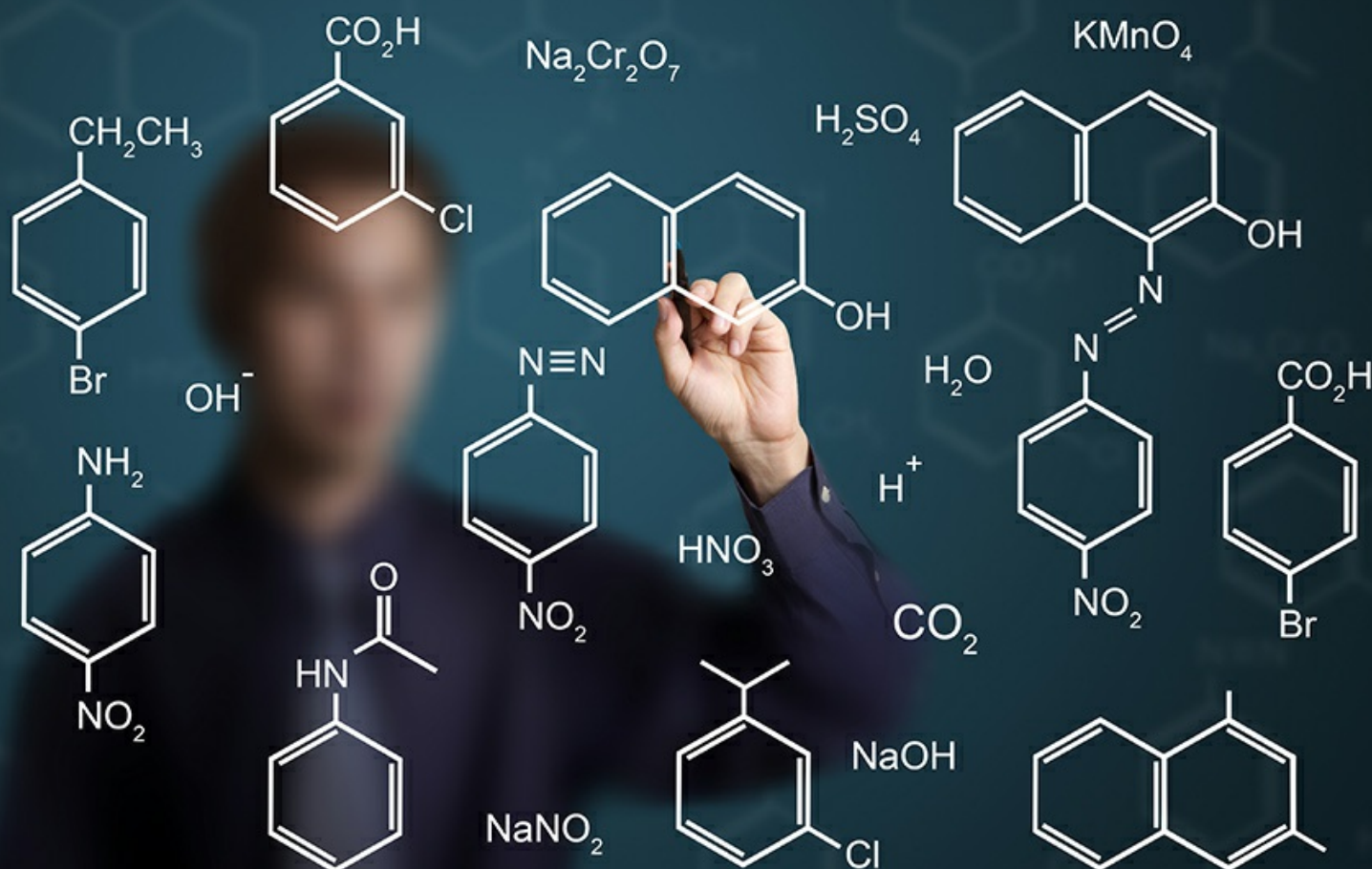


Introductory Chemistry

Edward W. Pitzer



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Introductory Chemistry



Introductory Chemistry

1st edition

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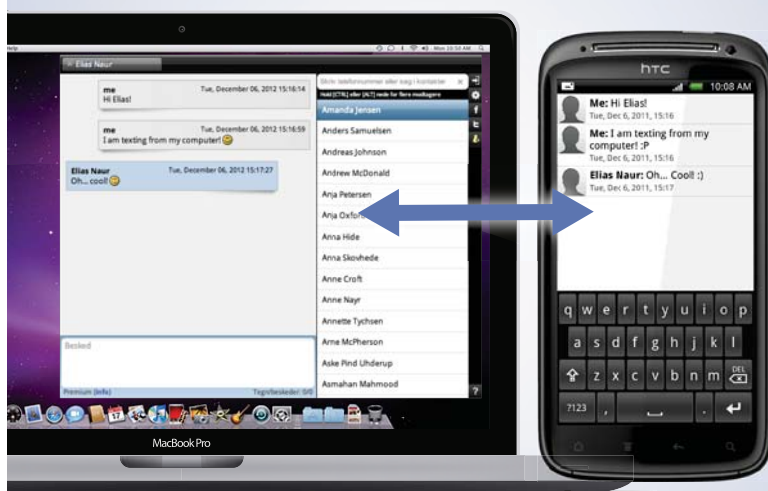
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Introduction

This textbook is intended for use by college level students who will take only one course in chemistry throughout their academic career.

The following is a list of areas that may require an introduction to chemistry but not a full two years of college chemistry.

Food Science	Pharmacy Technician
Safety and Health	Health Education
Mortuary Science	Nursing
Physical Therapy	Laboratory Technician
Environmental Science	Hazardous Material Control
Fire Investigation	Animal Science
Plant Science	Phlebotomy

If you are planning to go to medical school, you will need a more in depth course of “first year” chemistry. However, if you “live in fear” of college chemistry study my textbook as preparation. After all it’s free!

There are two goals that I have for this textbook. The first goal is to teach the “fundamentals” of chemistry without bogging the student down with heavy theory. The second goal is to teach basic critical thinking skills.

This is done by a textbook long building of a central problem solving theorem that is applied to nearly all of the problems in the book.

All of the problems presented in this text all fully worked with proper and correct answers. Do yourself a favor. Write the statement of the problems on a piece of paper, exit the text, and try to solve the problems. If you get stuck on a problem, refer back to the text. After several trials of the problems in this fashion you will probably find you have mastered the material.

If you have as much fun as I think you are going to reading and using this textbook, tell a friend about the textbook and the great services of bookboon.com.

1 Standard Measurements

1.1 Standard Units – The SI System

Chemistry is a science; all sciences measure things. It couldn't be a more direct application. However, one needs to see the value of measuring a thing the same way another person measures that same thing.

Some common measurements have anatomical origins. The thumb is approximately an inch wide, a foot is around a foot in length, and a yard is approximately the length of the forearm. But whose thumb, whose foot, and whose forearm? Very often it was the anatomical measurements of the king that prevailed.

Antoine-Laurent Lavoisier (known as the father of modern chemistry) was among a group of French scientists commissioned by King Louis XVI to develop a standardized system of units and measurements.

On December 10, 1799 the “Système international d'unités” was officially adopted. Today it is known simply as the SI System.

The following table lists the seven *basic* units of the SI system.

Measurement	Standard Unit	Symbol
Mass	kilogram	kg
Length	meter	m
Time	second	s
Temperature	Kelvin	K
Amount (of anything)	mole	mol
Electrical Current	Ampere	A
Luminous Intensity	candela	cd

Table 1.1.1 The SI System of Measurements

So what is a *basic* unit and where is the unit for volume? A *basic* unit is a unit that cannot be broken down into other units. Volume, like most of the units we will use, is a *derived* unit. That is to say it is derived from the seven basic units. The following table shows some of the derived units we will use in this text.

