **R** group. An example of a primary alcohol is 1-propanol. The structural formula and ball-and-stick model for 1-propanol are shown below.

$$CH_3CH_2-\overset{\displaystyle OH}{\underset{\displaystyle H}{C}}-H$$

1-propanol (a primary alcohol)

In **secondary (2º) alcohols**, *the carbon "carrying" the hydroxyl group* is bonded to ***two*** **R** groups. An example of a secondary alcohol is 2-butanol:



$$CH_3-\overset{\overset{OH}{|}}{\underset{\underset{H}{|}}{C}}-CH_2CH_3$$

2-butanol (a secondary alcohol)

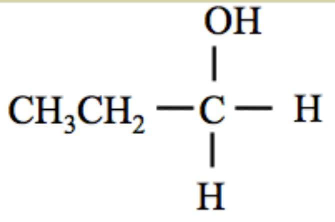
In **tertiary (3º) alcohols**, *the carbon "carrying" the hydroxyl group* is bonded to ***three*** **R** groups. An example of a tertiary alcohol is 2-methyl-2-propanol:

$$CH_3-\overset{\overset{OH}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3$$

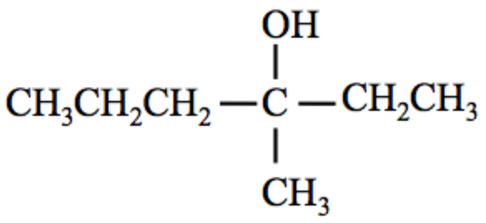
2-methyl-2-propanol (a tertiary alcohol)

Review 10.1: The Structure of Alcohols

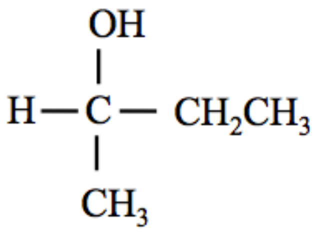
Identify each of the alcohols shown below as either primary (1º), secondary (2º), or tertiary (3º).

a. 

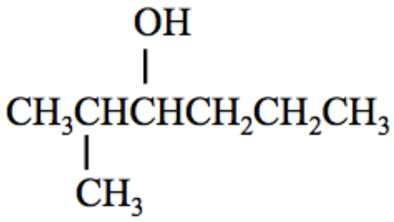
$$CH_3CH_2-\overset{\overset{OH}{|}}{\underset{\underset{H}{|}}{C}}-H$$

b. 

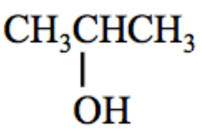
$$CH_3CH_2CH_2-\overset{\overset{OH}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2CH_3$$

c. 

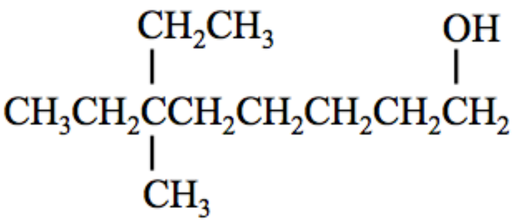
$$H-\overset{\overset{OH}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2CH_3$$

d. 

$$CH_3\underset{\underset{CH_3}{|}}{CH}\overset{\overset{OH}{|}}{CH}CH_2CH_2CH_3$$

e. 

$$CH_3\underset{\underset{OH}{|}}{CH}CH_3$$

f. 

$$CH_3CH_2\overset{\overset{CH_2CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}CH_2CH_2CH_2CH_2\overset{\overset{OH}{|}}{CH_2}$$

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

Naming Alcohols

The *systematic method* for naming alcohols is based on the hydrocarbon naming method.

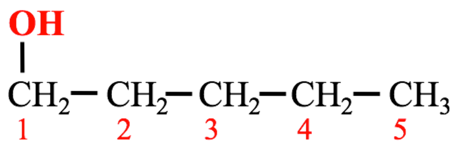
Step 1. Find and name the *parent chain*.

The *parent chain is the longest, continuous chain of carbon atoms that* ***contains the point of attachment to the hydroxyl group*** **(OH)**.

- Count the number of carbon atoms in the parent chain. Starting with the alkane name that corresponds to the number of carbon atoms in the parent chain, replace the "**e**" at the end of the alkane name with "**ol.**" For example, if the parent chain of an alcohol contains two carbons, it would be called ethanol.

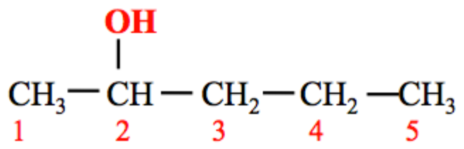
ethan***e*** ⟶ ethan***ol***

- For alcohols with ***more than two carbons***, the position of *the point of attachment to the* ***hydroxyl group*** must be indicated by adding a number before the parent chain name as described below.
  - Assign *position numbers* to the carbons in the parent chain. Position number **1** is assigned to the carbon at the *end of the parent chain* that is **closest to the *hydroxyl group***.
    - If the hydroxyl group is bonded to carbon number **1** of the parent chain, then "**1-**" is used as a prefix to the parent chain name. For example, in the molecule below, the parent chain is called **1**-pentanol.



$$\underset{1}{\overset{\mathbf{OH}}{\mathrm{CH_2}}}-\underset{2}{\mathrm{CH_2}}-\underset{3}{\mathrm{CH_2}}-\underset{4}{\mathrm{CH_2}}-\underset{5}{\mathrm{CH_3}}$$

    - If the hydroxyl group is bonded to carbon number **2** of the parent chain, then "**2-**" is used as a prefix to the parent chain name. For example, in the molecule below, the parent chain is called **2**-pentanol.



$$\underset{1}{\mathrm{CH_3}}-\underset{2}{\overset{\mathbf{OH}}{\mathrm{CH}}}-\underset{3}{\mathrm{CH_2}}-\underset{4}{\mathrm{CH_2}}-\underset{5}{\mathrm{CH_3}}$$

  - This is analogous to the numbers that you used as prefixes for the parent chain names of alkenes, to indicate the position of the double bond, and for amines, to indicate the point of attachment to the nitrogen.

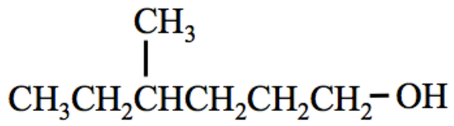
Steps 2, 3, and 4 are done the same way as you did when systematically naming *other organic molecules*.

Step 2. Name any alkyl group substituents.

Step 3: Determine the *point of attachments* of alkyl groups to the parent chain.

Step 4. Construct the name of the alcohol by placing the alkyl groups in alphabetical order and specifying their positions, followed by the name of the parent chain.

Example: Name the molecule that is shown below.



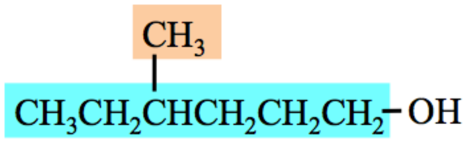
$$\mathrm{CH_3CH_2\overset{CH_3}{C}HCH_2CH_2CH_2}-\mathrm{OH}$$

Solution:

Step 1: Find and name the parent chain.

The *parent chain is the longest, continuous chain of carbon atoms that contains the point of attachment to the hydroxyl group* (OH).

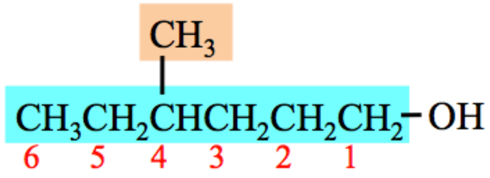
- Count the number of carbon atoms in the parent chain. There are six carbons in the parent chain. Starting with the alkane name that corresponds to the number of carbon atoms in the parent chain, replace the "**e**" at the end of the alkane name with "**ol**."



$$CH_3CH_2\overset{\overset{CH_3}{|}}{C}HCH_2CH_2CH_2-OH$$

hexan**e** ⟶ hexan***ol***

- For alcohols with ***more than two carbons***, the position of the *the point of attachment to the **hydroxyl group*** must be indicated by adding a number before the parent chain as follows:
    - Assign *position numbers* to the carbons in the parent chain. Position number **1** is assigned to the carbon at the *end of the parent chain* that is **closest to the *hydroxyl group*.**



$$\underset{6}{CH_3}\underset{5}{CH_2}\underset{4}{\overset{\overset{CH_3}{|}}{C}H}\underset{3}{CH_2}\underset{2}{CH_2}\underset{1}{CH_2}-OH$$

        - The hydroxyl group is bonded to carbon number **1** of the parent chain, then "**1-**" is used as a prefix to the parent chain name. **The parent chain is called 1-hexanol.**

Step 2: Name any alkyl group substituents.

Alkyl groups are named in the same manner as we did for *alkanes*. There is one alkyl group substituent: **methyl**. The methyl group substituent in the structure shown above is shaded orange.

Step 3: Determine the *point of attachments* of alkyl groups to the parent chain.

The carbons in the parent chain are assigned position numbers; the ***methyl group*** is attached to carbon number **4**.

Step 4: Construct the name of the alcohol by placing the alkyl groups in alphabetical order and specifying their position number, followed by the name of the parent chain. Use a ***dash*** between position *numbers* and *letters*.

    - The substituent is **4-methyl**. The parent chain name is **1-hexanol.**

- The name of the molecule is **4-methyl-1-hexanol**.

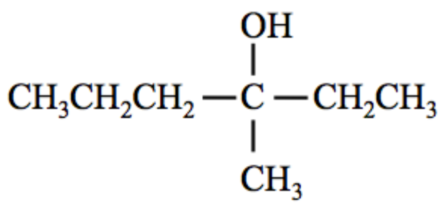
You try it:

Review 10.2: Naming Alcohols

Write the *systematic name* for each of alcohol molecules that are shown below.

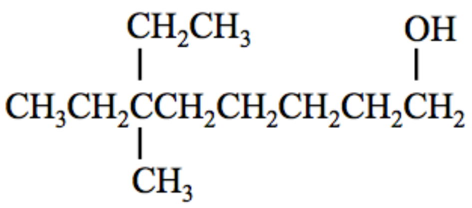
a. CH_3-OH

b.



$$CH_3CH_2CH_2-\underset{CH_3}{\underset{|}{\overset{\overset{OH}{|}}{C}}}-CH_2CH_3$$

c.



$$CH_3CH_2\underset{CH_3}{\underset{|}{\overset{\overset{CH_2CH_3}{|}}{C}}}CH_2CH_2CH_2CH_2\overset{\overset{OH}{|}}{C}H_2$$

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

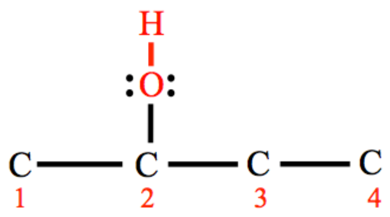
Let's do a problem where we are given the name of an alcohol, and wish to draw its structural formula.

Example: Draw the *line bond structure* of **3-methyl-2-butanol**.

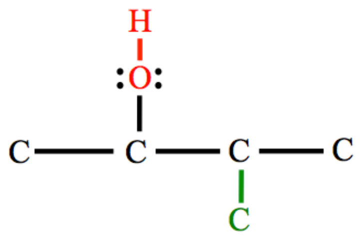
Solution:

First draw the **carbons** of the *parent chain*. The parent chain is **2-butanol**, therefore it contains *four* carbons.

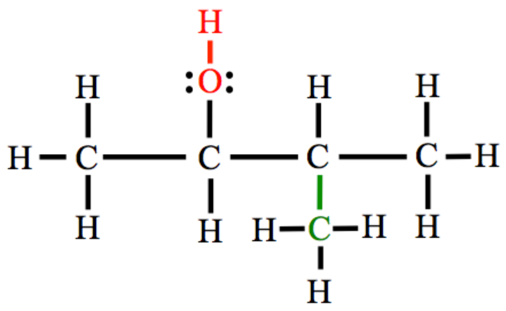
The "**2-**" prefix in **2-butanol** indicates that the *hydroxyl group* is bonded to carbon number **2** of the parent chain. Since we are drawing a line bond structure, we must include the lone pairs on oxygens. Add enough lone pairs to the ***oxygens*** so that the octet rule is satisfied.



Next, add the ***carbon*** of the methyl substituent. Since we are drawing the structure of **3-methyl**-2-butanol, the methyl group's carbon (shaded green) is attached to carbon number **3** of the parent chain.



To finish, add enough hydrogens to each carbon in order to satisfy the octet rule:



You try it:

Review 10.3: Drawing Alcohols

We just drew the line bond structure of 3-methyl-2-butanol. Draw the *condensed* ***and*** the *skeletal* structural formula of 3-methyl-2-butanol.

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

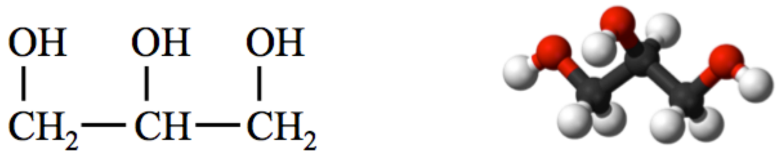
Review 10.4: Drawing Alcohols

Draw the ***line bond structure*** of 4-methyl-3-heptanol.

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

Polyhydroxy Alcohols

Molecules with more than one hydroxyl group are called **polyhydroxy alcohols**. An example of a polyhydroxy alcohol is ***glycerol*** (also known as glycerin and as propane-1,2,3-triol). Glycerol is an important biomolecule because it is one of the precursors to triglycerides (fats and vegetable oils) and some of the compounds found in cell membranes (glycerophospholipids and glycerooglycolipids). The condensed structure and the ball-and-stick model of glycerol are shown below.

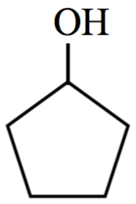


$$\begin{array}{ccccc} OH & & OH & & OH \\ | & & | & & | \\ CH_2 & - & CH & - & CH_2 \end{array}$$

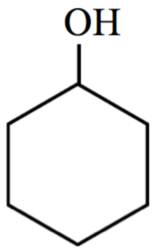
glycerol
(a polyhydroxy alcohol)

Cyclic Alcohols

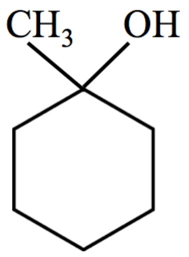
When the *hydroxyl group* of an alcohol is bound to a *ring structure* it is called a **cyclic alcohol**. Cyclic alcohols can be *secondary* or *tertiary* as shown below.



cyclopentanol
(2^{o} alcohol)



cyclohexanol
(2^{o} alcohol)



1-methylcylohexanol
(3^{o} alcohol)

Cyclic alcohols are named in a manner similar to that for cycloalkanes. Starting with the ***cyclo****alkane* name that corresponds to the number of carbon atoms in the *ring structure*, cyclic alcohols are named by replacing the "**e**" at the end of the ***cyclo***alkane name with "**ol.**" The ring-carbon that is carrying the **OH** is always designated as position number 1. Note the names of the cyclic alcohols that are shown above.

Properties of Alcohols

Water Solubility of Alcohols

Smaller alcohol molecules have significant water solubility because of their ability to interact with water through hydrogen bonding and dipole-dipole interactions. As their nonpolar (hydrocarbon) parts get larger, the water solubilities of alcohols decrease. This trend can be seen in Table 10.1.

Table 10.1
Water Solubility and Melting Points of Some Alcohols

Molecule Name	Condensed Structure	Water Solubility (g/100 mL)	Boiling Point (^{o}C)
methanol	CH_3OH	miscible*	65.0
ethanol	CH_3CH_2OH	miscible	78.5
1-propanol	$CH_3CH_2CH_2OH$	miscible	97.4
1-butanol	$CH_3CH_2CH_2CH_2OH$	8.0	117
1-pentanol	$CH_3CH_2CH_2CH_2CH_2OH$	2.2	138

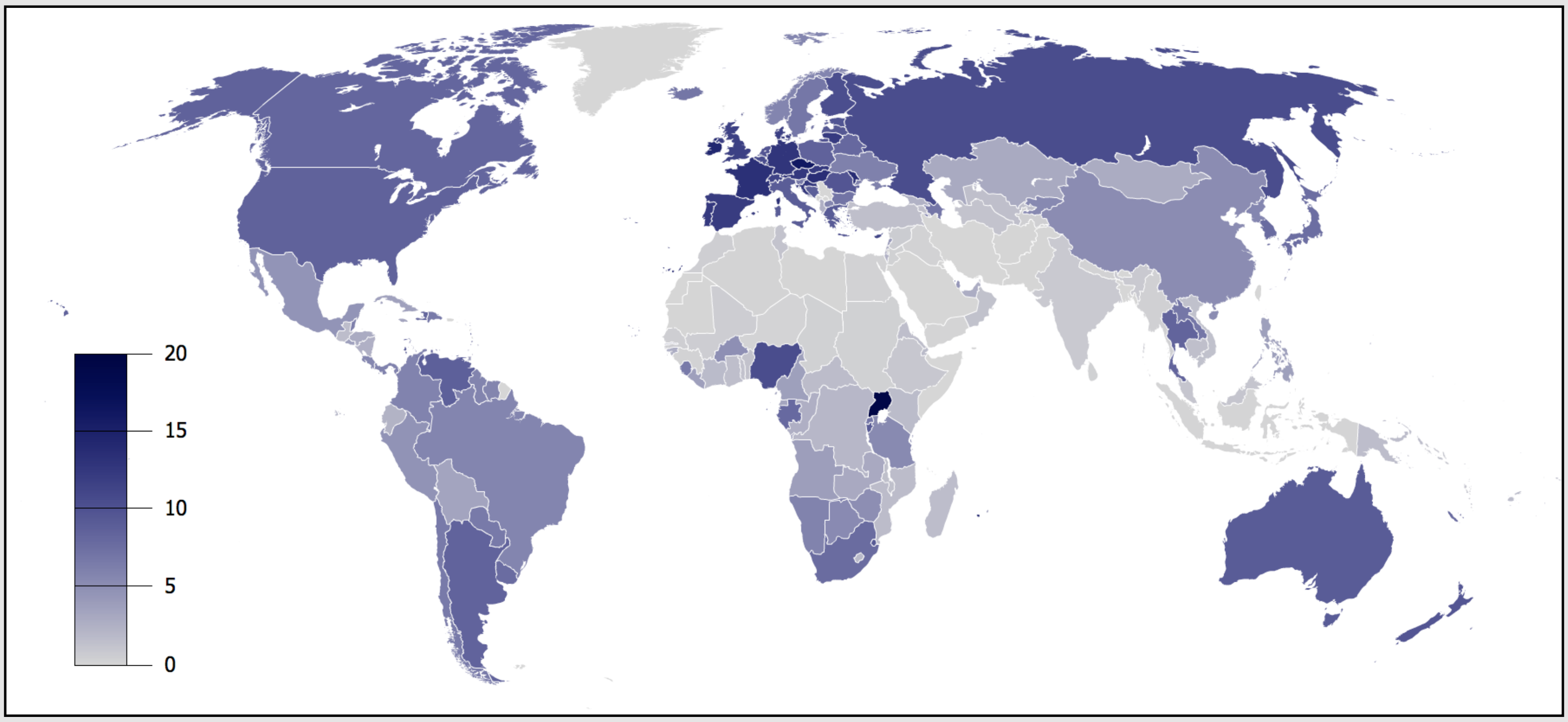
*miscible indicates that the substance will mix/dissolve at any alcohol to water ratio.

Melting and Boiling Points of Alcohols

Alcohol molecules have higher melting and boiling points than alkanes of similar size because of their ability to interact with each other through hydrogen bonding and dipole-dipole interactions. As their nonpolar (hydrocarbon) parts get larger, the melting and boiling points of alcohols increase because of increasing London forces. This trend can be seen in Table 10.2.

Alcohols have biological, industrial, and medical applications. Alcohols are used as fuels, medications, recreational drugs, antiseptic agents, industrial solvents, antifreeze, detergents, and preservatives. Humans have consumed ethanol as a recreational drug since the Neolithic age (stone age). Figure 10.1 shows the data for annual per capita ethanol consumption (liters) by country.

Figure 10.1 **Ethanol Consumption by Country**



Annual per capita recorded ethanol consumption (liters) by country in 2004. Based on the data of WHO Global Status Report on Alcohol 2004 and Statistical Information System (WHOSIS). Source: PD

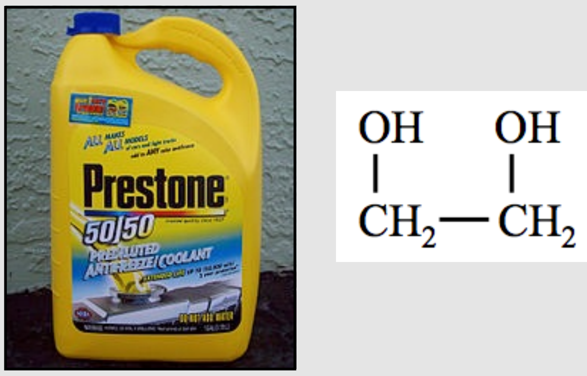
Ethanol, 1-propanol, and 2-propanol are used, with about 10-30% water, as ***antiseptic*** (surface antimicrobial) agents. One or more of these three alcohols serve as the active ingredients in many hand sanitizers, such as Purell.

Methanol is added to automotive windshield washer fluid, de-icers, and gasoline additive products as an antifreeze agent. Antifreeze agents lower the melting points of liquids. Aqueous ethylene glycol (50% v/v), a polyhydroxy alcohol, is used as engine antifreeze. It is quite effective as an antifreeze because of its ability to disrupt water-water hydrogen bonding (because of its own ability to hydrogen bond with water). A trace of fluorescent color is added to antifreeze to facilitate in leak detection. The structure of ethylene glycol is shown in Figure 10.2.

Methanol, ethanol, and some other small alcohol molecules are used as fuel. This includes use in internal combustion engine automobiles. Since alcohol can be produced by *renewable resources* and lowers pollutant emissions, many countries require the addition of alcohol to gasoline. In the United States, many states mandate that alcohol be added to gasoline.

Alcohols are used as preservatives for specimens in biological sciences, and as solvents for medical drugs, perfumes, and the preparation of plant extracts, such as vanilla.

Figure 10.2
Engine Antifreeze



$$\overset{\displaystyle OH}{\overset{|}{CH_2}}-\overset{\displaystyle OH}{\overset{|}{CH_2}}$$

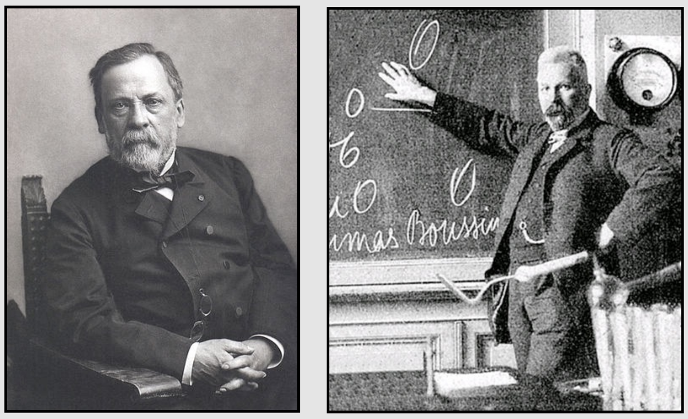
Left: Prestone brand engine antifreeze.
Right: Ethylene glycol structural formula.
Engine antifreeze is often composed of an aqueous, 50% (v/v), ethylene glycol.
Source: Wikimedia Commons, Author: DNO1967

Formation of Alcohols

1) Alcohol Fermentation

Ethanol is produced in nature in a process called ***alcohol fermentation***. In the 1850s and 1860s, Louis Pasteur (Figure 10.3, left) discovered that fermentation involved living organisms. It was not until 1897 that Eduard Buchner (Figure 10.3, right) found that ground fragments of dead yeast could produce ethanol and CO_2. As a result of Buchner's work, the term "enzyme" was applied to materials that enabled fermentation, and the understanding that fermentation was a result of enzymatic processes gained acceptance. Buchner's results are often regarded as the birth of *biochemistry*, and he was awarded the Nobel Prize in chemistry for this work in 1907. Alcohol fermentation is a series of chemical reactions that convert sugar molecules, such as glucose, into ethanol and CO_2. The final step in this reaction series involves an enzyme which is only present in yeast and some bacteria. The overall reaction of ethanol formation from a sugar molecule (glucose) is shown below:

Figure 10.3
Louis Pasteur and Eduard Buchner



Left: Louis Pasteur (1822-1895) French microbiologist and chemist.
Right: Eduard Buchner (1860-1917) German chemist and zymologist.
Source: PD

$$\underset{\textbf{glucose}}{C_6H_{12}O_6} \longrightarrow \underset{\textbf{ethanol}}{\mathbf{2}\,CH_3CH_2OH} + \underset{\textbf{carbon dioxide}}{\mathbf{2}\,CO_2}$$

2) Alcohol Formation in Nucleophilic Substitution Reactions

If you were a chemistry major, you would take a year-long organic chemistry class in which you would study the mechanisms of all of the reactions that we cover in this textbook. A reaction mechanism is a description of the sequence of bond-breaking and bond-formation that occurs in a chemical reaction. Since the intention of this book is to cover general, organic, and biochemistry *in just one semester*, we don't have the time - or need - to study the reaction mechanisms for all of the chemical reactions that I present. However, I do wish to introduce you to one very commonly observed reaction mechanism - the "nucleophilic substitution II" (S_N2) reaction mechanism. In the S_N2 reaction for the formation of alcohols, a hydroxide ion is attracted to the *partial* positive charge of a carbon in an ***alkyl halide*** molecule. An **alkyl halide** is a hydrocarbon that had one of its hydrogens replaced with a halogen (group VII element: F, Cl, Br, or I). The general form of the equation for alcohol formation by an S_N2 reaction is shown below (**X** represents F, Cl, Br, or I).

$$\underset{\textbf{alkyl halide}}{R-X} + \underset{\textbf{hydroxide ion}}{OH^-} \rightleftharpoons \underset{\textbf{alcohol}}{R-OH} + \underset{\textbf{halogen ion}}{X^-}$$

The negative charge of the hydroxide ion is quite attracted to the *partial* positive charge of ***the carbon that is bonded to the halogen atom.*** The reaction mechanism is called ***nucleophilic substitution*** because the nucleophile (OH^-) is attracted to the *nucleus* of the partially positive carbon, and then ***substitutes** for* (*replaces)* the halogen (**X**).

Specific examples of nucleophilic substitution reactions for the formation of alcohols are shown below.

$$CH_3-Cl + OH^- \rightleftharpoons CH_3-OH + Cl^-$$

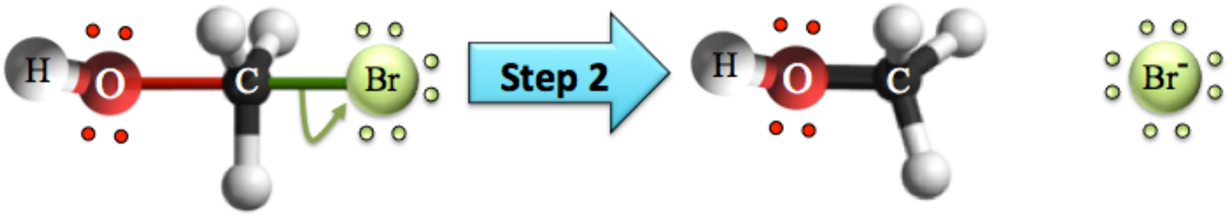
$$CH_3-Br + OH^- \rightleftharpoons CH_3-OH + Br^-$$

$$CH_3CH_2CH_2-I + OH^- \rightleftharpoons CH_3CH_2CH_2-OH + I^-$$

The S_N2 chemical reaction involves ***making one new bond and breaking one old bond***. First, a lone pair from the hydroxide nucleophile forms a bond to the carbon that is carrying (bonded to) the halide.

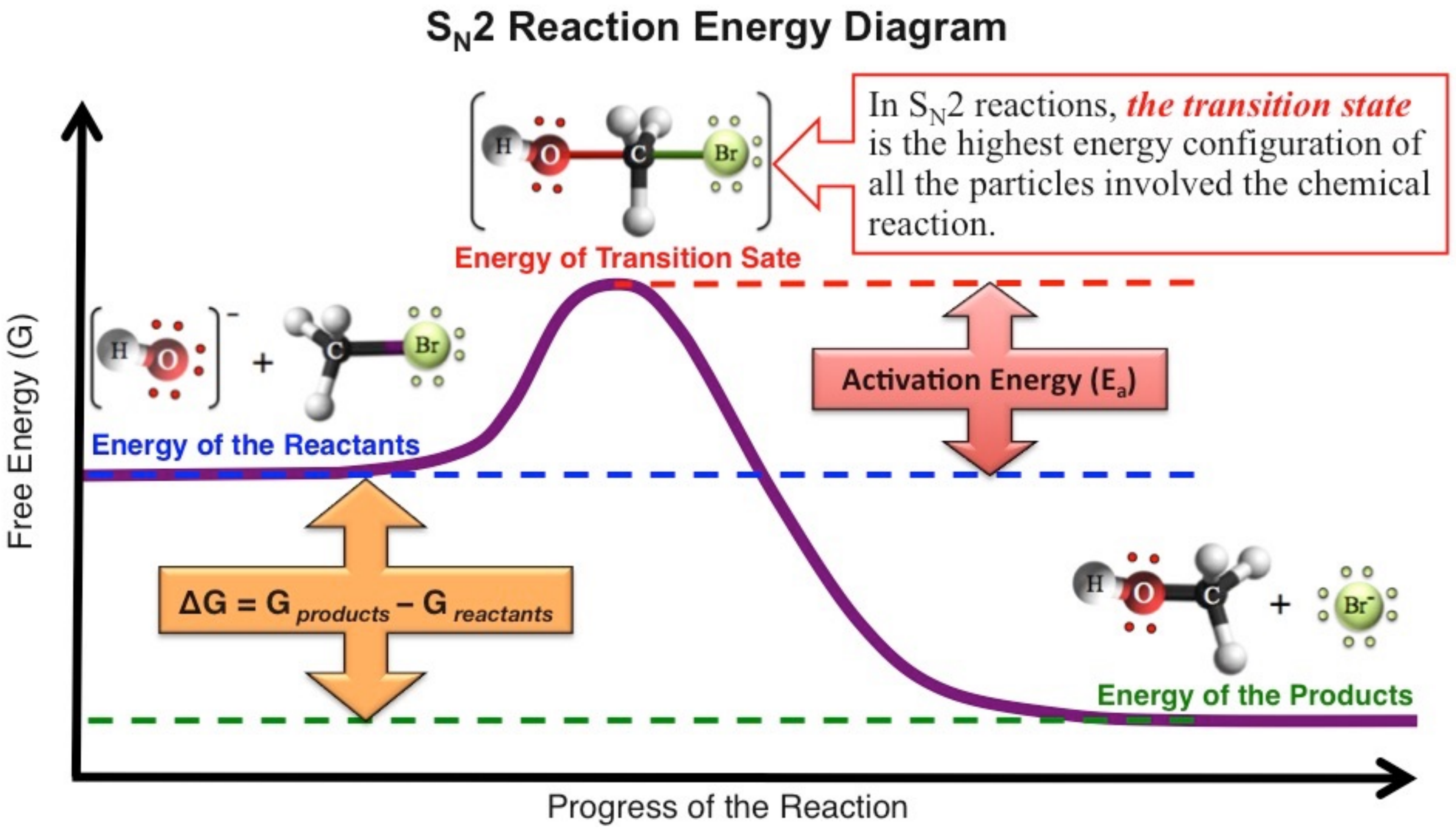
hydroxide ion **bromomethane** (an alkyl halide) **transition state**

The species which is formed by the newly-made bond is called a **transition state**. The transition state is a ***high-energy molecule*** because there are *ten* electrons (five single bonds) around a carbon atom instead of the lower-energy octet. The *transition state* has a ***high energy***, which means that it is unstable, and the weakest of these five bonds will quickly break. The weakest bond is the bond to the halogen (bromine in this example). When this bond breaks, the halogen takes with it the two electrons that were in its bond to the carbon, and an alcohol is produced, as shown below for our example reaction.



intermediate (from step 1) **methanol** (an alcohol) **bromide ion**

I introduced you to reaction energy diagrams, **ΔG**, activation energy (**E_a**), and transition states in chapter 6. The ***transition state*** is the highest energy arrangement of all the particles involved in the S_N2 reaction. The reaction energy diagram for our example S_N2 reaction is shown below.



In S_N2 reactions, ***the transition state*** is the highest energy configuration of all the particles involved the chemical reaction.

Review 10.5: Nucleophilic Substitution Reactions

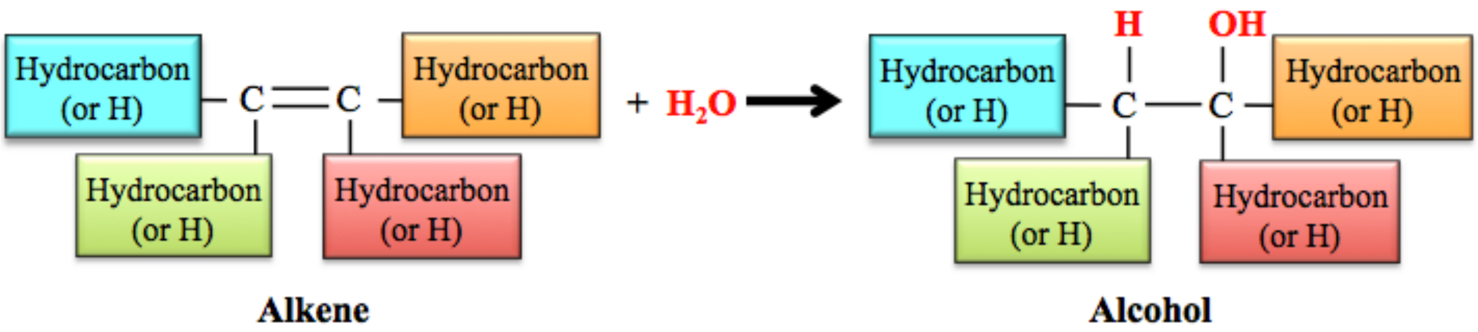
Predict the products of the following nucleophilic substitution reaction.

$$CH_2CH_3{-}Br \quad + \quad OH^- \quad \rightleftharpoons$$

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

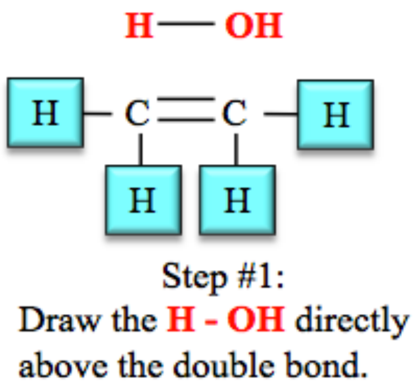
3) Hydration of Alkenes

In chapter 6, you learned that an *alkene* can react with *water* to produce an *alcohol*. A hydrogen from H_2O is added to one of the double-bonded carbon atoms and **OH** from the H_2O is added to the ***other*** double-bonded carbon atom in the ***alkene***, to produce the corresponding ***alcohol.*** The ***general form*** of the chemical equation for the hydration of an alkene reaction is shown below:

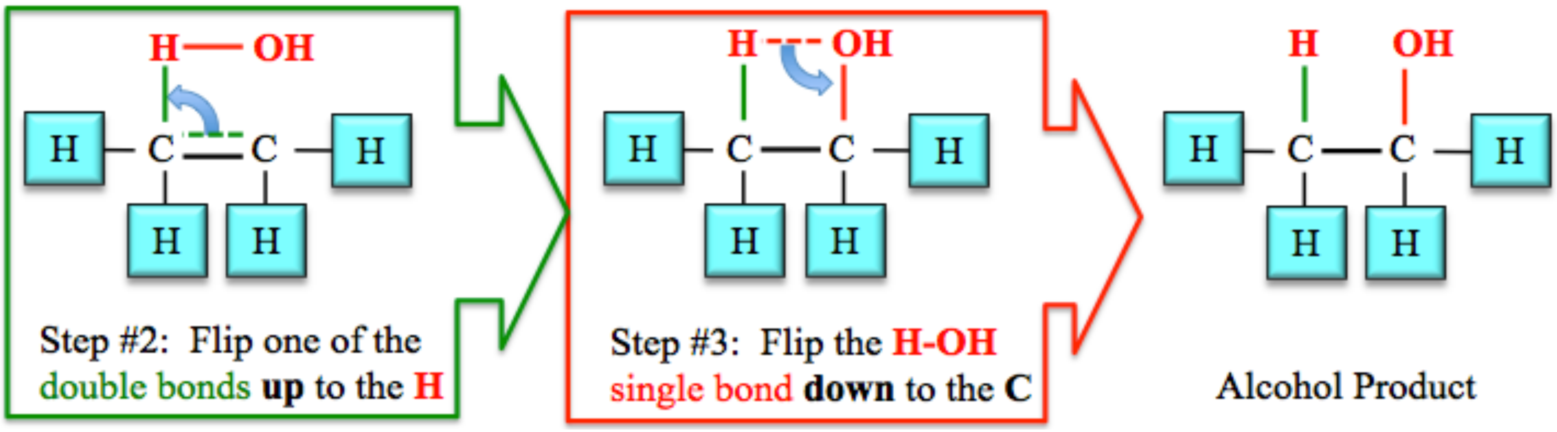


In chapter 6, I showed you a *bond flipping method* to help you predict the structure of the alcohol that is produced when you add H_2O "*across a double bond*." Let's review that method now by adding H_2O across the double bond of **ethene** (hydration of ethene).

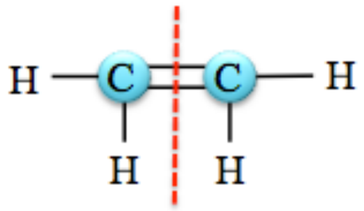
Step 1: Draw the H_2O to be added *across the double bond* and the alkene as shown below.



Steps 2 and 3: ***Flip*** the bonds, as shown below, to get the alcohol product of the reaction.

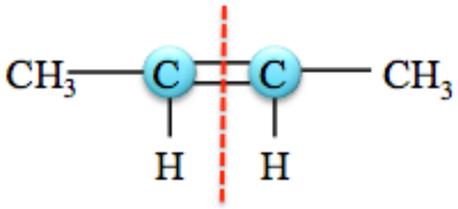


In chapter 6, we always began with ***symmetric*** alkenes when doing hydration reactions. An alkene is ***symmetric*** when a line drawn perpendicular to, and through, the middle of the double bond of its structural formula results in ***identical parts*** on each side of the line. For example, the alkene (*ethene*) from the hydration reaction shown on the previous page is *symmetric* because the dashed line drawn through the the double bond results in ***identical parts*** on each side of the line.



ethene (a symmetric alkene)

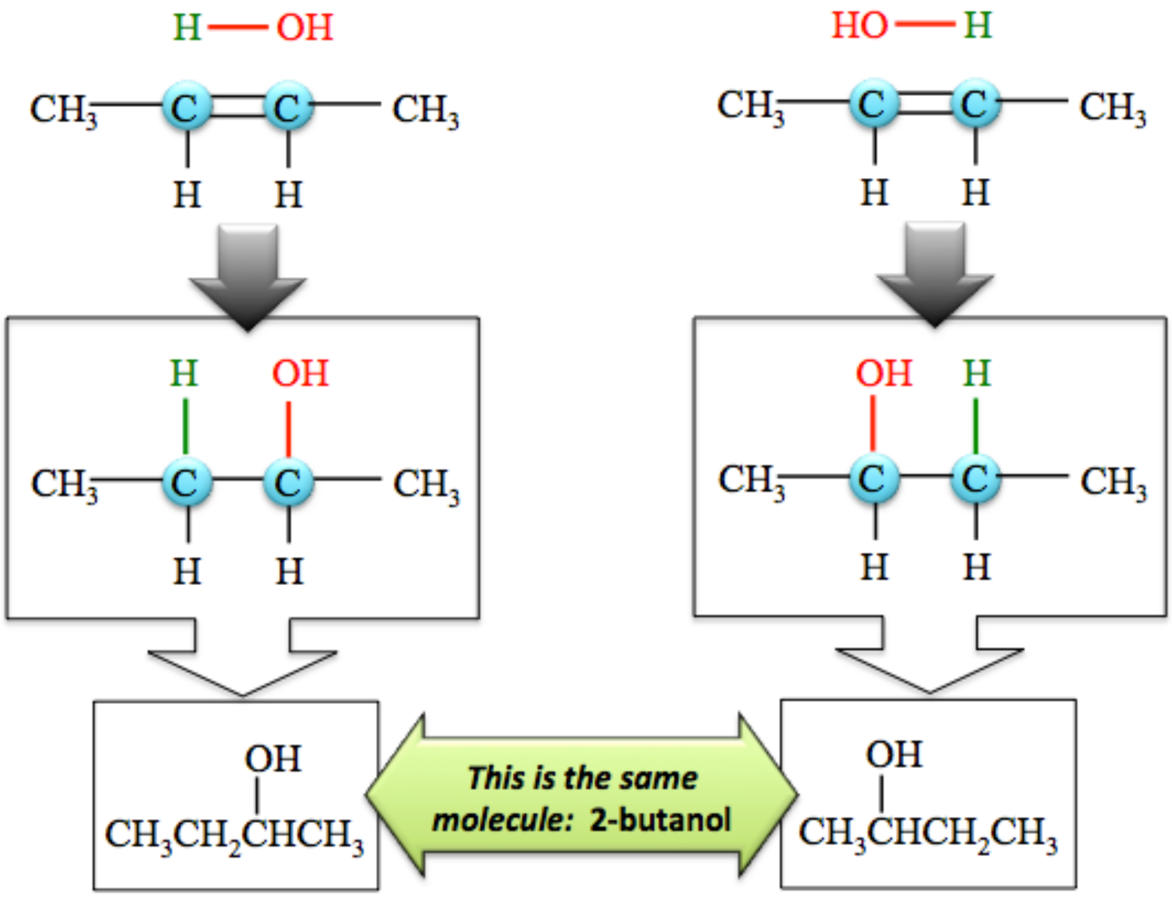
Another example of a ***symmetric alkene*** is *2-butene*. Note that parts of the molecule on each side of the red dashed line bisecting the carbon-carbon double bond are ***identical***.



2-butene (a symmetric alkene)

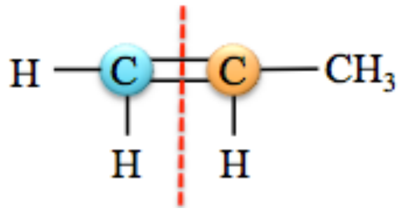
When a symmetric alkene undergoes a hydration reaction, there is only ***one possible product***. For example, the illustration below shows that the same alcohol molecule is produced regardless of which of 2-butene's double-bonded carbons gets the added **OH** group.

$$CH_3CH{=}CHCH_3 \quad + \quad H_2O$$



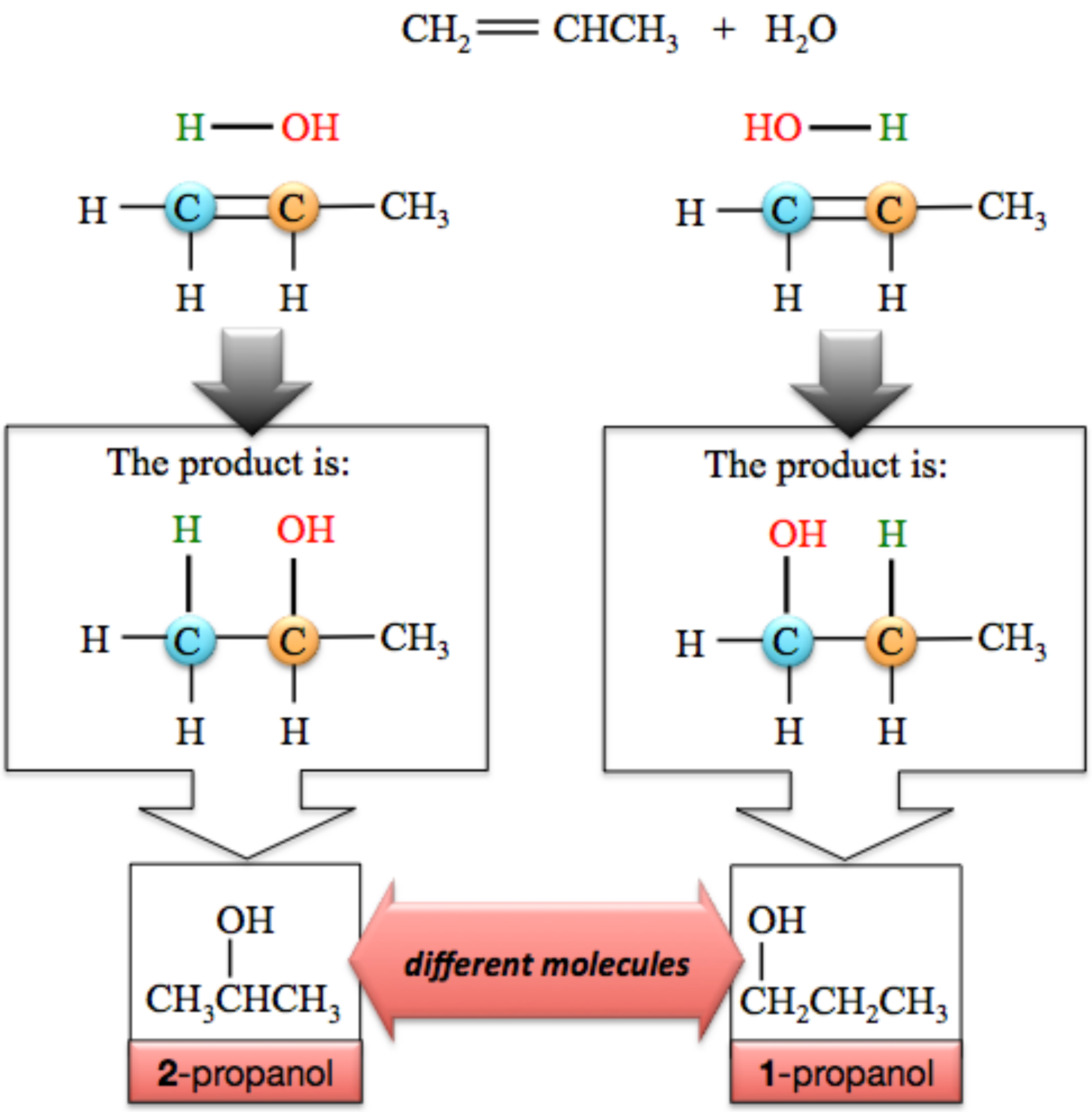
The reason that the addition of the **OH** to ***either*** double-bonded carbon results in the same alcohol (2-butanol) is that the 2-butene is ***symmetric***.

An example of an ***asymmetric alkene*** is *propene*. Note that the dashed line bisecting the carbon-carbon double bond results in ***nonidentical parts*** on each side of the line.

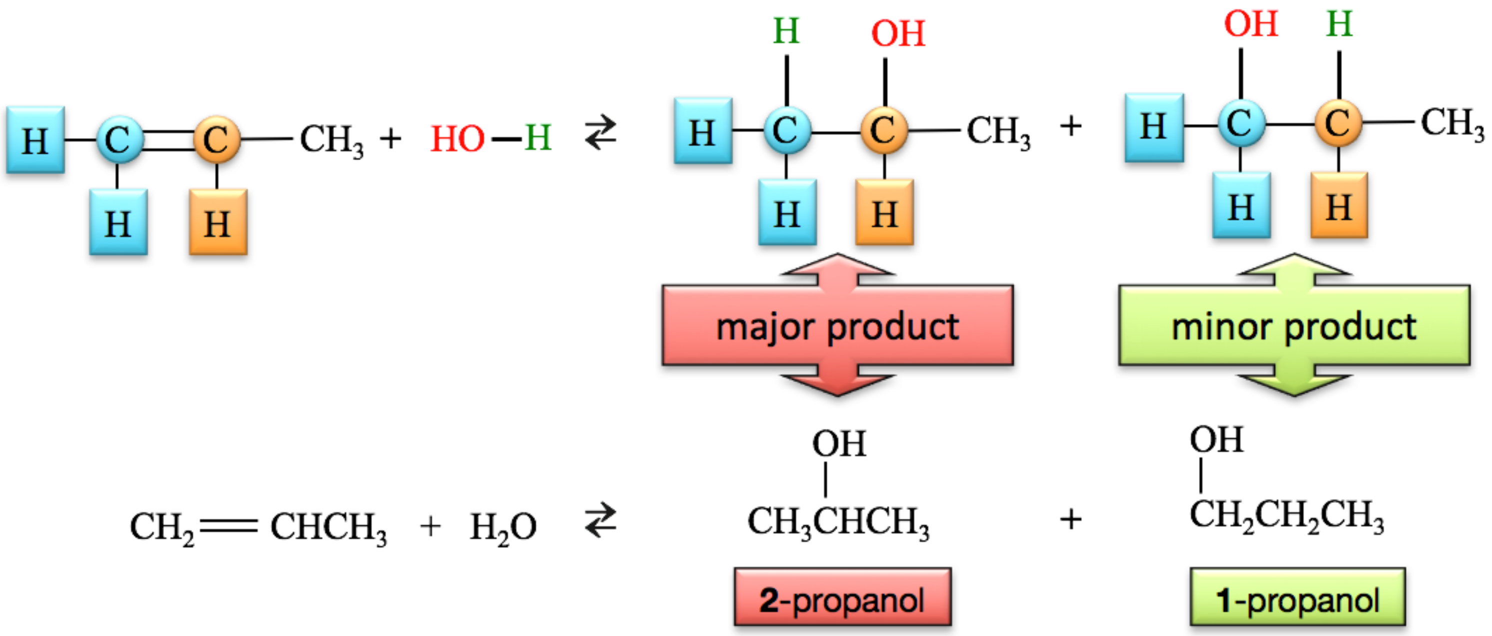


propene (an asymmetric alkene)

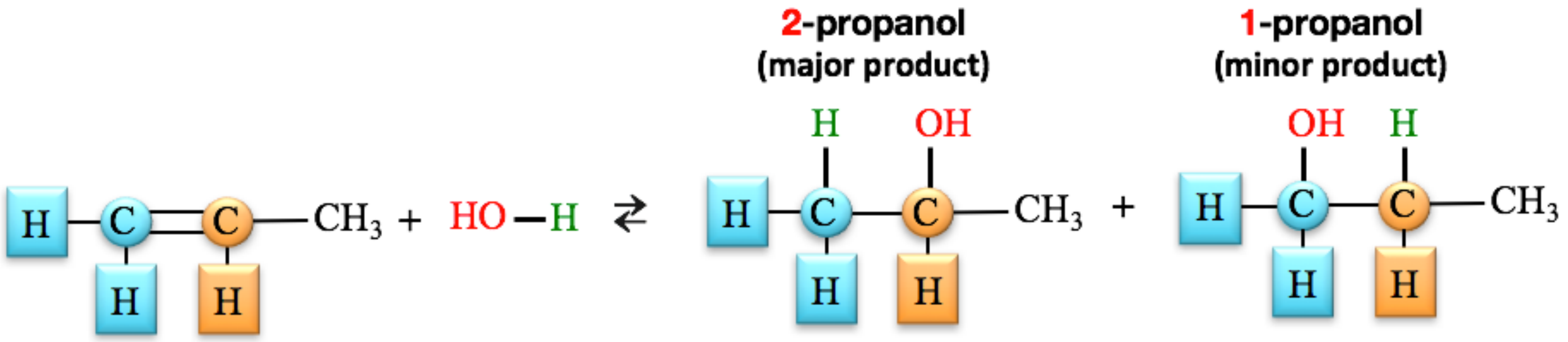
When an **asymmetric alkene** undergoes a hydration reaction, there are ***two different alcohol molecules produced***. For example, the illustration below shows that the addition of the **OH** group to propene's *right-most* double-bonded carbon (shaded orange) produces **2**-propanol; whereas adding the **OH** group to the left-most double-bonded carbon (shaded blue) produces **1**-propanol.



The hydration of an asymmetric alkene ***does not produce an equal amount of each alcohol product***. For example, in the hydration of propene (shown below), there is more **2**-propanol than **1**-propanol produced. The product made in greater quantity is called the "**major product**," and the product made in lesser quantity is called the "**minor product**."



The reason that there is more 2-propanol than 1-propanol produced is that the *activation energy* for the production of 2-propanol is less than that of 1-propanol. It is possible to predict the major and minor products for the hydration of an asymmetric alkene using **Markovnikov's Rule**. This rule says that, the ***major product*** is formed by adding the **H** - from water - to the alkene's double-bonded carbon that ***originally carried the most hydrogens***, and adding the **OH** to the *other* double-bonded carbon. An easy way to remember this rule is by using the old saying, "*the rich get richer*," where the **H**'s represent money. The ***minor product*** is formed by adding the **H** and **OH** in a manner opposite to that described for the *major product*. Consider the hydration of propene:

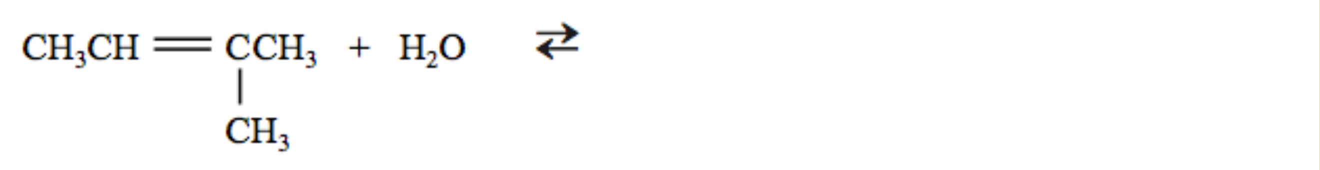


The left-most double-bonded carbon (shaded blue) in propene is bonded to two hydrogens (shaded blue). The right-most double-bonded carbon (shaded orange) is bonded to only one hydrogen (shaded orange). The ***major product*** is formed by adding the **H** - from water - to the double-bonded carbon that originally carried the most hydrogens - *the rich get richer* - and the **OH** is added to the *other* double-bonded carbon.

You try one:

Review 10.6: Predicting the Major and Minor Products in the Hydration of Alkenes

Draw and name the major and minor products for the hydration of 2-methyl-2-butene:

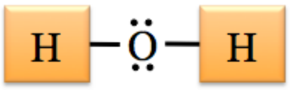


$$CH_3CH{=}C(CH_3)CH_3 + H_2O \rightleftarrows$$

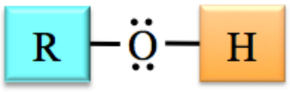
For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

10.3 Compounds that are Related to Alcohols

Water and **alcohols** are said to be "***structurally related***" because of their bonding patterns. If one of the hydrogens from water is *replaced* by an alkyl group (**R**), then an ***alcohol*** is obtained.

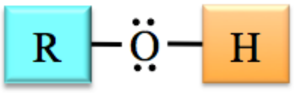


water

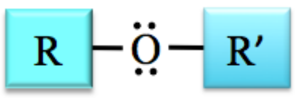


alcohol

Ethers and **alcohols** are *structurally related* compounds. If the hydrogen (highlighted in orange) from an alcohol is replaced by an alkyl group (R'), then an ***ether*** is obtained.

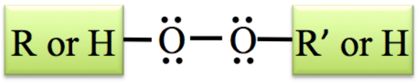


alcohol



ether

Peroxides are *structurally related* to **water, ethers,** and **alcohols.** If a *second* oxygen is added to water, ethers, or alcohols, as in the arrangement shown below, then a ***peroxide*** is obtained.

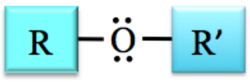


general form of a peroxide

Ethers

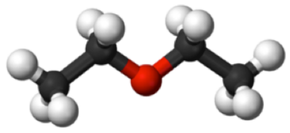
The Structure of Ethers

Ethers contain an oxygen atom that is attached to ***two*** alkyl (**R**) groups. The general form of an *ether* is shown below.

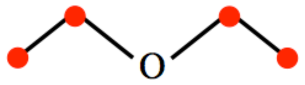


A specific example of an ether is *diethyl ether*. Diethyl ether was introduced as a surgical anesthetic in the 1840s. It is rarely used as an anesthetic currently because of the availability of more desirable substances. Both of the alkyl (**R**) groups in diethyl ether are ethyl groups ($-CH_2CH_3$). Condensed structural formulas and a ball-and-stick model for diethyl ether are shown below (black sphere = carbon, red sphere = oxygen, and white sphere = hydrogen).

$CH_3CH_2{-}O{-}CH_2CH_3$ *or* $CH_3CH_2OCH_2CH_3$



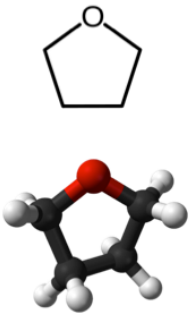
The *skeletal structure* of diethyl ether is shown below. I have added red dots to indicate the carbon atom positions.



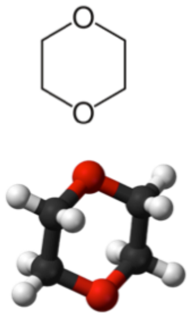
Cyclic Ethers

A cyclic compound that has an oxygen atom in one of the ring positions is called a **cyclic ether**. Cyclic ethers are *hetero*cyclic compounds because their rings contain more than one type of element. A few examples of cyclic ethers are shown below.

ethylene oxide



tetrahydrofuran (THF)



dioxane

Naming Ethers

IUPAC naming is rarely used for *small* ether molecules. Because we will focus on *small* ether molecules, we will use what is referred to as the “common names” for ethers. This *trivial* method for naming ethers **is *not*** based on the IUPAC hydrocarbon naming method.

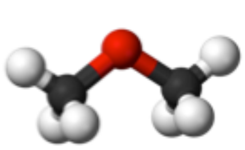
Step 1. Identify the alkyl group names for the two alkyl (R) groups.

- If the two **R** groups are *identical* use the “di” prefix before alkyl group name.

Step 2. Construct the name of the ether by placing the alkyl groups in alphabetical order followed by the word “ether.”

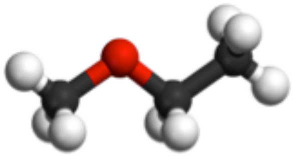
- Use a space between the alkyl group names and before the word “ether.”

Examples:



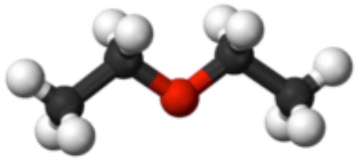
CH_3-O-CH_3

dimethyl ether



$CH_3-O-CH_2CH_3$

ethyl methyl ether



$CH_3CH_2-O-CH_2CH_3$

diethyl ether

You try a one:

Review 10.7: Naming Ethers

Name the molecule that is shown below.

$CH_3CH_2-O-CH_2CH_2CH_3$

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

Properties of Ethers

Water Solubility of Ethers

Smaller ethers have significant water solubility because of their ability to interact with water through hydrogen bonding and dipole-dipole interactions. As their nonpolar (hydrocarbon) parts get larger, the water solubilities of ethers decrease.

Melting and Boiling Points of Ethers

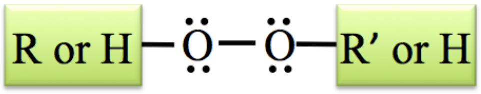
Ethers have higher melting and boiling points than *hydrocarbons* of similar size because they can interact with each other through dipole-dipole interactions - they are polar molecules. As their nonpolar (hydrocarbon) parts get larger, the melting and boiling points of ethers increase because of increasing London forces. Ethers are ***unable*** to hydrogen bond *with each other*, and therefore, they have lower melting and boiling points than *alcohols* and *carboxylic acids* of similar size.

Ethers in Nature and Industry

Ethers have natural, industrial, and biochemical applications. Dimethyl ether and ethyl methyl ether are used as aerosol spray propellants. Dimethyl ether is used as an industrial solvent and in the perfume industry for the extraction of fragrant compounds from their natural sources. Ethylene oxide, a cyclic ether, is used in the medical industry and hospitals as a disinfectant or sterilization agent for heat sensitive equipment. For example, disposable plastic syringes are sterilized using pure ethylene oxide.

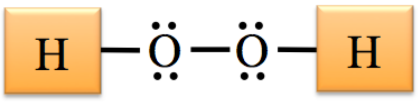
Peroxides

Peroxides contain two oxygen atoms that are single-bonded to each other and situated between hydrogens, alkyl groups, or any other organic groups.



Peroxides are quite reactive because of the two oxygen atoms that are single-bonded to each other. A much more stable configuration (lower energy) results when the oxygen-oxygen single bond breaks, and the oxygen atoms acquire more electrons by oxidizing another molecule. It is for this reason that peroxides are very effective oxidizing agents, and are frequently used as disinfectants and bleaching agents.

A specific example of a peroxide is *hydrogen peroxide*.



hydrogen peroxide

Hydrogen peroxide is important in human and animal metabolism. An extremely toxic byproduct of the production of ATP in the mitochondria is the superoxide ion (O_2^-) ion. This is not the *monoatomic* oxide ion (O^{2-}); it is an unstable *diatomic* ion with a 1^- charge. The superoxide ion is extremely toxic to cells because it can react with and damage (oxidize) DNA, proteins, and membrane component compounds. Almost all organisms have evolved enzymes called superoxide dismutases (SOD) to quickly remove superoxide ions. These enzymes are *antioxidant agents*. SOD enzymes catalyze the reaction of superoxide ions and water to produce hydrogen peroxide, oxygen, and hydroxide ions.

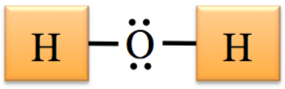
$$2\,O_2^- + 2\,H_2O \xrightarrow{\text{SOD}} \mathbf{H_2O_2} + O_2 + 2\,OH^-$$

Though not quite as strong an oxidizer as superoxide, hydrogen peroxide is also an oxidizing agent, and is therefore quite toxic to cells. However, the hydrogen peroxide produced from superoxide is quickly converted to oxygen and water by an enzyme called catalase.

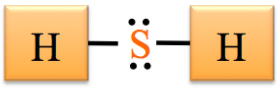
$$2\,\mathbf{H_2O_2} \xrightarrow{\text{catalase}} 2\,H_2O + O_2$$

Sulfur Analogs

When the oxygen atoms of water, an alcohol, ether, or peroxide is replaced by sulfur, the resulting compound is called a **sulfur analog**. For example, the ***sulfur analog of water,*** dihydrogen sulfide, is obtained if the oxygen in a water molecule is replaced by sulfur.



H_2O



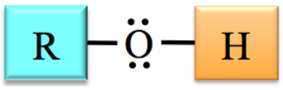
H_2S

dihydrogen sulfide

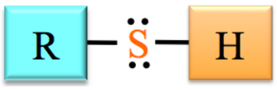
Dihydrogen sulfide (H_2S) is often called hydrogen sulfide. Although H_2S is heavier than H_2O, it is a gas at room temperature. The reason for this difference is that, unlike water, H_2S molecules are unable to hydrogen bond with each other. H_2S has the foul odor of rotten eggs. It is toxic and very reactive (explosive, flammable, and corrosive). H_2S occurs in nature when bacteria metabolize organic matter in the absence of oxygen. This often happens in sewers and swamps. It is also found in natural gas, some water wells, and volcanic gases. It is found in very low concentration in humans, where it acts as a chemical signaling molecule.

Thiols

The ***sulfur analog of an alcohol*** is obtained if the oxygen atom in an alcohol is replaced by sulfur. The resulting molecule is called a **thiol**.



alcohol



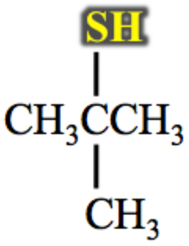
thiol

The term “thiol” is a portmanteau of "thion" + "alcohol," where “thion” comes from the Greek word for sulfur. Thiols are often referred to as *mercaptans*. Many thiols have the aroma of garlic. Thiol aromas can be pungent and annoying. There are several thiols in the spray of skunks - *as I learned while looking for compounds that could remove the skunk spray from my dog*.

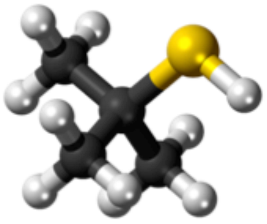
Figure 10.4 A Skunk

Thiol odors can be pungent and annoying. There are several thiols in the spray of skunks.
Source: Wikimedia Commons, Author: Diotime
CC-BY-SA
http://creativecommons.org/licenses/by-sa/3.0/deed.en

A specific example of a thiol is *2-methyl-2-propanethiol*. A condensed structural formula and ball-and-stick model for 2-methyl-2-propanethiol are shown below (black sphere = carbon, yellow sphere = sulfur, and white sphere = hydrogen).



$$\begin{array}{c} SH \\ | \\ CH_3CCH_3 \\ | \\ CH_3 \end{array}$$



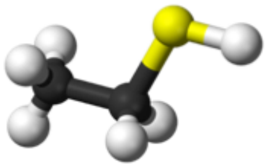
2-methyl-2-propanethiol is added, in very small amounts, to natural gas as an odorant in order to help detect gas leaks or mistakenly-opened valves. The **-SH** functional group, which defines the thiol family of organic compounds, is referred to as a ***thiol group*** or a ***sulfhydryl group***.

Naming Thiols

Thiols are systematically named in the same way as *alcohols* ***with only one exception***:

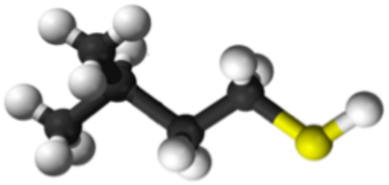
- The term “thiol” is added to the end the alkane name that indicates the number of carbons in the parent chain (***instead of*** replacing the “e” from the alkane name with “ol,” as we did for alcohols).

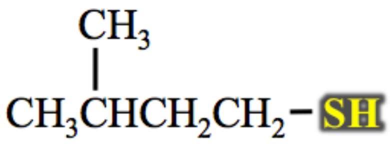
Examples:



$CH_3CH_2{-}SH$

ethanethiol





$$CH_3\overset{\displaystyle CH_3 \atop |}{C}HCH_2CH_2{-}SH$$

3-methyl-1-butanethiol

As was the case for alcohols, the point of attachment of the ***thiol group*** (-SH) must be indicated for thiols with more than two carbons in their parent chain. The point of attachment to the thiol group is indicated by writing the position number *in front of* the parent chain name.

You try one:

Review 10.8: Naming Thiols

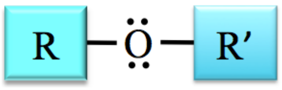
Name the molecule that is shown below.

$CH_3CH_2CH_2CH_2CH_2SH$

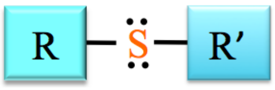
For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

Sulfides

The ***sulfur analog of an ether*** is obtained if the oxygen in an ether molecule is replaced by sulfur. The resulting molecule is called a **sulfide**. Sulfides are also referred to as **thioethers.**



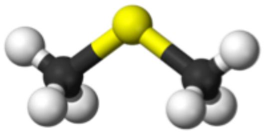
ether



sulfide

A specific example of a sulfide is *dimethyl sulfide (DMS)*. A condensed structural formula and a ball-and-stick model for *dimethyl sulfide* are shown below.

CH_3-S-CH_3



dimethyl sulfide (DMS)

DMS is found in the atmosphere in greater concentration than any other organic sulfur-containing compound because it is produced by phytoplankton. It is also produced by bacteria in sewers. DMS has a characteristic cabbage-like odor. It is produced from cooking certain vegetables - corn, cabbage, beetroot - and seafood.

Naming Sulfides

We will use *common* names for sulfides, as we did for ethers.

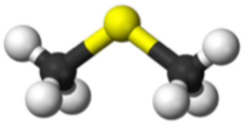
Step 1. Identify the alkyl group names for each of the R groups.

- If the two **R** groups are *identical* use the "di" prefix before the alkyl group name.

Step 2. Name the sulfide by placing the alkyl groups in alphabetical order followed by the word "sulfide."

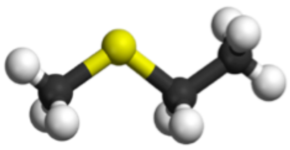
- Use a space between the alkyl group names and before the word "sulfide."

Examples:



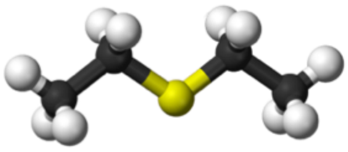
CH_3-S-CH_3

dimethyl sulfide



$CH_3-S-CH_2CH_3$

ethyl methyl sulfide



$CH_3CH_2-S-CH_2CH_3$

diethyl sulfide

You try one:

Review 10.9: Naming Sulfides

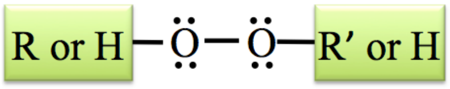
Name the molecule that is shown below.

$CH_3CH_2-S-CH_2CH_2CH_3$

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

Disulfides

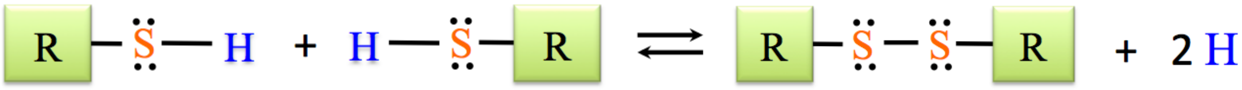
The ***sulfur analog of a peroxide*** is obtained if the two oxygens in a peroxide molecule are replaced by two sulfurs. The resulting molecule is called a **disulfide.**



peroxide

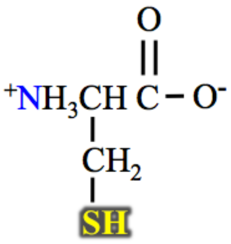
disulfide

The S-S bond is called a **disulfide bond**. Disulfides can be made from the reaction of two thiols. In this reaction, the thiols are oxidized to form a disulfide. The general form of the oxidation of thiols to a disulfide is shown below.



You can recognize that the thiol reactants were *oxidized* because they *lose hydrogen* in the reaction.

The disulfide bond is important in protein biochemistry. ***Cysteine*** is one of the twenty common amino acid molecules that make up proteins. Cysteine, shown below, contains a thiol group that is capable of forming disulfide bonds with other cysteine-thiols.

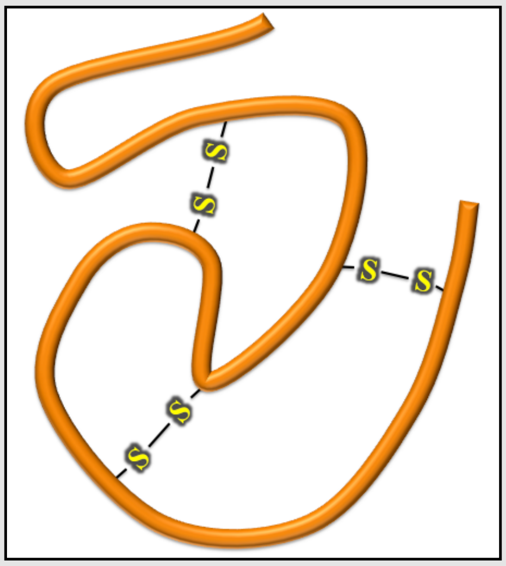


cysteine

Two thiol (SH) groups *on the same protein molecule* ***or*** two thiol groups on two *different protein molecules* can react to form disulfide bonds. Disulfide bonds in protein are called *disulfide bridges*. The disulfide bridges in protein play an important role in how many proteins maintain their shape, which is critical in their biological function. This concept is illustrated in Figure 10.5 by a large protein molecule - represented as a thick orange ribbon - that is held into a particular shape with the help of some disulfide bonds. You will learn more details of protein structure and function in chapter 15.

Figure 10.5 Disulfide Bonds in Proteins

The orange ribbon represents a large protein molecule that is held into a particular shape with the help of three disulfide bonds. Disulfide bonds in protein may also be called disulfide bridges. The disulfide bridges (S-S) play an important role in how many proteins maintain their shape, which is critical in their biological function.



Review 10.10: Understanding Disulfides

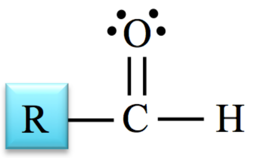
Draw the condensed structure of the disulfide that is formed by the reaction of two methanethiol molecules.

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

10.4 Aldehydes and Ketones

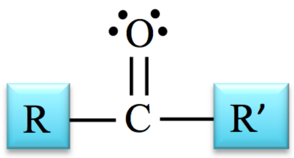
The Structure of Aldehydes and Ketones

The general forms of aldehydes and ketones are shown below.



$$\mathrm{R-\overset{O}{\overset{\|}{C}}-H}$$

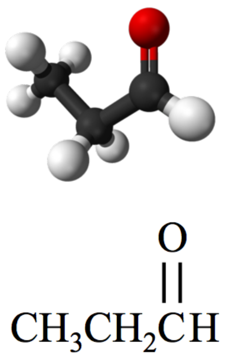
aldehyde



$$\mathrm{R-\overset{O}{\overset{\|}{C}}-R'}$$

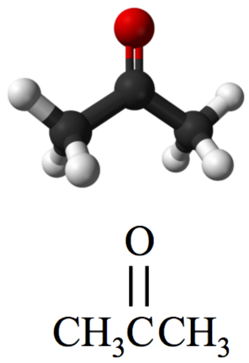
ketone

In ***aldehydes***, the carbonyl carbon is bonded to ***one*** **R** group **and** ***one*** hydrogen (**H**), except for the simplest aldehyde, formaldehyde, which has the carbonyl carbon bonded to *two* hydrogens. In ***ketones***, the carbonyl carbon is bonded to ***two*** **R** groups. For example, consider the aldehyde and ketone that are shown below.



$$\mathrm{CH_3CH_2\overset{O}{\overset{\|}{C}}H}$$

an aldehyde



$$\mathrm{CH_3\overset{O}{\overset{\|}{C}}CH_3}$$

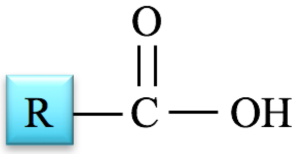
a ketone

Sometimes a shorthand notation "**CHO**" is used for the carbonyl group *and* the hydrogen that is bonded to the carbonyl carbon when drawing ***aldehydes***, as shown below.

$$\mathrm{CH_3CH_2\overset{O}{\overset{\|}{C}}H \qquad CH_3CH_2CHO}$$

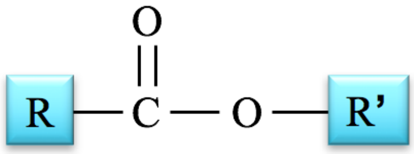
two *equivalent* ways to draw an aldehyde

Any molecule that contains a ***carbonyl group*** **(C=O)** is called a **carbonyl compound**. In addition to aldehydes and ketones, you have been introduced to several *carbonyl compounds*: carboxylic acids, esters, and amides. As a review, and for comparison, the general form for each of these families is shown below.



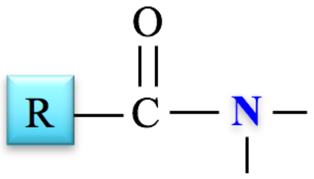
$$\mathrm{R-\overset{O}{\overset{\|}{C}}-OH}$$

carboxylic acid



$$\mathrm{R-\overset{O}{\overset{\|}{C}}-O-R'}$$

ester



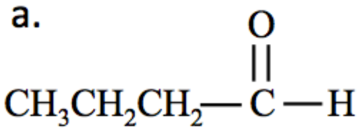
$$\mathrm{R-\overset{O}{\overset{\|}{C}}-\underset{|}{N}-}$$

amide

Review 10.11: The Structure of Aldehydes and Ketones

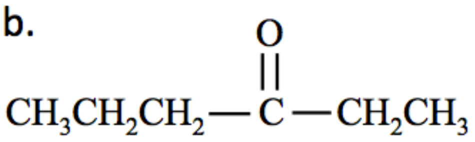
Classify each of the following molecules as either an aldehyde or a ketone.

a.



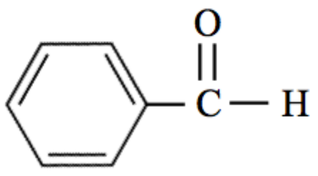
$$\mathrm{CH_3CH_2CH_2-\overset{O}{\overset{\|}{C}}-H}$$

b.



$$\mathrm{CH_3CH_2CH_2-\overset{O}{\overset{\|}{C}}-CH_2CH_3}$$

c.

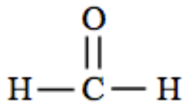


For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

Naming Aldehydes and Ketones

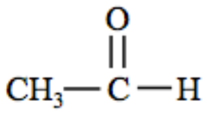
Common Names for Aldehydes and Ketones

Small aldehydes and ketones, those with a relatively few number of carbon atoms, are often identified by ***common names***. Some examples of common names for *aldehydes* are shown below.



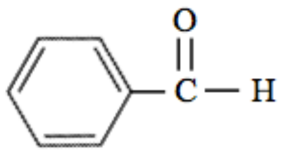
$H-\overset{\overset{O}{\|}}{C}-H$

formaldehyde



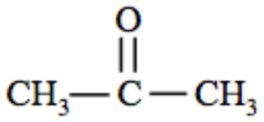
$CH_3-\overset{\overset{O}{\|}}{C}-H$

acetaldehyde



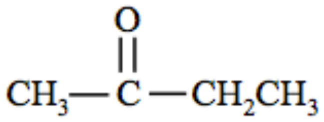
benzaldehyde

Sometimes, *common names* for ***ketones*** list the names of the alkyl groups bonded to the *carbonyl group* followed by the word ***ketone***. Examples of *common names* for *ketones* are shown below.



$CH_3-\overset{\overset{O}{\|}}{C}-CH_3$

dimethyl ketone (or acetone)



$CH_3-\overset{\overset{O}{\|}}{C}-CH_2CH_3$

methyl ethyl ketone

Systematic Names for Aldehydes and Ketones

The ***systematic method*** for naming aldehydes and ketones is based on the hydrocarbon naming method.

Step 1. Find and name the *parent chain*.

The *parent chain is the longest, continuous chain of carbon atoms that **contains the carbonyl carbon**.*

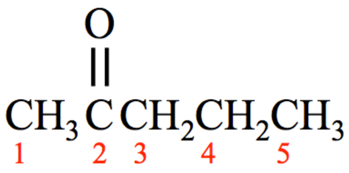
- Count the number of carbon atoms in the parent chain.
    - **For aldehydes**, starting with the alkane name that corresponds to the number of carbon atoms in the parent chain, replace the "**e**" at the end of the alkane name with "**al.**" For example, if the parent chain of an aldehyde contains two carbons, it would be called ethanal.

      ethan***e*** ⟶ ethan***al***

    - **For aldehydes**, the carbonyl carbon will ***always*** be at the end of the parent chain and is assigned position number **1**.
    - **For ketones**, starting with the alkane name that corresponds to the number of carbon atoms in the parent chain, replace the "**e**" at the end of the alkane name with "**one.**" For example, if the parent chain of a ketone contains three carbons, it would be called propanone.

      propan***e*** ⟶ propan***one***

    - **For ketones** with ***more than four carbons***, the position of the ***carbonyl carbon*** must be indicated by adding a number as a prefix to the parent chain name as described below.
        - Position number **1** is assigned to the carbon at the ***end** of the parent chain* that is **closest to the carbonyl carbon.**
            - For example, if the carbonyl carbon is in position number **2** of a parent chain that contains five carbon atoms, then the parent chain is called **2**-pentanone.



$\underset{1}{CH_3}\underset{2}{\overset{\overset{O}{\|}}{C}}\underset{3}{CH_2}\underset{4}{CH_2}\underset{5}{CH_3}$

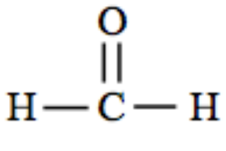
Steps 2, 3, and 4 are done the same way as you did when systematically naming *other organic molecules*.

Step 2. Name any alkyl group substituents.

Step 3: Determine the *point of attachments* of alkyl groups to the parent chain.

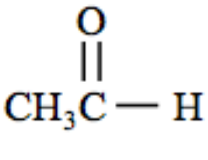
Step 4. Construct the name of the molecule by placing the alkyl groups in alphabetical order and specifying their positions, followed by the name of the parent chain.

Aldehyde *Systematic Name* Examples:



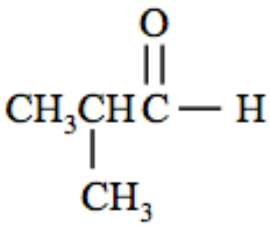
$H-\overset{\overset{O}{\|}}{C}-H$

methanal



$CH_3\overset{\overset{O}{\|}}{C}-H$

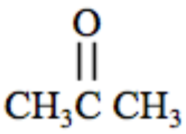
ethanal



$CH_3\underset{\underset{CH_3}{|}}{CH}\overset{\overset{O}{\|}}{C}-H$

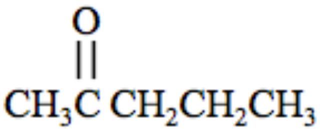
2-methylpropanal

Ketone *Systematic Name* Examples:



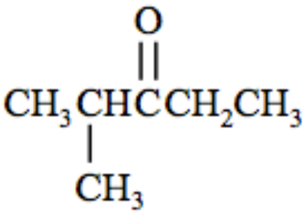
$CH_3\overset{\overset{O}{\|}}{C}CH_3$

propanone



$CH_3\overset{\overset{O}{\|}}{C}CH_2CH_2CH_3$

2-pentanone



$CH_3\underset{\underset{CH_3}{|}}{CH}\overset{\overset{O}{\|}}{C}CH_2CH_3$

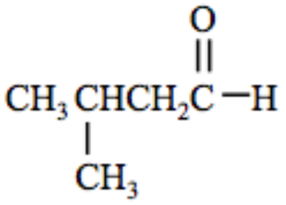
2-methyl-3-pentanone

You try it:

Review 10.12: Naming Aldehydes and Ketones

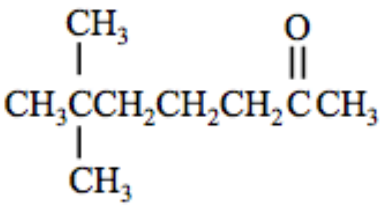
Write the ***systematic names*** for each of the molecules shown below:

a.



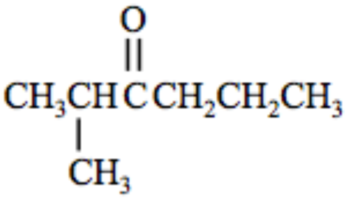
$CH_3\underset{\underset{CH_3}{|}}{CH}CH_2\overset{\overset{O}{\|}}{C}-H$

b.



$CH_3\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}CH_2CH_2CH_2\overset{\overset{O}{\|}}{C}CH_3$

c.



$CH_3\underset{\underset{CH_3}{|}}{CH}\overset{\overset{O}{\|}}{C}CH_2CH_2CH_3$

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

Review 10.13: Drawing the Structural Formulas of Aldehydes and Ketones

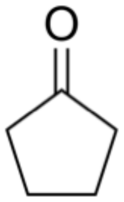
Draw the *condensed* ***and*** *skeletal* structure for each of molecules listed below.

a. 4-methyl-2-pentanone
b. 5,5-dimethylhexanal
c. 3-ethyl-4-octanone

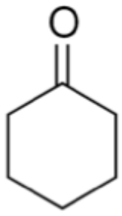
For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

Cyclic Ketones

A **cyclic ketone** is a molecule in which a *carbonyl carbon* occupies a position *between two other carbons* in a ring structure. Two examples of cyclic ketones are shown below.



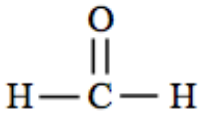
cyclopentanone



cyclohexanone

Cyclic ketones are named in a manner similar to that for *cyclic alcohols*. Starting with the cycloalkane name that corresponds to the number of carbon atoms in the ring structure chain, replace the "**e**" at the end of the *cyclo*alkane name with "**one**," as in the naming of the two cyclic ketones shown above.

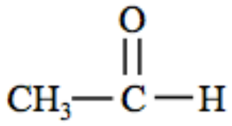
Frequently Encountered Aldehydes and Ketones



$$\mathrm{H{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}H}$$

methanal (*or* formaldehyde)

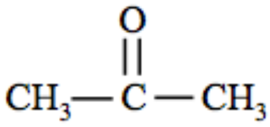
Methanal, (common name *formaldehyde*) is quite toxic; however, it is frequently used because of its ability to kill viruses, fungi, and bacteria. It is used to disinfect and sterilize equipment. Formaldehyde will react with other compounds, and chemically bond multiple molecules together into "polymers." Polymers are molecules *composed of multiple repeated subunits*. The polymers that are formed using formaldehyde as linking agents are used to make plastics and adhesives, and for binding plywood. Formaldehyde-linked polymers may "out-gas" formaldehyde in the curing process, therefore it is important to use safety precautions when handling these materials. In 2011, the US National Toxicology Program categorized formaldehyde as "known to be a human carcinogen".



$$\mathrm{CH_3{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}H}$$

ethanal (*or* acetaldehyde)

Ethanal (common name *acetaldehyde*) has a sweet aroma. It is narcotic if taken in large enough amounts. It occurs in smaller quantities, naturally, in coffee, bread, and ripe fruit, especially in apples. Its use is widespread in industry, notably in the formation of polymer adhesives such as carpenter's glue (also known as white glue or Elmer's glue). I will discuss acetaldehyde's biological significance in the next section of this chapter.



$$\mathrm{CH_3{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CH_3}$$

propanone (*or* acetone)

Propanone (common name *acetone*) is often used as a solvent and cleaning agent. It has the ability to dissolve many organic compounds and is also miscible with water. It is used as household nail-polish remover. Acetone has a high vapor pressure, and is highly flammable. It is not significantly toxic and is not currently regarded as a carcinogen, a mutagenic chemical, or a concern for chronic neurotoxicity issues.

Properties of Aldehydes and Ketones

Water Solubility of Aldehydes and Ketones

Smaller aldehyde and ketone molecules have significant water solubility because of their ability to interact with water through hydrogen bonding and dipole-dipole interactions. As their nonpolar parts get larger, the solubilities of aldehydes and ketones decrease. This trend can be seen in Table 10.2.

Boiling Points of Aldehydes and Ketones

As their nonpolar parts get larger, the boiling points of aldehydes and ketones increase because of increasing London forces. This trend can be seen in Table 10.2.

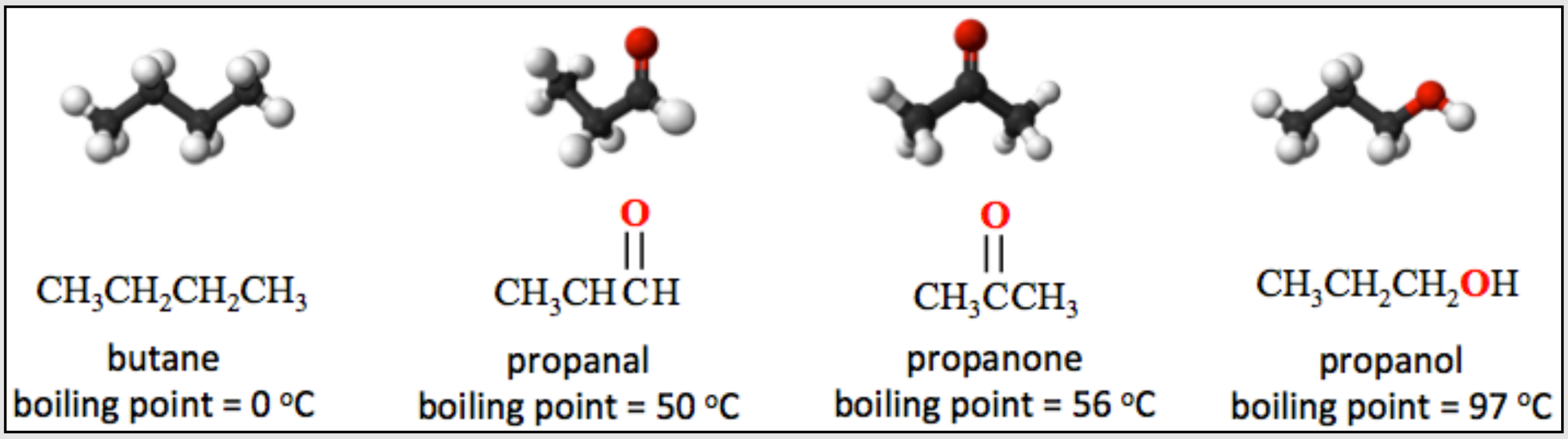
Table 10.2
Water Solubility and Boiling Points of Some Aldehydes and Ketones

Aldehyde Name	Condensed Structure	Water Solubility (g/100 mL)	Boiling Point (°C)
ethanal	CH_3CHO	miscible	21
propanal	CH_3CH_2CHO	16	49
butanal	$CH_3CH_2CH_2CHO$	7	76
pentanal	$CH_3CH_2CH_2CH_2CHO$	1	103

Ketone Name	Condensed Structure	Water Solubility (g/100 mL)	Boiling Point (°C)
propanone	CH_3COCH_3	miscible	56
2-butanone	$CH_3COCH_2CH_3$	26	80
2-pentanone	$CH_3COCH_2CH_2CH_3$	6	102

Aldehydes and ketones have ***higher*** boiling points than ***hydrocarbons*** of similar size because of their ability to interact with each other through *dipole-dipole interactions*. Aldehydes and ketones have ***lower*** boiling points than ***alcohols*** or ***carboxylic acids*** of similar size because aldehydes and ketones *are **not** capable* of interacting with each other through *hydrogen bonding*. Although they do have lone pairs of electrons on their oxygen atoms, they do not contain a hydrogen bonded to an N, O, or F that would be needed for hydrogen bonding with each other. Figure 10.6 shows the boiling points of an alkane, aldehyde, ketone, and alcohol - all of approximately the same size. The boiling points of the aldehyde and ketone are greater than that of the hydrocarbon (butane), but less than that of the alcohol (2-propanol).

Figure 10.6
Boiling points of Propanal and Propanone vs. Butane and Propanol



From left to right, an alkane, aldehyde, ketone, and alcohol - all of approximately the same size. The boiling points of the aldehyde (propanal) and ketone (propanone) are ***greater*** than that of the *hydrocarbon* (butane) because of their ability to interact with each other through dipole-dipole forces. The boiling points of the aldehyde and ketone are ***less*** than that of the alcohol (propanol) because, unlike alcohols, aldehydes and ketones *are **not** capable* of interacting with each other through *hydrogen bonding*.

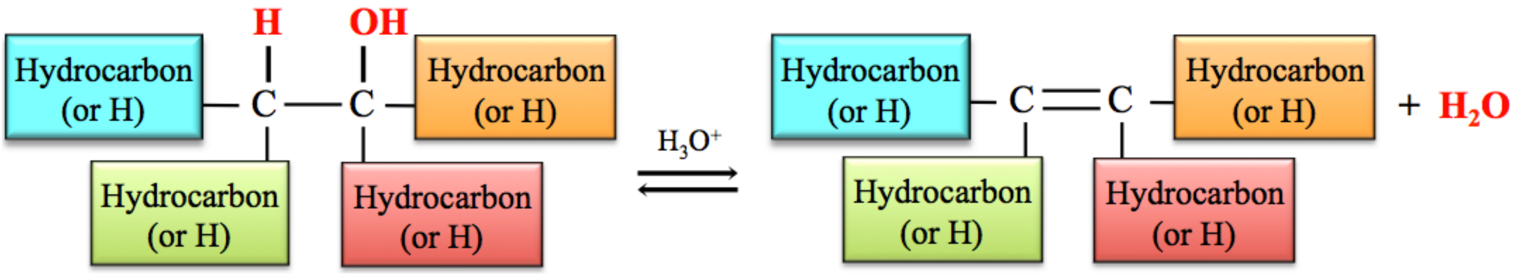
10.5 Reactions Involving Alcohols, Aldehydes, and Ketones

I waited to discuss the reactions of alcohols until after you learned about aldehydes and ketones because the products of some reactions of alcohols are aldehydes or ketones. All of the reactions that I will show you in this chapter are important in biology and will be seen again in the biochemistry that I will discuss in the next four chapters of this book.

Reactions of Alcohols

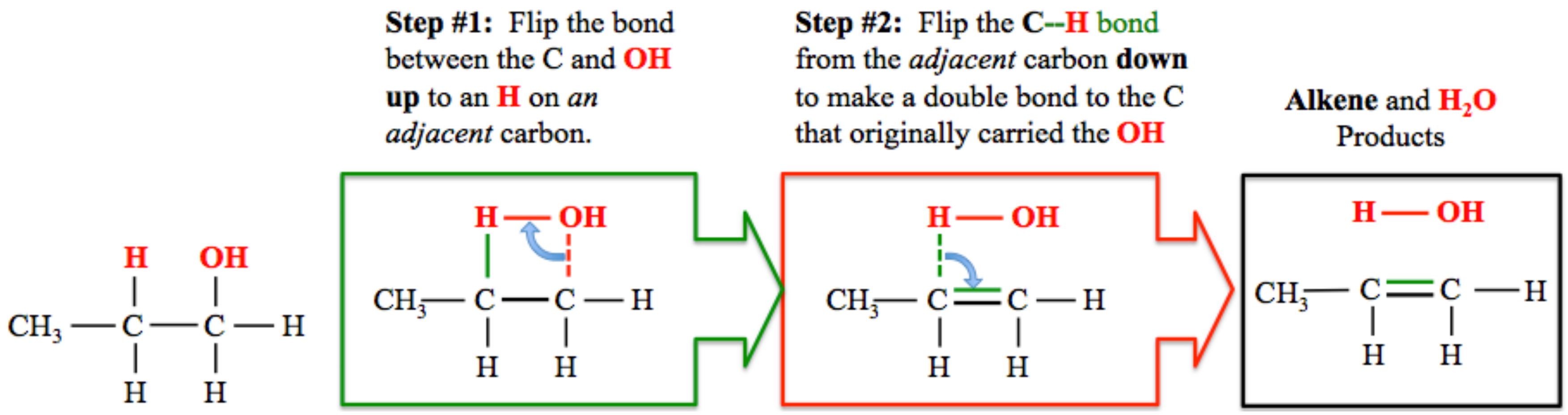
1) The *Dehydration* of Alcohols

I introduced you to the *dehydration of alcohols* reaction in chapter 6. Dehydration of alcohols is the ***reverse*** of the hydration of alkenes. H_2O is removed from an alcohol to form an alkene. In the dehydration of an alcohol, a hydroxyl group (**OH**) is removed from one carbon, and an **H** is removed from *another carbon* that is *adjacent* to the carbon from which the hydroxyl group was removed. A double bond forms between these two carbons. This reaction is catalyzed by a strong acid or an enzyme. The ***general form*** of the equation for the *hydration of an alcohol reaction* is shown below.



alcohol **alkene**

In chapter 6, I showed you a *bond flipping method* to help you predict the structure of the alkene that is produced when you "remove H_2O" to form a double bond." Let's review that method now by removing H_2O from 1-propanol (dehydration of 1-propanol). Beginning with the structure of the alcohol, perform the following steps:



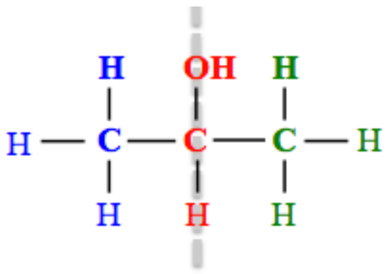
Step #1: Flip the bond between the C and **OH** **up** to an **H** on *an adjacent* carbon.

Step #2: Flip the **C--H** bond from the *adjacent* carbon **down** to make a double bond to the C that originally carried the **OH**

Alkene and H_2O Products

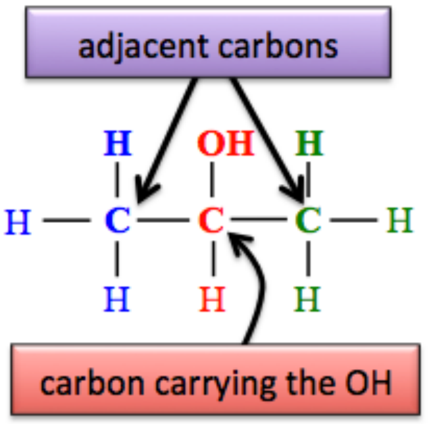
1-propanol

For the dehydration of a ***primary*** **(1°)** ***alcohol*** there is only one carbon that is adjacent to the *carbon carrying the* **OH**, therefore there is only one possible alkene product. The dehydration of a ***symmetric secondary*** **(2°)** or a ***symmetric tertiary*** **(3°)** ***alcohol*** only produces a single alkene product. A ***2° or 3° alcohol*** is ***symmetric*** if the *alkyl groups* bonded to the *carbon carrying the* **OH** are ***identical***. For example, **2-propanol**, shown below, is *symmetric*. Note that its alkyl groups - on each side of the dashed line - are ***identical***; they are both methyl groups.



2-propanol

When a *symmetric alcohol* is dehydrated, it makes no difference from which *adjacent carbon* a hydrogen is removed to form the double bond; the alkene product is the same. I will elaborate using *2-propanol* (shown below), which is a *symmetric* secondary alcohol, as an example.

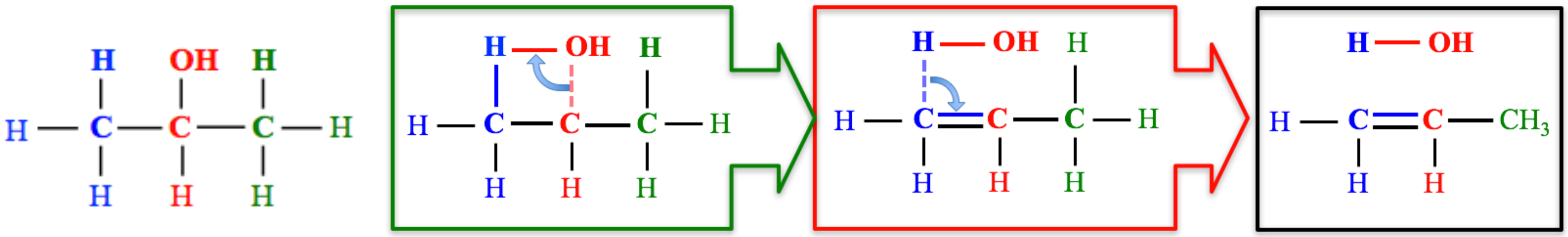


If we remove the **OH**, and an **H** from the *adjacent carbon* on the ***left-hand side*** of the *carbon carrying the* **OH**, then the products are **propene** and **H_2O**, as shown below.

Step 1: Flip the bond between the **C** and **OH** **up** to an **H** on *an adjacent* carbon.

Step 2: Flip the **C-H** bond from the *adjacent* carbon **down** to make a double bond to the **C** that originally carried the **OH**.

propene and **H_2O**

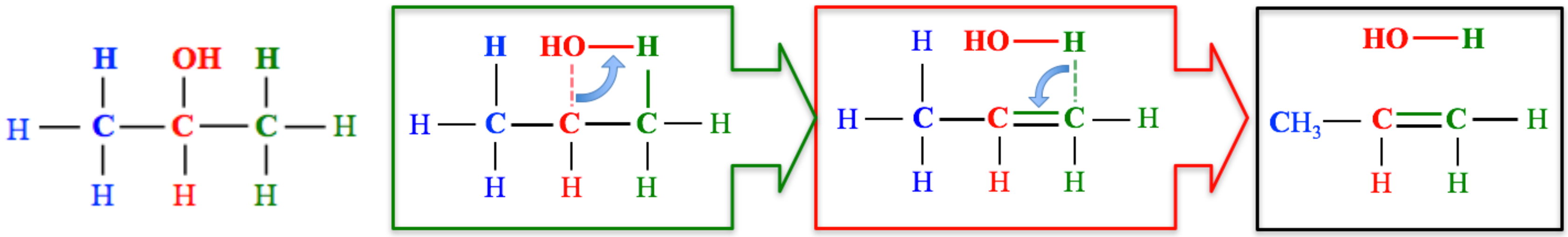


Since 2-propanol is a *symmetric alcohol*, **propene and H_2O are also the products** when we remove the **OH,** and then an **H** from the *adjacent carbon* on the ***right-hand side*** of the *carbon carrying the* **OH**, as shown below.

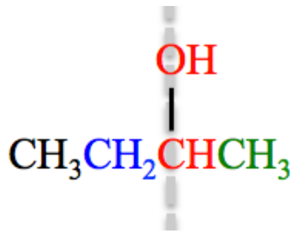
Step 1: Flip the bond between the **C** and **OH** **up** to an **H** on *an adjacent* carbon.

Step 2: Flip the **C-H** bond from the *adjacent* carbon **down** to make a double bond to the **C** that originally carried the **OH**.

propene and **H_2O**



When an **asymmetric alcohol** undergoes a dehydration reaction, there are ***two different alkene molecules produced***. *Asymmetric* alcohols are **2° or 3° alcohols** in which the alkyl groups bonded to the carbon *carbon carrying the* **OH** are ***not*** identical. An example of an ***asymmetric alcohol*** is 2-butanol, shown below. Note that the alkyl groups that are bonded to the *carbon carrying the* **OH**, ***are not identical***; one is a methyl group and the other is an ethyl group.

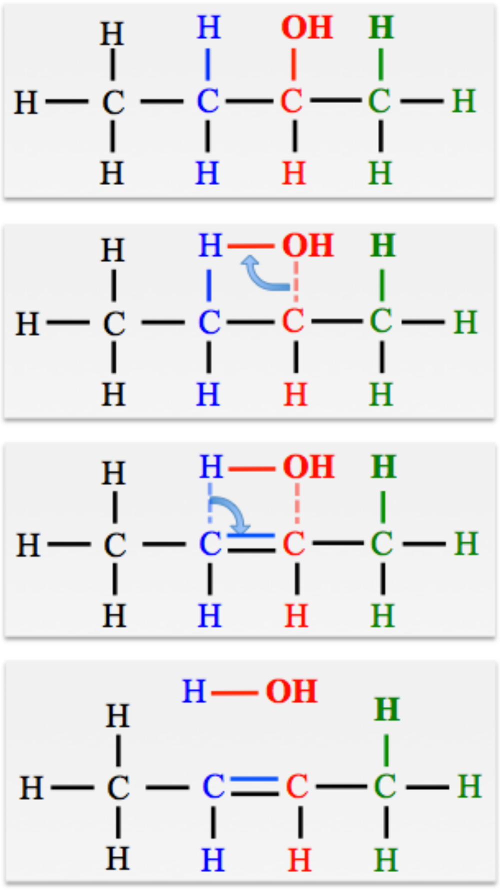


$$CH_3CH_2\overset{OH}{C}HCH_3$$

2-butanol (an asymmetric alcohol)

As an example, let's take a look at the ***two different alkenes that are produced*** when **2-butanol** (an asymmetric alcohol) undergoes the dehydration reaction. The illustration below shows that removing an **H** from the *adjacent carbon* on the *left-hand* side of the *carbon carrying the* **OH** produces **2-butene** (and water); whereas removing an **H** from the *adjacent carbon* on the *right-hand* side of the *carbon carrying the* **OH** produces a ***different*** alkene, **1-butene**.

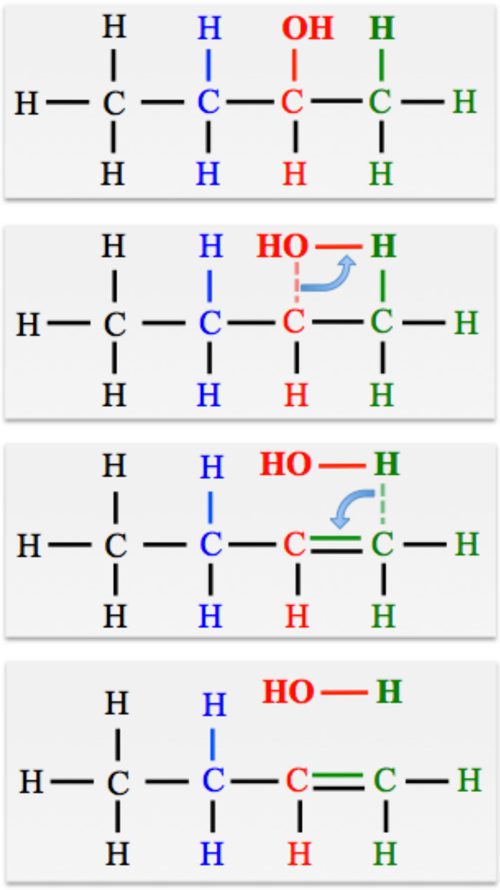
Left Column: remove an **H** from the *adjacent carbon* on the left-hand side of the carbon carrying the **OH**.



$CH_3CH{=}CHCH_3 + H_2O$

2-butene and water

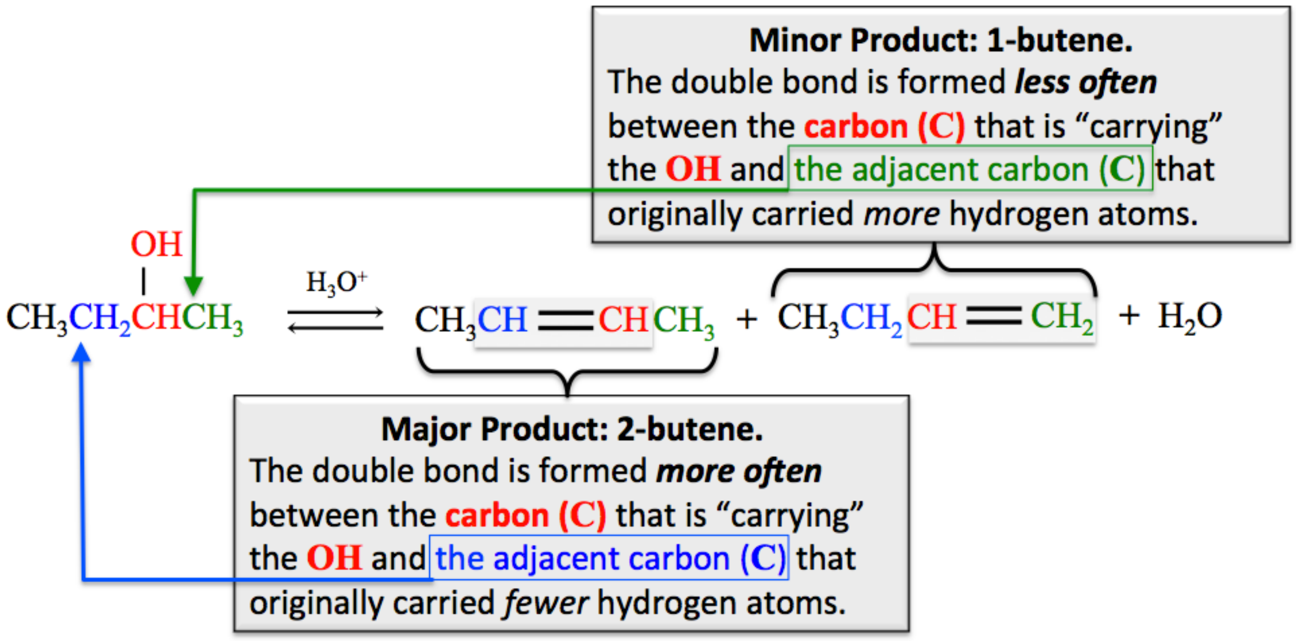
Right Column: remove an **H** from the *adjacent carbon* on the right-hand side of the carbon carrying the **OH**.



$CH_3CH_2CH{=}CH_2 + H_2O$

1-butene and water

You have previously learned that the *hydration* of an asymmetric *alkene* ***does not produce equal amounts of both alcohol products***. A similar situation occurs for the *dehydration* of alcohols. For example, in the dehydration of 2-butanol (above), about *four times* as much **2**-butene (*major product*) as **1**-butene (*minor product*) is produced. It is possible to predict the major and minor products for the dehydration of an alcohol; in the ***major product***, the double bond is formed between the *carbon that was carrying the* **OH** and the adjacent carbon that ***originally carried fewer hydrogens***. The ***minor product*** is formed between the *carbon that was carrying the* **OH** and the adjacent carbon that ***originally carried more hydrogens***.



Minor Product: 1-butene.
The double bond is formed ***less often*** between the **carbon (C)** that is "carrying" the **OH** and the adjacent carbon (C) that originally carried *more* hydrogen atoms.

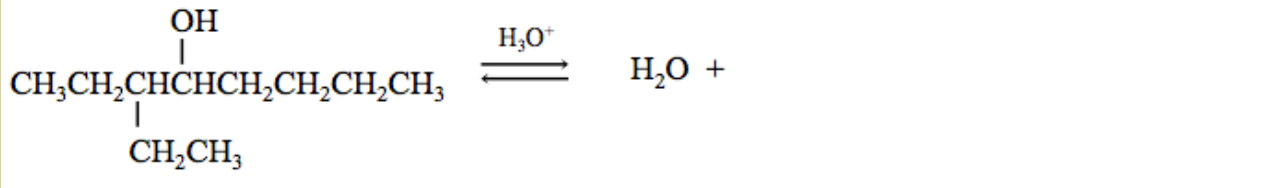
$$CH_3CH_2\overset{OH}{CH}CH_3 \xrightleftharpoons{H_3O^+} \underbrace{CH_3CH{=}CHCH_3}_{} + \overbrace{CH_3CH_2CH{=}CH_2}^{} + H_2O$$

Major Product: 2-butene.
The double bond is formed ***more often*** between the **carbon (C)** that is "carrying" the **OH** and the adjacent carbon (C) that originally carried *fewer* hydrogen atoms.

In the formation of the ***major alkene product,*** the adjacent carbon that originally contained fewer hydrogens will lose ***another*** hydrogen when the double bond is formed. An easy way to remember this alcohol dehydration rule is with the old saying, "*the **poor** get **poorer***," where hydrogen atoms (**H**) represent money.

Review 10.14: The Dehydration of Alcohols

Draw *and* name the major and minor products for the dehydration of 3-ethyl-4-octanol.



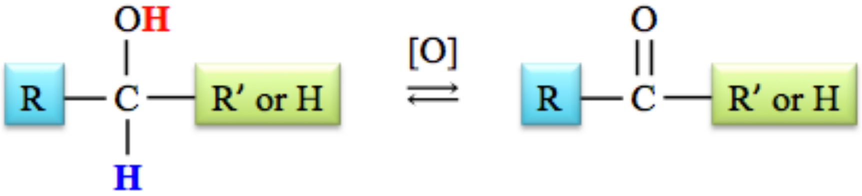
$$CH_3CH_2\underset{\underset{CH_2CH_3}{|}}{C}H\overset{\overset{OH}{|}}{C}HCH_2CH_2CH_2CH_3 \overset{H_3O^+}{\rightleftharpoons} H_2O +$$

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

2) The *Oxidation* of Alcohols

An ***oxidation can*** only occur when it is accompanied by a ***reduction***. The species that is oxidized loses one or more electrons and the species that is reduced gains those electrons. You learned that the ***oxidation*** of an organic compound in a reaction can be identified by ***the addition of oxygen and/or loss of hydrogen***. For the ***reduction*** of an organic compound, the opposite occurs; ***the addition of hydrogen and/or loss of oxygen***.

When an alcohol is oxidized, the hydrogen from the hydroxyl group (**OH**) and a hydrogen (**H**) attached to *the carbon that is carrying the hydroxyl group* are both removed, *and* the C-O *single* bond is changed to a *double* bond. The general form of the equation for the ***oxidation of an alcohol*** is shown below.

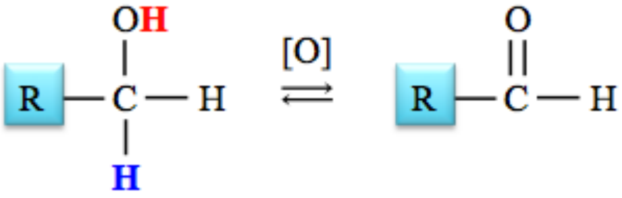


The reason that this reaction is classified as an ***oxidation*** (loss of electrons) is that the hydrogen (shown above in bold blue font) that is bonded to the hydroxyl-carrying carbon, leaves the alcohol and takes ***both of the electrons*** from the bond with it. A hydrogen with ***two electrons*** is called a ***hydride ion*** ($H:^-$).

The "**[O]**," drawn above (or below) the arrows in a chemical equation, is often used to indicate that the reactant is being *oxidized,* and should not be confused with the presence of a catalyst. When oxidation is indicated by using "**[O]**," then the identity of the oxidizing agent - which is actually a reactant - and the destination of the hydrogens are often omitted from the chemical equation. When doing so, it is acceptable - and expected - that the equation is not balanced. When relevant, I will discuss the identity of specific oxidizing agents seen in nature, research, and industry.

a) Oxidation of Primary (1°) Alcohols

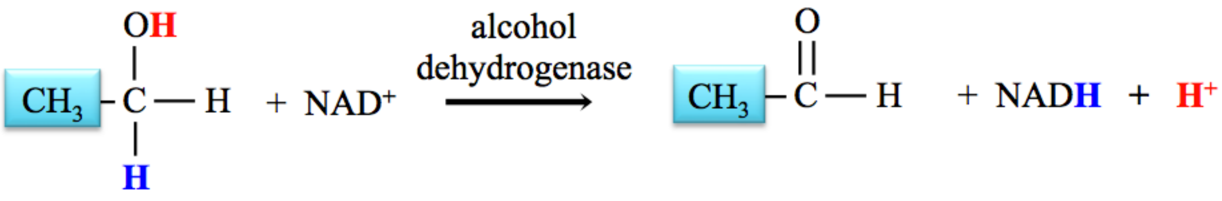
In section 2 of this chapter, I discussed the structural differences between primary, secondary, and tertiary alcohols. The structure of the alcohol determines the identity of its oxidation product. Oxidation of a ***primary (1°) alcohol*** produces an ***aldehyde***:



a primary alcohol **an aldehyde**

The oxidation of a primary alcohol produces an aldehyde because the hydroxyl group of a primary alcohol is attached to a carbon *at an end of the parent chain*, and therefore the carbonyl group in the product is *at the end of the chain*.

A specific example of the oxidation of a primary alcohol is the oxidation of *ethanol*. In humans and many animals, this reaction is catalyzed by the ***alcohol dehydrogenase*** enzyme, and the *oxidizing agent* is an ion called *nicotinamide adenine dinucleotide* (NAD^+). In this reaction ethanol and NAD^+ are converted to ethanal, NADH, and an H^+ ion, as shown below.

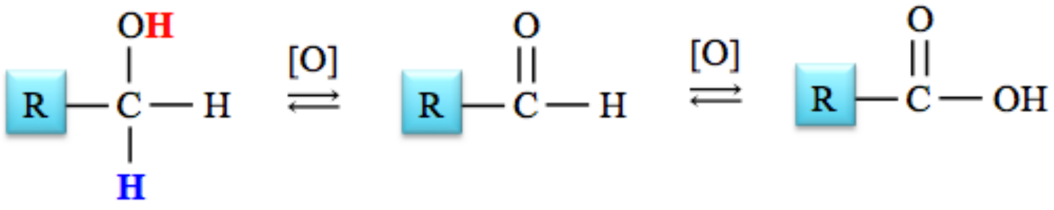


CH_3CH_2OH
ethanol (a 1° alcohol)

CH_3CHO
ethanal (an aldehyde)

The H^+ that is produced will quickly react with water to form a hydronium ion (H_3O^+). The evolution of the alcohol dehydrogenase enzyme for this reaction was important in order to remove naturally-occurring ethanol that we consume in some foods. Ethanol is toxic to cells. Although not an evolutionary requirement, the existence of this enzyme allows for the consumption of alcoholic beverages. The drug **disulfiram** (sold as *Antabuse*), is designed to deter individuals from drinking. It works by inhibiting the alcohol dehydrogenase enzyme, and thereby produces very undesirable effects when alcohol is consumed. You will learn more about enzyme inhibition in chapter 13.

Certain organic molecules and inorganic oxidizing agents, such as CrO_3, MnO_4^-, can further oxidize aldehydes to produce carboxylic acids.



1° alcohol **aldehyde** **carboxylic acid**

For humans (and many animals) the conversion of the ethanal (an aldehyde) to acetic acid (a carboxylic acid) in the second step of the alcohol oxidation reaction, shown below, is catalyzed by an enzyme called ***acetaldehyde dehydrogenase***.

$$CH_3CH_2OH \xrightarrow[\text{[O]}]{\text{alcohol dehydrogenase}} CH_3CHO \xrightarrow[\text{[O]}]{\text{acetaldehyde dehydrogenase}} CH_3COOH$$

ethanol

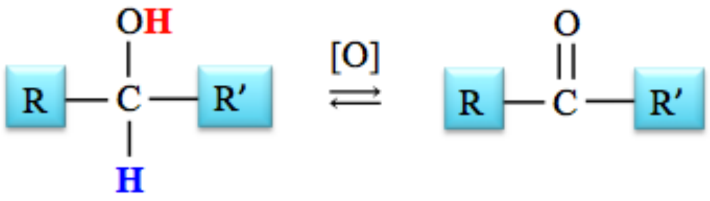
ethanal
(acetaldehyde)

ethanoic acid
(acetic acid)

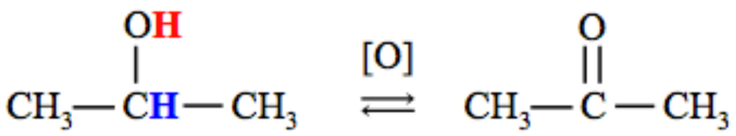
Most individuals of Asian descent have one of two variations in their DNA that each result in an ***especially efficient*** form of the *alcohol dehydrogenase* enzyme that catalyzes the *first* reaction (ethanol to ethanal). These individuals convert ethanol to ethanal very quickly. About half of the Asian individuals who have one of those DNA variants, also have ***a second DNA variation*** that results in a ***less*** *functional* acetaldehyde dehydrogenase enzyme to catalyze the *second reaction* above. For individuals with both of these DNA variants, *high* ethanal levels occur when consuming alcoholic beverages, which cause the red blotches/flushes (erythema) on the face, neck, shoulders, and, sometimes, the entire body. This condition is known as ***alcohol flush***. *Alcohol flush* has been correlated with a greatly-increased risk of esophageal cancer ***for those who drink*** (http://www.nih.gov/news/health/mar2009/niaaa-23.htm). The DNA variants leading to alcohol flush are most common among individuals of Asian descent, but do also occur, though much less frequently, in individuals of other geographical descents.

b) Oxidation of Secondary (2º) Alcohols

The oxidation of a secondary alcohol produces a ***ketone*** because the hydroxyl group of a secondary alcohol is attached to a carbon *that **<u>not</u> at an end** of a carbon chain*. The general form of the equation for the oxidation of a 2º alcohol is shown below.



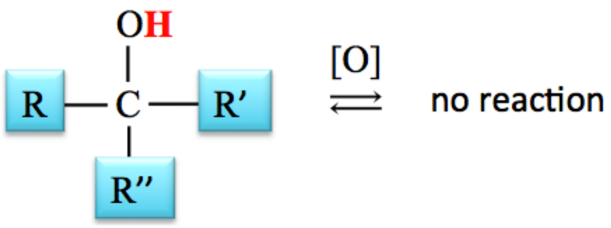
A specific example of the oxidation of a secondary alcohol is the oxidation of 2-propanol.



$$CH_3-\overset{\overset{OH}{|}}{CH}-CH_3 \underset{}{\overset{[O]}{\rightleftharpoons}} CH_3-\overset{\overset{O}{||}}{C}-CH_3$$

c) Oxidation of Tertiary (3º) Alcohols

A tertiary alcohol ***cannot*** be oxidized to an aldehyde or a ketone because tertiary alcohols do not have a hydrogen attached to the *carbon that is carrying the hydroxyl group*.



You try a couple of alcohol oxidation problems:

Review 10.15: The Oxidation of Alcohols

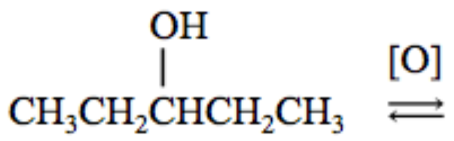
MnO_4^- will first oxidize a primary alcohol to an aldehyde, and then it will oxidize the aldehyde to produce a carboxylic acid. Draw <u>*and*</u> name the ***aldehyde*** that is initially formed, and then the ***carboxylic acid*** that is subsequently formed in the oxidation of butanol when MnO_4^- is used as the oxidizing agent.

$$CH_3CH_2CH_2CH_2OH \overset{[O]}{\rightleftharpoons} \text{an aldehyde} \overset{[O]}{\rightleftharpoons} \text{a carboxylic acid}$$

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

Review 10.16: The Oxidation of Alcohols

Draw ***<u>and</u>*** name the organic molecule that is formed in the reaction shown below.



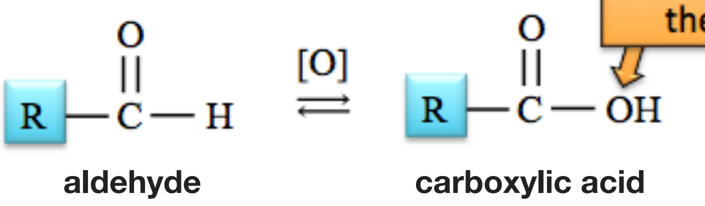
$$CH_3CH_2\overset{\overset{OH}{|}}{C}HCH_2CH_3 \overset{[O]}{\rightleftharpoons}$$

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

Reactions of Aldehydes and Ketones

1) The Oxidation of Aldehydes

Aldehydes can be oxidized to ***carboxylic acids***. You read about the oxidation of aldehydes - on the previous page- when I discussed the oxidation of *primary alcohols* to form *aldehydes*, which, under certain conditions are further oxidized to *carboxylic acids.* The general form of the equation for the oxidation of an aldehyde is shown below.

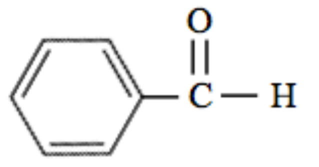


This oxygen comes from the oxidizing agent.

A specific example of the *oxidation of an aldehyde* is a reaction that my students do in a laboratory activity. They use the permanganate ion (MnO_4^-) to oxidize benzaldehyde. The **R** group in benzaldehyde is a *benzene ring*. In the following review problem, I would like you to draw the carboxylic acid that is produced when this reaction occurs.

Review 10.17: The Oxidation of Aldehydes

The structure of ***benzaldehyde*** is shown below. Draw the structure of the *carboxylic acid* that is formed in the oxidation of benzaldehyde.

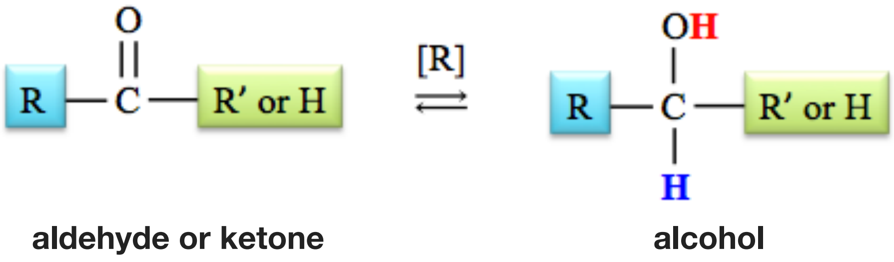


benzaldehyde

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

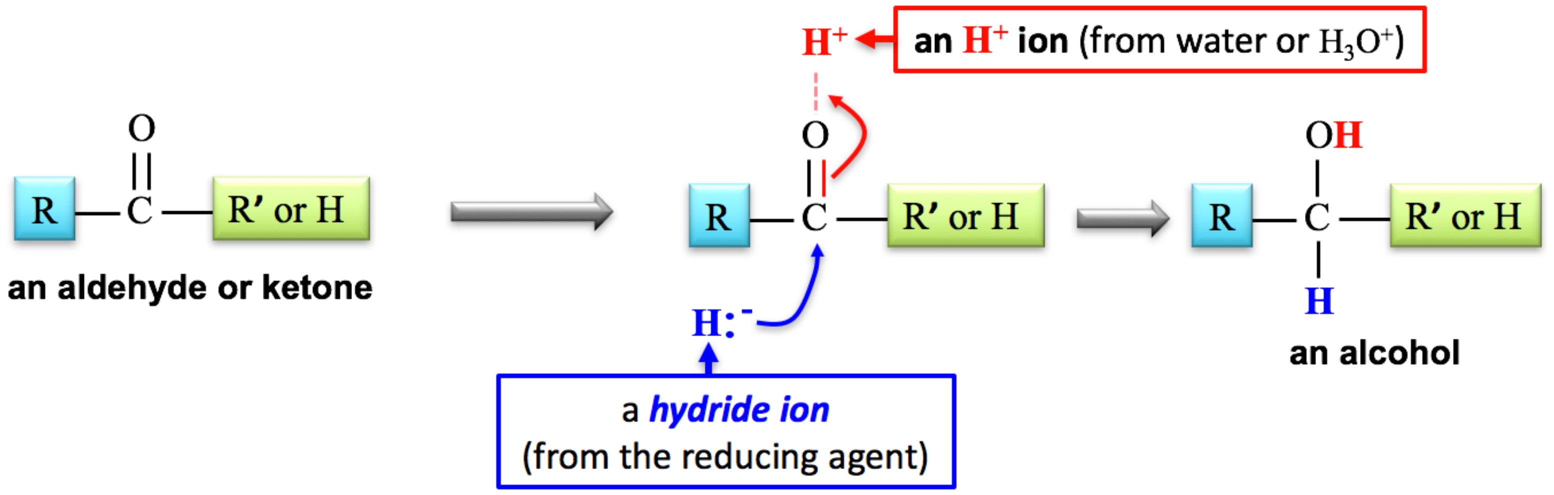
2) The Reduction of Aldehydes and Ketones

Reduction of aldehydes and ketones is the reverse of the oxidation of alcohols reaction. The general form of the equation for the ***reduction of an aldehyde or ketone*** is shown below.

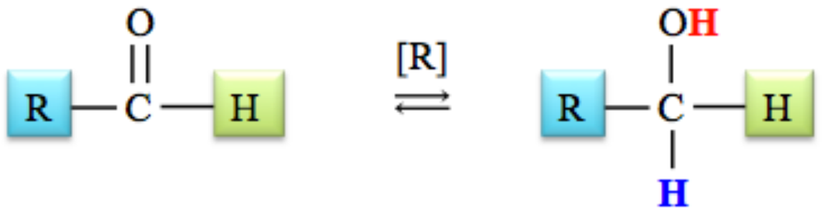


As was the case for "**[O]**," an "**[R]**" is often written above the arrows in a chemical equation to indicate that the reactant is being *reduced*. When reduction is indicated by using "**[R]**," then the identity of the reducing agent reactant and the source of the hydrogens (or destination of oxygens) are often omitted from the chemical equation. In this case, the equation need not be balanced.

Reduction of aldehydes or ketones involves the formation of a bond to the *carbonyl carbon* by a ***hydride ion*** ($H:^-$), accompanied by the bonding of an H^+ ion to the carbonyl-oxygen atom, and the conversion of the carbon-oxygen double bond into a single bond. This produces an alcohol as illustrated below.



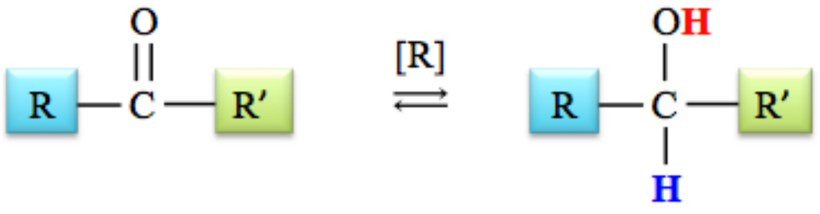
Aldehydes are reduced to ***primary alcohols***.



aldehyde **a primary (1°) alcohol**

Recall that the reduction of aldehydes and ketones is the reverse of the oxidation of alcohols reaction. Since the oxidation of primary alcohols produces aldehydes, the ***reverse reaction,*** the reduction of aldehydes produces primary alcohols.

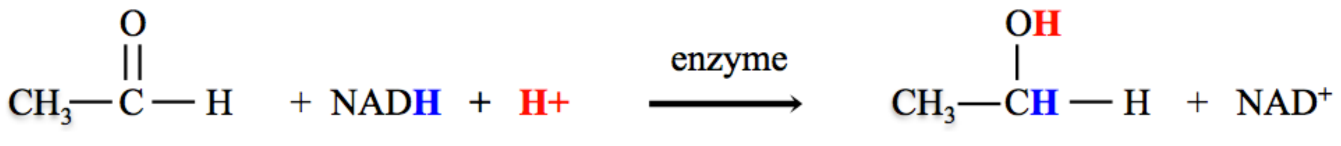
Ketones are reduced to ***secondary alcohols***.



ketone **a secondary (2°) alcohol**

Since the oxidation of secondary alcohols produces ketones, the ***reverse reaction,*** the reduction of ketones produces secondary alcohols.

In **biological systems**, the ***hydride ion*** ($H:^-$) used in the reduction of aldehydes or ketones is supplied by *nicotinamide adenine dinucleotide hydride (*NADH) or other organic hydride ion sources. A specific example of a *biochemical reduction* is the reaction of ethanal with NADH and an H^+ to form ethanol (shown below).



$$CH_3-\overset{\overset{\displaystyle O}{||}}{C}-H + NADH + H^+ \xrightarrow{\text{enzyme}} CH_3-\overset{\overset{\displaystyle OH}{|}}{CH}-H + NAD^+$$

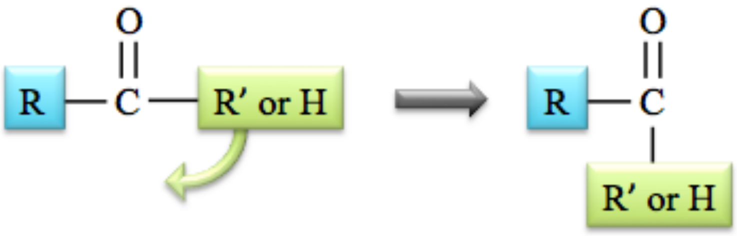
ethanal **ethanol**

This is the final reaction in yeast's alcohol fermentation process. The H^+ ion is supplied by H_2O or H_3O^+

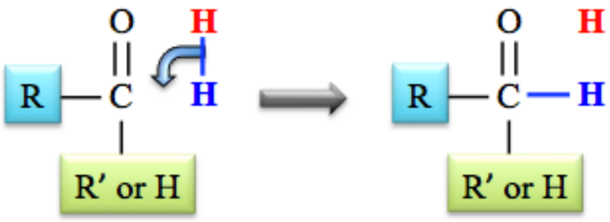
In the laboratory, hydride ions from aluminum hydride (AlH_4^-), or borohydride (BH_4^-) are used as reducing agents. Hydrogen gas (H_2) is also used as a reducing agent in laboratory and industrial applications.

Reductions that use hydrogen gas (H_2) are called **hydrogenation reactions**. They occur at high temperatures and in the presence of metal catalysts - often platinum (Pt) metal surfaces. Hydrogenation reactions do not use the mechanism of the addition of ***hydride*** ($H:^-$) and H^+ ions that I previously described. A discussion of the mechanism for catalytic hydrogenation is beyond the scope of this book; however, you can predict the products for the reduction/hydrogenation of aldehydes or ketones by adding H_2 "across" the carbon-oxygen double bond (the carbonyl group), as we did for adding H_2 and H_2O "across" a C=C double bond.

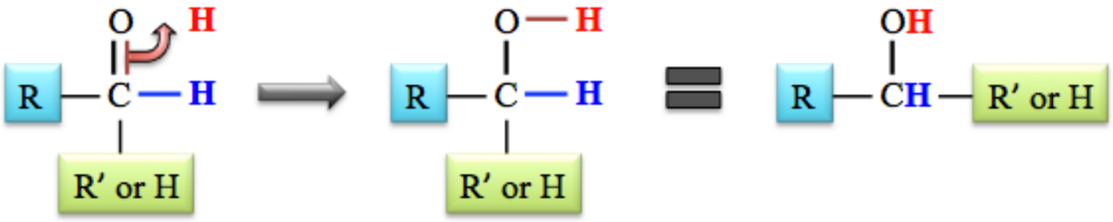
To more easily visualize the addition of H_2 across the carbonyl group, it is convenient to redraw the aldehyde or ketone reactant with the **R'** or **H** group flipped downward, as shown below.



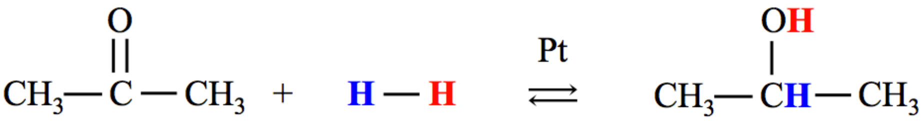
Next, draw the H_2 molecule to the side of the carbonyl group, and then flip the bond between the hydrogens downward to make a new bond to the carbonyl carbon:



Finally, flip one pair of electrons from the carbonyl group's double bond upward to form a bond with the remaining *unbound* hydrogen (H).



A specific example of the hydrogenation of a ketone is the reaction of propanone with H_2:



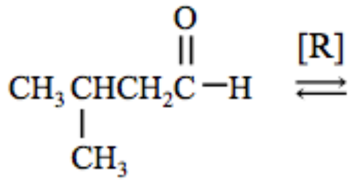
$$CH_3-\overset{\overset{O}{\|}}{C}-CH_3 + H-H \xrightleftharpoons{Pt} CH_3-\overset{\overset{OH}{|}}{CH}-CH_3$$

propanone H_2 **2-propanol**

Review 10.18: Predicting the Product for the Reduction of an Aldehyde or Ketone

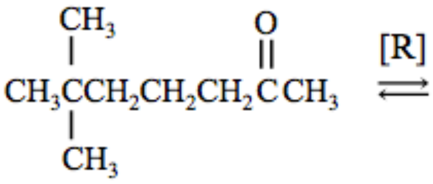
Draw the condensed structure ***and*** name the alcohol produced in the reduction of each of the following aldehydes or ketones. **NOTE:** When reduction reactions are indicated by "**[R]**," you do not need to include the source of hydrogens, and the equation will therefore not be balanced.

a.



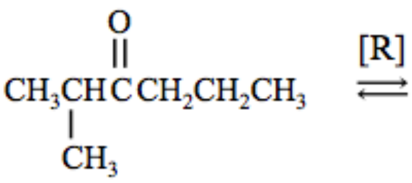
$$CH_3\underset{\underset{CH_3}{|}}{CH}CH_2\overset{\overset{O}{\|}}{C}-H \xrightleftharpoons{[R]}$$

b.



$$CH_3\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}CH_2CH_2CH_2\overset{\overset{O}{\|}}{C}CH_3 \xrightleftharpoons{[R]}$$

c.

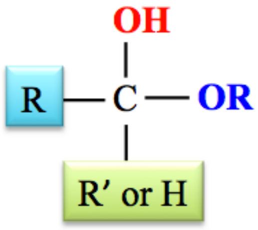


$$CH_3\underset{\underset{CH_3}{|}}{CH}\overset{\overset{O}{\|}}{C}CH_2CH_2CH_3 \xrightleftharpoons{[R]}$$

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

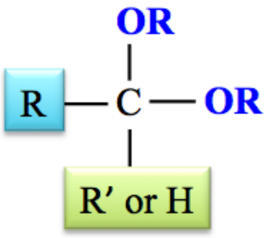
3) The Reaction of Aldehydes or Ketones with Alcohols: Hemiacetal and Acetal Production

A **hemiacetal** is a molecule that contains ***both*** an **OR** group *and* **OH** group that are bonded to the ***same*** carbon. The general form of a hemiacetal is shown below.



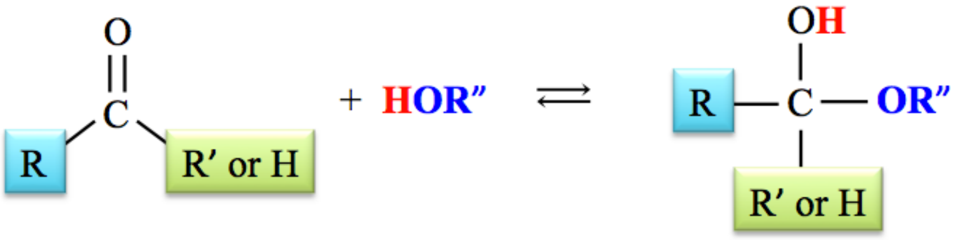
general form of a hemiacetal

An **acetal** is a molecule that contains ***two*** **-OR** groups, where *both* **-OR** groups are bonded to the ***same*** carbon. The general form of an acetal is shown below.



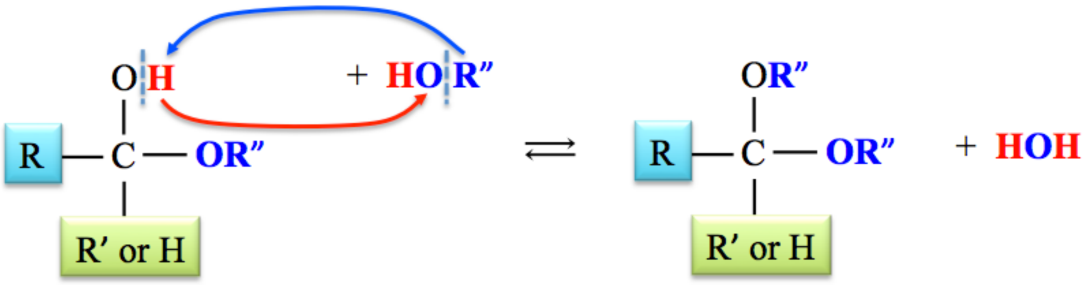
general form of an acetal

An ***aldehyde or a ketone*** will react with an ***alcohol*** to form a **hemiacetal**. This reaction is catalyzed by acid. The **OR"** from the ***alcohol*** forms a bond to the carbonyl-carbon of the aldehyde or ketone, the **H** from the alcohol bonds to the carbonyl-*oxygen*, and the carbonyl group's double bond is changed to a single bond.



aldehyde or ketone **alcohol** **hemiacetal**

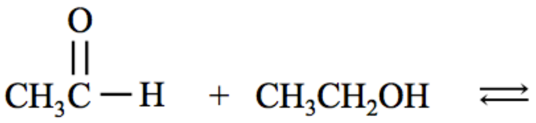
The ***hemiacetal*** that is formed can react with a *second alcohol molecule* to form an **acetal** and an **H_2O** molecule. The structure of the ***acetal*** that is produced is drawn by ***exchanging*** the **R"** group *of the alcohol* and the **H** from the *hemiacetal's* hydroxyl group (**OH**), as shown below.



hemiacetal **alcohol** **acetal** **H_2O**

The formation of acetals and hemiacetals is very important in biochemistry, particularly in carbohydrate chemistry (next chapter). I will show you an example problem for hemiacetal and acetal production, then ask you to try a couple of problems on your own.

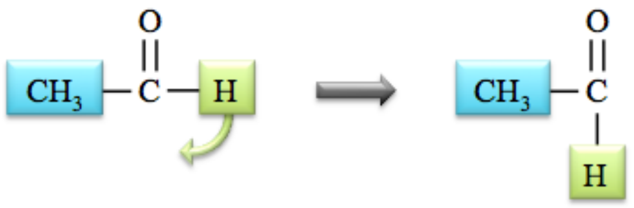
Example: Draw the structure of the hemiacetal - and then the acetal - that is formed by the reaction of ethanal with ethanol.



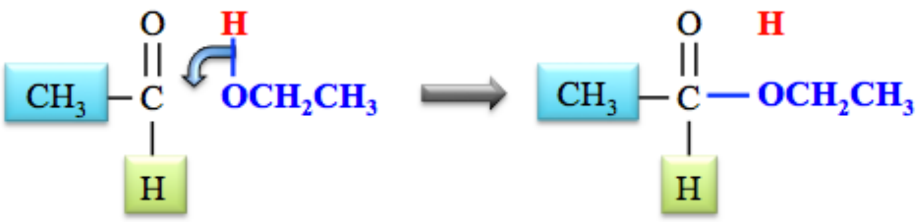
$$CH_3\overset{\overset{\displaystyle O}{\|}}{C}-H \;+\; CH_3CH_2OH \;\rightleftharpoons$$

Solution: To form the ***hemiacetal***, the **OR** from the ***alcohol*** forms a bond to the carbonyl carbon of the aldehyde or ketone, the **H** from the alcohol bonds to the carbonyl *oxygen*, and the carbonyl group's double bond is changed to a single bond. A simple way to do this is to add the alcohol "across" the carbonyl double bond. This is done in the same way as for the hydrogenation/reduction of aldehydes or ketones when we added H_2 across the carbonyl double bond.

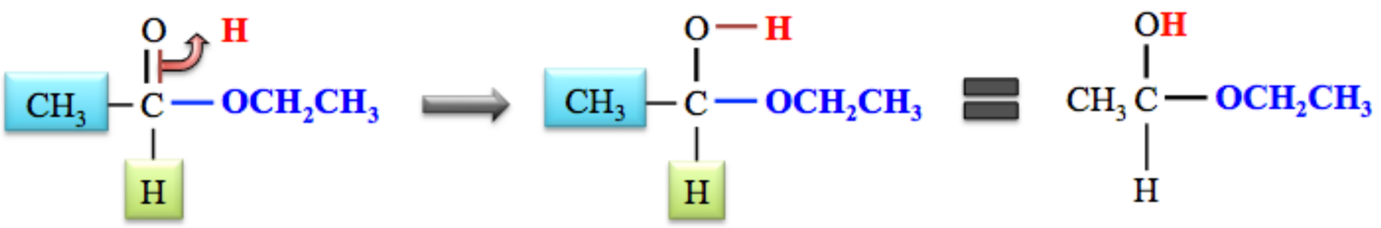
To add the alcohol (CH_3CH_2OH) across the carbonyl group, it is convenient to redraw the aldehyde as shown below.



Next, draw the *alcohol molecule* to the side of the carbonyl group, as shown below, and then flip the bond from the *alcohol's hydroxyl group* downward to make a new bond to the carbonyl carbon.

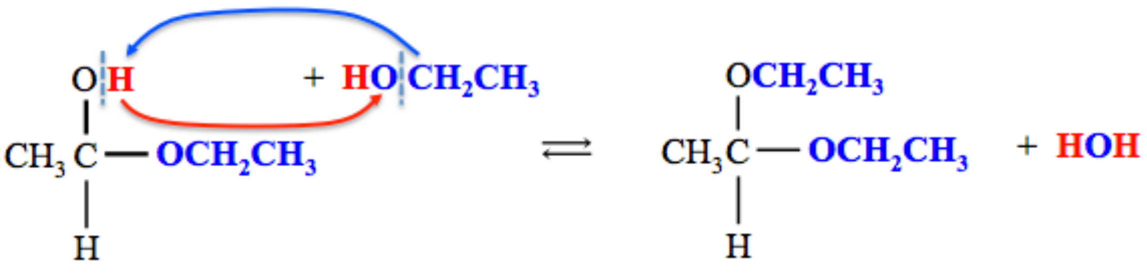


Finally, flip one pair of electrons from the carbonyl group upward to form a bond to the remaining *unbound* hydrogen (**H**).



hemiacetal

The ***hemiacetal*** that is formed can react with a *second ethanol molecule* to form an **acetal** and an H_2O molecule. The structure of the **acetal** can be drawn by ***exchanging*** the **R** group *of the alcohol* (CH_3CH_2) and the **H** from the *hemiacetal's* hydroxyl group:

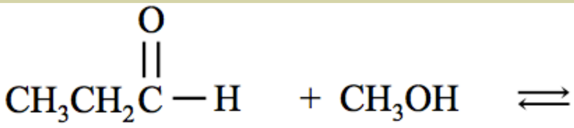


hemiacetal **ethanol** **acetal** **H_2O**

Now you try it:

Review 10.19: The Formation of Hemiacetals and Acetals

Draw *and* name the hemiacetal, and then the acetal, that are formed in the reaction shown below.

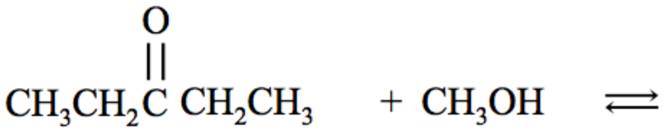


$$CH_3CH_2\overset{\overset{O}{\|}}{C}-H \quad + CH_3OH \rightleftharpoons$$

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

Review 10.20: The Formation of Hemiacetals and Acetals

Draw *and* name the hemiacetal, and then the acetal, that are formed in the reaction shown below.



$$CH_3CH_2\overset{\overset{O}{\|}}{C}\,CH_2CH_3 \quad + CH_3OH \rightleftharpoons$$

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

10.6 Review of the Reactions of Chapter 10

1) Alcohol Fermentation

Alcohol fermentation is a series of chemical reactions that convert sugar molecules, primarily glucose, into ethanol and CO_2. The overall reaction of ethanol formation from glucose is shown below:

$$\underset{\text{glucose}}{C_6H_{12}O_6} \longrightarrow \underset{\text{ethanol}}{\mathbf{2}\ CH_3CH_2OH} + \underset{\text{carbon dioxide}}{\mathbf{2}\ CO_2}$$

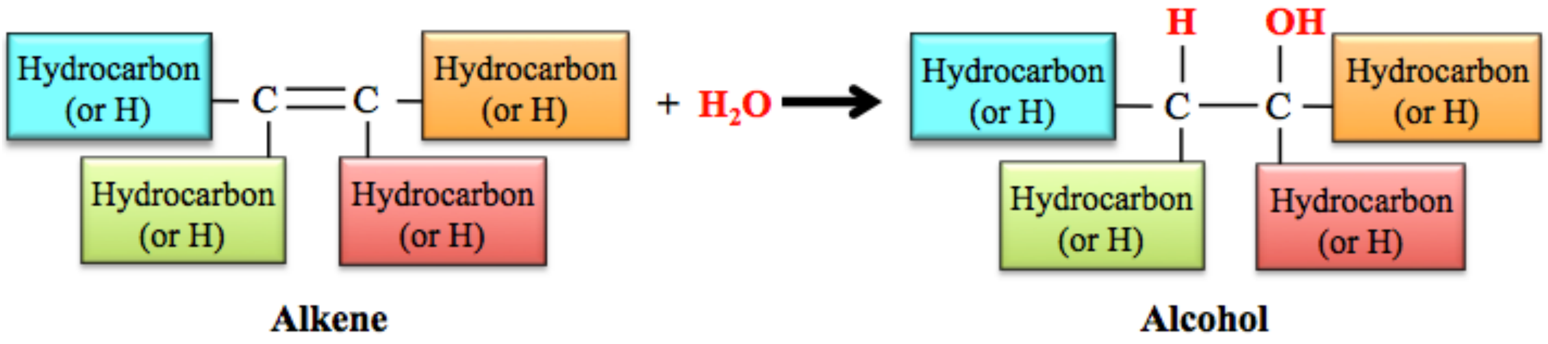
2) Alcohol Formation in Nucleophilic Substitution Reactions

The general form of the equation for an S_N2 reaction for the formation of alcohol is shown below (**X** represents F, Cl, Br, or I).

$$\underset{\text{alkyl halide}}{\boxed{R}{-}X} + \underset{\text{hydroxide ion}}{OH^-} \rightleftharpoons \underset{\text{alcohol}}{\boxed{R}{-}OH} + \underset{\text{halide ion}}{X^-}$$

3) Hydration of Alkenes

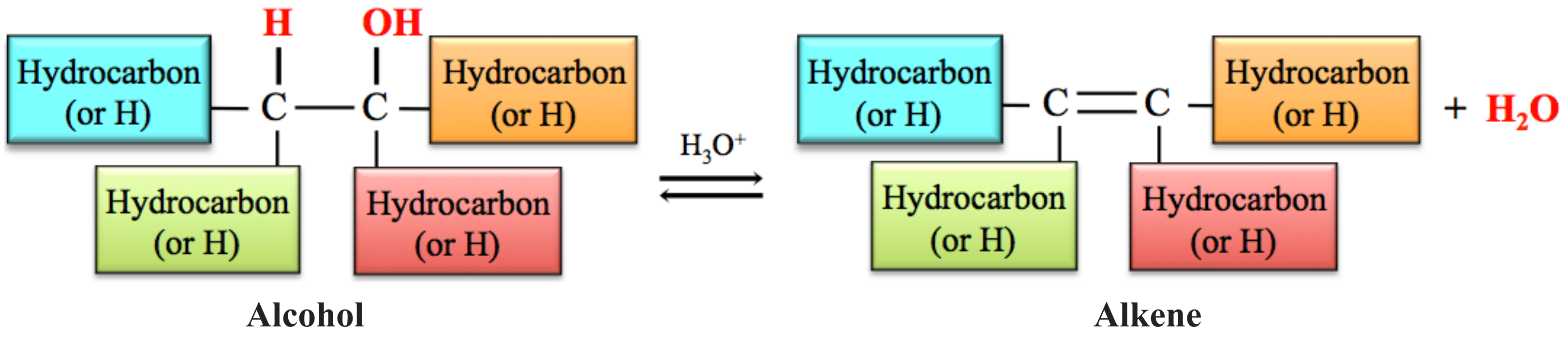
A hydrogen atom from **H_2O** is added to one of the double bonded carbon atoms and the **OH** from the **H_2O** is added to the ***other*** double bonded carbon atom in the ***alkene*** to produce the corresponding ***alcohol.*** The ***general form*** of the equation for the hydration of an alkene reaction is shown below.



When an **asymmetric alkene** undergoes a hydration reaction, there are ***two different alcohol molecules produced*** - the product which is produced in greater quantity is called the **major product**, the product made in lesser quantity is called the **minor product**. It is possible to predict the major and minor products for the hydration of an asymmetric alkene using **Markovnikov's Rule.**

4) The *Dehydration* of Alcohols

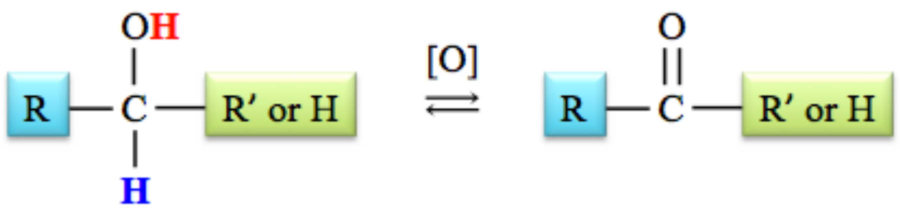
A hydroxyl group (**OH**) is removed from an ***alcohol*** and then an **H** is removed from a carbon that is *adjacent* to the carbon that was bonded to the hydroxyl group. A double bond forms between these two carbons. The ***general form*** of the chemical equation for the *hydration of an alcohol reaction* is shown below.



When an **asymmetric *2º or 3º* alcohol** undergoes a dehydration reaction, there are ***two different alkene molecules produced*** (*major* and *minor* products).

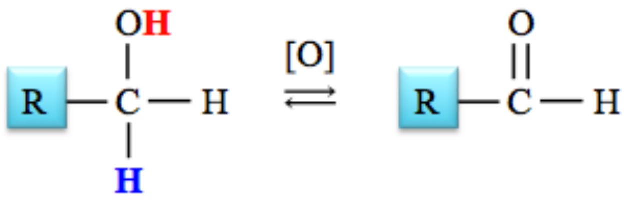
5) The *Oxidation* of Alcohols

When an alcohol is oxidized, the hydrogen from the hydroxyl group (**OH**) and a hydrogen attached to *the carbon that is carrying the hydroxyl group* are both removed, and the C-O *single* bond is changed to *double* bond. The general form of the equation for the ***oxidation of an alcohol*** is shown below.



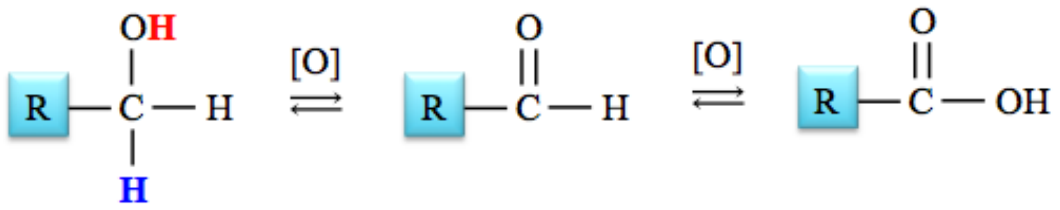
Oxidation of Primary (1°) Alcohols

Oxidation of a ***primary (1°) alcohol*** produces an ***aldehyde***:



primary alcohol **aldehyde**

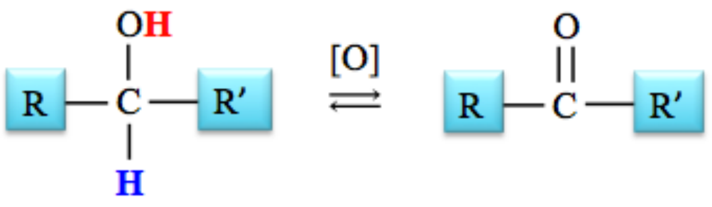
Certain organic molecules and inorganic oxidizing agents, such as CrO_3, MnO_4^-, can further oxidize aldehydes to produce carboxylic acids.



1° alcohol **aldehyde** **carboxylic acid**

Oxidation of Secondary (2°) Alcohols

The oxidation of a secondary alcohol produces a ***ketone*** as shown below.

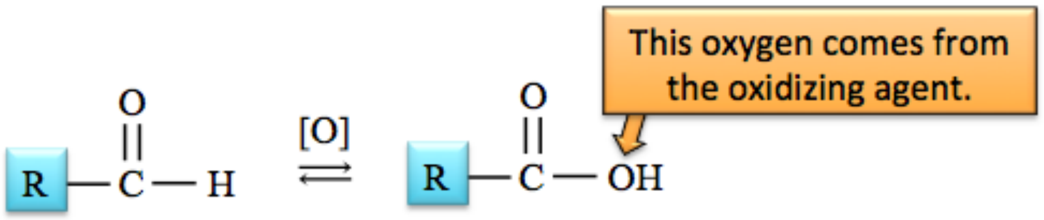


2° alcohol **aldehyde**

Tertiary (3°) alcohols cannot be converted to aldehydes or ketones by oxidation.

6) The Oxidation of Aldehydes

Aldehydes can be oxidized to ***carboxylic acids***. The general form of the chemical equation for the oxidation of an aldehyde is shown below.

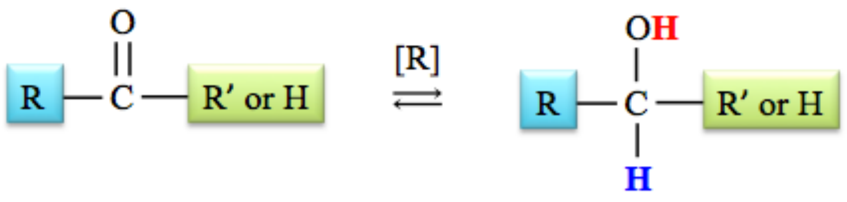


This oxygen comes from the oxidizing agent.

aldehyde **carboxylic acid**

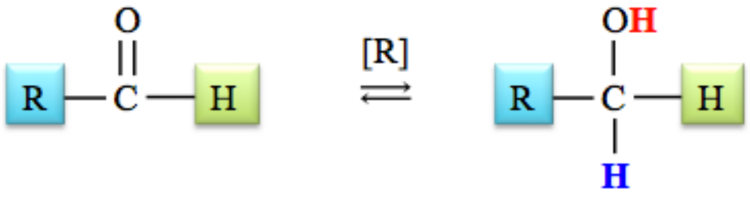
7) The Reduction of Aldehydes and Ketones

Reduction of aldehydes and ketones is the reverse of the oxidation of alcohol reactions. The general form of the equation for the ***reduction of an aldehyde or ketone*** is shown below.



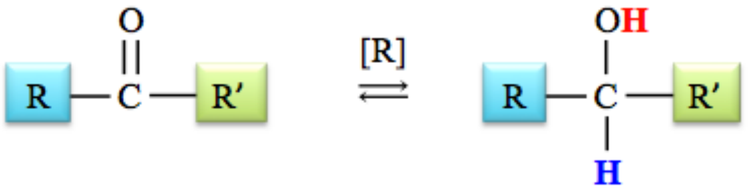
aldehyde or ketone **alcohol**

Aldehydes are reduced to ***primary alcohols*.**



aldehyde **primary (1°) alcohol**

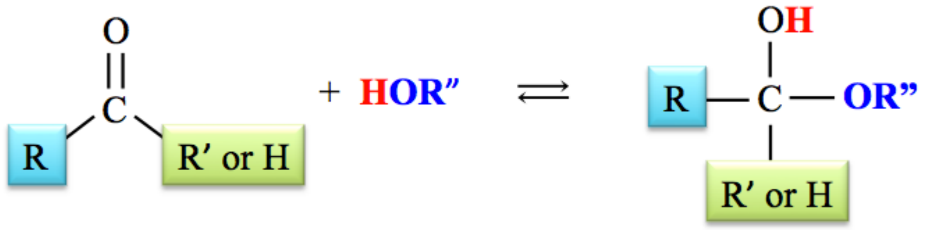
Ketones are reduced to ***secondary alcohols*.**



ketone **secondary (2°) alcohol**

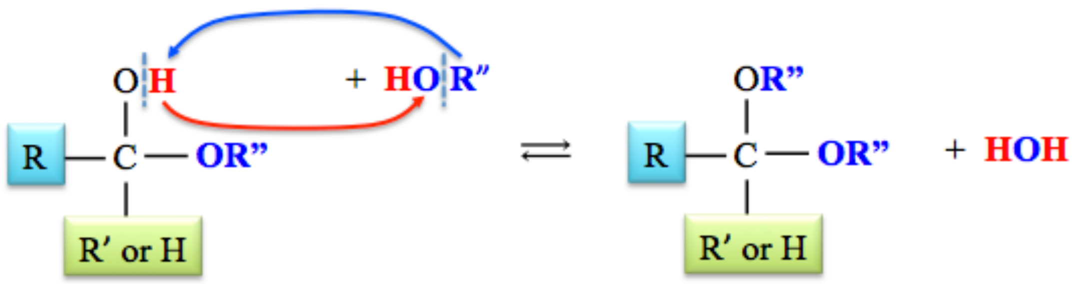
8) The Reaction of Aldehydes or Ketones with Alcohols: Hemiacetal and Acetal Production

An ***aldehyde <u>or</u> a ketone*** will react with an ***alcohol*** to form a **hemiacetal**.



aldehyde or ketone **alcohol** **hemiacetal**

The ***hemiacetal*** that is formed can react with a *second alcohol molecule* to form an **acetal** and an H_2O molecule.



hemiacetal **alcohol** **acetal** **H_2O**

Use the link below for more practice *naming the compounds* of chapter 10:

http://www.zovallearning.com/GOBlinks/ch10/naming-ch10-compounds-worksheet-and-key.pdf

Use the link below for more practice ***predicting the products of the reactions*** of chapter 10:

http://www.zovallearning.com/GOBlinks/ch10/ch10-reactions-worksheet-and-key-GOB.pdf

Chapter 11:
Carbohydrates

A photograph of California redwood trees (*Sequoia sempervirens),* taken in Big Basin Redwoods State Park. Carbohydrates account for about 60% of the mass of dry wood.
Source: Wikimedia Commons, Author: Allie_Caulfield, CC-BY, http://creativecommons.org/licenses/by/2.0/legalcode

Carbohydrates are also referred to as **sugars** or **saccharides**. We are all familiar with "table sugar," which is a particular carbohydrate molecule. Carbohydrates are quite abundant in nature. More than half of the carbon found in living organisms is contained in carbohydrate molecules, most of which are contained in plants (e.g. the California redwood trees shown above). The primary reason for such an abundance is that a carbohydrate is produced by a series of chemical reactions that we call photosynthesis. Energy from sunlight is used by plants to provide energy to drive the photosynthesis process. In the photosynthesis process, carbon dioxide and water are converted to oxygen gas and a ***carbohydrate*** called *glucose*. Plants can use *glucose* to produce the ATP molecules that are needed to do the work necessary for life. Plants store excess glucose as *starch*, for later use. Animals obtain energy that is stored in *starch* by eating plants, or by eating animals that ate plants or had herbivores in their food-chain. So, in one sense, we are *solar powered*!

In this chapter, you will learn the details of carbohydrate chemistry; then in chapter 15, you will learn how the potential energy in glucose or starch is eventually used to do physical work or drive cellular processes that require energy.

11.1 Chapter 11 Educational Goals

1. Given a ***Fischer projection*** of a monosaccharide, classify it as either **aldoses** or **ketoses**.
2. Given a ***Fischer projection*** of a monosaccharide, classify it by the number of carbons it contains.
3. Given a ***Fischer projection*** of a monosaccharide, identify it as a **D-sugar** or **L-sugar**.
4. Given a ***Fischer projection*** of a monosaccharide, identify **chiral carbons** and determine the ***number of stereoisomers*** that are possible.
5. Identify *four* common types of **monosaccharide derivatives**.
6. Predict the products when a monosaccharide reacts with **a reducing agent** or with ***Benedict's reagent***.
7. Define the term **anomer** and explain the difference between **α** and **β** ***anomers***.
8. Understand and describe **mutarotation.**
9. Given its ***Haworth projection***, identify a monosaccharide either a **pyranose** or a **furanose**.
10. Identify the **anomeric carbon** in ***Haworth structures.***
11. Compare and contrast **monosaccharides**, **disaccharides**, **oligosaccharides**, and **polysaccharides.**
12. Given the structure of an oligosaccharide or polysaccharide, identify the **glycosidic bond**(s) and characterize the glycosidic linkage by the bonding pattern [for example: **β**(1⟶4)].
13. Given the ***Haworth structures*** of two monosaccharides, be able to draw the **disaccharide** that is formed when they are connected by a **glycosidic bond**.
14. Understand the difference between **homopolysaccharides** and **heteropolysaccharides**.
15. Compare and contrast the ***two components*** of **starch.**
16. Compare and contrast **amylopectin** and **glycogen.**
17. Identify **acetal** and **hemiacetal** bonding patterns in carbohydrates.

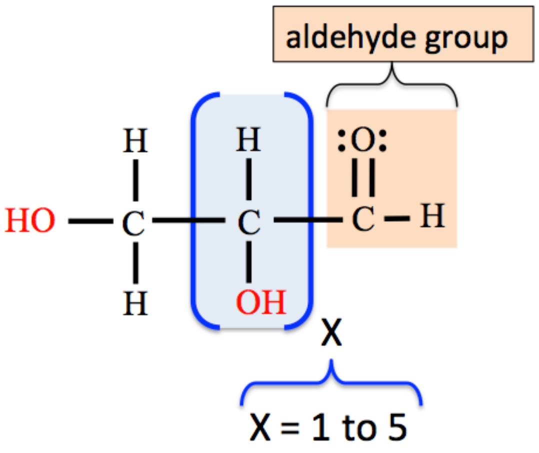
11.2 Introduction to Monosaccharides

Monosaccharides are the smallest carbohydrates and serve as the building blocks of larger carbohydrates. They are also referred to as **simple sugars.** Monosaccharides have the general chemical formula of $C_n(H_2O)_n$; where **n** (the number of carbon atoms) can be ***three*** to ***seven***. They are *polyhydroxyl* aldehydes or ketones:

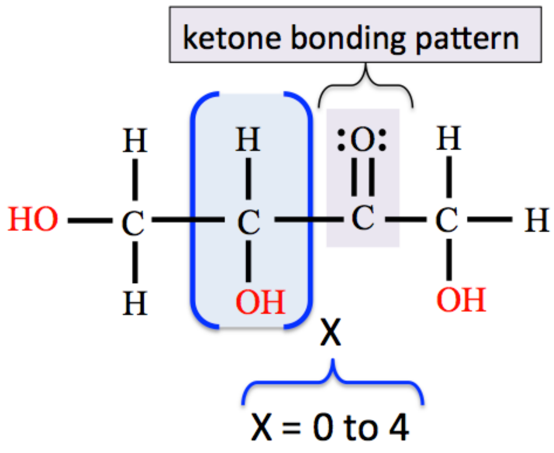
1) Monosaccharides contain either an ***aldehyde*** group <u>*or*</u> a ***ketone*** bonding pattern.

2) Monosaccharides contain ***more than one*** *hydroxyl* (**OH**) *group*.

A monosaccharide that contains an *aldehyde group* is called an **aldose.** A monosaccharide that contains the *ketone bonding pattern* is called a **ketose.** The general form of an *aldose* and a *ketose* are shown below:

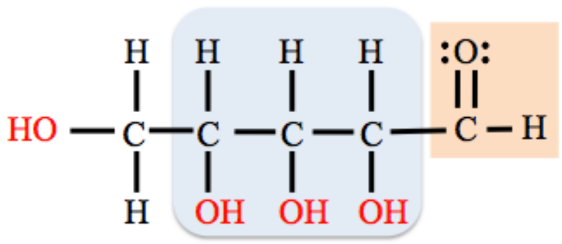


general form of an aldose

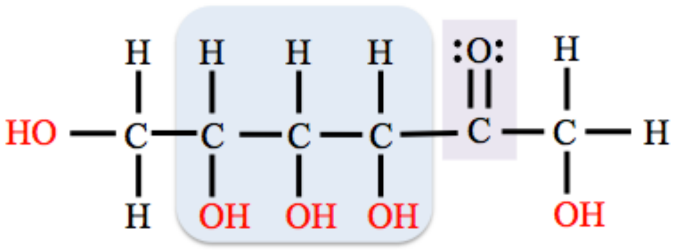


general form of a ketose

Note that the group in the blue-shaded region can repeat. For example, I have drawn (below) an aldose and a ketose structure where **X** = **3**:



an aldose

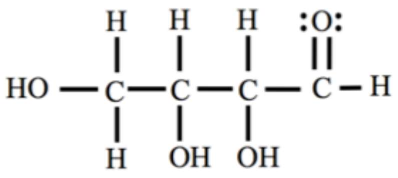


a ketose

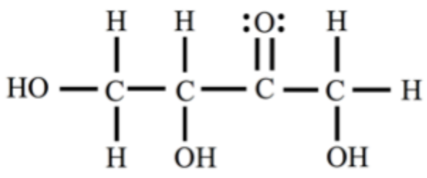
Review 11.1: Aldose vs. Ketose

Classify each of the following monosaccharides as either an ***aldose*** or a ***ketose***.

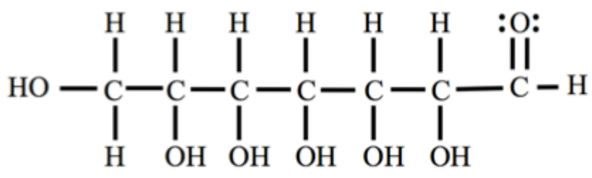
a.



b.



c.



For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

Monosaccharides can be classified according to the number of carbons they contain. These classifications are as shown in Table 11.1.

Table 11.1
Classification of Monosaccharides by the Number of Carbons they Contain

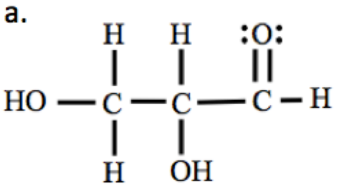
Number of Carbons	Classification
3	triose
4	tetrose
5	pentose
6	hexose
7	heptose

A monosaccharide may also be classified by ***both*** the number of carbons ***and*** whether it is an aldose or a ketose. This is done by using the prefix “aldo” for aldoses, or “keto” for ketoses, in front of “triose,” “tetrose,” “pentose,” “hexose,” or “heptose.” For example, an ***aldose*** that contains ***five*** carbons is an ***aldopentose***.

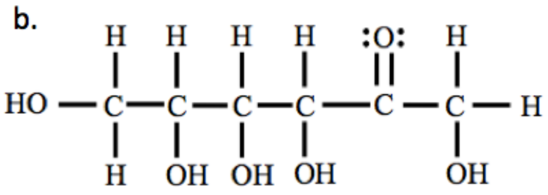
Review 11.2: Classification of Monosaccharides

Classify each of the following monosaccharides using the prefix “aldo” for aldoses, or “keto” for ketose, in front of “triose,” “tetrose,” “pentose,” “hexose,” or “heptose.”

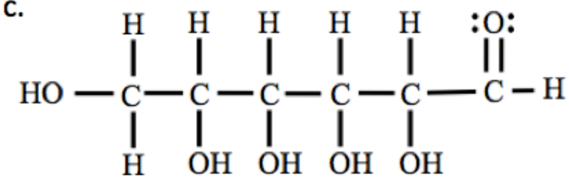
a.



b.



c.

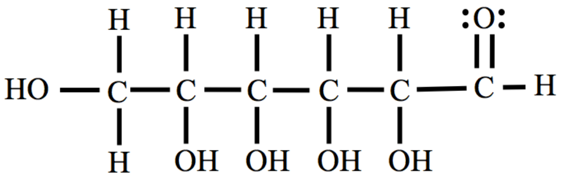


For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

Stereochemistry of Monosaccharides

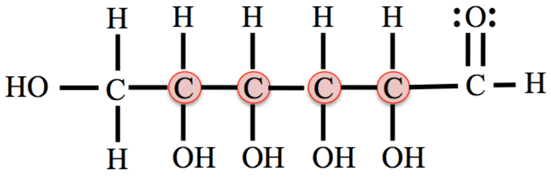
Except for the *ketotriose*, monosaccharides contain ***at least one chiral carbon***. You learned that a chiral carbon is a carbon that is surrounded by *four* ***different*** *groups*. Molecules with just ***one*** chiral carbon have a pair of ***geometric isomers*** called ***enantiomers***. Enantiomers have the same atomic connections, but a different three-dimensional arrangement of atoms, and are *nonsuperimposable mirror images* of each other. If a molecule has ***more than one*** *chiral carbon*, then it will have more than one pair of enantiomers. The number of stereoisomers that a molecule has can be *calculated* from the *number of chiral carbons*. If a monosaccharide has **n** chiral carbons, then it will have $\mathbf{2^n}$ stereoisomers. For example, if a molecule has *three* chiral carbons, then it will have $\mathbf{2^3}$ = (2 x 2 x 2) = 8 stereoisomers (***four*** pairs of enantiomers). For more details on chiral carbons and enantiomers, review section 5 of chapter 9.

Example: How many stereoisomers are possible for the monosaccharide shown below?



Solution: Identify the number of chiral carbons, and then calculate the number of stereoisomers.

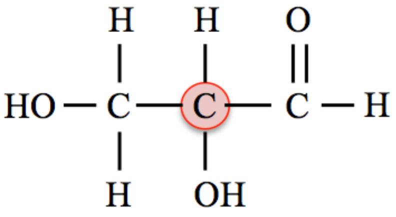
- There are ***four*** chiral carbons in this molecule. The chiral carbons are highlighted red in the structure below.



- Recall that a carbon is chiral if it is surrounded by *four different* ***groups***; you must consider whether each of the ***entire groups*** bonded to the carbon are different from each other. In this example, the left-most carbon is not chiral because it is bonded to *two* hydrogen atoms. The *right-most* carbon is not chiral because it is only bonded to *three groups*.

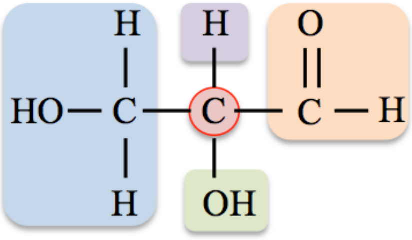
Since this monosaccharide structure has ***four*** chiral carbons, there are 2^4 = (2 x 2 x 2 x 2) = **16 possible stereoisomers (*eight pairs of enantiomers).***

The monosaccharide in the previous example has a molecular formula of $C_6H_{12}O_6$. We found that there are **16** different molecules (stereoisomers) that share this molecular formula and structural formula. Most of the physical properties of these 16 stereoisomers are quite similar; however, the way they each behave in biological systems can be very different. Let's consider the three dimensional arrangement of the atoms in the smallest monosaccharide, *glyceraldehyde*. Glyceraldehyde has only **one** chiral carbon.

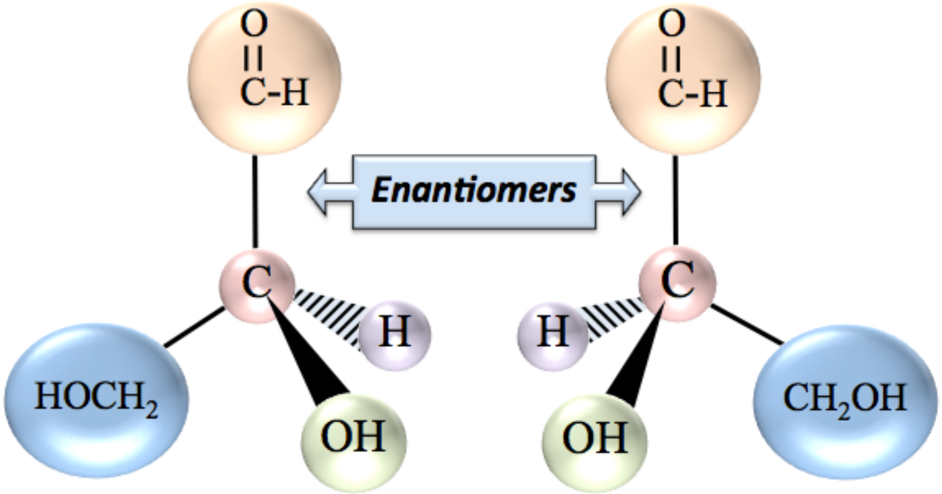


glyceraldehyde

The *chiral carbon* in the structural formula above is highlighted in red; it is bonded to *four different groups*. In the structure below, I have highlighted the *four different groups* that surround the chiral carbon.

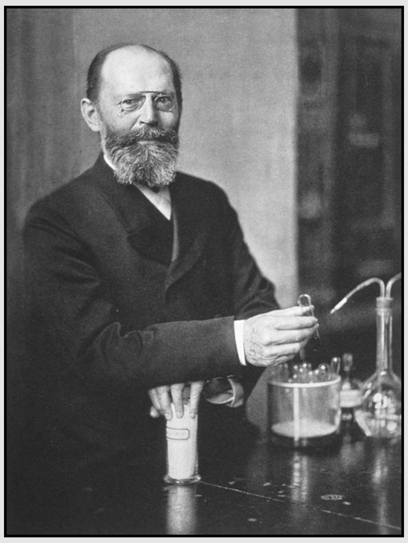


Since there is *one* chiral carbon in glyceraldehyde, then there are $2^n = 2^1 = 2$ stereoisomers (one pair of enantiomers/ nonsuperimposable mirror images). Wedge and dash models of the pair of *glyceraldehyde* enantiomers are shown below.



the pair of *glyceraldehyde* enantiomers (nonsuperimposable mirror images)

Emil Fischer



In order for professionals in healthcare, engineering, and science fields to discuss and depict the various monosaccharide stereoisomers, it is necessary to be able to draw two-dimensional (flat) structural formulas on a page or computer display, such that they still contain the ***three-dimensional information*** particular to each stereoisomer. In previous chapters, we used the wedge and dash system to retain the three-dimensional information on a flat surface. For monosaccharides, **Fischer projections** are used for this purpose. They were first described and used by Emil Fischer (1852 – 1919). Fischer was the 1902 recipient of the Nobel Prize in Chemistry for his work on carbohydrates and other organic molecules called purines.

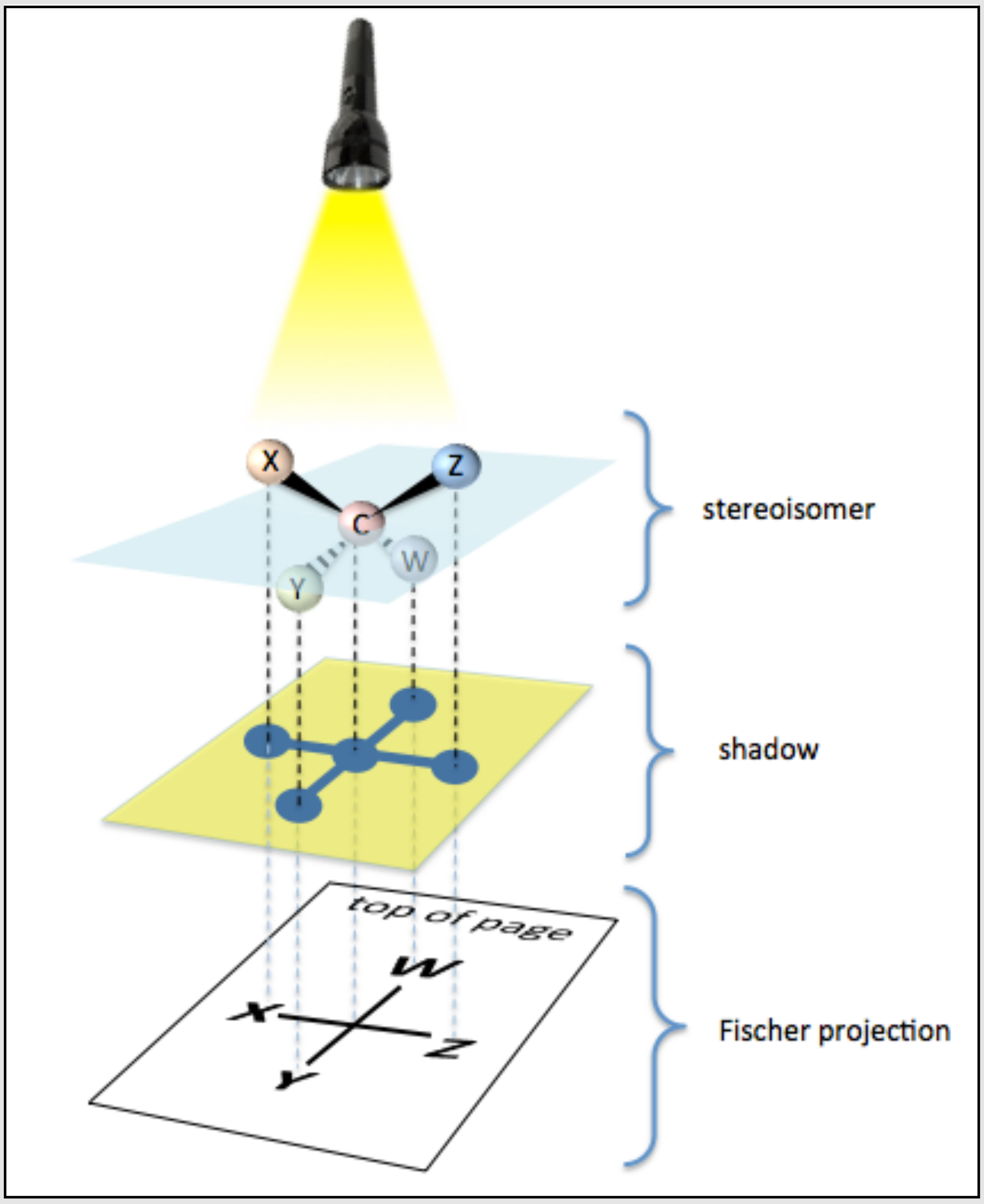
Fischer Projections

Fisher projections are related to an imaginary "shadow" that would be produced if a chiral carbon and its four bonded groups were placed in a particular orientation between a light source and a surface. Of course, this is an imaginary concept since it is impossible to get a real shadow from a molecule. The concept is illustrated in Figure 11.1.

The ***chiral carbon*** in the stereoisomer shown in Figure 11.1 is labeled with the letter "C" and shaded red. In Fischer projections, *chiral carbons are implied to be at the* ***intersection*** *of a vertical and horizontal line*, as shown in the Fischer projection drawn in the bottom of Figure 11.1.

Fischer's choice of the particular orientation of the chiral carbon and its four groups was arbitrary, ***any*** orientation could have been used; *however*, for consistency, one specific orientation needed to be chosen. The chosen orientation of a chiral carbon and the four groups that are bonded to it ***relative to the drawing surface/page in all Fischer Projections*** is as follows:

Figure 11.1
An Illustration of the Fischer Projection Concept



A fictitious light projector (represented by a flashlight) generates the *imaginary* "shadow" that would be produced when a chiral carbon and its four bonded groups are placed *in a particular orientation* in between the light projector and the surface. Fischer projections are based on these imagined shadows of the groups and bonds around each chiral carbon in a monosaccharide.

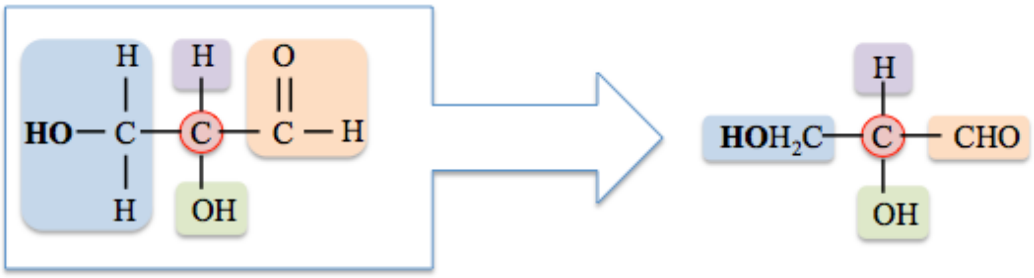
1) The ***bonds*** from the *chiral* carbon to the *other* ***carbon*** *atoms* ***point at a downward angle*** (see the bonds from the chiral carbon (**C**) to **W** and **Y** in Figure 11.1), ***and*** their shadows form ***vertical lines*** on the drawing surface/ Fischer projection.

2) The ***bonds*** from the chiral carbon to *the* ***noncarbon*** *groups* (which will be an **H** and an **OH**) ***point at a upward angle*** (see the bonds from the chiral carbon (**C**) to **X** and **Z** in Figure 11.1), **and** their shadows form ***horizontal lines*** on the drawing surface/Fischer projection.

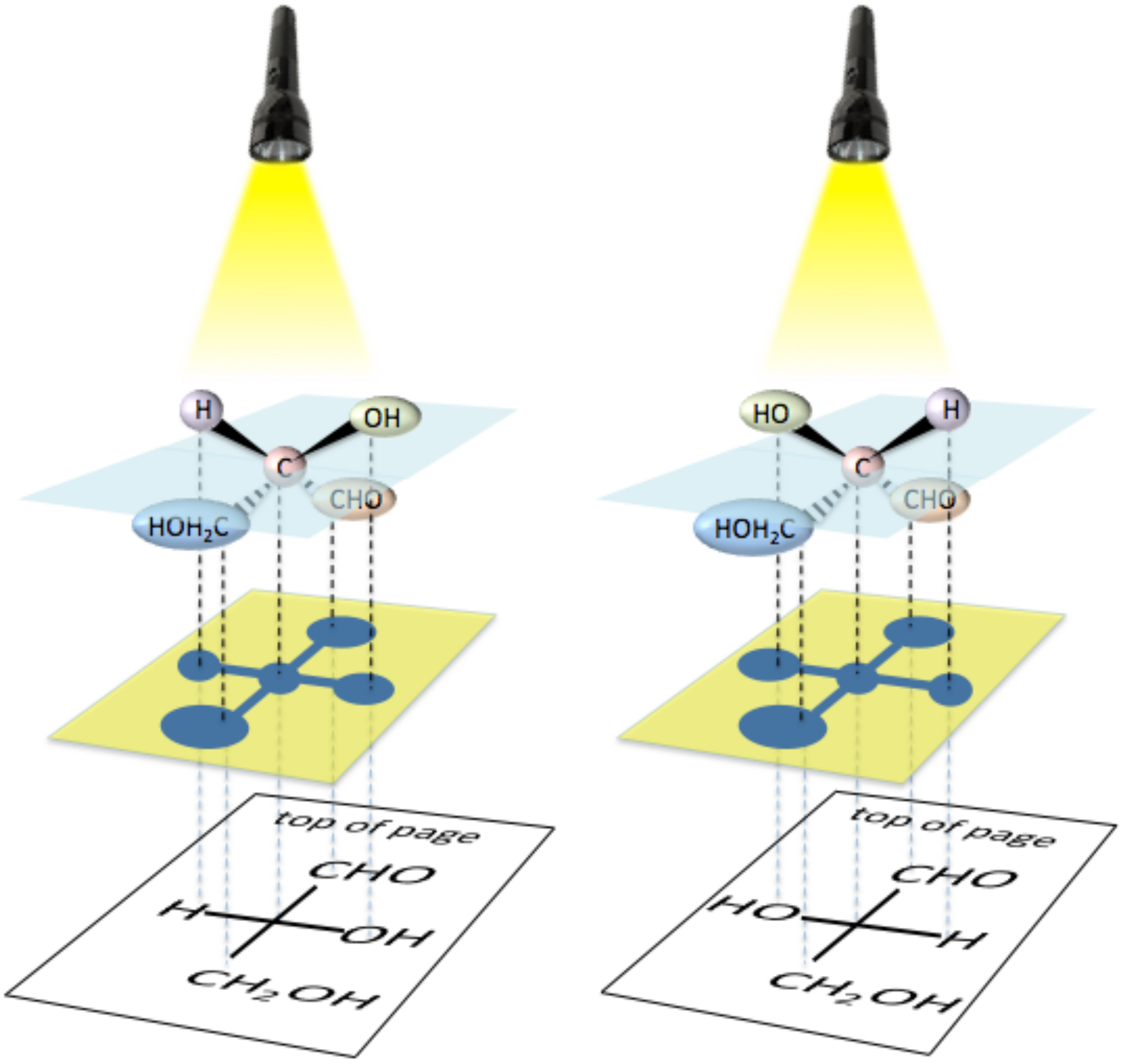
3) For ***aldoses***, the *aldehyde group* is positioned at the end of the molecule that is closest to the top of the page (position **W** in Figure 11.1). For ***ketoses***, the *carbonyl carbon* is positioned as close as possible to the end molecule that is nearest the top of the page.

Orienting the groups around chiral carbons in relation to the drawing surface, as describe above, results in a preservation of the three-dimensional information that distinguishes each monosaccharide.

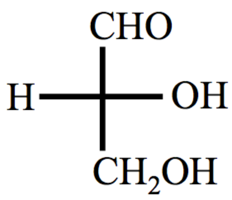
Let’s consider the **Fischer projections** for both of the *glyceraldehyde* stereoisomers. Recall that *glyceraldehyde* has ***one*** chiral carbon (shaded red below). Since the other two carbons in *glyceraldehyde* are ***not chiral***, I can use shorthand notation to simplify the structure. The aldehyde group is represented by “**CHO.**”

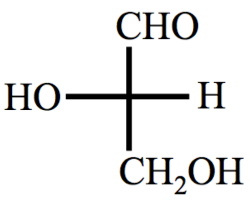


The derivation for the Fischer projections of glyceraldehyde’s enantiomers is illustrated below.



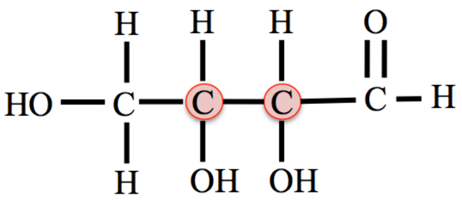
The Fischer projections for the two enantiomers of *glyceraldehyde* are:





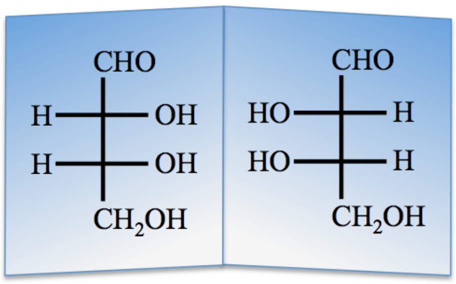
We do not need to draw the bonds around the top or bottom carbon atoms because they are ***not chiral***. Note that we draw the hydroxyl groups that are on the ***left-hand side*** of Fischer projections as “**HO.**”

For monosaccharides with ***more than one*** chiral carbon, Fischer projections must be drawn (or interpreted) by considering the orientation around *each* of the chiral carbons. This is done one chiral carbon at a time. As an example, let's consider aldotetroses, which contain ***two*** chiral carbons:

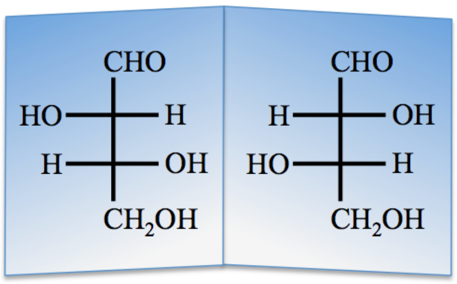


an aldotetrose

Since aldotetroses each have ***two*** chiral carbons, there are $2^2 = (2 \times 2) = 4$ **stereoisomers** (***two pairs of enantiomers).*** I have drawn the Fischer projections for the four aldotetrose stereoisomers (below).



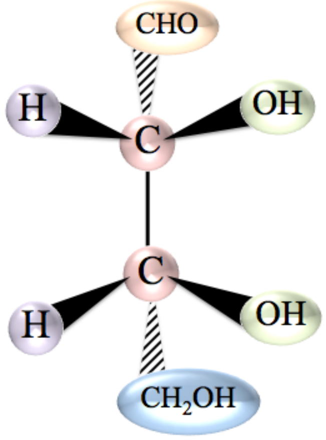
enantiomer pair
(mirror images)



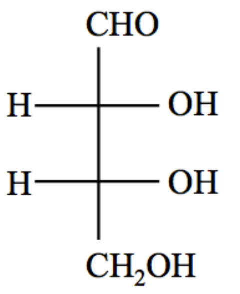
enantiomer pair
(mirror images)

Remember that a chiral carbon is located wherever lines cross (intersect) in Fischer projections. Note that the hydrogen (**H**) and the hydroxyl group (**OH**) positions are reversed on chiral carbons for each particular enantiomer pair. This is the case for all monosaccharide enantiomer pairs.

The illustration below is meant to help you understand the three-dimensional implications of Fischer projections for monosaccharides with **more than one *chiral* carbon.** In this illustration, I have drawn both the *wedge and dash representation* and the Fischer projection of one of the aldotetrose stereoisomers.



Wedge and Dash Representation



Fischer Projection

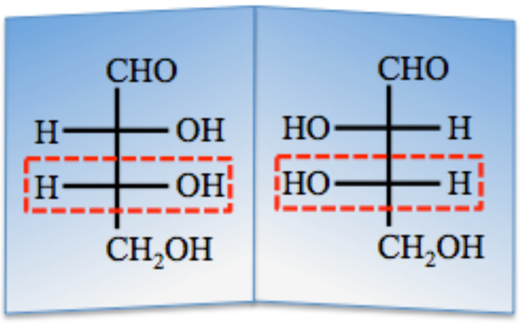
Review 11.3: Fischer Projections

An aldopentose contains **three** chiral carbons, and therefore there are $2^3 = 8$ aldopentose stereoisomers. Draw Fischer projections of the ***eight*** stereoisomers. **Hint:** First draw the Fisher projection's aldehyde group, three chiral carbons, and non chiral carbon (as shown here) for all eight of the stereoisomers. On your first Fischer projection, draw all of the hydroxyl groups on the right side of the chiral carbons and all hydrogens on the left side. Next, draw its mirror image (enantiomer) that has all hydroxyl groups on the left side of the chiral carbons and all hydrogens on the right side. That will give you two of the eight stereoisomers. Construct your third Fischer projection by exchanging the positions of a hydroxyl group and a hydrogen that are bonded to the same chiral carbon in order to obtain a structure that differs from your previous ones. Then, draw its mirror image to get your fourth projection. Continue like this until you have eight different Fischer projections.

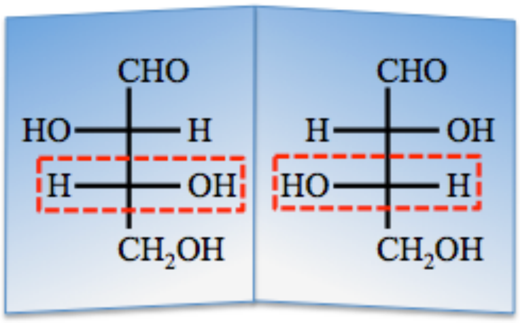
For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

D- and L- Designations for Monosaccharides

Carbohydrates are most often referred to by their common names, all of which use the “-ose” suffix. A common name is assigned to each pair of enantiomers. In order to differentiate the *two* individual monosaccharides of an enantiomer pair, ‘**D-**’ or ‘**L-**’ designations are used with the common name. The ‘**L-**’ designation is used for the enantiomer in which **the *chiral carbon* that is furthest from the top of the Fischer projection** has its *hydroxyl group* on the ***left***. To remember this, you can think “**L-** for **L**EFT.” The ‘**D-**’ designation is used for the ***other enantiomer*** of the pair. For example, you learned that aldotetroses each have ***two*** chiral carbons, therefore there are $2^2 = 4$ **aldotetrose stereoisomers** (***two pairs of enantiomers).*** I have drawn and used **D-** and **L-** designations for the Fischer projections of the *four* aldotetrose stereoisomers (below).



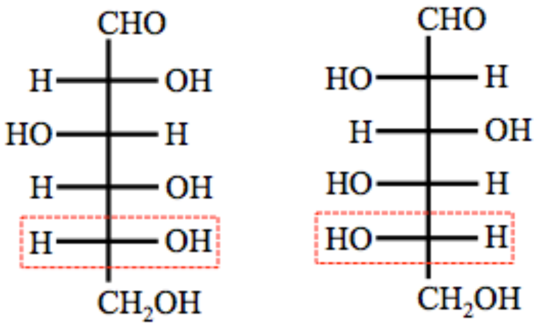
D-erythrose L-erythrose
(an enantiomer pair)



D-threose L-threose
(an enantiomer pair)

I drew red-dashed boxes around the chiral carbons that are furthest from the top of their Fischer projections. It is the position of the *hydroxyl group* on these carbons that is responsible for the **D-** vs. **L-** designations. Note that when determining the **D-** vs. **L-** designations, we are interested in the orientation of the *hydroxyl group* on the *chiral carbon* that is furthest from the top of the Fischer projection; this will always be the ***second to the last (bottom) carbon*** because the *bottom* carbon is *never chiral*.

Monosaccharides are produced in living organisms by chemical reactions, some of which require enzymes that can only produce **one** particular enantiomer. For example, the stereoisomer of ***glucose*** that is made in photosynthesis is **D-glucose**. Fischer projections for both of the glucose enantiomers are shown below. I drew red-dashed boxes around the chiral carbons and hydroxyl groups responsible for the **D-** and **L-** designations.

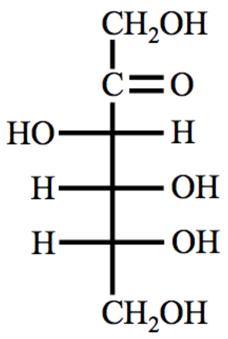


D-glucose L-glucose
(an enantiomer pair)

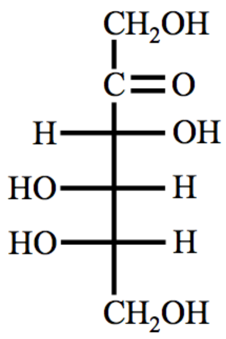
The glucose enantiomer pair (D-glucose and L-glucose) are ***two*** of the ***sixteen*** aldohexose stereoisomers. There are ***seven*** more aldohexose enantiomer pairs that can be drawn by varying the positions of the H and OH on each side of a Fischer projection (as you did for the aldopentoses in the previous review problem). These seven other *enantiomer pairs* are differentiated from glucose, and each other, by their ***common names***.

I do not require my students to memorize the common names and structures for particular monosaccharides, however, you should check with your own instructor to see if you are required to do so.

An example of a ***ketose*** is **fructose**. *D-Fructose* is one of our major dietary carbohydrates. Fischer projections of the *fructose* enantiomers are shown below.