Example 1.2.2

Alpha Centauri, the brightest star in the southern constellation Centaurus, is approximately 26,000,000,000,000 miles from Earth. Let's express this in scientific notation.

- 1) Even though there is no decimal point expressed in this number its location is at the end of the number. Establish a new location for the decimal point between the 2 and the 6.

$$a = 2.6$$

- 2) Count the number of spaces from the new to the old location of the decimal point. $b = 13$.
- 3) Multiply a by ten raised to the power of b .

$$2.6 \times 10^{13}$$

Again a number like 2.6×10^{13} miles is much easier to work with and enter into a calculator. All scientific calculators have scientific notation operations.

Refer to the following two figures to get a good overview of the scientific notation system.

Scientific Notation for Large Numbers					
<u>Numbers</u>					
1	10	100	1,000	1,000,000	1,000,000,000
<u>Number of Decades (tens)</u>					
0	1	2	3	6	9
<u>Exponent</u>					
10^0	10^1	10^2	10^3	10^6	10^9

Figure 1.2.1 Scientific Notation for Large Numbers

Scientific Notation for Small Numbers					
<u>Numbers</u>					
1	0.1	0.01	0.001	0.000001	0.000000001
<u>Number of Decades (tenths)</u>					
0	1	2	3	6	9
<u>Exponent</u>					
10^0	10^{-1}	10^{-2}	10^{-3}	10^{-6}	10^{-9}

Figure 1.2.2 Scientific Notation for Small Numbers

As you can, see the number of decades, whether counting tens or tenths, is equal to the absolute value of the exponent of ten.

Exercise 1.2.1

Convert 0.00000000124 to scientific notation.

Let $a = 1.24$. Let $b = -9$.

Therefore 1.24×10^{-9} .

Exercise 1.2.2

Convert 234,000,000 to scientific notation.

Let $a = 2.34$. Let $b = 8$.

Therefore 2.34×10^8 .

Exercise 1.2.3

Convert 1.09×10^{-7} to standard notation.

$a = 1.09$. $b = -7$.

You need 6 zeroes to position the decimal point 7 spaces to the left of its present position.

Therefore 0.000000109.

Exercise 1.2.4

Convert 3.62×10^{12} to standard notation.

$a = 3.62$. $b = 12$.

You need 10 zeroes to position the decimal point 12 spaces to the right of its present position.

Therefore 3,620,000,000,000.

1.3 The Part per Million (ppm) System

Another popular method used to express large and small numbers is the part per million (ppm) system.

The best way to understand the part per million system is to compare it to the percent system. The percentage system is a system that everyone should be familiar with. In the percentage system numbers are viewed as a fraction or decimal part of one hundred, Therefore 50% could be viewed as 50/100 or 0.50.

The part per million system is similar to the percent system in that numbers are viewed as a fraction or decimal part of one million. Another way of rationalizing this comparison is to realize that a percent could be referred to (but never is) as a part per hundred.

The one important difference between percent and part per million values is that while percent can be used to represent concentration, part per million values are always used to represent concentration.

The best way to become familiar with the part per million system is to practice converting from percent to part per million and the reverse.

The symbol for percent is % and the symbol for part per million is ppm.

Let's do some exercises.

Exercise 1.3.1

The air we breathe is 0.9% argon. Convert this value to ppm. The number 10,000 is always used in these conversions because one million is 10,000 times as large as one hundred.

$$0.9\% = \frac{0.9}{100} \times \frac{10,000}{10,000} = \frac{9,000}{1,000,000} = 9,000 \text{ ppm}$$

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Exercise 1.3.2

The air we breathe is also around 0.036% carbon dioxide. Convert this value to ppm.

$$0.036 \% = \frac{0.036}{100} \times \frac{10,000}{10,000} = \frac{360}{1,000,000} = 360 \text{ ppm}$$

Exercise 1.3.3

Whole milk is around 48,000 ppm lactose.

Convert this value to %.

$$48,000 \text{ ppm} = \frac{48,000}{1,000,000} \times \frac{\frac{1}{10,000}}{\frac{1}{10,000}} = \frac{4.8}{100} = 4.8\%$$

Exercise 1.3.4

A solution of salt (NaCl) water contains 520 ppm of the sodium ion (Na⁺). Convert this value to %.

$$520 \text{ ppm} = \frac{520}{1,000,000} \times \frac{\frac{1}{10,000}}{\frac{1}{10,000}} = \frac{0.052}{100} = 0.052\%$$

1.4 Significant Figures

Significant numbers, and the rules that govern them, are not as difficult as one might imagine. The figure below lists some simple rules that make it easy to determine the number of significant figures in a particular number.

1. Numbers that are not zeroes are considered significant figures.
2. If a number is a zero between nonzero numbers it is a significant figure.
3. If a number is a zero at the end of a number in decimal formation it is a significant figure.
4. Any number in the coefficient of a number expressed in scientific notation is a significant figure.
5. If a zero precedes a nonzero number in a number expressed in decimal form it is **not** a significant figure.
6. If a zero comes after nonzero numbers in a very large number that is not in decimal form it is **not** a significant figure.

Let's do some exercises.

Exercise 1.4.1

How many significant figures are in 7.8 km?
Rule #1 tells us there are **2** significant figures.

Exercise 1.4.2

How many significant figures are in 408 kg?
Rule #2 tells us there are **3** significant figures.

Exercise 1.4.3

How many significant figures are in 37.0 °C?
Rule #3 tells us there are **3** significant figures.

Exercise 1.4.4

How many significant figures are there in 7.000×10^4 m?
Rule #4 tells us there are **4** significant figures.

Exercise 1.4.5

How many significant figures are there in 0.000075 kg?
Rule #5 tells us there are **2** significant figures.

Exercise 1.4.6

How many significant figures are there in 26,000,000 km?
Rule #6 tells us there are **2** significant figures.

But what happens when you multiply, divide, add, or subtract numbers with specific numbers of significant figures?

Doing mathematical operations with significant figures is relatively straightforward. Do the mathematical operations as usual. Assign your answer the same number of significant figures as the number that contained the **least** number of significant figures. When rounding off round down if the number to be dropped is 4 or less and round up if the number to be dropped is 5 or more.

Let's do some exercises.

Exercise 1.4.7

Report the product of 1.46 and 2.5 with the correct number of significant figures.

$$1.46 \times 2.5 = 3.65 \text{ or } \mathbf{3.7} \text{ to the 2 significant figures of 2.5}$$

Exercise 1.4.8

Report the sum of 1.9834 and 2 with the correct number of significant figures.

$$1.9834 + 2 = 3.9834 \text{ or } \mathbf{4} \text{ to the 1 significant figure of 2.}$$

Exercise 1.4.9

Report the difference of 6.3 minus 1.2546 with the correct number of significant figures.

$$6.3 - 1.2546 = 5.0454 \text{ or } \mathbf{5.0} \text{ to the 2 significant figures of 6.3.}$$

Exercise 1.4.10

Report the quotient of 29 divided by 2.5 with the correct number of significant figures.

$$29/2.5 = 11.6 \text{ or } \mathbf{12} \text{ to the 2 significant figures of either number.}$$



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1.5 Unit Conversions

Again, I make the point that measuring values is an essential part of any science. Once you have collected these measured values you must know how to manipulate them if they are to be useful.

Let's say that you directed Sam to calculate the fuel consumption efficiency of his car by measuring the amount of fuel added to the car in liters and the distance the car traveled in kilometers.

After several days you ask Sam to report on the fuel consumption efficiency of his car. Sam responds, "Six liters." A bit confused you ask Sam the question again and he responds, "One hundred and two kilometers."

Apparently, Sam does not know how to **convert** his measured values into the fuel consumption efficiency of his car.