D-fructose



L-fructose

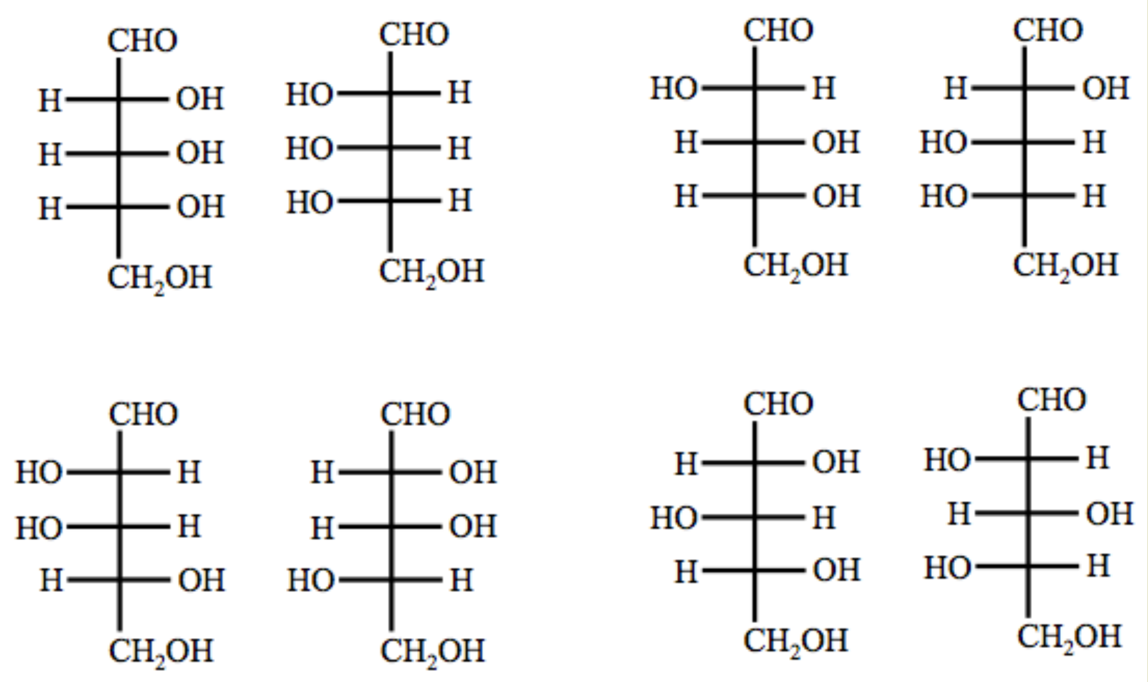
Monosaccharides with the **L-** designation are sometimes referred to as "**L-sugars**," and those with the **D-** designation are sometimes referred to as "**D-sugars**."

Summary of D- and L- Designations:

- In **L-sugars**, the ***chiral carbon*** that is furthest from the top of the Fischer projection has its ***hydroxyl group*** on the ***left***.
- In **D-sugars**, the ***chiral carbon*** that is furthest from the top of the Fischer projection has its ***hydroxyl group*** on the ***right***.

Review 11.4: D- vs. L- Monosaccharides

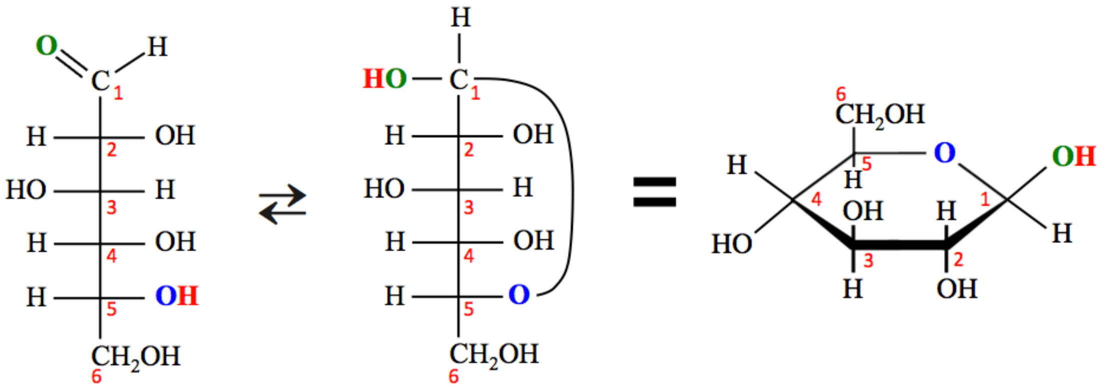
Classify each of the eight stereoisomers shown below as either **D-** or **L-** stereoisomers.



For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

11.3 The Cyclic Forms of Monosaccharides

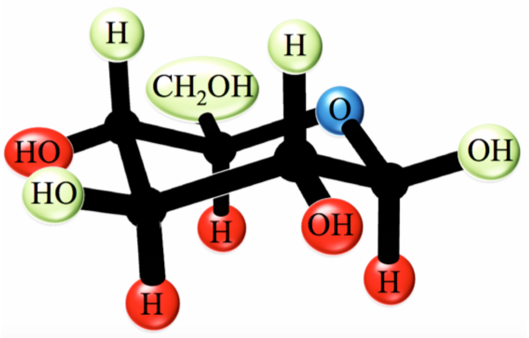
When monosaccharides that contain five to seven carbons are in aqueous solutions, they can undergo a reaction in which they ***rearrange*** their bonding pattern to form *cyclic structures*. The process is considered to be a chemical reaction since some chemical bonds are broken and new bonds are formed. It is a reversible reaction in which the open-chain form (also referred to as the *linear form*, *noncyclic form*, or *acyclic form*) is interconverted with the cyclic form. The cyclic form is *lower in energy* and is therefore the dominant form. In most solutions, the equilibrium ratio of *cyclic form* to *open-chain form* is about *one hundred* to *one*. A specific example of the cyclization rearrangement reaction is shown below for a *D-glucose* molecule. The open-chain form of D-glucose can be converted to its cyclic form when a new bond is formed between the oxygen bonded to carbon number **5** and the carbonyl carbon (carbon number **1**)



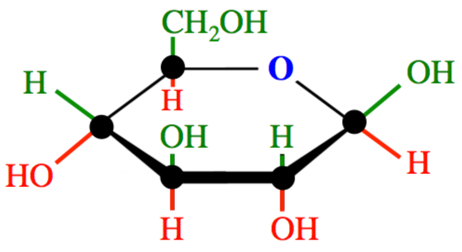
D-glucose
Fischer projection
(open-chain form)

D-glucose
Haworth projection
(cyclic form)

You have seen *side-view structures* of cyclic compounds in previous chapters. The *side view structures* of cyclic monosaccharides, such as I drew above, are called **Haworth projections** *or* **Haworth structures**. The carbon atoms that form the ring are not drawn explicitly, but are implied to occur where lines/bonds meet. To help you understand the *three-dimensional* implications of Haworth projections, I have drawn a ball-and-stick model that shows the actual geometry/bond angles of the cyclic form of D-glucose, next to its Haworth Projection representation:



ball-and-stick model
(actual molecular geometry)



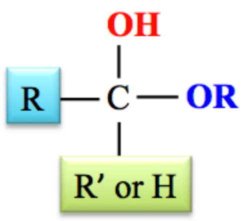
Haworth projection

I used large black dots at the ring-carbon positions in both structures. Each ring-carbon is bonded to *two other ring-atoms* ***and*** two *other groups*. Groups that are oriented *upward* relative to the ring-carbons are shaded ***green***. Groups oriented *downward* from ring-carbons are shaded ***red***.

Haworth projections were first introduced and named after Sir (Walter) Norman Haworth. Haworth received the 1937 Nobel Prize in Chemistry because of his research on carbohydrates and vitamin C.

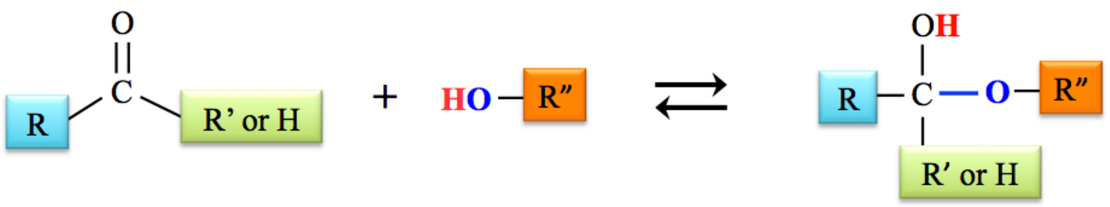
The rearrangement/cyclization reaction of a monosaccharide is actually a form of the ***hemiacetal formation*** reaction that you learned about at the end of the previous chapter. Let's take a moment to review that reaction.

A **hemiacetal** is a molecule containing ***both*** an **OR** group *and* an **OH** group that are bonded to the ***same*** carbon. The general form of a hemiacetal is shown below.



general form of a hemiacetal

The general form of the chemical equation for an ***aldehyde (or a ketone)*** reacting with an ***alcohol*** to form a **hemiacetal** is:



aldehyde or ketone **alcohol** **hemiacetal**

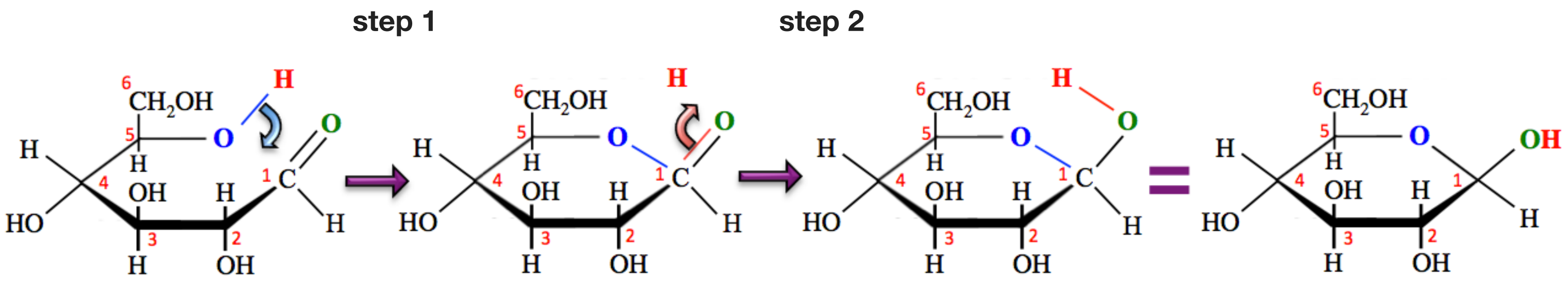
You learned how to predict the structure of the hemiacetal that is produced from a specific aldehyde (or ketone) and alcohol by adding the alcohol "across" the carbonyl double bond. To add the alcohol (**R"**-**OH**) across the carbonyl group, it is convenient to redraw the aldehyde (or ketone) as shown below.

Next, draw the *alcohol molecule* to the side of the carbonyl group, as shown below, and then flip the bond from the *alcohol's hydroxyl group* downward to make a new bond to the carbonyl carbon.

Finally, flip one bond from the carbonyl group upward to form a bond with the remaining *unbound* hydrogen (**H**).

hemiacetal

Now let's think about how this reaction can occur **for a monosaccharide.** The open-chain form of an ***aldose*** monosaccharide contains both an ***aldehyde group*** and at least two ***hydroxyl groups***. The open-chain form of a ***ketose*** monosaccharide contains both the ***ketone*** bonding pattern and at least two ***hydroxyl groups***. A *hemiacetal* is formed when a monosaccharide's *hydroxyl group* reacts with its *carbonyl group*. The monosaccharide is "reacting with itself." I will elaborate by showing the steps of the hemiacetal formation during the cyclization of D-glucose:

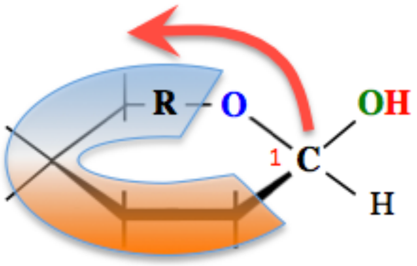


D-glucose
(*open-chain form*, drawn curved)

D-glucose
(cyclic hemiacetal form)

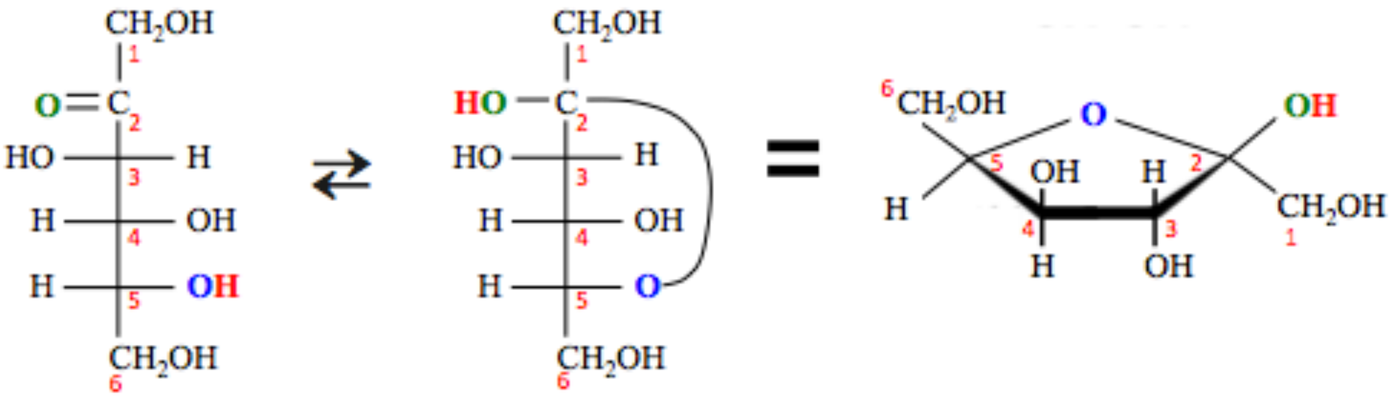
Hemiacetal formation occurs *within* an individual monosaccharide molecule in the same way as it did for an aldehyde (or ketone) with a separate alcohol molecule; the *hydroxyl group* is added "across" the carbonyl double bond. Note that the ***left-most*** structure of D-glucose (above), although drawn curved, is still in its *open-chain form*. In **step 1**, the *hydroxyl group (on carbon number* ***5****) is drawn* to the side of the carbonyl group, and then the bond from the *hydroxyl group* is flipped downward to make a new bond to the *carbonyl carbon* (carbon number **1**). Next, in **step 2**, one bond from the *carbonyl group* is flipped upward to form a bond with the remaining *unbound* hydrogen (**H**), to produce the cyclic form of D-glucose.

The cyclic form of D-glucose is a **cyclic hemiacetal.** Recall that a **hemiacetal** is a molecule that contains ***both*** an **OR** group *and* an **OH** group that are bonded to the ***same*** carbon. Carbons that are bonded to ***both*** an **OR** group *and* an **OH** group are called **hemiacetal carbons.** Carbon number **1** in the cyclic form of D-glucose meets this criterium. The **OH** that is bonded to carbon number **1** is obvious, but the **OR** may not be immediately obvious to you. However, note that, beginning at carbon number **1** and moving *counter-clockwise*, as indicated by the **red arrow** in the structure shown below, the **OR** bonding pattern is seen. When the **OR** bonding pattern occurs in this way, ***forming a ring***, the molecule is referred to as a **cyclic hemiacetal.**



a cyclic hemiacetal

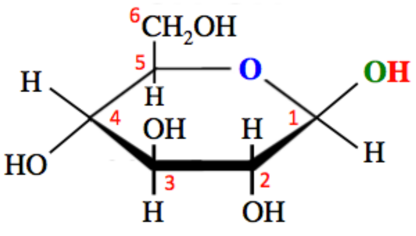
An example of the cyclization of a ***ketose*** (*fructose*) is shown below.



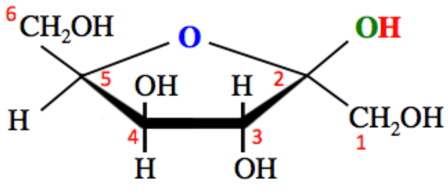
D-fructose
Fischer projection
(open-chain form)

D-fructose
Haworth projection
(cyclic form)

The most common cyclic monosaccharide structures are five- and six-member rings. The reason for this is that the bond angles in rings with five or six members are close to the low-energy, 110° angle arrangement of four electron groups. This is not only true for cyclic forms of monosaccharides, but for all cyclic compounds found in nature. Cyclic monosaccharides with five-member rings are called **furanoses**, and those with six-member rings are called **pyranoses**. These terms are often used as suffixes when naming cyclic monosaccharide structures. For example, the cyclic form of D-glucose shown below (with a six-member ring) is called ***D-glucopyranose***, and the cyclic form of D-fructose shown below (with a five-member ring) is called **D-*fructofuranose***.

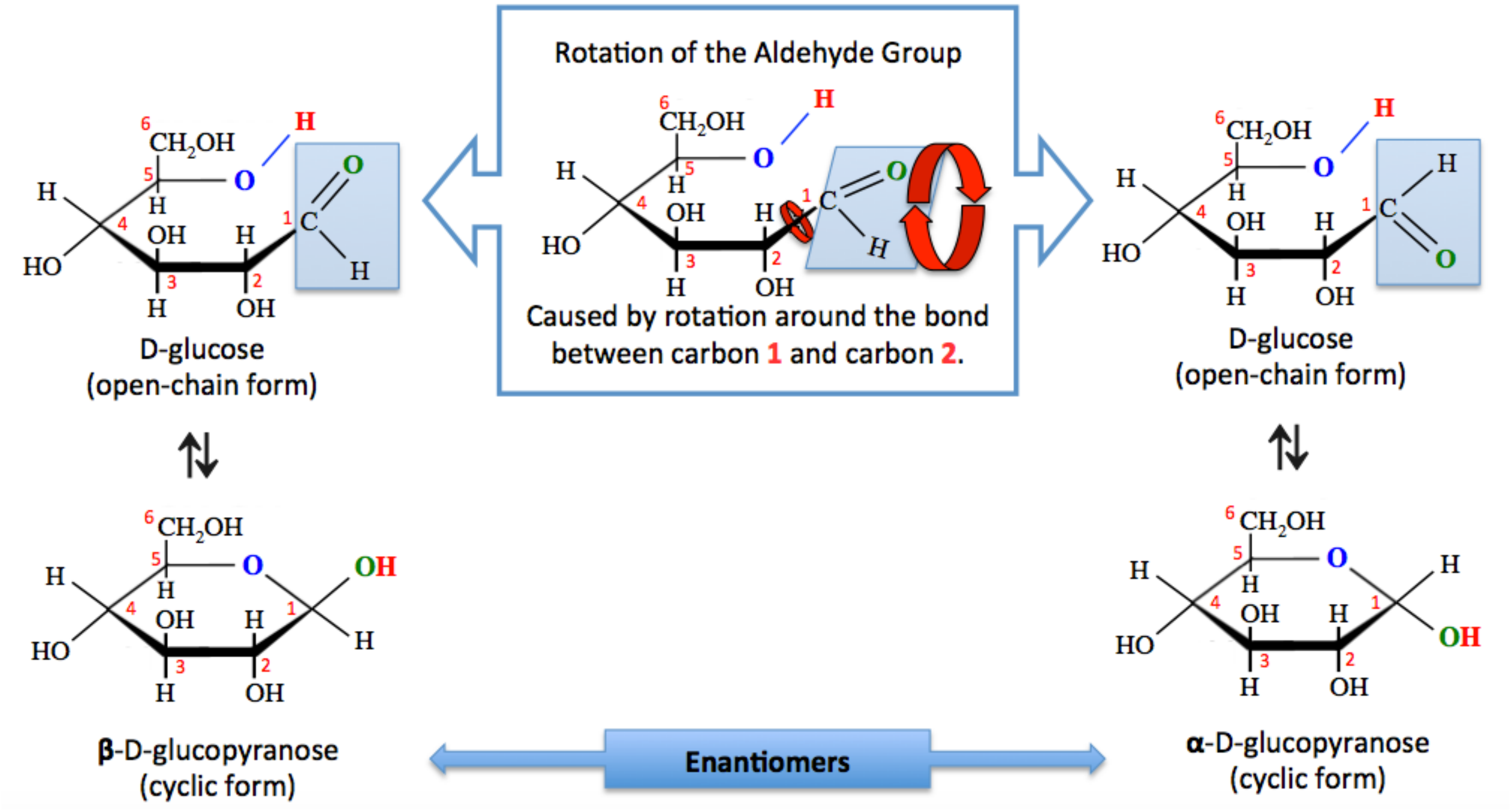


D-glucopyranose
(a pyranose)



D-fructofuranose
(a furanose)

The cyclization reaction is reversible; the cyclic form interconverts with the open-chain form when monosaccharides are in solution. Each time that the open-chain form is converted to the cyclic form, one of two cyclic ***enantiomers*** will be formed. This process is illustrated below for an aldose (D-glucose).

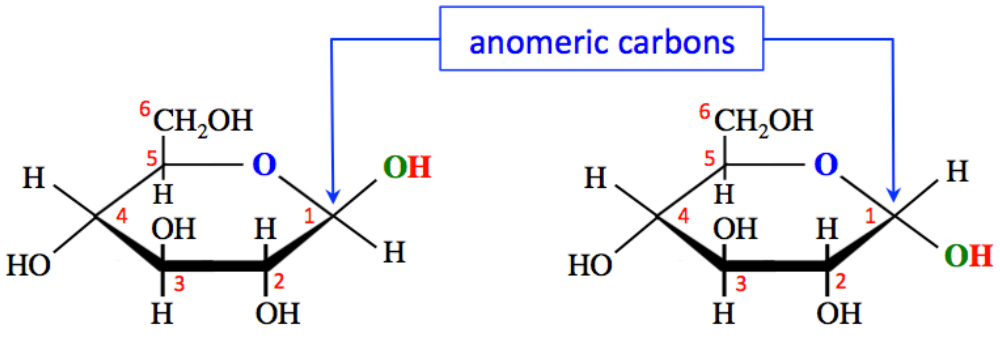


In the open-chain form of D-glucose that is shown in ***top-left*** of the illustration above, the carbonyl group (C=O) is oriented ***upward*** from the ring that is forming; therefore, when the *cyclic hemiacetal* is formed (***bottom, left***), the *new* hydroxyl group (OH) will be oriented ***upward*** from carbon number **1**. *Free rotation* occurs around single bonds in the open-chain form (as depicted in the box in the ***top-middle*** of the illustration). Rotation around the bond between carbon number **1** and carbon number **2** of the open-chain form causes the carbonyl group to, at times, be oriented ***downward*** from the ring (as seen in the open-chain form in the ***top-right*** of the illustration). In this arrangement, when the cyclization reaction occurs, the cyclic hemiacetal is formed with the *new* hydroxyl group (OH) oriented ***downward*** from carbon number **1** (as seen in the ***bottom-right*** structure of the illustration).

The formation of either of two different cyclic structures, ***a cyclic enantiomer pair,*** is possible because of the four different groups bonded to a ***chiral hemiacetal carbon*** (the carbon which contains an OH and an OR). This carbon is called the **anomeric carbon**. It is the carbon that ***was*** the *carbonyl carbon* in the open-chain form. The cyclic enantiomers are *almost identical*; the ***only*** difference is that the bonding pattern around the *anomeric carbons* are mirror images.

The sugar produced in photosynthesis, and almost all of the other monosaccharides found in plants and animals, are **D-sugars**. At some point in the history of Earth, nature chose D-sugars. It is easy to identify the **anomeric carbon** in a Haworth projection of a D-sugar; it is the ring-carbon to the ***right-hand side*** of the ***ring-oxygen***. You will only see D-sugars in the remainder of this book.

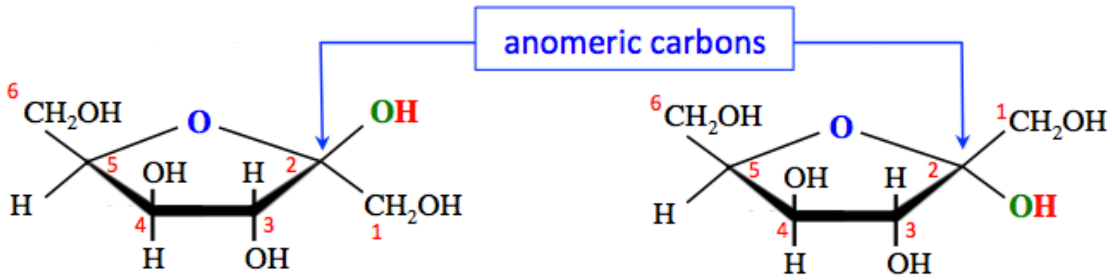
Although ***all*** of the ring-carbons in cyclic monosaccharides are chiral, the only possible change in stereochemistry that may occur in cyclization is that of the *anomeric carbon*. The two enantiomers that can be formed during the cyclization process are called **anomers**. They are classified, based on the orientation of the *hydroxyl group* (**OH**) on the *anomeric carbon*, as the **α-anomer** (alfa anomer) or the **β-anomer** (beta anomer). The **α-anomer** has the **OH** on the anomeric carbon oriented ***downward*** from the ring. The **β-anomer** has the **OH** on the anomeric carbon oriented ***upward*** from the ring. The **anomers** of *D-glucopyranose* are drawn below.



β-anomer
(**β**-D-glucopyranose)

α-anomer
(**α**-D-glucopyranose)

The formation of **β-anomers** or **α-anomers** also occurs, for the same reason, for *ketoses*. For example, the cyclization of *D-fructose* results in the formation of two possible **anomers**, as shown below.



β-anomer
(**β**-D-fructofuranose)

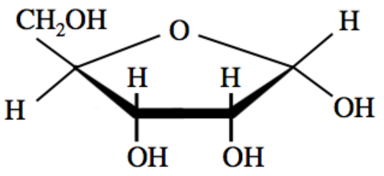
α-anomer
(**α**-D-fructofuranose)

The conversion from **α-anomer**, to the ***open-chain form***, then to the **β-anomer** (and vice versa) is called **mutarotation**.

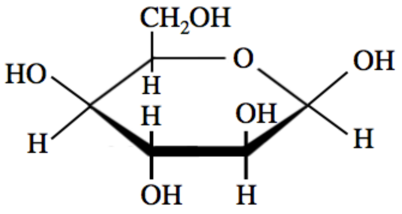
Review 11.5: Pyranoses vs. Furanoses

Classify each of the molecules shown below as either a pyranose ***or*** a furanose.

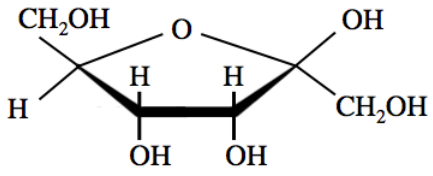
a.



b.



c.



For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

Review 11.6: Anomeric Carbon Identification

Identify the **anomeric carbon** in each of the molecules shown in the *previous review problem* (**Review 11.5**).

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

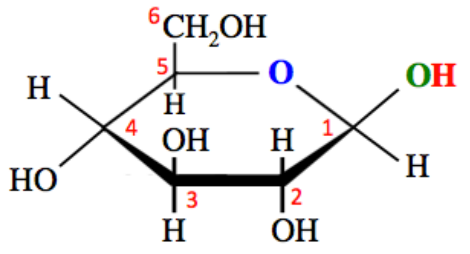
Review 11.7: Identification of β- and α-anomers.

Classify each of the molecules from **Review Problem 11.5** as either a β-anomer ***or*** an α-anomer.

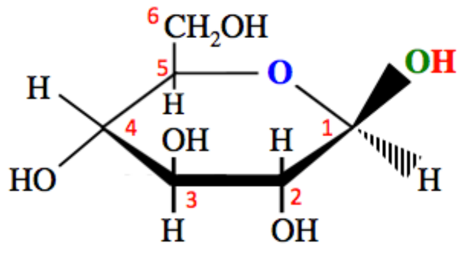
For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

Alternative Methods for Drawing Cyclic Forms of Monosaccharides

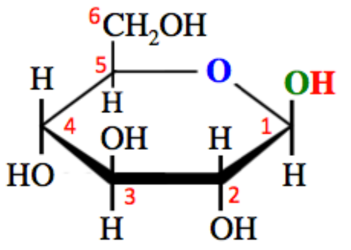
Some auto-grading systems for online problem sets may require you to use wedge and dash bonds to indicate their orientation (upward vs. downward) from *anomeric carbons* in Haworth projections. This is necessary in order for the auto-grader to determine if you have drawn the **α-anomer** or the **β-anomer** correctly. One other method for drawing Haworth projections, which you may encounter in other textbooks or online problems, uses vertical lines (straight up or down) for all of the bonds to ring-carbons. Below, I have drawn a Haworth projection of the **β-anomer of D-glucopyranose** using the method that you have seen so far (***left-most structure***), using wedge and dash bonds on the *anomeric carbon* (***middle structure***), and using vertical lines for bonds to all of the ring-carbons (***right-most structure***):



β-D-glucopyranose
drawn in the *style that*
I will use ***in this book***.

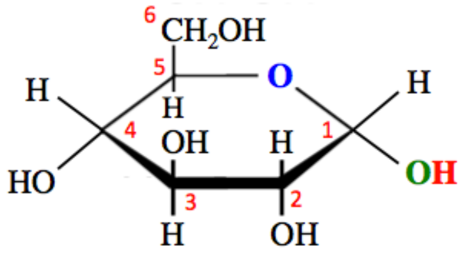


β-D-glucopyranose
drawn *using wedge and dash*
notation <u>at the anomeric carbon</u>.

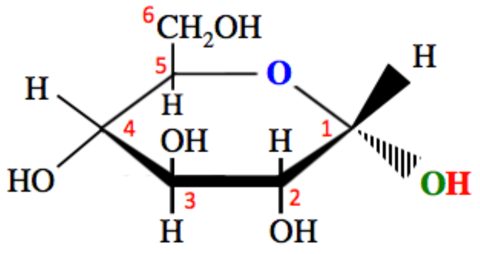


β-D-glucopyranose
drawn using vertical lines
for bonds to ring-carbons.

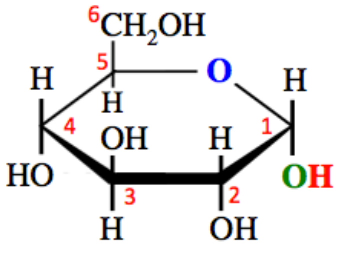
Note that in the wedge and dash method, the wedge (solid) represents a bond oriented in the upward direction relative to the anomeric carbon; the dashed bond represents a bond oriented in the downward direction. For a comparison of **α-** vs. **β-** for each of the Haworth projection styles, I have drawn the **α-anomer of D-glucopyranose** below using the three different styles.



α-D-glucopyranose
drawn in the *style that*
I will use ***in this book***.

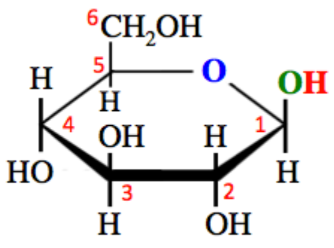


α-D-glucopyranose
drawn *using wedge and dash*
notation <u>at the anomeric carbon</u>.

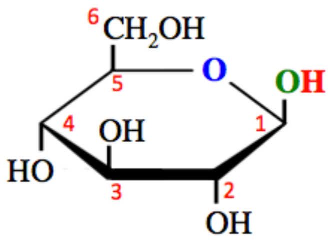


α-D-glucopyranose
drawn using vertical lines
for bonds to ring-carbons.

Sometimes, the *hydrogens* are not drawn for *ring-carbons*, as shown in the *right-most structure* of **β**-D-glucopyranose below.



all hydrogens drawn



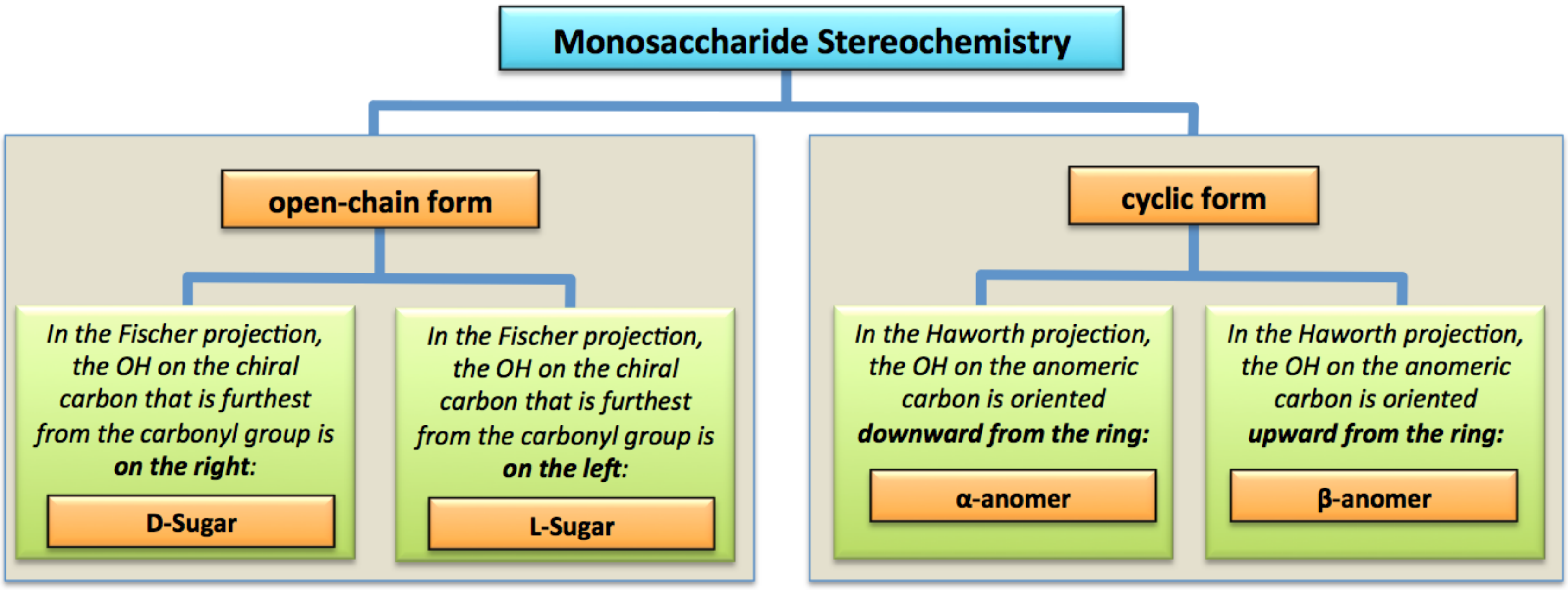
hydrogens bonded to
ring-carbons omitted

I have given you many details about the cyclization of monosaccharides in this section. I would like you to be able to do the following on an examination:

Given a **Haworth projection** of a **D-**monosaccharide:

1) Identify the molecule as a **pyranose** or a **furanose**.
2) Identify the **anomeric** carbon.
3) Identify the molecule as the **β-anomer** or the **α-anomer**.
4) Understand the definition of **mutarotation.**
5) Understand how the three-dimensional arrangement of atoms in a monosaccharide (as seen in a ball-and-stick model) is implied by a **Haworth projection**.

Summary of Monosaccharides Stereochemistry



Monosaccharide Stereochemistry

open-chain form

*In the Fischer projection, the OH on the chiral carbon that is furthest from the carbonyl group is **on the right**:*

D-Sugar

*In the Fischer projection, the OH on the chiral carbon that is furthest from the carbonyl group is **on the left**:*

L-Sugar

cyclic form

*In the Haworth projection, the OH on the anomeric carbon is oriented **downward from the ring:***

α-anomer

*In the Haworth projection, the OH on the anomeric carbon is oriented **upward from the ring:***

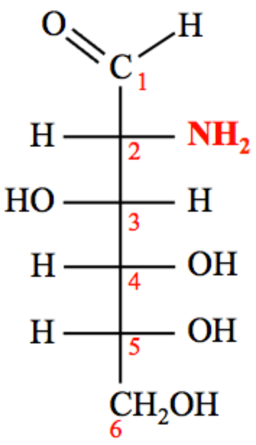
β-anomer

11.4 Monosaccharide Derivatives and Reactions

Monosaccharide derivatives are compounds that are derived from monosaccharides. In this section, I will introduce you to ***four*** classes of monosaccharide derivatives, some examples, and some of the reactions that produce them.

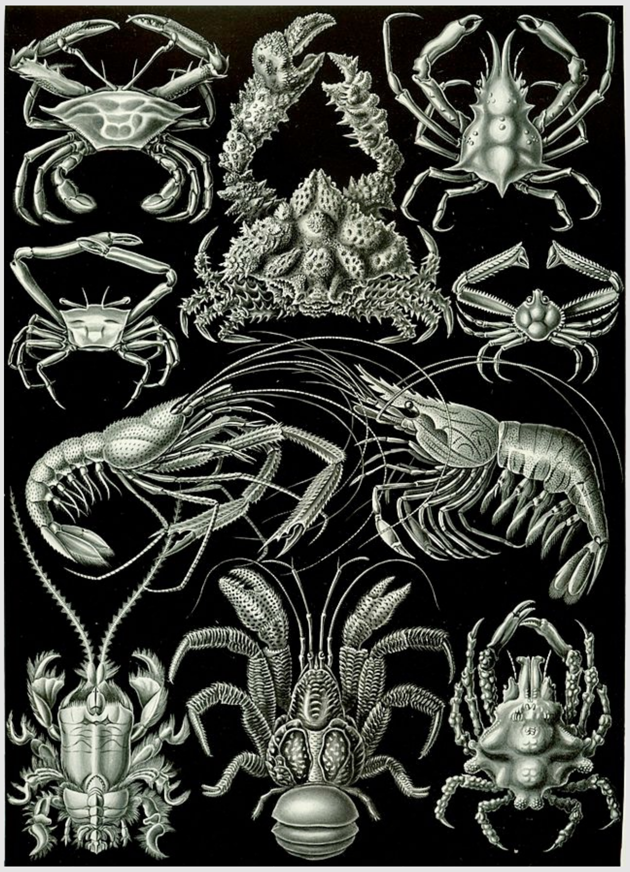
Amino Sugars

In an **amino sugar**, a hydroxyl group (**OH**) of a monosaccharide has been replaced by an ***amino group*** (**NH_2**). An example of an amino sugar is *D-glucosamine*. *D-Glucosamine* is derived when the hydroxyl group on carbon number **2** of *D-glucose* is replaced by an ***amino group***. The open-chain from of D-glucosamine is shown below.



D-glucosamine

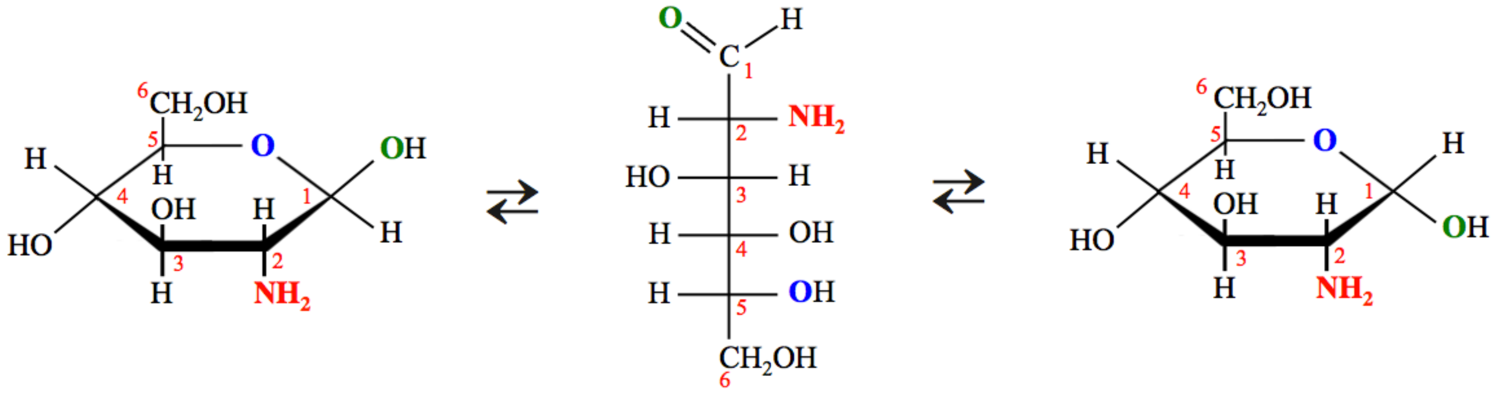
Figure 11.2 Some Crustaceans



The exoskeleton of crustaceans contain carbohydrate polymers that are made from monosaccharide derivatives (amino sugars).
Source: Ernst Haeckel's 1904 work published in Kunstformen der Natur, PD

Like monosaccharides, ***amino sugars*** undergo *mutarotation* as shown below:

mutarotation of *D-glucosamine*

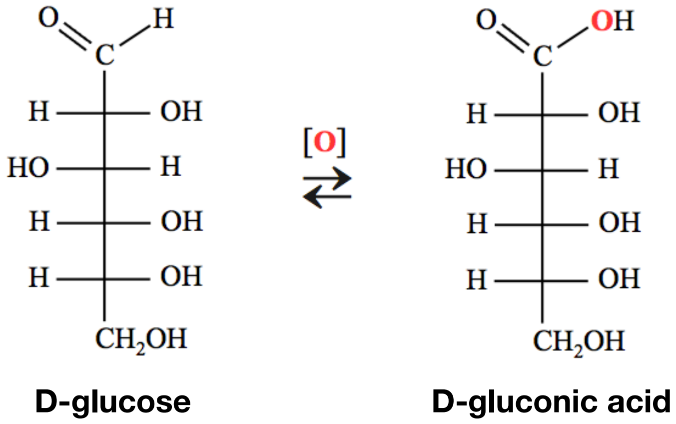


β-D-glucosamine **open-chain D-glucosamine** **α-D-glucosamine**

D-glucosamine is a precursor for the production of glycolipids. It is a component of the larger monosaccharide-containing polymers that make up the exoskeletons of crustaceans (e.g. shrimp, lobster, crab) and other arthropods. D-glucosamine is purified for commercial use by processing exoskeletons or other organic material that contains it. Although it has been deemed safe for human consumption and sold as a "dietary supplement," its ***actual effectiveness*** in the treatment of any health/medical condition, according to the US National Institutes of Health, ***has not been established***.

Carboxylic Acid Sugars

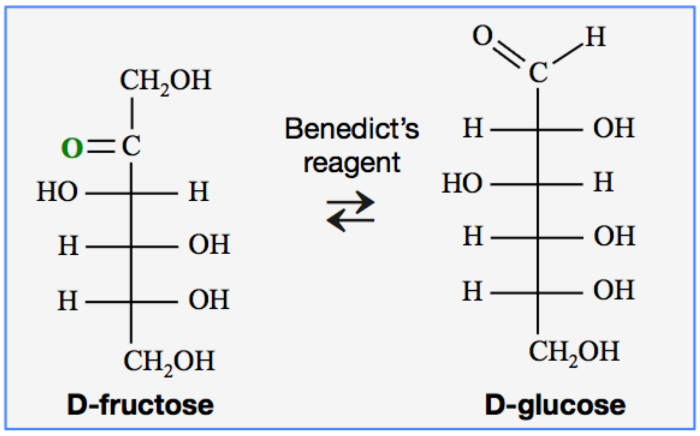
In a **carboxylic acid sugar**, an aldehyde group (**CHO**) of a monosaccharide has been replaced by a ***carboxyl group*** (**COOH**). This is done by a reaction that you have previously seen, ***oxidation*** of *aldehydes* to *carboxylic acids*. For example, the open-chain form of *D-glucose* can be oxidized to produce *D-gluconic acid*, as shown in the chemical equation below.



It is the ***open-chain form*** of glucose and other aldoses that undergo the oxidation reaction; the cyclic forms *do not* have an ***aldehyde group***. Even though the cyclic form is predominant in solution, it is in *equilibrium* with the open-chain form. Therefore, there are always some *open-chain forms* present to react with an oxidizing agent.

This *oxidation of aldoses* reaction was used for about 50 years in the measurement of blood sugar levels. Stanley Benedict first discovered and published a method in which a solution containing Cu^{2+} ions acts as an oxidizing agent in the conversion of ***aldoses*** to *carboxylic acid sugars*. This solution is now referred to as **Benedict's reagent**. It is used as a test for aldoses since it will oxidize the aldehyde groups *but not the hydroxyl groups* **or** the *ketone bonding patterns*. Benedict's reagent is a *basic* solution that contains Cu^{2+} ions. Cu^{2+} ions appear clear-blue when in solution. If a sample that contains an ***aldose*** is placed in a test tube that contains hot Benedict's reagent, the Cu^{2+} will be reduced to Cu^{1+}. The Cu^{1+} then reacts with hydroxide to form a colored solid. As the aldose concentration in a sample increases, more of the colored solid is made and the color of the Benedict's test goes from blue to green to orange to red to brown. Sugars that produce a color change in Benedict's reagent are called "reducing sugars," since they reduce Cu^{2+} to Cu^{1+}. When a color change is observed, we say that it is a "positive" test.

Although *fructose* is a ***ketose*** (*not an aldose*), it gives a positive Benedict's test result. The reason for this is that when fructose is in a hot basic solution, it will undergo either of two rearrangement reactions (shown below), in which it is converted to *glucose* or *mannose*. It is actually the *glucose* and *mannose* ***aldoses***, *not fructose*, that are subsequently oxidized to produce a color change in Benedict's test.



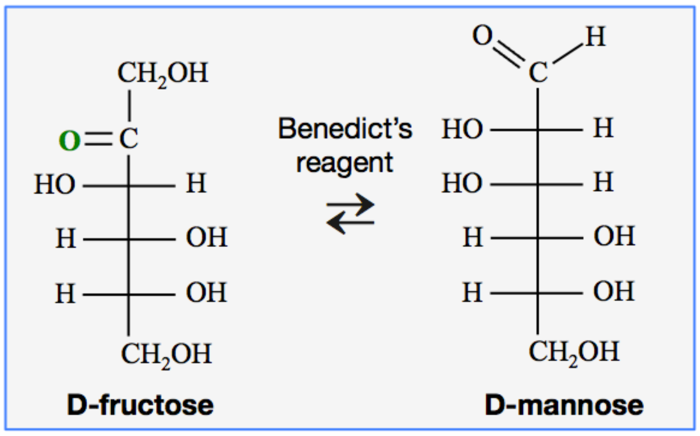


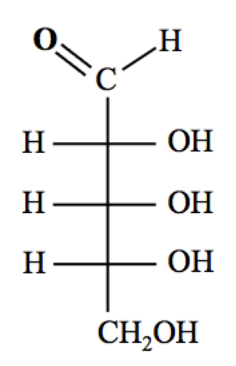
Figure 11.3
A Glucometer

A modern glucometer is very specific for D-glucose since it uses a naturally-occurring enzyme that will only oxidize D-Glucose.

Since Benedict's reagent is *not specific* for D-glucose, which is the important blood sugar species in diabetes monitoring, its use in most medical diagnostic work has been replaced by glucometers. Glucometers are much more specific than the Benedict's test in sensing ***only*** D-glucose. This is because glucometers use an enzyme (**g**lucose **o**xidase **d**ehydrogenase, GOD), which only catalyzes the oxidation of D-glucose.

Review 11.8: Oxidation of Monosaccharides: Carboxylic Acid Sugars

Draw the Fischer projection of the *carboxylic acid sugar* that is formed when the aldehyde group of D-ribose (shown below) is oxidized.

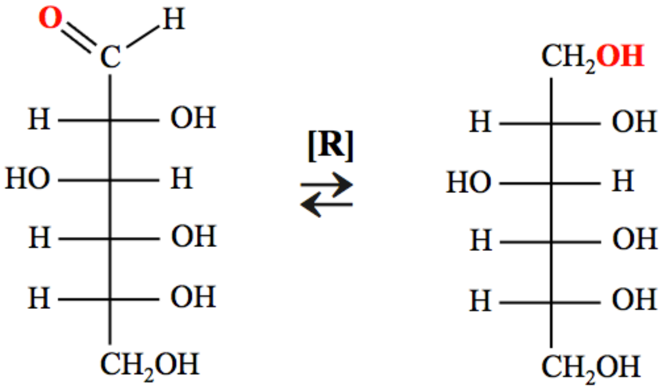


D-ribose

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

Alcohol Sugars

Alcohol sugars, sometimes called "***sugar alcohols***," are derived when the carbonyl group (**C=O**) of a monosaccharide is ***reduced*** to a hydroxyl group. This is done by a reaction that you have previously seen, ***reduction*** of *aldehydes* and *ketones* to *alcohols*. In chapter 10, you learned how to predict the structure of the alcohol formed in this reaction by adding H_2 "across" the carbonyl group's double bond. An example of the reduction of a monosaccharide (*D-glucose*) to form an *alcohol sugar* (*sorbitol*) is shown in the chemical equation below.

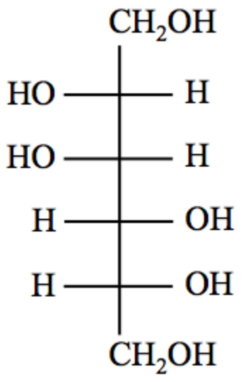


D-glucose

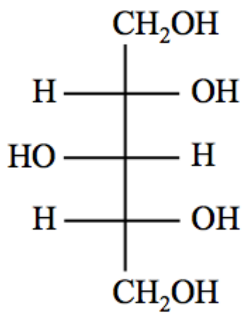
sorbitol
(an alcohol sugar)

Alcohol sugars are used in the food and beverage industry as thickeners and sweeteners. Unlike sugars, alcohol sugars cannot be metabolized by oral bacteria, and therefore do not cause tooth decay. Unfortunately for chefs, alcohol sugars do not caramelize, as do natural sugars. ***Sorbitol*** can be manufactured by the reduction of *D-glucose* and it also occurs naturally in pears, peaches, prunes, and apples. *Sorbitol* is used as a sugar substitute, mostly to replace natural sugars in order to prevent tooth decay. It is not so effective as a dietary aid because it can be metabolized by humans for energy. On a per gram basis, it provides 65% of the energy of natural sugars, yet is only 60% as sweet as table sugar (*sucrose*). *Sorbitol* is used in toothpaste, mouthwash, and chewing gum. It is also used, in greater quantities, as an orally or rectally administered laxative.

Other examples of alcohol sugars are *mannitol* and *xylitol*:



mannitol

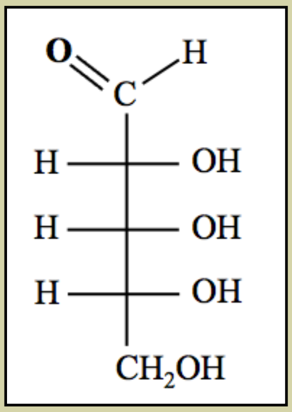


xylitol

Mannitol is used as a sweetener and has many applications in medicine. It is frequently used as a filler in the production of tablets of medicine. *Xylitol* is used as a sweetener in chewing gum. Like other alcohol sugars, it is unusable by oral bacteria. However, unlike the other alcohol sugars, *xylitol* aids in the recalcification of teeth.

Review 11.9: Reduction of Monosaccharides: Alcohol Sugars

Draw the Fischer projection of the **alcohol sugar** that is formed when D-ribose (shown below) is **reduced.**

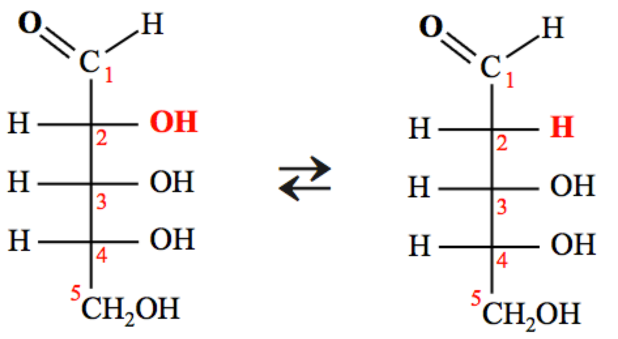


D-ribose

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

Deoxy Sugars

Deoxy sugars are derived when a hydroxyl group (**OH**) in a monosaccharide is replaced by a ***hydrogen atom***. For example, D-*2-deoxyribose* (a deoxy sugar) is derived when the hydroxyl group on carbon number 2 of D-ribose (a monosaccharide) is replaced by a hydrogen atom:

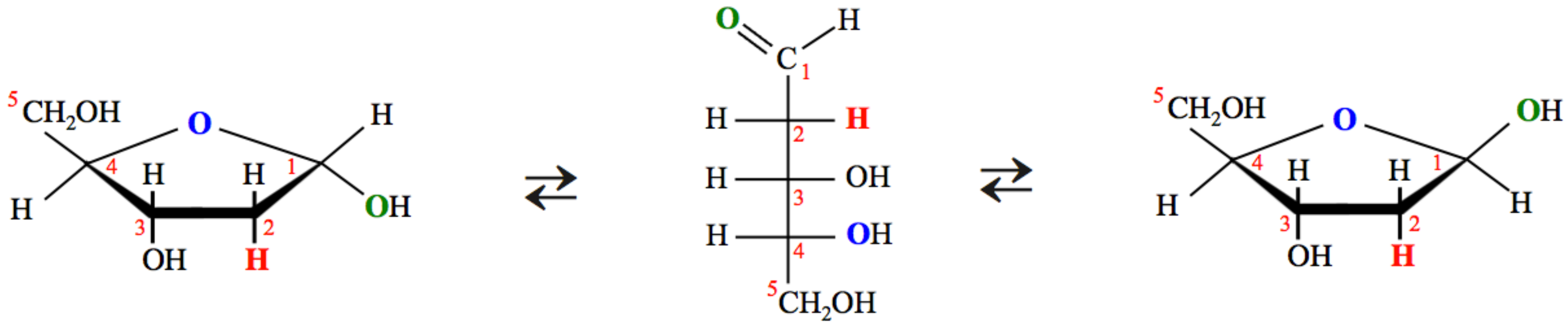


D-ribose
(a monosaccharide)

D-2-deoxyribose
(a deoxy sugar)

The "2" in D-2-deoxyribose indicates the carbon position where a hydrogen (**H**) replaces a hydroxyl group (**OH**) of the D-ribose monosaccharide.

Like monosaccharides, ***deoxy sugars*** undergo *mutarotation* as shown below:

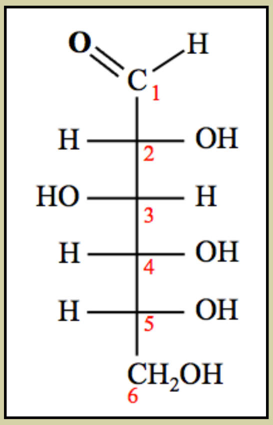


α-D-2-deoxyribofuranose **D-2-deoxyribose** **β-D-2-deoxyribofuranose**

D-2-deoxyribofuranose is one of the residues that make deoxyribonucleic acids (DNA). One of the differences between DNA and RNA (ribonucleic acid) is that RNA contains D-ribofuranose, whereas DNA contains D-2-deoxyribofuranose. You will learn much more about DNA and RNA in chapter 14.

Review 11.10: Deoxy Sugars

D-2-deoxyglucose is currently being used in the development of anticancer strategies. Using the Fischer projection of **D-glucose** (shown below) as the *starting point*, draw the **Fischer projection** of D-2-deoxyglucose.



D-glucose

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

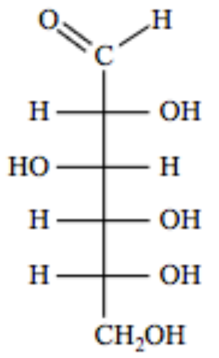
Table for the Review of Monosaccharide Derivatives

Monosaccharide Derivative	Defining Structural Trait
Amino Sugar	A hydroxyl group (OH) of a monosaccharide is replaced by an amino group (NH_2)
Carboxylic Acid Sugar	The aldehyde group (CHO) of an aldose is oxidized to a carboxyl group (COOH).
Alcohol Sugar	The carbonyl group of a monosaccharide is reduced to a hydroxyl (OH) group.
Deoxy Sugar	A hydroxyl group (OH) of a monosaccharide is replaced by a hydrogen.

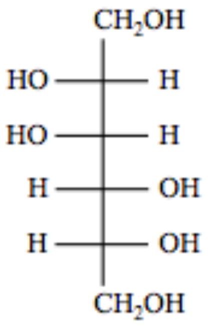
Review 11.11: Identification of Monosaccharides and Monosaccharide Derivatives

Identify each of the molecules shown below as either a monosaccharide, amino sugar, carboxylic acid sugar, alcohol sugar, or a deoxy sugar.

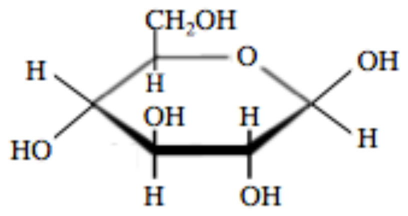
a.



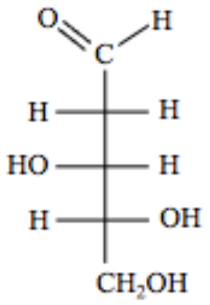
b.



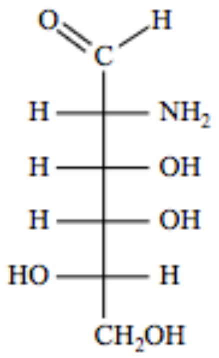
c.



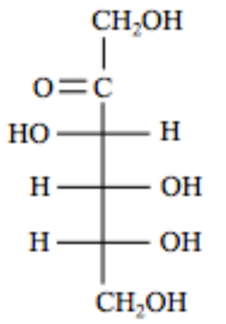
d.



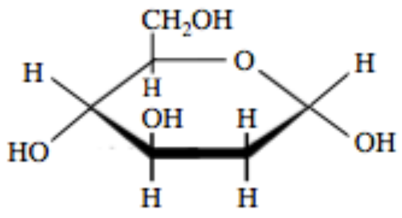
e.



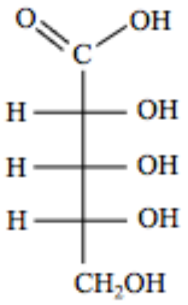
f.



g.



h.



For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

11.5 Oligosaccharides

Carbohydrates can be classified into three major groups based on their size: *monosaccharides, oligosaccharides, and polysaccharides.* **Oligosaccharides** are molecules that are made when ***two*** to ***ten*** monosaccharides chemically bond to each other. Molecules from particular organic families (such as monosaccharides) are referred to as "**residues**" when they bond together to form a large molecule. Oligosaccharides are often subcategorized by the number of monosaccharide ***residues*** that they contain. For example, an oligosaccharide that is composed of ***two*** monosaccharide *residues* is called a **disaccharide**. Likewise, an oligosaccharide made from ***three*** monosaccharide *residues* is called a **trisaccharide.**

The Glycosidic Bond

I will begin this section by introducing you to the bonding pattern in which monosaccharide residues are bonded to each other. Let's begin by considering the bond formed between two **α**-D-glucose monosaccharides. For the remainder of this chapter, I will sometimes use **large black dots** at the position of the ***anomeric carbons*** in order to draw your attention to them.

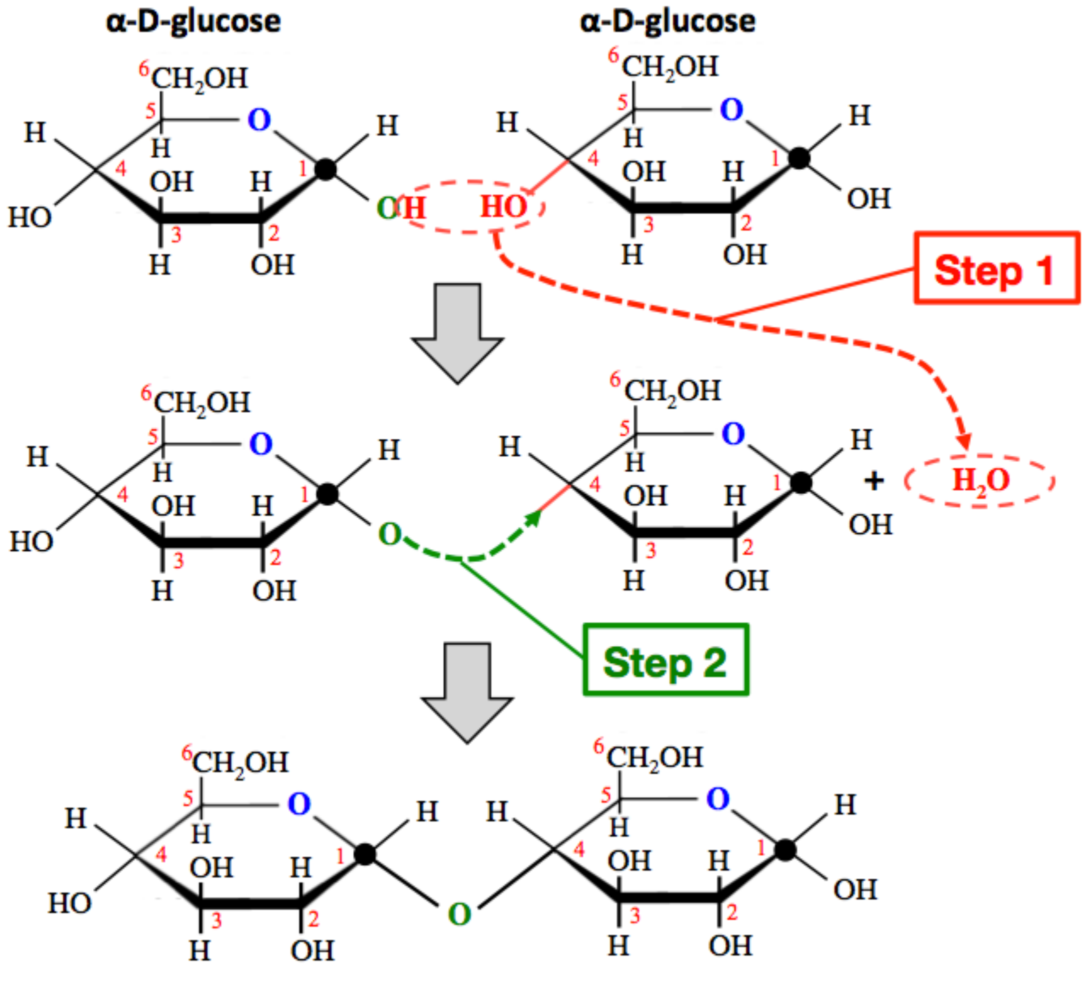
Step 1: An **H** atom is removed from the hydroxyl group (**OH**) ***that is bonded to the anomeric carbon*** of the left-most residue, and an **OH** is removed from ***any carbon*** in the right-most residue.

- In this example, the **OH** is removed from carbon number **4** of the right-most sugar residue.

The **H** and **OH** that were removed form a water molecule.

Step 2: Draw a ***new bond*** **from** the oxygen (**O**) that remains on the *anomeric carbon* in the left-most residue (shaded green in the illustration) **to** the carbon from which the **OH** was removed in the right-most residue. This ***new bond*** is oriented in the same direction as *was* the bond to **OH** that was removed.

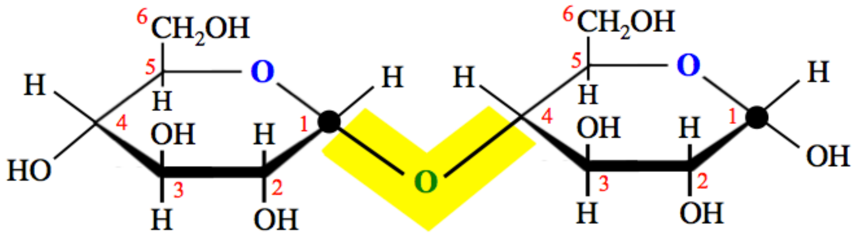
This method can be used to form a bond ***between any two sugar residues***.



maltose (a disaccharide)

The *disaccharide* that is formed when the anomeric carbon of **α**-D-glucose is linked to carbon number **4** of a second D-glucose residue (as in the illustration above) is called **maltose.** *Maltose* is found in malt, which is purified from germinated grains. Brewers interrupt the barley grain germination to obtain what is referred to as *malted barley*. Malted barley has a high concentration of *maltose*, which is fermentable, and therefore used in making beer and some other adult beverages. It is also used as a sweetener and thickener in frozen beverages called "malts."

The covalent bonding pattern linking the ***anomeric carbon*** of one residue to an oxygen, then to a carbon in the ***other*** sugar residue is referred to as a **glycosidic bond** (even though it actually contains ***two*** single bonds). I have highlighted the glycosidic bond (yellow) in the drawing of *maltose* shown below.



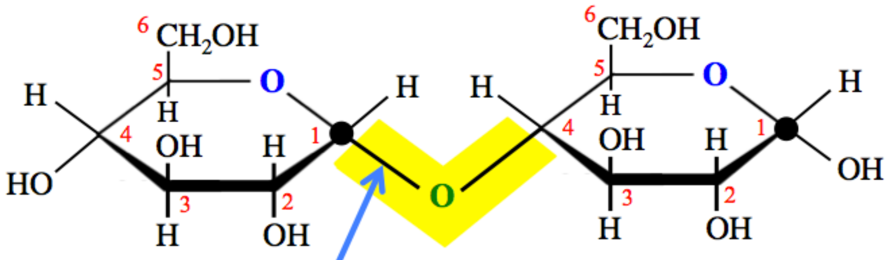
Glycosidic bonds are described using **alpha (α)** or **beta (β)** designations based on the orientation (stereochemistry) of the ***glycosidic bond*** *relative to the anomeric carbon*. This is done in a manner similar to the **α** and **β** designations for cyclic monosaccharides, which was based on the orientation of the ***hydroxyl group*** relative to the anomeric carbon.

For glycosidic bonds:

- The **alpha (α)** designation indicates that the bond ***from the anomeric carbon to the oxygen* (O) *in the glycosidic bond*** is oriented ***downward*** from the ring.
- The **beta (β)** designation indicates that the bond ***from the anomeric carbon to the oxygen* (O) *in the glycosidic bond*** is oriented ***upward*** from the ring.

A glycosidic bond is characterized by its **α**/**β** orientation, ***and*** a description of ***which two carbons are linked*** by the glycosidic bond. For example, the glycosidic bond in *maltose* is classified as **α-(1⟶4).**

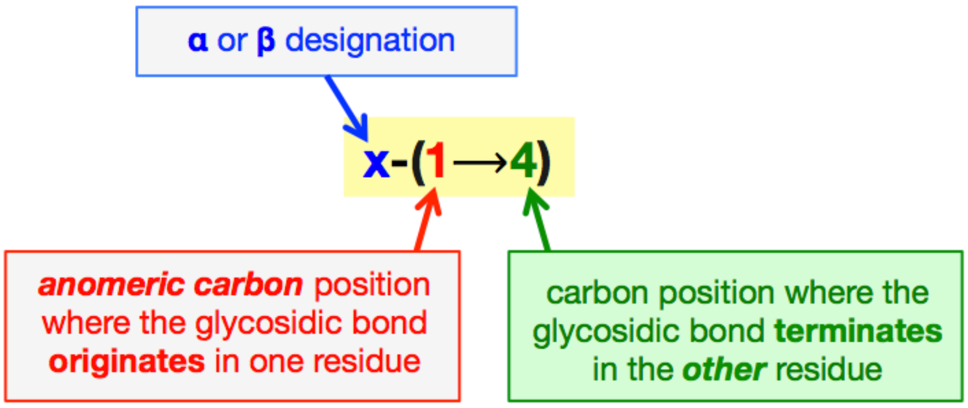
an α-(1⟶ 4) glycosidic bond



Maltose has the **"α"** designation because the bond ***from the anomeric carbon to the oxygen* (O) *of the glycosidic bond*** is oriented ***downward*** from the ring.

Maltose has the **(1⟶4)** designation because the ***glycosidic bond*** links the *anomeric* carbon (carbon number **1**) to carbon number **4** of the *other* residue.

The numbers and arrow that are seen in the parenthesis (the "1⟶4" in the case of *maltose*) begins with the position number of the ***anomeric carbon*** where the glycosidic bond **originates**, then the arrow followed by the carbon position number where the glycosidic bond **terminates** in the ***other*** residue.



α or **β** designation

x-(1⟶4)

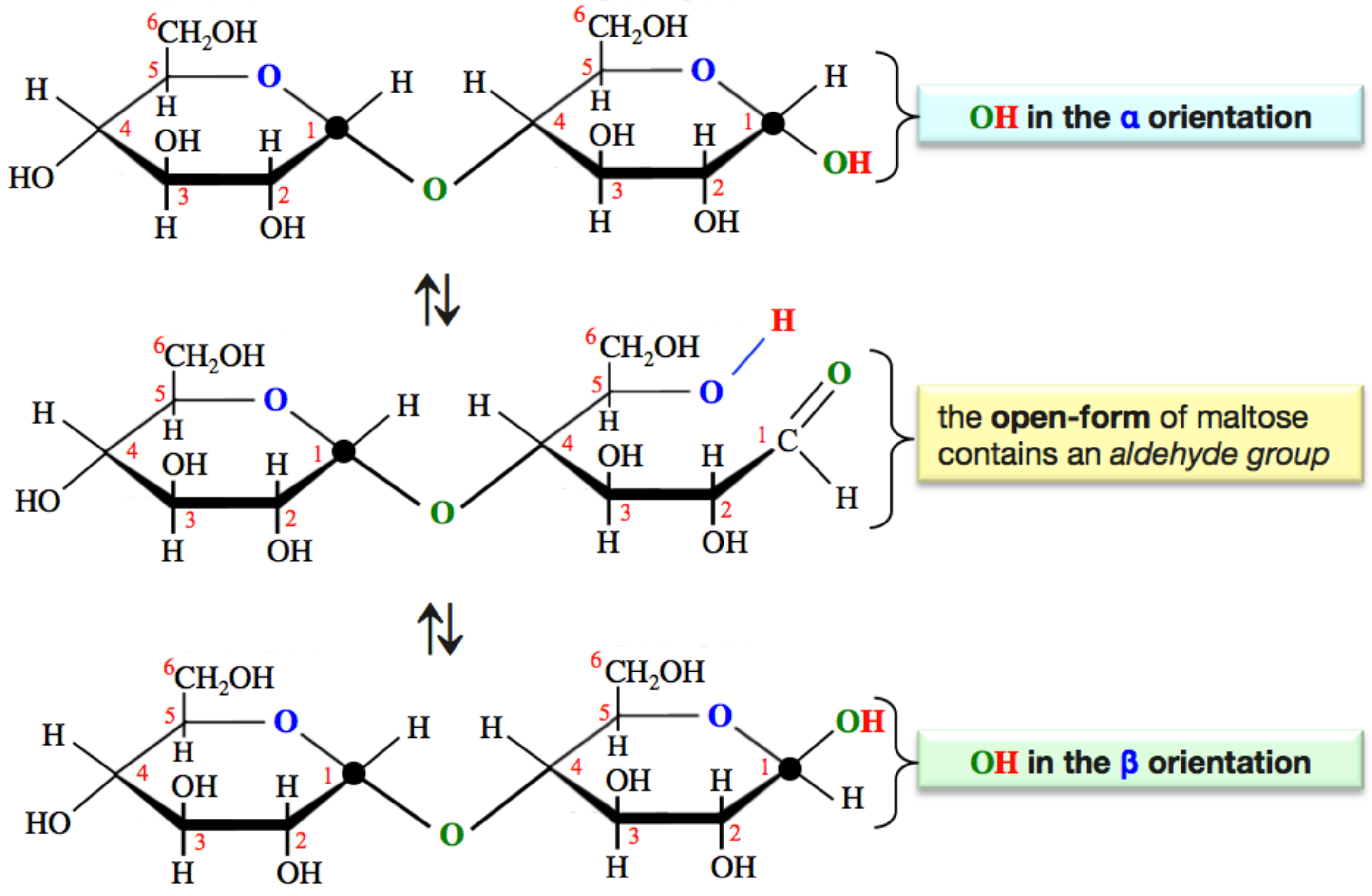
anomeric carbon position where the glycosidic bond **originates** in one residue

carbon position where the glycosidic bond **terminates** in the ***other*** residue

Note that the glycosidic bond in *maltose* has the **α** designation because it is formed from the **α**-anomers: two **α**-D-glucose monosaccharides. Later in this section, you will see that when a glycosidic bond is formed between two **β**-anomers, it will have the β orientation.

Note that the *anomeric carbon* on the left-most residue in *maltose* (shown below) is no longer a *hemiacetal carbon*. That carbon is still bonded to an OR, however it is no longer bonded to an OH. Since it is no longer a hemiacetal, it can no longer interconvert between open-chain and cyclic forms. It is "locked" in the cyclic form. This is ***not the case*** for the anomeric carbon in the ***right-most*** residue; it is a *hemiacetal* and can therefore undergo mutarotation as shown below.

mutarotation of maltose



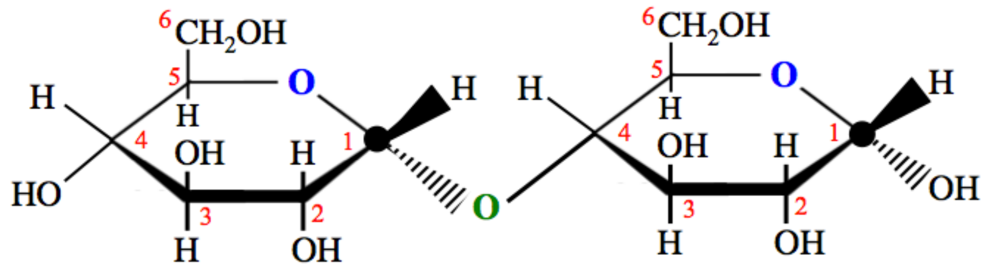
OH in the α orientation

the **open-form** of maltose contains an *aldehyde group*

OH in the β orientation

Oligosaccharides, such as maltose, *with a residue that contains a hemiacetal anomeric carbon* will interconvert between closed anomers and an open-form. Mutarotation does not change the **α**/**β** orientation of the **glycosidic bond**. If the open-form of an oligosaccharide contains an aldehyde group, it will give a positive Benedict's test.

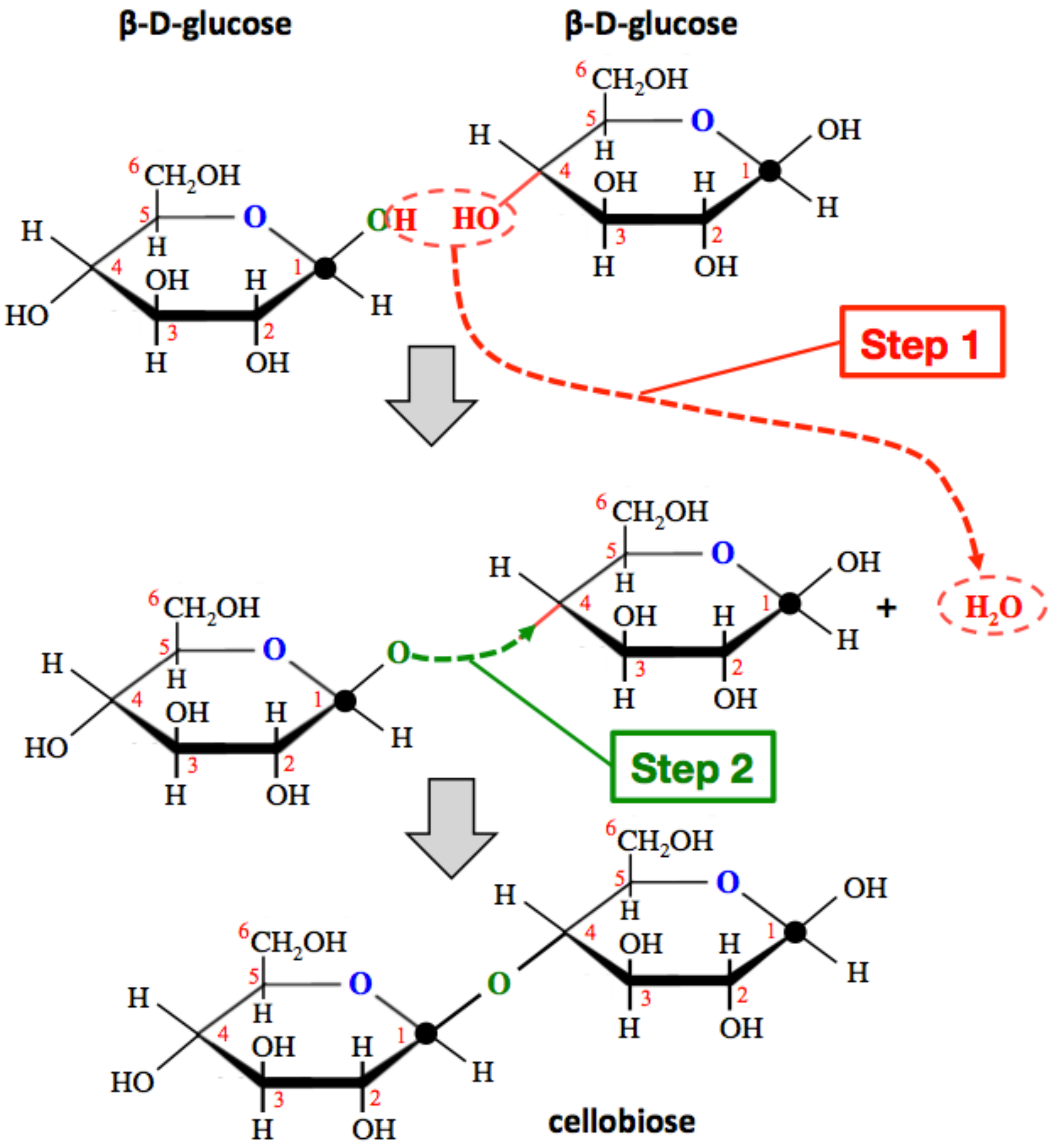
Some online problem auto-graders will require that you use the wedge and dash bonds to indicate the stereochemistry (**α**/**β**) at the anomeric carbons (only). In this case, the *maltose* disaccharide would be drawn as shown below.



maltose drawn with wedge and dash notation at the chiral carbons (only)

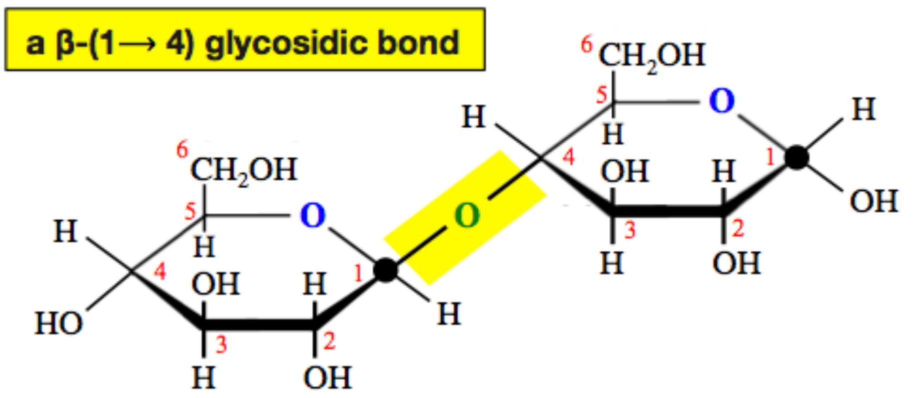
Since the anomeric carbon in the ***right-most*** residue is a hemiacetal and undergoes mutarotation, the orientation of the the OH and H that are bonded to it constantly changes. I *arbitrarily* chose to draw the *right-most* residue with the the OH in the **α** orientation; it would have been *equally correct* to draw that OH in the **β** orientation.

Let’s now visualize the way that a glycosidic bond connects two **β**-D-glucose monosaccharides in the illustration below.



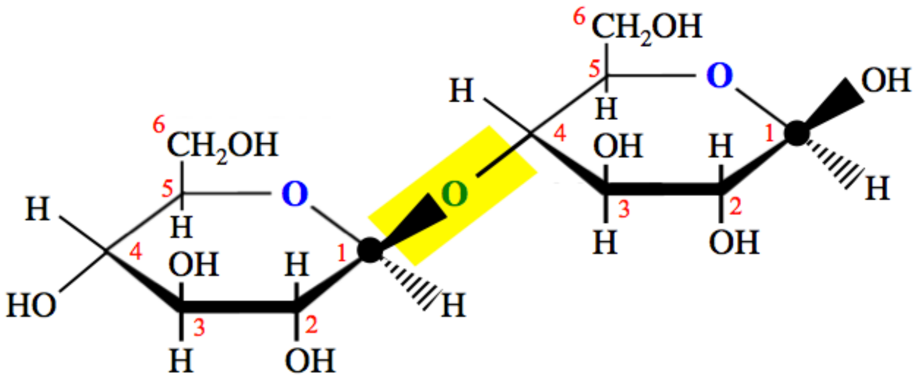
The *disaccharide* that is formed when the anomeric carbon of **β**-D-glucose is linked to carbon number 4 of a second D-glucose residue (as in the illustration above) is called ***cellobiose***.

Note that since we began with **β-**anomers of the monosaccharides, the glycosidic bond, necessarily, has the **β** orientation. The **beta (β)** designation indicates that the bond ***from the anomeric carbon to the oxygen*** (O) ***in the glycosidic bond*** is oriented ***upward*** from the ring. The glycosidic bond in *cellobiose* is classified as **β-(1⟶4).**



Cellobiose has the **“β”** designation because the bond ***from the anomeric carbon to the oxygen*** (O) ***of the glycosidic bond*** is oriented ***upward*** from the ring.

For online problem auto-graders that require you to use the wedge and dash bonds from the anomeric carbons, the *cellobiose* disaccharide should be drawn as shown below.

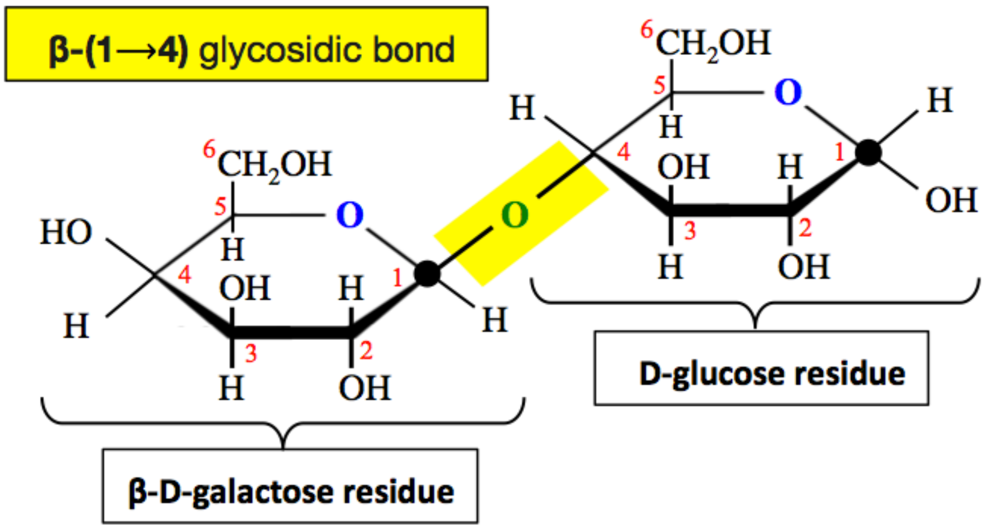


cellobiose drawn with wedge and dash notation at the chiral carbons (only)

The anomeric carbon in the ***right-most*** residue undergoes mutarotation. I *arbitrarily* chose to draw the *right-most* residue with the **OH** in the **β** orientation; it would have been *equally correct* to draw that **OH** in the **α** orientation

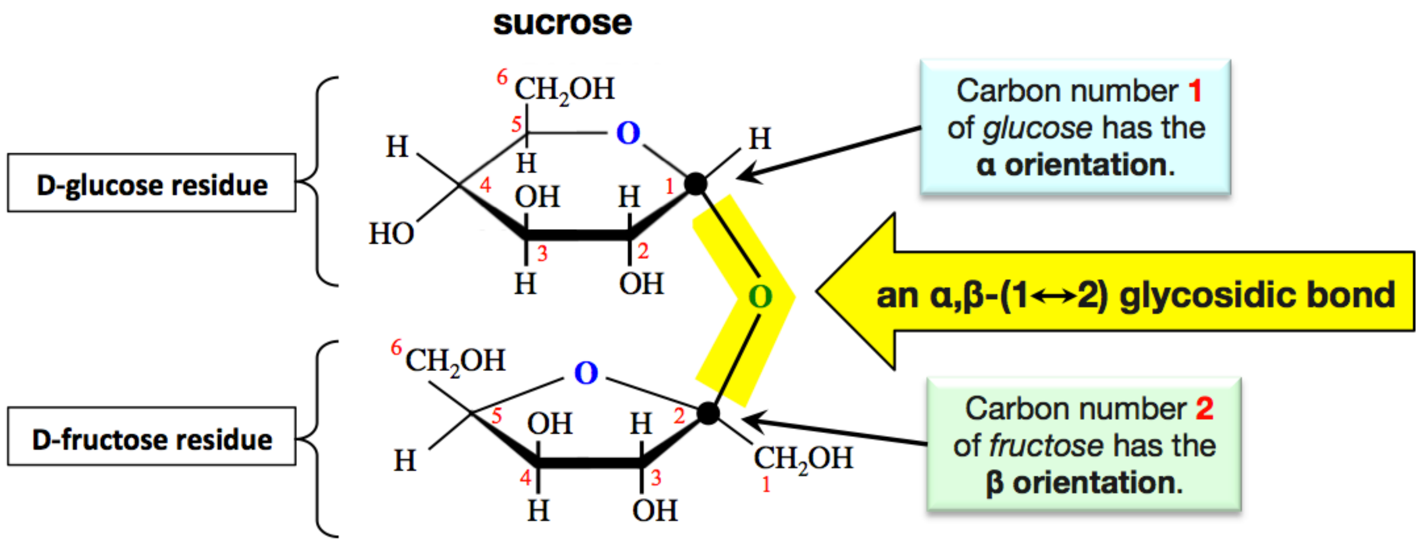
Lactose is a disaccharide that contains a β-D-galactose residue bonded to a D-glucose residue by a **β-(1⟶4)** glycosidic bond.

lactose



Most of us have an enzyme, called lactase, that will break *galactose*-glucose **β-(1⟶4)** glycosidic bonds so that we can digest and metabolize *lactose*. Lactose is a nutrient that is found in milk and dairy food made from milk. A small percentage of individuals are born with a mutation in the gene that is responsible for the production of the lactase enzyme, and are therefore unable to metabolize lactose. This condition is called **congenital lactose intolerance**. In many mammals, including humans, production of the lactase enzyme ceases at a very young age, this condition is known as **primary lactose intolerance**. Over the last five to ten thousand years, human populations have evolved a genetic variant in a “lactose persistence DNA sequence” that allows them to continue to produce the lactase enzyme, and therefore continue *lactose* metabolism into adolescence and adulthood. The presence of this DNA variation was evolutionally beneficial and has spread to about half of the world’s population. Individuals who lack the lactose persistent DNA variation suffer from *primary lactose intolerance*. Both congenital and primary lactose intolerance results in the build-up of undigested lactose in the large intestine. Intestinal bacteria ferment the lactose and produce gases such as carbon dioxide, hydrogen, and methane. The presence of these gases is quite uncomfortable since it results in flatulence and bloating. In order for individuals with lactose intolerance to enjoy dairy foods, they can add the lactase enzyme (produced by fungi or yeast) directly to their food or ingest it in tablet form. Milk that has been supplemented with the yeast lactase enzyme is sold in many countries for lactose intolerant consumers.

Sucrose, also referred to as “*table-sugar*” or just “*sugar*,” is a *disaccharide* formed from an α-D-glucose residue and a β-D-fructose residue. Its glycosidic bonding pattern is a bit different from the ones that you have seen so far because it involves ***two*** *anomeric carbons*. The glycosidic bond in *sucrose* links the *anomeric carbon* in the *glucose* residue to the *anomeric carbon* in the *fructose* residue:



sucrose

Carbon number **1** of *glucose* has the **α orientation.**

an α,β-(1⟷2) glycosidic bond

Carbon number **2** of *fructose* has the **β orientation.**

Note that the *anomeric carbon* in the D-fructose residue is carbon number **2** (the anomeric carbon for D-sugars is ***always*** the ring-carbon that is to the right of the ring-oxygen in Haworth projections). The glycosidic bond in *sucrose* is classified as **α,β-(1⟷2)**. This is because the stereochemistry at the anomeric carbon of the *glucose* residue (position number **1**) has the **α** orientation, and the anomeric carbon of the *fructose* residue (position number **2**) has the **β** orientation. The double arrow (⟷) used in this notation indicates that the glycosidic bond is between *two* ***anomeric*** carbons.

Since the glycosidic bond in *sucrose* links the *anomeric carbon* of one residue to the *anomeric carbon* of the other residue, ***neither of these anomeric carbons are hemiacetal carbons***. Since neither residue contains a hemiacetal carbon, they cannot interconvert/mutarotate between open-chain and cyclic forms. Both residues are “locked” in their cyclic forms. For this reason, *sucrose*, *unlike* the other disaccharides that you have seen, will give a ***negative*** Benedict's test and is therefore *not* classified as a **reducing sugar**.

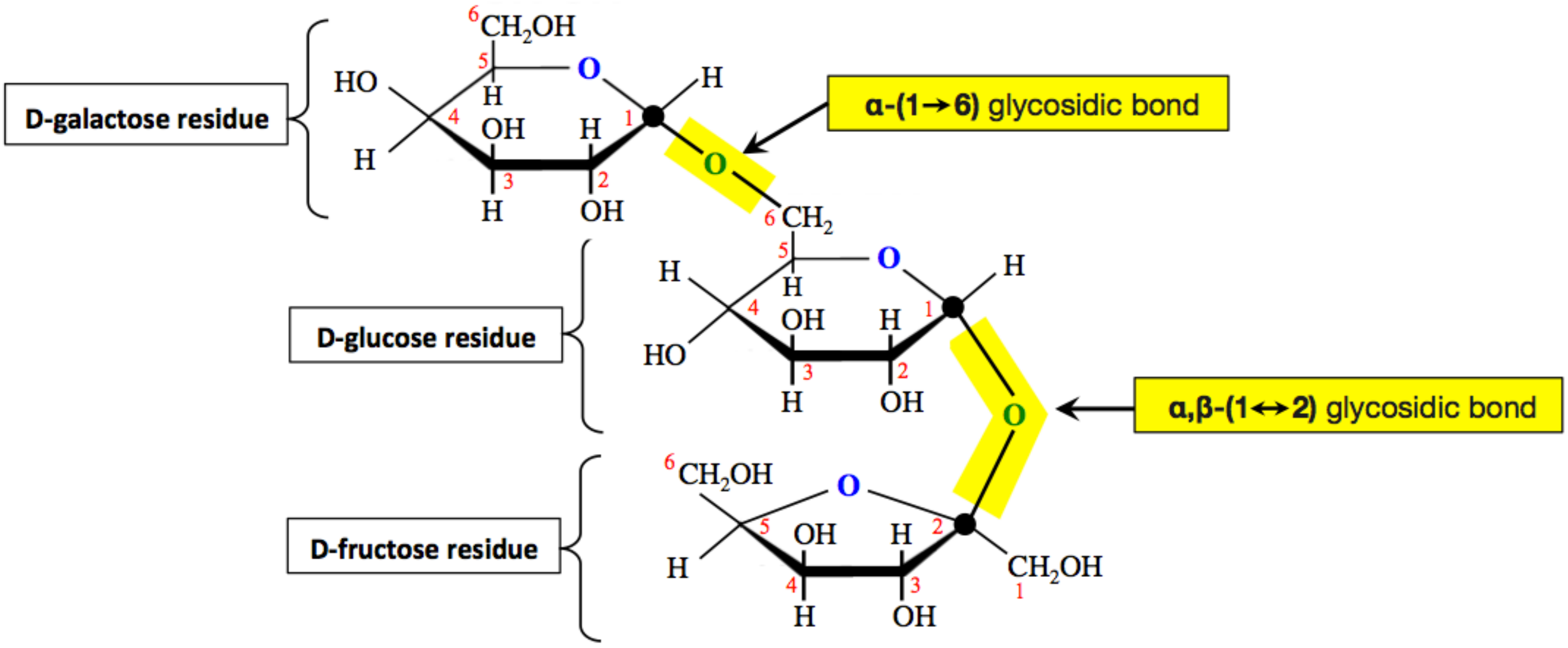
Sucrose is consumed in relatively large quantities because of its desired “sweet” taste. It is manufactured by purification from sugar cane or sugar beets (Figure 11.4). Overconsumption of sucrose has been linked to tooth decay and obesity.

Figure 11.4 **Sugar Cane and Sugar Beets**

Left: Cut and bundled sugar cane.
Right: Illustration of the sugar beet plant and root. Sucrose is extracted from the root of the sugar beet.
Source: Wikimedia Commons, Author: Rufino Uribe, CC-BY, http://creativecommons.org/licenses/by/2.0/legalcode

Examples of oligosaccharides that contain ***more than two*** monosaccharide residues are ***raffinose*** and ***stachyose***. ***Raffinose*** is categorized as a **trisaccharide** because it contains ***three*** monosaccharide residues. It is made from a *galactose*, a *glucose*, and a *fructose* residue, bonded to each other as shown below.

raffinose



Note that *raffinose* contains an **α-(1⟶6)** glycosidic bond, which you have not seen in previous examples. This glycosidic bond connects carbon number **1** of D-galactose, an anomeric carbon, with carbon number **6** of D-glucose.

Stachyose is categorized as a **tetrasaccharide** because it contains ***four*** monosaccharide residues. It is made from ***two*** *galactose* residues, a *glucose* residue, and a *fructose* residue, bonded to each other as shown below.

stachyose

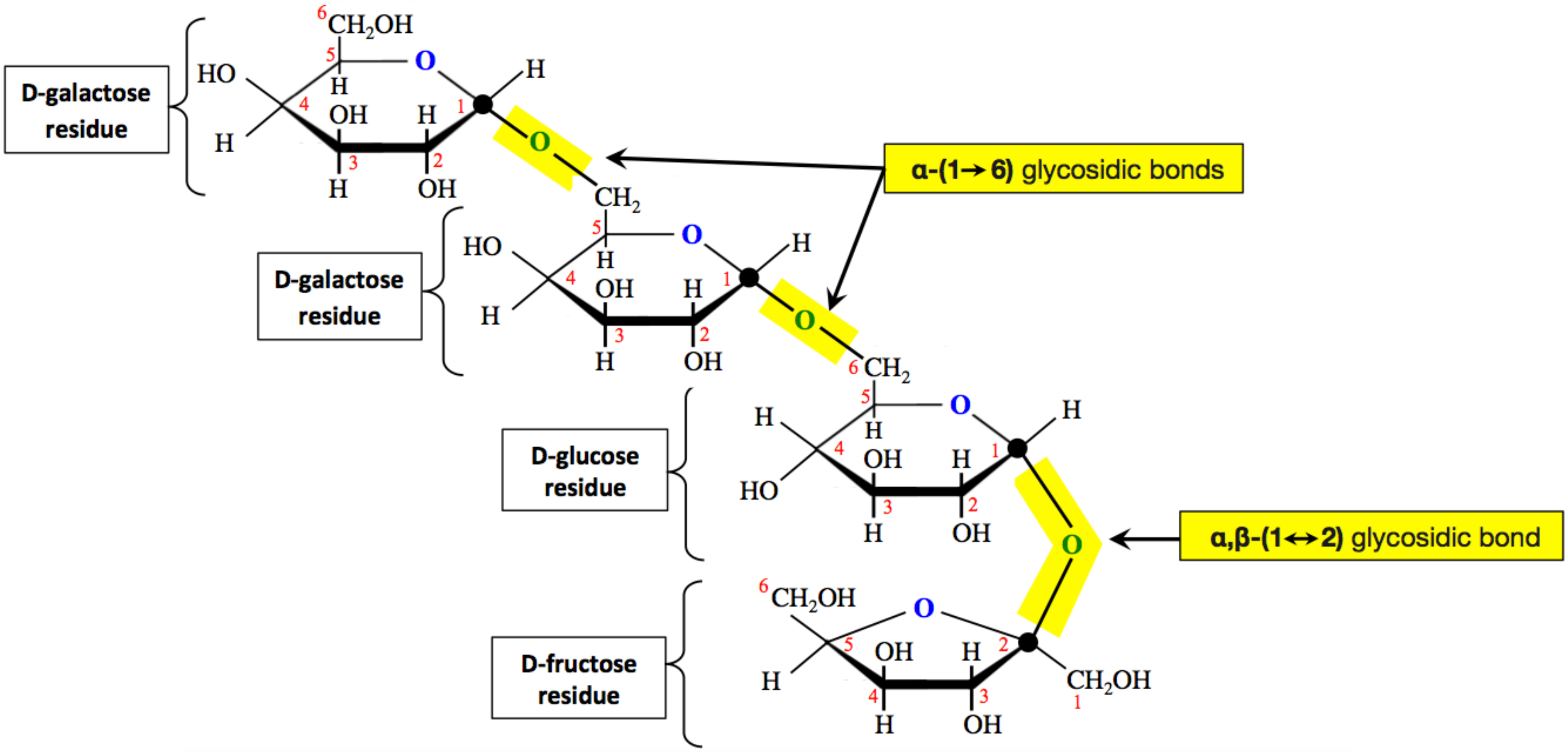


Figure 11.5 Beano Dietary Supplement

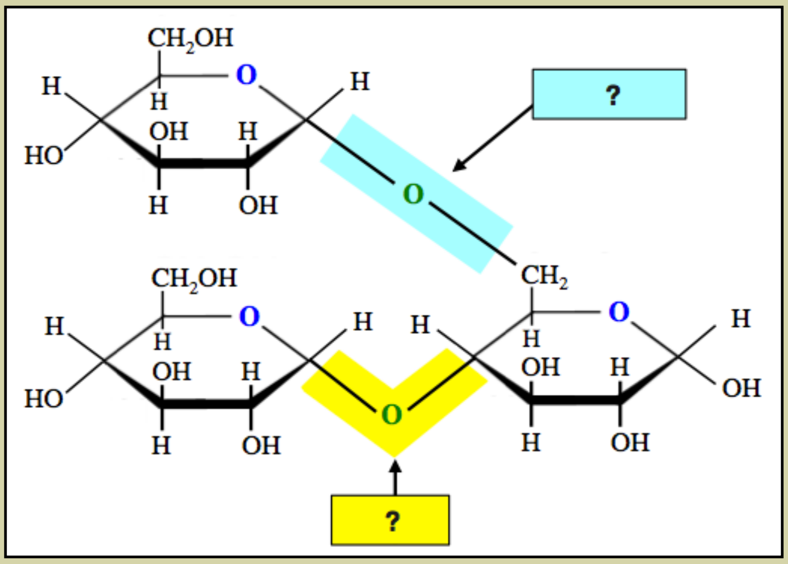
Source: Beanogas.com

Raffinose and *Stachyose* are found together in many foods, most notably legumes (e.g. beans and peanuts) and cruciferous vegetables (e.g. broccoli, cauliflower, brussels sprouts, and cabbage). Monogastric (single stomach) animals, including humans, pigs, and poultry, cannot completely digest *raffinose* or *stachyose* because we do not have the enzyme, α-galactosidase (α-GAL), that is needed to break their α-galactose glycosidic bonds. Since *raffinose* and *stachyose* pass through the digestive track without being completely digested, they can be fermented by digestive microbes to produce gases. To avoid the discomfort of bloating and flatulence associated with such gases, the α-GAL enzyme can be taken as a nutritional supplement (marketed by Prestige Holdings Inc. using the brand name of Beano, Figure 11.5).

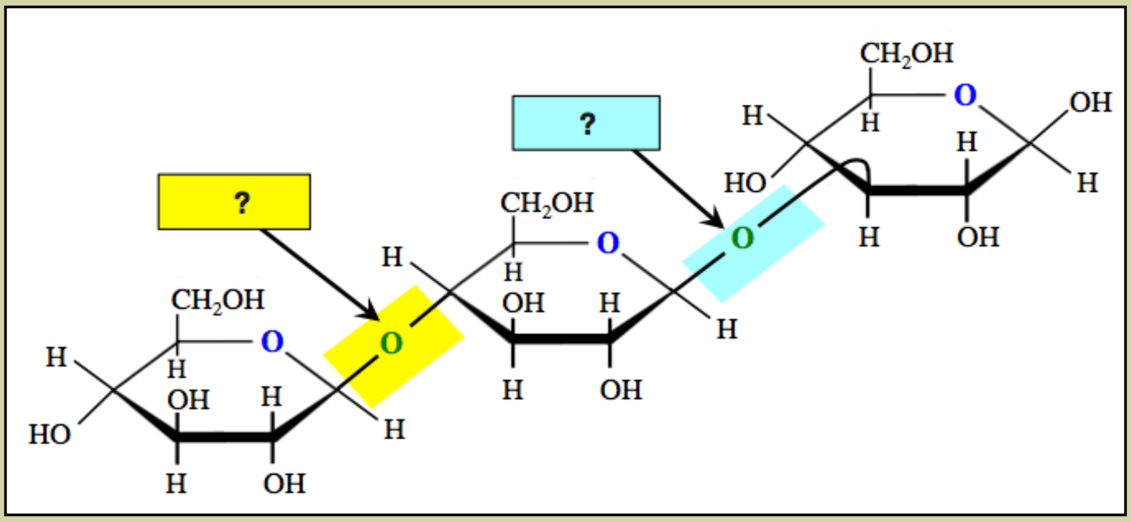
Review 11.12: Alpha (α) and Beta (β) Designations for Glycosidic Bonds

Classify each of the highlighted glycosidic bonds using the **alpha "α-(?⟶?)"** *or* **beta "β-(?⟶?)"** designation.

a.



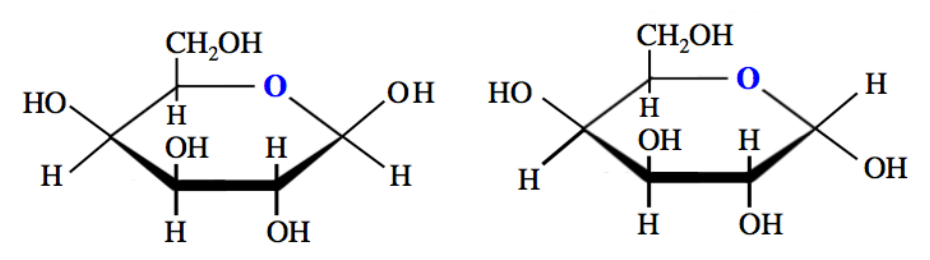
b.



For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

Review 11.13: Glycosidic Bonds

Draw the disaccharide that is formed when the two monosaccharide molecules below are connected by a **β-(1⟶4)** glycosidic bond.



For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

Review 11.14: Glycosidic Bonds

Draw the disaccharide from the **previous** review problem (**Review 11.13**) using wedge and dash notation at the anomeric carbons (only).

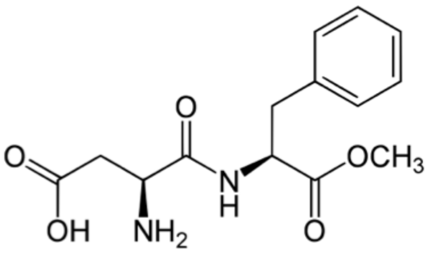
For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

Sweeteners

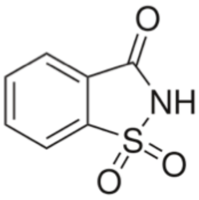
A sweetener is a compound that is added to food in order to impart the sweet taste of sucrose, but with significantly fewer calories. Sweeteners can be classified as "**artificial sweeteners**" or "**natural sweeteners**." *Natural sweeteners* are carbohydrates, naturally occurring carbohydrate derivatives, or other naturally occurring non carbohydrate compounds. *Artificial sweeteners* do not occur in nature; they are synthesized in commercial laboratories. The structural formulas of some artificial sweeteners are shown below.

Figure 11.6 Packaged Sweeteners

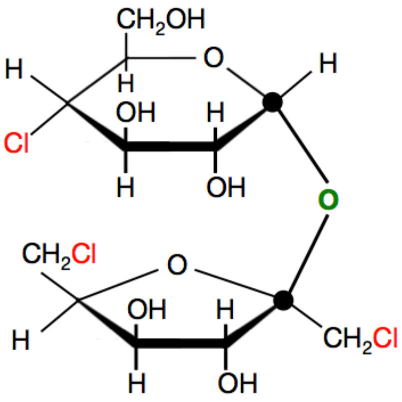
Many restaurants offer a variety of sucrose alternatives. Frequently encountered brand names include Splenda, Sweet'N Low, Nutrasweet, and Equal. Source: Wikimedia Commons, Author: Allie_Caulfield, CC-BY, http://creativecommons.org/licenses/by/2.0/legalcode



aspartame
(Equal, NutraSweet)



saccharin
(Sweet'N Low)



sucralose
(Splenda)

Sucrose is the reference standard for “sweetness.” A “sweetness value” of 100 is assigned to sucrose, and then other sweeteners are assigned sweetness values relative to the taste of the same mass of sucrose. Table 11.2 lists some natural and artificial sweeteners and their sweetness values.

The sweeteners that are currently approved for sale in the US are: stevia, aspartame, sucralose, neotame, acesulfame potassium (Ace-K), saccharin, and advantame. Although there are rumors to the contrary, ***none of these sweeteners***, artificial or natural, have ever been shown to cause cancer in humans.

Table 11.2
Sweetness Relative to the Same Mass of Sucrose

Sweetener	Sweetness Value
Natural Sweeteners	
Fructose	170
Xylitol (an alcohol sugar)	100
Glucose	75
Sorbitol (an alcohol sugar)	55
Maltose	32
Galactose	30
Lactose	15
Stevia (a plant extract)	25,000
Artificial Sweeteners	
Sucralose (Splenda, Kaltame)	60000
Saccharin (Sweet’N Low)	30000
Aspartame (Equal, NutraSweet)	18,000

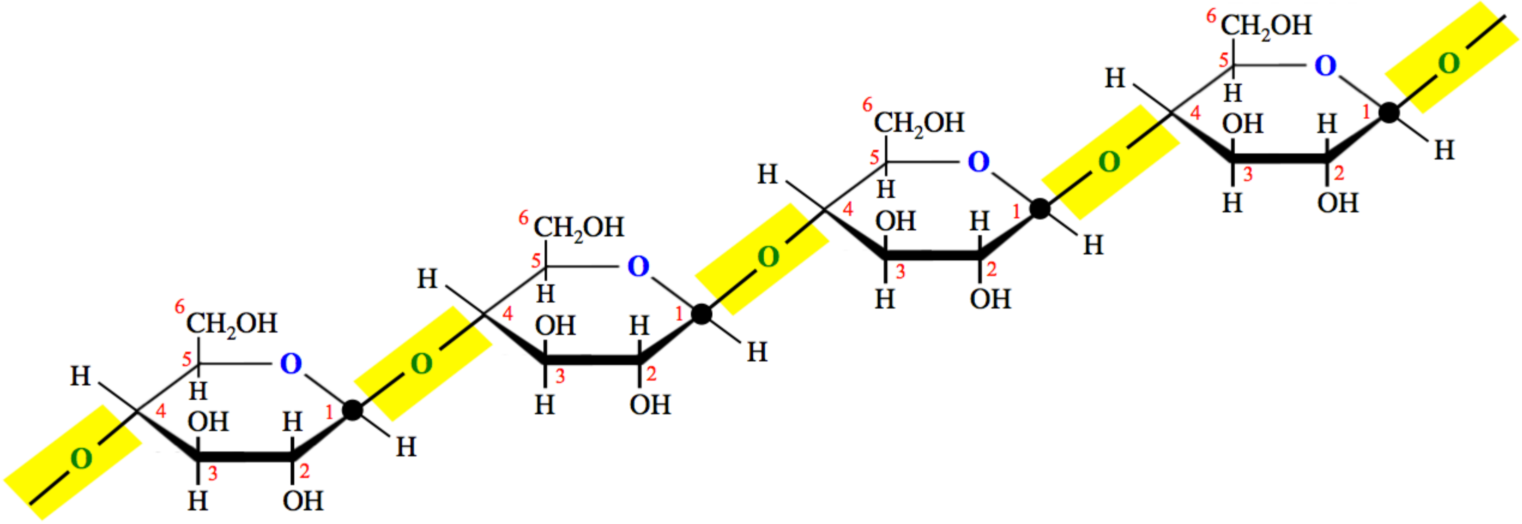
11.6 Polysaccharides

Polysaccharides are composed of ***more than ten*** residues. The residues can be monosaccharides or monosaccharide derivatives. Polysaccharides are often subcategorized as either **homopolysaccharides** or **heteropolysaccharides**. ***Homopolysaccharides*** are composed of ***only one type*** *of* residue. ***Heteropolysaccharides*** are composed of ***more than one type*** of residue. I will elaborate using examples.

Homopolysaccharides

Cellulose

An example of a homopolysaccharide is **cellulose**. *Cellulose* is composed of multiple D-glucose residues (only). The residues are bonded to each other by **β-(1⟶4)** glycosidic bonds, as shown below.



a small section (four D-glucose residues) of a *cellulose* molecule

The structure shown above represents a ***small section*** of a *cellulose* molecule. A *cellulose* molecule contains hundreds (sometimes thousands) of glucose residues.

Cellulose is the most abundant polymer found on Earth. It is found in the cell walls of green plants, some algae, and oomycetes. *Cellulose* accounts for approximately 45% of the mass of dry wood and about 90% of the mass of cotton fibers (Figure 11.7).

Figure 11.7 Cotton

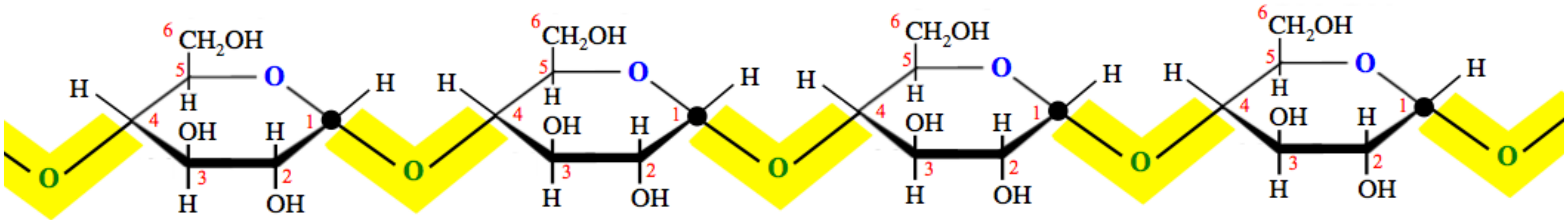
Cotton fibers have the highest cellulose content, 90% (w/w), of any natural material.
Source: PD

The major industrial use for *cellulose* is the production of paper. Humans lack the enzyme necessary to break the *glucose-glucose* β-(1⟶4) glycosidic bond, therefore we cannot metabolize cellulose to get energy. It is for this reason that we do not eat paper, cotton, wood, and many other plants. Some animals (ruminants and termites) are able to metabolize cellulose, not because they produce an enzyme that can break the *glucose-glucose* β-(1⟶4) glycosidic bond, but because they contain bacteria in their digestive track that can do so. In humans, dietary *cellulose* acts as a bulking agent for feces, and eases defecation. When consumed, it is classified as a ***dietary fiber.***

Much of the rigidity of plant cell walls comes from the strong intermolecular forces, especially hydrogen bonding, that are present between the very long and straight cellulose molecules that lie next to each other in a side-by-side fashion.

Starch

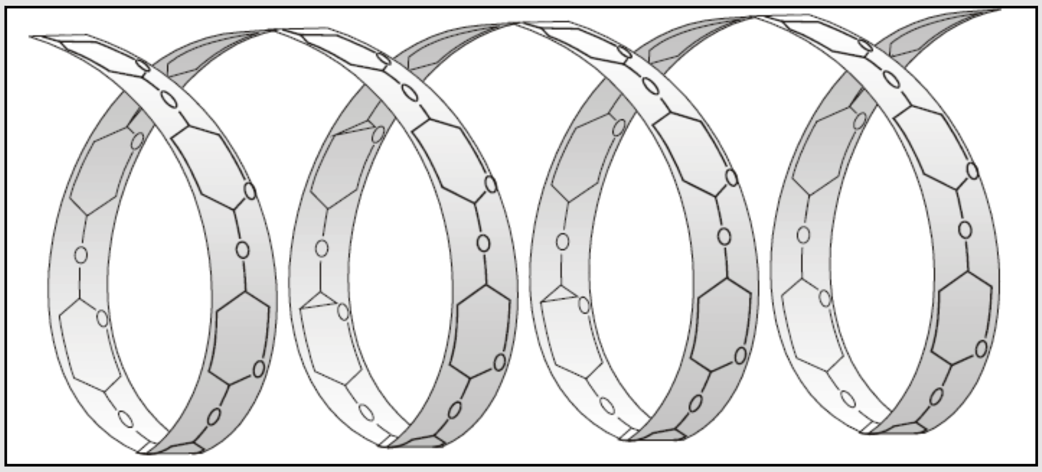
Starch is a common component of plants. The excess *glucose* produced in photosynthesis is stored as *starch* in plants. *Starch* is composed of two different polysaccharides, both of which are *homopolysaccharides*. The two components of *starch* are **amylose** and **amylopectin**. ***Amylose*** is composed of multiple D-glucose residues (only), bonded to each other by **α-(1⟶4)** glycosidic bonds, as shown below.



a small section (four D-glucose residues) of an *amylose* molecule

The structure shown above represents a ***small section*** of an amylose molecule. An *amylose* molecule contains hundreds to many thousands of D-glucose residues. Note that, except for the **α** and **β** orientation of the glycosidic bonds, *amylose* and *cellulose* have the same bonding pattern; they are homopolysaccharides of D-glucose, and their glycosidic linkages are between carbon number **1** and carbon number **4**. The difference in stereochemistry (**α** vs. **β**) *does* result in a significant difference in the three-dimensional arrangement of the residues. While *cellulose* molecules are relatively straight, the residues in amylose form a helical coil (helix) as illustrated in Figure 11.8.

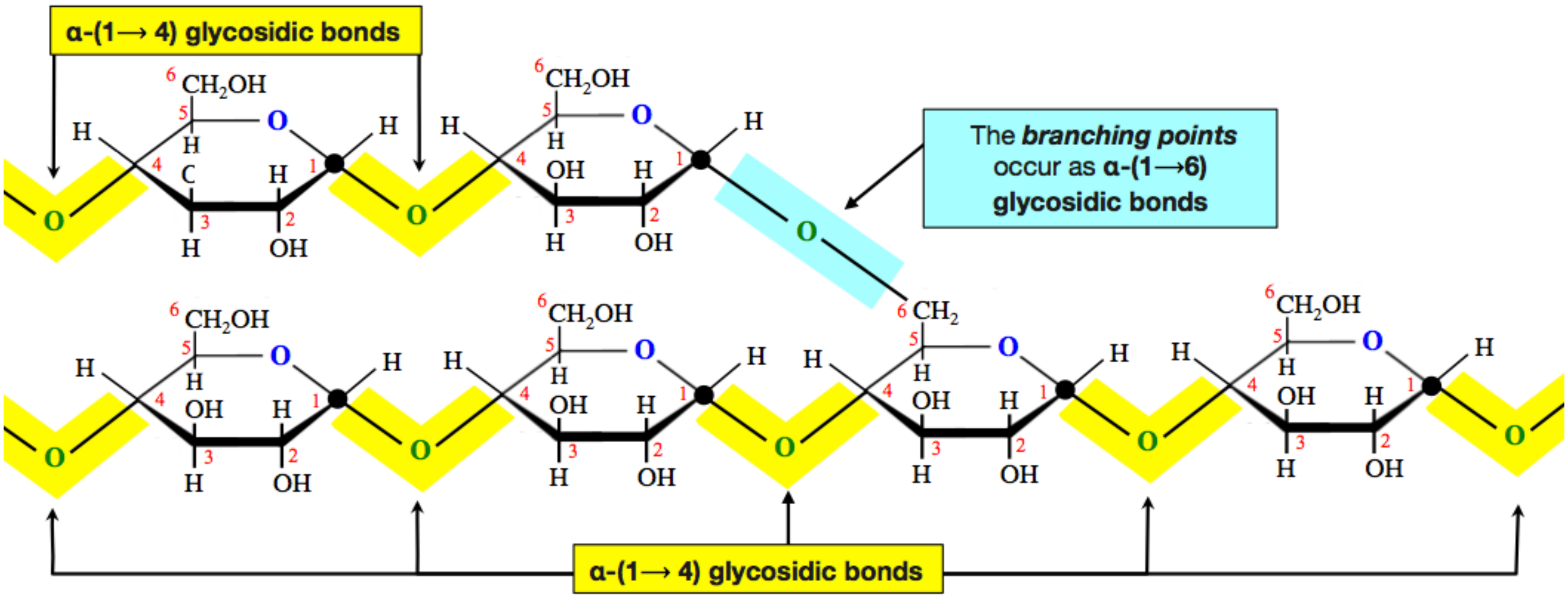
Figure 11.8 Helical Molecular Geometry of Amylose



An illustration of the helical structure of a small section of an amylose molecule.
Source: Wikimedia Commons, GNU Free Documentation License Author: H. Hoffmeister

The difference in stereochemistry (**α** vs. **β**) in amylose vs. cellulose makes a big difference in our ability to digest these two compounds. Humans (and many other animals) have digestive enzymes that are capable of breaking *glucose-glucose* **α-(1⟶4)** glycosidic bonds. It is for this reason that we can digest *amylose/starch*.

The second component of starch, ***amylopectin***, is also a *homopolysaccharide* composed of multiple D-glucose residues (only), bonded to each other by **α-(1⟶4)** glycosidic bonds (as in *amylose*) ***with other chains of D-glucose that originate (branch) from carbon number 6***. The branching occurs as an **α-(1⟶6)** glycosidic bond, as shown below.



a small section (six D-glucose residues) of an *amylopectin* molecule

The structure shown above represents a ***small section*** of an *amylopectin* molecule. An *amylopectin* molecule typically contains 2,000 to 200,000 D-glucose residues.

Branching usually occurs every ***24 to 30 glucose residues*** in *amylopectin*, as illustrated below.

Figure 11.9 **Bonding Pattern of Amylopectin**

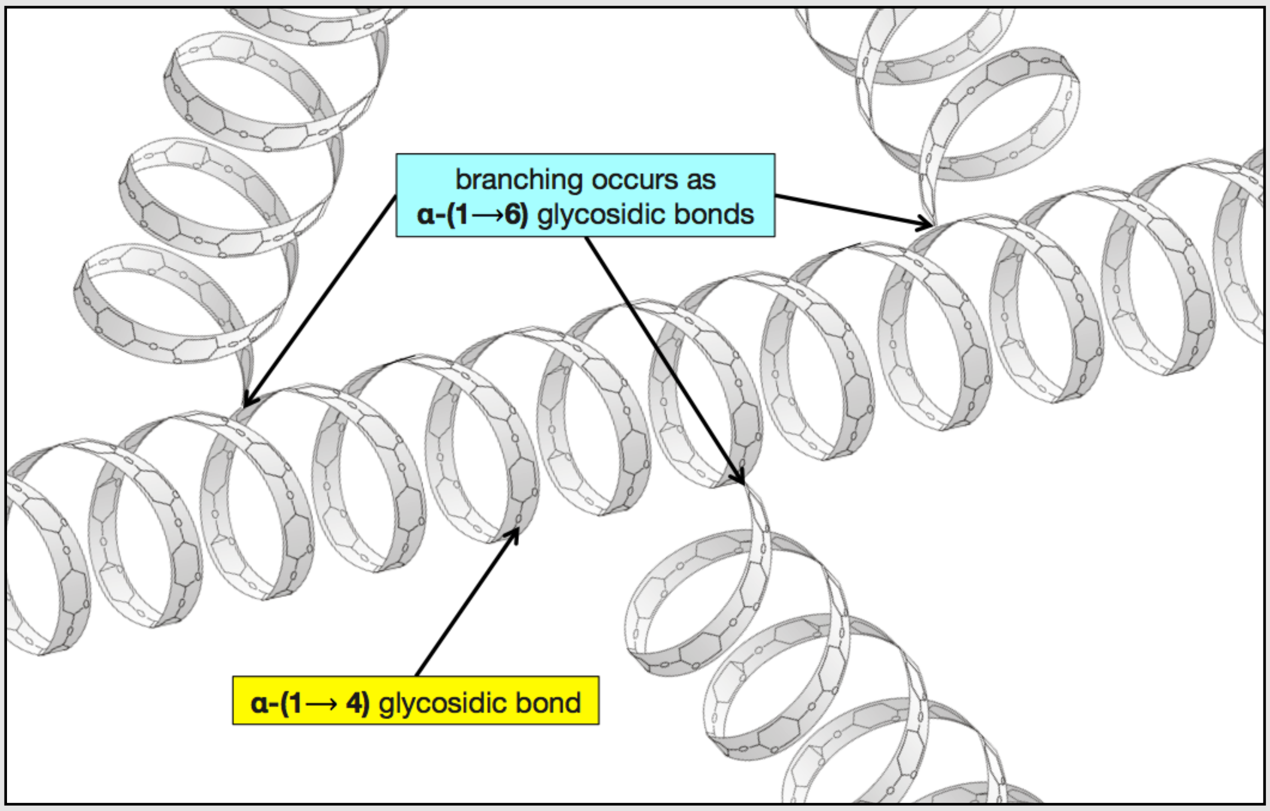


Illustration of the bonding pattern and molecular geometry in a small section of an *amylopectin* molecule. Three branching points are shown in this illustration.

Source: Wikimedia Commons, GNU Free Documentation License,
Adapted from original work at: http://commons.wikimedia.org/wiki/Category:Amylose#/media/File:Amylosekette.png
Author: H. Hoffmeister

Because of branching, *amylopectin* molecules have a large number of *endpoints*. Since the *amylase digestive enzymes* attach to starch molecules at the endpoints, *amylopectin* can be digested more quickly than *amylose*. Starch contains about 70-80% *amylopectin* and 20-30% *amylose*. One of the three *amylase digestive enzymes* is capable of breaking the branching **α-(1⟶6)** glycosidic bonds.

Glycogen

Plants store excess glucose as *starch*; animals and fungi store excess glucose as **glycogen**. *Glycogen* is a *homopolysaccharide* composed of multiple D-glucose residues (only). It is almost identical to *amylopectin*, the only difference is that it ***branches more frequently***. Branching in *glycogen* usually occurs every ***8 to 10 glucose residues***. In humans, *glycogen* is made and stored primarily in liver and muscle cells.

Review 11.15: Amylose vs. Amylopectin

Identify the following as properties of either amylose, amylopectin, or **both** amylose ***and*** amylopectin.

a. contains **α-(1⟶4)** glycosidic bonds
b. homopolysaccharide
c. contains glucose residues only
d. contains **α-(1⟶6)** glycosidic bonds
e. contains branching points
f. more quickly digested (amylose ***or*** amylopectin?)

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

Review 11.16: Amylose vs. Cellulose

Identify the following as properties of either amylose, cellulose, or **both** amylose ***and*** cellulose.

a. contains **α-(1⟶4)** glycosidic bonds
b. contains glucose residues only
c. found in plants
d. has a helical structure
e. is a homopolysaccharide
f. contains **β-(1⟶4)** glycosidic bonds
g. can be digested by humans
h. is a major component of cell walls

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

Review 11.17: Glycogen vs. Amylopectin

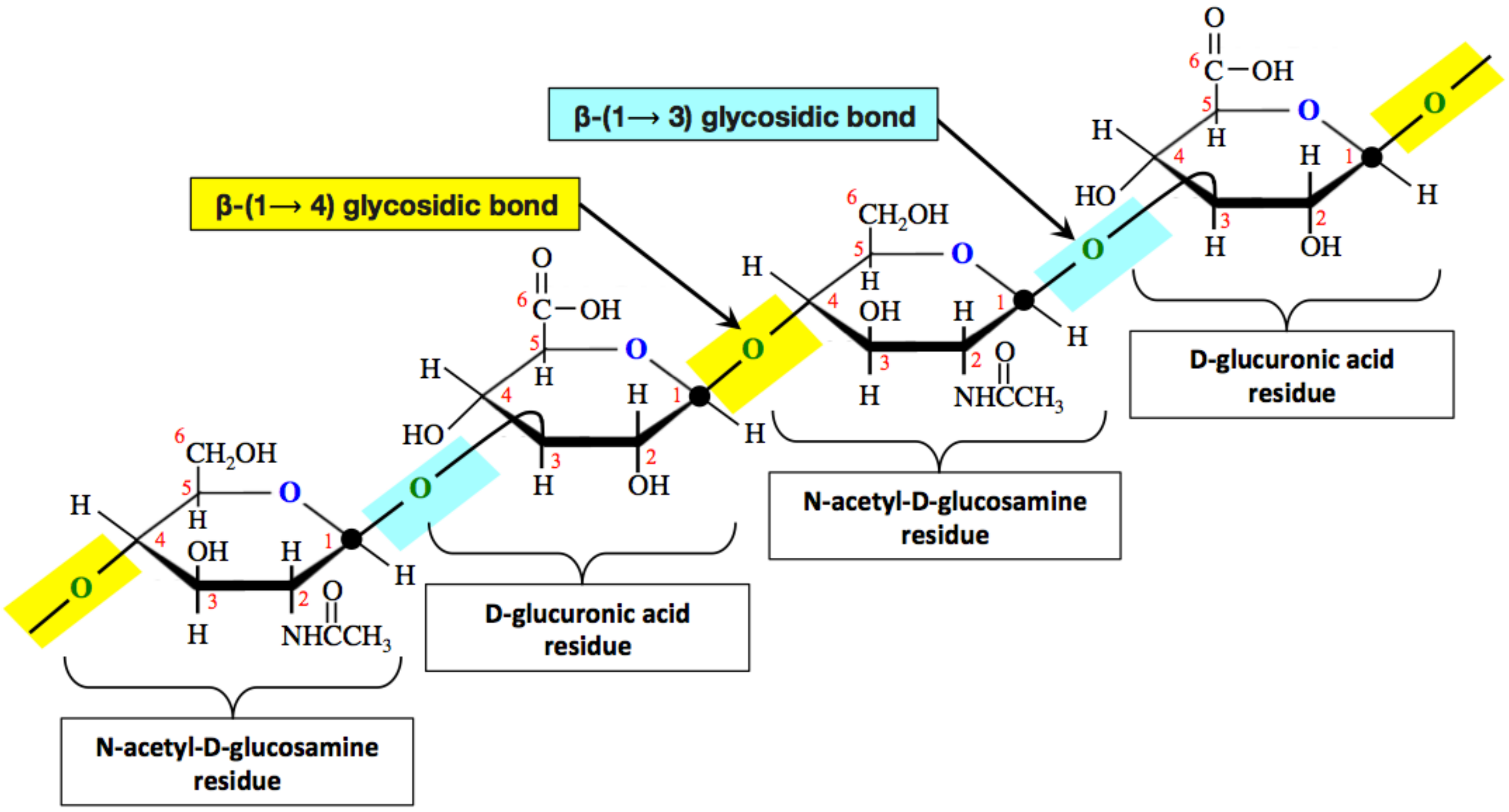
Identify the following as properties of either glycogen, amylopectin, or **both** glycogen ***and*** amylopectin.

a. contains **α-(1⟶4)** glycosidic bonds
b. contains glucose residues only
c. contains **α-(1⟶6)** glycosidic bonds
d. contains branching points
e. is a homopolysaccharide
f. produced by plants
g. produced by animals
h. branching occurs more frequently (glycogen ***or*** amylopectin)?

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

Heteropolysaccharides

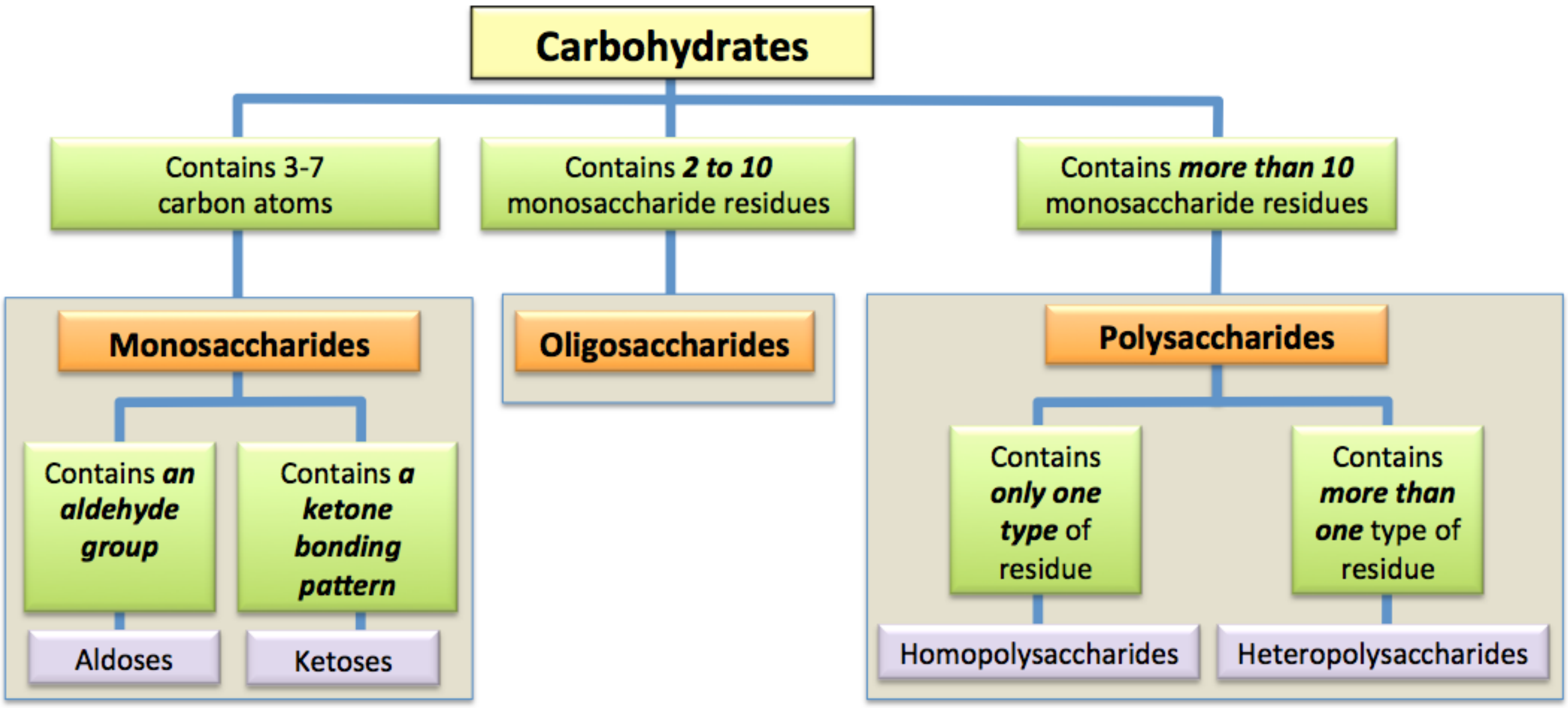
Heteropolysaccharides are composed of ***more than one type*** of residue. The residues can be monosaccharides and/or monosaccharide derivatives. An example of a ***heteropolysaccharide*** is *hyaluronic acid*, which contains *D-glucuronic acid* and *N-acetyl-D-glucosamine* residues, connected to each other in the bonding pattern shown below.



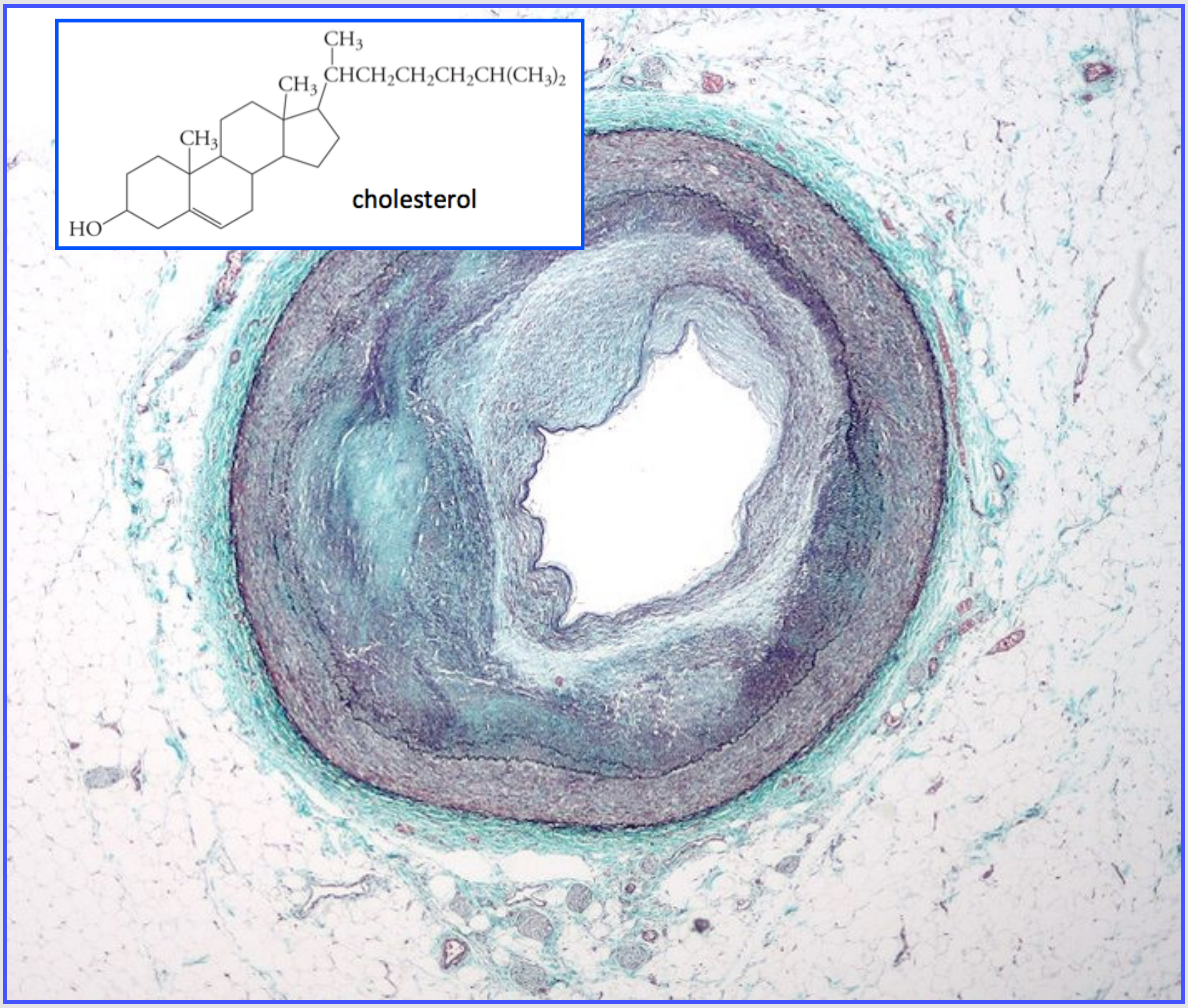
a small section of a hyaluronic acid molecule

The D-glucuronic acid and N-acetyl-D-glucosamine residues are connected by alternating **β-(1⟶4)** and **β-(1⟶3)** glycosidic bonds. The structure shown above represents only a ***small section*** of a *hyaluronic acid* molecule, *which* can contain *up to* about 50,000 residues. *Hyaluronic acid* is found in the lubricating fluid that surrounds joints, and also in the vitreous humor inside the eye.

The key to differentiating ***homopolysaccharides*** from ***heteropolysaccharides*** is to know that *homopolysaccharides* contain ***only one type*** of residue, whereas *heteropolysaccharides* contain ***more than one type*** of residue. A review of carbohydrate classification is shown below.



Chapter 12: Lipids and Membranes



Low magnification micrograph of a cross section of a ***coronary artery with atherosclerosis***. The tunica intima (inner layer) in this artery is severely thickened; it measures 330 micrometers in some places. In healthy individuals, it is only about 10 micrometers thick. The thickening of the inner layer of the artery is caused by the accumulation of **plaque**, which is made from both living white blood cells and remnants of dead cells, including **cholesterol** and **triglycerides**. ***Cholesterol*** and ***triglycerides*** are **lipids**. A cholesterol molecule is shown in the figure insert. Constriction (occlusion) of the coronary artery makes the heart work harder, and can lead to myocardial infarction (heart attack).
Source: Wikimedia Commons, Author: Nephron, CC-BY-SA http://creativecommons.org/licenses/by-sa/3.0/deed.en

Lipids and **membranes** play an important role in nature. Lipids are used as: cell membrane components, energy storage compounds, insulation, signaling compounds, and hormones. Membranes are composed primarily of certain types of lipid molecules. In this chapter, you will be introduced to the various classes of lipids and learn about their structures, physical properties, some important chemical reactions in which they are involved, and their biological roles. You will also learn about the chemical structure and properties of biological membranes.

12.1 Chapter 12 Educational Goals

1. Know the *factors* which characterize a compound as being a **lipid**.
2. Describe the structure of **fatty acids** and explain how *saturated, monounsaturated, and polyunsaturated fatty acid* structures differ from one another.
3. Predict how the *number of carbons* and *the degree of unsaturation* affect the melting points of fatty acids.
4. Describe the *structure* of waxes, how they are made, and understand the *biological function* of waxes.
4. Describe the general ***structure of triglycerides*** and list their biological functions.
5. Describe the reaction involved in the *formation of triglycerides* from fatty acid residues and glycerol.
6. Describe three reactions in which *triglycerides are reactants*.
7. Explain how the structures of *saturated* and *unsaturated triglycerides* differ from one another.
8. Explain the difference in melting points of ***vegetable oils*** vs. ***animal fats***.
9. Distinguish **phospholipids** from **glycolipids**.
10. Distinguish **glycerophospholipids** from **sphingophospholipids**.
11. Distinguish **glyceroglycolipids** from **sphingoglycolipids.**
12. Identify the structural component that is common to all **steroids** and identify *three important members* of this class of lipids.
13. Describe the *structure and function* of **bile salts**.
14. Describe the *structure and function* of **lipoproteins**. List *five types* of lipoproteins.
15. Understand what is meant by the terms "total cholesterol," "good cholesterol," and "bad cholesterol" as they relate to lipid panel blood tests.
16. Understand the structural basis of the lipid class called **eicosanoids**.
17. Explain how *aspirin, ibuprofen, and acetaminophen* work to reduce fever, swelling, and pain.
18. Describe the *components and structure* of a ***cell membrane***.
19. Compare and contrast **passive transport** and **active transport**.
20. Compare and contrast **simple diffusion** and **facilitated diffusion**.

12.2 Introduction to Lipids

In chapter 4, you learned that organic compounds are categorized into various *families* based on the presence of certain *functional groups*. For example, an organic molecule with a hydroxyl group (OH) bonded to a hydrocarbon part is in the *alcohol* family. **Lipids**, in contrast, ***are not*** defined by the presence of specific functional groups. **Lipids are defined as biological compounds that are insoluble in water but soluble in nonpolar solvents.** *Biological compounds* are organic compounds that occur in *living* organisms. There are three *solubility classes* for biological compounds: **hydrophilic, hydrophobic,** and **amphipathic**. Of these three classes, ***hydrophobic and amphipathic*** are ***water-insoluble***. Amphipathic molecules are ***water-insoluble*** because they do not dissolve when placed in water; they form ***monolayers*** and ***micelles***.

You will be introduced to ***seven*** **classes of lipids** in this chapter:

1) **Fatty Acids**
2) **Waxes**
3) **Triglycerides**
4) **Steroids**
5) **Phospholipids**
6) **Glycolipids**
7) **Eicosanoids**

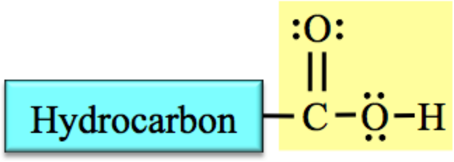
Figure 12.1
Triglycerides are One of the Classes of Lipids

Triglycerides are a class of lipids that includes two subcategories - ***vegetable oils*** and ***animal fats***.
Left: A *vegetable oil* (cotton seed oil).
Right: A beef steak, the white regions are primarily composed of *animal fat*.
Source (left): Wikimedia Commons, Author: cottonseedoil,
CC-BY, http://creativecommons.org/licenses/by/2.0/legalcode (right): USDA, PD

12.3 Fatty Acids

The Structure of Fatty Acids

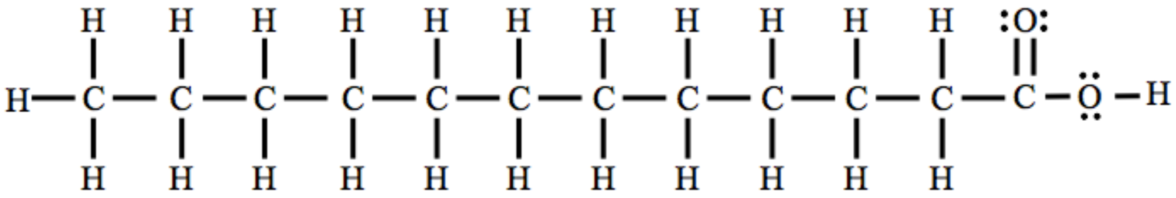
Fatty acids are ***carboxylic acids*** with *long-chain* hydrocarbon parts. Let's do a quick review of *carboxylic acids*. ***Carboxylic acids*** contain a ***carboxyl functional*** group attached to a hydrocarbon part. A *carboxyl group* contains both a ***carbonyl group***, which is a carbon double bonded to an oxygen (**C=O)**, ***and*** a hydroxyl group **(-OH)**. The carboxyl group is *connected to* the hydrocarbon part, as shown below. The carboxyl group is highlighted in yellow.

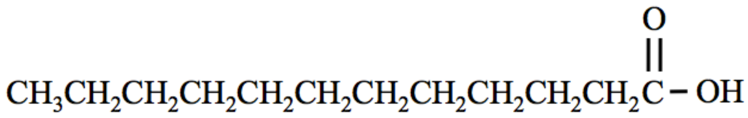


general form of a carboxylic acid

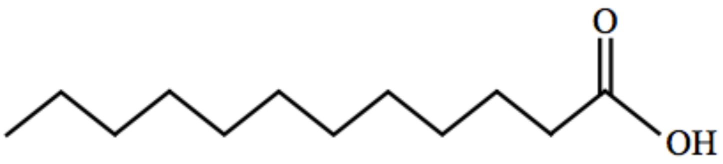
Fatty acids typically ***contain between twelve and twenty carbon atoms***. A specific example of a fatty acid is ***lauric acid***. The line-bond, condensed, skeletal, and ball-and-stick structure of lauric acid are shown below.

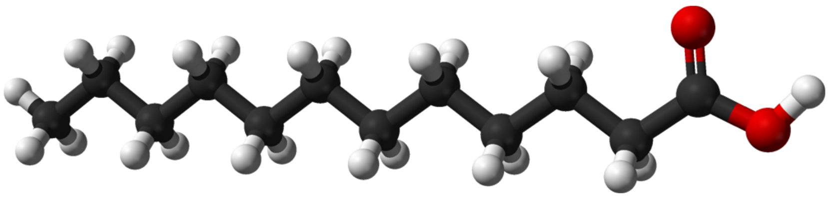
lauric acid (a carboxylic acid)



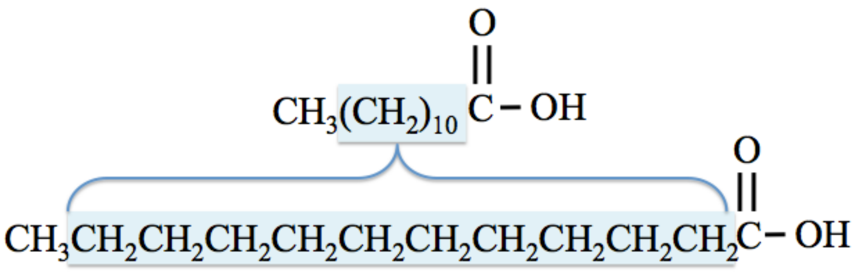


$$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2\overset{O}{\overset{\|}{C}}-OH$$





In order to save time when drawing structural formulas for large molecules such as fatty acids, an *abbreviated condensed structure* is used. Repeating structural units are shown in parenthesis with a subscripted number where the subscript is equal to the number of times that the structural unit within the parenthesis is repeated. For example, carbons that are single bonded to each other in a linear sequence, along with the hydrogens that are bonded to them, are abbreviated as $(CH_2)_n$, where **n** is equal to the number of number of times that the CH_2 is repeated. The *abbreviated condensed structure (top) and the standard condensed structure (bottom)* for lauric acid are both drawn below.



$$CH_3(CH_2)_{10}\overset{O}{\overset{\|}{C}}-OH$$

$$CH_3\overbrace{CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2}\overset{O}{\overset{\|}{C}}-OH$$

Fatty acids usually contain an ***even number of carbon atoms*** because they are made in nature by combining *two-carbon* molecules. You will learn about how this occurs in chapter 15. Fatty acids can differ from one another in the **number of carbon atoms** they contain, and in the **number of carbon-carbon double bonds** they contain. Table 12.1 shows some fatty acids that are frequently encountered in biological systems.

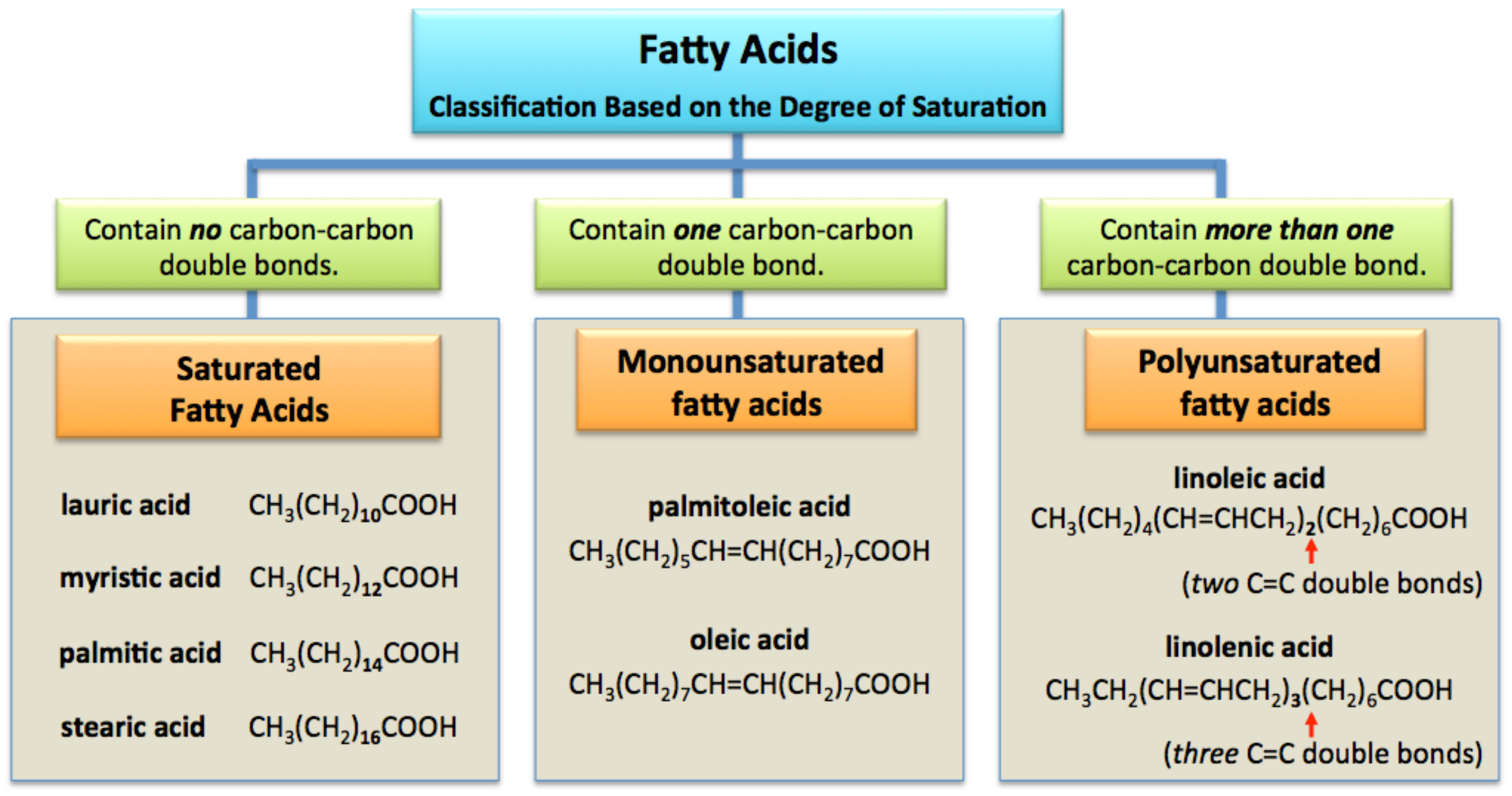
Table 12.1 Table of Some Fatty Acids

Number of Carbons	Number of Carbon-Carbon Double Bonds	Common Name	Condensed Structure	Major Source
12	0	lauric acid	$CH_3(CH_2)_{10}COOH$	coconut
14	0	myristic acid	$CH_3(CH_2)_{12}COOH$	nutmeg
16	0	palmitic acid	$CH_3(CH_2)_{14}COOH$	palm
16	1	palmitoleic acid	$CH_3(CH_2)_5CH{=}CH(CH_2)_7COOH$	macadamia, animals
18	0	stearic acid	$CH_3(CH_2)_{16}COOH$	animal fat
18	1	oleic acid	$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$	olives
18	2	linoleic acid	$CH_3(CH_2)_4(CH{=}CHCH_2)_2(CH_2)_6COOH$	safflower, soy
18	3	linolenic acid	$CH_3CH_2(CH{=}CHCH_2)_3(CH_2)_6COOH$	flax, corn

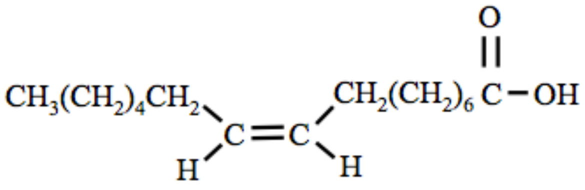
Classification of Fatty Acids

Fatty acids are classified as **saturated**, **monounsaturated**, or **polyunsaturated** based on the number of *carbon-carbon* double bonds they contain. **Saturated fatty acids** contain ***no*** carbon-carbon double bonds. **Monounsaturated fatty acids** contain ***one*** carbon-carbon double bond. **Polyunsaturated fatty acids** contain ***more than one*** carbon-carbon double bond. In Figure 12.2, the fatty acids in Table 12.1 are placed into one of these classes, based on their ***degree of saturation***.

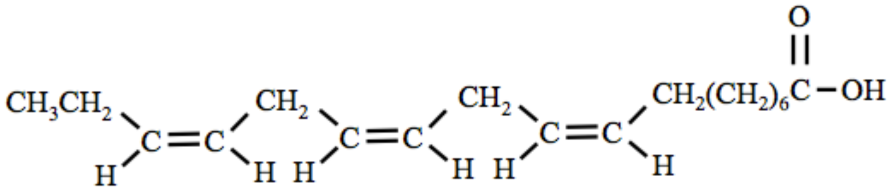
Figure 12.2 Saturated, Monounsaturated, and Polyunsaturated Fatty Acids



Another way in which fatty acids can be classified is by their ***stereochemistry***. They are categorized as either ***cis*** or ***trans***, based on the stereochemistry of the carbon-carbon double bonds in their hydrocarbon parts. Fatty acids that contain ***one or more*** double-bonded carbons with the trans geometry are referred to as ***trans* fatty acids**. Fatty acids that contain ***only*** the *cis* geometry are called ***cis* fatty acids**. For a review of *cis* and *trans* stereoisomers, see chapter 4, section 9. Most of the fatty acids that are produced in nature are *cis*; the only known exceptions are the fatty acids produced by some bacteria. A couple of examples of ***cis* fatty acids** are shown below.



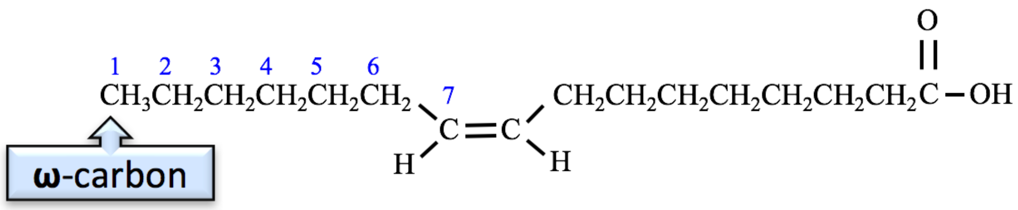
palmitoleic acid



linolenic acid

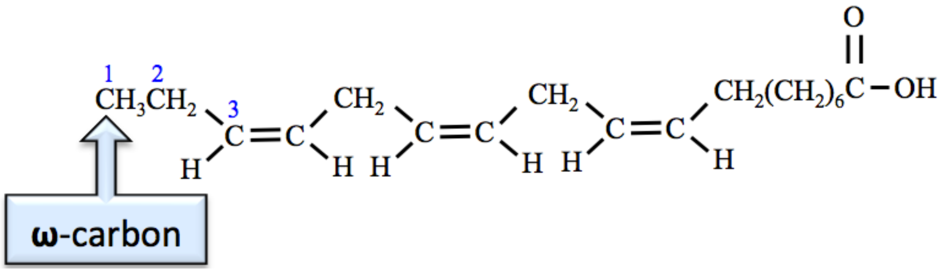
Omega Notation and Classification of Unsaturated Fatty Acids

Although not used in IUPAC naming, ***omega notation*** is frequently seen in popular nutrition literature. In omega notation, the carbon at the ***end*** of a fatty acid's hydrocarbon chain is designated as the "***omega*** carbon" or "**ω**-carbon." Omega (**ω**) is the last letter of the Greek alphabet, making the omega designation appropriate for the "last" carbon in a fatty acid's hydrocarbon chain. *Unsaturated* fatty acids are put into omega notation classes by the position of the *first* double bond that occurs, counting from the omega carbon. For example, if a carbon-carbon double bond in a fatty acid occurs at the ***seventh*** carbon, counting from the *omega* carbon, then it is classified as an *omega-7* fatty acid (or ω-7 fatty acid). An example of a *omega-7* fatty acid is palmitoleic acid.



palmitoleic acid (an *omega-7* fatty acid)

An example of an *omega-3* fatty acid is linolenic acid.



linolenic acid (an *omega-3* fatty acid)

Chemical reactions involved in digestion and metabolism of fish oils provide relatively high concentrations of *omega-3* fatty acids, and vegetable oils provide *omega-6* fatty acids. *Omega-3* and *omega*-6 fatty acids are important precursors used in the biosynthesis of a class of signaling compounds called *eicosanoids*.

Review 12.1: Omega Notation for Unsaturated Fatty Acids

Use the structures shown in Table 12.1 to give the omega notation classification of (a) oleic acid ***and*** (b) linoleic acid.

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

Properties of Fatty Acids

Melting Points of Fatty Acids

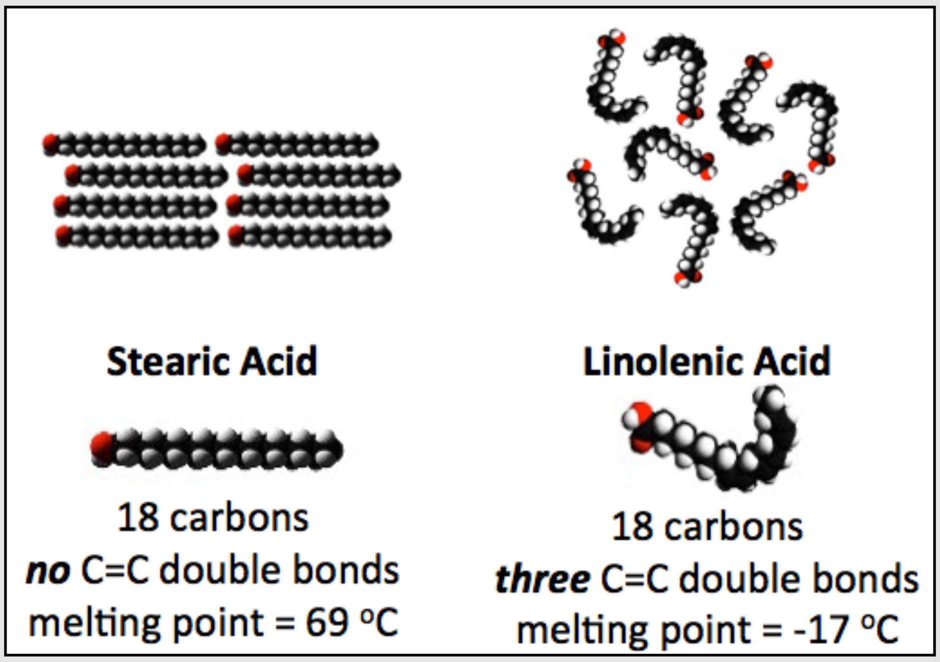
Fatty acids are attracted to each other through hydrogen bonding and dipole-dipole interactions of their carboxyl groups, and also through London forces. The melting points of fatty acids are related to the size of their hydrocarbon part - as are, in general, the melting points of all organic compounds. The larger the nonpolar hydrocarbon part, the stronger the London forces and the higher the melting point. Table 12.2 shows this trend in melting points for several *saturated fatty acids*.

Table 12.2
Melting Points of some Saturated Fatty Acids

Number of Carbons	Common Name	Condensed Structure	Melting Point (^{o}C)
12	lauric acid	$CH_3(CH_2)_{10}COOH$	43
14	myristic acid	$CH_3(CH_2)_{12}COOH$	54
16	palmitic acid	$CH_3(CH_2)_{14}COOH$	62
18	stearic acid	$CH_3(CH_2)_{16}COOH$	69

Another factor that influences the melting points of fatty acids is their ***degree of saturation***. The more carbon-carbon double bonds that are present in a fatty acid, the lower the melting point. The inability of rotation around double bonds prevents less saturated molecules from getting as close to each other as is possible for more highly saturated molecules. The strength of London forces - and all other noncovalent interactions - are distant dependent; the closer the particles are to each other, the stronger the attractive force. This is similar to what you have experienced if you have ever brought two opposite poles of magnets together. When the magnets are far apart from each other, you do not even feel their attraction. The closer together that the magnets are to each other, the more forcefully they pull toward each other.

Figure 12.3
Comparison of Stearic Acid and Linolenic Acid



Stearic acid (***left***) and Linolenic acid (***right***) both contain 18 carbon atoms. Linolenic acid has more carbon-carbon double bonds than stearic acid, and its inability to freely rotate around double bonds prevents linolenic acid molecules from getting as near to each other as is possible for stearic acid molecules. This limits the strength of the intermolecular forces for fatty acids that contain carbon-carbon double bonds, and results in lower melting points when compared to more saturated fatty acids.
Source: Wikimedia Commons (then altered), Author: anonymous, CC-BY-SA http://creativecommons.org/licenses/by-sa/3.0/deed.en

If two fatty acids have the same number of carbon atoms but differ in degree of saturation, molecules of the fatty acid with the fewest carbon-carbon double bonds can pack closer to each other, and so the fatty acid with the higher degree of saturation will therefore have a higher melting point. It is for this reason that *stearic acid* has a higher melting point than *linolenic acid*. Consider the difference in shape and flexibility between *stearic acid* (18 carbons and ***no*** carbon-carbon double bonds) and *linolenic acid* (18 carbons and ***three*** double bonds). Space-filing models of these two molecules are shown in Figure 12.3. *Stearic acid* is solid at room temperature, whereas *linolenic acid* is liquid at room temperature.

Review 12.2: Melting Points of Fatty Acids

Which fatty acid would you expect to have the higher melting point, oleic acid or palmitoleic acid? Refer to Table 12.1 structures of these fatty acids.

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

Review 12.3: Melting Points of Fatty Acids

Which fatty acid would you expect to have the higher melting point, oleic acid or linolenic acid? Refer to Table 12.1 structures of these fatty acids.

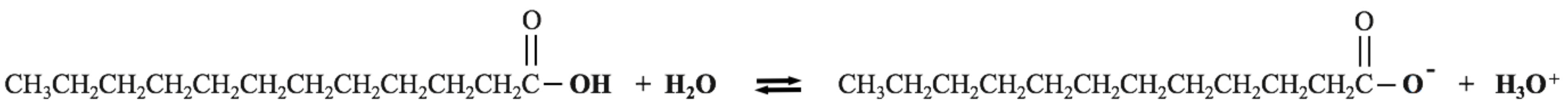
For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

Water Solubility of Fatty Acids

Fatty acids are ***hydrophobic*** and therefore *do not dissolve in water*. This is because they contain eleven or more carbon atoms in their *hydrocarbon part*.

Formation of Carboxylate Ions from Fatty Acids

Fatty acids, *like all carboxylic acids*, can react with *water* to produce their corresponding ***carboxylate ion*** forms (**base forms**). For example, the reaction *lauric acid* and water produces the corresponding carboxylate ion - the laur*ate* ion - and a hydronium ion, as shown below.



$$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2\overset{\displaystyle O}{\overset{\|}{C}}-\mathbf{OH} + \mathbf{H_2O} \rightleftharpoons CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2\overset{\displaystyle O}{\overset{\|}{C}}-\mathbf{O^-} + \mathbf{H_3O^+}$$

lauric acid (a fatty acid)
(acid form)

laurate ion (a carboxyate ion)
(base form)

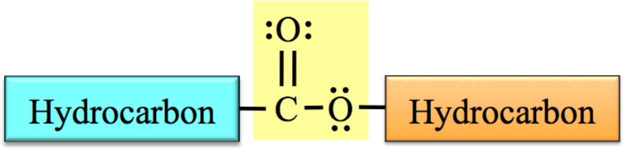
In previous chapters, you learned that the relative amounts of a conjugate pair's ***acid form*** and ***base form*** that are present in an aqueous solution depends on the pH of the solution ***and*** the pK_a of the particular acid (as described by the Henderson-Hasselbalch Equation). The pK_a of carboxylic acids (including fatty acids) is about **5.** Since the physiological pH in cells, blood, and intercellular solutions is *greater than* **5**, the *carboxylate form* of a fatty acid is predominant in these solutions ($pH > pK_a$).

Carboxylate ions are named by replacing the "-ic acid" suffix of the ***fatty acid*** name with "-ate ion." A few examples are shown below.

laur**ic acid** → laur**ate ion**
ole**ic acid** → ole**ate ion**
palmit**ic acid** → palmit**ate ion**

12.4 Waxes

Waxes are members of the ***ester*** family of organic compounds. Let's do a quick review of *esters*. ***Esters*** contain a ***carboxylate group*** that is bonded *between* ***two*** hydrocarbon parts, as shown below. The *carboxylate group* is highlighted in yellow.



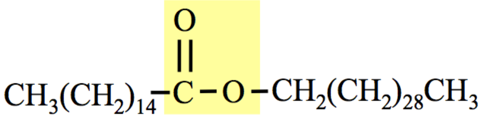
general form of an ester

The boxes that represent the hydrocarbon parts are shaded with different colors because the two hydrocarbon parts *are not necessarily identical*.

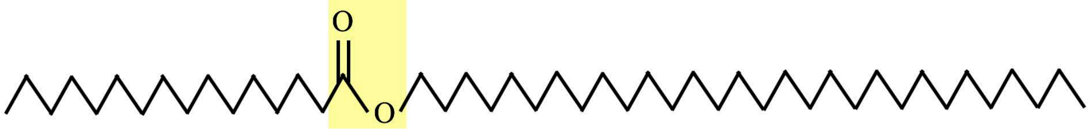
Figure 12.4 **Beeswax**

Left: Natural honeycomb made by bees in order to contain their larvae and store honey and pollen.
Middle: A commercial beekeeper's artificial honeycomb fabricated from real beeswax.
Right: Beekeepers harvesting honey from artificial honeycombs.
Sources (top): Wikimedia Commons, Author: Merdal, CC-BY, http://creativecommons.org/licenses/by/2.0/legalcode, (middle): Wikimedia Commons, Author: Waugsberg CC-BY, http://creativecommons.org/licenses/by/2.0/legalcode, Source (bottom): PD

Waxes are ***esters*** with ***relatively long hydrocarbon parts***. They are produced by plants and animals. Insects use wax to contain their larvae and store food or pollen. Examples of waxes are the esters in beeswax (Figure 12.4). Beeswax is a mixture of compounds, of which about 80% are waxes. The condensed and skeletal structural formulas for the *most abundant wax* molecule found in beeswax are shown below.



$$CH_3(CH_2)_{14}-\overset{\overset{\large O}{||}}{C}-O-CH_2(CH_2)_{28}CH_3$$



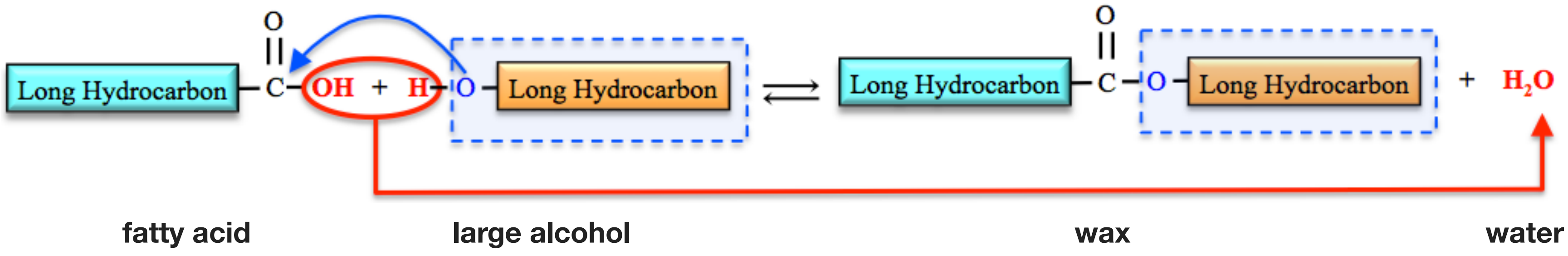
Waxes are ***hydrophobic*** because of their large and nonpolar hydrocarbon parts. Sheep secrete a wax called *lanolin* which protects their wool and skin from the environment and helps shed water from their coats. Plants secrete waxes which help them control hydration and evaporation. A list of some waxes, their most abundant wax molecule, and how we use them are shown in Table 12.3.

Table 12.3 **Examples of Esters Found in Waxes**

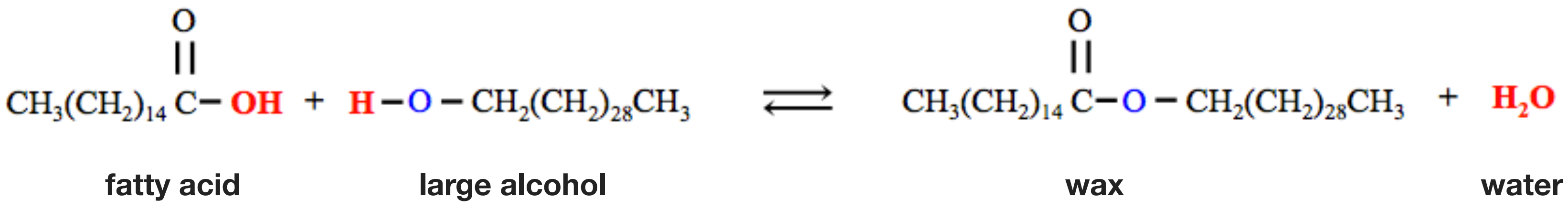
Common Name	Most Abundant Ester	Source	Uses
beeswax	$CH_3(CH_2)_{\mathbf{14}}\mathbf{COO}CH_2(CH_2)_{\mathbf{28}}CH_3$	honeycomb	candles, shoe polish, wax paper
carnauba wax	$CH_3(CH_2)_{\mathbf{24}}\mathbf{COO}CH_2(CH_2)_{\mathbf{27}}CH_3$	Brazilian palm	furniture, car, and floor wax
insect wax	$CH_3(CH_2)_{\mathbf{24}}\mathbf{COO}CH_2(CH_2)_{\mathbf{27}}CH_3$	insects	shoe polish
spermaceti	$CH_3(CH_2)_{\mathbf{30}}\mathbf{COO}CH_2(CH_2)_{\mathbf{14}}CH_3$	whale's head	lubricant
jojoba wax	$CH_3(CH_2)_{\mathbf{18}}\mathbf{COO}CH_2(CH_2)_{\mathbf{18}}CH_3$	jojoba bush	candles, cosmetics, soap additive

Formation of Waxes

In chapter 9, you learned that in ***esterification***, carboxylic acids react with alcohols to form esters. ***Waxes*** are formed by the *esterification* reaction of *fatty acids* with *large alcohols*. In this reaction, the **OH** from the fatty acid and an **H** from the alcohol are removed, and then combined to form H_2O. The oxygen (**O**) and hydrocarbon that was originally part of the alcohol, forms a new bond to the fatty acid's carbonyl carbon. This process is illustrated below.



A specific example of the formation of a wax molecule in an esterification reaction is shown below.

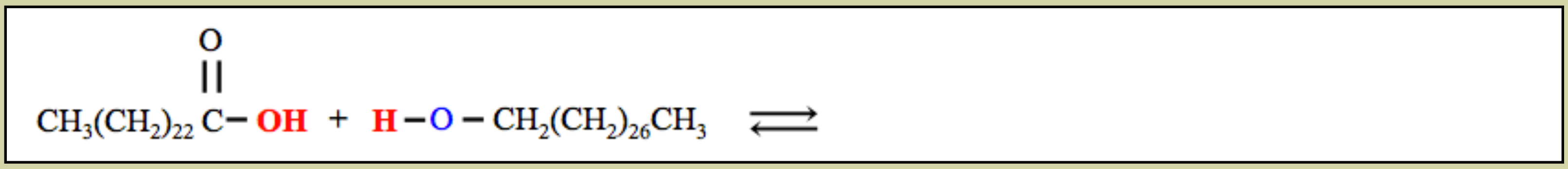


$$\mathrm{CH_3(CH_2)_{14}}\overset{\overset{\displaystyle \mathrm{O}}{\|}}{\mathrm{C}}-\mathrm{OH} + \mathrm{H}-\mathrm{O}-\mathrm{CH_2(CH_2)_{28}CH_3} \rightleftharpoons \mathrm{CH_3(CH_2)_{14}}\overset{\overset{\displaystyle \mathrm{O}}{\|}}{\mathrm{C}}-\mathrm{O}-\mathrm{CH_2(CH_2)_{28}CH_3} + \mathrm{H_2O}$$

You try one:

Review 12.4: Formation of Waxes: Esterification Reaction

Draw the condensed structure of the wax that is produced in the following reaction.



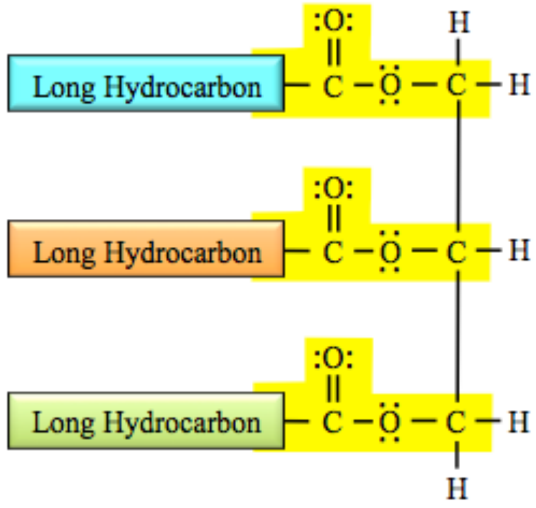
$$\mathrm{CH_3(CH_2)_{22}}\overset{\overset{\displaystyle \mathrm{O}}{\|}}{\mathrm{C}}-\mathrm{OH} + \mathrm{H}-\mathrm{O}-\mathrm{CH_2(CH_2)_{26}CH_3} \rightleftharpoons$$

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

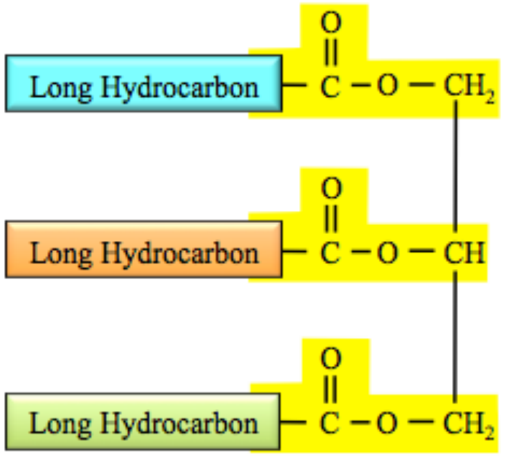
12.5 Triglycerides

The Structure of Triglycerides

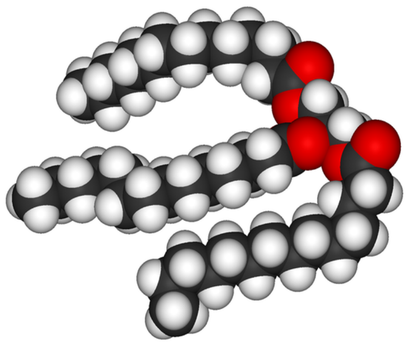
Triglycerides - also referred to as *triacylglycerides* - are ***triesters***. The reason for this classification is that they contain ***three*** ester-type bonds. The triglyceride bonding pattern can be seen in the line bond, condensed, and space-filling structures shown below. The ester bonding patterns are highlighted in yellow.



line bond structure

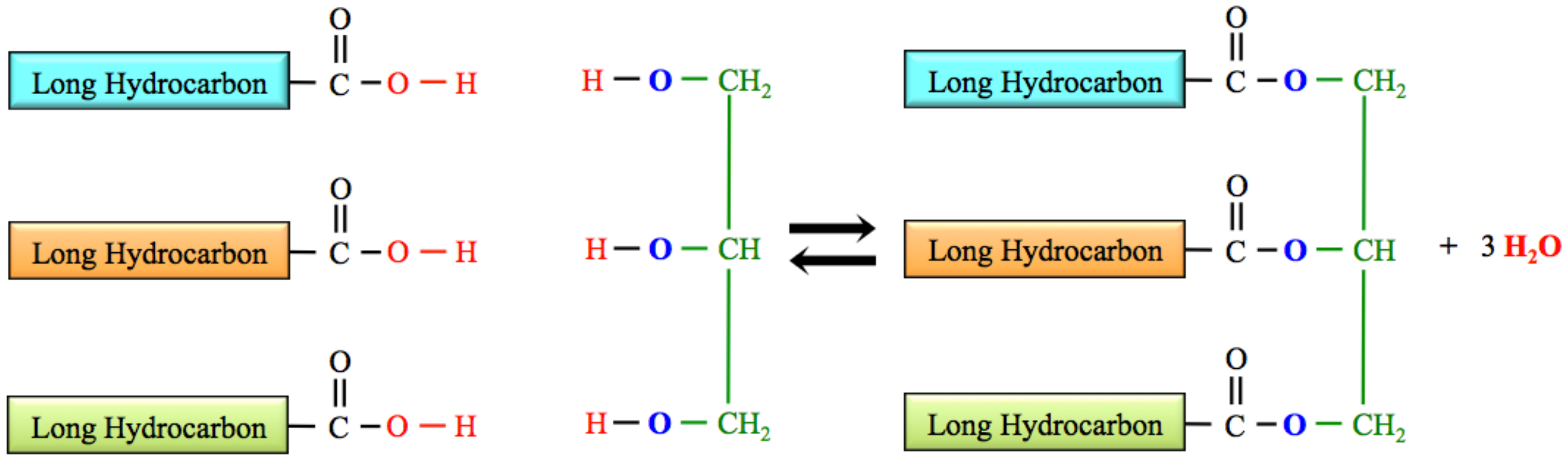


condensed structure



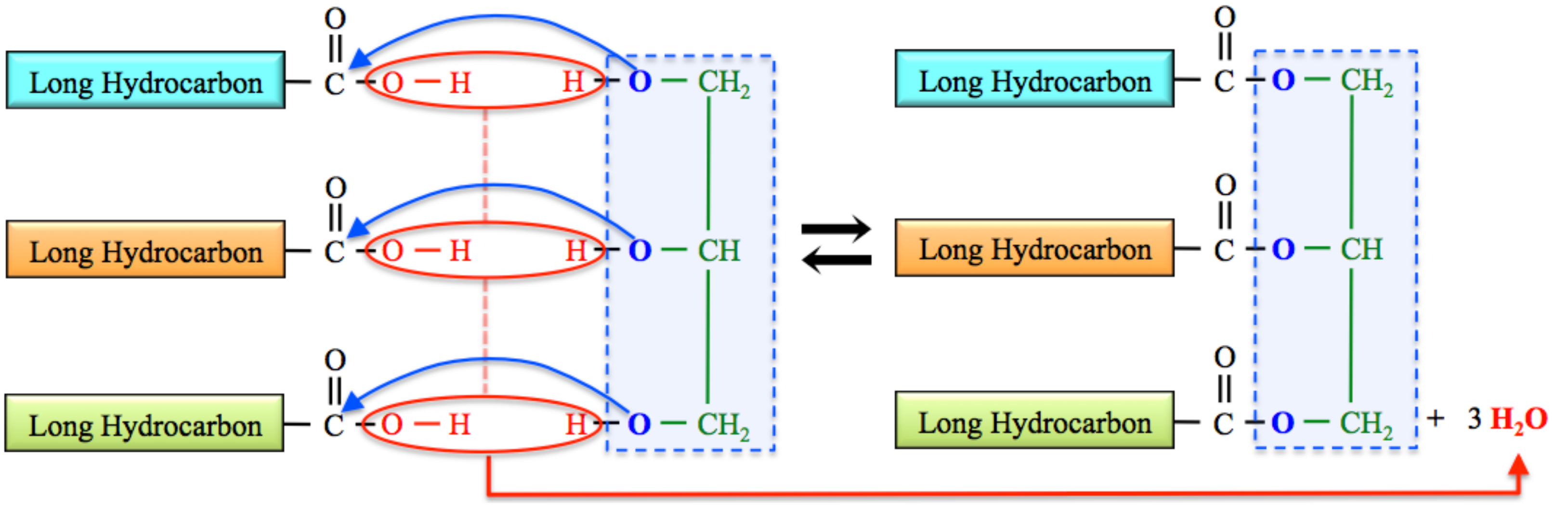
space-filling model

The boxes representing the long-chain hydrocarbon parts are shaded in different colors to emphasize that they are not necessarily identical hydrocarbons. *Triglycerides* are formed in the esterification reaction of ***three*** *fatty acid molecules* with *glycerol* (an alcohol with three hydroxyl groups).



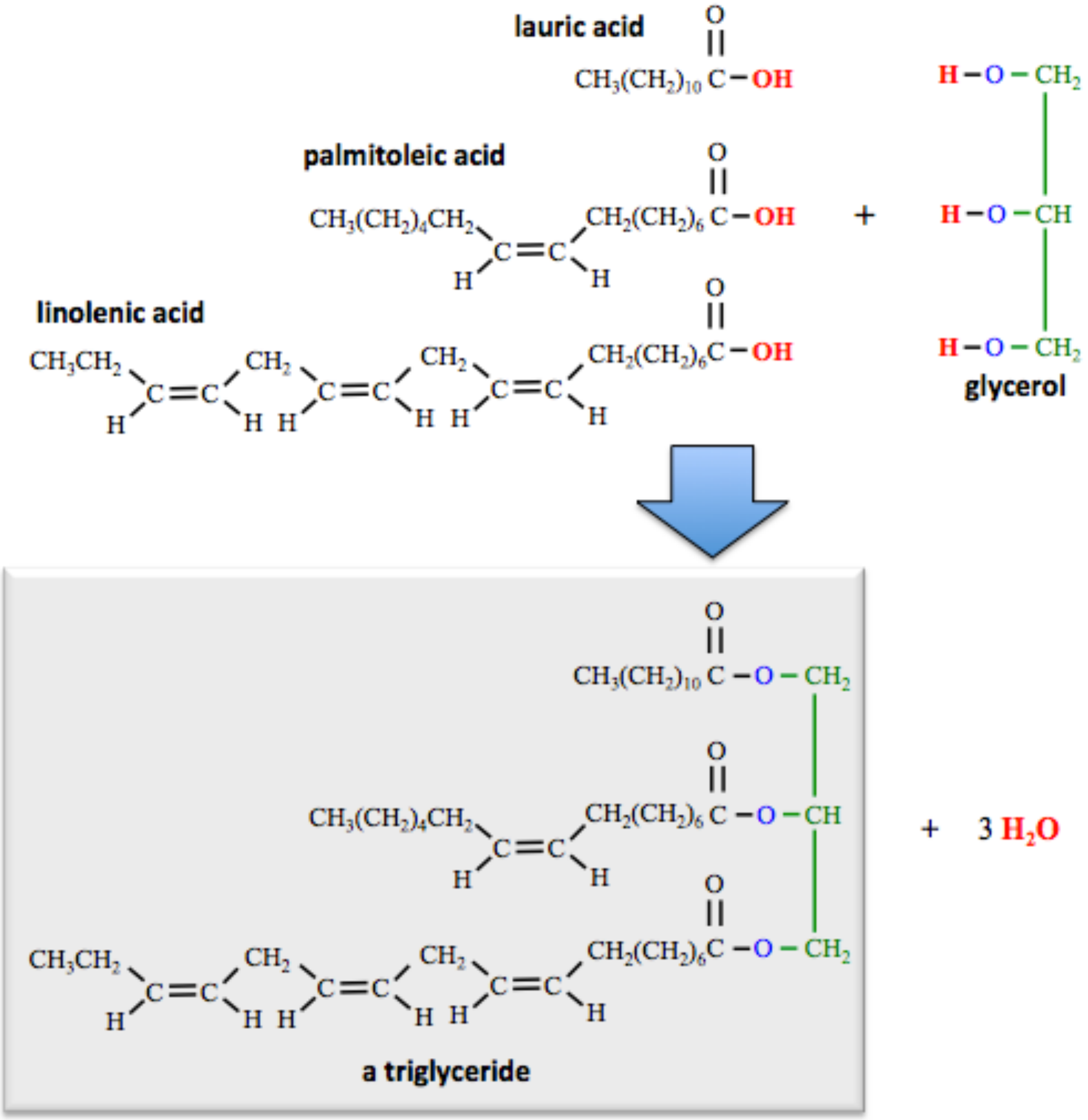
three **fatty acid molecules** **a glycerol molecule** **a triglyceride** **+** ***three*** **H_2O molecules**

In this esterification reaction, the **OH**s from the fatty acids and *three* **H**s from glycerol's hydroxy groups are removed, and then combined to form *three* **H_2O** molecules. The three oxygens, (**O**) that were originally in glycerol, each form a new bond to a fatty acid's carbonyl carbon. This process is illustrated below.

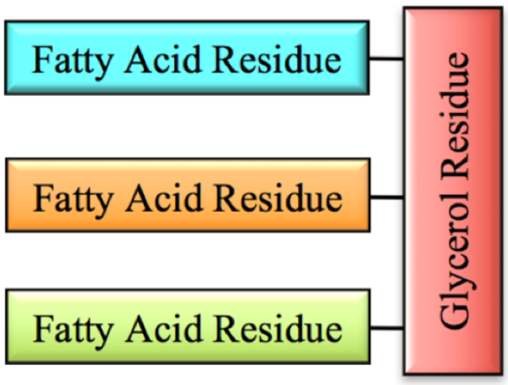


three **fatty acid molecules** **glycerol** **a triglyceride** ***three*** **water molecules**

An example of the formation of a triglyceride molecule from lauric acid, palmitoleic acid, linoleic acid, and glycerol is shown below.



When molecules from particular organic families - such as the three fatty acids and glycerol in the formation of a triglyceride - react to form a large molecule, or when a large molecule is broken down to form them, they are often referred to as "**residues.**" For example, a *triglyceride* contains *three* **fatty acid residues** and a **glycerol residue**. The part that was originally from glycerol - shaded red in the image below - is sometimes called the "**glycerol backbone.**"



You try one:

Review 12.5: Formation of Triglycerides: Esterification Reaction

Draw the *condensed* structure of the triglyceride that is formed from the esterification reaction of three lauric acid molecules and a glycerol molecule. Refer to Table 12.1 for the structure of lauric acid.

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Classification of Triglycerides

Fat vs. Oil

The terms “fat” and “oil” can each have multiple meanings and, worse, are often used ambiguously. In the most general sense, the term “*oil”* is defined as any nonpolar, viscous liquid. In the context of *triglycerides*, the term “**oil**” is generally used for a triglyceride that is ***liquid** at room temperature*. The term “**fat**” is generally used for a triglyceride that is ***solid** at room temperature*. Our use of the term “fat” in this context should not be confused with the common practice using the term “fat” for adipose tissue in humans and animals. Adipose tissue is composed of cells that store triglycerides (Figure 12.5).

Solid triglycerides made by ***animals*** are referred to as **animal fat**. The primary biological roles of triglycerides in animals are: energy storage, the production of energy when metabolized, provision of fatty acids for the production of other lipids, and insulation.

Figure 12.5
Triglyceride Molecule Storage

The mouse on the left has more triglyceride molecules stored in adipose tissue than the mouse on the right.
Source: Oakridge National Laboratory, USA, PD

Animal fat can be separated from other animal parts in a process called **rendering**. Fat from *pigs* is used in food products and is called **lard**. Fat from *chickens* that is used in food products is called **schmaltz**. Fat from *beef and sheep* is called **tallow**, and is used primarily for producing soap and in animal feed. Fat from *milk* is called ***butterfat***, ***clarified butter***, or ***ghee***. The food product that is commercially marketed as “butter” contains about 80% fat, 15% water, and 5% protein and other substances. Butterfat is usually, but not always, made from *cow’s milk*.

Liquid triglycerides that are made by plants are referred to as **vegetable oils**. Vegetable oils are used for cooking and in food products, biofuels, cosmetics, and soaps. Evidence of human purification of vegetable oils goes as far back as 4000 years[1]. Table 12.4 lists various vegetable oils, amounts of their world-wide consumption, common uses, and their source.

Table 12.4 Some Vegetable Oils and Their World Consumption, Primary Uses, and Sources

Vegetable Oil	Worldwide Consumption (metric tons)	Primary Uses and Sources
palm oil	41.3	cooking oil, biofuel (from palm fruit mesocarp pulp)
soybean oil	41.3	cooking oil
canola oil	18.2	cooking oil (comes from a variety of rapeseeds)
sunflower oil	9.9	cooking oil, biodiesel (from sunflower seed)
cottonseed oil	5.0	food products
palm kernel oil	4.8	cooking oil, food products (from palm seed)
peanut oil	4.8	cooking oil
coconut oil	3.5	cooking oil and soap making
olive oil	2.8	cooking oil, cosmetics, soaps, fuel for traditional oil lamps (from whole olives)

Worldwide Consumption data is from the US Department of Agriculture for 2007/2008

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[1] "4,000-year-old 'kitchen' unearthed in Indiana". Archaeo News. January 26, 2006.

Fish oil is purified from tissue and belly cavities of oily fish, such as sardines, herring, anchovies, salmon, trout, tuna, and mackerel. Some fish, such as shark and cod, have significant amounts of oil stored in their liver.

In nutritional labeling, all triglycerides, whether from plants or animals, solid or liquid, are often grouped together and called "**fat**" or included in the **"total fat"** category. Triglycerides supply more than twice as much energy per gram than do the other two types of food energy nutrients (proteins and carbohydrates).

Saturated vs. Unsaturated Triglycerides

We classify triglyceride molecules as either ***saturated*** or ***unsaturated*** using the same criteria as we used for fatty acids. Saturated triglyceride molecules ***do not*** contain *carbon-carbon* double bonds. Unsaturated triglyceride molecules contain ***one or more*** carbon-carbon double bonds. Unsaturated triglycerides are often further subcategorized as either **monounsaturated** or **polyunsaturated**. *Monounsaturated* triglycerides contain only ***one*** carbon-carbon double bond. *Polyunsaturated* triglycerides contain ***two or more*** carbon-carbon double bonds.

Just like *fatty acids*, triglycerides with higher degrees of saturation (fewer carbon-carbon double bonds) are more flexible and can pack closer to each other than less saturated triglycerides. It is for this reason that the noncovalent interactions, and therefore the melting points of triglycerides increase with the degree of saturation.

Since animal fats have a relatively ***high*** *degree of saturation*, they are solid at room temperature [consider beef-fat or lard (Figure 12.6), or butter]. Vegetable oils and fish oils have a ***lower*** *degree of saturation* than animal fats, and are therefore ***liquid*** at room temperature (consider olive and corn oil). Palm and coconut oil are *semi-solid* at room temperature because they contain a higher degree of saturation than the other vegetable oils.

Figure 12.6

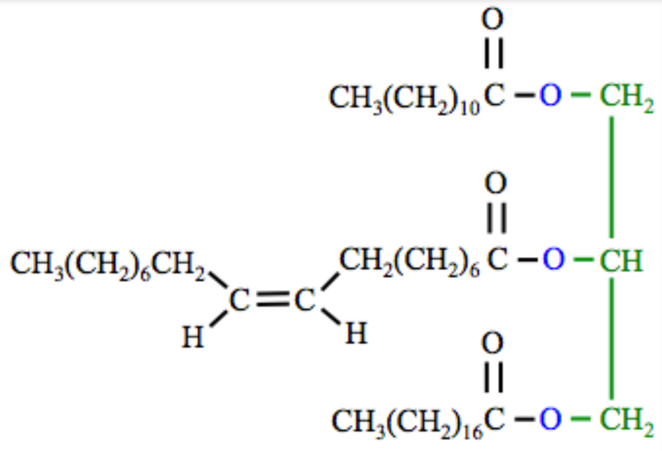
Animal Fat is Solid at Room Temperature

Since animal fats have a relatively ***high*** *degree of saturation*, they are solid at room temperature.
Left: A beef steak, the white regions are primarily composed of animal fat.
Right: Lard (pork fat).
Source (left): USDA, PD, (right) Wikimedia Commons, Author: Peter G. Werner, CC-BY-SA
http://creativecommons.org/licenses/by-sa/3.0/deed.en

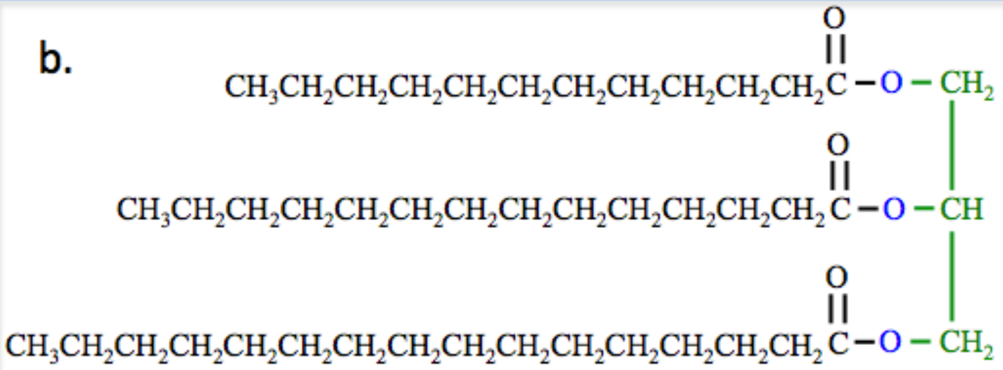
Review 12.6: Saturated vs Unsaturated Triglycerides

Categorize each one of the following triglycerides as being either saturated or unsaturated.

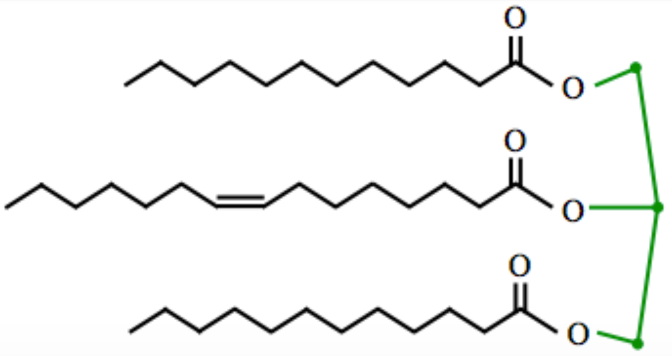
a.



b.



c.



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Review 12.7: Saturated vs Unsaturated Triglycerides

Draw the **skeletal structure** of a *saturated* triglyceride.

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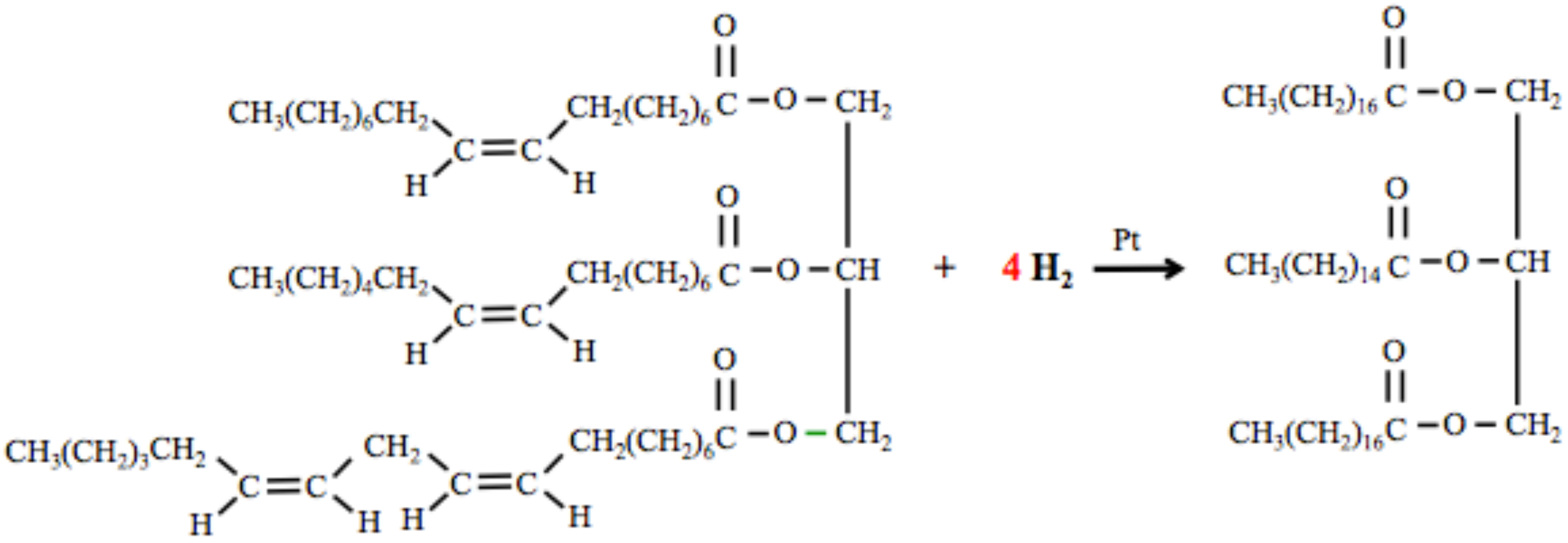
Reactions of Triglycerides

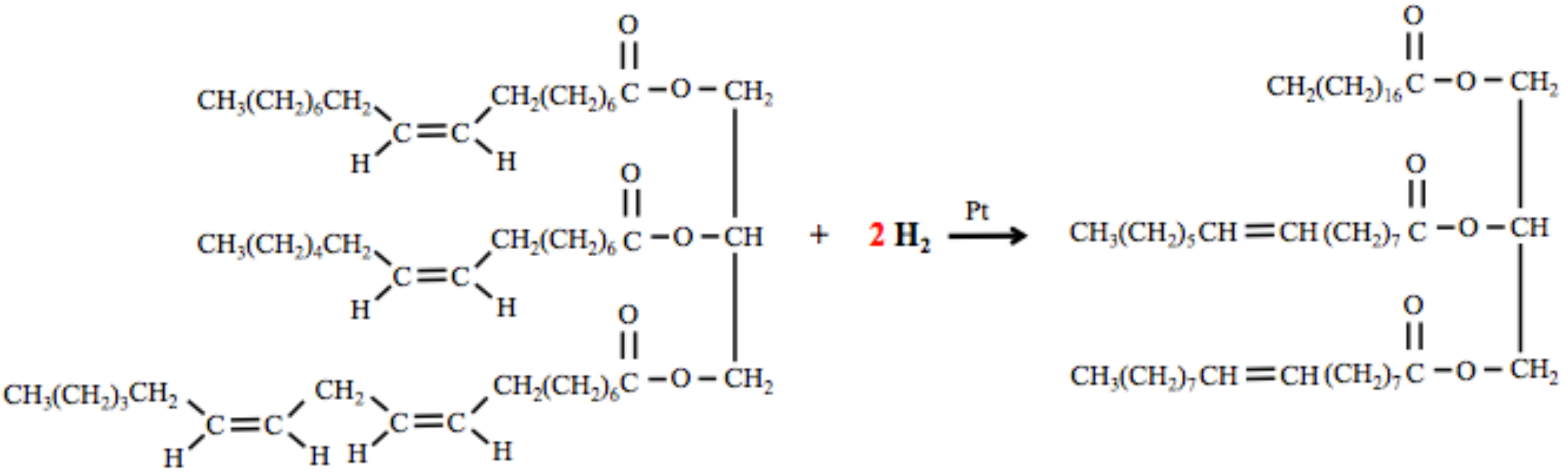
1. Catalytic Hydrogenation

The *carbon-carbon* double bonds of triglycerides will react with hydrogen gas (H_2) in the presence of a catalyst (at high temperatures). In chapter 6, you learned about the ***hydrogenation*** of carbon-carbon double bonds in alkenes. We were able to predict the product by "adding H_2 across the carbon-carbon double bond." *We can do the same for triglycerides*. If enough H_2 is supplied, the carbon-carbon double bonds in *unsaturated triglycerides* become completely saturated; a *saturated triglyceride* is formed. A hydrogen atom is added to each of the double-bonded carbons, thereby converting them into single bonds. The reaction must be done at a high temperature and on the surface of a *metal catalyst*. The catalysts used are typically platinum, palladium, rhodium, or ruthenium. An example of a chemical equation for *complete saturation* during a ***catalytic hydrogenation reaction*** is shown below.



an unsaturated triglyceride **a saturated triglyceride**

Note that the unsaturated triglyceride reactant (above) contains four double bonds, therefore four moles of H_2 are needed to achieve ***complete saturation***. If the amount of H_2 is limited, or the chemical reaction time is reduced, then the triglyceride product will contain *some unreacted* carbon-carbon double bonds. We call this process **partial hydrogenation**. An example of a chemical equation for ***partial hydrogenation*** during a ***catalytic hydrogenation reaction*** is shown below.