The simplest unit conversion is the ratio of two measured values. While a calculation of liters per kilometer (L/km) would reflect the fuel consumption efficiency of Sam's car it is customary to measure fuel consumption efficiency in kilometers per liter (km/L).

So the fuel consumption efficiency of Sam's car is calculated as follows.

$$102 \text{ km} / 6.0 \text{ L} = 17 \text{ km/L}$$

American scientists and engineers certainly use the SI system of units. However, generally speaking, the US has yet to officially adopt any type of metric system. For this reason it is often necessary to **convert** the units of one system to the units of another system.

Listed in the table below are some approximate conversions of US units to customary metric units.

Measurement	US Unit	Metric Unit	Conversion
Mass	Pound	Kilogram	0.454 kg/lb
Volume	Gallon	Liter	3.785 L/gal
Area	Square Foot	Square Meter	0.093 m ² /ft ²
Length	Mile	Kilometer	1.61 km/mi
Temperature	°F	°C	°C = $\frac{5(°F-32)}{9}$
Force	Poundforce	Newton	4.45 N/lbf

Table 1.5.1 US to Metric Unit Conversions

There are no example problems in this section. The next section is all problem solving using the concept of unit conversion.

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1.6 Problem Solving and Critical Thinking Skills

I would like to help each student develop problem solving abilities prior to encountering the chemical calculations in the rest of the text.

For this reason the statements of these problems are not necessarily chemical in nature but deal with everyday situations.

The skills developed working these problems are *directly applicable* to the chemical calculations that follow.

These problems are worked out in full step-by-step detail. They are relatively simple calculations irrespective of the amount of space they occupy in the text.

All of the following problems use my unit conversion problem solving *mantra* as follows:

- Draw a long horizontal line.
- Make an equals sign.
- Skip some space.
- Write down the units you are asked to solve for.
- Go back to the beginning of the horizontal line and write down the numbers and units you have been given.
- Make a vertical line.

Here's what all that means.

- The horizontal line is the division line in a series of fractions.
- The equals sign is self-explanatory.
- The skipped space is where the numerical answer will go.
- The units you enter after the skipped space are your target.
- The units at the beginning are the units to be converted.
- The vertical line establishes the first fraction and indicates multiplication.

Exercise 1.6.1

Calculate the number of centimeters in a mile.

(1 mi = 1.61 km).

Set the calculation up in the style of my problem solving *mantra* established in the previous section.

$$\frac{1 \text{ mi}}{\quad} = \quad \text{cm}$$

Now convert *mi* to *km*.

$$\frac{1 \text{ mi} | 1.61 \text{ km}}{1 \text{ mi}} = \text{cm}$$

Notice that *mi* canceled *mi*. Now convert *km* to *m*.

$$\frac{1 \text{ mi} | 1.61 \text{ km} | 1000 \text{ m}}{1 \text{ mi} | 1 \text{ km}} = \text{cm}$$

Notice that *km* canceled *km*. Now convert *m* to *cm*

$$\frac{1 \text{ mi} | 1.61 \text{ km} | 1000 \text{ m} | 100 \text{ cm}}{1 \text{ mi} | 1 \text{ km} | 1 \text{ m}} = 1.61 \times 10^5 \text{ cm}$$

Notice that *m* canceled *m*. You are left with *cm* which was your target and by doing the arithmetic you have your answer.



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Exercise 1.6.2

Calculate the number of milliliters in five US gallons.

$$(1 \text{ gal} = 3.785 \text{ L})$$

Set the calculation up in the style of my problem solving *mantra* established in the previous section.

$$\frac{5 \text{ gal}}{1} = \text{ml}$$

Now convert *gal* to *L*.

$$\frac{5 \text{ gal} \left| \frac{3.785 \text{ L}}{1 \text{ gal}} \right.}{1} = \text{ml}$$

Notice that *gal* canceled *gal*. Now convert *L* to *mL*.

$$\frac{5 \text{ gal} \left| \frac{3.785 \cancel{\text{L}} \left| \frac{10^3 \text{ ml}}{1 \cancel{\text{L}}} \right. \right.}{1}}{1} = 1.9 \times 10^4 \text{ ml}$$

Notice that *L* canceled *L* and by doing the arithmetic you have your answer.

Exercise 1.6.3

Marie is considering purchasing a US knock-off brand of her favorite French perfume. The French perfume contains 150 mg/L of essential oils. The US knock-off perfume contains 0.01 oz/gal of essential oils. If Marie decides to purchase the knock-off perfume, will she get a good deal? (1 g = 0.035 oz and 1 gal = 3.785 L)

The strategy for this example is to convert the 0.01 oz/gal of the US knock-off perfume to mg/L and compare that to the 150 mg/L of the French perfume.

Set the calculation up in the style of my problem solving *mantra* established in the previous section.

$$\frac{0.01 \text{ oz}}{1 \text{ gal}} = \frac{\text{mg}}{\text{L}}$$

Now convert *gal* to *L*.

$$\frac{0.01 \text{ oz}}{1 \text{ gal}} \left| \frac{1 \text{ gal}}{3.785 \text{ L}} \right. = \frac{\text{mg}}{\text{L}}$$

Notice that **gal** canceled **gal**. Now convert **oz** to **g**.

$$\frac{0.01 \cancel{\text{oz}}}{1 \cancel{\text{gal}}} \left| \frac{1 \cancel{\text{gal}}}{3.785 \text{ L}} \right| \frac{1 \text{ g}}{0.035 \cancel{\text{oz}}} = \frac{\text{mg}}{\text{L}}$$

Notice that **oz** canceled **oz**. Now convert **g** to **mg**.

$$\frac{0.01 \cancel{\text{oz}}}{1 \cancel{\text{gal}}} \left| \frac{1 \cancel{\text{gal}}}{3.785 \text{ L}} \right| \frac{1 \cancel{\text{g}}}{0.035 \cancel{\text{oz}}} \left| \frac{1000 \text{ mg}}{1 \cancel{\text{g}}} \right| = 75.5 \frac{\text{mg}}{\text{L}}$$

Notice that **g** canceled **g**. You are left with **mg** in the numerator and **L** in the denominator. That was your target and by doing the arithmetic you have your answer.

The US knock-off perfume has approximately half the essential oils as the French perfume. Marie will not get a good deal.

Take notice that in Example 1.6.2 we used the conversion factor 3.785 gal/1 L and in Example 1.6.3 we used the conversion factor 1 gal/3.785 L. Can we do that? The answer is **yes**. Even though the numbers have different units they are equal to one another. So inverting the fractional units does not change the value of the fraction.

Exercise 1.6.4

An area rug is 3 meters wide by 4 meters long. What is the area of the rug in square yards (yd²)? (1 ft² = 0.093 m²)

First calculate the area of the rug in square meters (m²).

$$3 \text{ m} \times 4 \text{ m} = 12 \text{ m}^2$$

Set the calculation up in the style of my problem solving **mantra** established in the previous section.

$$\frac{12 \text{ m}^2}{\quad} \left| \frac{\quad}{\quad} \right| = \text{yd}^2$$

Now convert **m²** to **ft²**.

$$\frac{12 \text{ m}^2}{\quad} \left| \frac{1 \text{ ft}^2}{0.093 \text{ m}^2} \right| \left| \frac{\quad}{\quad} \right| = \text{yd}^2$$

Notice that m^2 canceled m^2 . Now you get to **deduce** your first conversion factor. You know that there are 3 ft in 1 yd. So $3 \text{ ft} \times 3 \text{ ft} = 9 \text{ ft}^2$ and $1 \text{ yd} \times 1 \text{ yd} = 1 \text{ yd}^2$. So $1 \text{ yd}^2 = 9 \text{ ft}^2$.