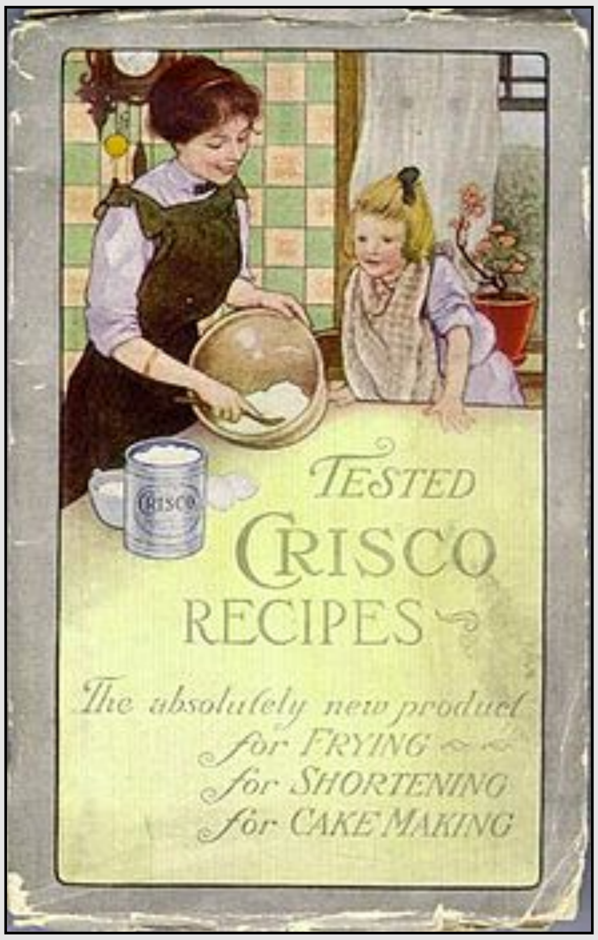


an unsaturated triglyceride **a *partially hydrogenated* triglyceride**

Note that the triglyceride reactant in the reation above contains four double bonds, however, only two moles of H_2 were supplied, therefore only two of the carbon-carbon double bonds became saturated. Triglycerides that are found in nature, with few exceptions, contain only ***cis*** fatty acid residues. Note that the ***reactant*** for the reaction shown above is drawn using ***cis*** configurations around *all of the carbon-carbon double bonds*.

The catalytic hydrogenation of vegetable oils is a very important reaction for the food industry. Solid triglycerides are advantageous in baking because of the texture that is achieved when they are mixed with flour. Animal fat - butter - can be used, however it is more expensive than vegetable oils. The partial hydrogenation of vegetable oils produces what is referred to as **partially hydrogenated vegetable oil** or **shortening**. ***Margarine*** and ***Crisco*** are examples of partially hydrogenated vegetable oil products. Partially hydrogenated oils are solid - but soft - at room temperature and have culinary-desired melting points in the range of 30 to 40 °C. Partially hydrogenated vegetable oils are quite resistant to oxidation, and therefore they will have a longer shelf-life than the unprocessed, natural vegetable oils. In 1911, the Proctor and Gamble corporation marketed a shortening call Crisco by offering a free cookbook (Figure 12.7) in which the use of butter and other animal fats in recipes could be replaced by their shortening. Partially hydrogenated vegetable oils began to be widely used in the 1920s.

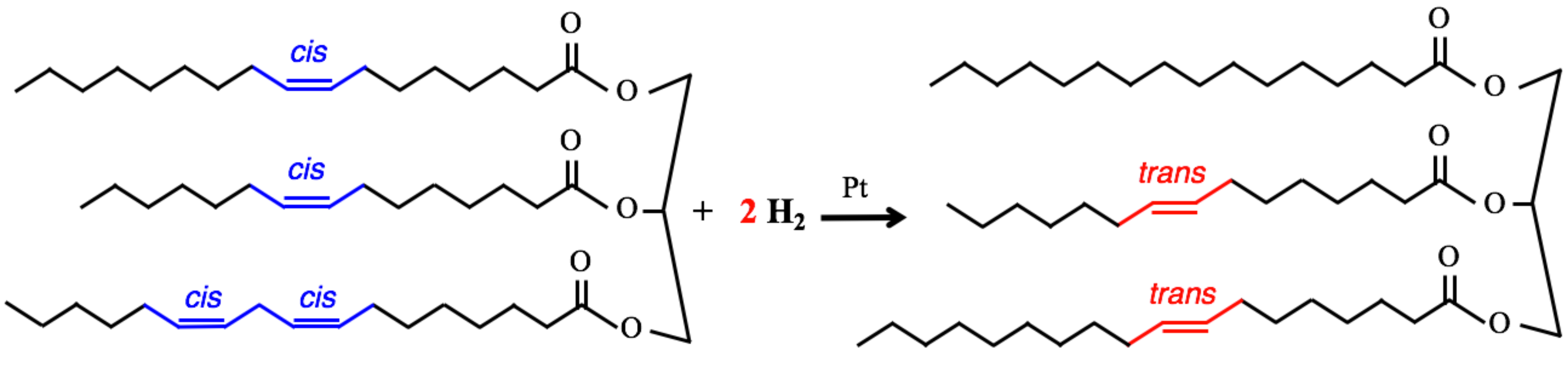
Figure 12.7
The Free Crisco Cookbook



Procter and Gamble corporation promoted their partially hydrogenated vegetable oil - Crisco - by the distribution of free cookbooks with recipes that replaced butter with Crisco. Source: PD

An undesirable consequence of partial hydrogenation is the formation of ***trans* fats** - fats containing one or more carbon-carbon double bonds that have the *trans* configuration. In the partial hydrogenation process, many of the ***unreacted cis*** carbon-carbon double bonds are converted to the ***trans*** configuration. *Trans* fat intake has been correlated with a higher risk of coronary artery disease. The United States Food and Drug Administration product labelling definition of "zero grams *trans* fats per serving" is that a serving has less that 0.5 grams, or is no greater 7% (w/w), *trans* triglycerides. This definition may be problematic since eating several servings of foods that are labeled as "zero grams *trans* fats" may add up to a dangerous level of *trans* fat intake. In order for Proctor and Gamble to be able to label their Crisco product as "zero grams trans fats per serving," they increased their saturation levels (more H_2 reacted), and diluted the product with unprocessed (*cis*) vegetable oil. The State of California (USA) has banned the use of partially hydrogenated vegetable oils in restaurants.

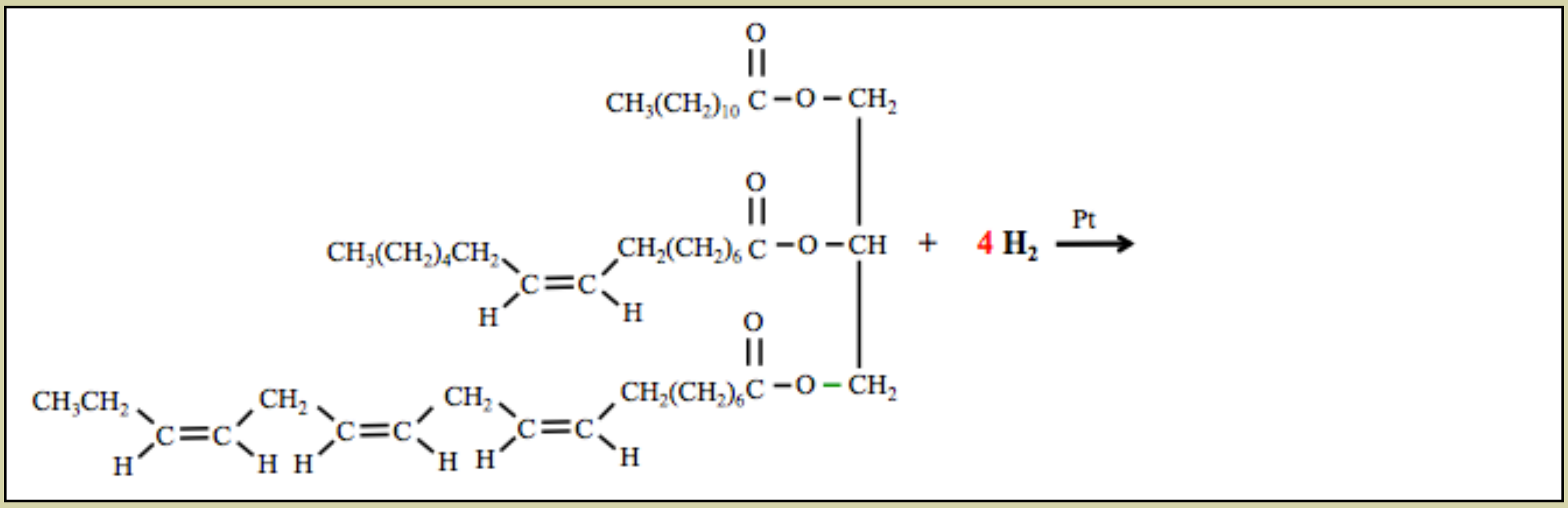
A chemical equation showing the partial hydrogenation of a naturally-occurring unsaturated *cis*-triglyceride (vegetable oil) to a partially hydrogenated *trans*-triglyceride is shown below.



The product is a partially hydrogenated vegetable oil molecule, which typically contains one or more ***trans*** fatty acid residues.

Review 12.8: Catalytic Hydrogenation

Draw the *condensed structure* of the saturated triglyceride that is produced from the **complete hydrogenation** of the triglyceride shown below.

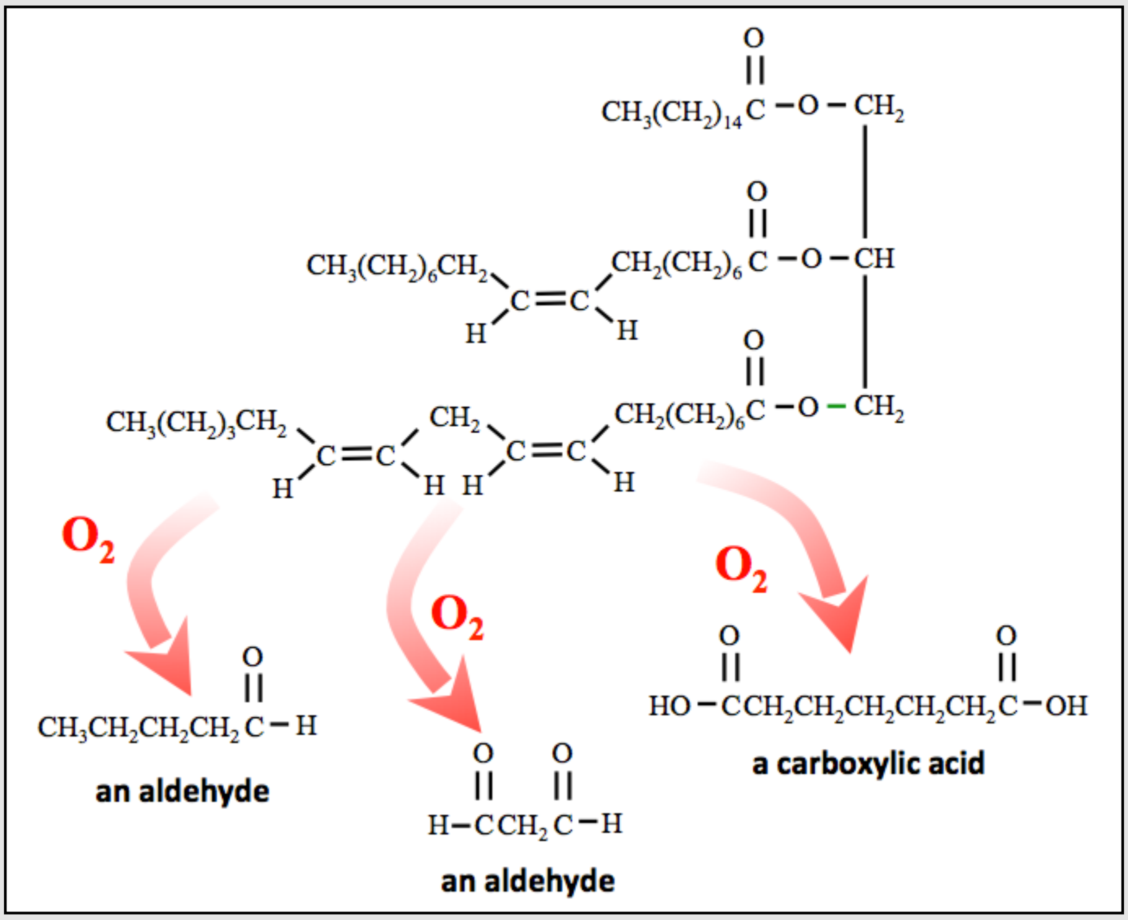


For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

2. Oxidation of Triglycerides

Triglycerides are oxidized by oxygen gas (O_2) to form *carboxylic acids* and *aldehydes*. The details of the mechanism for the oxidations, and the prediction of the *specific* aldehydes and carboxylic acids that are produced are beyond the scope of this book. Many of the aldehydes and carboxylic acids that are produced in this reaction have foul odors. When triglyceride food products undergo this reaction, it is called "**rancidification**"; the food substances are said to become "**rancid**." In order to prevent or slow the rancidification of foods, the oxygen supply can be limited by air-tight containers and packaging, and the food can be stored at low temperatures. Examples of a couple of typical aldehydes and a carboxylic acid that are produced in the oxidation of triglycerides are shown in Figure 12.8

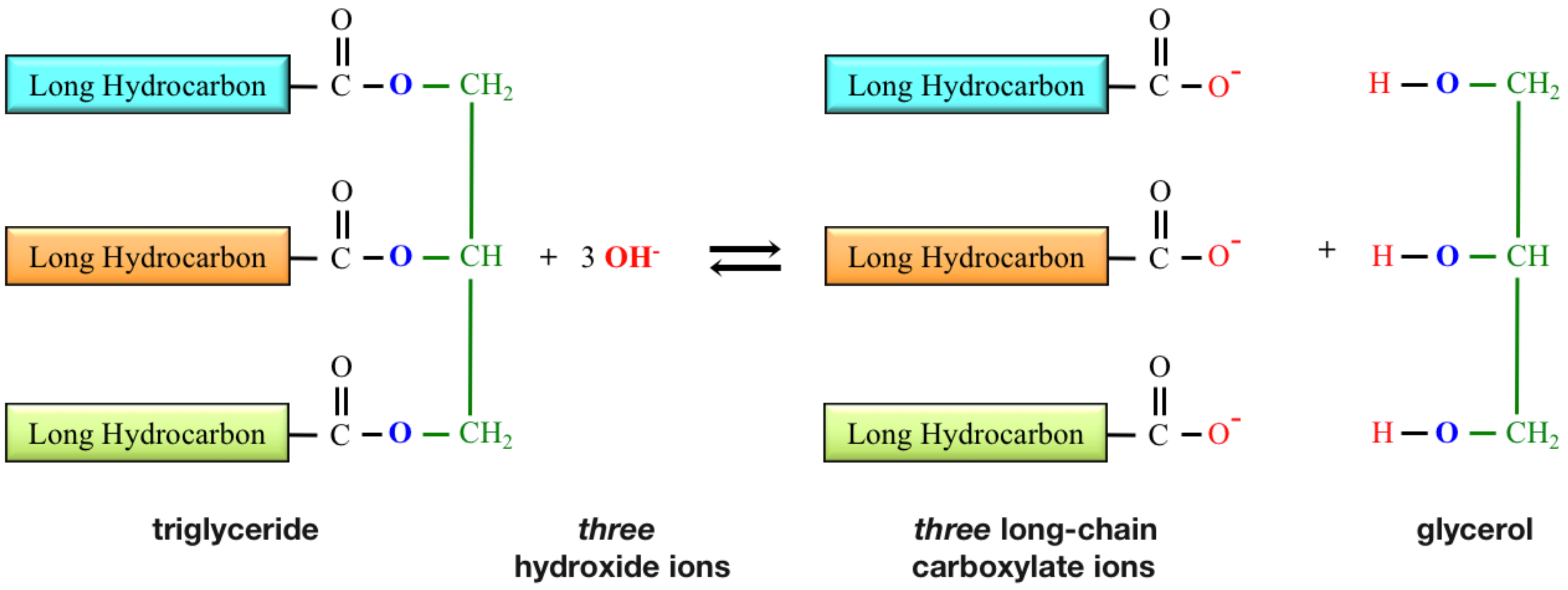
Figure 12.8
Oxidation of Triglycerides



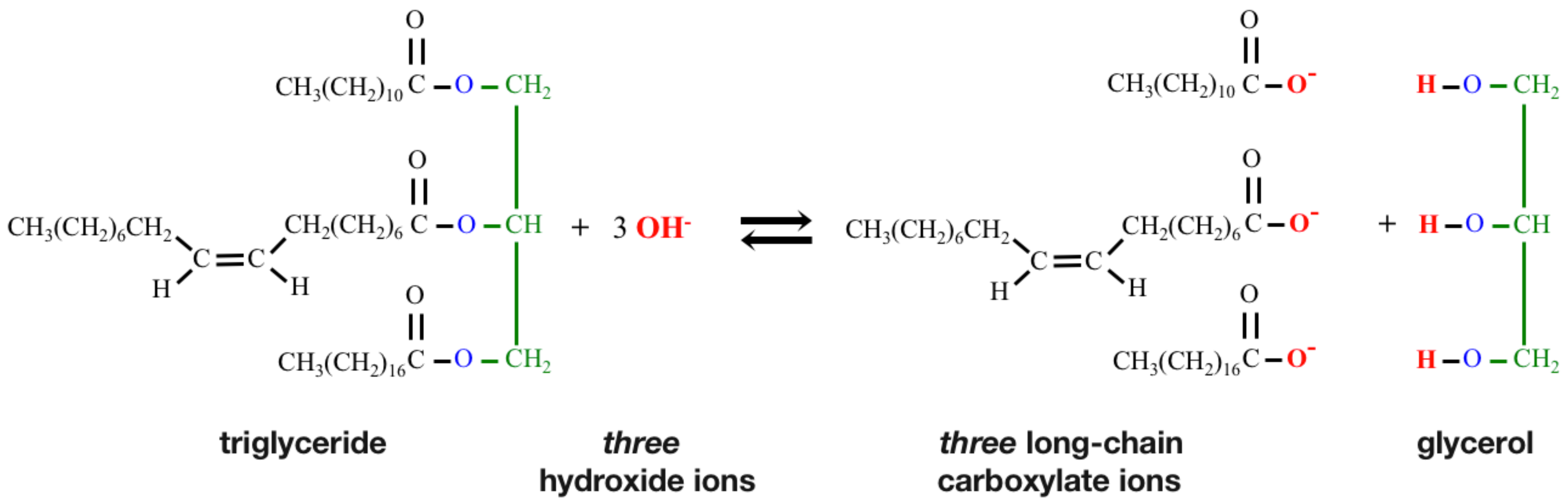
Triglycerides are oxidized by oxygen gas (O_2) to form *aldehydes* and *carboxylic acids*. The aldehydes and carboxylic acids that are produced in this reaction tend to have unpleasant odors. Prediction of the *specific* aldehydes and carboxylic acids that are produced is beyond the scope of this book, however a couple of typical aldehydes and a carboxylic acid that can be produced in this reaction are shown.

3. Saponification

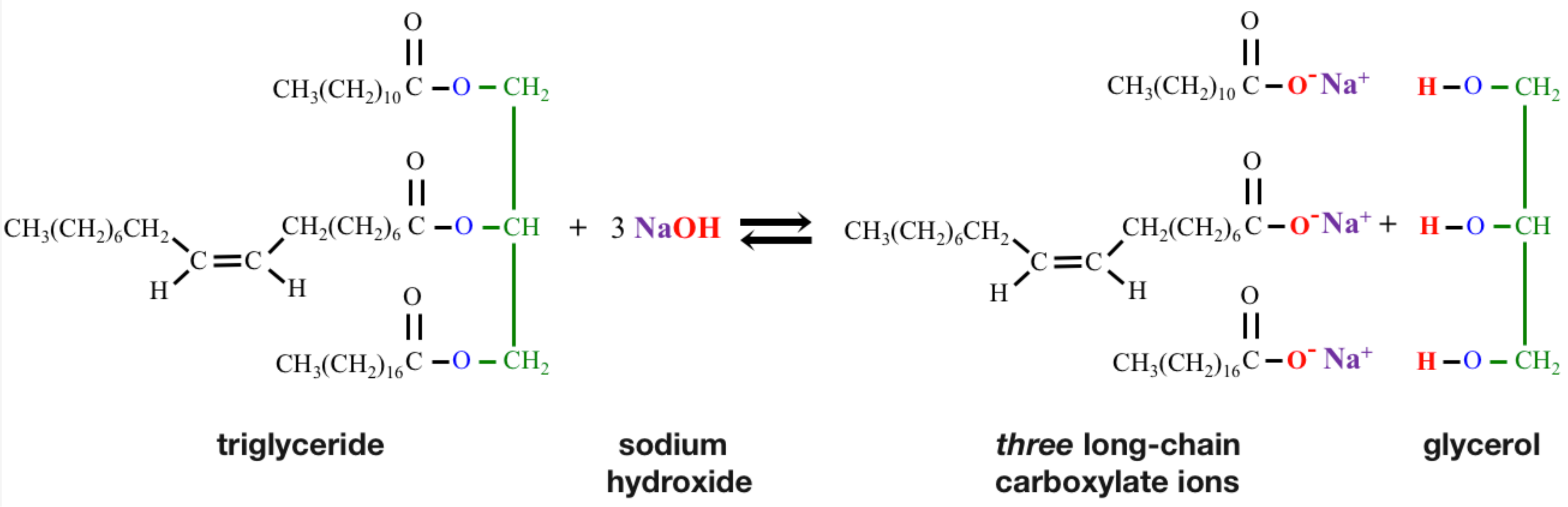
In the ***saponification*** reaction***,*** a ***triglyceride*** reacts with ***hydroxide ions*** to produce ***three long-chain carboxylate ions*** and ***glycerol*** (an alcohol). The general form of the chemical equation for the saponification of triglycerides is shown below.



An example of the saponification of a specific triglyceride is shown below.



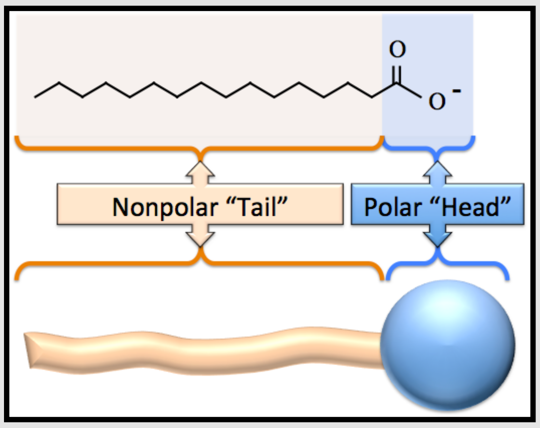
The hydroxide ions in the saponification reaction come from hydroxide-containing ionic compounds, usually sodium hydroxide ($NaOH$) or potassium hydroxide (KOH). When the cation of the hydroxide-containing compound is specified, it is often written after the long-chain carboxylate ion products as shown below:



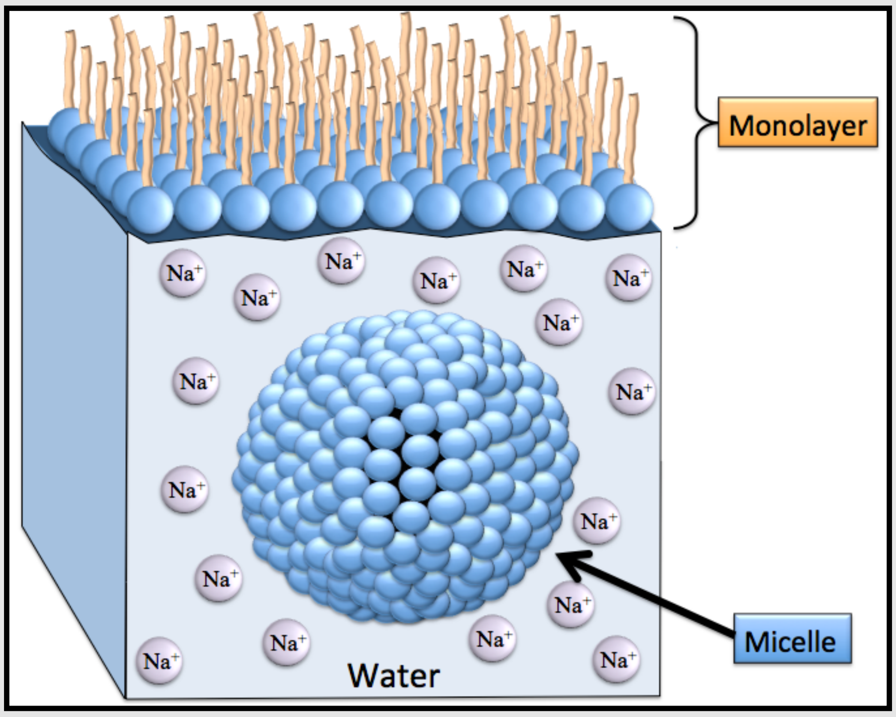
When the Na^+ or K^+ *cations* are included in chemical equations, as shown above, be careful to avoid the ***common misconception*** of interpreting the negative sign of the carboxylate ion's *formal charge* for a covalent bond to the sodium or potassium ion. The compounds formed from the long-chain carboxylate anions and the Na^+ or K^+ cations are ***ionic*** and are called ***fatty acid salts***. When *fatty acid salts* are formed or placed in water, ***only*** the cations, Na^+ in the example above, are solvated (dissolve); the long-chain carboxylate ions are amphipathic and form **monolayers** and **micelles**, as illustrated in the ***middle insert*** of Figure 12.9.

The saponification reaction is used to make **soap**. The long-chain carboxylate ions that are produced are ***amphipathic***, and act as emulsifying agents to remove nonpolar molecules (i.e. grease or oil) from surfaces, including - very importantly - skin and clothing. An illustration of an oil droplet emulsified by a long-chain carboxylate ion micelle is shown in the ***bottom insert*** of Figure 12.9. You can review amphipathic compounds and how they act as emulsifying agents in chapter 7, section 6.

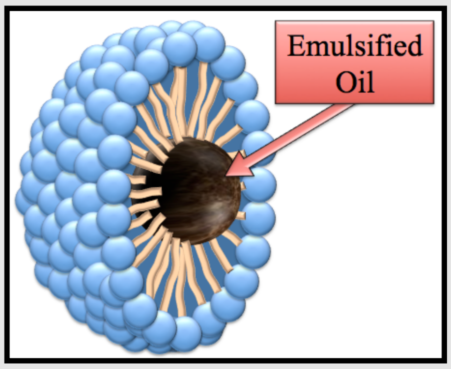
Figure 12.9 Fatty Acid Salts



Top: Representation of an amphipathic long-chain carboxylate ion using a sphere (blue) as the polar "head" for the carboxylate group (COO-) and long cylindrical shape (orange) for the nonpolar "tail".



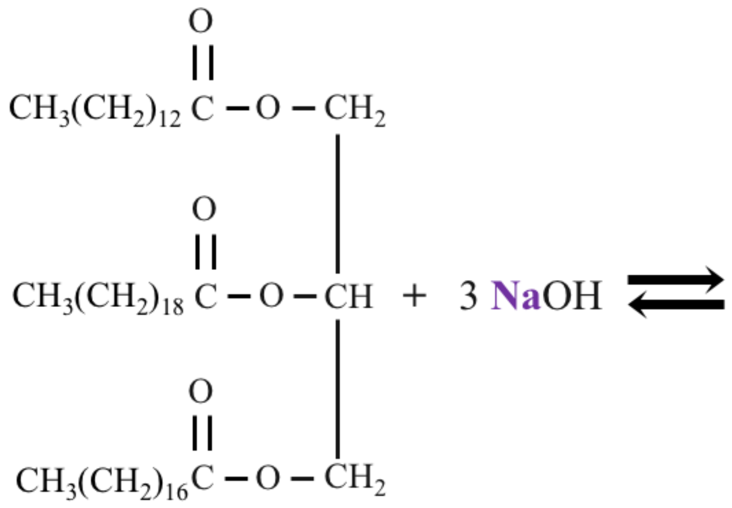
Middle: A *fatty acid salt* and water. ***Only the cations*** - Na^+ in this example - are solvated (dissolve); the long-chain carboxylate ions form **monolayers** and **micelles**.



Bottom: An illustration of an oil droplet emulsified by the long-chain carboxylate ions of fatty acid salts (soap).

Review 12.9: Saponification

Draw the *condensed structure* of the products for the saponification of the triglyceride shown below. Include the cations when drawing fatty acid salts.



For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

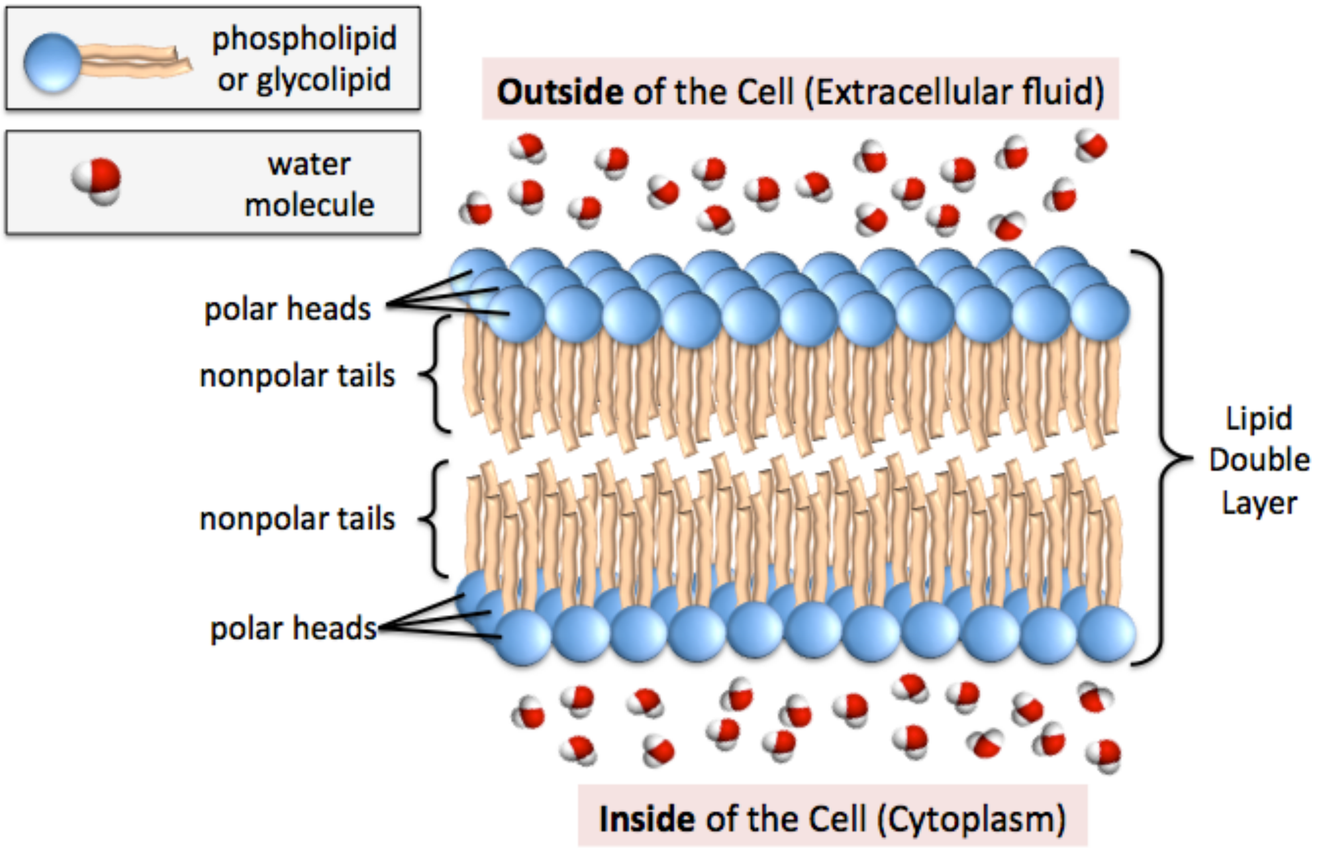
Use the link below for more practice ***with the structures of fatty acids and triglycerides***:

http://www.zovallearning.com/GOBlinks/ch12/fatty-acid-and-triglyceride-worksheet.pdf

Get the entire course as a series of video lectures at: www.zovallearning.com

12.6 Phospholipids and Glycolipids

Phospholipids and glycolipids are best known for their presence in biological membranes. They are amphipathic compounds that contain a polar "head" group that is very hydrophilic, and hydrophobic nonpolar "tail" groups. They are found in nature as either monolayers, micelles, or in a layer that is two molecules-thick called a "**lipid double layer**" or a "**lipid bilayer**." An illustration of a section of a cell membrane's lipid double layer is shown below.



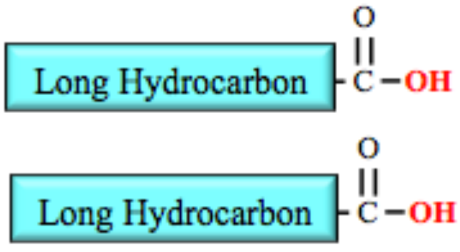
Note that the polar heads are oriented either toward the water that is inside the cell, or toward the water that is outside of the cell. The nonpolar tails in the top of the double layer are much more attracted to the nonpolar tails in the bottom of the double layer than to water or polar head groups. It is for this reason that the two monolayers have the tail-to-tail orientation. In the last section of this chapter, you will see that there are other components distributed throughout the lipid double layer of biological membranes, however, for simplicity, those other components are not included in the illustration shown above. Lipid double layer membranes not only occur as cell membranes, they also form specialized compartments within cells. For example, intracellular double layer membranes occur in liposomes and form the outer boundary of a cell's nucleus.

Phospholipids

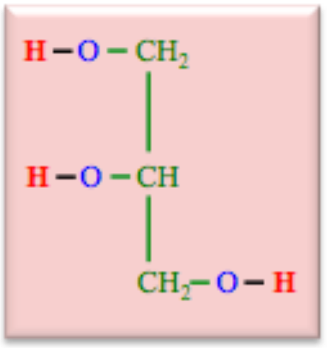
There are two main classes of **phospholipids**: ***glycerophospholipids*** and ***sphingophospholipids***. Both of these classes contain a phosphate residue in their structure, it is for this reason that they are called ***phospho***lipids. I will elaborate on the difference between these two classes of lipids in the following discussions of their structures.

1) Glycerophospholipids

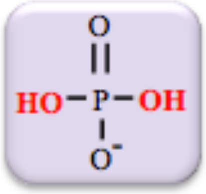
Glycerophospholipids are made from the components shown below.



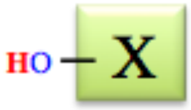
one *or* two fatty acids



glycerol

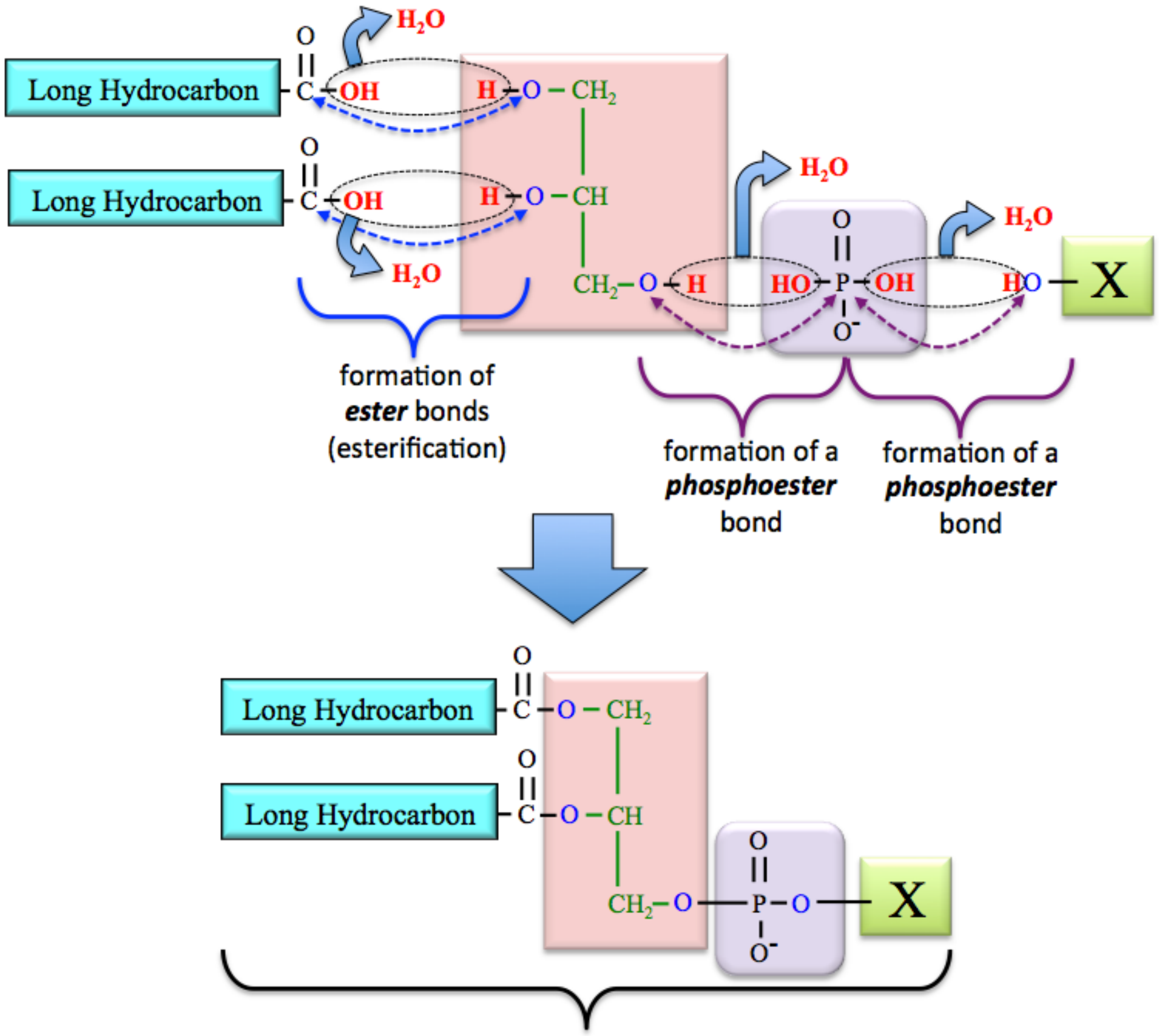


a phosphate (dihydrogen phosphate ion)



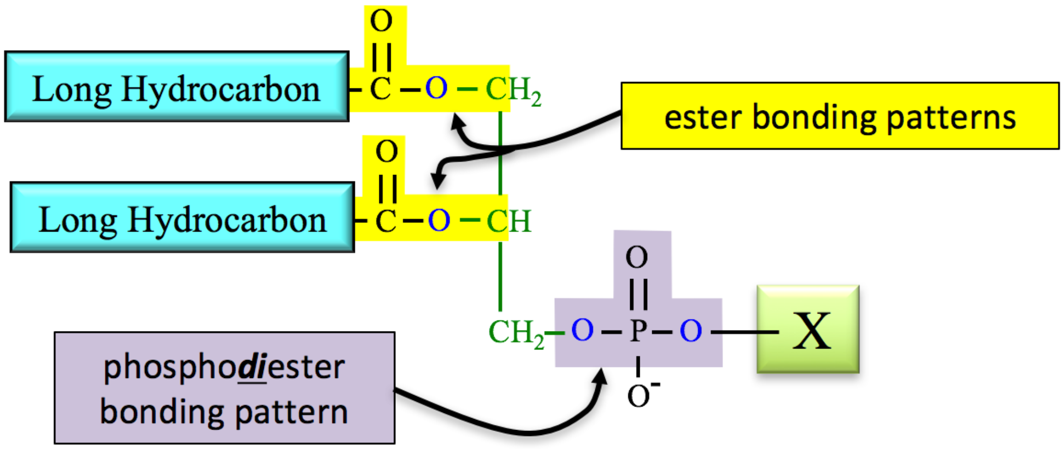
an alcohol (X = an organic group)

These components are bonded to each other by ***esterification reactions*** to form glycerophospholipids:



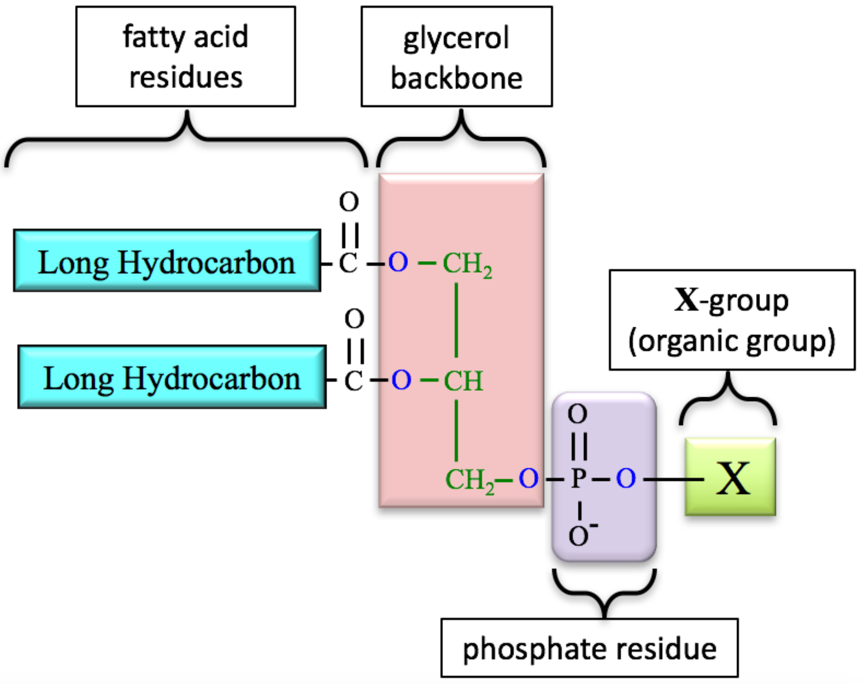
general form of a glycerophospholipid

You have seen the esterification reaction of fatty acids with alcohols (glycerol) when you learned about triglycerides. As shown above, this same reaction occurs between *fatty acids* and *glycerol* in the formation of a glycerophospholipid. A **phosphoester bond** is formed when a *phosphate* reacts with an *alcohol*, as seen in ***two*** cases above. The hydroxyl group on the left-hand side of the *phosphate* reacts with glycerol. The hydroxyl group on the right-hand side of the phosphate reacts with the *other alcohol* (HO-**X**). When ***both*** OH's of a phosphate form phosphoester bonds, the bonding pattern is called a phospho***diester*** bond. Note the similarity in the way that a carboxyl group (COOH) of a fatty acid reacts with an alcohol, and the way that a phosphate reacts with an alcohol. The *ester* and *phosphodiester* bonding patterns in a *glycerophospholipid* are highlighted and labeled in the structure below.



bonding pattern of glycerophospholipids

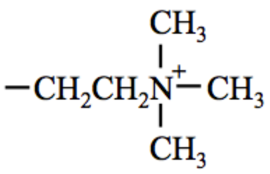
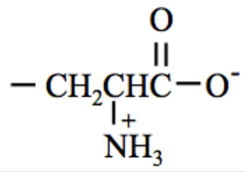
The various “residues” that make up a glycerophospholipid are labeled in the structure below.



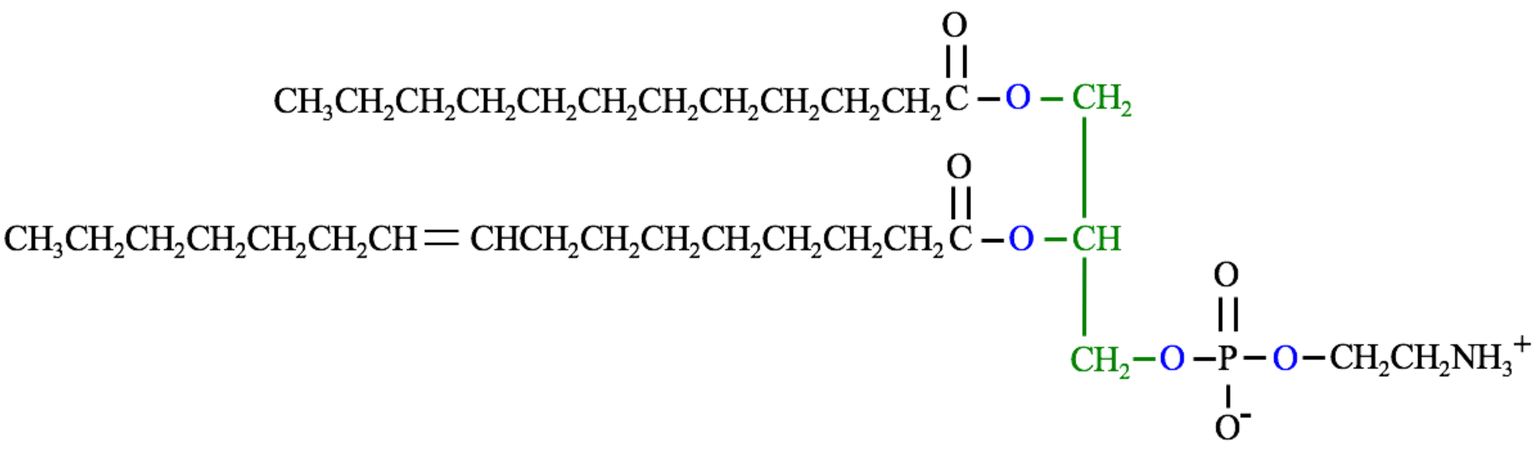
The atoms that came from glycerol (in the red box above) are referred to the “**glycerol backbone**.”

The identity of the organic “X-group” varies. Table 12.5 shows the three X-groups that are most frequently seen in glycerophospholipids. The subclasses of glycerophospholipids are determined by the identity of their X-groups, and are listed in Table 12.5. **Phosphatidylethanolamines** and **phosphatidylserines** are components of *cephalin*. Cephalin is found throughout the body, with especially large amounts present in the brain and nerve tissue. **Phosphatidylcholines** are a component of *lecithin*. Lecithin is a term for the yellow-brown fatty substances present in animal and plant tissues.

Table 12.5
The Three Most Common “X-Groups” found in Glycerophospholipids

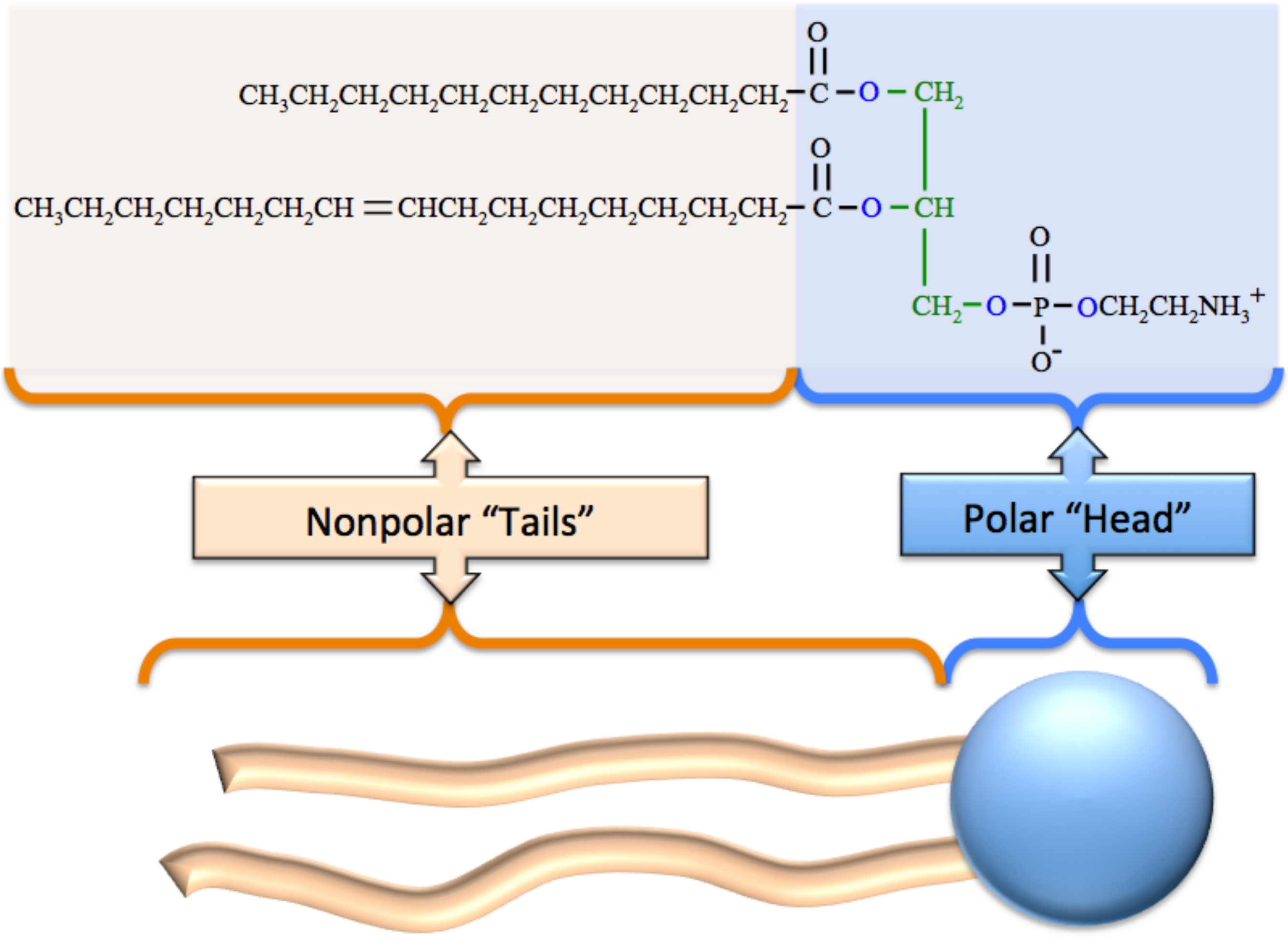
Organic “X group”	Glycerophospholipid Class
$-CH_2CH_2NH_3^+$	Phosphatidylethanolamine (present in *Cephalin*)
 $-CH_2CH_2\overset{+}{N}(CH_3)_3$	Phosphatidylcholine (present in *Lecithin*)
 $-CH_2\underset{NH_3^+}{CH}\overset{O}{\overset{\|}{C}}-O^-$	Phosphatidylserine (present in *Cephalin*)

A specific example of a *glycerophospholipid* is shown below.



The three carbons of the *glycerol backbone* are shaded green. This particular glycerophospholipid is classified as a phosphatidylethanolamine because the X-group is **- $CH_2CH_2NH_3^+$**. I arbitrarily chose to use stearic and palmitoleic fatty acid residues; any two fatty acids could have been used.

Now that you have been introduced to the structures of glycerophospholipids, you can understand why they are amphipathic. These lipids have a polar head region and nonpolar tails, as depicted for the glycerophospholipid below.

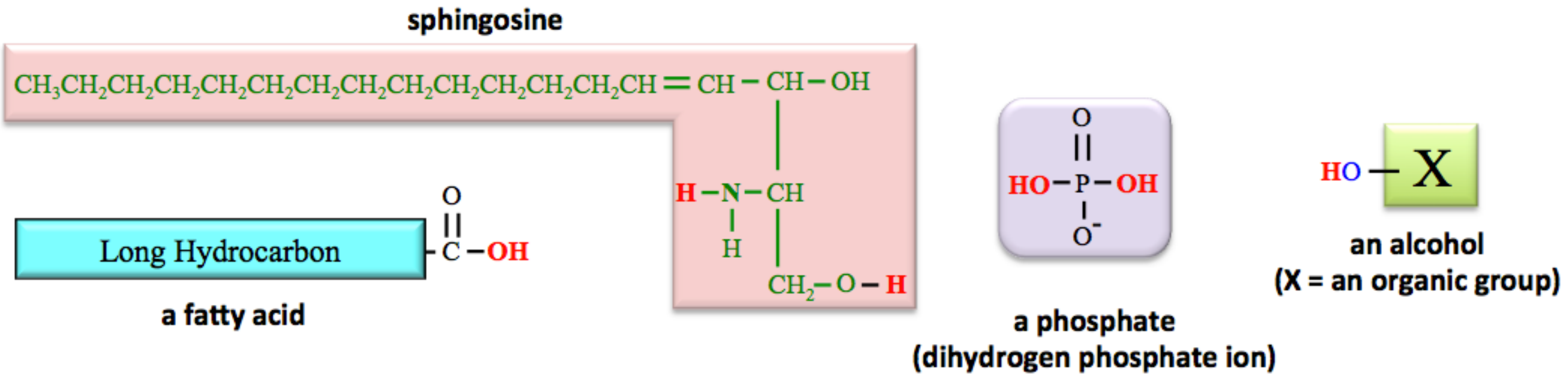


The *polar head* region is quite ***hydrophilic***. This region is attracted to water through ***dipole-dipole*** interactions because it contains several "highly polar" bonds. It can ***hydrogen bond*** with water. The polar head is also attracted to water through ***ion-dipole interactions*** because of the *formal charge* on both an oxygen *and* a nitrogen. The hydrocarbon chains of the fatty acid residues make up the nonpolar tails.

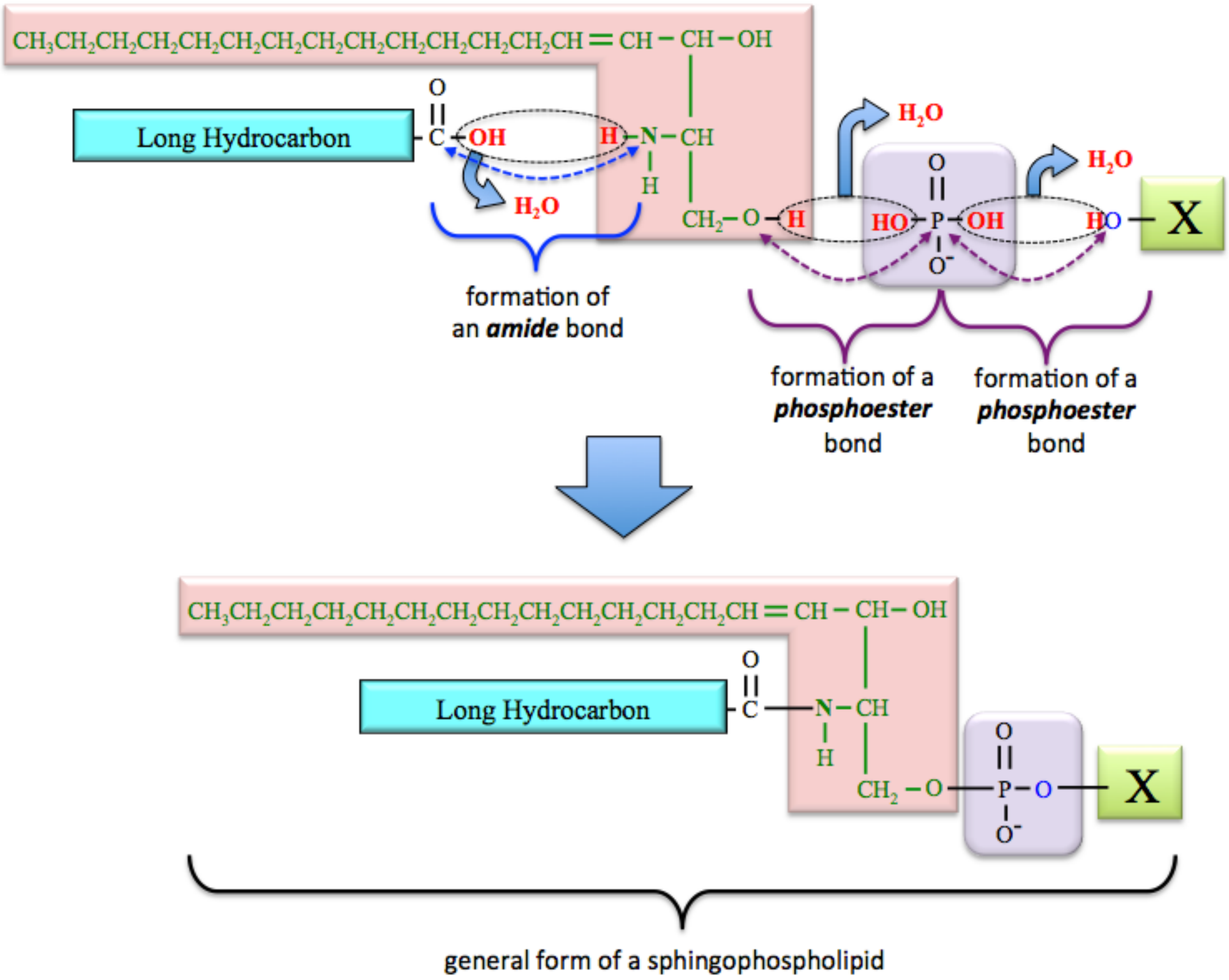
2) Sphingophospholipids

The difference between the two classes of phospholipids - *glycerophospholipids* and *sphingophospholipids* - is that ***sphingophospholipids*** have a "*sphingosine backbone*" instead of a *glycerol backbone*.

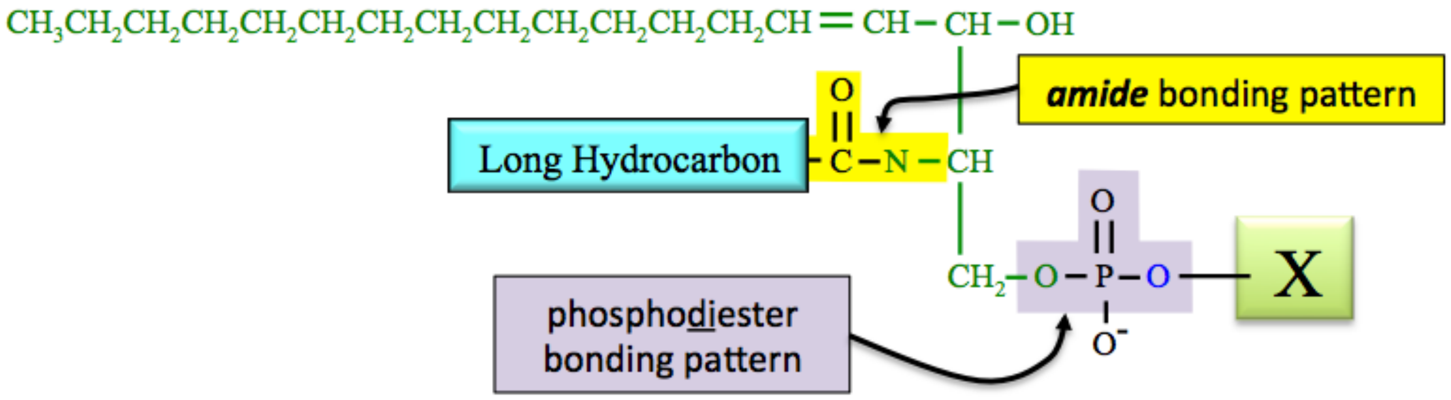
Sphingophospholipids are made from the components shown below.



These four components combine to make a sphingophospholipid:

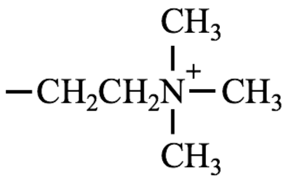


In sphingophospholipids, we refer to the sphingosine residue (highlighted red above) as the "sphingosine backbone." A fatty acid reacts with sphingosine's ***amino group*** ($-NH_2$) to form an **amide bond**, as shown above. ***Amide bonds***, which were discussed in detail in chapter 9, are single bonds between a carbonyl carbon and a nitrogen. A phosphodiester is formed when the phosphate reacts with both sphingosine ***and*** the alcohol. The ***amide*** and ***phosphodiester*** bonding patterns for a sphingophospholipid are indicated in the structure shown below.



bonding pattern for sphingophospholipids

Table 12.6
The Most Common “X-Groups” found in Sphingophospholipids

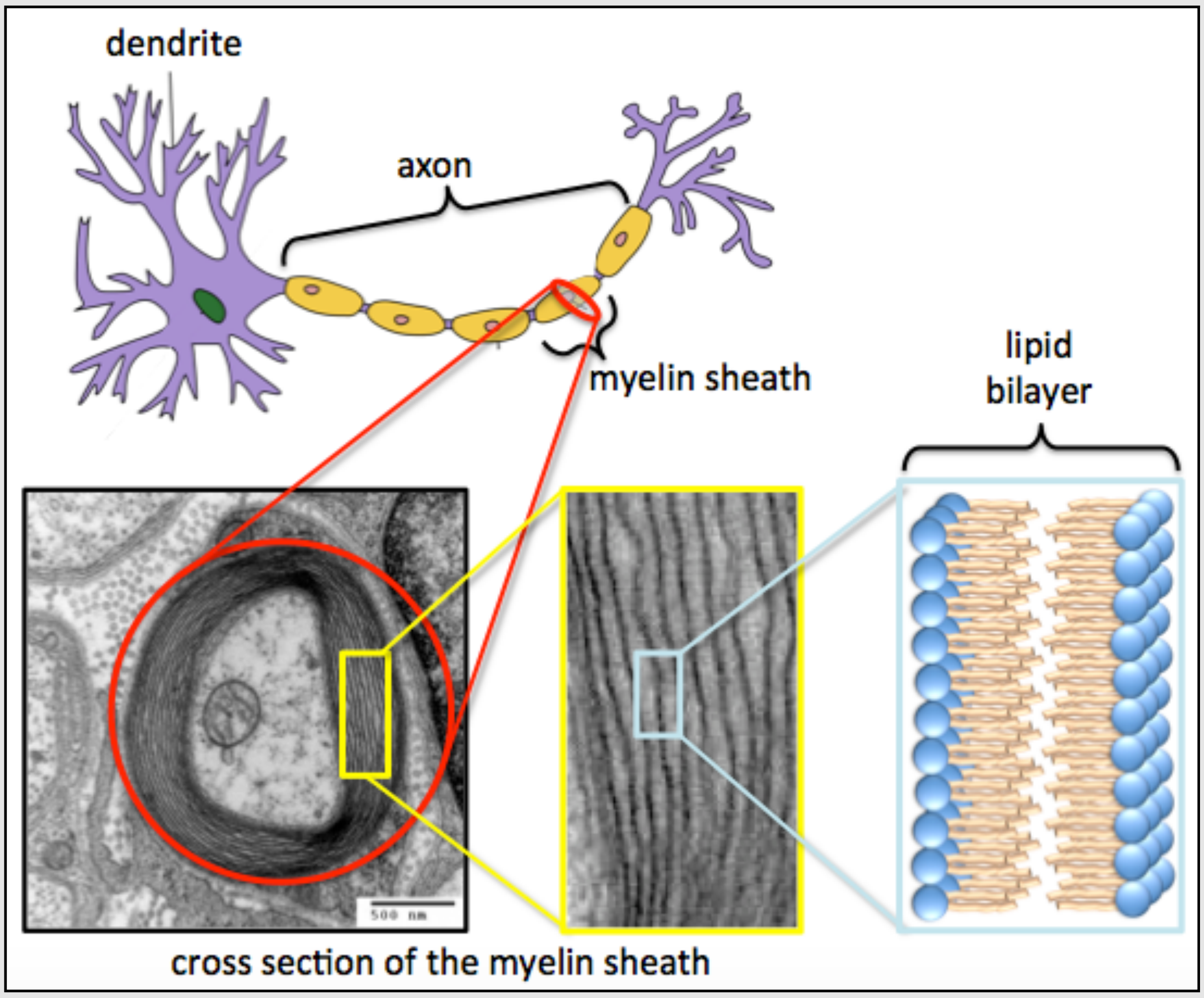
“X-group”	**Sphingophospholipid Class**
$-\mathrm{H}$	Ceramide
$-\mathrm{CH_2CH_2NH_3^+}$ or  $-\mathrm{CH_2CH_2\overset{+}{N}(CH_3)_3}$	Sphingomyelin

As was the case for glycerophospholipids, the identity of sphingophospholipids’ “**X**-group” varies. Sphingophospholipids are classified based on their **X**-group. The three most common sphingophospholipid **X**-groups are shown in Table 12.6

If the **X**-group of a sphingophospholipid is [- $\mathbf{CH_2CH_2N^+(CH_3)_3}$], or [- $\mathbf{CH_2CH_2NH_3^+}$], then it is classified as a **sphingomyelin**. Sphingomyelins have this name because they are the most abundant class of *phospholipid* found in myelin (although they are the most abundant ***phospho****lipids* found in myelin, the most abundant *lipids* in myelin are *glycolipids*, which I will discuss soon). Myelin is a combination of lipids (85%) and proteins (~15%), assembled as a ***bilayer*** that wraps around nerve cell axons, as illustrated in Figure 12.10. The myelin sheath is an electrical insulator and its main function is to increase the speed at which nerve impulses are propagated along axons.

Figure 12.10

TEM Image of a Myelin Sheath Cross Section



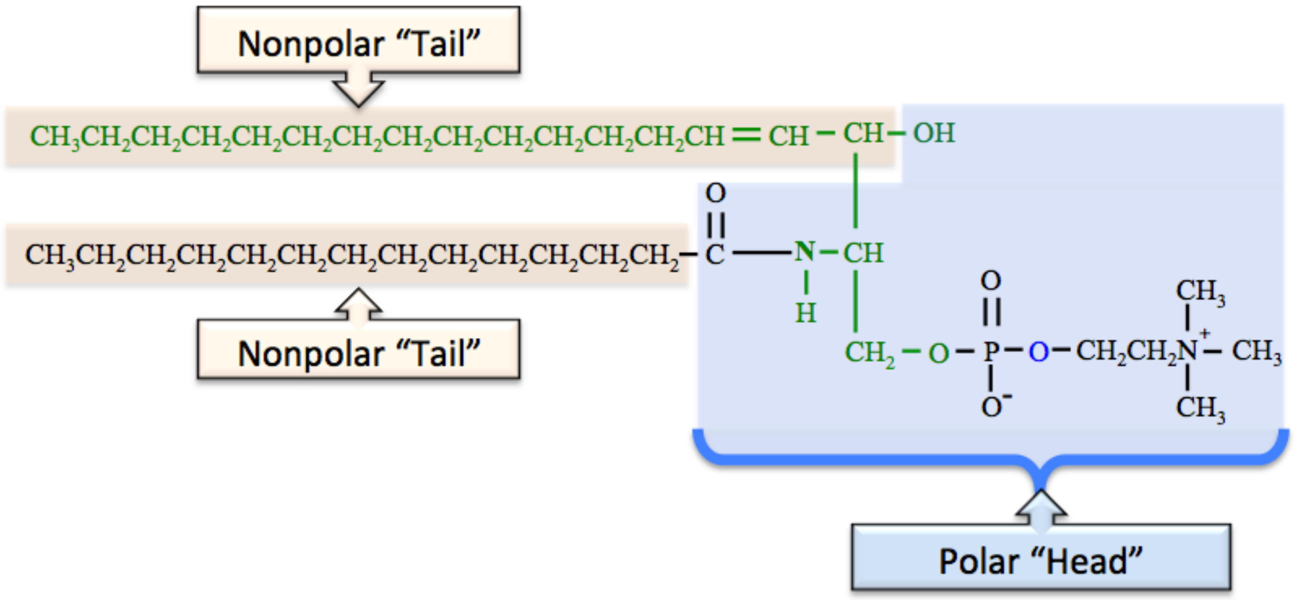
Top: An illustration of a nerve cell.
Source: Wikimedia Commons, Author: Quasar Jarosz, CC-BY-SA http://creativecommons.org/licenses/by-sa/3.0/deed.en (adapted from original work)

Bottom, left and middle: Transmission electron micrograph (TEM) of a myelinated axon cross section. The myelin bilayer (concentric) surrounds the axon.
Source: Wikimedia Commons, Author: roadnottaken, CC-BY-SA http://creativecommons.org/licenses/by-sa/3.0/deed.en (adapted from original work)

Bottom, right: An illustration of a small section of a myelin lipid bilayer. Although myelin is about 15% protein, the proteins are omitted from the illustration for simplicity in viewing.

If the X-group of a sphingophospholipid is a hydrogen (-H), instead of an organic group, then it is classified as a **ceramide**. *Ceramides* are found in cell membranes and in the myelin sheath of nerve cells.

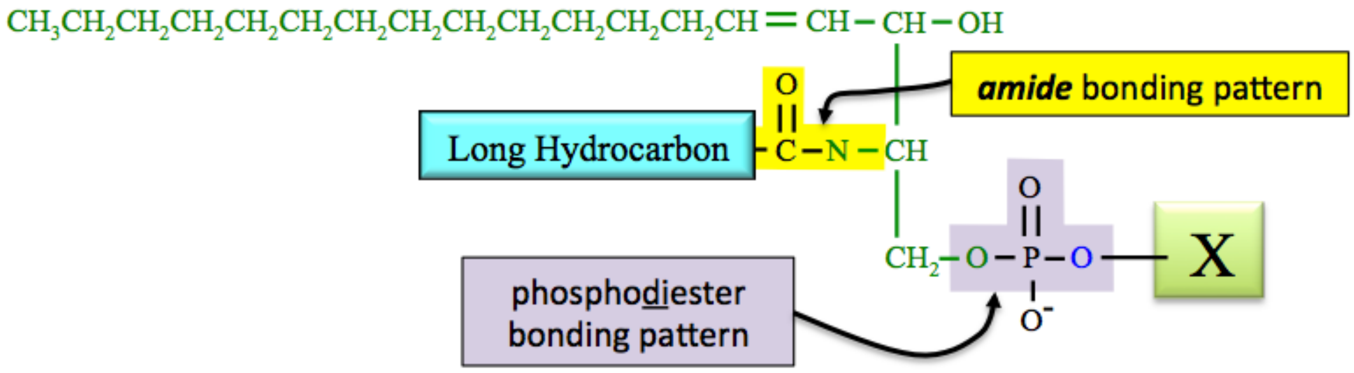
A specific example of a sphingophospholipid (a sphingomyelin) is shown below.



The atoms from sphingosine are in green font. I arbitrarily chose to use *myristic acid* as the fatty acid residue; any fatty acid could have been used. This particular sphingophospholipid is classified as a *sphingomyelin* because the X-group is **$-CH_2CH_2N^+(CH_3)_3$**. Sphingophospholipids are amphipathic. They have a polar head region and nonpolar tails, which are labeled in the structure above. Note that most of the atoms from sphingosine are part of one of the lipid's nonpolar tails.

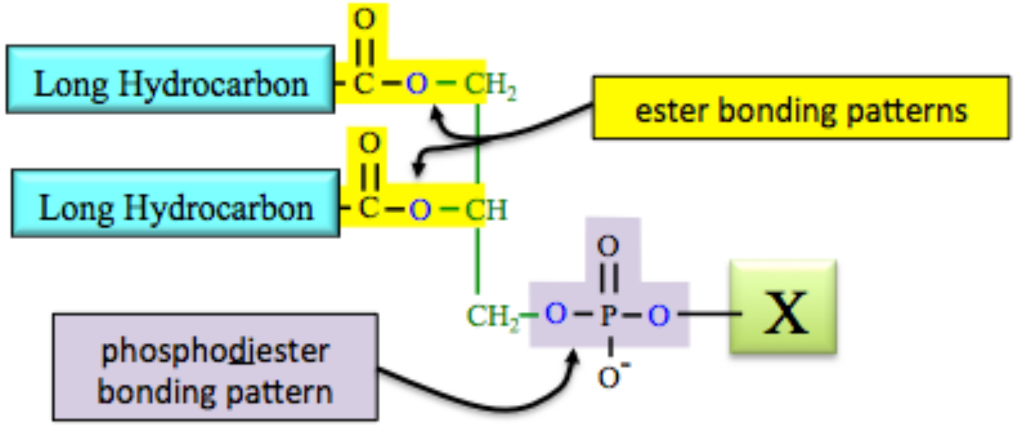
Review of Phospholipid Structure: Glycerophospholipids vs. Sphingophospholipids

If you are given the structure of a **phospholipid**, you should be able to determine if it is a ***glycerophospholipid*** or a ***sphingophospholipid***. The key to doing so is to identify either a *glycerol backbone* (for glycerophospholipids) or a *sphingosine backbone* (for sphingophospholipids). An easy way to do so is to look for the ***nitrogen*** in the ***amide bond*** between the fatty acid residue and the *sphingosine backbone*. This *amide* bonding pattern is ***present in sphingophospholipids, but not in glycerophospholipids***.



bonding pattern for sphingophospholipids

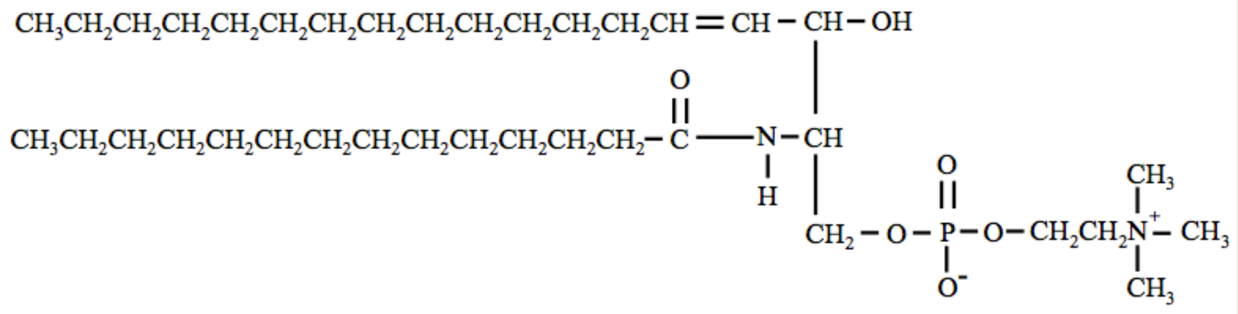
Alternatively, you can differentiate glycerophospholipids from sphingophospholipids by the presence the ***ester bonding pattern*** between the fatty acid resides and the *glycerol backbone*. This *ester* bonding pattern is ***present in glycerophospholipids, but not in sphingophospholipids***:



bonding pattern of glycerophospholipids

Review 12.10: Identification of Glycerophospholipids vs. Sphingophospholipids

Identify (circle) the ***nitrogen atom*** that is contained in the amide bond in the sphingophospholipid shown below.

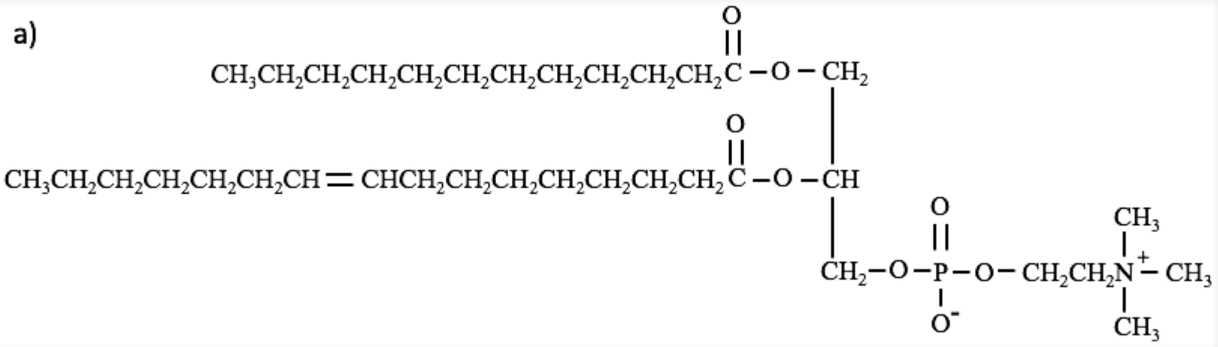


For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

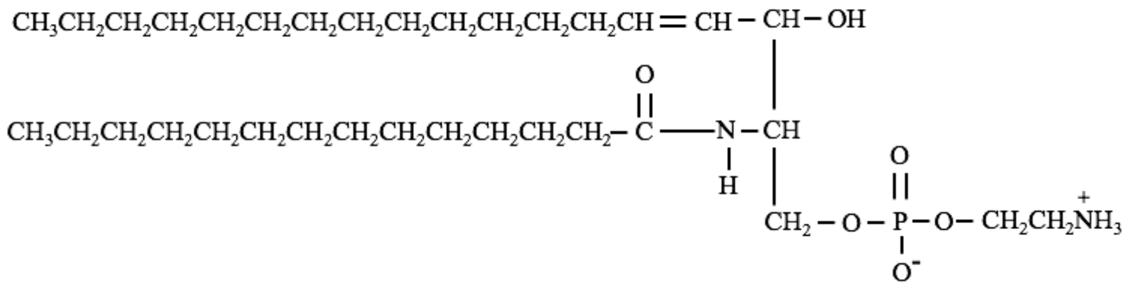
Review 12.11: Identification of Glycerophospholipids vs. Sphingophospholipids

Categorized each of the following compounds as being either a ***glycerophospholipid*** or a ***sphingophospholipid***.

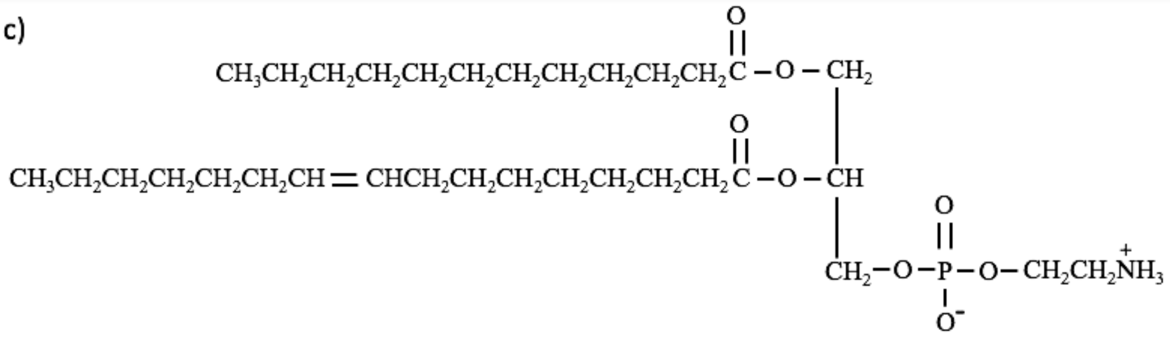
a)



b)



c)



For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

Review 12.12: Classification of Glycerophospholipids and Sphingophospholipids

Categorize each of the compounds from the previous problem (12.11) as being either a phosphatidylethanolamine, a phosphatidylcholine, a phosphatidylserine, a ceramide, or a sphingomyelin.
Hint: use Table 12.5 or Table 12.6.

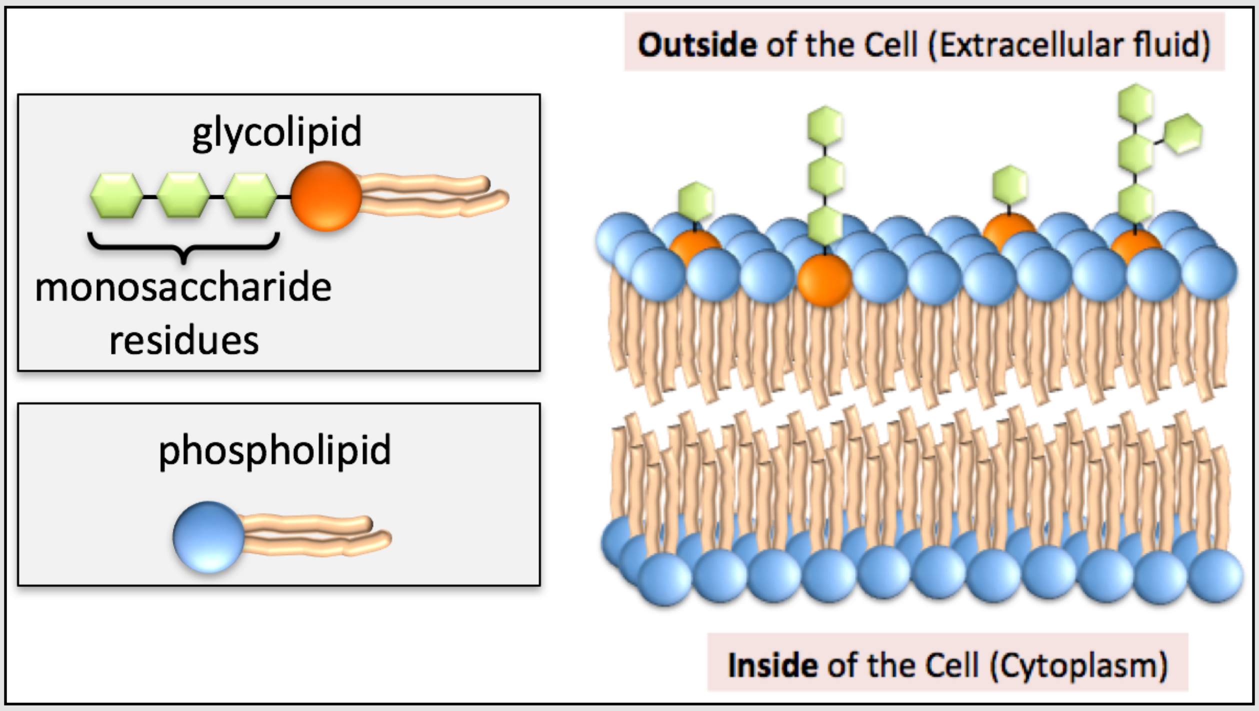
For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

Glycolipids

Glycolipids are *lipids* that contain ***one or more monosaccharide residues***. *Glycolipids* are easily distinguished from *phospholipids* by the *presence* of a monosaccharide residues and the *absence* of a phosphate residues. Glycolipids are found in the cell membranes of plants and animals. In all eukaryotic cells, the monosaccharide residues of the glycolipid extend from the outer surface of the cell membrane double layer into the aqueous region outside of the cell, as shown in Figure 12.11.

Figure 12.11

Illustration of Glycolipids in a Cellular Lipid Double Layer

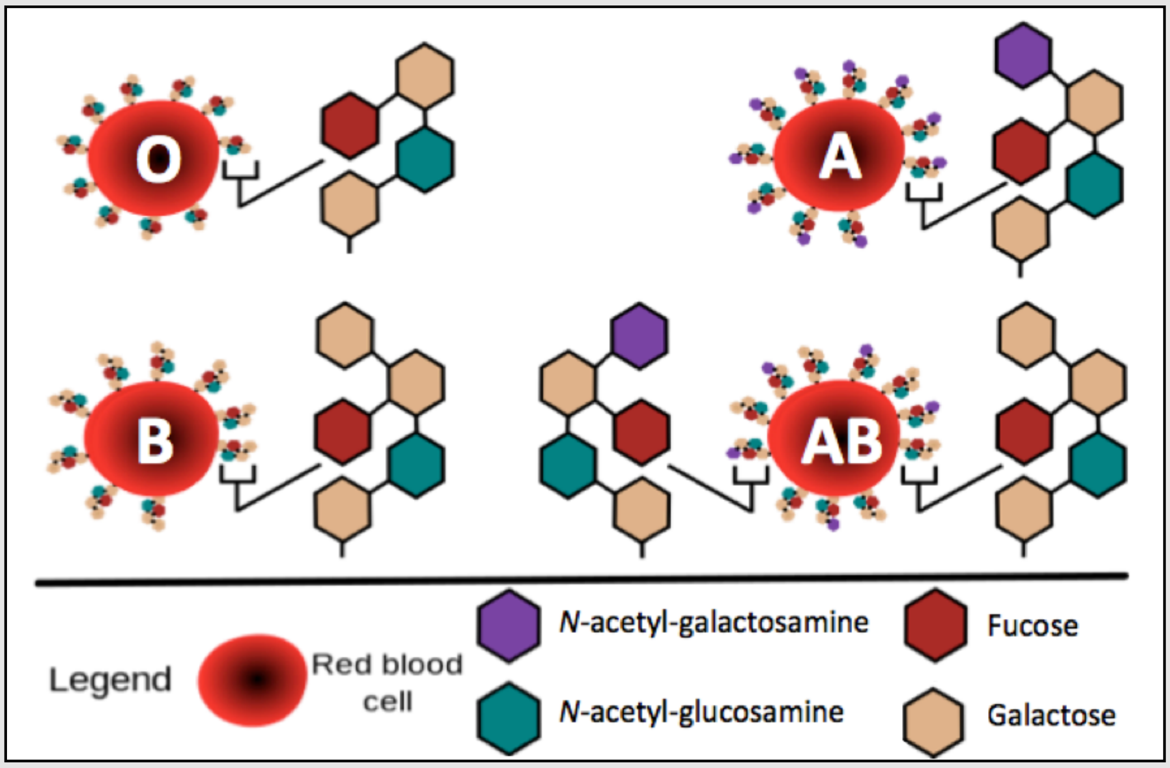


Glycolipids extend from the outer surface of the cell membrane double layer into the aqueous region outside of the cell. The monosaccharides residues are drawn as green hexagons.

The specific monosaccharide residues that protrude from the membrane serves in maintaining membrane stability, attaching cells to one another to form tissues, and as a "recognition site" for "cell signaling" chemicals. Cell signaling chemicals make it possible for the cells to respond to their environment in order to enable functions such as tissue homeostasis, immunity, and the development of the organism. When signaling systems are not operating correctly to process the communication between cells and their environments, diseases such as cancer, diabetes, and autoimmune disorders occur. An example of glycolipid recognition sites are the monosaccharide residues that protrude from red blood cells and form the basis of ABO blood typing. Figure 12.12 shows the various bonding patterns of glycolipid-monosaccharides used for ABO blood typing and their classification.

Figure 12.12

The Glycolipid Monosaccharides in ABO Blood Typing



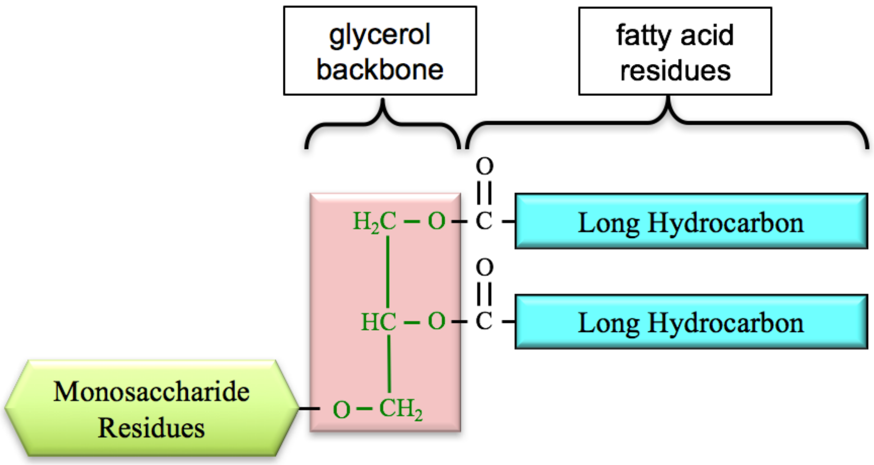
This image shows the glycolipid monosaccharide residues that define the four "ABO" blood types. Note that type AB red blood cells contain both type-A and type B glycolipids.

Source: PD

Glycolipids can be classified by their structures as **glyceroglycolipids** or **sphingoglycolipids.**

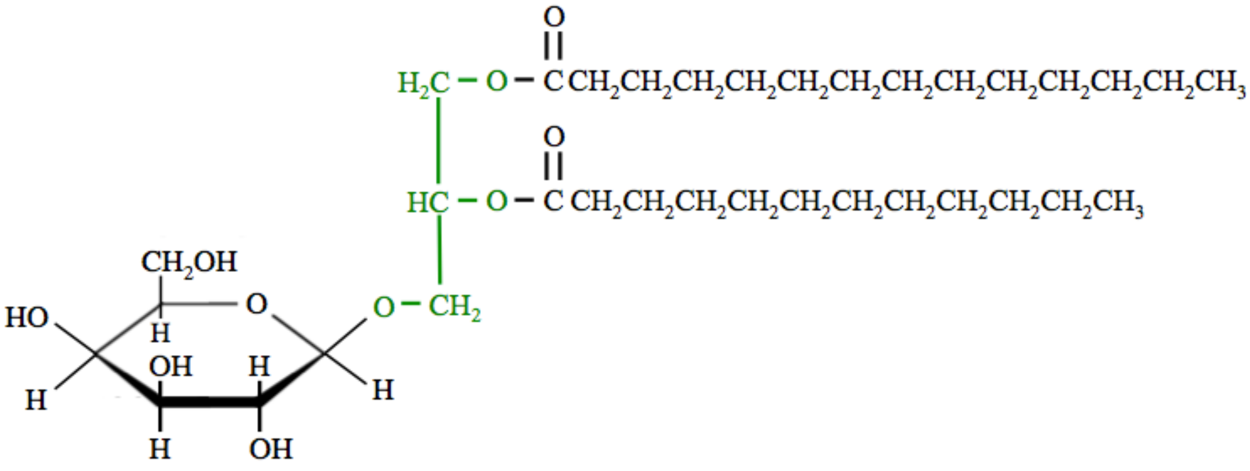
1) Glyceroglycolipids

Glycolipids often have glycerol or sphingosine backbones. Glycolipids with a ***glycerol backbone*** are called **glyceroglycolipids**. The general form of a glyceroglycolipid is shown below.



general form of a glyceroglycolipid

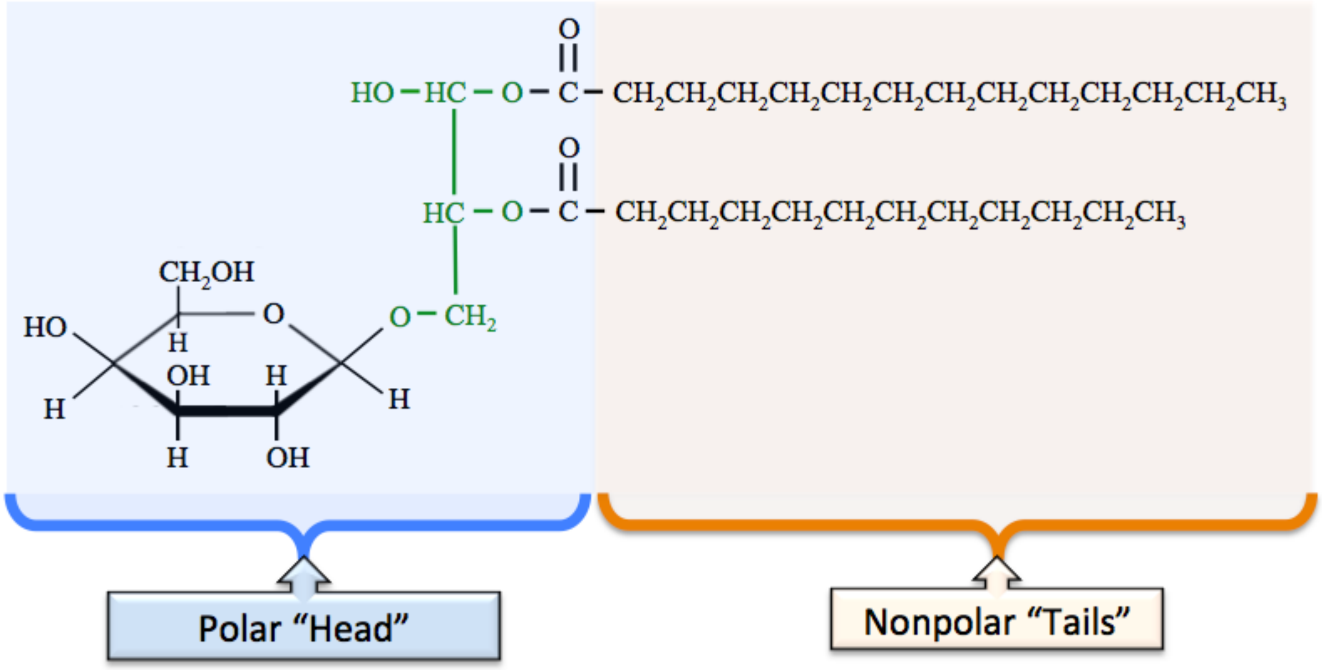
A specific example of a glyceroglycolipid is the monogalactosyldiglyceride (MGDG) shown below.



monogalactosyldiglyceride (a glyceroglycolipid)

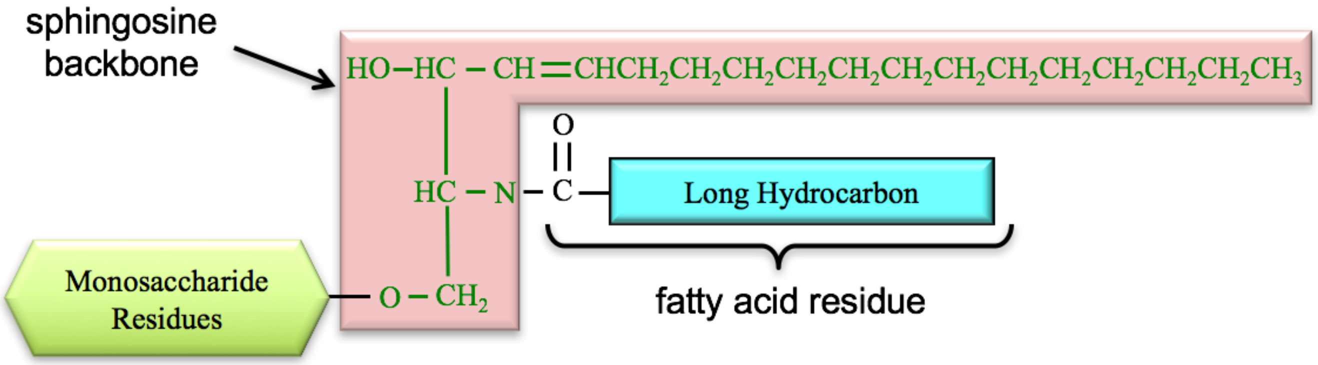
The monosaccaride residue in all monogalactosyldiglycerides is galactose. The fatty acid residues of monogalactosyldiglycerides vary; I arbitrarily chose the two fatty acid residues in the structure shown above. MGDG occurs in high quantity in the membranes that surround chloroplast organelles.

All glycolipids are *amphipathic*. They have a polar head region and nonpolar tails, which are labeled in the structure of MGDG shown below. The multiple highly-polar **OH** groups from the monosaccharide reside make the polar head region quite hydrophilic.



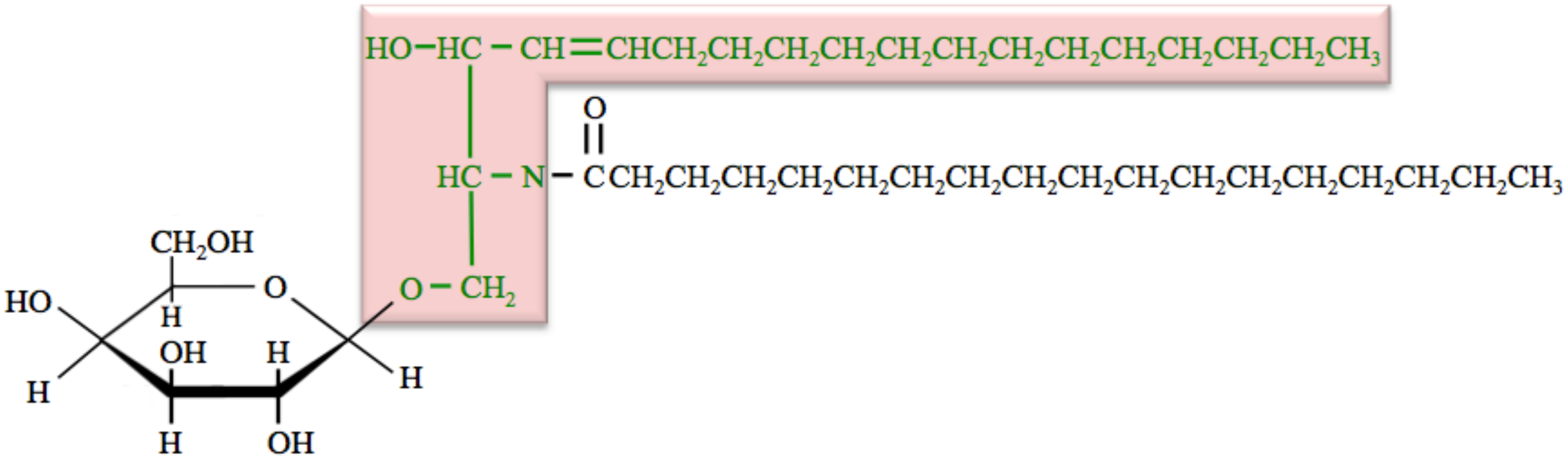
2) Sphingoglycolipids

Glycolipids with a ***sphingosine backbone*** are called **sphingoglycolipids**. Sphingoglycolipids are found predominantly in nerve and muscle cells. They are the major lipid component of the myelin sheath (Figure 12.10). The general form of a sphingoglycolipid is shown below.



general form of a sphingoglycolipid

An example of a sphingoglycolipid is the glucosylceramide shown below:

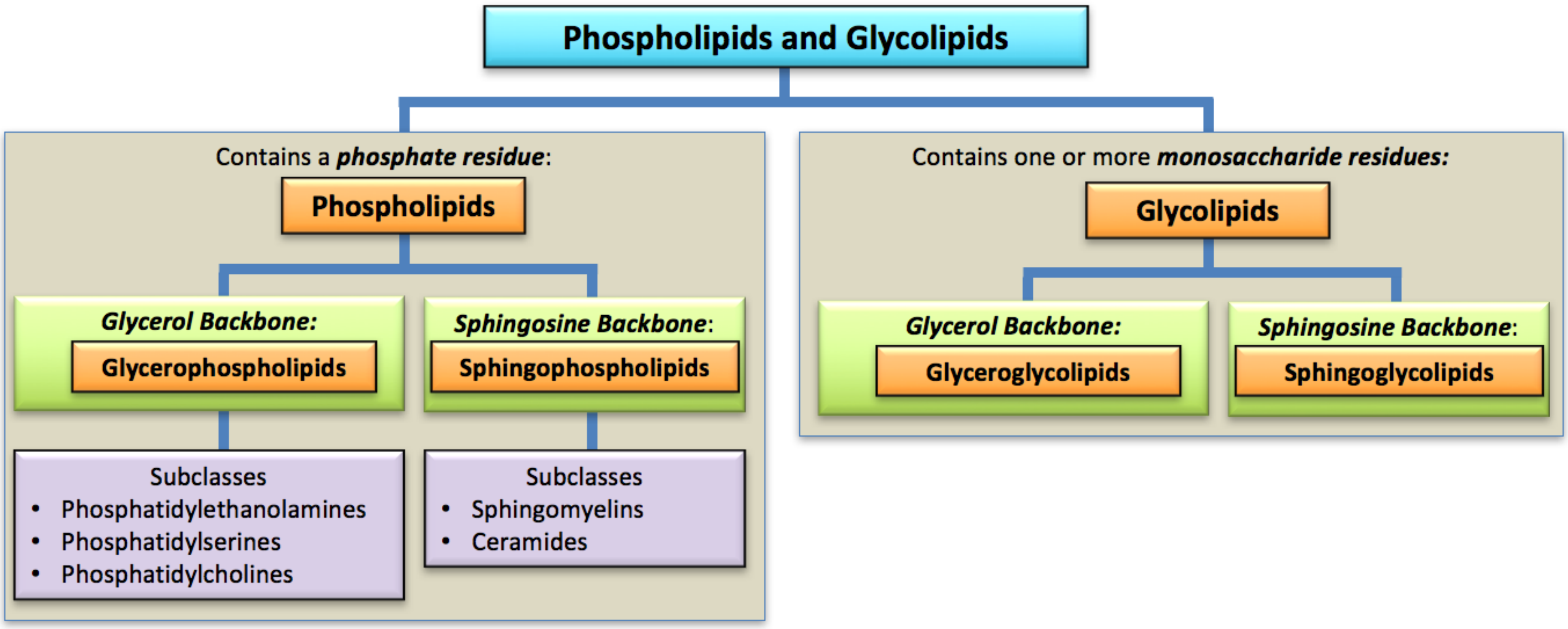


a glucosylceramide (a sphingoglycolipid)

The monosaccharide residue in all glucosylceramides is glucose. The fatty acid residue in glucosylceramides varies; I arbitrarily chose a stearic acid residue for the structure shown above.

The accumulation of large quantities of sphingolipids in cells and organs results from certain genetic diseases called ***lipidosis***. The body normally controls the amount of sphingolipids that accumulate by using enzymes that catalyze reactions that break down sphingolipids. Genetic disorders result in a deficiency of an enzyme responsible for the breakdown of a sphingolipid. Gaucher's disease is caused by a deficiency in the enzyme that breaks down glucosylceramide. Krabbe disease is caused from a deficiency in the enzyme responsible for catalyzing the breakdown of galactosylceramine (a sphingolipid in which the monosaccharide residue a galactose). Tay-Sachs disease is a genetic disorder that causes a deficiency of the enzyme responsible for the breakdown of GM2-ganglioside (a sphingolipid in which the monosaccharide residues are a particular oligosaccharide). The other sphingolipidosis diseases are Fabry disease, Sandhoff disease, and metachromatic leukodystrophy. Some of these diseases can be treated by a very costly enzyme replacement therapy, however most sphingolipidosis cases result in death before five years of age.

Review of Phospholipid and Glycolipid Classification

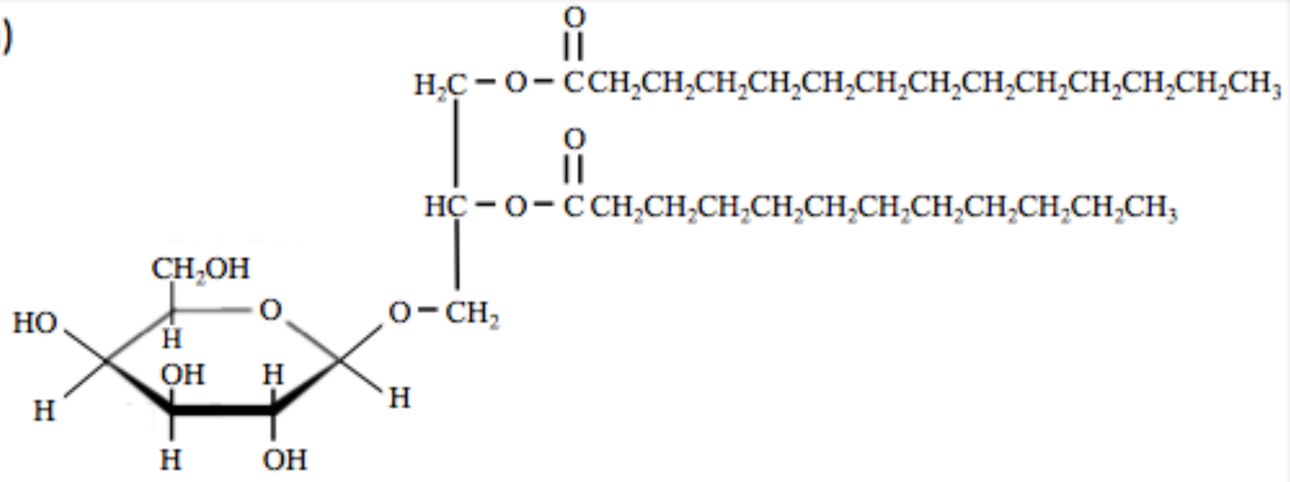


Refer to Table 12.5 and Table 12.6 for phospholipid *subclass* identification.

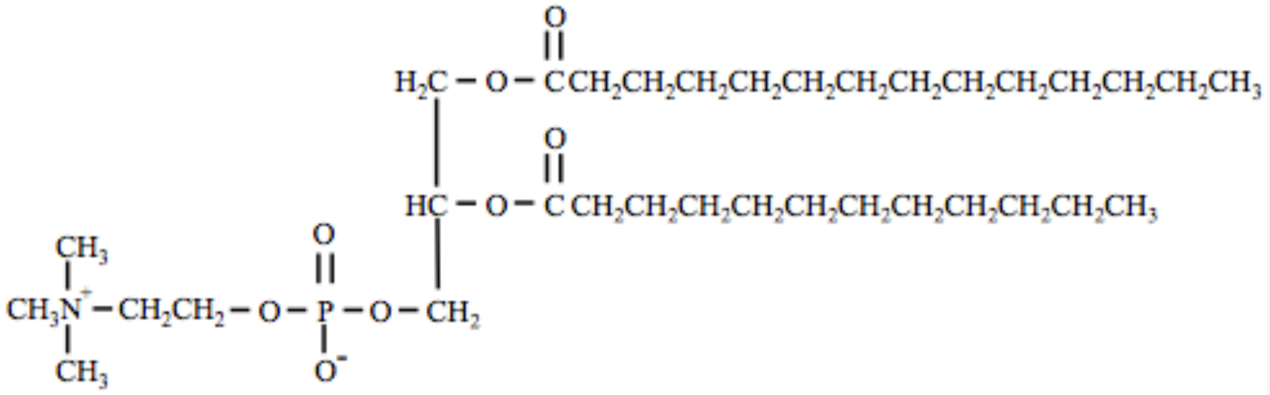
Review 12.13: Identification of Phospholipids vs. Glycolipids

Categorized each of the following compounds as being either a ***phospholipid*** or a ***glycolipid***.

a)

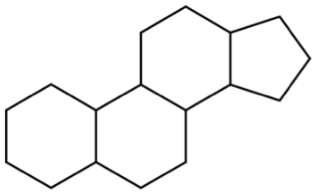


b)



12.7 Steroids

Steroids are lipids that contain a particular ***fused***, four-ring structure. *Fused rings* are rings that *share* atoms. The fused four-ring structure, which is common to all steroids, contains three six-member rings and one five-member ring, that are fused to each other in the pattern shown below.



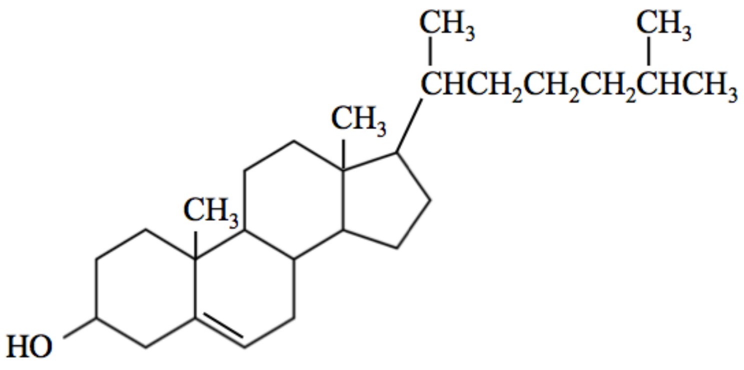
the fused, four-ring structure common to steroids

Outside of the health and scientific communities, the term “steroid” is often only associated with the performance enhancing drugs (*steroid hormones*) that are used by *some* athletes/bodybuilders. Those *steroid hormones* are just one type of steroid. The ***three types of steroids are***:

1) **cholesterol**
2) **steroid hormones**
3) **bile salts**

Cholesterol

Cholesterol is the name of the molecule shown below.



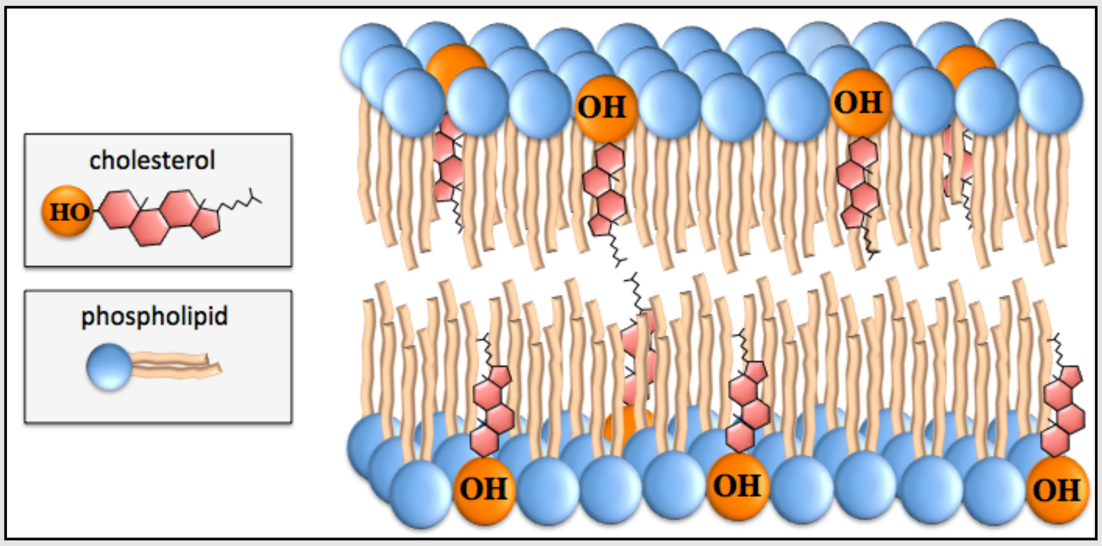
cholesterol

Cholesterol’s primary biological roles are as a structural component of animal biological membranes and as a starting material for the biosynthesis of other steroids (steroid hormones and bile salts). Cholesterol is not found in significant quantities in plants. Animals can make cholesterol from other compounds; therefore cholesterol is present in your body even if you don’t ingest it.

Cholesterol maintains the structural integrity and rigidity of biological membrane double layers by embedding its hydrophobic fused-ring structure within the nonpolar tails of the double layer, as shown in Figure 12.13. Cholesterol imparts rigidity to membranes because of the lack of free rotation within its fused-ring structure.

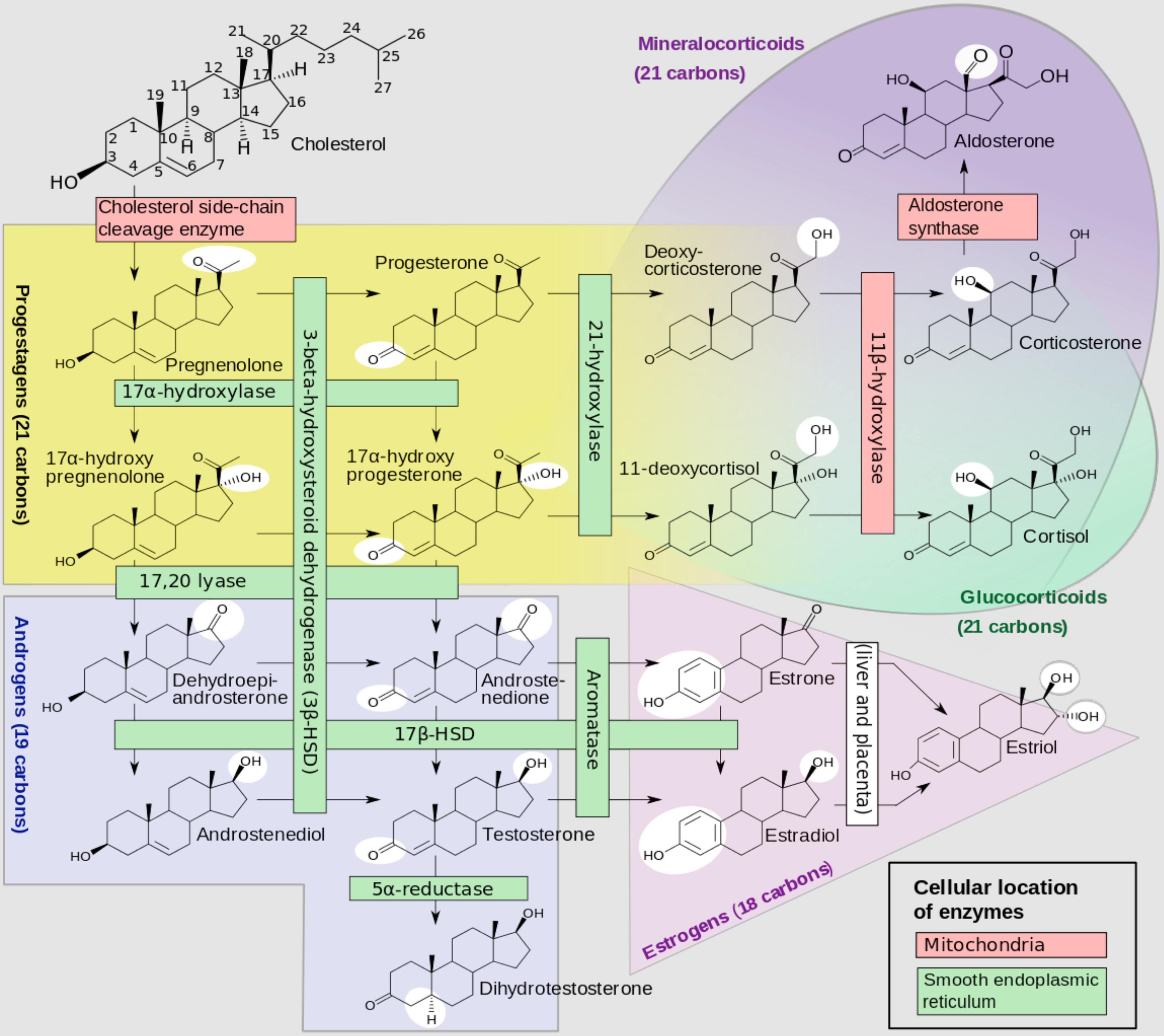
Figure 12.13 **Cholesterol in a Lipid Bilayer**

An illustration of a small section of a lipid bilayer. Cholesterol imparts rigidity to membranes because of the lack of free rotation within its fused-ring structure.



Animals produce other essential steroids (steroid hormones and bile salts) using cholesterol as a starting material. The production of steroids is called **steroidogenesis**. Figure 12.14 shows the pathways in which human ***steroid hormones*** are produced from cholesterol. Note that cholesterol (upper left) is the precursor for *all of the other steroid hormones*. Relax, **I do not expect you to memorize this diagram**; I included it only for you to get the *general idea of steroidogenesis* and to emphasize that the steroid hormones are made using *cholesterol* as a starting material.

Figure 12.14 **Production of Steroid Hormones from Cholesterol**



A diagram of the processes in which steroid hormones are produced from cholesterol. The enzymes that catalyze these reactions and their locations are indicated by the colored boxes drawn atop the reaction arrows. The white circles and ovals indicate the groups that were changed in the synthesis reactions. The cholesterol structure (upper left) has the *carbon positions* numbered. Wedges and dashes are used to indicate bonds that are oriented upward or downwards, respectively, relative to the ring structure. *α* and *β* designations have the same meaning as used for carbohydrates.

Source: Häggström M, Richfield D (2014). "Diagram of the pathways of human steroidogenesis". *Wikiversity Journal of Medicine* **1** (1). DOI: 10.15347/wjm/2014.005. ISSN 20018762. Author: David Richfield and Mikael Häggström, CC-BY-SA, http://creativecommons.org/licenses/by-sa/3.0/deed.en

Steroid Hormones

Hormones are a class of signaling compounds that are produced by the glands of the endocrine or exocrine system, then released into the bloodstream (or sap in the case of plants). Hormones vary in their chemical structure; those that are derived from cholesterol, as shown in the steroidogenesis diagram on the previous page (Figure 12.14), are called **steroid hormones**.

An example of a ***steroid hormone*** is a "male sex hormone" called **testosterone**. Testosterone and other male sex hormones (androgens) are responsible for the development of male characteristics such as larger muscle growth, thick facial hair, male sex organs, and sperm production. Although testosterone is classified as one of the male sex hormones, it is also present, at lower levels, in females. The structure of testosterone and other androgens are shown in the steroidogenesis diagram (Figure 12.14).

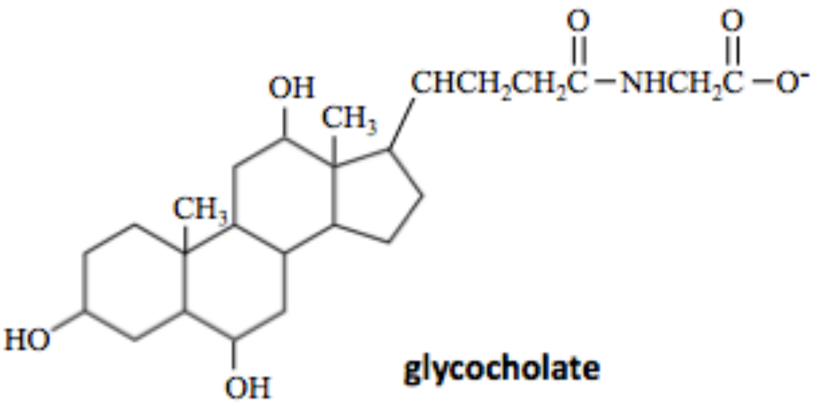
Testosterone acts to decrease body fat and increase muscle mass. Synthetic derivatives of testosterone, called **anabolic steroids**, will enhance these effects. You have probably heard much in the news about the use of anabolic steroids by athletes. Most professional sports organizations ban their use, and periodically test athletes to enforce the policy. Anabolic steroids are currently used in medical practice to increase muscle growth and appetite, induce male puberty, and to treat chronic wasting conditions including cancer and AIDS. It is considered unwise to use anabolic steroids in order to enhance athletic performance and for recreational bodybuilding because of the detrimental side effects; this is especially true for high doses and/or long-term use. Such side effects for males include pattern baldness, breast development, a reduction in testicle size, low sperm count, and infertility. The side effects for females include abnormal menstrual function, breast atrophy, increased facial hair, voice-deepening, and baldness. Other possible adverse side effects - for both men and women - include liver disease, heart disease, and depression.

Other examples of steroid hormones are **estrogens** and **progestogens**, the "female sex hormones." They are responsible for the development of female characteristics related to menstruation and reproductive cycles, such as broadening of the pelvis, fat deposited in breasts, and uterus size increase. An example of a female sex hormone is ***progesterone***, which is responsible for many of the biological functions associated with pregnancy. For example, it causes the mucous membrane of the uterus to prepare for the implantation of eggs. If pregnancy does not occur, then progesterone levels decrease and cause menstruation. The structure of *progesterone* and other *progestogens* are shown in the steroidogenesis diagram (Figure 12.14).

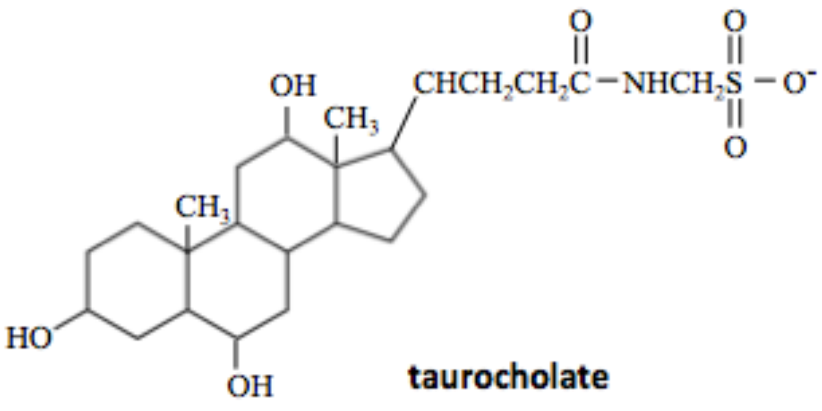
Although the adrenal gland is best-known for its production of *adrenaline* (a ***non****steroidal* hormone), it does produce several *steroid hormones*. Steroid hormones produced by the adrenal gland are called **adrenal corticosteroids**. Examples of *adrenal corticosteroids* are ***cortisol*** and ***aldosterone***. One of the many roles of *cortisol* is to suppress immune responses. It is administered *as a therapeutic medication* under the name ***hydrocortisone***. *Aldosterone* plays an important role in regulating blood pressure and the concentration of some electrolytes. The structure of *cortisol* and *aldosterone* are shown in the steroidogenesis diagram (Figure 12.14).

Bile Salts

Bile salts are *amphipathic* compounds produced using cholesterol as a starting material. They are produced in the liver and stored in the gall bladder. The biological role of bile salts is to emulsify and transport dietary triglycerides (fats and vegetable oils) and assist in their metabolism. The structures of two bile salts are shown below; note the four *fused-ring* structures, which are present in *all steroids.*

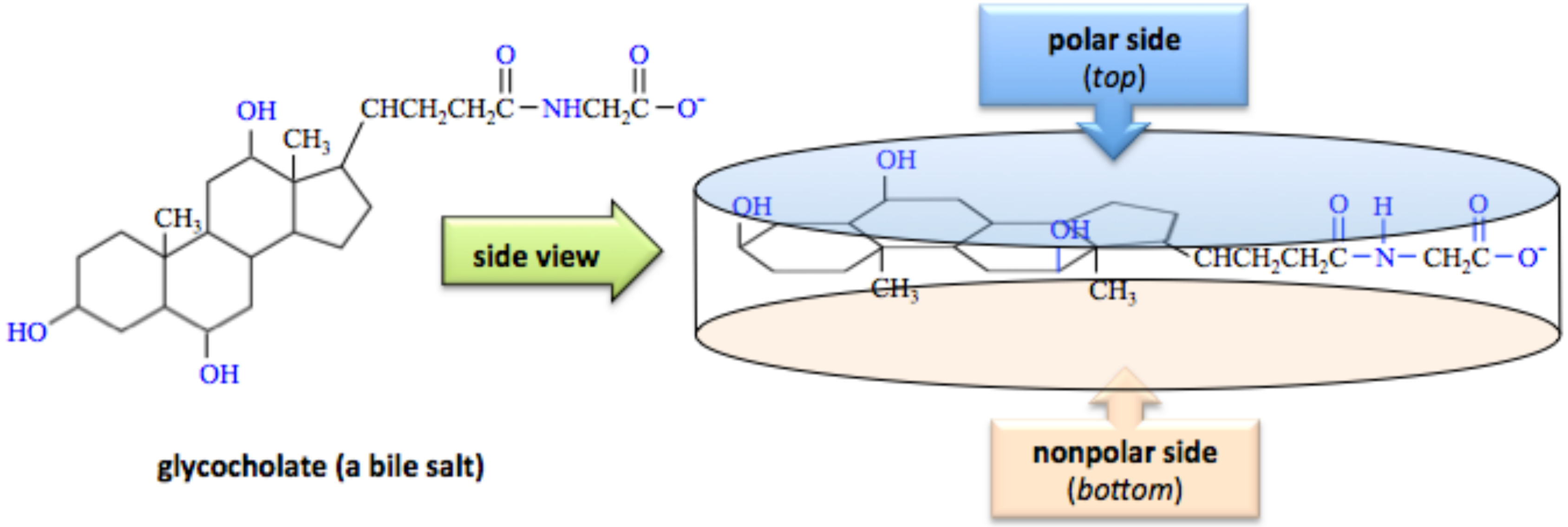


glycocholate

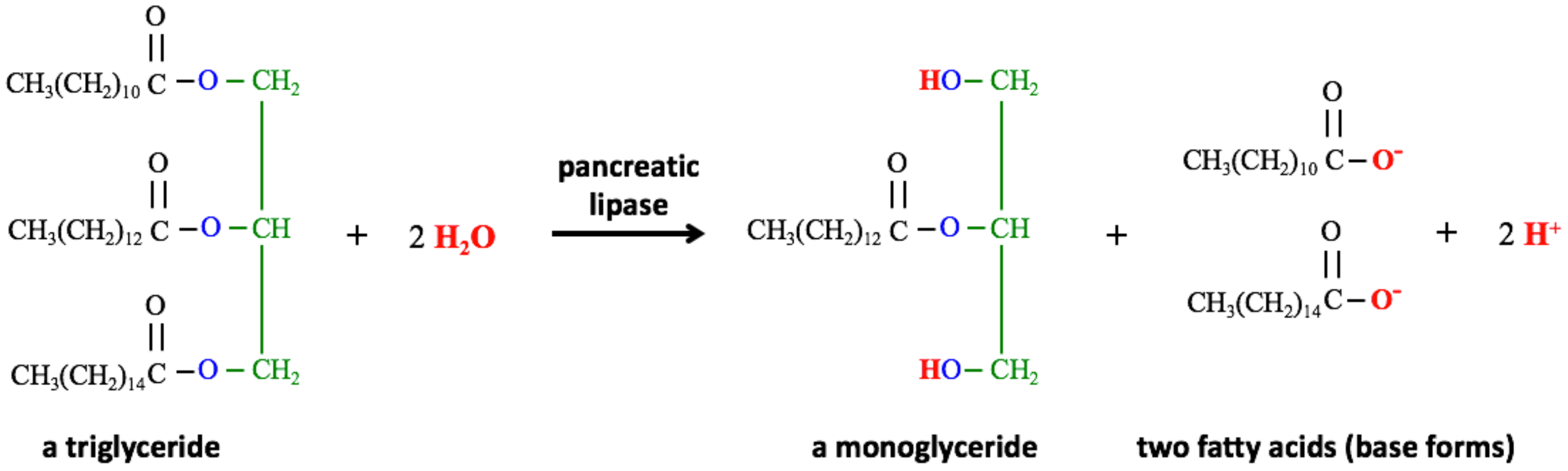


taurocholate

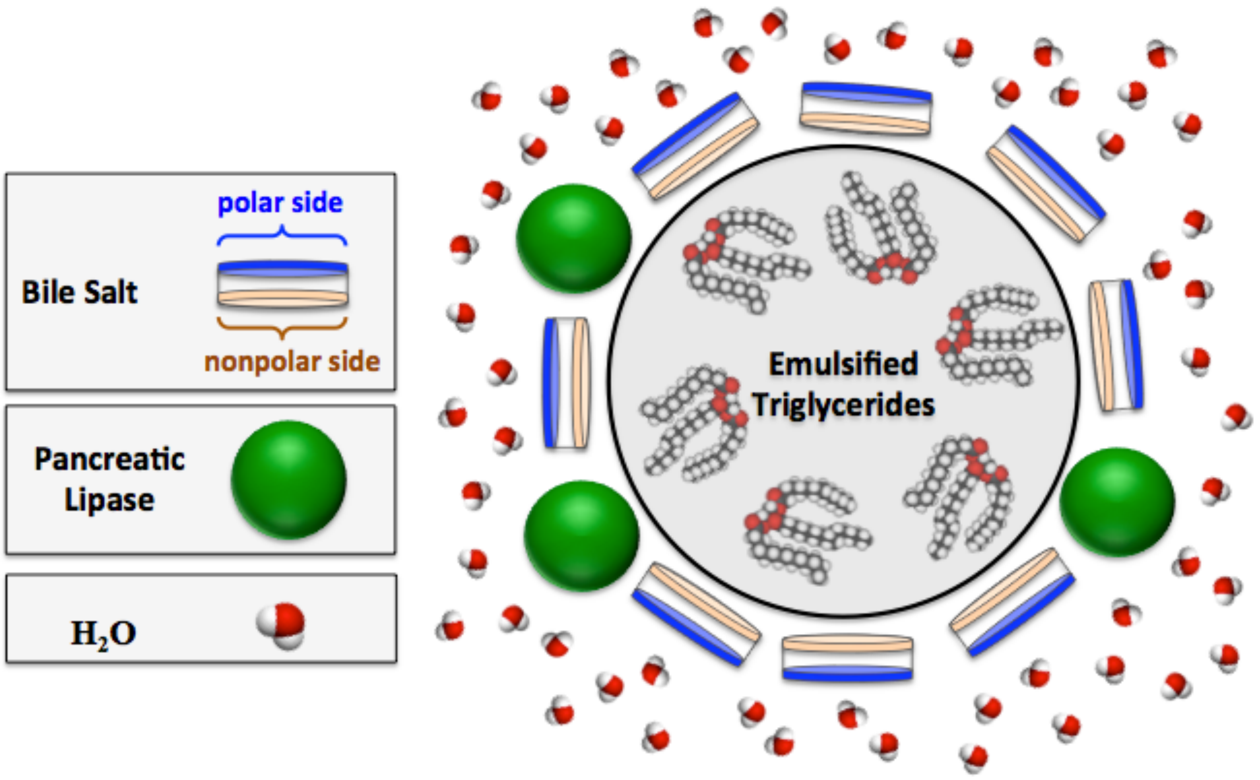
The amphipathic structure of a bile salt differs from the arrangement that you have seen for other amphipathic compounds. All of the amphipathic compounds that you have previously seen had polar “heads” connected to nonpolar “tails”. *This is not the case for bile salts*, which are better described as oblong disks that have a ***polar side*** and a ***nonpolar side***, as illustrated below.



The triglycerides (fats and oils) that we eat are unable to pass through the intestine wall. In order for these nutrients to be used by the body, they must be broken down into smaller molecules, in a process called digestion. Digestion of fats and oils involves the *partial hydrolysis* of triglycerides (esters) to produce fatty acids and monoglycerides, as shown for a typical triglyceride in the chemical equation below.



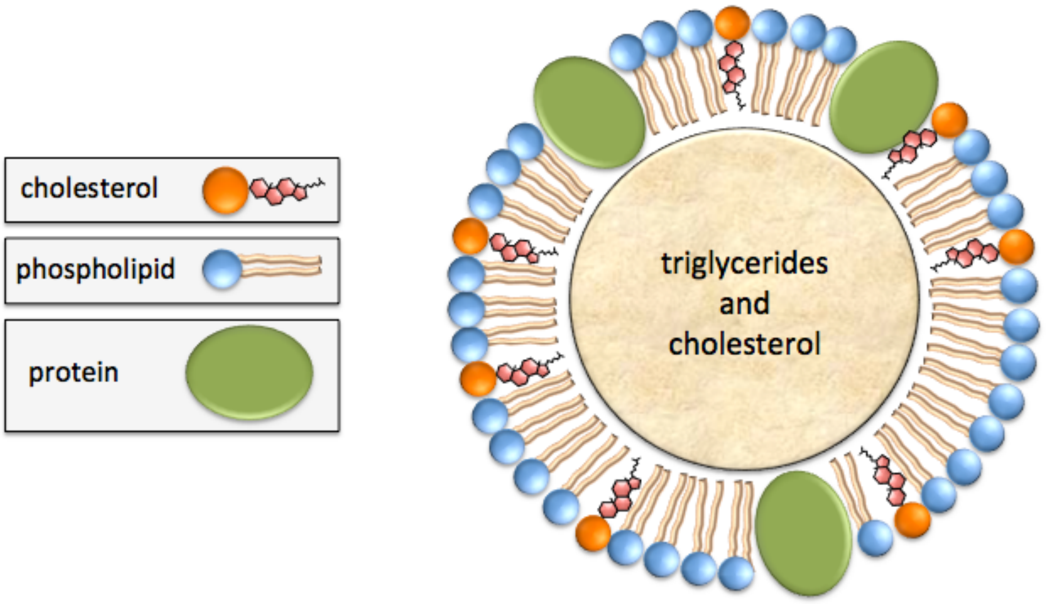
The enzyme responsible for catalyzing this reaction is called *pancreatic lipase*. Bile salts disassemble the large globules of dietary triglycerides and cholesterol within the intestine into small droplets emulsified in micelles. Pancreatic lipase enzymes are incorporated into the bile salt micelle monolayer, as illustrated in the cross sectional view shown below.



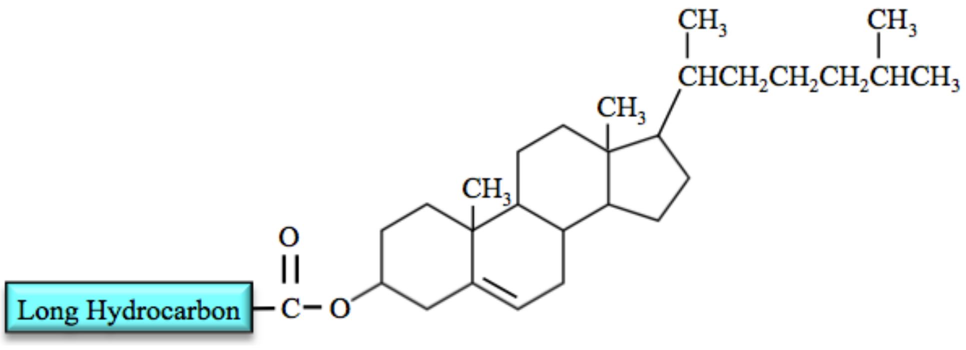
The fatty acids and monoglycerides that are formed by the digestion of fats and oils can pass through the walls of the intestine and then can be used by the body. After being absorbed into the intestine walls, the fatty acids and monoglycerides are re-assembled (by esterification) back into triglycerides. They are then emulsified and transported, along with cholesterol, in a colloid called a **lipoprotein**. Other functions of bile salts include emulsifying nonpolar vitamins so they can be more easily adsorbed, eliminating cholesterol and other molecules from the body, and aiding in the adsorption of dietary cholesterol into the intestinal mucosa.

Transport of Cholesterol and Triglycerides

Since blood, lymph, and intercellular fluid are *aqueous mixtures*, cholesterol and triglycerides must be ***emulsified*** in order to be transported throughout the body. This is done by ***lipoproteins***. *Lipoproteins* are composed of a core that contains emulsified triglycerides and cholesterol, which is surrounded by a micelle monolayer made from proteins, phospholipids, and cholesterol. A *cross sectional* illustration of a lipoprotein is shown below.



Lipoproteins contain cholesterol in their micelle monolayers, ***and*** in their emulsified cores. The cholesterol *in the emulsified core* of lipoproteins is in the form of *cholesterol esters (shown below),* formed by the esterification reaction of cholesterol with a fatty acid.



structure of cholesterol ester

There are five classes of lipoproteins: *chylomicrons, very low-density lipoproteins* (VLDL)*, intermediate-density lipoproteins* (IDL), *low-density lipoproteins* (LDL), and *high-density lipoproteins* (HDL). These classifications are based on the density of the lipoprotein particles. Since protein is more dense than lipid, the greater the percentage of protein, the higher the density of the lipoprotein. Table 12.7 lists the density ranges and % (w/w) compositions of the lipoprotein classes.

Table 12.7 Density Ranges and Percent (w/w) Compositions for Lipoprotein Classes

Lipoprotein Classification	Density (g/cm^3)	% Protein	% Cholesterol	% Phospholipids	% Triglycerides and Cholesterol Esters
chylomicrons	< 0.94	< 2	8	7	84
VLDL	< 1.006	10	22	18	50
IDL	1.006 - 1.019	18	29	22	31
LDL	1.019 - 1.063	25	50	21	8
HDL	1.063 - 1.21	33	30	29	4

Figure 12.15
Arterial Plaque

Atherosclerotic plaque from a carotid endarterectomy specimen.
Source: Wikimedia Commons,
Author: Ed Uthman, MD, CC-BY, http://creativecommons.org/licenses/by/2.0/legalcode

The amounts of HDL and LDL in the blood have been correlated with the constriction (occlusion) of the coronary artery, which makes the heart work harder and can lead to myocardial infarction (heart attack). The thickening of the inner layer of the artery is caused by the accumulation of **plaque**, which is made from living white blood cells and remnants of dead cells, including **cholesterol** and **triglycerides**. A high LDL level is correlated with a greater risk of heart disease. A high HDL level is correlated with a lowered risk of heart disease. For these reasons, it is recommended that adults have the lipid levels in their blood tested ***at least*** once every five years. The test is called a **lipoprotein panel**. Although the concentration of cholesterol is not directly measured in these tests, the terms "total cholesterol," "bad cholesterol", and "good cholesterol" are often used by practitioners when describing or discussing the results of lipid panels. Cholesterol is the name of a *particular molecule*, however, ***in lipid panels***, the term "total cholesterol" is used for the concentration of HDL + LDL + 20% of the triglycerides. The term "bad cholesterol" is used for the concentration of LDL. The term "good cholesterol" is given to HDL since it transports cholesterol back to the liver (the liver can remove cholesterol from the body) and lowers the risk of heart disease. The lipid panel level concentration categories, guidelines, and recommendations from the US National Institutes of Health are shown in Table 12.8.

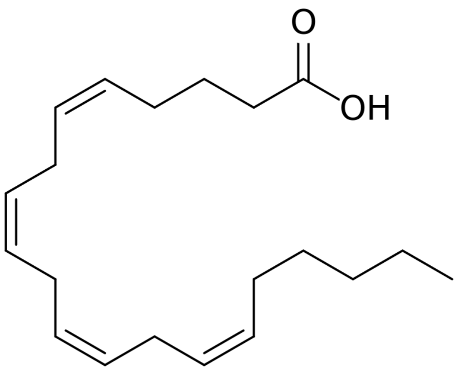
Table 12.8 Lipid Panel Level Concentration Categories

Substance	**Desirable/Recommended Level**	**Borderline High Level**	**High Level**
"Total Cholesterol" (HDL + LDL + 20% of the triglycerides)	below 200 mg/dL	200-239 mg/dL	240 mg/dL and above
Triglycerides	below 150 mg/dL	150-199 mg/dL	200 mg/dL and above
LDL "Bad Cholesterol"	below 100 mg/dL (ideal)* 100-129 mg/dL (near ideal)	130-159 mg/dL	160-189 mg/dL (high) 190 and above mg/dL (very high)
	Considered *Protective* Against Heart Disease	**Intermediate Values (the higher, the better)**	**A Major *Risk Factor* for Heart Disease**
HDL "Good Cholesterol"	60 mg/dL and above	40-59 mg/dL	less than 40 mg/dL

Lipid and lipoprotein concentrations are measured in milligrams (mg) of substance per deciliter (dL) of blood.
*The LDL desirable values are lower than those shown in the table for persons at risk of heart attack.
Source: National Institutes of Health, *Medline Plus* (2012). Volume 7 Number 2 Page 6-7
http://www.nlm.nih.gov/medlineplus/magazine/issues/summer12/articles/summer12pg6-7.html

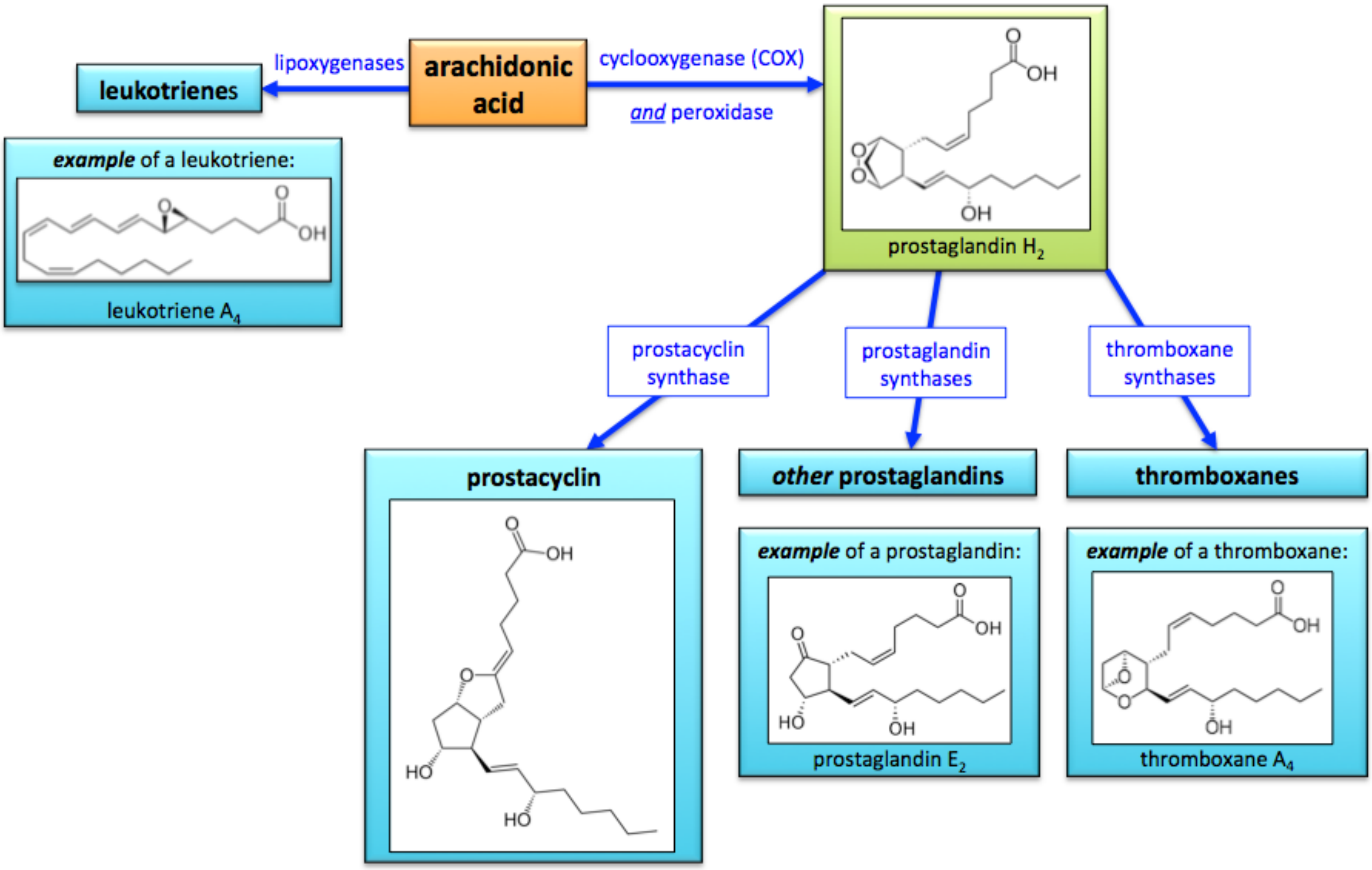
12.8 Eicosanoids

The "*eicosa*" prefix in *eicosanoids* is from the Greek "*eicosa*," which means twenty. The lipids called **eicosanoids** are *signaling molecules* that contain twenty carbon atoms. They are derived from one of three, twenty-carbon polyunsaturated fatty acids (arachidonic acid, eicosapentaenoic acid, or dihomo-gamma-linolenic acid). Arachidonic acid, shown below, is the major precursor of eicosanoids.



arachidonic acid

Arachidonic acid, eicosapentaenoic acid, or dihomo-gamma-linolenic acid undergo *reactions* that transform them into the various classes of *eicosanoids* - such as ***prostaglandins***, ***thromboxanes***, ***leukotrienes***, and ***prostacyclin***. For example, *arachidonic acid* can be converted to various eicosanoids as shown in the diagram below.



You are ***not*** responsible for memorizing the names of the enzymes for these reactions or the structures of the various eicosanoids.

Prostaglandins

Prostaglandins have a wide range of biological effects, including causing pain, causing inflammation, causing fever, affecting blood pressure, inducing sleep, regulating blood flow to particular organs, controlling ion transport across membranes, and inducing labor.

Thromboxanes

Thromboxane A_2 is the major biologically-active form of thromboxanes. It acts as vasodilator and is involved in the facilitation of blood clotting.

Leukotrienes

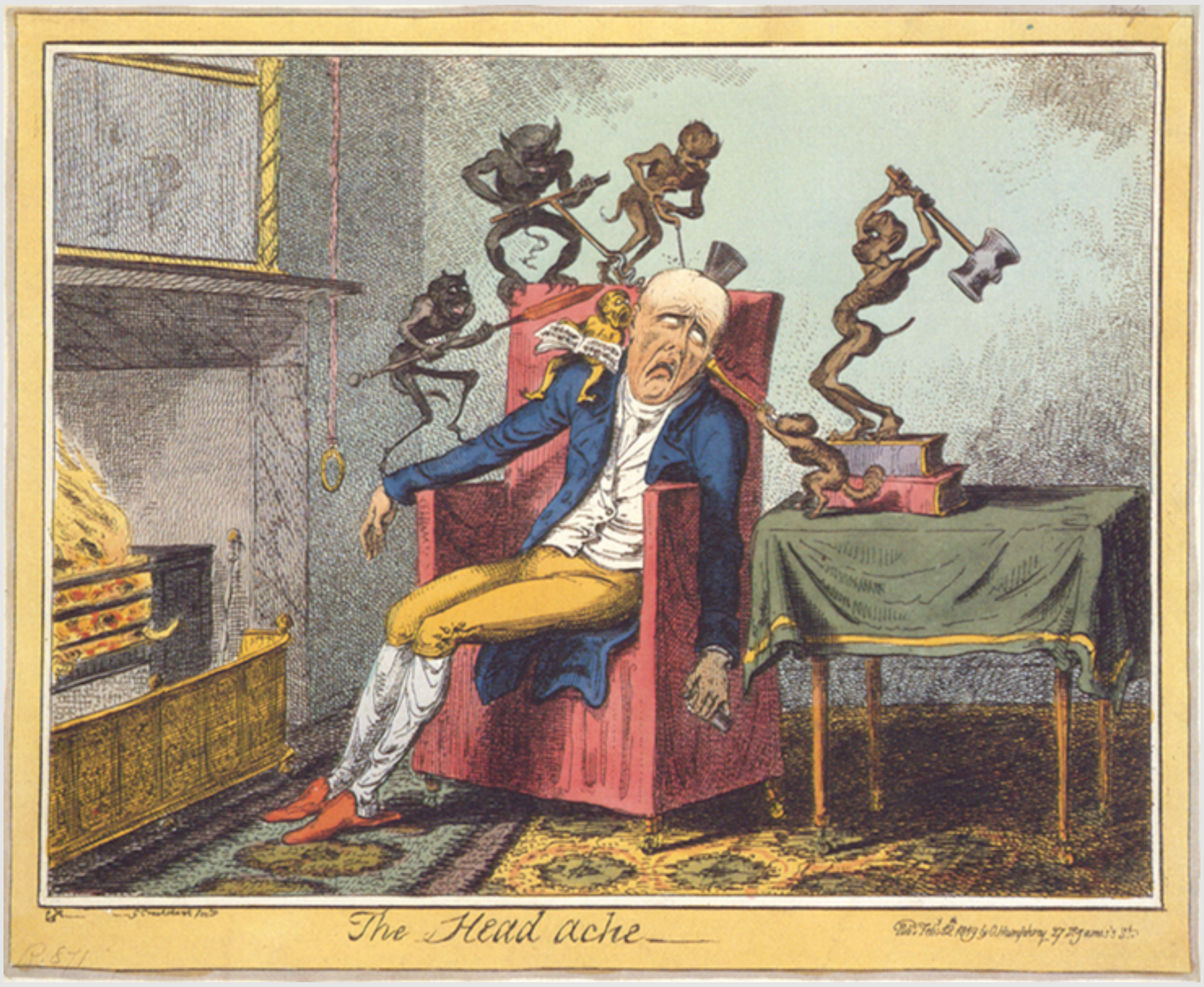
Leukotrienes are involved in the regulation of immune responses and in induced muscle contractions in the lungs. The overproduction of a particular leukotriene (leukotriene D_4) is a major cause of inflammation in asthma. Some anti-asthma drugs block the production of leukotrienes.

Prostacyclin

Prostacyclin is involved in vasodilatation, *inhibition* of blood clotting, regulation of the contraction of smooth muscle, and inflammation.

Nonsteroidal Anti-inflammatory Drugs (NSAIDs)

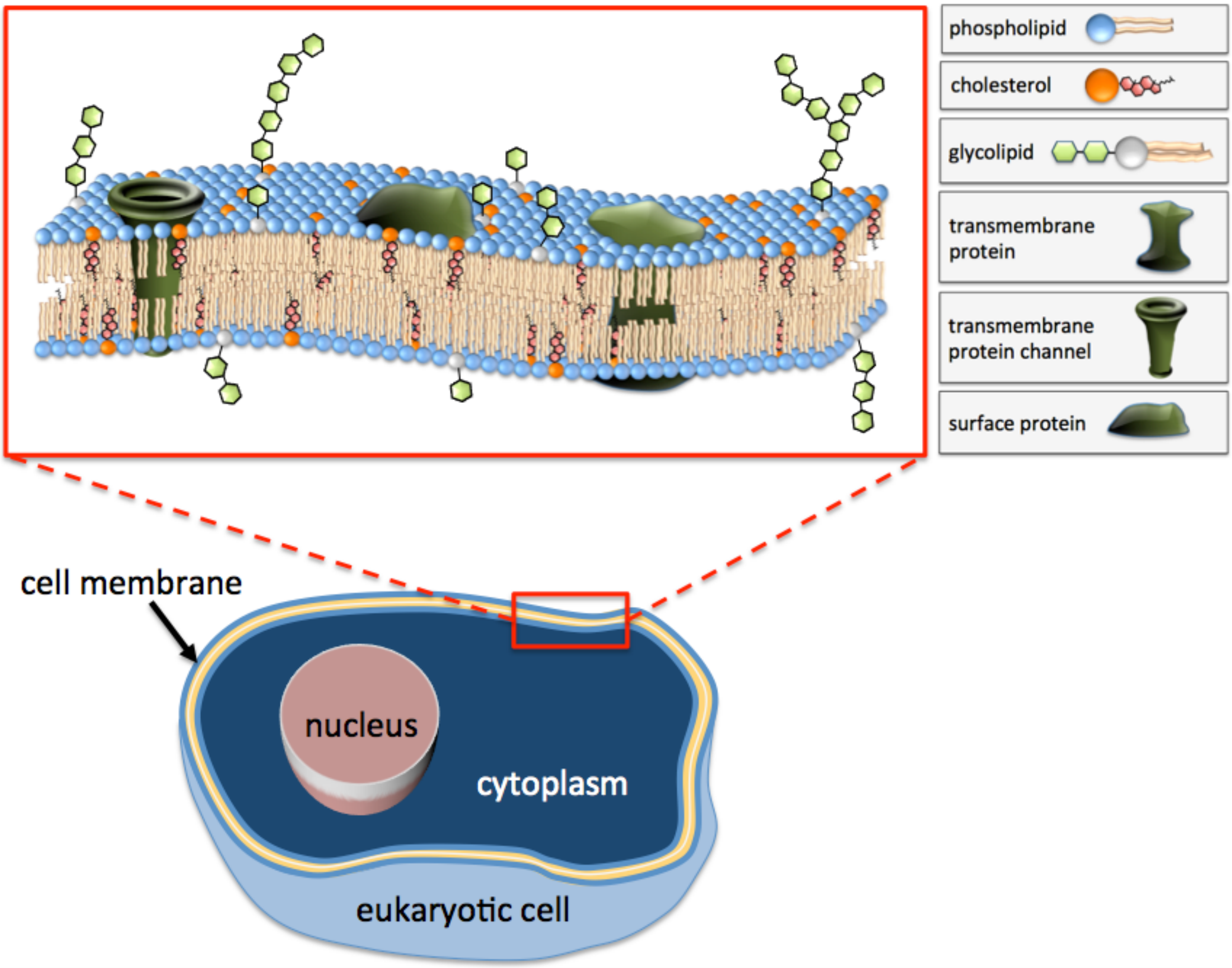
NSAIDs such as aspirin, acetaminophen, and ibuprofen are taken to reduce pain, fever, and inflammation by blocking the action of the cyclooxygenase enzyme (COX) that catalyzes the conversion of arachidonic acid into prostaglandins and thromboxanes (see the eicosanoids formation diagram on the previous page).



The Head Ache, by George Cruikshank (1792 – 1878).

12.9 Biological Membranes

Biological membranes are semipermeable physical barriers. Biological lipid double layer membranes not only function as cell membranes, but also exist within cells in order to form specialized compartments. For example, intracellular lipid double layer membranes surround a cell's nucleus, chloroplasts, and mitochondria. The lipid double layers in biological membranes contain components other than phospholipids and glycolipids. These other components, which include cholesterol and various proteins, are distributed throughout the lipid double layer, as illustrated below for a eukaryotic cell membrane.



The forces holding the lipids and other components together in each of the two monolayer sheets are relatively weak. For this reason, membranes are flexible, and the membrane components are not locked in place; they are able to "slide" past each other. The flexibility of membranes ***decreases*** as the *chain lengths* and *degree of saturation* of the lipid nonpolar tails increase. This is because flexibility decreases as London forces get stronger. In animals, the amount of membrane-cholesterol also regulates membrane flexibility. The flexibility of a membrane decreases as the amount of membrane-cholesterol increases.

The Transport of Molecules and Ions Across Membranes

Certain compounds must be able to pass through cell membranes in order for cells to perform their biological functions. The processes in which species are transported through membranes are classified as either **passive transport** or **active transport**.

Passive Transport

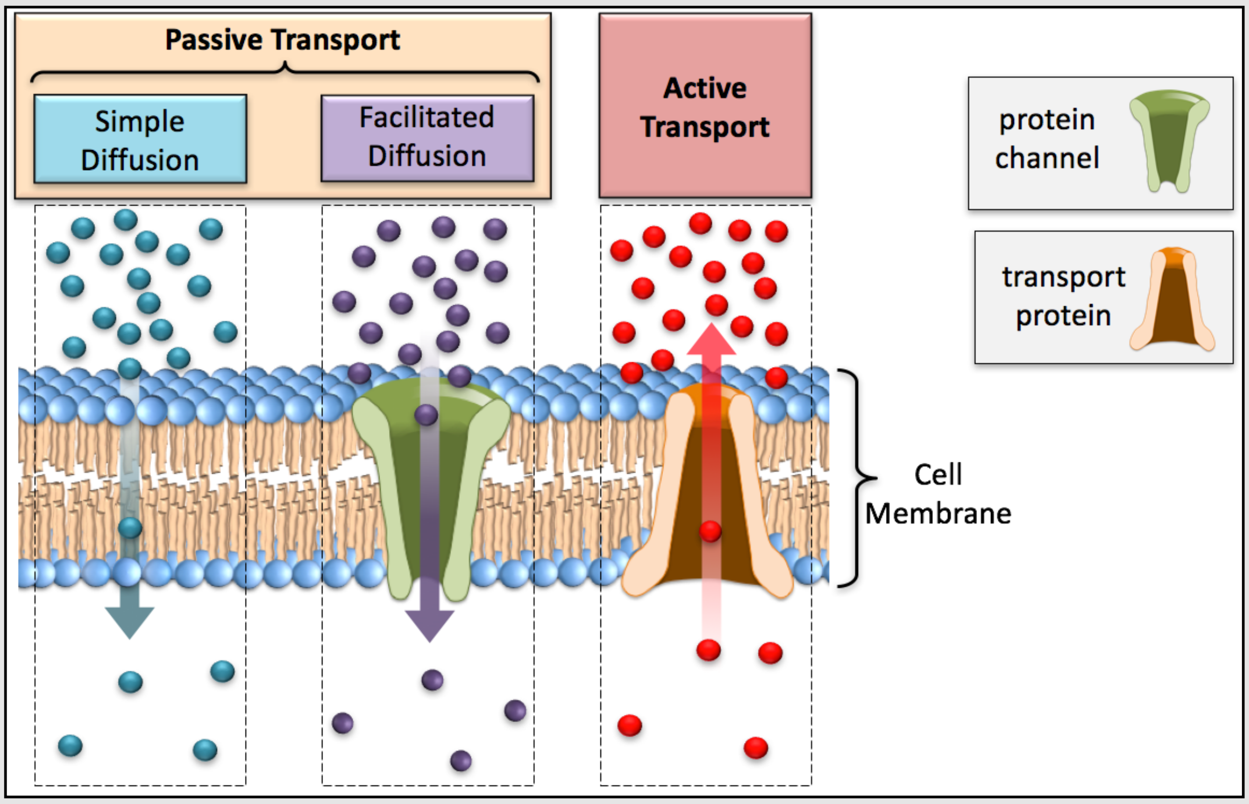
Some *nonpolar* and *amphipathic* compounds can pass through a membrane because of their attraction to the phospholipids in the membrane by noncovalent interactions. Species that are able to move through membranes in this way are called ***lipophilic compounds***. Examples of lipophilic compounds are steroid hormones. The direction of the net transport of a *lipophilic* compound is determined by diffusion; there will be a net transport from the side of the membrane where its concentration is greater, to the side where its concentration is less. Recall, from chapter 7, that we described this type of transport as "with the concentration gradient." The energetic driving force for diffusion is the potential energy of the diffusing species' concentration gradient. It is lower in energy to have equal concentrations of the diffusing species on ***both*** sides of a membrane; therefore, diffusion occurs. This diffusive movement of lipophilic compounds through a membrane is referred to as **simple diffusion**.

Diffusion of small ions and polar molecules, which are *not* lipophilic, through membranes is facilitated by ***protein channels*** that pass through the cell membrane. This diffusion of ions and polar molecules though protein channels is referred to as ***facilitated diffusion***. In *facilitated diffusion,* as with *simple diffusion*, a molecule or ion is transported from the side of the membrane where its concentration is greater to the side where its concentration is less, or "with the concentration gradient," and the energetic driving force is the potential energy of the diffusing species' concentration gradient. Both ***simple diffusion*** and ***facilitated diffusion*** are called **passive transport** because they do not require an energetic input from sources other than the concentration gradient of the transported species. The transport of water molecules through membranes is a passive transport process, and is best described by ***osmosis*** (see chapter 7, section 11). The protein channels in which water molecules pass are called *aquaporins*.

Active Transport

In order for molecules or ions to be transported in the direction "against the concentration gradient" - from the side of the membrane where their concentration is less to the side where their concentration is greater - ***energy must be supplied***. This type of transport is referred to as **active transport**. Unlike the ***passive transport*** processes that are driven by the potential energy provided by the transported species' concentration gradient, in ***active transport***, energy must be supplied by ***some other source***. In the *active transport* process, the ions or molecules cross the membrane with assistance from a **transport protein**. An example of active transport is the transport of ions, amino acids, sugars, lipids, drugs, or other molecules "against their concentration gradient" through **ATP binding cassette transport proteins (ABC transporters)**. *ABC transporters* use chemical energy, supplied by **ATP**, to transport compounds through a membrane. An illustration of the passive and active transport processes can be seen in Figure 12.16.

Figure 12.16 Passive and Active Transport Processes



An illustration of the passive and active transport processes. In passive transport, there is a net transport of ions or molecules "***with** the concentration gradient.*" In active transport, there is a net transport of ions or molecules "***against** the concentration gradient.*"

Review 12.14: Simple Diffusion vs. Facilitated Diffusion

Compare and contrast **simple diffusion** with **facilitated diffusion.**

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

Review 12.15: Passive Transport vs. Active Transport

Describe the difference between **passive transport** and **active transport**.

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

Now that you know about phospholipids and membranes, you can understand how the venom of some snakes work. One of the toxins in the venom of some snakes, such as the *eastern diamondback rattlesnake* shown in Figure 12.17, is an enzyme called ***phospholipase A2***. This enzyme hydrolyzes a glycerophospholipid's ester bond and its phosphodiester bonds. Receiving relatively large amounts of this toxic enzyme, such as are delivered from snakebites, causes the breakdown of phospholipids within cell membranes, which weakens the membrane double layer structure, and results in hemolysis (breaking apart) of red blood cells. *Phospholipase A2* is also secreted in some insect bites, and is present *at very low concentration,* in mammalian tissues.

Figure 12.17 An Eastern Diamondback Rattlesnake

The eastern diamondback rattlesnake secrets a venom in its bite containing an enzyme (phospholipase A2) that breaks chemical bonds in glycerophospholipids. The breakdown of phospholipids within cell membranes weakens the membrane structure and results in hemolysis (breaking apart) of red blood cells.
Source: Wikimedia Commons, Author: Tad Arensmeier,
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Chapter 13:
Peptides, Proteins, and Enzymes

Proteins are present in all life forms on Earth. They play various roles in nature. Many of the chemical reactions that are needed for life would occur too slowly if they were not catalyzed by members of a class of proteins called enzymes. Proteins play a role in replicating DNA and also in using the information in DNA to make other proteins. They are used to transport and store compounds and in chemical signaling. Proteins provide structure (rigidity and stiffness) in skin, connective tissue, hair, horns, hooves, and feathers. They are the major component of muscles because of their role in locomotion.

In this chapter, you will learn about proteins through the *lens of chemistry*. You will begin by learning about their chemical structures and shapes in order to better understand how they are able to perform their functions. You will see how changes in a protein's structure or environment will affect its ability to perform its biological function, which can affect the well-being of an organism. The primary causes of many human diseases are protein-related.

Horns, such as those of the impala in this image, are made up of a protein (keratin) that covers live bone.

Source: Wikimedia Commons, Author: Muhammad Mahdi Karim, GNU Free Documentation License (http://www.gnu.org/licenses/old-licenses/fdl-1.2.html)

13.1 Chapter 13 Educational Goals

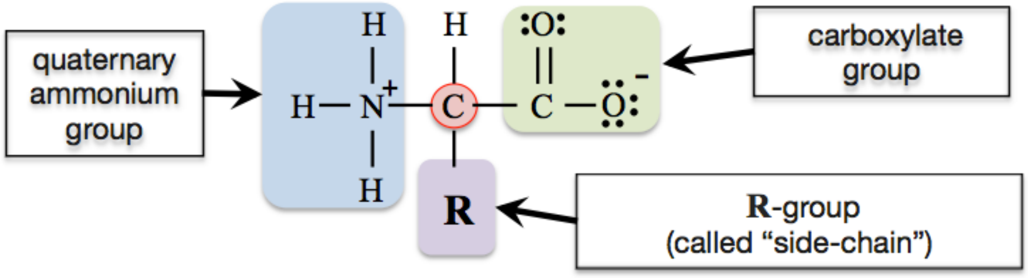
1. Describe the general bonding pattern of **α-amino acids** and understand how amino acids are classified by the ***polarity*** and ***charge of their side-chains***.
2. Given the table of twenty common amino acids (Table 13.1), determine the ***total charge*** of the dominant form of an amino acid (at physiological **pH**, at **pH** < 2, and at **pH** > 11).
3. Understand the three-dimensional information contained in the Fischer projection of an amino acid.
4. Given a Fischer projection of an amino acid, determine if it is an ***L****-amino acid* or ***D****-amino acid*.
5. Understand and define the term **peptide**.
6. Given the table of twenty common amino acids, be able to draw the structural formula of the peptide that is obtained when two or more particular amino acids are connected by **peptide bonds**.
7. Given the structural formula of a **peptide**, be able to identify the **peptide bonds,** the **C-terminus,** the **N-terminus,** *and* the **peptide groups**.
8. Given the structural formula of a peptide, and the table of twenty common amino acids, determine the ***total charge*** of the peptide's dominant form (at physiological **pH**, at **pH** < 2, and at **pH** > 11).
9. Given the structure of a peptide and the table of twenty common amino acids, name a particular peptide using amino acid residue *abbreviations.*
10. Compare and contrast **peptides** and **proteins**.
11. Understand and define **primary, secondary, tertiary, and quaternary protein structure**. Name the noncovalent interactions that are responsible for each level of structure.
12. Explain what is meant by the term **denaturation**, and list the ways to denature a protein.
13. Understand the difference between **globular, fibrous, and membrane proteins**.
14. Compare and contrast **simple proteins** and **conjugated proteins**.
15. Understand the terms **cofactor** and **coenzyme**.
16. Understand how **enzymes** work and distinguish between **absolute specificity, relative specificity, and stereospecificity**.
17. Understand and define the terms: **essential amino acid, complete protein, incomplete protein, and complimentary protein**.
18. Understand how changes in **pH** and *temperature* can affect the reaction **rate** of an enzymatically-catalyzed reaction.
19. Understand how **enzyme inhibitors** and **activators** control enzymatic reactions, and compare and contrast **reversible** and **irreversible inhibitors**.
20. Understand organisms regulate **metabolic pathways** using **feedback inhibition** and **positive feedback**.

13.2 Amino Acids

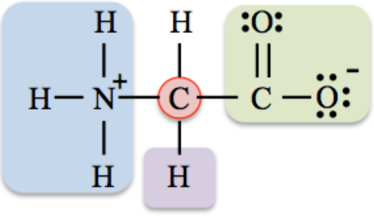
Peptides are composed of ***amino acid residues*** that are bonded to each other in a linear (non branched) pattern. A **protein** consists of ***one or more large peptides*** and has ***a specific biological function***. In order to best understand how proteins function, you must first learn about their building blocks: **amino acids**. In addition to their role in proteins, amino acids play other important biological roles, for example they act as neurotransmitters and are contained in other biological compounds.

Structural Formulas of Amino Acids

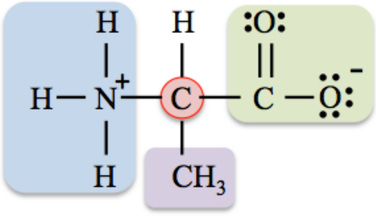
Amino acids are organic compounds that contain a ***quaternary ammonium group*** *and* a ***carboxylate functional group***. The bonding pattern in a typical amino acid is shown below.



Note that the nitrogen (**N**) in a quaternary ammonium group has a *formal charge* of (1+), and one of the oxygen atoms in the carboxylate group has a *formal charge* of (1-). For amino acids, the **R-group** is often called the "**variant group**" or "**side-chain.**" I will refer to it as the *side-chain*. It can be a hydrogen atom, hydrocarbon, or various other groups of bonded atoms. Amino acids are named based on the identity of their *side-chain*. For example, if the side-chain is a hydrogen atom (**H**), then the amino acid is called *glycine*; if the side-chain is a methyl group (**CH_3**), then the amino acid is called *alanine*. The structures of *glycine* and *alanine* are shown below.

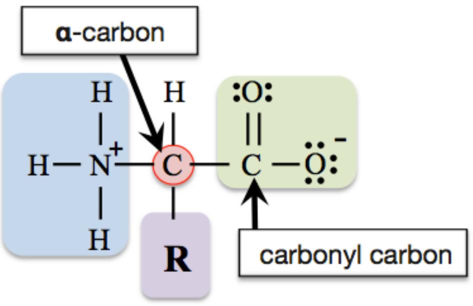


glycine



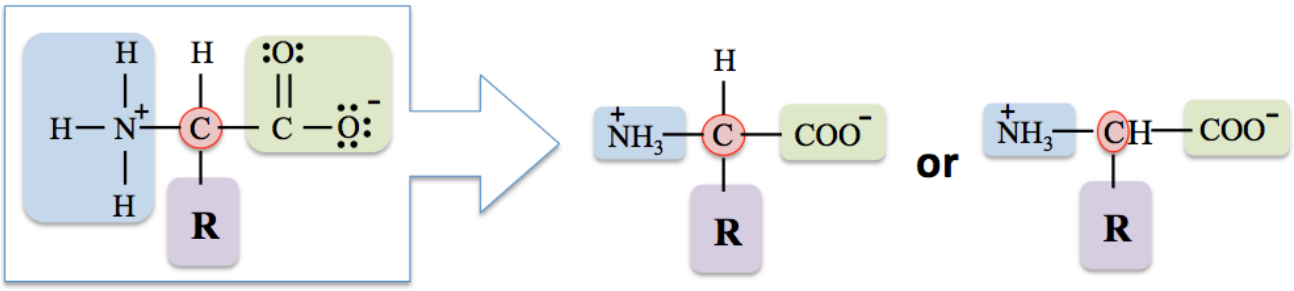
alanine

There are twenty-three amino acids that make up the proteins in plants and animals. Of these twenty-three amino acids, *twenty* of them are directly specified by the genetic code in DNA. These twenty amino acids are called the "**common**" or "**standard**" amino acids. All twenty *common amino acids* are **alpha (*α*)** amino acids. They are called ***α***-amino acids because their *side-chains* are attached to ***α*-carbons**. The ***α***-carbon, highlighted in a red circle in all of the amino acid structures on this page, is the carbon that is ***bonded*** to the *carbonyl* carbon.



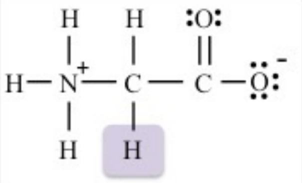
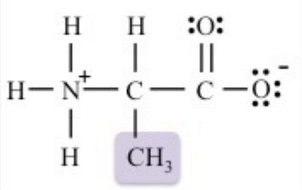
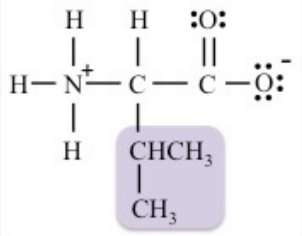
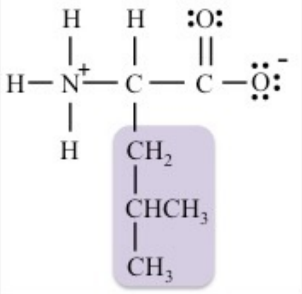
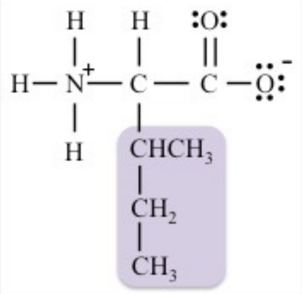
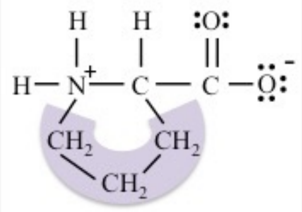
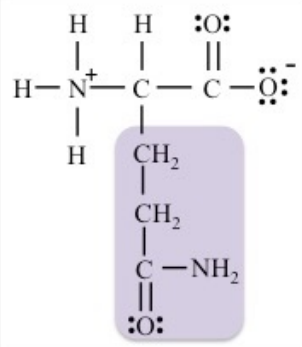
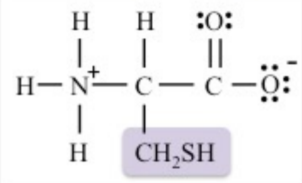
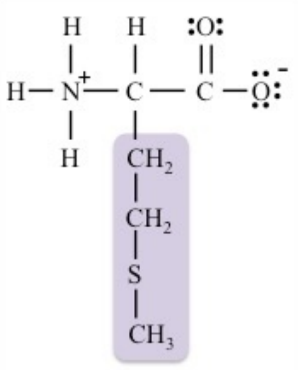
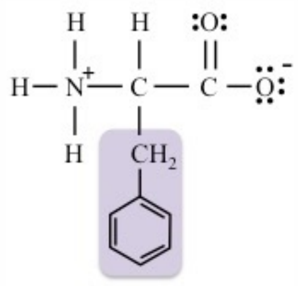
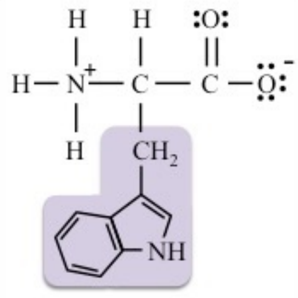
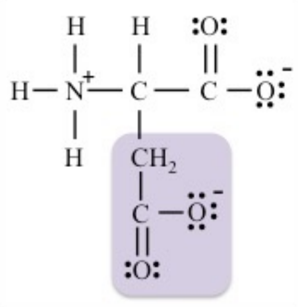
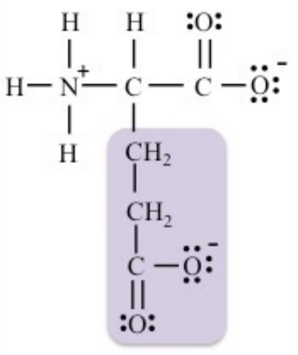
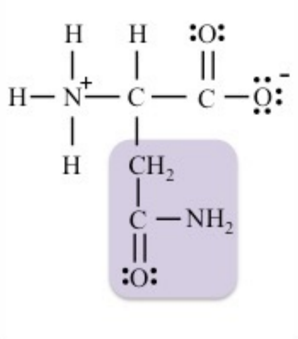
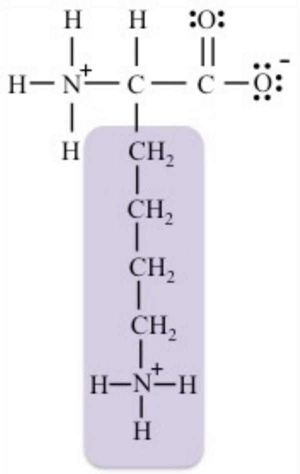
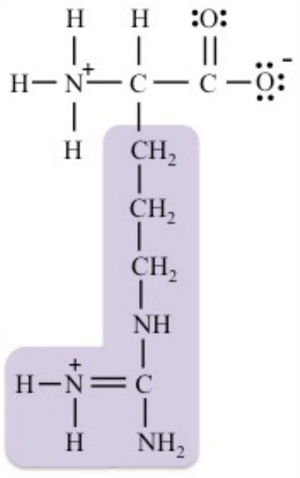
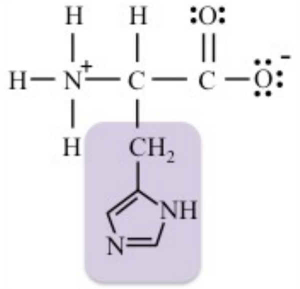
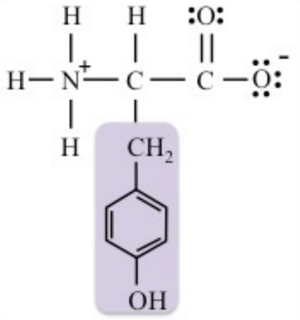
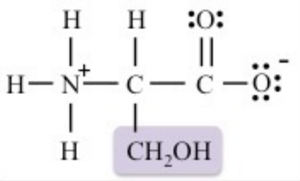
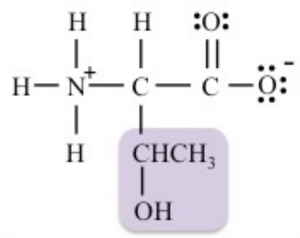
general form of an alpha (*α*) amino acid

For convenience, amino acid structures are sometimes further simplified as shown below:



The ***twenty common amino acids*** are often referred to using three-letter abbreviations. The structures, names, and abbreviations for the twenty common amino acids are shown in Table 13.1. Note that they are all ***α*-amino acids.**

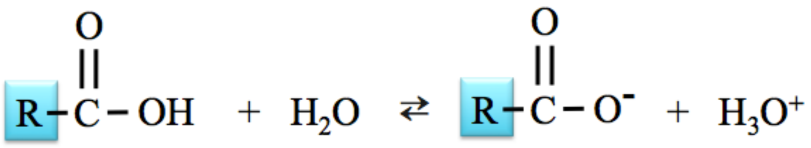
Table 13.1 **Table of the Twenty Common Amino Acids**

Name (abbreviation)	Structural Formula
Glycine (Gly)	
Alanine (Ala)	
Valine (Val)	
Leucine (Leu)	
Isoleucine (Ile)	
Proline (Pro)	
Glutamine (Gln)	
Cysteine (Cys)	
Methionine (Met)	
Phenylalanine (Phe)	
Tryptophan (Trp)	
Aspartic Acid (Asp)	
Glutamic Acid (Glu)	
Asparagine (Asn)	
Lysine (Lys)	
Arginine (Arg)	
Histidine (His)	
Tyrosine (Tyr)	
Serine (Ser)	
Threonine (Thr)	

Structural formulas of the twenty common amino acids. The side-chains are highlighted.

Charge of Amino Acids

The structural formulas of the common amino acids in Table 13.1 all contain at least one ***carboxylate group***. You may recall that when a carboxylate ion is in an aqueous solution, the carboxylate ion (base form) and carboxylic acid (acid form) conjugates are both present because they are in equilibrium, as shown in the equation below.



$$R-\overset{O}{\overset{\|}{C}}-OH + H_2O \rightleftarrows R-\overset{O}{\overset{\|}{C}}-O^- + H_3O^+$$

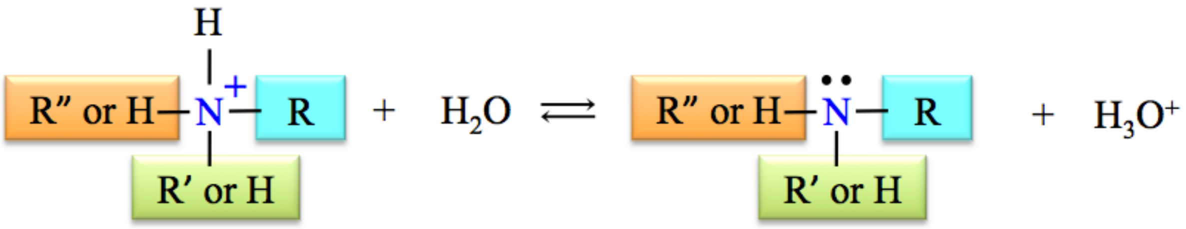
carboxylic acid *(acid form)*

carboxylate ion *(base form)*

pK$_a$ = **2 to 5,** depends on **R** group

From the ***Henderson-Hasselbalch*** relation, we know that when the **pH** is less than the **pK**$_a$ of a carboxyl group, then the carboxylic acid form (**R-COOH**) is predominant, and when the **pH** is greater than the **pK**$_a$, then the carboxylate ion form (**R-COO**$^-$) is predominant.

The structural formulas of the common amino acids all contain at least one ***quaternary ammonium group***. In chapter 9, you learned that when a quaternary ammonium compound is in an aqueous solution, the quaternary ammonium ion (acid form) and amine (base form) conjugates are both present because they are in equilibrium, as shown in the equation below.



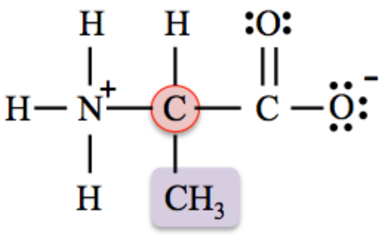
$$\text{R'' or H}-\overset{H}{\overset{|}{\underset{\underset{\text{R' or H}}{|}}{N^+}}}-R + H_2O \rightleftharpoons \text{R'' or H}-\overset{\cdot\cdot}{\underset{\underset{\text{R' or H}}{|}}{N}}-R + H_3O^+$$

quaternary ammonium ion (*acid form,* **pK**$_a$ **~9.5**)

amine (*base form*)

The relative amounts of the acid form and base form can be predicted from the Henderson-Hasselbalch relation. Therefore, when the **pH** of a solution is less than the **pK**$_a$ (**~9.5**), then the *quaternary ammonium group* (acid form) is predominant, and when the **pH** is greater than the **pK**$_a$, then the amine group (base form) is predominant.

Since amino acids involve the **carboxyl group/carboxylate group conjugate pair** *and* the **quaternary ammonium group/amine group** *conjugate pair*, then the *total charge of the predominant form of an amino acid* will depend on the **pH**. Let me elaborate with an example. Let's consider the predominant form of *alanine* at physiological **pH** (**pH** ~7.4). The **pK**$_a$ values of amino acid carboxyl groups are between **2** and **5** (depending on which amino acid), therefore, at **pH** = **7.4**, the base form (carboxylate ion) is predominant. *Quaternary ammonium groups* that are attached to the ***α***-carbons of amino acids have **pK**$_a$ values of about **9.5**, therefore, at **pH** = **7.4**, the acid form (quaternary ammonium group) is predominant. I have drawn the structure of *alanine* that is predominant at **pH** = **7.4**.

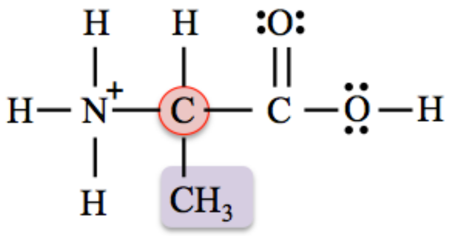


predominant form of *alanine* at **pH** = **7.4**

The predominant form of *alanine* has a negative (1-) formal charge on the *carboxylate group* and a positive (1+) formal charge on the *quaternary ammonium group*, which gives it a *total charge* of **zero**. When an amino acid has a total charge equal to zero, it is called a **zwitterion** (zwitter is German for *hermaphrodite* or *hybrid*).

The amino acid structures in Table 13.1 **are the predominant forms at physiological pH.** In sufficiently acidic or basic solutions, the *total charge* of the predominant form of an amino acid *will change* from its physiological value. Let's consider the *total charge* of the predominant form of *alanine* in an extremely *acidic* solution, and then in an extremely *basic* solution.

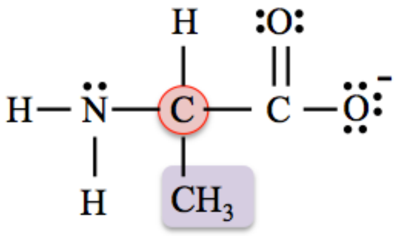
At **pH = 1.0** (an extremely *acidic solution*) the **pH** is less than the **pK**$_a$ of *both* the carboxyl group and the quaternary ammonium group, therefore both groups exist in their ***acid forms***, as shown below.



predominant form of *alanine* at **pH** = **1.0**

The predominant form of *alanine at* **pH = 1.0** has an uncharged carboxyl group (**COOH**) and has a positive (1+) formal charge on the nitrogen of the quaternary ammonium group, which results in a **positive (1+) *total charge***.

At **pH = 12.0** (an extremely *basic solution*) the **pH** is greater than the **pK**$_a$ of *both* the carboxyl group and the quaternary ammonium group, therefore both groups exist in their ***base forms***, as shown below.



predominant form of *alanine* at **pH** = **12.0**

The predominant form of *alanine at* **pH = 12.0** has a negative (1-) formal charge on the single-bonded oxygen of the carboxylate group and an *uncharged* nitrogen in the amine group, which results in a **negative (1-)** *total charge*.

Review 13.1: The Charge of Amino Acids

The amino acid structures in Table 13.1 are the predominant forms at physiological **pH**.

a. Draw the predominant form of valine when the **pH = 7.4**
b. Draw the predominant form of valine when the **pH = 1.0**
c. Draw the predominant form of valine when the **pH = 12.0**
d. What is the *total charge* of the predominant form of valine when the **pH = 7.4**?
e. What is the *total charge* of the predominant form of valine when the **pH = 1.0**?
f. What is the *total charge* of the predominant form of valine when the **pH = 12.0**?

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

Classification of Amino Acids

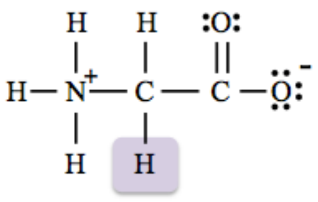
Amino acids are classified by the ***polarity of their side-chains*** and the ***ability of their side-chains to acquire formal charge*** (at physiological **pH**). You can think of this classification as a convenient way to predict how a side-chain will interact with water. It will also be helpful in understanding how the side-chains of amino acids in proteins interact with each other. These interactions help a protein to maintain the particular shape that is responsible for its biological function. The classes of amino acids and their descriptions are listed in Table 13.2.

Table 13.2 **Classification of Amino Acids**

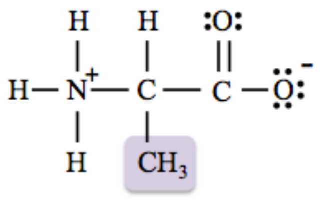
Amino Acid Class	Side Chain Polarity	Side-Chain Charge at Physiological pH
Nonpolar	nonpolar (hydrophobic side-chain)	zero
Polar neutral	polar (hydrophilic side-chain)	zero
Polar acidic	polar (hydrophilic side-chain)	negative
Polar basic	polar (hydrophilic side-chain)	positive

1) Nonpolar Amino Acids

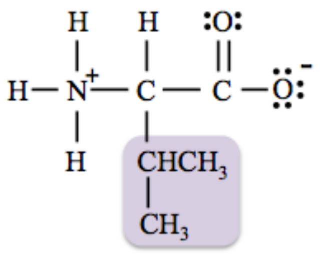
Nonpolar amino acids have ***nonpolar (hydrophobic) side-chains*** and their predominant forms have ***uncharged*** side-chains at physiological **pH**. The *nonpolar amino acids* (their predominant forms at physiological **pH**) are shown below.



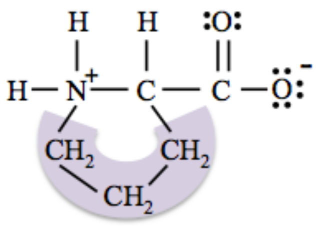
glycine



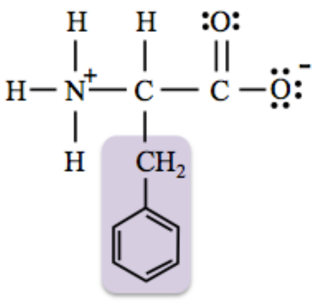
alanine



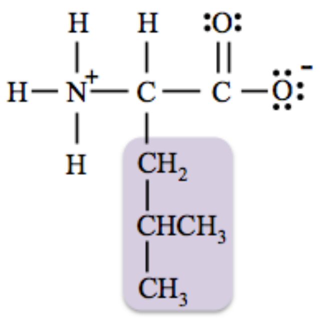
alanine



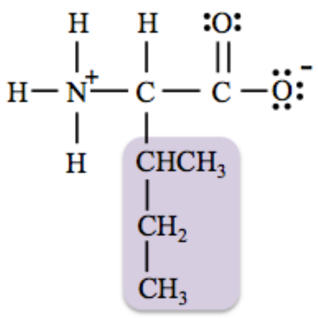
proline



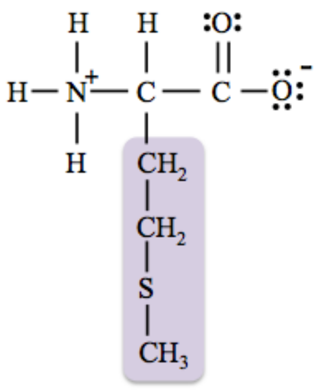
phenylalanine



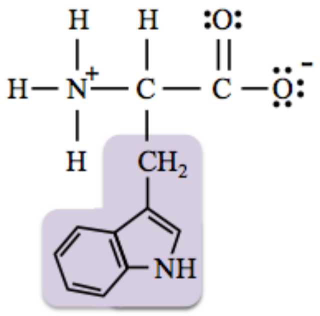
leucine



isoleucine



methionine

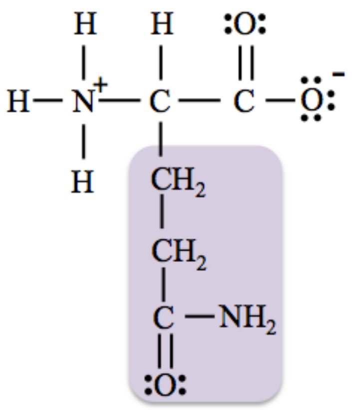


tryptophan

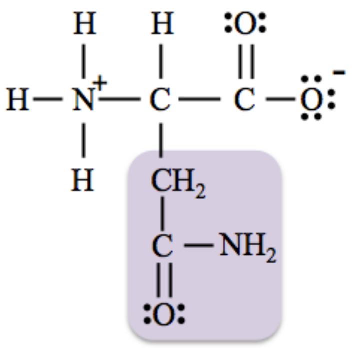
Note that although the side-chain of *tryptophan* contains a few highly-polar bonds, the hydrocarbon part is so large that it dominates the interactions, making the side-chain *hydrophobic*. For this reason, tryptophan is put into the *nonpolar* class.

2) Polar Neutral Amino Acids

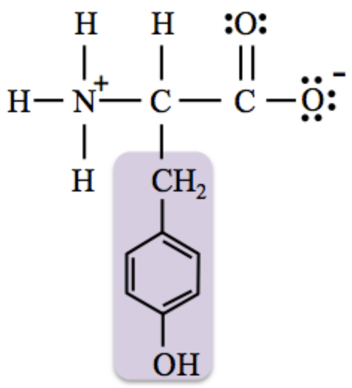
Polar neutral amino acids have ***polar (hydrophilic) side-chains*** and their predominant forms have ***uncharged*** side-chains at physiological **pH**. The *polar neutral amino acids* (their predominant forms at physiological **pH**) are shown below.



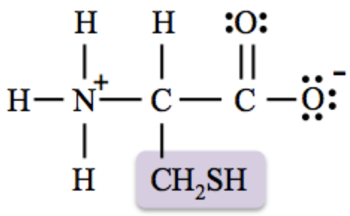
glutamine



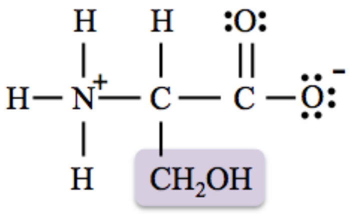
asparagine



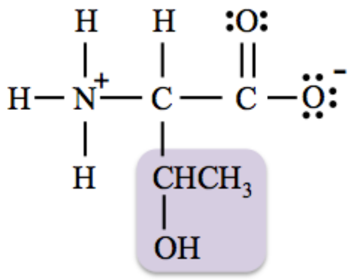
tyrosine



cysteine



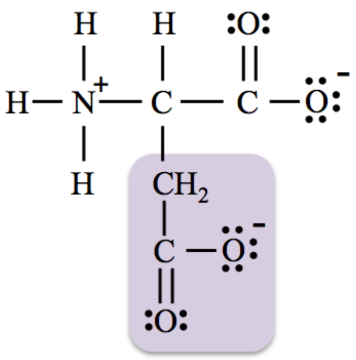
serine



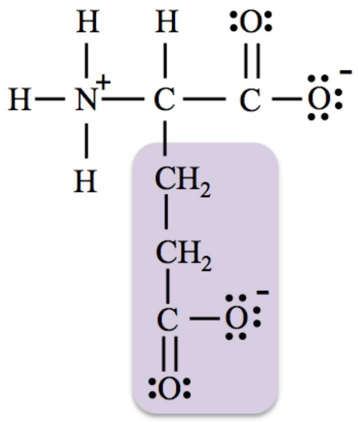
threonine

3) Polar Acidic Amino Acids

Not *all* predominant forms of amino acids have *uncharged side-chains* at physiological **pH**. **Polar acidic amino acids** have ***polar (hydrophilic) side-chains*** and, at physiological **pH**, their predominant forms have side-chains with **negative (1-) *formal charge.*** This formal charge is from a ***carboxylate group***. The *polar acidic amino acids* (their predominant forms at physiological **pH**) are shown below.



aspartic acid

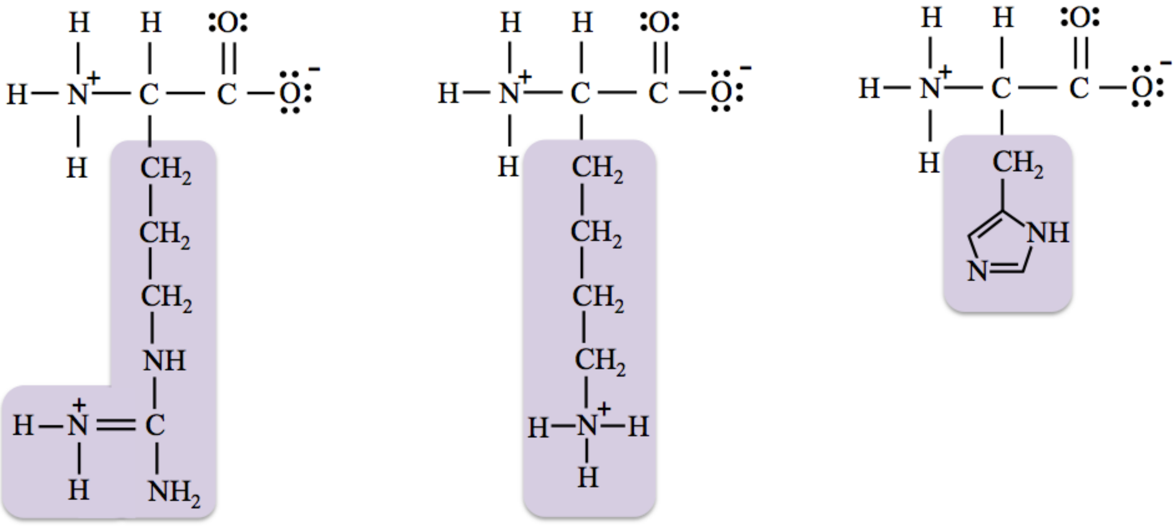


glutamic acid

Polar *acidic* amino acids are given the "*acidic*" term in their classification because the acid forms of their side-chains are stronger acids than those of the polar "*basic*" amino acids (discussed next).

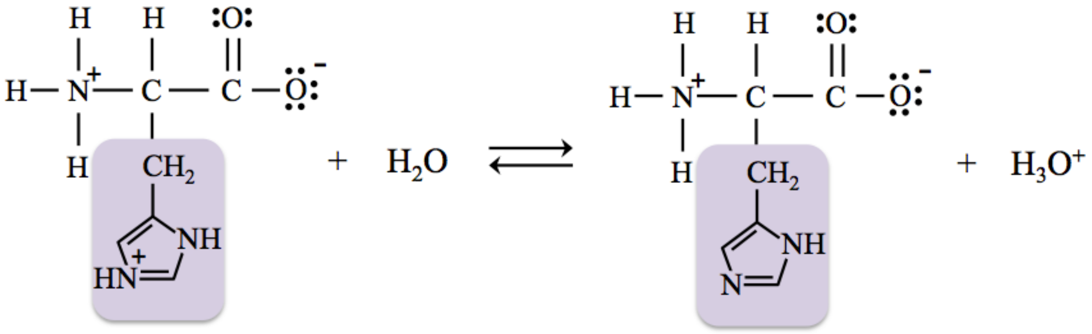
4) Polar Basic Amino Acids

Polar basic amino acids have ***polar (hydrophilic) side-chains*** and, except for *histidine*, their predominant forms have side-chains with **positive (1+) *formal charge*** at physiological **pH**. This formal charge is from a ***quaternary ammonium group***. The *polar basic amino acids* (their predominant forms at physiological **pH**) are shown below.



arginine **lysine** **histidine**

The reason that *histidine's side-chain* behaves differently than those of *arginine* and *lysine* is related to the presence of its ring structure. Although the *predominant form* of ***histidine's side-chain*** is its *uncharged* (base) form at physiological **pH,** it is in equilibrium with its *charged* quaternary group form (acid form), as shown in the equation below.



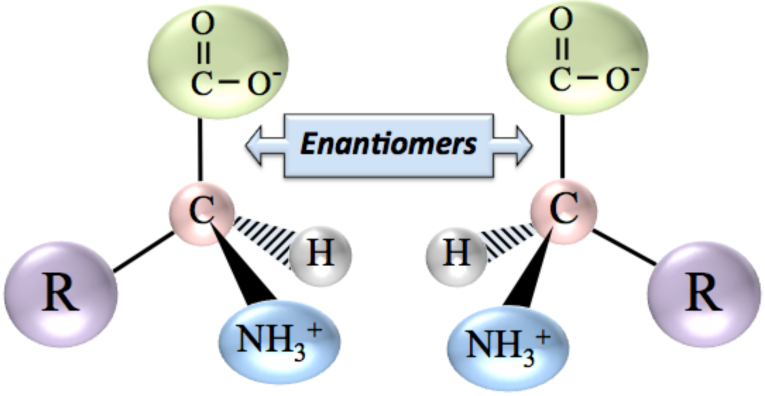
histidine's acid form (10%)

histidine's base form (predominant 90%)

At physiological **pH**, a significant amount (10%) of histidine side-chains are in their quaternary ammonium group forms, which have **positive (1+) *formal charge***. Since a significant amount of histidine has *positively-charged side-chains*, it is put into the *polar basic amino acid* class.