Now convert ft^2 to yd^2 .

$$\frac{12 \cancel{m^2} | 1 \cancel{ft}^2 | 1 \text{ yd}^2}{0.093 \cancel{m^2} | 9 \cancel{ft}^2} = 14 \text{ yd}^2$$

Notice that ft^2 canceled ft^2 and by doing the arithmetic you have your answer.

Exercise 1.6.5

In 2010, the Deepwater Horizon oil spill released 4.9 million barrels (bbl) of oil into the Gulf of Mexico. How many cubic centimeters of oil was released into the Gulf? (1 bbl = 55 gal and 1 gal = 3.785 L and $1 \text{ L} = 10^3 \text{ cm}^3$)

Set the calculation up in the style of my problem solving **mantra** established in the previous section.

$$\frac{4.9 \times 10^6 \text{ bbl}}{\quad} = \quad \text{cm}^3$$

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Now convert *bbl* to *gal*.

$$\frac{4.9 \times 10^6 \text{ bbl} | 55 \text{ gal}}{1 \text{ bbl}} = \text{cm}^3$$

Notice that *bbl* canceled *bbl*. Now convert *gal* to *L*.

$$\frac{4.9 \times 10^6 \text{ bbl} | 55 \text{ gal} | 3.785 \text{ L}}{1 \text{ bbl} | 1 \text{ gal}} = \text{cm}^3$$

Notice that *gal* canceled *gal*. Now convert *L* to *cc*³.

$$\frac{4.9 \times 10^6 \text{ bbl} | 55 \text{ gal} | 3.785 \text{ L} | 10^3 \text{ cm}^3}{1 \text{ bbl} | 1 \text{ gal} | 1 \text{ L}} = 1 \times 10^{12} \text{ cm}^3$$

Notice that *L* canceled *L* and by doing the arithmetic you get your answer.

Exercise 1.6.6

A light year is the distance light will travel (in a vacuum) in one year. The speed of light is 6.7×10^8 miles per hour. How many centimeters are there in a light year? (1 mi = 1.6 km)

Set the calculation up in the style of my problem solving *mantra* established in the previous section.

$$\frac{6.7 \times 10^8 \text{ mi}}{1 \text{ hr}} | \frac{\text{cm}}{\text{yr}} =$$

Now convert *mi* to *km*.

$$\frac{6.7 \times 10^8 \text{ mi} | 1.61 \text{ km}}{1 \text{ hr} | 1 \text{ mi}} = \frac{\text{cm}}{\text{yr}}$$

Notice that *mi* canceled *mi*. Now convert *km* to *m*.

$$\frac{6.7 \times 10^8 \text{ mi} | 1.61 \text{ km} | 10^3 \text{ m}}{1 \text{ hr} | 1 \text{ mi} | 1 \text{ km}} = \frac{\text{cm}}{\text{yr}}$$

Notice that **km** canceled **km**. Now convert **m** to **cm**.

$$\frac{6.7 \times 10^8 \cancel{\text{mi}}}{1 \text{ hr}} \times \frac{1.61 \cancel{\text{km}}}{1 \cancel{\text{mi}}} \times \frac{10^3 \cancel{\text{m}}}{1 \cancel{\text{km}}} \times \frac{10^2 \text{ cm}}{1 \cancel{\text{m}}} = \frac{\text{cm}}{\text{yr}}$$

Notice that **m** canceled **m**. Now convert **hr** to **d**.

$$\frac{6.7 \times 10^8 \cancel{\text{mi}}}{1 \cancel{\text{hr}}} \times \frac{1.61 \cancel{\text{km}}}{1 \cancel{\text{mi}}} \times \frac{10^3 \cancel{\text{m}}}{1 \cancel{\text{km}}} \times \frac{10^2 \text{ cm}}{1 \cancel{\text{m}}} \times \frac{24 \cancel{\text{hr}}}{1 \text{ d}} = \frac{\text{cm}}{\text{yr}}$$

Notice that **hr** canceled **hr**. Now convert **d** to **yr**.

$$\frac{6.7 \times 10^8 \cancel{\text{mi}}}{1 \cancel{\text{hr}}} \times \frac{1.61 \cancel{\text{km}}}{1 \cancel{\text{mi}}} \times \frac{10^3 \cancel{\text{m}}}{1 \cancel{\text{km}}} \times \frac{10^2 \text{ cm}}{1 \cancel{\text{m}}} \times \frac{24 \cancel{\text{hr}}}{1 \cancel{\text{d}}} \times \frac{365 \cancel{\text{d}}}{1 \text{ yr}} = 9.4 \times 10^{17} \frac{\text{cm}}{\text{yr}}$$

Notice that **d** canceled **d**. You are left with **cm** in the numerator and **yr** in the denominator. The question was how many centimeters are there in a light year. There are 9.4×10^{17} centimeters per light year.

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2 Distinctions and Classifications of Matter

2.1 Types of Properties of Matter

Matter can be described as anything that has mass and occupies space.

However, when studying a fundamental science like chemistry it is necessary to make more distinct classifications of matter.

The first major classification of matter is the division of *physical* and *chemical* properties.

The *physical properties* of a substance are those properties that do not depend on a chemical change in the substance in order to be defined.

Some examples of physical properties are listed below.

- Mass
- Volume
- Color
- Freezing Point
- Boiling Point
- Viscosity

The *chemical properties* of a substance are those properties that depend on a chemical change or reaction to occur in order to be defined.

Some examples of chemical properties are listed below.

- Corrosion Rate
- Heat of Combustion
- Enthalpy of Formation
- Electromotive Force
- Toxicity
- Reactivity with Solvents

When asked to identify a property of a substance as either physical or chemical simply decide whether a reaction or change is necessary in order to measure the property. If reaction or change is necessary, the property is chemical in nature. If no reaction or change is necessary, the property is physical in nature.

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Another way that chemical properties differ from physical properties is that chemical properties can be used to classify a substance. Different materials can be ranked or classified according to a chemical property.

For example, by measuring flammability of various materials, one can classify them as being flammable or inflammable.

Another important distinction of matter is the distinction between *intensive* and *extensive* properties.

An *intensive* property of a substance is a property that does not depend on the amount of the substance present. Some examples of intensive properties would be *color*, *odor*, *density*, and *electrical conductivity*. In other words, a single red brick would be the same color as a ton of the same red brick.

An *extensive* property of a substance is a property that does depend on the amount of the substance present. Some examples of extensive properties are *mass*, *volume*, and *weight*. If you add one red brick to your system containing one red brick, you double the system's mass, volume, and weight.

A final and more fundamental distinction of a substance is whether a substance is an *element* or whether the substance is a *molecule*.

An *element* is a substance that cannot be broken down and retain the identity of the substance. Think of a "pure" gold ring. The ring is comprised of nothing but gold *atoms*. If you were to succeed in breaking apart a gold atom it would cease to be gold.

A *molecule* is a substance comprised of a fixed proportion of two or more atoms. Water is a molecule comprised of two hydrogen atoms and one oxygen atom. If a molecule is comprised of a different ratio of hydrogen and oxygen atoms, it is a different molecule.

2.2 The History of Atomic Structure

One very important way to classify matter is to describe what it is made of.

Democritus (ca. 460–370 BC) is usually accredited as the originator of *atomism*. Atomism is the theory that matter is made up of tiny particles called *atoms*. This single concept is the basis of modern day atomic theory. Throughout history some have claimed that the theory was no more than a lucky guess. The fact that his theory aligns so well with the theories of the 19th and 20th century has led others to name Democritus as "the father of science".

In the early 19th century John Dalton (1766–1844) developed what is now considered the foundation of modern atomic theory. The table below list his five postulates of atomic theory.

Dalton's Atomic Theory
1) Elements are made up of extremely small particles called atoms.
2) Atoms of a given element are identical in size, mass, and other properties.
3) Atoms cannot be created or destroyed.
4) Atoms of different elements combine in fixed whole number proportions to form molecules.
5) In chemical reactions atoms are separated and recombined into different molecules.

Figure 2.2.1 Dalton's Atomic Theory

Ernest Rutherford (1871–1937) is credited with the discovery of sub-atomic particles by performing his famous gold foil experiment. He bombarded a thin gold foil with radioactive particles and noticed two things. First, that in some areas the radioactive particles were reflected. Second, that in other areas the radioactive particles passed right through the foil. From these observations he theorized that the gold was comprised of dense centers of mass but was mostly open space. He theorized that the dense centers of mass were sub-atomic particles. He reasoned that hydrogen, the lightest element, contained one of these particles that he called a *proton*.

Joseph John (J.J.) Thomson (1856–1940) is credited with the discovery of the *electron*. By working with cathode rays, Thomson noticed that the particles were well over a thousand times smaller than other subatomic particles. He also noticed that these particles generated the same amount of heat and had the same magnetic deflection no matter what material they came from. Thomson named these new fundamental particles *corpuscles* which was later changed to electrons.

James Chadwick (1891–1974) discovered a subatomic particle of approximately same mass as the proton that had a neutral charge. This had already been predicted and was named the *neutron*. He later worked on the Manhattan project and helped in the development of the first atomic bombs.

History notwithstanding, here is a brief review of what we have learned.

An atom is comprised of the following:

- Positively charged particles called *protons*.
- Neutrally charged particles called *neutrons*.
- A *nucleus* containing the protons and neutrons.
- Negatively charged particles orbiting the nucleus known as *electrons*.

2.3 The Periodic Table

Early on during the development of atomic theory other researchers were observing and developing theories on the behavior of matter. That is to say they characterized different types of matter based on how their properties were alike or unlike.

Dimitri Mendeleev (1834–1907) is credited with developing the first viable periodic table of the elements. There were others that had developed tables that showed the properties of different elements. The genius of Mendeleev was that his table contained gaps where he predicted as yet undiscovered elements would later fill those gaps. Some of the elements he predicted were discovered during his lifetime. These discoveries vindicated Mendeleev's notion of periodic behavior and is now the very bedrock of modern day periodic tables.

The following figure displays the 117 known elements with their atomic numbers and *average* atomic weights in atomic mass units (amu).



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The Periodic Table of the Elements

	I A																			VIII A									
1	1 H 1.008																				2 He 4.003								
2	3 Li 6.941	II A	4 Be 9.012																		10 Ne 20.179								
3	11 Na 22.990		12 Mg 24.305																		18 Ar 39.95								
4	19 K 39.10		20 Ca 40.08	III B	21 Sc 44.96	IV B	22 Ti 47.87	V B	23 V 50.94	VIB	24 Cr 52.00	VII B	25 Mn 54.94	VIII B	26 Fe 55.85	27 Co 58.93	28 Ni 58.70	IB	29 Cu 63.55	II B	30 Zn 65.39	31 Ga 69.72	32 Ge 72.61	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80		
5	37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc 98	44 Ru 101.07	45 Rh 106.42	46 Pd 106.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.76	52 Te 127.60	53 I 126.90	54 Xe 131.29											
6	55 Cs 132.91	56 Ba 137.33	57-71 La Ac	72 Hf 178.49	73 Ta 180.95	74 W 183.85	75 Re 186.21	76 Os 190.23	77 Ir 192.22	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	84 Po (209)	85 At (210)	86 Rn (222)											
7	87 Fr (223)	88 Ra (226)	89-103 La Ac	104 Rf (261)	105 Db (262)	106 Sg (263)	107 Bh (262)	108 Hs (264)	109 Mt (266)	110 Uun (264)	111 Uuu (272)	112 Uub (277)	113 Uut (284)	114 Uuq (289)	115 Uup (288)	116 Uuh (292)	117 Uus (294)	118 Uuo (294)											
			Lanthanides	57 La 138.91	58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm (145)	62 Sm 151.96	63 Eu 151.96	64 Gd 157.25	65 Tb 158.93	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.04	71 Lu 174.97											
			Actinides	89 Ac (227)	90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np (237)	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (262)											

Figure 2.3.1 The Periodic Table of the Elements

This presentation of The Periodic Table has several main objectives.

- 1) To distinguish between metals, non-metals, and semi-metals. Here, the metals are colored blue, the non-metals are colored yellow, and the semi-metals are colored orange.
- 2) To enumerate the eighteen groups. The eighteen groups are divided between the Main Group elements, groups I A through VIII A, and the Transition Metals, groups I B through VIII B. Note that group VIII B is actually comprised of three vertical columns.
- 3) To enumerate the seven periods which are the vertical column of numbers on the left hand side of the table.
- 4) To list the number of protons, or *Z* number, the average mass, or *A* number, and the chemical symbol.

The following figure shows an example of this presentation.

6	Z Number = 6 protons
C	Elemental Symbol C for Carbon
12.011	Average mass A = 12.011 amu

Figure 2.3.3 Element Presentation

The nucleus of the carbon atom is comprised of six protons and six neutrons for a total of twelve *nucleons*. A neutron has essentially the same mass as a proton so that each nucleon is assigned a mass of 1 amu. The mass of an electron is 1/1800 that of a nucleon, therefore its mass is not *significant*.

To calculate the number of neutrons in a carbon atom you must calculate the mass of a specific isotope. For example the number of neutrons in a carbon 12 atom would be the A number 12 minus the Z number 6 for a total of 6 neutrons.

So the number of neutrons in an element is as simple as this formula: # **neutrons** = **A** - **Z** (A expressed as the nearest whole number). Here is a more specific look at what you should know about the Periodic Table.

- The vertical columns are known as **groups** and are populated by elements with similar properties.
- The horizontal rows are known as **periods** and are populated by elements that increase by one proton for each position.
- Groups IA through VIIIA are known as the **Main Group Elements**.
- Groups IB through VIIIB are known as the **Transition Elements**.
- The Lanthanide and Actinide series are known as the **Inner Transition Elements**.

The color coordinated divisions on the Periodic Table represent the following.

- The blue entries are **metals**. Metals have a shine or “metallic luster”, conduct electricity, are malleable (hammered into sheets), and ductile (drawn into wire).
- The yellow entries are **non-metals**. Overall non-metals are the complete opposite of metals. They are poor conductors of heat and, with the exception of the graphite form of carbon, are poor conductors of electricity.
- The orange entries are **semi-metals**. Semi-metals properties lie between those of metals and nonmetals (as does their position on the periodic table). Silicon and germanium (semiconductors) are semi-metals.

The 117 elements listed on the Periodic Table in Figure 2.3.1 are also listed, with their chemical names, in Table 2.3.1 at the end of this chapter.

2.4 Electronic Structure of Atoms

Before we look at how atoms interact with one another, we must first know how their electrons are arranged about the nucleus of the atom.

Electrons are arranged about the nucleus of the atom in ever increasing energy levels.

These energy levels are known as **shells**. The shells are divided into **subshells** and each subshell is divided into **orbitals**.

These divisions of energy levels for electrons are exactly structured in a **periodic** manner.

The electron shells are numbered from 1 to infinity. However, it may be difficult to imagine an atom with an infinite number of electron shells.