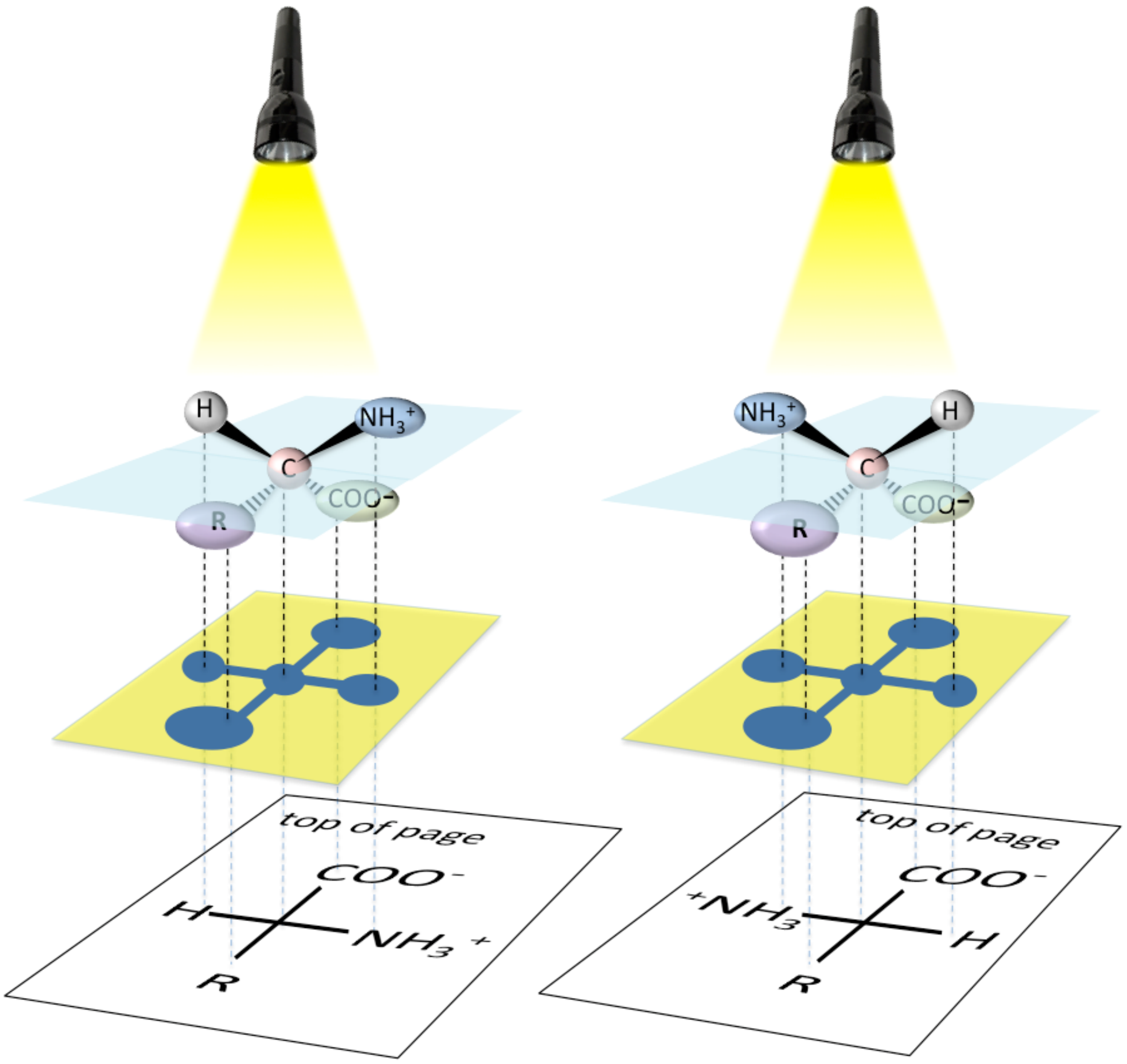
Amino Acid Stereoisomers

Except for *glycine*, the ***α***-carbons of the common amino acids are ***chiral***. *Glycine* is an exception because there are *two* hydrogen atoms bonded to its ***α***-carbon. The chirality of an amino acid's ***α***-carbon results in a ***pair*** of amino acid ***stereoisomers***. The pair of stereoisomers are ***enantiomers*** because they are *nonsuperimposable mirror images*. You have seen *two ways* to retain the three-dimensional information while drawing the structures of chiral compounds: ***wedge and dash representations*** (as shown below) and ***Fischer projections***.

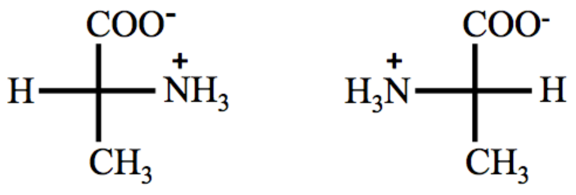


wedge and dash models of an amino acid enantiomer pair

When drawing or interpreting a Fischer projection of an ***α***-amino acid, we imagine the amino acid oriented between a projected light and a surface, as illustrated for the enantiomer pair shown in the illustration below.



This method is very similar to the method we used for monosaccharide Fischer projections. In the Fischer projection of an ***amino acid***, the positions of the chiral carbon and the groups around the chiral carbon correspond to their imagined shadow positions. The *side-chain* must be drawn toward the bottom of the page, and the *carboxylate group* toward the top of the page. Fischer projections of amino acids have the quaternary ammonium ion and a hydrogen atom on either side of the chiral carbon. The enantiomer that has a quaternary ammonia group (NH_3^+) on the *left-hand side* of its Fischer projection is called the "**L-isomer,**" and the one that has a quaternary ammonia group on the right-hand side of its Fischer projection is called the "**D- isomer**." Fisher projections of the **L-isomer** and **D-isomer** of *alanine* are shown below.



D-alanine ***L-alanine***

Fischer projections of the alanine enantiomer pair

You learned that **D-*sugars*** were much more common in nature than **L-*sugars***, however, nature favors **L-*amino acids*** over **D-*amino acids***. It is ***only L-amino acids that make up proteins***. **D-*amino acids*** do exist in nature, however, they are rare.

Review 13.2: Fischer Projections of Amino Acids

Draw Fisher projections of the **D-isomer** and the **L-isomer** of *serine.*

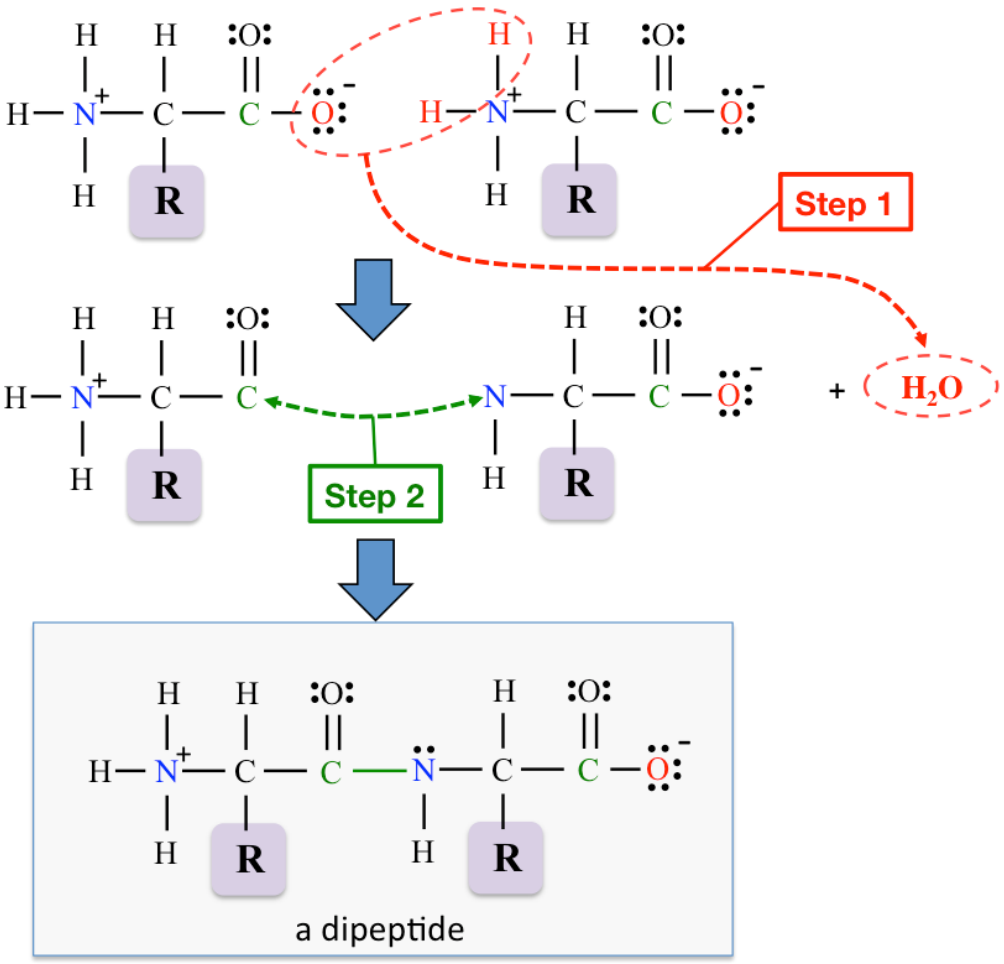
For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

13.3 Peptides

Peptides (sometimes called **polypeptides**) are composed of ***amino acid residues*** bonded to each other in a linear (non branched) pattern. I will elaborate using an example. Let's consider the bonding pattern in ***peptides*** by forming a **dipeptide** from *two* amino acids. The *carboxylate group* of one amino acid covalently bonds to the *quaternary ammonium group* of the *other* amino acid. The structure of the dipeptide that is produced can be obtained by the method described and illustrated below.

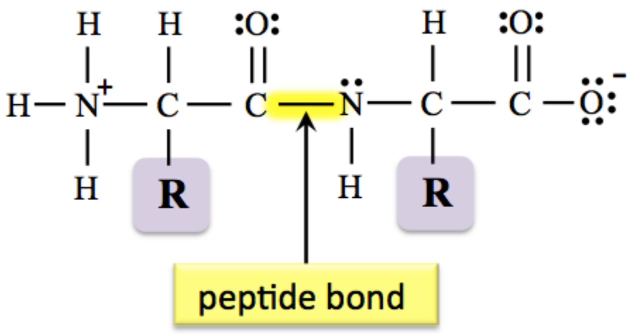
Step 1: The two amino acids are drawn side-by-side. The single-bonded *oxygen atom* is removed from the *carboxylate group* on the *left-most* amino acid. *Two* hydrogen atoms are removed from the *quaternary ammonium group* on the *right-most* amino acid. The oxygen atom and the two hydrogen atoms combine to form a water molecule

Step 2: A ***new bond*** is made between the carbonyl carbon and the nitrogen.



The peptide formed in this example is called a **dipeptide** because it contains ***two*** amino acid residues.

The ***new bond*** between the two amino acid residues is called a **peptide bond**.



I used "**R**" for the *side-chains* of the amino acids and dipeptide in the illustrations above. The method for the formation of the peptide bond works with *any of the **α**-amino acids*, regardless of the particular side-chains. In the review problem that follows, I ask you to form a peptide bond between two specific amino acid residues.

You try one:

Review 13.3: Formation of the Peptide Bond

Draw the *structural formula* of the ***dipeptide*** that contains ***two valine*** amino acid residues. Label the **peptide bond**.

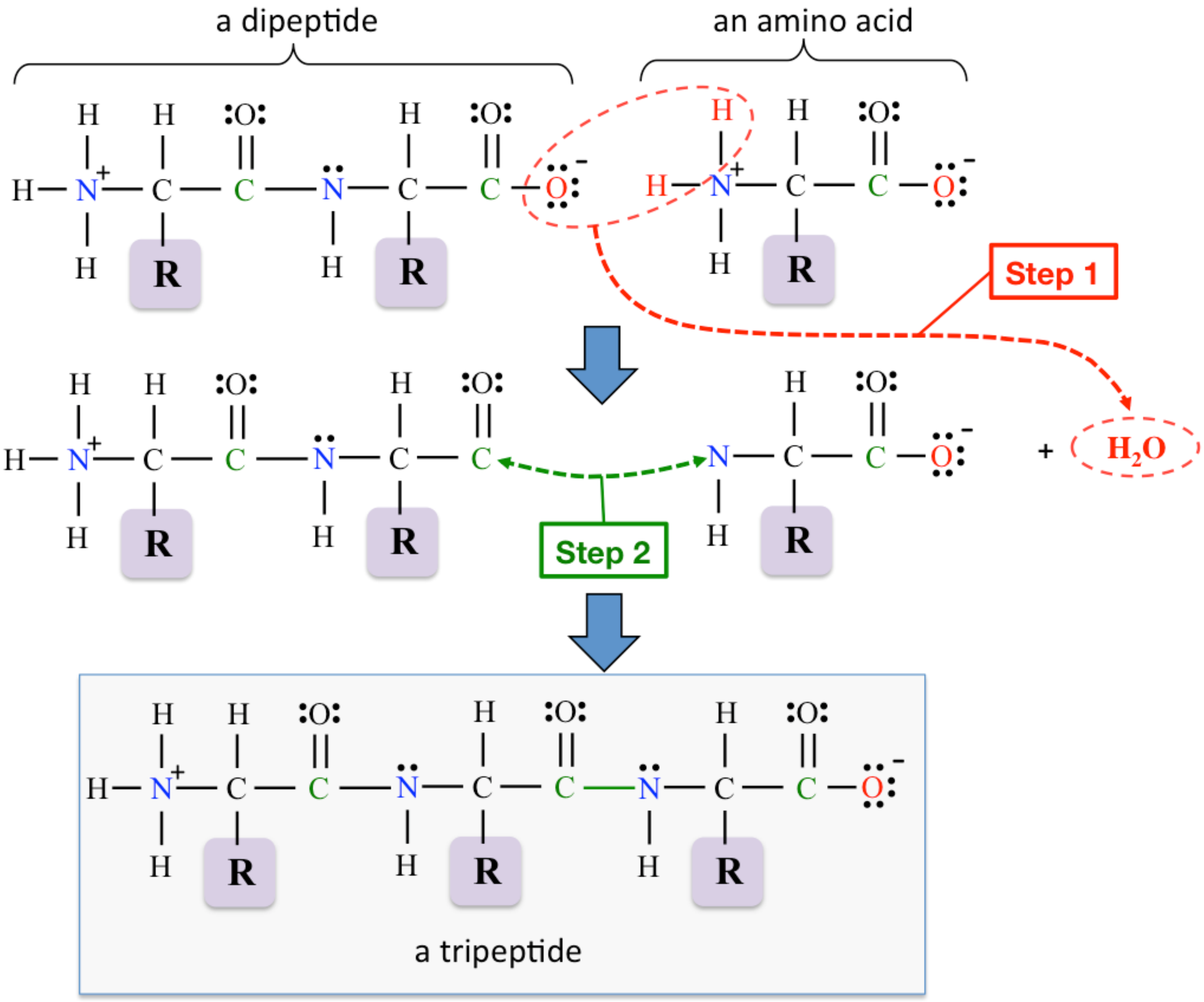
For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

In nature, peptide chains are produced by bonding specific amino acid residues, one by one, to a growing peptide chain. You may recall this process, called **translation**, from your biology courses. The identity of each new amino acid residue that is added to a growing chain is determined by the genetic code in a particular gene. Let's examine the chemical bonding process that occurs as a ***new*** amino acid residue is added to a growing peptide chain. We will begin with the general form of a ***dipeptide*** and then add a *new amino acid residue to it*. Since the *dipeptide* has a *carboxylate group*, and the *new* amino acid has a *quaternary ammonium group*, the new ***peptide bond*** can be made using the same two steps as we used when bonding two amino acids to each other.

Step 1: The dipeptide and the amino acid to be joined are drawn side-by side. The single-bonded *oxygen atom* is removed from the *carboxylate group* on the *dipeptide*. *Two* hydrogen atoms are removed from the *quaternary ammonium group* on the *amino acid*. The oxygen atom and the two hydrogen atoms combine to form a water molecule.

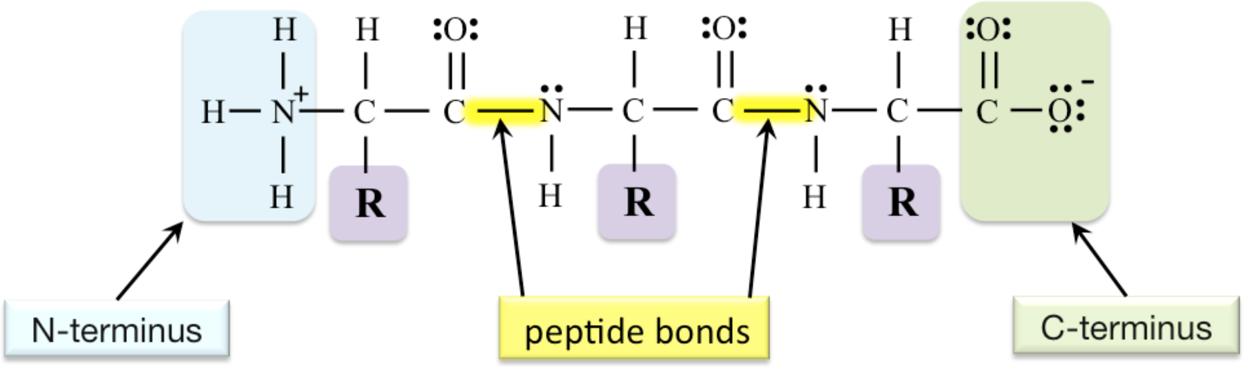
Step 2: A ***new bond*** is made between the carbonyl carbon and the nitrogen.

The peptide formed in this example is called a **tripeptide** because it contains ***three*** amino acid residues.

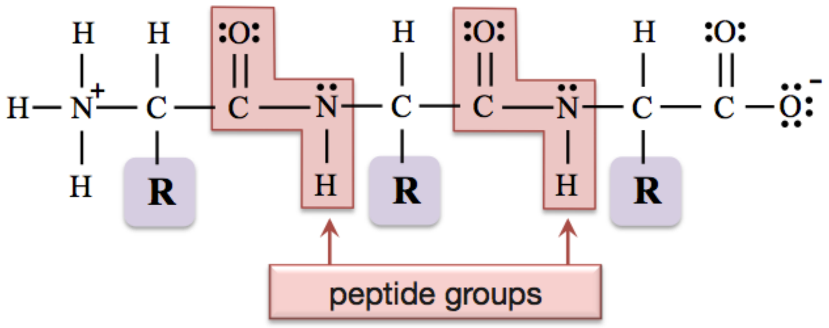


This process can continue and larger peptides can be formed by adding more amino acids, one by one, to a growing peptide.

I will use the tripeptide structure to introduce you to some important peptide terminology. The ***end*** of the peptide structural formula that has a ***quaternary ammonium group*** is called the **N-terminus**, and the ***end*** that has a ***carboxylate group*** is called the **C-terminus**.

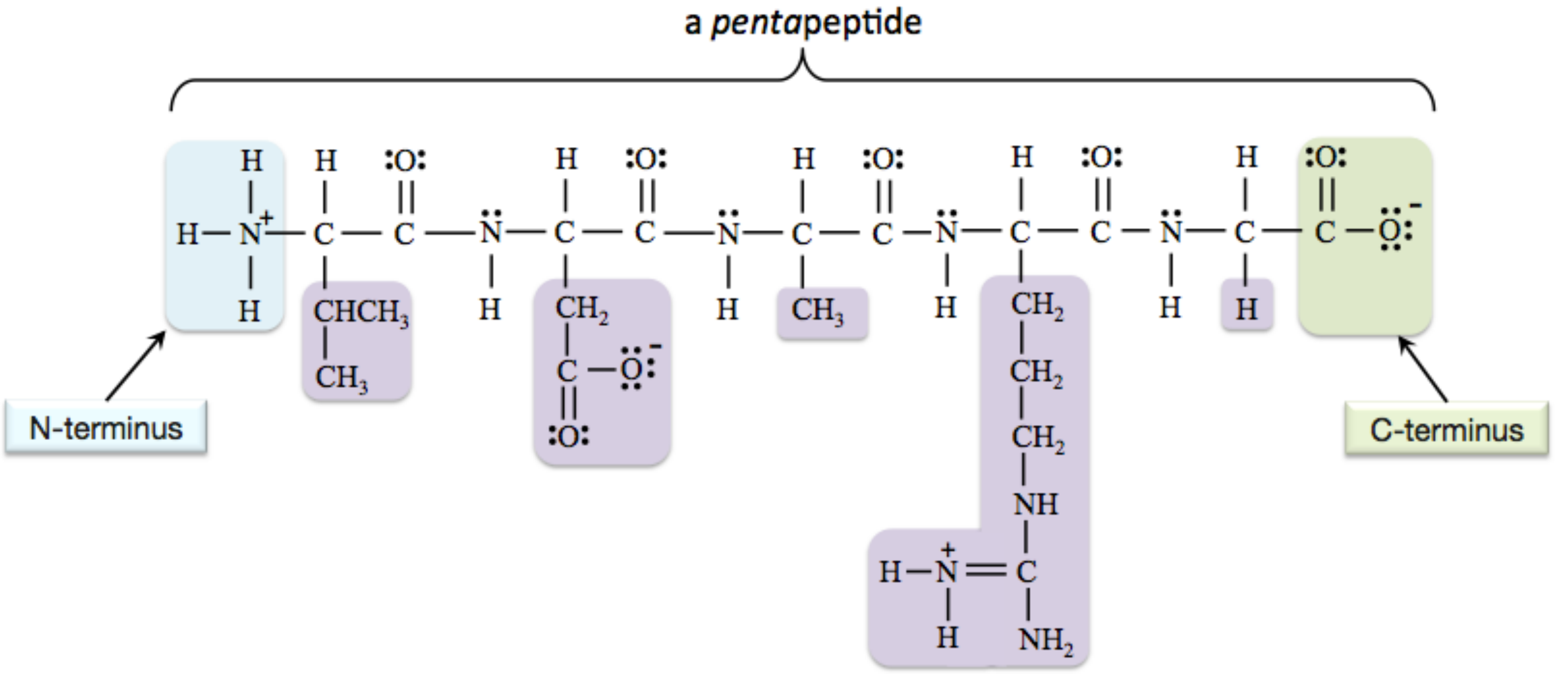


The bonding pattern around a *peptide bond* is called the **peptide group**. The atoms of the ***peptide groups*** in the tripeptide shown below are highlighted and labeled.



Note that the ***nitrogen in a peptide group does not*** carry a (1+) formal charge, as does the *nitrogen in the quaternary ammonium group at the N-terminus.*

Particular peptides are identified by the use of a common name ***or*** by listing its amino acid residues' *abbreviations* in order from N-terminus to C-terminus. The abbreviations for the amino acids are given in Table 13.1. As an example of identifying a peptide from its amino acid residue's *abbreviations*, the *penta*peptide shown below is called **Val-Asp-Ala-Arg-Gly**.



Val-Asp-Ala-Arg-Gly

I drew this pentapeptide by forming peptide bonds between the predominant forms of the amino acids at physiological **pH** (as shown in Table 13.1), therefore the resulting pentapeptide is also in the form that is predominant at physiological **pH**. Note that *two* of the *side-chains* in this peptide carry a formal charge. This peptide has a total charge equal to ***zero*** because the *two negative formal charges* and *two positive formal charges* add up to ***zero***.

Review 13.4: Drawing and Naming Peptides

Draw the *structural formula* for the predominant form of Gly-Lys-Tyr-Ala at physiological **pH**. Label the **peptide bonds** and circle the **peptide groups**. If you correctly connect the amino acid structural formulas from Table 13.1, then the peptide that you draw will be the predominant form at physiological **pH**.

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

Review 13.5: Total Charge of Peptides

What is the ***total charge*** of the peptide that you drew for Review problem 13.4?

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Examples of Biologically-Relevant Peptides

A **protein** consists of one or more ***large peptides*** and has ***a specific biological function***. Although shorter peptide chains (less than about *fifty* amino acid residues) have specific biological functions, they are generally not classified as proteins. Short peptide chains function as chemical signaling compounds; over one hundred of them have been identified.

Endorphins are examples of chemical signaling peptides. They are natural painkillers that are produced in the body. They interact with receptors in the brain to inhibit the transmission of pain signals. Five endorphins have been found (so far). An example of an endorphin peptide is ***α****-endorphin*. It contains sixteen amino acid residues, which are connected in the sequence (N-terminus to C-terminus) shown below:

Tyr-Gly-Gly-Phe-Met-Thr-Ser-Glu-Lys-Ser-Gln-Thr-Pro-Leu-Val-Thr

Another example of a peptide is *oxytocin*. It is produced by the pituitary gland, and stimulates uterine contractions in labor. *Oxytocin* contains *nine* amino acid residue, which are connected in the sequence shown below:

Cys-Tyr-Ile-Gln-Asn-Cys-Pro-Leu-Gly

Oxytocin was the first naturally-occurring hormone to be produced in a laboratory. It was synthesized and purified by Vincent du Vigneaud in 1953, who won the 1955 Nobel Prize in Chemistry for this work.

13.4 Proteins

The image above is a photograph of a Song dynasty painting of women ironing, sewing, and pounding ***silk***. Silk is a protein fiber that is obtained from the cocoons of certain insects, most notably the silkworm. Silk's biological ***function*** is to provide structure (rigidity) to the cocoon in order to protect the worm during metamorphosis.

A **protein** consists of ***one or more large peptides*** and has ***a specific biological function***. Proteins are present in all life forms on Earth. They can be classified according to their *biological function*. A list of these protein classes, their descriptions, and some examples are shown in Table 13.3.

Table 13.3 Protein Classification Based on Biological Function

Protein Class	Description	Examples
Contractile	Used for muscle movement	*Actin* and *myosin* work together to contract and expand muscles.
Enzyme	Catalyze biological chemical reactions	*Amylase* catalyzes the hydrolysis of starch.
Hormone	Released from glands and organs to regulate body functions	*Insulin* helps to regulate the level of glucose in blood.
Protective	Binds to foreign substances to begin the process that eliminates potentially dangerous substances from an organism.	*Antibodies,* for example, the antibodies that recognize and bind to influenza viruses
Structural	Provides rigidity and stiffness	*Keratin* in hair, skin, and nails
Storage	Stores other substances	*Myoglobin* stores oxygen in muscles.
Transport	Assists in moving other substances within a cell or organism	*Hemoglobin* transports oxygen.

Protein Structure

It is very important to understand the chemical bonding patterns and shapes of proteins in order to better understand how proteins are able to perform their biological functions. The bonding pattern and shape of a protein is referred to as "**protein structure.**" To describe a protein's structure, we use four "levels," which we call **primary**, **secondary**, **tertiary**, and **quaternary structure**.

1) Primary Structure

The **primary structure** of a protein is the ***sequence of amino acid residues*** in its peptide chain(s). The specific sequence of amino acid residues in each protein is determined by the genetic code in a particular gene. You will learn about **protein synthesis** (how the information in DNA is used to make proteins) in chapter 14. Proteins generally contain between 50 and 35,000 amino acid residues. One of the smaller proteins is *insulin,* a hormone that signals cells to allow glucose to enter. Human *insulin* contains 51 amino acid residues. The largest known protein is *titin*, which is found in muscle. Human *titin* contains about 34,000 amino acid residues.

The primary structure of peptides and proteins is analogous to the arrangement of letters in a word. In a word, it is not only which letters are present that is important; the sequence of the letters is also important. For example, the words below all contain the same *four* letters (**t**, **e**, **i**, and **d**), however, each word has a different meaning.

tide diet edit tied

The letters of a word are analogous to amino acid residues. For example, there are *twenty-four* different peptides that each contain one glycine, one alanine, one aspartic acid, and and one serine residue:

gly-ala-asp-ser	gly-asp-ala-ser	gly-ser-asp-ala	gly-ser-ala-asp	gly-asp-ala-ser	gly-asp-ser-ala
ala-gly-asp-ser	ala-asp-gly-ser	ala-ser-asp-gly	ala-ser-gly-asp	ala-asp-ser-gly	ala-gly-ser-asp
asp-ala-gly-ser	asp-ala-ser-gly	asp-gly-ala-ser	asp-gly-ser-ala	asp-ser-gly-ala	asp-ser-ala-gly
ser-asp-ala-gly	ser-asp-gly-ala	ser-gly-asp-ala	ser-gly-ala-asp	ser-ala-gly-asp	ser-ala-asp-gly

Because the ***primary structure*** is different in each of the *twenty-four* peptides listed above, each has a different shape and unique physical and chemical properties.

The ability of a protein to perform its biological function depends on its particular shape. The shape of a protein ultimately comes from the sequence of amino acids in its peptide chain (its primary structure). There are about 50,000 types of proteins in the human body, which means that nature needed to come up with 50,000 different protein shapes. At first, this may seem a bit fantastical, however, when we calculate the number of distinct peptide chains that can be made from the twenty common amino acids, the 50,000 value does not seem so large. The number of distinct peptides that are possible depends on the number of amino acids the peptide chain contains. If there are **n** amino acid residues in a peptide, then there can be 20^{n} different amino acid sequences, therefore 20^{n} possible shapes. The number "20" comes from the number of common amino acids. Let's calculate how many distinct dipeptides (peptides that contain only two amino acids) are possible:

- There are 20^{2} = **400** possible dipeptides (each with a different primary structure).

If we allow for one more amino acid residue to be added, then we have a tripeptide:

- There are 20^{3} = **8000** possible tripeptides (each with a different primary structure).

Next, let's do the calculation for a ***relatively small*** protein that contains *only* **100** amino acid residues:

- There are 20^{100} = **1.3 x 10^{130}** possible peptides (each with a different primary structure).

This number is too large for me to comprehend, other than thinking of it as "*almost infinite.*" It is about 100 million times greater than the number of atoms on Earth. If there are **1.3 x 10^{130}** distinct primary structures, then there are **1.3 x 10^{130}** distinct shapes that are possible (and this is for a relatively ***small*** protein). When compared to the **1.3 x 10^{130}** possible shapes *for a small protein*, the 50,000 protein shapes needed for human life does not at all seem too fantastical. This is the type of variety on which *evolutionary theory* is based.

2) Secondary Structure

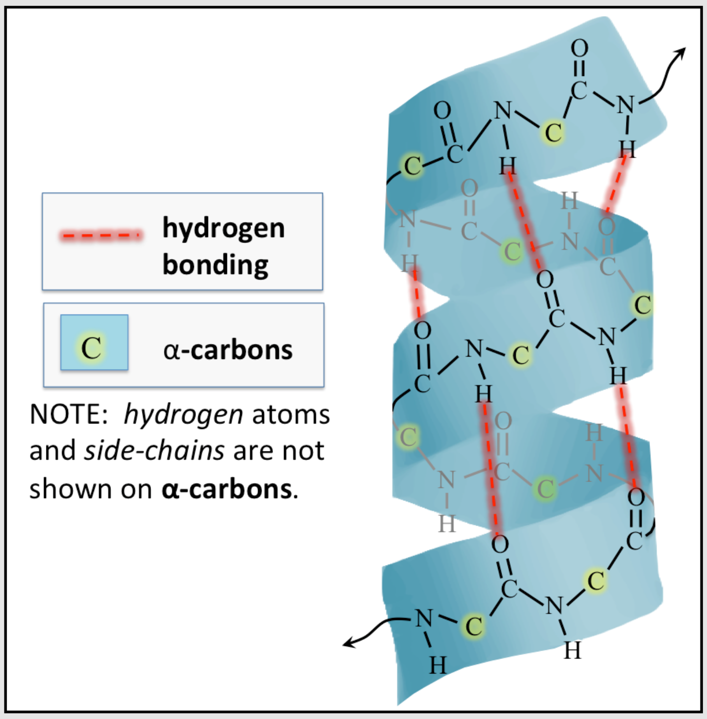
Secondary protein structure describes the geometric patterns that occur when individual peptide chains “fold” back on themselves, more specifically, the patterns that result from **hydrogen bonding** interactions between ***peptide groups*** within an individual peptide. There are ***two common types*** of secondary structures, the **alpha helix (*α* helix)** and the **beta sheet (β sheet)**.

The Alpha Helix

A peptide chain takes a shape that resembles a spring in the *alpha helix* structure. A model of the alpha helix geometry is shown in Figure 13.1. For simplicity in viewing, I have not drawn the hydrogen atom or side-chain on any of the ***α***-carbons. The alpha helix geometry is formed and maintained by ***hydrogen bonding between peptide groups***. There about 3.5 amino acid residues in each complete turn/coil of the peptide chain.

In the 1930’s, experiments that involved measuring the intensity and angles that x-rays are reflected from protein crystals (x-ray diffraction) implied the existence of a helical geometric pattern in proteins. The details of the alpha helix, such as the hydrogen bonding pattern, was first postulated by Linus Pauling in 1948. Pauling was awarded the Nobel Prize in Chemistry for his work on protein structure and other topics.

Figure 13.1
Alpha Helix Geometry

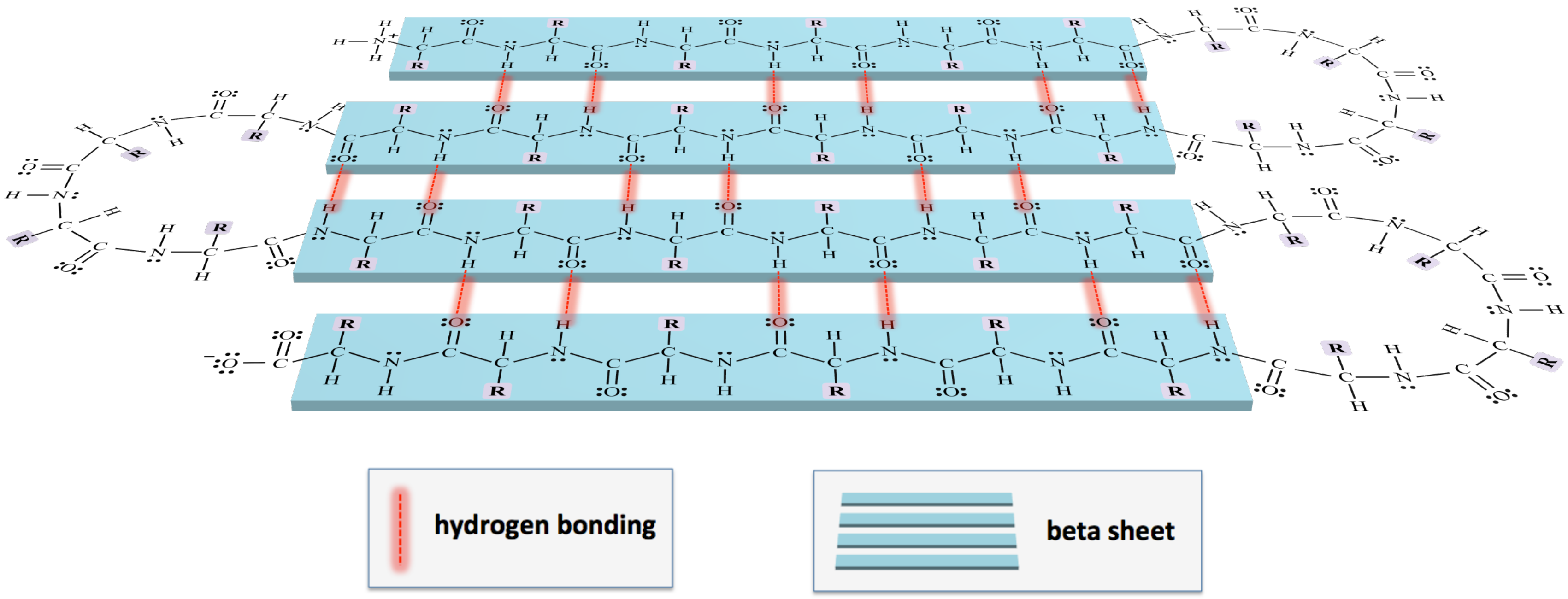


NOTE: *hydrogen* atoms and *side-chains* are not shown on **α-carbons**.

The Beta Sheet

The **beta sheet** geometry occurs when a peptide folds back on itself in a ***side-by-side*** arrangement. A illustrative model of a beta sheet is shown below.

Illustrative Model of a Beta Sheet



A beta sheet is held together through ***hydrogen bonding*** attractions between ***peptide groups***. Just like the discovery of the alpha helix, the existence of beta sheets was first inferred from the results of x-ray diffraction experiments.

In addition to *alpha helices* and *beta sheets*, there are a few other, much less frequently seen geometries that are also categorized as secondary structures. Since these other secondary structures are relatively rare, I will not discuss their particularities. A key feature of *secondary protein structure* is that it **only** involves ***hydrogen bonding between peptide groups within an individual peptide chain***.

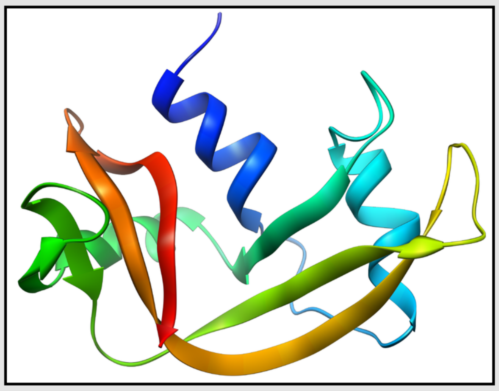
3) Tertiary Structure

Not all of the amino acids in a peptide are organized in well-defined secondary structures such as alpha helices or beta sheets. These *unorganized sections* of a peptide chain, along with the alpha helices and beta sheets, "***fold***" into a more compact shape. The compacted shape of a peptide is called **tertiary structure**.

"Ribbon models" are often used in order to visualize tertiary protein structure. These illustrative models use ribbon-like shapes to represent the geometry of secondary structures, such as the four shaded rectangles in the beta sheet illustration and the blue shaded coil in the alpha helix illustration on the previous page. Sometimes arrows are used at the ends of ribbons to indicate the direction (from N-terminus to C-terminus). Lines or thin tubes are used for *unorganized sections* of a peptide chain.

Tertiary structure*, the compact shape of a peptide*, is easily visualized from the protein's ribbon model. Ribbon models have been developed for most proteins. The primary information used to construct the models is x-ray diffraction measurements. The ribbon model for *ribonuclease A* protein (RNase A), an enzyme used to break down RNA, is shown in Figure 13.2. RNAse is composed of ***only*** one peptide chain.

Figure 13.2
Ribbon Model of Ribonuclease A



The ribbon model for *ribonuclease* makes it easy to visualize the protein's tertiary structure.
Source: Wikimedia Commons,
Author: Vossman, CC-BY-SA,
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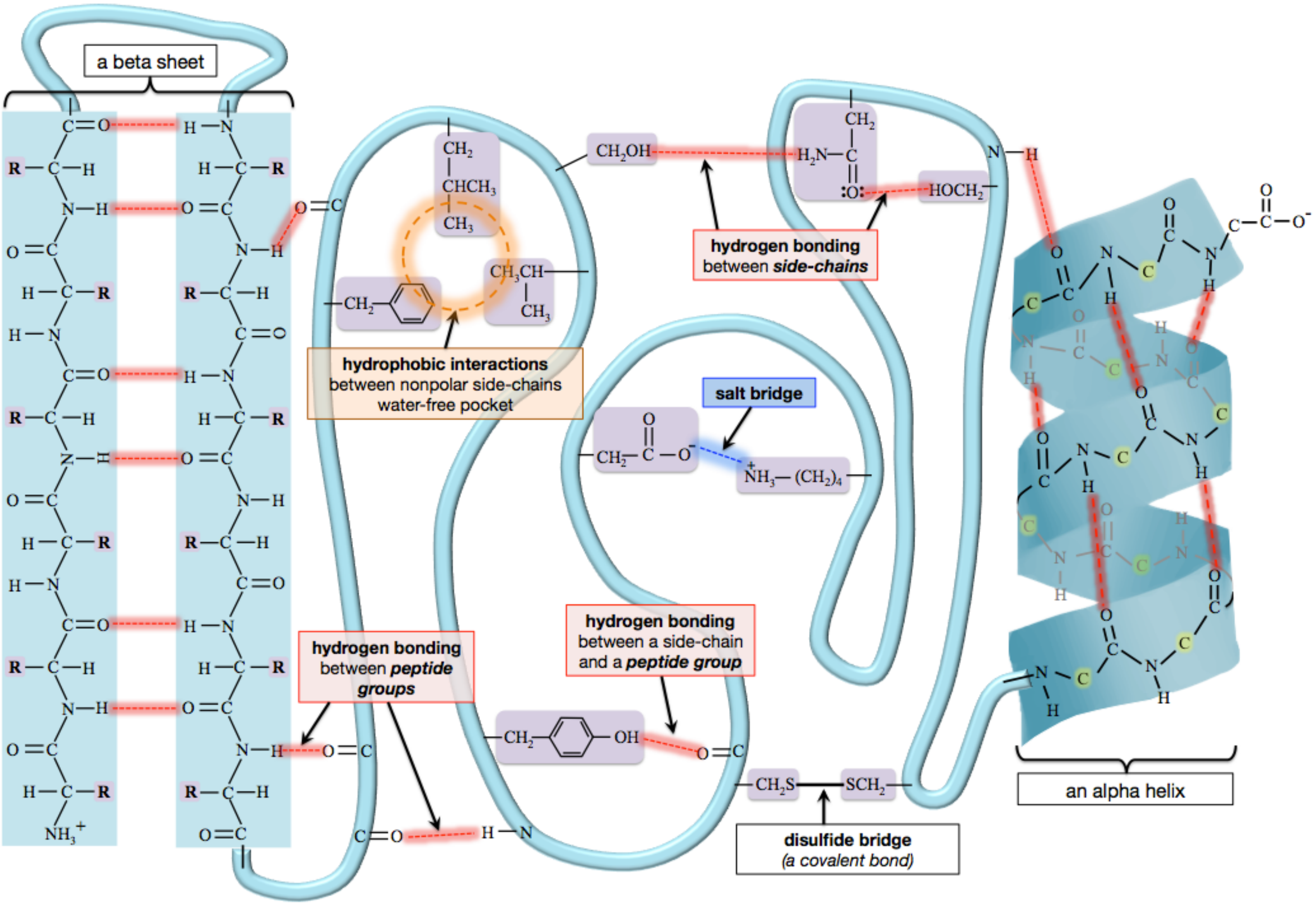
How do proteins ***fold*** into the compacted tertiary structures that are necessary for them to function? Unfortunately, science does not offer a complete explanation at this time, although it is currently an area of much research. We do have a good understanding of the ***attractive interactions*** that hold peptide chains in their compacted tertiary structures. Some of the interactions that are involved in **tertiary structure** are illustrated below.

An Illustration of Hydrophobic Interactions, Salt-Bridge, Disulfide Bridge, and Hydrogen Bonding in Tertiary Structure



Description of Tertiary Structure Interactions:

a) Hydrophobic Interactions

Nonpolar side-chains are hydrophobic and therefore tend to orient themselves away from the water molecules that surround proteins in aqueous solutions. They are attracted to ***other*** *nonpolar side-chains* through *London forces,* and form "**water-free pockets**" in the interior region of the folded and compacted peptide (see the illustration on the previous page). This phenomenon is called a **hydrophobic interaction.** It is a *lower energy state* for nonpolar side-chains to be next to other nonpolar side-chains in the interior of the tertiary structure than it is for them to be on the outer surface of the structure where they would protrude into the polar aqueous solution.

b) Hydrogen bonding

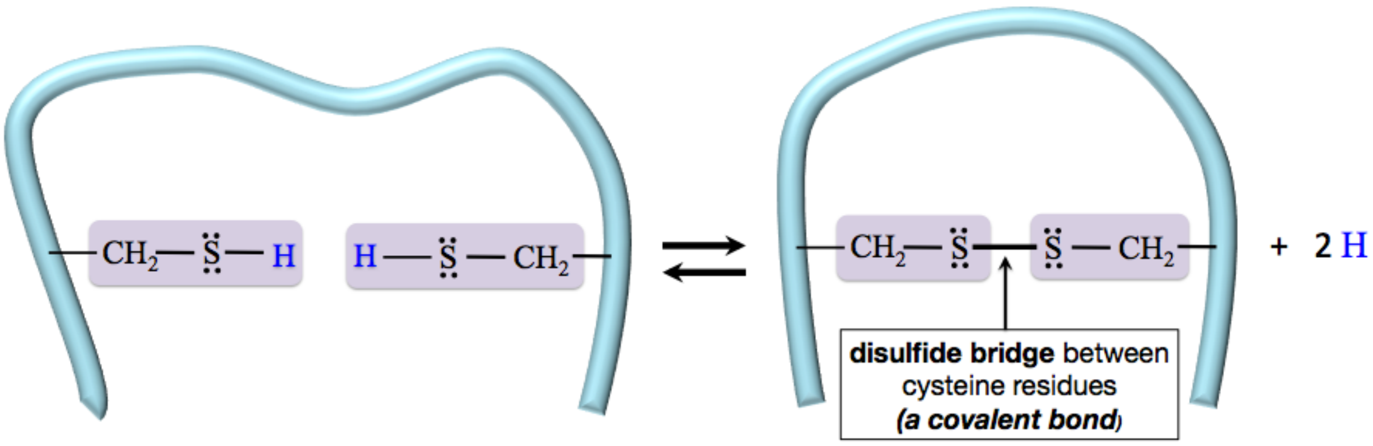
Hydrogen bonding in *tertiary structures* can occur between polar side chains (that contain the features necessary for hydrogen bonding) and/or peptide groups. Tertiary structure hydrogen bonding *does not include* the hydrogen bonding in alpha helices or beta sheets.

c) Salt Bridges

In chapter 4, I briefly introduced ***salt bridges*** as one of the *five noncovalent interactions*. A *salt bridge* is an attractive force between the ***positive*** formal charge on *polar basic* amino acid residue and a ***negative*** formal charge on a *polar acidic* residue. An example of a salt bridge between an *aspartic acid* residue (polar acidic) and a *lysine* residue (polar basic) can be seen in the illustration on the previous page.

d) Disulfide Bridges

In chapter 10, you learned that *disulfide (covalent) bonds* can be formed by the oxidation of two thiol (**SH**) groups. *Disulfide bonds* in proteins are called ***disulfide bridges***. Each *cysteine* residue contains a thiol group in its side-chain that is capable of forming a disulfide bridge with *another* cysteine residue**,** as shown below.



disulfide bridge between cysteine residues ***(a covalent bond)***

Formation of a Disulfide Bridge

e) Dipole-Dipole and Ion-Dipole Forces

Dipole-dipole attractive forces can occur between polar side-chains and/or peptide groups. ***Ion-dipole attractive forces*** can occur between a side-chain with a formal charge *and* another polar side-chain or peptide group. These interactions are not included in the illustration on the previous page. If needed, you can review dipole-dipole and ion-dipole interactions in section 6 of chapter 4.

4) Quaternary Structure

Some proteins only contain *one* peptide chain, and others contain *multiple* peptide chains. Quaternary protein structure is the overall shape that occurs when two or more *individual peptide chains* assemble to make a protein. The forces that hold the subunits together in quaternary structures are the same as those involved in tertiary structures. I will elaborate on quaternary protein structure by showing you a couple of examples.

Hemoglobin is a protein that contains *four* individual peptide chains. In proteins composed of two or more peptide chains, the individual peptide chains are referred to as "**subunits.**" The **quaternary structure** of hemoglobin is the description of the overall shape of the four ***assembled*** *subunits*. Hemoglobin has *two pairs* of identical subunits; two of the subunits are shaded red, and the other two subunits are shaded blue in the protein ribbon model shown in Figure 13.3. The four small, green structures that are seen in the hemoglobin ribbon model (above) are called *heme* prosthetic groups. I will discuss prosthetic groups a bit later in this section.

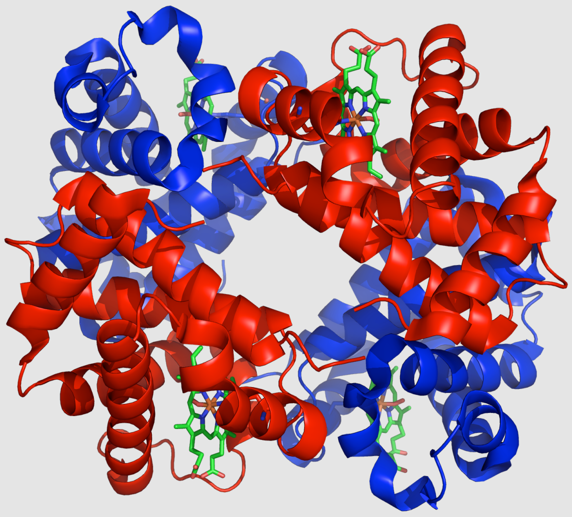


Figure 13.3
The Quaternary Structure of Human Hemoglobin

A ribbon model of human *hemoglobin*. Hemoglobin is composed of ***four*** individual peptide chains (subunits). Two of the subunits are shaded red, and the other two subunits are shaded blue in this ribbon model. Quaternary structure is a description of the overall shape that occurs when *multiple* peptide chains (residue) are assembled in a protein.

Source: Wikimedia Commons, Author: Richard Wheeler, CC-BY-SA, http://creativecommons.org/licenses/by-sa/3.0/legalcode

The quaternary structures of large proteins are sometimes depicted using *space-filling models*. In these models, the various subunits are often shaded with different colors or greyscale tones. For example, the quaternary structure of *ATP synthase*, an enzyme that catalyzes the formation of ATP, can be seen in the space-filling model shown in Figure 13.4.

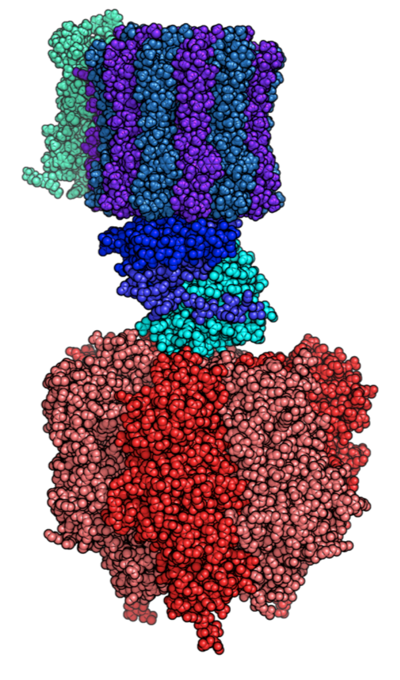


Figure 13.4
The Quaternary Structure of ATP Synthase

A space-filling model of *ATP synthase.* ATP synthase is composed of ***several*** individual peptide chains (subunits). The various subunits are shaded with different colors.

Source: Wikimedia Commons, Author: Alex.X, CC-BY-SA, http://creativecommons.org/licenses/by-sa/3.0/legalcode

If a protein is composed of just ***one*** peptide chain, then it has only primary, secondary, and tertiary structure. Quaternary structure is the arrangement of ***multiple*** peptide chains (subunits), therefore it does not apply to single-peptide proteins. Secondary, tertiary, and quaternary structures ***all depend on primary structure***, and a protein's primary structure is determined by information in DNA.

Review 13.6: Protein Structure

Write the names (using the three letter abbreviation method) of *all of the tripeptides* that can be made by combining one glycine (gly), one alanine (ala), and one aspartic acid (asp) residue. For example, one of the tripeptides is gly-ala-asp.

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

Review 13.7: Protein Structure

How many distinct ***tetra****peptides* can be made (using any of the twenty common amino acids)?

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

Review 13.8: Protein Structure

Answer the following questions using ***one or more*** of the following choices: hydrogen bonding, glycosidic bonds, covalent bonding, disulfide bridges, hydrophobic interactions, salt bridges.

a. Which are involved in maintaining secondary structure?
b. Which are involved in maintaining tertiary structure?
c. Which are involved in maintaining quaternary structure?

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

A note about language: protein vs. proteins. When referring to *a particular* protein particle, it is customary to use "protein" for ***both*** the singular (one protein particle) *and* the plural (more than one of *the* <u>*same*</u> *protein particle*). For example, when discussing ***all*** of the hemoglobin particles in an organism's blood, you would say, "...the hemoglobin *protein* in the organism's blood...." When referring to *more than one* ***particular*** protein, it is customary to use "protein**s**" as the plural. For example, when discussing ***all*** *types of protein particles* in an organism's blood, you would say, "...the *proteins* in the organism's blood...."

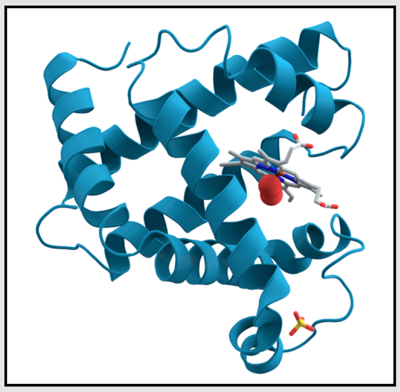
Globular, Fibrous, and Membrane Proteins

Proteins generally fall into one of three categories: **globular**, **fibrous**, or **membrane** proteins.

Globular Proteins

Globular proteins have highly-folded and compact shapes. The term *globular (*from Latin *"globus"* meaning *round mass* or *sphere)* is used because the overall shapes of these proteins are more "sphere-like" than "string-like." The globular shape allows for *hydrophobic* side-chains to be directed to the protein's interior (forming "water-free pockets"), while *polar* side-chains are oriented outward to form a *hydrophilic* exterior. The hydrophilic exterior allows globular proteins to be more easily dispersed in solutions (intercellular and extracellular). The water-solubility of these proteins is related to the fact that they evolved to function in roles that required them to move freely in aqueous solutions within cells, blood, and interstitial fluids. *Hemoglobin* is an example of a globular protein. As you saw from its ribbon model (Figure 13.3), it has a quite compacted shape. Globular proteins function as enzymes, chemical signaling compounds, transporters of other compounds, and antibodies.

Figure 13.5 Myoglobin



A ribbon model of *myoglobin* (a globular protein).

Myoglobin is another example of a globular protein. It is used to store oxygen (O_2) in muscle tissue, thereby allowing organisms to function while holding their breath. *Myoglobin* is responsible for the red color of meat. It is found in especially high concentration in diving animals, such as seals and whales. Myoglobin was the first protein to have its structure determined by x-ray diffraction. This work was done in 1958 by John Kendrew and his coworkers. In 1962, the Nobel Prize in chemistry was awarded to Kendrew for his work on myoglobin, and also to Max Perutz for determining the structure of hemoglobin. A ribbon model of myoglobin is shown in Figure 13.5. It is composed of just one peptide chain. Human myoglobin contains 153 amino acid residues and eight alpha helices. It also contains a *heme* prosthetic group (shown in grey) that binds oxygen (shown as red spheres next to the heme group).

Figure 13.6 Human Serum Albumin (HSA)

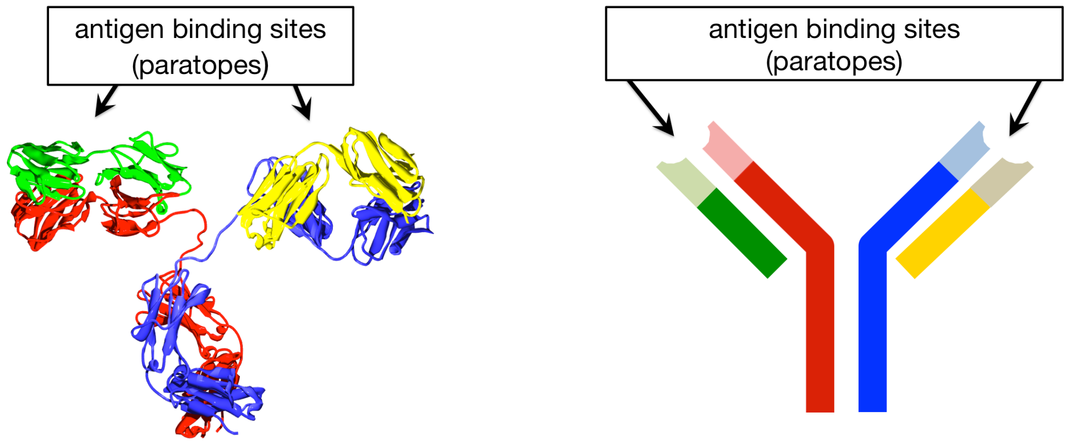
A ribbon model of **albumin** (a globular protein).

Another example of a globular protein is ***albumin***. Human *albumin* is the most abundant protein in human blood plasma. Its biological functions include transporting hormones, fatty acids, and other compounds, acting as a buffer, and maintaining osmotic pressure. A ribbon model of *human serum albumin* (HSA) is shown in Figure 13.6. This image shows four palmitic acid molecules (grey structures) bound to HSA, as would occur in its role as a fatty acid transporter.

Antibodies, also referred to as **immunoglobulins** (Ig), are globular proteins. Antibodies are able to act as protective agents by binding to specific, usually harmful, objects - called *antigens*. Antigens are often foreign (nonself) objects such as harmful bacteria or viruses. When an antibody binds to an antigen, it either directly neutralizes the antigen, or marks it so that the antigen can be subsequently neutralized by other components of the immune system.

The smallest antibodies are composed of a *single* immunoglobulin unit, called an **immunoglobulin monomer**. The ribbon model of an *immunoglobulin monomer* is shown on the *left-hand side* of Figure 13.7. An immunoglobulin monomer is shaped a bit like the letter "Y," and is often illustrated using a Y-shape, as shown on the *right-hand side* of Figure 13.7.

Figure 13.7 The Structure of an Immunoglobulin Monomer



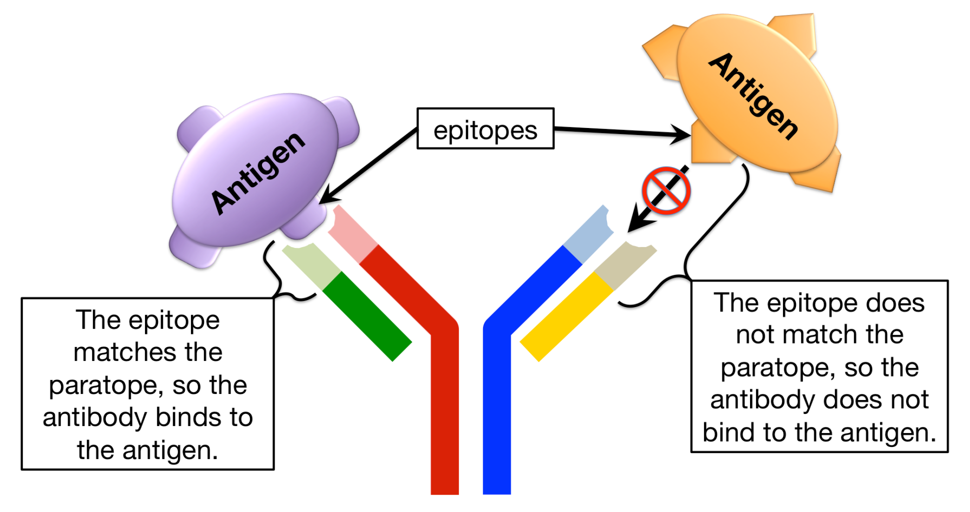
Ribbon model of an immunoglobulin monomer

"Y-shape" model of of an immunoglobulin monomer

The tops of the two upper parts of the Y-shape are the **antigen binding sites**. An antigen binding site, called the **paratope**, binds to a particular part of an antigen called the **epitope**. The binding between antigen and antibody occurs because of ***noncovalent attractive forces***, *which are maximized due to the complementary shapes of the paratope and epitope.* You can think of this as analogous to a lock-and-key system. Note that in the Y-shape antibody model shown in Figure 13.8, the *paratope* will only bind with one of the two antigens - the antigen that has a complementary epitope. We say that the paratope (or antibody binding site) is "*specific*" for a particular epitope.

The immune system can produce an almost infinite variety of paratope shapes by varying the paratope region's amino acid sequence (and therefore its shape). By doing so, antibodies are produced to be *specific* for one particular antigen, much like a lock is *specific* for one key.

Figure 13.8 Antigen-Antibody Binding



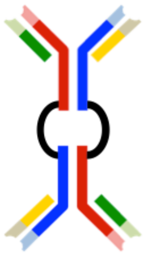
The epitope matches the paratope, so the antibody binds to the antigen.

The epitope does not match the paratope, so the antibody does not bind to the antigen.

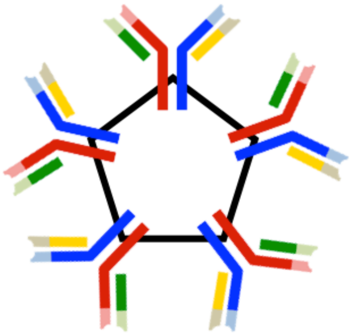
A **vaccine** contains epitopes of a potentially-dangerous, microbial pathogen for which the vaccine is intended to provide protection. The source of the vaccine's epitopes is either epitopes that have been extracted from the pathogen, a weakened or inert form of the pathogen, or a "safe" microbe that contains the same epitope as the dangerous pathogen. When the vaccine is injected, the immune system begins a process that varies the amino acid sequence in antibody paratopes until an antibody capable of binding to the vaccine's epitope is produced. Once this occurs, the immune system retains the antibody information so that if the lethal pathogen appears in the future, the effective antibody can be quickly produced. The amount of time that the immune system can retain antibody information varies, and re-vaccination is often necessary. The re-vaccination is referred to as a **booster**.

Some antibodies contain ***more than one*** *immunoglobulin unit.* Placental mammals, which includes humans, have immunoglobulin monomer, immunoglobulin dimer, and immunoglobulin pentamer antibodies. Immunoglobulin *dimers* are made from ***two*** immunoglobulin monomers, and immunoglobulin *pentamers* are made from ***five*** immunoglobulin monomers. These three types of antibody structures are illustrated below.

immunoglobulin monomer
(single immunoglobulin unit)



immunoglobulin
dimer



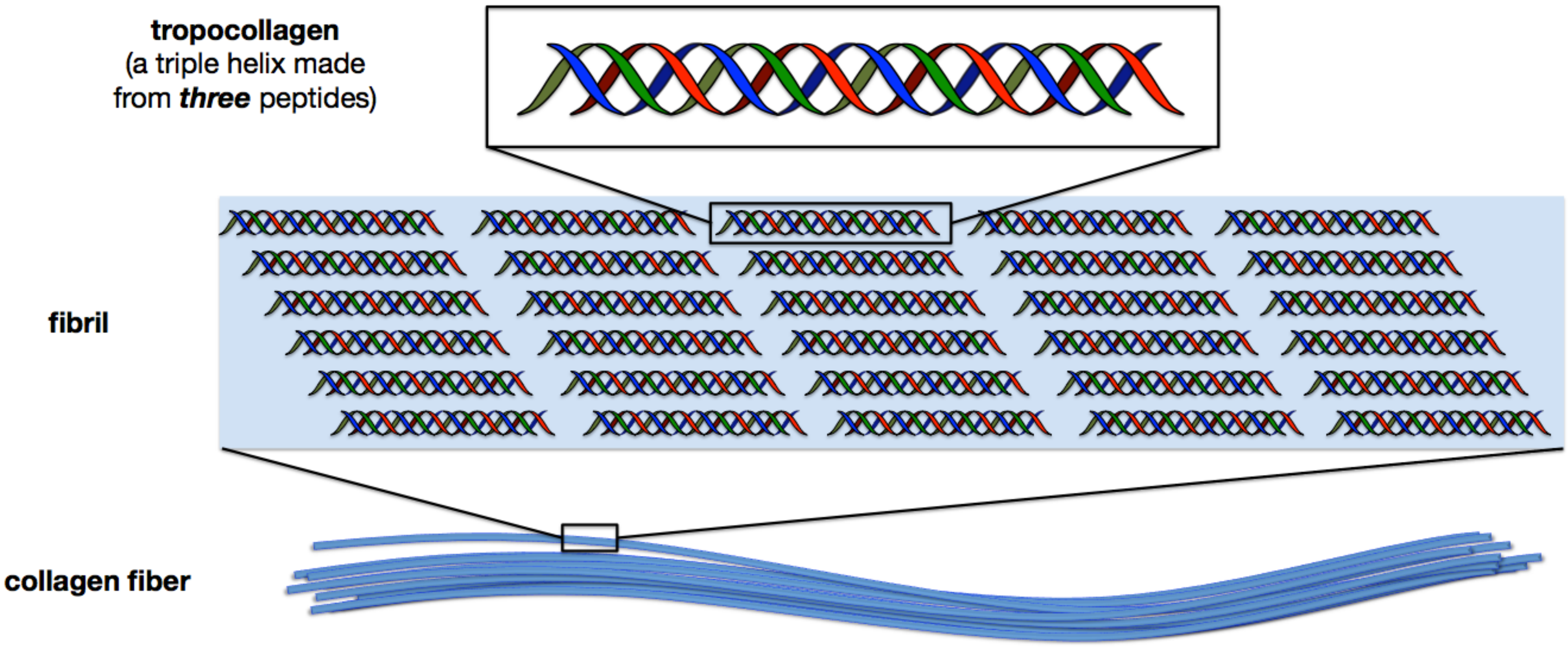
immunoglobulin
pentamer

One last note about antibodies. ***Antibodies*** have *carbohydrates* (oligosaccharides) that are covalently bound to ***some*** of their amino acid residue *side-chains*. Proteins, such as antibodies, that contain carbohydrates are called **glycoproteins**.

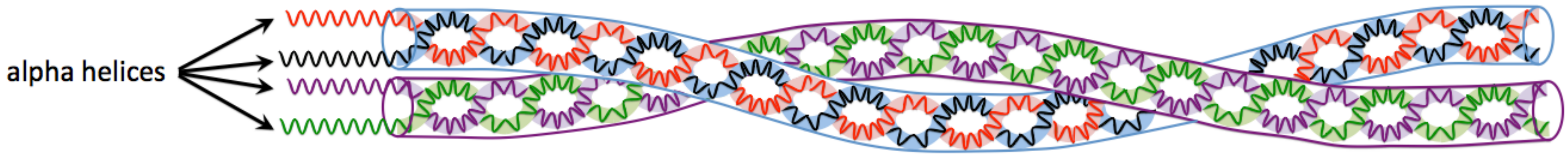
Fibrous Proteins

Fibrous proteins are much less compact than globular proteins. They have long and narrow "string-like" shapes. The narrower shape makes it difficult for hydrophobic side-chains to be oriented toward the interior region of a fibrous protein, and results in a *hydrophobic* exterior. For this reason, fibrous proteins tend to be water-insoluble. Fibrous proteins play important roles in providing structural rigidity and in contractile movement (muscles).

An example of a *fibrous protein* is ***collagen***. *Collagen* is the most abundant protein in the body. Its function is to provide structural rigidity and stiffness. It is found in skin, ligaments, tendons, and other parts of the body. **Collagen fibers** are made from bundles of **collagen fibrils**. *Collagen fibrils* are composed of **tropocollagen**, which consists of three peptide chains that are twisted around each other in a *triple helix* coil (not to be confused with the single-peptide alpha helix). An illustration of the components of *collagen* are shown below.



Other examples of fibrous proteins are **keratins**. Like *collagen*, they are abundant in nature, and their primary role is to provide structural rigidity and stiffness. *Keratins* are some of the strongest natural materials. K*eratins* can be classified as **alpha-keratins** or **beta-keratins**. ***Alpha-keratins*** are found in places such as hair, wool, horns, hooves, claws, and nails. The term *keratin* is derived from the Greek term *kerato* (κέρατο) that means *"horn-like."* An example of an *alpha-keratin* structure can be seen in human hairs. In hair, *two* peptide ***double*** helices are twisted around each other to form a **protofibril**, as shown below.



a protofibril

two peptide ***double helices*** that are twisted around each other

Protofibrils bundle together to form **microfibrils**. *Microfibrils* bundle together to form **macrofibrils**. Each ***hair cell*** is primarily composed of bundled *macrofibrils*. Finally, a **single hair** consists of bundled hair cells. An illustration of the structure of hair is shown below.

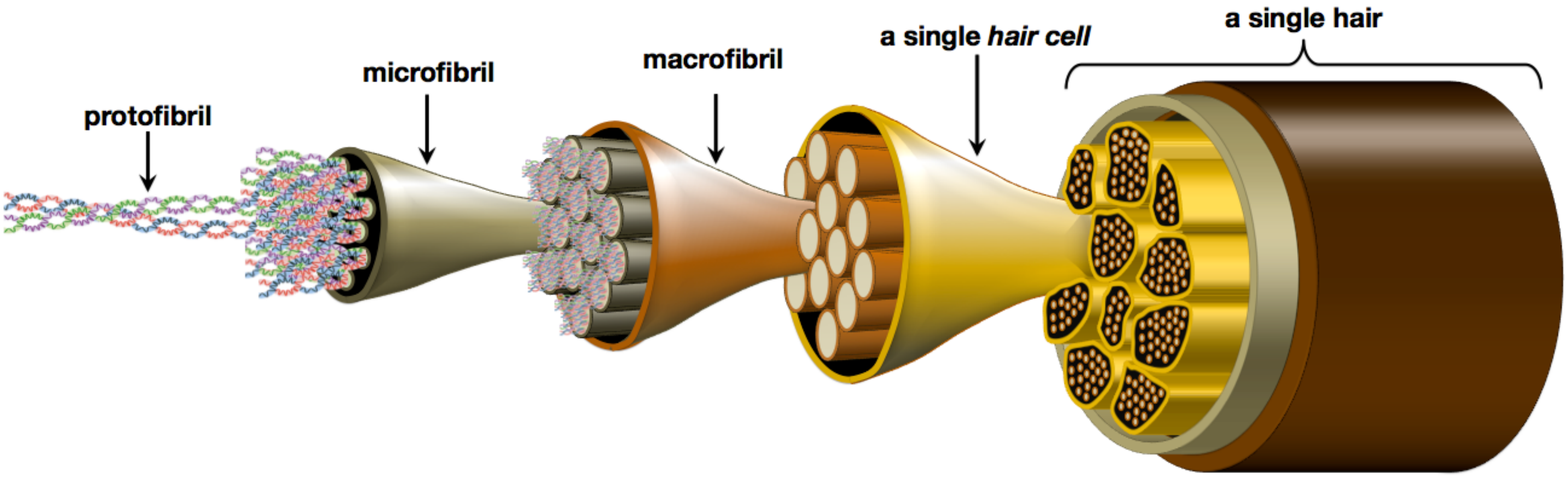
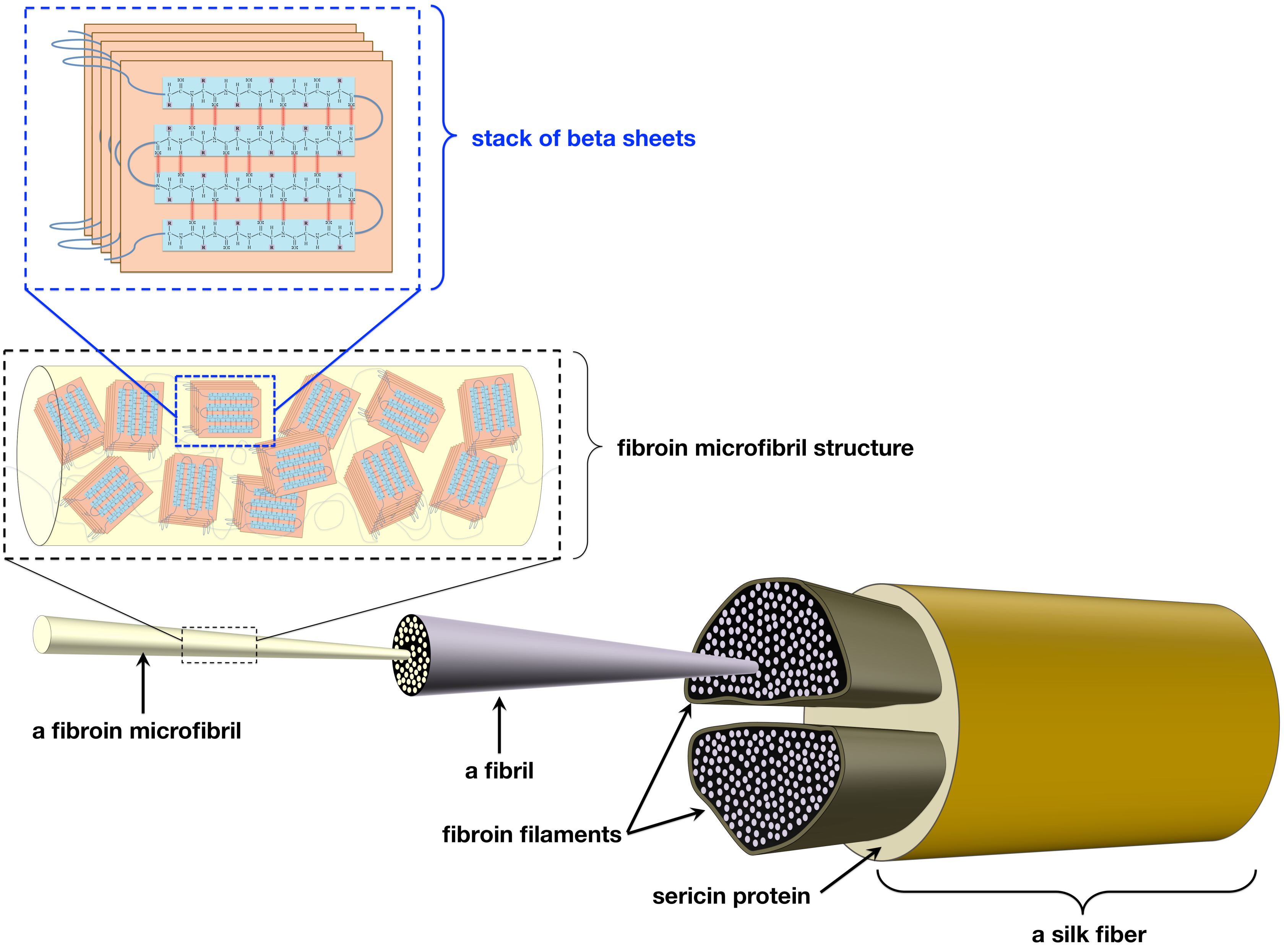


Illustration of the Alpha-Keratin Structure in a Single Hair

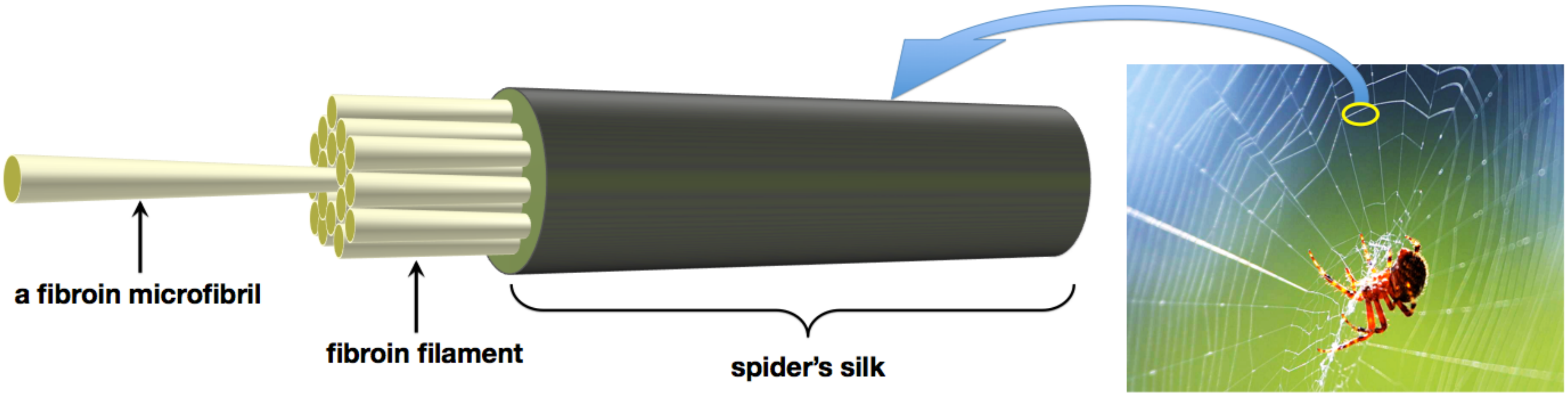
Beta-keratins, which are also fibrous proteins, are found in places such as reptilian skin, the outer layer of human skin, bird feathers and beaks, turtle shells, silk, and the tongue. Beta-keratins are composed of fibers that primarily contain ***beta sheet*** *secondary* structures. The *beta sheets* are arranged in ***layered*** *tertiary* structures. An example of a beta-keratin structure can be seen in **silk**. An illustration of the structure of silk is shown and discussed on the next page.

In silk, *beta sheets* form stacks, as shown at the *top* of the illustration below. The stacks, which are held together by disulfide bridges and noncovalent interactions, entwine to form a **fibroin microfibril**. *Fibroin microfibrils* assemble to form **fibrils.** *Fibrils* assemble to form **fibroin filaments**. Two *fibroin filaments* are held together by *sericin protein*, which acts like a glue to hold the two fibroin filaments together in a single silk fiber, as shown below.

.



Fibroin microfibril keratin fibers are also found in spider webs. It is for this reason that spider webs are sometimes referred to as *spider's silk*. The structure of *spider's silk* is illustrated below.

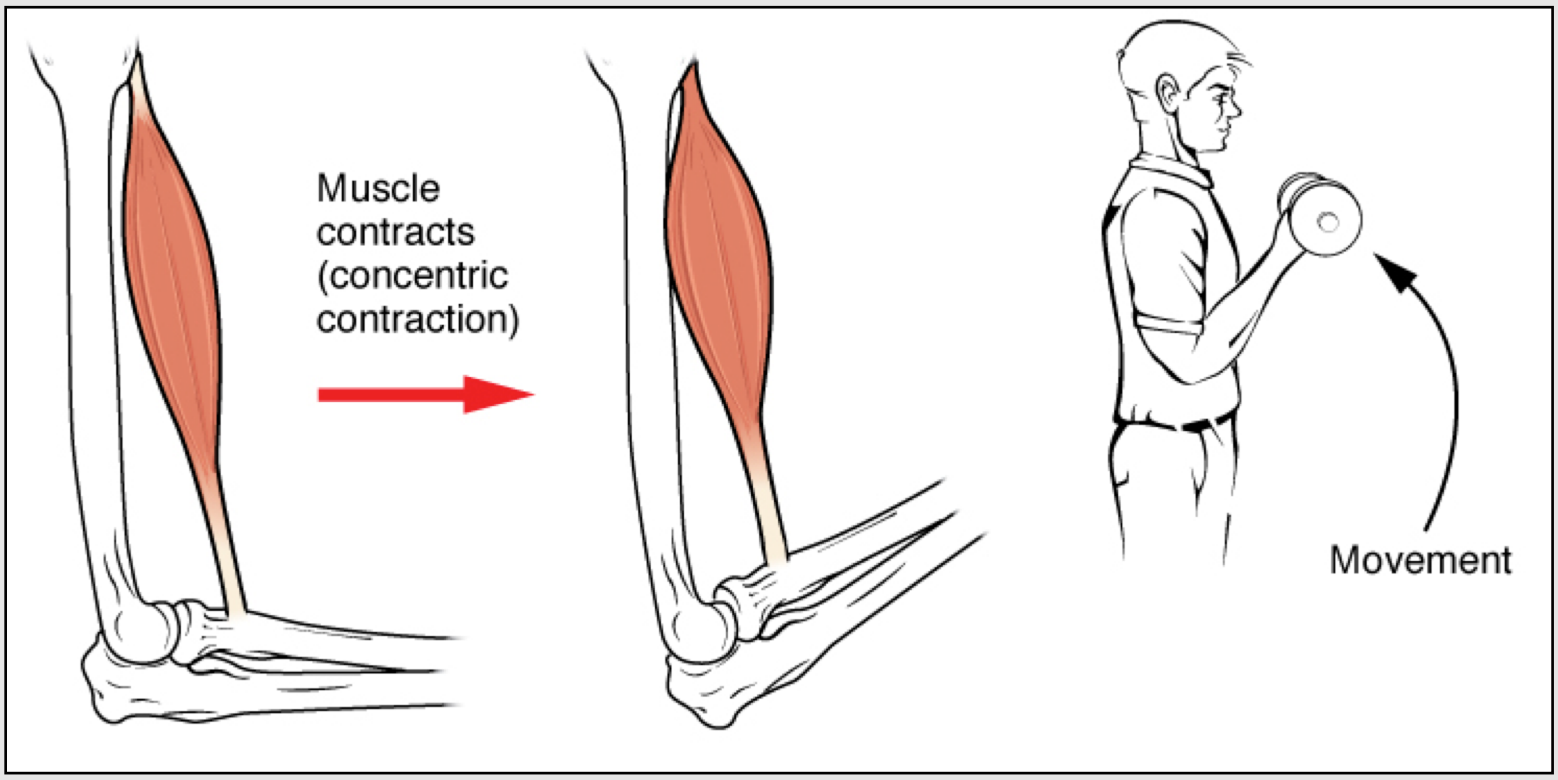


Fibrous Proteins in Muscles

Muscle contraction involves the interaction of fibrous proteins. A discussion of muscle fibers will not only provide you with another example of fibrous proteins, it will allow you to better understand how muscles work. Furthermore, this topic will also allow me to "complete the loop" as to how energy that was generated by the sun is transformed into chemical potential energy and then into kinetic energy of locomotion (movement).

Muscle contraction allows movement to occur. For example, in concentric contraction, the shortening of a muscle causes movement around a joint. This process is illustrated for a bicep contraction in Figure 13.9.

Figure 13.9 **Muscle Contraction in the Upper Arm (Bicep)**



Movement occurs when a muscle is shortened. The shortening of a muscle is called *muscle contraction*. This figure shows how the shortening of the bicep muscle results in movement of the arm.

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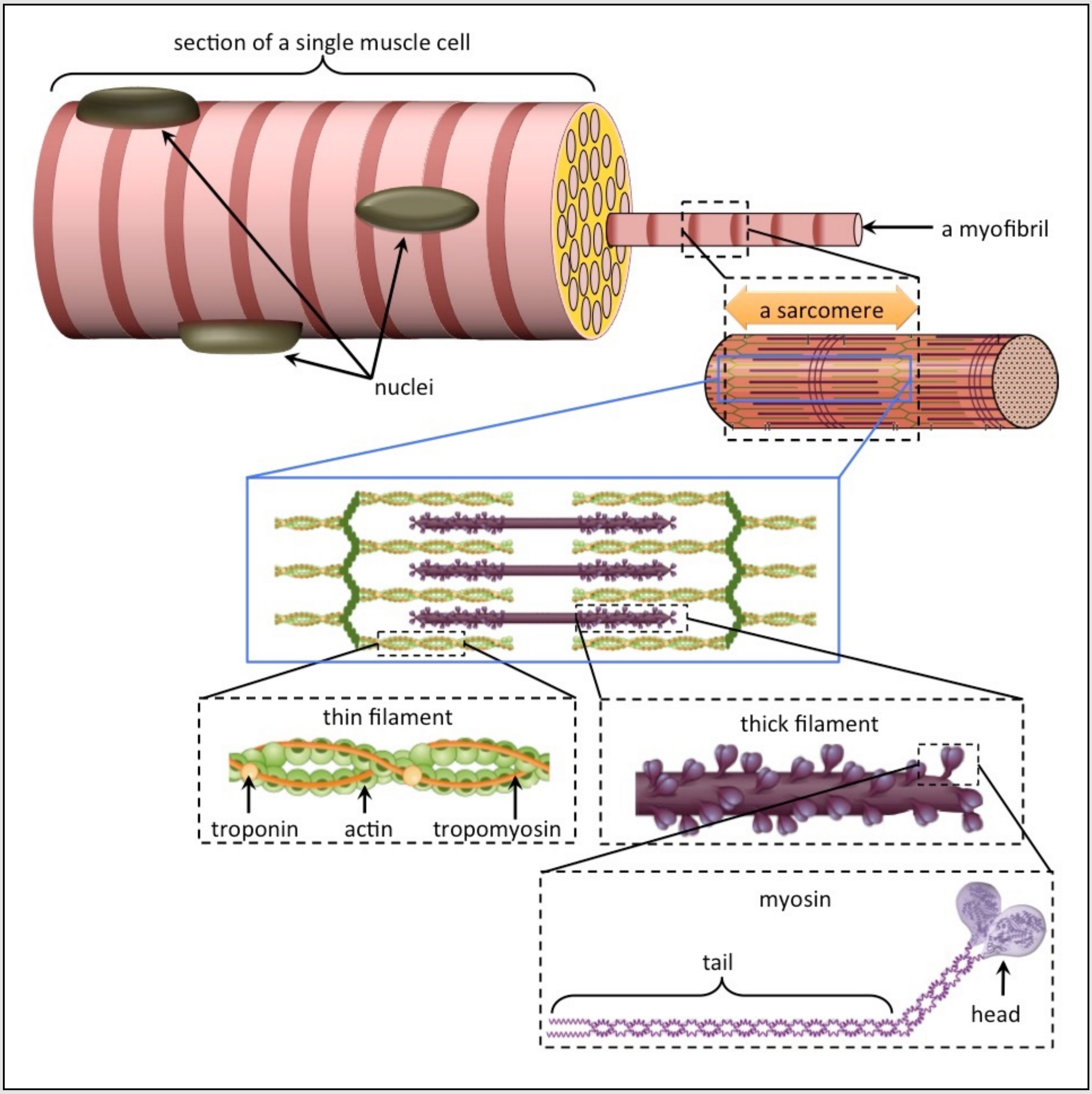
Muscle contraction is a complicated physiological process that can be described by a model called the "**sliding filament theory.**" I will first give you an introduction to the structure of muscles, and then discuss the *sliding filament theory*.

Muscles are composed of bundled muscle cells. The structure of a section of a single muscle cell is illustrated in Figure 13.10.

Figure 13.10 **An Illustration of the Structure within a Muscle Cell**



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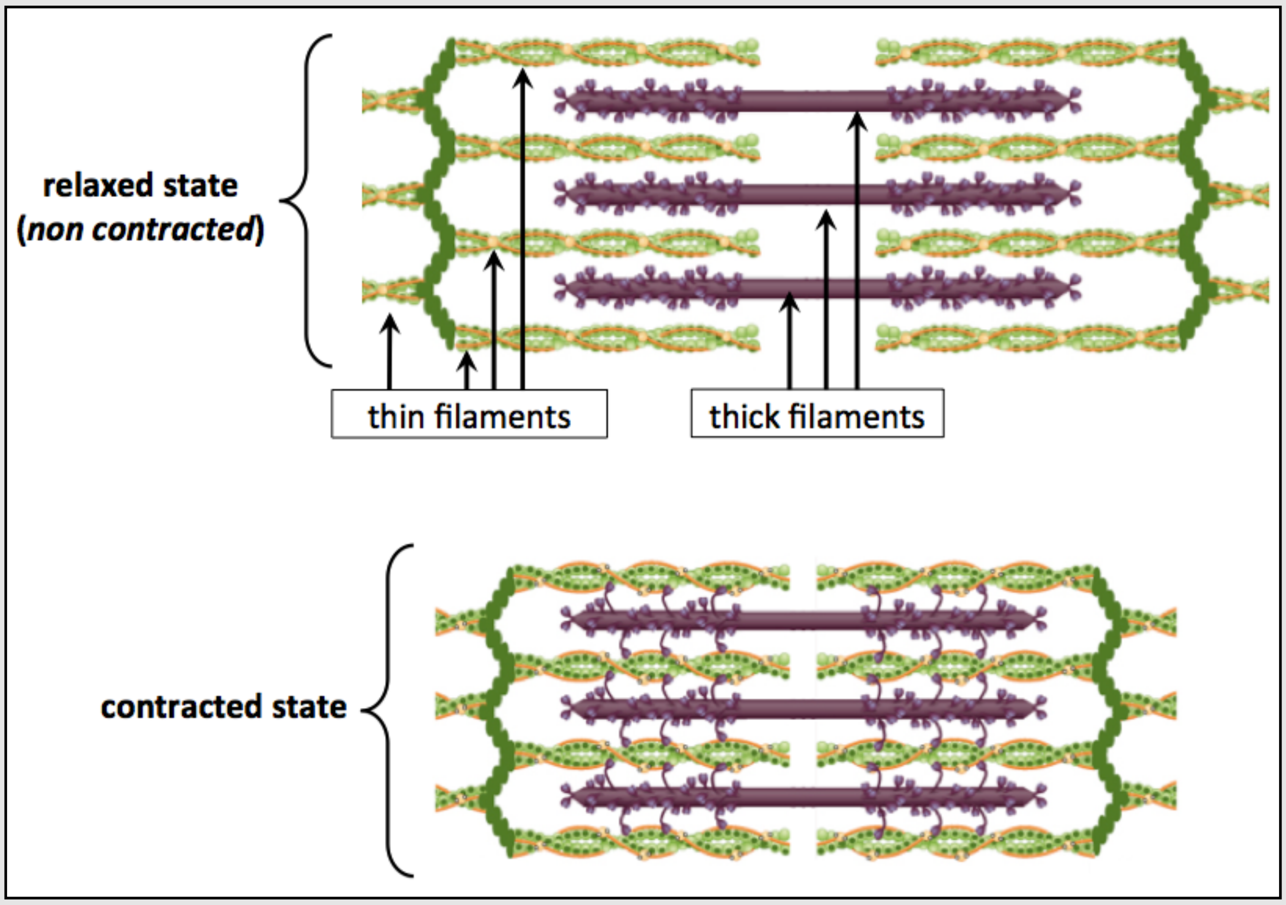
A muscle cell is a polynuclear (many nuclei) cell that contains long protein fibers called **myofibrils**. *Myofibrils* are composed of individual contractile units called **sarcomeres**. *Sarcomeres* contain fibrous proteins called "**thick filaments**" and "**thin filaments**."

Thick filaments are composed of **myosin** fibrous protein (see bottom-right in Figure 13.10). The ***myosin tail region*** is composed of two alpha helices that are twisted around each other. In the ***myosin head region***, the individual alpha helices split apart from each other and fold into more compacted tertiary structures.

Thin filaments are composed of three proteins: actin, troponin, and tropomyosin, as illustrated in Figure 13.10.

Now that you have seen the general structure of muscles, let's take a look at how they contract. For muscle contraction (or relaxation) to occur, the thick and thin filaments must "slide" past each other, as illustrated in Figure 13.11.

Figure 13.11 **Sliding Filament Model of Muscle Contraction**



Before contraction, the thick and thin filaments are in a relaxed state (non contracted), as shown in the top of this figure. During muscle contraction, the *thick filaments* and *thin filaments* "slide" past each other to shorten (contract) the overall structure, as shown in the contracted state in the bottom of the figure. Muscles will stay in the contracted state so long as a signal from the brain persists. When the signal ends, the filaments will slide past each other in the opposite direction, back to the relaxed state.

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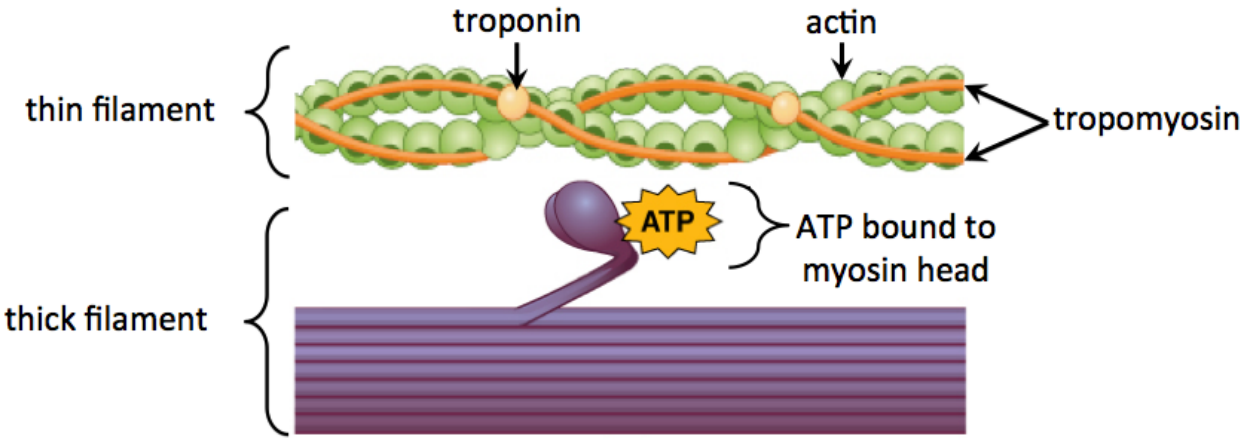
Let's now consider *how* and *when* the filaments "slide" past each other. We will begin with a small section of a thick and a thin filament in the *state* illustrated below.



This image, as well as the next eight, were adapted from: Wikimedia Commons, Author: OpenStax College, CC-BY-SA, https://creativecommons.org/licenses/by/3.0/deed.en

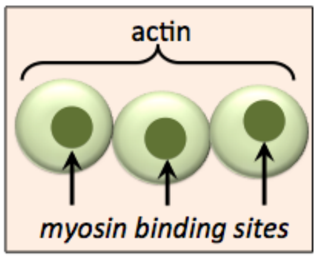
In this initial state, ***a****denosine* ***t****ri****p****hosphate* (**ATP**) is attached to the *head* region of *myosin.* You will learn more about ATP and its structure in chapter 14, but for now I want you to understand that all organisms rely on the chemical potential energy of ATP. Electromagnetic energy (light) from the sun is converted to chemical potential energy in glucose. The energy in glucose is eventually converted to chemical potential energy of aqueous ATP. Chemical potential energy can be stored in *covalent bonds* and *non-covalent attractive interactions*. Energy must be ***used*** to break covalent bonds or noncovalent attractive interactions, and energy is ***released*** when covalent bonds or noncovalent attractive interactions are formed. In a chemical reaction, if there is more energy released by the formation of new bonds and/or noncovalent interactions involving products than was used to break the bonds and interactions involving reactants, then the reaction will occur spontaneously and the excess energy is released. The reaction of ATP with water is capable of releasing energy:

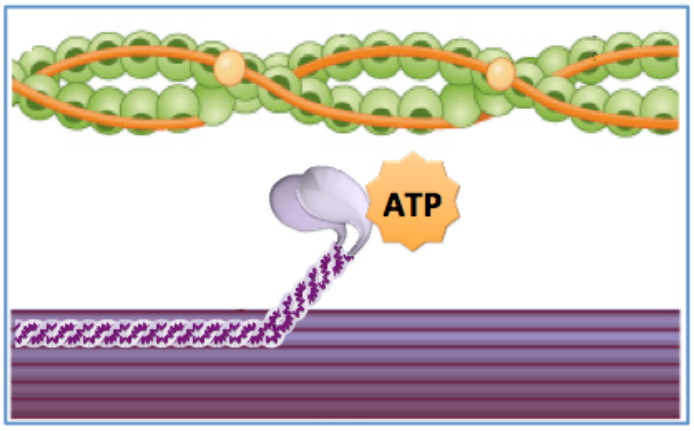
$$\text{ATP}\ (aq) + H_2O\ (l) \rightleftarrows \text{ADP}\ (aq) + P_i\ (aq) + H^+\ (aq) \qquad \mathbf{\Delta G = -7{,}300}\ \text{Joules per mole of ATP}$$

P_i is an frequently used abbreviation for a hydrogen phosphate ion (HPO_4^{2-}), and ADP is an abbreviation for ***a****denosine* ***di****phosphate*. The H^+ produced in this reaction can quickly react with a water molecule to form H_3O^+. ***The energy released by this reaction can be used to slide the thin and thick filaments past each other.***

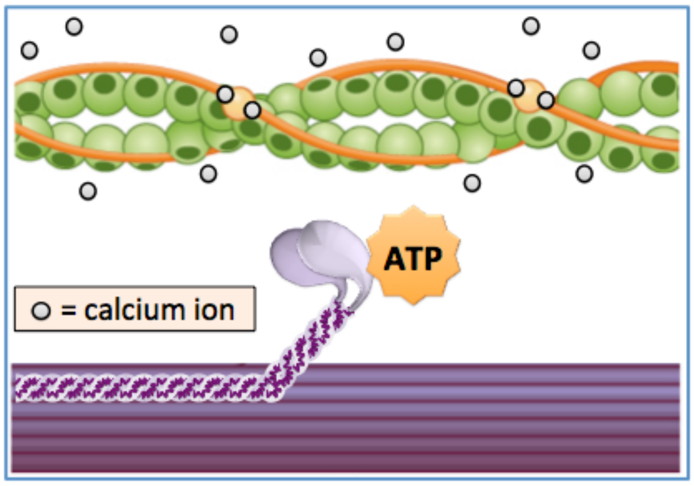
1) *Actin* contains sites to which *myosin heads* can bind. These sites are represented as dark green spots on *actin fibers*.

In our initial state, *tropomyosin fibers* block actin's *myosin binding sites* so that the myosin heads are unable to attach to the thin filament, as shown in the illustration on the right.

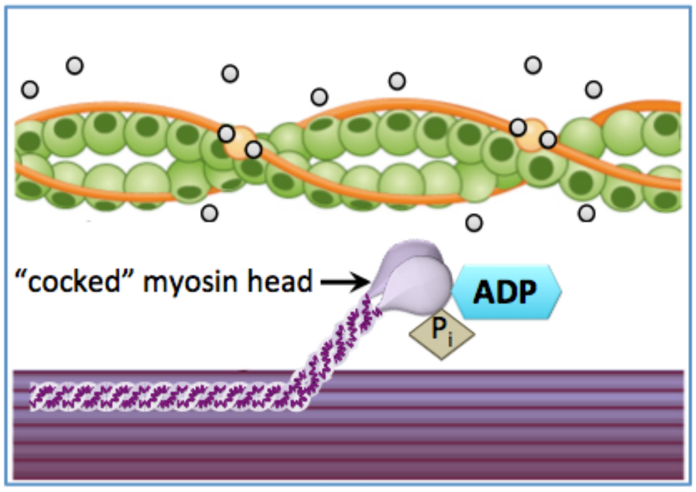




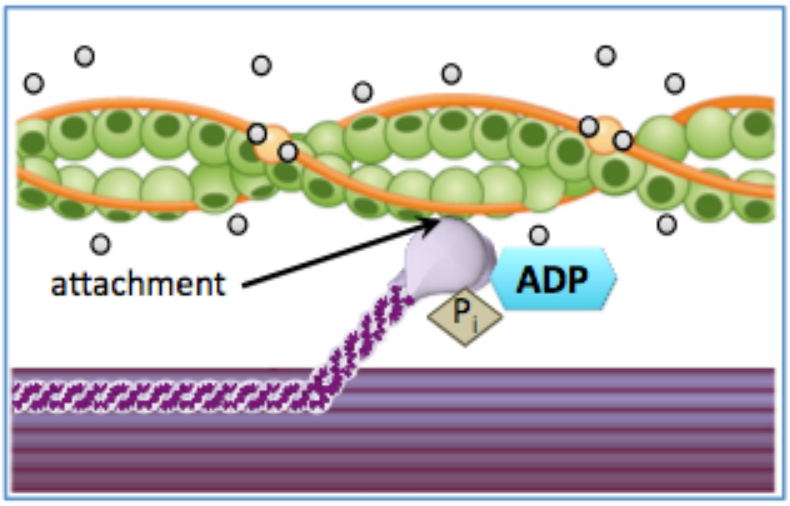
2) Muscle contraction begins in response to an action potential (nerve impulse) that originates in the central nervous system. The electrical signal is transferred to a particular muscle and causes an organelle called the sarcoplasmic reticulum to release calcium ions. When calcium ions are released, they bind to *troponin,* which causes the *tropomyosin fibers* to move and thereby exposes the *myosin binding sites*.



3) ATP is hydrolyzed to ADP and P_i. Energy released from the hydrolysis of ATP reaction is **used to change the conformation (shape) of *myosin***. This results in a "cocked" myosin head. In this step, the energy released from the conversion of ATP and H_2O to ADP, P_i, and H^+ is used to *change myosin's bond angles and atomic locations from a low energy configuration to a high energy configuration.* This is analogous to "cocking the hammer" of a pistol, or pulling back on the string of a bow-and-arrow. In this step, the ADP and P_i that are produced remain attached to the "cocked" myosin head, as shown on the right.

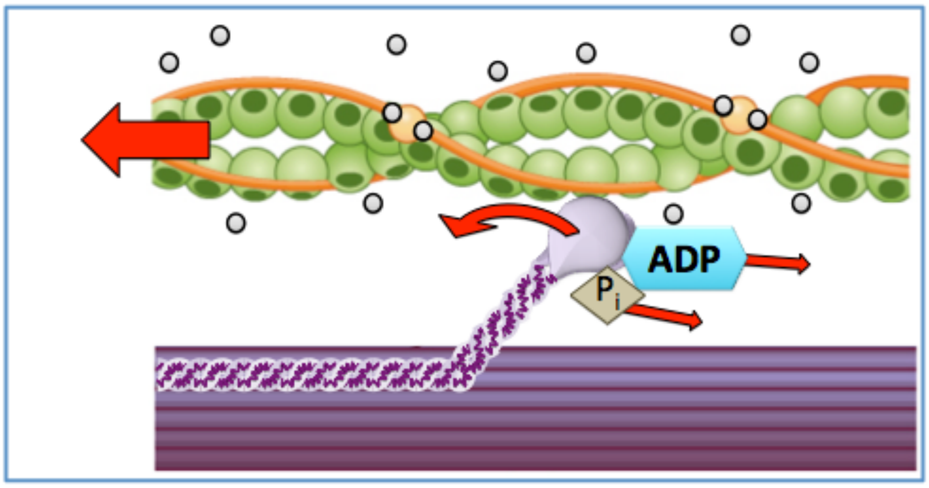


4) The “cocked” myosin head attaches to a myosin binding site on the thin filament. This attachment is a noncovalent interaction.

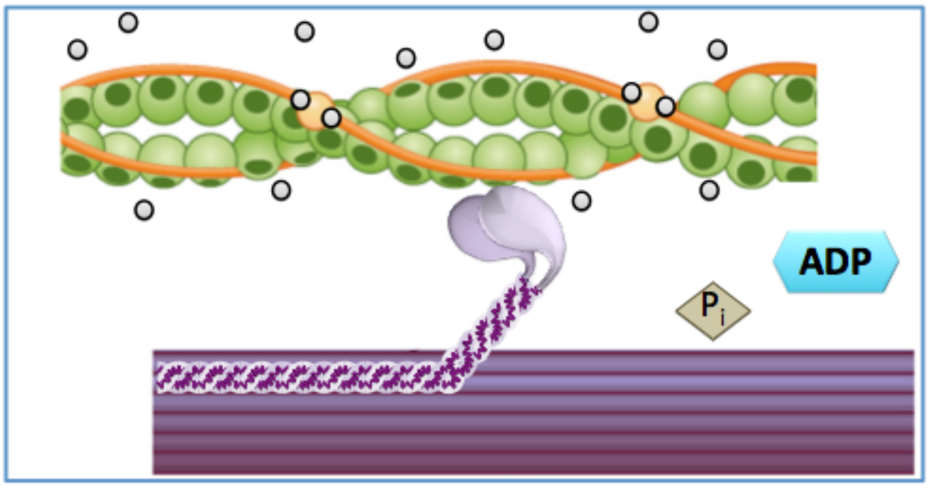


5) ADP and P_i are released from the myosin head. This allows the myosin to bend back to its original “un-cocked” position.

- In our “cocked” pistol analogy, this step represents what happens when the trigger of a pistol is pulled: the pistol’s “hammer” springs forward (to strike the bullet’s cartridge).
- In our *bow-and-arrow* analogy, this step represents what happens when the string is released: it moves forward and accelerates the arrow.

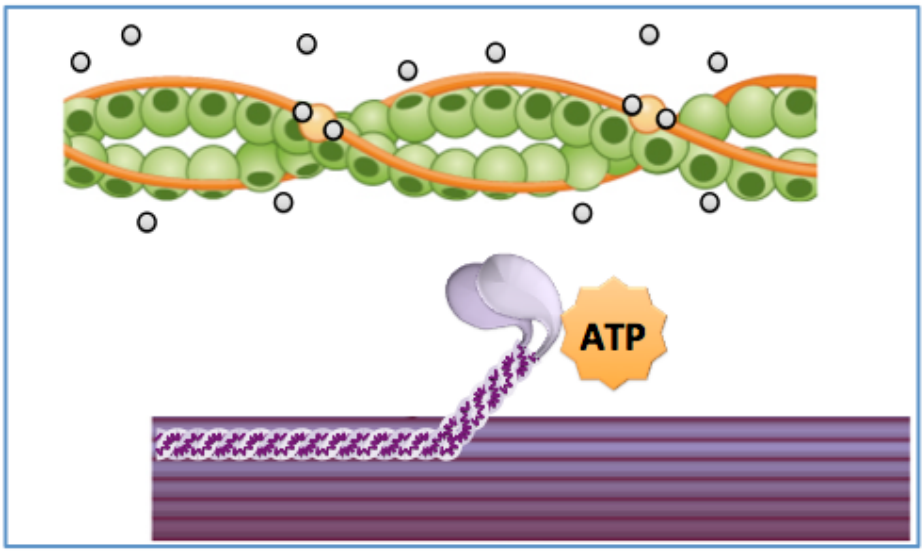


Because the myosin head is attached to the thin filament, as the myosin bends, the thin filament “slides” past the thick filament.



6) ATP binds to the myosin head, which causes the head to detach from the thin filament. ***This completes the cycle***; the system is now back to its original configuration and the cycle can repeat so long as calcium and ATP are present. As this cycle repeats, the muscle can continue to shorten. Since calcium ions are constantly being transported ***back*** *into the sarcoplasmic reticulum*, their release must be continuously induced by central nervous system impulses in order for muscle contraction to continue.

If ATP is not present, the myosin remains bound to the thin filament. This state is observed after death, since ATP is no longer produced, and is called *rigor mortis*.

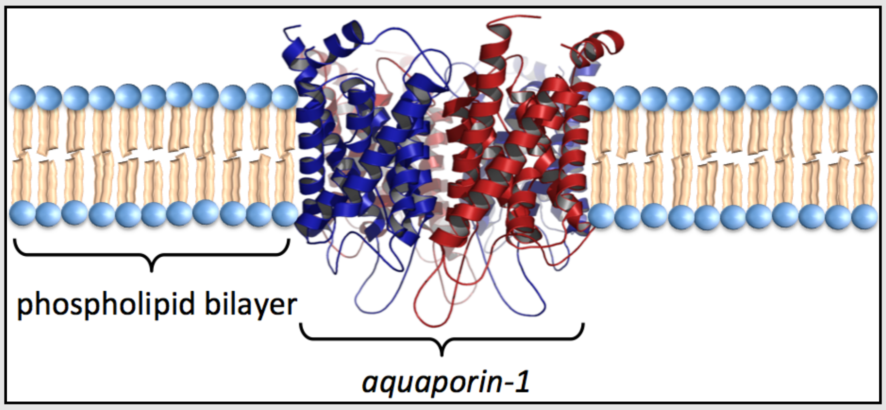


Membrane Proteins

Membrane proteins are proteins that are attached to biological membranes. Membrane proteins function as enzymes, cell recognition markers, receptors (allowing chemical signals to be relayed between the interior and exterior of cells), and transporters of compounds in and out of cells. Some membrane proteins extend through the entire membrane and are called **transmembrane proteins.** Other membrane proteins do not completely extend through the membrane; these are called **monotopic proteins**. Note the derivation of this name; ***mono*** = one or single, ***topic*** = side.

Examples of ***transmembrane proteins*** include the ***aquaporins***. *Aquaporins* function as *transporter proteins;* they facilitate the transport of water molecules (only) in and out of cells. There are several types of aquaporins, one of them, *aquaporin-1*, is illustrated in Figure 13.12. The discovery of aquaporins was first reported in 1992 by John Agree. Agree won the 2003 Nobel Prize in Chemistry for this work. Before Agree's discovery of aquaporins, it was assumed that water simply "leaked" through cell membranes.

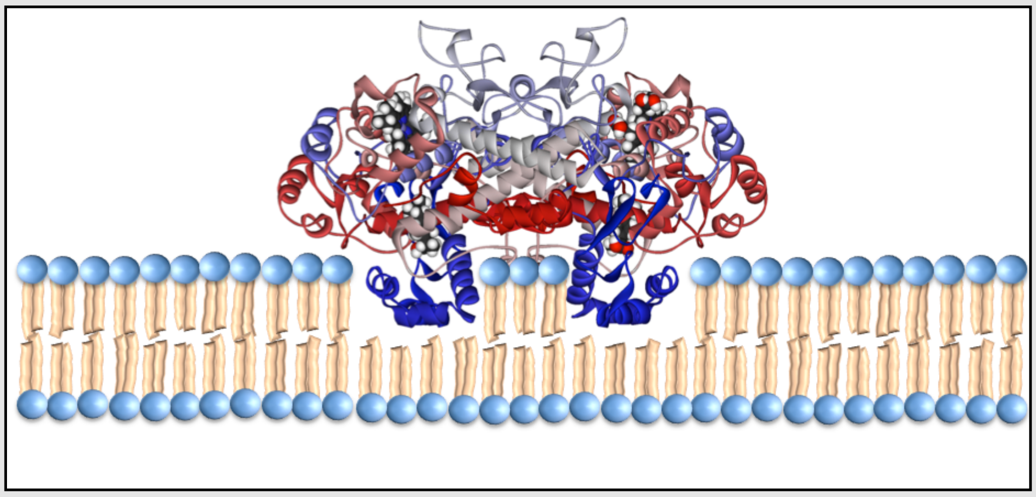
Figure 13.12 Illustration of a Transmembrane Protein (Aquaporin-1)



Source: The protein structure is from Wikimedia Commons, Author: Vossman, CC-BY-SA, http://creativecommons.org/licenses/by-sa/3.0/legalcode

An example of a ***monotopic protein*** is *cyclooxygenase-2*, an enzyme that is responsible for converting eicosanoic acid into prostaglandins, prostascyclin, and thromboxane (you learned about this enzyme and these reactions in section 8 of chapter 12). An illustration of cyclooxygenase-2 attached to a membrane is shown in Figure 13.13.

Figure 13.13 Illustration of a Monotopic Membrane Protein (Cyclooxygenase-2)



Source: Wikimedia Commons, PD

Review 13.9: Globular vs. Fibrous vs. Membrane Proteins

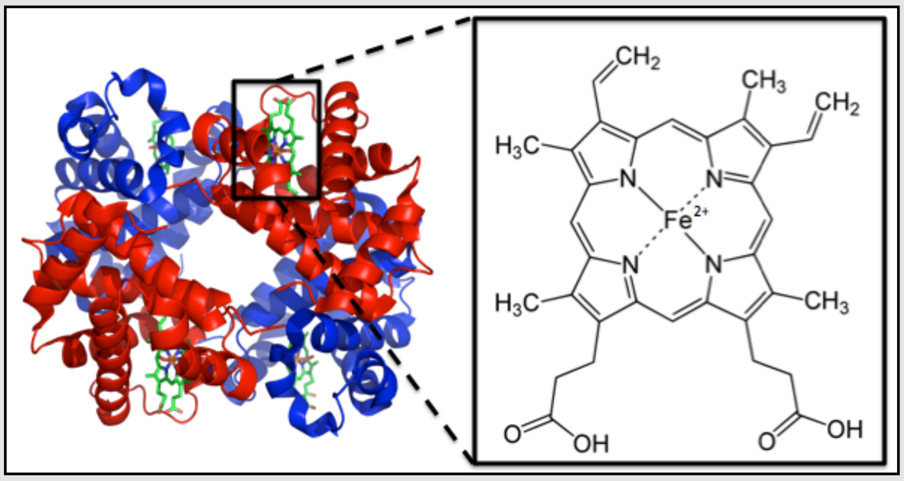
Do a bit of online research to determine if *succinate dehydrogenase* is a globular, fibrous, or membrane protein.

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

Prosthetic Groups: Simple vs. Conjugated Proteins

Some proteins contain only amino acid residues, these are called **simple proteins**. Other proteins contain amino acid residues ***and*** *non* amino acid components. Proteins that contain non amino acid components are called **conjugated proteins**. The *non* amino acid components of these proteins are called **prosthetic groups**. An example of a *prosthetic group* is the *heme* group, which is present in *hemoglobin*. The main role of *hemoglobin* is to transport oxygen (O_2) molecules. Heme groups contain an iron ion, to which an oxygen molecule can be quite strongly attached. A ribbon model of human hemoglobin, with a magnification insert showing the bonding pattern in one of its four heme groups, is shown in Figure 13.14.

Figure 13.14 **The Heme Prosthetic Groups in Human Hemoglobin**



Left: A ribbon model of human hemoglobin. Hemoglobin contains ***four*** heme groups (shaded green in this structure).
Source: Wikimedia Commons, Author: Richard Wheeler, CC-BY-SA, http://creativecommons.org/licenses/by-sa/3.0/legalcode
Right: A magnification insert showing the bonding pattern of a heme group.

Hemoglobin contains *four* heme groups (shaded green in the figure above). Each heme group is capable of binding one oxygen molecule. Heme prosthetic groups are also found in myoglobin, catalase, and other proteins.

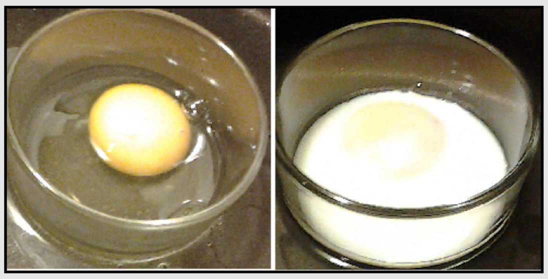
Denaturation of Proteins

The shape of a protein is the key factor in its ability to perform its biological role. It is therefore critical that an organism's proteins maintain their shapes. Protein shape is maintained by the attractive forces involved in secondary, tertiary, and quaternary structures. When these attractive forces are disrupted, the native shape of proteins can be changed enough that a partial or complete loss of bioactivity (function) occurs. When a protein loses some or all of its biological activity in such a manner, this is referred to as "**protein denaturation.**" In most cases, unless the shape change is very minor, the denaturation is ***irreversible***. Any mechanical or chemical agent that causes the denaturation of a protein is called a **denaturing agent**.

An example of protein denaturation that you have experienced is the cooking of eggs. In its native form, albumin is *soluble* and *colorless* in the *non yolk* part of eggs, as seen on the *left-hand side* of Figure 13.15. When denatured by heating, the shape of albumin changes to such an extent that it is no longer soluble and therefore precipitates as a white solid (Figure 13.15, *right-hand side*). This observation is the basis of the term "egg white."

The *deformation of* a *paper clip* can be used as an analogy for protein denaturation. Let a paper clip represent a protein. Just like a real protein, a paper clip has a function (holding multiple sheets of paper together) and it must maintain its shape in order to function. Small changes in the shape of the paper clip will not significantly affect its ability to function. Larger changes in its shape will begin to affect its ability to hold sheets of paper together. If large enough changes are made to the shape of the paper clip, then it will completely lose it ability to hold sheets of paper together (function).

Figure 13.15 Denaturation of Egg Protein



Left: An egg before cooking.
Right: An egg after cooking.
A*lbumin* protein in egg is soluble in its native state (left). After denaturation from cooking (right), it becomes insoluble and precipitates as a white solid.
Adapted from: Wikimedia Commons, Author: RMALDA CC-BY, https://creativecommons.org/licenses/by/3.0/deed.en

Some of the most common ***denaturing agents*** are listed and described below:

1) **Heating.** The noncovalent attractive forces involved in ***secondary, tertiary, and quaternary structures*** in proteins are easily disrupted by heating. The cooking of an egg was an example of heat denaturation.

Figure 13.16
Mechanical Denaturation of Raw Eggs

Source: Wikimedia Commons, Author: Anonymous, CC-BY-SA, http://creativecommons.org/licenses/by-sa/3.0/legalcode

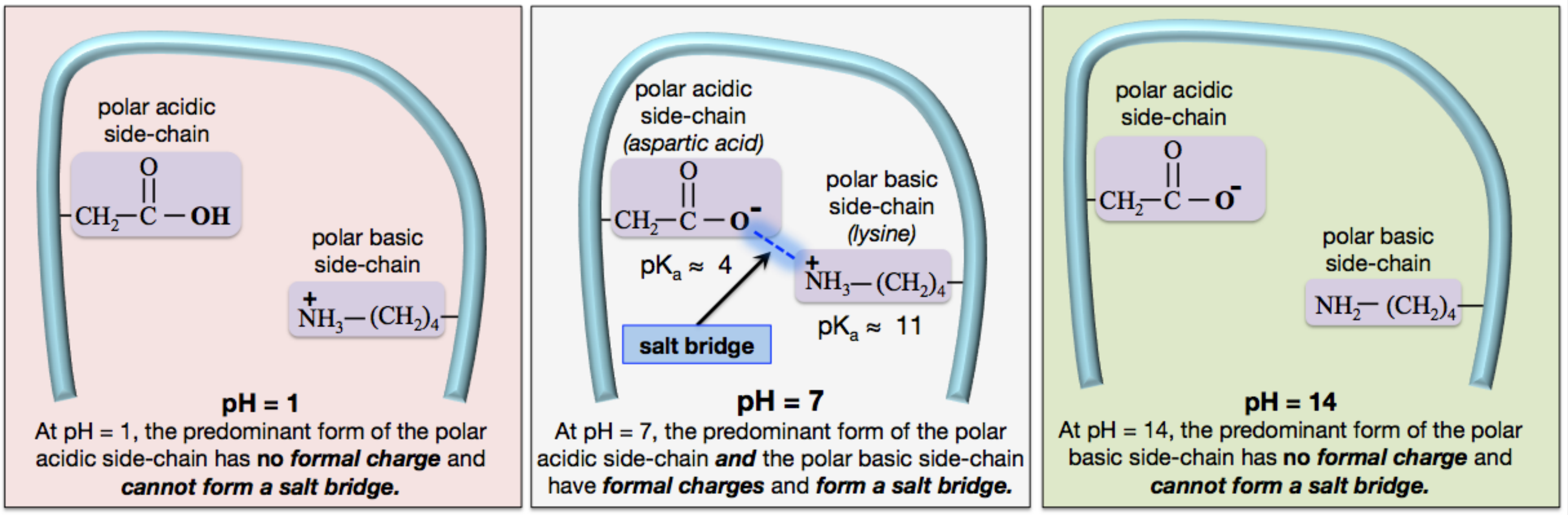
2) **Mechanical Agitation.** Mechanical agitation can disrupt the noncovalent attractive forces involved in secondary, tertiary, and quaternary structures. An example of denaturation of protein by mechanical agitation is the foaming that occurs during beating of raw egg (yolks removed). (Figure 13.16). Chefs use this process to make *meringue*.

3) **Amphipathic Compounds.** Some amphipathic compounds can cause denaturation by inserting their nonpolar ends into an association of hydrophobic side chains and thereby displacing some of the side chains. For example, *detergents* are capable of denaturing proteins.

4) **Polar Solvents.** Polar solvents, such as acetone or ethanol, can interfere with hydrogen bonding, dipole-dipole, and ion-dipole interactions by competing for a protein's existing interactions.

5) **pH Changes.** pH changes can disrupt a protein's ***salt bridges*** and ***ion-dipole interactions.*** Near physiological pH, the predominant form of *polar acidic* side-chains and *polar basic* side-chains (except for histidine) have a *formal charge*. These charged side-chains help proteins maintain their tertiary and/or quaternary structure because they participate in *salt bridges* and *ion-dipole* interactions. The box in the *middle* of Figure 13.17 illustrates a salt bridge that can form between a *polar acid (aspartic acid)* and polar basic (lysine) *side-chain* at **pH = 7.**

Figure 13.17 **The Disruption of a Salt Bridge by pH Changes**



Middle: Illustration of a salt bridge that can form between a *polar acid* and polar basic *side-chain* at pH = 7.
Right: When the pH is changed to a value greater than the pK$_a$ of a polar basic side-chain, then its *uncharged* base form becomes predominant. This uncharged side-chain cannot participate in salt bridge interactions.
Left: When the pH is changed to a value less than the pK$_a$ of a polar acid side-chain, then its *uncharged* acid form becomes predominant. This uncharged side-chain cannot participate in salt bridge interactions.

If the pH is changed to a value ***greater than*** the pK$_a$ of a *polar basic* side-chain's quaternary ammonium group, then its ***uncharged*** base form becomes predominant, as illustrated in the box on the *right-hand* side of Figure 13.17. If the pH is changed to a value ***less than*** the pK$_a$ of a *polar acidic* side-chain's carboxyl group, its ***uncharged*** acid form becomes predominant, as illustrated in the box on the *left-hand* side of Figure 13.17. Either of these pH changes can disrupt a protein's ***salt bridges*** and ***ion-dipole*** interactions.

An example of the denaturation of proteins by a pH change is the use of citric acid in the marination (soaking) of fish and shellfish in a dish called ***ceviche*** (Figure 13.18). The citric acid comes from citric juices such as lemon, lime, orange, or grapefruit juice. Marination in these citric juices lowers the pH to denature the proteins in the fish/shellfish, which gives them a "cooked" appearance. You should be aware that, unlike cooking at a sufficiently high temperature, acidic marinades ***do not*** kill bacteria or other parasitic worms.

Figure 13.18 Ceviche

Essential Amino Acids: Complete, Incomplete, and Complementary Proteins

Organisms produce (synthesize) protein from dietary amino acids. Our bodies are capable of producing ***eleven*** of the twenty common amino acids (from other amino acids or certain other compounds), therefore we do not necessarily need to obtain these eleven amino acids in our diet. However, the other ***nine*** amino acids *can only be obtained by eating proteins that contain them*. These nine amino acids are called **essential amino acids**, and are listed below.

Histidine (His)	Methionine (Met)	Lysine (Lys)
Leucine (Leu)	Threonine (Thr)	Valine (Val)
Isoleucine (Ile)	Tryptophan (Typ)	Phenylalanine (Phe)

Foods that contain ***all*** of the essential amino acids are called **complete proteins** (although they are not actually true proteins, a more accurate name would be "*complete protein foods*"). Most animal products are *complete proteins*. Examples of complete proteins are eggs, meat, milk, fish, and poultry. Foods that contain proteins but do not contain *all of the essential amino acids* are called **incomplete proteins**. These include most plant proteins. Examples of *incomplete proteins* and their missing essential amino acids are listed in Table 13.4.

Table 13.4
Some Incomplete Proteins and their Missing Amino Acids

Food	Amino Acid Deficiency
rice, wheat, oats	lysine
beans	methionine, tryptophan
peas	methionine
soy	low in methionine
corn	lysine, tryptophan
almonds, walnuts	lysine, tryptophan

A combining of two or more *incomplete proteins* that are deficient in *different* amino acids is a dietary strategy used to ensure the intake of all nine essential amino acids. For example, if you eat beans and rice, you obtain all of the essential amino acids since rice contains the amino acids that beans lack, and vice versa. When proteins are combined in this way, they are called **complementary proteins**.

Review 13.10: Essential Amino Acids

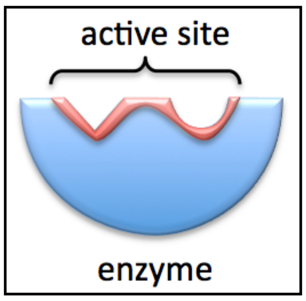
Which two foods from Table 13.4 could ***each*** be eaten with corn as a complementary protein?

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

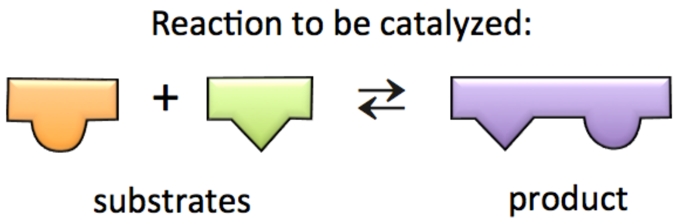
13.5 Enzymes

You learned about catalysts in chapter 6. Catalysts are substances that increase the rates of chemical reactions. Life requires that many chemical reactions occur within organisms. The human body employs over a thousand chemical reactions. Many of these reactions would occur too slowly to be useful in the absence of a catalyst. Nature provides humans and other biological organisms with proteins that are capable of catalyzing reactions. Protein catalysts are called **enzymes**. Among all plants and animal species, over 5,000 chemical reactions are catalyzed by enzymes. Enzymes are capable of increasing the rate of a chemical reaction by up to a factor of one thousand.

Scientists who specialize in studying enzymes are called *enzymologists*. Enzymologists refer to the reactants of catalyzed reactions as **substrates**. Most enzymes are composed of hundreds or thousands of amino acid residues, however only a small region of the enzyme makes contact with the *substrates*. The part of the enzyme that makes contact with substrates is called the "**active site**." Let's take a look at a model that describes enzymatic catalysis. In this model, we will represent an enzyme and its active site as illustrated *on the right*.

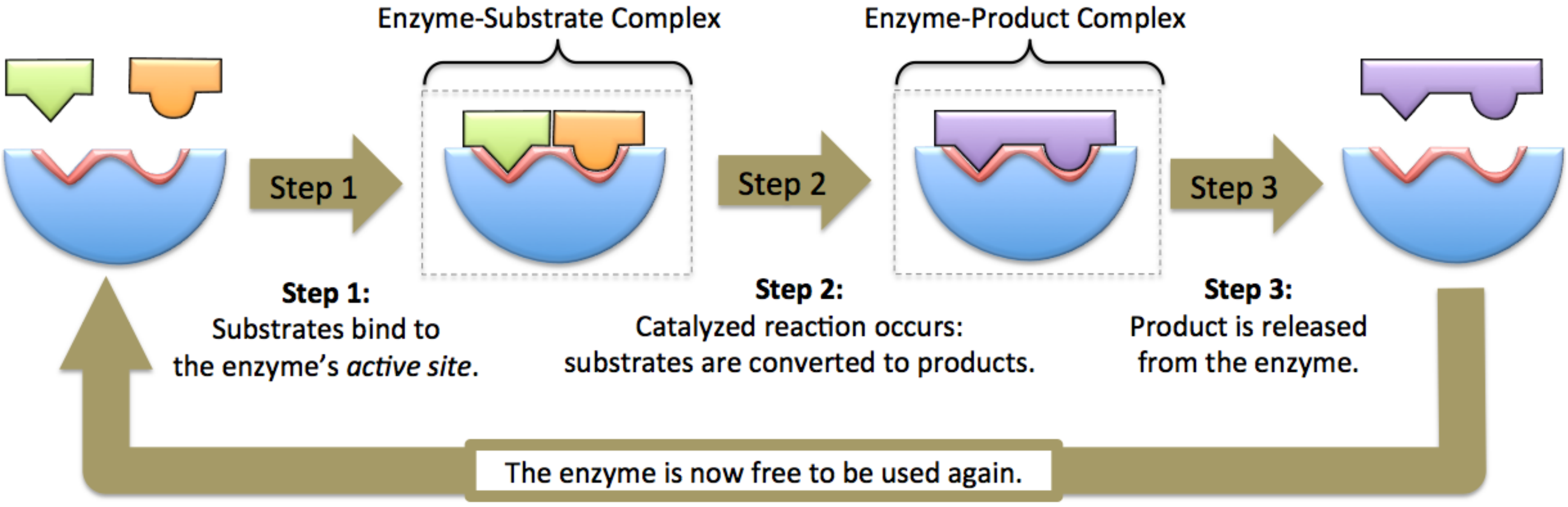


We will consider a reaction where ***two*** substrates (reactants) are converted to ***one*** product, as illustrated below.



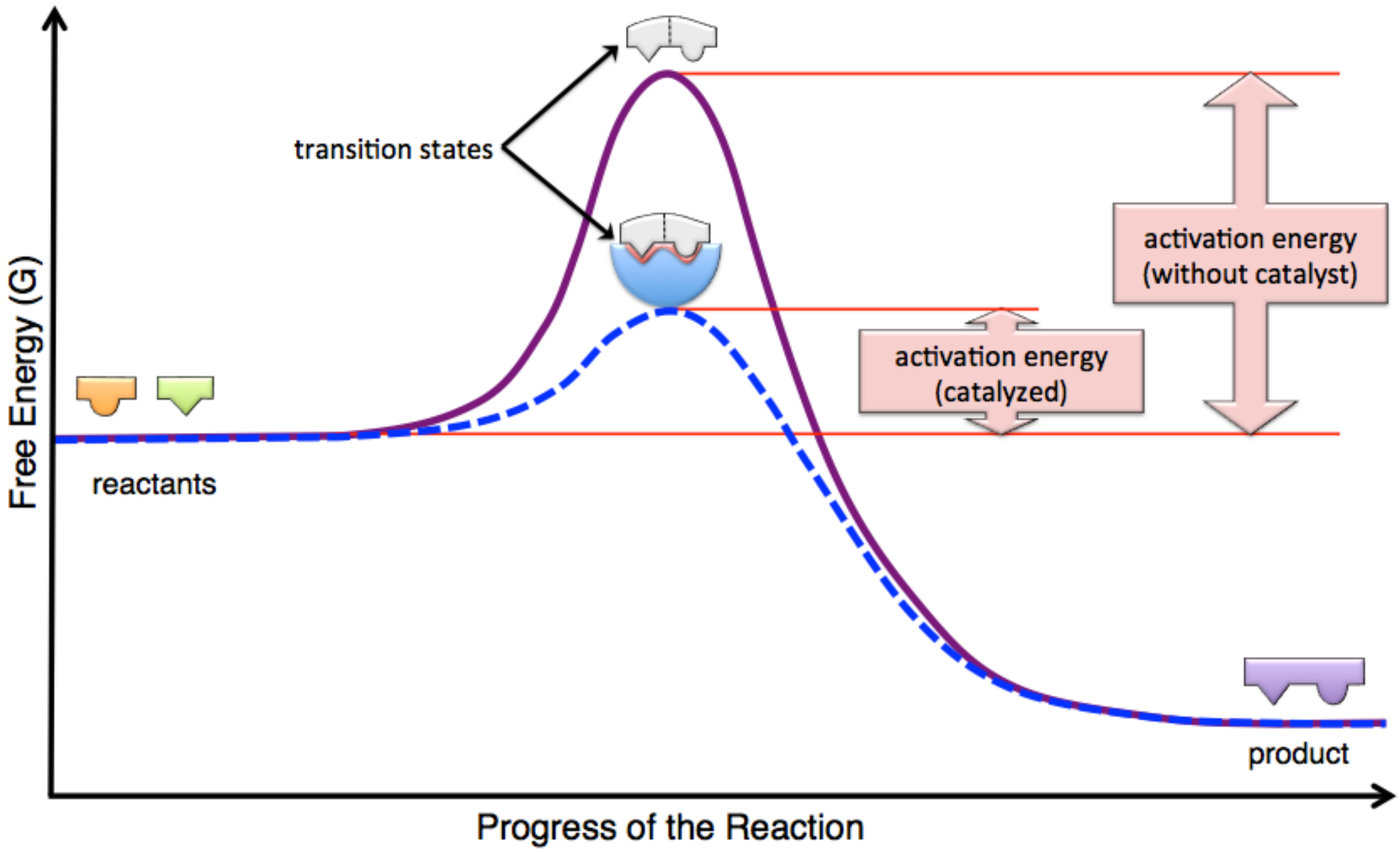
In this example, *two* substrates react to form *one* product, however this model *will also apply to other cases* such as *one* substrate compound forming *two* products, or *two* substrate compounds forming *two* products.

The *enzymatic catalysis process* is illustrated below.



In **Step 1**, the substrates bind to the ***active site*** of an enzyme. The substrates are held tightly in the active site by ***noncovalent attractive forces****, which are maximized due to the complementary shapes of the substates and active site*. These complementary shapes are depicted by matching geometric shapes in the illustration. The particle that is formed when the *substrates* are bound to the enzyme is called the **enzyme-substrate complex**. In **Step 2**, the chemical reaction occurs. Substrates are converted to products when covalent bonds within the substrates are broken **and/or** new bonds are made. The particle that is formed when the *product* is bound to the enzyme is called the **enzyme-product complex**. In **Step 3**, the newly formed product is released. Note that after products are released from enzymes, the enzymes are free to accept new substrates and the cycle can repeat. Enzymes ***do not affect*** the *equilibrium concentrations* of products and reactants (substrates), they only increase the reaction rates, and therefore equilibrium is reached more quickly.

All catalysts, including enzymes, lower the *activation energy* of a reaction and thereby *increase the reaction rate*. For a review of *activation energy*, see section 5 of chapter 6. Let's compare the reaction energy diagram of an ***enzymatically catalyzed*** reaction with that of an ***un-catalyzed*** reaction:



The *un-catalyzed* reaction is represented by the solid curve and the *enzymatically catalyzed* reaction is represented by the dashed curve. In catalyzed <u>and</u> un-catalyzed reactions, one or more of a reactant's covalent bonds and/or several noncovalent attractive interactions involving reactants are disrupted or completely broken. This process *requires* energy. At some point in the progress of the reaction, the energy reaches a *maximum value*. This state is a *temporary*, short-lived configuration of atoms called the ***transition state***. In chapter 6, you learned that the amount of *energy* required to reach the *transition state* is called the ***activation energy***. As the reaction progresses, *new* covalent bonds and/or noncovalent attractive interactions form and generate the product; these processes *release* energy. The formation of the new covalent bonds and/or noncovalent attractive interactions are responsible for the *decrease in energy* that is seen in the diagram as the transition state changes to product.

How does an enzyme *increase the rate of a reaction*? When substrates bind to an enzyme's active site, ***interactions with the enzyme*** change the shape of the substrates (and enzyme) to a configuration that lowers the energy of the transition state (relative to an un-catalyzed reaction). Detailed descriptions of these interactions for particular enzymes are a current area of focus for many researchers.

Review 13.11: Enzymatic Catalysis

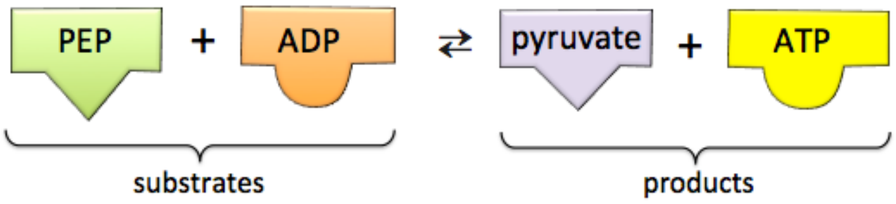
Determine whether each of the following statements are true or false.

a. A catalyzed reaction has a lower activation energy than an un-catalyzed reaction.
b. The greater the activation energy, the faster the reaction rate.
c. At equilibrium, a catalyzed reaction will result in a greater amount of products than would an un-catalyzed reaction.

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

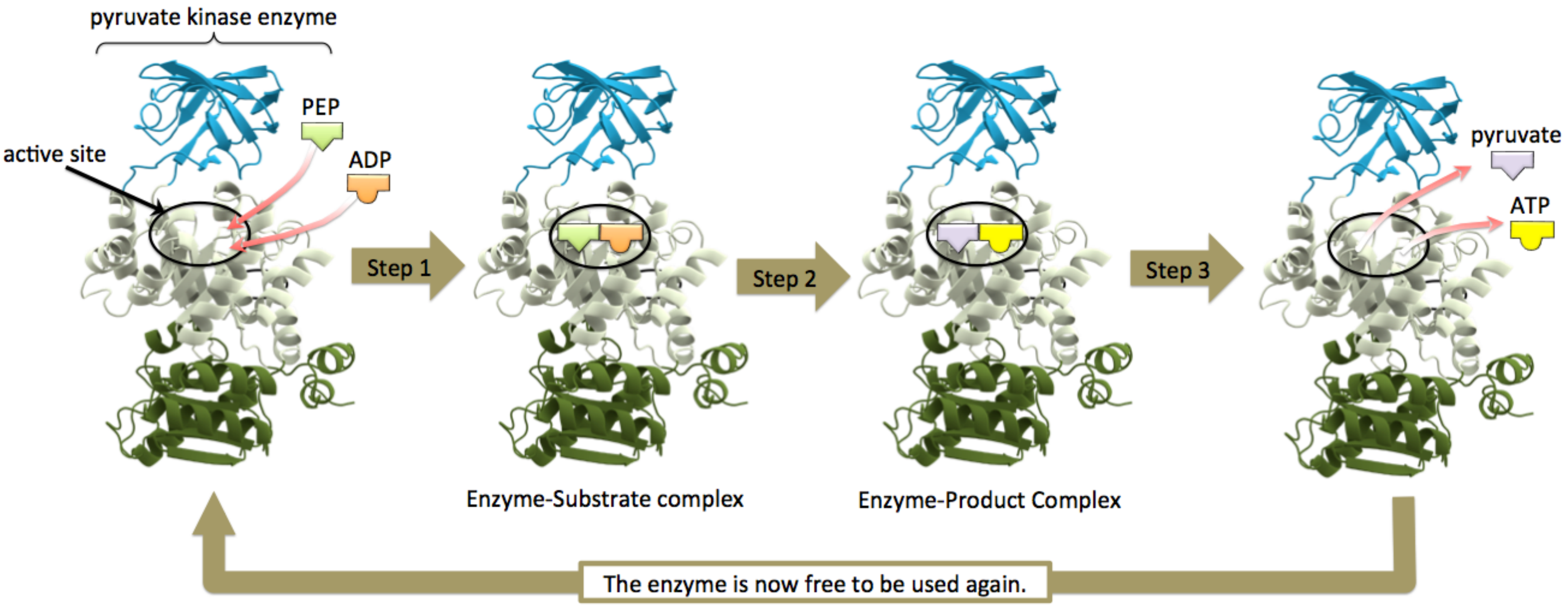
An Example of Enzymatic Catalysis

As an example of enzymatic catalysis, let's consider an enzyme called *pyruvate kinase*. Pyruvate kinase catalyzes the reaction of ***p**hospho**e**nol**p**yruvate* (**PEP**) with **ADP**, thereby forming *pyruvate* and **ATP**, as in the equation shown below.



A detailed knowledge of the bonding patterns involved in this reaction ***is not important*** at this time. This is the last reaction that occurs in glycolysis, which is a series of reactions that organisms use to capture energy from food. One of the goals of the glycolysis process is to transfer potential energy stored within glucose (from our diet) to potential energy in the form of **ATP**. In chapter 15, I will discuss the details of how this is done, in part, by the reaction shown above.

The illustration below depicts the three steps of our enzymatic process model for the case of catalysis by *pyruvate kinase*.

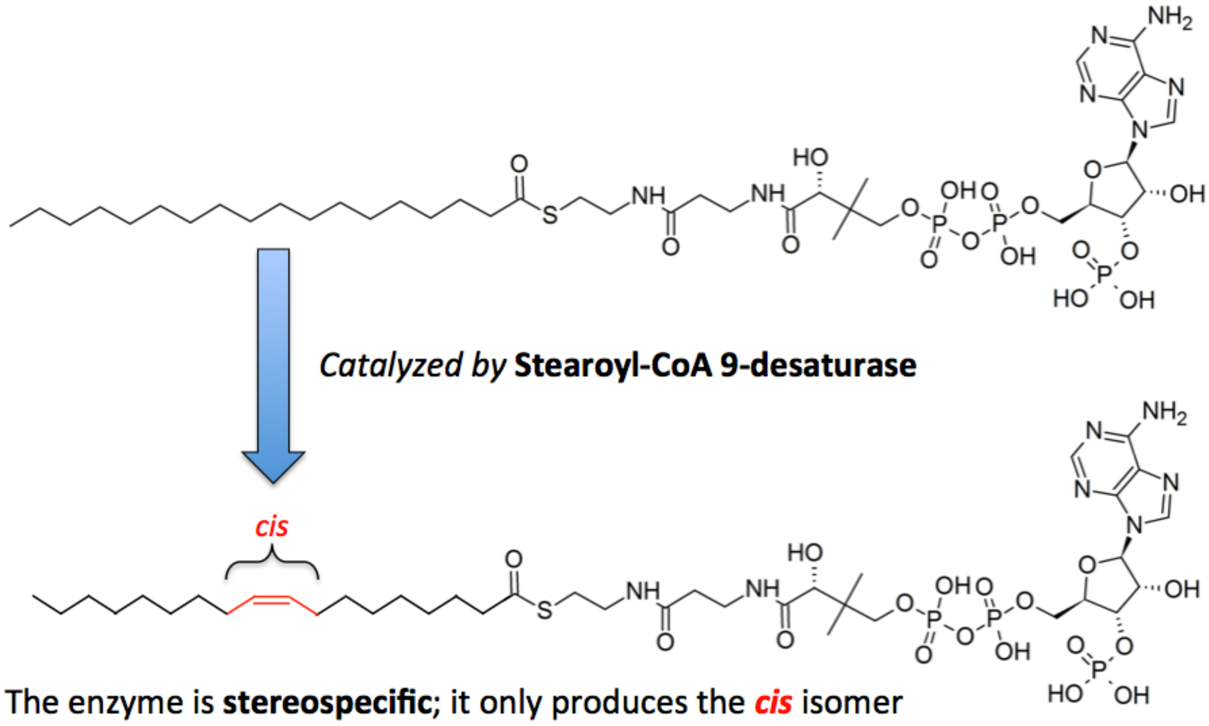


Enzyme image from: Wikimedia Commons, Author: Thomas Splettstoesser, CC-BY https://creativecommons.org/licenses/by/3.0/deed.en

In **Step 1**, the substrates, PEP and ADP, bind to the ***active site*** of the *pyruvate kinase* enzyme. In **Step 2**, the chemical reaction occurs. A phosphoryl group (PO_3^-) is transferred from PEP to ADP to form pyruvate and ATP. In **Step 3**, the products, pyruvate and ATP, are released and the enzyme is free to accept new substrates so that the cycle can repeat.

Enzyme Specificity

Enzymes are *specific* for particular substrates *or* groups of substrates. Their specificity is due to both the selective geometry of their active site and their ability to lower activation energy for particular substrates. Some enzymes will only catalyze the reaction of a particular substrate; this is called **absolute specificity**. An example of an enzyme with *absolute specificity* is *urease. Urease* is used by some plants, fungi, and bacteria to catalyze a reaction in which *urea* (only) is converted to ammonium and bicarbonate. Some enzymes are *less specific*, and will catalyze reactions for a particular family of substrates; this is called **relative specificity**. Examples of enzymes with *relative specificity* include *proteases,* which catalyze the hydrolysis of various proteins. Many enzymes will only catalyze the reaction of, or production of, *one particular stereoisomer*; this is called **stereospecificity**. An example of an enzyme with stereospecificity is *stearoyl-CoA 9-desaturase, an enzyme that is involved in fatty acid metabolism and is present in every cell in the body. Stearoyl-CoA 9-desaturase* only catalyzes the production of the *cis* stereoisomer, as shown below.



Catalyzed by **Stearoyl-CoA 9-desaturase**

The enzyme is **stereospecific**; it only produces the ***cis*** isomer

Almost all enzyme names use the "*ase*" suffix. Enzymes are named and categorized based on their substrates *and/or* the reactions that they catalyze. Table 13.5 lists some of the classes of enzymes, the reactions they catalyze, and some examples.

Table 13.5 **Some Classes of Enzymes and their Reactions**

Enzyme Class	Reaction Involved	Examples
Isomerases	Catalyze rearrangement reactions: The reactant and the product contain the same atoms, only the bonding pattern changes.	Cis-trans isomerases - Convert *cis* to *trans* or vice versa.
Ligases	Use energy from ATP to form chemical bonds between substrates	DNA ligase - forms bonds between two DNA fragments.
Hydrolases	Catalyze hydrolysis reactions	• Lipases - hydrolyze ester bonds in lipids • Proteases - hydrolyze peptide bonds • Phosphatases - hydrolyze phosphoester bonds • Nucleases - hydrolyze bonds in DNA and RNA • Carbohydrases - hydrolyze glycosidic bonds
Oxidoreductases	Catalyze oxidation-reduction reactions	• Oxidases - oxidize a substrate • Reductases - reduce a substrate • Dehydrogenases - remove two hydrogens from neighboring carbons and form a double bond
Transferases	Catalyze the transfers of a group of atoms	• Kinases - transfer a phosphoryl group (PO_3^-) • Transaminases - transfer an amino group

Review 13.12: Enzyme Specificity

Choose one of the enzyme classes from Table 13.5 that would catalyze each of the following reactions.

a. The conversion of a *cis* double bond to a *trans* double bond.
b. The digestion of fat.
c. The conversion of starch to D-glucose.
d. The conversion of a dipeptide into two amino acids.
e. The hydrolysis of ATP to form ADP and P_i.

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

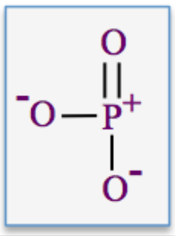
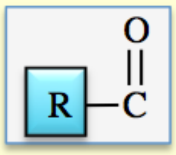
Cofactors

A **cofactor** is defined as a non protein compound that must be permanently *or* temporarily bound to an enzyme in order for the enzyme to function. For example, a nickel ion (Ni^{2+}) must be bound to a *urease* enzyme in order for the enzyme to catalyze the conversion of urea to ammonium and bicarbonate. Likewise, Zn^{2+} must be attached to an *alcohol dehydrogenase* enzyme, and Fe^{2+} to the *peroxidase* enzyme, in order for catalysis to occur. *Cofactors* are either inorganic ions (e.g. Ni^{2+}, Fe^{2+}, or Zn^{2+}) or organic compounds.

When *cofactors* are *organic compounds*, they are often referred to as ***coenzymes***. In most cases, coenzymes are actually one of the substrates in the catalyzed reaction. The reason that certain substrates are also referred to as *coenzymes* is that they are ***common substrates to many different enzymatic reactions*** in which they the ***donate atoms, groups of atoms, or electrons*** to other substrates ***or*** accept ***atoms, groups of atoms, or electrons*** from other substrates. For example, ATP and ADP are considered to be coenzymes because they are involved in the *transfer* of phosphoryl groups (PO_3^-) ***in many different enzymatically catalyzed reactions***. Because ATP and ADP are used so often and in so many *different* reactions, ***each*** ATP particle in your body is converted to ADP and then back to ATP about 500 times per day.

Many *coenzymes* are derived from dietary *vitamins*. Some *substrates* that are also classified as *coenzymes* and their dietary sources are listed in Table 13.6.

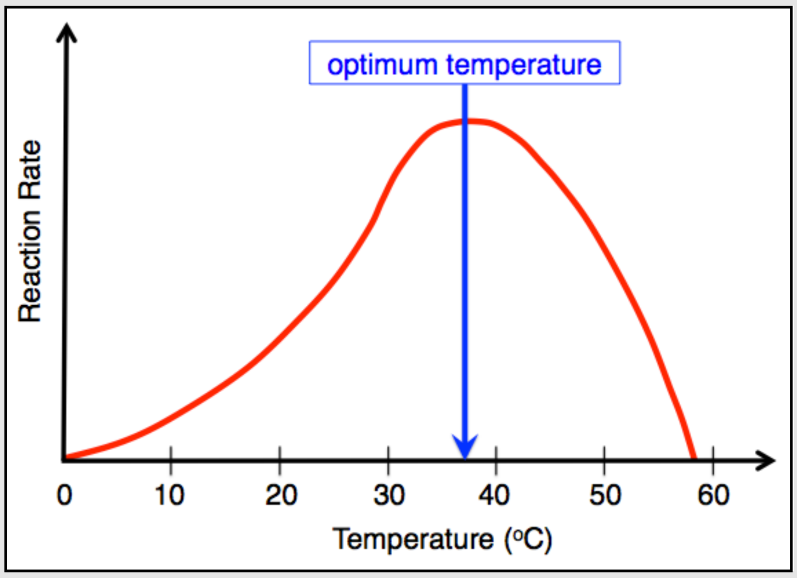
Table 13.6 Some Coenzymes, the Species they Transfer, and their Dietary Source

Coenzyme	Species that is Transferred	Dietary Source
ATP/ADP	phosphoryl group = 	meat and sugars
NAD^+/NADH	hydride ion ($H:^-$) **or** electrons	niacin (vitamin B_3)
FAD/$FADH_2$	hydride ion ($H:^-$) **or** electrons	riboflavin (vitamin B_2)
coenzyme A	acyl group = 	pantothenic acid (vitamin B_5)

Effect of Temperature on the Rates of Enzymatically Catalyzed Reactions

A typical graph of the rate of an enzymatically catalyzed reaction vs. temperature is shown in Figure 13.19. As the temperature begins to increase there is an *initial* increase in the rate of the reaction. This is the case for both catalyzed and uncatalyzed reactions; the elevated temperatures provide more energy for reactants to overcome the *activation energy*. As the temperature continues to increase, the reaction rate of an enzymatically catalyzed reaction reaches a maximum value (the peak of the curve in Figure 13.19). The temperature at which the rate of the reaction is greatest is called the enzyme's **optimum temperature**. The reason that the reaction rate does not continue to increase after reaching the optimum temperature is that the enzyme begins to denature at the higher temperature. As the temperature increases past the optimum temperature, the rate of the reaction quickly decreases because the enzyme becomes more severely denatured.

Figure 13.19
The Rate of an Enzymatically Catalyzed Reaction vs. Temperature



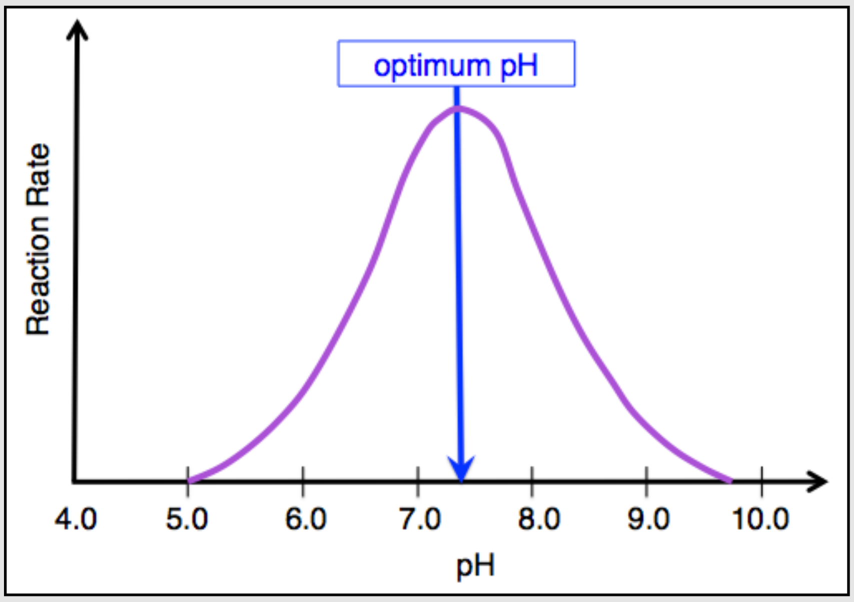
At elevated temperatures, enzymes lose their ability to catalyze because they become denatured. The temperature at which the rate of the reaction is greatest is called the enzyme's **optimum temperature**.

An enzyme's optimum temperature is usually very close to the normal temperature of the organism in which it exists. For example, the optimum temperature of most human enzymes is at normal body temperature (~37 ºC), as depicted in Figure 13.19. You may find it interesting that enzymes present in organisms that exist in extreme thermal environments (thermophiles) have extreme thermal optimums. For example, a species of bacteria (*thermus aquaticus*), which evolved in hot springs, has enzymes with optimum temperatures near 75 ºC (167 ºF).

Effect of pH on the Rates of Enzymatically Catalyzed Reactions

The rate of an enzymatically catalyzed reaction depends on the **pH**. A typical graph of the rate of an enzymatically catalyzed reaction vs. pH is shown in Figure 13.20. The pH at which the rate of an enzymatically catalyzed reaction is greatest is called the enzyme's **optimum pH**. An enzyme's *optimum* pH is usually very close to the normal pH of the region of an organism in which the enzyme exists. For example, the normal pH in most regions of the body is about 7.4 (physiological pH), so the *optimum* pH for enzymes found in these regions is also near 7.4 (as depicted in Figure 13.20). As the pH increases *or* decreases from its ***optimum* pH** value, the reaction rate decreases because of enzyme denaturation. It is for this reason that nature has employed biological buffers.

Figure 13.20
The Rate of an Enzymatically Catalyzed Reaction vs. pH



As pH values increase or decrease from their **optimum pH** value, enzymes lose their ability to catalyze because they become denatured.

Not all parts of the body have a normal pH near 7.4. For example, the stomach has a normal pH range of 1 to 3. It is not surprising that the digestive enzyme called *pepsin,* which functions in the stomach, has an *optimum* pH of 2.

Control of Enzymatic Reactions

There are thousands of different chemical reactions that occur in the human body. It would be very inefficient (and unhealthy) for all of these reactions to be occurring simultaneously at fast rates. It is critical that reaction rates be controllable so that they match the body's immediate physiological needs. All life forms employ reaction regulation mechanisms that involve *controlling* enzymatically catalyzed reactions by processes called **enzyme inhibition** and **enzyme activation**.

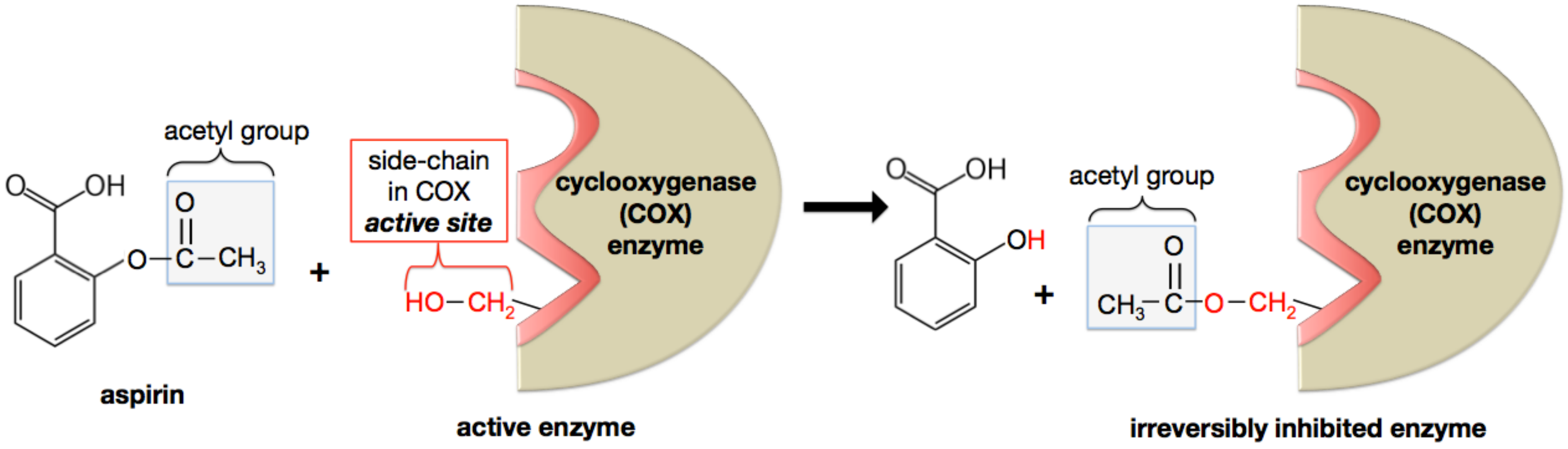
1) Enzyme Inhibition

The body uses chemical feedback systems that can increase or decrease an enzyme's ability to catalyze a reaction. The amount of substrate that an enzyme converts to product (per second) is referred to as the enzyme's "**activity.**" When a particular molecule (or ion) forms a covalent or noncovalent bond with an enzyme, it can result in a decrease in the enzyme's *activity*. A species that decreases a particular enzyme's activity is called an **inhibitor**. Unlike temperature, pH, and denaturing agents, which affect all types of enzymes, inhibitors will only affect specific enzymes. *Enzyme inhibition* can be classified as **irreversible inhibition** or **reversible inhibition**.

i) Irreversible inhibition

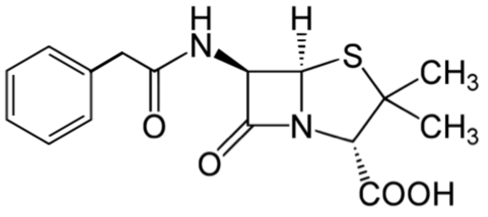
Irreversible inhibition occurs when an *inhibitor* ***reacts*** with an enzyme, forming a ***new*** and ***permanent*** *covalent bond to* the enzyme. In almost all cases of irreversible inhibition, the new bond is made to the enzyme's *active site*, which results in *complete and permanent loss* of the enzyme's activity. In order to re-initiate catalysis, an organism must produce *new enzymes* (in the absence of the inhibitor).

An example of *irreversible inhibition* is ***aspirin's*** **mode of operation**. In an earlier chapter, I discussed how *arachidonic acid* undergoes a series of reactions to produce *prostaglandins* and other *eicosanoids*. *Prostaglandins* have a wide range of biological effects, including causing pain, inflammation, and fever. Although these effects may seem nonbeneficial, in some situations they do play an important biological role. In other situations, it is beneficial to *prevent* pain, inflammation, and fever, therefore we use *aspirin,* or other **n**on**s**teroidal **a**nti **i**nflammatory **d**rugs (NSAIDs). Aspirin *irreversibly inhibits* the *cyclooxygenase* (COX) enzyme, which catalyzes one of the reactions involved in prostaglandin production. Irreversible inhibition occurs when aspirin reacts with an amino acid side-chain in the COX enzyme's *active site,* as illustrated below.

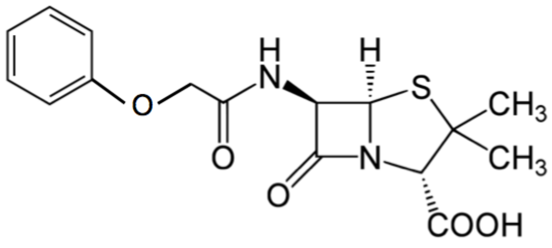


In this reaction, an *acetyl group* from **aspirin** is exchanged for a hydrogen atom (**H**) from a particular side-chain in the COX enzyme's active site. When an acetyl group is bonded to the enzyme's active site, it is no longer possible for *substrates* to bind to the enzyme, and therefore the enzyme is permanently inactivated.

Another example of *irreversible inhibition* can be seen in the mode of action of the antibiotic drug called ***penicillin***. The structural formulas of the intravenously-administered *penicillin G* and the orally-administered *penicillin V* are shown below.



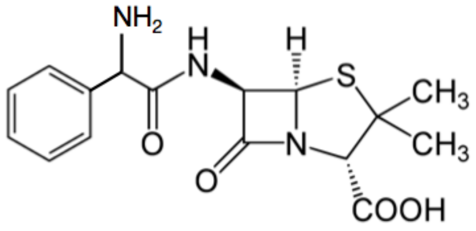
penicillin G
(given intravenously)



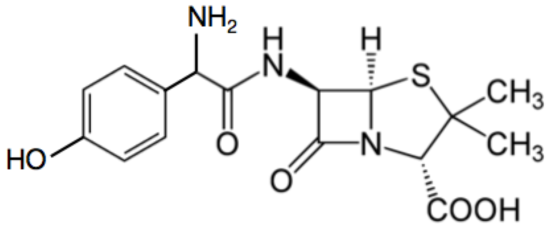
penicillin V
(given orally)

Penicillins are a class of antibiotics that work by *irreversibly inhibiting* a bacterial enzyme called DD-*transpetidase*. This enzyme is involved in constructing cell walls in some types of bacteria. If the cell wall cannot be correctly assembled, then the bacteria cannot divide (reproduce), and therefore do not persist. *Penicillin is* ***specific*** for the DD-*transpetidase* enzyme's active site because the shapes of the *penicillins* are quite similar to the shape of the substrate that is normally catalyzed by the enzyme. Once a penicillin is in the active site of this enzyme, a chemical reaction occurs in which *penicillin forms a* ***covalent bond*** to a particular side-chain in the active site. The reaction is *irreversible* and results in the complete loss of the enzyme's activity.

Some bacteria develop a resistance to *penicillin* G and V. In response, medical researchers have developed penicillin derivatives to which most bacteria have not yet developed a resistance. The structural formulas for a couple of these penicillin derivatives, *ampicillin* and *amoxicillin*, are shown below.



ampicillin

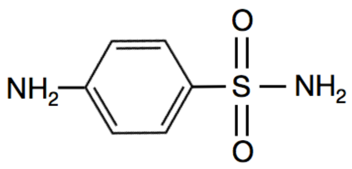


amoxicillin

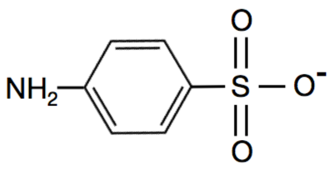
ii) **Reversible Inhibition**

Reversible inhibition occurs when an inhibitor is weakly bound to an enzyme and decreases its activity. This type of inhibitor is called a **reversible inhibitor**. Like the substrates, ***reversible inhibitors*** are *specific* for particular enzymes. *Reversible inhibitors* do not form covalent bonds to the enzyme, therefore they repeatedly attach to and detach from enzymes. When a reversible inhibitor detaches from an enzyme, the enzyme's activity is completely restored. The greater concentration of the inhibitor, the more frequently it will attach to enzymes, and the greater the reduction in enzyme activity. Reversible inhibitors decrease an enzyme's activity by attaching to either an enzyme's *active site* **or** to a region of an enzyme *other than the active site*.

An example of a *reversible inhibitor* is the antibacterial drug called *sulfanilamide*. *Sulfanilamide*, like most reversible inhibitors, reversibly binds to an enzyme's active site, forcing the enzyme's substrate to *compete* for access. Binding of reversible inhibitors to the active sites of enzymes can occur because the inhibitors' shapes often resemble the shapes of substrates, and are therefore complementary to the active sites. *Sulfanilamide* inhibits a bacterial enzyme that catalyzes the production of a compound that is essential for bacterial growth. As shown below, *sulfanilamide* very closely resembles *p-aminobenzoate ion*, which is the bacterial enzyme's substrate.



sulfanilamide
(antibacterial drug)

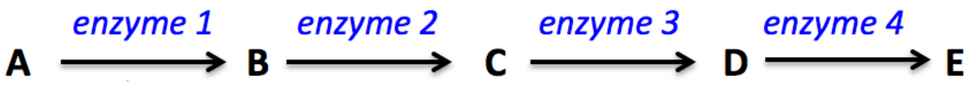


p-aminobenzoate ion
(substrate)

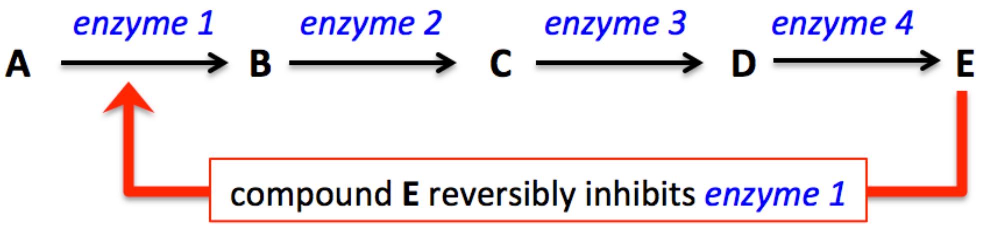
Sulfanilamide was first used extensively as an antibacterial agent in World War II. Since then, many other antibacterial agents have been synthesized by exchanging the amino group (that is bound to the sulfur) with other organic groups. These *sulfanilamide analogs* are called **antibacterial sulfa drugs**.

Organisms often use several reactions in series (one after another) in order to carry out the chemical changes they require to meet their physiological needs. These reaction series are referred to as **metabolic pathways**. *Photosynthesis*, *glycolysis,* and the *citric acid cycle* are examples of *metabolic pathways*. Many of the reactions in metabolic pathways require enzymes, therefore organisms can regulate (slow down) a metabolic process, according to their needs, by *inhibiting* one (or more) of the enzymes involved in the metabolic pathway.

The *product* of a reaction in a metabolic pathway often acts as a *reversible inhibitor* for one (or more) of the reactions in the pathway. This biological strategy makes sense because when there is a relatively high concentration of a product in a metabolic pathway, it would be inefficient, and in some cases harmful, to continue its production. For example, consider the following hypothetical metabolic pathway involving *four enzymatically-catalyzed reactions* that eventually converts compound "**A**" into compound "**E**."



When the concentration of compound **E** is high enough to meet the organism's needs, it would be inefficient, and in some cases dangerous, for the metabolic pathway to proceed. For this reason, compound **E** acts as a *reversible inhibitor* of ***enzyme 1***:



If compound **E** is not present, or is present in relatively low concentration, the reactions proceed, and therefore compound **E** is produced at a significant rate. If compound **E** is produced at a greater rate than the organism uses it, its concentration will increase. As the concentration of **E** increases, more **E** is available to bind to and inhibit, ***enzyme 1***, and this results in a decrease in the production of **B**, **C**, **D**, and, ultimately, a decrease in the production of **E**. Until the organism uses or breaks down a significant amount of compound **E**, compound **E** will continue to *inhibit its own production*.

The *regulation* of a metabolic pathway by *the inhibition of an enzyme* by ***products*** *of any of the reactions* in the pathway is called **feedback inhibition**. An example of *feedback inhibition* is the regulation of *glycolysis*. Glycolysis is a metabolic pathway that involves a series of ten chemical reactions. It is used by organisms to convert glucose to ATP, NADH, and pyruvate. If the concentrations of these products are sufficient, it would be inefficient and potentially harmful to continue to produce them. Each of the ten reactions in the glycolysis pathway requires an enzyme. Three of the enzymes in the pathway are regulated by inhibitors in the feedback inhibition process.

2) Enzyme Activation

Enzyme activation can occur when an "**activator**" binds to an enzyme and ***increases*** its activity. Binding of the *activator* species to an enzyme induces changes in the active site that increases the enzyme's activity. Just like the substrates and enzyme inhibitors, ***enzyme activators*** are specific for a particular enzyme or group of enzymes. *Enzyme activators* can regulate metabolic pathways by activating one or more of the pathway's enzymes. An example of *enzyme activation* is the activation of *pyruvate kinase*, a glycolysis pathway enzyme, by its own substrate, phosphoenolpyruvate (PEP).

One last note on the *control of enzyme activity*: In this section, I discussed how enzyme activity can be decreased or increased by the binding of inhibitors or activators (respectively). Nature employs additional strategies in order to increase or decrease enzyme activity. In some cases, one enzyme catalyzes the breaking of chemical bonds, or the formation of new bonds, in a ***second enzyme*** in order to activate or deactivate the second enzyme. The details of these processes are beyond the scope of this book; however, you should know that this type of activation and deactivation is commonly employed by organisms to regulate metabolic pathways.

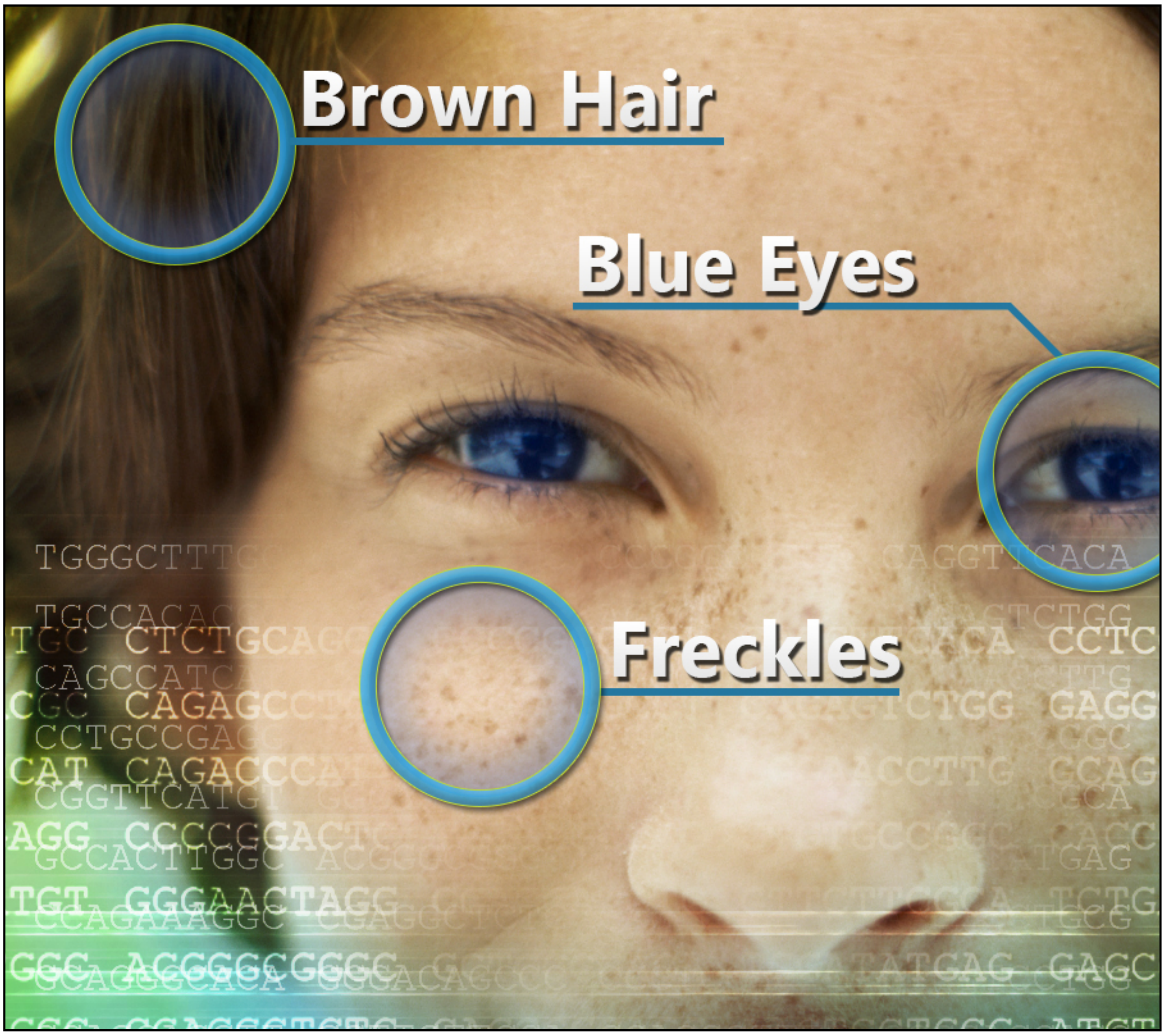
Examples of the Involvement of Enzymes in Disease

The underproduction or overproduction of enzymes, or the inability of an organism to control enzymes can lead to diseases. When such diseases result from a defect (mutation) in a gene that is responsible for the production of a particular enzyme, they are categorized as **genetic diseases**. In the next chapter, you will learn details of how the information in DNA is used to produce proteins (including enzymes). There are thousands of different types of enzymes that are produced in the body, and the inability to correctly produce or control just one type of enzyme could result in death. You may recall that I discussed ***Tay-sach's*** and other ***sphingolipidosis*** genetic diseases that result from a deficiency of the enzymes responsible for the breakdown of sphingolipids. Although some forms of *sphingolipidosis* are treatable with **enzyme replacement therapy**, most sphingolipidosis cases result in death before five years of age. *Enzyme replacement therapy* is also used to treat other enzyme deficiencies, such as *lactose intolerance* (deficient lactase enzyme activity) and *exocrine pancreatic deficiency* (insufficient pancreatic production of digestive enzymes).

Another example of disease that is related to enzymes occurs when DNA is replicated. Before a cell divides, a duplicate copy of its DNA must be made. The new DNA is “proofread” for errors and then repaired. *DNA repair enzymes* catalyze the repair of mistakes made in the DNA replication process. If an individual's *DNA repair enzymes* are not functional, this results in an accumulation of new mutations, and leads to various types of cancers.

Phenylketonuria (PKU) is an enzyme-related disease that can be controlled by a special diet. PKU is caused by deficient activity of the *phenylalanine hydroxylase* enzyme (PAH). This enzyme is responsible for breaking down excess phenylalanine (an amino acid). When the PAH enzyme is not fully functional, high levels of phenylalanine result, which affects brain development and causes intellectual disabilities, seizures, and other medical issues. If PKU is diagnosed and treated early, the damaging effects can be minimized and normal mental development can occur. For individuals with PKU, the consumption of foods rich in phenylalanine residues, such as meats and nuts, can be poisonous. Treatment of PKU is a strict life-time diet that *restricts* phenylalanine-containing foods, and *includes* dietary supplementation of the non phenylalanine amino acids and other nutrients. Individuals with PKU must be careful not to consume the artificial sweetener, *aspartame* (NutraSweet) because phenylalanine is produced when aspartame is broken down in the body.

Chapter 14: Nucleic Acids



Nucleic acids (DNA and/or RNA) are present in every known form of life. The information that is needed for organisms to exist and function is contained in DNA. This information enables cells to grow and divide. It is responsible for your physical characteristics, such as your height, the color or your eyes, skin, and hair, and even the sound of your voice. The information contained in DNA is accessed and put to use by RNA and proteins.

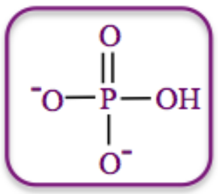
In this chapter, you will learn about the chemical structures of DNA and RNA and how their structures allow them to perform their biological roles. I will discuss the chemistry of DNA replication, how information in DNA is used to direct the formation of proteins, viruses and viral diseases, and the field of study called genetics.

14.1 Chapter 14 Educational Goals

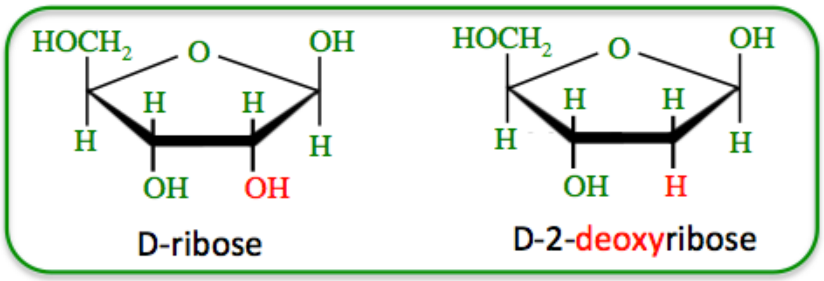
1. Know the *three* chemical components of a **nucleotide**: a *monosaccharide residue* (either ribose or deoxyribose), at least one *phosphate group*, and an "*organic base*."
2. Identify **phosphoester** bonding patterns and ***N*-glycosidic bonds** within *nucleotides*.
3. Compare and contrast **ribonucleotides** and **deoxyribonucleotides**.
4. Understand the bonding patterns within **nucleotide diphosphates** and **nucleotide triphosphates**.
5. Predict the products for the hydrolysis of **ATP** and **ADP**.
6. Describe the bonding patterns within **cyclic nucleotides**.
7. Describe the chemical structure of **polynucleotides** (DNA and RNA) and identify the **phosphodiester bonding patterns** within *polynucleotides*.
8. Draw the structural formula of a **dinucleotide** that is formed by combining two specified nucleotides.
9. Compare and contrast the monosaccharide residues present in DNA vs. RNA.
10. Know the names of the **organic bases** that are present in DNA and RNA.
11. Given the structure of a DNA or RNA strand, identify the **sugar-phosphate backbone**, the **3' terminus**, and the **5' terminus**.
12. Describe the DNA **double helix structure**, and understand and define the term "**complementary base pairing**."
13. Understand how DNA folds back on itself and wraps around *histones* to form **chromatin**. Define, compare, and contrast **chromatin**, **genes**, and **chromosomes**.
14. Understand and explain how **DNA replication** takes place and how **DNA polymerase** is involved in the replication process.
15. Describe the **polymerase chain reaction**.
16. Know how **DNA fingerprinting** works and how it is used in forensic science.
17. Understand and explain **transcription** and how **RNA polymerase** is involved in the transcription process.
18. Understand and explain **translation** and define the term "**codon**."
19. Given the primary structure of DNA or mRNA, use the **genetic code** table to predict the sequence of amino acids in the polypeptide that would be produced in translation.
20. Describe the ***three types of RNA*** and understand the role of each in translation.
21. Define the term "**gene expression**."
22. Define the term "**operon**." Describe how the ***lac* operon** is *regulated* in order to control *gene expression* in *E. coli*.
23. Describe the structure of **viruses** and understand the way in which they can cause infections/diseases. Understand how the **reverse transcriptase** enzyme is used by HIV viruses.
24. Define and understand the terms "**mutation**," "**genome**," and "**gene therapy**." Explain how mutations can lead to **genetic diseases**. Give an example of a **monogenic disease**.
25. Define the terms: **recombinant DNA**, **genetically modified organism (GMO)**, **transfection**, and **bioethics**.

14.2 Nucleotides

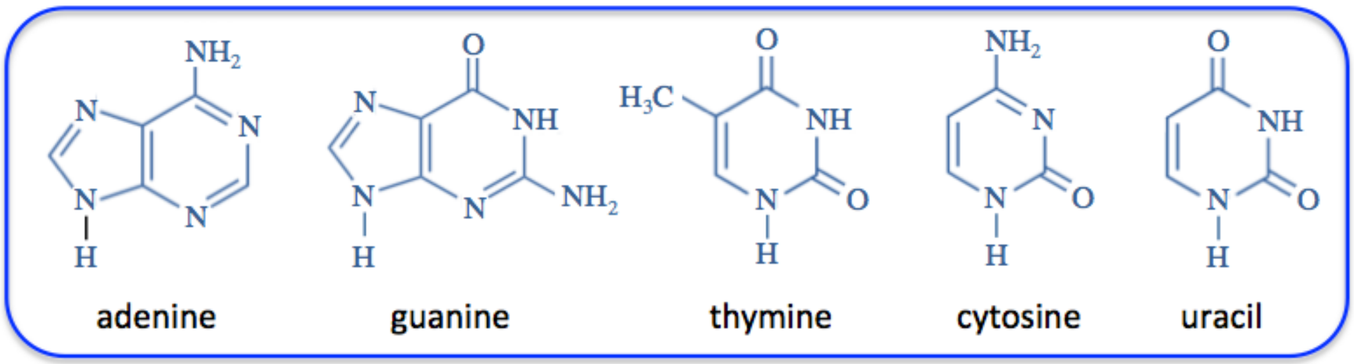
Nucleic acid is a term used for the class of biological polymers consisting of deoxyribonucleic acid **(DNA)** *and* ribonucleic acid (**RNA**). These polymers consist of *linear sequences* of ***nucleotide*** residues. A ***nucleotide*** is formed from by *three* chemical components: a *monosaccharide* (either ribose or deoxyribose), at least one *phosphate*, and one "*organic base*." The structures of these components are shown below.



a phosphate
(hydrogen phosphate ion)

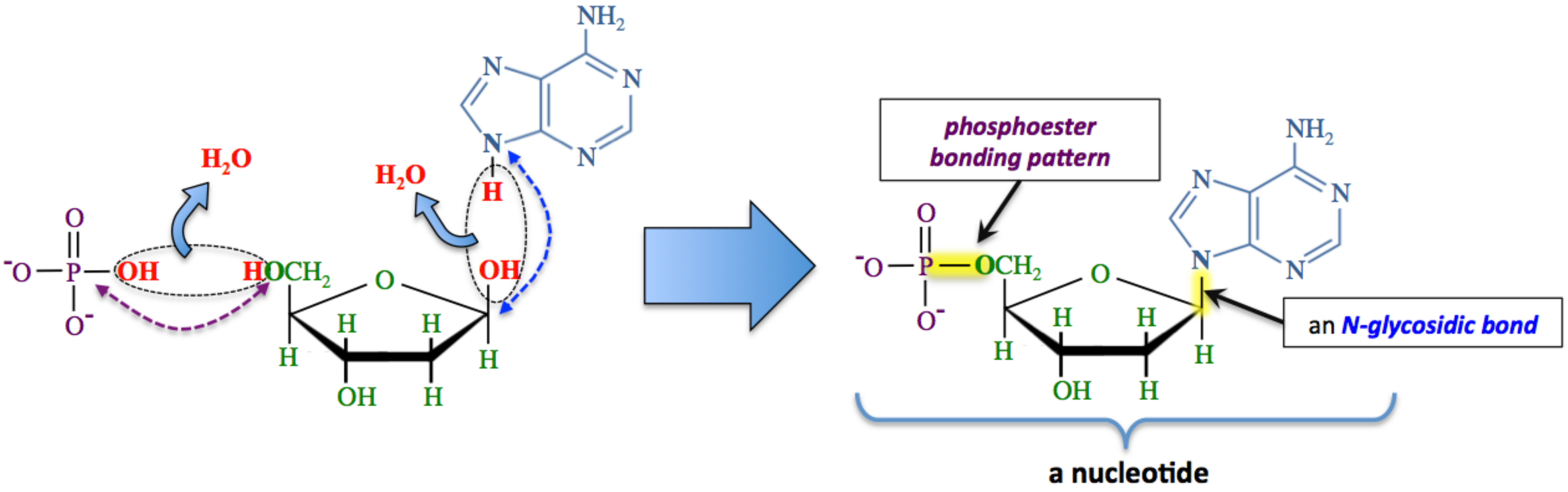


nucleotides contain one of these monosaccharides



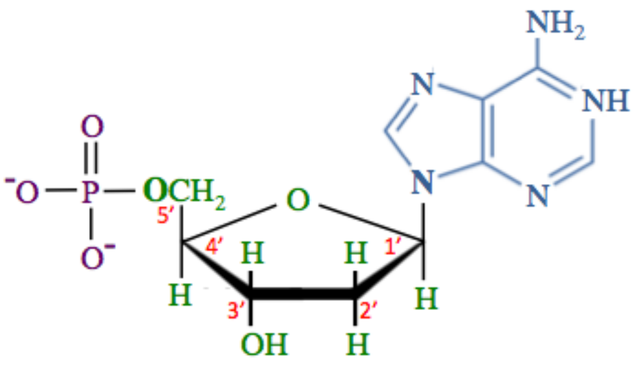
nucleotides contain one organic base
(the five most common organic bases are shown)

I will elaborate on the structure of *nucleotides* by illustrating the formation of one from a *monosaccharide*, a *phosphate* (HPO_4^-), and an "*organic base*." In this example, I will use *deoxyribose* as the monosaccharide and therefore form a ***deoxyribo****nucleotide*. I will use *adenine* as the *organic base*.



We see a familiar bonding pattern in the formation of nucleotides; the ***phosphoester*** bonding pattern occurs when a monosaccharide bonds with the phosphate group. We also see a *new* type of bonding pattern; an ***N*-glycosidic bond** is made when the monosaccharide bonds to a nitrogen in the *organic base*. *N-glycosidic* bonds should not be confused with the "standard" *glycosidic* bonds, which connect two carbohydrate residues.

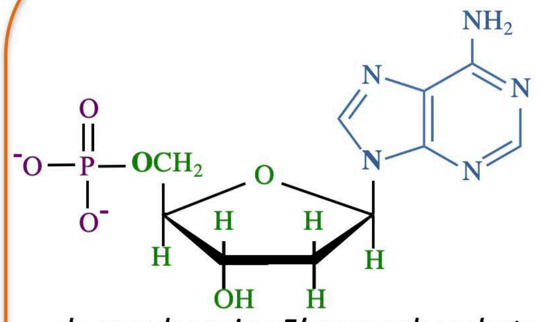
The nucleotide in the example on the previous page was formed by bonding a phosphate to the carbon in position number **5** of the monosaccharide ring. I have redrawn that nucleotide (on the right), showing the position numbers of the monosaccharide ring.



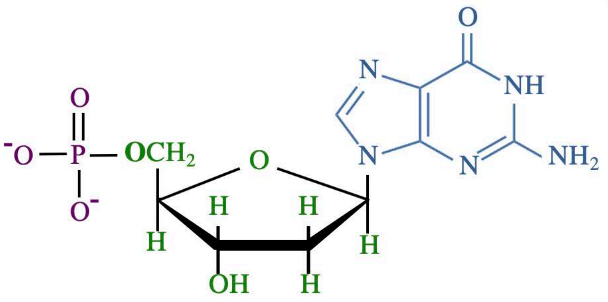
Note that when assigning numbers to the *monosaccharide* ring positions, we use apostrophes in order to distinguish these positions from the *organic base* ring positions. Because the nucleotide in this example is formed from one *phosphate,* ***deoxy****ribose,* and an *adenine* organic base, we write its name as “***deoxy****adenosine* **5’**-monophosphate,” and we say “deoxyadenosine five prime monophosphate.” It is common to use abbreviations when naming nucleotides. In this case, we would abbreviate the name as “**5’**-dAMP,” the lowercase “d” indicates “*deoxy*.”

Organisms synthesize **DNA** from **5’**-nucleotides. The nucleotides that make up **DNA** contain a ***deoxy****ribose residue, a phosphate residue,* and either *adenine, guanine, cytosine, or thymine* organic bases. The structures, names, and abbreviations of the four nucleotides (deoxyribonucleotides) that make up **DNA** are shown *on the right*.

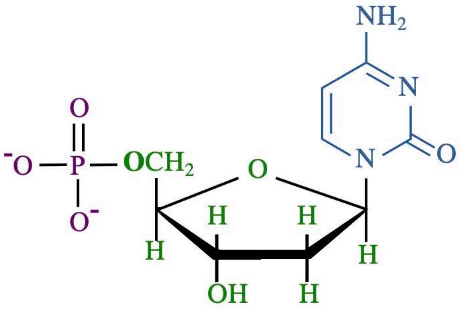
The deoxyribonucleotide residues that comprise DNA



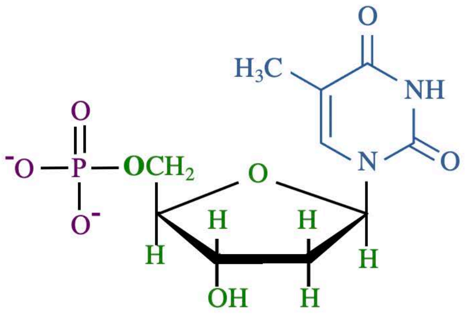
deoxyadenosine 5’-monophosphate
(5’-dAMP)



deoxyguanosine 5’*-monophosphate*
(5’-dGMP)



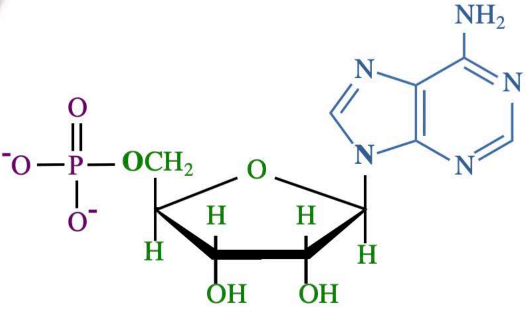
deoxycytidine 5’-monophosphate
(5’-dCMP)



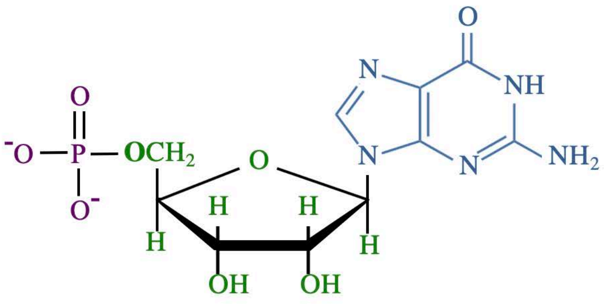
deoxythymidine 5’*-monophosphate*
(5’-dTMP)

The nucleotides that make up **RNA** contain a *ribose* residue, a *phosphate residue,* and either *adenine, guanine, cytosine,* or *uracil*. The structures, names, and abbreviations of the four nucleotides (ribonucleotides) that make up **RNA** are shown on the left.

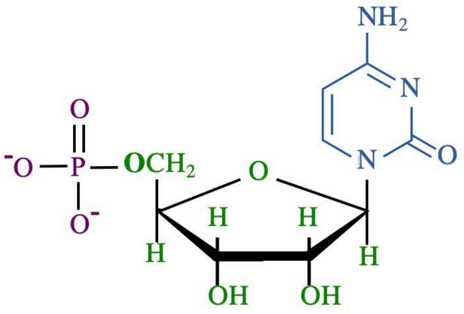
The ribonucleotide residues that comprise RNA



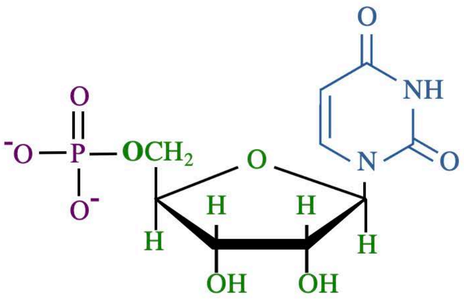
adenosine 5’-monophosphate
(5’-AMP)



guanosine 5’*-monophosphate*
(5’-GMP)



cytidine 5’-monophosphate
(5’-CMP)



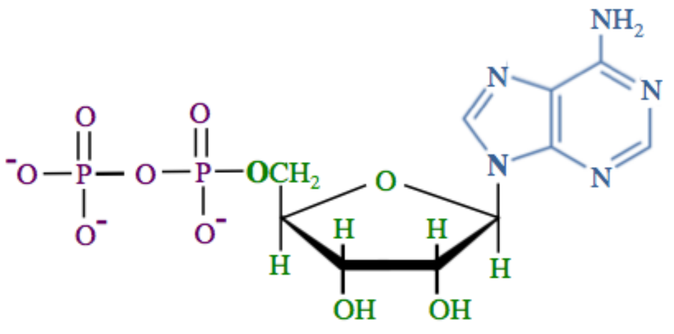
uridine 5’*-monophosphate*
(5’-UMP)

Note that both DNA and RNA have *adenine, guanine*, and *cytosine* organic bases, however *thymine* is present only in DNA and *uracil* is present only in RNA.

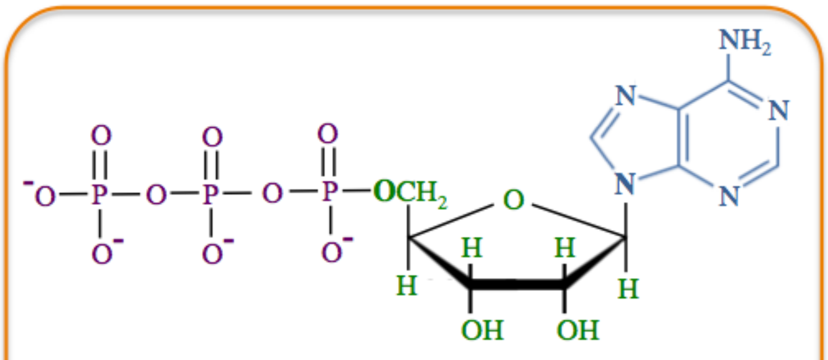
These **5’**-nucleotides are so frequently encountered in biology that the “**5-**” is usually omitted in the names and abbreviations. **3’**-nucleotides do exist, but they are rare.

Nucleotide Diphosphates and Nucleotide Triphosphates

Nucleotides have biological roles other than forming DNA and RNA. One of these roles involves transferring energy. The two most important energy-transfer nucleotides are *adenosine triphosphate* (ATP) and *adenosine diphosphate* (ADP). The structural formulas for ATP and ADP are shown below:



adenosine diphosphate **(ADP)**

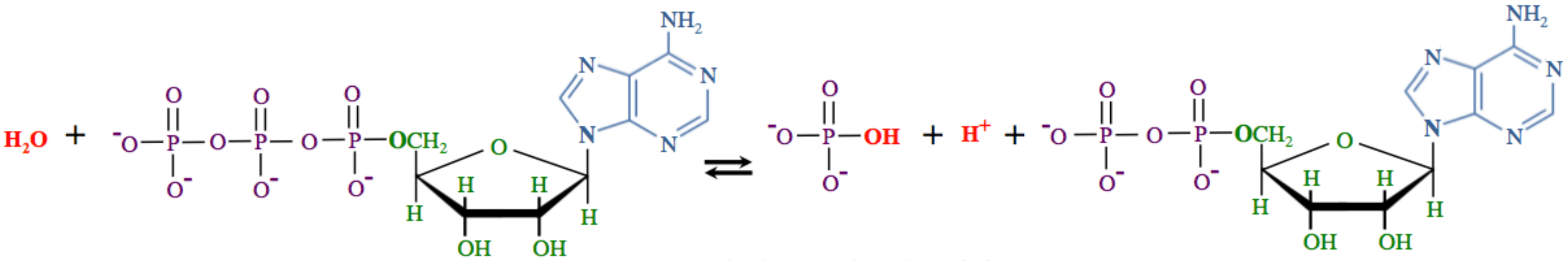


adenosine triphosphate **(ATP)**

ATP contains ***more*** *chemical potential energy* than does ADP. Organisms obtain energy from their environment (sunlight or chemical potential energy in food) when they use it to convert ADP to ATP. This is analogous to filling a car's fuel tank or charging a battery. You will learn the details of how chemical potential energy in food is used to convert ADP to ATP in chapter 15.

Energy is ***released*** from ATP when it is converted to back to ADP. Organisms can do mechanical ***work,*** or drive chemical reactions that require energy by converting ATP to ADP. This is analogous to burning fuel in order to move a car, or discharging a battery while powering an electrical device. *One* way that energy can be released from ATP is by reacting it with H_2O to form ADP, hydrogen phosphate (abbreviated as P_i), and an H^+ ion. The chemical equation for this reaction is shown below.

H_2O *(l)* + ATP *(aq)* ⇌ P_i *(aq)* + H^+ + ADP *(aq)*   **ΔG = -*7300*** Joules per mole of ATP

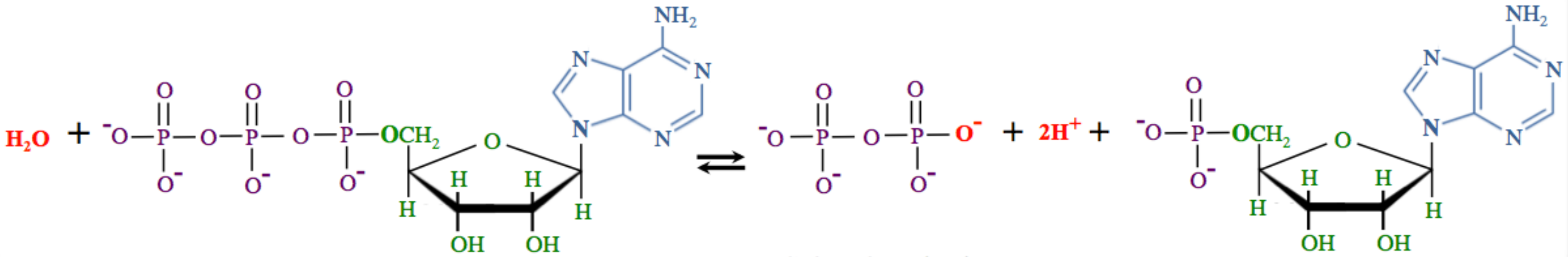


adenosine triphosphate **(ATP)**   *hydrogen phosphate* **(P_i)**   *adenosine diphosphate* **(ADP)**

The reaction of ATP with H_2O is quite slow at physiological pH, however it can occur at useful rates when catalyzed by enzymes. The hydrogen ion (**H^+**) formed in this reaction will quickly react with water to form H_3O^+ (aq). In the last chapter, you saw how the energy released by the reaction of ATP and water provides the energy needed to make muscles contract. In that process, the myosin head acts as an enzyme to catalyze the reaction, in addition to providing the power stroke.

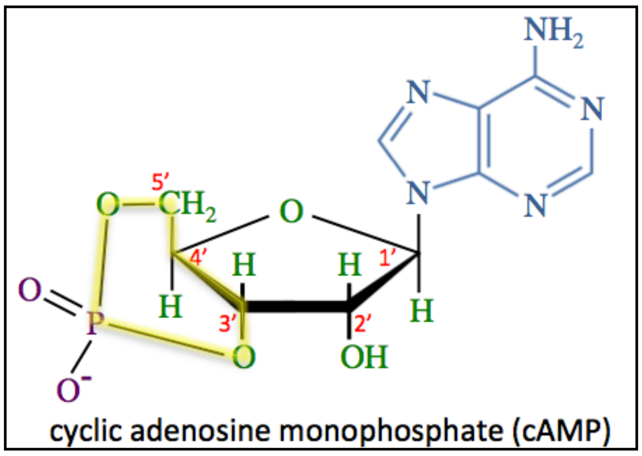
Not as common, but ATP can also release energy by reacting with water to produce *adenosine monophosphate* (AMP), diphosphate (abbreviated as PP_i), and an H^+ ion, as shown below.

H_2O *(l)* + ATP *(aq)* ⇌ PP_i *(aq)* + H^+ + AMP *(aq)*   **ΔG = -*10,900*** Joules per mole of ATP



adenosine triphosphate **(ATP)**   *diphosphate* **(PP_i)**   *adenosine monophosphate* **(AMP)**

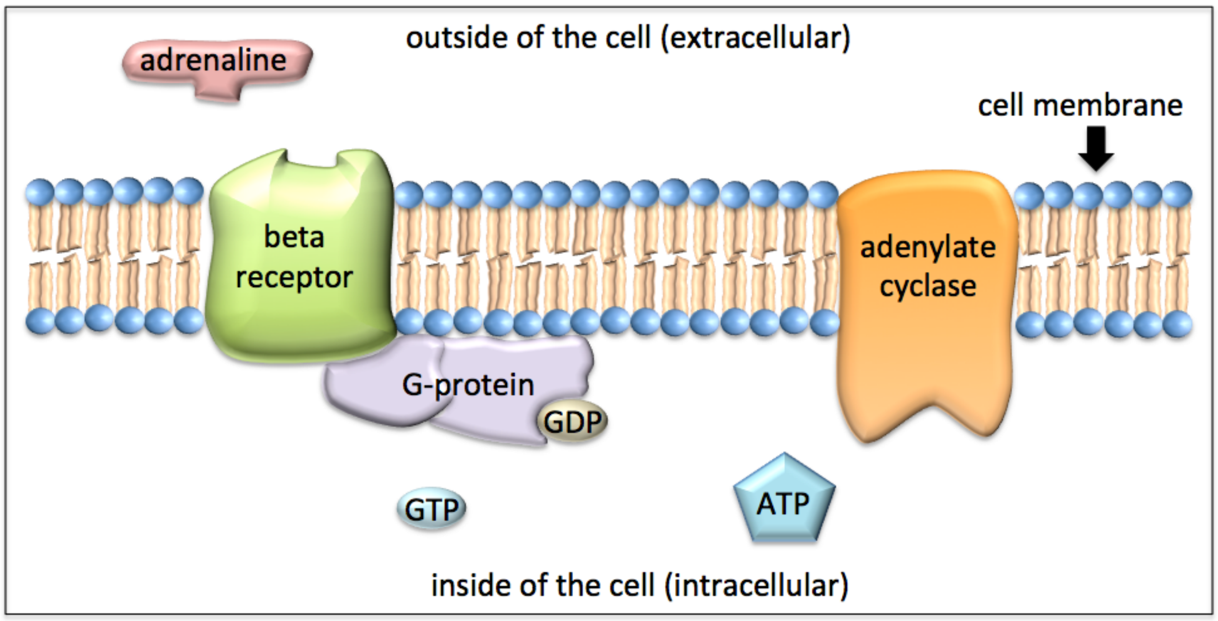
Cyclic Nucleotides



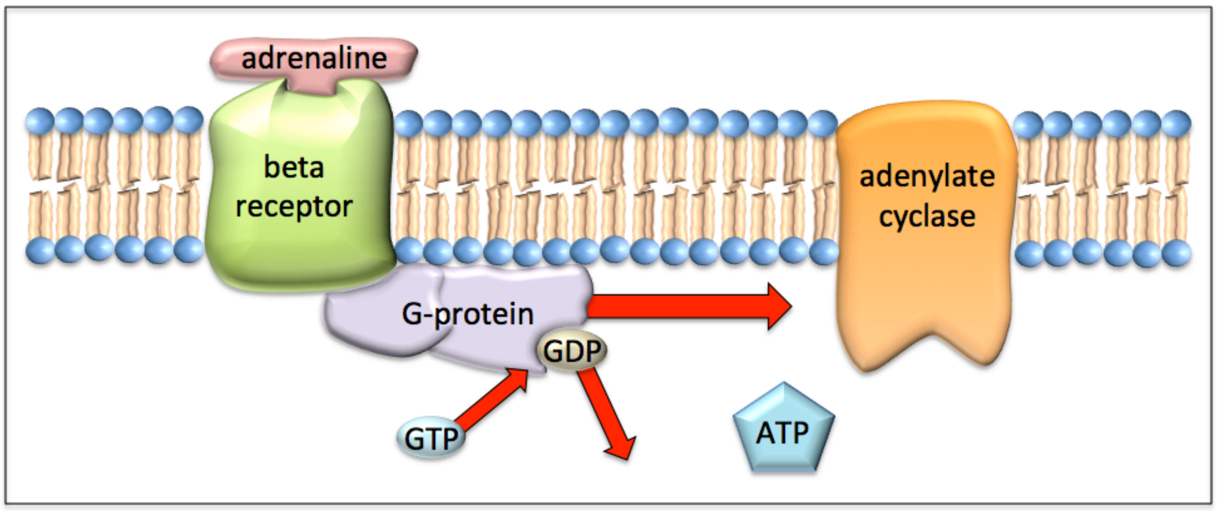
cyclic adenosine monophosphate (cAMP)

Another biological role of nucleotides is to act as chemical signaling compounds. A type of nucleotide, called a **cyclic nucleotide**, is often used for this purpose. Cyclic nucleotides are nucleotides that contain a phosphate group *that bonds to the monosaccharide residue at two locations*, thereby forming a *phosphorus-containing* ring. A structural formula of a cyclic nucleotide, with its phosphorus-containing ring (shaded yellow), is shown on the right. Because this nucleotide is cyclic and is made from *ribose*, an *adenine* organic base, and one *phosphate group*, it is called *cyclic adenosine monophosphate* and is abbreviated as cAMP. The lower case "c" indicates that it is a *cyclic* nucleotide.

Cyclic nucleotides play an important role in chemical signaling. For example, cAMP is involved in *adrenaline's* "fight or flight" response. I have discussed chemical signaling compounds in previous parts of this book. This example of cAMP chemical signaling will allow you to look a bit deeper into how signaling compounds and protein receptors can cause a response in the cells of an organ or a tissue.



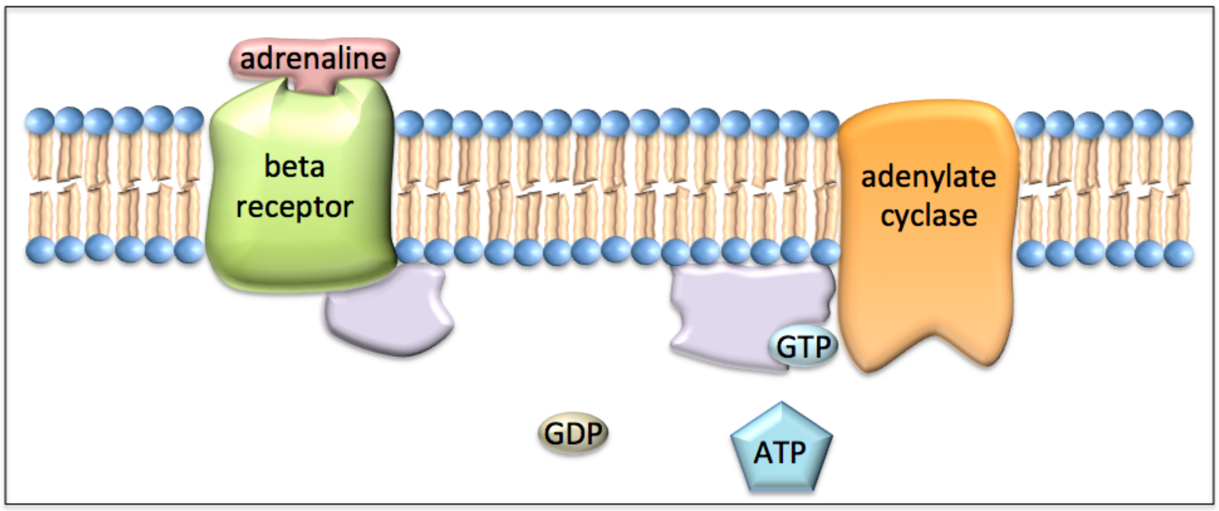
When adrenaline (also called epinephrine) is released from the adrenal gland in response to stress, such as a physical threat, excitement, noise, or bright lights, it can bind to a transmembrane "beta-receptor" protein. On the inside of the cell, a protein called "G-protein" is bound to the beta-receptor. The "G-" in "G-protein" is used because this protein is bound to GDP or GTP nucleotides.



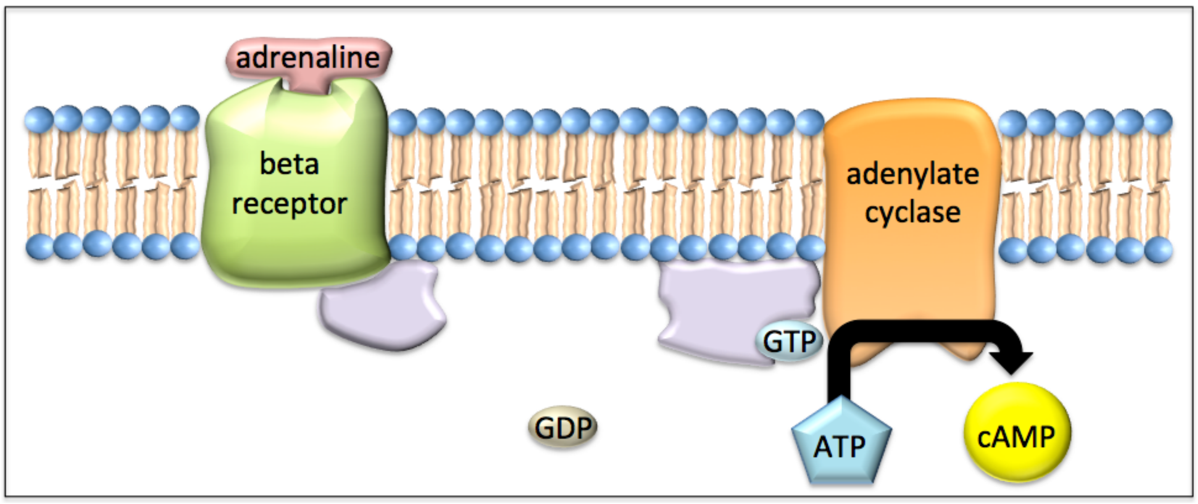
When adrenaline binds to the beta-receptor, a conformation change occurs in the beta-receptor. This induces a conformation change in the G-protein, which has two effects:

(1) GTP replaces the GDP on G-protein.

(2) The G-protein splits into two fragments. The fragment that contains the GTP is free to move along the inner membrane surface.



Next, the fragment of G-protein that contains GTP binds to the *adenylate cyclase* enzyme.



The G-protein/GTP fragment ***activates*** the *adenylate cyclase* enzyme, which catalyzes the conversion of ATP to *cyclic adenosine monophosphate* (cAMP):

ATP + H_2O ⇄ **cAMP** + PP_i + H^+

Note that for each adrenaline that binds to the exterior of a cell, ***many*** ATPs react to produce ***many*** cAMPs; this is called **signal amplification.**

Next, cAMP triggers several biological processes, most of which come about because **cAMP activates the *protein kinase A (PKA)* enzyme.** The PKA enzyme is involved in many metabolic processes. For example, PKA stimulates glycolysis by phosphorylating (and thereby activating) an enzyme used in the glycolysis metabolic pathway. You may recall that I briefly mentioned the activation of enzymes by phosphorylation while discussing enzyme activation/inhibition in chapter 13. Other effects of the activation of PKA by cAMP include: inhibition of glycogen production, activation of the breakdown of glycogen into glucose (glycogenesis), and increasing the production of certain proteins.

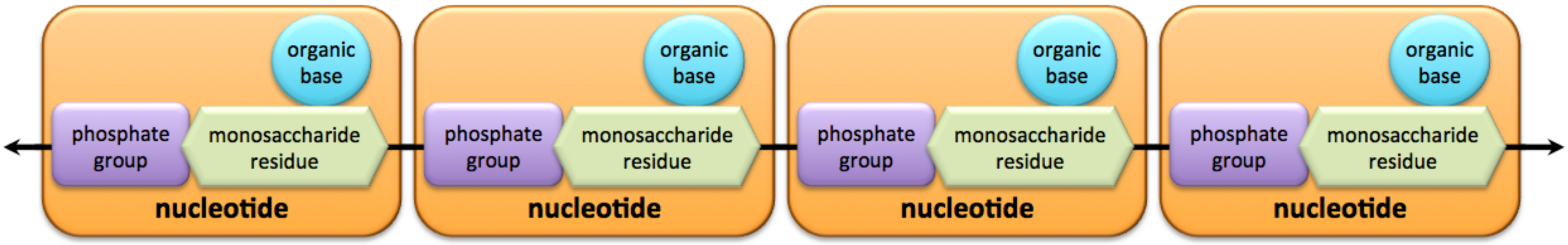
Review 14.1: Nucleotides

Cyclic guanosine monophosphate (**cGMP**) acts in a way that is similar to cAMP by activating the *protein kinase G* (PKG) enzyme. Draw the structural formula of ***cyclic*** guanosine monophosphate (cGMP) by making the *phosphoester bonds* to carbon number **3'** *and* carbon number **5'** of the monosaccharide. Label the ***N-glycosidic*** bond.

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

14.3 Polynucleotides: DNA and RNA

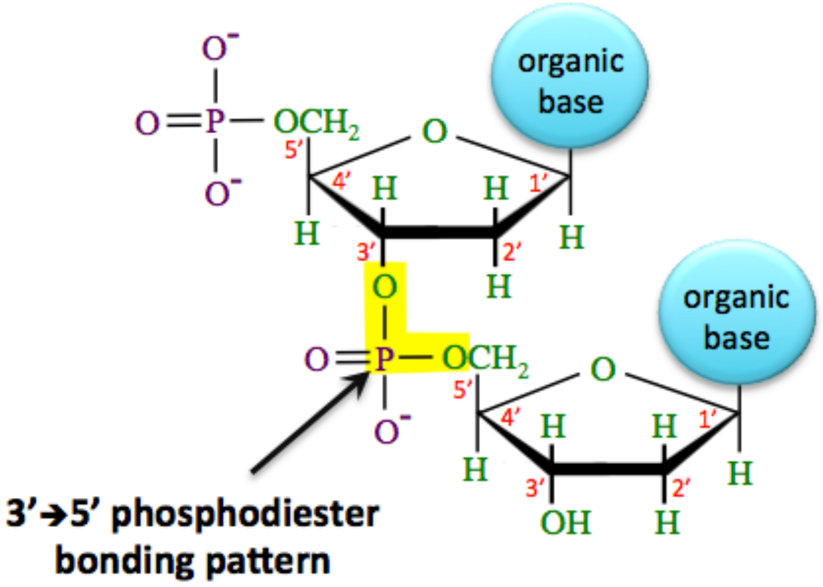
A **polynucleotide** is a polymer made from ***nucleotide*** residues. Nucleotides bond to each other in a linear sequence (not branched) as illustrated below.



This diagram only shows four nucleotide residues, however polynucleotides generally contain between about 20 nucleotide residues (the smallest RNA) and about 250 million residues (human chromosome 1). A chain of covalently bonded nucleotides is referred to as a "**strand.**"

I will elaborate on the bonding pattern in polynucleotide strands by first describing a **di**nucleotide. In a dinucleotide, two nucleotides are covalently bonded to each other by a phosphodiester bonding pattern between a **3'** carbon on one monosaccharide and a **5'** carbon on the other monosaccharide, as shown below.

a dinucleotide



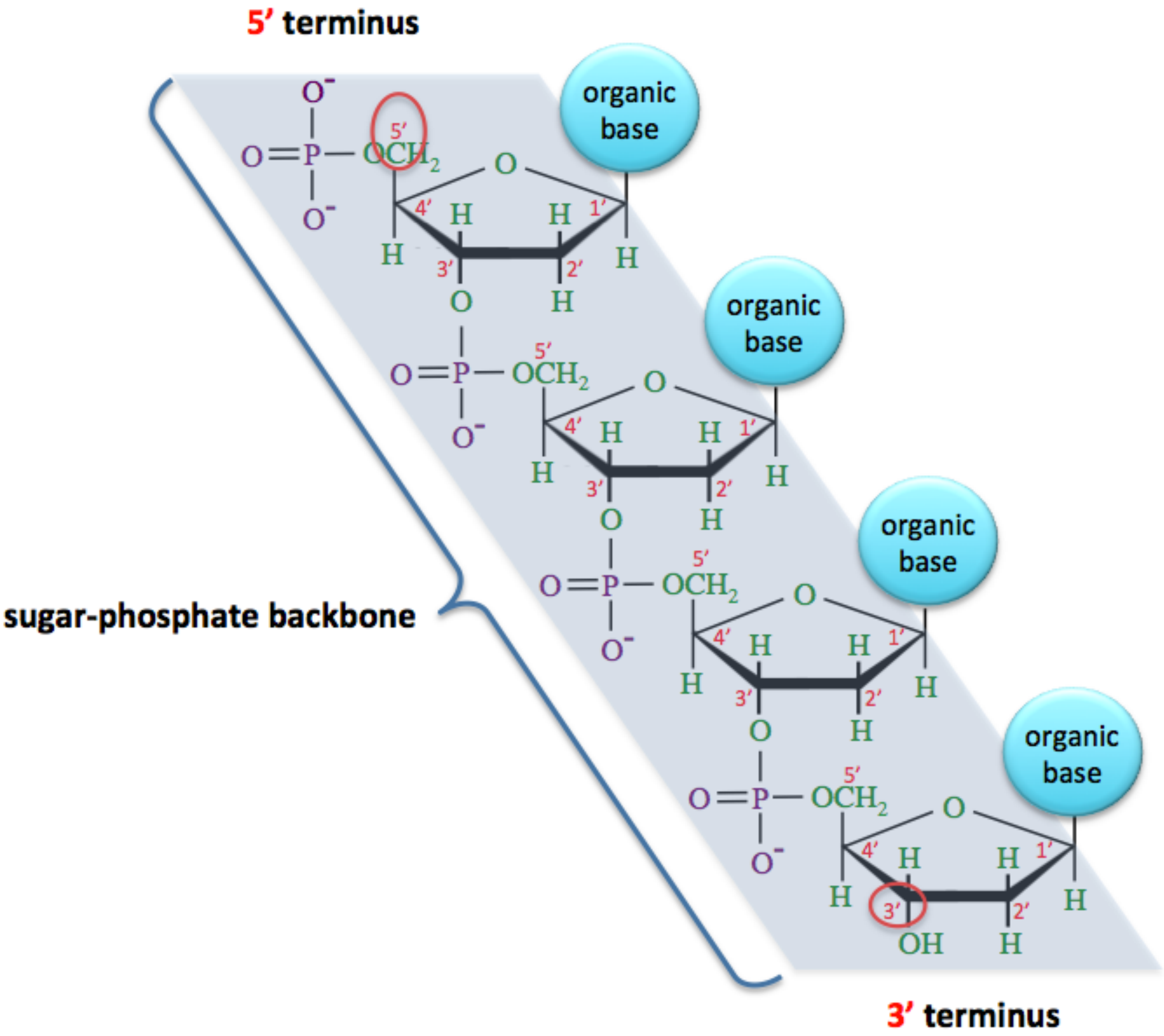
As you have seen in a previous chapter, a *phospho**di**ester bonding* pattern occurs when a phosphate group is bonded between ***two*** other groups of atoms. In the case of *polynucleotides*, we call this bonding pattern a **3'**→**5'** *phosphodiester* because the phosphate group is between the **3'** and **5'** carbons.

Review 14.2: The Bonding Pattern of Polynucleotide Strands

Starting with the dinucleotide that I formed in the above example, draw a ***tri**nucleotide* by adding another nucleotide to the 3' carbon of the *bottom nucleotide residue*. Highlight the ***phosphodiester*** bonding patterns. You may use a circle to represent the organic base structures, as I did in the dinucleotide.

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

Additional details of the bonding pattern in a polynucleotide strand can be seen below in the structural formula of a ***small section*** of DNA.



The nucleotides are connected to each other by covalent bonds between the monosaccharide residues and the phosphate residues (only). For this reason, the *alternating* monosaccharide and phosphate residues in a polynucleotide strand are referred to as the "**sugar-phosphate backbone**." The *organic groups branch* off of the sugar-phosphate backbone, much like side-chains branch from a peptide chain. You learned that the ends of peptide chains are different from each other and are labeled as the N-terminus or the the C-terminus. A similar situation occurs at the ends of polynucleotide strands. One end of the strand is terminated with a phosphate group that is attached to a **5'** carbon; we call that end of the strand the **5' terminus**. The other end of the strand is terminated with a *hydroxyl group* (**OH**) that is attached to a **3'** carbon; we call that end of the strand the **3' terminus**.

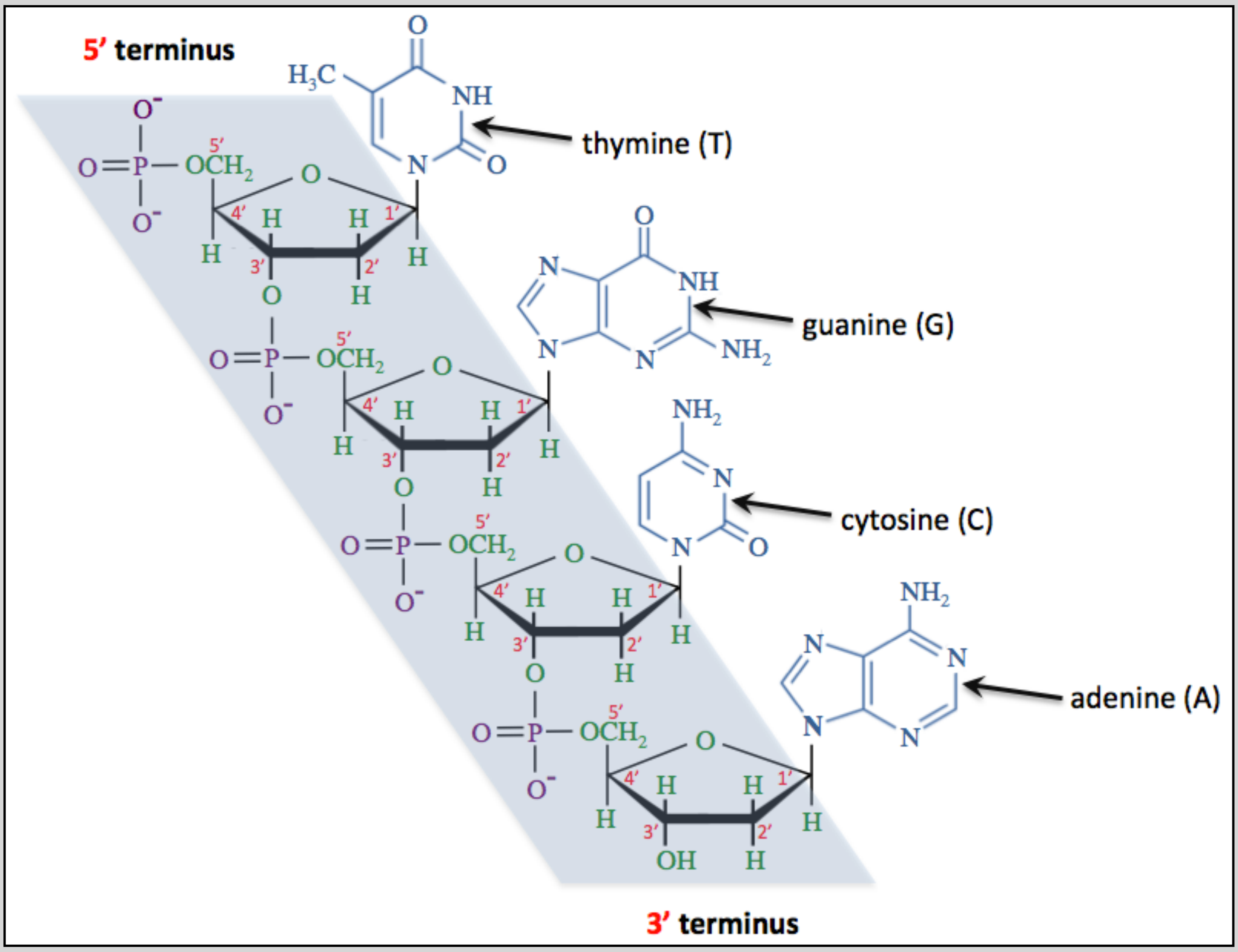
DNA Structure

DNA contains the "information" needed for life. This information enables cells to grow and divide. It is responsible for your physical characteristics, such as your height, skin tone, and eye color. Human DNA contains about three million deoxyribonucleotide residues. Eukaryotic cells, which are cells having membrane-bound nuclei, have most of their DNA in the nucleus, and small amounts in other organelles such as chloroplasts and mitochondria. The DNA of prokaryotic cells is contained in the cytoplasm.

DNA is composed of a combination of ***deoxy****ribonucleotides* that contain either adenine, guanine, thymine, or cytosine organic bases. In some cases, the organic bases are chemically modified after they are incorporated into DNA. The details of these modifications are beyond the scope of this course.

Genetic information, the information used to make the various proteins and thereby enabling life, is contained in the ***sequence of nucleotides*** in DNA. The sequence of nucleotides in DNA is referred to as **DNA's primary structure**. As an example, let's consider the primary structure of the small section of DNA that is shown in Figure 14.1.

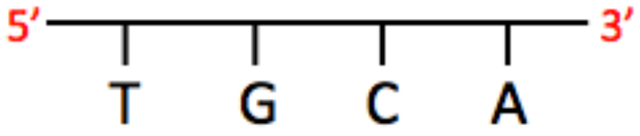
Figure 14.1 Primary Structure of a Small Section of DNA



A sequence of nucleotides (primary structure) in a small section of DNA.

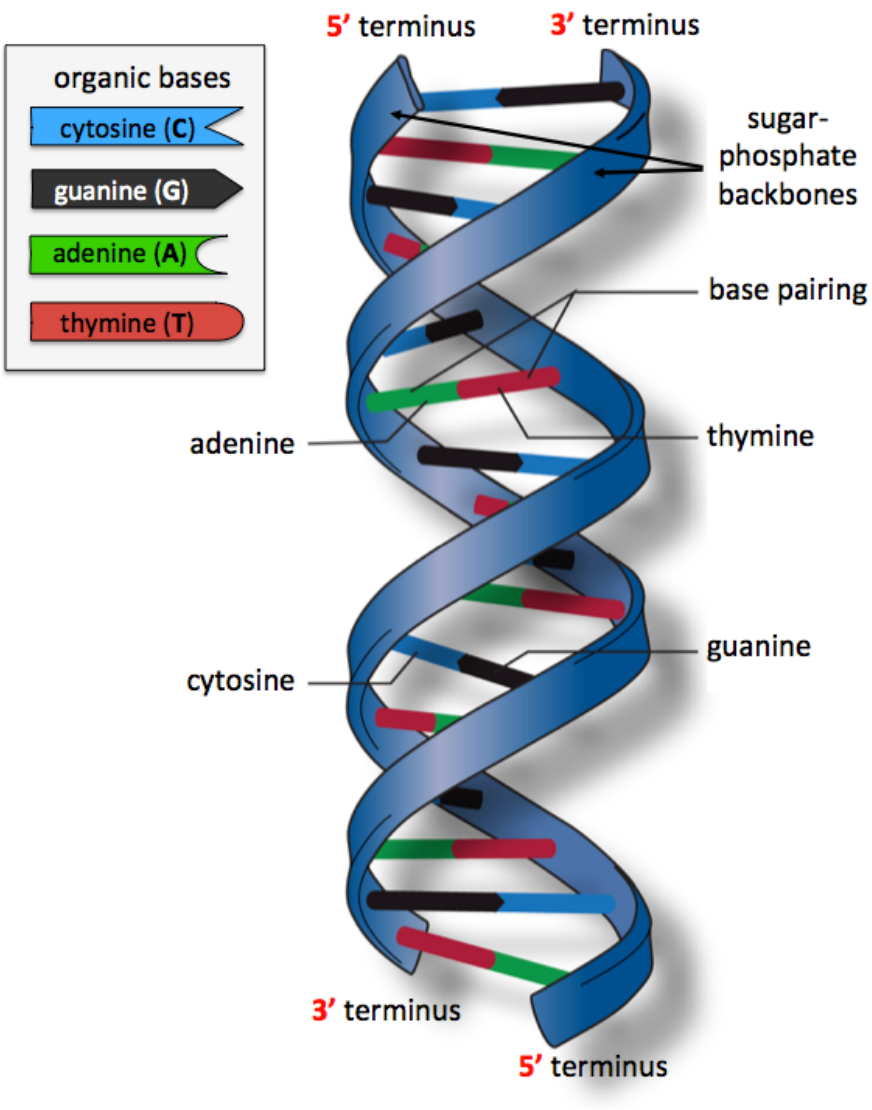
Nucleotides are given a one-letter abbreviation based on the first letter in the name of their *organic base*. In order to describe the primary structure of a DNA strand, it is customary to list the nucleotides' one-letter abbreviations in the order that the nucleotide residues appear in the strand. For example, the primary structure of the DNA strand drawn above is written as **5'-TGCA-3'**.

A common method used to represent the primary structure of DNA and RNA is to draw the one-letter abbreviations of the organic bases branching from a line that represents the sugar-phosphate backbone. For example, the DNA strand shown above is represented as:



In later sections of this chapter, you will learn the details of how the sequence of nucleotides in a strand of DNA is used to direct the assembly of specific amino acid residues during the biosynthesis of proteins.

DNA exists as a **double helix,** which is made from ***two polynucleotide strands***. A *ribbon model* of a DNA double helix structure is shown below.



I would like to draw your attention to a few important *structural details* that are seen in this model of DNA:

1) The sugar-phosphate backbones for each of the two DNA strands are illustrated as blue ribbons.

2) The two DNA strands of a DNA double helix have their **5'** terminuses and **3'** terminuses with opposite orientations. Note that at the *top* of the double helix illustration, the **5'** terminus of one DNA strand is present and the **3'** terminus of the other DNA strand is present. The same is true at the bottom of the double helix. We call this opposing orientations of the DNA strands an "**antiparallel**" arrangement.

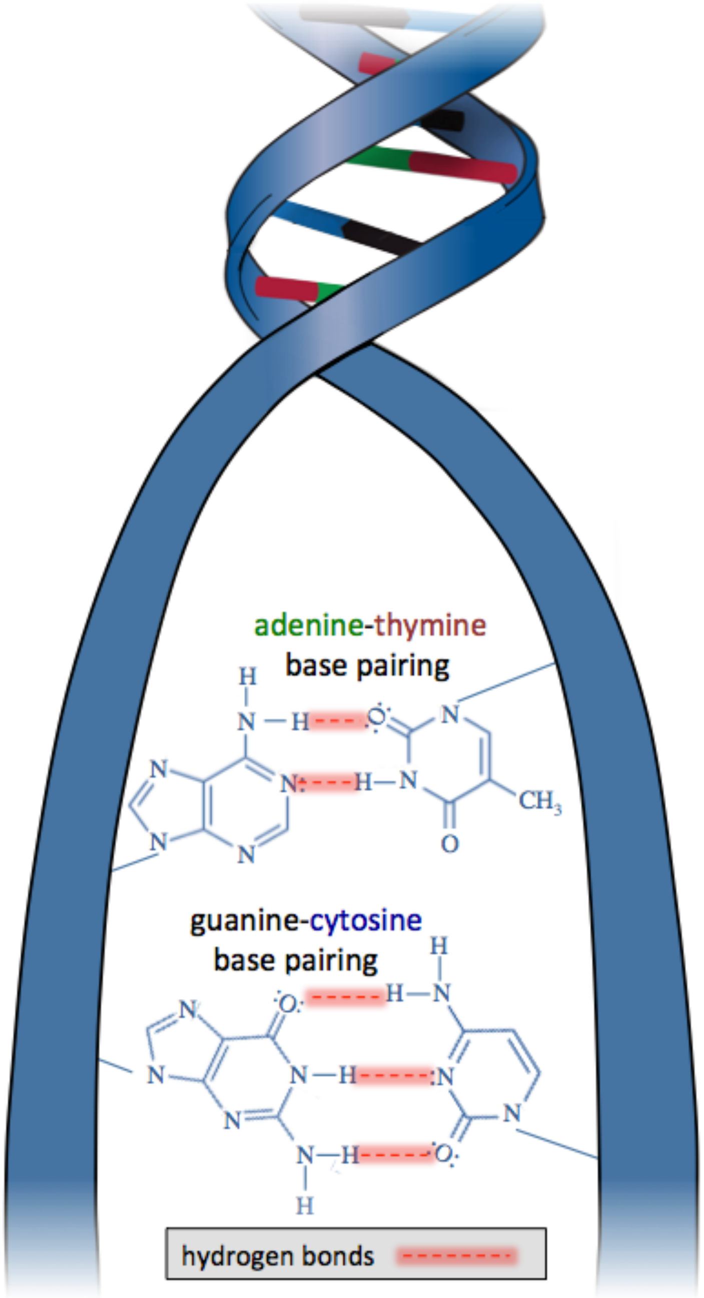
3) The two DNA strands are held together by especially strong *hydrogen bonding* between ***specific*** pairs of organic bases.

- *Adenine* (**A**) bases hydrogen bond with *thymine* (**T**) bases.
- *Guanine* (**G**) bases hydrogen bond with *cytosine* (**C**) bases.

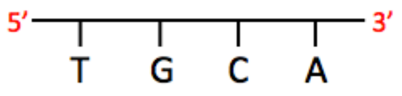
The reason for the strong hydrogen bonding between these organic base pairs is that they have *complementary shapes*.

The hydrogen bonding between these pairs of organic bases is referred to as **base pairing** *or* **complementary base pairing**. We say that the two polynucleotide strands in a double-stranded DNA particle are "***complementary***." The details of the hydrogen bonding patterns involved in complementary base pairing are shown in the illustration on the right.

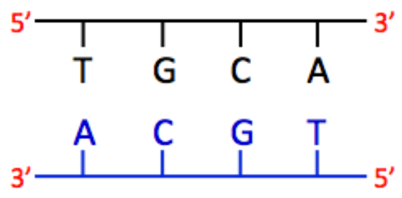
The double helix structure of DNA was first postulated by James Watson and Francis Crick in 1953. Their postulation was based, in large part, on an x-ray diffraction image that was generated by Rosalind Franklin and Raymond Gosling in 1952. Watson and Crick were awarded the Nobel Prize for their work toward the discovery of the DNA double helix.



I drew the structural formula of small section of single-stranded DNA as an example (two pages back). The sequence of nucleotides in that particle was written as **5'**-TGCA-**3'** and represented as shown below.

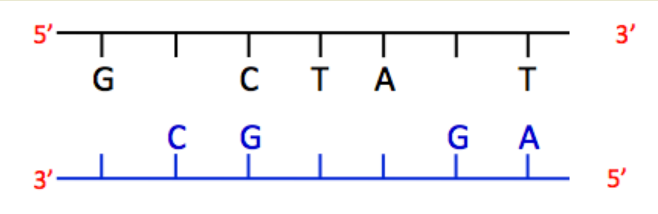


Since **G** base pairs with **C**, and **A** base pairs with **T**, the ***complement*** *of the strand shown above* is **3'**-ACGT-**5'**, and is drawn under the original strand in the representation below.



Review 14.3: DNA Base Pairing

Fill in the missing one-letter abbreviations for the organic bases in the image below to show the correct complementary base pairing.



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Chromatin and Chromosomes

In eukaryotic organisms (plants, animals, and fungi), the DNA double helix coils into a more compact structure, as illustrated in the figure on the right. This coiling is necessary in order for the DNA to be contained in a cell's nucleus. In humans, if a typical DNA particle were uncoiled, it would be about six feet long.

In the coiling process, the double helix wraps around histone proteins, as shown in figure on the right. The DNA/histone further condenses into a fiber that is called **chromatin**. Depending on the cell life cycle, *chromatin* can undergo further coiling. For example, before a cell divides chromatin is coiled into its tightest, *most compact shape*, which is called a **chromosome**. The amount of *chromosomes* that a cell contains depends on the organism. Humans have a total of 46 chromosomes per cell, 23 from each parent. Dogs have a total of 78 chromosomes, 39 from each parent. Fruit flies have a total of eight chromosomes. The smallest human chromosome contains about 50 million base pairs, and the largest one contains about 250 million base pairs.

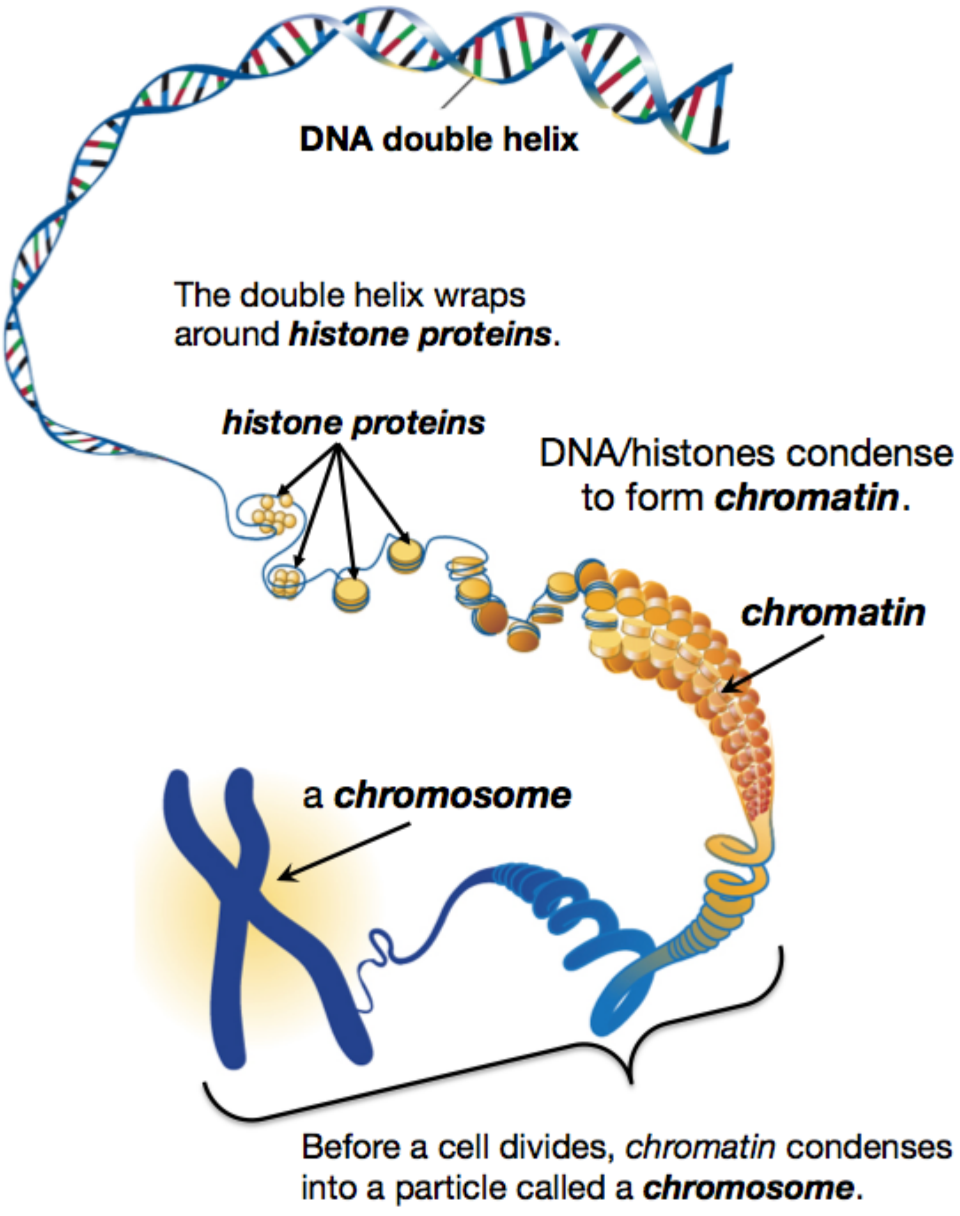
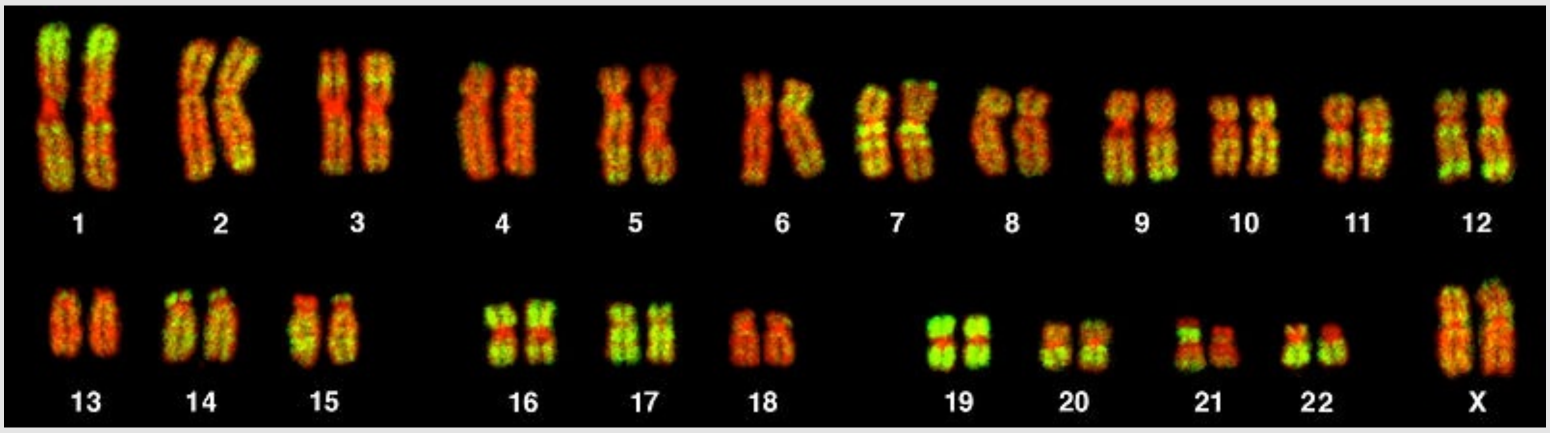


Figure 14.2 is a compilation of images of the human chromosomes (during mitosis).

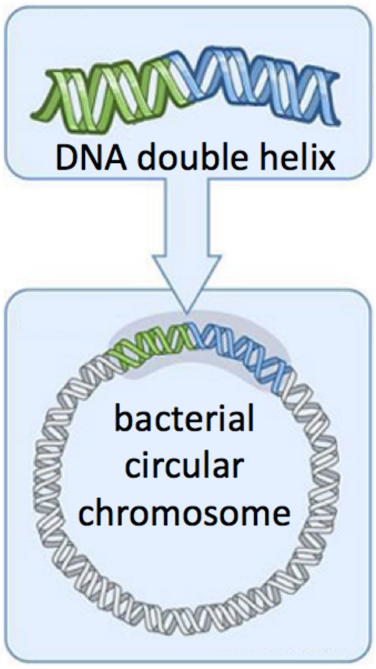
Figure 14.2 **Human Chromosomes**



Optical microscope images of human (female) chromosomes.

Source: Wikimedia Commons, Authors: Andreas Bolzer, Gregor Kreth, Irina Solovei, Daniela Koehler, Kaan Saracoglu, Christine Fauth, Stefan Müller, Roland Eils, Christoph Cremer, Michael R. Speicher, Thomas Cremer, CC-BY, https://creativecommons.org/licenses/by/2.5/deed.en

In *bacteria*, which do not have nuclei, chromosomes exist as circular units, called **circular chromosomes**, as illustrated on the right. Circular chromosomes can twist/fold into more compact shapes. In addition to circular chromosomes, bacteria contain smaller, *yet still circular*, double-stranded DNA units called **plasmids**.



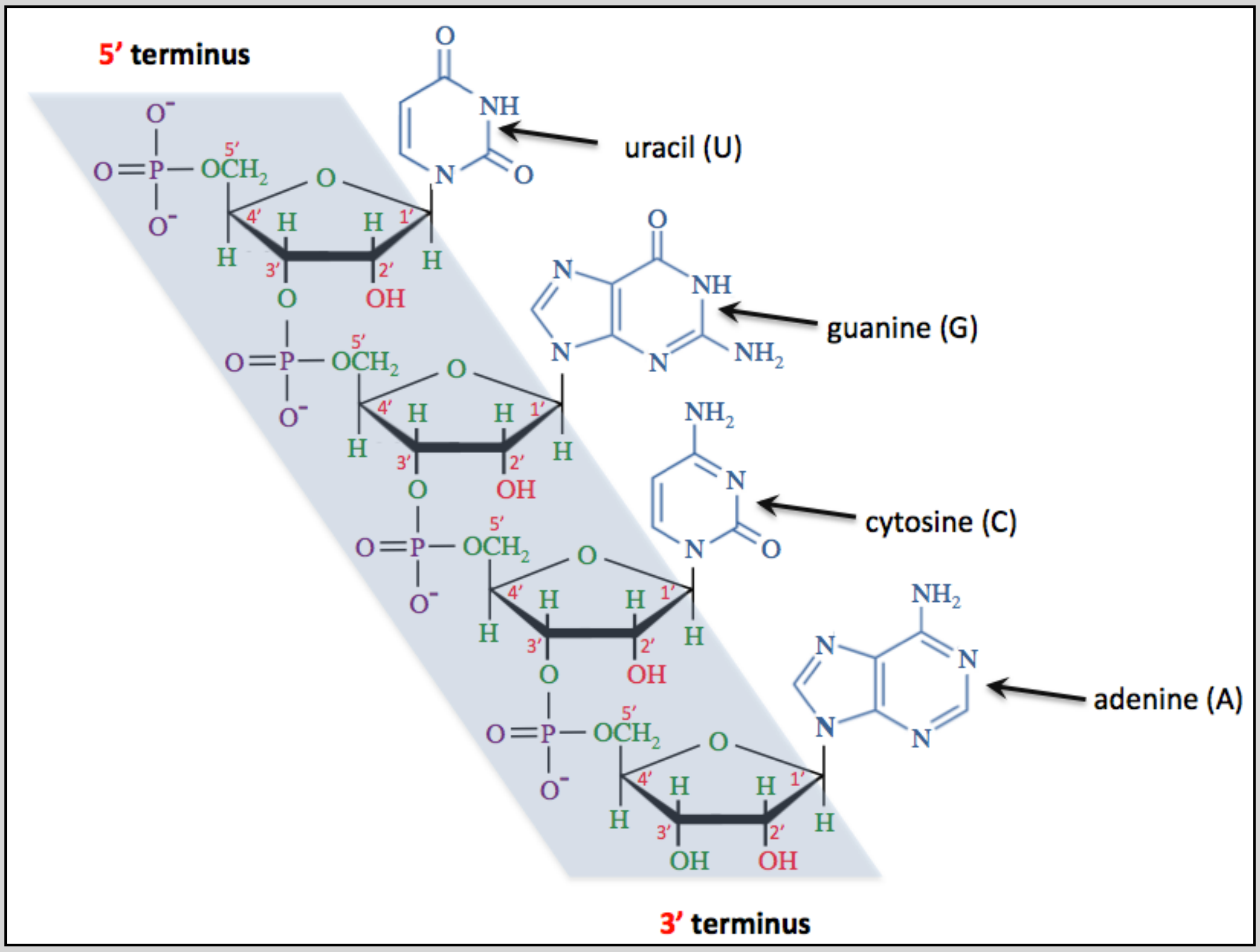
Denaturation of the DNA Double Helix

DNA double helices are held together by hydrogen bonding between complementary base pairs. Disruption of these attractive interactions is called **DNA denaturation**. If enough disruption occurs, the DNA strands of a double helix will completely separate from each other. DNA can be denatured by the same agents that are responsible for the denaturation of proteins. Many important laboratory processes that are involved in biological research and clinical diagnostics use heat to denature the double helix structure of DNA. Unlike *protein* denaturation, when *DNA* is denatured by heat and then allowed to cool to room temperature, the DNA strands will recombine into the original double helix shape. When complementary DNA strands re-form their double helix structure, it is referred to as **annealing**. Annealing of DNA strands is possible because of complementary base pairing. In *protein* denaturation, anything more than extremely small temperature changes usually results in *irreversible* denaturation.

RNA Primary Structure

RNA is a polynucleotide that contains *ribose* residues, phosphate groups, and adenine, guanine, cytosine and uracil organic bases. The sequence of nucleotides in RNA is referred to as **RNA's primary structure**. The primary structure of a small section of RNA is illustrated in Figure 14.3.

Figure 14.3 Primary Structure of a Small Section of RNA



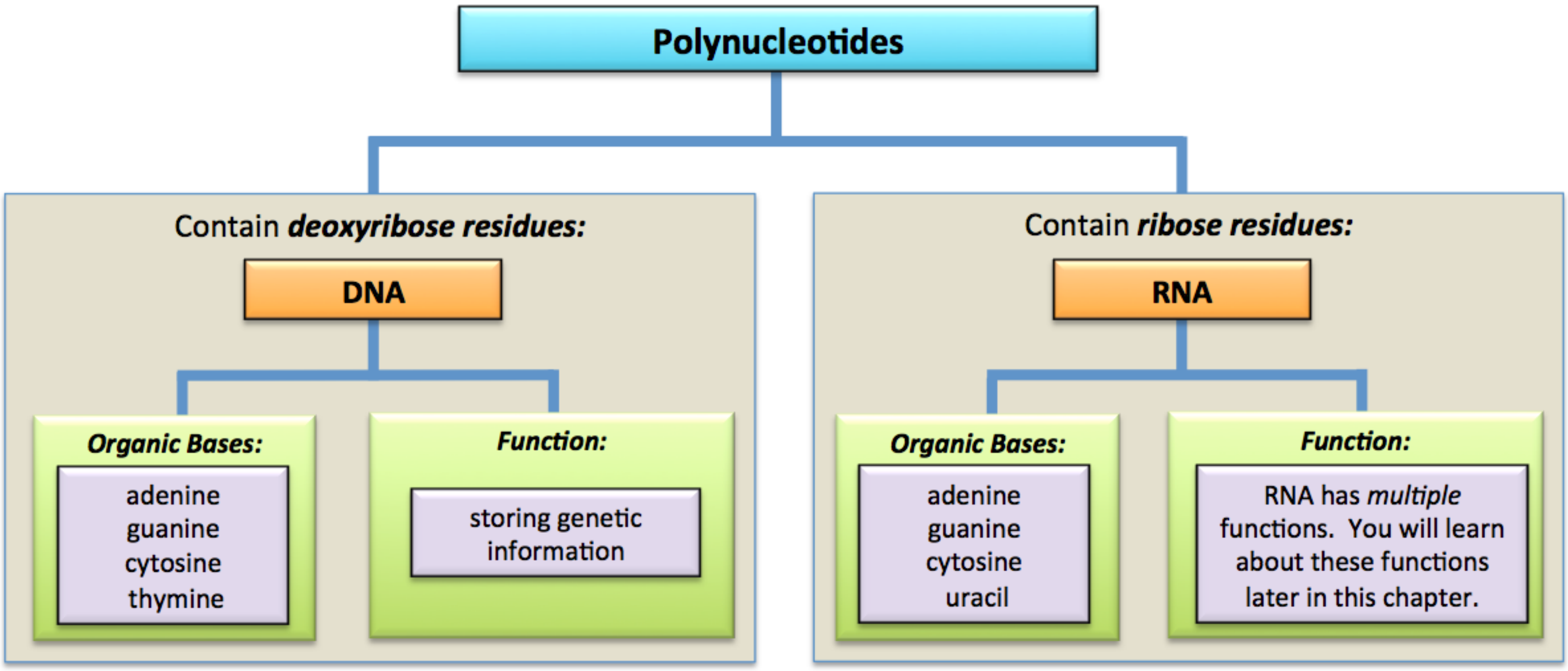
A sequence of nucleotides (primary structure) in a small section of RNA.

DNA contains ***deoxy****ribonucleotide* residues, which have two hydrogen atoms bonded to the carbons in the **2'** positions. **RNA** contains *ribonucleotide residues,* which have one hydrogen atom and one hydroxyl group (OH) bonded to the carbons in the **2'** positions.

The primary structures of DNA and RNA differ in another way; **DNA** contains *thymine* organic bases, however **RNA** does not; it contains *uracil* organic bases instead.

DNA has just one function - storing genetic information. RNA has several functions. The overall shape of an RNA particle depends on its function. I will discuss the three types of RNA that are involved in protein synthesis in a later section of this chapter.

Differences Between the Two Classes of Polynucleotides: RNA vs. DNA



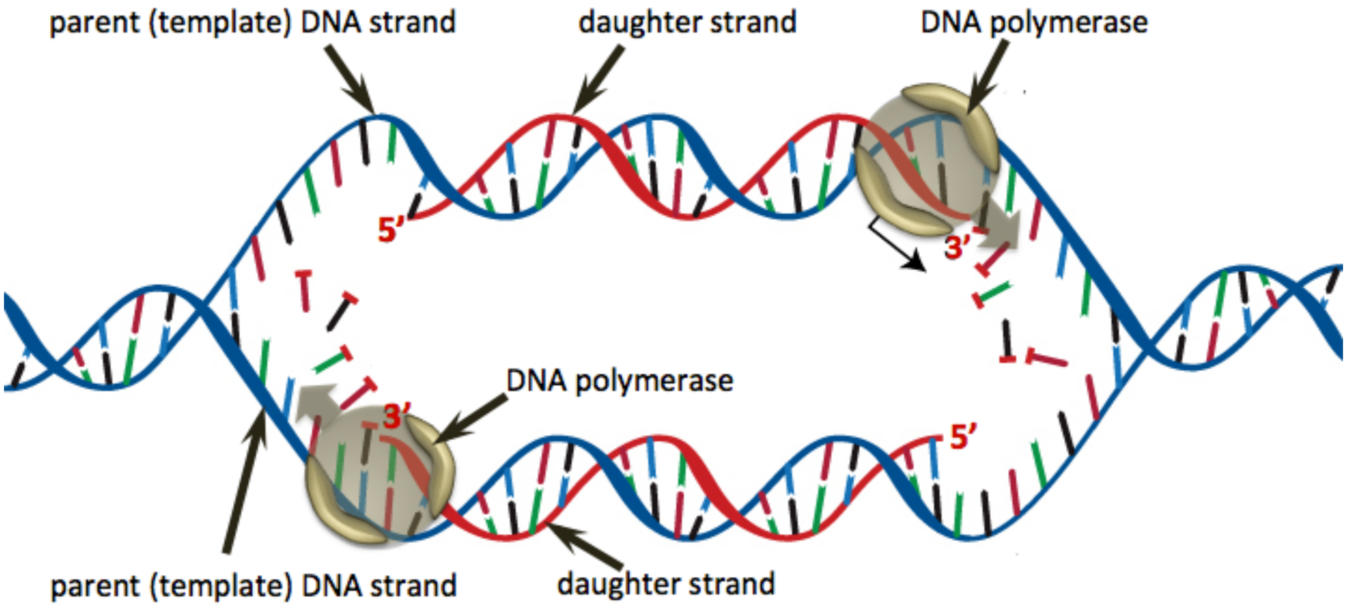
14.4 DNA Replication

Figure 14.4 An Onion Cell Dividing

In the beginning of the division of somatic cells, DNA coils into compact structures called chromosomes (stained dark grey/black in the image). Next, the DNA/chromosomes are replicated. As the cell divides, the new cells each receive identical versions of the original DNA.
Source: Wikimedia Commons, Author: Martin Bahmann, CC-BY-SA, http://creativecommons.org/licenses/by-sa/3.0/legalcode

Self-replication is a common characteristic to all known life forms. In order for organisms to grow and reproduce, cells must divide. When a cells divides, the original cell, called the *parent cell*, forms two new cells that are called the *daughter cells*. Before a somatic cell (non germ/sex cell) physically splits into two daughter cells, an exact duplicate of all of the parent cell's DNA must be made so that a copy can be placed in each daughter cell. Figure 14.4 shows the duplicate copies of darkly-stained onion DNA being separated from each other so they can be distributed into the forming daughter cells.

The process in which a duplicate copy of a DNA double helix is made is called **DNA replication**. In DNA replication, each of the two original DNA strands (called the ***parent strands***) is used as a "template" for the formation of a new "**daughter strand.**" This process begins in a period of the cell lifecycle when DNA is in the form of chromatin (not chromosomes). In eukaryotic cells, proteins called "helicases" unwind and then open sections of the double helices by disrupting the hydrogen bonds between base pairs. Once a double helix has opened, DNA polymerase enzymes catalyze the formation of complementary daughter strands *on* ***each*** *of the parent strands*. The daughter strands are formed by adding *free deoxyribonucleotides*, from within the nucleus, one-by-one to the growing daughter strands, as illustrated below.



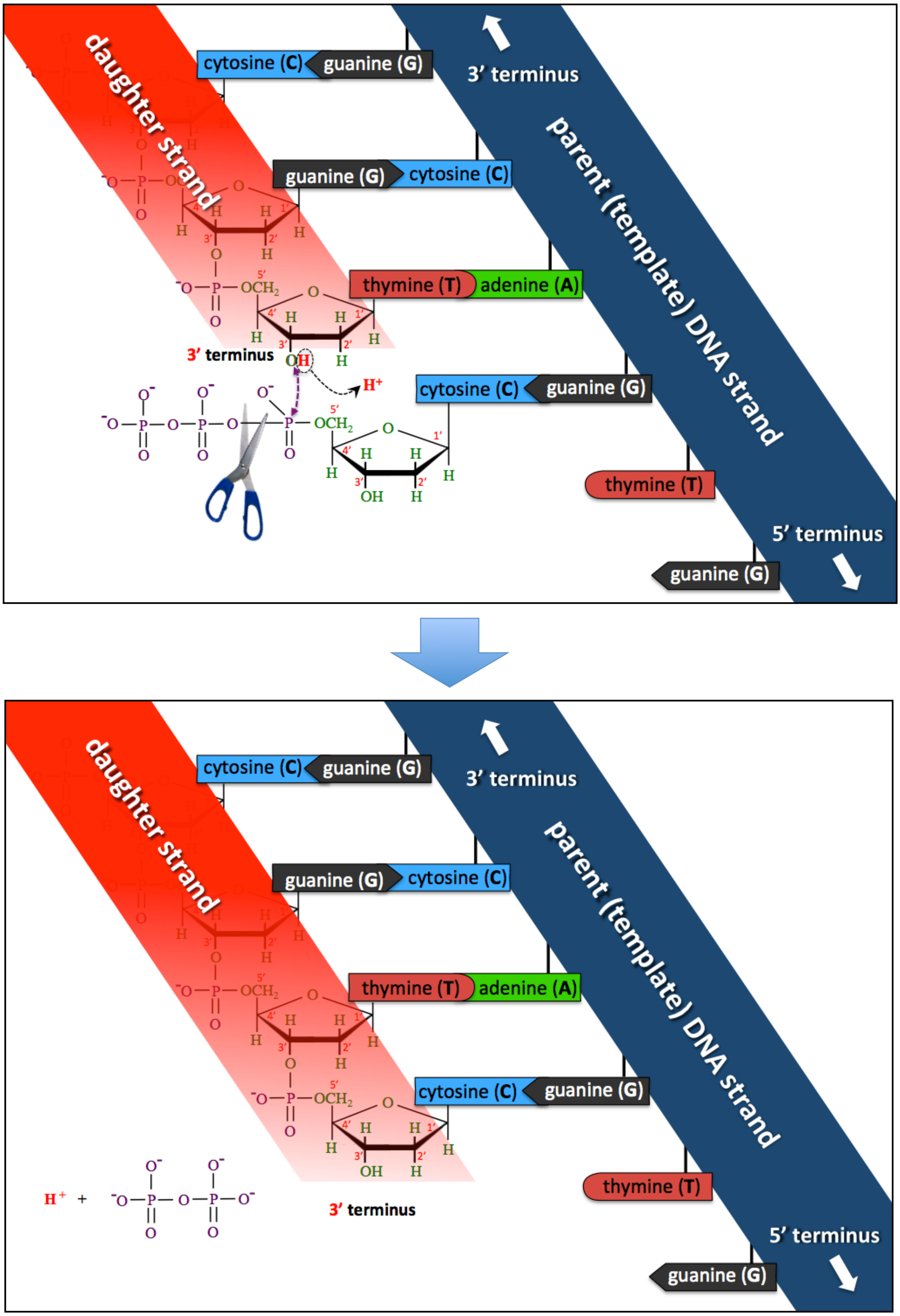
In this image, the sugar-phosphate backbone of the parent DNA strands are shaded blue and daughter strands are shaded red. I would like to draw your attention to a few important points:

1) Because each daughter strand is assembled, nucleotide by nucleotide, with organic bases that are *complementary* to one of the parent strands, then both of the double-stranded DNA particles that result from the replication process are ***identical to the original DNA particle***. This is often referred to as **semiconservative replication**.

2) DNA polymerase enzymes catalyze the addition of nucleotides to the **3'** terminus of the growing ***daughter strand***. In order to do this, DNA polymerase moves along the ***parent (template) strand*** in the direction from **3'** terminus to **5'** terminus of the ***parent*** strand. Only the *daughter* strand terminuses are labeled (**3'** or **5'**) in this figure. The arrows drawn on the DNA polymerase enzymes in the illustration indicate their paths along the parent strands.

3) In plants and animals, this process occurs simultaneously *at multiple places along each parent strand*. Although ***not shown*** *in the image above*, these multiple sections of a daughter strand are linked/bonded together with the help of *DNA ligase enzymes*.

Let’s take a closer look at the chemical reaction that is involved in adding a nucleotide residue to a growing daughter strand. After helicase proteins unwind and open the DNA double helix parent strands, DNA polymerase enzymes catalyze the formation of ***phosphodiester bonds*** between free nucleotide triphosphates and the **3’** terminus of a growing daughter strand. The daughter strands that are produced are complementary to their template parent strands because ***DNA polymerase directs the addition of nucleotide triphosphates that are complementary to the adjacent parent strand bases***. This reaction is illustrated below for the addition of deoxy*cytidine* triphosphate to a growing daughter strand.



In this case, a triphosphate with the *cytosine* (C) base was added because of the adjacent complementary *guanine* (G) base in the template parent strand.

Review 14.4: DNA Replication

Using the illustration on the previous page, name the next nucleotide triphosphate that would be added to the growing daughter strand.

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

DNA polymerase is quite accurate in adding the nucleotides to the daughter strand that are complementary to nucleotides in the template parent strand. Daughter strands are produced with an error rate (wrong, missing, or extra base pairs added) that is on the order of *one error* every 10,000 bases. Some DNA polymerase enzymes are capable of proofreading. They can remove incorrectly matched (noncomplementary) nucleotides from the growing end of a daughter strand. Finally, ***DNA repair enzymes*** can check daughter strands for errors and replace the incorrect nucleotides with the correct ones. At the end of these processes, DNA can be replicated with error rates of about *one error* every 10^9 base pairs. This is quite impressive; it would be analogous to typing about 100 lengthy novels while making only *one mistake*! Nature is amazing. When an error is not corrected in DNA replication, it is referred to as a **mutation**. Mutations are responsible for many diseases. I will discuss diseases that result from mutations in a later section of this chapter.

Can you think of a reason why life, as we know it, would be quite different (or nonexistent) if DNA replication could be accomplished error-free? Think about it, then compare your thoughts with what I tell you in the next paragraph.

Mutations can result in daughter cells that are *less functional* than the parent cell. In most cases, this is not a major problem for multicellular organisms. However, if a mutation occurs in a sex cell (i.e. sperm or ovarian cell), and the cell is used in reproduction, then the mutation will be present in the DNA of *every* cell nucleus of the organism's offspring. Depending on the location of the mutation in the DNA sequence, the mutation usually results in equally ***or*** less functional cells. In very rare cases, the mutation will result in an organism that functions in a superior manner, allowing the organism and its descendants to reproduce more frequently. This is process called ***natural selection*** and is central to the ***theory of evolution***. ***Errors in DNA replication make evolution possible***. Nature has found a balance between having too many and too few DNA replication errors.

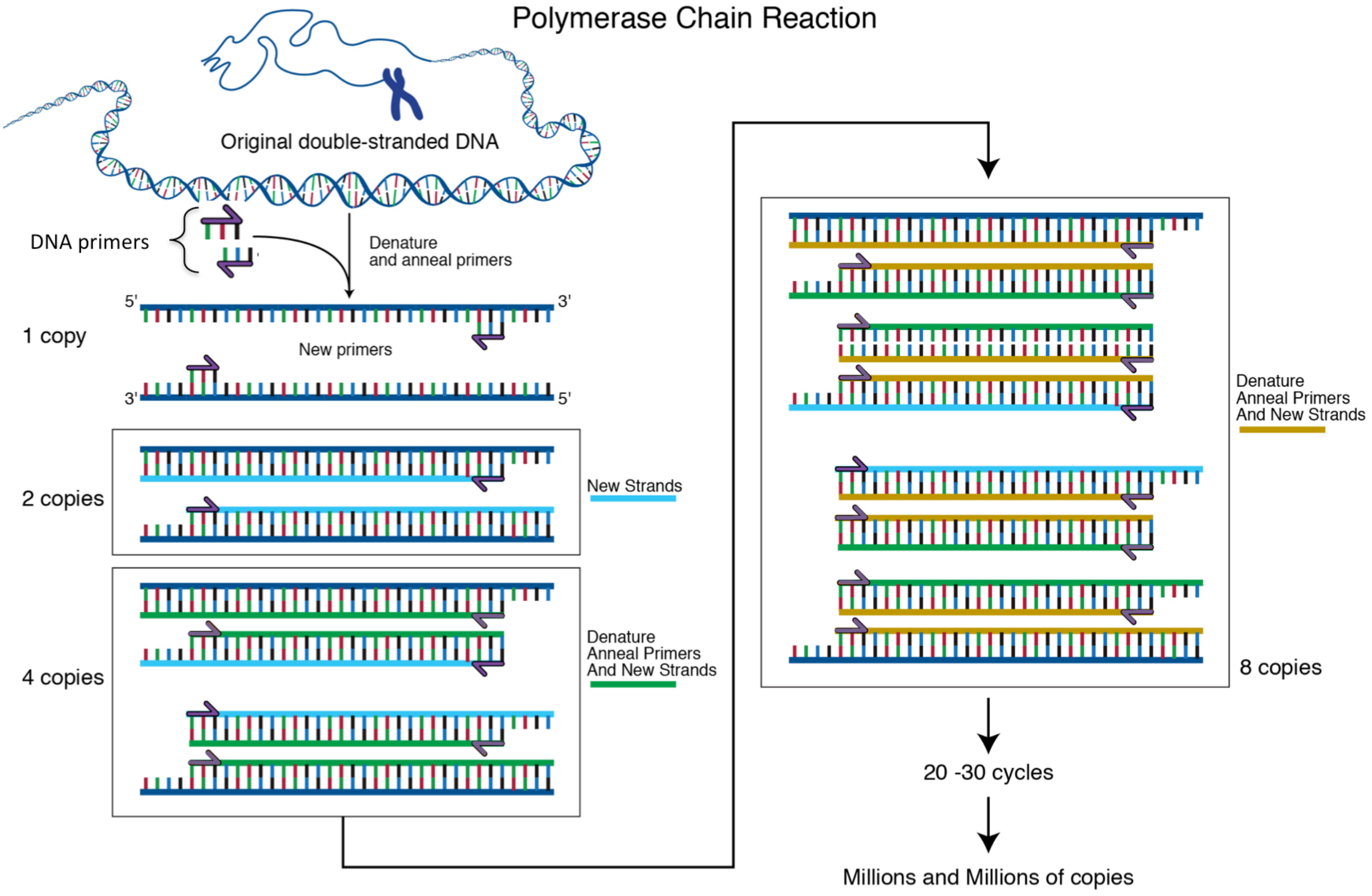
Review 14.5: DNA Replication

Choose whether each of the following statements about DNA replication is ***true*** or ***false***.

a. A double helix can be converted to two identical double helices.
b. If the sequence within a parent template strand is **5'**-CGCGTTA-**3'**, then the sequence of its daughter strand would be **5'**-GCGCAAT-**3'**.
c. If the sequence within a parent template strand is **5'**-CGCGTTA-**3'**, then the sequence of its daughter strand would be **3'**-GCGCAAT-**5'**.
d. One of the double helices produced in DNA replication contains the two parent strands, and the other double helix contains the two daughter fragments.
e. The two parent strands are complementary to each other and therefore, the two daughter strands are complementary to each other.
f. DNA polymerase moves in the direction from **5'** terminus of the parent (template) DNA strands toward the **3'** terminus of the parent strands.
g. DNA polymerase catalyzes the addition of nucleotides to the **3'** terminus of the growing daughter strand.

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

It is possible to perform DNA replication in vitro (outside of a cell, e.g. in a test tube) using a process called the **polymerase chain reaction (PCR)**. Starting with just a single DNA double helix, *millions of replications* of a desired section of the double helix can be made. This process involves the use of DNA polymerase that has been extracted from organisms such as bacteria. PCR was invented by Dr. Kary Mullis in 1983, and he was awarded the 1993 Nobel Prize in Chemistry for this work. PCR was a major breakthrough in the field of biochemistry and has enabled many new technologies such as DNA fingerprinting used in forensic science, and the testing for genetic and infectious diseases. The PCR process is illustrated and described below.



PCR begins by adding DNA polymerase enzyme and small single stranded "DNA primers" to a sample of DNA.   The DNA double helices in the sample are each separated into two single strands by heat ***denaturation*** (~95^{o}C). Next, in an ***annealing*** step, the mixture is cooled and the primers bind to specific regions of the sample DNA strands. The DNA primers are chosen to be complementary to a specific nucleotide sequence on the sample DNA, based on the section of the DNA that is to be replicated. Primers are represented by small purple arrows (⇀) in the figure. Daughter strand production, catalyzed by DNA polymerase, proceeds in the direction of the primer arrows, and results in the replication of a desired section of the sample DNA (as shown in the box labeled "**2 copies**"). The two original DNA strands are shaded dark blue and the daughter strands are shaded light-blue. The process of *denaturing*, then *annealing*, then daughter strand *growth* is referred to as a **PCR cycle**. In the next PCR cycle, the two copies are denatured to give ***four*** template DNA strands, then primers bind (anneal) to the four template strands and a second generation of daughter strands are produced, as shown in the box labeled "4 copies." The second generation of daughter strands are shaded green. Note that there are now ***four*** copies of the desired section of original DNA. In the next PCR cycle, a third generation of daughter strands are made, giving ***eight*** copies of the original DNA section. As this process repeats, each new PCR cycle doubles the number of copies present. After 20-30 cycles, millions of copies are made. Note that the DNA polymerase used in PCR must not be denatured in the heating part of the cycle. It is for this reason that the polymerase used in PCR comes from the *Thermus aquaticus* (Taq) bacterium extremophile, which evolved in hot springs. To get an idea of how doubling the number of copies 30 times leads to millions of copies, think of it in terms of money.   If you were to give someone a penny on the first day of the month, then double the amount you give them every day for 30 days, you would pay them over 10 million dollars! This is called exponential growth and it allows for just a few sample DNA particles to be replicated into an amount that can be readily detected (and quantified) with standard laboratory equipment.

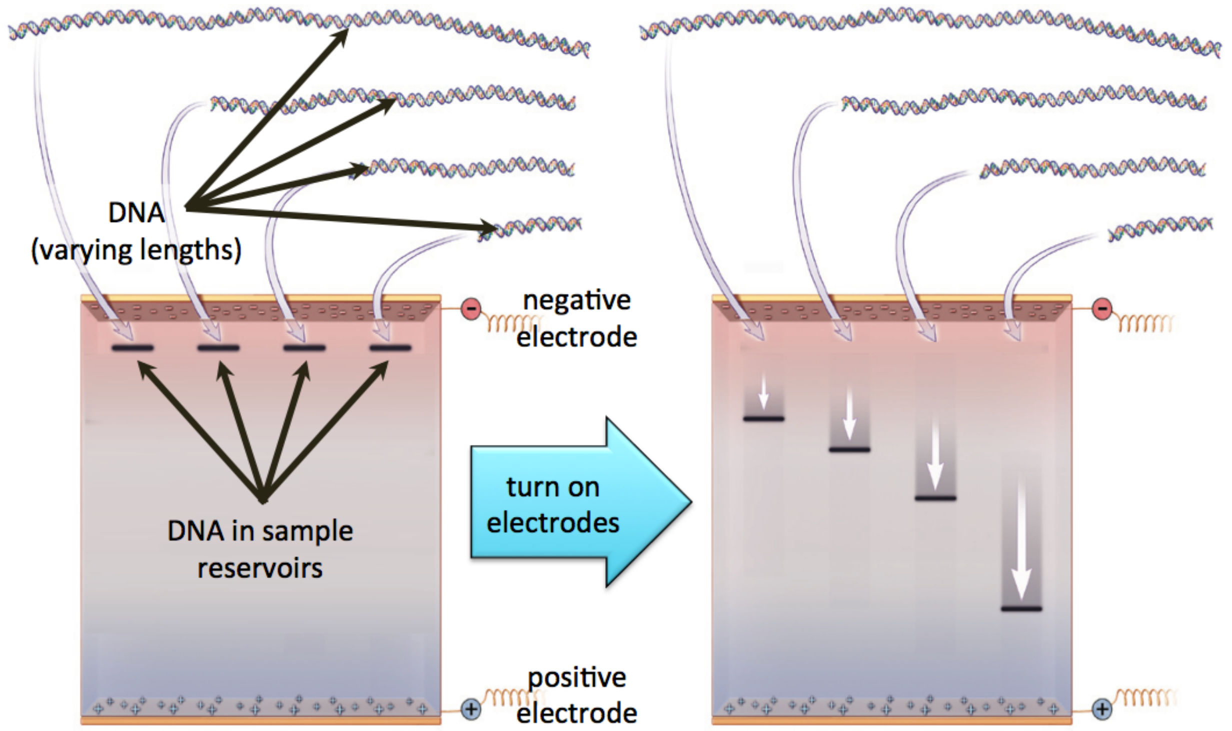
An example of the use of PCR can be seen in **DNA fingerprinting** (also called **DNA profiling**), which is used in forensic science. If a very small sample of DNA evidence, such as a single hair or small amount of bodily fluid, is collected at a crime scene, the DNA present in the sample can be replicated by PCR, then analyzed and compared with the DNA of a suspect. In humans, 99.9% of DNA is identical. However, since human DNA contains about 30 billion base pairs, there remains a considerable amount of variation in the 0.1 % of DNA that is *not the same* in all humans.

In *DNA fingerprinting*, specific regions of DNA that are known to be quite variable among different individuals (like a fingerprint) are analyzed so that they can be used for identification. These specific regions of DNA, called **short tandem repeats** (**STR**s), do not directly code for protein production, and contain *repeating nucleotide sequences*. For example, a particular STR, referred to as TH01, used for DNA fingerprinting in the US, has a repeating sequence of AATG. The number of times that a sequence is repeated in a particular STR varies from individual to individual; it is this variance that allows individuals to be identified. For example, one person may have *three* repeats of AATG in their TH01 STR, whereas another person can have *five* repeats:

Person #1: - AATG AATG AATG -
Person #2: - AATG AATG AATG AATG AATG -

Forensic scientists in the US currently analyze thirteen different STRs for DNA fingerprinting. PCR is carried out using thirteen pairs of PCR primers; one unique pair is used for *each STR*. Each primer pair has nucleotide sequences that are complementary to human DNA such that DNA polymerase will replicate the STR of interest. After PCR, there will be millions of copies of each of the thirteen STRs. The number of repeating units contained in each STR is determined by measuring *the number of total base pairs it contains*. This is done using a technique called **gel electrophoresis.** In gel electrophoresis, samples to be analyzed are placed in small reservoirs in a hydrophilic polymer called a ***gel***. The gel has electrodes on opposite sides, as illustrated on the left. Since DNA has a negative formal charge on the phosphate group, when the electrodes are powered, the DNA moves toward the positive electrode. The fewer base pairs that DNA has, the smaller it is, therefore the more readily it passes through pores in the gel and the faster it moves. An illustration of the gel electrophoresis process is shown on the left.

Illustration of Gel Electrophoresis



PCR and gel electrophoresis is done for the thirteen STRs in the DNA evidence that was collected at the crime scene ***and*** in the suspect's DNA. The STR analysis of the DNA evidence is then compared to the analysis of the suspect's STRs (or with a DNA data bank containing STR analysis data of many individuals). If just *one* of the suspect's STRs were inspected and found to have the same number of base pairs as an STR found at the crime scene, this would not be very strong evidence. There is about a 5-20% chance of two individuals having the same number of repeating base pairs *for a particular STR*. However, when thirteen STRs are compared, the chance of two individuals having the same number of repeating base pairs *for all thirteen STRs* is less than one in a billion (10^9). The exception to this is for individuals who are related, especially *identical twins*.

Review 14.6: Electrophoresis

If one DNA particle containes 187 nucleotides and another DNA particle contains 96 nucleotides, which of the two particles would move faster during gel electrophoresis?

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14.5 Protein Synthesis

In the previous section, you learned how **DNA replication** enables the information in DNA to be passed from generation to generation of cells and organisms. In this section, you will learn how the information contained in the sequence of DNA nucleotides is used to generate proteins. This process is central to the existence of all known lifeforms because proteins are critical in directing and controlling cell growth and function, and in regulating an organism's metabolism. The process of making proteins from the information in DNA is called **protein synthesis** or **gene expression**. The diagram below summarizes the flow of DNA information.

Protein synthesis can be divided into two sequential processes: **transcription** and **translation.**

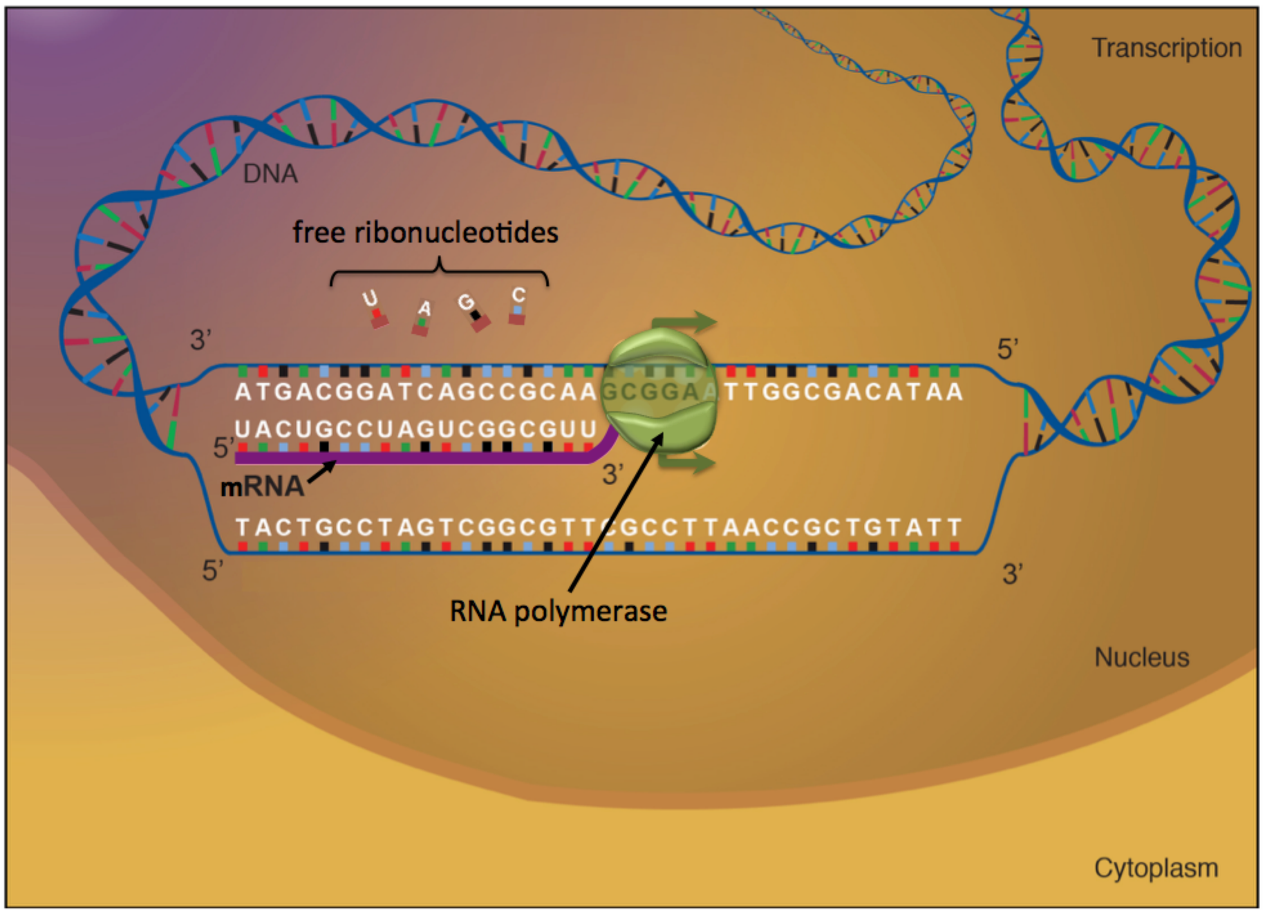
Transcription: DNA to mRNA

A **gene** is generally defined as *a region of DNA that carries the information needed to produce a protein*. Human DNA contains about 25,000 genes. The first step in *protein synthesis* is called **transcription**. In the transcription process, the information (sequence of nucleotides) in a gene is used to create a specific sequence of *ribo*nucleotides in a single-stranded **messenger RNA** (**mRNA**) particle. Another way to say this is, "the information in a gene is ***transcribed*** to mRNA."

The *transcription process* is similar to DNA replication, with three main differences:

1) RNA is produced in transcription, whereas DNA is produced in DNA replication.
2) In transcription, only ***one*** of the DNA double helix strands is used as a template to produce ***one mRNA strand***, whereas in DNA replication, ***each*** of the two DNA strands in a double helix produce a daughter strand.
3) Different enzymes are used.

Transcription begins when an **RNA polymerase enzyme** binds to a "**promoter site**" on the gene to be transcribed. ***Promoter sites*** are specific sequences of nucleotides at the beginning of a gene. When RNA polymerase binds to the promoter site, the hydrogen bonding between base pairs within the DNA double helix is disrupted. This unwinds and opens a section of the gene's double helix. Next, *RNA polymerase* moves along one strand of the gene while catalyzing the addition of *free ribonucleotides,* that are complementary to the DNA template, to the **3'** end of a growing mRNA strand. When the RNA polymerase reaches a nucleotide sequence in the gene, called the **termination site**, the mRNA strand is released. This process occurs in the nucleus of eukaryotic cells and in the cytoplasm of prokaryotic cells. A simplified visualization of transcription (in a eukaryotic cell) is illustrated on the left.



The DNA-to-RNA base pairing is a bit different from the DNA-to-DNA base pairing because RNA contains *uracil* (U) and does not contain *thymine* (T). DNA organic bases C,G,T, and A base pair with RNA bases G, C, A, and U, respectively, as shown in the illustration.

Although not shown in the illustration on the previous page, in eukaryotic cells, there are regions of RNA that undergo additions and deletions of nucleotides in a process called **co-transcriptional modifications**. A discussion of the details of co-transcriptional modifications is beyond the scope of this book.

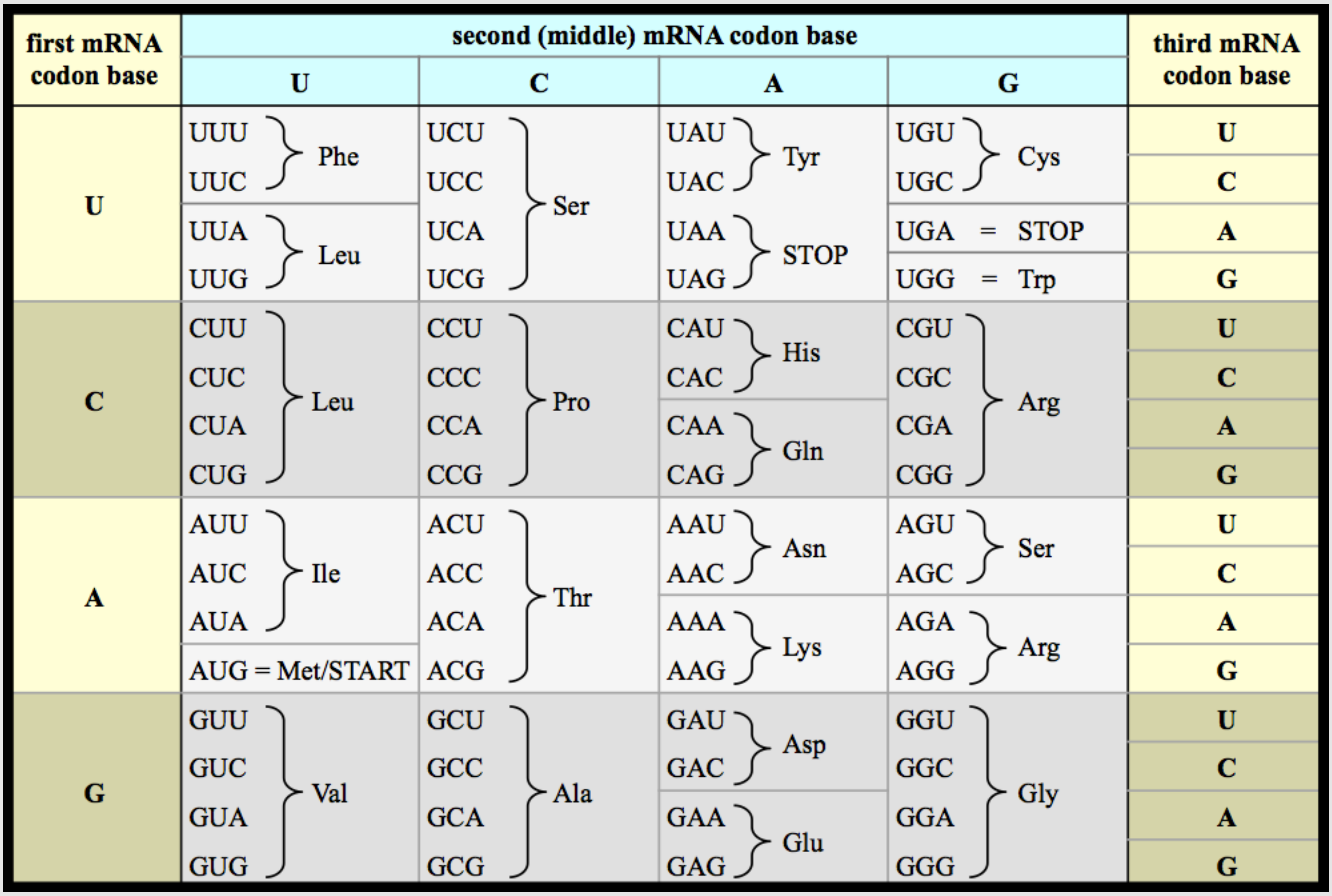
Messenger RNA produced in the transcription process contains the information (message) from a gene that is required to produce a protein. In eukaryotic cells, mRNA exits the nucleus through pores in the nuclear membrane and enters the cytoplasm where the *protein synthesis* process will be completed.

About 1.5% of human DNA is in the form of a gene; the remaining 98.5% is called **noncoding DNA**. Until recently, the noncoding DNA was called “junk DNA.” It was thought that all noncoding DNA is extraneous DNA that has been passed down, through evolution, from ancestral species. More recently, research has shown that not all noncoding DNA is “junk.” For example, noncoding DNA has been found to play a role in the regulation of transcription.

Translation: mRNA to Protein

The next step in *protein synthesis* is called **translation**. In this process, the information that was in a gene and is now contained in mRNA is used to construct the polypeptide chains that make up proteins. In the last chapter, you learned that the sequence of *amino acids* in a polypeptide is referred to as its *primary structure*, and that the *primary structure* of a protein ultimately determines its secondary, tertiary, and quaternary structure. In *translation*, the sequence of nucleotides in mRNA, is converted (translated) to a sequence of amino acid residues in a *polypeptide*. This is done using the **genetic code**. The *genetic code* is based on three-nucleotide sequences, called **codons**. A *codon* directs the addition of a specific amino acid residue to a polypeptide that is being formed. For example, the mRNA three-nucleotide sequence (codon) **GAU** codes for the addition of an *aspartic acid* (Asp) amino acid residue to a growing polypeptide chain. The genetic code was completely known by the late 1950’s and is shown in Table 14.1.

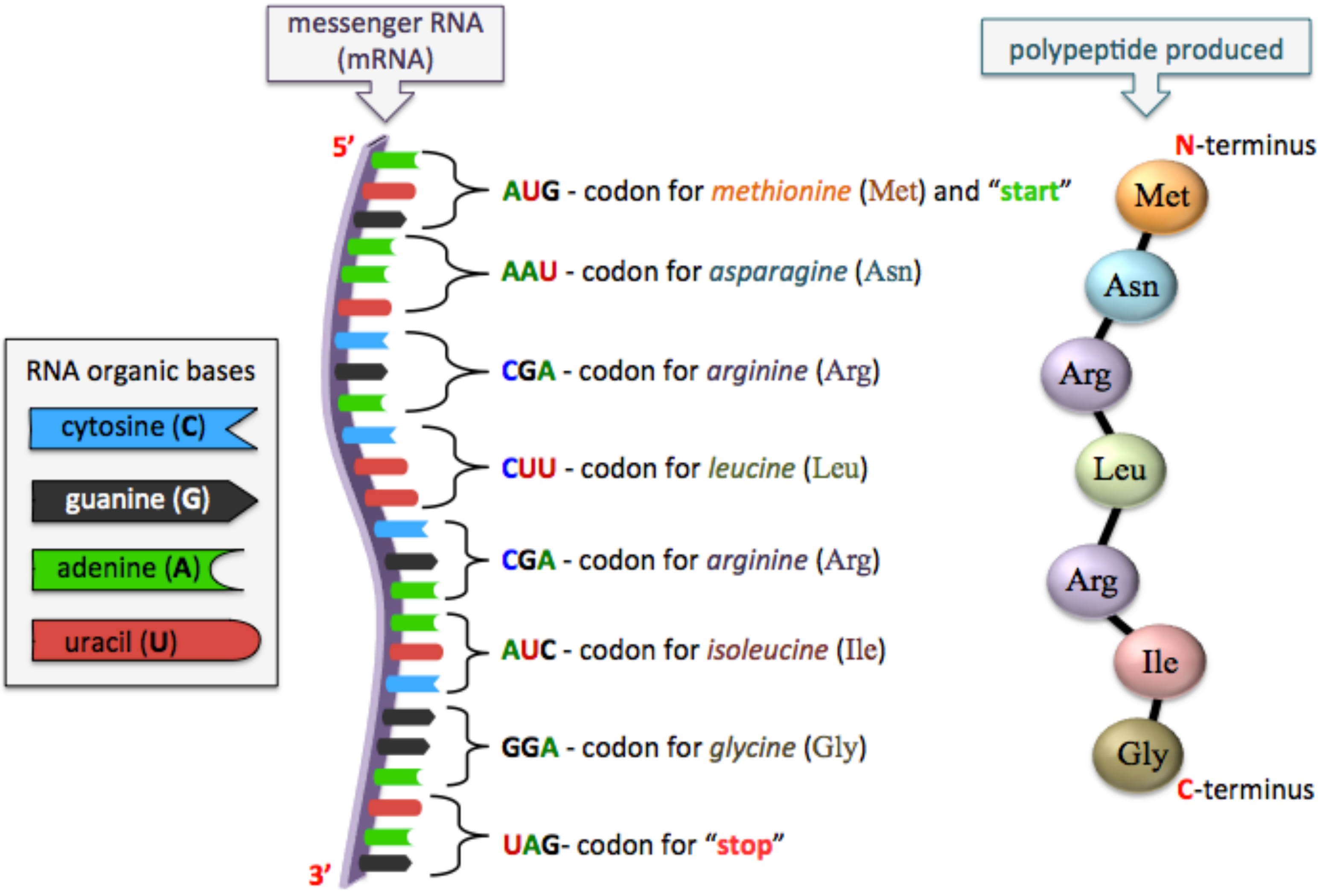
Table 14.1 **Genetic Code Table: The mRNA Codons and the Amino Acids for which they Code**



first mRNA codon base	second (middle) mRNA codon base								third mRNA codon base
	U		C		A		G		
U	UUU	Phe	UCU	Ser	UAU	Tyr	UGU	Cys	U
	UUC		UCC		UAC		UGC		C
	UUA	Leu	UCA		UAA	STOP	UGA	= STOP	A
	UUG		UCG		UAG		UGG	= Trp	G
C	CUU	Leu	CCU	Pro	CAU	His	CGU	Arg	U
	CUC		CCC		CAC		CGC		C
	CUA		CCA		CAA	Gln	CGA		A
	CUG		CCG		CAG		CGG		G
A	AUU	Ile	ACU	Thr	AAU	Asn	AGU	Ser	U
	AUC		ACC		AAC		AGC		C
	AUA		ACA		AAA	Lys	AGA	Arg	A
	AUG	= Met/START	ACG		AAG		AGG		G
G	GUU	Val	GCU	Ala	GAU	Asp	GGU	Gly	U
	GUC		GCC		GAC		GGC		C
	GUA		GCA		GAA	Glu	GGA		A
	GUG		GCG		GAG		GGG		G

The mRNA nucleotide sequences in the codons are listed in the direction of the mRNA 5’ terminus toward the 3’ terminus.

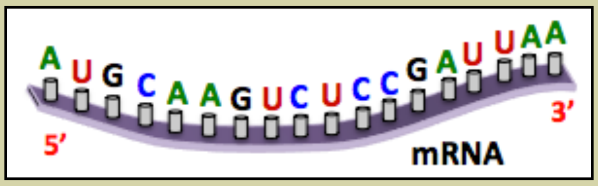
The “start” codon (**AUG**) determines the first amino acid residue to be used in the polypeptide. Peptides are synthesized in the direction from their **N-**terminus to their **C-**terminus. The “stop” codons determine the final amino acid to be added to the polypeptide. I will elaborate using an illustration. In nature, mRNA sequences contain hundreds to many thousands of nucleotide residues, however, for simplicity, I will use a very short mRNA sequence in the illustration. An example of an mRNA sequence, its codons, and the polypeptide chain that it produces are illustrated below.



Since there are ***twenty-one*** common amino acids, and only ***four*** types of RNA nucleotides (**C**, **G**, **A**, **U**), it was necessary for nature to use ***three nucleotides per codon***. ***If*** there were only *one* nucleotide per codon, then only *four* amino acids could have been specified. ***If*** there were *only two nucleotides per codon*, then only *sixteen amino acids* could have been specified.

Review 14.7: Understanding Translation

Write the three-letter abbreviations for the amino acid residues, in order from **N**-terminus to **C**-terminus, of the polypeptide that would be produced in the translation of the mRNA shown below. Recall that in translation, polypeptides are formed in the direction from their **N**-terminus to the **C**-terminus.



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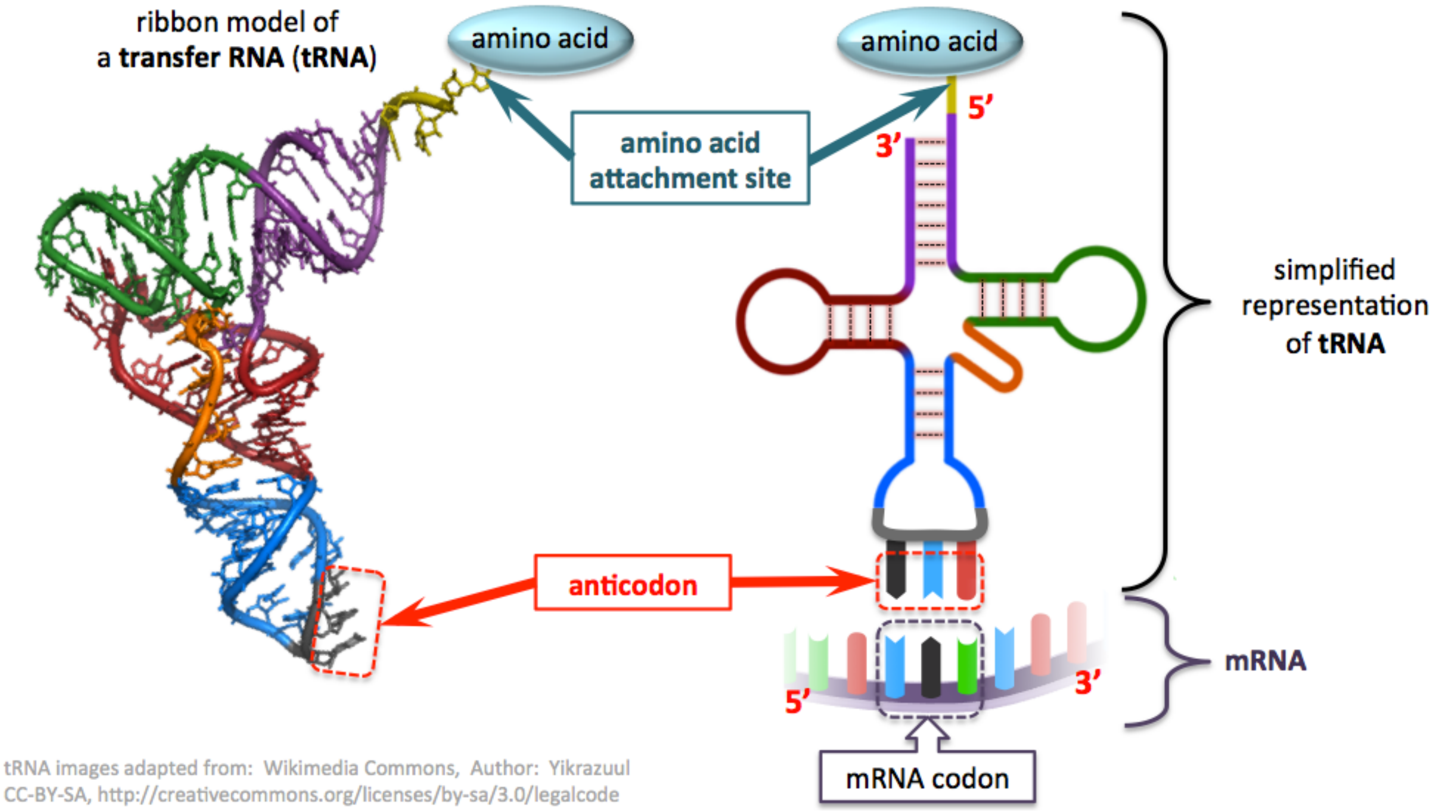
In order for you to understand how the codon information is used to direct the addition of specific amino acids to a growing peptide chain, I must take a moment to tell you about another type of RNA, called **transfer RNA** (**tRNA**). The function of a tRNA particle is to carry and then transfer the amino acid that is specified by an mRNA codon to a growing peptide chain. A ribbon model and a simplified representation of a tRNA particle are shown below.



tRNA images adapted from: Wikimedia Commons, Author: Yikrazuul
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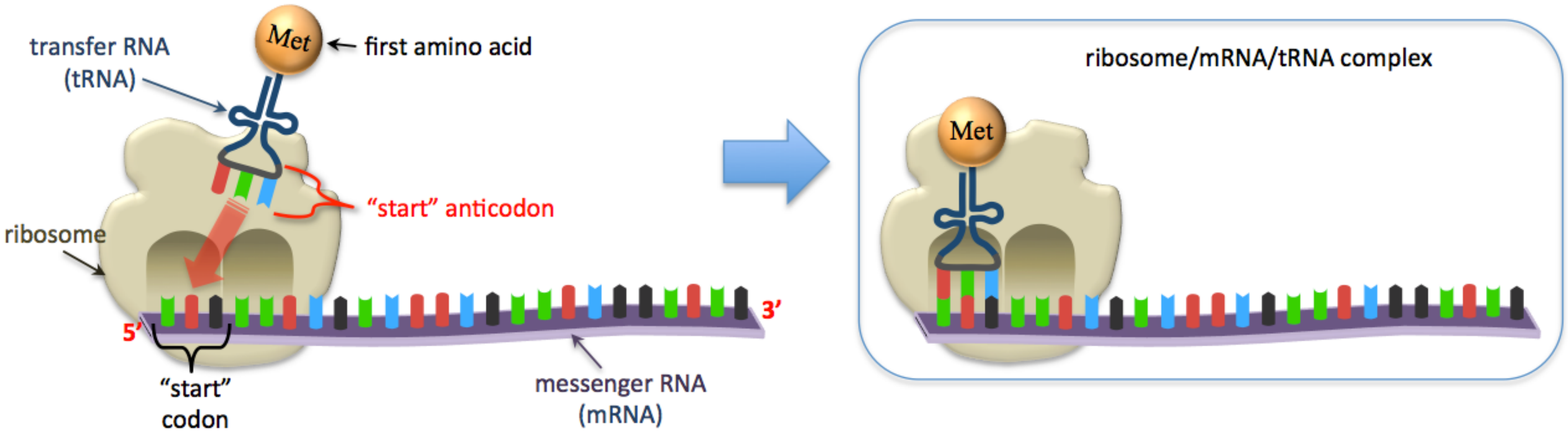
tRNA particles are single-stranded polynucleotides that contains 73 to 93 ribonucleotides. Base pairing causes the single tRNA strand to *fold back on itself*. Hydrogen bonding between tRNA base pairs is represented by the dotted lines that are highlighted red in the simplified tRNA representation. One region of tRNA has a site that attaches to an *amino acid residue,* and another region contains a three-nucleotide sequence called an **anticodon**. The particular amino acid that a tRNA carries depends on the three-nucleotide sequence in its *anticodon*. Anticodons are *complementary* to mRNA codons, as illustrated in the bottom-right of the image above. In the illustration, the mRNA codon (in the **5'** to **3'** direction) is **CGA**, therefore the tRNA anticodon (in the **3'** to **5'** direction) is **GCU**. Using the mRNA codon in this example (**CGA**), and the genetic code table, we find that this tRNA would carry an *arginine* (Arg) amino acid residue. I will discuss the importance of the matching of mRNA codon/tRNA anticodon/amino acid in the following discussion of the translation process.

Translation is a complicated process. We will take a step-by-step overview of its key features in order to understand *how* the nucleotide sequence in mRNA is used to direct the synthesis of a polypeptide. Translation occurs in *three* steps: **initiation**, **elongation**, and **termination**.

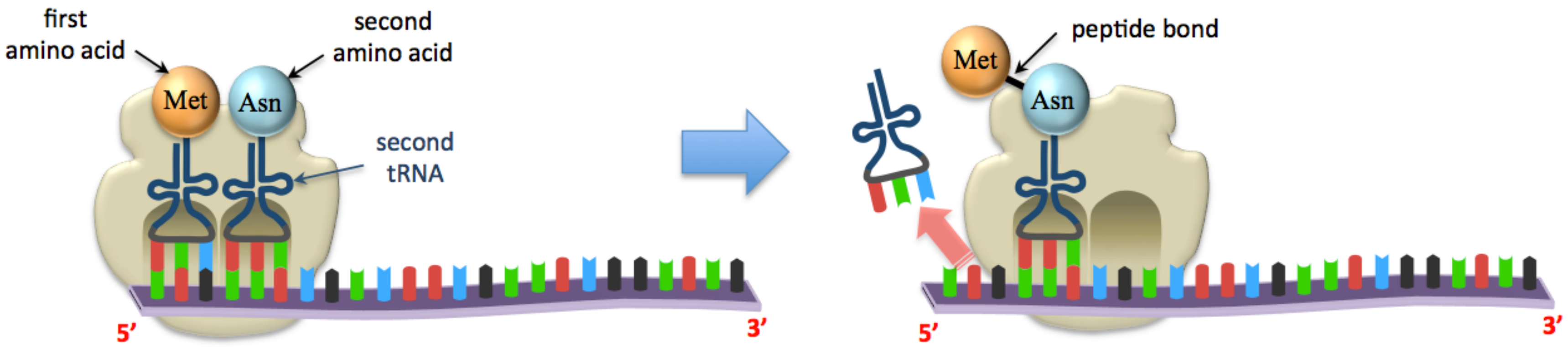
Initiation

Once the *messenger RNA* leaves the nucleus and enters the cytoplasm, a **ribosome** attaches to its "start" codon (**AUG**). *Ribosomes* are relatively large particles that contain protein *and* very long RNA strands called **ribosomal RNA** (**rRNA**). The function of *ribosomes* is to provide a structure upon which polypeptides can be produced. Next, a *transfer* RNA with a "start" *anticodon* (**UAC**) binds to the mRNA start codon to form a ribosome/mRNA/tRNA complex. The formation of this complex, as illustrated below, is called the **initiation step**.

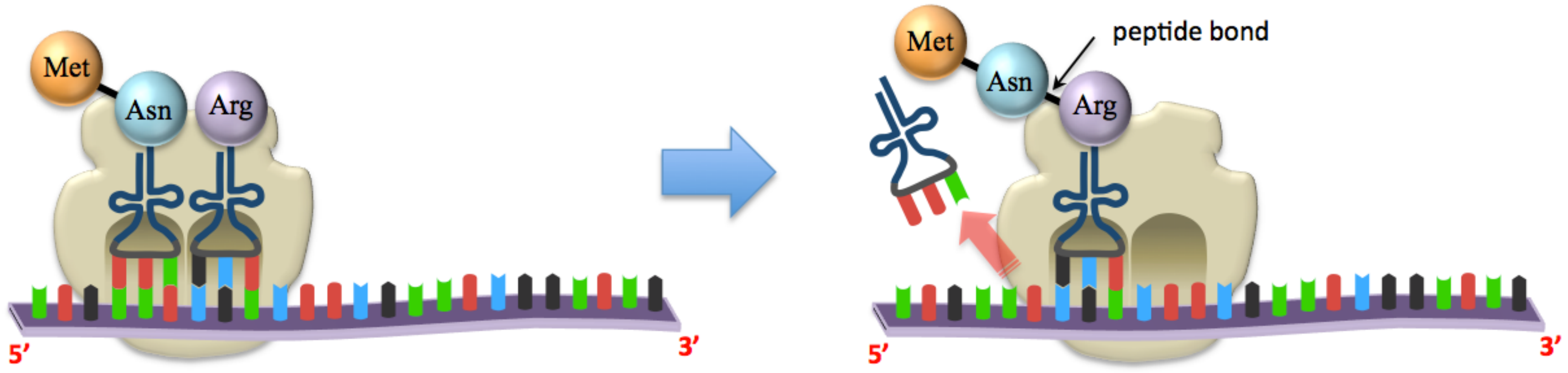


Elongation

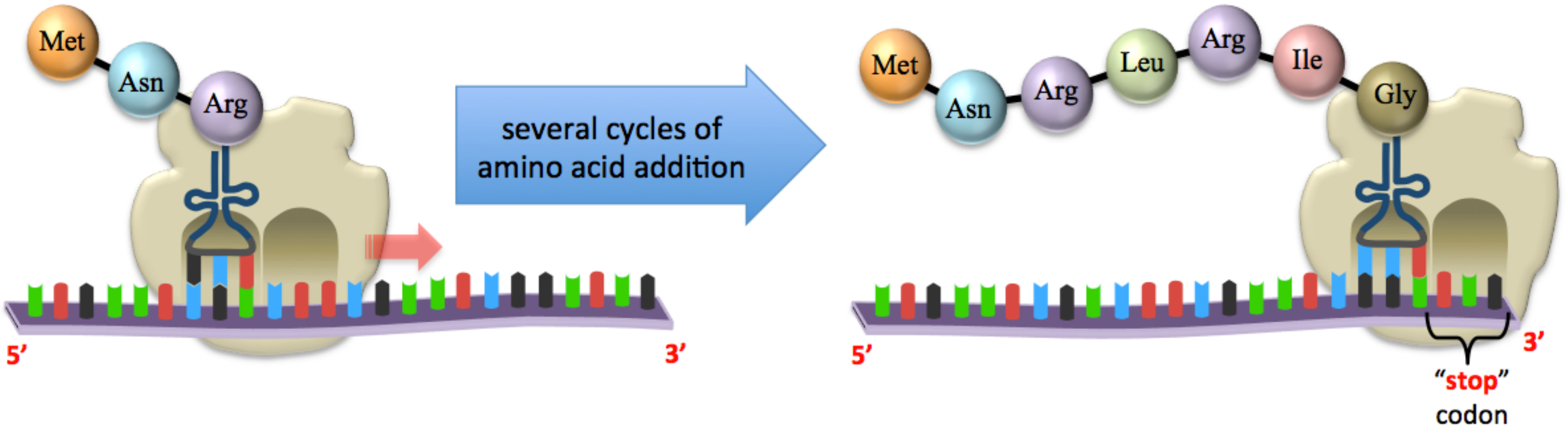
The next step in the *translation process* is called ***elongation***. In elongation, a polypeptide chain is made by the formation of *peptide bonds* between the amino acid residues that are specified by the genetic code in mRNA. Elongation begins when a second tRNA binds to the ribosome/mRNA/tRNA complex, as illustrated below.



The second tRNA delivers the amino acid that corresponds to the codon that follows the start codon. In the illustration, the second tRNA delivers an asparagine (Asn) amino acid. A part of the ribosome, called the *transferase center*, catalyzes the formation of a *peptide bond* between the first amino acid and the second amino acid. Next, the ribosome moves a distance of three bases (a codon) along the mRNA strand in the **5'** to **3'** direction. The tRNA that was attached to the first amino acid detaches from the mRNA and diffuses throughout the cytoplasm where it will encounter an enzyme that catalyzes its reattachment *to an amino acid that matches its anticodon*. This entire process is repeated when a third tRNA/amino acid binds to the next mRNA codon, as illustrated below.



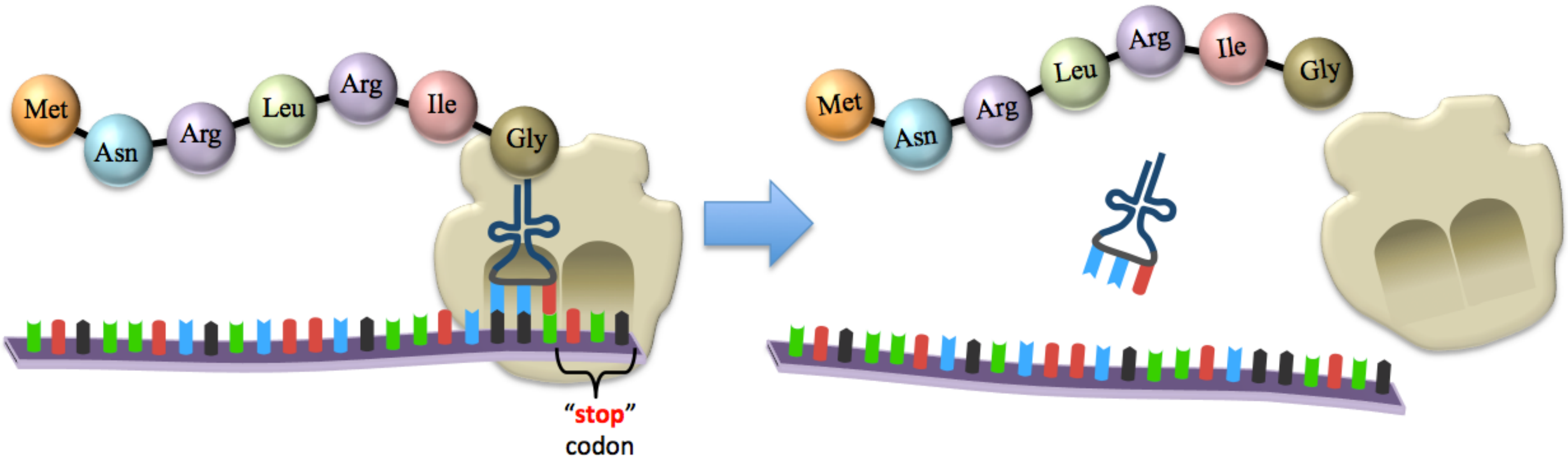
Peptides are synthesized in the direction from the **N-**terminus to the **C-**terminus because the new amino acid residues form peptide bonds with the **C-**terminus of a growing peptide chain. Elongation happens at a fast pace; in bacteria, amino acids are added to the growing polypeptide chain at a rate of about 40 per second. After many cycles of amino acid addition, the ribosome will reach a "***stop***" codon as illustrated below.



For simplicity, I used a very short mRMA stand in this example. Recall that in nature, mRNA contains hundreds to thousands of nucleotide residues.

Termination

The ***termination*** step occurs when the ribosome reaches a ***stop*** codon (**UAA**, **UGA**, or **UAG**). When this happens, the polypeptide, mRNA, tRNA, and ribosome become separated, as illustrated below.



In some cases, the polypeptide that is produced in translation is a fully-functional protein. In other cases, the polypeptides undergo further folding to acquire the secondary and tertiary structures that they need in order to function. In many cases, multiple polypeptide subunits must assemble into a quaternary structure in order to form a fully-functional protein. For example, hemoglobin contains *four* polypeptide chains (two pairs of identical polypeptides); each polypeptide is individually transcribed and then translated.

Some proteins require covalent bonding modifications after they are transcribed. These modifications are called **post-translational modifications**. An example of a *post-translational modification* is the addition of *heme groups* to heme-containing proteins, such as hemoglobin and myoglobin.

Although not discussed in this section, there are some differences in how prokaryotic and eukaryotic cells synthesize proteins. Many antibiotics take advantage of these differences in order to inhibit protein synthesis in prokaryotic pathogens while not harming the human (or animal) hosts. Table 14.2 lists some of these antibiotics and their effects on prokaryotic protein synthesis.

Table 14.2
Some antibiotics and their effects on prokaryotic protein synthesis.

Antibiotic	Mode of Action
chloroamphenicol	inhibits peptide bond formation
erythromycin	prevents ribosome from moving along mRNA
streptomycin	inhibits initiation and cause misreading of mRNA
tetracycline	inhibits the binding of tRNA to mRNA/ribosome

Some pathogenic microorganisms cause infection by producing toxic proteins that inhibit translation in their host organisms. An example of a bacterium that produces a potentially lethal protein is the *C. diptheriae*. Infection from this organism is called **diphtheria**. Before the development of antibiotics, diphtheria was a major cause of death in children. The toxic protein produced by *C. diptheriae* inhibits the *elongation* process in translation by preventing the ribosome from moving along the mRNA.

Review 14.8: Understanding Transcription and Translation

Write the three-letter abbreviations for the amino acid residues, in order from **N**-terminus to **C**-terminus, of the polypeptide that would be produced by the transcription and translation of **DNA** with a sequence of **3'**-TACGGGGTACACACT-**5'**. **CAUTION:** In this question, you were given the sequence of DNA, *not* mRNA.

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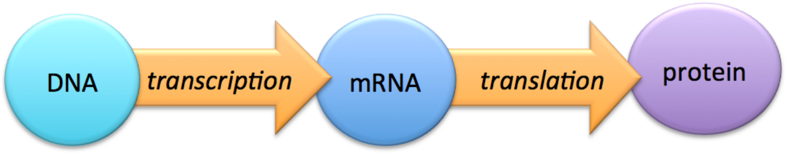
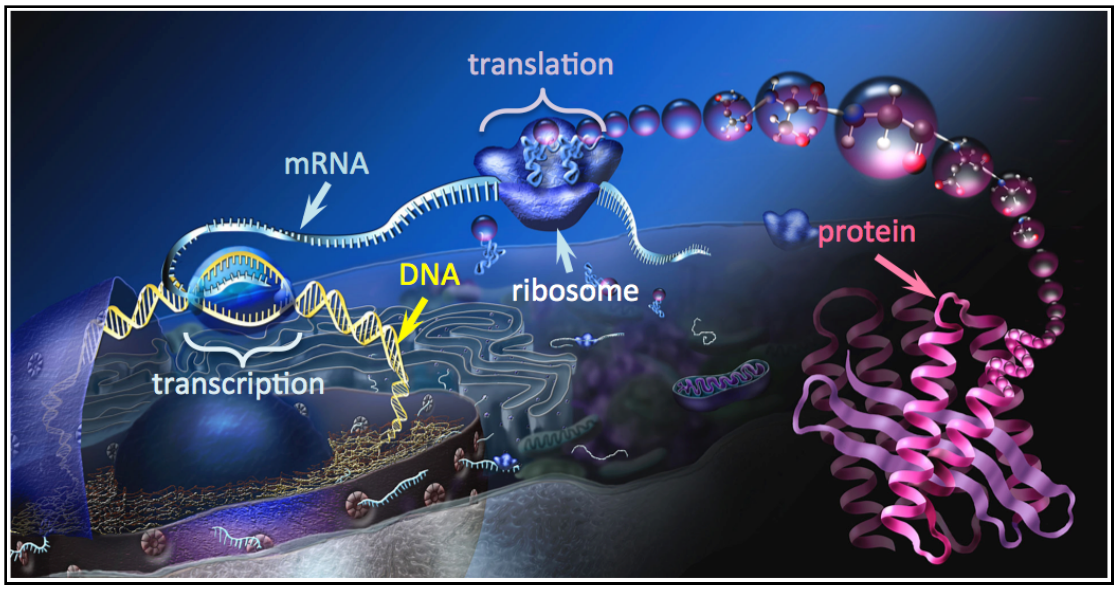
Protein Synthesis Summary Diagram and Illustration



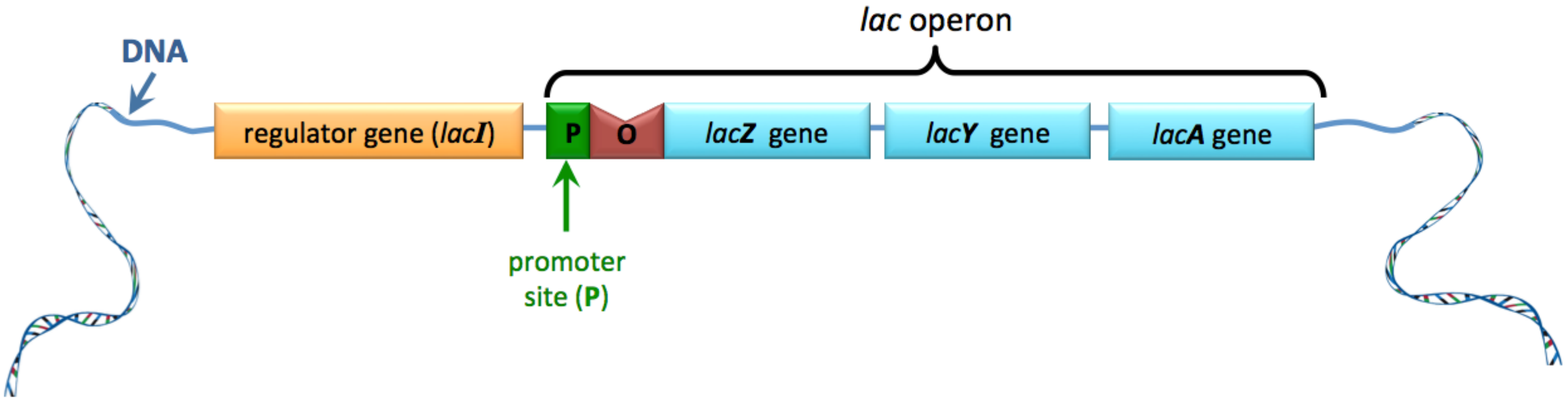


Control of Gene Expression

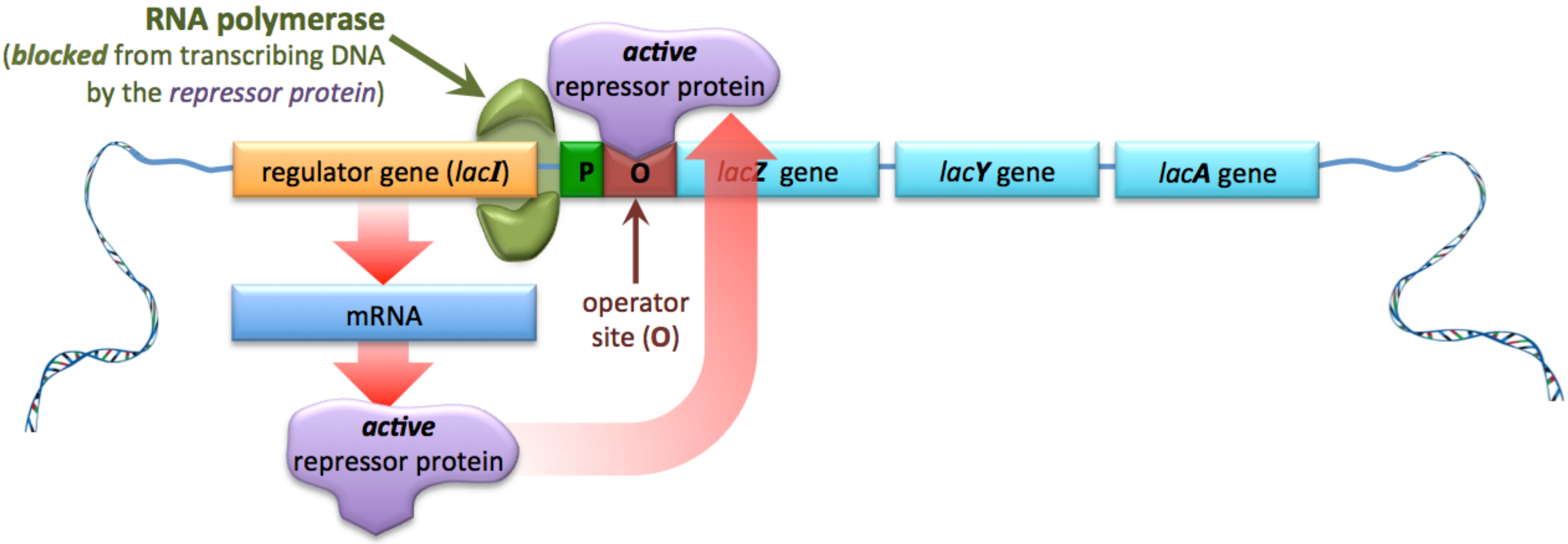
In chapter 13, I explained how organisms often use several reactions in series, called **metabolic pathways**, in order to carry out the chemical changes they require to meet their physiological needs. You also learned that many of the reactions in metabolic pathways require enzymes and that organisms can regulate (slow down or speed up) a metabolic process, according to their needs, by *inhibiting* or *activating* one (or more) of the enzymes involved in the metabolic pathway. ***Another way to control metabolic pathways***, or other conditions that involve proteins, is to **regulate the rate of production of a protein/enzyme**. This is called controlling ***gene expression*** (*gene expression* is another term used for *protein synthesis*). Because organisms have several thousand genes, it would be inefficient and harmful to *continually express* (continually make proteins from) all genes. Increasing the rate of gene expression is called **upregulation** of the gene; decreasing the rate of gene expression is called **downregulation** of the gene.

Gene expression can be regulated by controlling *transcription* (DNA to mRNA) or controlling the rate of post-transcriptional modifications. A complete discussion of these processes is far beyond the scope of this text. Instead, I will just give an example of the regulation of gene expression by controlling *transcription*.

Recall that *transcription*, the creation of mRNA from the information in a DNA, involves the *RNA polymerase enzyme*. In order for transcription to begin, *RNA polymerase* must bind to a "**promoter site**" on the DNA to be transcribed. ***Promoter sites*** are specific sequences of nucleotides near the beginning of a gene. Sometimes, several genes are transcribed from the *same promoter site*. A section of DNA made up from genes that are *transcribed from the same promoter site* is called an **operon.** *Escherichia coli* (*E. coli*) and many other bacteria contain an operon comprised of three genes that code for proteins involved in the metabolism or transport of lactose. This *operon*, called the *lac* operon, was the first operon to be discovered. Since then, many other operons have been found in both prokaryotic and eukaryotic organisms. Research on the *lac* operon resulted in the first gene expression process to be fully understood. The three genes of the *lac* operon are called *lac*Z, *lac*Y, and *lac*A. The *lac* operon is preceded by a *lac regulator gene*, as illustrated below.

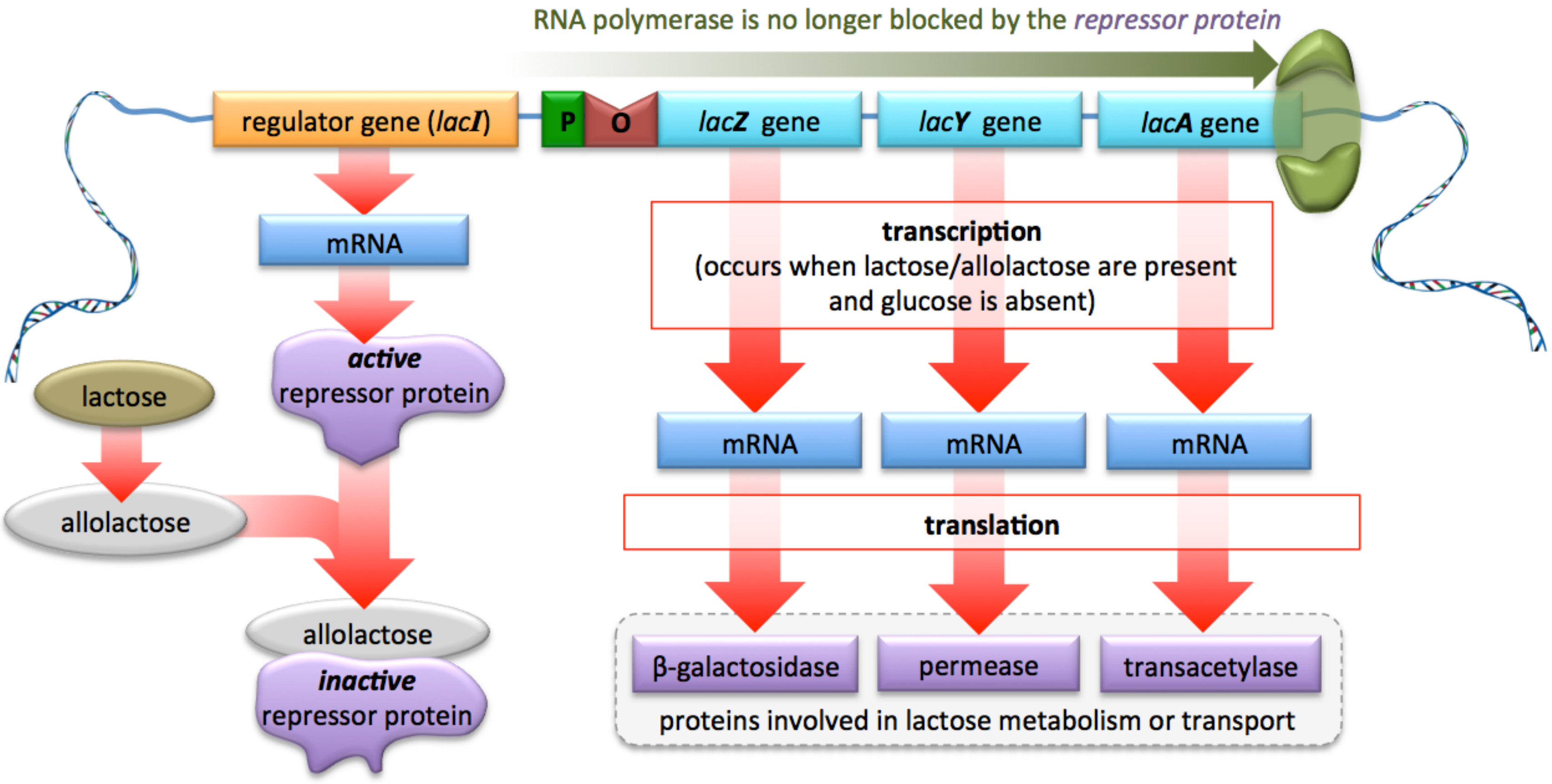


The primary energy source of the *E. coli* and most other bacteria is usually glucose. In the presence of glucose, lactose is not needed as an energy source and almost zero lactose is allowed into the bacterial cell, therefore it is not necessary for the genes of the *lac* operon to be expressed. It is for this reason that nature has provided a regulator gene (*lacI* gene). The *lacI* gene produces an ***active repressor protein,*** which binds to a segment of DNA called an **operator site**, as illustrated below.



When the active repressor protein is bound to the operator site, ***RNA polymerase is blocked from moving along the lac operon* to transcribe the *lacZ*, *lacY*, and *lacA* genes**. Under normal conditions (glucose present), this is ideal for the *E. coli* because there is plenty of glucose present, and lactose is *not* being taken in, therefore the bacteria do not need the lactose metabolism or transport proteins that the genes of the *lac* operon express.

Let's consider the scenario in which *lactose* is present ***in the absence of glucose***. In this case, lactose is allowed to enter the *E. coli*. Whenever lactose is present in the bacteria, some of it is converted to a compound called *allolactose*. Allolactose will bind to, and thereby *inactivate the repressor protein*. The *inactive* repressor protein cannot bind to the operator site, therefore RNA polymerase is no longer blocked and will move along the *lac* operon to transcribe the *lac* operon genes, as illustrated below.



The mRNAs from the *lac* operon genes are *translated* to the three proteins: *β-galactosidase*, *permease*, and *transacetylase. β-galactosidase* is an enzyme involved in lactose metabolism. *Permease* is a transmembrane protein that transports lactose into cells. *Transacetylase* is an enzyme thought to be involved in the breakdown of some non lactose species that are transported into cells by *permease*. The presence of lactose within *E. coli*, and the subsequent presence of allolactose, **upregulate** the genes of the *lac* operon. The bacteria are continuously using up allolactose and lactose. Whenever lactose is no longer obtained from the surroundings, the concentration of allolactose within the cells will decrease, and then *active regulator proteins* become available again to **downregulate** the *lac* operon.

Review 14.9: Understanding Gene Expression

Determine whether each of the following conditions would result in the genes of the *lac* operon being ***upregulated*** or ***downregulated***.

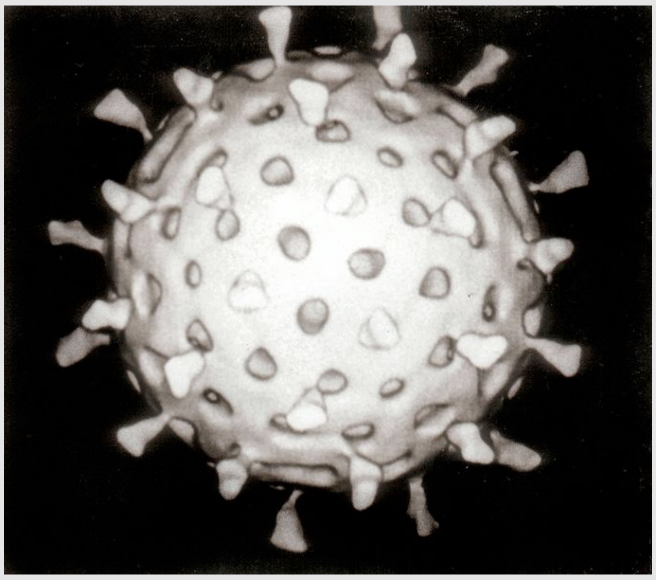
a. RNA polymerase is blocked from moving along the *lac* operon
b. Allolactose binds to the repressor protein
c. Lactose concentration within a cell is decreased
d. Allolactose concentration within a cell is increased
e. Glucose is available
f. Active repressor proteins are present in the absence of allolactose

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

14.6 Viruses

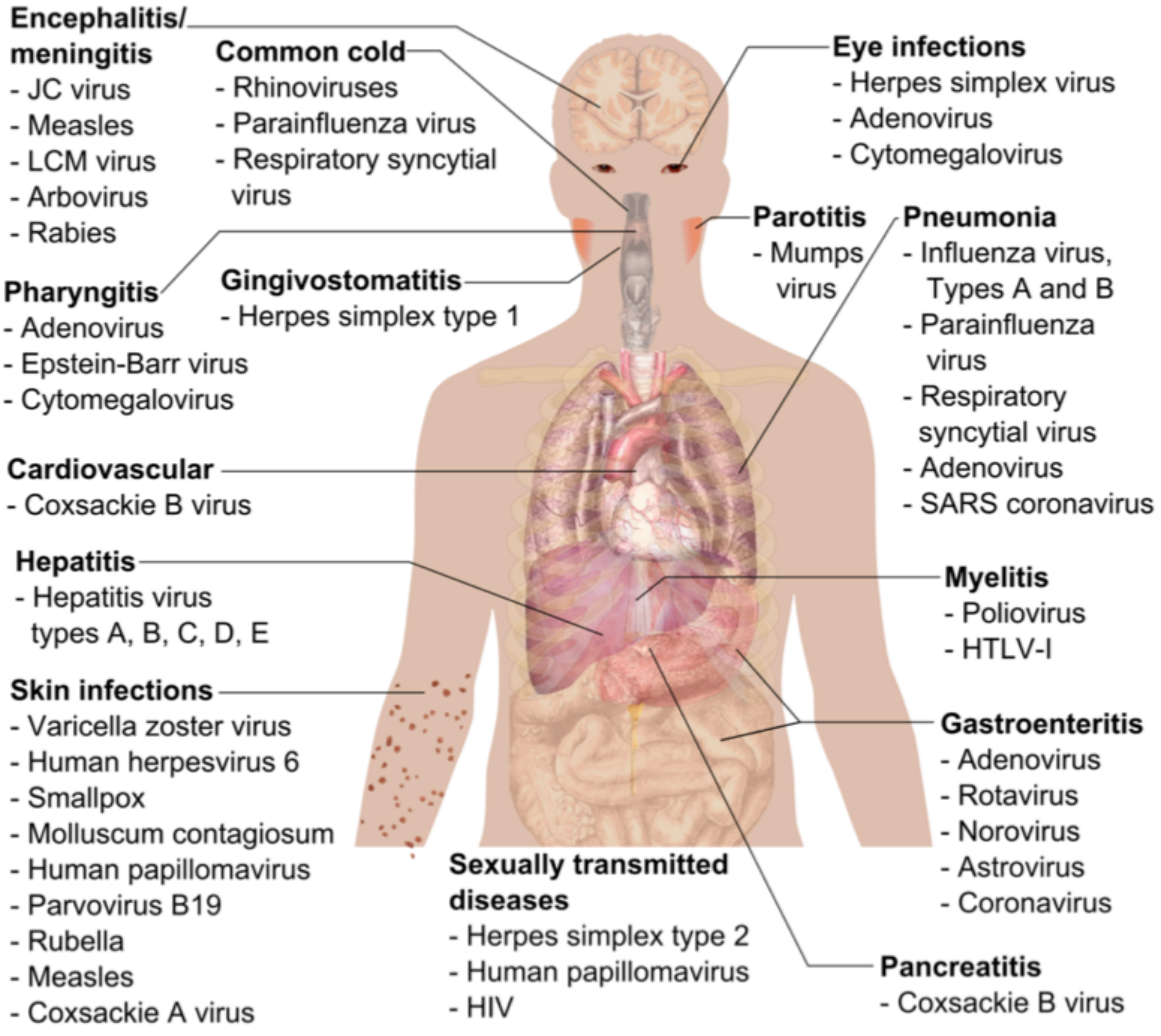
Viruses are small particles that are not able to reproduce on their own. A typical virus is about 1/100 the size of a bacteria. In order for a virus to reproduce, it must invade a cell of *another* organism. A cell that is invaded by a virus is called a **host cell**. Viruses have much less-complicated structures and contents than do cells; they do not have the components, such as nucleotides and certain enzymes, that are needed in order to self-replicate. Viruses come in a variety of shapes, one of which is shown in Figure 14.5. All viruses have a protein shell that encapsulates *either* DNA *or* RNA, and some viruses contain a small set of enzymes. A virus that contains DNA is called a **DNA virus**. A virus that contains RNA is called an **RNA virus**. Some viruses have a lipid coating that surrounds their protein shell.

Figure 14.5 **A Virus Particle**



A computer regenerated reconstruction of a virus particle.
Source: Wikimedia Commons
Author: Dr. Graham Beards

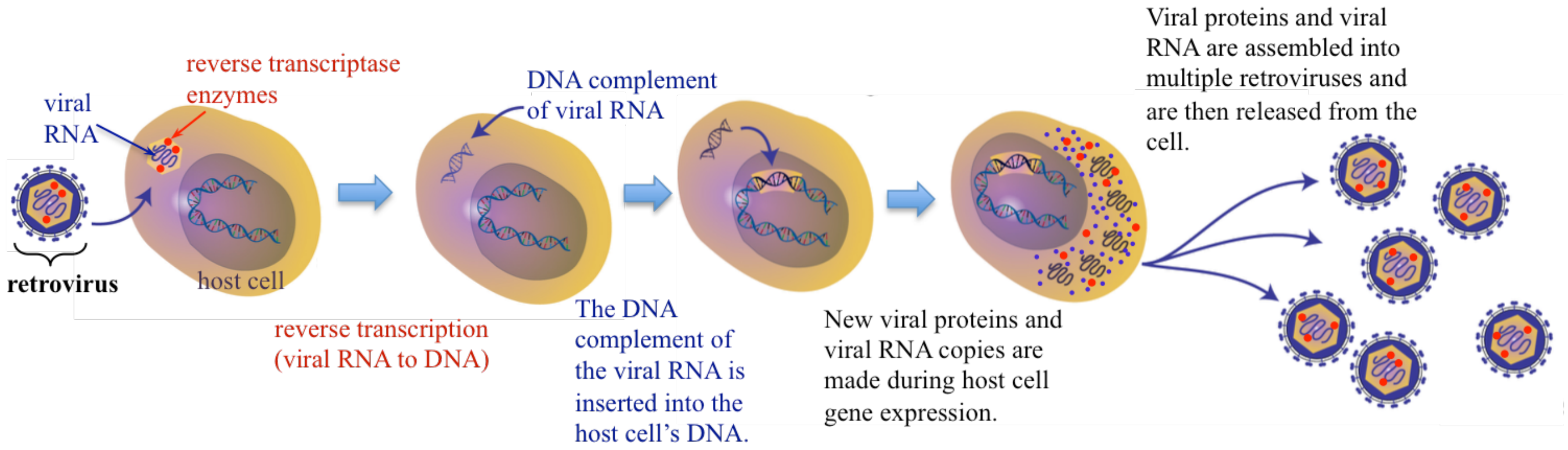
All forms of life can have their cells invaded by viruses. When viruses take over plant or animal cells, we call this a **viral infection**. Several human *infectious diseases*, some of which are *chronic diseases*, are caused by viral infection. Some of these diseases, the location of the infections, and the most common viral species involved are shown below.



Viruses infect cells by introducing their DNA or RNA and, in some cases, a few types of enzymes, into the host cell. This is done in various ways depending on the particular virus. Once the viral DNA or RNA is introduced to the host cell, enzymes, nucleic acids, and amino acids ***from the host cell*** are employed to make more viral DNA or viral RNA, and viral proteins. The viral DNA or RNA and viral proteins are ***reassembled into multiple, new virus particles*** within the host cell. These new viral particles cause the host cell to burst or release the viral particles using the exocytosis process. The infection spreads as the new viruses infect other cells.

Viral DNA or RNA self-replicates and expresses viral proteins in several different ways, depending of the type of virus. A detailed description of each of these processes is beyond the scope of this book. Instead, I will give one example by describing how the *human immunodeficiency virus* (HIV) infects cells.

HIV is in a category of viruses called **retroviruses**. When taken into the host cell, the information in the *retroviral* RNA is converted to complementary DNA. This is called **reverse transcription** and is catalyzed by a viral enzyme called ***reverse transcriptase***. The name "*reverse transcriptase*" is applied because the chemical process is the *reverse* of transcription. The newly formed DNA is inserted into the host cell's DNA, and then *transcribed* into new *retroviral* RNA and viral proteins during the host cell's normal gene expression. The *retroviral* RNA and viral proteins are ***assembled into multiple retroviruses*** and then released from the cell. This process is illustrated below.



Animals are capable of producing immune responses that eliminate most viral infections. Vaccinations are effective as anti-viral agents because they allow vaccinated individuals to produce artificially acquired immune responses to many viral infections. Some viruses, such as HIV, herpes simplex virus (HSV), and hepatitis C virus (HCV), are capable of evading immune responses and therefore result in chronic (persistent or long-lasting) disease.

Review 14.10: Enzymes Involved in DNA and RNA Formation

Which enzyme, DNA polymerase, RNA polymerase, or reverse transcriptase is involved in the processes below:

a. Transcription
b. Replication
c. Using a DNA template to make RNA
d. Using an RNA template to make DNA

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

14.7 Genetics

Genetics is the study of genes, variation in genes, and heredity. The field of genetics was founded by Gregor Mendel, a Moravian (now Czech Republic) scientist and friar. Mendel used results from his famous experiments on peas to provide a set of rules that describe inherited traits. In an 1865 publication, he showed that organisms passed a discreet set of “factors” that could be used with statistics to predict inherited traits. These “factors” are now called *genes*. In this section, I will discuss some of the chemical concepts that are important in the field of genetics.

Figure 14.6
Gregor Mendel (1822-1884)

Gregor Mendel is known as the founder of the science of genetics.

The information contained in the DNA of an organism is called its **genome**. Individuals, other than identical twins, have different inherited traits because the DNA of each person is not exactly the same as that of another person. Even identical twins have about *one hundred* incidents of differences in nucleotide sequences in their genome, although that is not enough to make differences in their appearances. Small differences in the appearances of identical twins are attributed to environmental, not genetic, differences. Examples of inherited traits in humans include eye, skin, and hair color. Sometimes, diseases result from an abnormal DNA sequence in a parent being passed to the next generation.

A **mutation** is a permanent change in the nucleotide sequence in an organism's genome. Changes in the nucleic acid sequence of a gene (a mutation) can result in changes in the amino acid sequence of the protein that is expressed, and can thereby give rise to partially or completely *nonfunctional proteins*. If the mutated gene results in a partially or completely nonfunctional protein that is important for an individual to function, the health of the individual may be diminished. Some mutations result in premature death.

Mutations can come about from errors that occur during DNA replication/proofreading, spontaneous DNA chemical changes, or induced DNA chemical changes. Spontaneous DNA chemical changes can occur when DNA undergoes chemical reactions in the absence of external agents or extreme conditions. Induced DNA chemical changes occur when DNA undergoes chemical reactions that result from the introduction of external chemical agents or high energy radiation. A chemical or physical agent that induces mutations is called a **mutagen**. Examples of **physical mutagens** are ultraviolet light (UV) and x-rays. These types of radiation can break the covalent bonds in DNA directly or can break bonds in other species to form high energy intermediate products that can react with DNA. Examples of **chemical mutagens** are hydrogen peroxide, superoxide ion (O_2^-), polyaromatic hydrocarbons (PAHs), benzene, and some metals (I.e. arsenic and cadmium).

Types of Mutations

Mutations that occur in multicellular organisms can be categorized as either **somatic mutations** or **germ line mutations**. ***Somatic mutations***, also called *acquired mutations*, are mutations that occur within cell types that *are not involved in reproduction* (**somatic cells**). When a mutation arises in a *somatic cell*, then the mutation is limited to that cell or any of its cell-division descendants ***within the organism***. Cancer is a disease that results from *somatic mutations* in genes that are responsible for cell growth or cell differentiation. Such mutations cause the formation of a mass of mutated cells (cancer cells) called a **tumor**. For example, a skin cell can acquire a mutation, very often from exposure to UV radiation, which causes it to begin to rapidly divide/replicate and form a tumor.

Germ line mutations are mutations that occur within germ line cells. Germ line cells are the cells that are involved in reproduction (e.g. sperm and ovarian cells). If a mutated germ line cell is passed to an offspring, then it results in a **constitutional mutation**, which is a mutation occurring in the nuclei of ***every cell of the offspring***. When a *constitutional mutation* causes a negative health condition, it is referred to as a ***genetic disease***. Note that mutations in germ line cells can be transmitted to offspring, whereas somatic cell mutations cannot.

Mutations can be classified as **small-scale** or **large-scale**, depending on the *number of nucleotides involved in the mutation*. *Small-scale mutations* involve a change in a small number of nucleotides (usually one to three nucleotides) within a single gene. *Large-scale mutations*, sometimes called ***chromosomal mutations***, involve changes in large sections of chromosomes.

Small-Scale Mutations

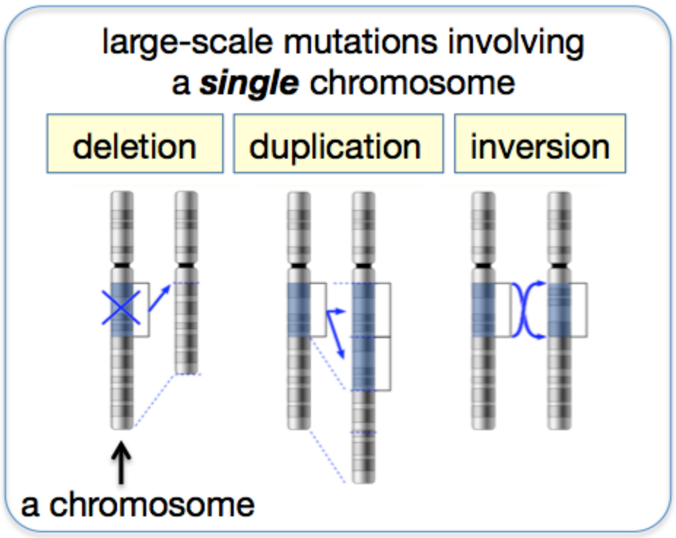
1) **Point:** A single, incorrect nucleotide takes the place of the original nucleotide. This often happens during DNA replication.
2) **Insertions**: One or more extra nucleotides are inserted between two of the original nucleotides in a gene.
3) **Deletions**: A single nucleotide or a short sequence (usually 2 or 3 nucleotides) are removed from a gene.

Large-Scale Mutations

There are five common types of *large-scale mutations*. Some occur within a single chromosome, and some involve the exchange of DNA between two different chromosomes.

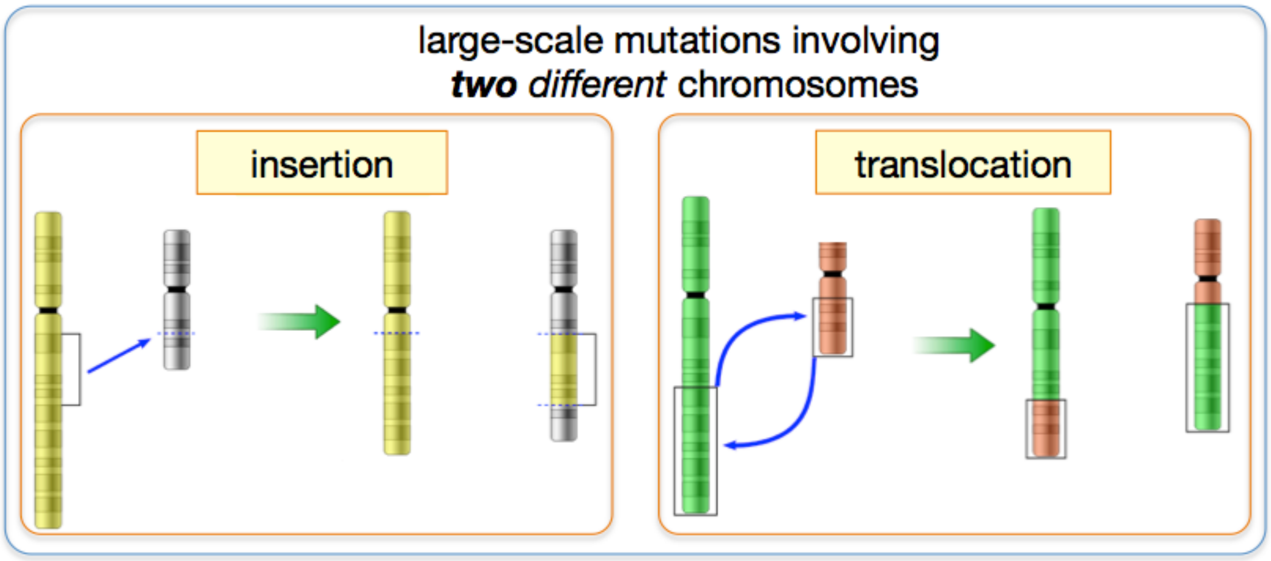
Large-scale mutations involving a ***single chromosome*** (illustrated on the right):

1) **Deletions:** A large section of DNA within a single chromosome is removed/deleted.
2) **Duplication:** A large section of DNA within a single chromosome is duplicated and reinserted.
3) **Inversion:** A large section of DNA within a single chromosome is inverted (**3'** and **5'** directions reversed).



Large-scale mutations involving ***two different chromosomes***:

4) **Insertion**: A large section of DNA within one chromosome is inserted into ***another*** chromosome (illustrated below, left).
5) **Translocation:** Large sections of DNA in two different chromosomes are exchanged (illustrated below, right).



Human Genetic Diseases

The inheritance of one or more mutated genes can result in a **genetic disease**. Some genetic diseases involve a particular gene, others involve multiple genes.

Normally, individuals have two copies of each gene in the nucleus of every somatic cell in their bodies. One copy of the gene was inherited from mother, and one copy from father. The exceptions to this are *some genes* on the human X chromosome. A **monogenic disease** occurs when *one or both* copies ***of a particular gene*** contains a harmful mutation. "**Dominant diseases**" are monogenic diseases that occur when ***both copies*** of a gene are mutated. "**Recessive diseases**" are monogenic diseases that occur when one copy of the gene *is not* mutated *and* one copy *is* mutated. Although I will not discuss the details, be aware that these definitions of *recessive* and *dominant* are applied a bit differently to mutations on the X chromosome because a father's X chromosome is only passed to daughters.

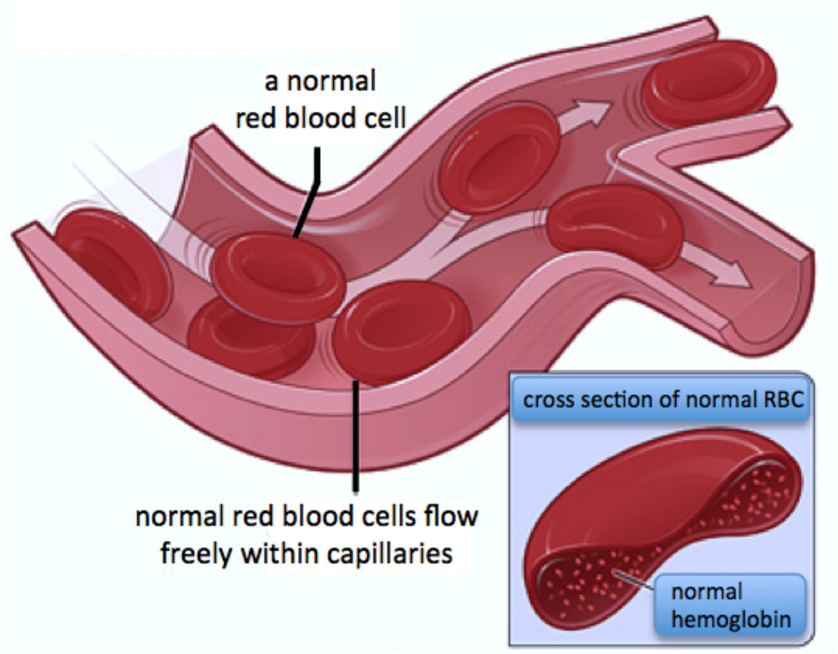
More than 7,000 different *monogenic diseases* have been identified. Despite this large number of diseases, monogenic diseases are quite rare. Most types of diseases occur in less than one in several thousand individuals. Table 14.3 lists some monogenic diseases and their prevalences.

Table 14.3 Approximate Prevalence of Some Monogenic Diseases

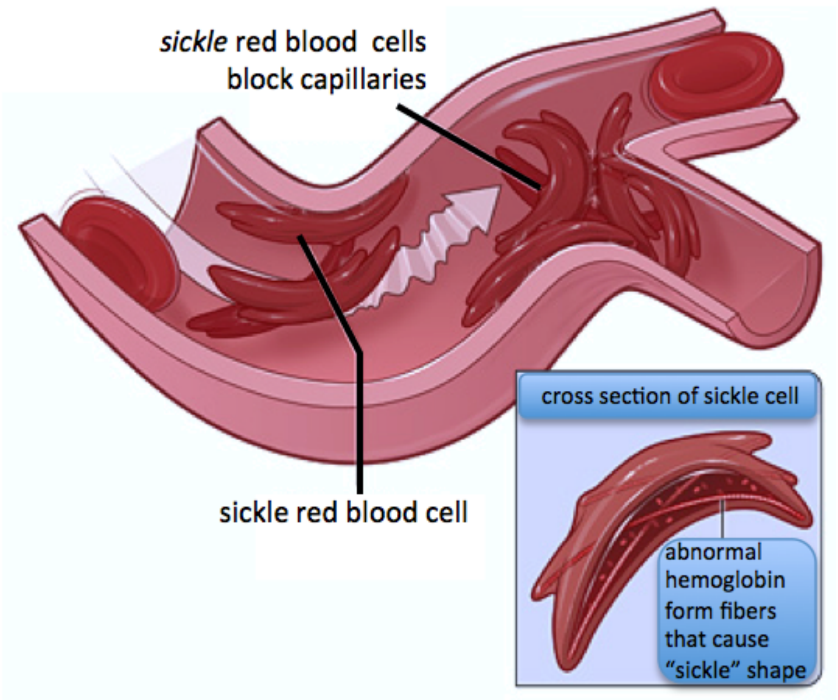
monogenic disease	prevalence
familial hypercholesterolemia	1 in 500
polycystic kidney disease	1 in 1,250
Huntington's disease	1 in 15,000
sickle cell disease	1 in 625
cystic fibrosis	1 in 2,000
Tay-Sachs disease	1 in 3,000
Phenylketonuria (PKU)	1 in 12,000
glycogen storage diseases	1 in 50,000
Duchenne muscular dystrophy	1 in 7,000
hemophilia	1 in 10,000

The prevalences shown here are approximate values and can vary significantly between populations with different ancestral ethnicities as well as gender.

An example of a monogenic disease is ***sickle cell disease*** *(sometimes called* ***sickle cell anemia****)*. Sickle cell disease is a recessive disease that occurs when a mutated *hemoglobin gene* is inherited from both parents. The mutated hemoglobin gene results in the production of abnormal hemoglobin protein. These abnormal hemoglobin protein particles stick to each other to form fibers that cause a distortion in the shape, and loss of elasticity, of the red blood cells (RBCs). The distortion in the red blood cells is referred to as "sickling." Normal (non sickle) red blood cells are relatively elastic (flexible), which allows them to move through capillary paths and junctions. Sickle cells are less flexible, and therefore block capillary blood-flow, as illustrated below.



normal red blood cells (RBC)



abnormal, *sickle* red blood cells

The symptoms and health issues of sickle cell disease result from blocked blood-flow or the relatively short cell lifetime of sickle cells (10-20 days vs. 90-120 days for normal red blood cells).

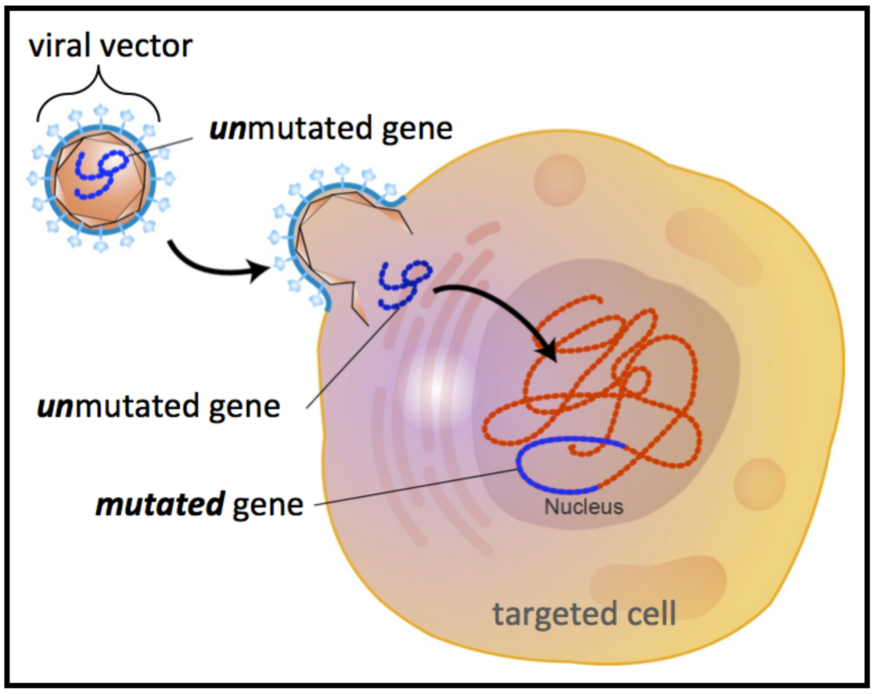
A **polygenic disease** occurs when *one or both* copies ***of multiple, different genes*** contain a harmful mutation. Although polygenic diseases do "run in families," they are not predictable by the simple statistical methods that apply to monogenic diseases. Hypertension, coronary heart disease, and diabetes are examples of polygenic diseases.

Not all genetic diseases are caused by mutations. **Aneuploidy** is a disorder that occurs when a person is missing a chromosome or has extra chromosomes. An example of *aneuploidy* is *Trisomy 21*, which is caused from having a third copy chromosome 21. The parents of individuals with Trisomy 21 are usually genetically normal. Trisomy 21 is one of the diseases that give rise to ***Down Syndrome***. The presence of the extra chromosome results in the overexpression of the chromosome's genes and leads to the physical and mental symptoms of the disease.

Treating Genetic Diseases: Gene Therapy

Some genetic diseases can be treated by **gene therapy**, which involves the delivery of functional (***un***mutated) genes to the cells of an individual who has a monogenic disease. In some cases, the genes are introduced to the body by "infecting" the patient with inert DNA viruses that have had their genomes replaced with the gene that is to be delivered. A biological agent (a virus in this case) that is used to artificially deliver DNA to a cell is called a "**vector.**" An overview of this process is illustrated on the right.

Alipogene tiparvovec (marketed under the trade name *Glybera*) was the first gene therapy agent to be approved for use in the United States and Europe. It is used to treat *lipoprotein lipase deficiency,* which is caused by a mutation in the gene that codes for the *lipoprotein lipase* enzyme. When individuals have this mutation, they cannot effectively break down fatty acids and therefore acquire severe pancreatitis (inflammation of the pancreas). Gene therapy treatment of this conditio*n by Alipogene tiparvovec* is administered using a viral vector that has been genetically engineered to contain the ***un***mutated, *lipoprotein lipase gene*.



Recombinant DNA: Genetically Modified Organisms

As the scientific community learned about the DNA replication process, scientists discovered that it is possible to extract copies of a gene from one organism and then insert that gene into another organism's genome. This process forms "**recombinant DNA**," which is ***DNA made from two or more sources***. Actually, this has been done in the farming industry for thousands of years by "crossbreeding" plants and "selective breeding" of animals. Modern molecular recombinant DNA techniques allow for faster results, precisely specified changes, and the ability to exchange DNA between any two organisms and between plants *and* animals. Molecular recombinant DNA techniques involve extracting and purifying a particular gene of interest from its source, and then inserting it into the DNA of another cell. An organism that contains recombinant DNA is called a **genetically modified organism (GMO)** or a ***mutant***. There are several variations on how the gene can be transferred, and many applications for recombinant DNA technologies. I will give you three examples of how recombinant DNA technology is used to produce genetically modified organisms.

GMO Example: Glyphosate Resistant Crops

Glyphosate is currently the most widely used herbicide (weed killer) in the US agricultural industry and the second most used household weed killer. It is marketed by the Monsanto Corporation under the trade name "*RoundUp*." Farmers can increase the yield of their food crops by eliminating weeds, which compete with their crops for nutrients and sunlight. Glyphosate works by inhibiting an enzyme (ESPS synthase) that is responsible for the production of some amino acids.

Glyphosate is effective in killing most types of plants, including food crops, therefore it is not practical to apply glyphosate to *unmodified* crops; it would kill the crops as well as the weeds! Monsanto wished to develop crops that were not affected by glyphosate. This would allow farmers to spray glyphosate on the modified crops, ***yet only kill the weeds***. To do so, they needed to find an organism with a gene that produced an ESPS synthase enzyme that is not inhibited by glyphosate, then introduce that gene into the ***germ line*** of a crop.

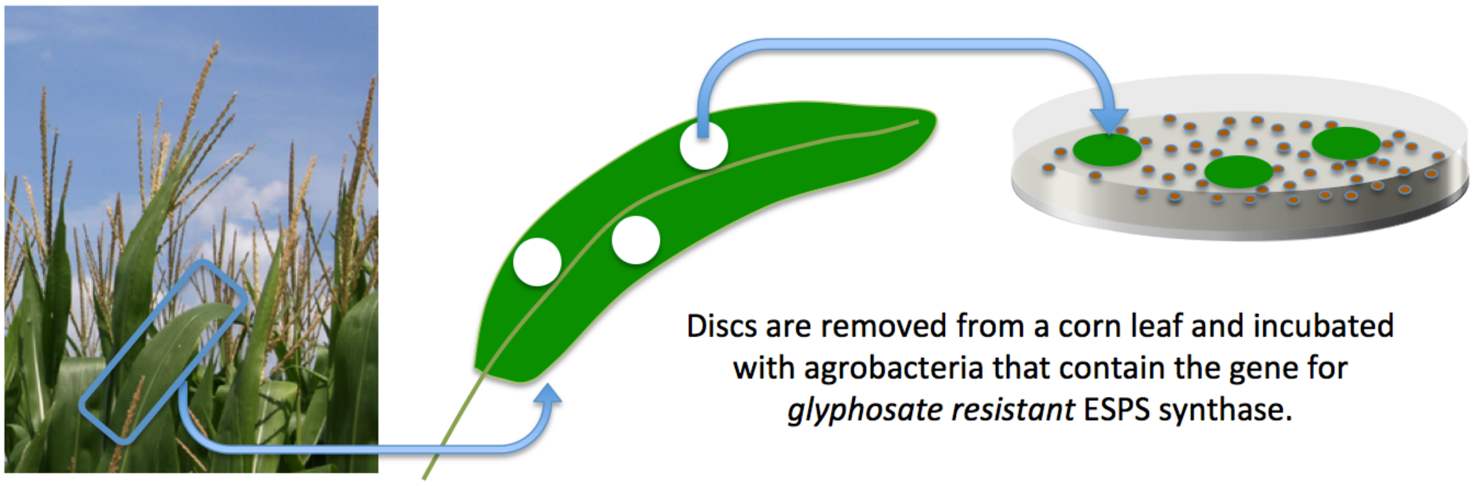
A key step in the production of any genetically modified organism is placing the new gene into the target cell in such a way that the target cell remains viable. A way to do this in plants is to use bacteria called *Agrobacteria*. *Agrobacteria* naturally infect plants by injecting their own (tumor-causing) DNA into plant cells. Figure 14.7 shows an electron microscope image of a species of agrobacteria called tumefaciens (*A. tumefaciens*) binding to, and transferring their DNA to a carrot cell. Scientists take advantage of this natural process in order to make recombinant DNA by transferring the gene of interest to the target cell's genome through intermediate agents, such as agrobacterium. The intermediate agents are referred to as **vectors**. Before agrobacteria are used as DNA transfer vectors, their tumor-causing genes are removed. In addition to agrobacterium, viruses are also used as DNA transfer vectors.

Researchers at Monsanto were able to locate an *A. tumefaciens* strain that had an ESPS synthase enzyme that is not affected (inhibited) by glyphosate by looking in the plumbing used for glyphosate *at the glyphosate production facility*! Once the *glyphosate resistant agrobacterium* were found and cultured, glyphosate resistant crops could be prepared, as described below.

1) **Transfection:** Infect some of the target plant cells with the *A. tumefaciens* agrobacterium strain that contains a glyphosate resistant ESPS synthase enzyme. In this example, I will use corn as the target crop. Discs are removed from a corn leaf and incubated with glyphosate resistant *A. tumefaciens* agrobacteria. The agrobacteria will ***transfect*** (transfer their glyphosate resistant ESPS synthase genes to) ***some*** of the corn leaf cells.

Figure 14.7
Agrobacterium Transferring DNA to a Plant Cell

Electron microscope image of *Agrobacterium tumefaciens* [bacteria] as they "transfect" a carrot cell. In the process, the bacteria's plasmid DNA material will enter the plant cells.

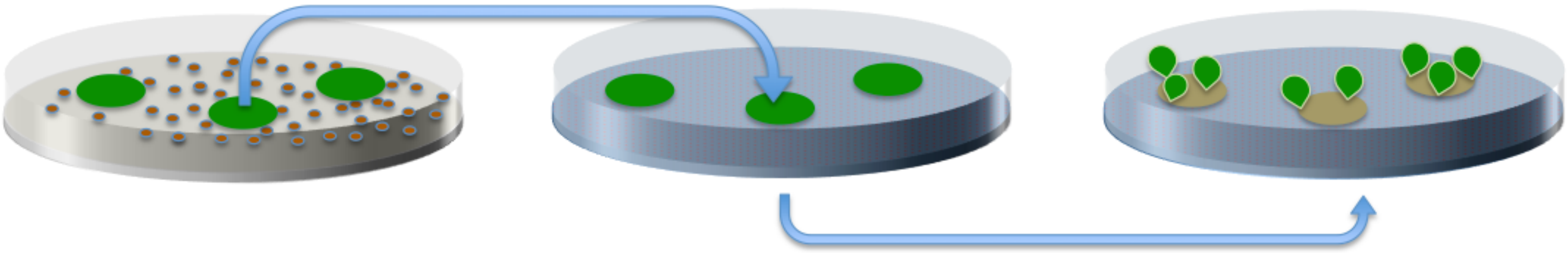


Discs are removed from a corn leaf and incubated with agrobacteria that contain the gene for *glyphosate resistant* ESPS synthase.

unmodified corn

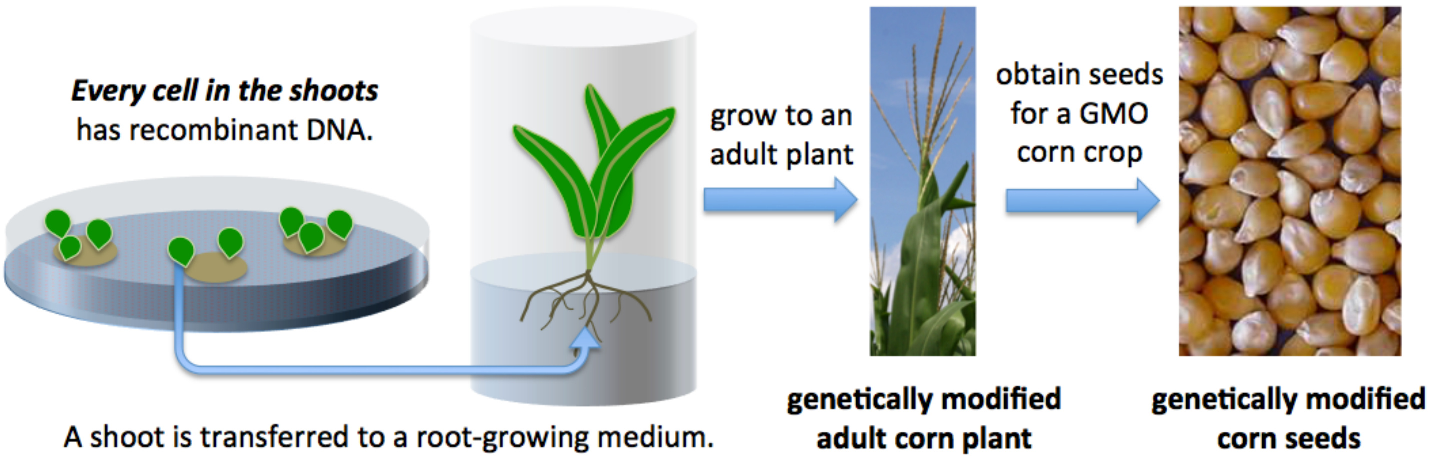
2) Next, the corn leaf discs are moved to a growth medium that *also* contains ***glyphosate***. Because *glyphosate* is present, only the cells that received the glyphosate resistant ESPS synthase gene will survive. The surviving corn cells will replicate and produce corn *shoots*. ***Every one of the cells*** in the shoots *contains recombinant DNA*.

Discs are placed in a cell-growth medium that *also* contains **glyphosate** herbicide.



Because glyphosate is present, **only the cells that were *transfected*** with the glyphosate resistant ESPS synthase gene survive to produce shoots.

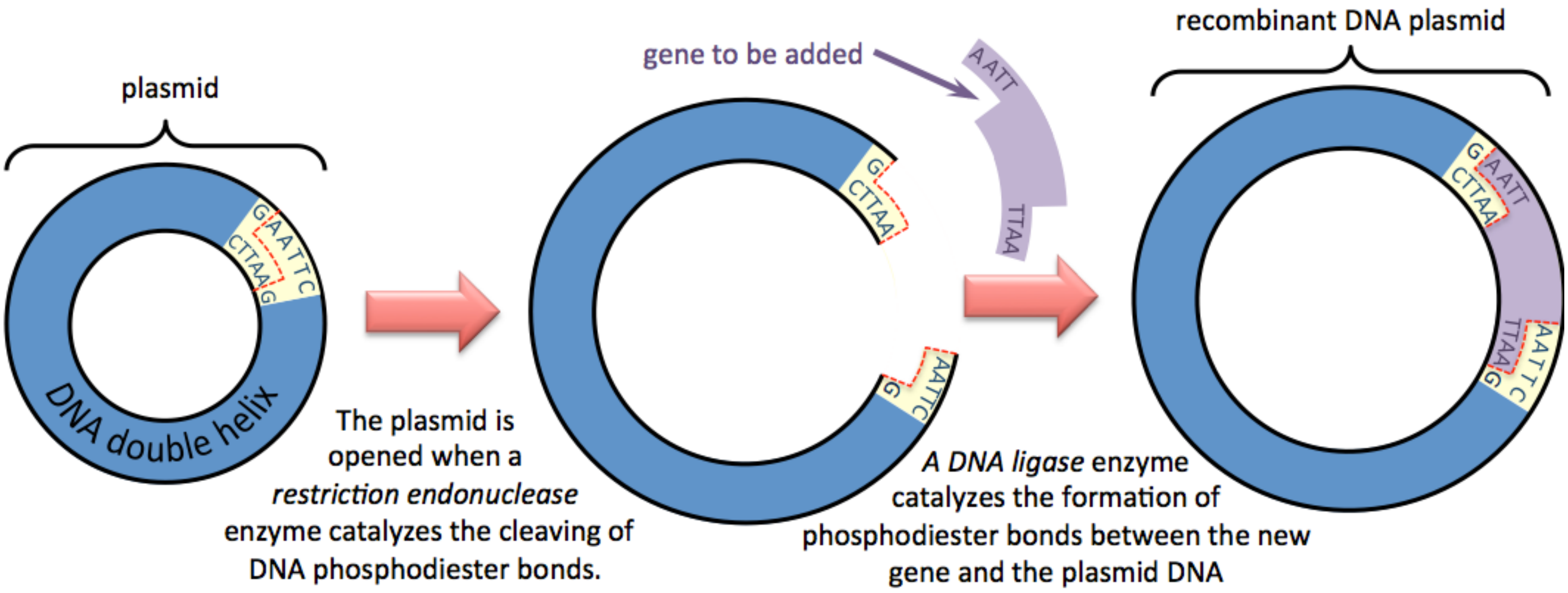
3) A shoot is transferred to a root-growth inducing medium, then the small plant is grown to a *genetically modified adult corn plan*t. Every cell in the plant, including its seeds, contains the glyphosate resistant ESPS synthase gene. The seeds are harvested and can be used to plant a genetically modified corn *crop*.



Contrary to what you may have heard reported in popular media, there is no *definitive research* that indicates GMO corn has negative health effects. The general scientific community currently has the understanding that GMO crops pose no greater health risks than do non GMO crops.

GMO Example: Human Insulin from Bacteria

In the previous example of genetically modified crops, the process was made a bit easier because the researchers found an Agrobacterium strain that ***already*** contained a gene for glyphosate resistant ESPS synthase. In other cases, DNA splicing techniques are used to insert a desired gene into a ***plasmid***. Recall that a plasmid is a relatively small, circular, double-stranded DNA particle. Plasmids occur naturally in bacteria, yeast, and some other single-cell organisms. New genes can be artificially inserted into plasmids. This is done with the help of enzymes to break open the natural plasmid and to catalyze the formation of phosphodiester bonds between the opened plasmid and the gene that is to be inserted. This process is illustrated below.



Once the genetically engineered plasmid is made, it can be inserted into an agrobacterium vector, or it can be directly inserted into the cells of an organism to be modified. This process made it possible to introduce the gene for *human insulin* into *E. coli* bacteria so that human insulin could be produced and purified from genetically modified *E. coli*. Insulin is normally secreted by the pancreas in response to elevated blood glucose levels. It acts as a protein hormone that signals cells to uptake glucose from the blood. When an individual's pancreas cannot produce enough insulin, the cells are starved and results in a condition called *diabetes type I*. People with this condition must monitor their blood sugar and take insulin (as a drug) when their blood sugar is elevated. Before insulin could be produced by recombinant DNA techniques, diabetics were given insulin made by harvesting the pancreas' of cows or other animals. This process sometimes resulted in insulin that contained harmful impurities that caused allergic reactions. The cows didn't like it either. To address these issues, human insulin genes were inserted into *E. coli* plasmids, and then the recombinant DNA plasmids were re-inserted into *E. coli*. The genetically modified *E. coli* are cultured to obtain large quantities of *E. coli* that produce human insulin. The human insulin is then purified and used as a therapeutic drug. Insulin made by genetic engineering was the first drug produced by GMOs that was approved for use in the United States.

GMO Example: Measuring Gene Expression using Green Fluorescent Protein Mutants

Figure 14.8 GFP Mutant Mice

Fluorescence from GFP-containing recombinant DNA can be seen in two of the three mice.
Source: Wikimedia Commons, Authors: Ingrid Moen, Charlotte Jevne, Jian Wang, Karl-Henning Kalland, Martha Chekenya, Lars A Akslen, Linda Sleire, Per Ø Enger, Rolf K Reed, Anne M Øyan and Linda EB Stuhr: Gene expression in tumor cells and stroma in dsRed 4T1 tumors in eGFP-expressing mice with and without enhanced oxygenation. In: BMC Cancer. 2012, 12:21. doi:10.1186/1471-2407-12-21 PDF
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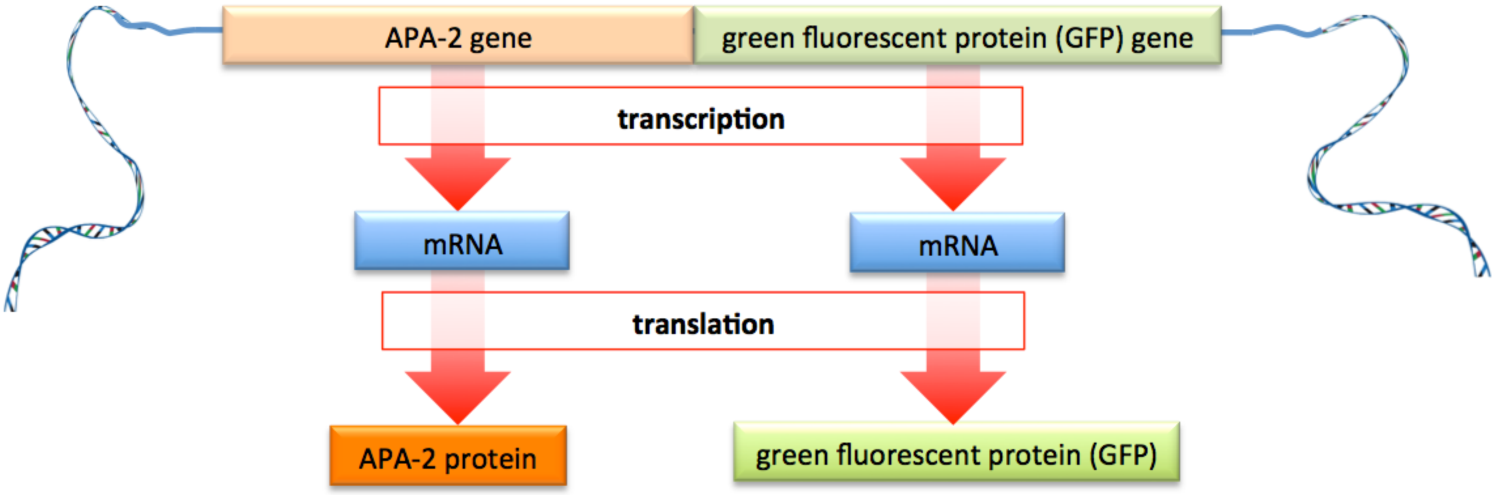
Jellyfish have a naturally occurring protein that emits green light when it is illuminated by UV light. We call this protein *green fluorescent protein* (**GFP**). The jellyfish gene for *green fluorescent protein* can be inserted into recombinant DNA plasmids. Once the engineered plasmid is made, it can be incorporated into another organism's genome. An organism that is genetically engineered to contain the GFP gene is called a **GFP mutant**. The GFP gene has been successfully incorporated into bacteria, yeast and other fungi, fish, plants, flies, and mammals. When the GFP gene is placed in the first cell of a multicellular organism (the zygote), the nuclei of all the cells within the organism will contain the GFP gene and can express the GFP protein. Fluorescence from GFP-containing recombinant DNA can be seen in two of the three mice shown in Figure 14.8.

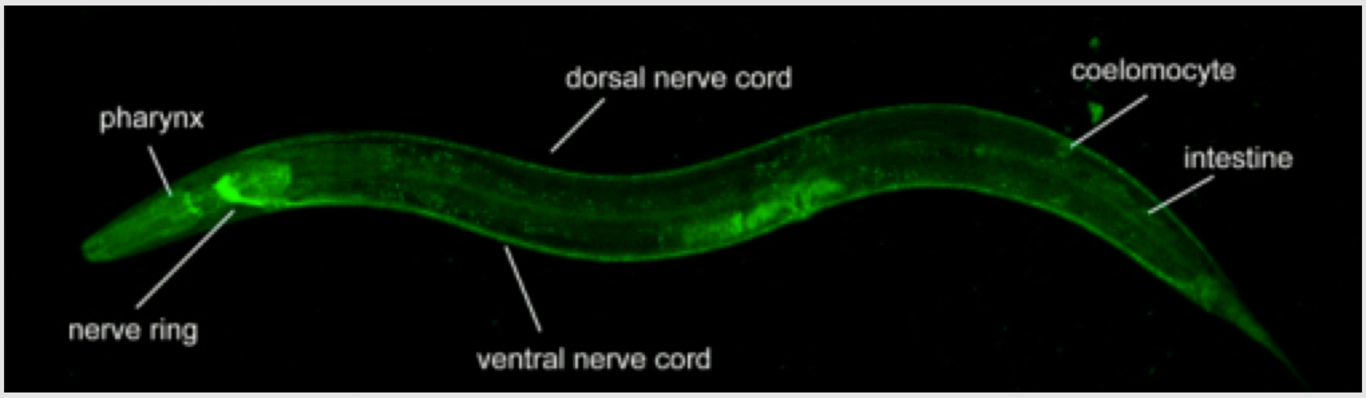
GFP mutants are often used to measure gene expression rates. Recall that genes *are not* continuously expressed at the same rate. It is of great medical importance to understand what agents or environments can increase or decrease gene expression rates. Measuring gene expression rates provides information that can lead to new or better treatments for diseases, and to better understanding of other health and biological phenomena. Before GFP mutants were used to measure the expression rates for genes of interest, organisms often had to be sacrificed so that the amount of protein or mRNA that was generated by the genes of interest could be extracted and measured. More recently, using a genetic engineering technology called *gene targeting*, GFP mutants are made by inserting a GFP gene ***next to*** the gene in which the expression rate is to be measured. Then, whenever the gene of interest is expressed, a green fluorescent protein is also expressed. The rate of gene expression is determined by illuminating the animal (or cells) with ultraviolet light and then measuring the amount of green light that is emitted. The intensity of the fluorescent light is proportional to the rate that the gene of interest is expressed. An advantage of this technique is that the expression levels can be studied over long periods of time because the measurements can be made on live organisms.

A common GFP mutant for studying gene expression is a nematode (worm) called *C. elegans*. This worm is about 1 mm in length and has a diameter close to that of a human hair. *C. elegans* is a popular model organism because it is small enough to easily grow in labs, but larger than single-cell organisms, so it contains small organs such as nerve cords, intestine, pharynx, etc. It is of interest to some researchers to study the expression of the **APA-2** gene. This gene codes for a protein that transforms the cell membrane into vesicles that are involved in transporting substances into the cells (endocytosis). In order to study expression of the APA-2 gene, a GFP gene is inserted *next to* the APA-2 gene in the *C. elegans* genome, as illustrated below.



A microscope image of a *C. elegans* GFP mutant in which the GFP gene was inserted next to an APA-2 gene is shown in Figure 14.9.

Figure 14.9 **A *C. elegans* GFP Mutant**



Fluorescence microscope image of a *C. elegans* GFP mutant in which the GFP gene was inserted next to an APA-2 gene. The intensity (brightness) of the green color in the image shown above is proportional to the expression rate of the APA-2 gene.

Source: Wikimedia Commons, Authors: Gu M, Liu Q, Watanabe S, Sun L, Hollopeter G, Grant BD, Jorgensen EM (adapted from original file). CC-BY, http://creativecommons.org/licenses/by/3.0/

When a small organism, such as a *C. elegans*, is imaged, it is possible to observe and measure the differences in expression rates between various parts of the organism. The intensity (brightness) of the green color in the image shown above is proportional to the expression rate of the APA-2 gene. The tissues/organs with greater expression rates have a brighter green color.

Bioethics: Using What We Know

Research in the field of genetics has made it possible to know the makeup of *your personal genome*. Information of this kind can lead to positive outcomes, such as predicting and treating many diseases. However, human genetic research can also result in negative consequences if we do not carefully consider its ethical, legal, and social implications. **Bioethics** is a term used to describe *the study of ethical issues that arise from biological technologies*. Some of the bioethical concerns that involve human genetics include the following questions:

- What individuals or corporate entities can have access to personal genetic information?
- Is genetic information something that can be patented and owned?
- Who should be genetically tested and at what age should genetic testing be performed?
- Should we re-engineer the genes we pass on to our children?

These are complicated questions. The best solutions for complicated questions are usually not found by simple yes/no, or “one-size-fits-all” approaches. Furthermore, new research and emerging technologies make it necessary to frequently reconsider prior policies. Complicated questions often require complicated solutions. In order to reasonably address these bioethical questions, it is necessary to have an understanding of the fundaments of genetics and nucleic acid chemistry. It was my intention to provide you with such an understanding in this chapter.

Chapter 15: Metabolism

In this final chapter, you will be able to see how the chemistry concepts that you learned in previous chapters provide a foundation for a better understanding of biological sciences. I think you will find that your understanding of chemistry will allow you to more deeply understand the life science topics that you first studied in elementary school, high school, and prior college courses. In chapter 15, you will learn about a topic that will be immediately useful to most health science students: the metabolism of food in humans.

15.1 Chapter 15 Educational Goals

1. Define the terms **metabolism**, **metabolic pathway**, **catabolism**, and **anabolism**.
2. Understand how **ATP** is formed from **ADP** and inorganic phosphate (**P_i**), and vice versa.
3. Understand how **Coenzyme-A** is used to *transfer* **acyl groups**.
4. Understand the roles of the **NAD^+/NADH** and **FAD/$FADH_2$** coenzymes in the *transfer of electrons*. Identify the **oxidized** and **reduced form** of each of these pairs.
5. Understand the differences between **linear**, **circular**, and **spiral** *metabolic pathways* and give an example of each.
6. Name the products formed during the **digestion** of *polysaccharides*, *triglycerides*, and *proteins*, and know the part(s) of the digestive track where each occurs.
7. Identify the initial reactant and final products of **glycolysis**, and understand how this pathway is controlled.
8. Understand and compare **glycolysis** and **gluconeogenesis** pathways.
9. Know the *fate of pyruvate* under **aerobic** and **anaerobic** conditions.
10. Define the terms ***hyperglycemic*** *and* ***hypoglycemic****.*
11. Understand how the body controls **blood glucose concentration** by the release of **insulin** or **glucagon** into the bloodstream.
12. Understand and compare **glycogenesis** and **glycogenolysis**. Understand how these processes are involved in maintaining normal blood glucose concentration.
13. Understand and compare **type I**, **type II**, and **gestational diabetes**.
14. Identify the initial reactant and final products of the **citric acid cycle**; understand how this pathway is controlled.
15. Understand how the *oxidation of coenzymes* during **oxidative phosphorylation** is used to produce **ATP**.
16. Compare the **malate-aspartate shuttle** and the **glycerol 3-phosphate shuttle** and understand their significance in affecting the amount of **ATP** that can be produced from glucose.
17. Predict how many **ATP** are formed when **acetyl-CoA** undergoes ***stages*** **3** and **4** of catabolism.
18. Describe the **catabolism of triglycerides**, the **β-oxidation spiral**, and how *β-oxidation* differs from **fatty acid anabolism** (biosynthesis).
19. Given the structure of a **fatty acid**, predict how many **ATP** are formed when it undergoes the ***β-oxidation spiral***.
20. Understand and compare **lipolysis** and **fatty acid synthesis**.
21. Explain the biological origins of **ketosis** and **ketoacidosis**.
22. Understand how **transamination** and **oxidative deamination** are involved in the **catabolism of amino acids**.
23. Given the structure of an **amino acid** and **α-ketoglutarate**, predict the products of a **transamination reaction**.
24. Explain how ***quaternary ammonium groups*** ($-NH_3^+$) are removed from amino acids ***and*** eliminated from the body.

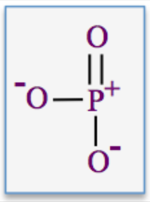
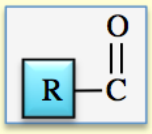
15.2 Overview of Metabolism

Metabolism is defined as *the entire set of life-sustaining chemical reactions that occur in organisms*. These reactions number in the thousands and include reactions such as those responsible for getting energy from food, processing and removal of waste, building up muscles, growth, photosynthesis in plants, cell division, and reproduction. The entire set of metabolic reactions is organized into smaller sets of sequential reactions called **metabolic pathways**. The species produced in the various reactions of a metabolic pathway are sometimes referred to as **metabolites**. Many of the reactions in metabolic pathways require enzymes, therefore organisms can control (accelerate or suppress) metabolic pathways, according to their current needs, by *upregulating*, *downregulating*, *inhibiting*, or *activating* one or more of the enzymes involved in the pathway.

Metabolic pathways can usually be classified as **catabolic** (catabolism) or **anabolic** (anabolism). ***Catabolic pathways*** involve the *breakdown* of larger organic compounds into smaller compounds. ***Anabolic pathways*** involve *building up* of larger organic compounds from smaller ones. An example of an *anabolic pathway* is *photosynthesis*. In this pathway, plants build glucose from CO_2 and H_2O. An example of a catabolic pathway, is *glycolysis*. This pathway is a series of reactions that break down glucose into smaller compounds.

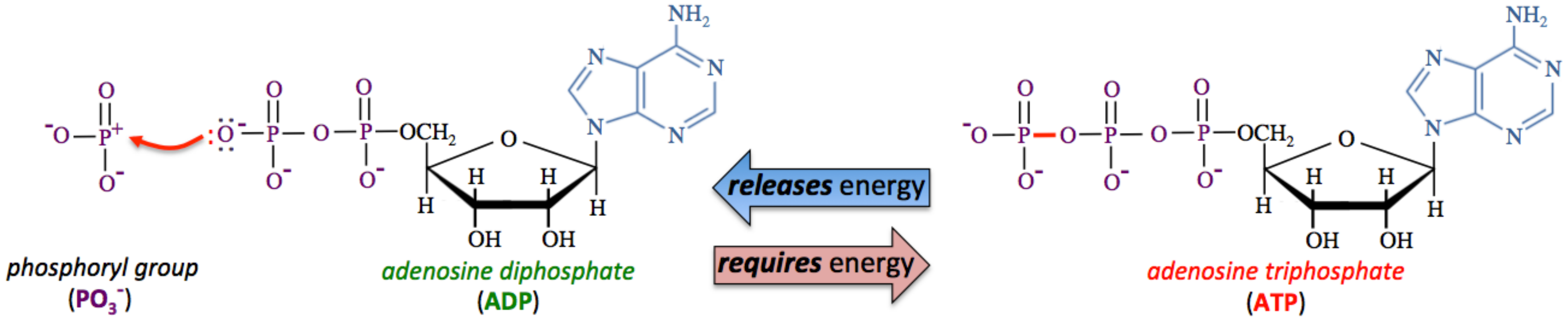
In this chapter, you will learn about the pathways that are involved in the metabolism of carbohydrates, proteins, and fats. An ultimate goal of these reactions is to convert the chemical potential energy contained in food into chemical potential energy in the form of **ATP**. This is a key metabolic strategy because chemical energy from **ATP** is used by organisms to do cellular work *and* provide the energy required for life-sustaining reactions that otherwise do not occur spontaneously. The advantage of converting chemical energy from food to **ATP** is that **ATP** is an energy source that can be instantaneously used by organisms. For example, if a person needs to move suddenly, **ATP** is immediately used to make muscles contract.

Before I discuss the metabolism of food, I will discuss the ***coenzymes*** that are involved. You may recall that a *coenzyme* is a species that must bind to an enzyme in order for the enzyme to function. In most cases, a coenzyme is actually one of the *substrates* (reactants) in the catalyzed reaction. The reason that certain *substrates* are ***also*** referred to as *coenzymes* is that these *substrates* are ***common substrates in many different enzymatic reactions*** in which they ***donate electrons, atoms, or groups of atoms*** to other substrates, ***or accept electrons***, ***atoms or groups of atoms*** from other substrates. The five group-transfer coenzymes that are central to the metabolization of food, along with the species each transfers are listed below.

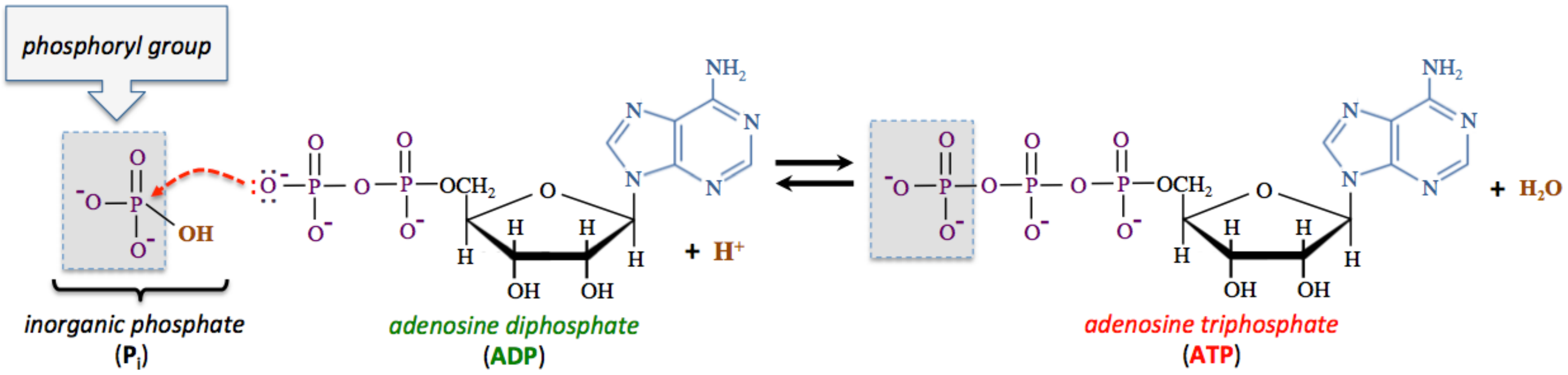
Coenzyme	Species that is Transferred
ADP/ATP	phosphoryl group =  $^{-}O-P^{+}(=O)-O^{-}$
NAD^+/NADH	hydride ion ($H:^-$) **or** electrons
FAD/$FADH_2$	hydride ion ($H:^-$) **or** electrons
coenzyme A	acyl group =  $R-C(=O)$
coenzyme Q	hydride ion ($H:^-$) **or** electrons

Phosphoryl Group-Transfer Coenzymes: ATP and ADP

ATP and **ADP** are classified as **coenzymes** because they are involved in the *transfer* of **phosphoryl groups** (PO_3^-) ***in many different enzymatically catalyzed reactions***. When a compound gains/accepts a *phosphoryl group* in a reaction, we say that the compound became "**phosphorylated.**" When a compound loses/donates a *phosphoryl group* in a reaction, we say that it was "**dephosphorylated.**" Because **ATP** and **ADP** are used so often and in so many *different* reactions, ***each*** **ATP** particle in your body is converted to **ADP** and then back to **ATP** *about 500 times per day*. **ATP** and **ADP** are interconverted by the transfer of a *phosphoryl group*, as shown below.

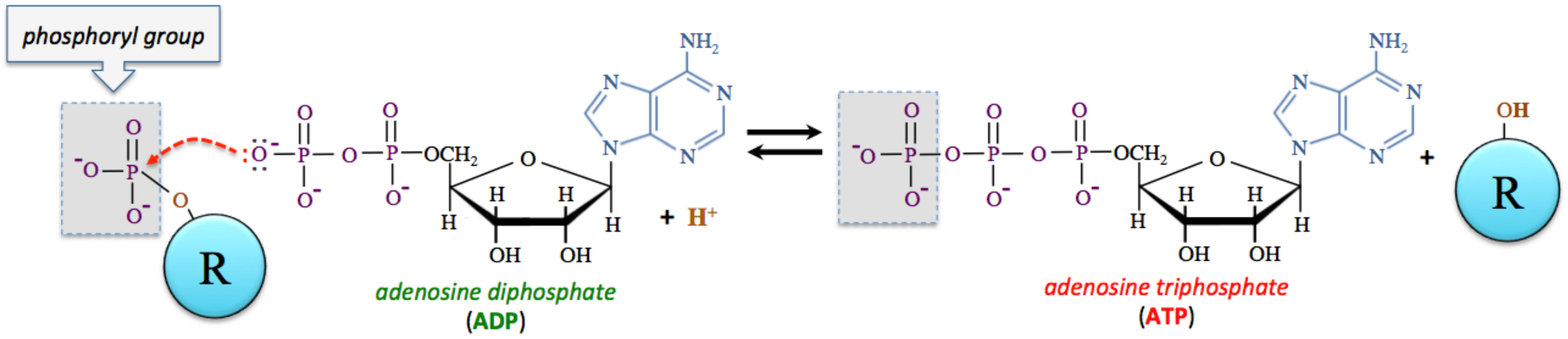


Adding a *phosphoryl group* to **ADP** in order to form **ATP** ***requires*** energy. Catabolic metabolic pathways often use the energy contained in food to drive the transfer of *phosphoryl groups* to **ADP**, thereby forming **ATP**. **ATP** is often formed by the reaction of **ADP** with *hydrogen phosphate* (HPO_4^{2-}) and an $\mathbf{H^+}$ ion. Biological literature refers to *hydrogen phosphate* as "**inorganic phosphate"** (abbreviated as $\mathbf{P_i}$). The chemical equation for the transfer of a *phosphoryl group* ($\mathbf{PO_3^-}$) ***from*** *inorganic phosphate* ($\mathbf{P_i}$) ***to*** **ADP** is shown below.