The electron subshells are not numbered. They are given letter designations arising from the spectral lines that each subshell generates. They are labeled as follows:

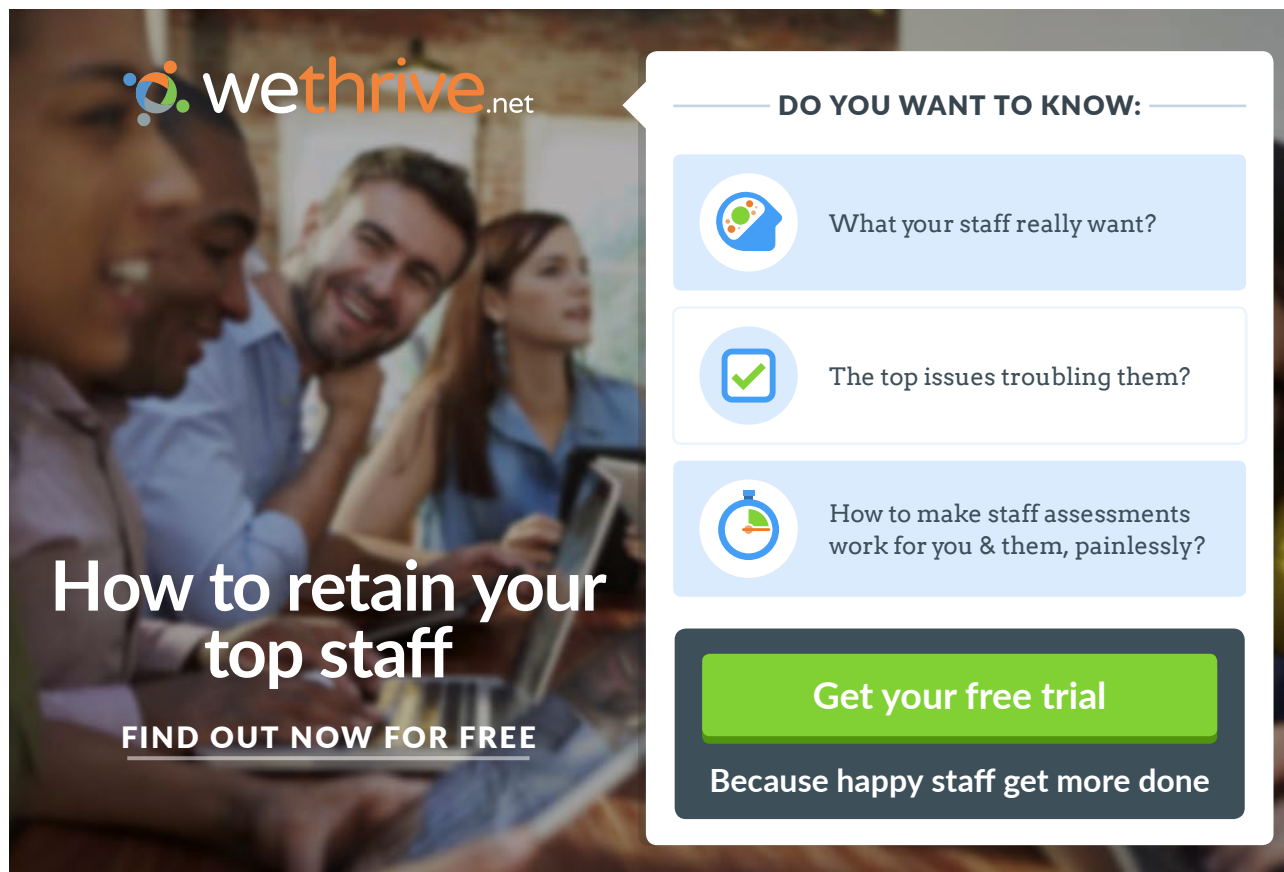
s from the *sharp* spectral line

p from the *principal* spectral line

d from the *diffuse* spectral line

f from the *fundamental* spectral line

Understanding that each electron subshell contains a discrete number of electron orbitals and that each electron orbital can contain up to two electrons, the following table is a first step to understanding the electronic structure of atoms.



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Shell #	Subshell	Configuration	# of Orbitals	Max. # e ⁻
1	s	1s	1	2
2	s	2s	1	2
	p	2p	3	6
3	s	3s	1	2
	p	3p	3	6
	d	3d	5	10
4	s	4s	1	2
	p	4p	3	6
	d	4d	5	10
	f	4f	7	14

Table 2.4.1 The Electronic Structure of Atoms

Note: The maximum number of electrons in the far right column of Table 2.4.1 are staggered to emphasize the periodic nature of the elements.

Let's explore filling electron shells across the Periodic Table with three simple rules.

Aufbau Principle: Electrons will fill the lower energy levels first and build up to the higher energy levels.

Pauli Exclusion Principle: Each electron orbital is limited to a maximum of two spin-opposed electrons.

Hund's Rule: Unfilled orbitals will be occupied before occupied orbitals are paired. (Fill orbitals so there is a minimum number of electron pairs.)

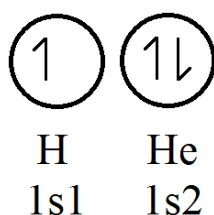
The following are examples of elements in each of the electron shells.

Electron Shell 1

This shell contains a single "s" subshell that in turn contains one electron orbital.

This subshell, designated "1s", can contain 0, 1, or 2 electrons in its one orbital.

The only two elements that contain only a 1s subshell are hydrogen and helium.



Note that the circle in my electronic structure diagrams represents an orbital. The half-barbed arrows represent electrons. In a full (two electron) orbital the two half-barbed arrows point in the opposite direction representing two spin-opposed electrons.

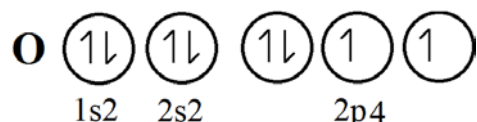
Electron Shell 2

This shell contains a single “s” subshell and a single “p” subshell.

The 2s subshell is the same as the 1s subshell. It contains one orbital that can contain 0, 1, or 2 electrons but at a higher energy level.

The 2p subshell contains three orbitals that can contain 0, 1, or 2 electrons each for a total of six electrons.

Let’s look at oxygen-8. $Z=8$ so there are 8 electrons. Place the electrons in the subshells and orbitals thus. $1s^2 2s^2 2p^4$



Please notice that, *as per Hund’s Rule*, 2p electron distribution forms as few electron pairs as possible.

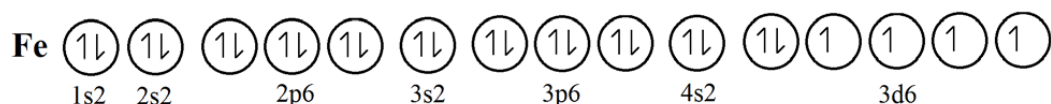
Electron Shell 3

This electron shell contains single s, p and d subshells.

The s and p subshells are identical to the previous s and p subshells. They have the same number of orbitals and electron capacity.

The 3d subshell contains five orbitals that can contain from 0 to 10 electrons.

Let’s look at iron. $Z=26$ so there are 26 electrons. Place the electrons in the subshells and orbitals thus. $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$

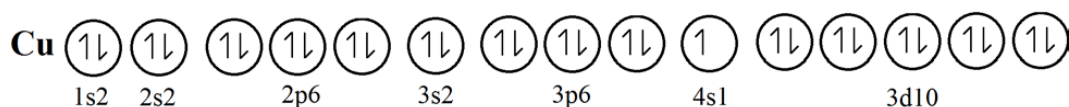


Oops! Did I make a mistake and fill the 4s2 subshell prior to filling the 3d6 subshell? Actually, I did not make a mistake.

It seems whenever Mother Nature sets up some elegant rules or relationships there are always exceptions. In filling of electron shells there are two important exceptions.

1. The *next* “s” subshell will fill *before* the *present* “d” subshell begins to fill.
2. *Except* when a *half filled* or *fully filled* “d” subshell can exist.

Let’s look at the example of chromium (Z=24) and copper (Z=29).



Here you see that the chromium is in a 4s¹ 3d⁵ configuration rather than a 4s² 3d⁴ configuration. Also, copper is in a 4s¹ 3d¹⁰ configuration rather than a 4s² 3d⁹ configuration. In both cases it is this way because the demonstrated configurations are at a lower energy level.

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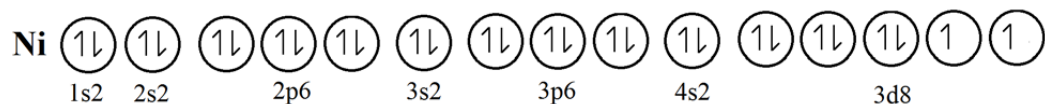
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Exercise 2.4.1

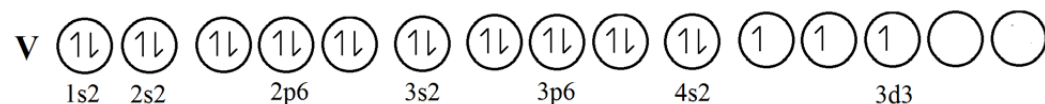
Draw and label the proper electron configuration for nickel (Ni) in the provided diagram.

Nickel has a Z-number of 28 therefore 28 electrons. It is not capable of a perfectly half filled or fully filled 3d level. The configuration should be $4s^2 3d^8$.

**Exercise 2.4.2**

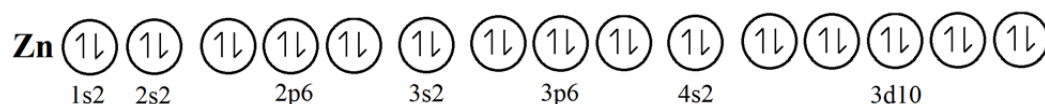
Draw and label the proper electron configuration for vanadium (V) in the provided diagram.

Vanadium has a Z-number of 23 therefore 23 electrons. It is not capable of a perfectly half filled or fully filled 3d level. The configuration should be $4s^2 3d^3$.

**Exercise 2.4.3**

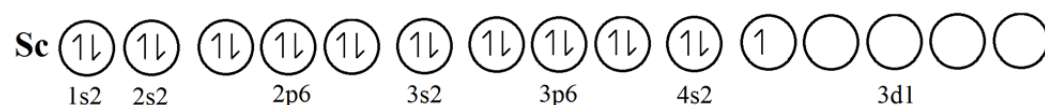
Draw and label the proper electron configuration for zinc (Zn) in the provided diagram.

Zinc has a Z-number of 30 therefore 30 electrons. It has a perfectly fully filled 3d level but not at the expense of a 4s electron. The configuration should be $4s^2 3d^{10}$.

**Exercise 2.4.4**

Draw and label the proper electron configuration for scandium (Sc) in the provided diagram.

Scandium has a Z-number of 21 therefore 21 electrons. It is not capable of a perfectly half filled or fully filled 3d level. The configuration should be $4s^2 3d^1$.



Exercise 2.4.5

Draw and label the proper electron configuration for chromium (Cr) in the provided diagram.

Chromium has a Z-number of 24 therefore 24 electrons. It is capable of a perfectly half filled 3d level. The configuration should be $4s^1 3d^5$.



I have reemphasized the special nature of Cr (don't forget copper) in the 4th period of the Periodic Table. Be aware that molybdenum (Mo) and silver (Ag) in the 5th period and tungsten (W) and gold (Au) in the 6th period share the same special nature.

2.5 Elements and Their Isotopes

An element is listed as a unique entry on the Periodic Table due solely to the number of protons that element contains. As you proceed from the left to the right on any period of the Periodic Table the atomic number (Z) increases by one whole number for each new element. This is because the atomic number (Z) equals the number of protons.

Each element represented on the Periodic Table is represented as a neutral species. That is to say a species with a neutral charge. Therefore, the number of electrons for each element as it is represented on the Periodic Table is equal to the number of protons for that element.

Two atoms that contain the same number of protons (and therefore the same number of electrons) but different numbers of neutrons are known as *isotopes* of the same element with different atomic masses.

The figure below shows examples of a nucleus of pure carbon-12 containing 6 protons and 6 neutrons and a nucleus of carbon-14 containing 6 protons and 8 neutrons.

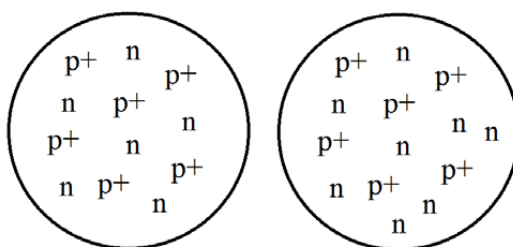


Figure 2.5.1 Two Isotopes of Carbon

I have made the point that different atoms of elements are the same element if they contain the same number of protons. I could take that point a little further and say they are the same elements because they have the same number of electrons. Remember that in a neutral atom the Z number equals the number of protons as well as the number of electrons.

We will learn later in the text that different elements react with one another only by sharing of electrons or by attraction of negative and positive charges resulting from the presence or absence of electrons.

In the figure above the Carbon-14 atom has the same number of electrons as the Carbon-12 atom. However, Carbon-14 differs from Carbon-12 by two additional units of atomic mass and in one other important way.

Carbon-14 is slightly radioactive and has a half-life of over 5,600 years. This property allows the technique of *carbon dating* to succeed in accurately determining the ages of ancient carbonaceous materials.



Z-Number	Element Name	Element Symbol	Average Atomic Mass
1	Hydrogen	H	1.008
2	Helium	He	4.003
3	Lithium	Li	6.941
4	Beryllium	Be	9.012
5	Boron	B	10.81
6	Carbon	C	12.011
7	Nitrogen	N	14.007
8	Oxygen	O	15.999
9	Fluorine	F	18.998
10	Neon	Ne	20.179
11	Sodium	Na	22.990
12	Magnesium	Mg	24.305
13	Aluminum	Al	26.98
14	Silicon	Si	28.09
15	Phosphorous	P	30.97
16	Sulphur	S	32.07
17	Chlorine	Cl	35.45
18	Argon	Ar	39.95
19	Potassium	K	39.10
20	Calcium	Ca	40.08
21	Scandium	Sc	44.96
22	Titanium	Ti	47.57
23	Vanadium	V	50.94
24	Chromium	Cr	52.00
25	Manganese	Mn	54.94
26	Iron	Fe	55.85
27	Cobalt	Co	58.93
28	Nickel	Ni	58.70
29	Copper	Cu	63.55
30	Zinc	Zn	65.39
31	Gallium	Ga	69.72
32	Germanium	Ge	72.61
33	Arsenic	As	74.92
34	Selenium	Se	78.96
35	Bromine	Br	79.90
36	Krypton	Kr	83.80

Z-Number	Element Name	Element Symbol	Average Atomic Mass
37	Rubidium	Rb	85.47
38	Strontium	Sr	87.62
39	Yttrium	Y	88.91
40	Zirconium	Zr	91.22
41	Niobium	Nb	92.91
42	Molybdenum	Mo	95.94
43	Technetium	Tc	(98)
44	Ruthenium	Ru	101.07
45	Rhodium	Rh	102.91
46	Palladium	Pd	106.42
47	Silver	Ag	107.87
48	Cadmium	Cd	112.41
49	Indium	In	114.82
50	Tin	Sn	118.71
51	Antimony	Sb	121.76
52	Tellurium	Te	127.60
53	Iodine	I	126.90
54	Xenon	Xe	131.29
55	Cesium	Cs	132.91
56	Barium	Ba	137.33
57	Lanthanium	La	138.91
58	Cerium	Ce	140.12
59	Praseodymium	Pr	140.91
60	Neodymium	Nd	144.24
61	Promethium	Pm	(145)
62	Samarium	Sm	150.36
63	Europium	Eu	151.96
64	Gadolinium	Gd	157.25
65	Terbium	Tb	158.93
66	Dysprosium	Dy	162.50
67	Holmium	Ho	164.93
68	Erbium	Er	167.26
69	Thulium	Tm	168.93
70	Ytterbium	Yb	173.04
71	Lutetium	Lu	174.97
72	Hafnium	Hf	178.49