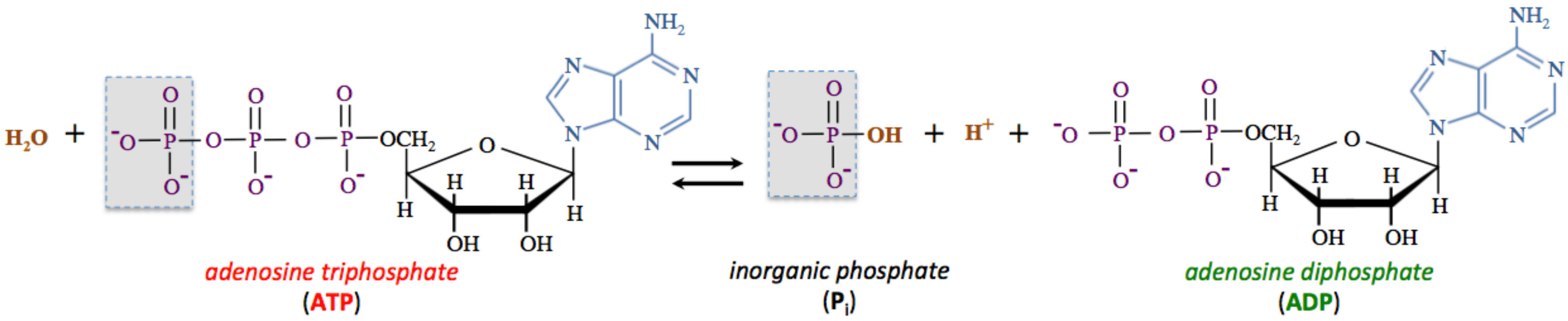
This reaction will not occur spontaneously unless external energy is provided. Later in this chapter, you will see how energy that is ***released*** from the catabolism of food is *converted* to electrochemical energy within cells' mitochondria, and then the electrochemical energy is used to provide the energy needed to enable this reaction to occur spontaneously.

Another way that organisms convert **ADP** to **ATP** is by the reaction of **ADP** with an organic molecule *that contains a phosphoryl group*. In this case, a *phosphoryl group* is transferred ***from*** the organic molecule ***to*** **ADP,** as shown in the chemical equation below.



You will see hydrogen ions ($\mathbf{H^+}$) as reactants *in many of the reactions in this chapter*. Because these reactions occur in aqueous solutions, $\mathbf{H^+}$ is ***readily available*** from $\mathbf{H_2O}$, and can also come from $\mathbf{H_3O^+}$ or the *acid forms* of other species that are present.

Energy is ***released*** from **ATP** when it is converted to **ADP**. This energy is used by organisms to drive energy-requiring reactions or physical processes that would otherwise not occur spontaneously. *One* way that energy can be released from **ATP** is by reacting it with **H_2O** to ***form*** **ADP**, *inorganic phosphate*, and an **H^+** ion. Although this reaction is spontaneous (ΔG is negative), the reaction rate is quite slow, therefore organisms employ enzymes in order for the reaction to proceed at a useful rate. The chemical equation for this reaction is shown below.



ΔG = *-7300* Joules per mole of **ATP**

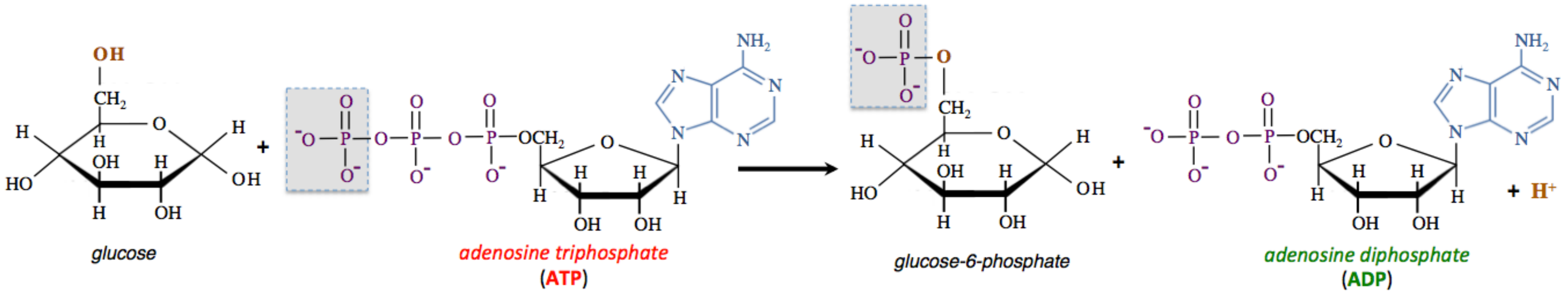
Note that **H^+** is *produced* in this reaction. You will see **H^+** ions as products *in many of the reactions in this chapter*. Keep in mind that the **H^+** ions that are produced in aqueous solutions do not remain solvated as *isolated ions*; they quickly react with water to form **H_3O^+**. Alternatively, **H^+** can react with **OH^-** or the *base form* of another species that is present.

Another way that organisms extract energy from **ATP** is to "energize" organic compounds by transferring a phosphoryl group *directly* to the compound. In this reaction, **ATP** is ***dephosphorylated*** and an organic compound is ***phosphorylated***, as shown in the reaction below:

ATP + organic compound ⇄ **ADP** + phosphorylated organic compound + **H^+**

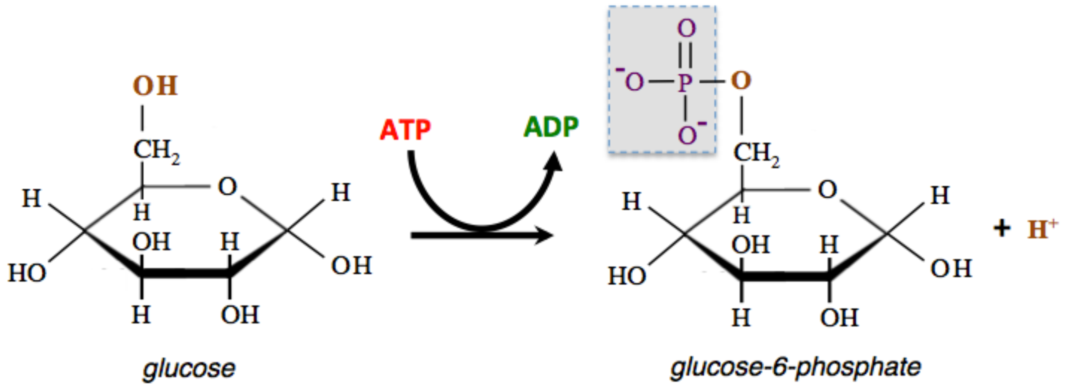
Chemical potential energy ***released*** by the conversion of **ATP** *to* **ADP** is *transferred to the phosphorylated organic product*. It is for this reason that we say "the organic compound is energized" in the reaction. It is common for organisms to "energize" organic compounds by phosphorylation in order to make subsequent metabolic pathway reactions occur spontaneously.

The first reaction of the glycolysis metabolic pathway is an example of "energizing" an organic compound by phosphorylation. In this reaction, glucose reacts with **ATP** to form glucose-6-phosphate, **ADP**, and an **H^+** ion, as shown below.



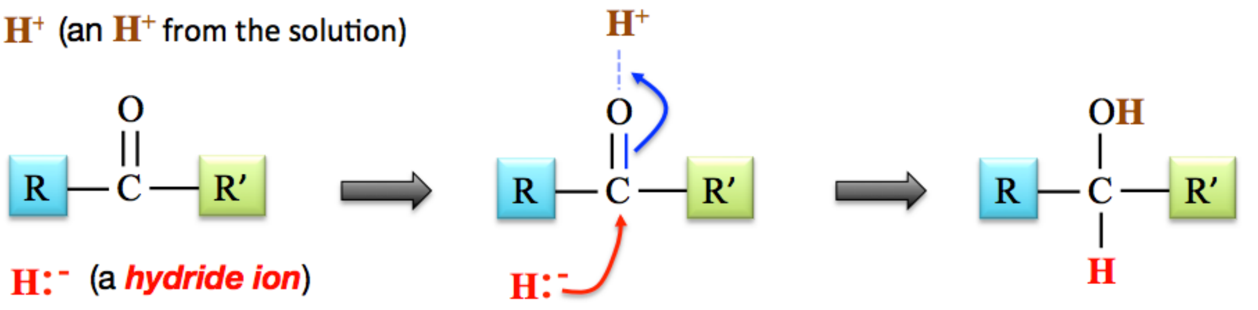
In this particular reaction, the reverse reaction occurs so slowly that it is negligible. In such cases, we refer to the reaction as an "**irreversible reaction.**" *Irreversible reactions* are frequently seen in biology. When writing a chemical equation for an irreversible reaction, only a forward (left to right) arrow is used, as shown *above*.

Biochemical literature often uses an *alternative* chemical equation format. For example, the reaction shown above is often written as:



Electron-Transfer Coenzymes and Their Role as Oxidizing and Reducing Agents

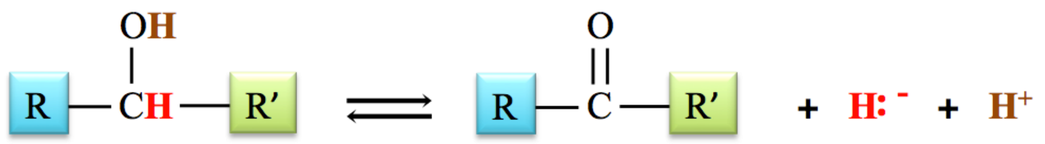
Oxidation-reduction reactions, which involve the transfer of one or more electrons, are quite common in organisms. Many of these reactions involve the transfer of an electron by way of the ***hydride ion*** (**$H:^-$**). Recall that a hydrogen *atom* has one electron, whereas a *hydride ion* has an "extra" (second) electron. A ***reduction*** occurs when a hydride ion forms a bond with an organic compound. The transfer of a hydride ion is a reduction because of hydride's "extra" electron. For example, you learned in chapter 10 that aldehydes or ketones are ***reduced*** when a ***hydride ion*** forms a bond with them. This is accompanied by the bonding of an **H^+** ion to produce an alcohol, as shown below.



a ketone

an alcohol

You learned that ***oxidation*** occurs when a *hydride ion* (**$H:^-$**) and an **H^+** ion are *removed* from an organic compound. For example, you saw that 2° alcohols can be ***oxidized*** to ketones, as shown in the chemical equation below.



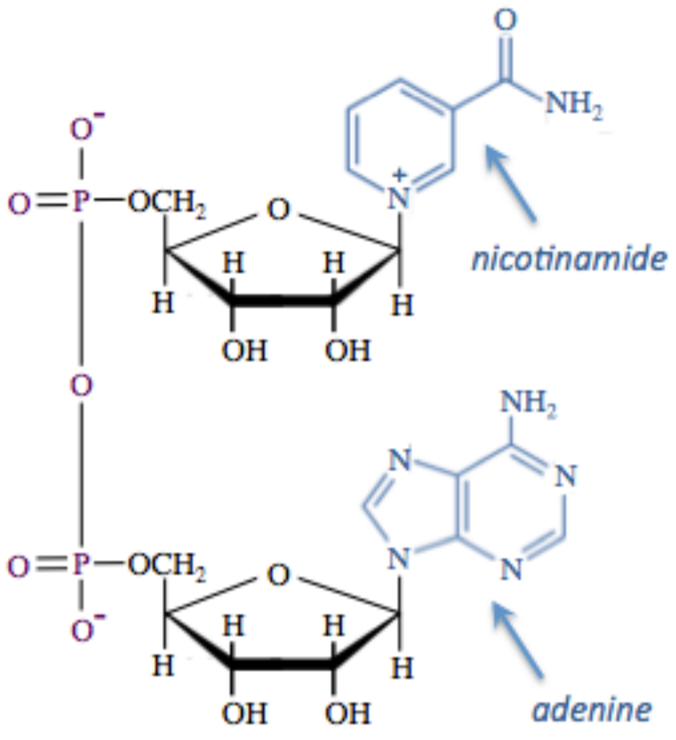
$$R-\overset{OH}{\overset{|}{C}}H-R' \rightleftharpoons R-\overset{O}{\overset{\|}{C}}-R' + H:^- + H^+$$

an alcohol

a ketone

This is considered an oxidation because the hydride ion carries away the "extra" electron.

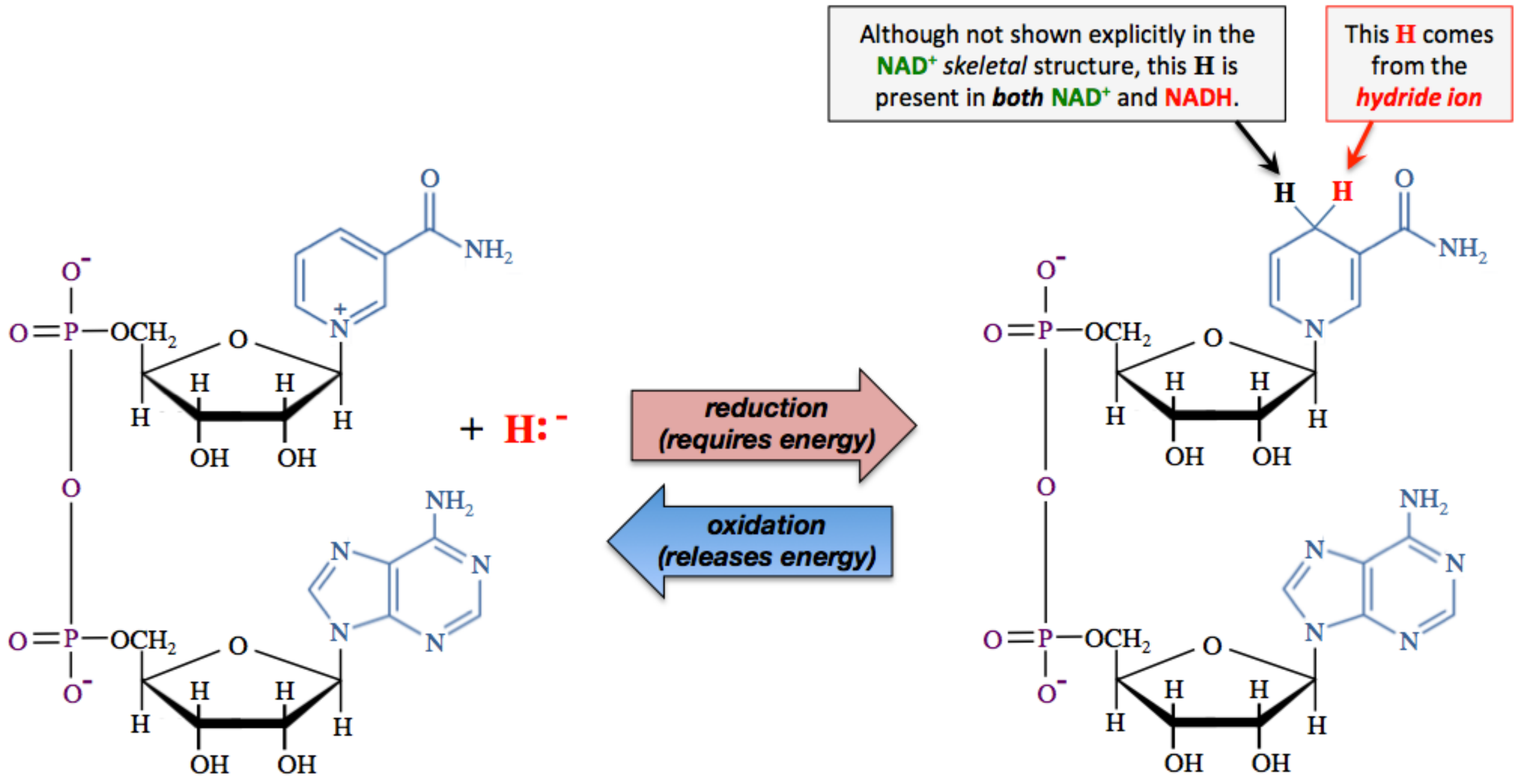
Nicotinamide adenine dinucleotide (**NAD^+**) and flavin adenine dinucleotide (**FAD**) are classified as **coenzymes** because they are common substrates, involved in the transfer of electrons, ***in many different enzymatically catalyzed reactions***.



nicotinamide adenine dinucleotide
(NAD^+)

Let's take a look at **NAD^+** first. The structural formula of **NAD^+** is shown on the left. **NAD^+** contains *two* nucleotide residues. One of the nucleotides has an ***adenine*** base, and the other contains a ***nicotinamide*** base. *Nicotinamide* is not one of the "*major*" bases (G,C,A,T, and U) that are found in DNA and/or RNA. Biological literature has historically abbreviated *nicotinamide adenine dinucleotide* (**NAD^+**) to include a positive (**+**) superscript. In this case, the "**+**" is referring *only to the formal charge on nicotinamide's ring-nitrogen*. It can be a bit misleading because the ***total charge*** of the nicotinamide adenine dinucleotide ion is actually (**1-**).

When **NAD$^+$** *accepts* a hydride ion from another species, it is ***reduced*** to **NADH**. It is for this reason that **NADH** is referred to as a ***reduced form of the coenzyme*** or a "**reduced coenzyme.**" The reduction of **NAD$^+$** ***requires*** energy. Note that this process is reversible. When **NADH** *donates* a hydride ion (to another species) it is ***oxidized*** to **NAD$^+$**. **NAD$^+$** is referred to as the ***oxidized form of the coenzyme*** or an "**oxidized coenzyme.**" Oxidation of **NADH** ***releases*** energy. A chemical equation for the oxidation/reduction of **NAD$^+$**/**NADH** is shown below.

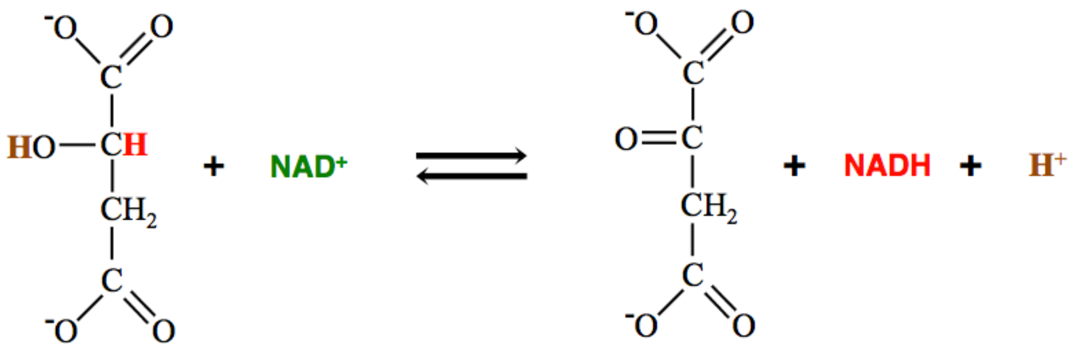

Although not shown explicitly in the NAD$^+$ *skeletal* structure, this **H** is present in ***both*** NAD$^+$ and NADH.

This **H** comes from the ***hydride ion***

oxidized form of the coenzyme
(**NAD$^+$**)

reduced form of the coenzyme
(**NADH**)

A specific example of the oxidation of an organic compound using **NAD$^+$** as the *oxidizing agent* is the oxidation of *malate*. This is one of the reactions that occurs in the metabolism of food, and that you will see again when I discuss the reactions of the citric acid cycle. In this reaction, *malate* is oxidized and **NAD$^+$** is reduced.

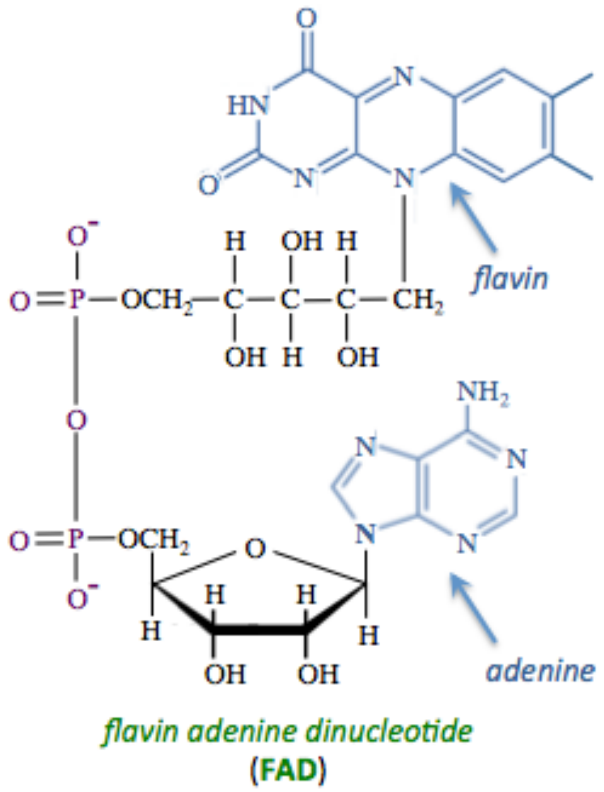


malate

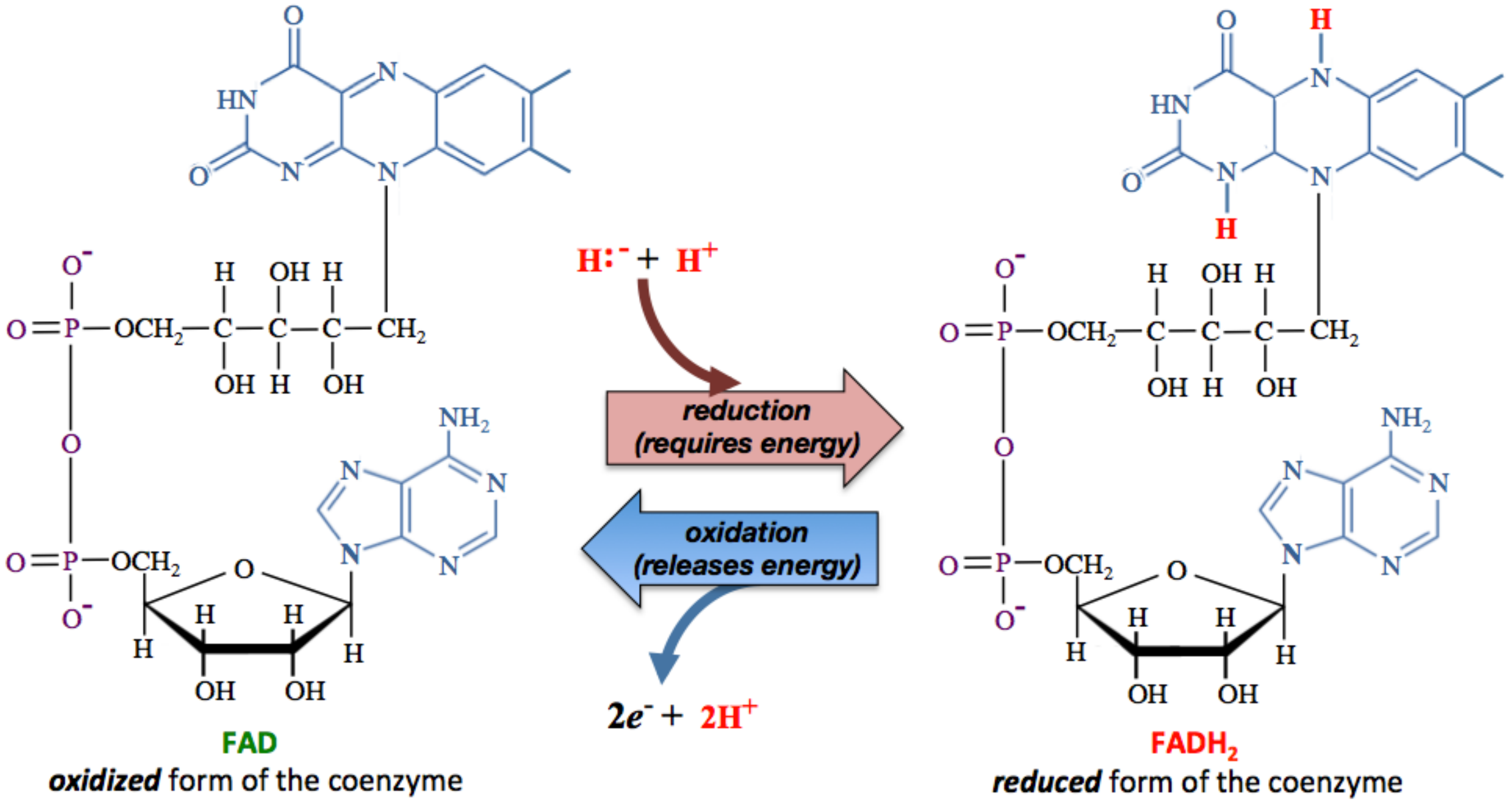
oxaloacetate

.

Let’s now consider flavin adenine dinucleotide (**FAD**), another electron-transfer coenzyme that is central to the metabolization of food. The structural formula of **FAD** is shown below.



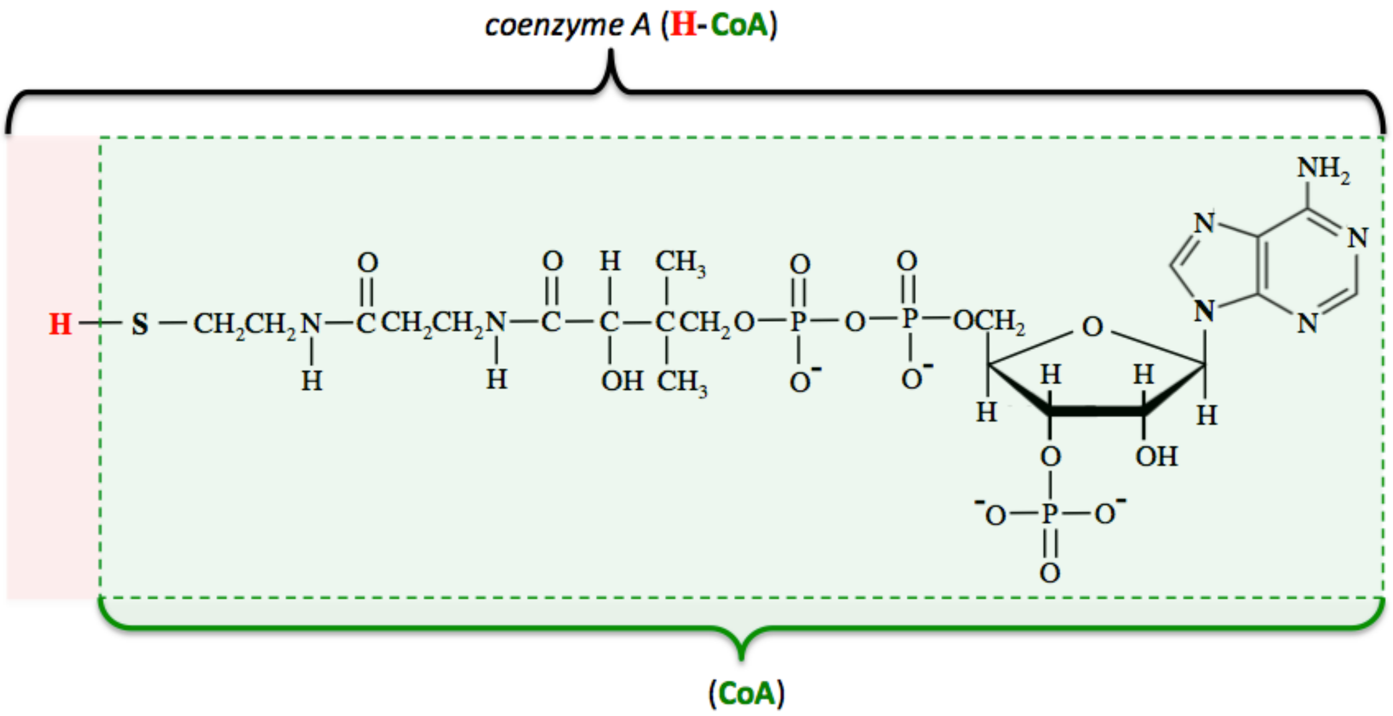
When **FAD** *accepts* a hydride ion from another species (and an H^+ from solution), it is ***reduced*** to **FADH₂**. **FADH₂** is **oxidized** to **FAD** by *donating* ***two*** electrons (and two H^+ ions) to other species. The oxidation of **FADH₂** *releases* energy, and the *reduction* of **FAD** requires energy. The structural formulas of **FAD** and **FADH₂** are shown below.

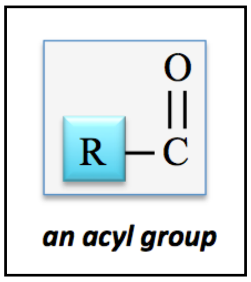


Much like **NAD⁺**/**NADH** and **FAD**/**FADH₂**, **Coenzyme Q** (*not shown*), transfers electrons and hydrogen ions when it cycles between its oxidized and reduced forms.

Acyl Group-Transfer Coenzyme: Coenzyme A

Coenzyme A (**H**-**CoA**) is used in many metabolic reactions. Its structural formula is shown below.

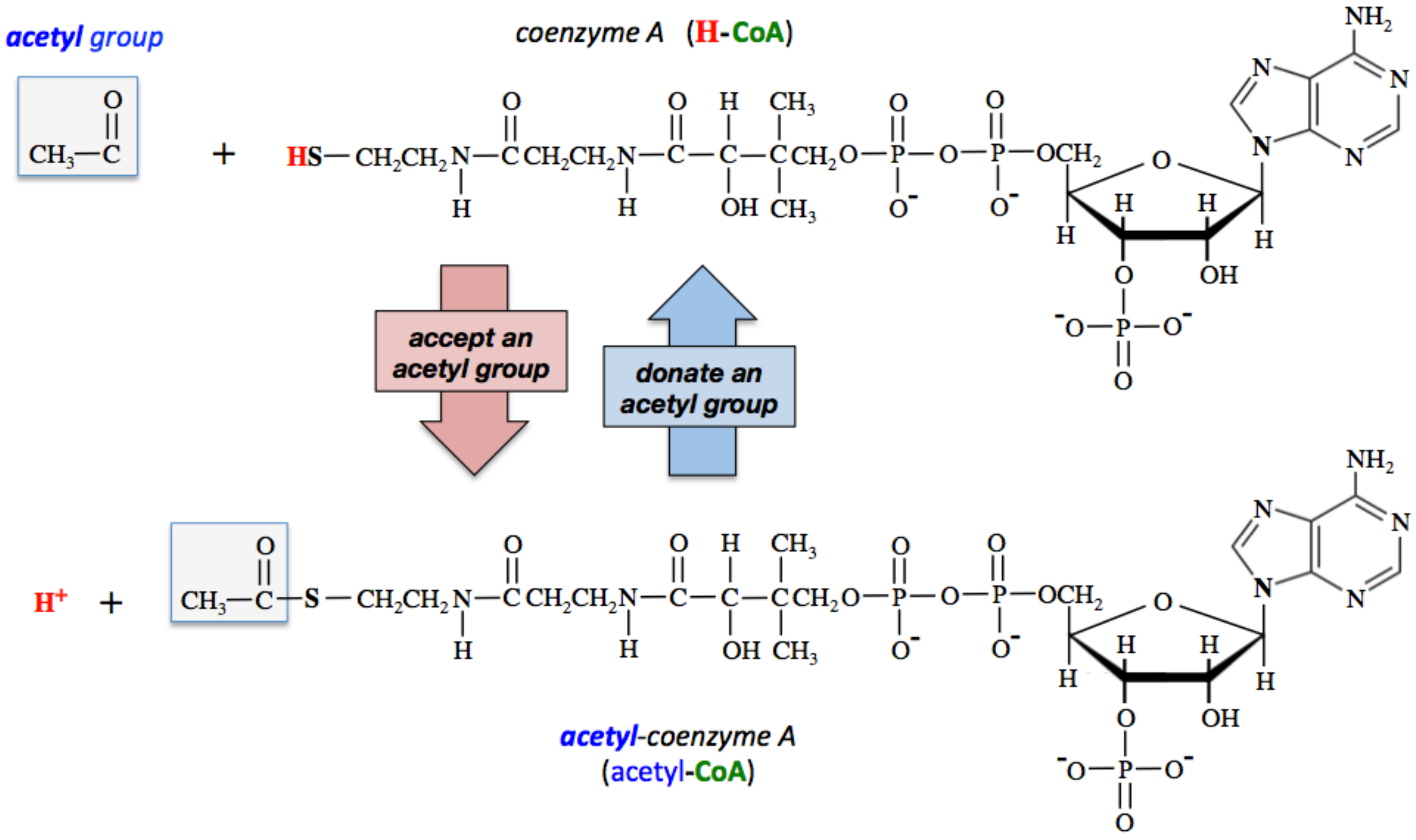




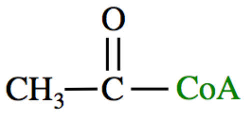
an acyl group

Coenzyme A is classified as a **coenzyme** because it is involved in the *transfer* of an ***acyl group in many different enzymatically catalyzed reactions***. An *acyl group* consists of a carbonyl group bonded to an organic group (**R**), as shown *on the left*. When *coenzyme A* (**H**-**CoA**) accepts an ***acyl group***, the *acyl group* replaces the *left-most* hydrogen (colored red) in the structure shown above.

An ***acyl group*** that is central to the metabolism of food is the **acetyl group**. *Acetyl groups* are donated and accepted by *coenzyme A*, as shown below:

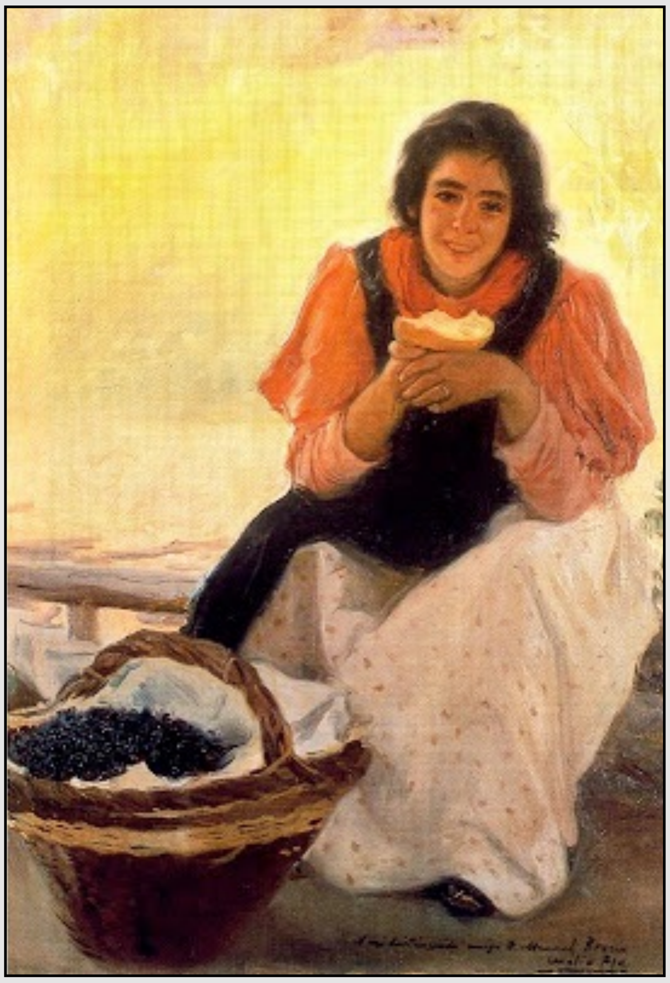


The structural formula of ***acetyl-coenzyme A*** (***acetyl*-CoA**) is often abbreviated as:


$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CoA$

15.3 Carbohydrate Metabolism

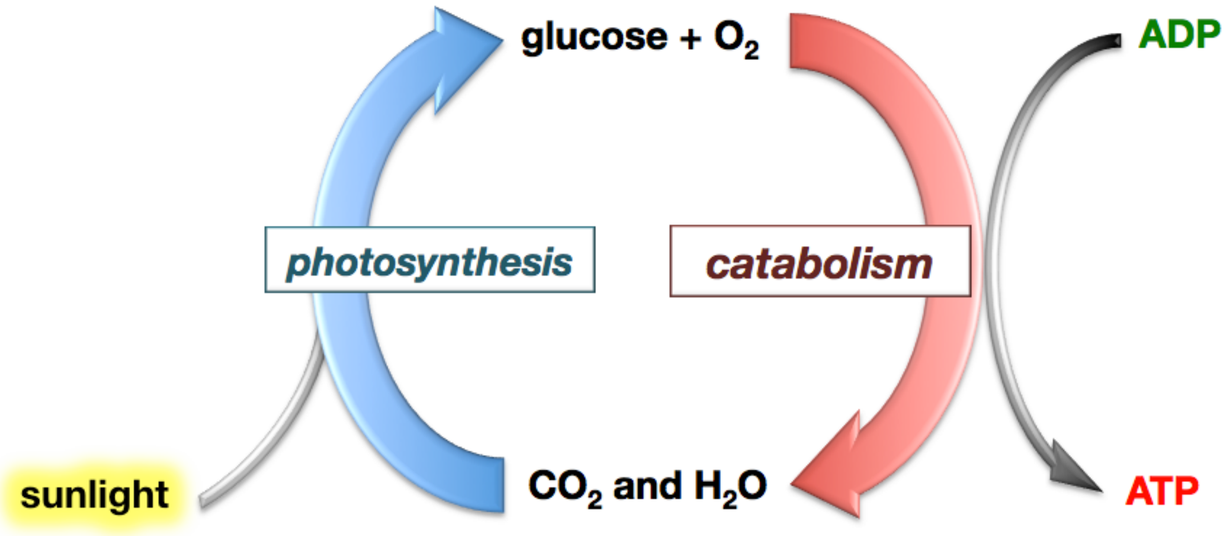
The energy that is contained in food can be traced back to the sun. Energy from sunlight is captured by plants during *photosynthesis* as they convert CO_2 and H_2O into *glucose* and O_2. Without energy from sunlight, the reaction of CO_2 with H_2O to produce glucose and O_2 is not spontaneous. You can convince yourself of this by exhaling CO_2 through a straw and into water. If glucose were produced spontaneously, then you would be able to taste the sweetness of glucose in the water; but the solution does not taste sweet. The reaction does not occur on its own (spontaneously) because glucose and O_2 gas are higher in free energy than are CO_2 and H_2O. However, the input of energy from sunlight provides the energy that is required to convert CO_2 and H_2O to glucose and O_2.



Title: Girl Eating Bread
Artist: Cecilio Plá y Gallardo

In photosynthesis, energy from the sun's light does not vanish; it is converted to ***chemical potential energy*** within *glucose*. Plants store excess *glucose* as ***starch***. One way to extract the energy from starch is to burn it. In fact, granaries (factories that extract and store starch in the form of flour) are very dangerous because of aerosolized starch/flour particles that are in the air. Huge explosions and fires have occurred in granaries when one spark ignites the aerosolized starch particles. In such fires and explosions, *the energy is wasted*; none of it is used to do work. If the starch were burned under a sealed container that has some water in it, the energy released from the starch would cause the water to boil and the resulting high-pressure vapor could be used to move a piston. This is how a steam engine works (although fuels other than starch are used to heat the water).

Humans did not evolve steam engines as power supplies. Instead, we use a series of **catabolic** chemical reactions to ***slowly oxidize food***, eventually converting it back to CO_2 and H_2O. Energy that is released in these oxidations is converted to chemical potential energy within **ATP**. Not *all* of the energy released by the oxidation of food is converted to energy within **ATP**, some is lost as heat. Organisms lose about 50% of food's energy as heat. It is this heat that allows us to maintain our normal body temperature in cooler environments. Note how nature cycles glucose and O_2 with CO_2 and H_2O using photosynthesis (an anabolic process) and glucose catabolism, as illustrated below.



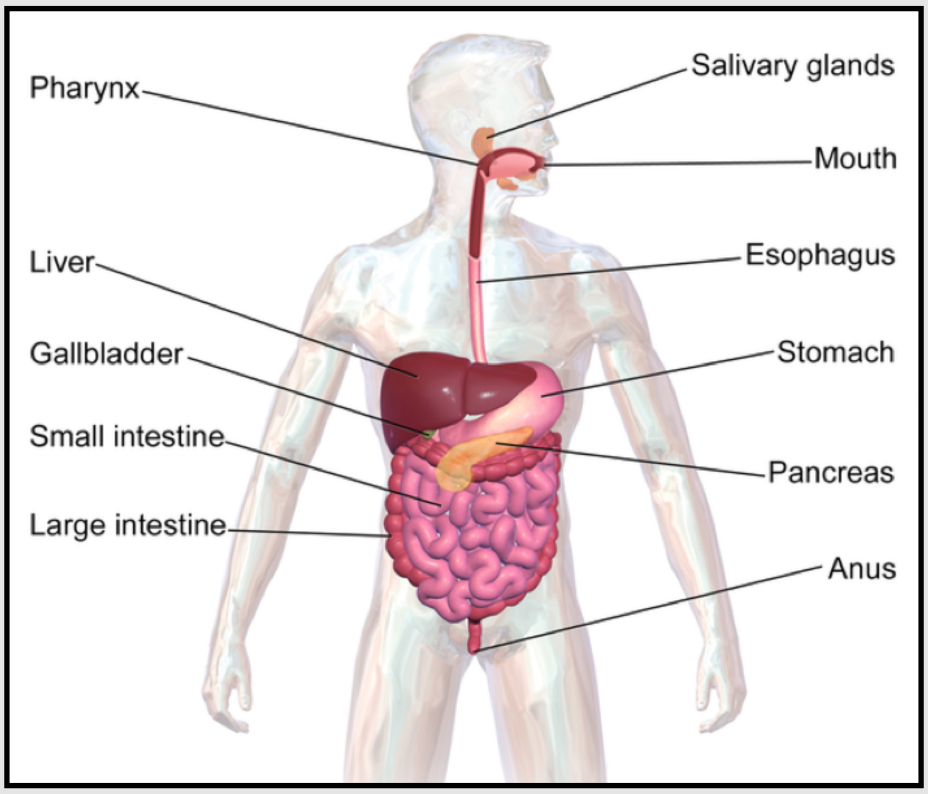
All three classes of macronutrients in food, carbohydrates, triglycerides (fats), and proteins, are catabolized in ***four stages***: digestion, acetyl-CoA production, the citric acid cycle, and oxidative phosphorylation.

Stage 1: Digestion of Carbohydrates

Digestion is the process in which the body breaks down carbohydrate, protein, and triglyceride polymers into their monomer residues. For example, carbohydrate polymers are converted to monosaccharides. Digestion occurs in the **digestive system**. The *digestive system*, sometimes referred to as the **digestive track** or **gastrointestinal (GI) track**, includes the organs that are responsible for digesting food and eliminating the *un*digestible components of food. The major organs of the human digestive system are shown in Figure 15.1.

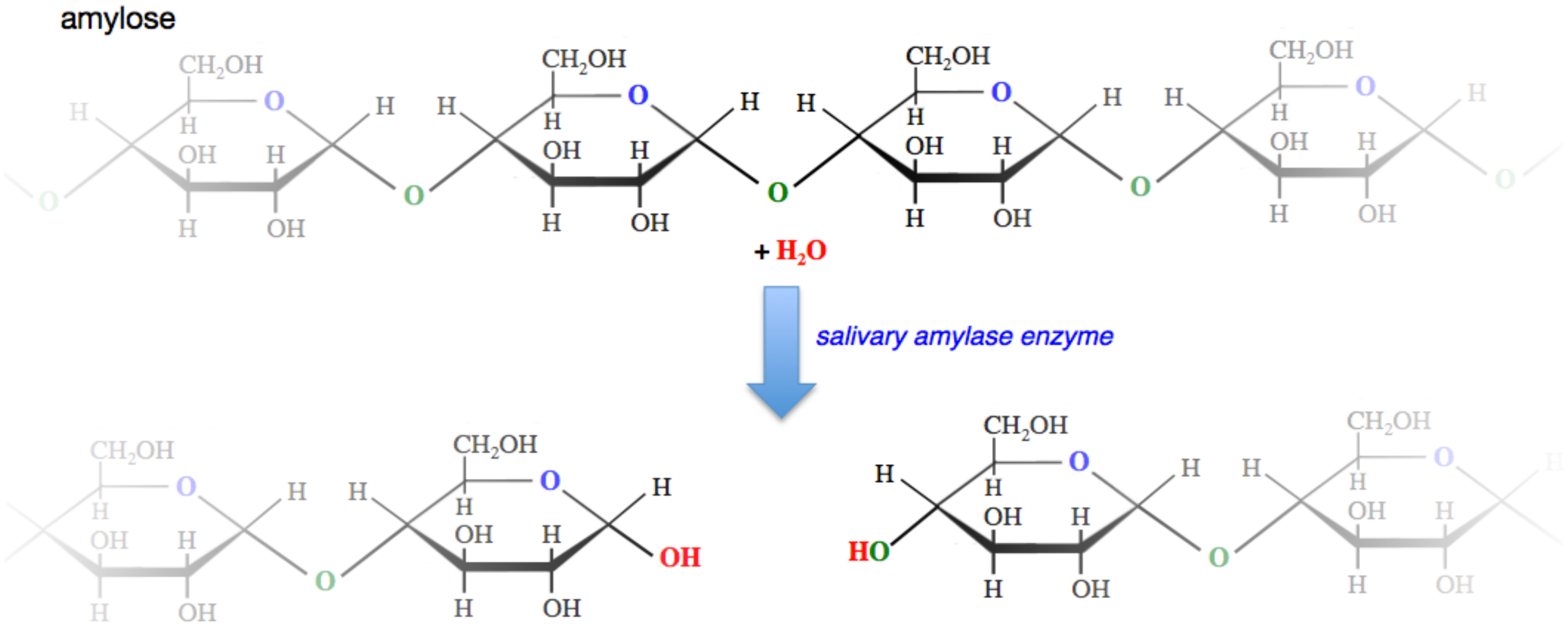
During the digestion of carbohydrate polymers, most oligosaccharides (2-10 monosaccharide residues) and polysaccharides (more than 10 monosaccharide residues) can be broken down to monosaccharides. These reactions are catalyzed by digestive enzymes.

Figure 15.1
Major Organs of the Human Digestive System



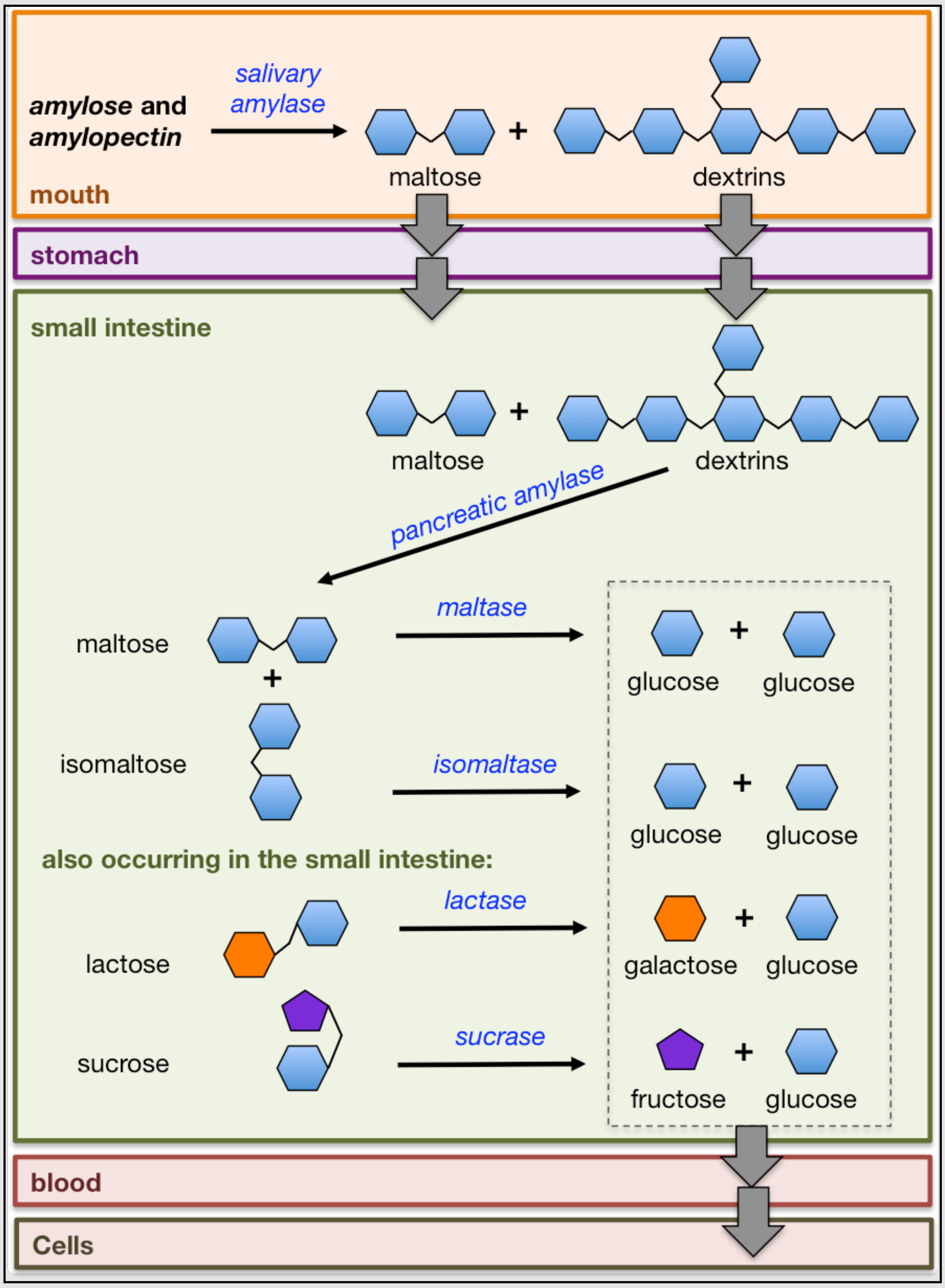
Source: Wikimedia Commons, Author: Blausen.com staff. "Blausen gallery 2014". *Wikiversity Journal of Medicine*. DOI:10.15347/wjm/2014.010. ISSN 20018762. CC-BY-SA, https://creativecommons.org/licenses/by-sa/4.0/deed.en

Approximately 50% of our dietary carbohydrates are in the form of **starch**. In chapter 11, you learned that starch has two components, amylose and amylopectin, both of which are composed entirely of glucose residues. Digestion of amylose and amylopectin begins in the mouth. Saliva contains *salivary amylase enzymes*, which catalyze the hydrolysis of some of the **α-(1⟶4)** glycosidic bonds in amylose and amylopectin. In the hydrolysis of carbohydrates, water molecules are used to lyse (break) ***glycosidic bonds***. The hydrolysis of a glycosidic bond is the reverse of the reaction that you learned in chapter 11 for the *formation* of a glycosidic bond. An example of the hydrolysis of *one* of amylose's **α-(1⟶4)** glycosidic bonds is shown below.



An illustrative overview of the digestion of carbohydrates is shown in Figure 15.2.

Figure 15.2 An Overview of Carbohydrate Digestion



Salivary amylase catalyzes the hydrolysis of amylose and amylopectin to form *maltose* (an **α-(1⟶4)** glucose-glucose disaccharide) and small oligosaccharides called **dextrins**. ***Dextrins*** are oligosaccharides that generally contain between *three* and *eight* glucose residues. The maltose, dextrins, and other non-starch dietary carbohydrates then pass through the stomach, where carbohydrate digestion temporarily stops because the *salivary amylase* is denatured by the stomach's low pH (very acidic) environment.

Digestion continues in the small intestine with the help of more digestive enzymes. *Pancreatic amylase* catalyzes the hydrolysis of *dextrins* to form *maltose* and *isomaltose. Isomaltose is an* **α-(1⟶6)** glucose-glucose disaccharide that comes from the **α-(1⟶6)** branching points in *amylopectin*. *Maltase* and *isomaltase* enzymes catalyze the hydrolysis of maltose and isomaltose (respectively) into glucose.

The ***non starch*** dietary carbohydrates, *lactose* and *sucrose,* are converted to monosaccharides with the help of *lactase* and *sucrase* enzymes, respectively. Lactose is hydrolyzed to galactose and glucose. Sucrose is hydrolyzed to fructose and glucose.

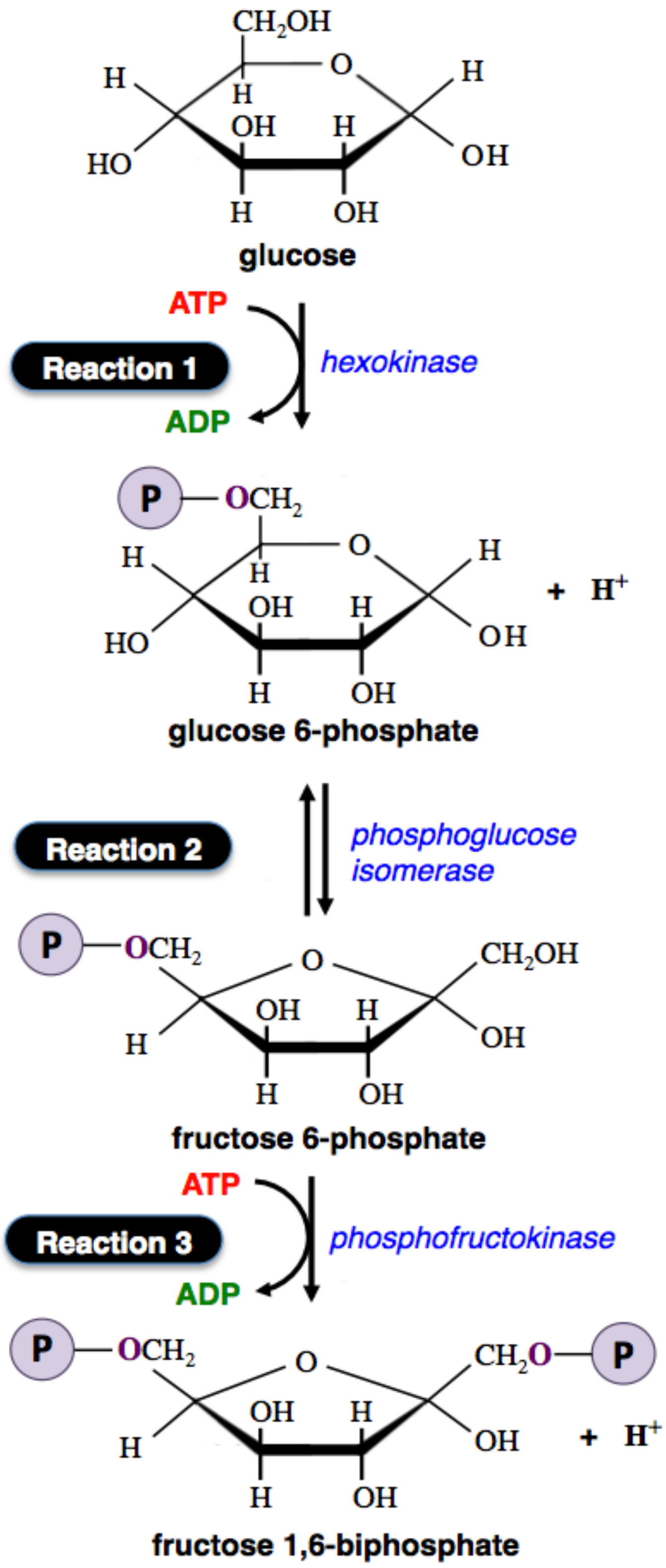
It is critical that oligosaccharides and polysaccharides be converted to monosaccharides in order for the sugars to pass through the intestine wall and into the bloodstream so that they are available to cells throughout the body. Monosaccharides are transported into the cells by passive diffusion through transmembrane proteins.

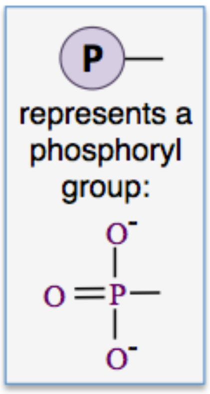
Not all dietary carbohydrates can be digested. For example, cellulose cannot be digested because humans do not have a dietary enzyme capable of hydrolyzing **β-(1⟶4)** glucose-glucose glycosidic bonds. Cellulose cannot pass through the small intestine and therefore passes through the digestive track until it is excreted in feces.

When glucose enters a cell, it can then undergo **stages 2**, **3**, and **4** of catabolism.

Stage 2: Acetyl-Coenzyme A Production

At this point in carbohydrate catabolism, the energy that originally came from sunlight is in the form of monosaccharides. Because of the nature of our diets, which is generally much higher in starch than other carbohydrate nutrients, about 90% of the monosaccharide products of digestion are glucose molecules. Non glucose monosaccharides, such as fructose and galactose, can be converted to glucose. I will discuss the conversion of non glucose monosaccharides to glucose a bit later. First, let's consider the *fate of glucose*. In **stage 2** of carbohydrate catabolism, ***glucose*** is converted into **acetyl-coenzyme A**, CO_2, and H_2O. This process begins with a *catabolic pathway* called **glycolysis**. ***Glycolysis*** is a series of ten sequential reactions that ultimately converts one glucose molecule to two pyruvate ions and two H_2O molecules. Before I describe these reactions, I want to minimize any possible student anxiety by informing you that is not my intention for you to memorize these reactions, the names of the intermediates, or the names of the enzymes that are involved. The **reactions of glycolysis** are listed and discussed below.

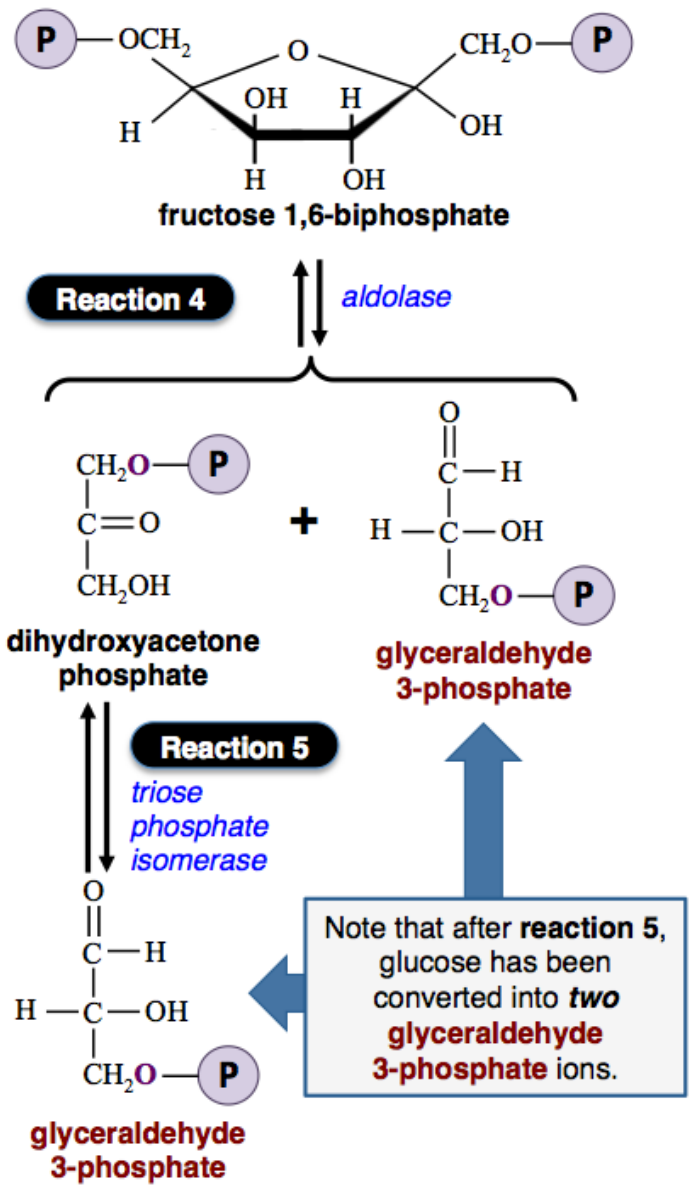




Reaction 1) Once glucose enters a cell, it is phosphorylated. In this reaction, a phosphoryl group is transferred from **ATP** to glucose. Note that this reaction requires a phosphoryl group ***that comes from*** **ATP**. Glucose would not spontaneously react with a free, aqueous phosphate ion. However, when a phosphoryl group is transferred from **ATP**, the reaction occurs spontaneously. The ultimate goal of glycolysis is to *produce* **ATP**, however this reaction ***consumed*** **ATP**. You will see that although this reaction did use an **ATP**, later reactions in glycolysis will result in **an overall net gain of ATP.** This reaction is **irreversible,** as indicated by the reaction arrows pointing toward the products only.

Reaction 2) This reaction is called an *isomerization* because it converts a compound to its "constitutional isomer." *Constitutional isomers* have the same molecular formula (same atoms), but different atomic connections. This reaction is **reversible,** as indicated by the reaction arrows pointing in *both forward and reverse directions*.

Reaction 3) In this reaction, a phosphoryl group is transferred from **ATP** to *fructose 6-phosphate*. As in **reaction 1**, this requires a phosphoryl group *that comes from the conversion of* **ATP** to **ADP**. For those keeping score, the glycolysis process has consumed a total of ***two*** **ATP** so far. This reaction is **irreversible**.



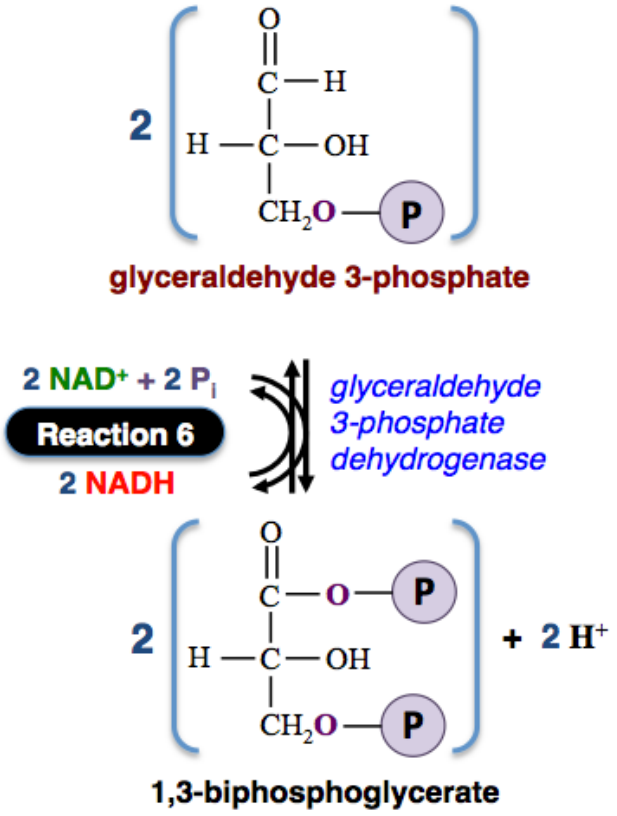
Note that after **reaction 5**, glucose has been converted into ***two*** **glyceraldehyde 3-phosphate** ions.

Reaction 4) Until now, the six carbons that were originally in glucose remain in ***fructose 1,6-biphosphate***. However, in reaction 4, the *six-carbon* compound is broken into two, *three-carbon* compounds (***dihydroxyacetone phosphate*** and ***glyceraldehyde 3-phosphate***). This reaction is **reversible.**

Reaction 5) In this isomerization reaction, ***dihydroxyacetone phosphate*** is converted to its constitutional isomer, ***glyceraldehyde 3-phosphate***. This reaction is **reversible.**

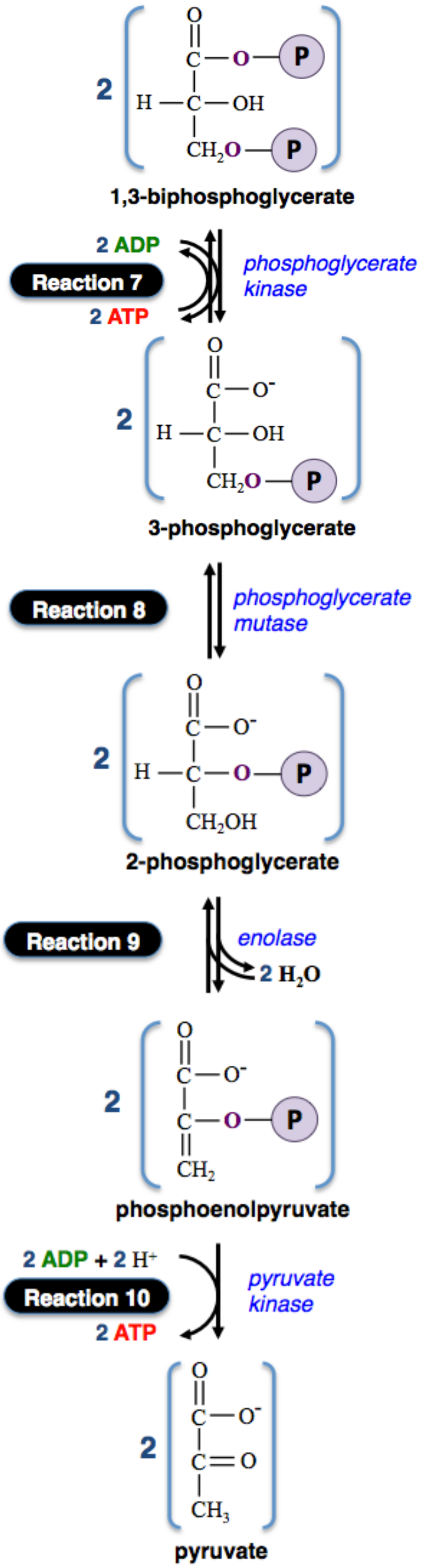
Notice that *one* ***glyceraldehyde 3-phosphate*** is produced in **reaction 4** and a second ***glyceraldehyde 3-phosphate*** is produced in **reaction 5.** Therefore, each of the *subsequent* reactions in the pathway ***will occur twice for each molecule of glucose that undergoes glycolysis***. It is for this reason the reactants and products in the chemical equations that follow have a stoichiometric coefficient of "**2.**"

The ***two glyceraldehyde 3-phosphate ions*** that were produced above will both undergo **reaction 6**:



Reaction 6) In this reaction, ***glyceraldehyde 3-phosphate*** is **oxidized**. *An oxidation cannot occur without a reduction.* In this case, **NAD^+** is ***reduced*** to **NADH**. This occurs when a hydride ion (**$H:^-$**) is transferred from glyceraldehyde 3-phosphate's carbonyl carbon to **NAD^+**. The reduction of **NAD^+** to **NADH** requires energy, that energy comes from glyceraldehyde 3-phosphate. Let's trace the energy back even further. The chemical potential energy in glyceraldehyde 3-phosphate comes from ***glucose*** (and a bit from the two **ATP** that are used in **reactions 1** and **3**). If we go back even further, the chemical energy in glucose comes from sunlight. Not ***all*** of the energy from glucose is transferred to the two **NADH** formed in **reaction 6.** Most of glucose's chemical potential energy remains in the two ***1,3-biphosphoglycerate ions*** that are produced.

You may be wondering what the benefit is of producing **NADH**. The energy that is acquired by **NADH** can later be used to convert **ADP** to **ATP**. You will read about how that happens when I discuss **stage 4** of metabolism.



Reaction 7) In this reaction, a phosphoryl group is transferred from *1,3-biphosphoglycerate* to **ADP**. The conversion of **ADP** to **ATP** requires energy. The energy was released from 1,3-biphosphoglycerate as it was converted to ***3-phosphoglycerate***. Since **two** *1,3-biphosphoglycerate* ions reacted, ***two*** **ATP** are produced. For those keeping score, this makes up for the two **ATP** that were used in **reactions 1** and **3**.

Reaction 8) In this reaction, a phosphoryl group is moved.

Reaction 9) This reaction is a ***dehydration of an alcohol***. A hydroxyl group (**OH**) is removed from carbon 3, an **H** is removed from carbon 2, and then a double bond is formed between carbons 2 and 3.

Reaction 10) In this final reaction of the glycolysis pathway, a phosphoryl group is transferred from *phosphoenolpyruvate* to **ADP**. In this reaction, potential energy in *phosphoenolpyruvate* is converted to potential energy in **ATP**. This reaction is *irreversible*. Because **two** phosphoenolpyruvate ions reacted, ***two*** **ATP** are produced. For those keeping score, the reactions of glycolysis result in a net gain of ***two*** **ATP** and ***two*** **NADH**.

When there is a sufficiently high concentration of **ATP**, pyruvate, or other pathway products, then the rate of glycolysis can be slowed down. If the **ATP** concentration becomes low, then glycolysis can be accelerated. The rate of the glycolysis pathway is controlled by enzyme inhibitors and enzyme activators of the enzymes involved in the **irreversible reactions** (**1**, **3**, and **10**). For example, **ATP** and phosphoenol pyruvate (the product of **reaction 9**) act as inhibitors of the *phosphofructokinase* enzyme that catalyzes **reaction 3**.

Summary of Glycolysis

The chemical equation for the ***overall*** glycolysis pathway is:

$$\textbf{glucose} + 2\,\textbf{ADP} + 2\textbf{P}_\textbf{i} + 2\,\textbf{NAD}^+ \rightleftarrows 2\,\textbf{pyruvate ions} + 2\,\textbf{ATP} + 2\,\textbf{NADH} + 2\,\textbf{H}_2\textbf{O} + 2\,\textbf{H}^+$$

Not ***all*** of the energy from **glucose** is transferred to the **ATP** and **NADH** formed in glycolysis. Some energy was lost as *heat* during the reactions, however, **most** of glucose's chemical potential energy remains in the two ***pyruvate ions***. Glycolysis is characterized as a ***linear pathway***. A *linear pathway* is a series of reactions that are not repeated.

Review 15.1: Understanding Glycolysis

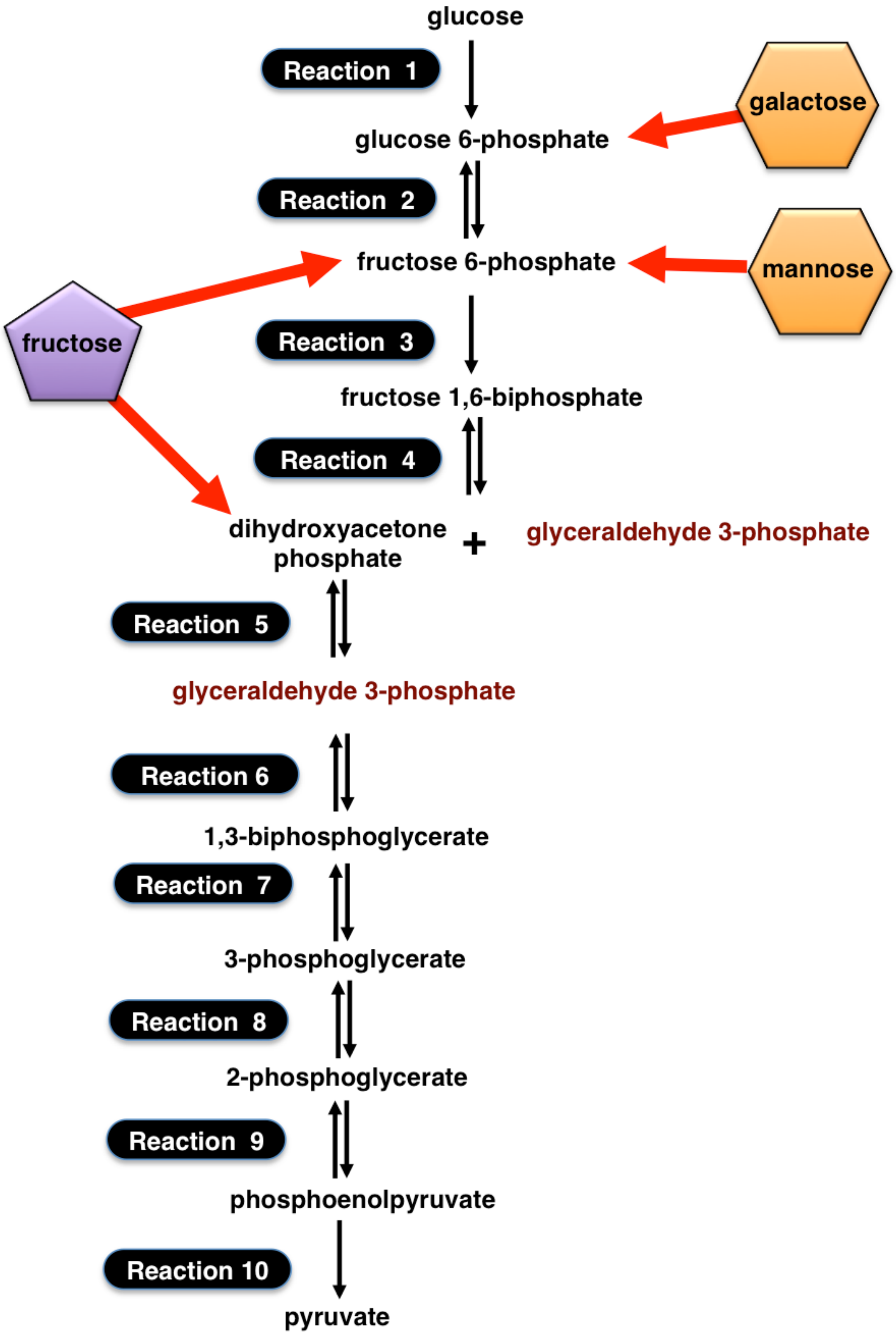
a. How many ATP are produced when ***six*** glucose molecules undergo glycolysis?
b. How many NADH are produced when ***six*** glucose molecules undergo glycolysis?

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

Before we take a look at the *fate of the pyruvate* that is produced in glycolysis, let's consider how ***non glucose monosaccharides*** are metabolized.

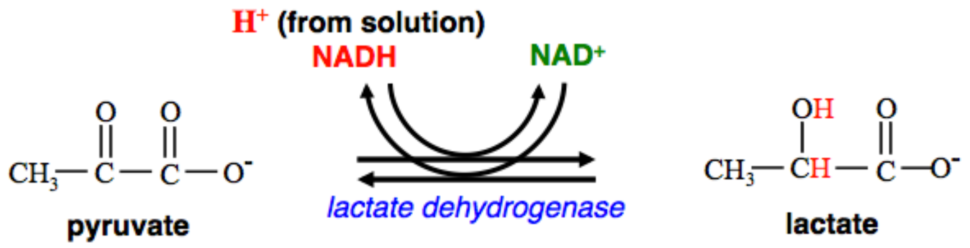
The Entry of Non Glucose Monosaccharides into Glycolysis

Although ***glucose*** is the major product of ***carbohydrate digestion***, *it is not the only monosaccharide that is produced*. ***Other monosaccharides*** can be catabolized when they are ***converted to intermediates in the glycolysis pathway***. For example, fructose, galactose, mannose, and pentose monosaccharides are produced in carbohydrate digestion (as shown a few pages back in Figure 15.2). These monosaccharides can be converted to the glycolysis intermediates that are indicated in the figure below.



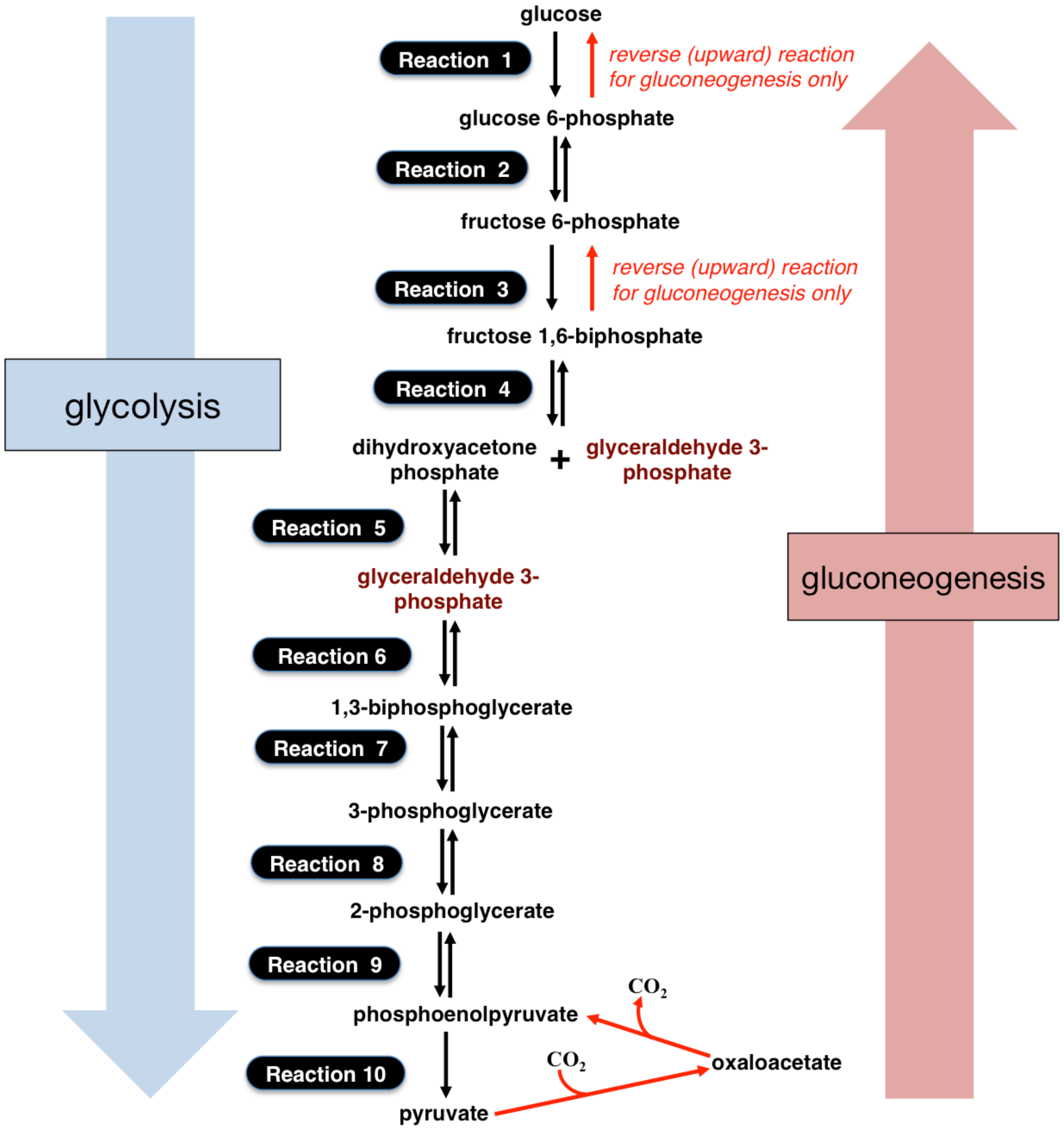
The Fate of Pyruvate

The fate of the pyruvate that is produced by *aerobic organisms* (organisms that require O_2 to grow), such as humans and most other organisms, *depends on the availability of oxygen in cells*. During strenuous physical activity, the oxygen in muscle cells becomes depleted (**anaerobic condition**). When this occurs, the *pyruvate* that is made in glycolysis remains in the cytoplasm and is converted (***reduced***) to ***lactate***, as shown in the reaction below.



The presence of lactate in a muscle causes the muscle to tire and feel sore. Lactate is released by muscle cells into the circulatory system and then taken up by liver cells. In the liver, lactate can be cycled *back to pyruvate*.

Glycolysis produces *two* pyruvate ions, *two* **ATP**, and *two* **NADH** from *each* glucose molecule. Since *two* **NADH** are used when *two* pyruvate ions are converted to lactate during *anaerobic* conditions, there is still a ***net gain*** of two **ATP** from each glucose. This is just a small fraction of the **ATP** that glucose is capable of producing when it undergoes ***all four*** stages of metabolism under aerobic conditions; however it is extremely important for single-cell organisms. The **ATP** from glycolysis (alone) can keep microorganisms alive in the absence of oxygen. Humans take advantage of lactate formation in microorganisms. The lactate produced by certain bacteria that are put into milk is responsible for denaturing milk protein in order to produce sour cream and yogurt. Certain yeast (*Saccharomyces cerevisiae*) convert dextrins into lactate, and then lactate into ethanol in the production of adult beverages.

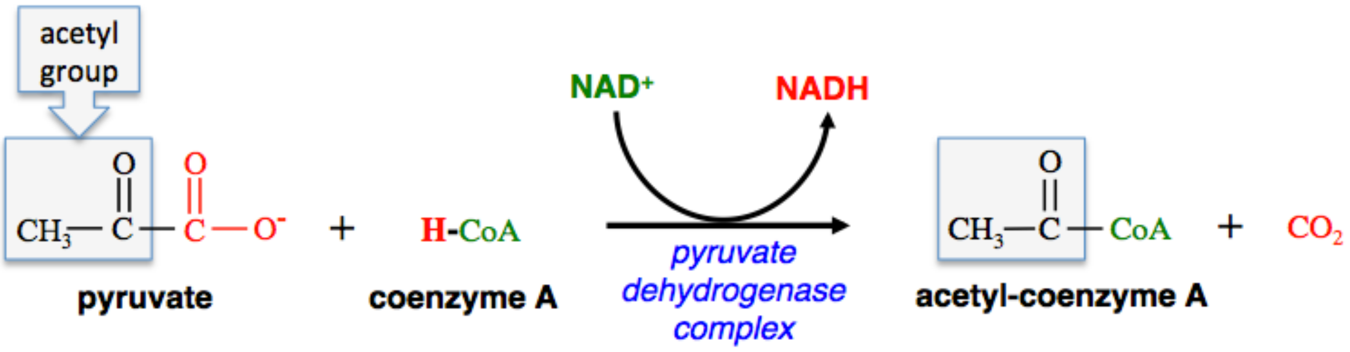


After lactate is transformed back to pyruvate, it can be converted to glucose and stored for future use. The conversion of ***non carbohydrate species to glucose*** is called **gluconeogenesis.** The conversion of lactate to glucose is an example of *gluconeogenesis*.

The *gluconeogenesis* and *glycolysis* pathways share many reactions. The differences occur at the three *irreversible* glycolysis reactions (reactions 1, 3, and 10), as shown in the figure on the left.

Gluconeogenesis does not use reaction 10 of glycolysis, and it uses different enzymes in order to enable the reverse of reactions 1 and 3 of glycolysis. In the figure on the left, *glycolysis* proceeds in the ***downward*** direction, and *gluconeogenesis* proceeds in the ***upward*** direction. Gluconeogenesis takes place primarily ***in the liver***.

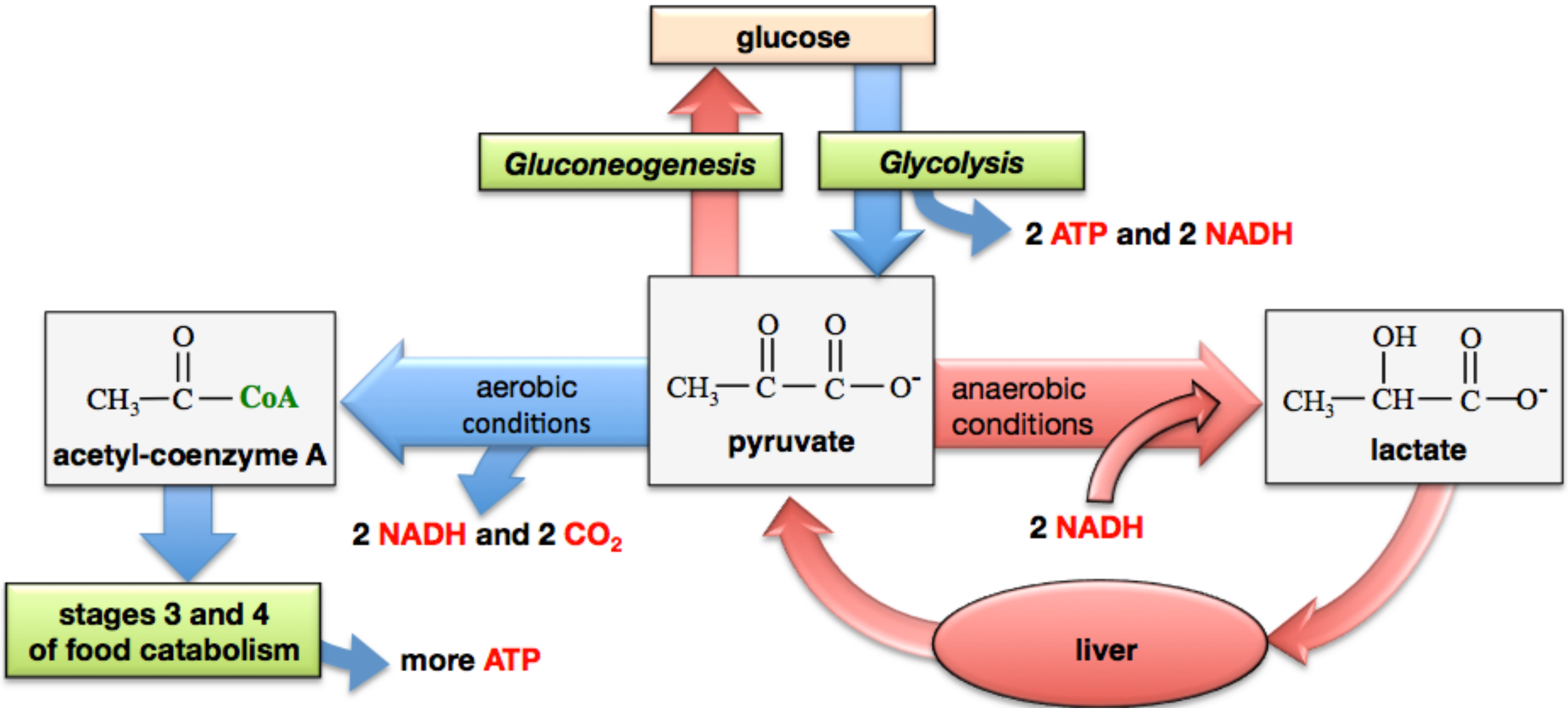
When oxygen is present (**aerobic conditions**), much more energy can be derived from pyruvate. Under aerobic conditions, pyruvate passes from the *cytoplasm* into the ***mitochondria*** and is then converted to ***acetyl-coenzyme A*** and CO_2, as shown in the reaction below.



There are few things that I would like to draw to your attention about this reaction. Pyruvate is ***oxidized*** and ***decarboxylated***. The decarboxylation produces **CO_2**. In the oxidation process, electrons from pyruvate are passed through intermediate compounds (not shown), until they are eventually transferred, along with a hydrogen, to **NAD$^+$**. Energy released by the oxidation of pyruvate is transferred to **NADH**.

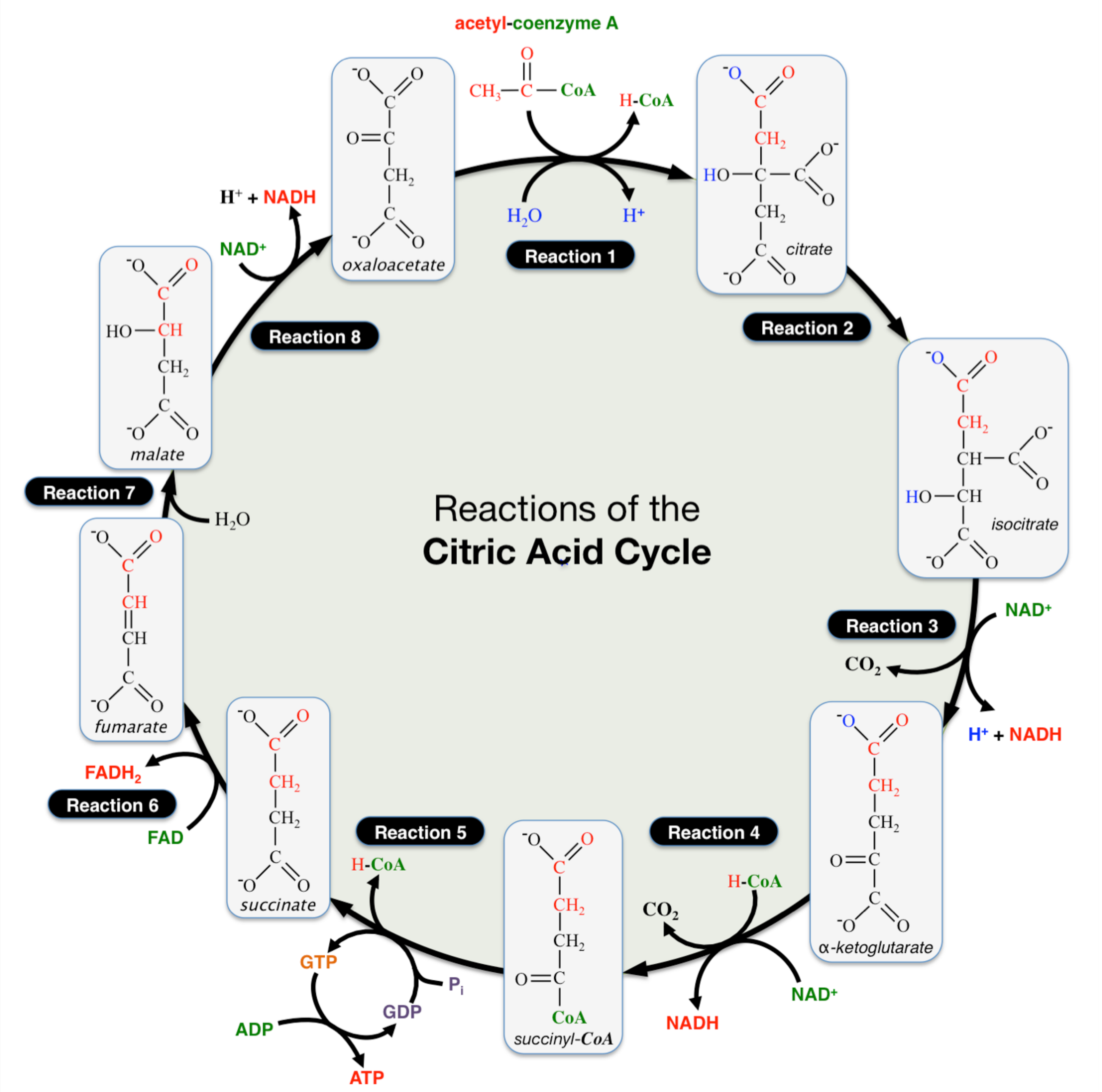
Up to this point in my discussion of **stage 2** of carbohydrate catabolism, under aerobic conditions, ***one*** glucose molecule has produced *two **acetyl-coenzyme A** ions,* and provided the energy for the formation of *four* **NADH** and *two* **ATP***.* The ***acetyl groups are relatively high-energy because they still contain much of the energy that was originally in glucose***. In the next stage of catabolism (the citric acid cycle), the energy contained in the acetyl groups is used to produce more **NADH** and more **ATP**.

An illustrative summary of **stage 2** of food catabolism and the ***fate of pyruvate*** is shown below:



Stage 3: The Citric Acid Cycle

The **citric acid cycle** is also referred to as the **Krebs Cycle** because it was H. A. Krebs who, in 1937, discovered these reactions and recognized their significance in energy-transfer reactions. In order to minimize learner anxiety so that you can focus on the overall concepts, be aware that you ***do not*** need to memorize these reactions, the names of the intermediates, or the names of the enzymes that are involved. The reactions of the citric acid cycle are shown below.



In the first reaction, acetyl-coenzyme A (acetyl-CoA) reacts with oxaloacetate. The *citric acid cycle* is characterized as a **circular pathway**. A *circular pathway* is a repeating series of reactions in which the final product is ***also*** an *initial reactant*. In the citric acid cycle, *oxaloacetate* is not only a *reactant* in the first reaction, it is ***also*** the *product* of the last reaction.

Acetyl-CoA brings two carbons in its acetyl group; these carbons are shown in red font in the diagram. It is not until the third pass through the cycle of reactions that those two carbons will be fully oxidized and released as CO_2. When one acetyl-CoA is completely processed in the citric acid cycle, ***three*** **NADH**, ***one*** **$FADH_2$**, ***one*** **ATP**, and ***two*** CO_2 molecules are produced. In this process, energy that was originally contained in acetyl-CoA is converted to chemical potential energy within **NADH**, **$FADH_2$** and **ATP.** Some energy is lost as heat.

Table 15.1 contains more information about the eight reactions of the citric acid cycle.

Table 15.1 **Reactions of the Citric Acid Cycle**

Reaction	Type of Reaction	Enzyme	Energy Transferred to:	Notes
1	acetyl group transfer	*citrate synthase*		An ***acetyl group*** is transferred to oxaloacetate.
2	isomerization	*aconitase*		The product and reactant are *constitutional isomers*.
3	oxidation/reduction *and* decarboxylation	*isocitrate dehydrogenase*	**NADH**	This reaction is irreversible. ***Isocitrate*** is decarboxylated and its hydroxyl group is oxidized to a carbonyl group. A *hydride ion* (**$H:^-$**) is transferred from *isocitrate* to **NAD^+**, thereby reducing **NAD^+** to **NADH**. This reaction is the body's main regulation point for the citric acid cycle. When cells are "energy rich," **ATP** and **NADH** concentrations are high. **ATP** and **NADH** ***inhibit*** the *isocitrate dehydrogenase* enzyme. When energy is in demand, **ADP** and **NAD^+** concentrations are high. **ADP** and **NAD^+** ***activate*** *isocitrate dehydrogenase*.
4	oxidation/reduction and decarboxylation	*α-ketogulutarate dehydrogenase*	**NADH**	This irreversible process has multiple steps (not shown). Two electrons are transferred from α-ketogulutarate to an intermediate species. Ultimately, the two electrons and a **H^+** ion are transferred from an intermediate to **NAD^+** to form **NADH**.
5	acyl group transfer *and* phosphorylation	*succinyl-CoA synthase*	**ATP**	Humans have a *succinyl-CoA synthase* enzyme that produces **GTP** (*guanosine triphosphate*). Energy in **GTP** is used to produce an **ATP**. We have another *succinyl-CoA synthase* enzyme that produces **ATP** directly.
6	oxidation/reduction	*succinate dehydrogenase*	**$FADH_2$**	$-CH_2-CH_2-$ is ***oxidized*** to -CH=CH- **FAD** is ***reduced*** to **$FADH_2$**. The **FAD**/**$FADH_2$** coenzyme is permanently bound to the succinate dehydrogenase enzyme.
7	hydration	*fumarase*		Hydration of an alkene.
8	oxidation/reduction	*malate dehydrogenase*	**NADH**	***Malate's*** 2^{o} alcohol is ***oxidized*** to a ketone. **NAD^+** is ***reduced*** to **NADH**.

The CO_2 produced in the *citric acid cycle* and in **stage 2** of metabolism, is one of the end-products of food metabolism. CO_2 is the most-oxidized form of carbon in organic compounds, and therefore has a very low energy content. Energy that was present in the food and food metabolites that contained these carbons has been extracted in the catabolism process.

Summary of Stage 3 (the Citric Acid Cycle).

The ***overall*** chemical equation for the ***citric acid cycle*** is:

$$\textit{acetyl-}\mathrm{CoA} + 3\,\mathrm{NAD^+} + \mathrm{FAD} + \mathrm{ADP} + \mathrm{P_i} + 2\,\mathrm{H_2O} \rightleftarrows 2\,\mathrm{CO_2} + 3\,\mathrm{NADH} + \mathrm{FADH_2} + \mathrm{ATP} + \mathrm{H\text{-}CoA} + 3\,\mathrm{H^+}$$

Potential energy from an acetyl-CoA that undergoes the citric acid cycle is converted to potential energy in ***three*** **NADH**, ***one*** **$FADH_2$**, and ***one*** **ATP**. Some energy is lost as *heat*.

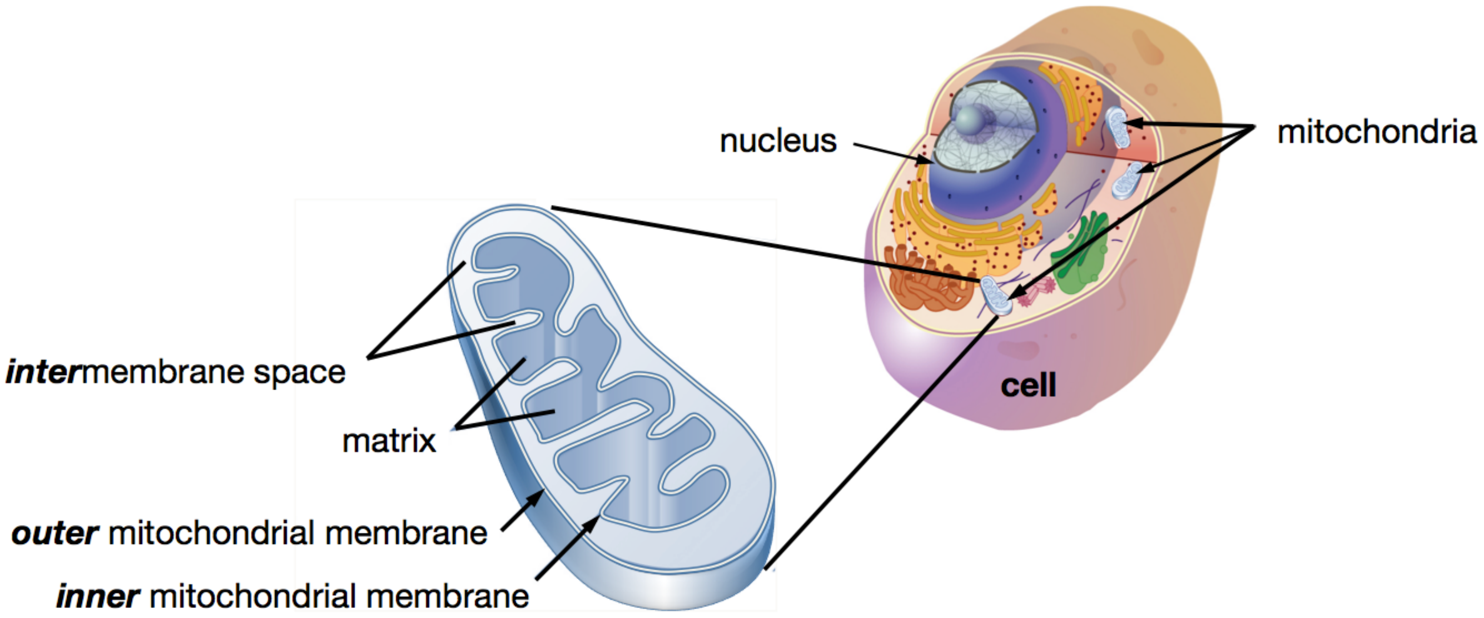
Review 15.2: Understanding Glucose Catabolism

Calculate the net gain of NADH, $FADH_2$, and ATP from *one glucose molecule* that undergoes the *first three stages of catabolism*. Keep in mind that glycolysis produces two pyruvate ions, which results in the production of two acetyl-CoA.

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

Stage 4: Oxidative Phosphorylation

Glycolysis occurs in the **cytoplasm** of the cell. The *cytoplasm* is about 80% water and includes everything within the cell membrane (except for the nucleus). The reactions of the citric acid cycle occur in the **mitochondria**. The illustration below shows the structure of the cell and a magnification of an individual mitochondrion.



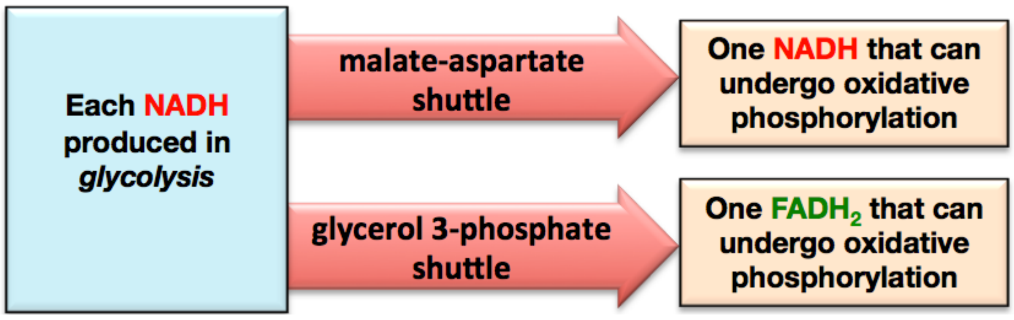
A mitochondrion consists of an ***outer* membrane** bilayer and an ***inner* membrane** bilayer. The region ***between*** the *outer* and *inner membranes* is called the ***inter*membrane space**. This can be easy to remember because "***inter***" means "between" and this space is between the inner and outer membranes. The region within the inner membrane is called the **matrix.**

The pyruvate that is produced in **glycolysis** is able to pass from the cytoplasm, through both the inner *and* outer mitochondrial membranes, into the ***matrix*** region. Pyruvate oxidation/decarboxylation and *the reactions* of the citric acid cycle occur in the ***matrix*** region.

The next stage of carbohydrate catabolism, **oxidative phosphorylation** (**stage 4**), requires that **NADH** be located ***within* the *mitochondrial matrix***. Since pyruvate oxidation/decarboxylation ***and*** the reactions of the citric acid cycle occur in the *mitochondrial matrix*, the **NADH** created in those processes can immediately undergo oxidative phosphorylation. The **NADH *that is produced by glycolysis*** is able to pass through the ***outer*** *mitochondrial membrane* and enter the *intermembrane space*; however, it is ***not*** able to pass through the ***inner*** *mitochondrial* membrane to enter the ***matrix*** region. In order for the energy from this **NADH** to be utilized, it must be processed through "**NADH** shuttles."

The two most important **NADH** shuttles are the **malate-aspartate shuttle** and the **glycerol 3-phosphate shuttle**. The **malate-aspartate shuttle** works by oxidizing the **NADH** to **NAD^+** in the intermembrane space, then transferring the electrons through the inner mitochondrial matrix to an **NAD^+** that ***is already inside the matrix,*** *thereby producing an* **NADH** that *can undergo oxidative phosphorylation*. In the **glycerol 3-phosphate shuttle**, **NADH** is oxidized in the intermembrane space by transferring electrons to an inner mitochondrial membrane-bound **FAD**, ***thereby producing an*** **$FADH_2$** that *can undergo oxidative phosphorylation.*

A complete description of the intermediates involved in the transferring of electrons in these two shuttles is far beyond the scope of this text. I have summarized the information that I would like you to know about the **NADH** shuttles in the diagram shown below.



Review 15.3: Understanding the Malate-Aspartate Shuttle

From one glucose molecule, determine how many NADH and $FADH_2$ would be available for *oxidative phosphorylation* (stage 4 of catabolism). Assume that both NADH formed in glycolysis use the **malate-aspartate shuttle.**

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

Review 15.4: Understanding the Glycerol 3-Phosphate Shuttle

From one glucose molecule, determine how many NADH and $FADH_2$ would be available for *oxidative phosphorylation* (stage 4 of catabolism). Assume that both NADH formed in glycolysis use the **glycerol 3-phosphate shuttle.**

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

The primary goal of food catabolism is the production of **ATP**. As we saw in review problem 15.2, only ***four*** **ATP** have been produced from one glucose so far. At this point in my narrative of carbohydrate catabolism, most of the chemical potential energy that has been extracted from glucose is still in the form of **reduced coenzymes** (**NADH** and **$FADH_2$**). In **stage 4** of catabolism (*oxidative phosphorylation*), chemical potential energy contained in the *reduced coenzymes* is transferred to **ATP**.

Oxidative phosphorylation is the process in which electrons from **NADH** or **$FADH_2$** are transferred, through a series of electron transfer intermediates, to dissolved oxygen (O_2) in order to provide the energy required to produce **ATP**. In this process, ADP and an inorganic phosphate (P_i) are converted to **ATP**. The formation of **ATP** from **ADP** and P_i would ***not*** occur spontaneously without the input of energy that is provided when electrons are transferred to O_2. Because of the availability of H^+ in solution (from H_2O, H_3O^+, or the *acid form* of any other species present), when electrons are transferred to oxygen, the following reaction occurs:

$$O_2 + 4H^+ + 4 \text{ electrons} \rightarrow 2H_2O$$

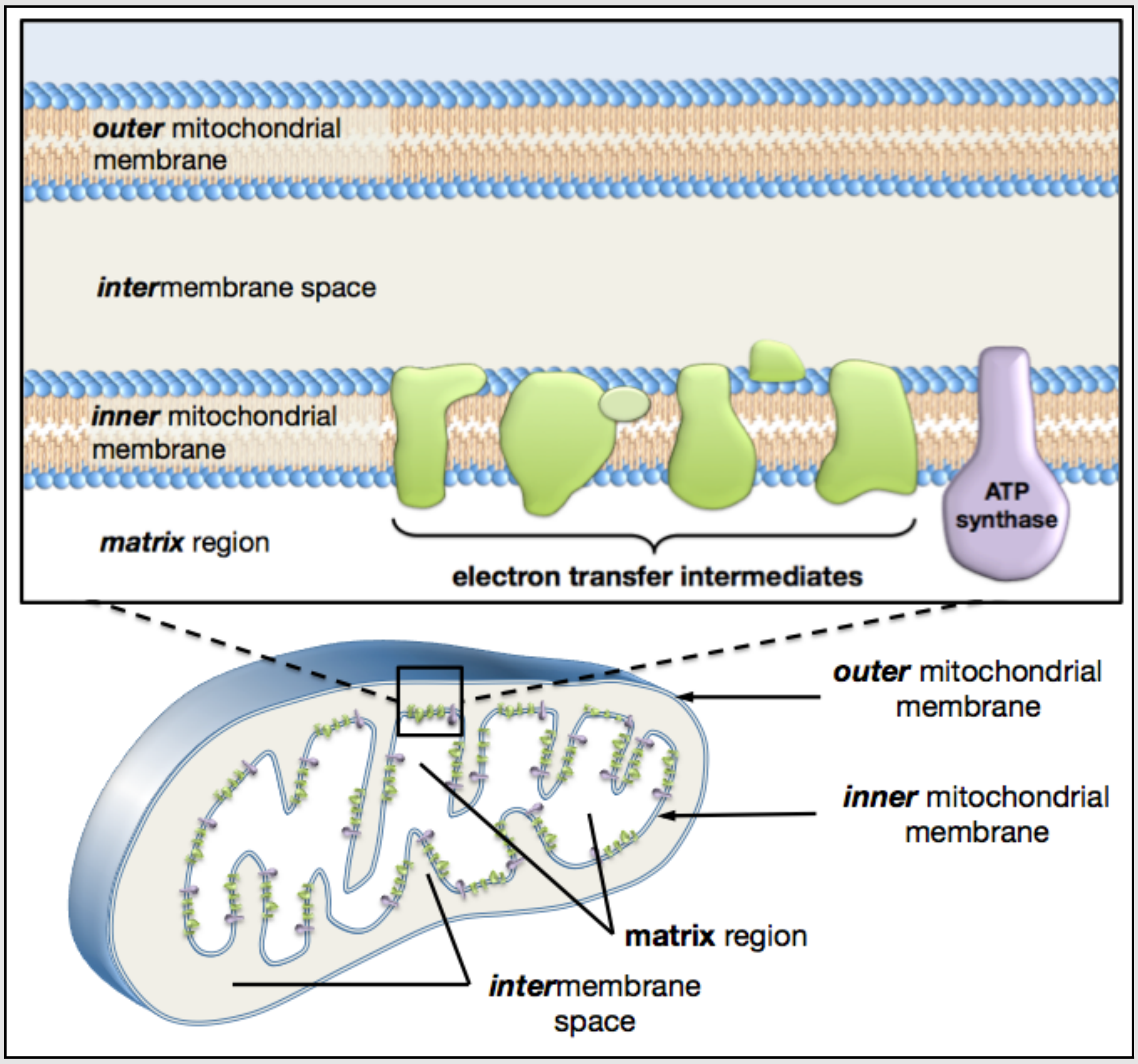
In the reaction above, O_2 is ***reduced***; it gains electrons. Energetically, this reaction is similar to one of the first chemical reactions that I told you about, the rocket fuel reaction:

$$O_2 + 2H_2 \rightarrow 2H_2O$$

Like the rocket fuel reaction, a relatively large amount of energy is released when electrons are transferred to O_2 in the oxidative phosphorylation process. O_2 is the ***final acceptor*** of electrons in food catabolism.

Figure 15.3 shows an illustration of a mitochondrion (***bottom***) with a magnification (***top***) that shows the location of the electron transfer intermediates (green) and the *ATP synthase* enzyme that catalyzes the formation of **ATP**.

Figure 15.3 Illustration of a Mitochondrion



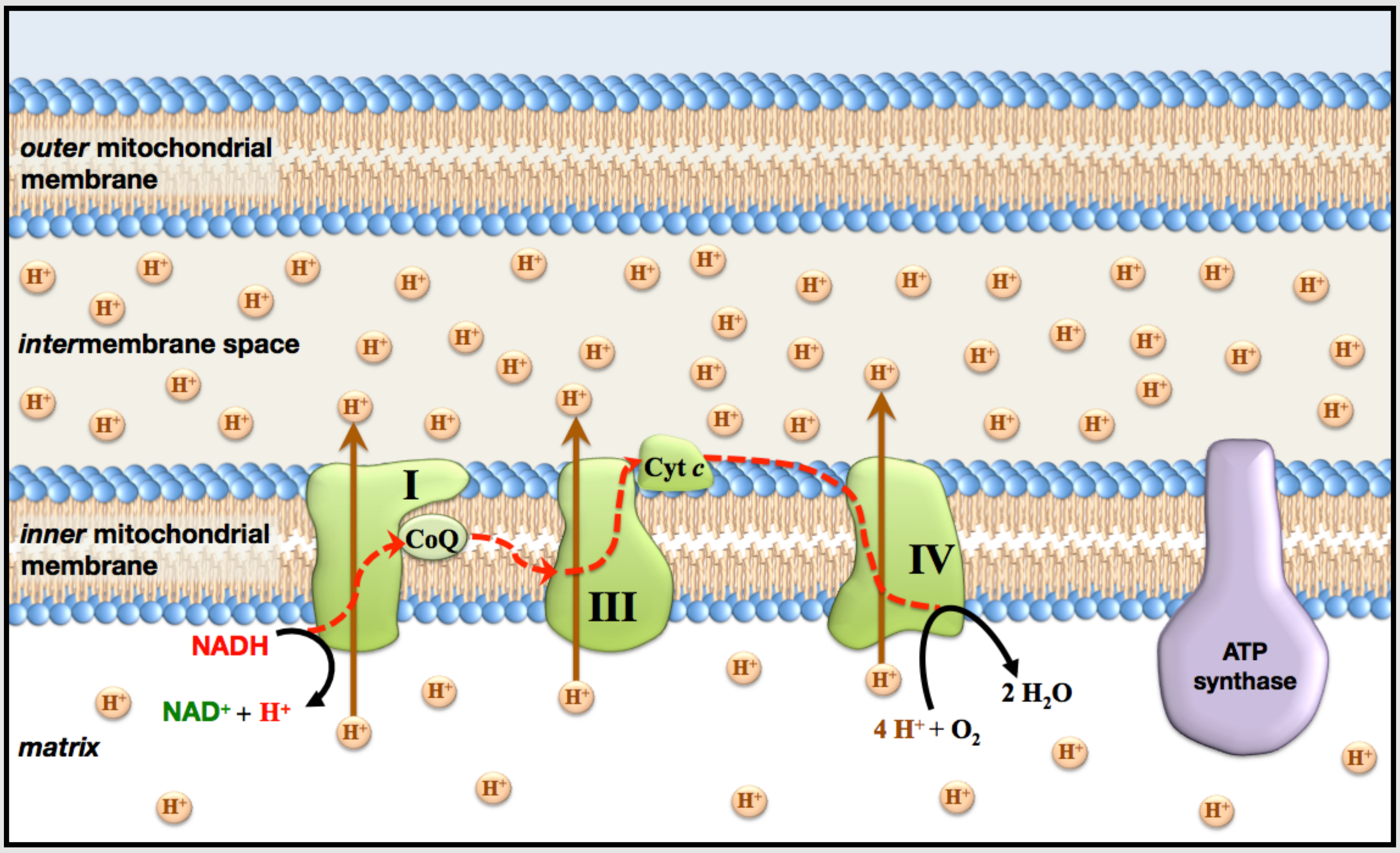
Bottom: Labeled illustration of a mitochondrion. **Top:** Magnification that shows the location of the electron transfer intermediates (green) and the enzyme that catalyzes the formation of ATP (purple).

The energy released by the transfer of electrons from **NADH** or **$FADH_2$**, through the electron transfer intermediates, to O_2 is not immediately used to drive the production of **ATP**. Instead, this energy is used to move hydrogen ions from a region of lower hydrogen ion concentration (the mitochondrial matrix) to a region of higher hydrogen ion concentration (the intermembrane space). By doing so, the energy that is released by the transfer of electrons is converted to **electrochemical potential energy**. Physically, this is very similar to "charging" a battery. It takes work to charge a battery. For example, to charge the battery in your smart-phone, work had to be done at the power plant that serves your home. If the power plant was a hydroelectric plant, water was released from a dam, it flowed downhill and then turned a paddle, which rotated a magnet near a wire and generated an electric potential that forces electrons into your battery.

Oxidative phosphorylation does not happen in exactly the same way for **NADH** as it does for **$FADH_2$**. Let's take a look at how oxidative phosphorylation happens for each of these reduced coenzymes. These are conceptually simple processes, but the mechanisms are quite complicated. I will not discuss every detail of the processes; instead I will provide an overview of the most important aspects.

An overview of the electron transfers and hydrogen ion transport that occur when **NADH** undergoes oxidative phosphorylation is shown below in Figure 15.4.

Figure 15.4 **Electron Transfers and Hydrogen Ion Transport From NADH Oxidation**



The electrons that are released in the oxidation of NADH are sequentially passed between electron transfer intermediates (shaded green) along the path that is indicated by the dashed red curve. The movement of electrons through the protein complexes (labeled I, III, and IV) releases energy. This energy is used by the complexes to actively transport hydrogen ions through the *inner* mitochondrial membrane in the direction indicated by the brown arrows.

The process begins with the oxidation of **NADH** in the matrix region. The electrons that are released in the oxidation of **NADH** are sequentially passed between electron transfer intermediates (shaded green) along the path that is indicated by the dashed red curve in Figure 15.4. Two of the electron transfer intermediates, ***coenzyme Q*** (**CoQ**) and ***cytochrome C*** (**Cyt c**), are quite *mobile*. **CoQ** is a nonpolar compound that is capable of diffusing through the non polar tails of the phospholipids in the membrane bilayer. **Cyt c** is a small protein that can move along the surface of the *inner* mitochondrial membrane.

The other electron transfer intermediates are *transmembrane* **proteins complexes** (labeled **I**, **III**, and **IV** in the figure). In order for the electrons to “move through” these protein complexes, they are transferred ***within*** *the complexes* by sequential oxidations and reductions of neighboring prosthetic groups or cofactors (not shown in the figure).

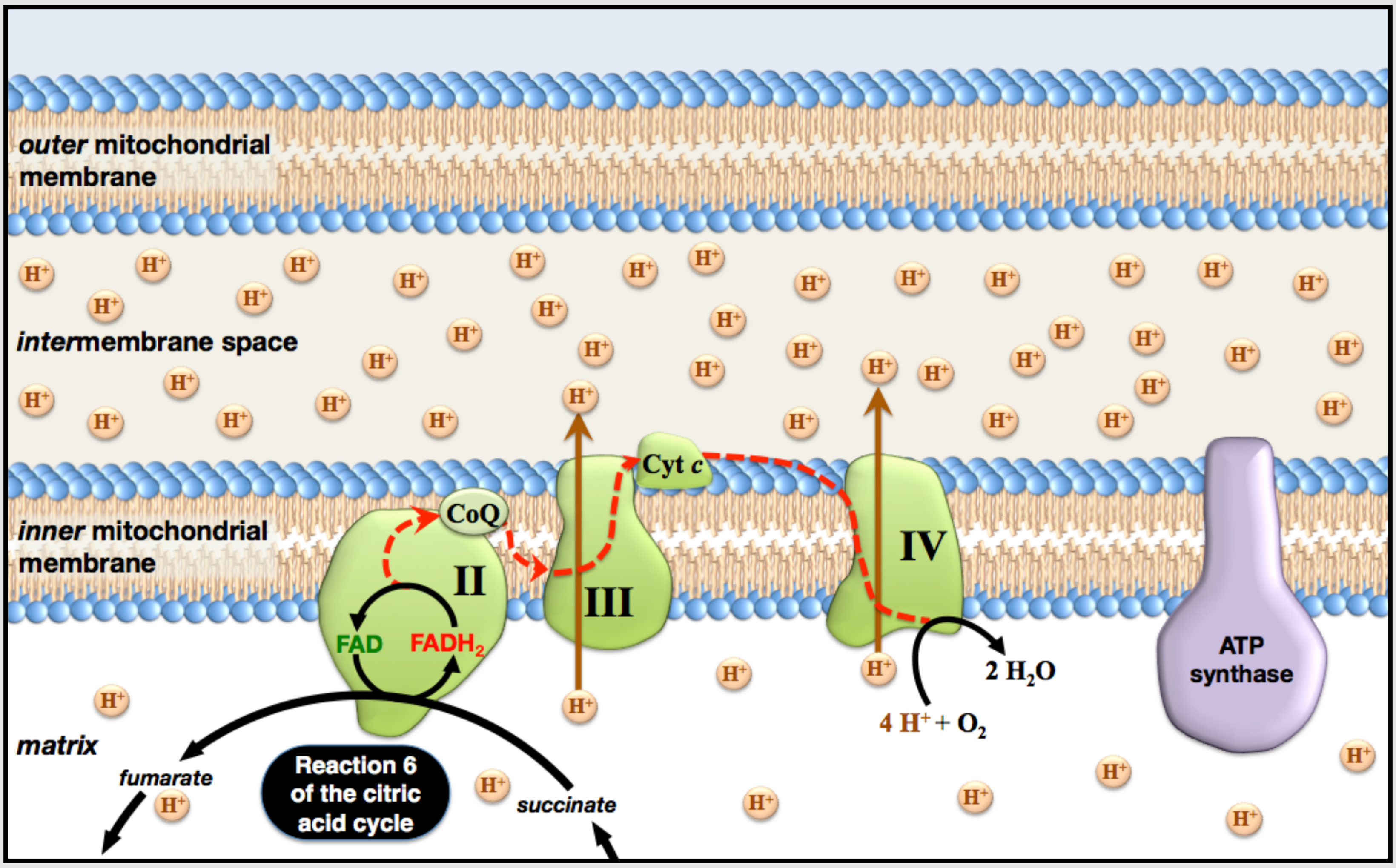
The movement of electrons through the protein complexes releases energy (analogous to water being released from a dam). This energy is used by the complexes to **actively transport** *hydrogen ions* from a region of ***lower*** hydrogen ion concentration (the mitochondrial matrix) to a region of ***higher*** hydrogen ion concentration (the *inter*membrane space), as indicated in the figure by the brown arrows. For *simplicity*, the illustration shows isolated hydrogen ions (**H^+**) in the matrix and intermembrane space. Be aware that although *individual* hydrogen ions are indeed transported *through the inner mitochondrial membrane*, they exist bound to water (as H_3O^+) before *and* after they move through the membrane.

Electrons are ultimately transferred to, and thereby ***reduce*** O_2. Four electrons (and four hydrogen ions) are required to react with each O_2 molecule, to produce water as shown in the chemical equation below:

$$O_2 + 4H^+ + 4 \text{ electrons} \rightarrow 2H_2O$$

Next, let's move our attention to how energy from **$FADH_2$** is used to generate electrochemical potential energy in mitochondria. An overview of the electron transfers and hydrogen ion transport that occur when **$FADH_2$** undergoes oxidative phosphorylation is shown below in Figure 15.5.

Figure 15.5 **Electron Transfers and Hydrogen Ion Transport From $FADH_2$ Oxidation**



The electrons that are released in the oxidation of $FADH_2$ are sequentially passed between electron transfer intermediates (shaded green) along the path that is indicated by the dashed (red) curve. The movement of electrons through protein complexes III and IV releases energy. This energy is used by these complexes to actively transport hydrogen ions through the *inner* mitochondrial membrane in the direction indicated by the brown arrows.

$FADH_2$ is produced in **reaction 6** of the *citric acid cycle*. The enzyme that catalyzes this reaction is part of an electron transfer intermediate called **complex II** (labeled **II** in Figure 15.5). In oxidative phosphorylation, **$FADH_2$** is oxidized and its electrons are sequentially passed between electron transfer intermediates, along the path that is indicated by the dashed curve, and ultimately transferred to O_2. The movement of electrons through protein complexes **III** and **IV** releases energy. This energy is used by these complexes to actively transport hydrogen ions through the inner mitochondrial membrane and into the intermembrane space.

Summary of the Oxidation of NADH and $FADH_2$ During Oxidative Phosphorylation

When **NADH** and **$FADH_2$** are oxidized, their electrons are transferred, through intermediates, to O_2. As electrons move through complexes I, III, and IV, energy is released. This energy is used by the complexes to **actively transport** hydrogen ions from a region of ***lower*** hydrogen ion concentration (the mitochondrial matrix) to a region of ***higher*** hydrogen ion concentration (the intermembrane space). In doing so, the ***energy*** from **NADH** and **$FADH_2$** (that was originally in food) is converted to ***electrochemical energy*** within mitochondria. This part of oxidative phosphorylation is often referred to as **electron transport***.* The electron transfer intermediates (shaded green in the three previous figures) that are involved in *electron transport* are sometimes called "***the electron transport chain***." Next, I will discuss how electrochemical energy within mitochondria is used to drive the production of **ATP**.

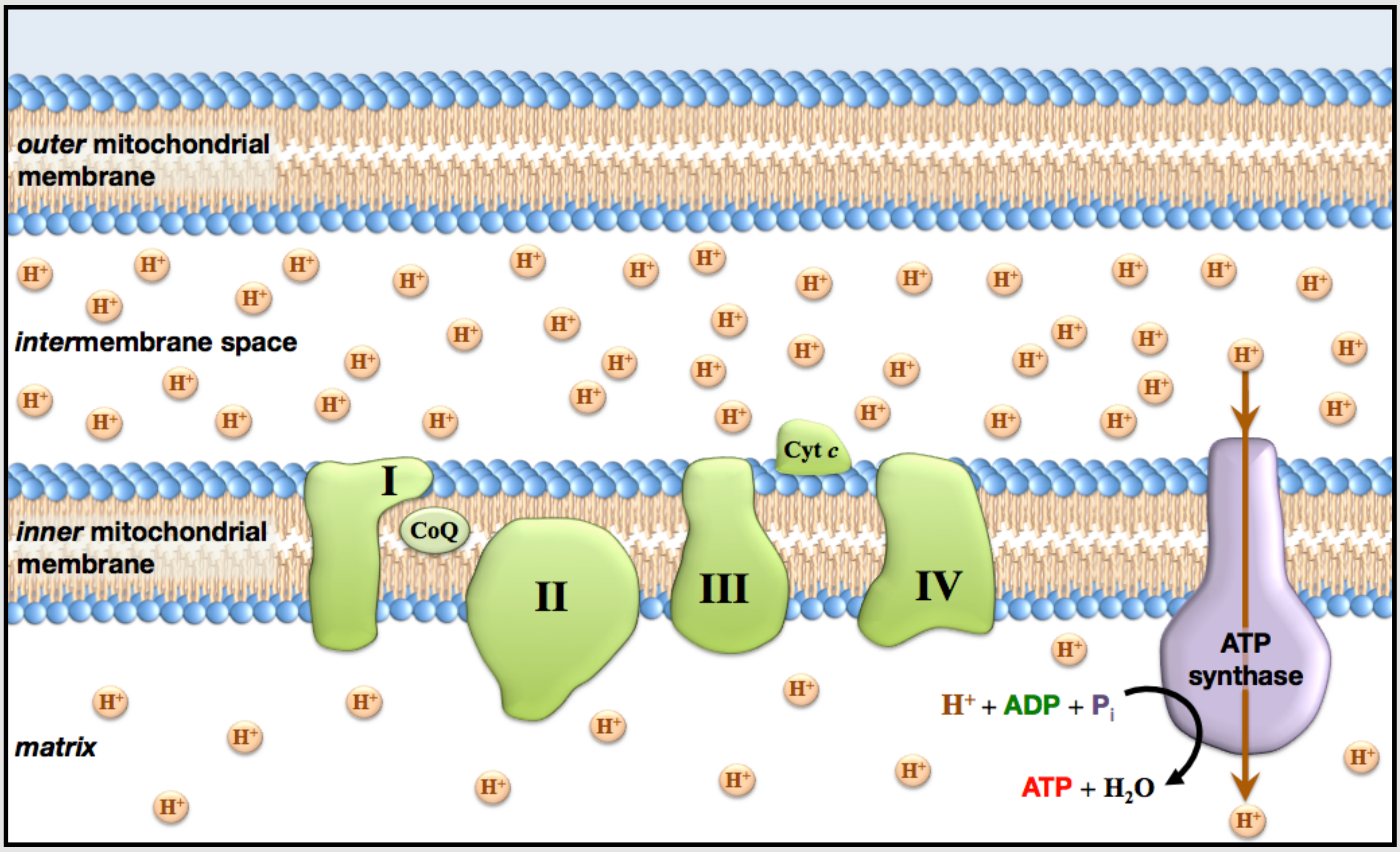
ATP Production in Oxidative Phosphorylation

When there are *unequal* concentrations of a species on opposite sides of a membrane, we say that a "concentration gradient" exists. Since hydrogen ions are charged, a hydrogen ion gradient contains significantly more energy than would an equivalent concentration gradient of an uncharged species. The reason for this is that the positive charge must be forced to move from a region of less positive charge to a region of more positive charge.

I told you that the creation of *electrochemical potential energy* in the form of an **H^+** concentration gradient was like charging a battery. The voltage (potential electrical energy) between the intermembrane space and the matrix region is about 0.15 volts. This is about 10% of the voltage of a "AA" battery.

As with any dissolved species, hydrogen ions will ***spontaneously*** diffuse from areas of high concentration to areas of low concentration. It is lower in energy for the hydrogen ions to be in the matrix region (low concentration) than it is for them to be in the intermembrane space (higher concentration). The only path between these regions in which hydrogen ions can passively diffuse is through the *ATP synthase* enzyme, as illustrated below in Figure 15.6.

Figure 15.6 **Diffusion of Hydrogen ions though ATP Synthase**



Hydrogen ions can spontaneously diffuse from the *inter*membrane space (high concentration) into the matrix (lower concentration). The passing of hydrogen ions through ATP synthase supplies the energy required to produce ATP.

Moving an object or compressing a spring requires that "work" be done. Much like electrical current passing through an electric motor does work, the passing of hydrogen ion current through an *ATP synthase* does work. This work is done by forcing the enzyme to change its shape and thereby supply the energy needed to form a bond between an inorganic phosphate (**P_i**) and **ADP**, to produce **ATP**. The *ATP synthase* enzyme not only catalyzes the reaction for the synthesis of **ATP**, it also plays a role in delivering the energy needed to make **ATP** synthesis occur ***spontaneously***.

The number of **ATP** that can be produced from **NADH** or **$FADH_2$** depends on the cell and its current conditions. The latest research indicates that, ***on average***, one **NADH** produces about **2.5** **ATP**, and one **$FADH_2$** produces about **1.5** **ATP**.

Let's calculate how many **ATP** can be produced from the catabolism of ***one glucose molecule***. For this calculation, we will assume that each **NADH** produces 2.5 **ATP**, and each **$FADH_2$** produces 1.5 **ATP**, and that **NADH** produced in glycolysis use the ***malate-aspartate shuttle***.

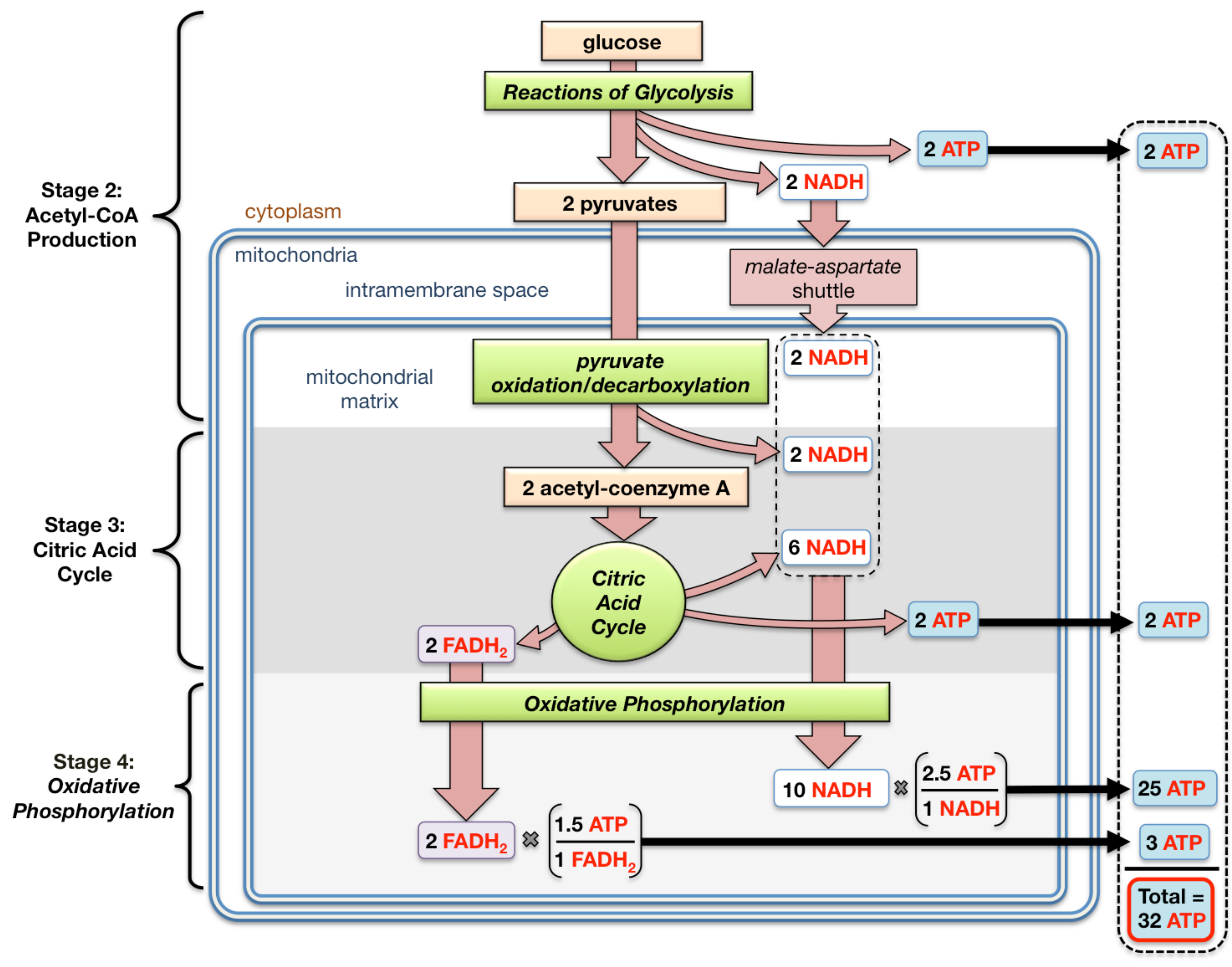
Stage 2: In *glycolysis*, glucose is converted to two pyruvate ions. In this process, two **NADH** and two **ATP** are formed. The two **NADH** undergo the ***malate aspartate shuttle*** and result in the formation of two **NADH** *within* the mitochondrial matrix.

The pyruvate ions can diffuse past both mitochondrial membranes, and enter the matrix region. There, the pyruvate ions undergo an oxidation/decarboxylation reaction. In this process, two **NADH** and two acetyl-CoA are formed.

Stage 3: In the *citric acid cycle*, the two acetyl-CoA produce a total of six **NADH**, two **$FADH_2$**, and two **ATP**.

Stage 4: In oxidative phosphorylation, the ***ten*** **NADH** and ***two*** **$FADH_2$** produced in **stages 2** and **3** are oxidized in order to produce **ATP**.

This gives total of **32 ATP**, as shown in the illustration below.



In the four stages of carbohydrate catabolism, chemical potential energy in carbohydrates is converted to chemical potential energy in **ATP**, a substance that can be used immediately by all cells to do cellular work. The carbon, hydrogen, and oxygen atoms in carbohydrates, along with the oxygen we inhale, are converted to CO_2 and H_2O. This is the CO_2 that we exhale.

Review 15.5: Understanding the Stages of Glucose Catabolism

Calculate how many ATP can be produced from the catabolism of one glucose molecule when the two NADH from glycolysis use the **glycerol 3-phosphate shuttle**. Assume that each NADH that undergoes oxidative phosphorylation produces 2.5 ATP, and each $FADH_2$ produces 1.5 ATP.

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

Regulation of Blood Glucose Concentration

It is important for human blood glucose concentration (sometimes called blood sugar level) to remain within a "normal" range. The normal range of glucose concentration in the blood is about 80 to 110 mg per dL of blood. Long term effects of having higher than normal blood glucose concentration (**hyperglycemia**) can include damage to kidneys, the neurological system, the cardiovascular system, eyes, feet, and legs. Between meals or during starvation, blood glucose levels fall below the normal range (**hypoglycemia**). This can result in confusion, loss of coordination, difficulties in speaking, a loss of consciousness, seizures, and even death. Symptoms can come on quite quickly and include hunger, shaking, sweating, and weakness.

In the "***fed***" state, which occurs *soon after a meal* when blood glucose levels are high, ***liver*** and ***muscle cells*** (primarily) take in *extra* glucose and store it in the form of ***glycogen***. The conversion of *glucose* to glycogen is called **glycogenesis**. *Glycogenesis* is an *anabolic pathway* in which glucose residues, with the help of enzymes, are connected to each other through glycosidic bonds to form *glycogen*. The chemical structure of glycogen is very similar to that of *amylopectin*; the only exception is that *glycogen* branches more frequently. For a review of glycogen and amylopectin structures, see chapter 11, section 6.

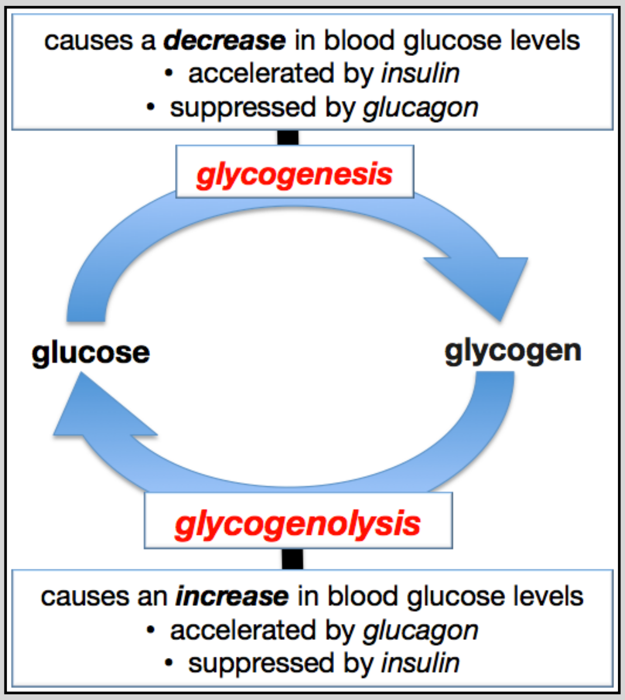
In the "***fasting state***," which occurs several hours after a meal, blood glucose levels become low, and glycogen is converted back to glucose in a process called **glycogenolysis**. ***Glycogenolysis*** occurs primarily in ***liver*** and ***muscle*** cells. It is the opposite of *glyco**genesis***. In *glycogeno**lysis***, the glycosidic bonds between glucose residues are hydrolyzed.

The body regulates blood glucose levels by releasing hormones that result in the production of compounds that ***inhibit and activate key enzymes in the glycogenesis and glycogenolysis pathways***. In response to increased blood glucose concentration (in the fed state), the pancreas releases a protein hormone called **insulin** into the blood stream. When insulin binds to liver and muscle cell receptors, it triggers a series of events that result in the ***activation*** of an enzyme in the *glyco**genesis*** pathway and the ***inhibition*** of an enzyme in the *glycogeno**lysis*** pathway. This acceleration of glycogenesis in muscle and liver cells and suppression of glycogenolysis in liver cells results in a decrease in blood glucose concentration. *Accelerating glycogenesis* increases the rate of the conversion of glucose to glycogen. *Suppressing glycogenolysis* inhibits the conversion of glycogen to glucose. Another way that insulin is involved in lowering blood glucose concentration is by initiating a process that increases facilitated diffusion of glucose from the bloodstream into **all cell types**.

In response to decreased blood sugar levels (in the "fasting state"), the pancreas releases a protein hormone called **glucagon** into the blood stream. Glucagon has the ***opposite effect of insulin*** on liver cells; it *accelerates* glycogenolysis and *suppresses* glycogenesis. This will result in increasing blood glucose concentration as glucose produced during glycogenolysis is transported from liver cells into the bloodstream. Glucagon also increases blood glucose concentration by accelerating ***gluconeogenesis*** (the production of glucose from non carbohydrate species). The roles of glycogenolysis and glycogenesis in controlling blood glucose levels are summarized in Figure -.-.

Figure 15.7

Roles of Glycogenesis and Glycogenolysis in the Regulation of Blood Glucose Concentration



causes a ***decrease*** in blood glucose levels
- accelerated by *insulin*
- suppressed by *glucagon*

causes an ***increase*** in blood glucose levels
- accelerated by *glucagon*
- suppressed by *insulin*

Diabetes

Diabetes Mellitus (**DM**), commonly referred to as **diabetes**, is a disease caused by ***chronic hyperglycemia***. There are three types of **diabetes mellitus**: type I, type II, and gestational diabetes. In diabetes type I, also called ***insulin-dependent diabetes***, the pancreas produces too little insulin. This can be a result of genetic disease, viral infection, or damage to the pancreas. Diabetes type I can be treated with insulin injections. Individuals must use a *glucometer* (Figure 15.8) to frequently measure the concentration of glucose in their blood, and then inject insulin when elevated glucose levels are observed. Because diabetes type I often begins in childhood, it is sometimes referred to as ***juvenile diabetes***.

Diabetes type II, also called ***insulin-resistant diabetes***, occurs when sufficient insulin is produced, however the insulin receptors are unable to respond appropriately. About 90% of diabetes cases are type II. This type of diabetes can be even more difficult to manage than type I diabetes because it does not respond to insulin injections. Diabetes type II occurs after childhood and is therefore sometimes referred to as ***adult-onset diabetes***.

Figure 15.8 A Glucometer

A digital glucometer. Accu-Chek Performa, by Roche.

Source: Wikimedia Commons, Author: Penarc, CC-BY-SA, http://creativecommons.org/licenses/by-sa/3.0/legalcode

Gestational diabetes occurs during pregnancy in individuals without a previous diagnosis of diabetes. It is thought to be caused by pregnancy-related factors that affect insulin receptors. It is usually manageable with special diets and exercise, however some individuals require antidiabetic drugs.

15.4 Triglyceride Metabolism

Dietary triglycerides, regardless of whether they came from plant or animal sources, are often referred to as **fat**. When triglycerides are catabolized, their chemical potential energy is converted to chemical potential energy in **ATP**. This process begins with the digestion of triglycerides. Triglycerides are also used in the formation of phospholipids and glycolipids, and as cellular signaling compounds.

Figure 15.9 Making Butter From Cream

Artist: Jahn Ekenæs (1847 -1920)
Title: Family in a Norwegian Fjord Landscape

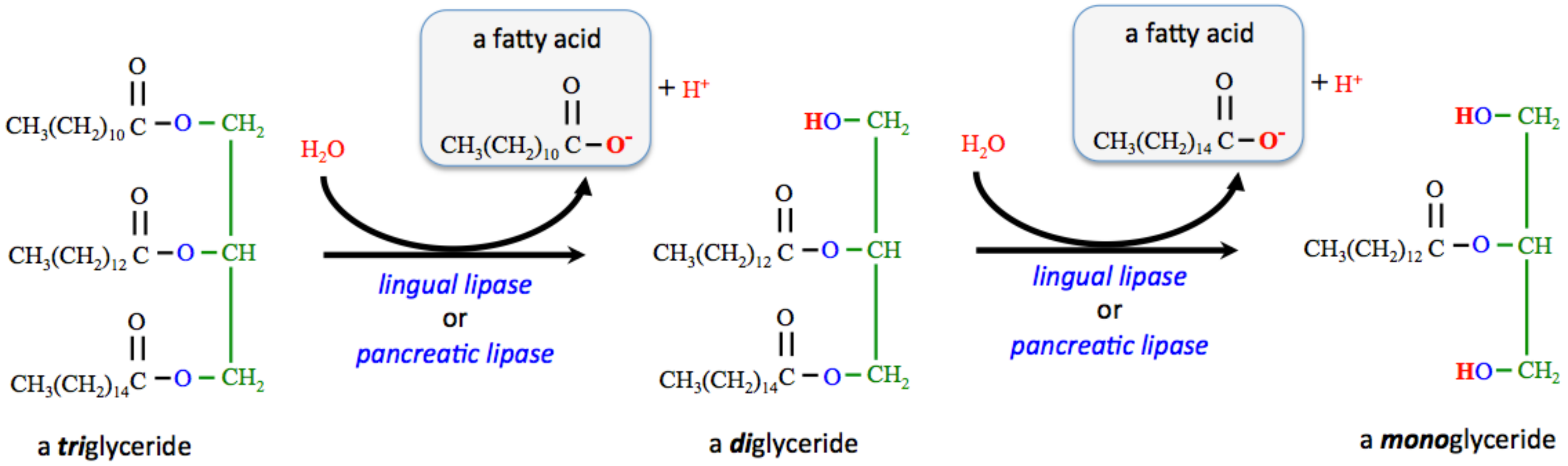
The body can store significant amounts of triglycerides, mostly in **adipose cells** (also called **fat cells**). Stored glucose (glycogen) can only sustain the body for about twenty-four hours, however, stored triglycerides will sustain the body for several weeks. Migratory birds that fly over oceans without feeding for very long periods are able to do so by using their reserves of triglycerides.

Digestion of Triglycerides

In order for triglycerides to pass through the intestine wall so that they can be used by the body, they must first undergo *partial* hydrolysis to produce ***fatty acids*** and ***monoglycerides***.

Let's take a moment to review the structure of *fatty acids*. Fatty acids are *carboxylic acids that contain long-chain hydrocarbon parts*. They usually contain between twelve and twenty carbon atoms. In regions of the body where the pH is greater than the pK_a of a fatty acid, the *base form* (the carboxylate ion) is predominant. Fatty acids have pK_a values of about 5. In most regions of the body, the pH is greater than 5, therefore the ***base forms*** of fatty acids are predominant. It is for this reason that I will use structures of the ***base forms*** of fatty acids in the chemical equations and figures in this section.

Triglycerides are first hydrolyzed to *diglycerides*, then to *monoglycerides*. Each one of these reactions produces a *fatty acid*, as shown below.



This is referred to as "***partial hydrolysis***" because one of the fatty acid residues *remains bound* to carbon number **2** of glycerol in the monoglyceride.

An overview of triglyceride digestion is shown in Figure 15.10. Triglyceride digestion begins in the ***mouth*** where *lingual lipase* catalyzes the partial hydrolysis of a very small percentage of the triglycerides. The ***majority*** of dietary triglycerides are digested in the ***small intestine***. Large hydrophobic (insoluble) globules, that are composed mostly of triglycerides and a small amount of diglycerides, monoglycerides, and fatty acids, enter the ***small intestine***. In the small intestine, bile salts disassemble these large hydrophobic globules and emulsify them into small micelles. When emulsified by bile salts, the ester bonds of the glycerides are oriented toward the surface of the micelle. This enables *pancreatic lipase* to catalyze the *partial* hydrolysis of emulsified triglycerides and diglycerides to produce ***fatty acids*** and ***monoglycerides***.

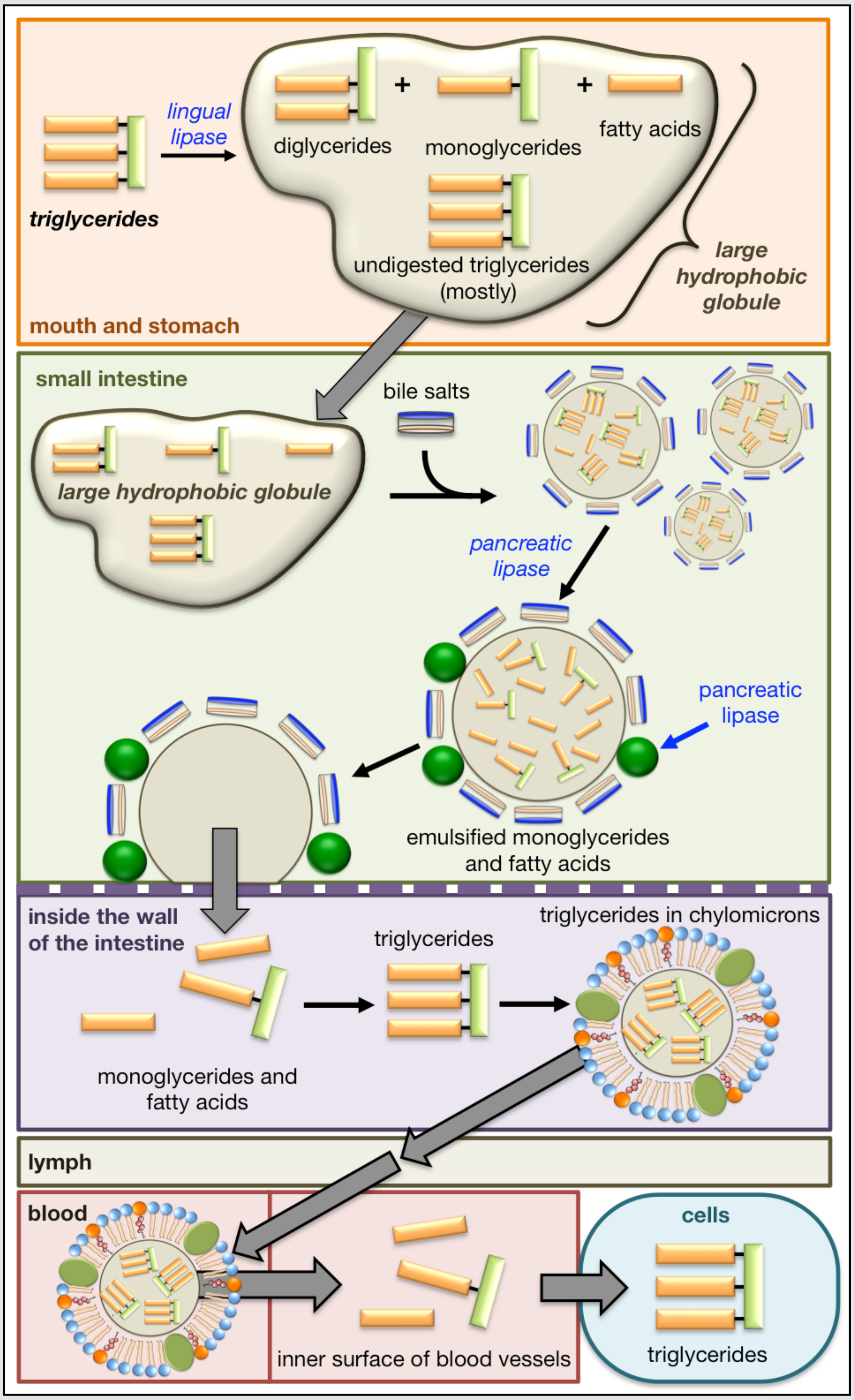
The fatty acids and monoglycerides that are formed inside the intestine can pass into the walls of the intestine. After being absorbed into the intestine walls, the fatty acids and monoglycerides are then re-assembled ***back into triglycerides***.

Since lymph, blood, and intercellular fluids are *aqueous mixtures,* and triglycerides are hydrophobic, the triglycerides must be ***emulsified*** in order to be transported throughout the body. This is done by ***chylomicrons***. Chylomicrons are small *lipoproteins* that are composed of a core that contains emulsified triglycerides (and some cholesterol and hydrophobic vitamins) surrounded by a lipid monolayer.

Triglycerides are emulsified in chylomicrons while in the wall of the intestine. The chylomicrons are then transferred into the lymph system, and then into the bloodstream. Triglycerides are released by the chylomicrons, and once again hydrolyzed to monoglycerides and fatty acids upon the inner surface of blood vessels. This occurs **primarily at blood vessels located in adipose (fat) tissue and muscles**. The monoglycerides and fatty acids can enter cells, where they are, once again, reassembled to triglycerides.

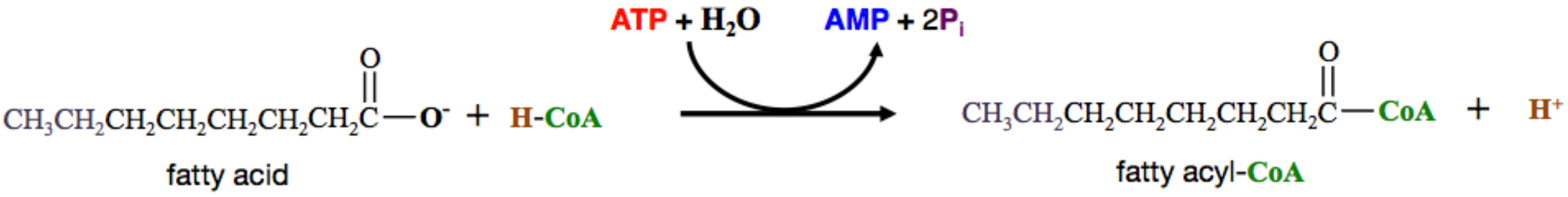
Adipose cells are the *major repository* for triglycerides; their primary function is to store triglycerides. Peripheral (other) cells/tissues can access this stored energy, as needed, when adipose cells ***completely*** *hydrolyze* the triglycerides to ***fatty acids*** and ***glycerol*** in a process called **lipolysis**. The fatty acids are released from the adipose cells into the blood, and carried by *serum albumin protein* to other cells. These fatty acids can then be catabolized to produce **ATP**.

Figure 15.10 Overview of Triglyceride Digestion



Catabolism of Fatty Acids

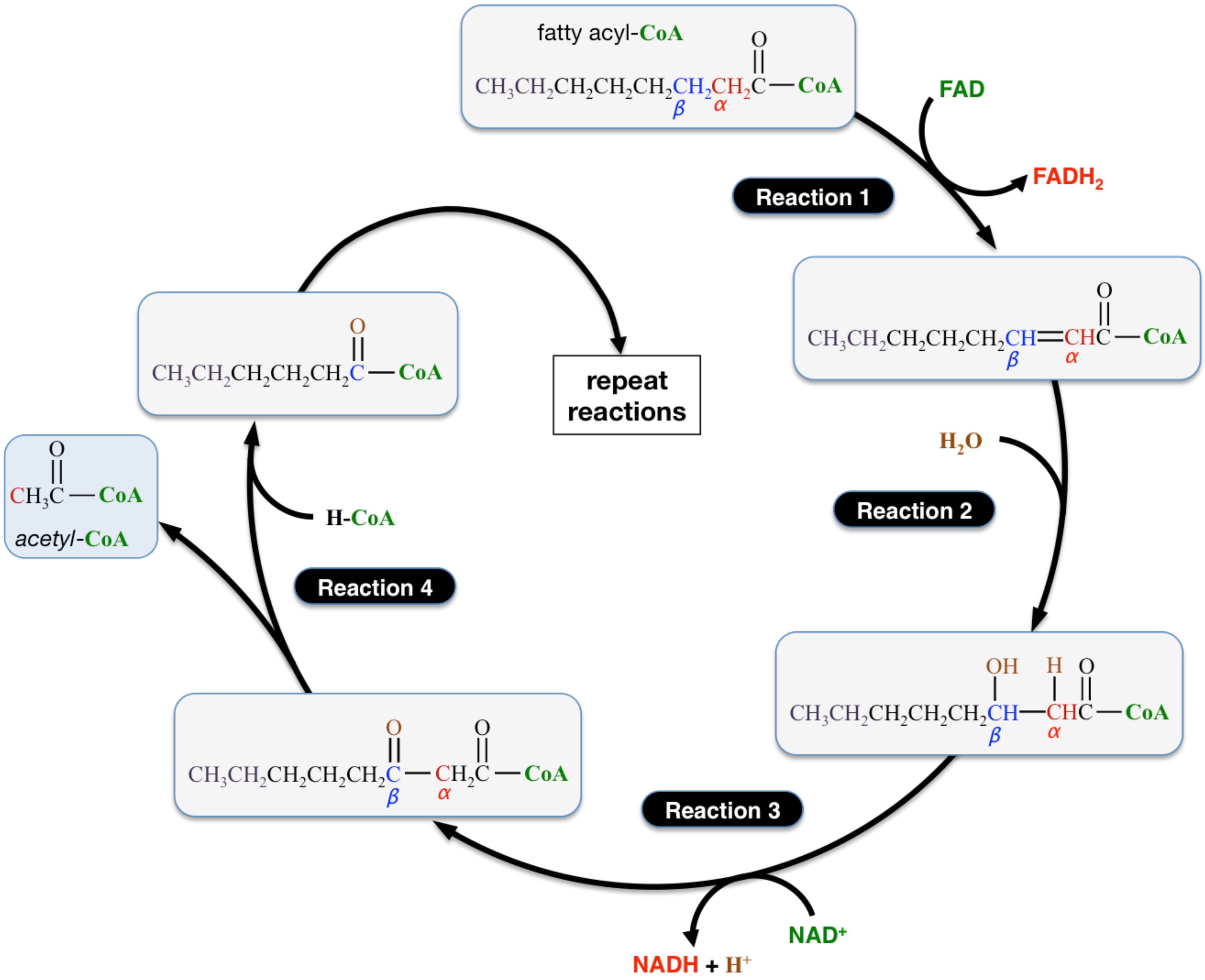
The first reaction in the catabolism of fatty acids is called ***activation***. In this reaction, the *acyl group* of a fatty acid is transferred to *coenzyme* A. For simplicity, I will show you an example of this reaction using a fatty acid that contains only ***eight*** carbons; in biological systems fatty acids typically contain twelve to twenty carbons. The reaction is shown below.



$$CH_3CH_2CH_2CH_2CH_2CH_2CH_2\overset{\overset{\displaystyle O}{\|}}{C}-O^- + H\text{-}CoA \xrightarrow[\quad]{ATP + H_2O \;\to\; AMP + 2P_i} CH_3CH_2CH_2CH_2CH_2CH_2CH_2\overset{\overset{\displaystyle O}{\|}}{C}-CoA + H^+$$

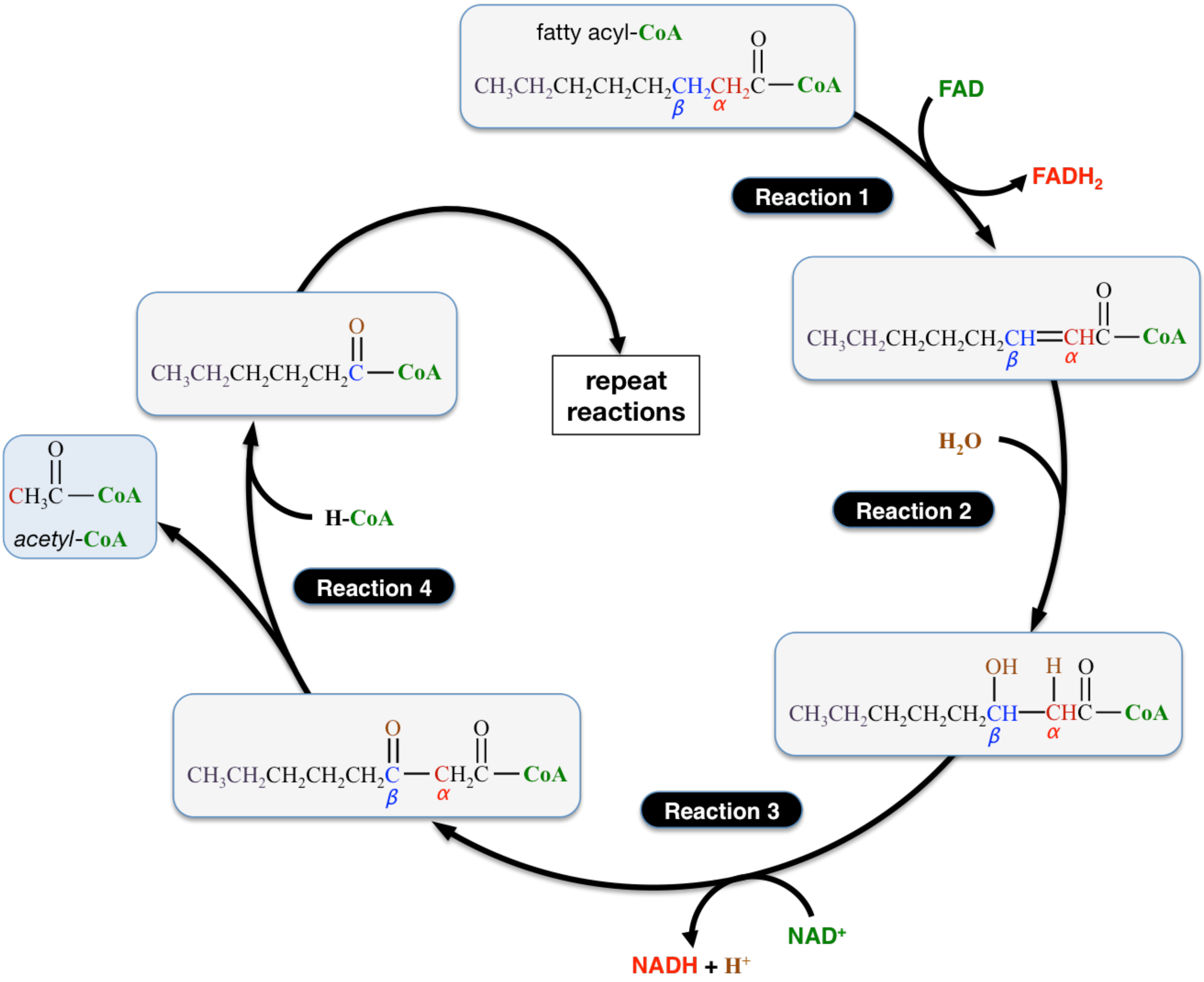
The fatty acid is converted to a **fatty *acyl*-coenzyme A**. This reaction does not occur spontaneously without the external energy input provided from the hydrolysis of two inorganic phosphates from **ATP**. In this case, **ATP** is converted to **AMP** and two inorganic phosphate (**P**$_i$) ions. The activation reaction is necessary in order for the acyl group from fatty acids to pass through the inner mitochondrial membrane and enter the matrix, where the subsequent reactions of fatty acid catabolism occur.

When fatty acyl-CoA enters the *mitochondrial matrix*, it undergoes a catabolic pathway called **beta-oxidation (*β*-*oxidation*)**. In ***β*-*oxidation***, a fatty acyl-CoA, goes through a ***repeated*** series of four reactions, ***each time*** losing two of its carbons. I will elaborate on ***β***-oxidation reactions using the *eight*-carbon fatty acyl-CoA that I used in the activation reaction example. The four reactions involved in ***β***-oxidation are shown below.



The carbon that is *next to* a fatty acyl's carbonyl group is designated as the "**α**-carbon," and the carbon that is two carbons away from the carbonyl group is designated as the "***β***-carbon." The **α**- and ***β***-carbons are labeled in the fatty acyl-CoA reactant. In **reaction 1** of ***β***-oxidation, the **α**- and ***β***-carbons are oxidized (they lose hydrogens and electrons). The hydrogens and electrons are transferred to **FAD** to produce **FADH$_2$**.

In **reaction 2** the double bond between the **α**- and ***β***-carbons is *hydrated*. The enzyme involved in this reaction directs the hydroxyl group to be added to the ***β***-carbon. *I have re-inserted the beta oxidation cycle figure on this page for convenient viewing*.

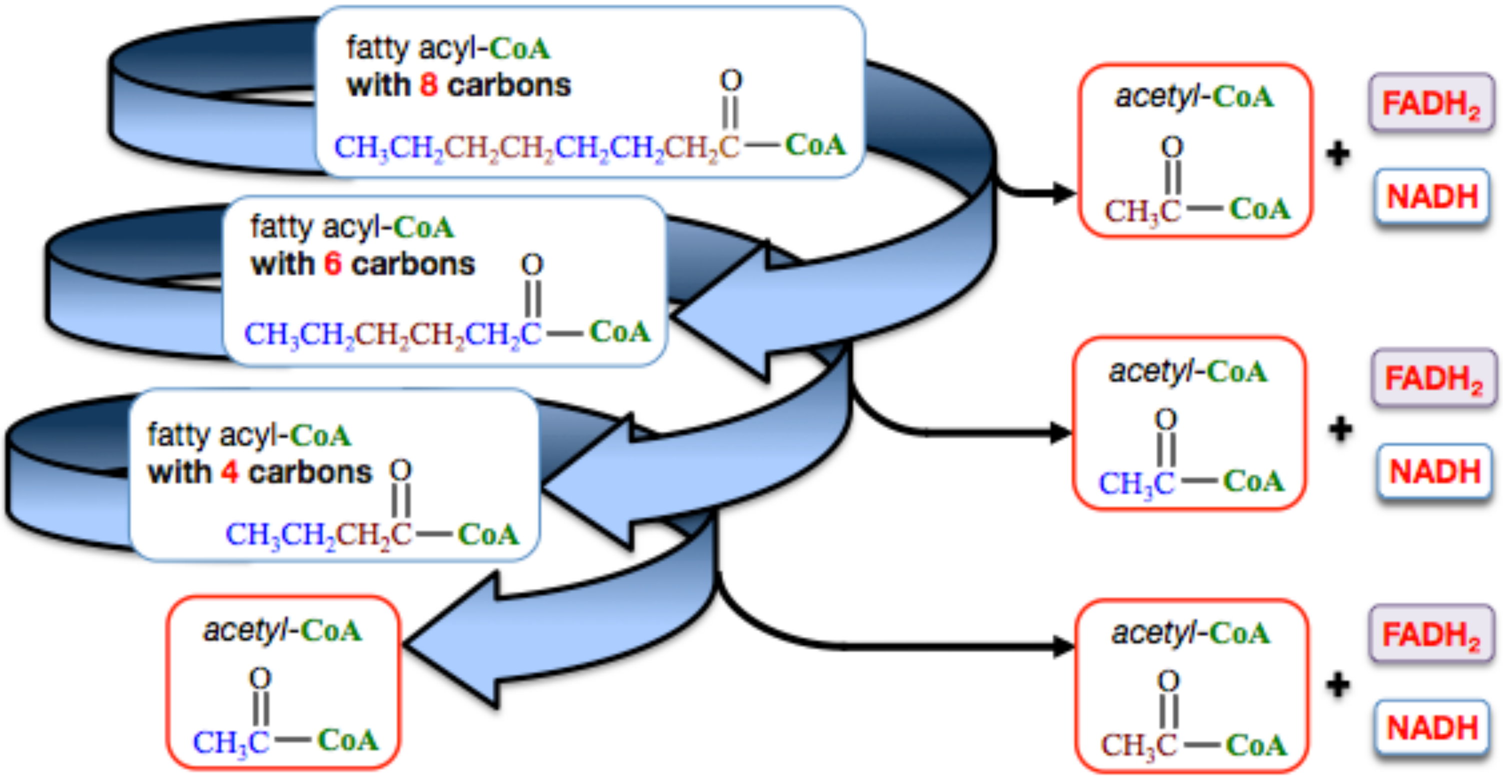


In reaction 3, the hydroxyl group on the ***β***-carbon is oxidized. It is for this reason that the reaction pathway is called ***β***-oxidation. In this oxidation, a hydrogen and electron are transferred to **NAD$^+$**, reducing it to **NADH**. Oxidation of this 2^o alcohol results in the formation of a *carbonyl group* at the ***β***-carbon.

In **reaction 4**, the bond between the **α**- and ***β***-carbon is broken. The acyl group, containing what was formerly the ***β***-carbon, is transferred to coenzyme A, thereby forming a ***new*** fatty acyl-CoA. A hydrogen forms a bond to what was formerly the **α**-carbon, thereby producing an acetyl-CoA. Because ***β***-oxidation occurs in the mitochondrial matrix, each acetyl-CoA can undergo the reactions of the citric acid cycle to produce an **ATP**, three **NADH**, and one **FADH$_2$**. More **ATP** is produced when the **NADH** and **FADH$_2$** formed in reactions 1 and 3, along with the **NADH** and **FADH$_2$** formed the citric acid cycle, undergo oxidative phosphorylation.

ATP production is not finished when the *original* fatty acid undergoes these four reactions, in fact it has just begun. Note that in addition to an acetyl-CoA, a ***new*** fatty acyl-CoA is also produced in **reaction 4.** The *new* fatty acyl-CoA is ***two carbons shorter*** than the original one. It will undergo the series of four reactions to produce more acetyl-CoA, **NADH**, and **FADH$_2$**. As this process repeats, the acyl group's length is decreased by ***two carbons*** with each successive ***β***-oxidation reaction series. This will continue until the fatty acyl-CoA contains *four* carbons, then it will undergo the reaction series ***one final time***. In the *final* pass through the four reactions, reaction 4 produces two ***acetyl***-CoA. The figure on the next page illustrates this process for the *eight-carbon* fatty acyl-CoA.

An *eight-carbon* fatty acyl-CoA will undergo ***three*** cycles of the ***β-oxidation*** reactions, as illustrated below:



If "**N**" equals the number of carbons that are contained in a fatty acyl-CoA, then it will undergo **[(N/2) -1]** ***β****-oxidation* cycles.

β-oxidation is classified a **"spiral" metabolic pathway**. A *spiral* metabolic pathway is a bit different than a *circular* pathway. In a circular pathway, such as the citric acid cycle, the final product is ***exactly*** the same as *one* of the *initial* reactants. This is not the case for a *spiral* pathway. A **spiral pathway** is a metabolic pathway in which a ***series of repeated reactions*** is used to break down (or build up) a compound.

Catabolism of Unsaturated Fatty Acids

Unsaturated fatty acids (derived from unsaturated fat) have ***double bonds*** in their hydrocarbon tails. Depending on the location of these double bonds, extra steps may be required to transform the double bonds in order to produce fatty acyl-CoA that can undergo ***β***-oxidation.

Review 15.6: β-oxidation

How many cycles of the ***β-oxidation*** spiral will occur for a *twelve-carbon* fatty acyl-CoA?

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

Review 15.7: β-oxidation

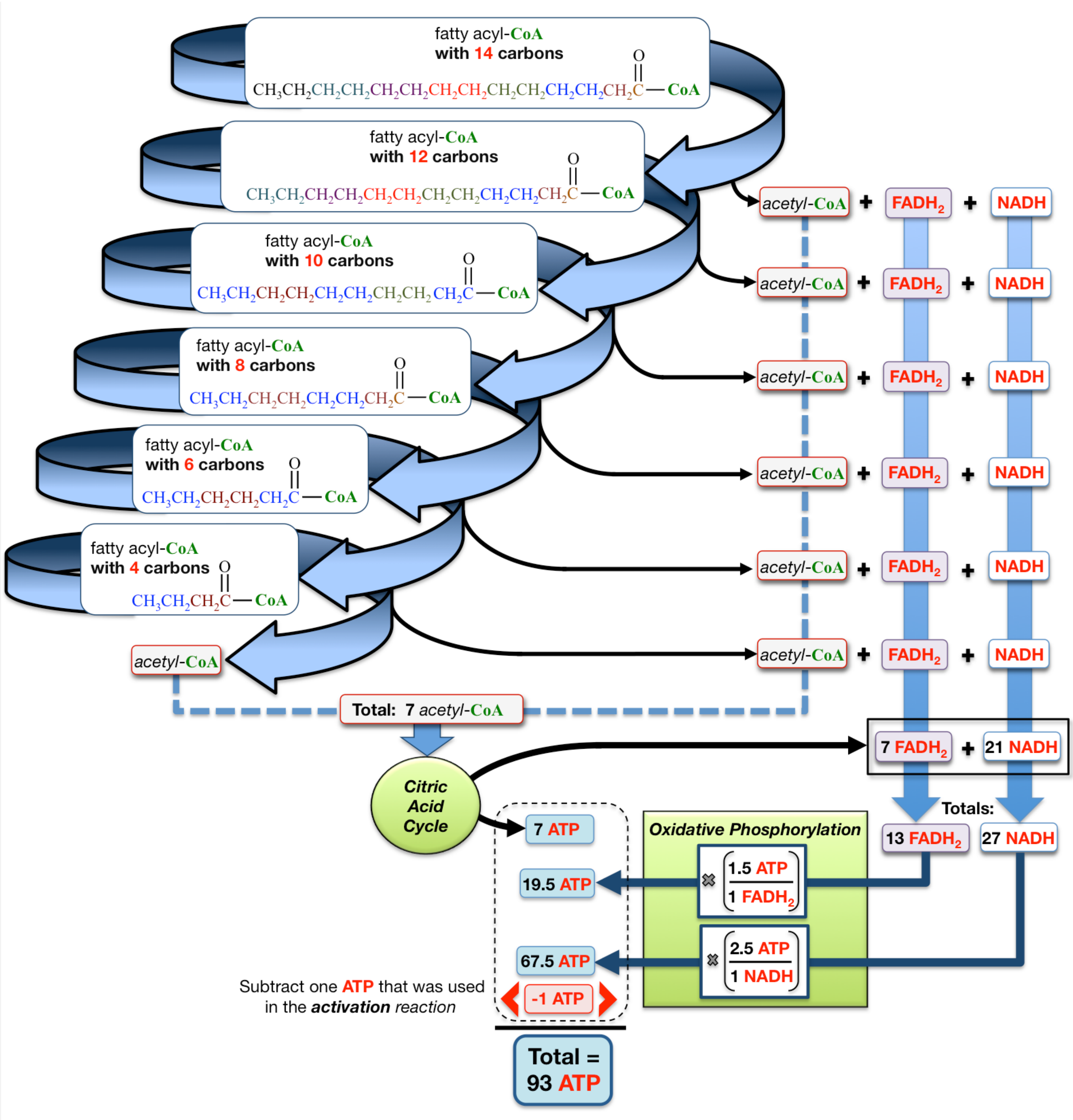
For the *twelve-carbon* fatty acyl-CoA in the previous review problem:

a. How many acetyl-CoA are produced after all of the ***β-oxidation*** cycles?
b. How many NADH are produced after all of the ***β-oxidation*** cycles?
c. How many FADH$_2$ are produced after all of the ***β-oxidation*** cycles?

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

ATP Production from Fatty Acids

As was the case for carbohydrate catabolism, the catabolism of triglycerides converts chemical potential energy in food to the form of chemical potential energy that is most useful in cells - **ATP**. Let's consider how many **ATP** are produced from the catabolism of a typical fatty acid, *myristate*, which contains 14 carbon atoms. First, myristate is activated to produce a 14-carbon fatty acyl-CoA. The activation step ***consumes*** one **ATP**. We will assume that *oxidative phosphorylation* produces, *on average*, 2.5 **ATP** per **NADH** and 1.5 **ATP** per **$FADH_2$**. The net gain of **ATP** from one 14-carbon fatty acid can be calculated as shown in the illustration below.



Each of the first *five* cycles of the ***β***-oxidation spiral produces one acetyl-CoA, one **NADH**, and one **$FADH_2$**. The *final cycle* of the spiral produces ***two*** acetyl-CoA, one **NADH**, and one **$FADH_2$**. The acetyl-CoA are processed through the citric acid cycle, producing **ATP** and *more* reduced coenzymes. The **NADH**, and **$FADH_2$** formed in ***β***-oxidation, and the **NADH**, and **$FADH_2$** formed in the citric acid cycle undergo oxidative phosphorylation. Since one **ATP** was consumed in the activation reaction, it is subtracted when calculating the *net gain* of **ATP**. ***β***-oxidation of myristate, *on average*, results in a net gain of **93 ATP**.

Some cells, primarily adipose, muscle, and liver cells, are capable of catabolizing **and** storing triglycerides. When these cells catabolize stored triglycerides, they begin by breaking the triglycerides down to fatty acids and glycerol. Not only can these cells catabolize the fatty acids for energy, they also use chemical potential energy in glycerol to produce **ATP**. This is done by converting glyceraldehyde to glyceraldehyde 3-phosphate, which is a glycolysis intermediate.

Review 15.8: ATP from β-*oxidation*

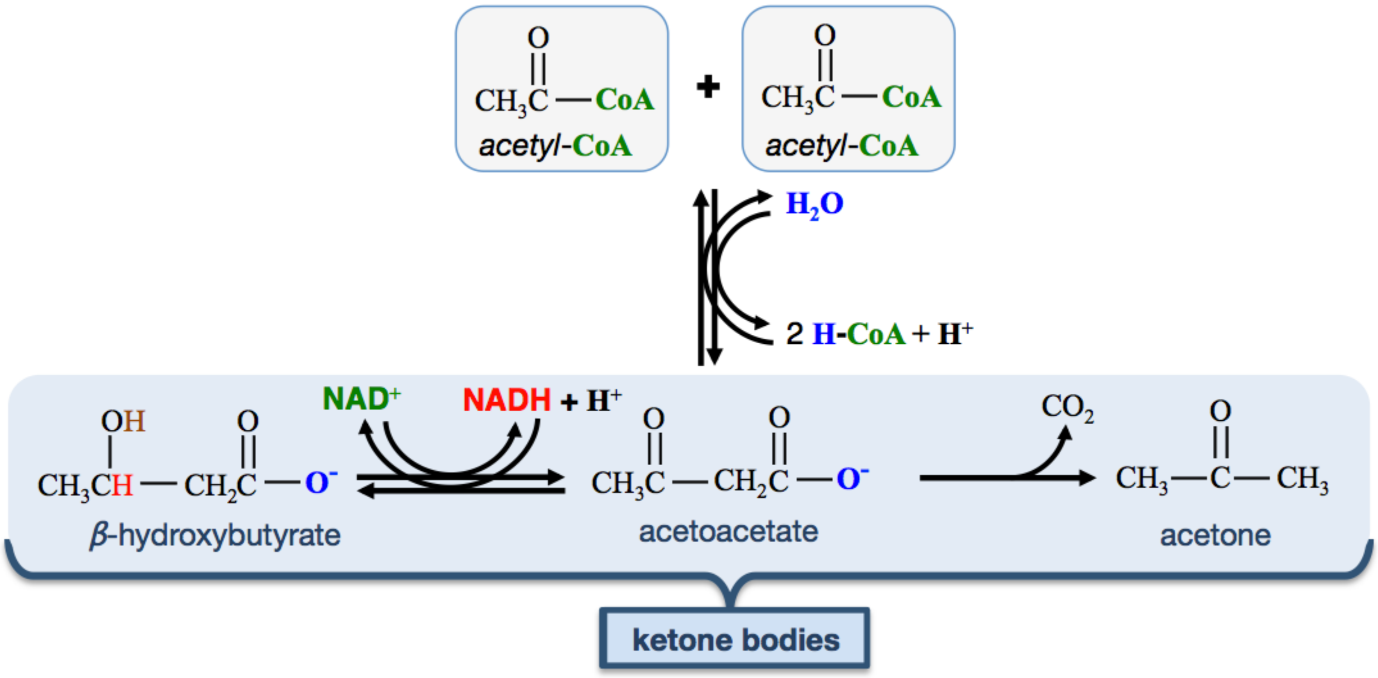
What is the net gain in ATP for **β-*oxidation*** of a twelve-carbon fatty acid? Assume that *oxidative phosphorylation* produces, ***on average***, 2.5 ATP per NADH and 1.5 ATP per $FADH_2$.

- **NOTE**: Because we are using average values for the calculation of ATP from oxidative phosphorylation, you will come up with fractional ATP subtotals; that is not a problem because you're calculating ***average*** ATP production. For example, you will calculate that, ***on average***, 16.5 ATP are produced from the $FADH_2$ in this problem.
- Remember to subtract one ATP to account for the ATP that was consumed in the activation step.

For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

Ketone Bodies

As you have seen in the previous example and review problem, the catabolism of a single fatty acid produces several acetyl-CoA. Catabolism of large quantities of triglycerides will therefore result in high concentrations of acetyl-CoA. Acetyl-CoA that is produced in excess of the amount that can be metabolized in the citric acid cycle results in a high concentration of acetyl-CoA in the mitochondrial matrix. When this occurs, acetyl-CoA reacts with *other* acetyl-CoA to produce the three compounds that are referred to as **ketone bodies**. This process is referred to as **ketogenesis**. Ketone bodies are produced as shown in the reactions below.



Two acetyl-CoA are first converted to *acetoacetate*. Acetoacetate can undergo two reactions. It can be reduced to ***β**-hydroxybutyrate*, or it can undergo a decarboxylation reaction to produce *acetone*. The easily identifiable aroma of acetone can be detected in the breath of an individual with high levels of ketone bodies. The name "ketone bodies" is historical, only one of them, acetone, is a ketone.

Ketone bodies are water-soluble, therefore easily dispersed from the liver to other parts of the body. Most cells, with liver cells being the notable exception, are capable of converting ketone bodies back into acetyl-CoA, and then metabolizing it in the citric acid cycle. Converting ketone bodies back to acetyl-CoA is the *reverse of ketogenesis* (different enzymes are involved). Some cell types rely on ketone bodies for **ATP** production more than others. Heart muscles and the renal cortex use ketone bodies more readily than glucose. The brain's primary energy source is glucose, but it is unable to store glucose and does not allow fatty acids (or amino acids) to enter. In the case of starvation, when there is very little glucose present, the brain gets 75% of its energy from ketone bodies.

When individuals diet, they begin to metabolize the triglycerides that are stored in fat cells. This leads to ***ketogenesis***. You can find many online videos of happy dieters excitedly holding up urine test strips that show elevated ketone body levels.

In cases of starvation, poorly treated diabetes, and conditions related to alcoholic binge drinking, the cells cannot get glucose and extremely high rates of fatty acid catabolism results in dangerous, and even fatal levels of ketone bodies. ***β***-*hydroxybutyric acid* and *acetoacetic acid* (the acid forms of ***β***-*hydroxybutyrate* and acetoacetate, respectively) have significant acid strength. Their production results in a higher concentration of H_3O^+, which can overcome the blood's buffering capacity. When this occurs, the blood becomes acidic. When blood pH is less than the normal range (7.35-7.45), the condition is called **acidosis**. *Acidosis* can result in tissue dysfunction and is especially damaging to the central nervous system. When *acidosis* is caused by excess *ketone bodies*, the condition is called **ketoacidosis**.

Fatty Acid Anabolism

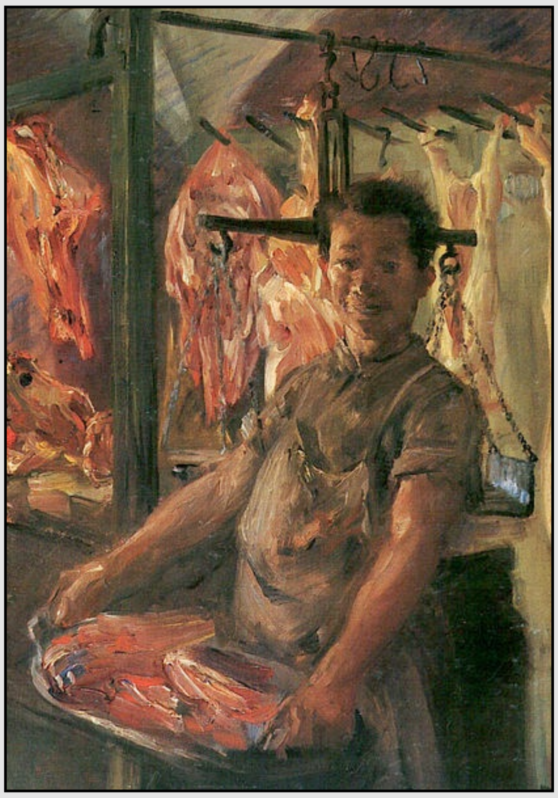
Fatty acids are produced by a *spiral metabolic pathway* that operates in the opposite direction as ***β***-oxidation; it builds up fatty acyl-CoA by a repeating series of reactions that add acetyl-CoA to a growing fatty acyl-CoA structure. This ***anabolic*** process of synthesizing fatty acids from acetyl-CoA is called **fatty acid synthesis**. Fatty acid synthesis occurs primarily in adipose and liver cells.

The body can synthesize almost all of the fatty acids it needs ***except for linoleic and linolenic acid***. The reason these two fatty acids cannot be biosynthesized is that we do not have an enzyme that is capable of *desaturating* carbons (forming carbon-carbon double bonds) beyond position number **10** of fatty acid chains. Linoleic and linolenic acid can ***only*** be obtained through dietary triglycerides, and are therefore classified as **essential fatty acids**.

When the body has plenty of glycogen stored, fat cells increase their intake of glucose. The glucose is catabolized to acetyl-CoA, which can then undergoes *fatty acid synthesis* to produce *fatty acids*. The fatty acids are stored as triglycerides in adipose cells. So, although individuals may consume a minimal amount of fats, they can still become obese if they consume carbohydrates in excess of their energy needs.

15.5 Protein Metabolism

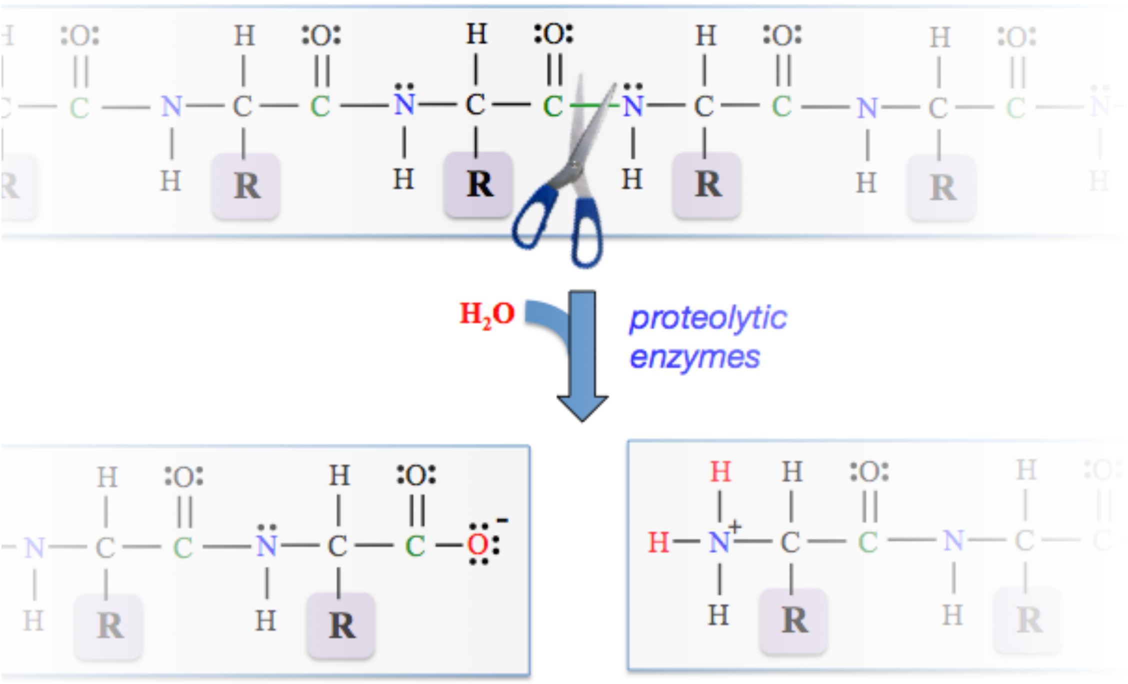
When ***dietary proteins*** are digested, they are converted to ***amino acids***. The *amino acids* are then used in various metabolic pathways. In an *anabolic* process, they are used to build proteins and peptides according to the body's needs. You learned about this process in chapter 14 when I discussed how proteins are synthesized in the ***translation*** process. *Amino acids* are also used as nitrogen sources for the biosynthesis of other amino acids and other nitrogen-containing compounds, such as nucleotide bases. Amino acids that are ingested in excess of what is needed for these biosynthesis needs are catabolized to produce **ATP**.



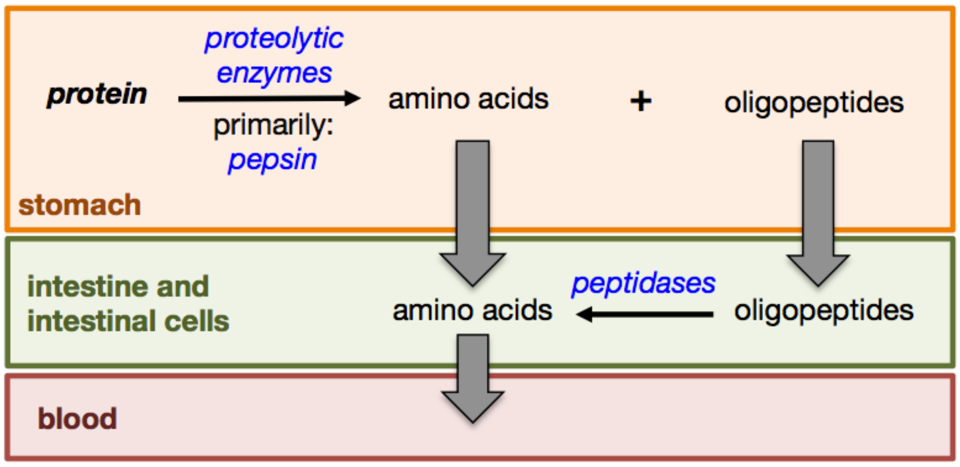
Artist: Lovis Corinth (1858 – 1925)

Digestion of Proteins

In the digestion process, dietary proteins are converted to ***amino acids*** by the *hydrolysis* of their ***peptide bonds***. In chapter 13, you learned how peptide bonds are formed between amino acids to produce proteins. The hydrolysis of peptide bonds is the reverse of that process. Recall that in proteins, the peptide bonds are between nitrogens and carbonyl groups. When a peptide bond is hydrolyzed, the peptide bond is broken and an oxygen is added to the carbonyl carbon and two hydrogens to the nitrogen. The hydrolysis of *one of the peptide bonds* in a small section of protein is shown below.



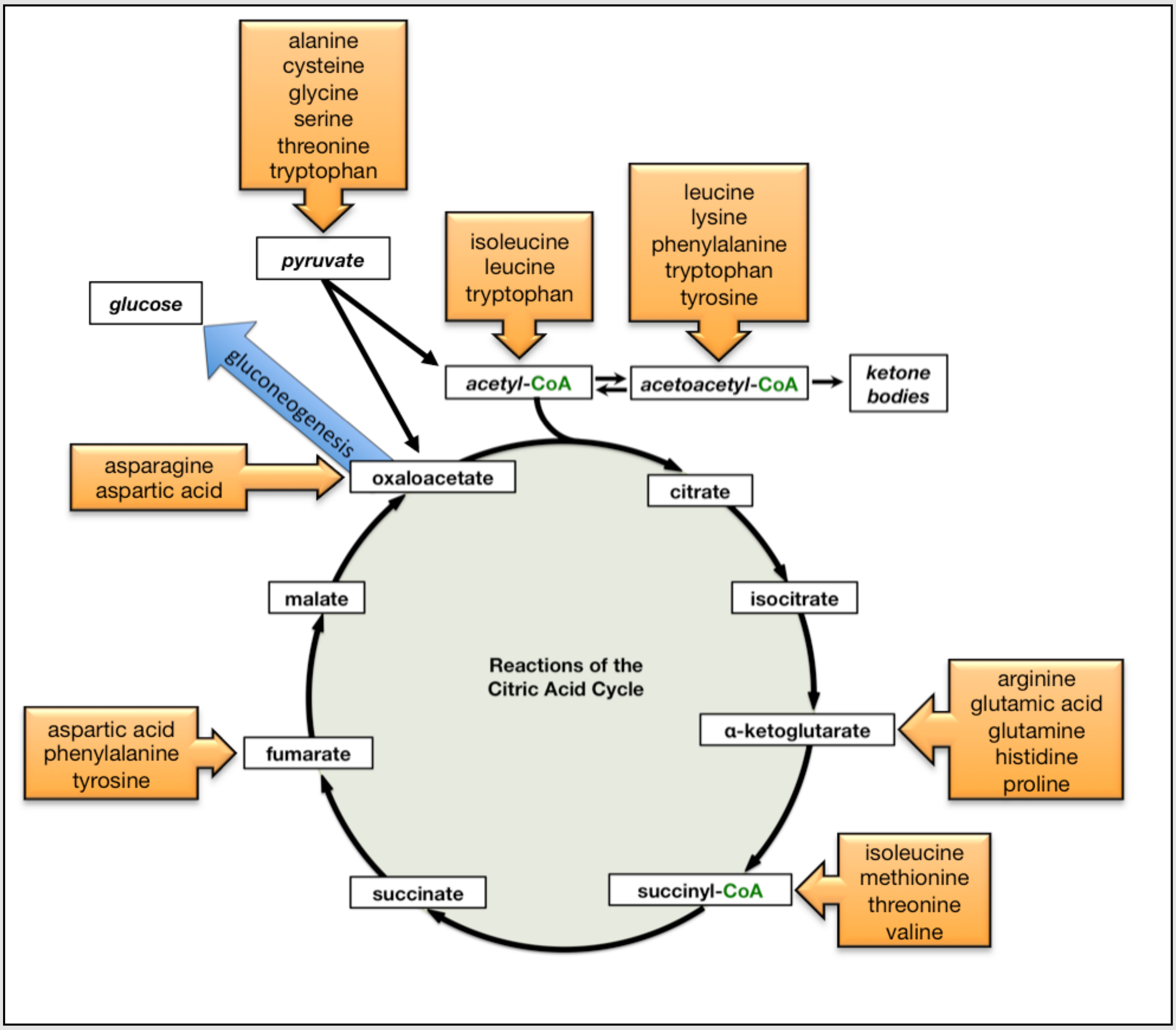
Protein digestion begins in the stomach and continues in the small intestine. In the stomach, an acidic environment and proteolytic enzymes (primarily *pepsin*) catalyze the hydrolysis of proteins to oligopeptides and amino acids. As these species move though the small intestine and enter the intestinal cells, the oligopeptides are further hydrolyzed to amino acids. This is done with the help of dietary enzymes called *peptidases*. The amino acids are released from the intestinal cells into the blood stream, and then transported to other cells. An overview of the digestion of proteins is shown below.



Catabolism of Amino Acids

Some of the amino acids produced in digestion are used for the synthesis of proteins, the synthesis of _other_ amino acids, and the synthesis of other nitrogen-containing compounds. Amino acids that are ingested in surplus of these biosynthesis needs are catabolized as fuel for the production of **ATP**. This is done by transforming them into intermediate metabolites that can be converted to glucose, ketone bodies, ***or*** undergo the citric acid cycle. The entry points of amino acids into the various metabolic pathways are indicated in Figure 15.11.

Figure 15.11 **Entry Points of Amino Acids into Metabolic Pathways**



A schematic diagram that shows entry points for the twenty common amino acid into metabolic intermediates that can be converted to glucose, ketone bodies, or undergo the citric acid cycle.

I do not expect students to memorize this table; however, there are a couple of important concepts that I want you to know:

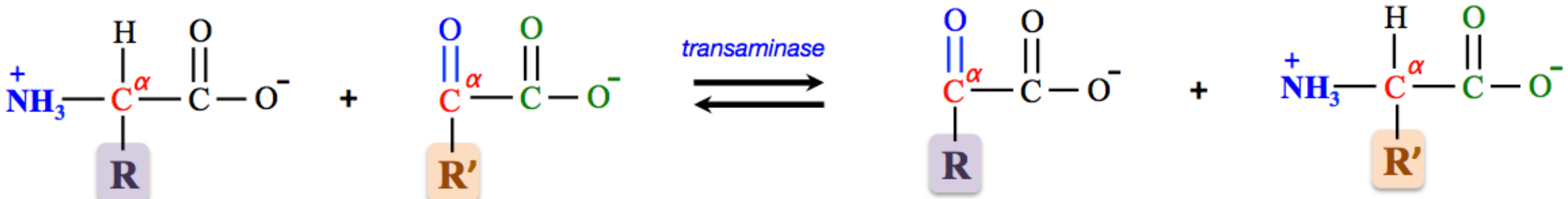
1) Amino acids can be converted to pyruvate, acetyl-CoA, acetoacetyl-CoA, or some citric acid cycle intermediates. These compounds are then converted to glucose, ketone bodies, ***or*** undergo the citric acid cycle.

2) All ***twenty common amino acids*** can be converted into either pyruvate, acetyl-CoA, acetoacetyl-CoA, or a citric acid cycle intermediate. Some amino acids are capable of being converted into more than one of these compounds.

The details of ***how*** the twenty common amino acids are converted into the metabolic intermediates shown in Figure 15.11 are far beyond the scope of this text. What is important to understand is that these conversions involve one or both of two important amino acid reactions: **transamination** and **oxidative deamination**. These reactions occur primarily in the liver. I will discuss these reactions and, in doing so, you will see a couple of examples of the transformations shown in Figure 15.11.

Transamination

Transamination involves the transfer of a quaternary ammonium group (NH_3^+). The NH_3^+ that is bound to the **α**-carbon of an amino acid is transferred to an **α-*keto* acid**. An **α**-keto acid is a *carboxylic acid* that has a ***carbonyl group*** (**C=O**) at the **α**-carbon. In a *transamination reaction*, an amino acid and an **α**-keto acid are converted to a ***new*** amino acid and a ***new* α**-keto acid. The general form of the transamination reaction is shown below.



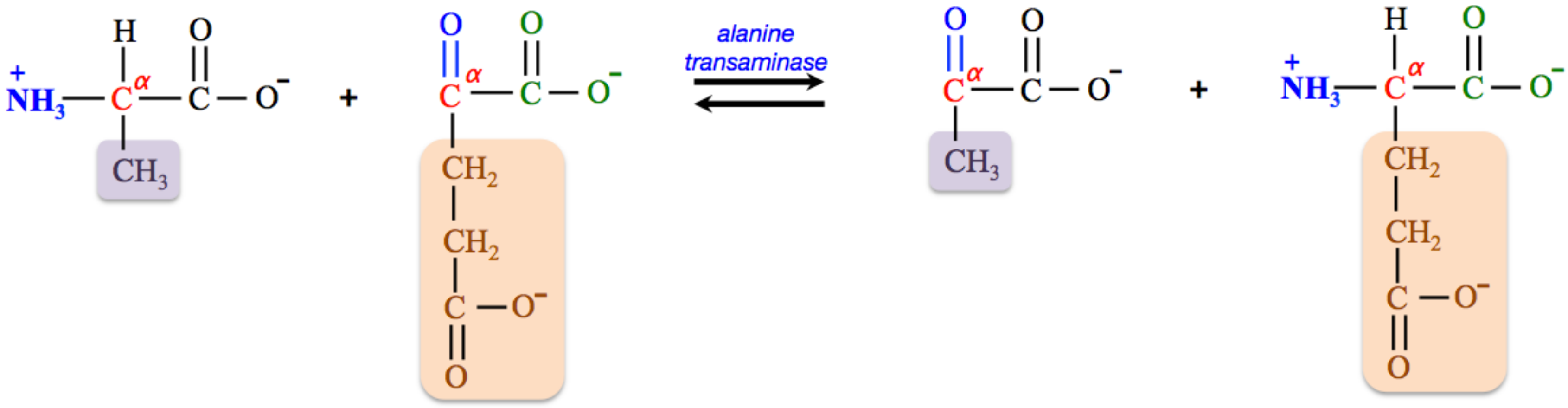
an amino acid

an α-*keto* acid

a **new** α-*keto* acid

a **new** amino acid

In *transamination reactions*, the NH_3^+ from an amino acid is ***usually*** transferred to **α-ketoglutarate** (an **α**-keto acid). A specific example of a *transamination reaction* is shown below.



alanine (Ala)
(an amino acid)

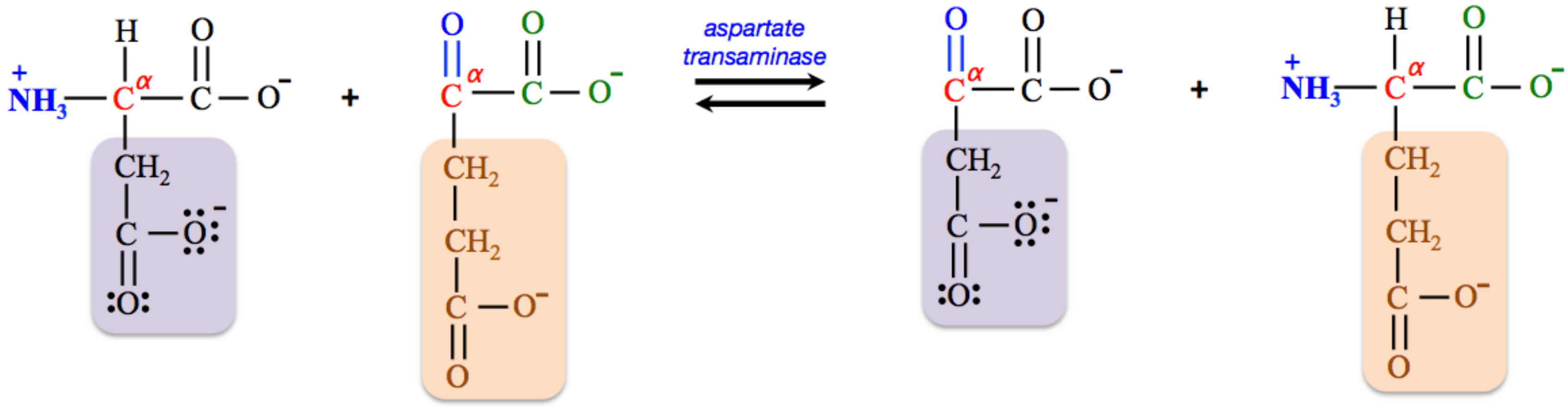
α-ketoglutarate
(an α-*keto* acid)

pyruvate
(a **new** α-*keto* acid)

glutamic acid (Glu)
(a **new** amino acid)

In this reaction, alanine is converted to pyruvate. If you look at Figure 15.11 (on the previous page), you will see that alanine is included as one of the amino acids that can be transformed into pyruvate.

Another example of a *transamination reaction* is the conversion of aspartic acid to oxaloacetate, as shown below.



aspartic acid (Asp)
an amino acid

α-ketoglutarate
an α-*keto* acid

oxaloacetate
a **new** α-*keto* acid

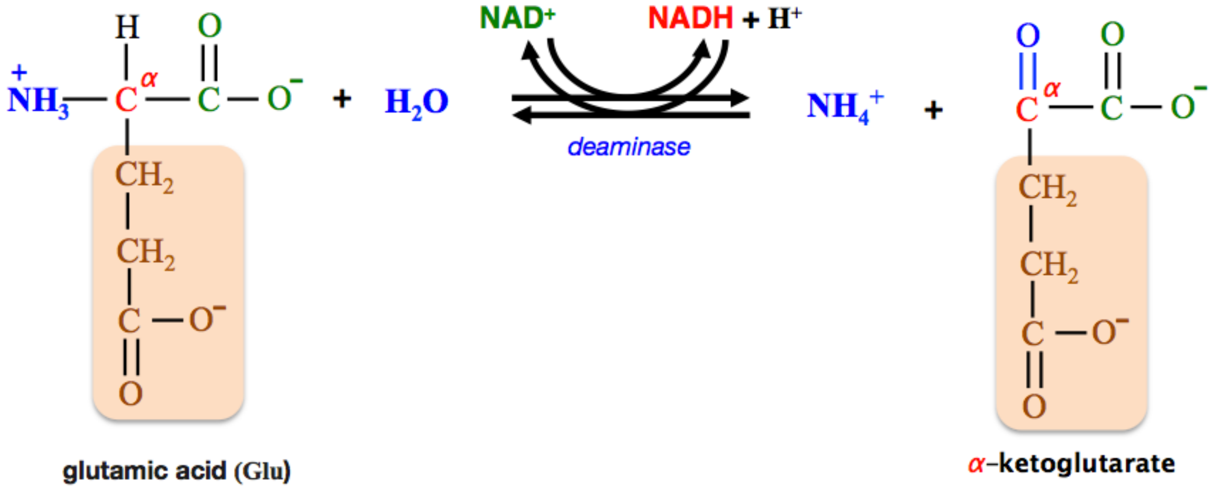
glutamic acid (Glu)
a **new** amino acid

If you look at Figure 15.11, you will see that aspartic acid is included as one of the amino acids that can be transformed into oxaloacetate.

In transamination reactions, **α**-ketoglutarate is converted to *glutamic acid*. We will now take a look at how *glutamic acid* is recycled back to **α**-ketoglutarate in the *oxidative deamination* reaction.

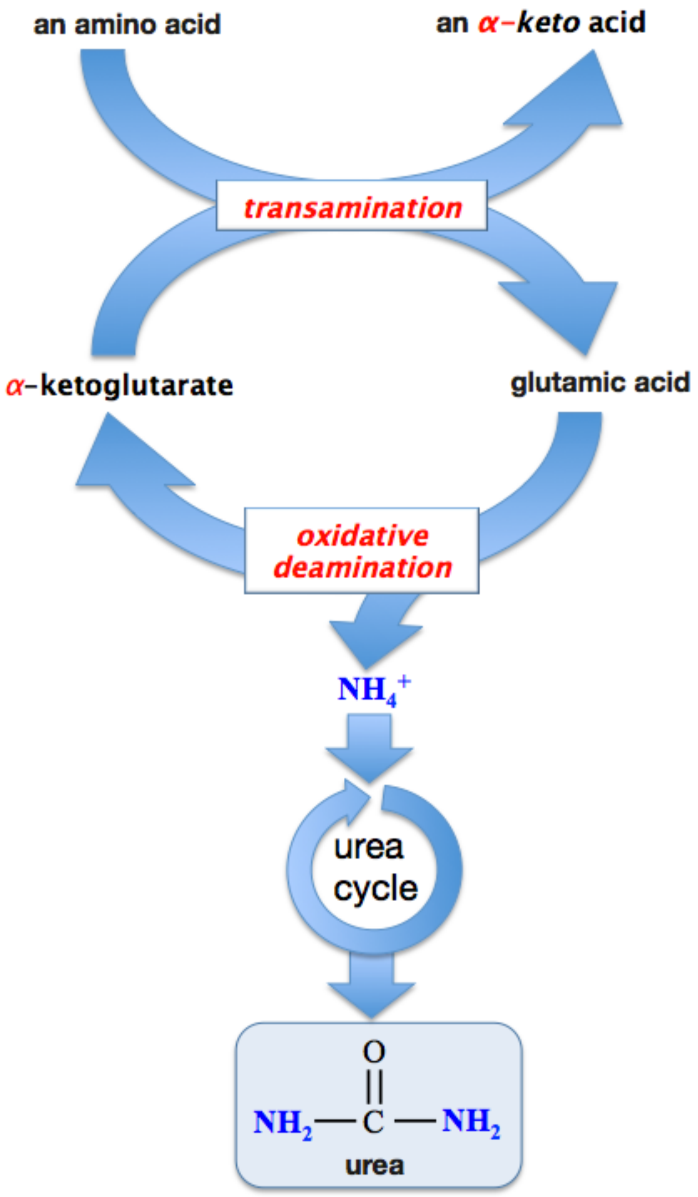
Oxidative Deamination

The other important reaction in amino acid catabolism is **oxidative deamination.** In both of the examples on the previous page, and most other transaminase reactions, **α**-ketoglutarate is converted to *glutamic acid* (an amino acid). In *oxidative deamination*, a *quaternary ammonium group* (-NH_3^+) is removed from *glutamic acid*, thereby producing ammonium (NH_4^+) and **α**-ketoglutarate, as shown below.



In addition to the removal of a *quaternary ammonium group*, *glutamic acid*'s **α**-carbon is oxidized (gains an oxygen *and* loses a hydrogen). This oxidation is accompanied by the reduction of **NAD^+**.

The **α**-ketoglutarate that is produced in the reaction is now free to accept a ***new*** *quaternary ammonium group* from another amino acid in a *transamination reaction,* as illustrated below.

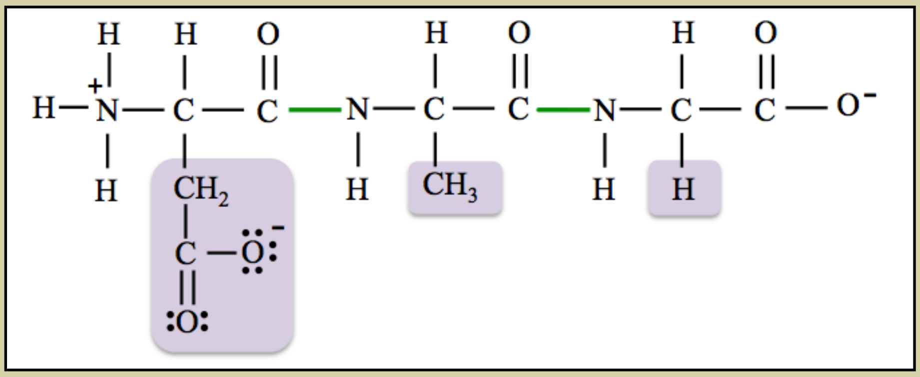


The free ammonium ions (NH_4^+) that are produced in oxidative deamination are ***toxic*** at elevated concentrations. Humans and most other terrestrial vertebrates are capable of converting the ammonium ions to ***urea***. A typical adult produces about 25 to 30 grams of *urea* per day. This occurs in a series of reactions called the **urea cycle**. Urea is filtered, by the kidneys, into the urinary track and then removed from the body during urination. Kidney disease can result in the build up of dangerous amounts of urea. The urea concentration in blood is referred to as ***blood urea nitrogen*** (**BUN**). In cases of ***end-stage renal (kidney) failure***, safe **BUN** levels are exceeded, and patients must undergo **dialysis treatments**. Dialysis involves artificial methods of urea removal. The most common of these is called **hemodialysis**. In *hemodialysis*, a patient's blood is passed along one side of a porous membrane, while a dialyzing (urea-free) solution is passed along the other. The pores allow the diffusion of urea (but not cells, proteins, or other large compounds) from the blood into the dialyzing solution. After the blood is dialyzed, it is continuously returned to the patient. Hemodialysis takes several hours and is usually done multiple times per week. This process is not only time-consuming, but far from ideal because of many complications and side effects. Bedside nocturnal dialyzers are now available.

In otherwise healthy patients with kidney failure, kidney transplants are possible. Kidney donations are fairly common since most humans have two kidneys, and one kidney is usually sufficient to eliminate urea. Current areas of research into other treatments involve the development of wearable artificial kidneys, and the growth of human kidneys in the lab.

Review 15.9: Predicting the Products of Hydrolysis of Peptides in Protein Digestion

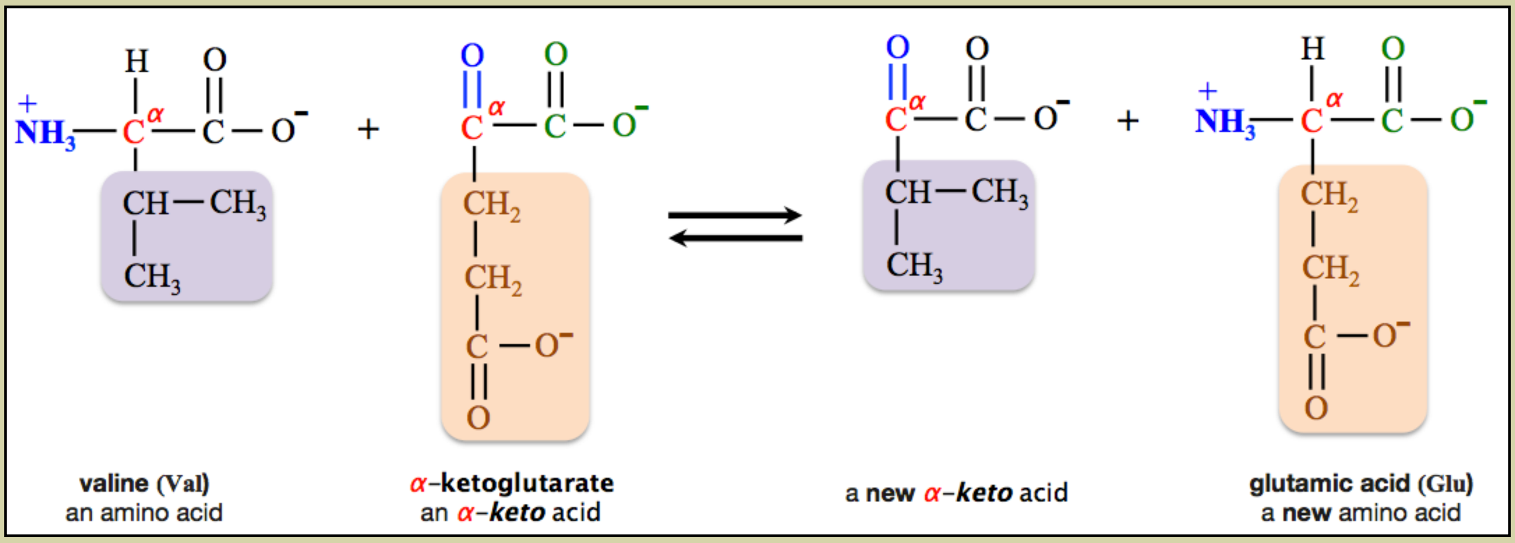
In the digestion of proteins, peptide bonds are hydrolyzed when proteins react with water in the presence of proteolytic enzymes. Draw the structural formulas of the three amino acids that are produced when all of the peptide bonds in the tripeptide shown below are hydrolyzed.



For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

Review 15.10: Understanding Transamination and Oxidative Deamination Reactions

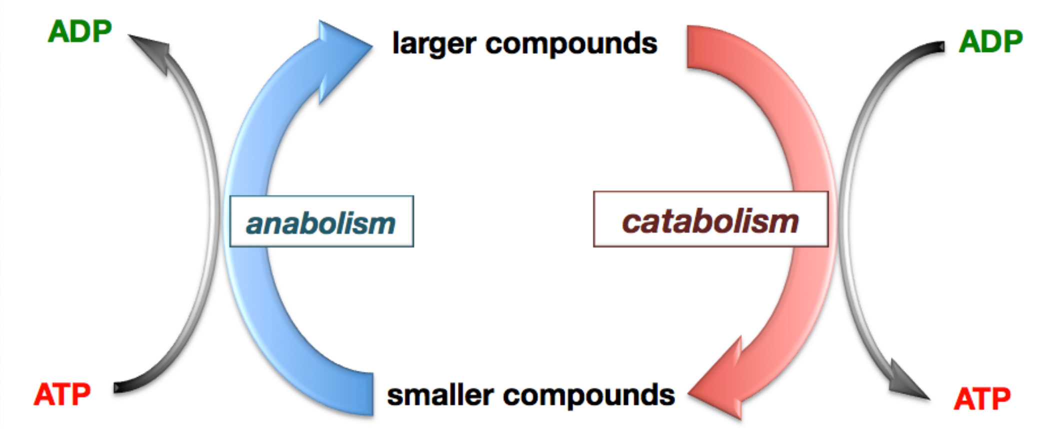
Identify the reaction shown below as either a *transamination* ***or*** an *oxidative deamination* reaction.



For ***i-books*** versions: **Click here to check answer** For **print or pdf versions**, see the answer key in Appendix 1.

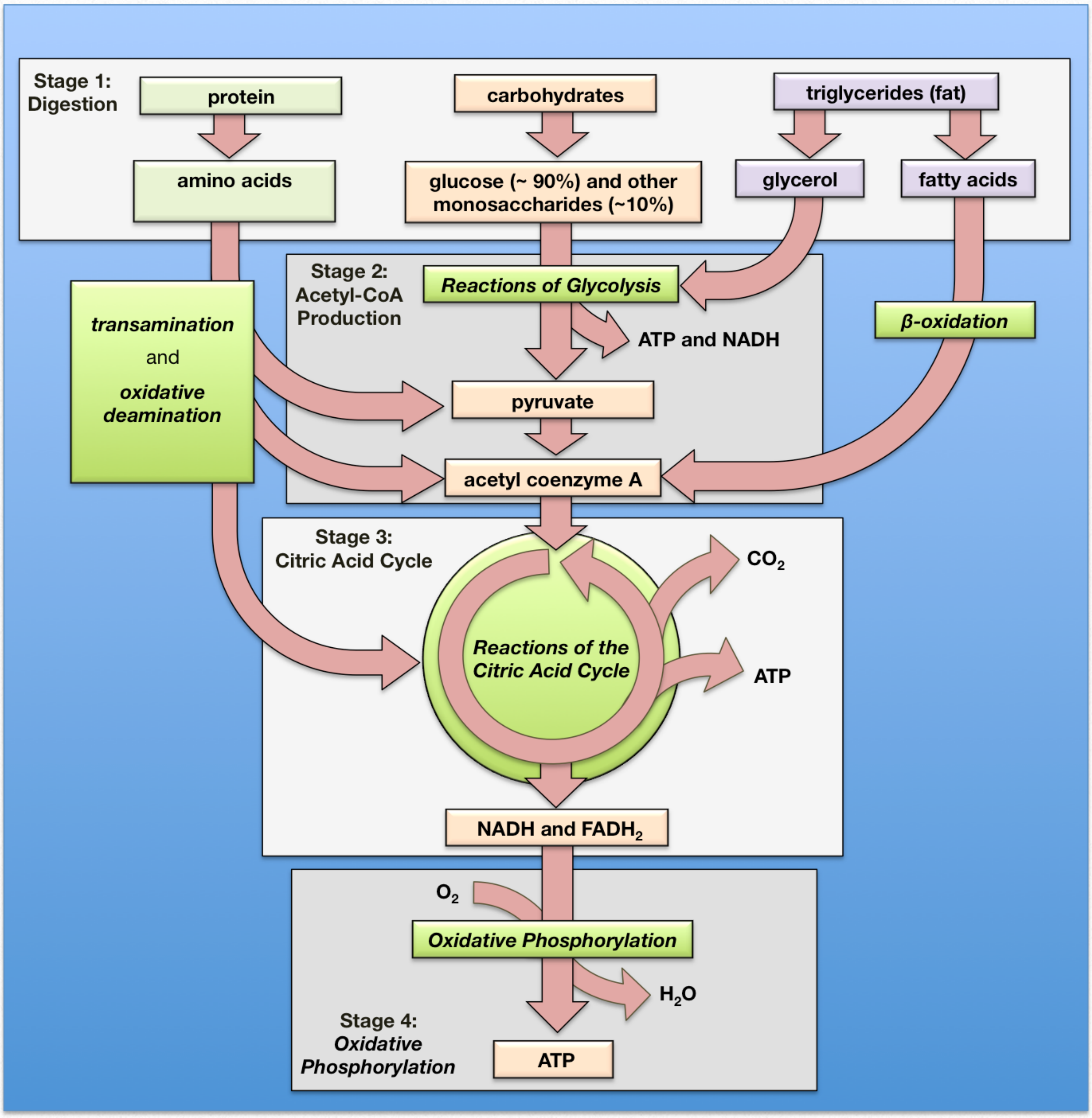
15.6 Summary of Metabolism

The body is able to build proteins, carbohydrates, and triglycerides from smaller organic compounds in anabolic processes. Anabolic processes generally require the input of external energy. This energy often comes from chemical potential energy in **ATP**. The body is able to break down proteins, carbohydrates, and triglycerides into smaller organic compounds in catabolic processes. Catabolic processes typically release energy. This energy is often used by the body to produce **ATP**. The metabolic strategy behind the production of **ATP** is that **ATP** is an energy source that can be instantaneously used by organisms to do cellular work and to provide the energy required for life-sustaining reactions that would otherwise not occur spontaneously. The metabolic strategies of catabolism and anabolism are summarized in the illustration on the right.



Catabolism

The catabolism of food is summarized in the image below:



In the four stages of food catabolism, chemical potential energy in food is converted to chemical potential energy in **ATP**, **NADH**, and **$FADH_2$**. The **NADH** and **$FADH_2$** can then be converted to electrochemical energy in the form of a hydrogen ion gradient. The electrochemical potential in this gradient is used to drive the production of **ATP**.

The ***catabolic processes*** discussed in this chapter are digestion, glycolysis, pyruvate oxidation/decarboxylation, the citric acid cycle, glycogenolysis, lipolysis, ***β***-oxidation, and oxidative deamination. These *catabolic processes* are listed and briefly described in the Table 15.2:

Table 15.2 The Catabolic Processes in Chapter 15

Name	Description	Notes
digestion	***Carbohydrates*** are *hydrolyzed* to ***monosaccharides***. ***Triglycerides*** are "***partially***" *hydrolyzed* to ***fatty acid salts*** and ***monoglyceride***. ***Proteins*** are *hydrolyzed* to ***amino acids***.	
glycolysis	A ***linear metabolic pathway*** in which *glucose* is converted into **two** *pyruvate ions.*	**High** concentrations of **ATP**, *pyruvate*, or *other pathway products* suppress this process.
pyruvate oxidation/ decarboxylation	*Pyruvate* is oxidized and decarboxylated to produce *acetyl*-**CoA**.	
citric acid cycle	A ***circular metabolic pathway*** in which *acetyl*-**CoA** is metabolized to produce **ATP**, **NADH**, and **$FADH_2$**.	
glycogenolysis	*Glycogen* is converted to *glucose.* Glycogenolysis occurs primarily in ***liver*** and ***muscle*** cells. Liver cells will release the glucose into the bloodstream so that it can be taken in by other types of cells.	***Low blood glucose*** and ***glucagon*** accelerate this process. ***High blood glucose*** and ***insulin*** suppress this process.
β-oxidation	A ***spiral metabolic pathway*** in which *fatty acids are converted to acetyl*-**CoA, NADH** and **$FADH_2$**.	
lipolysis	*Triglycerides* that are stored primarily in adipose (fat) cells and muscle cells are broken down into *fatty acids* and *glycerol*. Liver cells can release the fatty acids and glycerol into the bloodstream so that they can be taken in by other types of cells.	
oxidative deamination	A *quaternary ammonium group* ($-NH_3^+$) is removed from *glutamic acid*, thereby producing ammonium (NH_4^+) and ***α***-ketoglutarate.	

Anabolism

The ***anabolic processes*** discussed in this chapter are gluconeogenesis, glycogenesis, fatty acid synthesis, and protein synthesis. These *anabolic processes* are listed and briefly described in Table 15.3.

Table 15.3 The Anabolic Processes in Chapter 15

Name	Description	Notes
gluconeogenesis	The conversion of ***non-carbohydrate species into glucose***. This process is *similar* to the reverse of glycolysis. Gluconeogenesis occurs primarily in the liver. It increases blood glucose levels because liver cells can release the glucose that is produced into the bloodstream.	***Low blood glucose*** and ***glucagon*** accelerate this process.
glycogenesis	*Glucose* is converted to *glycogen.* Glycogenesis occurs primarily in ***liver*** and ***muscle*** cells. Glycogenesis lowers blood glucose levels because glucose is taken up by liver and muscle cells and then converted to glycogen.	***High blood glucose*** and ***insulin*** accelerate this process. ***Low blood glucose*** and ***glucagon*** suppress this process.
fatty acid synthesis	Fatty acids are produced by a spiral pathway that works in the opposite direction of ***β***-oxidation; it builds up fatty acyl-CoA by a repeating series of reactions that add acetyl-CoA to a growing fatty acyl-CoA structure. Fatty acid synthesis occurs primarily in adipose and liver cells.	
Protein synthesis	*Amino acids* are converted to *proteins.*	This process was mentioned briefly in this chapter, however it was ***thoroughly discussed chapter 14***.

Epilogue

I hope that the chemistry concepts that you learned in this course will provide a foundation for a better understanding of biological and health sciences. I believe you will find that your understanding of chemistry will allow you to see the world in a deeper and more interesting way than you did before this course. I hope that this new understanding will help you in future courses, your career, and in many other aspects of your life. **In these endeavors, I wish you the best!**

Appendices

Appendix 1: Answers to In-Chapter Review Problems

Appendix 2: Template and Examples for Drawing Line Bond Structures

Appendix 3: Determining Formal Charge

Appendix 4: Radioisotopes and Nuclear Reactions

Appendix 1: Answers to In-Chapter Review Problems

Chapter 1

1.1 a & c, because they do not involve motion.

1.2

a. 5.839×10^{3}

b. 7.4×10^{5} Note: you will learn why the answer is not 7.40000×10^{5} later in this chapter when we discuss significant figures.

c. 5.73×10^{-1}

d. 6×10^{-8}

1.3

a. 527.89

b. 0.00178538

c. 2340000

d. 0.00009583

1.4

a. 3

b. 5
  - decimal point present, starting from the left, we begin counting with the first non zero number (the 7), then count all numbers, including zeros

c. 3
  - Note that in scientific notation, we only consider the value in front of the power of ten. We only consider **6.70**.

d. 4

e. 2
  - decimal point absent, starting from the right, begin counting with the first non zero number (the 2), then count all numbers afterwards

f. 4
  - decimal point present, starting from the left, we begin counting with the first non zero number (the 6), then count all numbers, **including zeros**

g. 5

h. 4
  - Note that the zero to the **left** of the decimal point ***does not affect*** the number of significant figures. The extra zero is often used; it is especially important to use it when there is a non zero integer immediately to the **right** of the decimal point. This is done so the decimal point is more easily noticed: **0.6200** vs. **.6200**. The added zero is sometimes called the **"safety zero."**

i. 2

j. 2
  - decimal point absent, starting from the right, begin counting with the first non zero number (the 3), then count all numbers afterwards.

1.5

a. 5.047×10^{3} cal

b. 8.76290×10^{4} L

c. 8×10^{-5} g

d. 7.460×10^{-2} lb

1.6

a. 5070 or 5.07×10^{3} (not 505!!!)
  - Note: We do not round this number to 505 because that puts the 5 in the hundreds decimal place instead of the thousands place. Would you want to loan someone 5067 dollars, and have them pay you back $507. I don't think so. We keep digits in the correct decimal place, without adding significant figures, by using zeros that are not followed by decimal points (decimal point absent). Another way to do this is to express the number in scientific notation, and then round it.

b. 8760 or 8.76×10^{3}

c. 0.0000855 or 8.55×10^{-5}

d. 0.0746 or 7.46×10^{-2}

e. 5.00×10^{3}
  - Note: In some cases, as this one, it is only possible to express a number with the correct significant figures by using scientific notation.

1.7

a. 1.2

b. 58

c. 2.00
  - Did you use the addition/subtraction rule? A common mistake is to use the multiplication/division rule for addition or subtraction.

d. 16.6

1.8

a. 20.74 ft

$$\begin{array}{c|c|} 248.9\ \cancel{\text{inches}} & 1\ \text{ft} \\ \hline & 12\ \cancel{\text{inches}} \end{array} = 20.74\ \text{ft}$$

b. 90. eggs

$$\begin{array}{c|c|} 7.5\ \cancel{\text{dozen eggs}} & 12\ \text{eggs} \\ \hline & 1\ \cancel{\text{dozen eggs}} \end{array} = 90.\ \text{eggs}$$

- Did you put a decimal point after the 90? You must do so to have 2 significant figures in the answer.

c. 28.4 cal

$$\begin{array}{c|c|} 119\ \cancel{\text{J}} & 1\ \text{cal} \\ \hline & 4.184\ \cancel{\text{J}} \end{array} = 28.4\ \text{cal}$$

1.9

First convert meters to centimeters, and then convert centimeters to inches. You can do this by using two equations **or** by combining both steps into a *singe* equation.

i) using two equations:

$$\begin{array}{c|c|} 5.5\,\cancel{\text{m}} & 100\,\cancel{\text{cm}} \\ \hline & 1\text{ m} \end{array} = 0550\text{ cm}$$

$$\begin{array}{c|c|} 550\,\cancel{\text{cm}} & 1\,\cancel{\text{in}} \\ \hline & 2.54\,\cancel{\text{cm}} \end{array} = 220\text{ in}$$

ii) using a single equation:

$$\begin{array}{c|c|c|} 5.5\,\cancel{\text{m}} & 100\,\cancel{\text{cm}} & 1\text{ in} \\ \hline & 1\,\cancel{\text{m}} & 2.54\,\cancel{\text{cm}} \end{array} = 220\text{ in}$$

- NOTE: your answer should have 2 significant figures, we round 215.5 to 220 **or** 2.2 x 10^2

1.10

a. 0.001 kg = 1000 mg

b. 1 L = 1000 mL

- Note: liter (L) is the **base unit**, we know this because there is ***no metric prefix***. We use a "1" in the equivalence statement/conversion factor for the **base unit**)

c. 1 x 10^9 nm = 1 x 10^{-6} Mm

d. 1 g = 10 dg

- Note: g (gram) is the **base unit**.

1.11

a. 1750 (or 1.75 x 10^3) cL

- From the Equality Table, use (0.001 kL = 100 cL) to get the conversion factor.

$$\begin{array}{c|c|} 0.0175\,\cancel{\text{kL}} & 100\text{ cL} \\ \hline & 0.001\,\cancel{\text{kL}} \end{array} = 1750\text{ cL (or } 1.75 \times 10^3\text{ cL)}$$

b. 2.681 g

- From the Equality Table, use (1 g = 1000 mg) to get the conversion factor. Note that there is no prefix for (g), it is the base unit; we use a "1" in the conversion factor for the base unit.

$$\begin{array}{c|c|} 2681\,\cancel{\text{mg}} & 1\text{ g} \\ \hline & 1000\,\cancel{\text{mg}} \end{array} = 2.681\text{ g}$$

1.12

a. 175 °C = 448 K

b. 36 °C = 97 °F

c. 98.6 °F = 37.0 °C

- First do the subtraction, (98.6 - exactly 32) = 66.6, then do the division (66.6/exactly 1.8) = 37.0 (exact numbers have an infinite number of significant figures: exactly 32 is 32.00000000000000..... exactly 1.8 is 1.800000000000000......).

d. 87 °F = 304 K

- First convert 87 °F to 31°C , then convert 31 °C to 304 K

Chapter 2

2.1

a. ^{14}**N** number of protons = 7 number of neutrons = 7
atomic number =7 mass number = 14

b. ^{15}**N** number of protons = 7 number of neutrons = 8
atomic number =7 mass number = 15

c. ^{42}**Ca** number of protons= 20 number of neutrons = 22
atomic number = 20 mass number = 42

d. ^{1}**H** number of protons = 1 number of neutrons = 0
atomic number = 1 mass number = 1

2.2

a. 2.08 x 10^{24} atoms

$$\begin{array}{c|c|} 3.45\,\cancel{\text{moles}} & 6.022 \times 10^{23}\text{ atoms} \\ \hline & 1\,\cancel{\text{mole}} \end{array} = 2.08 \times 10^{24}\text{ atoms}$$

b. 7.0 moles

$$\begin{array}{c|c|} 4.2 \times 10^{24}\,\cancel{\text{atoms}} & 1\text{ mole} \\ \hline & 6.022 \times 10^{23}\,\cancel{\text{atoms}} \end{array} = 7.0\text{ moles}$$

- We round 6.974427 to 2 significant figures to get 7.0

2.3

The molar mass of argon (Ar) is **39.948 g/mole**.
Be sure to include the unit. The unit molar mass is **g/mole.**

2.4

a.

$$\begin{array}{c|c|} 12.3\,\cancel{\text{moles Ar}} & 39.948\text{ grams} \\ \hline & 1\,\cancel{\text{mole Ar}} \end{array} = 491\text{ g}$$

b.

$$\begin{array}{c|c|} 4.5\,\cancel{\text{moles Pb}} & 207.2\text{ grams} \\ \hline & 1\,\cancel{\text{mole Pb}} \end{array} = 930\text{ (or } 9.3 \times 10^2\text{) g}$$

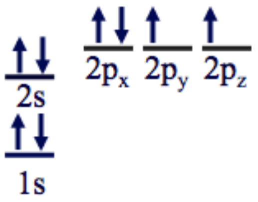
- two significant figures

2.5

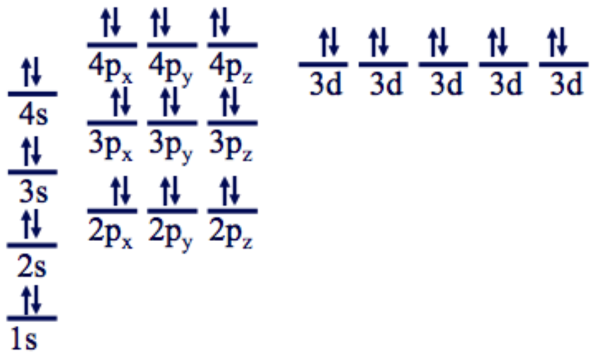
$$\begin{array}{c|c|} 5.00\,\cancel{\text{grams}} & 1\text{ mole} \\ \hline & 1.0079\,\cancel{\text{grams}} \end{array} = 4.95\text{ moles}$$

Chapter 3

3.1



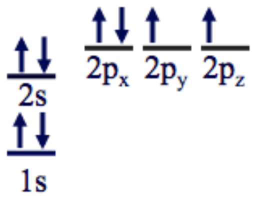
3.2



Note that 4**s** fills before the 3**d** because it is lower in energy.

3.3

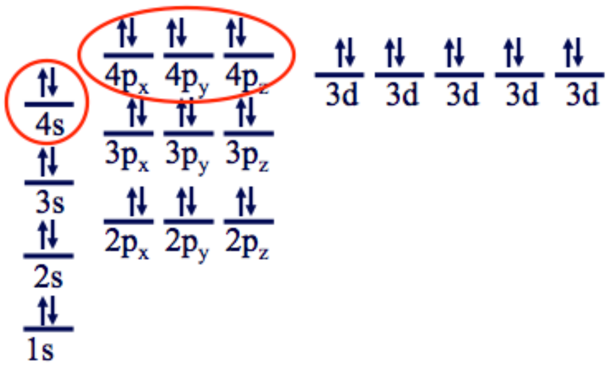
Start by constructing the energy level diagram for an oxygen atom:



Oxygen atoms have electrons in the **n**=1 and the **n**=2 levels. The valence electrons are the electrons in the **n**=2 level. There are 2 electrons in the 2**s** orbital and 4 electrons in the 2**p** orbitals, therefore **oxygen atoms have 6 valence electrons**.

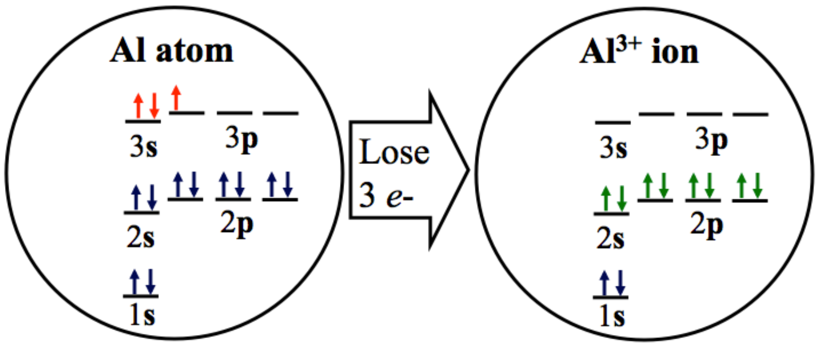
3.4

The valence electrons are in the **n**=4 level. **Krypton atoms have 8 valence electrons.** Note that although the 3**d** orbitals are greater in energy than the 4**s** orbital, electrons in the 3d orbitals are not valence electrons.



3.5

Answer: 3+ We can begin with the energy level diagram for an aluminum atom. Note that a aluminum **atom** has three valence electrons (shaded red in the figure below).



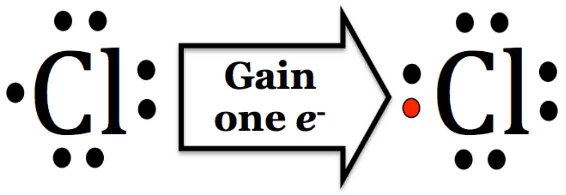
There are ***two*** ways that aluminum can achieve an octet of electrons in its outermost shell:

1) The aluminum atom could ***gain 5 electrons.*** This scenario would result in an aluminum ion with a *negative 5 charge*.
2) The aluminum atom could ***lose the three valence electrons in the 3s orbital*** as shown on the *right* in the figure. In this case, the valence electrons would be the *octet of electrons* in the **n**=2 shell (shaded green in the figure above).

Since the ion with the least amount of total charge will have lower energy, it is easier to lose three electrons than to gain five! An aluminum **atom** loses three electrons when an aluminum **ion** (Al^{3+}) is formed.

3.6

Chlorine is in **Group VII** on the periodic table because a chlorine atom has ***seven*** valence electrons. I have drawn an electron dot structure of a chlorine atom on the left side of the figure below.



There are ***two*** ways that chlorine can achieve an octet of electrons in its outermost shell:

1) The chlorine atom could ***lose the seven valence electrons.*** This scenario would result in an ion with a positive 7 charge.

2) The chlorine atom could ***gain one electron*** as shown on the right in the figure. This scenario would result in an ion with a *negative 1 charge.*

Since the ion with the least amount of total charge will have lower energy, it is easier to gain one electron than to lose seven. An chlorine **atom** gains one electron to become a $\mathbf{Cl}^-$ ion.

3.7

a. potassium ion

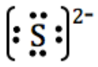
b. nitride ion

•Note that anions have the “-ide” suffix.

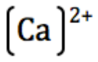
c. cobalt(III) ion

•Use Roman numerals to indicate the charge for elements that can occur with multiple charges.

d.



e.



3.8

a. S_2I_4 disulfur tetriodide

b. P_5F_8 pentaphosphorus octafluoride

c. N_2O_4 dinitrogen tetroxide

- The o or a at the end of the Greek pre-fix is usually dropped when the element name begins with a vowel NOTE, we did not write pentaoxygen because of this rule!

d. NBr_3 nitrogen tribromide

e. N_2O_5 dinitrogen pentoxide

f. PCl_3 phosphorus trichloride

g. H_2S dihydrogen monosulfide

h. N_2O dinitrogen monoxide

3.9

a. disulfur tetrafluoride S_2F_4

b. carbon trioxide CO_3

c. nitrogen pentoxide NO_5

d. nitrogen tribromide NBr_3

e. dinitrogen heptachloride N_2Cl_7

f. carbon tetrachloride CCl_4

g. hydrogen monochloride HCl

h. trihydrogen monophosphide H_3P

i. dihydrogen monoxide H_2O

3.10

a. sodium bicarbonate $NaHCO_3$

b. sodium fluoride NaF

c. iron(III) chloride $FeCl_3$

- From the (III) in the name, we know the iron has a 3+ charge

d. sodium carbonate Na_2CO_3

e. copper(II) sulfate $CuSO_4$

- We do not write $Cu_2(SO_4)_2$, we write the lowest ratio, 2:2 is equal to 1:1

f. magnesium hydroxide $Mg(OH)_2$

- Note: Hydroxide is a polyatomic ion, see the polyatomic ion table for its formula and charge.
- When the subscript for a polyatomic ion is ***greater than 1***, the polyatomic ion formula is written in parenthesis and the subscript is written after/outside of the parenthesis.

g. barium nitrate $Ba(NO_3)_2$

h. lithium sulfate Li_2SO_4

i. magnesium chloride $MgCl_2$

j. silver nitrate $AgNO_3$

k. aluminum sulfate $Al_2(SO_4)_3$

l. calcium hydroxide $Ca(OH)_2$

3.11

a. NaCl sodium chloride

b. $Fe_2(CO_3)_3$ iron(III) carbonate

c. $Cu(OH)_2$ copper(II) hydroxide

d. $(NH_4)_2SO_4$ ammonium sulfate

e. $LiNO_3$ lithium nitrate

f. $BaSO_4$ barium sulfate

g. $Mg(NO_3)_2$ magnesium nitrate

h. AgCl silver chloride

i. $Al(OH)_3$ aluminum hydroxide

j. $CaSO_4$ calcium sulfate

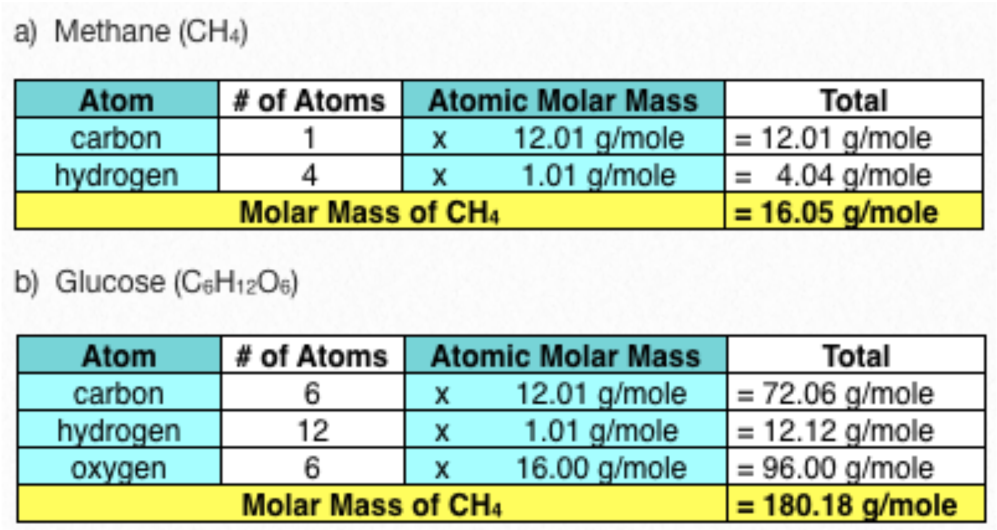
k. FeS Iron(II) sulfide

l. $PbCl_2$ lead(II) chloride

m. NaI sodium iodide

n. $MgCO_3$ magnesium carbonate

3.12



a) Methane (CH_4)

Atom	# of Atoms	Atomic Molar Mass	Total
carbon	1	x 12.01 g/mole	= 12.01 g/mole
hydrogen	4	x 1.01 g/mole	= 4.04 g/mole
Molar Mass of CH_4			**= 16.05 g/mole**

b) Glucose ($C_6H_{12}O_6$)

Atom	# of Atoms	Atomic Molar Mass	Total
carbon	6	x 12.01 g/mole	= 72.06 g/mole
hydrogen	12	x 1.01 g/mole	= 12.12 g/mole
oxygen	6	x 16.00 g/mole	= 96.00 g/mole
Molar Mass of CH_4			**= 180.18 g/mole**

3.13

a) 673 g

- The molar mass of CO_2 is 44.01 gram/mole.
- 15.3 mole x (44.01 gram / 1 mole) = 673 grams

b) 21 g

- The molar mass of HCl is 36.46 gram/mole.
- 0.57 mole x (36.46 gram / 1 mole) = 21 grams
- Note: 2 significant figures in the answer

3.14

$$\begin{array}{l|l|}2.93\ \cancel{g\ H_2O} & 1\ \text{mole}\ H_2O \\ \hline & 18.02\ \cancel{g\ H_2O}\end{array} = 0.163\ \text{moles}\ H_2O$$

3.15

Requires 2 steps. First convert from number of molecules to moles, and then convert moles to grams:

- **Conversion 1:** convert 2.25×10^{24} ***molecules*** to ***moles*** of H_2O
- **Conversion 2:** convert from ***moles*** of H_2O to ***grams***

Instead of doing two separate conversions, *we combine the equations*:

$$\begin{array}{l|c|c|}2.25 \times 10^{24}\ H_2O\ \text{molecules} & 1\ \text{mole}\ H_2O & 18.02\ \text{grams} \\ \hline & 6.022 \times 10^{23}\ \text{molecules} & 1\ \text{mole}\ H_2O\end{array} = \mathbf{67.3}\ \text{grams}$$

3.16

The molar mass of NaCl is 58.44 gram/mole.

$$\begin{array}{l|l|}95.2\ \cancel{g\ NaCl} & 1\ \text{mole NaCl} \\ \hline & 58.44\ \cancel{g\ NaCl}\end{array} = 1.63\ \text{mole NaCl}$$

Chapter 4

4.1 (a)

Guide for Drawing Line Bond Structures
Example: Draw the Line Bond Structure for Br_2

Step 1: Count the total number of valence electrons from all the atoms in the molecule.

Atom	Number of atoms		Number of valence electrons per atom		Totals
Br	2	x	7	=	14
		x		=	
Total number of electrons to appear in the line bond structure =					14

Step 2: Draw the “Skeleton" Structure

-Attach the atoms together with *single bonds* in the most symmetric way possible.

$$Br - Br$$

# of electrons used in skeleton = ___2___

(Multiply the number of bonds in skeleton by 2)

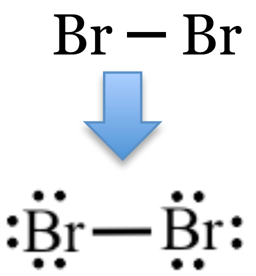
Step 3: Subtract the number of electrons used to make the skeleton structure from the total number of valence electrons.

Total # of valence electrons (from Step 1) _14__

# of electrons used in skeleton (from Step 2) - __2__

Remaining # electrons to be added = __12__

Step 4: <u>First:</u> Re-draw skeleton (from Step 2):

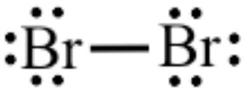


Next, add the remaining electrons to the above structure as <u>lone pairs</u> as evenly as possible on all atoms *except hydrogen*.

- Add remaining electrons to the skeleton as ***lone pairs.***

Step 5: Check for Octets

Check the structure in **Step 4** for octets of electrons around each atom (except hydrogen)



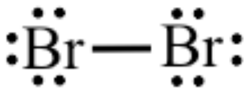
If octet rule is satisfied, you are done.

In this case, the octet rule is satisfied.

If octet rule is not satisfied go to **Step 6**

Step 6: Use **lone pairs** to make *double* or *triple bonds* **<u>until</u>** the octet rule is satisfied *for all atoms* in the molecule.

The octet rule was satisfied in Step 5, therefore Step 6 is not needed in this case.



4.1 (b)

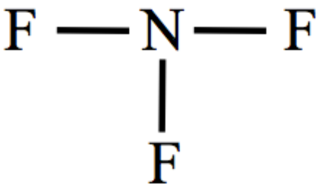
Guide for Drawing Line Bond Structures
Example: Draw the Line Bond Structure for NF_3

Step 1: Count the total number of valence electrons from all the atoms in the molecule.

Atom	Number of atoms		Number of valence electrons per atom		Totals
N	1	x	5	=	5
F	3	x	7	=	21
Total number of electrons to appear in the line bond structure =					26

Step 2: Draw the "Skeleton" Structure

-Attach the atoms together with *single bonds* in the most symmetric way possible.



# of electrons used in skeleton = 6

(Multiply the number of bonds in skeleton by 2)

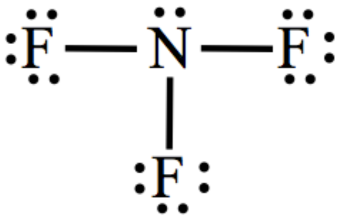
Step 3: Subtract the number of electrons used to make the skeleton structure from the total number of valence electrons.

Total # of valence electrons (from Step 1) 26

# of electrons used in skeleton (from Step 2) - 6

Remaining # electrons to be added = 20

Step 4: First: Re-draw skeleton (from Step 2):

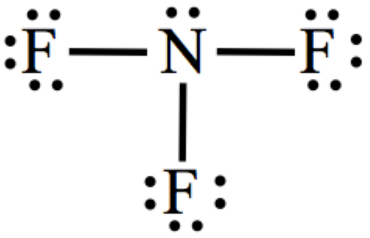


Next, add the remaining electrons to the above structure as lone pairs as evenly as possible on all atoms *except hydrogen*.

- Add remaining electrons to the skeleton as ***lone pairs.***

Step 5: Check for Octets

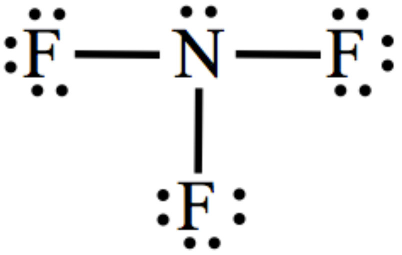
Check the structure in **Step 4** for octets of electrons around each atom (except hydrogen)



If octet rule is satisfied, you are done.
In this case, the octet rule is satisfied.
If octet rule is not satisfied go to **Step 6**

Step 6: Use **lone pairs** to make *double* or *triple bonds* **until** the octet rule is satisfied *for all atoms* in the molecule.

The octet rule was satisfied in Step 5, therefore Step 6 is not needed in this case.



4.1 (c)

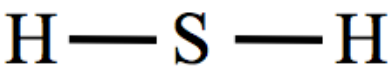
Guide for Drawing Line Bond Structures
Example: Draw the Line Bond Structure for H_2S

Step 1: Count the total number of valence electrons from all the atoms in the molecule.

Atom	Number of atoms		Number of valence electrons per atom	Totals
S	1	x	6 =	6
H	2	x	1 =	2
Total number of electrons to appear in the line bond structure =				8

Step 2: Draw the "Skeleton" Structure

-Attach the atoms together with *single bonds* in the most symmetric way possible.



# of electrons used in skeleton = ___4___

(Multiply the number of bonds in skeleton by 2)

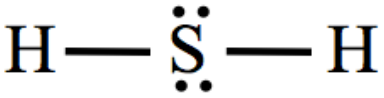
Step 3: Subtract the number of electrons used to make the skeleton structure from the total number of valence electrons.

Total # of valence electrons (from Step 1) __8__

# of electrons used in skeleton (from Step 2) - __4__

Remaining # electrons to be added = __4__

Step 4: First: Re-draw skeleton (from Step 2):

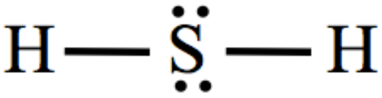


Next, add the remaining electrons to the above structure as lone pairs as evenly as possible on all atoms *except hydrogen*.

- Add remaining electrons to the skeleton as ***lone pairs.***

Step 5: Check for Octets

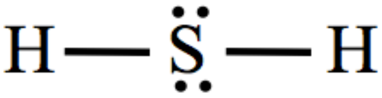
Check the structure in **Step 4** for octets of electrons around each atom (except hydrogen)



If octet rule is satisfied, you are done.
In this case, the octet rule is satisfied.
If octet rule is not satisfied go to **Step 6**

Step 6: Use **lone pairs** to make *double* or *triple bonds* **until** the octet rule is satisfied *for all atoms* in the molecule.

The octet rule was satisfied in Step 5, therefore Step 6 is not needed in this case.



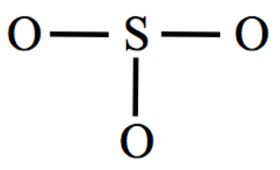
4.1 (d)

Guide for Drawing Line Bond Structures
Example: Draw the Line Bond Structure for SO_3

Step 1: Count the total number of valence electrons from all the atoms in the molecule.

Atom	Number of atoms		Number of valence electrons per atom	Totals
S	1	x	6 =	6
O	3	x	6 =	18
Total number of electrons to appear in the line bond structure =				24

Step 2: Draw the "Skeleton" Structure
Attach the atoms together with *single bonds* in the most symmetric way possible.



# of electrons used in skeleton = 6

(Multiply the number of bonds in skeleton by two)

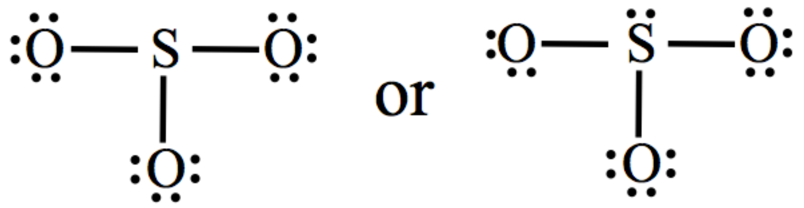
Step 3: Subtract the number of electrons used to make the skeleton structure from the total number of valence electrons.

Total # of valence electrons (from Step 1) 24

# of electrons used in skeleton (from Step 2) - 6

Remaining # electrons to be added = 18

Step 4: <u>**First:**</u> Re-draw skeleton (from Step 2):



Next, add the remaining electrons to the above structure as <u>lone pairs</u> as evenly as possible on all atoms *except hydrogen*.

- Add remaining electrons to the skeleton as ***lone pairs.***

Step 5: Check for Octets

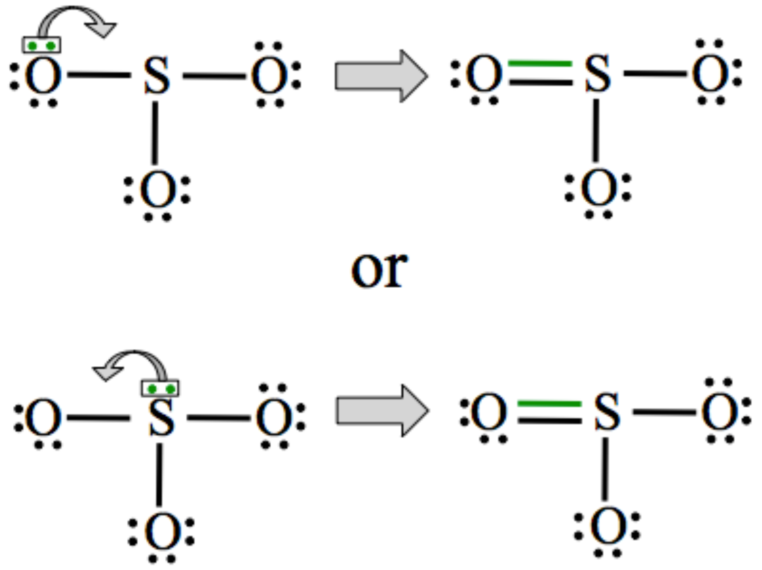
Check the structure in **Step 4** for octets of electrons around each atom (except hydrogen).

If octet rule is satisfied, you are done.
If octet rule is not satisfied, go to **Step 6.**

In this case, the octet rule **<u>is not</u>** satisfied, go to Step 6.

Step 6: Use **lone pairs** to make *double* or *triple bonds* **<u>until</u>** the octet rule is satisfied *for all atoms* in the molecule.

- ***Change*** *lone pairs* into double, or if needed, triple bonds in order to satisfy the octet rule.



4.1 (e)

Guide for Drawing Line Bond Structures
Example: Draw the Line Bond Structure for CO_2

Step 1: Count the total number of valence electrons from all the atoms in the molecule.

Atom	Number of atoms		Number of valence electrons per atom	Totals
C	1	x	4 =	4
O	2	x	6 =	12
Total number of electrons to appear in the line bond structure =				16

Step 2: Draw the “Skeleton" Structure
-Attach the atoms together with *single bonds* in the most symmetric way possible.

O — C — O

# of electrons used in skeleton = ___4___

(Multiply the number of bonds in skeleton by 2)

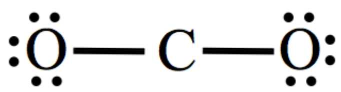
Step 3: Subtract the number of electrons used to make the skeleton structure from the total number of valence electrons.

Total # of valence electrons (from Step 1) __16__

# of electrons used in skeleton (from Step 2) - __4__

Remaining # electrons to be added = __12__

Step 4: <u>First:</u> Re-draw skeleton (from Step 2):



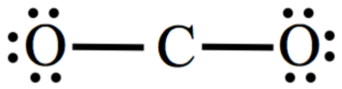
Note: there are other ways to add the lone pairs. No matter which way you use, if you do Steps 5 & 6 correctly, you will end up with the same correct line bond structure.

Next, add the remaining electrons to the above structure as <u>lone pairs</u> as evenly as possible on all atoms *except hydrogen*.

- Add remaining electrons to the skeleton as ***lone pairs.***

Step 5: Check for Octets

Check the structure in **Step 4** for octets of electrons around each atom (except hydrogen)

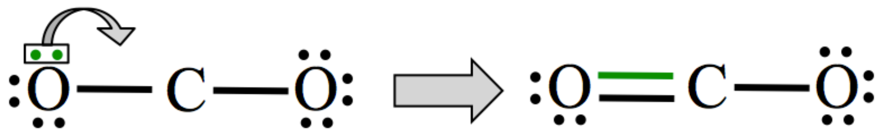


If octet rule is satisfied, you are done.
If octet rule is not satisfied go to **Step 6**

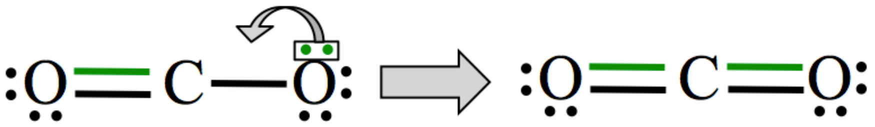
In this case, the octet rule **<u>is not</u>** satisfied, go to Step 6

Step 6: Use **lone pairs** to make *double* or *triple bonds* **<u>until</u>** the octet rule is satisfied *for all atoms* in the molecule.

- ***Change*** *lone pairs* into double, or if needed, triple bonds in order to satisfy the octet rule.



Now the octet rule is satisfied for the left-most oxygen, but not for the carbon or the right-most oxygen. So you must repeat Step 6 until the octet rule is satisfied for all atoms in the molecule.



4.1 (f)

Guide for Drawing Line Bond Structures
Example: Draw the Line Bond Structure for SO_2

Step 1: Count the total number of valence electrons from all the atoms in the molecule.

Atom	Number of atoms		Number of valence electrons per atom		Totals
S	1	x	6	=	6
O	2	x	6	=	12
Total number of electrons to appear in the line bond structure =					18

Step 2: Draw the “Skeleton" Structure
-Attach the atoms together with *single bonds* in the most symmetric way possible.

O — S — O

# of electrons used in skeleton = ___4___

(Multiply the number of bonds in skeleton by 2)

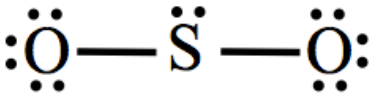
Step 3: Subtract the number of electrons used to make the skeleton structure from the total number of valence electrons.

Total # of valence electrons (from Step 1) __14__

# of electrons used in skeleton (from Step 2) - __4__

Remaining # electrons to be added = __14__

Step 4: <u>First:</u> Re-draw skeleton (from Step 2):



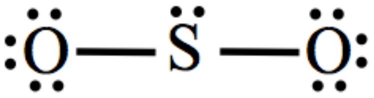
Note: there are other ways to add the lone pairs. No matter which way you use, if you do Steps 5 & 6 correctly, you will end up with the same correct line bond structure.

Next, add the remaining electrons to the above structure as <u>lone pairs</u> as evenly as possible on all atoms *except hydrogen*.

- Add remaining electrons to the skeleton as ***lone pairs.***

Step 5: Check for Octets

Check the structure in **Step 4** for octets of electrons around each atom (except hydrogen)

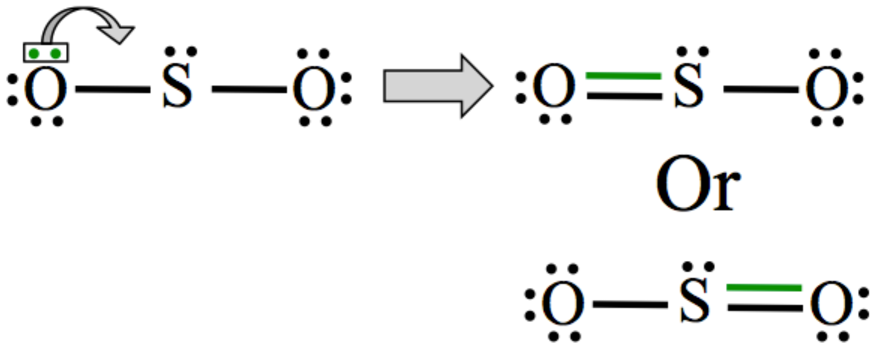


If octet rule is satisfied, you are done.
If octet rule is not satisfied go to **Step 6**

In this case, the octet rule **<u>is not</u>** satisfied, go to Step 6

Step 6: Use **lone pairs** to make *double* or *triple bonds* **<u>until</u>** the octet rule is satisfied *for all atoms* in the molecule.

- ***Change*** *lone pairs* into double, or if needed, triple bonds in order to satisfy the octet rule.



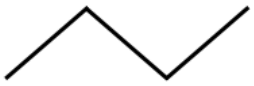
4.2

Condensed Structure:

$CH_3CH_2CH_2CH_3$

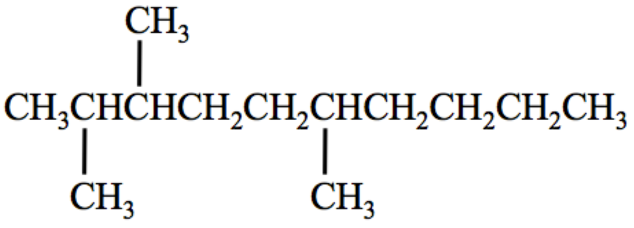
Skeletal Structure:

or



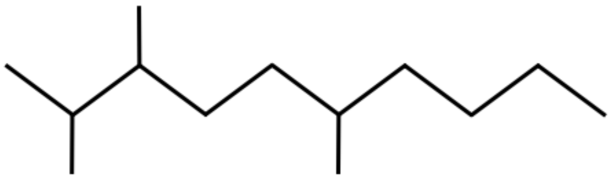
4.3

Condensed Structure:



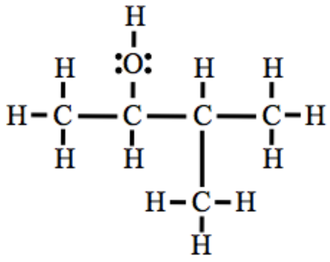
$$CH_3\underset{CH_3}{C}H\overset{CH_3}{C}HCH_2CH_2\underset{CH_3}{C}HCH_2CH_2CH_2CH_3$$

Skeletal Structure:

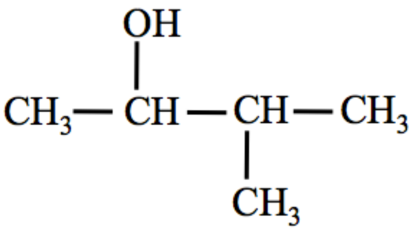


4.4

Line Bond Structure:

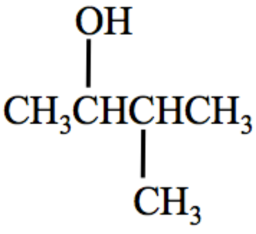


Condensed Structure:



$$CH_3-\overset{OH}{CH}-\underset{CH_3}{CH}-CH_3$$

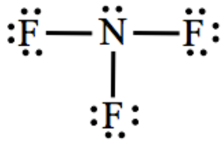
or



$$CH_3\overset{OH}{C}H\underset{CH_3}{C}HCH_3$$

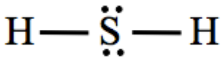
4.5

a. The line bond structure of NF_3 is:



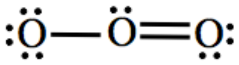
There are 4 electron groups *on the central atom*, three bonded atoms and one lone pair. NF_3 is in the AB_3E class and has the **pyramidal** shape with bond angles ***approximately*** equal to 110º.

b. The line bond structure of H_2S is:



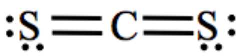
There are 4 electron groups *on the central atom*, two bonded atoms and two lone pairs. H_2S is in the AB_2E_2 class and has the **bent** shape with a bond angle ***approximately*** equal to 110º.

c. The line bond structure of ozone (O_3) is:



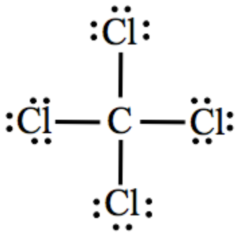
There are 3 electron groups *on the central ato*m, two bonded atoms and one lone pair. O_3 is in the AB_2E class and has the **bent** shape with a bond angle ***approximately*** equal to 120º.

d. The line bond structure of CS_2 is:



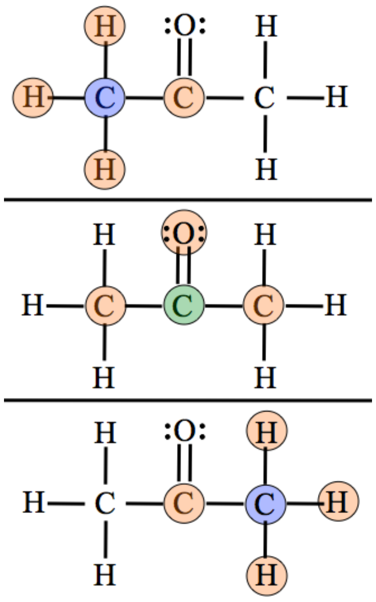
There are 2 electron groups *on the central atom*, two bonded atoms. CS_2 is in the AB_2 class and has the **linear** shape with a bond angle of 180º.

e. The line bond structure of CCl_4 is:



There are 4 electron groups *on the central atom*, four bonded atoms. CCl_4 is in the AB_4 class and has the **tetrahedral** shape with bond angles equal to 110º.

4.6

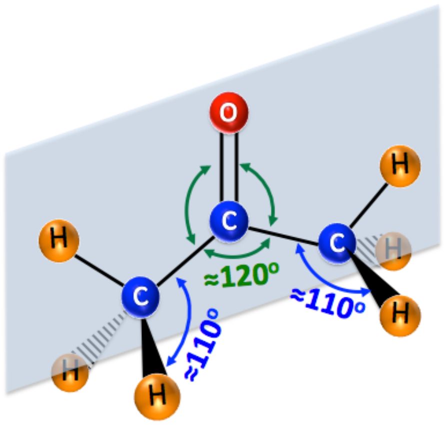


In the three line bond structures of acetone shown in the figure on the right, the ***left-most*** carbon in the **top** structure is shaded blue. Note that this carbon is surrounded by **four** electron groups (shaded orange), three hydrogens and *another* carbon atom. Since the left-most carbon is surrounded by four electron groups and all of the electron groups are bonded atoms, it is in the AB$_4$ class and therefore ***all*** bond angles around this carbon are approximately 110° (see TABLE 4.3).

Next, let's consider the **carbon in the middle** of acetone (**middle** structure, shaded green). Note that this carbon is surrounded by **three** electron groups (shaded orange), two *other* carbon atoms and one oxygen atom. Since this carbon is surrounded by four electron groups and all of the electron groups are bonded atoms, it is in the AB$_3$ class and therefore ***all*** bond angles around this carbon are approximately 120°.

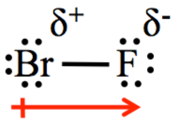
The ***right-most*** carbon in the **bottom** structure is shaded blue. Do you recognize that the the **right-most carbon** and the **left-most** carbon in acetone are *identical and indistinguishable*? If you were to view the right-most carbon f*rom behind the page*, it becomes the left-most carbon from that perspective! Since the right-most carbon is in the AB$_4$ class, ***all*** bond angles around this carbon are approximately 110°.

A wedge and dash representation of ethane is shown below.
Although not all bond angles are explicitly listed in the wedge and dash drawing, note that **all** bond angles around the ***middle carbon*** are approximately 120° and **al**l bond angles around the ***right- and left-most carbon*** are approximately 110°.



4.7

Fluorine is more electronegative than bromine. The electrons that are shared in the covalent bond spend more time nearer the fluorine atom therefore the fluorine has a partial negative charge (δ^-) and the bromine has a partial positive charge (δ^+).



4.8

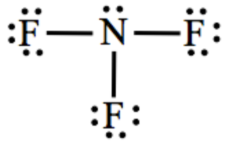
a. H_2, **nonpolar**. Homonuclear diatomic molecules contain *one* nonpolar bond, therefore the molecule is nonpolar.

b. carbon monoxide (CO), **polar**. Heteronuclear diatomic molecules contain *one* polar bond, therefore the molecule is polar.

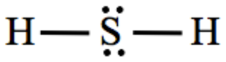
c. N_2 **nonpolar**. Homonuclear diatomic molecule

d. nitrogen monoxide (NO), **polar**. Heteronuclear diatomic molecule

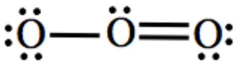
4.9



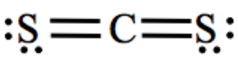
a. The line bond structure of NF_3 is: There are 4 electron groups *on the central atom*, three bonded atoms and one lone pair. Since the electron groups *on the central atom* are **not identical** (the lone pair on the nitrogen is an electron group!), the molecule is **non-symmetric = polar**.



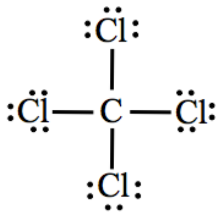
b. The line bond structure of H_2S is: There are 4 electron groups *on the central atom*, two bonded atoms and two lone pairs. Since the electron groups *on the central atom* are **not identical**, the molecule is ***non*****symmetric = polar**.



c. The line bond structure of ozone (O_3) is: There are 3 electron groups *on the central atom*, two bonded atoms and one lone pair. Since the electron groups *on the central atom* are **not identical**, the molecule is ***non*****symmetric = polar**.



d. The line bond structure of CS_2 is: There are 2 electron groups *on the central atom*, two bonded atoms. Since the electron groups *on the central atom* are **identical**, the molecule is **symmetric = nonpolar**.



e. The line bond structure of CCl_4 is: Since the electron groups *on the central atom* are **identical**, the molecule is **symmetric = nonpolar**.

4.10

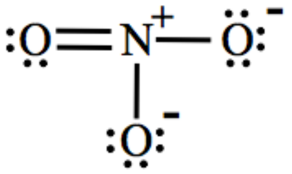
a. **polar**

- contains a highly polar bond (the bond between carbon and oxygen).

b. **nonpolar**

- Does not contain a highly polar bond.

4.11



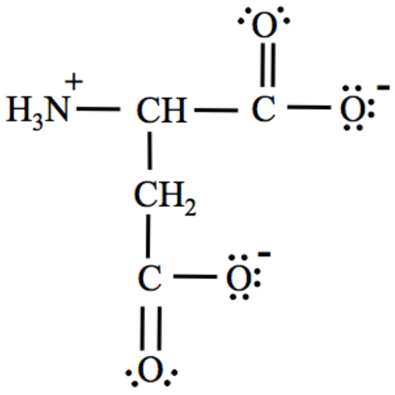
- The nitrogen has ***no lone pairs***, therefore it has a formal charge of 1+ (or +).
- The oxygens below and to the right of the nitrogen have ***just one single bond***, therefore they have a formal charge of 1- (or -).
- The oxygen to the left of the nitrogen ***does not have just one single bond*** (it has a double bond), therefore it has no formal charge (formal charge = zero).

4.12

There is no formal charge (formal charge = zero) on the nitrogen in NH_3.

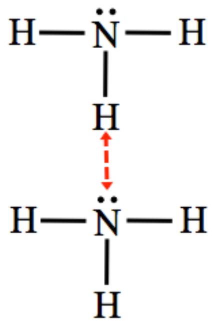
- Nitrogen will have a *no formal charge* when it has ***one or more lone pairs on it***.

4.13



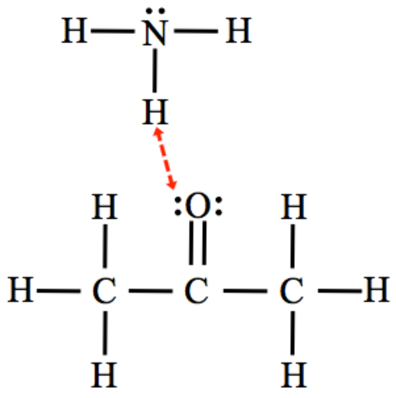
- The nitrogen has ***no lone pairs***, therefore it has a formal charge of 1+ (or +).
- The oxygens that have ***just one single bond***, have a formal charge of 1- (or -).
- The oxygens that ***do not have just one single bond*** (the ones with a double bond), have no formal charge (formal charge = zero).

4.14



a. **Yes**, ammonia molecules have both an H covalently bonded to an N, O, or F, and a lone pair on an N, O, or F. The attractive hydrogen bond force is indicated in the illustration as a dashed arrow.

b. **No**, although acetone does have an oxygen with lone pairs, a second acetone molecule ***does not*** have an H covalently bonded to an N, O, or F.



c. **Yes**, the ammonia molecule has an H covalently bonded to an N, O, or F, **and** the acetone molecule has a lone pair on an N, O, or F. The attractive hydrogen bond force is indicated in the illustration as a dashed arrow.

4.15

a. **Yes**, water is a polar molecule, all ***polar*** molecules are attracted to each other by dipole-dipole forces.

b. **No**, methane is a nonpolar molecule. Only polar molecules have permanent dipoles that can interact through dipole-dipole forces.

c. **Yes**, acetone is a polar molecule. You may wish to review Figure 4.28 on “polarity of large molecules” if you are not sure if acetone is polar or nonpolar. All polar molecules are attracted to each other by dipole-dipole forces.

4.16

The answer to both (a) and (b) is **yes**. London dispersion forces are present between ***any*** two molecules regardless of molecular polarity.

4.17

decane - The larger the molecule, the stronger the London dispersion forces, and therefore the higher the boiling point.

4.18

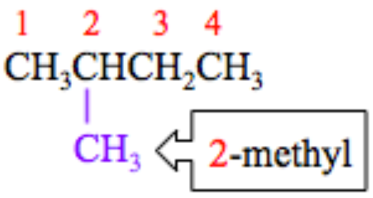
Yes, NH_4^+ is an ion and H_2O is a polar molecule. The positive charge of the ammonium cation is attracted to the negative end of the H_2O dipole.

4.19

No, although bromide is an ion, I_2 is not a polar molecule.

4.20

2-methylbutane

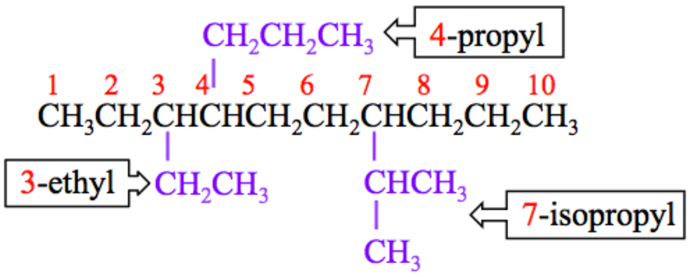


$CH_3CHCH_2CH_3$ with CH_3 on C2

4.21

3-ethyl-7-isopropyl-4-propyldecane

- note the difference between propyl and isopropyl.
- list substituents in alphabetical order
- put dashes between position numbers and letters

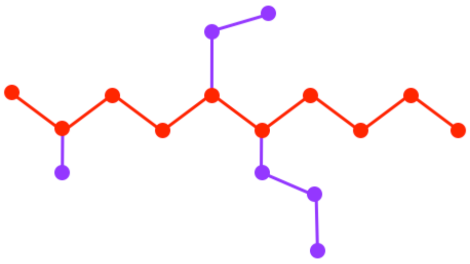


$CH_3CH_2CHCHCH_2CH_2CHCH_2CH_2CH_3$

4.22

5-ethyl-2-methyl-6-propyldecane

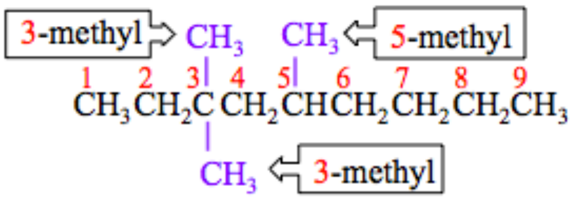
- Red shaded circles are at the positions of parent chain carbons and purple shaded circles are at the positions of the substituent carbons:



4.23

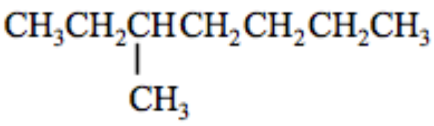
3,3,5-trimethylnonane

- Add the labels di, tri, or tetra in front of the alkyl group name **<u>if</u>** two, three, or four (respectively) identical substituents are present.

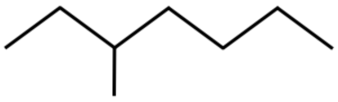


$CH_3CH_2CCH_2CHCH_2CH_2CH_2CH_3$

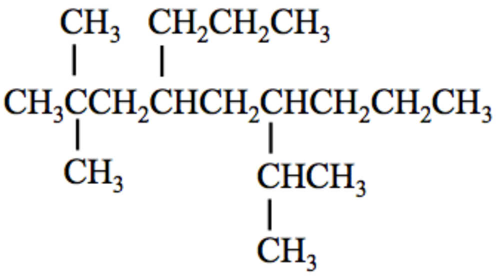
4.24



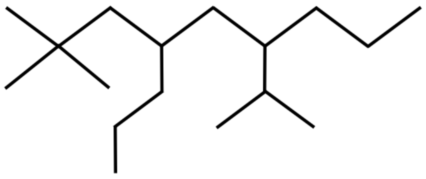
$CH_3CH_2CHCH_2CH_2CH_2CH_3$ with CH_3 on C3



4.25



$CH_3CCH_2CHCH_2CHCH_2CH_2CH_3$



4.26

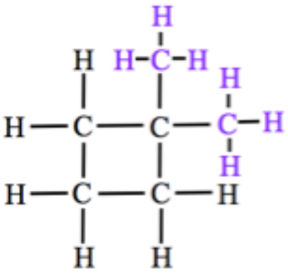
methylcyclopropane

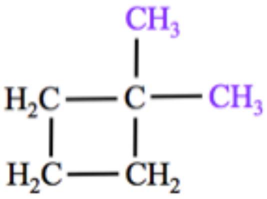
- When there is only one substituent, position numbers are not used for cycloalkanes
- You must include "cyclo" in the parent name.

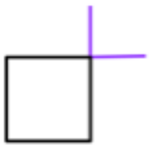
4.27

a. 1,1-dimethylcyclobutane

All four ring-carbons are identical and you could have attached ***both*** methyl substituents to any one of them.

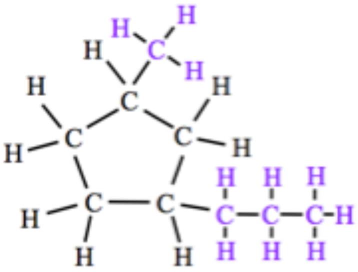


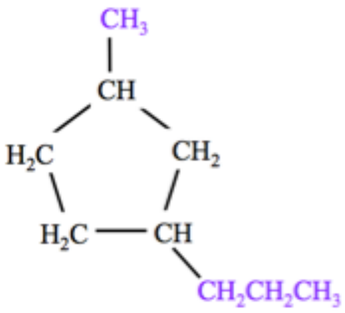


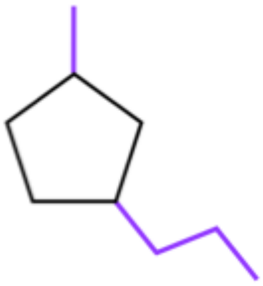


4.27 (continued)

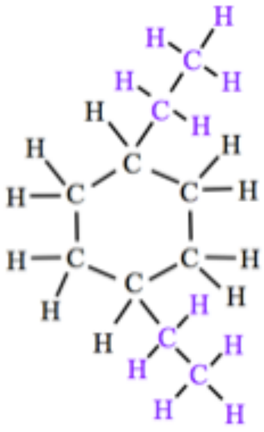
b. 1-methyl-3-propylcyclopentane

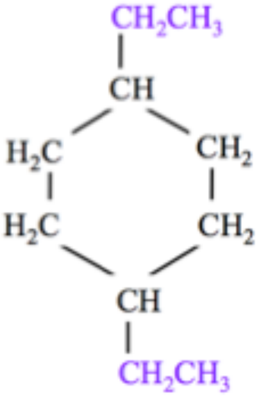






c. 1,4-diethylcyclohexane

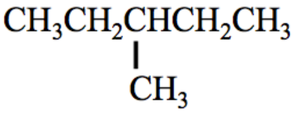




4.28

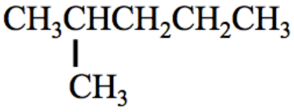
$CH_3CH_2CH_2CH_2CH_2CH_3$

hexane



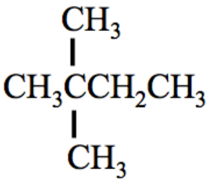
$CH_3CH_2\underset{CH_3}{CH}CH_2CH_3$

3-methylpentane



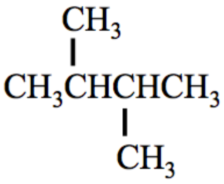
$CH_3\underset{CH_3}{CH}CH_2CH_2CH_3$

2-methylpentane



$CH_3\overset{CH_3}{\underset{CH_3}{C}}CH_2CH_3$

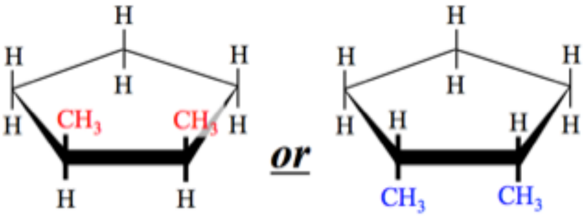
2,2-dimethylbutane



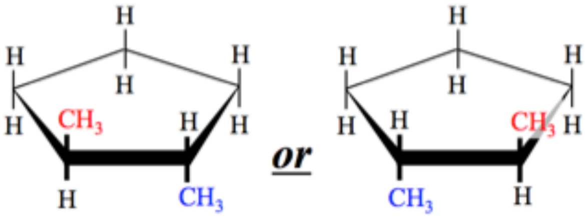
$CH_3\overset{CH_3}{CH}\underset{CH_3}{CH}CH_3$

2,3-dimethylbutane

4.29



cis-1,2-dimethylcyclopentane



trans-1,2-dimethylcyclopentane

4.30

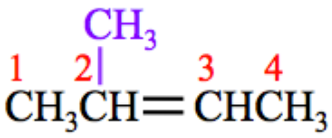
Both (a) 1,2-dimethylcyclopentane **and** **(b)** 1-ethyl-2-propylcyclobutane **will have** *cis* and *trans* isomers.

Neither (c) 1-methylcyclohexane **nor** **(d)** 1,1-dimethylcylcohexane have geometric isomers.

- **(c)** 1-methylcyclohexane only has *one substituent*.
- Although **(d)** 1,1-dimethylcylcohexane has two substituents, they are both on ***the same carbon***.

4.31

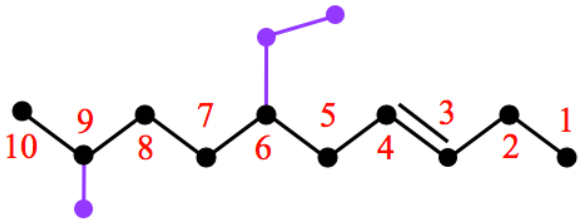
2-methyl-2-butene



$\overset{1}{CH_3}\overset{\overset{CH_3}{2}}{CH}=\overset{3}{CH}\overset{4}{CH_3}$

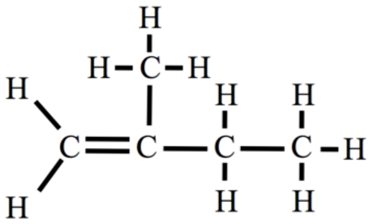
4.32

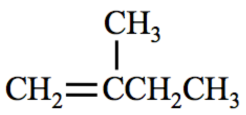
6-ethyl-9-methyl-3-decene



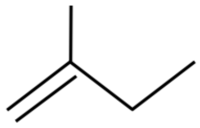
4.33

a) 2-methyl-1-butene

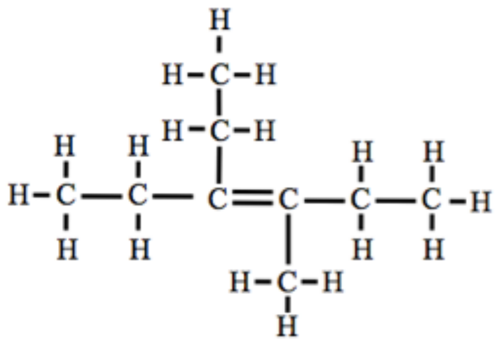


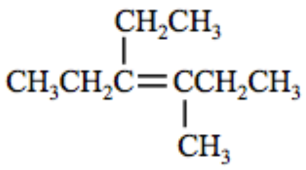


$$CH_2{=}\overset{\overset{CH_3}{|}}{C}CH_2CH_3$$

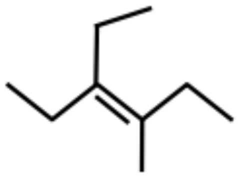


b) 3-ethyl-4-methyl-3-hexene



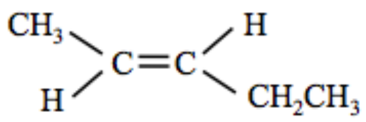


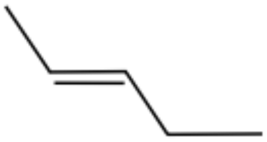
$$CH_3CH_2\overset{\overset{CH_2CH_3}{|}}{C}{=}\underset{\underset{CH_3}{|}}{C}CH_2CH_3$$



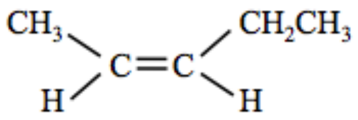
4.34

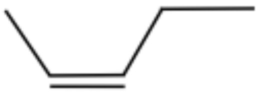
a) *trans*-2-pentene



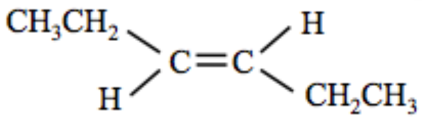


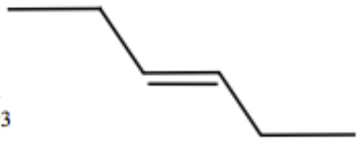
b) *cis*-2-pentene



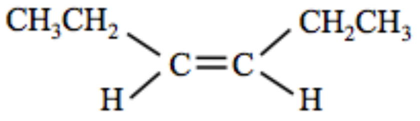


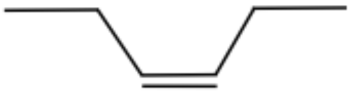
c) *trans*-3-hexene





d) *cis*-3-hexene





Chapter 5

5.1

78 J	1 cal	= 19 cal
	4.184 J	

Note: two significant figures

5.2

a) Use *Equation 5.1* for calculations involving temperature changes ($Q = S \cdot m \cdot (\Delta T)$).

$$\mathbf{Q} = \left(\frac{0.586\text{ cal}}{\cancel{g}\ \cancel{^{o}C}}\right)(12.00\ \cancel{g})(18.0\ \cancel{^{o}C}) = \mathbf{127\ cal}$$

(3 significant figures)

b) The specific heat of ice is 0.500 (cal/g °C), use this value in *Equation 5.1*:

$$\mathbf{Q} = \left(\frac{0.500\text{ cal}}{\cancel{g}\ \cancel{^{o}C}}\right)(128\ \cancel{g})(54.0\ \cancel{^{o}C}) = \mathbf{3460\ cal}$$

(3 significant figures)

c. Note that **ΔT is negative** in this problem!

$(\mathbf{\Delta T} = T_{final} - T_{initial}) = (00.0\ ^{o}C - 22.0\ ^{o}C) = \mathbf{-\ 22.0\ ^{o}C}$

$$\mathbf{Q} = \left(\frac{1.000\text{ cal}}{\cancel{g}\ \cancel{^{o}C}}\right)(584\ \cancel{g})(-22.0\ \cancel{^{o}C}) = \mathbf{-12800\ cal}$$

(3 significant figures)

- Whenever **ΔT is negative** in Equation 5.1, the calculated ***energy will be negative***.
- This is consistent with the convention of assigning *negative energy* values when energy is removed from a substance.

d. In this problem, **Q**, **S**, and **ΔT are known;** we must solve *Equation 5.1* for the **mass** (**m**).

- In order to solve equation *Equation 5.1* for **m**, we divide ***both sides*** of the equation by **S** and **ΔT**:

$$\frac{\mathbf{Q}}{\mathbf{S \cdot (\Delta T)}} = \frac{\mathbf{\cancel{S} \cdot m \cdot (\cancel{\Delta T})}}{\mathbf{\cancel{S} \cdot (\cancel{\Delta T})}}$$

$$\mathbf{m} = \frac{\mathbf{Q}}{\mathbf{S \cdot (\Delta T)}}$$

$$\mathbf{m} = \frac{1250\ \cancel{\text{cal}}}{\left(\frac{1.000\ \cancel{\text{cal}}}{g\ \cancel{^{o}C}}\right)12.4\ \cancel{^{o}C}} = \mathbf{101\ g}$$

(3 significant figures)

5.3

a. Use *Equation 5.2* for calculations involving **phase changes:**

$$\Delta E = (\text{mass}) \cdot (H_{fus} \text{ or } H_{vap})$$

- In this problem, we are interested in the phase change from ***solid to liquid*** (melting).
- We use Table 5.2 to find the **heat of fusion** (H_{fus}). The mass is **35 grams**.

$$\Delta E = (35\,\cancel{g})\left(\frac{540\text{ cal}}{\cancel{g}}\right) = \mathbf{19000\text{ cal}}$$

or **1.9×10^4 cal**

(2 significant figures)

b) In this problem, we are interested in a *phase change* from ***liquid to solid*** (freezing). We use Table 1.2 to find the **heat of fusion** (abbreviated as H_{fus}) for **ethanol**.

- Since we are ***freezing*** (*liquid to solid)* as apposed to *melting*, energy must be ***removed*** from ethanol in order to solidify it. We therefore **use a *negative sign*** with the heat of fusion (**$-H_{fus}$ = -26.05 cal/g**).

$$\Delta E = (224\,\cancel{g})\left(\frac{-26.05\text{ cal}}{\cancel{g}}\right) = \mathbf{-5840\text{ cal}}$$

or **-5.84×10^3 cal**

(3 significant figures)

- The use of a *negative sign* with H_{fus} or H_{vap} in *Equation 5.2* will *always* result in a negative energy (**ΔE**), which is consistent with energy being removed from a substance.

5.5

a) $$\frac{698\,\cancel{\text{Torr}}}{} \,\bigg|\, \frac{1\text{ atm}}{760\,\cancel{\text{Torr}}} = 0.918\text{ atm}$$

b) $$\frac{757\,\cancel{\text{mm Hg}}}{} \,\bigg|\, \frac{1\text{ atm}}{760\,\cancel{\text{mm Hg}}} = 0.996\text{ atm}$$

c) $$\frac{35.0\,\cancel{\text{psi}}}{} \,\bigg|\, \frac{1\text{ atm}}{14.7\,\cancel{\text{psi}}} = 2.38\text{ atm}$$

d) $$\frac{596\,\cancel{\text{mm Hg}}}{} \,\bigg|\, \frac{1\text{ Torr}}{1\,\cancel{\text{mm Hg}}} = 596\text{ Torr}$$

5.6

Use Boyle's Law:

$$\mathbf{P_1 \cdot V_1 = P_2 \cdot V_2}$$

Boyle's Law contains four variables, P_1, V_1, P_2, and V_2. When any three of these variables are known, the fourth variable can be found using algebra.

- It can be very helpful to make a table such as the one below when you are doing gas law problems.

Initial State
P_1 = 782 Torr
V_1 = 123 mL

Final State
P_2 = ???
V_2 = 63 mL

- We know P_1, V_1, and V_2; we wish to find $\mathbf{P_2}$:

$$\mathbf{P_1 \cdot V_1 = P_2 \cdot V_2}$$

- To solve for $\mathbf{P_2}$, we divide both sides of the equation by $\mathbf{V_2}$:

$$\frac{\mathbf{P_1 \cdot V_1}}{\mathbf{V_2}} = \frac{\mathbf{P_2 \cdot \cancel{V_2}}}{\mathbf{\cancel{V_2}}}$$

- $\mathbf{V_2}$ cancels on the right side; we have isolated the unknown variable ($\mathbf{P_2}$):

$$\frac{\mathbf{P_1 \cdot V_1}}{\mathbf{V_2}} = \mathbf{P_2}$$

- Insert the known values of P_1, V_1, and V_2 then solve for the final pressure ($\mathbf{P_2}$):

$$\mathbf{P_2} = \frac{(782\text{ Torr}) \cdot (123\,\cancel{\text{mL}})}{(63\,\cancel{\text{mL}})} = 1500\text{ Torr}$$

or 1.5×10^3 Torr

- Our answer has two significant figures.

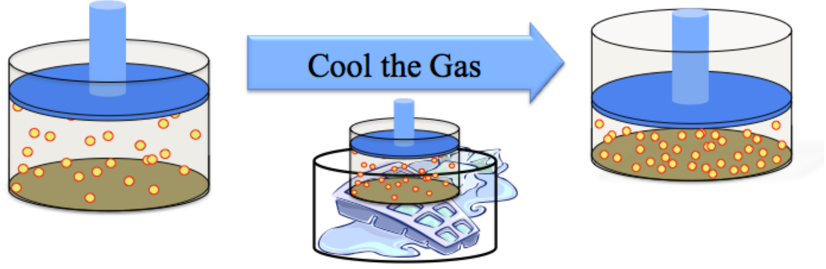
5.7

Use *Charles' Law*: $\frac{V_1}{T_1} = \frac{V_2}{T_2}$

Note that the question gave us the initial and final temperature in °C, we must convert to units of K.

- You learned the relationship between °C and °K in Chapter 1: K = °C + 273.15
  - Initial Temperature (T_1) = 125 + 273.15 = 398 K
  - Final Temperature (T_2) = 22 + 273.15 = 295 K
    - recall the significant figure rule for addition/subtraction

Make a *drawing and a table* such as the one below:



Before Cooling	
Initial Volume	= 1.80 L
Initial Temperature	= 398 K

After Cooling	
Final Volume	= ???
Final Temperature	= 295 K

- We know V_1, T_1, and T_2; we wish to find V_2: $\frac{V_1}{T_1} = \frac{V_2}{T_2}$
- To solve for V_2, we multiply both sides of the equation by T_2: $\frac{T_2 \cdot V_1}{T_1} = \frac{V_2 \cdot \cancel{T_2}}{\cancel{T_2}}$
- T_2 cancels on the right-hand side; we have isolated the unknown variable (V_2):

$$\frac{T_2 \cdot V_1}{T_1} = V_2$$

- Insert the known values of V_1, T_1, and T_2 then solve for the final volume (V_2):

$$V_2 = \frac{(295\ \cancel{K}) \cdot (1.80\ L)}{(398\ \cancel{K})} = 1.33\ L$$

  - Our answer has three significant figures.

5.8

Use *Gay-Lussac's Law*: $\frac{P_1}{T_1} = \frac{P_2}{T_2}$

- We know P_1, T_1, and T_2; we wish to find P_2: $\frac{P_1}{T_1} = \frac{P_2}{T_2}$
- To solve for P_2, we multiply both sides of the equation by T_2: $\frac{T_2 \cdot P_1}{T_1} = \frac{P_2 \cdot \cancel{T_2}}{\cancel{T_2}}$
- T_2 cancels on the right-hand side; we have isolated the unknown variable (P_2): $\frac{T_2 \cdot P_1}{T_1} = P_2$
- Insert the known values of P_1, T_1, and T_2 then solve for the final pressure (P_2):

$$P_2 = \frac{(525\ \cancel{K}) \cdot (15.7\ atm)}{(292\ \cancel{K})} = 28.2\ atm$$

  - Our answer has 3 significant figures.

5.9

We will use ***the combined gas law*** because the pressure, volume, and temperature ***are all changing***.

In this example, we know P_1, V_1, T_1, P_2, and T_2; we wish to find the V_2: $\frac{P_1 \cdot V_1}{T_1} = \frac{P_2 \cdot V_2}{T_2}$

- Make a table listing the variables that are known.

UNDER WATER	
Initial Pressure	= 2.00 atm
Initial Volume	= 10.0 mL
Initial Temperature	= 282 K

AT SURFACE	
Final Pressure	= 1.00 atm
Final Volume	= ???
Final Temperature	= 295 K

- To solve for V_2, we divide both sides of the equating by P_2 <u>and</u> multiply both sides by T_2:

$$\frac{T_2 \cdot P_1 \cdot V_1}{P_2 \cdot T_1} = \frac{\cancel{P_2} \cdot V_2 \cdot \cancel{T_2}}{\cancel{T_2} \cdot \cancel{P_2}}$$

- P_2 and T_2 cancel on the right-hand side; we have isolated the unknown variable (V_2):

$$\frac{T_2 \cdot P_1 \cdot V_1}{P_2 \cdot T_1} = V_2$$

- Insert the known values of P_1, V_1, T_1, P_2, and T_2 then solve for the final volume (V_2):

$$V_2 = \frac{(295\ \cancel{K}) \cdot (2.00\ \cancel{atm}) \cdot (10.0\ mL)}{(1.00\ \cancel{atm}) \cdot (282\ \cancel{K})} = 20.9\ mL$$

  - Our answer has three significant figures.

5.10

Use *Avogadro's Law*.

We know V_1, n_1, and n_2; we wish to find V_2: $\frac{V_1}{n_1} = \frac{V_2}{n_2}$

Make *a table* such as the one below.

Before Adding More Gas	
Initial Volume	= 4. 0 L
Initial Moles	= 0.56 moles

After Adding More Gas	
Final Volume	= ???
Final Moles	= 2.56 moles

  - The final number of moles (**n_2**) is 2.56 moles; initially there were 0.56 moles present, then ***another*** 2.00 moles were added.
- To solve for V_2, we multiply both sides of the equation by **n_2**: $\frac{n_2 \cdot V_1}{n_1} = \frac{V_2 \cdot \cancel{n_2}}{\cancel{n_2}}$
- n_2 cancels on the right-hand side; we have isolated the unknown variable (V_2):

$$\frac{n_2 \cdot V_1}{n_1} = V_2$$

- Insert the known values of V_1, n_1, and n_2, then solve for the final volume (V_2):

$$V_2 = \frac{(2.56\ \cancel{\text{moles}})\cdot(4.0\ \text{L})}{(0.56\ \cancel{\text{moles}})} = 18\ \text{L}$$

  - Our answer has two significant figures.

5.11

Since the gaseous system ***is not undergoing a change***, use the **ideal gas law**. Make *a table* such as the one to the right when doing an ideal gas law problem.

Variables:
$P = 8.63\ \text{atm}$
$V = 3.80\ \text{L}$
$n = ???$
$T = 295\ \text{K}$

- We know P, T, V, and R; we wish to find the number of moles (n):

$$P\cdot V = n\cdot R\cdot T$$

- To solve for n, we divide both sides of the equation by $R\cdot T$:

$$\frac{P\cdot V}{R\cdot T} = \frac{n\cdot\cancel{R\cdot T}}{\cancel{R\cdot T}}$$

- $R\cdot T$ cancels on the right-hand side of the equation so that we have isolated the unknown variable (n):

$$n = \frac{P\cdot V}{R\cdot T}$$

- Insert the known values of P, V, T, and R, then solve for the number of moles (n):

$$n = \frac{(8.63\ \cancel{\text{atm}})\cdot(3.80\ \cancel{\text{L}})}{\left(0.0821\ \frac{\cancel{\text{L}}\cdot\cancel{\text{atm}}}{\cancel{\text{K}}\cdot\text{mole}}\right)\cdot(295\ \cancel{\text{K}})} = 1.35\ \text{moles}$$

I have shaded the *gas constant* (**R**) and its units *green* so that you can see how to insert it into the equation.
Note that in this example atm, liters, and kelvin units cancelled with the units in the gas constant. The only unit that does not cancel is moles because we are solving for the number of moles.

5.12

Since the gaseous system ***is not undergoing a change***, use the **ideal gas law**. You were asked to find the volume (V), to do so, you must know the pressure, temperature, and number of moles of the carbon dioxide gas.

- You were not given the number of moles of CO_2 gas ***directly***, however you were given the mass.
  - Convert 17.0 g of CO_2 to moles of CO_2:

Number of moles (n) =

$$\begin{array}{c|c|} 17.0\ \text{g}\ CO_2 & 1\ \text{mole}\ CO_2 \\ \hline & 44.01\ \text{g}\ CO_2 \end{array} = 0.386\ \text{moles}\ CO_2$$

- Since the *gas constant* has units of **(L•atm/K•mole)**, when using the ideal gas law, the pressure must have **atm** units and the temperature must have **K** units:

Pressure (**P**) =

$$\begin{array}{c|c|} 568\ \text{Torr} & 1\ \text{atm} \\ \hline & 760\ \text{Torr} \end{array} = 0.747\ \text{atm}$$

Temperature (**K**) =
°C + 273.15 = (25 +273.15) = 298 K

- Make *a table* such as the one to the right when doing an ideal gas law problem.

Variables:
$P = 0.747\ \text{atm}$
$V = ???$
$n = 0.386\ \text{moles}$
$T = 298\ \text{K}$

- In this example, we know P, T, n, and R; we wish to find the volume (V):

$$P\cdot V = n\cdot R\cdot T$$

- To solve for V, we divide both sides of the equation by P:

$$\frac{\cancel{P}\cdot V}{\cancel{P}} = \frac{n\cdot R\cdot T}{P}$$

- P cancels on the left side of the equation; we have isolated the unknown variable (V):

$$V = \frac{n\cdot R\cdot T}{P}$$

- Insert the known values of P, T, R, and n, then solve for the volume (V):

$$V = \frac{(0.386\ \cancel{\text{mole}})\cdot\left(0.0821\ \frac{\text{L}\cdot\cancel{\text{atm}}}{\cancel{\text{K}}\cdot\cancel{\text{mole}}}\right)\cdot(298\ \cancel{\text{K}})}{(0.747\ \cancel{\text{atm}})} = 12.6\ \text{L}$$

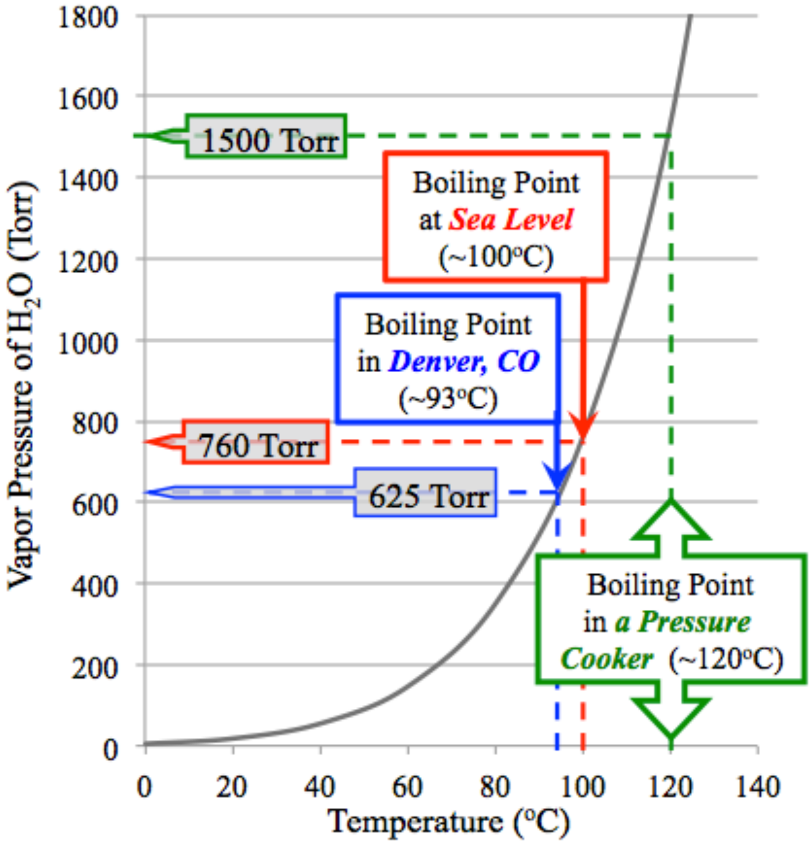
5.13

Dalton's Law states that the pressures of a mixture of gases in a container is equal to the sum of the pressures that each gas in the mixture would exert *if that gas were alone in the container*.

- The pressure of mixture = 625 Torr + 127 Torr = **752 Torr**

5.14

We estimate the boiling point by finding (extrapolating) the temperature at which the vapor pressure is equal to the pressure of the gas above it (1500 Torr).



Chapter 6

6.1

a. What are the reactants? H_2 and O_2

b. What is the product? H_2O

c. What do we call the number "2" in front of the H_2 (and H_2O)? Coefficient

d. Is the reaction balanced? yes

e. Why is there not a coefficient for O_2? When the coefficient is **1**, it is omitted.

f. How many hydrogen **atoms** are needed to produce **two** H_2O molecules? **4**

g. How many oxygen **atoms** are needed to produce **two** H_2O molecules? **2**

h. How many hydrogen **molecules** are needed to produce **two** H_2O molecules? **2**

i. How many oxygen **molecules** are needed to produce **two** H_2O molecules? **1**

j. Write the "word equation" that you would use to describe this reaction.

Hydrogen ***reacts*** with oxygen to ***produce*** dihydrogen monoxide (or water). **or** Hydrogen plus oxygen produces dihydrogen monoxide (or water).

- You can write "***forms***" instead of "***produces***"

6.2

a. $4\ Fe + 3\ O_2 \rightarrow 2\ Fe_2O_3$

b. $H_2 + Cl_2 \rightarrow 2\ HCl$

c. $2\ Ag + H_2S \rightarrow Ag_2S + H_2$

d. $CH_4 + 2\ O_2 \rightarrow CO_2 + 2\ H_2O$

e. $2\ HgO \rightarrow 2\ Hg + O_2$

f. $2\ Co + 3\ H_2O \rightarrow Co_2O_3 + 3\ H_2$

6.3

a. $2\ Al + 3\ CuCl_2 \rightarrow 2\ AlCl_3 + 3\ Cu$

b. $Pb(NO_3)_2 + 2\ NaBr \rightarrow PbBr_2 + 2\ NaNO_3$

c. $2\ Zn + O_2 \rightarrow 2\ ZnO$

d. $Al_2(SO_4)_3 + 3\ BaI_2 \rightarrow 2\ AlI_3 + 3\ BaSO_4$

e. $2\ NaHCO_3 \rightarrow Na_2CO_3 + CO_2 + H_2O$

f. $2\ Na + 2\ H_2O \rightarrow 2\ NaOH + H_2$

g. $PbS_2 + 3\ O_2 \rightarrow PbO_2 + 2\ SO_2$

h. $3\ Zn + 2\ H_3PO_4 \rightarrow Zn_3(PO_4)_2 + 3\ H_2$

6.4

a)

$$\begin{array}{c|c|} 1.32\ \cancel{\text{moles } C_3H_8} & 4\ \text{moles } H_2O \\ \hline & 1\ \cancel{\text{mole } C_3H_8} \end{array} = 5.28\ \text{moles } H_2O$$

b)

$$\begin{array}{c|c|} 12.6\ \cancel{\text{moles } C_3H_8} & 5\ \text{moles } O_2 \\ \hline & 1\ \cancel{\text{mole } C_3H_8} \end{array} = 63.0\ \text{moles } O_2$$

c)

$$\begin{array}{c|c|} 0.843\ \cancel{\text{moles } H_2O} & 5\ \text{moles } O_2 \\ \hline & 4\ \cancel{\text{moles } H_2O} \end{array} = 1.05\ \text{moles } O_2$$

6.5

You are given the ***theoretical yield*** (42 kg) _and_ the ***actual yield*** (33 kg). Enter these values into *Equation 6.1*:

$$\textbf{Percent Yield} = \left(\frac{\text{Actual Yield}}{\text{Theoretical Yield}}\right) \times 100\ \%$$

$$= \left(\frac{33\ \cancel{\text{kg}}}{42\ \cancel{\text{kg}}}\right) \times 100\ \% \ = \mathbf{79\ \%}$$

6.6

a. This reaction is **spontaneous**, **ΔG** is negative. This is the rocket fuel reaction; we know it occurs spontaneously or else the rocket would not move.

b. This reaction is **non-spontaneous**, **ΔG** is positive. This is the hydrolysis of water, it does not occur unless energy is ***continuously*** added, recall the image of the battery submerged in water.

- You may be wondering why **ΔG** does not have the exact same magnitude (but opposite sign) as the previous reaction. The reason is that the reaction in this problem _is not_ *the exact reverse* of the previous reaction because H_2O is in the *liquid phase* in this problem and H_2O is in the *gas phase* in the previous problem. The slight difference in the magnitude of **ΔG** for these two reactions is because of the difference in the amount of free energy contained in liquid H_2O vs. gaseous H_2O.

c. This reaction is **spontaneous**. We have all seen rusty nails, therefore the reaction must occur spontaneously.

6.7

a. **decomposition:** a *single* reactant (**H_2O**) breaks down into *two or more* substances (**H_2** + **O_2**)

$$2\,\mathbf{H_2O}\,(l) \rightarrow 2\,\mathbf{H_2}\,(g) + \mathbf{O_2}\,(g)$$

- Although there is a coefficient of “2” in front of the **H_2O**, this is a decomposition reaction because **H_2O** is the *single* (**only**) reactant. The coefficient is necessary for balancing.

b. **double-replacement:** two substances “***switch partners***”

$$\mathbf{KBr}\,(aq) + \mathbf{AgNO_3}\,(aq) \rightarrow \mathbf{KNO_3}\,(aq) + \mathbf{AgBr}\,(s)$$

c. **synthesis reaction:** a single compound (**MgO**) is formed from two or more substances (**Mg** + **O_2**)

$$2\,\mathbf{Mg}\,(s) + \mathbf{O_2}\,(g) \rightarrow 2\,\mathbf{MgO}\,(s)$$

d. **single-replacement reaction:** an element (**Mg**) *replaces* another element (**H**) in a compound (**HCl**)

$$\mathbf{Mg}\,(s) + 2\,\mathbf{HCl}\,(aq) \rightarrow \mathbf{MgCl_2}\,(aq) + \mathbf{H_2}\,(g)$$

6.8

$$2\,Li\,(s) + Br_2\,(g) \rightarrow 2\,LiBr\,(s)$$

a. What is the charge of each of the lithium atoms in the reactant [$Li\,(s)$]? **Answer: 0 (ZERO)**

$Li\,(s)$ is a pure element; since the ***total charge of any pure element or compound is always ZERO***, and $Li\,(s)$ is composed of *only one type of element*, the charge of each of the atoms in a piece of pure lithium metal ***is equal to ZERO***.

b. What is the charge of each of the lithium ions in the product? **Answer: 1+**

Since lithium bromide ($LiBr$) is a ***compound***, it has a total charge = ZERO. Lithium bromide is an ***ionic compound***, and although the compound’s total charge is ZERO, the lithium cations (and bromide anions) are charged particles; the charge of lithium ***ions*** is always **1+**.

c. Did each lithium atom ***gain*** or ***lose*** electron(s) in this reaction? If so, how many? **Answer: each lithium lost one electron.**

Since the charge of lithium ***increased by one charge units*** in the reaction, we can conclude that each lithium must have ***lost one electron***:

$$Li^{o} \rightarrow Li^{+} + e^{-}$$

d. Was lithium oxidized or reduced? **Answer: oxidized**
When a species loses electron(s), we call that *oxidation*.

e. What is the charge of each of the bromine atoms in the ***reactant*** [$Br_2\,(g)$]? **Answer: 0 (ZERO)** $Br_2\,(g)$ is a pure element, since the ***total charge of any pure element or compound is always ZERO***, and Br_2 is composed of *only one type of element*, the charge of each of the atoms in a Br_2 molecule ***is equal to ZERO***.

f. What is the charge of ***each*** of the bromide ions in the product? **Answer: 1-** See the discussion of lithium ions in the product for question (b). The charge of a bromide ***ion*** is always **1-**.

g. Did each of the bromine atoms gain or lose electron(s) in this reaction? If so, how many? **Answer: each bromine gained one electron.** As a reactant, bromine exists as $Br_2\,(g)$ and has a charge of ZERO. In the product, each bromide ion has a charge of 1-. Since the charge of bromine ***decreased by one charge unit*** in the reaction, we can conclude that each bromine must have ***gained one electron***:

$$Br^{o} + e^{-} \rightarrow Br^{-}$$

h. Was bromine oxidized or reduced? **Answer: reduced**
When a species gains electron(s), we call that *reduction*.

6.9

a. $$\mathbf{2}\,H_2(g) + O_2(g) \rightarrow \mathbf{2}\,H_2O(g)$$

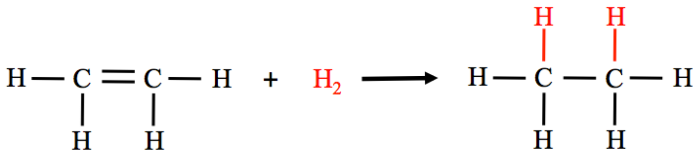
Each hydrogen atom in H_2 is bonded to ***one*** other *hydrogen atom* and **zero** *oxygen atoms* before reacting. After the reaction, each hydrogen in H_2O is bonded to zero *other* hydrogen atoms and to one oxygen atom (each hydrogen ***lost*** a bond to the other hydrogen and ***gained*** a bond to oxygen). An atom is **oxidized** if it ***gains*** *bond(s)* to ***oxygen*** and/or ***loses*** *bond(s)* to ***hydrogen***. **The hydrogens in $H_2\,(g)$ were oxidized in this reaction. We can alternatively say that $H_2\,(g)$ was oxidized.**

We consider *oxygen* next. *Each* oxygen atom in O_2 is bonded to ***one*** other *oxygen atom* and **zero** *hydrogen atoms* before reacting. After the reaction, the oxygen in H_2O is bonded to zero *other* oxygen atoms and to two hydrogen atoms (it ***lost*** a bond to oxygen and ***gained*** two bonds to hydrogen). An atom is **reduced** if it ***loses*** *bond(s)* to ***oxygen*** and/or ***gains*** *bond(s)* to ***hydrogen.*** **The oxygens in $O_2\,(g)$ were reduced in this reaction. We can alternatively say that $O_2\,(g)$ was reduced.**

6.9 (continued)

b) ethene + $H_2(g)$ → ethane

It may be helpful for you to draw the line bond structures of ethene and ethane in order to look for the loss and gain of bonds to hydrogen and oxygen:

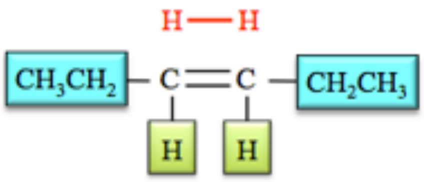


In **eth*ene***, each carbon atom is bonded to ***two*** *hydrogen atoms* before reacting. After the reaction, each carbon in **eth*ane*** is bonded to ***three*** hydrogen atoms. An atom is **reduced** if it ***loses*** *bond(s)* to ***oxygen*** and/or ***gains*** *bond(s)* to ***hydrogen.*** **The carbons in ethene were reduced in this reaction. We can alternatively say that ethene was reduced.**

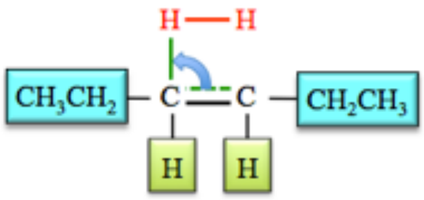
Each hydrogen atom in H_2 is bonded to ***one*** other *hydrogen atom* and **zero** *oxygen atoms* before reacting. After the reaction, each hydrogen in ethane is bonded to zero *other* hydrogen atoms (each hydrogen ***lost*** a bond to the other hydrogen). An atom is **oxidized** if it ***gains*** *bond(s)* to ***oxygen*** and/or ***loses*** *bond(s)* to ***hydrogen***. **The hydrogens in H_2 (g) were oxidized in this reaction. We can alternatively say that H_2 (g) was oxidized.**

6.10

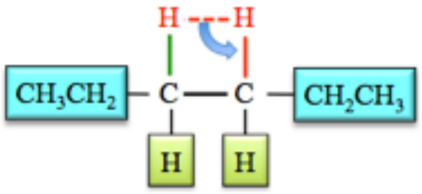
Step #1: Draw the **H-H** directly above the double bond.



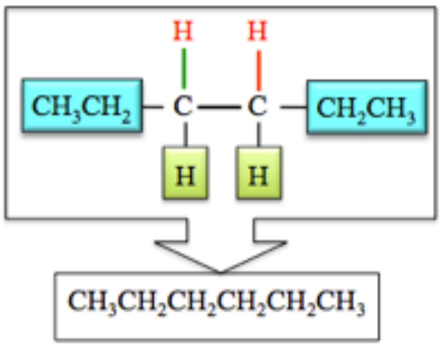
Step #2: Flip one of the bonds from the ***double bond*** up to the **H**



Step #3: Flip the **H-H** *single bond* down to the **C**

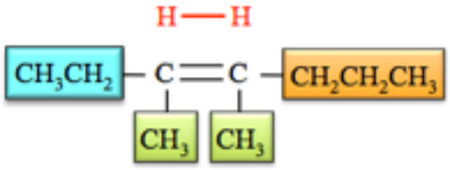


The product is hexane:

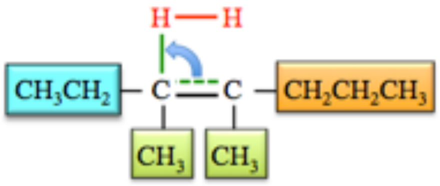


6.11

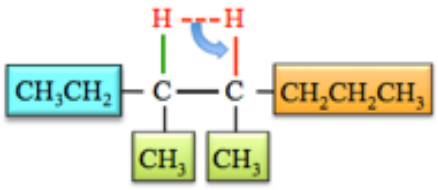
Step #1: Draw the **H-H** directly above the double bond.



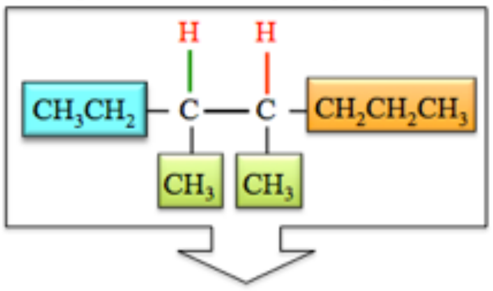
Step #2: Flip one of the bonds from the ***double bond*** up to the **H**

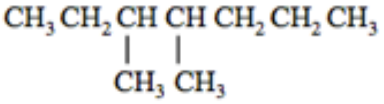


Step #3: Flip the **H-H** *single bond* down to the **C**



The product is 3,4-dimethylheptane:

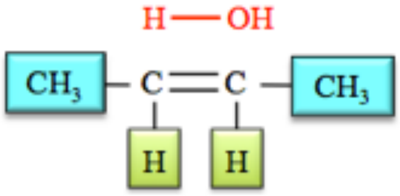




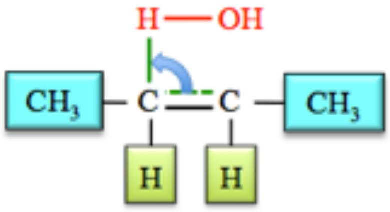
$$\begin{array}{ccccccc} CH_3 & CH_2 & CH & CH & CH_2 & CH_2 & CH_3 \\ & & | & | & & & \\ & & CH_3 & CH_3 & & & \end{array}$$

6.12

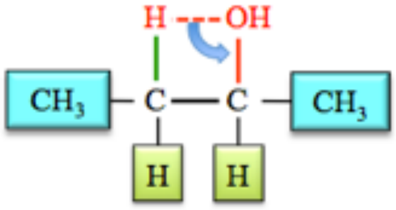
Step #1: Draw the **H-H** directly above the double bond.



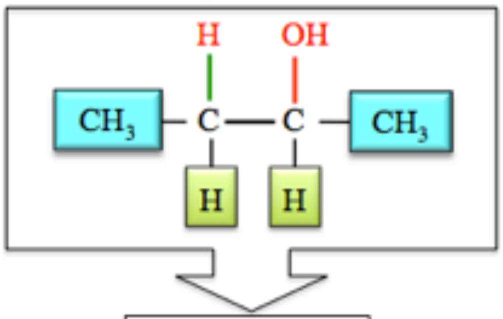
Step #2: Flip one of the bonds from the ***double bond*** up to the **H**

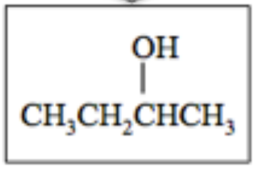


Step #3: Flip the **H-H** *single bond* down to the **C**



The product is:

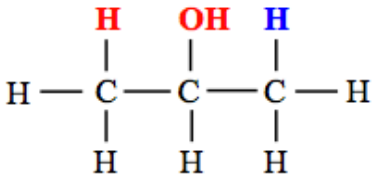




$$\begin{array}{l} \qquad\quad OH \\ \qquad\quad\, | \\ CH_3CH_2CHCH_3 \end{array}$$

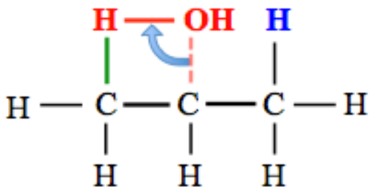
6.13

Although all of the bonding pattern information is contained in condensed and skeletal formulas, it may be helpful to draw the line bond structure in order to visualize the complete bonding pattern:

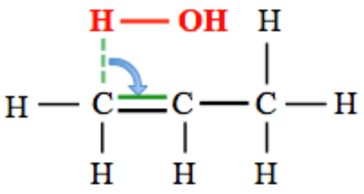


Step 1: Flip the bond between the C and **OH** **up** to an **H** on *an adjacent* carbon.

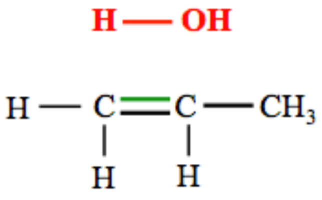
- Note that there are two carbons that are ***adjacent*** to the carbon that is carrying the **OH.** Since the adjacent carbons **are identical to each other** (because of the symmetry of the molecule), we can flip the bond toward either of them. I arbitrarily chose to flip the bond toward the **red H** instead of the **blue H**.



Step 2: Flip the **C--H** bond from the *adjacent* carbon **down** to make a double bond to the C that originally carried the **OH**.



This gives the ***alkene*** and water molecule products:



The correct condensed structural formula for the alkene is:

$$CH_2{=}CH\,CH_3 + H_2O$$

propene

Try to convince yourself that if you had flipped the bond between C and **OH** toward the **blue H** (in step 1), you would have obtained ***exact same product***: **propene**.

Chapter 7

7.1

The pure substance that is in the *greatest abundance* is referred to as the **solvent**. The other pure substance components of a solution is are called **solutes**.

a. **solute:** sodium chloride, **solvent:** water
b. **solute:** ethyl alcohol, **solvent** water
c. **solute:** water, **solvent:** acetone (since there is more acetone than water, ***acetone is the solvent***).

7.2

a. Sodium chloride dissociates when it dissolves. For every ***one mole*** of sodium chloride dissolved, the solution will contain *one mole* of solvated sodium ions ***plus*** *one mole* of solvated chloride ions, for a total of **2 moles of dissolved ions.**

$$NaCl\,(s) \rightarrow Na^+\,(aq) + Cl^-\,(aq)$$

b. Barium chloride dissociates when it dissolves. For every ***one mole*** of barium chloride dissolved, the solution will contain *one mole* of solvated barium ions ***plus*** ***two*** *moles* of solvated chloride ions, for a total of **3 moles of dissolved ions.**

$$BaCl_2\,(s) \rightarrow Ba^{2+}\,(aq) + 2\,Cl^-\,(aq)$$

7.3

a. oxygen gas dissolved in water: **hydrogen bonding, London forces**
   - hydrogen bonding occurs between the *H bonded to oxygen in water* and a *lone pair on an oxygen of O_2*

b. carbon dioxide gas dissolved in water: **hydrogen bonding, London forces**
   - hydrogen bonding occurs between the *H bonded to oxygen in water* and a *lone pair on an oxygen of CO_2*

c. potassium iodide dissolved in water: **ion-dipole forces (only)**
   - (since potassium and iodide are monatomic ions, we do not include London forces)

d. pentane dissolved in octane: **London forces (only)**

7.4

a. Potassium iodide is **water soluble**: iodides are in the water soluble class. There are some exceptions, however potassium is not one of them.

b. Iron(II) nitrate is **water soluble**: nitrates are in the water soluble class. There are no exceptions, all nitrates are water soluble.

c. Copper(II) hydroxide is **not water soluble**: hydroxides are in the water insoluble class. There are some exceptions, however Cu^{2+} is not one of them.

d. Silver bromide is **not water soluble**: bromides are in the water soluble class, however Ag^+ is listed as an exception.

e. sodium sulfate is **water soluble**: sulfates are in the water soluble class. There are some exceptions, however sodium is not one of them.

f. potassium hydroxide is **water soluble**: hydroxides are in the water insoluble class, however K^+ is a alkali (Group I) metal and is therefore an exception.

g. lead(II) chromate is **not water soluble**: chromates are in the water insoluble class. There are some exceptions, however Pb^{2+} is not one of them.

h. ammonium hydroxide is **water soluble**: hydroxides are in the water insoluble class, however NH_4^+ is an exception.

7.5

The **water soluble** ionic compounds are electrolytes: a) potassium iodide, b) iron(II) nitrate, e) sodium sulfate, f) potassium hydroxide, h) ammonium hydroxide.

7.6

The solubilities of most solids in water increase as the temperature increases. Since ionic compounds (in this case $NaNO_3$ and $CuCl_2$) and table sugar are solids, we expect their solubilities to increase with temperature.

We would expect the solubilities of the *gaseous substances* (in this case O_2, H_2, N_2) in water to decrease as the temperature increases.

7.7

a. **homogeneous**: at 20°C, the 30.0 g of NaCl would completely dissolve. (according to Figure 7.10, up to approximately 35 grams of NaCl will dissolve in 100 g of water at this temperature)

b. **No**: at 20°C, only up to about about 37 grams of NH_4Cl will dissolve in 100 g or water.

c. **Yes**: at 60°C, up to about 55 grams of NH_4Cl will dissolve in 100 g or water.

d. **heterogeneous**: **heterogeneous**: at 20°C, the 60.0 g of NaCl would not completely dissolve.

e. At 20°C, **approximately 35** of NaCl will dissolve in 100 g of water.

f. Since about 35 grams of the 60 grams of NaCl will dissolve in 100 g of water at 20°C, then **approximately 25 grams of solid will be present** (60 g - 35 g = 25 g).

7.8

Step 1: Write ***reactants*** and arrow for the chemical equations using ***word form*** (not formulas):

silver nitrate + barium chloride →

Step 2: Add the "*possible*" **products** to the word equation by switching ***anions***:

silver nitrate + barium chloride →
silver chloride + barium nitrate

Step 3: Convert the ***word*** equation to a ***formula*** equation:

$$AgNO_3 + BaCl_2 \rightarrow AgCl + Ba(NO_3)_2$$

Step 4: ***Balance*** the equation:

$$2\ AgNO_3 + BaCl_2 \rightarrow 2\ AgCl + Ba(NO_3)_2$$

Step 5: Add the phases of the reactants and "possible" products to the equation.

$$2\ AgNO_3\,(aq) + BaCl_2\,(aq) \rightarrow 2\ AgCl\,(s) + Ba(NO_3)_2\,(aq)$$

7.9

Step 1: Write ***reactants*** and arrow for the chemical equations using ***word form*** (not formulas):

iron(III) bromide + potassium phosphate →

Step 2: Add the "*possible*" **products** to the word equation by switching ***anions***:

iron(III) bromide + potassium phosphate →
iron(III) phosphate + potassium bromide

Step 3: Convert the ***word*** equation to a ***formula*** equation:

$$FeBr_3 + K_3PO_4 \rightarrow FePO_4 + KBr$$

Step 4: ***Balance*** the equation:

$$FeBr_3 + K_3PO_4 \rightarrow FePO_4 + 3\ KBr$$

Step 5: Add the phases of the reactants and "possible" products to the equation.

$$FeBr_3(aq) + K_3PO_4(aq) \rightarrow FePO_4\,(s) + 3KBr\,(aq)$$

7.10

a. As the *hydrocarbon part* of carboxylic acids gets larger, their water solubility **decreases**.

least soluble → most soluble
hexanoic acid, butanoic acid, ethanoic acid

b. As the *hydrocarbon part(s)* of esters gets larger, their water solubility **decreases**.

least soluble → most soluble
ethyl hexanoate, ethyl butanoate, ethyl ethanoate

7.11

Calculate the concentration using the equation/definition of % (w/w):

$$\% \text{ (w/w)} = \left(\frac{\text{mass of } \textit{solute}}{\text{mass of } \textit{solution}} \right) \times 100$$

To calculate the %(w/w), we need to know two quantities: the mass of the ***solute*** **AND** the mass of the ***solution.***

- Mass of the ***solute*** (magnesium chloride in this example) was given: **1.3 g**
- Mass of the ***solution:***
  - ***The solution is a mixture composed of water and magnesium chloride!***
  - The mass of the solution is equal to the mass of the ***solute*** (MgCl, 1.3 g) ***plus*** the mass of the ***solvent*** (water, 43.0 g):
  -

1.3 g + 43.0 g = **44.3 g**

Insert the mass of the solute and the mass of the solution into the equation for % (w/w):

$$\% \text{ (w/w)} = \left(\frac{1.3 \text{ g}}{44.3 \text{ g}} \right) \times 100 = 2.9 \ \% \text{ (w/w)}$$

7.12

Calculate the concentration using the equation/definition of % (v/v):

$$\% \text{ (v/v)} = \left(\frac{\text{volume of } \textit{solute}}{\text{volume of } \textit{solution}} \right) \times 100$$

To calculate the %(v/v), we need to know two quantities: the volume of the ***solute*** **AND** the volume of the ***solution.***

- Volume of the ***solute*** (acetone in this example) was given: **145 mL**
- Volume of the ***solution*** was given: **1914 mL**

Insert the volume of the solute and the volume of the solution into the equation for % (v/v):

$$\% \text{ (v/v)} = \left(\frac{145 \text{ mL}}{1914 \text{ mL}} \right) \times 100 = 7.58 \ \% \text{ (v/v)}$$

- three significant figures

7.13

Calculate the concentration using the equation/definition of % (w/v):

$$\%\ (\text{w/v}) = \left(\frac{\text{grams of } \textit{solute}}{\text{mL of } \textit{solution}}\right) \times 100$$

To calculate the % (w/v), we need to know two quantities: the **grams** of the ***solute*** **<u>AND</u>** the volume (in mL) of the ***solution.***

- grams of the ***solute*** (table sugar in this example) was given: **3.2 g**
- mL of ***solution*** was given: **735 mL**

Insert the grams of the solute and mL of the solution into the equation for % (w/v):

$$\%\ (\text{w/v}) = \left(\frac{3.2\ \text{g}}{735\ \text{mL}}\right) \times 100 = 0.44\ \%\ (\text{w/v})$$

7.14

Calculate the concentration using the equation/definition of parts per thousand (w/w):

$$\text{parts per thousand (w/w)} = \left(\frac{\text{mass of } \textit{solute}}{\text{mass of } \textit{solution}}\right) \times 1000$$

To calculate the parts per thousand (w/w), we need to know two quantities: the mass of the ***solute*** **<u>AND</u>** the mass of the ***solution***

- Mass of the ***solute*** (alcohol in this example) was given: **0.080 g**
- Mass of the ***solution*** (blood in this example) was given: **100.0 g**

Insert the mass of the solute and the mass of the solution into the equation for parts per thousand (w/w):

$$\text{parts per thousand (w/w)} = \left(\frac{0.080\ \text{g}}{100.0\ \text{g}}\right) \times 1000 = 0.80 \text{ parts per thousand (w/w)}$$

7.15

Calculate the solution's **molarity** using the equation/definition of molarity:

$$\text{Molarity} = \left(\frac{\text{moles of } \textit{solute}}{\text{liters (L) of } \textit{solution}}\right)$$

To calculate the ***molarity***, we need to know two quantities: the **moles** of the ***solute*** **<u>AND</u>** the volume (in L) of the ***solution.***

- moles of the ***solute*** (glucose).
  - You were not given the number of moles ***directly***, however, you were given the *number of grams* of glucose (3.83 g). Calculate the *molar mass* of glucose ($C_6H_{12}O_6$), and then convert from grams to moles:
    - The molar mass of glucose is [(6 x 12.01 g/mole) + (12 x 1.01 g/mole) + (6 x 16.00 g/mole)] = **180.18 g/mole**.

$$\begin{array}{c|c|l} 3.83\ \cancel{\text{grams } C_6H_{12}O_6} & 1\ \text{mole } C_6H_{12}O_6 & \\ \hline & 180.18\ \cancel{\text{grams } C_6H_{12}O_6} & \end{array} = 0.0213\ \text{moles } C_6H_{12}O_6$$

- liters (L) of ***solution*** was given: **5.00 L**

Insert the moles of the solute and L of the solution into the equation for molarity:

$$\text{Molarity} = \left(\frac{0.0213\ \text{moles}}{5.00\ \text{L}}\right) = 0.00426\ \text{moles/L} \ \text{ or } \ 0.00426\ \text{M}$$

The solution's concentration is **0.00426 moles/L.** Alternatively, you can write **0.00426 M** and say "**0.00426 molar**".

7.16

Calculate the concentration using the equation/definition of osmolarity:

$$\text{Osmolarity} = \left(\frac{\text{osmoles of } solute}{\text{liter (L) of } solution}\right)$$

To calculate the **os*molarity***, we need to know two quantities: the number of **osmoles** of the ***solute*** **<u>AND</u>** the volume (in L) of the ***solution.***

- **osmoles** of the ***solute*** ($BaCl_2$)
    - You were not given the number of osmoles ***directly***, however, you were given the *number of moles* of $BaCl_2$ (0.50 moles). $BaCl_2$ ionizes when dissolved. For every ***one mole*** of $BaCl_2$ is dissolved, **3** osmoles are formed (one osmole of Ba^{2+} and two osmoles of Cl^-).

$$\mathbf{BaCl_2}\,(s) \rightarrow \mathbf{Ba^{2+}}\,(aq) + \mathbf{2\ Cl^-}\,(aq)$$

-
    - Multiply the number of moles of $BaCl_2$ by a factor of **3** to convert ***moles*** of $BaCl_2$ to ***osmoles***:

$$0.50\ \text{moles}\ \mathbf{BaCl_2}\left[\frac{\mathbf{3}\ \text{osmoles}}{\text{mole}\ \mathbf{BaCl_2}}\right] = \mathbf{1.5\ osmoles}$$

-
    - 0.50 moles of $BaCl_2$ were dissolved, therefore the solution contains **1.5 osmoles**.
- liters (L) of ***solution*** was given: **2.00 L**

Insert the **osmoles** of the *solute* and liters (L) of *solution* into the equation for osmolarity:

$$\text{Osmolarity} = \left(\frac{1.5\ \text{osmoles}}{2.00\ \text{L}}\right) = 0.75\ \text{osmoles/L}\ \text{ or }\ 0.75\ \text{osmolar}$$

Even though we started with the same number of moles of solute and the same volume of solution in this example as we did in the previous two examples, the calculated osmolarity values were not the same because of the difference in the number of particles that are formed upon dissolution of the various solutes.

7.17

In order to convert to osmoles/L, we need to convert moles of $FeCl_3$ to osmoles. We know the relationship between moles of $FeCl_3$ and osmoles:

$FeCl_3$ dissociates when dissolved. For every ***one mole*** of $FeCl_3$ is dissolved, 4 osmoles are formed (<u>one</u> osmole of Fe^{3+} and <u>three</u> osmoles of Cl^-).

$$\mathbf{FeCl_3}\,(s) \rightarrow \mathbf{Fe^{3+}}\,(aq) + \mathbf{3\ Cl^-}\,(aq)$$

1 mole $FeCl_3$ = **4** osmoles

- Use this relationship as the conversion factor:

$$\underbrace{\frac{0.010\ \cancel{\text{moles FeCl}_3}}{\text{L}}}_{\text{Molarity (moles/L)}}\left|\underbrace{\frac{4\ \text{osmoles}}{1\ \cancel{\text{mole FeCl}_3}}}_{\text{Conversion Factor (osmoles/mole FeCl}_3)}\right| = \underbrace{\mathbf{0.040}\left(\frac{\text{osmoles}}{\text{L}}\right)}_{\text{Osmolarity (osmoles/L)}}$$

If the ***molarity*** of an $FeCl_3$ solution is 0.010 M, the ***osmolarity*** is 0.040 osmoles/L.

7.18

Calculate the solution's molality using the equation/definition of molality:

$$\text{Molality} = \left(\frac{\text{moles of } solute}{\text{kg of } solvent}\right)$$

To calculate the ***molarily***, we need to know two quantities: the **moles** of the ***solute*** **<u>AND</u>** the mass (in kg) of the ***solvent.***

- The moles of the ***solute*** (ethyl alcohol) was given: **1.34 moles.**
- The mass of the ***solvent*** (water) was given: **0.75 kg**

Insert the moles of the *solute* and *kg of solvent* into the equation for molality:

$$\text{Molality} = \left(\frac{1.34\ \text{moles}}{0.75\ \text{kg}}\right) = 1.8\ \text{moles/kg}\ \text{ or }\ 1.8\ m$$

7.19

a. When **one mole** of $\mathrm{Fe_2(SO_4)_3}$ is dissolved, ***12 Eq*** are formed.

b. There are 6 Eq of sulfate (three moles, each mole has a “2-” charge: 3 x 2 = 6)

c. There are 6 Eq of iron(III) (two moles, each mole has a “3+” charge: 2 x 3 = 6)

$$\mathbf{Fe_2(SO_4)_3}\,(s) \;\rightarrow\; \underbrace{\underbrace{\mathbf{2\ Fe^{3+}}\,(aq)}_{\boxed{\begin{array}{c}\mathbf{6\ Eq}\\ \mathbf{of\ Fe^{3+}}\end{array}}} \;+\; \underbrace{\mathbf{3\ SO_4^{2-}}\,(aq)}_{\boxed{\begin{array}{c}\mathbf{6\ Eq}\\ \mathbf{of\ SO_4^{2-}}\end{array}}}}_{\boxed{\mathbf{12\ total\ Eq}}}$$

7.20

Calculate the concentration using the equation/definition of Eq/L:

$$\text{Eq/L} = \left(\frac{\text{Eq of } \textit{solute}}{\text{liter (L) of } \textit{solution}}\right)$$

To calculate the **Eq/L** concentration, we need to know two quantities: the number of **equivalents (Eq)** present **AND** the volume (in L) of the ***solution.***

- **Eq** present:
  - As you calculated in the previous **review problem**, For every ***one mole*** of $\mathrm{Fe_2(SO_4)_3}$ that is dissolved, **12 Eq** are formed (**6** Eq of $\mathrm{Fe^{3+}}$ and **6** Eq of $\mathrm{SO_4^{2-}}$).

$$\mathbf{Fe_2(SO_4)_3}\,(s) \;\rightarrow\; \mathbf{2\ Fe^{3+}}\,(aq) \;+\; \mathbf{3\ SO_4^{2-}}\,(aq)$$

  - Multiply the number of moles of $\mathrm{Fe_2(SO_4)_3}$ by a factor of **12** to convert ***moles*** of $\mathrm{Fe_2(SO_4)_3}$ to **Eq**:

$$0.015\text{ moles } \mathrm{Fe_2(SO_4)_3}\left(\frac{\mathbf{12\ Eq}}{\text{mole } \mathrm{Fe_2(SO_4)_3}}\right) = \mathbf{0.18\ Eq}$$

  - 0.015 moles of $\mathrm{Fe_2(SO_4)_3}$ were dissolved, therefore the solution contains **0.18 Eq**.
- liters (L) of ***solution*** was given: **2.5L**

Insert the **Eq** present and liters (L) of *solution* into the equation for **Eq/L** concentration:

$$\text{Eq/L} = \left(\frac{0.18\text{ Eq}}{2.5\text{ L}}\right) = 0.072\text{ Eq/L}$$

7.21

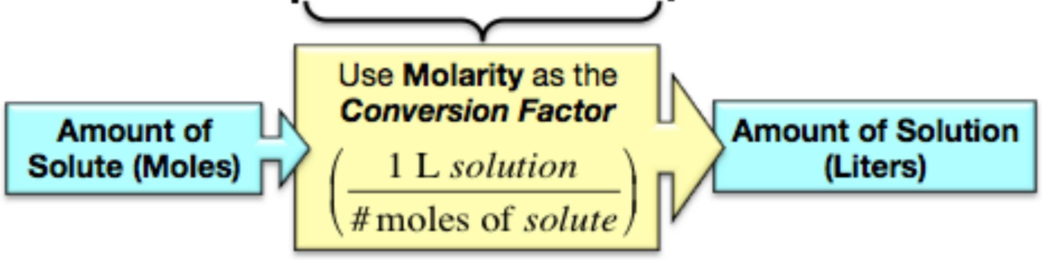
You must calculate how many liters of solution (wine) contain 10.4 moles of ethyl alcohol. Use the molarity as a ***conversion factor*** to convert between moles of solute (ethyl alcohol) and liters of wine.

STEP 1) Set up the equation using the given quantity:

$$\begin{array}{l|l|l} 10.4\ \text{moles ethyl alcohol} & \qquad\qquad & = \text{? L solution (wine)} \\ \hline & & \end{array}$$

STEP 2) Using the concentration as a conversion factor, we put the given units (moles ethyl alcohol) in the denominator so that the given units will cancel, and then put the desired units (L of solution/wine) in the numerator:

$$\begin{array}{l|l|l} 10.4\ \cancel{\text{moles ethyl alcohol}} & 1\text{ L solution (wine)} & = 3.7\text{ L solution (wine)} \\ \hline & 2.8\ \cancel{\text{moles ethyl alcohol}} & \end{array}$$



10.4 moles of ethyl alcohol would be contained in 3.7 L of this wine, therefore 3.7 L of wine is a lethal dose.

7.22

In the previous problem we determined that a legal dose of the wine for a 150 lb. individual is 3.7 L. Do a unit conversion using the given relationship between liters of wine and glasses of wine: 1L wine = 5 glasses.

$$\begin{array}{r|c|} 3.7\ \cancel{\text{L wine}} & 5.0\ \text{glasses wine} \\ \hline & 1\ \cancel{\text{L wine}} \end{array} = 19\ \text{glasses of wine}$$

7.23

First calculate the ***number moles*** of silver nitrate ($AgNO_3$) that are contained in 0.384 L of a 0.200 M silver nitrate solution, and then convert moles of $AgNO_3$ to grams.

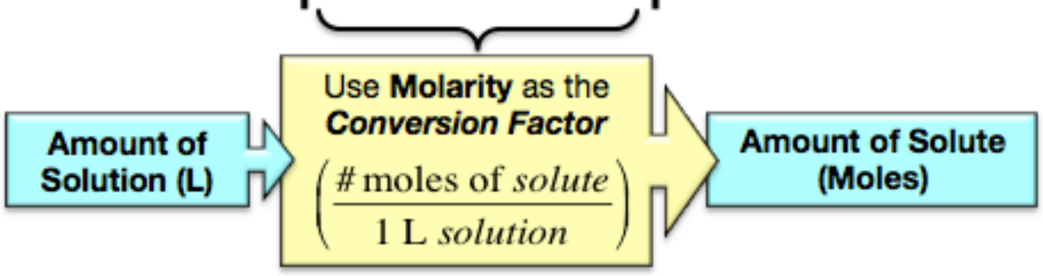
Use the molarity as a ***conversion factor*** to convert between *liters of solution* and *moles of solute* ($AgNO_3$).

- Set up the equation using the given quantity:

$$\begin{array}{r|c|} 0.384\ \text{L solution} & \qquad\qquad \\ \hline & \end{array} = ?\ \text{moles}\ AgNO_3$$

- Use the concentration as a conversion factor:

$$\begin{array}{r|c|} 0.384\ \cancel{\text{L solution}} & 0.200\ \text{moles}\ AgNO_3 \\ \hline & 1\ \cancel{\text{L solution}} \end{array} = 0.0768\ \text{moles}\ AgNO_3$$



- Convert 0.0768 ***moles*** of $AgNO_3$ to ***grams***:

The *molar mass* of $AgNO_3$ is [(1 x 107.88 g/mole) + (1 x 14.01 g/mole) + (3 x 16.00 g/mole)] = **169.89 g/mole.**

$$\begin{array}{r|c|} 0.0768\ \cancel{\text{moles}\ AgNO_3} & 169.89\ \text{grams}\ AgNO_3 \\ \hline & 1\ \cancel{\text{mole}\ AgNO_3} \end{array} = 13.0\ \text{grams}\ AgNO_3$$

0.384 L of the 0.200 M solution will contain 13.0 grams of $AgNO_3$.

7.24

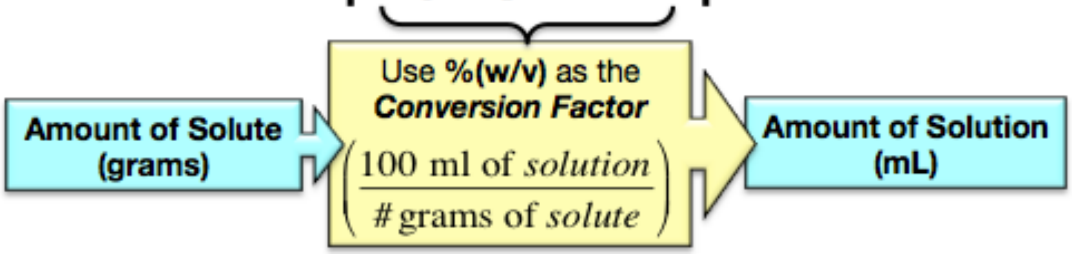
Use % (m/v) as a conversion factor to convert from grams of solute to volume (mL) of solution.

STEP 1) Set up the equation using the given quantity:

$$\begin{array}{r|c|} 0.0025\ \text{g morphine sulfate} & \qquad\qquad \\ \hline & \end{array} = ?\ \text{mL solution}$$

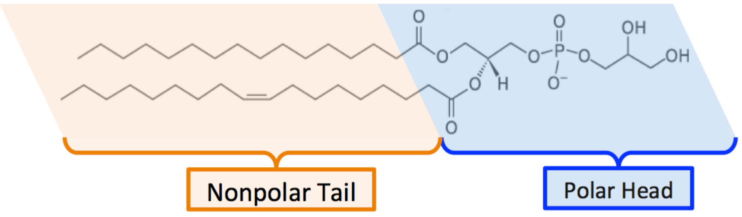
STEP 2) We need to convert grams of solute (morphine sulfate) to mL of solution. 1.0 % (w/v) means that there are 1.0 grams of solute (morphine sulfate) in every **100 mL** of solution. To use this concentration as a conversion factor, we put the given units (grams of morphine sulfate) in the denominator so that the given units will cancel, and then put the desired units (mL of solution) in the numerator:

$$\begin{array}{r|c|} 0.0025\ \cancel{\text{g morphine sulfate}} & 100\ \text{mL solution} \\ \hline & 1.0\ \cancel{\text{g morphine sulfate}} \end{array} = 0.25\ \text{mL solution}$$



7.25

a. **amphipathic:** this compound has a polar head and a nonpolar tail



NOTE: You may have noticed that the phosphorus in this compound *does not obey the octet rule*. This does occur on occasion for some elements. In this textbook, you will only see this occur for phosphorus and sulfur but *never* for carbon, nitrogen, or oxygen. Phosphorus and sulfur are larger than carbon, nitrogen, and oxygen, and it is therefore somewhat easier (lower in energy) for phosphorus and sulfur to accommodate so many electrons in their vicinity (because their "vicinity" is larger).

b. **hydrophobic:** there are no polar functional groups at all. As a general rule, molecules that have less than ***one polar functional group for every five carbon atoms*** do not dissolve in water and are therefore hydrophobic.

7.26

a. **hydrophilic:** the ratio of polar functional groups, hydroxyl groups (-OH) and a carbonyl group (C=O) in this case, to total carbon atoms is ***much greater than*** 1:5. As general rule, molecules that have at least ***one polar functional group for every five carbon atoms*** are water soluble and therefore are classified as **hydrophilic.**

b. **hydrophobic:** the ratio of polar functional groups, a single hydroxyl group (-OH) in this case, to total carbon atoms is ***much less than*** 1:5. As a general rule, molecules that have less than ***one polar functional group for every five carbon atoms*** do not dissolve in water and are therefore hydrophobic.

7.27

The polar head is on the right-hand side. Although lone pairs are not shown explicitly in skeletal structures, the oxygens do have lone pairs that can hydrogen bond with water. In addition, there is a **formal charge** on one of the the oxygens. Water molecules' dipoles are *strongly attracted* to the charged region of the compound through *ion-dipole interactions*. The left-hand side of the compound is composed of carbon and hydrogen only and is therefore the nonpolar tail.

7.28

Use the ***dilution equation***:

$$M_1 \bullet V_1 = M_2 \bullet V_2$$

- In this example, we know M_1, V_1, and V_2, and we wish to find the final concentration (**M_2**):

M_1 = 1.50 M
M_2 = **???** M
V_1 = 1.70 L
V_2 = 3.50 L

- To solve for **M_2**, we divide ***both sides*** of the equation by **V_2**. After doing so, **V_2** cancels on the right-hand side, and we have isolated the unknown variable (**M_2**):

$$M_2 = \frac{M_1 \bullet V_1}{V_2}$$

- Insert the know values of M_1, V_1, and V_2, and then solve for the final concentration (**M_2**):

$$M_2 = \frac{(1.50\ \text{M}) \bullet (1.70\ \cancel{\text{L}})}{(3.50\ \cancel{\text{L}})} = 0.729\ \text{M}$$

The final concentration of the diluted solution is 0.729 M. Check to **see if you answer makes sense**; the value of the calculated final concentration should be ***less than*** the initial concentration!

7.29

Use the ***dilution equation***:

$$M_1 \bullet V_1 = M_2 \bullet V_2$$

In this example, we know M_1, V_1. V_2 is *implied* but not given directly.

- The question states that "2.00 L i***s added*** to 0.50 L of a 0.200 M solution", therefore the final volume (**V_2**) is equal to **2.50 L.**

$$\mathbf{V_2} = V_1 + 2.00\ \text{L} = 0.50\ \text{L} + 2.00\ \text{L} = \mathbf{2.50\ L}$$

We wish to find the final concentration (**M_2**):

M_1 = 0.200 M
M_2 = **???** M
V_1 = 0.50 mL
V_2 = 2.50 L

To solve for **M_2**, we divide ***both sides*** of the equation by **V_2**. After doing so, **V_2** cancels on the right-hand side; we have isolated the unknown variable (**M_2**):

$$M_2 = \frac{M_1 \bullet V_1}{V_2}$$

Insert the know values of M_1, V_1, and V_2, then solve for the final concentration (**M_2**):

$$M_2 = \frac{(0.200\ \text{M}) \bullet (0.50\ \cancel{\text{L}})}{(2.50\ \cancel{\text{L}})} = 0.040\ \text{M}$$

The final concentration of the diluted solution is 0.040 M. Check to **see if you answer makes sense**; the value of the calculated final concentration should be ***less than*** the initial concentration!

7.30
The mixture would be a **suspension** because the grains of sand would settle to the bottom of the container.

7.31
The greater the difference in ***osmolarity*** between each side of the semipermeable membrane, the greater the *osmotic pressure*.

System #1 has a difference in osmolarity between each side of the membrane of **2.00 osmoles/L**.

- Each mole of dissolved $NaCl$ results in two osmoles. The $NaCl$ has a molarity of 1.00 moles/L = 2.00 osmoles/L.
- Pure water has an osmolarity = ZERO

System #2 has a difference in osmolarity between each side of the membrane of **1.00 osmoles/L**.

- The $NaCl$ has a molarity of 0.500 moles/L = 1.00 osmoles/L.
- Pure water has an osmolarity = ZERO

System #1 has a greater difference in osmolarity, it therefore has a greater osmotic pressure.

7.32
The greater the difference in ***osmolarity*** between each side of the semipermeable membrane, the greater the *osmotic pressure*.

System #1 has an osmolarity equal to **2.00 osmoles/liter**.

- Each mole of dissolved $NaCl$ results in *two* osmoles. The $NaCl$ has a molarity of 1.00 moles/L = 2.00 osmoles/L.
- Pure water has an osmolarity = ZERO

System #2 has an osmolarity equal to **5.00 osmoles/liter**.

- Each mole of $Fe_2(SO_4)_3$ results in *five* moles of dissolved particles (osmoles); two moles of iron and three moles of sulfate. The $Fe_2(SO_4)_3$ has a molarity of 1.00 moles/L = 5.00 osmoles/L.
- Pure water has an osmolarity = ZERO

System #2 has a greater difference in osmolarity, it therefore has a greater osmotic pressure.

Chapter 8

8.1

The equilibrium expression is written with the concentrations of the *products* (raised to their stoichiometric coefficient powers) in the numerator, and the concentrations of the *reactants* (raised to their stoichiometric coefficient powers) in the denominator.

- The stoichiometric coefficients are all equal to 1 in this reaction. When a number is raised to the power of 1, its value does not change so the "1" is omitted.

$$K_{eq} = \frac{[NO_2\ ][ClNO]}{[ClNO_2][NO]}$$

8.2

$$K_{eq} = \frac{[H_3O^+][Cl^-]}{[HCl]}$$

Since **H_2O (*l*)** is a liquid, it is omitted from the equilibrium expression. All of the coefficients are 1, therefore they are not written as exponents.

8.3

When we know $[H_3O^+]$, we can solve the equilibrium expression (*Equation 8.3*) for the hydroxide ion concentration:

$$[OH^-] = \frac{1.0 \times 10^{-14} M^2}{[H_3O^+]}$$

Inserting the known value for the hydronium ion concentration (3.6 x 10^{-11} M) allows us to solve for the hydroxide ion concentration:

$$[OH^-] = \frac{1.0 \times 10^{-14} M^2}{3.6\ \times\ 10^{-11} M} = 2.8\ \times\ 10^{-4} M$$

8.4

When we know $[OH^-]$, we can solve the equilibrium expression (*Equation 8.3*) for the hydronium ion concentration:

$$[H_3O^+] = \frac{1.0 \times 10^{-14} M^2}{[OH^-]}$$

Inserting the known value for the hydroxide ion concentration (2.4 x 10^{-9} M) allows us to solve for the hydronium ion concentration:

$$[H_3O^+] = \frac{1.0 \times 10^{-14} M^2}{2.4\ \times\ 10^{-9} M} = 4.2\ \times\ 10^{-6} M$$

8.5

When we know $[H_3O^+]$, we can solve the equilibrium expression (*Equation 8.3*) for the hydroxide ion concentration:

$$[OH^-] = \frac{1.0 \times 10^{-14} M^2}{[H_3O^+]}$$

Inserting the known value for the hydronium ion concentration (1.0 x 10^{-7} M) allows us to solve for the hydroxide ion concentration:

$$[OH^-] = \frac{1.0 \times 10^{-14} M^2}{1.0\ \times\ 10^{-7} M} = 1.0\ \times\ 10^{-7} M$$

8.6

a. $H_3BO_3\ (aq) + H_2O\ (l) \rightleftarrows H_2BO_3^-\ (aq) + H_3O^+\ (aq)$

acid **base**

- H_3BO_3 donated an H^+, so it is the **acid.** H_2O accepted an H^+, it is the **base.**

b. $HSO_4^-(aq) + HNO_3(aq) \rightleftarrows H_2SO_4\ (aq) + NO_3^-\ (aq)$

base **acid**

- HNO_3 donated an H^+ it is the **acid.** HSO_4^- accepted an H^+, so it is the **base.**

c. $CN^-\ (aq) + H_2O\ (l) \rightleftarrows HCN\ (aq) + OH^-\ (aq)$

base **acid**

- H_2O donated an H^+, so it is the **acid.** CN^- accepted an H^+, it is the **base.**

8.7

The species that *contains the extra hydrogen* (H^+) is the "***acid form***," and the species with one fewer hydrogen is the "***base form***".

a. H_3BO_3 is the ***acid form***, and $H_2BO_3^-$ is the ***base form***.
b. H_2O is the ***base form***, and H_3O^+ is the ***acid form***.
c. HSO_4^- is the ***base form***, and H_2SO_4 is the ***acid form***.
d. HNO_3 is the ***acid form***, and NO_3^- is the ***base form***.
e. CN^- is the ***base form***, and HCN is the ***acid form***.

8.8

Insert the $[H_3O^+]$ into *Equation 8.5* and use your calculator to solve for the pH.

pH = - log$[H_3O^+]$ = - log(3.8 x 10^{-9}) = - (-8.42) = **8.42**

8.9
First, use the $[OH^-]$ to solve the equilibrium expression (*Equation 8.3*) for the hydronium ion concentration:

$$[H_3O^+] = \frac{1.00 \times 10^{-14}\,M^2}{[OH^-]}$$

Inserting the known value for the hydroxide ion concentration (2.4 x 10^{-9} M) allows you to solve for the hydronium ion concentration:

$$[H_3O^+] = \frac{1.00 \times 10^{-14}\,M^2}{2.4 \times 10^{-9}\,M} = 4.2 \times 10^{-6}\,M$$

Then, insert the $[H_3O^+]$ into *Equation 8.5* and calculate the pH:

pH = - log$[H_3O^+]$ = - log(4.2 x 10^{-6}) = - (-5.38) = **5.38**

8.10
Insert the pH into *Equation 8.5* and use your calculator to solve for the $[H_3O^+]$.

pH = - log$[H_3O^+]$

12.65 = - log$[H_3O^+]$

To solve for the $[H_3O^+]$, isolate it on one side of the equation. First, get rid of the negative sign on the right-hand side of the equation by multiplying both sides by (-1):

-12.65 = log$[H_3O^+]$

Next, get rid of the "log" on the right-hand side by taking the "anti-log" of each side of the equation:

antilog(-**12.65)** = $[H_3O^+]$

Use your calculator to get the antilog of (-12.65).

antilog(-**12.65**) = $[H_3O^+]$

2.2 x 10^{-13} M = $[H_3O^+]$

An aqueous solution with a **pH** of **12.65** has a **$[H_3O^+]$** of **2.2 x 10^{-13} M.**

8.11
Insert the pH into *Equation 8.5* and use your calculator to solve for the $[H_3O^+]$.

pH = - log$[H_3O^+]$

0.25 = - log$[H_3O^+]$

To solve for the $[H_3O^+]$, isolate it on one side of the equation. First, get rid of the negative sign on the right-hand side of the equation by multiplying both sides by (-1):

-0.25 = log$[H_3O^+]$

Next, get rid of the "log" on the right-hand side by taking the "anti-log" of each side of the equation:

antilog(-**0.25)** = $[H_3O^+]$

Use your calculator to get the antilog of (-3.25).

antilog(-**0.25**) = $[H_3O^+]$

0.56 M = $[H_3O^+]$

An aqueous solution with a **pH** of **0.25** has a **$[H_3O^+]$** of **0.56 M** (or **5.6 x 10^{-1} M).**

8.12

a. Basic: pH > 7
b. Basic: $[H_3O^+]$ < 1 x 10^{-7} M
    - Note that the ***exponent is negative***, therefore 1 x 10^{-9} M < 1 x 10^{-7} M.
c. Neutral: from *Equation 8.3*, if $[H_3O^+]$= 1 x 10^{-7} M, then the $[OH^-]$ = 1 x 10^{-7} M.
d. Basic
e. Acidic
f. Acidic: pH < 7
g. Basic: pH > 7
h. Basic: $[OH^-]$ > 1 x 10^{-7} M
i. Acidic: pH < 7
j. Neutral
k. Neutral: pH = 7.00
l. Neutral: from *Equation 8.3*, if $[OH^-]$= 1 x 10^{-7} M, then the $[H_3O^+]$ = 1 x 10^{-7} M.

8.13
Phosphoric acid is a stronger acid than acetic acid. This can be determined by comparing their acidity constants (K_a). The larger the K_a, the stronger the acid. If an equal number of moles of each of these acids were dissolved in separate 1 liter portions of water, the phosphoric acid solution would have a greater $[H_3O^+]$. Both solutions would have pH < 7, however the phosphoric acid would have the lesser pH value since it has a greater $[H_3O^+]$.

8.14

a. $HCl\ (aq) + NaOH\ (aq) \rightleftarrows H_2O\ (l) + NaCl\ (aq)$

b. $HCl\ (aq) + KOH\ (aq) \rightleftarrows H_2O\ (l) + KCl\ (aq)$

9.15

a. HF (acid form) is predominant. The pK_a for HF is 3.18. When the pH < pK_a, then the [HA] > $[A^-]$.
b. HPO_4^{2-} (base form) is predominant. The pK_a for $H_2PO_4^-$ is 7.21. When the pH > pK_a, then the [A] > $[HA^-]$.
c. NH_4^+ (acid form) is predominant. The pK_a for NH_4^+ is 9.31. When the pH < pK_a, then the [HA] > $[A^-]$.

8.16
Choose the acid with a pK_a that is closest to the desired pH. The formula for the *base form* of the conjugate pair will have one fewer hydrogen than the acid, and the charge will be less positive by one charge unit.

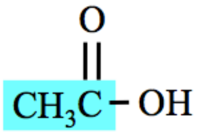
a. CH_3CO_2H and $CH_3CO_2^-$, pK_a = 4.74
b. HCO_3^- and CO_3^{2-}, pK_a = 10.25
c. $H_2PO_4^-$ and HPO_4^{2-}, pK_a = 7.21

Chapter 9

9.1

Step 1: Find and name the parent chain.

The parent chain of the molecule in this example is highlighted blue:



$$CH_3\overset{O}{\overset{\|}{C}}-OH$$

There are two carbon atoms in the parent chain. Replace the “**e**” at the end of the alkane name with “**oic acid.**”

ethan***e*** → ethan***oic acid***

The name of the parent chain is ethanoic acid.

Step 2: Name any alkyl group substituents.

Step 3: Determine the *point of attachment* of alkyl group(s) to the parent chain.

There are no substituents in this molecule.

Step 4: Construct the name of the carboxylic acid by placing the alkyl groups in alphabetical order and specifying their position numbers, followed by the name of the parent chain.

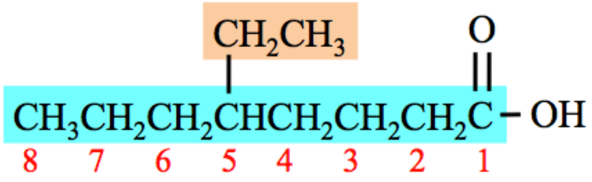
- Since there are no substituents in this molecule, the name of the molecule is simply the name of the parent chain:

ethanoic acid

9.2

Step 1: Find and name the parent chain.

The parent chain of the molecule in this example is highlighted blue:



$$\underset{8}{CH_3}\underset{7}{CH_2}\underset{6}{CH_2}\underset{5}{\overset{CH_2CH_3}{\overset{|}{C}}H}\underset{4}{CH_2}\underset{3}{CH_2}\underset{2}{CH_2}\underset{1}{\overset{O}{\overset{\|}{C}}}-OH$$

Replace the “**e**” at the end of the alkane name with “**oic acid.**” **There are eight carbon atoms in the parent chain.**

octan***e*** → octan***oic acid***

The name of the *parent chain* is **octanoic acid.**

Step 2: Name any alkyl group substituents.

- There is one alkyl group substituent (shaded orange): **ethyl.**

Step 3: Determine the *point of attachment* of alkyl group(s) to the parent chain.

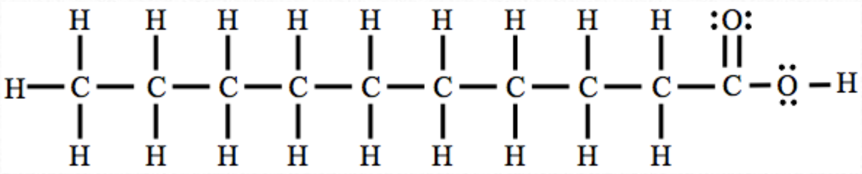
- The ethyl group is attached to carbon number **5** of the parent chain: **5-ethyl.**

Step 4: Construct the name of the carboxylic acid by placing the alkyl groups in alphabetical order and specifying their position numbers, followed by the name of the parent chain. Use a ***dash*** between position *numbers* and *letters*.

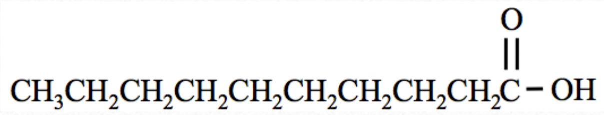
- The name of the molecule is **5-ethyloctanoic acid.**

9.3

Line bond structure (be sure to include all lone pairs in line bond structures):



Condensed structure:

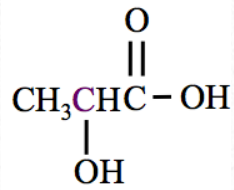


$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2\overset{\overset{O}{||}}{C}-OH$

Skeletal structure:

9.4

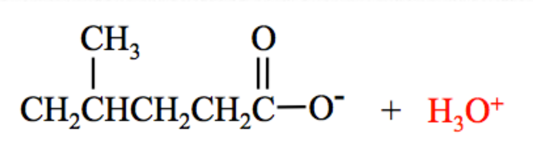
a.



$CH_3\underset{\underset{OH}{|}}{C}H\overset{\overset{O}{||}}{C}-OH$

b. 2-hydroxypropanoic acid.

9.5

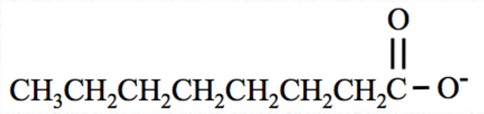


$CH_2\overset{\overset{CH_3}{|}}{C}HCH_2CH_2\overset{\overset{O}{||}}{C}-O^- + H_3O^+$

9.6

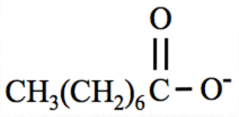
Carboxylate ions are named by replacing the "-ic acid" suffix of their ***acid form*** name with "-ate ion."

a. octanoate ion



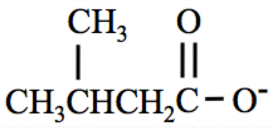
$CH_3CH_2CH_2CH_2CH_2CH_2CH_2\overset{\overset{O}{||}}{C}-O^-$

or



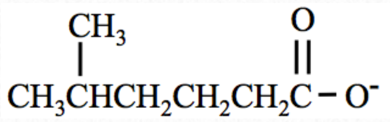
$CH_3(CH_2)_6\overset{\overset{O}{||}}{C}-O^-$

b. 3-methylbutanoate ion



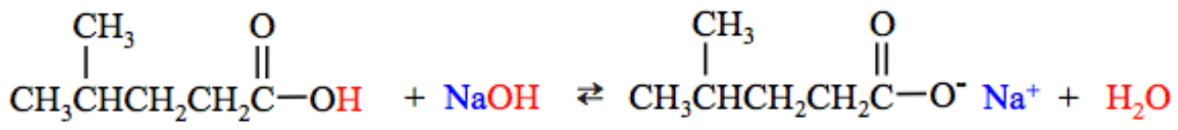
$CH_3\overset{\overset{CH_3}{|}}{C}HCH_2\overset{\overset{O}{||}}{C}-O^-$

c. 5-methylhexanoate ion



$CH_3\overset{\overset{CH_3}{|}}{C}HCH_2CH_2CH_2\overset{\overset{O}{||}}{C}-O^-$

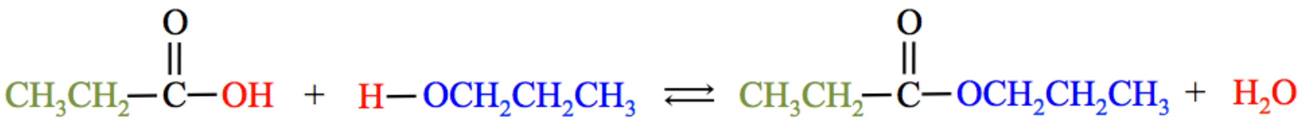
9.7



$$CH_3\overset{CH_3}{\overset{|}{C}}HCH_2CH_2\overset{O}{\overset{\|}{C}}-OH + NaOH \rightleftarrows CH_3\overset{CH_3}{\overset{|}{C}}HCH_2CH_2\overset{O}{\overset{\|}{C}}-O^- \, Na^+ + H_2O$$

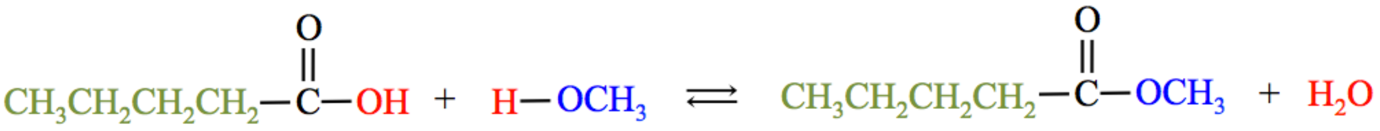
9.8

a.



$$CH_3CH_2-\overset{O}{\overset{\|}{C}}-OH + H-OCH_2CH_2CH_3 \rightleftharpoons CH_3CH_2-\overset{O}{\overset{\|}{C}}-OCH_2CH_2CH_3 + H_2O$$

b.



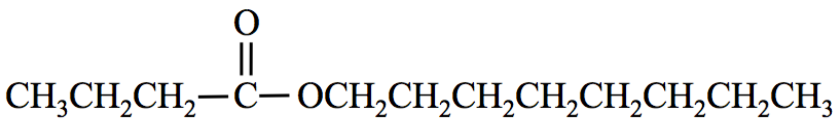
$$CH_3CH_2CH_2CH_2-\overset{O}{\overset{\|}{C}}-OH + H-OCH_3 \rightleftharpoons CH_3CH_2CH_2CH_2-\overset{O}{\overset{\|}{C}}-OCH_3 + H_2O$$

9.9

a. propyl propanoate

b. methyl pentanoate

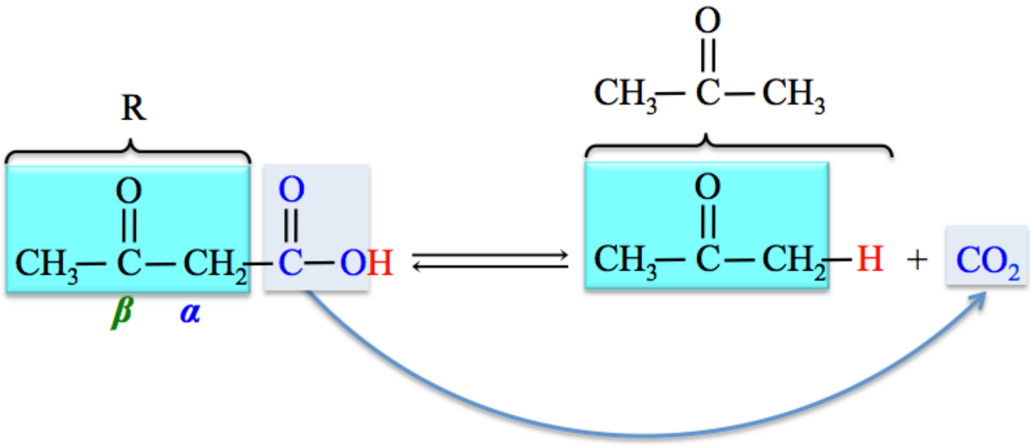
9.10



$$CH_3CH_2CH_2-\overset{O}{\overset{\|}{C}}-OCH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$$

9.11

Remove the carboxyl group (COOH) and replace it with a hydrogen. The products of this reaction are CO_2 and ***acetone***. Healthcare workers are trained to be aware of the odor of *acetone* in a patient's breath as a sign of dangerously high levels of ketone bodies (**ketoacidosis**).



9.12

a. **secondary (2°) amine** - The nitrogen is bonded to ***two*** **R** groups and ***one*** hydrogen atom.

b. **primary (1°) amine** - The nitrogen is bonded to ***one*** **R** group and ***two*** hydrogen atoms.

c. **tertiary (3°) amine** - The nitrogen is bonded to ***three*** **R** groups.

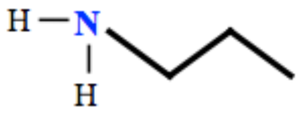
d. **primary (1°) amine**

e. **primary (1°) amine**

f. **secondary (2°) amine**

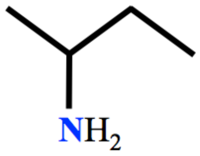
9.13

a.

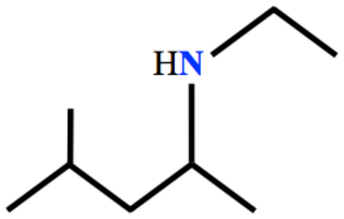


or

b.

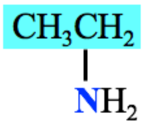


c.



9.14

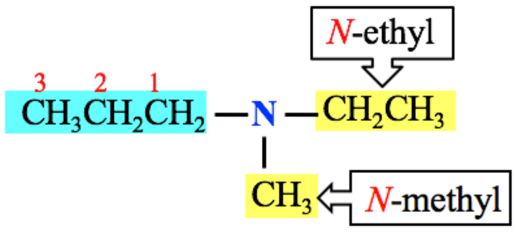
a.



$$\begin{array}{l} CH_3CH_2 \\ \quad | \\ \quad NH_2 \end{array}$$

ethanamine

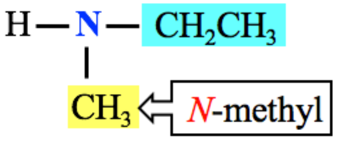
b.



$$\begin{array}{l} CH_3CH_2CH_2 - N - CH_2CH_3 \\ \qquad\qquad\quad\; | \\ \qquad\qquad\;\; CH_3 \end{array}$$

N-ethyl-*N*-methyl-1-propanamine

c.

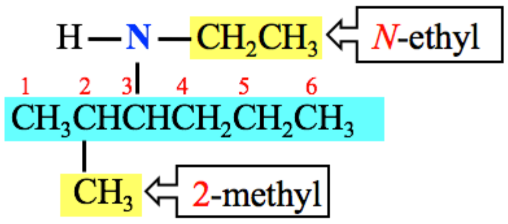


$$\begin{array}{l} H - N - CH_2CH_3 \\ \quad\;\; | \\ \quad CH_3 \end{array}$$

N-methylethanamine

octanamine

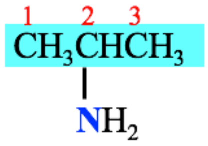
d.



$$\begin{array}{l} \qquad\; H - N - CH_2CH_3 \\ \qquad\qquad\;\; | \\ CH_3CHCHCH_2CH_2CH_3 \\ \qquad | \\ \quad\;\; CH_3 \end{array}$$

N-ethyl-2-methyl-3-hexanamine

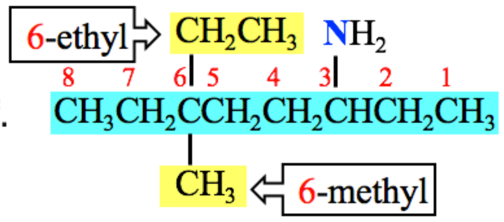
e.



$$\begin{array}{l} CH_3CHCH_3 \\ \qquad | \\ \quad\; NH_2 \end{array}$$

2-propanamine

f.

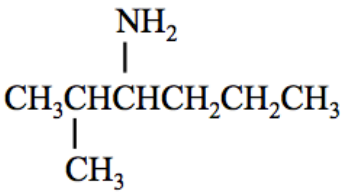


$$\begin{array}{l} \qquad\quad CH_2CH_3 \quad NH_2 \\ \qquad\qquad | \qquad\qquad | \\ CH_3CH_2CCH_2CH_2CHCH_2CH_3 \\ \qquad\qquad | \\ \qquad\quad CH_3 \end{array}$$

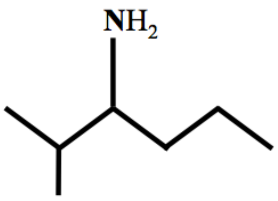
6-ethyl-6-methyl-3-octanamine

9.15

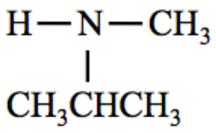
a. 2-methyl-3-hexanamine



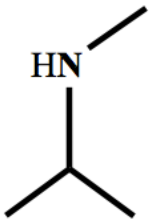
$$\begin{array}{l} \qquad\quad NH_2 \\ \qquad\qquad | \\ CH_3CHCHCH_2CH_2CH_3 \\ \qquad | \\ \quad\; CH_3 \end{array}$$



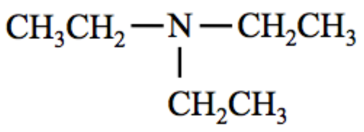
b. *N*-methyl-2-propanamine



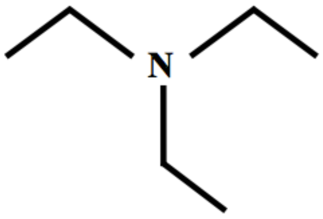
$$\begin{array}{l} H - N - CH_3 \\ \qquad | \\ CH_3CHCH_3 \end{array}$$



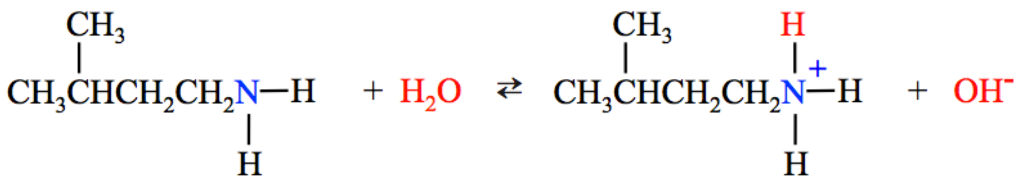
c. *N*,*N*-diethylethanamine



$$\begin{array}{l} CH_3CH_2 - N - CH_2CH_3 \\ \qquad\qquad\; | \\ \qquad\quad CH_2CH_3 \end{array}$$

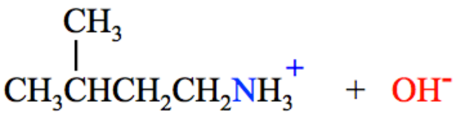


9.16



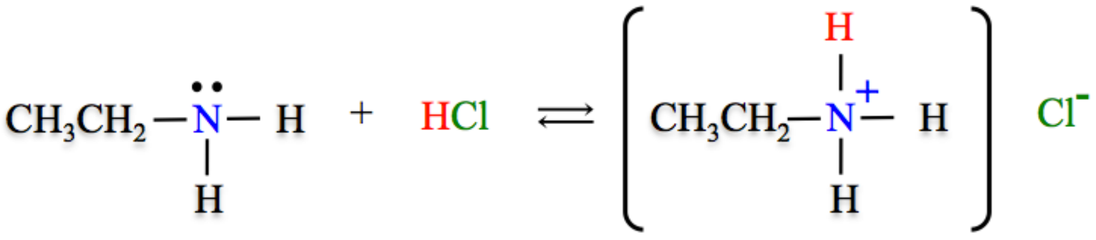
$$\underset{\substack{|\\ H}}{\overset{\substack{CH_3\\ |}}{CH_3CHCH_2CH_2N}}{-}H + H_2O \rightleftharpoons \overset{\substack{CH_3\\ |}}{CH_3CHCH_2CH_2}\underset{\substack{|\\ H}}{\overset{\substack{H\\ |}}{N^+}}{-}H + OH^-$$

or



$$\overset{\substack{CH_3\\ |}}{CH_3CHCH_2CH_2NH_3^+} + OH^-$$

9.17



$$CH_3CH_2{-}\underset{\substack{|\\ H}}{\ddot{N}}{-}H + HCl \rightleftharpoons \left[CH_3CH_2{-}\underset{\substack{|\\ H}}{\overset{\substack{H\\ |}}{N^+}}{-}H \right] Cl^-$$

or

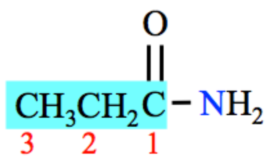
$CH_3CH_2NH_3^+\ Cl^-$

Note that the quaternary ammonium ion product is an ionic compound; there is not a covalent bond between the quaternary ammonium ion and the chloride ion.

9.18

Step 1: Find and name the parent chain.

The parent chain of the molecule in this example is highlighted blue:



$$\underset{3\ \ \ 2\ \ \ 1}{CH_3CH_2\overset{\substack{O\\ \|}}{C}}{-}NH_2$$

There are three carbon atoms in the parent chain. Replace the "**e**" at the end of the alkane name with "**amide**."

propan***e*** ⟶ propan***amide***

The name of the parent chain is ethanoic acid.

Step 2: Name any alkyl group substituents.

Step 3: Determine the *point of attachment* of any alkyl groups.

There are no substituents in this molecule.

Step 4: Construct the name of the amide by placing the alkyl groups in alphabetical order and specifying their position, followed by the name of the parent chain.

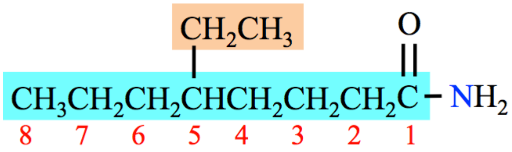
- Since there are no substituents in this molecule, the name of the molecules is simply the name of the parent chain:

  propanamide

9.19

Step 1: Find and name the parent chain.

The parent chain of the molecule in this example is highlighted blue:



$$CH_3CH_2CH_2\overset{CH_2CH_3}{\overset{|}{C}}HCH_2CH_2CH_2\overset{O}{\overset{\|}{C}}-NH_2$$

Replace the "e" at the end of the alkane name with "amide." **There are eight carbon atoms in the parent chain.**

octan***e*** ⟶ octan***amide***

The name of the *parent chain* is **octanamide.**

Step 2: Name any alkyl group substituents.

There is one alkyl group substituent (shaded orange): **ethyl.**

Step 3: Determine the *point of attachment* of any alkyl groups.

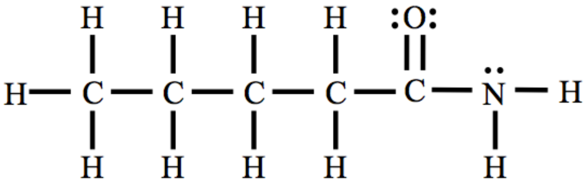
The ethyl group is attached to carbon number 5 of the parent chain: **5-ethyl.**

Step 4: Construct the name of the amide by placing the alkyl groups in alphabetical order and specifying their positions, followed by the name of the parent chain. Use a ***dash*** between position *positions* and *letters*.

- The name of the molecule is **5-ethyloctanamide.**

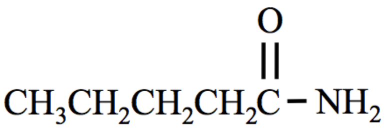
9.20

Line bond structure:



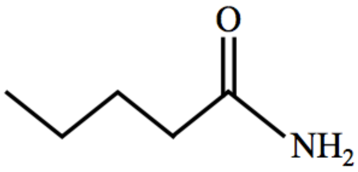
- Draw the bonds to *all atoms* and include *all lone pairs* in line bond structures.

Condensed structure:

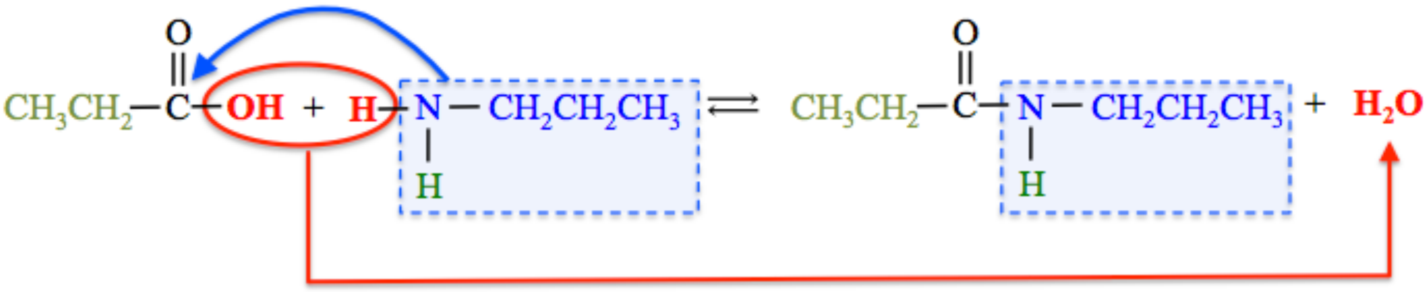


$$CH_3CH_2CH_2CH_2\overset{O}{\overset{\|}{C}}-NH_2$$

Skeletal structure:



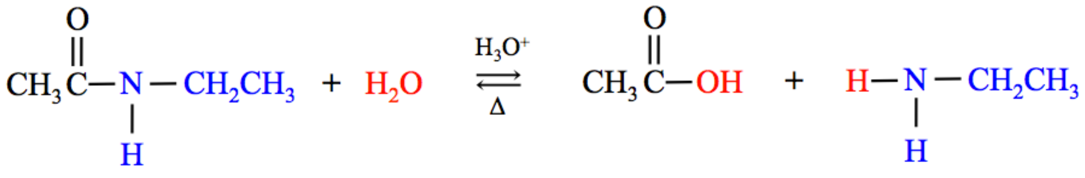
9.21



N-propylpropanamide

9.22

Answer:

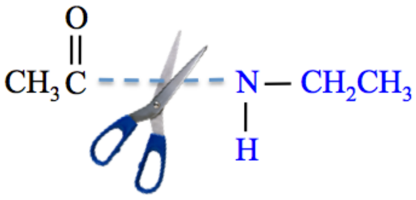


$$CH_3\overset{\overset{O}{\|}}{C}-\underset{\underset{H}{|}}{N}-CH_2CH_3 + H_2O \xrightleftharpoons[\Delta]{H_3O^+} CH_3\overset{\overset{O}{\|}}{C}-OH + H-\underset{\underset{H}{|}}{N}-CH_2CH_3$$

ethanoic acid **ethanamine**

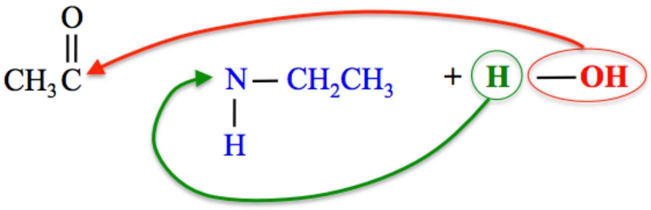
Detailed Solution:

1) Break the bond between the **carbonyl group** and the **nitrogen**.

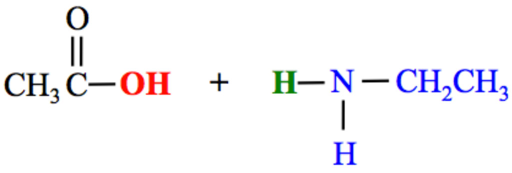


$$CH_3\overset{\overset{O}{\|}}{C} - - - - \underset{\underset{H}{|}}{N}-CH_2CH_3$$

2) Bond the **OH** from water to the **carbonyl carbon** and bond the **H** from water to the **nitrogen**.



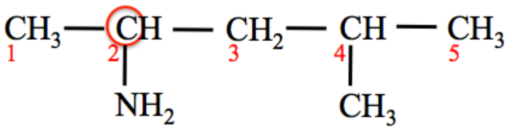
$$CH_3\overset{\overset{O}{\|}}{C} \quad \underset{\underset{H}{|}}{N}-CH_2CH_3 + H-OH$$



$$CH_3\overset{\overset{O}{\|}}{C}-OH + H-\underset{\underset{H}{|}}{N}-CH_2CH_3$$

9.23

There is <u>one chiral carbon</u> - carbon number 2.



$$\underset{1}{CH_3}-\underset{\underset{NH_2}{|}}{\overset{2}{CH}}-\underset{3}{CH_2}-\underset{\underset{CH_3}{|}}{\overset{4}{CH}}-\underset{5}{CH_3}$$

Carbon number 1 is bonded to three identical groups - three hydrogens.

Carbon number 2 is chiral - it is bonded to ***four*** different groups - a hydrogen, a methyl group, an amino group (NH_2), and a larger alkyl group.

Carbon number 3 is bonded to two identical groups - two hydrogens.

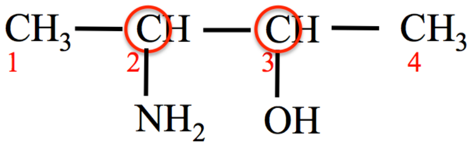
Carbon number 4 is bonded to two identical groups - two methyl groups.

Carbon number 5 is bonded to three identical groups - three hydrogens.

9.24

If **n** = the number of chiral carbons, then the maximum number of stereoisomers is 2^n.

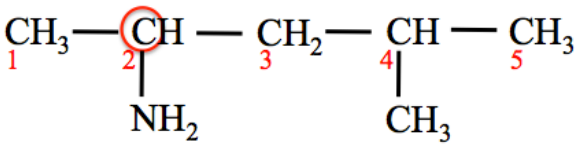
a) **Four stereoisomers:** There are *<u>two</u>* chiral carbons - carbons number 2 and 3.



$$\underset{1}{CH_3}-\underset{\underset{NH_2}{|}}{\overset{2}{CH}}-\underset{\underset{OH}{|}}{\overset{3}{CH}}-\underset{4}{CH_3}$$

Maximum Number of Stereoisomers $= 2^n = 2^2 = 4$

b) **Two stereoisomers**: There is *<u>one</u>* chiral carbon - carbon number 2.



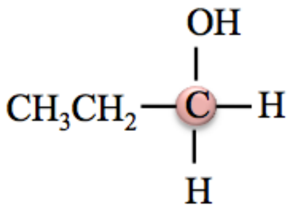
$$\underset{1}{CH_3}-\underset{\underset{NH_2}{|}}{\overset{2}{CH}}-\underset{3}{CH_2}-\underset{\underset{CH_3}{|}}{\overset{4}{CH}}-\underset{5}{CH_3}$$

Maximum Number of Stereoisomers $= 2^n = 2^1 = 2$

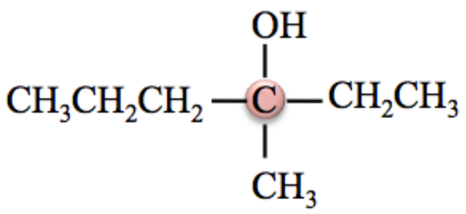
Chapter 10

10.1

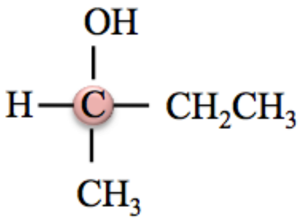
The carbons that are “carrying” the hydroxyl group in the structures shown below are shaded red.

a.


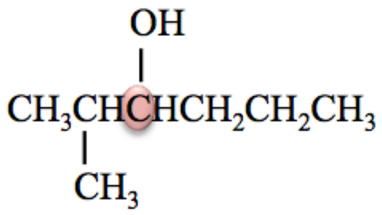
$CH_3CH_2-\overset{\overset{OH}{|}}{\underset{\underset{H}{|}}{C}}-H$

b.


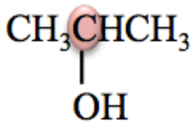
$CH_3CH_2CH_2-\overset{\overset{OH}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2CH_3$

c.


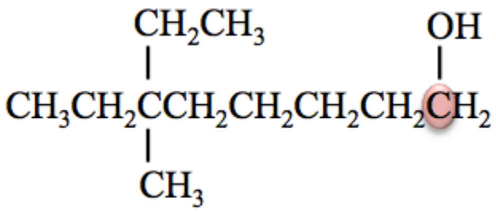
$H-\overset{\overset{OH}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2CH_3$

d.


$CH_3\underset{\underset{CH_3}{|}}{CH}\overset{\overset{OH}{|}}{C}HCH_2CH_2CH_3$

e.


$CH_3\underset{\underset{OH}{|}}{CH}CH_3$

f.


$CH_3CH_2\overset{\overset{CH_2CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}CH_2CH_2CH_2CH_2\overset{\overset{OH}{|}}{CH_2}$

a. **primary (1°) alcohol** - *The carbon “carrying” the hydroxyl group* is bonded to ***one*** **R** group.

b. **tertiary (3°) alcohol** - *The carbon “carrying” the hydroxyl group* is bonded to ***three*** **R** groups.

c. **secondary (2°) alcohol** - *The carbon “carrying” the hydroxyl group* is bonded to ***two*** **R** groups.

d. **secondary (2°) alcohol** - *The carbon “carrying” the hydroxyl group* is bonded to ***two*** **R** groups.

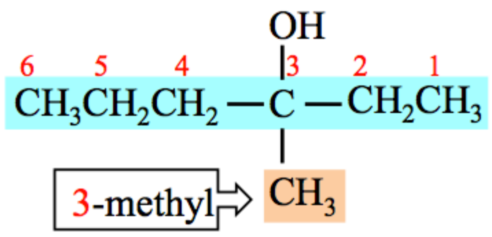
e. **secondary (2°) alcohol** - *The carbon “carrying” the hydroxyl group* is bonded to ***two*** **R** groups.

f. **primary (1°) alcohol** - *The carbon “carrying” the hydroxyl group* is bonded to ***one*** **R** group.

10.2

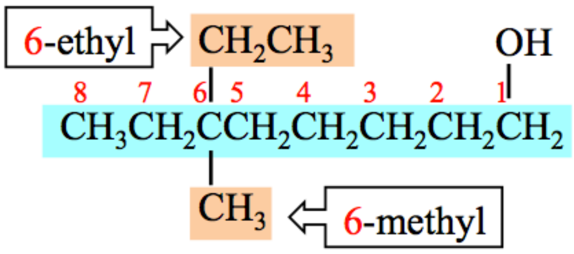
a. CH_3-OH

methanol

b.


$CH_3CH_2CH_2-\overset{\overset{OH}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2CH_3$

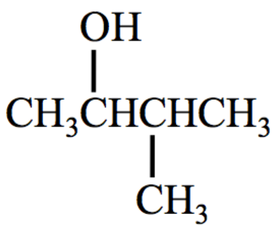
3-methyl-3-hexanol

c.


$CH_3CH_2\overset{\overset{CH_2CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}CH_2CH_2CH_2CH_2\overset{\overset{OH}{|}}{CH_2}$

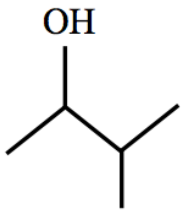
6-ethyl-6-methyl-1-octanol

10.3



$$CH_3CH(OH)CH(CH_3)CH_3$$

condensed structure



skeletal structure

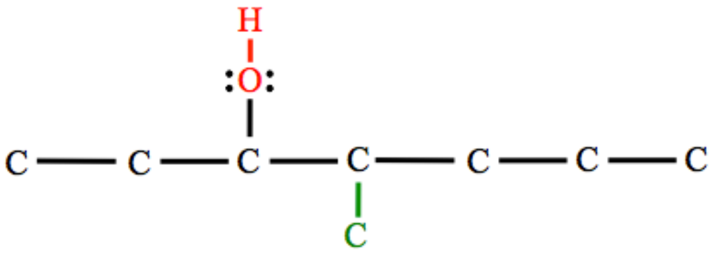
10.4

First draw the **carbons** of the *parent chain*. The parent chain is **3-heptanol**, therefore it contains *seven* carbons.

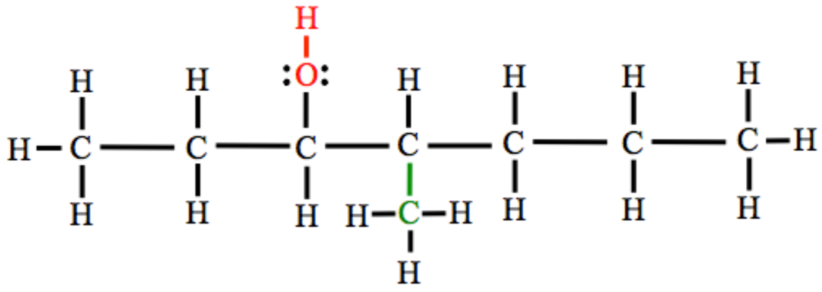
$$C-C-C-C-C-C-C$$

The “**3-**” prefix in **3-heptanol** indicates that the *hydroxyl group* is bonded to carbon number **3** of the parent chain. Since we are drawing a line bond structure, we must include the lone pairs on oxygens. Add enough lone pairs to the ***oxygens*** so that the octet rule is satisfied.

Next, add the ***carbon*** of the methyl substituent. Since we are drawing the structure of **4-methyl**-3-heptanol, the methyl group’s carbon (shaded green) is attached to carbon number **4** of the parent chain.



To finish, add enough hydrogens to each carbon in order to satisfy the octet rule:



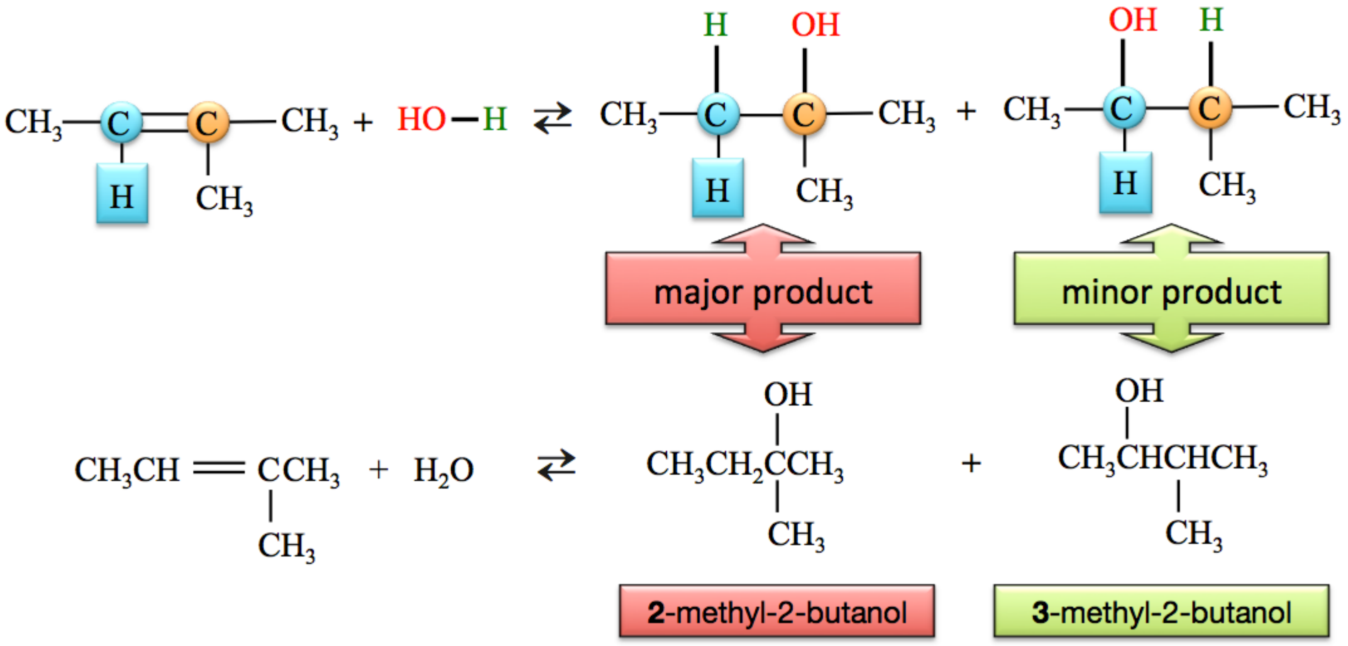
10.5

In a ***nucleophilic substitution reaction,*** the nucleophile (OH^-) ***substitutes*** for (*replaces)* the halogen (F, Cl, Br, or I).

$$CH_3CH_2-Br \quad + \quad OH^- \quad \rightleftharpoons \quad CH_3CH_2-OH \quad + \quad Br^-$$

10.6

The left-most double-bonded carbon in 2-methyl-2-butene (shaded blue) is bonded to ***one*** hydrogen (shaded blue). The right-most double-bonded carbon (shaded orange) is ***not bonded to any*** hydrogens. The ***major product*** is formed by adding the **H** (from water) to the double-bonded carbon that originally carried the most hydrogens - *the rich get richer* - and the **OH** is added to the *other* double-bonded carbon. The ***minor product*** is formed by adding the **H** and **OH** in a manner opposite to that described for the *major product*.



10.7

Step 1. Identify the alkyl group names for each of the R groups.

- There is an **ethyl** and a **propyl** alkyl group in this molecule.

Step 2. Construct the name of the ether by placing the alkyl groups in alphabetical order followed by the word "ether."

- Use a space between the alkyl group names and before the word "ether."
  - **ethyl propyl ether**

10.8

Step 1: Find and name the parent chain.

The *parent chain is the longest, continuous chain of carbon atoms that contains the point of attachment to the thiol group* (SH).

- Count the number of carbon atoms in the parent chain. There are ***five*** carbons in the parent chain. The term "**thiol**" is added to the end of the alkane name that indicates the number of carbons in the parent chain.

pentane ⟶ pentane**thiol**

- For thiols with ***more than two carbons***, the position of the *the point of attachment to the* ***thiol group*** (-**SH**) must be indicated by adding a number before the parent chain name as described below. Position number **1** is assigned to the carbon at the *end of the parent chain* that is ***closest to the point of attachment to the thiol group*.**
  - The **thiol group** is bonded to carbon number **1** of the parent chain, then "**1-**" is used as a prefix to the parent chain name. **The parent chain is called 1-pentanethiol.**

Step 2: Name any alkyl group substituents. *There are no substituents in this example*.
Step 3: Determine the *point of attachment* of alkyl group) to the parent chain.

- **There are no substituents in this example.**

Step 4: Construct the name of the thiol by placing the alkyl groups in alphabetical order and specifying their position numbers, followed by the name of the parent chain. Use a ***dash*** between position *numbers* and *letters*.

- The name of the molecule is **1-pentanethiol.**

10.9

Step 1. Identify the alkyl group names for each of the R groups.

- There is an **ethyl** and a **propyl** alkyl group in this molecule.

Step 2. Construct the name of the sulfide by placing the alkyl groups in alphabetical order followed by the word "sulfide."

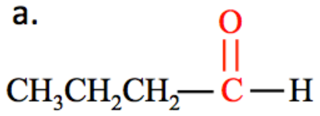
- Use a space between the alkyl group names and before the word "sulfide."
  - **ethyl propyl sulfide**

10.10

$CH_3-S-S-CH_3$

10.11

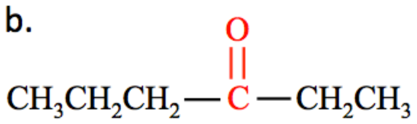
a.



$CH_3CH_2CH_2-\overset{O}{\overset{||}{C}}-H$

An aldehyde - the carbonyl carbon is bonded to ***one*** **R** group **and** ***one*** hydrogen.

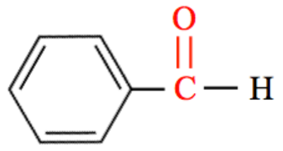
b.



$CH_3CH_2CH_2-\overset{O}{\overset{||}{C}}-CH_2CH_3$

A ketone - the carbonyl carbon is bonded to ***two*** **R groups.**

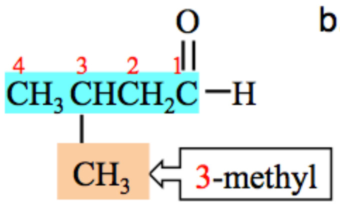
c.



An aldehyde - the carbonyl carbon is bonded to ***one*** **R** group **and** ***one*** hydrogen.

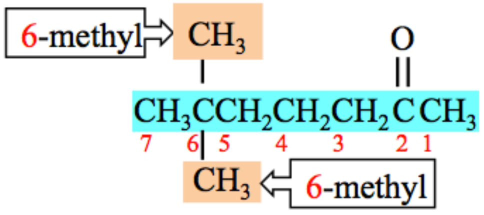
10.12

a.



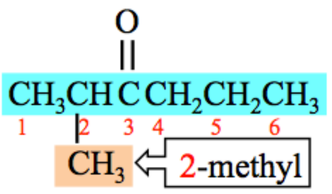
3-methylbutanal

b.



6,6-dimethyl-2-heptanone

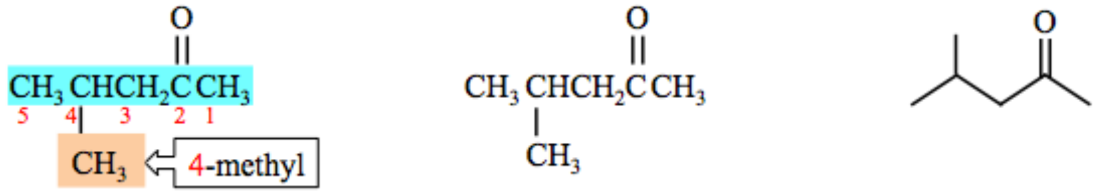
c.



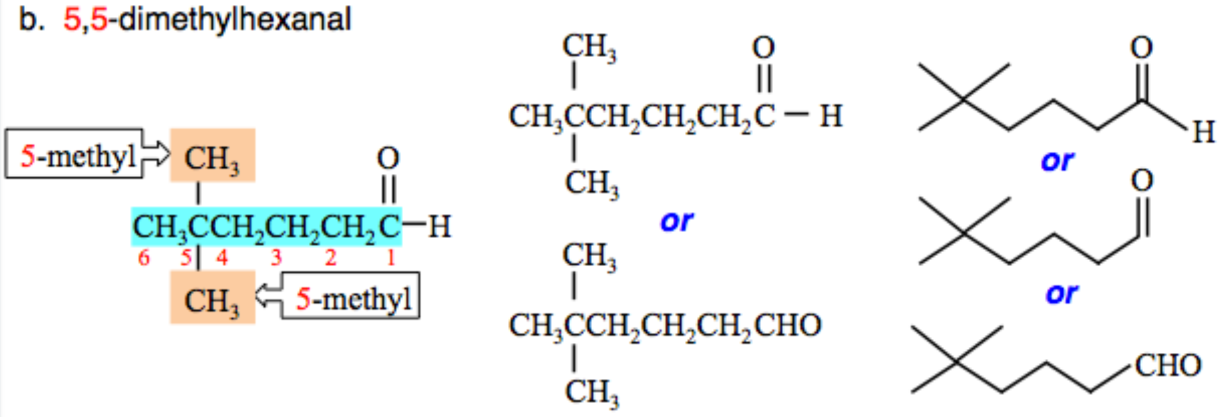
2-methyl-3-hexanone

10.13

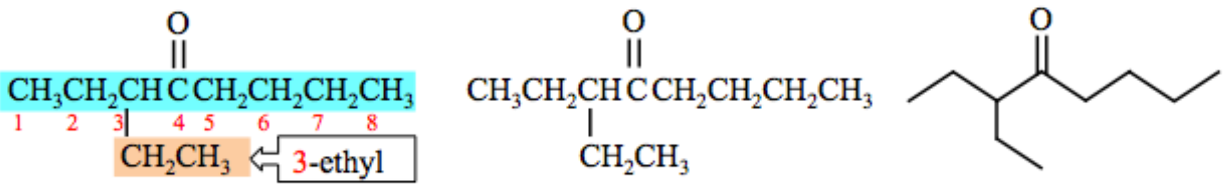
a. 4-methyl-2-pentanone



b. 5,5-dimethylhexanal

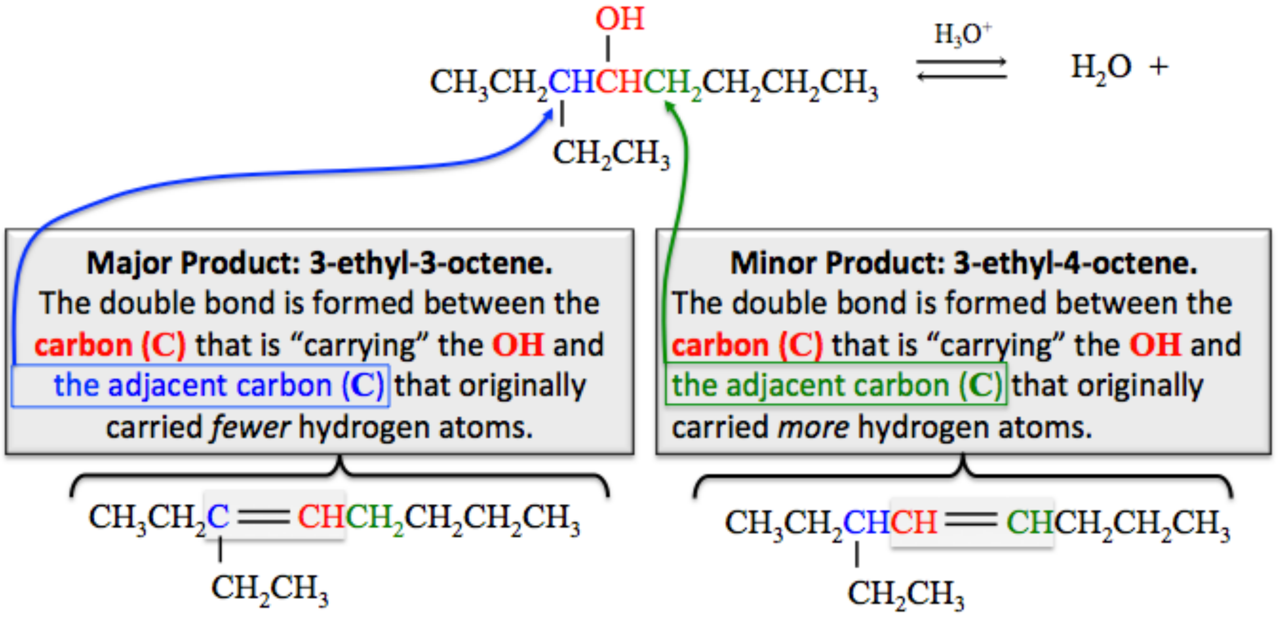


c. 3-ethyl-4-octanone



10.14

In the formation of the major alkene product, the adjacent carbon that originally contained fewer hydrogens (in blue font) will lose ***another*** hydrogen when the double bond is formed in the product- "*the **poor** get **poorer***" - where the **H**s represent money.



$$CH_3CH_2\underset{\displaystyle CH_2CH_3}{CH}\overset{\displaystyle OH}{CH}CH_2CH_2CH_2CH_3 \overset{H_3O^+}{\rightleftharpoons} H_2O +$$

Major Product: 3-ethyl-3-octene. The double bond is formed between the **carbon (C)** that is "carrying" the **OH** and the adjacent carbon (**C**) that originally carried *fewer* hydrogen atoms.

$$CH_3CH_2\underset{\displaystyle CH_2CH_3}{C}{=}CHCH_2CH_2CH_2CH_3$$

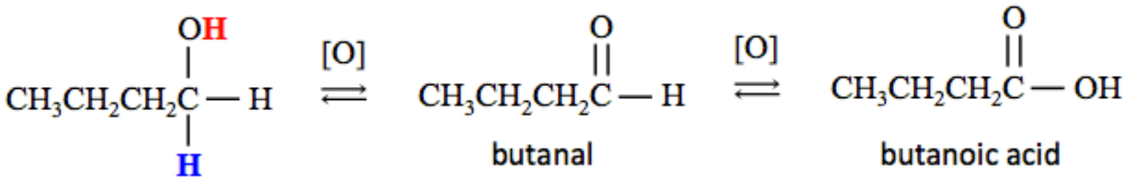
Minor Product: 3-ethyl-4-octene. The double bond is formed between the **carbon (C)** that is "carrying" the **OH** and the adjacent carbon (**C**) that originally carried *more* hydrogen atoms.

$$CH_3CH_2\underset{\displaystyle CH_2CH_3}{CH}CH{=}CHCH_2CH_2CH_3$$

10.15

Aldehyde Formation: When an alcohol is oxidized to an ***aldehyde***, the hydrogen from the hydroxyl group (**OH**) and a hydrogen (**H**) attached to *the carbon that is carrying the hydroxyl group* are both removed, <u>and</u> the C-O *single* bond is changed to *double* bond.

Carboxylic Acid Formation: Certain oxidizing agents, such as CrO_3 and MnO_4^-, can further oxidize aldehydes to produce carboxylic acids.

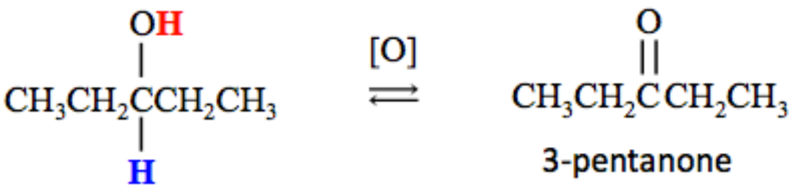


$$CH_3CH_2CH_2\underset{\displaystyle H}{\overset{\displaystyle OH}{C}}-H \overset{[O]}{\rightleftharpoons} CH_3CH_2CH_2\overset{\displaystyle O}{\overset{\|}{C}}-H \overset{[O]}{\rightleftharpoons} CH_3CH_2CH_2\overset{\displaystyle O}{\overset{\|}{C}}-OH$$

When oxidation is indicated by using "**[O]**," then the identity of the oxidizing agent and the destination of the hydrogens and/or source of oxygen atoms may be omitted from the chemical equation. When doing so, the equation does not need to be balanced.

10.16

Ketone Formation: When an alcohol is oxidized to an ***aldehyde***, the hydrogen from the hydroxyl group (**OH**) and a hydrogen (**H**) attached to *the carbon that is carrying the hydroxyl group* are both removed, <u>and</u> the C-O *single* bond is changed to *double* bond. The oxidation of a secondary alcohol produces a ***ketone.***

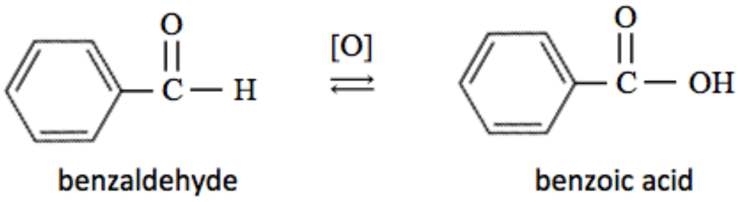


$$CH_3CH_2\underset{\displaystyle H}{\overset{\displaystyle OH}{C}}CH_2CH_3 \overset{[O]}{\rightleftharpoons} CH_3CH_2\overset{\displaystyle O}{\overset{\|}{C}}CH_2CH_3$$

When oxidation is indicated by using "**[O]**," then the identity of the oxidizing agent and the destination of the hydrogens may be omitted from the chemical equation. When doing so, the equation does not need to be balanced.

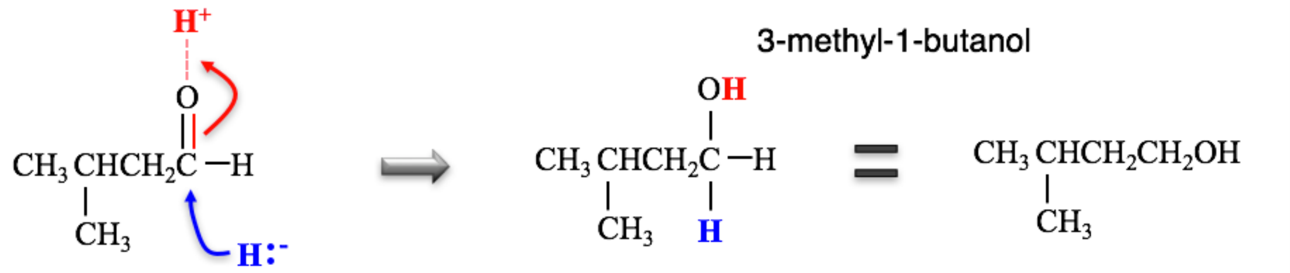
10.17

Aldehydes can be oxidized to ***carboxylic acids***. In this reaction, benzaldehyde is oxidized to form benzoic acid.



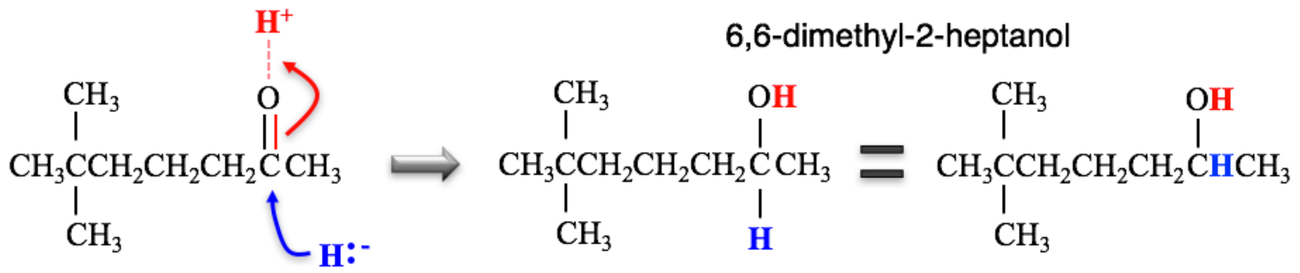
10.18

a. **Aldehydes** are reduced to **primary alcohols**.



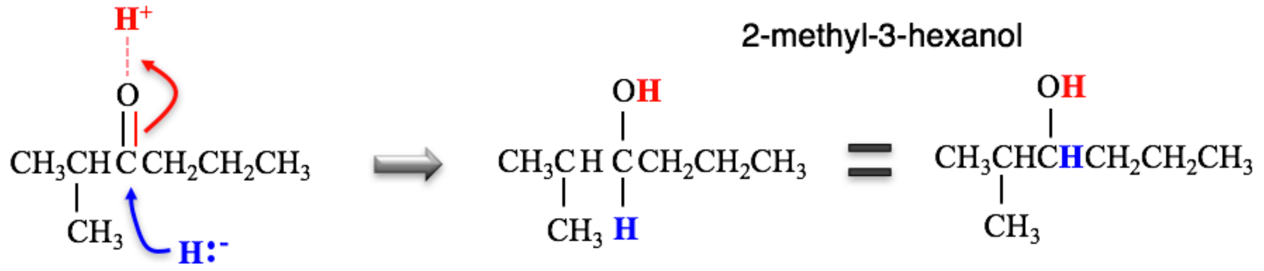
3-methyl-1-butanol

b. **Ketones** are reduced to **secondary alcohols**.



6,6-dimethyl-2-heptanol

c. **Ketones** are reduced to **secondary alcohols**.

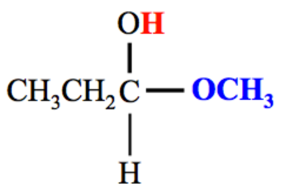


2-methyl-3-hexanol

10.19

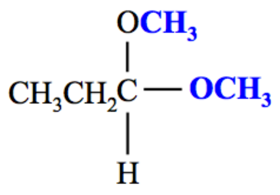
Answer:

Hemiacetal



$$\mathrm{CH_3CH_2}\overset{\mathrm{OH}}{\underset{\mathrm{H}}{\mathrm{C}}}\mathrm{-OCH_3}$$

Acetal

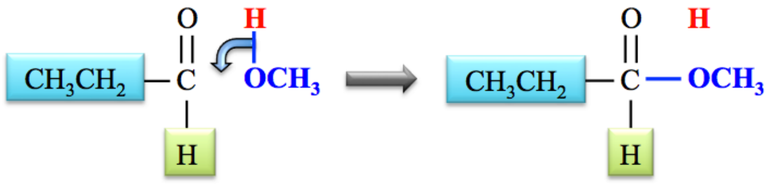


$$\mathrm{CH_3CH_2}\overset{\mathrm{OCH_3}}{\underset{\mathrm{H}}{\mathrm{C}}}\mathrm{-OCH_3}$$

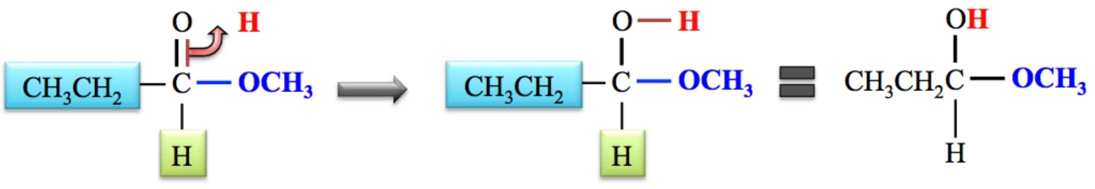
Detailed Solution:

1) Redraw the aldehyde as shown below.

2) Draw the *alcohol molecule* to the side of the carbonyl group, and then flip the bond from the *alcohol's hydroxyl group* downward to make a new bond to the carbonyl carbon.

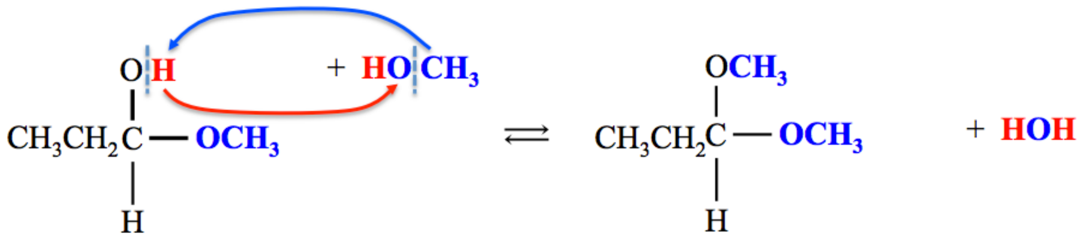


3) Flip one pair of electrons from the carbonyl group upward to form a bond to the remaining *unbound* hydrogen.



hemiacetal

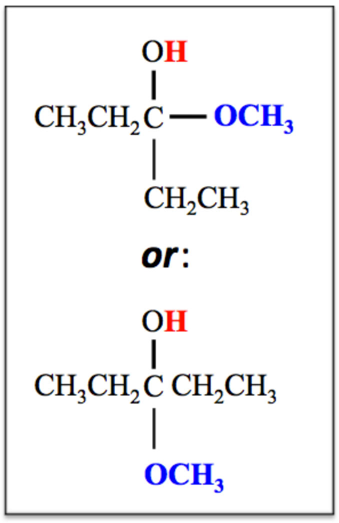
4) The ***hemiacetal*** that is formed can react with a *second ethanol molecule* to form an **acetal** and an H_2O molecule. The structure of the **acetal** can be drawn by ***exchanging*** the **R** group *of the alcohol* (CH_3) and the **H** from the *hemiacetal's* hydroxyl group:



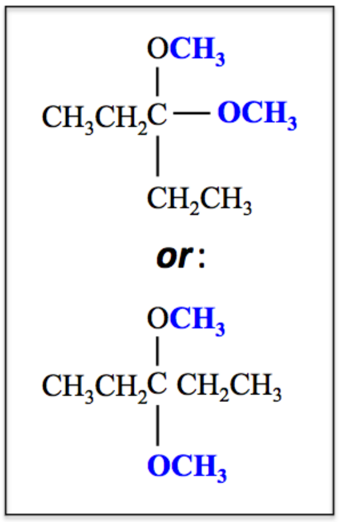
10.20

Answer

Hemiacetal

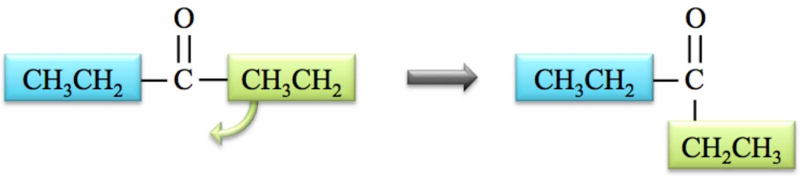


Acetal

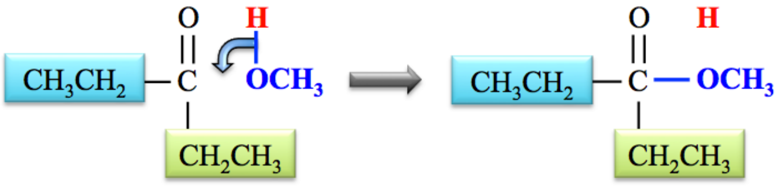


Detailed Solution:

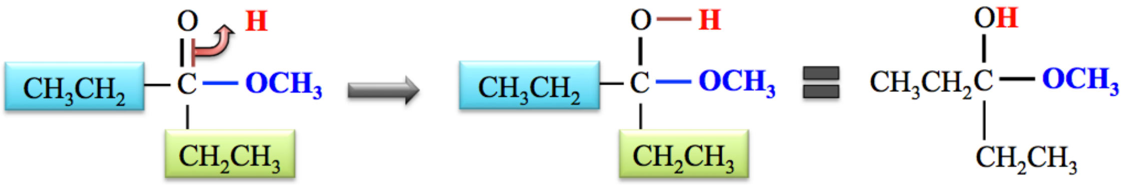
1) Redraw the ketone as shown below.



2) Draw the *alcohol molecule* to the side of the carbonyl group, and then flip the bond from the *alcohol's hydroxyl group* downward to make a new bond to the carbonyl carbon.

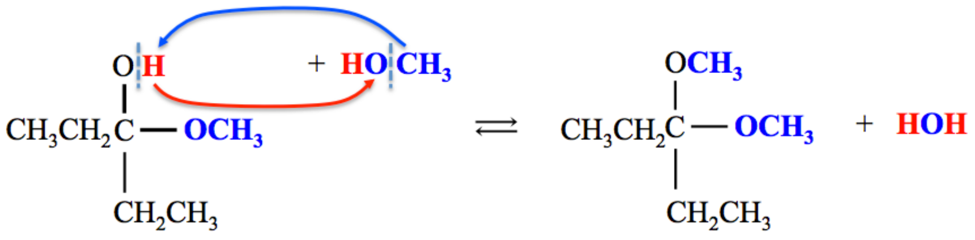


3) Flip one pair of electrons from the carbonyl group upward to form a bond to the remaining *unbound* hydrogen.



hemiacetal

4) The ***hemiacetal*** that is formed can react with a *second ethanol molecule* to form an **acetal** and an H_2O molecule. The structure of the **acetal** can be drawn by ***exchanging*** the **R** group *of the alcohol* (CH_3) and the **H** from the *hemiacetal's* hydroxyl group:

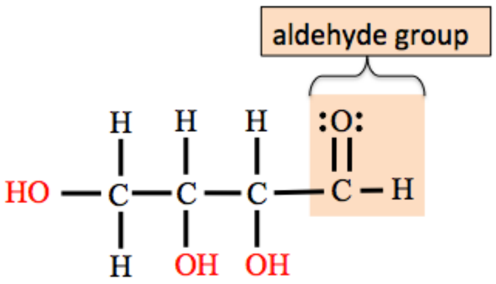


hemiacetal **methanol** **acetal** **H_2O**

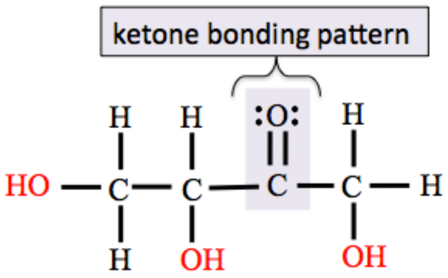
Chapter 11

11.1

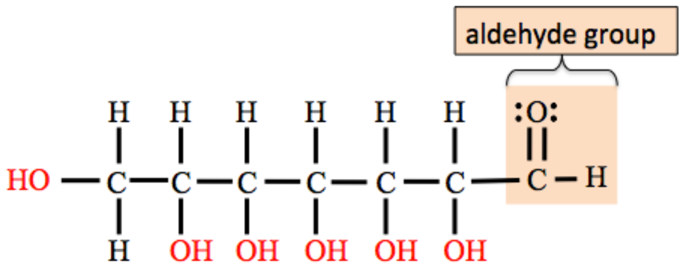
a. **Aldose:** contains an aldehyde group (**CHO**).



b. **Ketose:** contains the ketone bonding pattern.

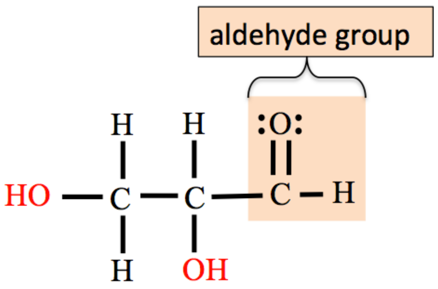


c. **Aldose:** contains an aldehyde group (**CHO**).

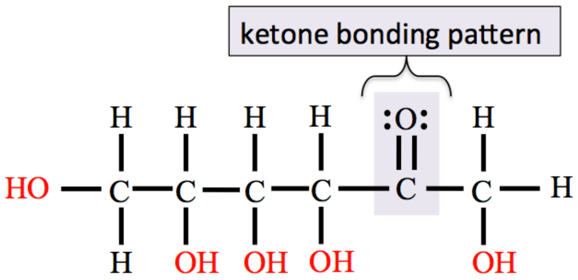


11.2

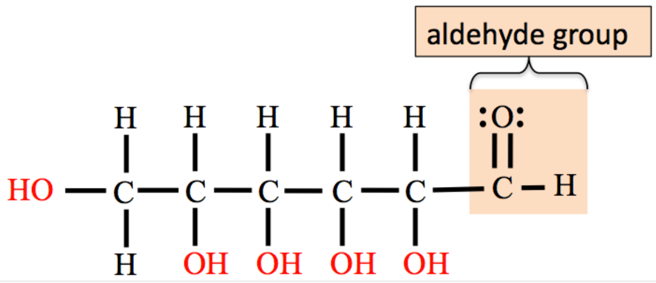
a. **Aldotriose:** contains an aldehyde group (aldose) and three carbons (triose).



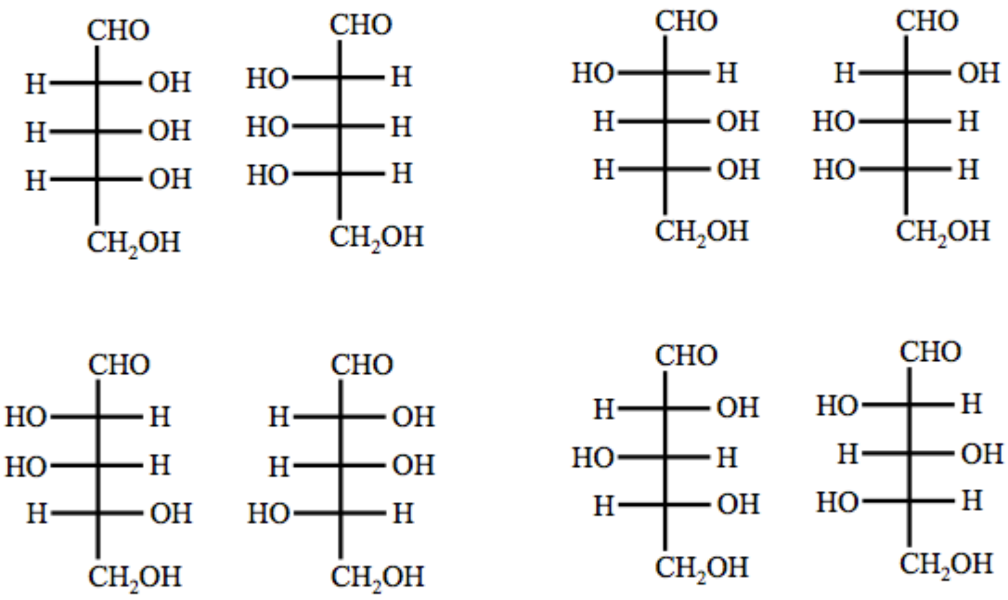
b. **Ketohexose:** contains the ketone bonding pattern (ketose) and six carbons (hexose).



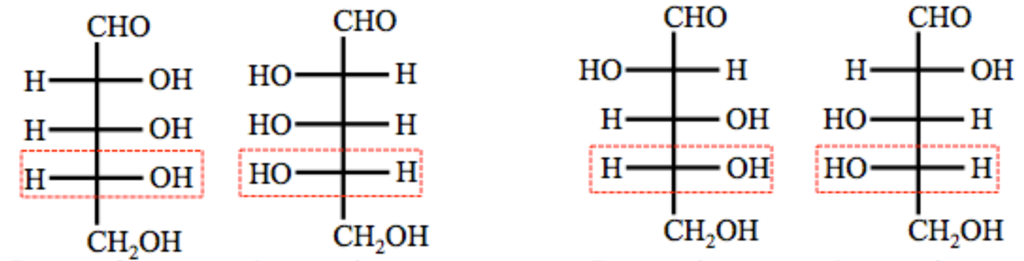
c. **Aldohexose:** contains an aldehyde group (aldose) and six carbons (hexose).



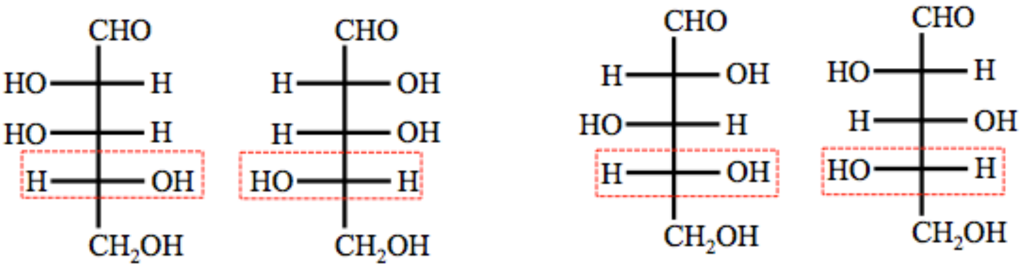
11.3



11.4



D-stereoisomer L-stereoisomer D-stereoisomer L-stereoisomer



D-stereoisomer L-stereoisomer D-stereoisomer L-stereoisomer

11.5

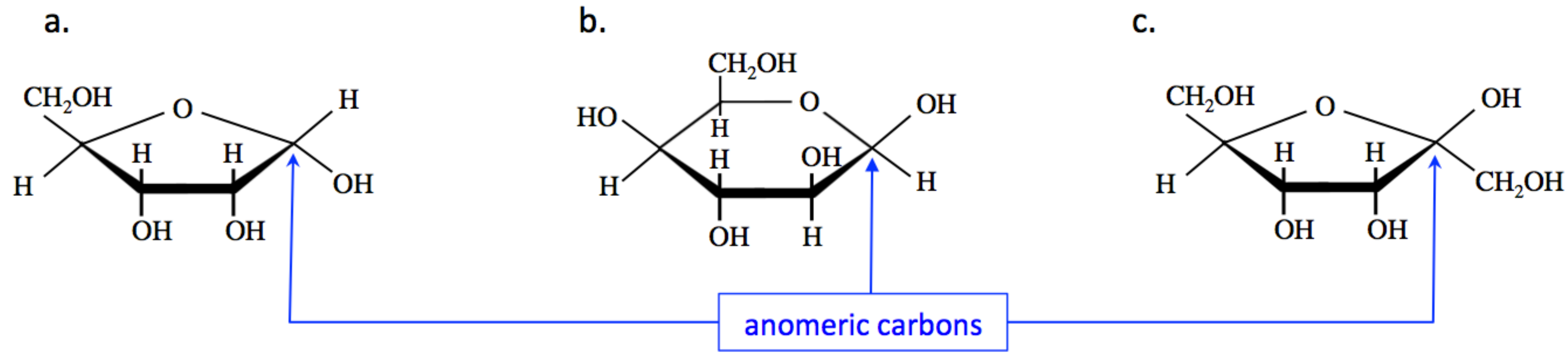
a. **furanose:** the ring contains ***five*** atoms

b. **pyranose:** the ring contains ***six*** atoms

c. **furanose:** the ring contains ***five*** atoms

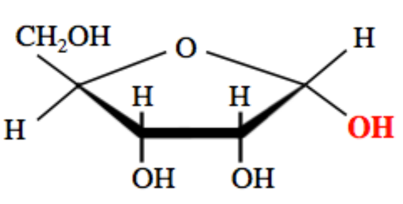
11.6

The **anomeric carbon** is the ***chiral hemiacetal carbon***. It is easy to identify the anomeric carbon in a Haworth projection of a D-sugar; it is the ring-carbon to the ***right-hand side*** of the the ***ring-oxygen***. You will only see D-sugars in the remainder of this book.



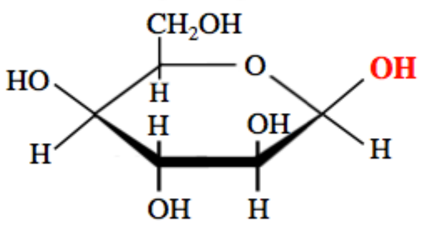
11.7

a.



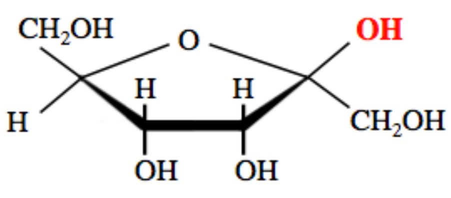
α-anomer: the **OH** on the *anomeric carbon* is oriented ***downward*** from the ring.

b.



β-anomer: the **OH** on the *anomeric carbon* is oriented ***upward*** from the ring.

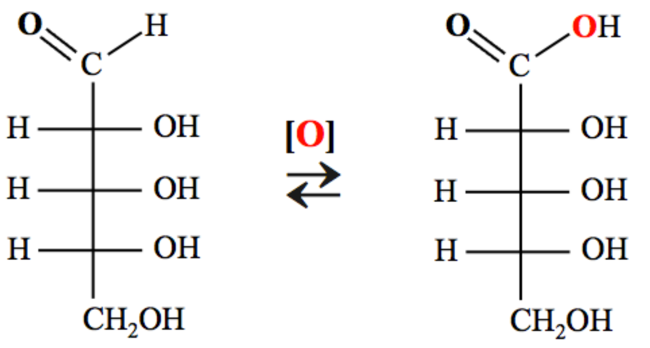
c.



β-anomer: the **OH** on the *anomeric carbon* is oriented ***upward*** from the ring.

11.8

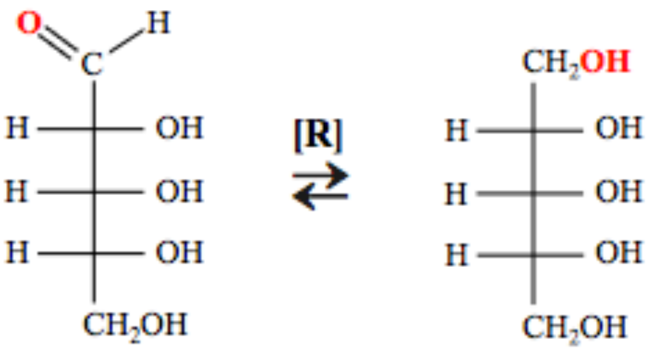
In a **carboxylic acid sugar**, an aldehyde group ($\mathbf{-CHO}$) of a monosaccharide is ***oxidized*** to a ***carboxyl group*** ($\mathbf{-COOH}$).



D-ribose **a carboxylic acid sugar**

11.9

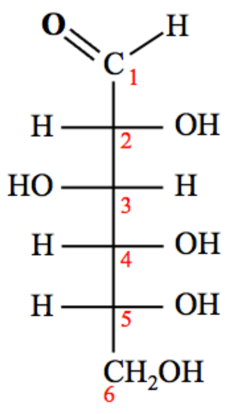
Alcohol sugars are derived when the carbonyl group ($C{=}O$) of a monosaccharide is ***reduced*** to a hydroxyl group.



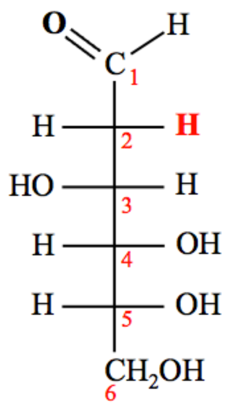
D-ribose **an alcohol sugar**

11.10

Deoxy sugars are derived when a hydroxyl group ($\mathbf{-OH}$) in a monosaccharide is replaced by a ***hydrogen atom***.



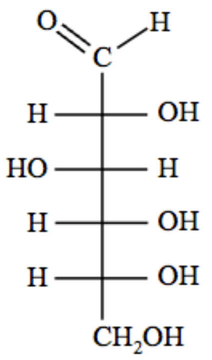
D-glucose



D-2-deoxyglucose

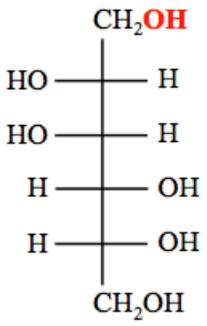
11.11

a.



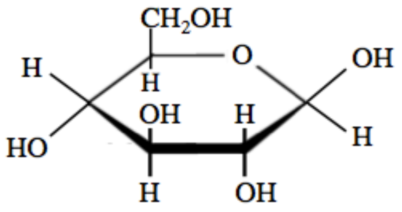
monosaccharide
a polyhydroxyl *aldehyde*

b.



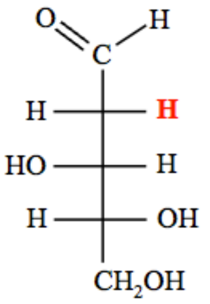
alcohol sugar
The carbonyl group (C=O) of a monosaccharide is *reduced* to a *hydroxyl group*.

c.



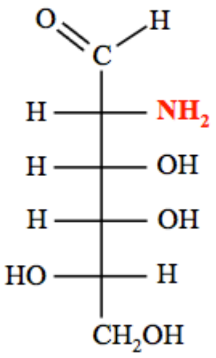
monosaccharide
the cyclic form

d.



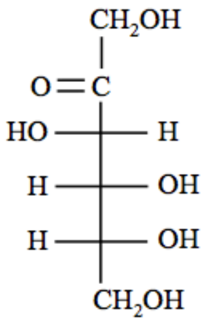
deoxy sugar
A hydroxyl group (OH) in a monosaccharide is replaced by a *hydrogen*.

e.



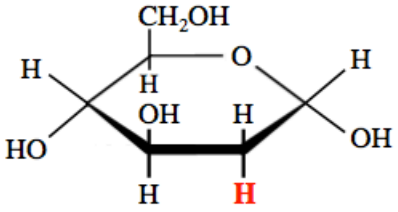
amino sugar
A hydroxyl group (OH) in a monosaccharide is replaced by an *amino group* (NH_2).

f.



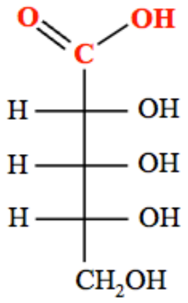
monosaccharide
a polyhydroxyl *ketone*

g



deoxy sugar
(cyclic form)
A hydroxyl group (-OH) in a monosaccharide is replaced by a *hydrogen*.

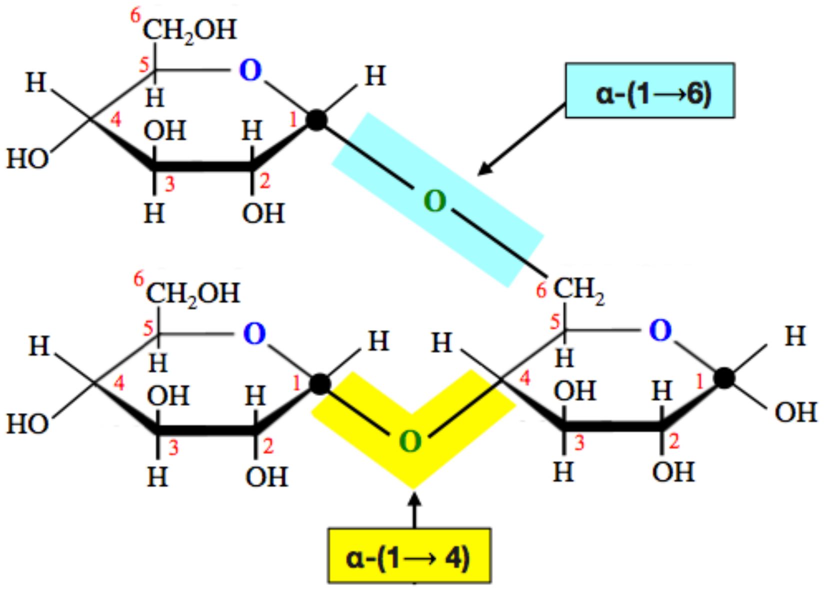
h.



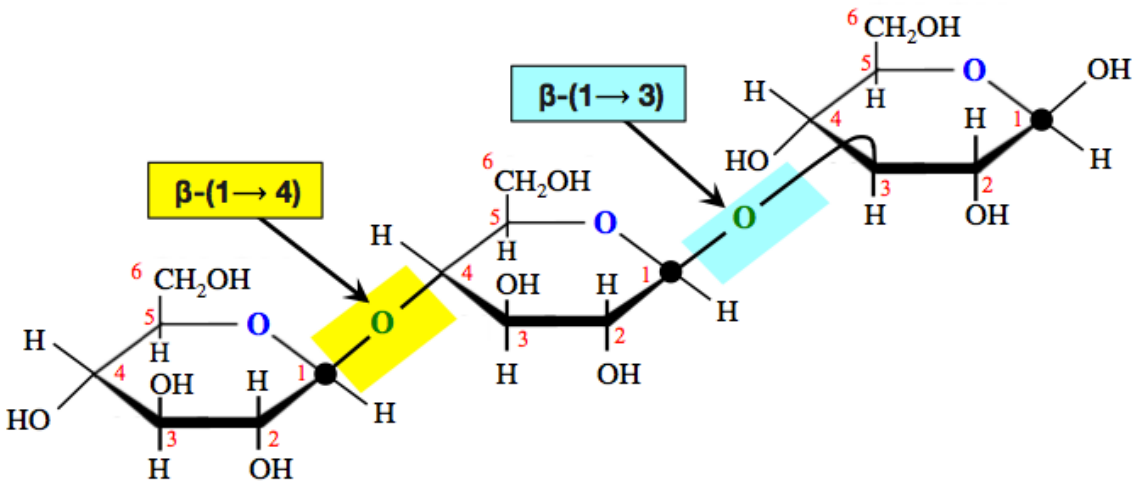
carboxylic acid sugar
The aldehyde group (CHO) of an aldose is oxidized to a *carboxyl group* (COOH).

11.12

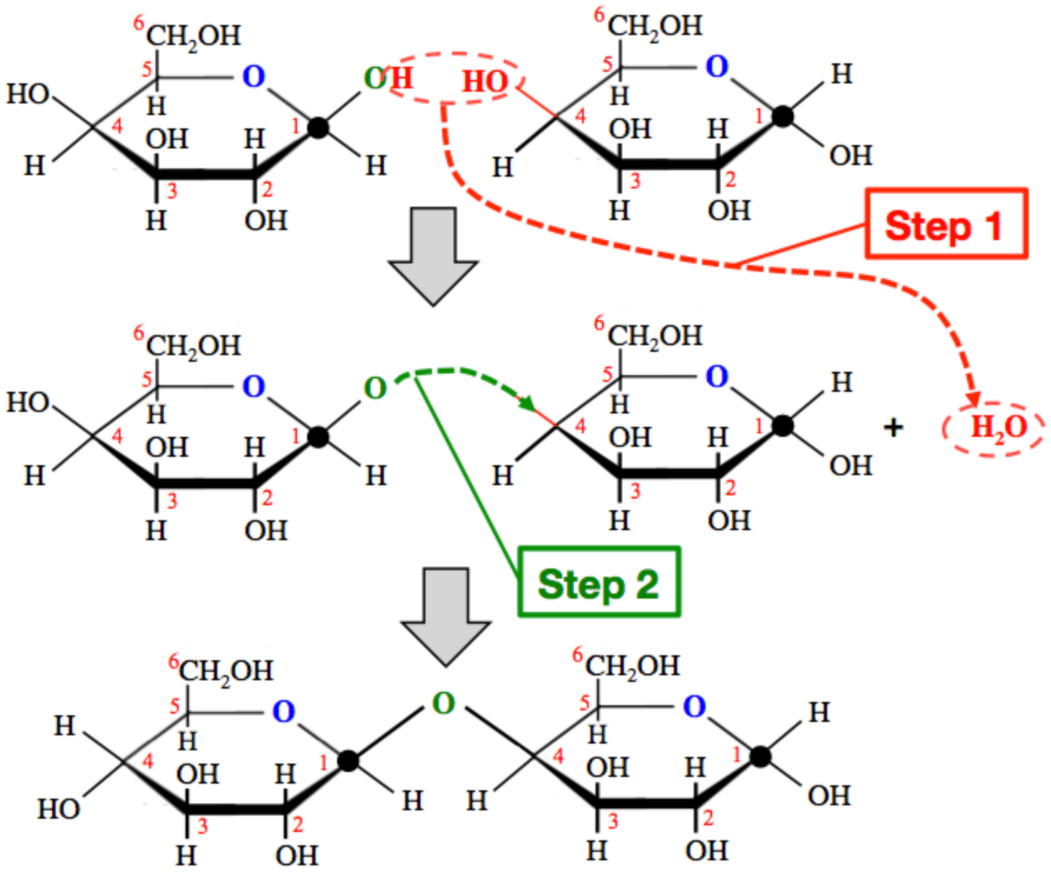
a.



b.



11.13



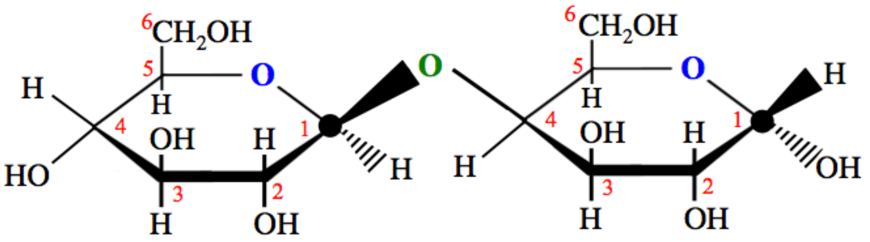
Step 1: An H atom is removed from the hydroxyl group (OH) ***that is bonded to the anomeric carbon*** of the left-most residue, and an OH is removed from ***any carbon*** in the right-most residue.

- In this example, the OH is removed from carbon number 4 of the right-most sugar residue.

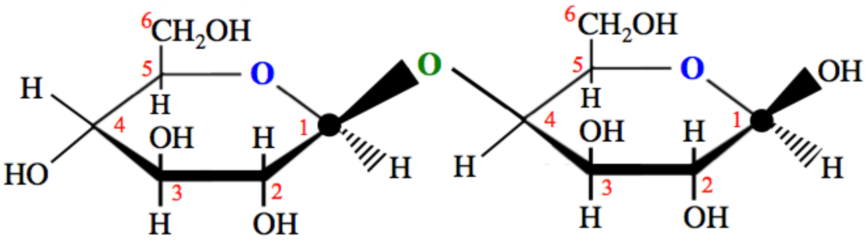
The H and OH that were removed to form a water molecule.

Step 2: Draw a ***new bond*** **from** the oxygen (O) that remains on the *anomeric carbon* in the left-most residue (shaded green in the illustration) **to** the carbon from which the OH was removed in the right-most residue. This ***new bond*** is oriented in the same direction as *was* the bond to OH that was removed.

11.14



or



Since the anomeric carbon in the ***right-most*** residue is a *hemiacetal* and therefore undergoes ***mutarotation***, the orientation of the OH and H that are bonded to is reversible. In the **top** structure, the *right-most* residue is drawn with the **α** orientation; it is *equally correct* to draw that residue in its **β** orientation, as I did in the **bottom** structure.

11.15

a. contains **α-(1⟶4)** glycosidic bonds: **both amylose *and* amylopectin**
b. homopolysaccharide: **both amylose *and* amylopectin**
c. contains glucose residues only: **both amylose *and* amylopectin**
d. contains **α-(1⟶6)** glycosidic bonds: **amylopectin**
e. contains branching points: **amylopectin**
f. more quickly digested: **amylopectin**

11.16

a. contains **α-(1→4)** glycosidic bonds: **amylose**
b. contains glucose residues only: **both amylose *and* cellulose**
c. found in plants: **both amylose *and* cellulose**
d. has a helical structure: **amylose**
e. is a homopolysaccharide: **both amylose *and* cellulose**
f. contains **β-(1→4)** glycosidic bonds: **cellulose**
g. can be digested by humans: **amylose**
h. is a major component of cell walls: **cellulose**

11.17

a. contains **α-(1→4)** glycosidic bonds: **both glycogen *and* amylopectin**
b. contains glucose residues only: **both glycogen *and* amylopectin**
c. contains **α-(1→6)** glycosidic bonds: **both glycogen *and* amylopectin**
d. contains branching points: **both glycogen *and* amylopectin**
e. is a homopolysaccharide: **both glycogen *and* amylopectin**
f. produced by plants: **amylopectin**
g. produced by animals: **glycogen**
h. branching occurs more frequently (glycogen ***or*** amylopectin): **glycogen**

Chapter 12

12.1

Unsaturated fatty acids are put into classes by the position of the ***first*** double bond that occurs, *counting from the omega carbon*.

a. Oleic Acid: omega-9 (or ω-9). In oleic acid, a carbon-carbon double bond occurs at the ***ninth*** carbon, counting from the *omega* carbon.

b. Linoleic Acid: omega-6 (or ω-6). In linoleic acid, a carbon-carbon double bond occurs at the ***third*** carbon, counting from the *omega* carbon.

12.2

Oleic Acid. Explanation: Since oleic acid and palmitoleic acid have the same number of *carbon-carbon double bonds* (one); we must compare the *number of carbons atoms*. Oleic acid has **18** carbons and palmitoleic acid has only **16** carbons. Since oleic acid is a larger/longer molecule it will have stronger London force interactions, therefore, a higher melting point.

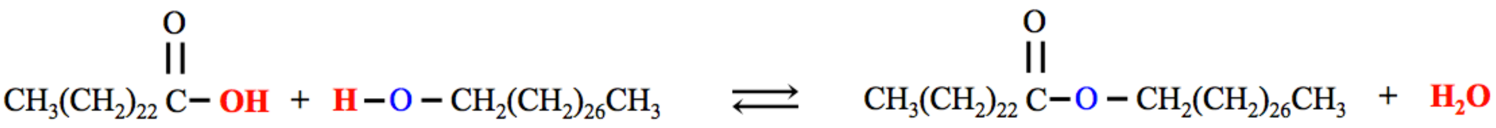
The melting point of oleic acid is 13 °C. The melting point of palmitoleic acid is 0 °C.

12.3

Oleic Acid. Explanation: Since oleic acid and linolenic acid have the same number of carbons (18); we must compare the *number of carbon-carbon double bonds*. Oleic acid has **one** carbon-carbon double bond and linolenic acid has **three** carbon-carbon double bonds. Since **oleic acid** has fewer double bonds, the molecules can pack closer together, which results in stronger London force attractions and a higher melting point.

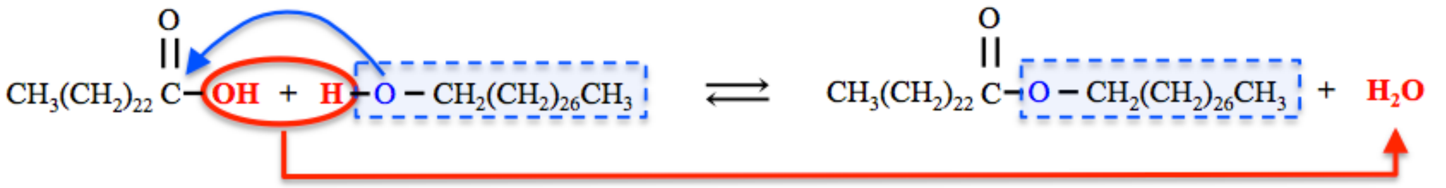
12.4

Answer:



$$CH_3(CH_2)_{22}\overset{\overset{O}{\|}}{C}-OH + H-O-CH_2(CH_2)_{26}CH_3 \rightleftharpoons CH_3(CH_2)_{22}\overset{\overset{O}{\|}}{C}-O-CH_2(CH_2)_{26}CH_3 + H_2O$$

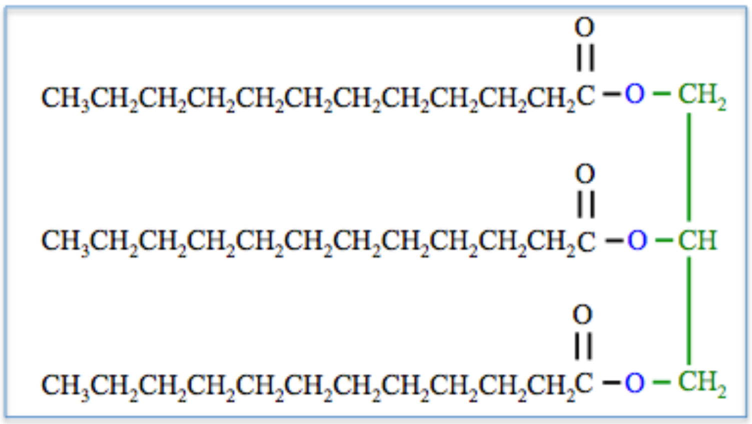
Detailed Solution: The **OH** from the fatty acid and an **H** from the alcohol are removed, and then combine to form **H_2O**. The oxygen (**O**) and hydrocarbon that was originally part of the alcohol, forms a new bond to the fatty acid's carbonyl carbon.



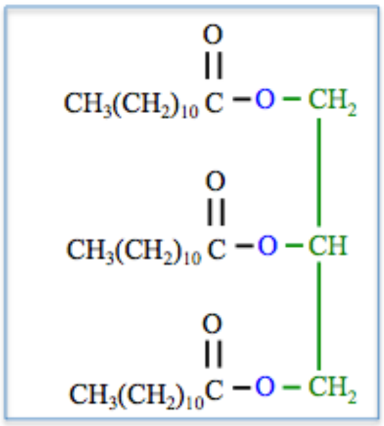
$$CH_3(CH_2)_{22}\overset{\overset{O}{\|}}{C}-OH + H-O-CH_2(CH_2)_{26}CH_3 \rightleftharpoons CH_3(CH_2)_{22}\overset{\overset{O}{\|}}{C}-O-CH_2(CH_2)_{26}CH_3 + H_2O$$

12.5

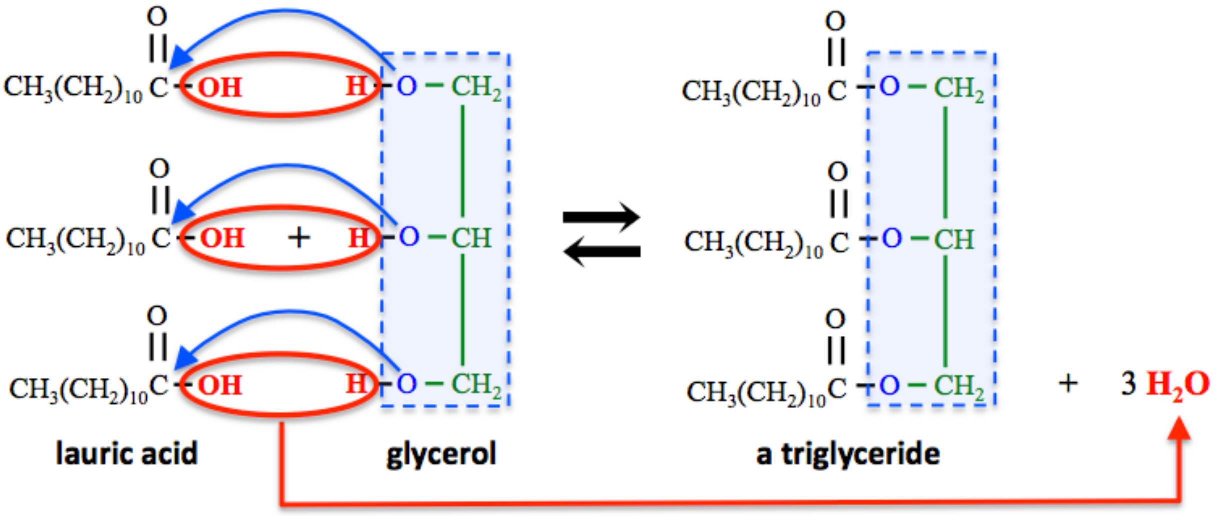
Answer:



or



Detailed Solution: The **OH**s from the fatty acids and *three* **H**s from glycerol's hydroxy groups are removed, and then combined to form *three* H_2O molecules. The three oxygens (**O**), that were originally in glycerol, each form a new bond to a fatty acid's carbonyl carbon. This process is illustrated below.



12.6

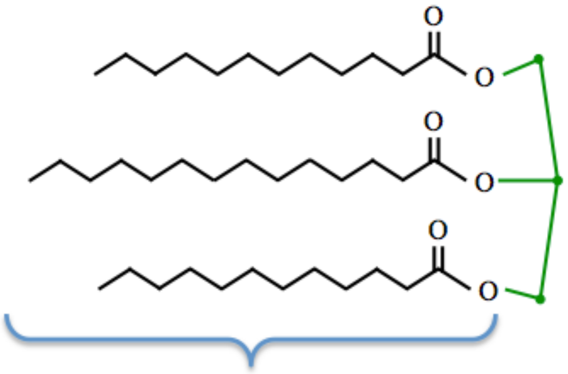
a. **Unsaturated:** The triglyceride contains one or more *carbon-carbon* double bonds.

b. **Saturated:** The triglyceride does not contain a *carbon-carbon* double bond.

c. **Unsaturated:** The triglyceride contains one or more *carbon-carbon* double bonds.

12.7

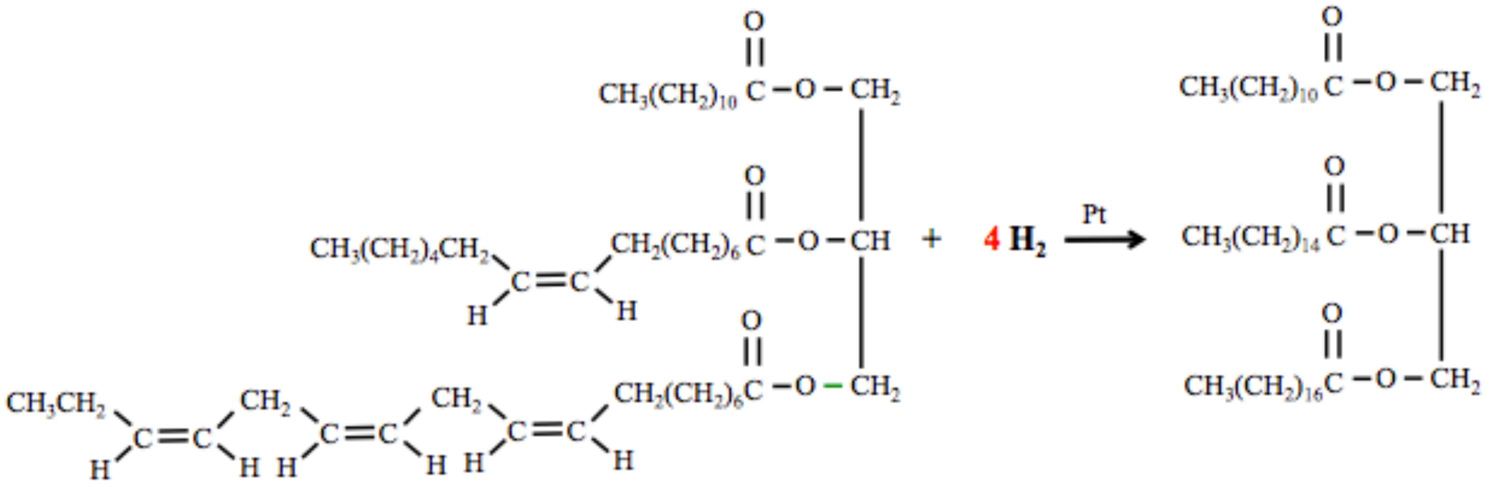
Saturated triglycerides do not contain *carbon-carbon* double bonds.



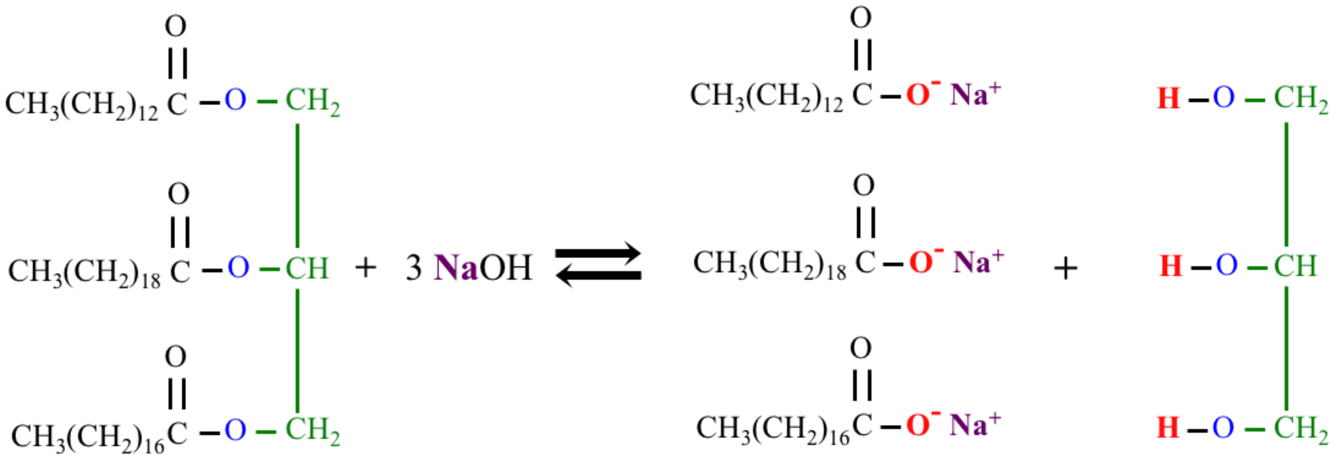
You can use any three saturated fatty acid residues.

12.8

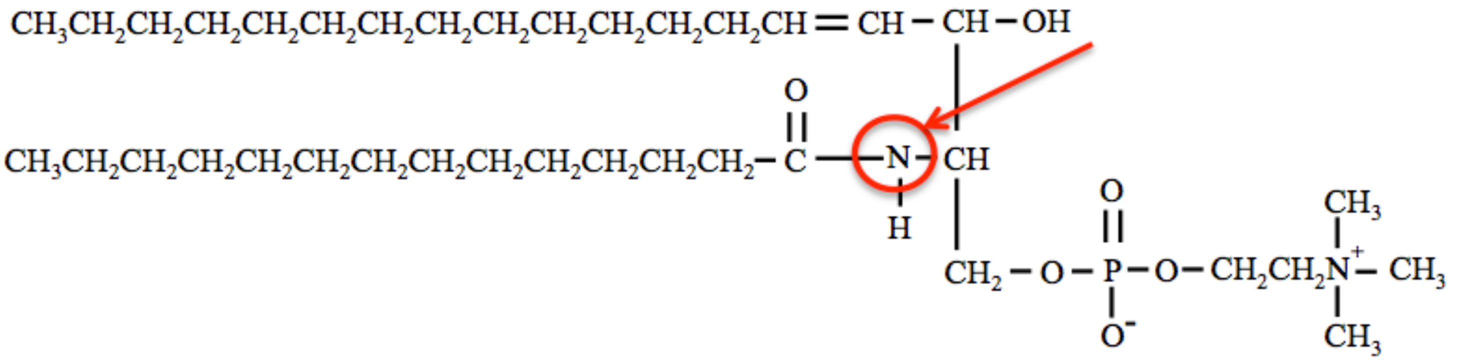
In the ***complete*** *catalytic hydrogenation of a triglyceride*, H_2 is added across ***all*** of the carbon-carbon double bonds of the unsaturated fatty acid residues to produce the corresponding saturated triglyceride. In this example there are **four** carbon-carbon double bonds in the triglyceride reactant, therefore **four** moles of H_2 are required for every mole of the triglyceride.



12.9

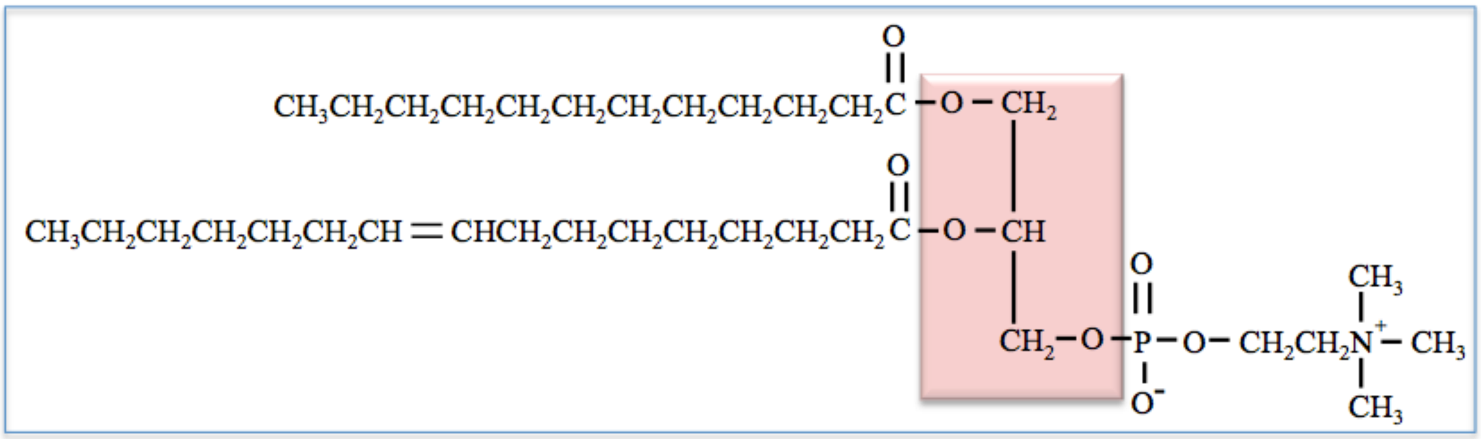


12.10

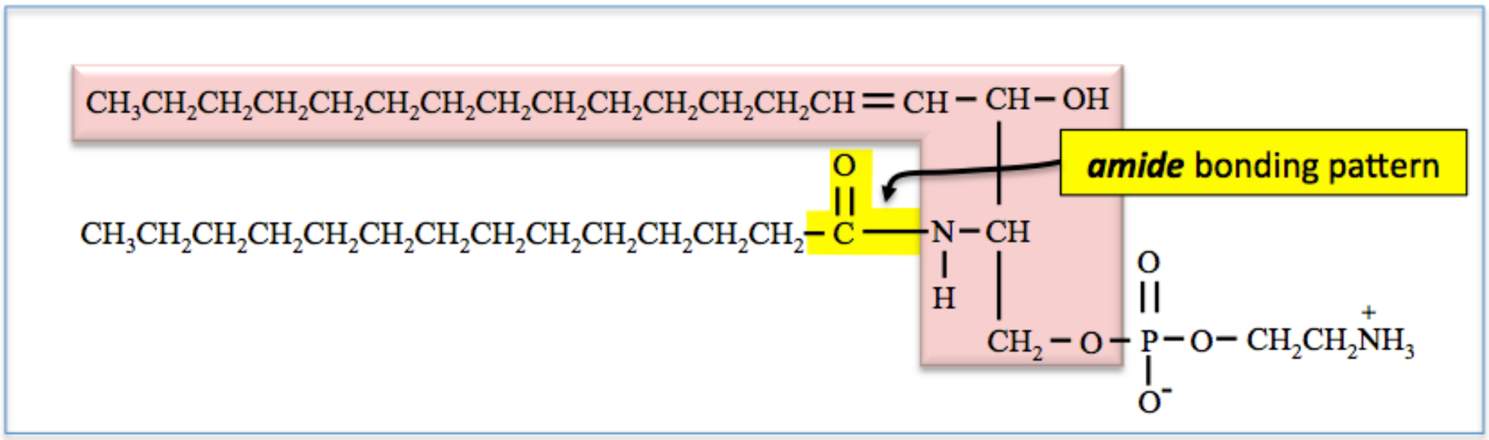


8.11

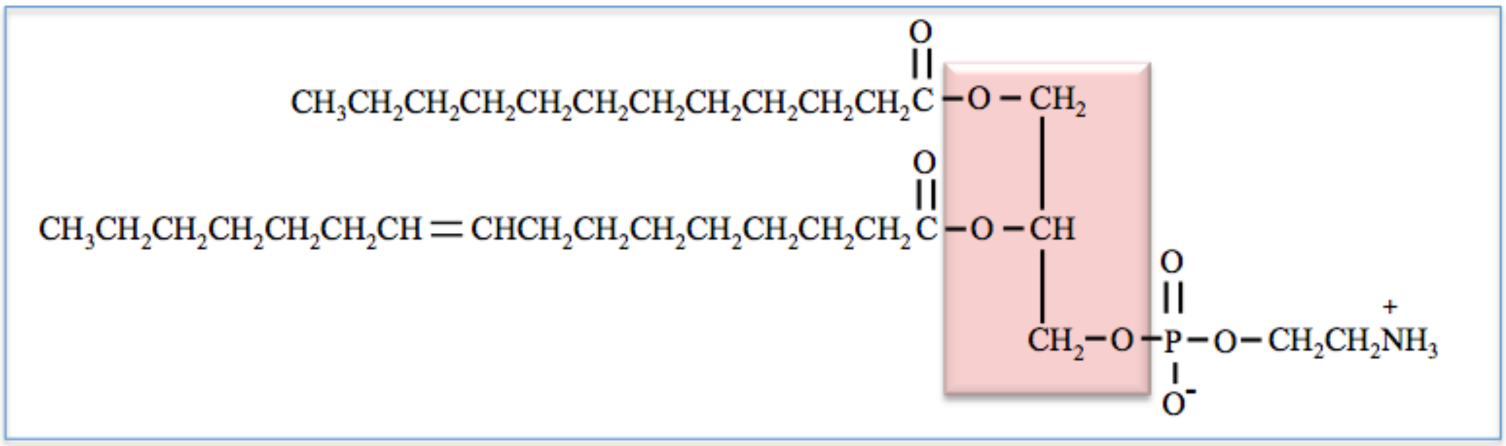
a. ***Glycerophospholipid:*** Note the ***glycerol backbone*** (highlighted red)



b. **Sphingophospholipid:** Note the ***sphingosine backbone*** (highlighted red) and the amide bonding pattern.

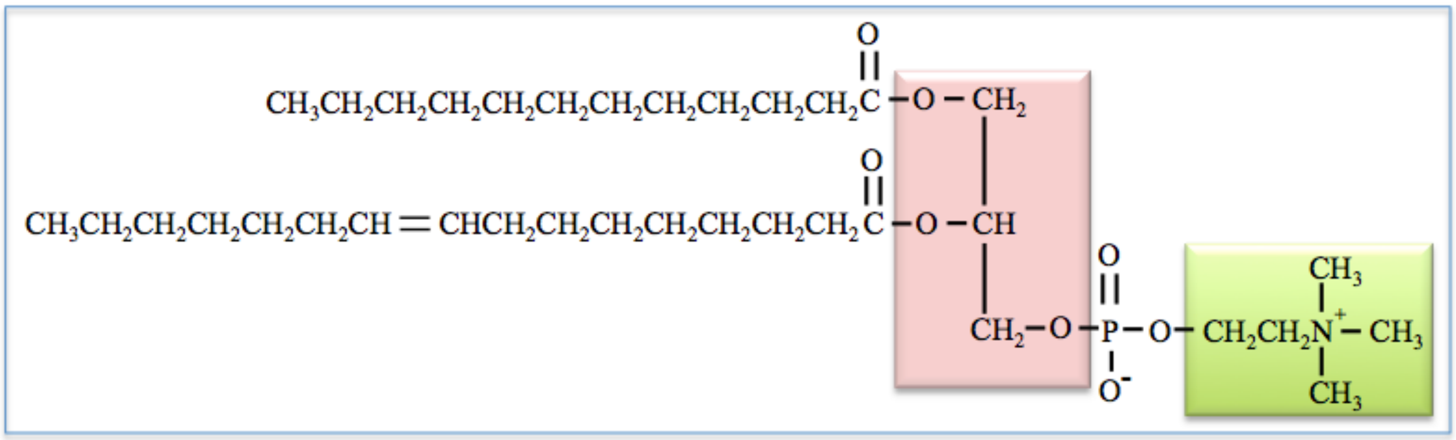


c. **Glycerophospholipid:** Note the ***glycerol backbone*** (highlighted red).

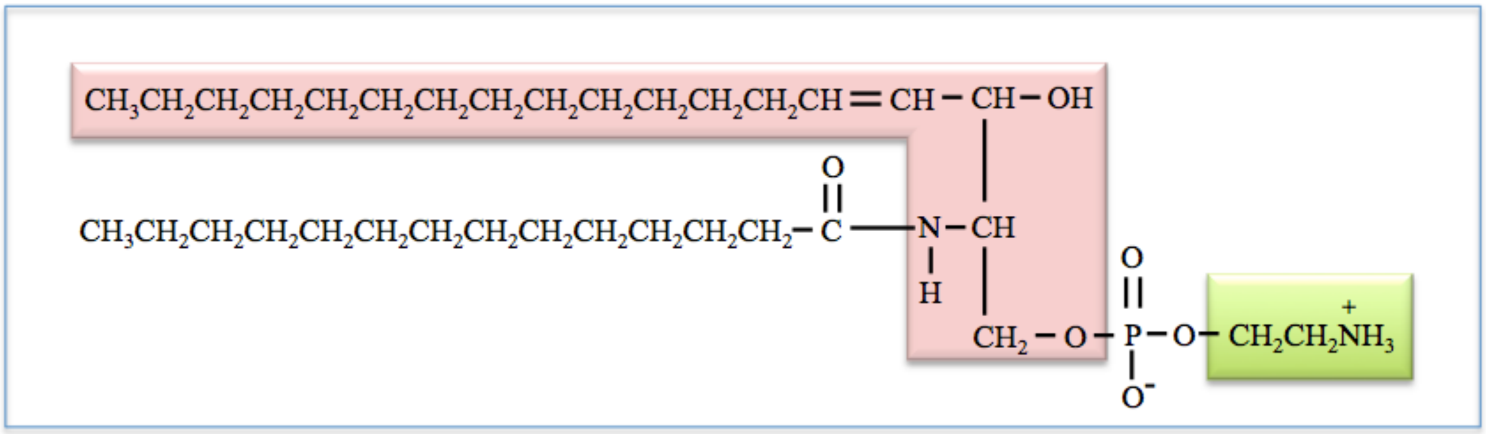


12.12

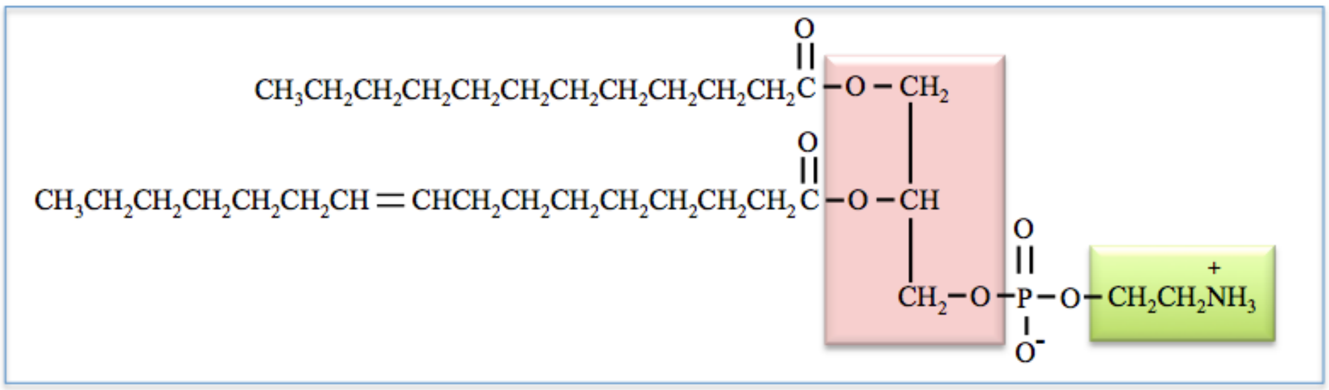
a. This *glycerophospholipid* is a **phosphatidylcholine**. The subclasses of ***glycerophospholipids,*** corresponding to specific X-groups, are listed in Table 12.5. The X-group in the molecule below is highlighted green.



b. This *sphingophospholipid* is a **sphingomyelin**. The subclasses of ***sphingophospholipids,*** corresponding to specific X-groups, are listed in Table 12.6. The X-group in the molecule below is highlighted green.



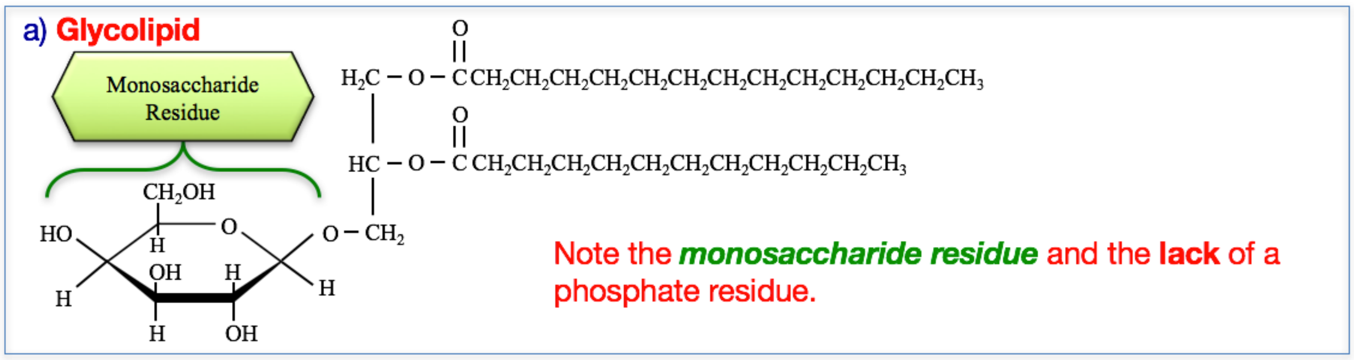
c. This *glycerophospholipid* is a **phosphatidylethanolamine**. The subclasses of ***glycerophospholipids***, corresponding to specific X-groups, are listed in Table 12.5. The X-group in the molecule below is highlighted green.

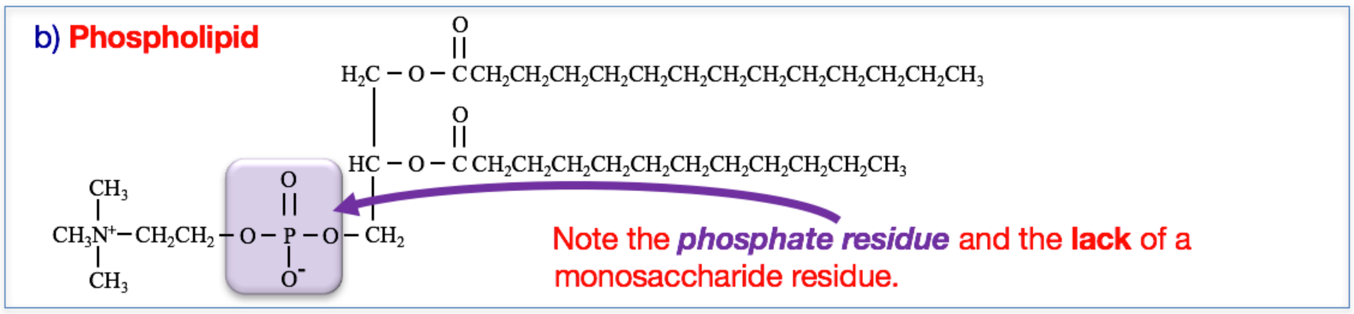


12.13

a. **Glycolipid:** Note the ***monosaccharide residue*** and the lack of a phosphate residue.

b. **Phospholipid:** Note the ***phosphate residue*** (highlighted purple) and the lack of a monosaccharide residue.





12.14

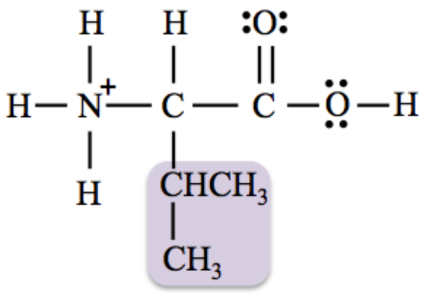
Both ***simple diffusion*** and ***facilitated diffusion*** result from the net transport of molecules or ions through a membrane, from a region where their concentration is ***greater*** to a region where their concentration is ***less*** (they move "*with the concentration gradient*"). In ***simple diffusion***, *lipophilic* molecules pass directly through the phospholipid bilayer membrane, whereas in ***facilitated diffusion***, small ions and polar molecules, which are *not lipophilic*, can only pass through membranes when facilitated by ***protein channels***. See the illustration in Figure 12.16.

12.15

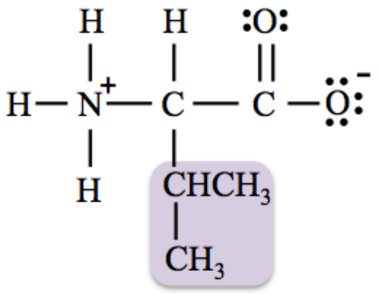
Passive transport (both simple diffusion and facilitated diffusion) results from the net transport of molecules or ions through a membrane, from a region where their concentration is ***greater***, to a region where their concentration is ***less*** (species are transported "***with** the concentration gradient*"). The energetic driving force for **passive transport** is the potential energy contained in the concentration gradient of the *diffusing species*. **Active transport** involves the net transport of molecules or ions, through a membrane, from a region where their concentration is ***less***, to a region where their concentration is ***greater*** (species are transported "***against** the concentration gradient*"). Because **active transport** occurs in the direction *against the concentration gradient,* the transported species' concentration gradient does not provide energy, *it must therefore* use some other energy source. This energy is often supplied by "energy rich" compounds such as ATP.

Chapter 13

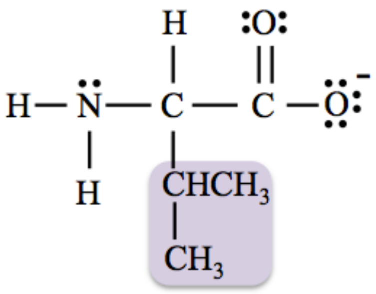
13.1



pH = 1.0
total charge = 1+

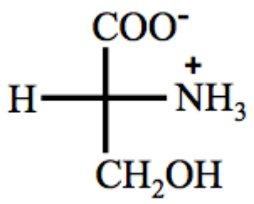


physiological pH (pH = 7.4)
total charge = 0

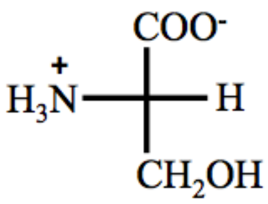


pH = 12.0
total charge = 1-

13.2



D-serine

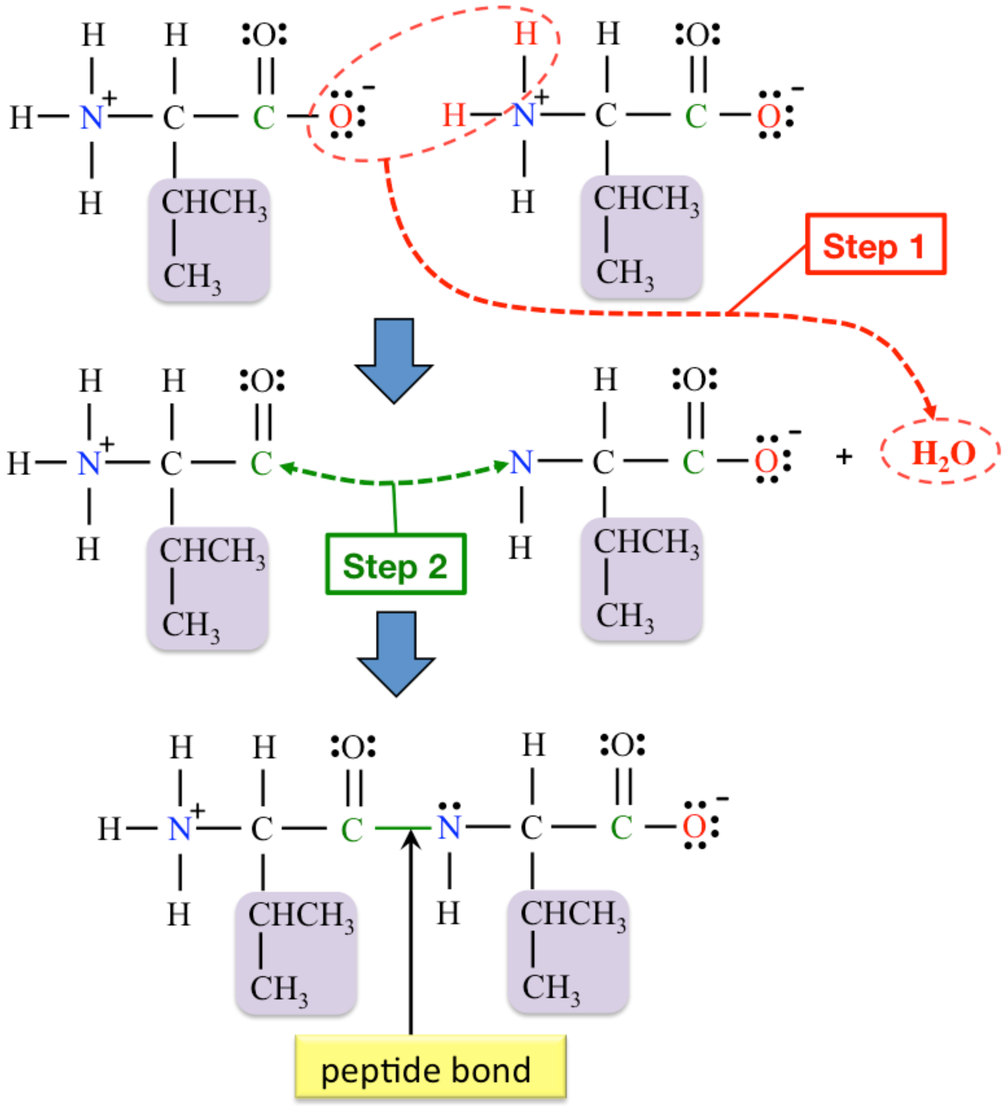


L-serine

13.3

Step 1: The single-bonded *oxygen atom* is removed from the *carboxylate group* on the *dipeptide*. *Two* hydrogen atoms are removed from the *quaternary ammonium group* on the *amino acid*. *Combine* the oxygen atom and the two hydrogen atoms to form a water molecule.

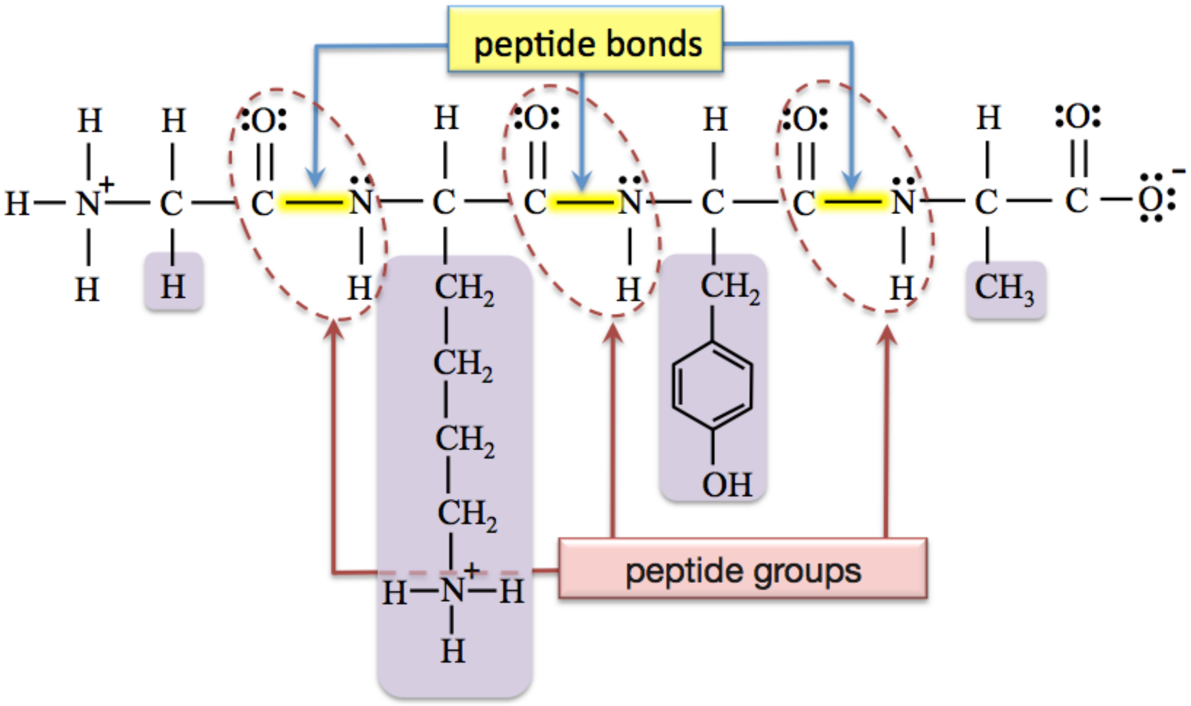
Step 2: A ***new bond*** is made between the carbonyl carbon and the nitrogen.



13.4

Because the peptide was drawn based on the predominant forms of the amino acids at physiological **pH** (as they are shown in Table 13.1), the resulting peptide is the form that is predominant at physiological **pH**.

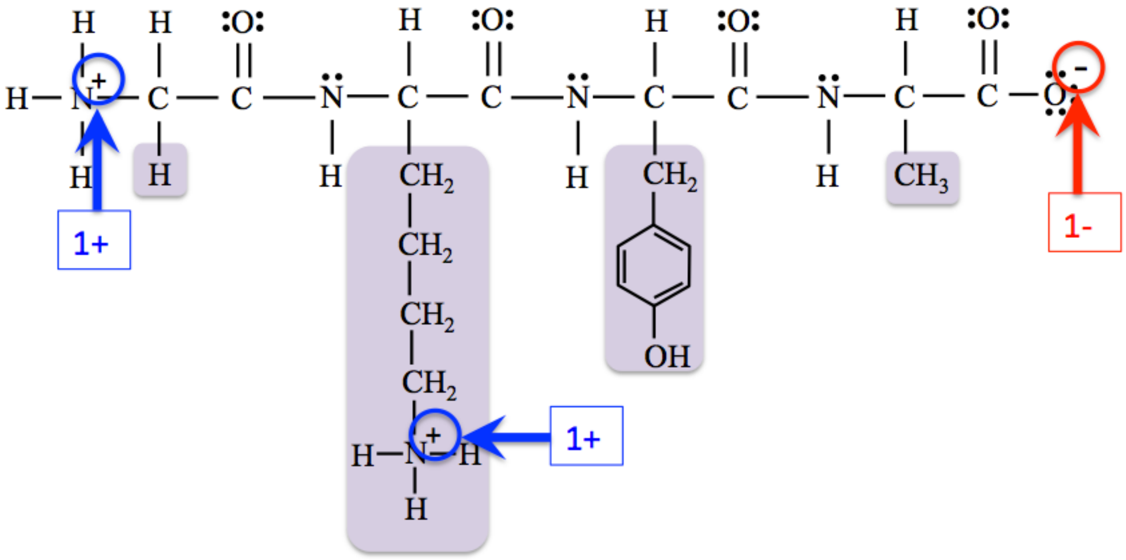
Gly-Lys-Tyr-Ala



13.5

Note that the ***nitrogens*** *in the peptide groups* ***do not*** carry a (1+) formal charge, as does the *nitrogen in the quaternary ammonium group at the N-terminus.* You can find the total charge of a peptide by adding up all of the formal charges that are present.

((1+) + (1+) + (1-)) = a *total charge* of **1+**



13.6

You can combine these three peptides in the following primary structures (listed from N-terminus to C-terminus):

gly-ala-asp
ala-gly-asp
asp-gly-ala
gly-asp-ala
ala-asp-gly
asp-ala-gly

There are **six** distinct tripeptides that can be formed from these three amino acids.

13.7

If there are **n** amino acid residues in a peptide, then there can be 20^n different amino acid sequences, therefore 20^n distinct peptides.

- There are 20^4 = **160,000** distinct tetrapeptides.

13.8

a. Which are involved in secondary structure?
  - hydrogen bonding

b. Which are involved in tertiary structure?
  - hydrogen bonding, disulfide bridges, hydrophobic interactions, salt bridges, covalent bonding (only in disulfide bridges).

c. Which are involved in quaternary structure?
  - same as tertiary: hydrogen bonding, disulfide bridges, hydrophobic interactions, salt bridges, covalent bonding (only in disulfide bridges).

13.9

Succinate dehydrogenase is a ***membrane protein***.

13.10

soy or peas. All of the other foods in the table are deficient in either lysine or tryptophan, or both lysine and tryptophan.

13.11

a. A catalyzed reaction has a lower activation energy than an uncatalyzed reaction. **True**
  - Catalyst increase the rate of a reaction by decreasing the activation energy from its uncatalyzed value.

b. The greater the activation energy, the faster the reaction rate. **False**
  - The lower the activation energy, the greater the reaction rate.

c. At equilibrium, a catalyzed reaction will result in a greater amount of products than would an uncatalized reaction. **False**
  - Enzymes ***do not effect*** the *equilibrium concentrations* of products and reactants (substrates), they only increase the reaction rates, and therefore equilibrium is reached more quickly.

13.12

a. The conversion of a *cis* double bond to a *trans* double bond. **Isomerases**

b. The digestion of fat. **Hydrolases**
  - The digestion of fat involves the hydrolysis of ester bonds within triglycerides. This is catalyzed by *lipase* enzymes.

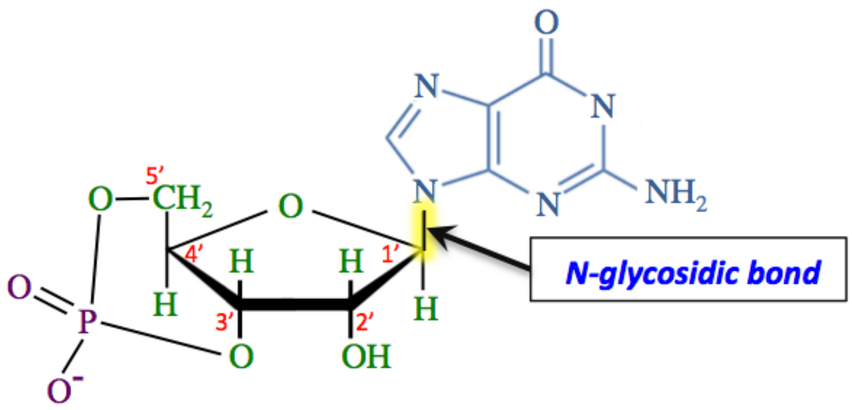
c. The conversion of starch to D-glucose. **Hydrolases**
  - This reaction involves the hydrolysis of glycosidic bonds within starch. This is catalyzed by a *carbohydrase* enzyme (amylase).

d. The conversion of a dipeptide into two amino acids. **Hydrolases**
  - This reaction involves the hydrolysis a peptide bond. This is catalyzed by *protease* enzymes.

e. The hydrolysis of ATP to form ADP and P_i. **Hydrolases**
  - This reaction involves the hydrolysis of a phosphoester bond. This is catalyzed by *phosphatase* enzymes.

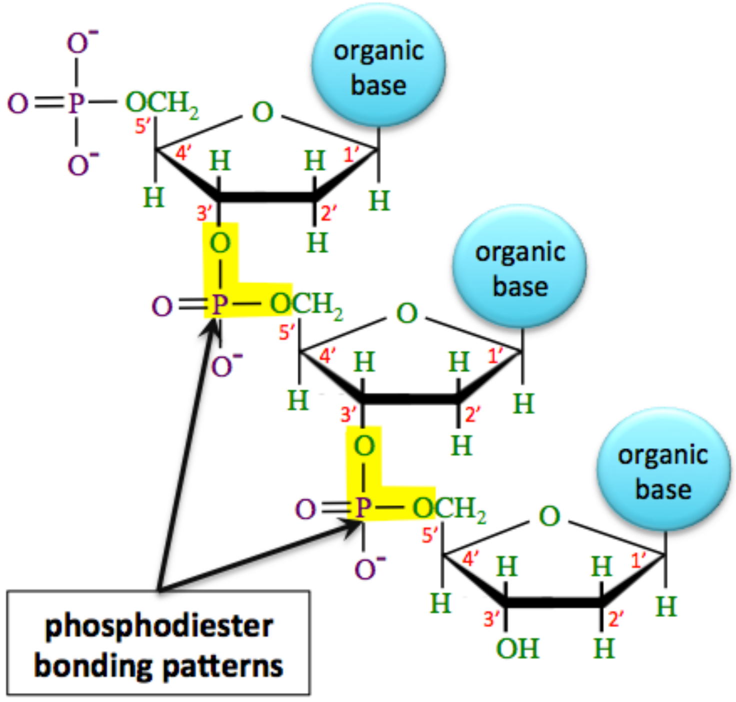
Chapter 14

14.1

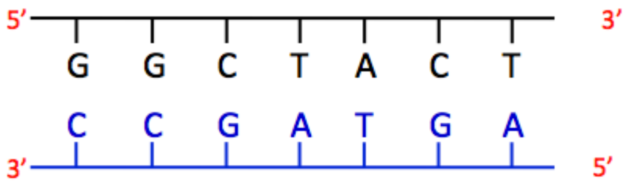


cyclic guanosine monophosphate (cGMP)

14.2



14.3



14.4

The daughter strands are complementary to the parent strands because *DNA polymerase directs the addition of nucleotides that are complementary to the parent strand*. Because the next base on the parent chain is thymine (**T**), the nucleotide triphosphate with an adenine (**A**) organic base would be added to the parent chain. The name of this nucleotide is *deoxyadenosine triphosphate* (or *deoxyadenosine* **5'**-*triphosphate*).

14.5

a. **True**, this is DNA replication

b. **False**, see part c for the correct daughter sequence

c. **True**

d. **False**, each double helix that is made in replication contains one parent strand and one daughter strand

e. **True**

f. **False**

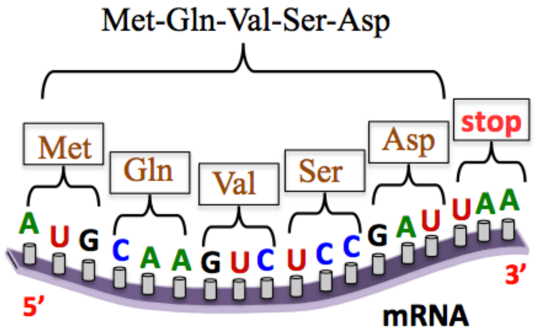
g. **True**

14.6

The particle with 96 nucleotides would move faster because it is smaller.

14.7

Peptides are formed in the direction from the **N**-terminus toward the **C**-Terminus. Use Table 14.1 to find the amino acids that correspond to the codons in mRNA. RNA polymerase moves in the **5'** to **3'** direction along mRNA.



14.8

DNA: **3'**-TACGGGGTACACACT-**5'**

This sequence of DNA would be ***transcribed*** to:

mRNA: **5'**-AUGCCCCAUGUGUGA-**3'**

These five codons would be ***translated*** to the amino acid sequence:

(**N**-terminus) Met-Pro-His-Val (**C**-terminus)

14.9

a. RNA polymerase is blocked from moving along the *lac* operon: **downregulated**

b. allolactose binds to the repressor protein: **upregulated**

c. lactose concentration within a cell is decreased: **downregulated**

d. allolactose concentration within a cell is increased: **upregulated**

e. glucose is available: **downregulated**

f. active repressor proteins are present in the absence of allolactose: **downregulated**

14.10

a. Transcription: **RNA polymerase**

b. Replication: **DNA polymerase**

c. Using a DNA template to make RNA: **RNA polymerase**

d. Using an RNA template to make DNA: **reverse transcriptase**

Chapter 15

15.1

The *overall* chemical equation for the glycolysis pathway is:

glucose + 2 ADP + 2 NAD$^+$ $\rightleftarrows$ 2 pyruvate ions + 2 ATP + 2 NADH + 2 H_2O + 2 H^+

Each glucose produces 2 ATP + 2 NADH, therefore six glucose produce:

a. 6 x 2 ATP = 12 ATP
b. 6 x 2 NADH = 12 NADH

15.2

Stage 1: No **ATP** or reduced coenzymes are produced in digestion.

Stage 2:

- glycolysis of ***one*** glucose molecule:

  glucose + 2 **ADP** + 2 **NAD$^+$** $\rightleftarrows$ **2** pyruvate ions + **2 ATP** + **2 NADH** + 2 H_2O + 2 H^+

- pyruvate oxidation and decarboxylation of ***the two pyruvate ions*** produced in glycolysis:

  2 pyruvate + 2 **NAD$^+$** **2 H-CoA** $\rightleftarrows$ **2 *acetyl*-CoA** + **2 NADH** + **2 CO_2**

Stage 3:

- reactions of the *citric acid cycle* ***for the two acetyl*-CoA** produced in **stage 2**:

2 *acetyl*-CoA + **6 NAD$^+$** + **2 FAD** + **2 ADP** + 2P_i + **4 H_2O** $\rightleftarrows$ **4 CO_2** + **6 NADH** + **2 $FADH_2$** + **2 ATP** + **2 H-CoA** + **6 H^+**

Total: 4 ATP, **10 NADH** , and **2 $FADH_2$**

15.3

Start this problem with the amount of **NADH** and **$FADH_2$** that are formed ***from one glucose*** molecule in stages 1 to 3 of glucose catabolism. In the previous review problem (**Review 15.2**), you found that **10 NADH**, and **2 $FADH_2$** are produced from one glucose molecule.

The ***two*** **NADH** that are produced in ***glycolysis*** cannot pass through innermitochondrial membrane and enter the matrix region where oxidative phosphorylation takes place. Therefore, it is necessary that "**NADH** *shuttles*" be used. In the **malate-aspartate shuttle**, each NADH produced in *glycolysis* results in one **NADH** that can undergo oxidative phosphorylation. In this case, there would be **10 NADH** and **2 $FADH_2$** available for oxidative phosphorylation.

15.4

As discussed in the previous review problem, we begin this problem with the **10 NADH**, and **2 $FADH_2$** that are formed ***from one glucose*** molecule in stages 1 to 3 of glucose catabolism. In the **glycerol 3-phosphate shuttle**, each **NADH** produced in *glycolysis* results in one **$FADH_2$** that can undergo oxidative phosphorylation. In this case, there would be **8 NADH** and **4 $FADH_2$** available for oxidative phosphorylation.

15.5

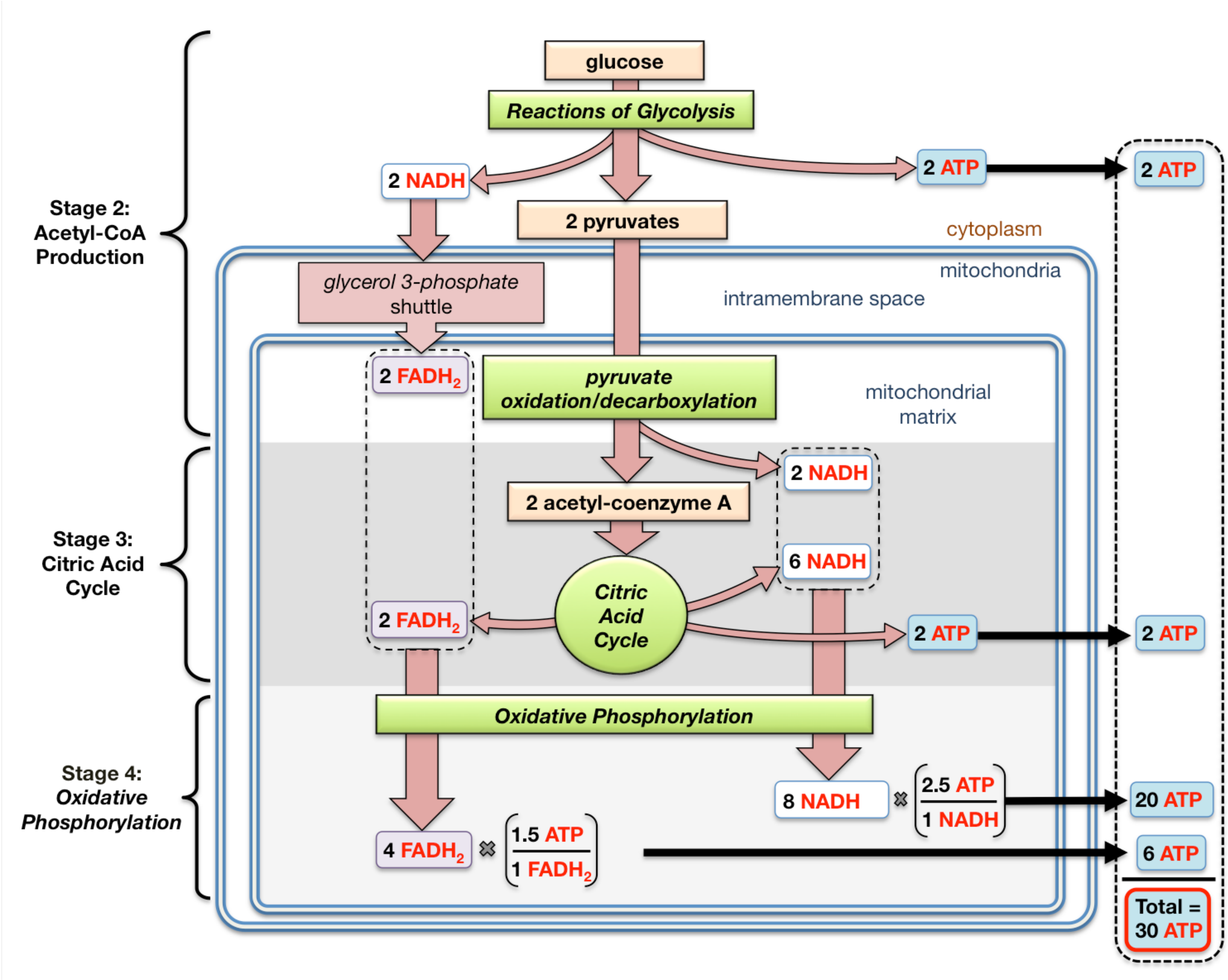
Stage 2: In *glycolysis*, glucose is converted to two pyruvate ions. In this process, two **NADH** and two **ATP** are formed. The two **NADH** undergo the **glycerol 3-phosphate shuttle** and result in the formation of two **$FADH_2$** *within* the mitochondrial matrix.

The pyruvate ions can diffuse past both mitochondrial membranes, and enter the matrix region. There, the pyruvate ions undergo an oxidation/decarboxylation reaction. In this process, two **NADH** and two acetyl-CoA are formed.

Stage 3: In the *citric acid cycle*, the two acetyl-CoA produce a total of six **NADH**, two **$FADH_2$**, and two **ATP**.

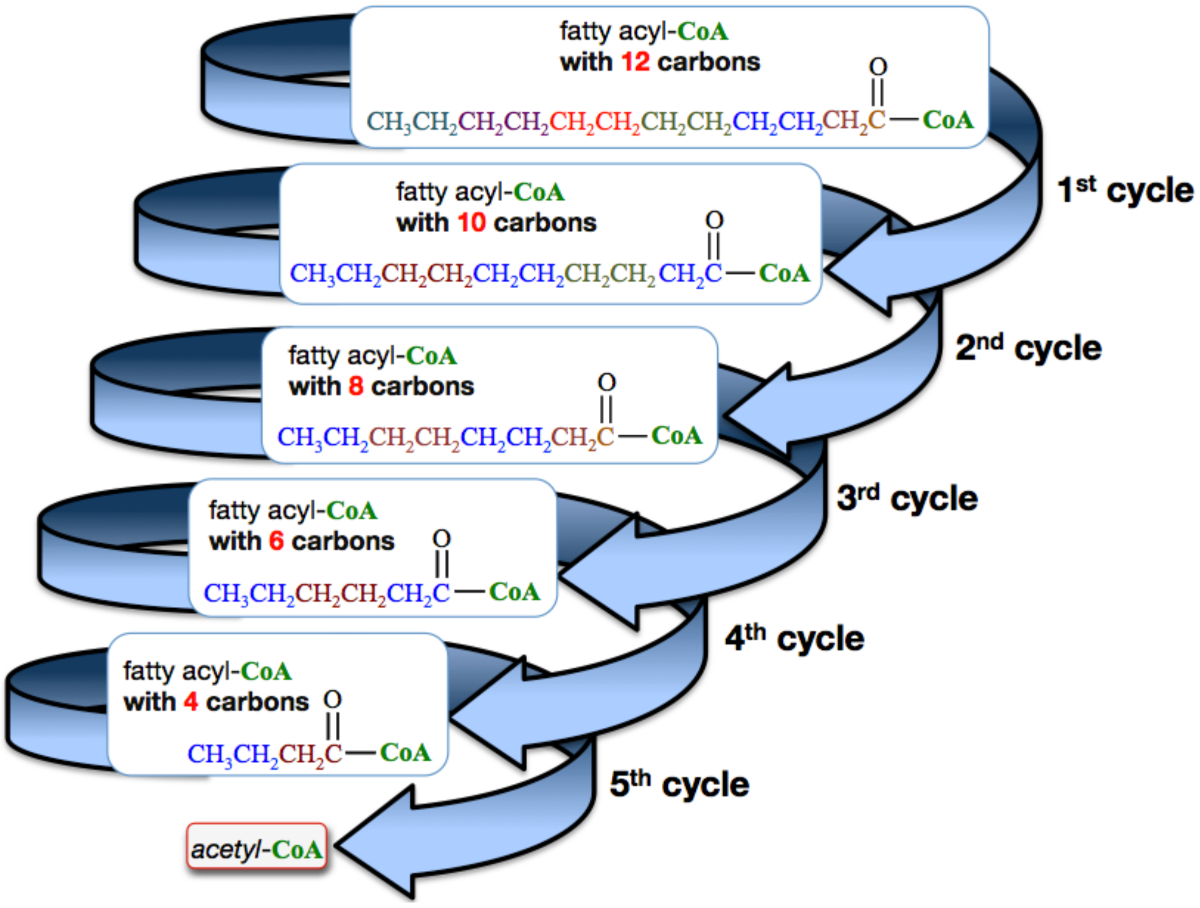
Stage 4: In oxidative phosphorylation, the ***eight*** **NADH** and ***four*** **$FADH_2$** produced in **stages 2** and **3** are oxidized in order to produce **ATP**.

This gives total of 30 ATP, as shown in the illustration below.



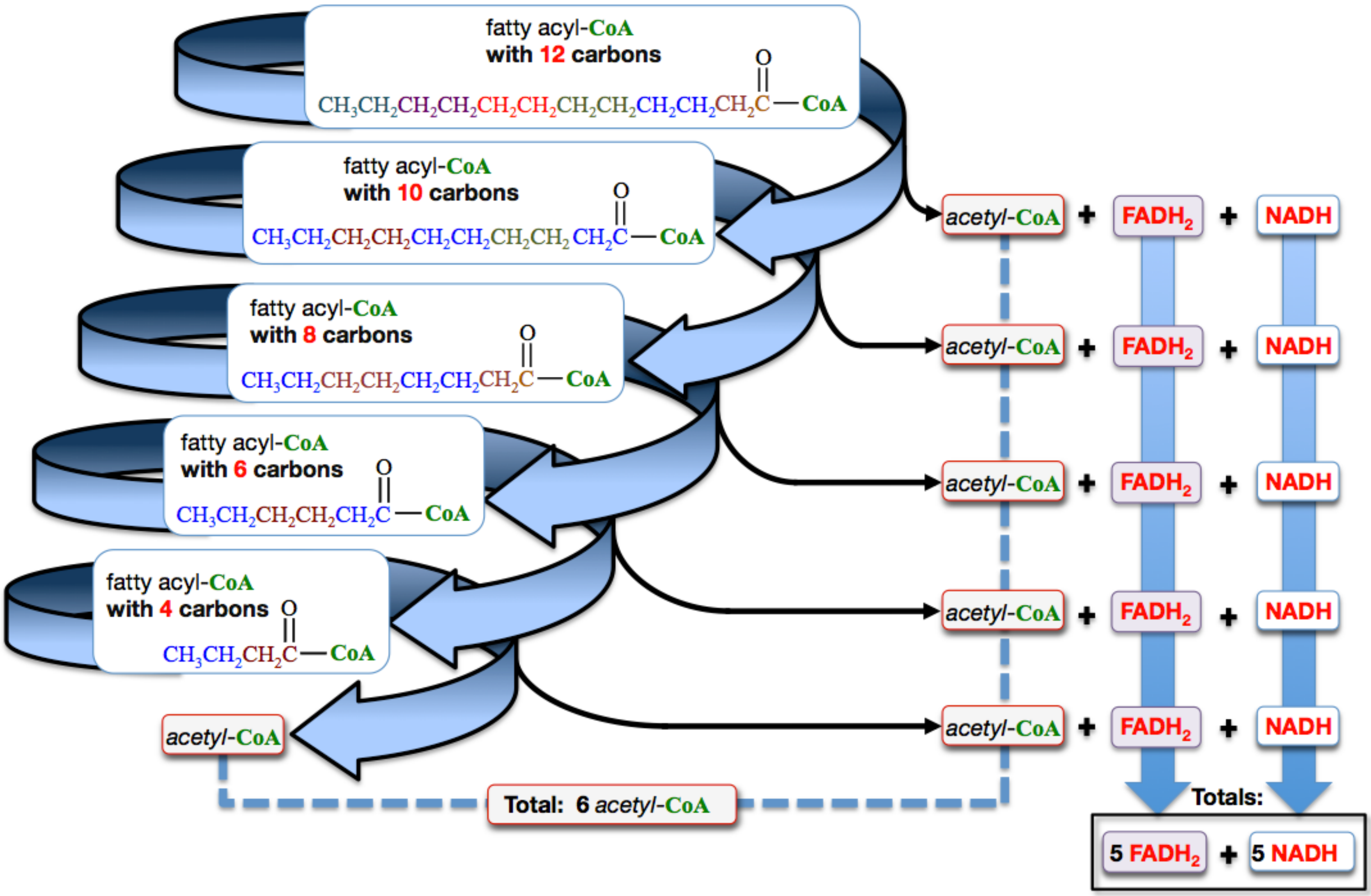
15.6

A *twelve-carbon* fatty acyl-CoA will undergo ***five*** cycles of the ***β-oxidation*** spiral. If **N** = the number of carbons that are contained in a fatty acyl-CoA, then it will undergo **[(N/2) -1]** ***β**-oxidation* cycles. This is illustrated for a *twelve-carbon* fatty acyl-CoA below:



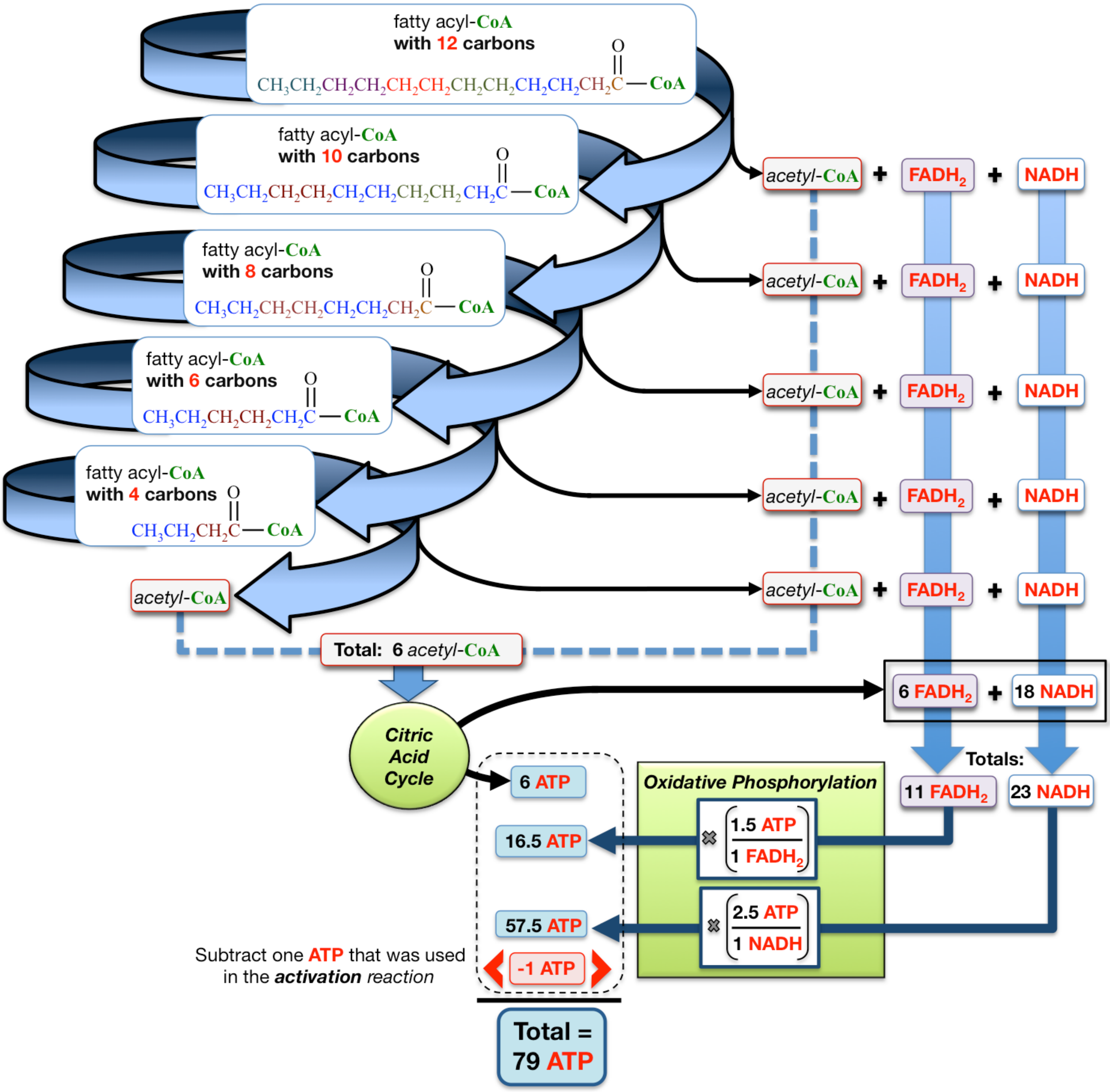
15.7

A twelve-carbon fatty acyl-CoA goes through five ***β**-oxidation* cycles. On each of the first four cycles, one acetyl-CoA, one **$FADH_2$**, and one **NADH** are produced. On the final cycle (fifth cycle), **two** acetyl-CoA, one **$FADH_2$**, and one **NADH** are produced. This adds to a **total** of **six** acetyl-CoA, **five $FADH_2$**, and **five NADH**.



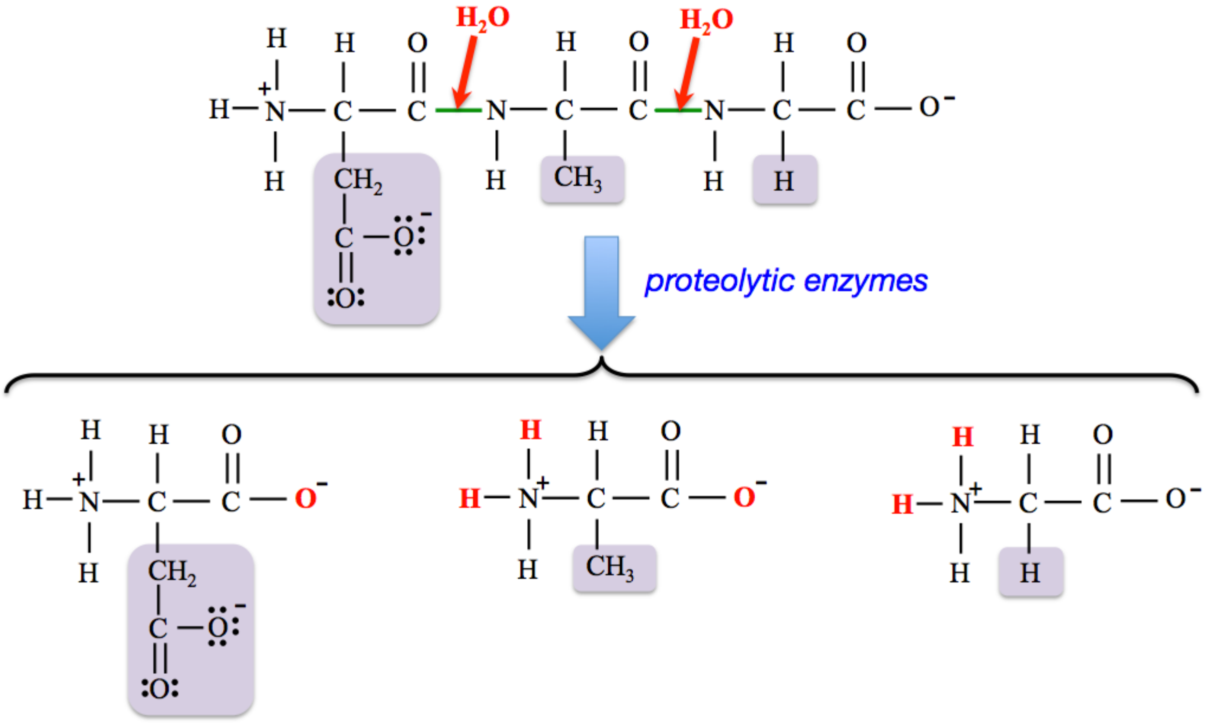
15.8

There is a net gain of **79 ATP** for **β-*oxidation*** of a twelve-carbon fatty acid, as illustrated below.



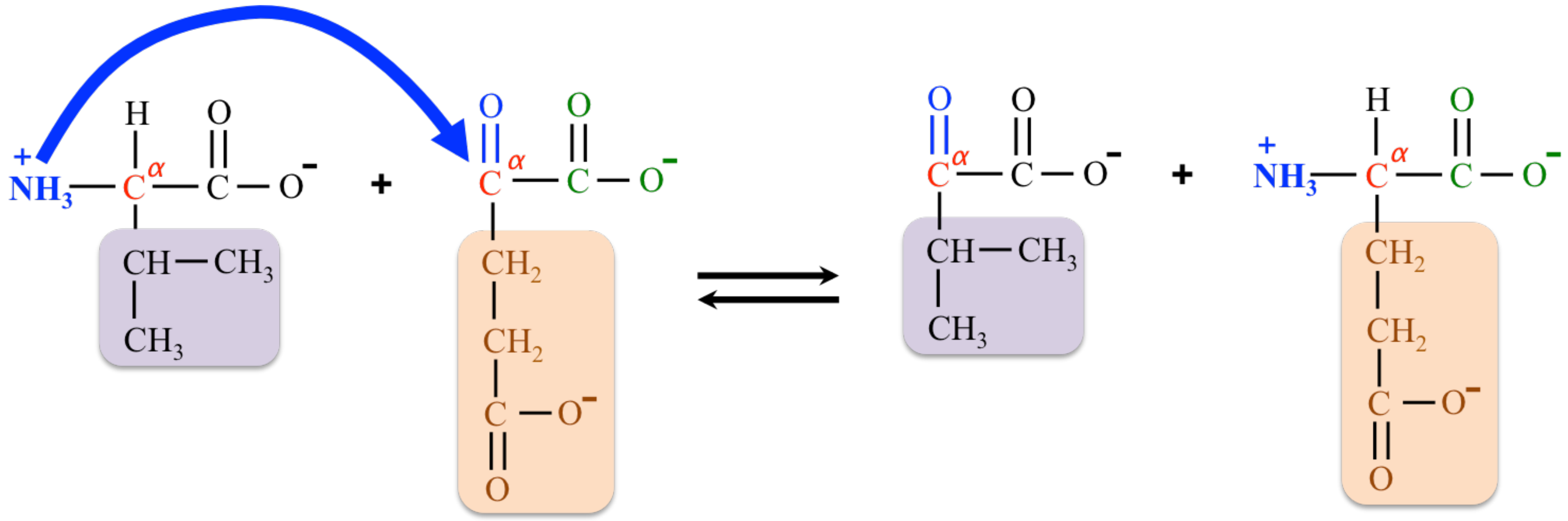
15.9

The peptide bonds are hydrolyzed. These are the bonds between the nitrogens and carbonyl groups.



15.10

This is a ***transamination*** reaction; it involves the ***transfer*** of a quaternary ammonium group (-NH_3^+). *Oxidative deamination* reactions produce ***free*** ammonium ions (NH_4^+).



valine (Val)
an amino acid

***α*-ketoglutarate**
an *α*-***keto*** acid

a **new** *α*-***keto*** acid

glutamic acid (Glu)
a **new** amino acid

Appendix 2: Template for Drawing Line Bond Structures

See the next two pages ***for examples*** of how to use this template.

Guide for Drawing Line Bond Structures of Diatomic or Small Binary Molecules

Step 1: Count the total number of valence electrons from all the atoms in the molecule.

Atom	Number of atoms		Number of valence electrons per atom	Totals
		x	=	
		x	=	
Total number of electrons to appear in the line bond structure =				

Step 2: Draw the “Skeleton" Structure
-Attach the atoms together with *single bonds* in the most symmetric way possible.

# of electrons used in skeleton = ______
(Multiply the number of bonds in skeleton by 2)

Step 3: Subtract the number of electrons used to make the skeleton structure from the total number of valence electrons.

Total # of valence electrons _____
(from Step 1)

# of electrons used in skeleton - _____
(from Step 2)

Remaining # electrons to be added = _____

Step 4: First: Re-draw skeleton (from Step 2):

Next, add the remaining electrons to the above structure as lone pairs as evenly as possible on all atoms *except hydrogen*.

- Add remaining electrons to the skeleton as ***lone pairs.***

Step 5: Check for Octets

Check the structure in **Step 4** for octets of electrons around each atom (except hydrogen)

If octet rule is satisfied, you are done.

If octet rule is not satisfied go to **Step 6**

Step 6: Use **lone pairs** to make *double* or *triple bonds* **until** the octet rule is satisfied *for all atoms* in the molecule.

- ***Change*** *lone pairs* into double, or if needed, triple bonds in order to satisfy the octet rule.

Guide for Drawing Line Bond Structures
Example: Draw the Line Bond Structure for H_2O

Step 1: Count the total number of valence electrons from all the atoms in the molecule.

Atom	Number of atoms		Number of valence electrons per atom	Totals
O	1	x	6 =	6
H	2	x	1 =	2
Total number of electrons to appear in the line bond structure =				8

Step 2: Draw the "Skeleton" Structure

-Attach the atoms together with *single bonds* in the most symmetric way possible.

$$H-O-H$$

# of electrons used in skeleton = ___4___

(Multiply the number of bonds in skeleton by 2)

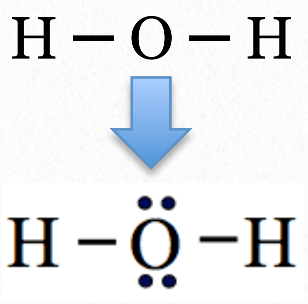
Step 3: Subtract the number of electrons used to make the skeleton structure from the total number of valence electrons.

Total # of valence electrons (from Step 1) __8__

# of electrons used in skeleton (from Step 2) - __4__

Remaining # electrons to be added = __4__

Step 4: **<u>First:</u>** Re-draw skeleton (from Step 2):

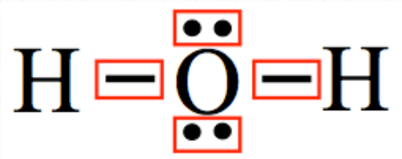


Next, add the remaining electrons to the above structure as <u>lone pairs</u> as evenly as possible on all atoms *except hydrogen*.

- Add remaining electrons to the skeleton as ***lone pairs.***

Step 5: Check for Octets

Check the structure in **Step 4** for octets of electrons around each atom (except hydrogen)



If octet rule is satisfied, you are done.

- In this case, the octet rule is satisfied.

If octet rule is not satisfied go to **Step 6**

Step 6: Use **lone pairs** to make *double* or *triple bonds* **<u>until</u>** the octet rule is satisfied *for all atoms* in the molecule.

- ***Change*** *lone pairs* into double, or if needed, triple bonds in order to satisfy the octet rule.

Step 6 is **<u>not needed</u>** in this example since the octet rule was satisfied in **Step 5**.

Guide for Drawing Line Bond Structures
Example: Draw the Line Bond Structure for O_2

Step 1: Count the total number of valence electrons from all the atoms in the molecule.

Atom	Number of atoms		Number of valence electrons per atom	Totals
O	2	x	6 =	6
		x	=	
Total number of electrons to appear in the line bond structure =				12

Step 2: Draw the "Skeleton" Structure

-Attach the atoms together with *single bonds* in the most symmetric way possible.

O – O

# of electrons used in skeleton = ___2___

(Multiply the number of bonds in skeleton by 2)

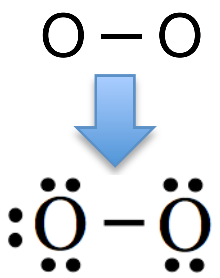
Step 3: Subtract the number of electrons used to make the skeleton structure from the total number of valence electrons.

Total # of valence electrons (from Step 1) _12__

# of electrons used in skeleton (from Step 2) - _2__

Remaining # electrons to be added = __10__

Step 4: First: Re-draw skeleton (from Step 2):

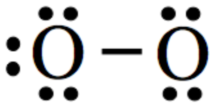


Next, add the remaining electrons to the above structure as lone pairs as evenly as possible on all atoms *except hydrogen*.

- Add remaining electrons to the skeleton as ***lone pairs.***

Step 5: Check for Octets

Check the structure in **Step 4** for octets of electrons around each atom (except hydrogen)



Only 6 electrons surround the oxygen on the right; the octet rule is not satisfied!

If octet rule is satisfied, you are done.

If octet rule is not satisfied go to **Step 6**

Step 6: Use **lone pairs** to make *double* or *triple bonds* **until** the octet rule is satisfied *for all atoms* in the molecule.

- ***Change*** *lone pairs* into double, or if needed, triple bonds in order to satisfy the octet rule.

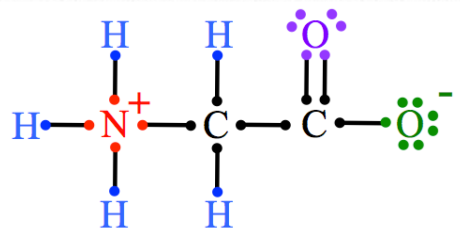
Appendix 3: Determining Formal Charge

To determine the formal charge (or lack of formal charge) for any particular atom in a molecule or polyatomic ion, we "formally" assign ***one electron*** from each of the atom's shared electron pair(s) ***and*** *all of the atom's lone pair electrons* to the atom. Then we compare the number of electrons that are "formally" assigned to the particular atom to the number of valence electrons that the atom would have if it was alone. If there are more electron(s) "formally" assigned to the atom than the number of valence electrons the atom would have if it was alone, then it is assigned a ***negative*** formal charge. Conversely, If there are fewer electrons "formally" assigned to the atom than the number of valence electrons the atom would have if it was alone, then it is assigned a positive formal charge. I realize this may sound complicated ***at first***, however it will become much easier as you consider a few examples.

Example: Glycine is one of the twenty common amino acids that make up the proteins in our bodies. The line bond structure of glycine is shown on the right.   Calculate the **formal charge** for *each* of the atoms in glycine.

Solution: To calculate the formal charge for a particular atom in a compound, we assign to that particular atom ***one electron*** from each shared electron pair ***and*** all electrons from lone pairs surrounding that atom. This process of "formally" assigning electrons to an atom gives us a reasonable approximation of how many electrons are in the vicinity of a particular atom. While considering formal charge, we ignore unequal sharing of electrons.

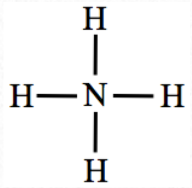
- Recall that *pairs of shared electrons* are drawn as lines in line bond structures.
- In the figure below, I have represented each electron in a bond as a dot on the end of a line/bond.



- In order for you to visualize the formal assignment of the electrons in the above structure, the electrons (dots) and the atoms to which they are "formally" assigned have been shaded the same color.

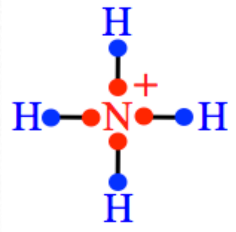
Let's calculate the **formal charge** for *each* of the atoms in glycine.

- **Hydrogens:** Each hydrogen (shaded blue) has 1 electron (dot shaded blue) *formally* assigned to it. An isolated hydrogen atom (electrically neutral) has one valence electron. In this case, there is neither an excess nor a deficiency of electrons in the vicinity of the hydrogen atoms. We say that the *formal charge* on the hydrogens in glycine is ***zero*** (no formal charge).
- **Nitrogen:** The nitrogen (shaded red) is formally assigned four electrons (dots shaded red). An isolated nitrogen atom (electrically neutral) has five valence electrons. In this case, there is a deficiency of electrons in the vicinity of the nitrogen atom. There is one more proton (in the nitrogen nucleus) than there are electrons in the vicinity of the nitrogen, therefore the nitrogen has a formal charge of 1+ (or +). Note that the formal charge (+) is superscripted to right of the nitrogen.
- **Carbons:** Each carbon (shaded black) has four electrons (dots shaded black) *formally* assigned to it. An isolated carbon atom (electrically neutral) has 4 valence electrons. In this case, there is neither an excess nor a deficiency of electrons in the vicinity of the carbon atoms. We say that the *formal charge* on the carbons in glycine equals ***zero*** (no formal charge).
- **Oxygen:** There are two oxygen atoms in glycine and each one has a different bonding pattern, therefore we need to determine the formal charge of each of them independently. Lets begin with the oxygen atom that is shaded purple and double-bonded to carbon.
    - The **oxygen that is shaded purple** is formally assigned six electrons (dots shaded purple). An isolated oxygen atom (electrically neutral) has six valence electrons.   In this case, there is neither an excess nor a deficiency of electrons in the vicinity of this oxygen atom, therefore the *formal charge* on this oxygen equals ***zero*** (no formal charge).
    - The **oxygen that is shaded green** is formally assigned seven electrons (dots shaded green). An isolated oxygen atom (electrically neutral) has six valence electrons. In this case, there is an excess of electrons in the vicinity of this oxygen atom, therefore it has a formal charge of 1- (or -). Note that the formal charge (-) is superscripted to right of the oxygen.



Example: The line bond structure of the ammonium ion (NH_4^+) is shown on the right: Calculate the **formal charge** of *each* of the atoms in the NH_4^+ ion.

Solution:



Assign ***one electron*** from each shared electron pair ***and*** all electrons from lone pairs surrounding to each atom.

- In the structure to the right, the electrons in bonds are shown as a dots on the end of a line/bond. The electrons (dots) and the atoms to which they are "formally" assigned have been shaded the same color.

- Calculate the **formal charge** for *each* of the atoms in NH_4^+.
    - **Hydrogens:** Each hydrogen (shaded blue) has one electron (dot shaded blue) *formally* assigned to it. An isolated hydrogen atom (electrically neutral) has one valence electron. In this case, there is neither an excess nor a deficiency of electrons in the vicinity of the hydrogen atoms. The hydrogens in glycine equals ***zero*** (no formal charge).
    - **Nitrogen:** The nitrogen (shaded red) is formally assigned four electrons (dots shaded red). An isolated nitrogen atom (electrically neutral) has five valence electrons. In this case, there is a deficiency of electrons in the vicinity of the nitrogen atom, so it has a formal charge of 1+ (or +).

What Do You Need to Know About Formal Charge?

For the purposes of this book, I will only need you to be able to determine the formal charge on two elements - **nitrogen and oxygen.** We will soon be focusing on organic biomolecules. Biomolecules consist primarily of **C**, **H**, **O**, and **N**. In the molecules that you will come across in this book, *carbon* and *hydrogen* atoms ***will never*** have a formal charge. *Oxygen* and *nitrogen* ***may or may not*** have a formal charge. The formal charge on oxygen and nitrogen atoms in compounds is based on the compound's bonding pattern as described below.

1) The Formal Charge on Oxygen:

- Oxygen has a formal charge of 1- when it has ***just one single bond*** (three lone pairs).
- In ***all other cases that we discuss in this text***, oxygen will not have a formal charge (formal charge = zero).

2) The Formal Charge on Nitrogen:

- Nitrogen will have *no formal charge* when it has ***one or more lone pairs on it***.
- In ***all other cases***, nitrogen has a 1+ formal charge.

Appendix 4: Radioisotopes and Nuclear Reactions

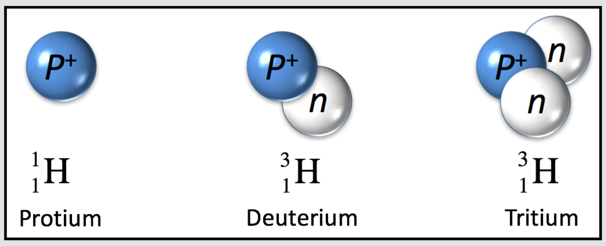
Educational Goals for Radioisotopes and Nuclear Reactions

1. Know and understand the terms: **nuclear reaction**, **transmutation**, **nuclear equation**, **parent isotope**, **daughter isotope**, **radioisotope**, **nuclear radiation**, **radioactive decay, fusion reaction, fission reaction,** and **radiolabeling**.
2. Describe the *four types* of **nuclear decay reactions.**
3. Given the *type of decay reaction* and the identity of the parent isotope, predict the products and write the **nuclear equation.**
4. Given the **half-life** and mass of a particular radioisotope present in a sample, calculate the amount of that radioisotope that will be present after a specified number of half-lives have passed.
5. Know and understand the definitions of the various **radiation dosage units.**
6. Given the dosage of a particular type of radiation in **rad** units, convert it to **rem** units.
7. Describe and understand the following medical practices: **brachytherapy**, **unsealed source radiotherapy**, **external beam radiotherapy (EBRT)**, **thyroid scans**, **positron emission tomography** (**PET**) **scans.**

Radioisotopes and Nuclear Recactions

At the time of writing this, there are 118 known elements. 98 of these elements occur naturally on earth. The other 20 elements are made artificially by man. Most elements have more than one isotope. Remember that isotopes are different forms of the same element whose atoms differ only in the number of neutrons.)" There are about 300 known isotopes of the 98 naturally occurring elements. For example, hydrogen can exist as ^{1}H, ^{2}H, or ^{3}H (see Figure 16.1) and carbon can exist as ^{12}C, ^{13}C, and ^{14}C. The neutrons and protons are attracted to each other by a fundamental property of nature called the strong nuclear force. This force is about 100 times stronger than electromagnetic forces and about 1000 times stronger than gravitational forces. It is responsible for the energy that is released in nuclear reactors and nuclear weapons.

Figure 16.1 Isotopes of Hydrogen



The nuclei of the isotopes of hydrogen.

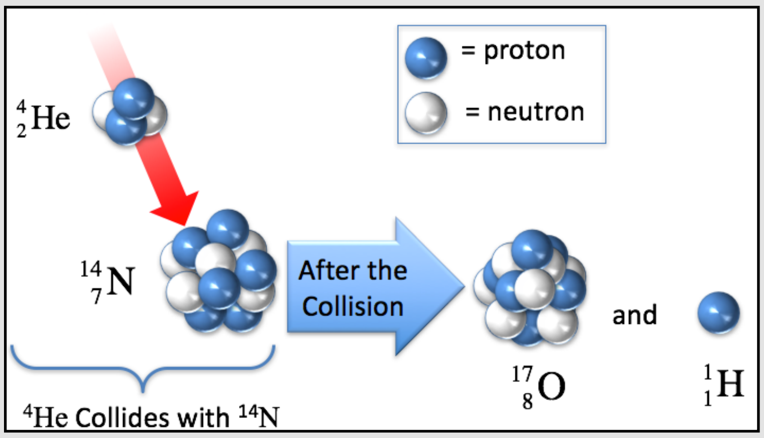
A **nuclear reaction** is a process in which there is a change in the nucleus of one or more isotopes. The first man-made nuclear reaction was recorded by Earnest Rutherford in 1917. Rutherford generated fast-moving ^{4}He nuclei and collided them with ^{14}N to produce ^{17}O and ^{1}H as illustrated in Figure 16.2. Note that *new* isotopes (^{17}O and ^{1}H) were created. The conversion of one isotope into another is called **transmutation**.

Nuclear reactions can be represented using **nuclear equations**. The symbols (including mass numbers and atomic numbers) for the *original* species, which are present before the nuclear reaction occurs, are drawn on the left-hand side of the arrow. The symbols for the species that are *produced* in the nuclear reaction are drawn on the right-hand side of the arrow. The nuclear equation for the Rutherford's nuclear reaction is:

$$^{14}_{7}\mathrm{N} + {}^{4}_{2}\mathrm{He} \rightarrow {}^{17}_{8}\mathrm{O} + {}^{1}_{1}\mathrm{H}$$

The *original* isotopes are called the **parent isotopes**. The isotopes that are *produced* in a nuclear reaction are called **daughter isotopes**. In the above reaction, parent isotopes are ^{14}N and ^{4}He, and the daughter isotopes are ^{17}O and ^{1}H.

Figure 16.2 A Nuclear Reaction



Protons are represented by blue spheres and neutrons are white spheres. A fast-moving ^{4}He nuclei and collides with ^{14}N to produce ^{17}O and ^{1}H.

Note that the terms hydrogen-1, protium, and proton are interchangeable because they are referring to the same particle:

$$\text{hydrogen-1} = {}^{1}_{1}\mathrm{H} = \mathrm{H} = {}^{1}\mathrm{H} = p = {}^{1}_{1}p = {}^{1}p$$

Radioactive isotopes

The nuclei of some isotopes are unstable and undergo nuclear reactions called **radioactive decay**. Henri Becquerel is credited with the discovery of radioactivity from uranium in 1896. It was later seen in thorium, polonium and radium by Marie Skłodowska-Curie and Pierre Curie. All three of these scientists, shown in Figure 16.3, won the 1903 Nobel Prize in Physics for these discoveries. Marie Curie went on to win a second Nobel Prize in Chemistry in 1911. She was the first woman to win a Nobel Prize, and the only woman to win the prize in two fields (chemistry and physics).

Figure 16.3 Scientists Involved in the Discovery of Radioactive Isotopes

The scientists that were honored with the 1903 Nobel Prize in Physics for their work on radioactivity. Left: Henri Becquerel, Middle: Marie Sklodowska-Curie, Right: Pierre Curie.

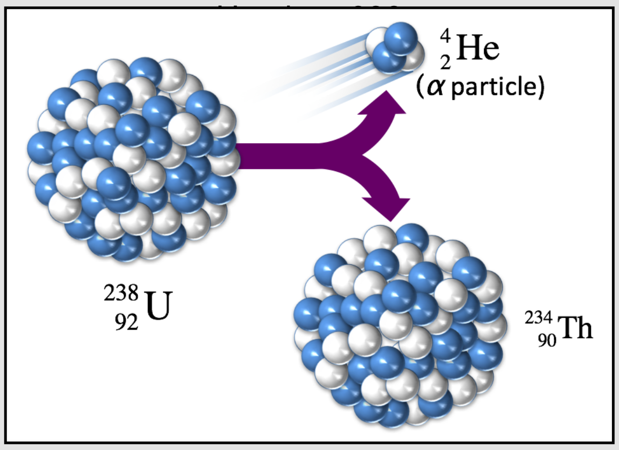
In radioactive decay, unstable isotopes lose energy in the form of radiated particles and/or "high energy" light. These emitted particles and/or high energy light are referred to as **nuclear radiation**. Unstable isotopes which emit nuclear radiation are called **radioisotopes** or **radioactive isotopes**. For example, ^{1}H, and ^{2}H do not undergo radioactive decay and are therefore classified as stable isotopes. ^{3}H, on the other hand, is unstable, undergoes radioactive decay, and is classified as a radioisotope.

Nuclear Decay Reactions

1) Alpha Decay

One way that a radioactive isotope can lose energy is to emit (radiate) an **alpha (α) particle**. Alpha particles are actually ^{4}He nuclei. The alpha particles that are emitted have high speeds of about 5-10% of the speed of light (~15,000 km/second) and therefore have high energies.

Figure 16.4 Illustration of the Alpha Decay of



Alpha decay of uranium-238 produces an alpha particle (^{4}He) and thorium-234.

An example of alpha decay is the decay of uranium-238 (^{238}U), which is illustrated in Figure 16.4. The nuclear equation for this reaction is shown below.

$$^{238}_{92}\mathrm{U} \rightarrow {}^{234}_{90}\mathrm{Th} + {}^{4}_{2}\mathrm{He}$$

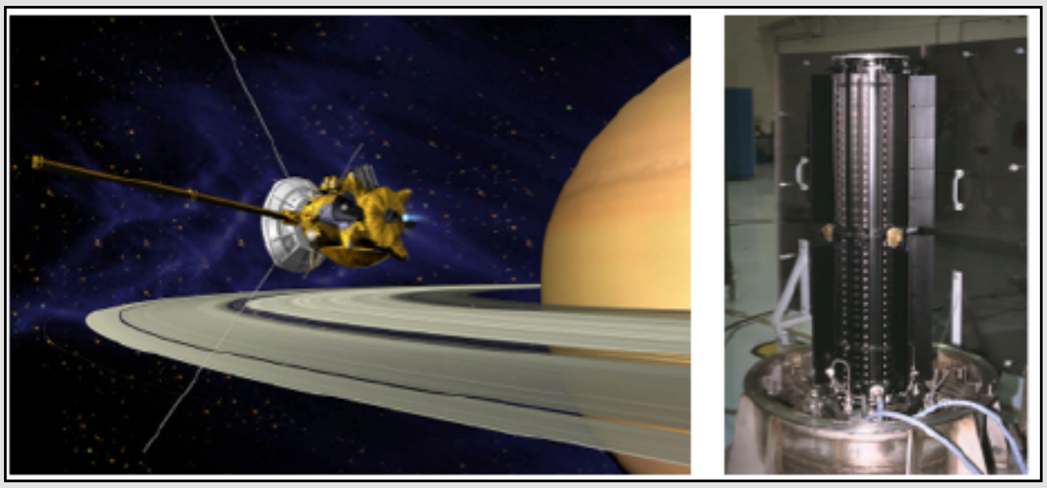
We use the symbol (**α**) to represent the helium nucleus, so the nuclear equation above can also be written as:

$$^{238}_{92}\mathrm{U} \rightarrow {}^{234}_{90}\mathrm{Th} + {}^{4}_{2}\alpha$$

The uranium-238 nuclei "radiate" alpha particles. Alpha particles are one type of nuclear radiation. You will hear about other types of nuclear radiation when I discuss other types of nuclear decay reactions.

An interesting example of alpha decay is its use in radioisotope thermoelectric generators (RTGs). RTGs convert the heat energy released in alpha decay into electricity. They have been used to power satellites, spacecraft, and unmanned remote facilities such as lighthouses in the Arctic Circle. They are especially useful in space missions too far from the sun to rely on solar panels for electricity. RTG's have been used in Pioneer 10, Pioneer 11, Voyager 1, Voyager 2, Galileo, Ulysses, Cassini, New Horizons, and the Mars Science Laboratory spacecraft. An illustration of the Cassini spacecraft, which was launched in 1997 and has orbited Saturn from 2004 to 2017, is shown on the left-hand side of Figure 16.5. A picture of one of Cassini's three radioisotope thermal generators before it was installed is shown on the right in Figure 16.5.

Figure 16.5
An Illustration of Cassini Spacecraft and One of its Radioisotope Thermoelectric Generators (RTGs)



Left: NASA artist's rendering of the Cassini spacecraft in Saturn orbit.
Right: One of the three Cassini radioisotope thermal generators before installation.

The Cassini spacecraft's RTG fuel was 33 kg (73 lb) of Plutonium-238. Plutonium-238 fuel is in the form of small pellets that glow red from their own heat. Plutonium-238 undergoes alpha decay. When the radiated high velocity alpha particles collide with the fuel pellet itself or the surroundings, the temperature increases. A glowing, hot plutonium-238 pellet is show in Figure 16.6.

Review Problem 1

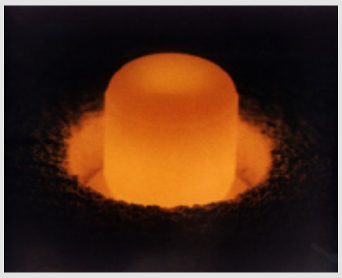
You just learned that the Cassini spacecraft's RTG fuel was plutonium-238.

a. What isotope is formed by alpha decay of plutonium-238?
b. Write the nuclear equation form the reaction.

For ***i-books*** versions: **Click here to check answer**

For **print or pdf versions**, see the answer key **at the end of *this* appendix**.

Figure 16.6 Plutonium-238

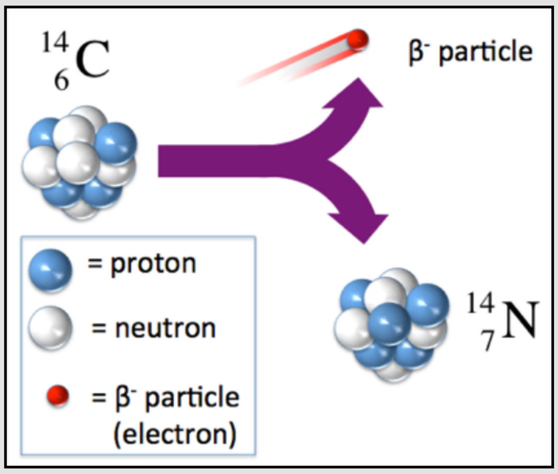


A plutonium-238 pellet glowing red hot from its own alpha decay energy.

2) Beta Minus (β^-) Decay

Another way that a radioactive isotope can lose energy is to emit (radiate) a **beta (β) particle**. The velocity of the β particle that is emitted depends on the particular parent isotope. There are two types of beta particles: beta minus (β^-) and beta plus (β^+).

Figure 16.7 β^- Decay of Carbon-14



An illustrative example of β^- decay. In the β^- decay of carbon-14, a neutron in the carbon-14 patent isotope is converted to a proton and a β^- particle. The proton that is produced remains in the nucleus and the β^- particle is ejected (radiated).

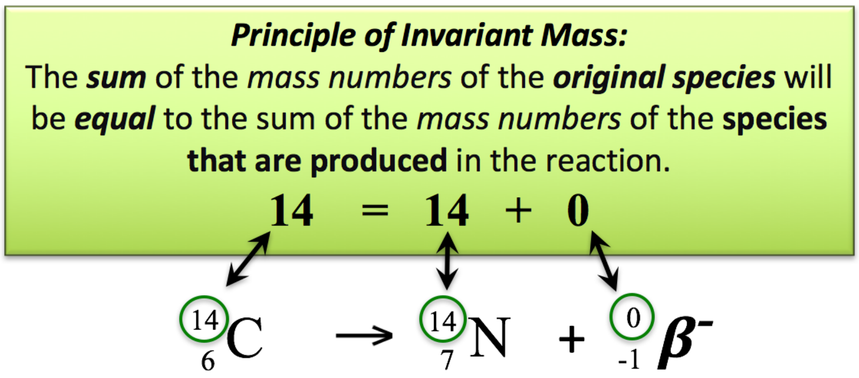
β^- particles are actually *fast-moving* electrons. Isotopes with a relatively high ratio of neutrons to protons tend to undergo β^- decay. In β^- decay, a *neutron* in the nucleus of the parent isotope is converted to a *proton* and a β^- particle. The proton remains in the nucleus and the β^- particle is ejected (radiated). An example of β^- decay is the decay of carbon-14 which is illustrated in Figure 16.7.

The nuclear equation for the β^- decay of carbon-14 can be written as:

$${}^{14}_{6}\text{C} \rightarrow {}^{14}_{7}\text{N} + {}^{0}_{-1}\beta^-$$

Because a β^- particle has no neutrons or protons, it has a mass number of zero. For species that have no protons such as β^- particles, instead of a subscripted atomic number, we write the *charge of the particle* as a subscript. The charge of a β^- particle is "-1" because it is an electron.

The **principle of invariant mass**, which is applicable to all nuclear reactions, states that the *sum of the mass numbers of the original species* will be ***equal*** to the *sum of the mass numbers of the species that are produced in the reaction*. Let's consider how the *principle of invariant mass* applies to the β^- decay of carbon-14. The mass number of the parent isotope (carbon-14) is **14**, and the *sum of the mass numbers of the species that are produced in the reaction is* **14**. The illustration below shows how the *principle of invariant mass* applies to the β^- decay of carbon-14.

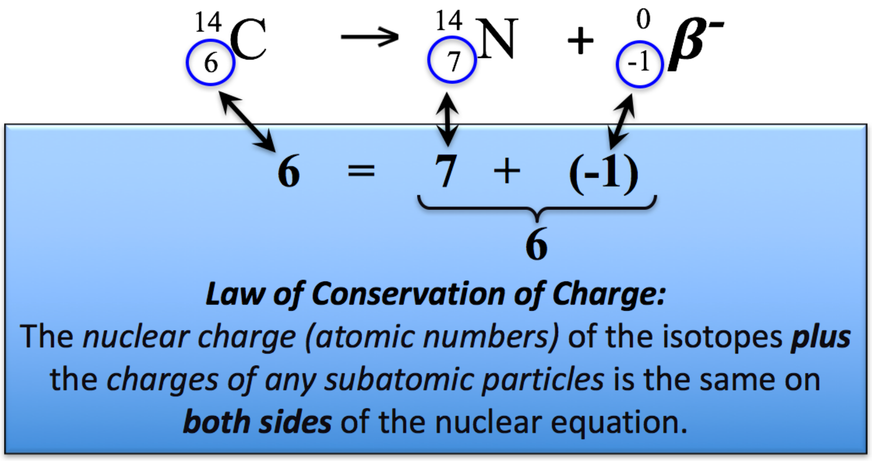


Principle of Invariant Mass:
The ***sum*** of the *mass numbers* of the ***original species*** will be ***equal*** to the sum of the *mass numbers* of the **species that are produced** in the reaction.

$$14 = 14 + 0$$

$${}^{14}_{6}\text{C} \rightarrow {}^{14}_{7}\text{N} + {}^{0}_{-1}\beta^-$$

There is another important principle that applies to all nuclear reactions. The **law of conservation of charge** states that the *nuclear charge (atomic numbers)* of the isotopes ***plus*** the *charges of any subatomic particles* is the same on ***both sides*** of the nuclear equation. As an example, let's consider how the *law of conservation of charge* applies to the β^- decay of carbon-14. The *nuclear charge (atomic number)* of the parent isotope (carbon-14) is **6**. For the daughter species, we have a *nuclear charge* of 7 from ${}^{14}\text{N}$, ***plus*** a "-1" charge from the β^- particle to give a total of **6**. The illustration below shows how the law of conservation of charge applies to the β^- decay of carbon-14.



$${}^{14}_{6}\text{C} \rightarrow {}^{14}_{7}\text{N} + {}^{0}_{-1}\beta^-$$

$$6 = \underbrace{7 + (-1)}_{6}$$

Law of Conservation of Charge:
The *nuclear charge (atomic numbers)* of the isotopes ***plus*** the *charges of any subatomic particles* is the same on ***both sides*** of the nuclear equation.

Review Problem 2

Complete the nuclear equation below for the *β*⁻ decay of potassium-40.

$$^{40}_{19}\text{K} \;\longrightarrow$$

For ***i-books*** versions: **Click here to check answer**

3) Beta Plus (β^+) Decay

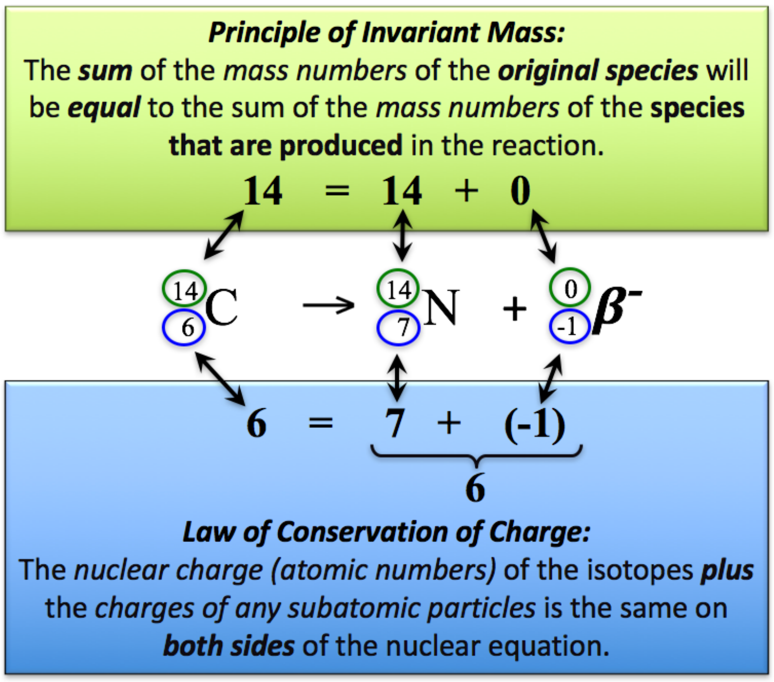
In β^+ decay, a *proton* in the nucleus of the parent isotope is converted to a *neutron* and a β^+ particle. The neutron that is produced remains in the nucleus and the β^+ particle is ejected (radiated) at very high speed (about 90% of the speed of light). β^+ particles, also referred to as ***positrons***, have the same mass as electrons but have a *positive* charge (+1). β^+ particles have an important role in medicine because of their use in *positron emission tomography* (PET) diagnostic imaging. I will discuss PET in more detail later. An example of β^+ decay is the decay of fluorine-18 which is illustrated in Figure 16.8.

The nuclear equation for the β^+ decay of fluorine-18 is show below.

$$^{18}_{9}\text{F} \;\longrightarrow\; ^{18}_{8}\text{O} \;+\; ^{0}_{+1}\boldsymbol{\beta}^{+}$$

Because the β^+ particle has no neutrons or protons it has a mass number of zero. For species that have no protons such as β^+ particles, instead of a subscripted atomic number, we write the *charge of the particle* as a subscript. The charge of a β^+ particle is positive one (+1).

The illustration below shows how the *principle of invariant mass* and the *law of conservation of charge* apply to the β^+ decay of fluorine-18.



Principle of Invariant Mass:
The ***sum*** of the *mass numbers* of the ***original species*** will be ***equal*** to the sum of the *mass numbers* of the **species that are produced** in the reaction.

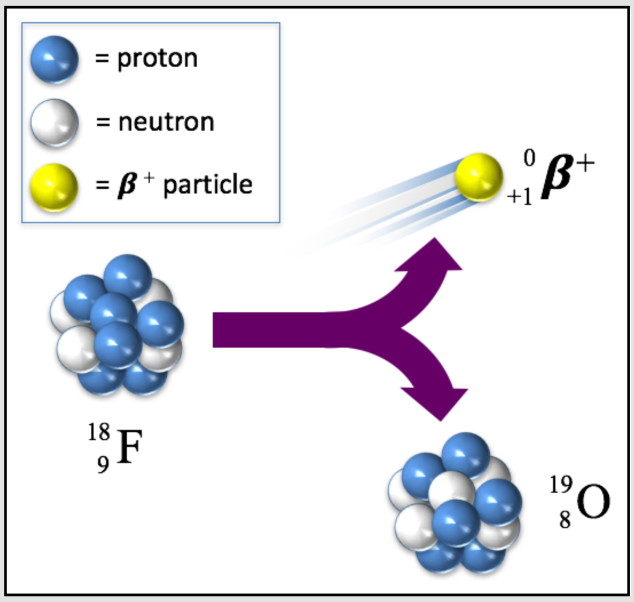
$$14 \;=\; 14 \;+\; 0$$

$$^{14}_{6}\text{C} \;\longrightarrow\; ^{14}_{7}\text{N} \;+\; ^{0}_{-1}\boldsymbol{\beta}^{-}$$

$$6 \;=\; \underbrace{7 \;+\; (-1)}_{6}$$

Law of Conservation of Charge:
The *nuclear charge (atomic numbers)* of the isotopes ***plus*** the *charges of any subatomic particles* is the same on ***both sides*** of the nuclear equation.

Figure 16.8 β^+ Decay of Fluorine-18



An illustrative example of β^+ decay. In the β^+ decay of fluorine-18, a proton in the fluorine-18 patent isotope is converted to a neutron and a β^+ particle. The neutron that is produced remains in the nucleus and the β^+ particle is ejected (radiated).

Review Problem 3

Complete the nuclear equation below for the β^+ decay of Iridium-192.

$$^{192}_{77}\text{Ir} \;\longrightarrow$$

For ***i-books*** versions: **Click here to check answer**

4) Gamma (γ) Decay

The emission of **α** particles, $\boldsymbol{\beta}^-$ particles, or $\boldsymbol{\beta}^+$ particles is often accompanied by gamma (γ) decay. In γ decay, a gamma ray is emitted. Gamma rays are a form of "high energy" light. An example of gamma (and $\boldsymbol{\beta}^-$) decay is the shown in nuclear equation below:

$$^{99}_{42}\text{Mo} \rightarrow {}^{99}_{43}\text{Tc} + {}^{0}_{-1}\boldsymbol{\beta}^- + \gamma$$

In this reaction, there is a delay of several hours before the gamma ray is emitted. The use of the ^{99}Mo decay to generate gamma rays is used in millions of medical diagnostic procedures per year.

Fission and Fusion Nuclear Reactions

Fission and **fusion** are nuclear reactions in which large amounts of energy are released. The energy is released in the form of nuclear radiation and *heat*.

In **fission reactions**, the nucleus of one isotope is split into two or more smaller nuclei. An example of a fission reaction is the reaction of uranium-235 that is used to generate power in nuclear power reactors. In this reaction a ^{235}U nucleus (the nuclear fuel) absorbs a neutron (from a "starter source") and then splits into ^{91}Kr, ^{142}Ba, and three neutrons. The three neutrons that are produced can then react with three more ^{235}U nuclei. This process will continue, in what is known as a ***nuclear chain reaction***, until the ^{235}U fuel is depleted. The energy that is released in the fission process is used to heat water to produce pressurized steam that subsequently generates electricity by rotating a shaft in an electrical generator.

In a **fusion reaction**, two or more isotopes collide to form one or more *different* isotopes and subatomic particles. The energy that comes from the sun is produced by fusion reactions. In a series of fusion reactions occurring in the sun and many similar "small stars," four ^{1}H nuclei are converted to a ^{4}He nuclei and two $\boldsymbol{\beta}^+$ particles.

Radioisotopes in Medicine

Nuclear Radiation Dosages

All four types of nuclear radiation, **α** particles, $\boldsymbol{\beta}^-$ particles, $\boldsymbol{\beta}^+$ particles, and gamma rays can change the composition of substances that they encounter. This can be quite detrimental to humans and other living creatures because it can result in damage to substances, such as DNA and proteins, that are essential for normal cell function. It is for this reason that we must be careful about exposure to nuclear radiation.

In order to consider safe levels of exposure, you should be aware of the units that are used for radiation dosages. The **becquerel** (**Bq**) unit is related to the number of nuclei per second that undergo radioactive decay within a sample. One **Bq** is defined as one radioactive nucleus decaying per second. The **rad** unit (*radiation absorbed dose*) is related to the amount of energy that an object absorbs when it is exposed to a radioactive sample. One **rad** is defined as a dose of 0.01 Joules per kilogram of the absorbing object. The **rem** dosage unit is obtained by multiplying the **rad** value by a "*quality factor* (**QF**)" which takes into account the biological damage done by the different types of decay radiation. The **rem** is defined as:

$$\textbf{rem} = \textbf{rad} \cdot (\textbf{QF})$$

The approximate values for *quality factors* are shown in Table 16.1. These values are approximate because they vary depending on the energy of the radiation, the time period in which the object was exposed to the radiation, and the particular part of the body that received the dose. The larger the value of the *quality factor*, the more damaging the exposure event.

Table 16.1 **Quality Factors (QF) for Various Types of Radiation**

Type of Radiation	Quality Factor (QF)
X-rays, gamma rays, $\boldsymbol{\beta}^+$ particles, $\boldsymbol{\beta}^-$ particles	1
neutrons, protons	10
$\boldsymbol{\alpha}$ particles, fission reaction daughter isotopes	20

In medical applications, the **gray** (**Gy**) and **sievert** (**Sv)** are often used instead of the **rad** and **rem**: 1**Gy** = *exactly* 100 **rads** and 1 **Sv** = *exactly* 100 **rem.** All four of these radiation units are also used for X-rays. X-rays, like gamma rays, are high energy forms of light.

Review Problem 4

a. If a patient receives a dose of 0.15 **rad** of β^- radiation, what is the dosage in **rem** units?

b. If a patient receives a dose of 0.15 **rad** of **α** particle radiation, what is the dosage in **rem** units?

For ***i-books*** versions: **Click here to check answer**

For **print or pdf versions**, see the answer key **at the end of *this* appendix**.

Exposure to Radiation

Exposure to radiation can have harmful or beneficial effects. The key to using radioisotopes in medicine is *controlling the exposure* to radiation. Table 16.2 shows the harmful *short-term* health effects of exposure to increasing dosages of radiation. *Delayed effects* of exposure include an increase in the risk of cancer, genetic diseases, and cataracts.

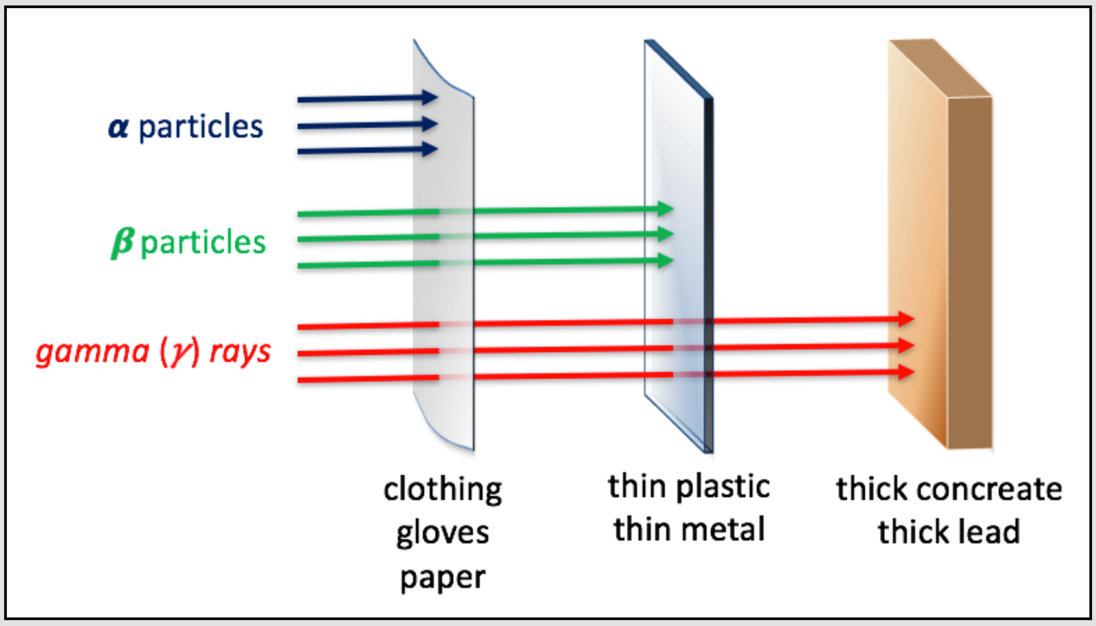
Table 16.2 **Harmful Short-Term Health Effects of Exposure to Increasing Dosages of Radiation**

Exposure/Dose (rem)	Effect on Health	Time for symptoms to appear (without treatment)
5-10	Changes in blood chemistry	
50	Nausea	hours
55	Fatigue	
70	Vomiting	
75	Hair loss	2-3 weeks
90	Diarrhea	
100	Hemorrhage	
400	Possible death	within 2 months
1000	Destruction of intestinal lining, internal bleeding, death	1-2 weeks
2000	Central nervous system damage, loss of consciousness, death	minutes to days

Source: US Environmental Protection Agency

Exposure to radiation can be controlled by proper shielding that blocks radiation. You have probably experienced this when having dental x-rays. Figure 16.9 illustrates the shielding ability of various substances for **α** particles, β particles, and γ radiation.

Figure 16.9 **Ability of Various Substances to Block Nuclear Radiation**



An illustration of the ability of some substances to block **α** particles, β particles (both β^- particles, or β^+), and γ radiation.

Half-life

In order to prevent unnecessary or undesired exposure to radiation, it is useful to know the time period in which a sample of a particular radioisotope will remain hazardous. We use the concept of **half-life** to describe the amount of time required for ***one half*** of a sample of a particular radioisotope to decay. As an example, let's consider a sample that contains 100 mg of iridium-192. ^{192}Ir is used in medicine for internal radiation therapy. It undergoes $\boldsymbol{\beta}^-$ decay as shown in the nuclear equation below.

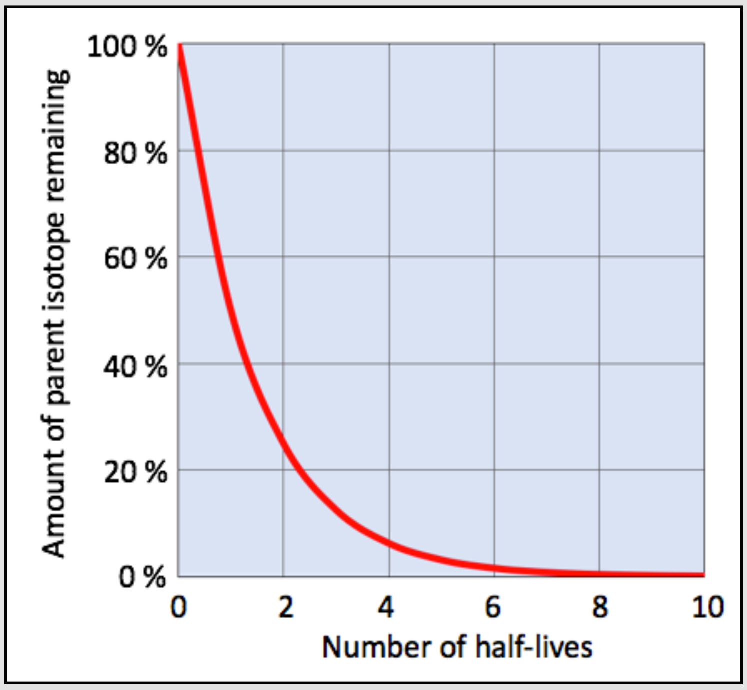
$$^{192}_{77}\text{Ir} \longrightarrow {}^{192}_{78}\text{Pt} + {}^{0}_{-1}\boldsymbol{\beta}^- + \gamma$$

The ***half-life*** of ^{192}Ir is 74 days. After 74 days (one half-life), 50 mg of ^{192}Ir remains. Note the ^{192}Ir nuclei are not simply vanishing; they are being converted to daughter isotopes (^{192}Pt) and nuclear decay products. Over the following 74 days, half of the *remaining* 50 mg of ^{192}Ir decays to leave just 25 mg of ^{192}Ir. Over the *next* 74 days, the mass of the remaining ^{192}Ir is once again decreased by 50%. This will continue until the last ^{192}Ir nucleus decays. ^{192}Ir internal radiation therapy involves implanting small capsules of ^{192}Ir near cancer tumors. The gamma rays that are emitted can kill some types of cancer cells. The general concept of half-life is graphically illustrated in Figure 16.10.

Figure 16.10

Illustration of the Half-Life Concept

After one half-life, 50% of the parent isotope remains remains. After two half-lives, 25% of the parent isotope remains. After three half-lives, 12.5% of the parent isotope remains. The mass of the parent isotope decreases by 50% every successive half-life period until the last parent nucleus decays.



You may be wondering how it is possible that a radioisotope with a relatively short half-life, such as ^{192}Ir, could exist based on the age of our solar system. ^{192}Ir can be produced by placing a sample of ^{191}Ir (a stable isotope) in the core of a nuclear reactor where it is bombarded with neutrons. In this process, a neutron will combine with a ^{191}Ir nucleus in a *fusion reaction* to form ^{192}Ir.

A small sample that contains nuclei of a radioisotope that has a relatively short half-life will not remain radioactive (hazardous) for a long time; however, because the decay rate is so fast, it could deliver a *large dose* of radiation during a short exposure time. Conversely, a small sample that contains nuclei of a radioisotope that has a long half-life will remain radioactive for a long time; however, its decay rate can be slow enough that it would only deliver a *small dose* of radiation during a short exposure time. Table 16.3 shows the half-lives of some radioisotopes. Note that the half-lives vary from less than one second to more than a billion years.

Table 16.3 Half-lives of Some Radioisotopes

Radioisotope	**half-life**	**Type of Decay**
Polonium-214	0.0016 seconds	α and γ
Carbon-11	20 minutes	β^+
Sodium-24	15 hours	β^- and γ
Iodine-131	8.1 days	β^- and γ
Strontium-90	28.1 years	β^-
Carbon-14	5,370 years	β^-
Uranium-238	4.5×10^9 years	α and γ

Review Problem 5

^{59}Fe undergoes β^- decay and has a half-life of 45 days.

a. Complete the nuclear equation for the β^- decay of ^{59}Fe.

$$^{59}_{26}\text{Fe} \rightarrow \boxed{?} + ^{0}_{-1}\beta^-$$

b. If a sample contains 88 mg of ^{59}Fe, how many mg of ^{59}Fe will remain after 135 days (***three*** half lives)?

For ***i-books*** versions: **Click here to check answer**

For **print or pdf versions**, see the answer key **at the end of *this* appendix**.

Radioisotopes as Therapeutic Medicine

I have discussed how nuclear radiation can be detrimental to your health; however, it is important to understand that it can also be beneficial when appropriate doses are administered. Radioisotopes are frequently used as treatment (therapy) for cancer. Nuclear radiation tends to kill fast-growing cells (such as cancerous cells). In **brachytherapy**, a ***sealed radiation source*** is placed within (or near) a region of the body that requires treatment. It is used to treat cervical cancer, prostate cancer, breast cancer, skin cancer, and several other types of cancer. An advantage of *brachytherapy* is that the radiation source can be positioned near the tumor so it will minimize damage to other areas of the body.

In **unsealed source radiotherapy**, unsealed radioisotopes are administered by injection or ingestion. The radioisotopes tend to accumulate in specific organs or tissues depending on how/where they are administered and the particular properties of the radioisotope that is used. Unsealed source radiotherapy is often used to treat thyroid and bone cancer. Patients undergoing unsealed source radiotherapy are kept a safe distance from other individuals because of the amount of gamma rays that are being emitted. It can take several days before the patient stops emitting dangerous quantities of gamma rays. Special safety procedures must be used when handling the patient's urine because the radioisotopes tend to be concentrated by the kidneys and then passed into the urine. It is for these reasons that patients often remain in the hospital for up to several days after the treatment. Health care professionals must obtain specialized training in order to work with radioisotopes.

In **external beam radiotherapy (EBRT)**, gamma rays or X-rays are emitted from a radiation source outside of the body. The radiation is projected in a narrow beam that can be directed to a particular organ or tissue.

Radioisotopes as Diagnostic Tools

Radioisotopes are often used to diagnose medical conditions. Examples include **thyroid scans** and **positron** (β^+ particles) **emission tomography** (**PET**) scans.

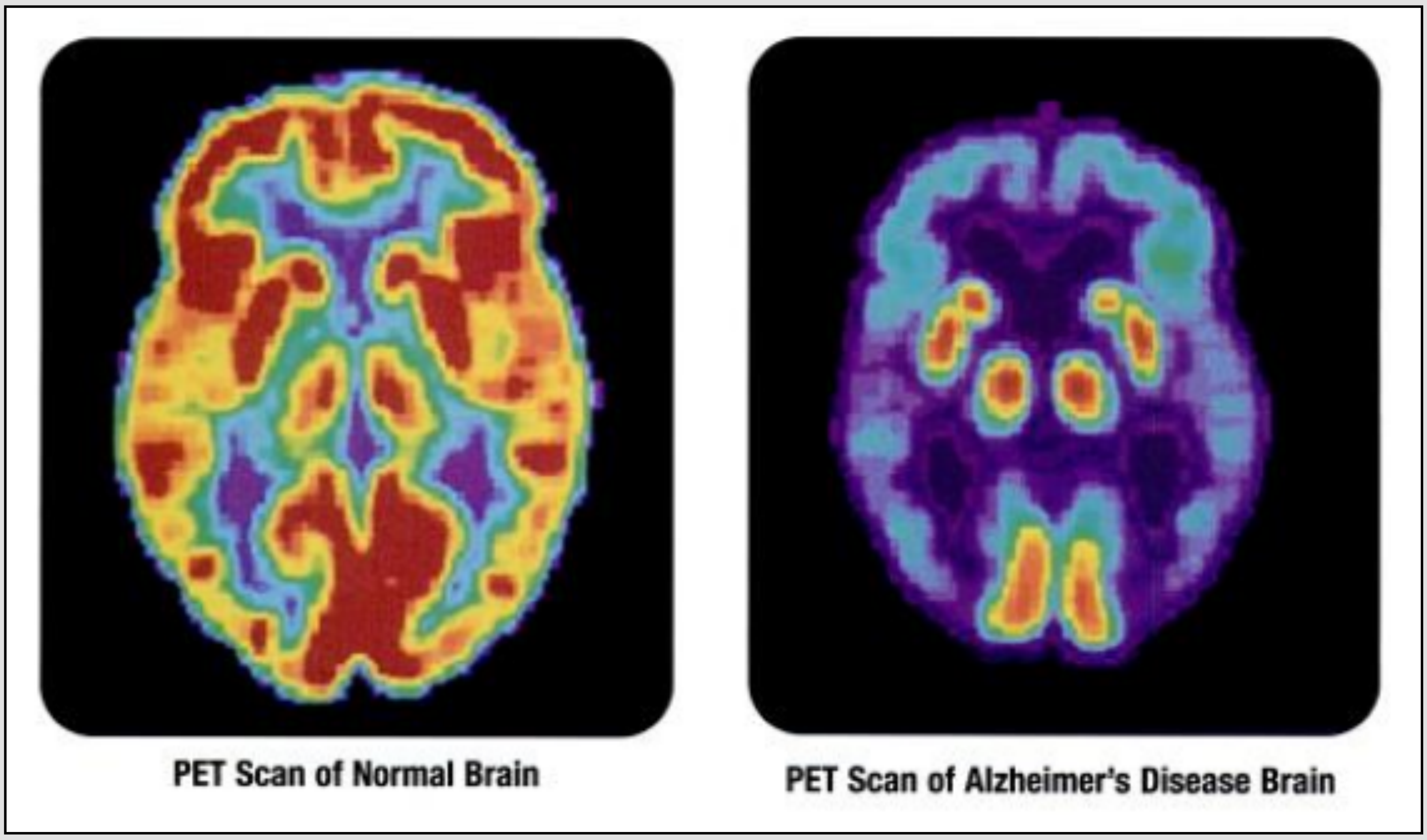
In a *thyroid scan*, iodine-131 is administered to patients in order to examine the thyroid gland. The rate at which ^{131}I accumulates in the thyroid gland is indicative of conditions such as thyroid cancer, hyperthyroidism, and other thyroid disorders. ^{131}I nuclei emit gamma rays and a β^- particle when they decay. The gamma rays that are emitted can be collected by detectors (gamma ray cameras) in order to generate an image that shows the amount of gamma rays being emitted from regions within the thyroid gland. A thyroid scan image is shown in Figure 16.11. The more intense (brighter) white areas are indicative of greater quantities of gamma ray emission.

Figure 16.11 A Thyroid Scan Image

An image of the gamma rays emission pattern in a thyroid scan. The grayscale indicates the quantity of gamma rays being emitted.

Fluorine-18 is used in **positron emission tomography** (**PET**) to monitor biochemical processes within the body. ^{18}F decays by emitting a **β^+** particle (a *positron*). The **β^+** particles that are produced will undergo subsequent "*annihilation*" that results in the emission of a *gamma ray*. ^{18}F can be incorporated into chemicals that are routinely used by the body and then administered to the patient. The incorporation of radioisotopes into other chemicals is referred to as "**radiolabeling.**" I will elaborate on *positron emission tomography* (PET) by discussing its use in monitoring brain activity. In this application, glucose (a sugar that is contained in our normal diet) is radiolabeled with ^{18}F. The radiolabeled glucose is administered intravenously to the patient. After about one hour, the radiolabeled glucose will have migrated to parts of the body where it is in greatest demand. At this time, the gamma rays that are emitted by the radiolabeled glucose are imaged by detectors (gamma ray cameras). Knowing where glucose is in high demand gives healthcare professionals information that is useful in diagnosing and monitoring conditions such as brain disorders. For example, PET scans are used as a tool to diagnose and monitor Alzheimer's disease because glucose usage is *decreased* in the brain of a patient with Alzheimer's disease. Figure 16.12 show a PET brain scan of a normal brain (left) and the brain of a patient with Alzheimer's disease (right). The warmer colors (red, orange, and yellow) indicate areas of greater gamma ray emission (more glucose use) and the cooler colors (green, blue, and violet) indicate areas of lesser gamma ray emission (less glucose use).

Figure 16.12 **Positron Emission Topography (PET) Scans**



A PET brain scan of a normal brain (left) and the brain of a patient with Alzheimer's disease (right). The warmer colors (red, orange, and yellow) indicate areas of greater gamma ray emission (more glucose use) and the cooler colors (green, blue, and violet) indicate areas of lesser gamma ray emission (less glucose use).

Answers to Radioisotopes and Nuclear Chemistry Appendix Review Problems

Problem 1:

a. The parent isotope is plutonium-238. Because this is an ***alpha-decay*** nuclear reaction, one of the daughter isotopes is ^{4}He ($^{4}\boldsymbol{\alpha}$). We can deduce the identity of the other daughter isotope from knowing that the parent lost two protons and two neutrons in the form of an alpha particle. All plutonium isotopes will contain 94 protons. Therefore, a daughter isotope with 92 protons and a mass number of 234 will be produced. A glance at the periodic table tells us this isotope is Uranium-234.

b. The nuclear equation for the reaction is: $^{238}_{94}\text{Pu} \rightarrow {}^{234}_{92}\text{U} + {}^{4}_{2}\alpha$

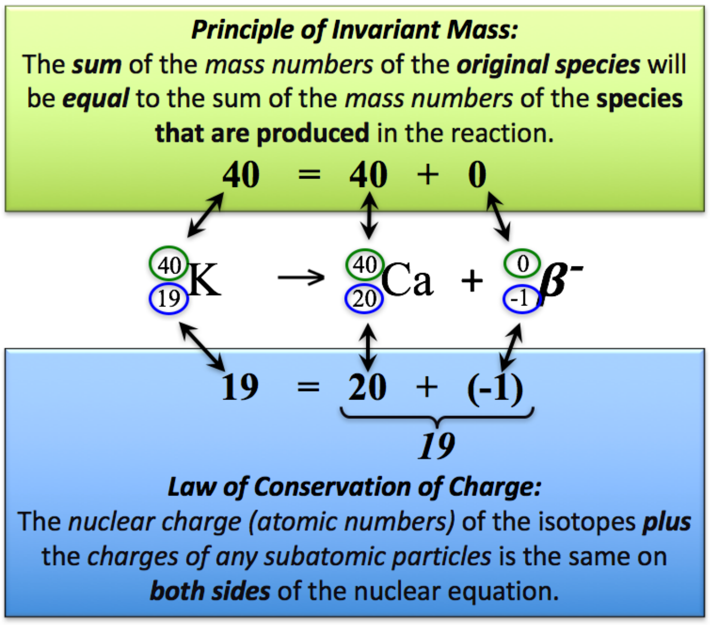
Problem 2:

In $\boldsymbol{\beta}^-$ decay, a neutron in the nucleus of the parent isotope is converted to a proton and a $\boldsymbol{\beta}^-$ particle. The proton remains in the nucleus and the $\boldsymbol{\beta}^-$ particle is ejected (radiated).

The nuclear equation for the reaction is: $^{40}_{19}\text{K} \rightarrow {}^{40}_{20}\text{Ca} + {}^{0}_{-1}\boldsymbol{\beta}$

The **principle of invariant mass** states that the *sum of the mass numbers of the original species* will be ***equal*** to the *sum of the mass numbers of the species that are produced in the reaction*. The mass number of the parent isotope (potassium-40) is **40**, and the *sum of the mass numbers of the species that are produced in the reaction is* **40**.

The **law of conservation of charge** states that the *nuclear charge (atomic numbers)* of the isotopes ***plus*** the *charges of any subatomic particles* is the same on ***both sides*** of the nuclear equation. The *nuclear charge (atomic number)* of the parent isotope (potassium-40) is **19**. For the daughter species, we have a *nuclear charge* of 20 from ^{40}Ca, ***plus*** a "-1" charge from the $\boldsymbol{\beta}^-$ particle to give a total of **19**.


Principle of Invariant Mass:
The ***sum*** of the *mass numbers* of the ***original species*** will be ***equal*** to the sum of the *mass numbers* of the **species that are produced** in the reaction.

Law of Conservation of Charge:
The *nuclear charge (atomic numbers)* of the isotopes ***plus*** the *charges of any subatomic particles* is the same on ***both sides*** of the nuclear equation.

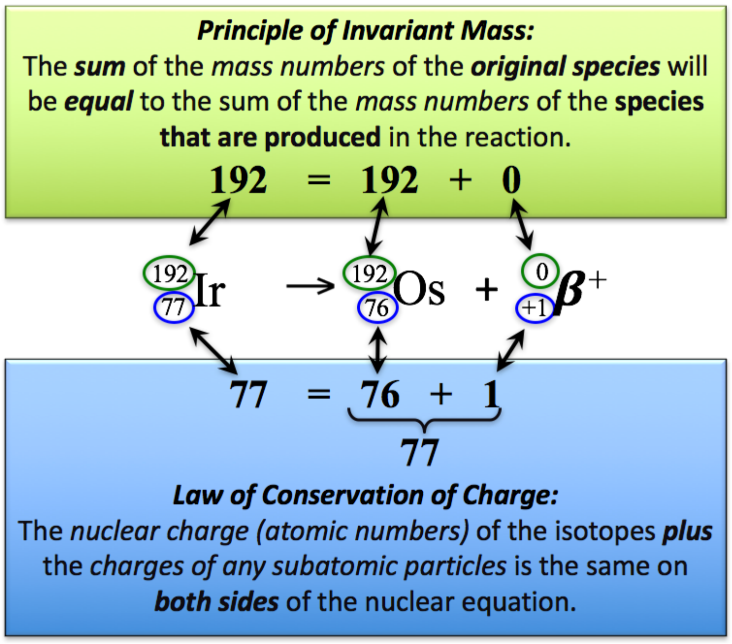
Problem 3:

In $\boldsymbol{\beta}^+$ decay, a proton in the nucleus of the parent isotope is converted to a neutron and a $\boldsymbol{\beta}^+$ particle. The neutron that is produced remains in the nucleus and the $\boldsymbol{\beta}^+$ particle is ejected (radiated).

The nuclear equation for the reaction is: $^{192}_{77}\text{Ir} \rightarrow {}^{192}_{76}\text{Os} + {}^{0}_{+1}\boldsymbol{\beta}^+$

The **principle of invariant mass** states that the *sum of the mass numbers of the original species* will be ***equal*** to the *sum of the mass numbers of the species that are produced in the reaction*. The mass number of the parent isotope (iridium-192) is **192**, and the *sum of the mass numbers of the species that are produced in the reaction is* **192**

The **law of conservation of charge** states that the *nuclear charge (atomic numbers)* of the isotopes ***plus*** the *charges of any subatomic particles* is the same on ***both sides*** of the nuclear equation. The *nuclear charge (atomic number)* of the parent isotope (iridium-192) is **77**. For the daughter species, we have a *nuclear charge* of 76 from ^{192}Os, ***plus*** a "+1" charge from the $\boldsymbol{\beta}^+$ particle to give a total of **77**.


Principle of Invariant Mass:
The ***sum*** of the *mass numbers* of the ***original species*** will be ***equal*** to the sum of the *mass numbers* of the **species that are produced** in the reaction.

Law of Conservation of Charge:
The *nuclear charge (atomic numbers)* of the isotopes ***plus*** the *charges of any subatomic particles* is the same on ***both sides*** of the nuclear equation.

Problem 4:

The **rem** dosage unit is obtained by multiplying the **rad** value by a "*quality factor* (**QF**)" that takes into account the biological damage done by the different types of decay radiation. The **rem** is defined as:

rem = **rad** • (**QF**)

a. If a patient receives a dose of 0.15 **rad** of $\boldsymbol{\beta}^{-}$ radiation, what is the dosage in **rem** units?

The QF for $\boldsymbol{\beta}^{-}$ radiation is 1; therefore

$$\begin{aligned} \textbf{rem} &= \textbf{rad} \cdot (\textbf{1}) \\ &= (0.15) \cdot (\textbf{1}) \\ &= 0.15\ \textbf{rem} \end{aligned}$$

b. If a patient receives a dose of 0.15 **rad** of **α** particle radiation, what is the dosage in **rem** units?

The QF for **α** particle radiation is **20**; therefore

$$\begin{aligned} \textbf{rem} &= \textbf{rad} \cdot (\textbf{20}) \\ &= (0.15) \cdot (\textbf{20}) \\ &= 3.0\ \textbf{rem} \end{aligned}$$

Problem 5:

a. Complete the nuclear equation for the $\boldsymbol{\beta}^{-}$ decay of ^{59}Fe.

$$^{59}_{26}\text{Fe} \longrightarrow {}^{59}_{27}\text{Co} + {}^{0}_{-1}\boldsymbol{\beta}^{-}$$

b. If a sample contains 88 mg of ^{59}Fe, how many mg of ^{59}Fe will remain after 135 days (***three*** half lives)?