Z-Number	Element Name	Element Symbol	Average Atomic Mass
73	Tantalum	Ta	180.95
74	Tungsten	W	183.85
75	Rhenium	Re	186.21
76	Osmium	Os	190.23
77	Iridium	Ir	192.22
78	Platinum	Pt	195.08
79	Gold	Au	196.97
80	Mercury	Hg	200.59
81	Thallium	Tl	204.38
82	Lead	Pb	207.2
83	Bismuth	Bi	208.98
84	Polonium	Po	(209)
85	Astatine	At	(210)
86	Radon	Rn	(222)
87	Francium	Fr	(223)
88	Radium	Ra	(226)
89	Actinium	Ac	(227)



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Z-Number	Element Name	Element Symbol	Average Atomic Mass
90	Thorium	Th	232.04
91	Protactinium	Pr	140.91
92	Neodymium	Nd	144.24
93	Promethium	Pm	(145)
94	Plutonium	Pu	(244)
95	Americium	Am	(243)
96	Curium	Cm	(247)
97	Berkelium	Bk	(247)
98	Californium	Cf	(251)
99	Einsteinium	Es	(252)
100	Fermium	Fm	(257)
101	Mendelevium	Md	(258)
102	Nobelium	No	(259)
103	Lawrencium	Lr	(262)
104	Rutherfordium	Rf	(261)
105	Dubnium	Db	(262)
106	Seaborgium	Sg	(263)
107	Bohrium	Bh	(262)
108	Hassium	Hs	(264)
109	Meitnerium	Mt	(266)
110	Ununnilium	Uun	(264)
111	Ununium	Uuu	(272)
112	Ununbium	Uub	(277)
113	Ununtrium	Uut	(284)
114	Ununquadium	Uuq	(289)
115	Ununpentium	Uup	(288)
116	Ununhexium	Uuh	(292)
117	Ununseptium	Uus	
118	Ununoctium	Uuo	(294)

Table 2.3.1 The Periodic Table of the Elements

3 Chemical Bonding

3.1 Types of Compounds

At this level of instruction all possible chemical compounds will be divided into two major categories. These two categories are *ionic compounds* and *molecular compounds*.

Ionic Compounds

Ionic compounds are those compounds that are bonded together by *strong opposite ionic attractions*.

For example look at the common ionic compound sodium chloride, or ordinary table salt, in Figure 3.1.1.

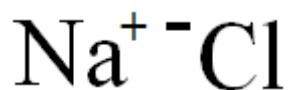


Figure 3.1.1 Sodium Chloride

Here the strong positive charge of sodium (Na) is attracted to the strong negative charge of chlorine (Cl) in order to form the molecule sodium chloride (NaCl). One unit of charge, which is sometimes referred to as the *elementary charge*, is equal to 1.6×10^{-19} coulombs.

Molecular Compounds

Molecular compounds are those compounds that are bonded together by the *sharing of electrons*. When a bond is formed by this sharing it is referred to as a *covalent bond*.

For instance look at the common molecular compound water (H_2O) in Figure 3.1.2.

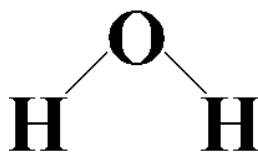


Figure 3.1.2 Water

Here the lines connecting the hydrogen atoms to the oxygen atom represent a covalent bond made up of two electrons. These two electrons are comprised of one electron from the hydrogen atom and one electron from the oxygen atom. They are being *shared* in the *covalent bond*.

It should be noted that seven elements of the Periodic Table exist naturally as diatomic molecules.

Figure 3.1.3 list these seven elements in their natural diatomic, *molecular* state.

Molecule	Formula	Molecule	Formula
Hydrogen	H ₂	Chlorine	Cl ₂
Nitrogen	N ₂	Bromine	Br ₂
Oxygen	O ₂	Iodine	I ₂
Fluorine	F ₂		

Table 3.1.1 Diatomic Elemental Molecules

These compounds were listed under the molecular compounds section because they are molecular compounds. Each of these diatomic molecular compounds are *covalently bonded*.

3.2 Chemical Formulae

It is necessary to be familiar with all of the components of a chemical formula. One should also realize that not all of the components of a chemical formula are used with every chemical formula. This depends on the complexity of the given chemical formula.

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The following is the correct chemical formula for two molecules of urea, a common airport runway deicer.



The following is a list of the different components present in the chemical formula for two molecules of urea.

Chemical Symbols: The chemical symbols present in the chemical formula are C (carbon), O (oxygen), N (nitrogen), and H (hydrogen).

Subscripts: Subscripts are used to represent the presence of multiple atoms or groups of atoms. Here a subscript 2 is used to indicate 2 H atoms in the NH_2 group and 2 NH_2 groups in the $\text{CO}(\text{NH}_2)_2$ molecule.

Parentheses: Parentheses are used to direct the multiplication of subscripts. In the $\text{CO}(\text{NH}_2)_2$ chemical formula the parentheses are necessary to assure that the subscript 2 outside the parentheses indicates that there are two NH_2 groups.

Coefficients: Coefficients at the beginning of a chemical formula simply indicate a multiple number of molecules. In the $2\text{CO}(\text{NH}_2)_2$ chemical formula the coefficient 2 indicates two molecules of urea.

One additional symbol is used when indicating the number of **waters of hydration** in a given ionic compound.

Waters of hydration are necessary for some ionic compounds to form a crystalline structure. When the positive sodium ion (Na^+) and the negative chlorine ion (Cl^-) come together they are capable of forming the NaCl crystal without using waters of hydration. Other ionic combinations are not so fortunate.

Let's look at the hydrated crystalline form of copper sulfate (CuSO_4). Alone copper sulfate does not form a crystalline structure and appears as a white amorphous powder.

When hydrated with a specific number of water molecules per each copper sulfate molecule it appears as a brilliant blue orthorhombic crystal with the following formula.

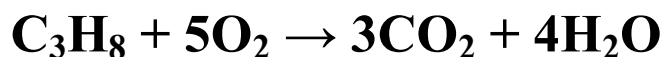


This molecule is known as copper sulfate pentahydrate. The "dot" in the center of the chemical formula indicates that the water molecules are **not** a part of the copper sulfate but **are** a part of the copper sulfate pentahydrate crystal.

When copper sulfate pentahydrate is heated it loses its blue color and its crystalline structure in a process known as **dehydration**. This simply means that the waters of hydration have been driven off and the molecule reverts to the white amorphous copper sulfate.

3.3 Chemical Equations

Let's look at the chemical equation for the combustion of propane (C_3H_8).



By definition a chemical equation **describes what happens** in a chemical reaction.

So what happened in the above chemical reaction?

First, the propane (C_3H_8) and oxygen (O_2) were consumed.

Second, carbon dioxide (CO_2), and water (H_2O) were produced.

A better way of stating the reaction is as follows: Propane and oxygen **reacted to produce** carbon dioxide and water.

This then makes the propane and oxygen (the components left of the arrow) the **reactants**. Accordingly, this makes the carbon dioxide and water (the components right of the arrow) the **products**.

Now that you have been introduced to a chemical equation, I will introduce you to one additional component of chemical formulae. Often when expressing a chemical equation it is necessary to indicate what state a given reactant or product is in.

The following four states of reactants and products are commonly used:

Solid	A reactant is a solid or a product precipitates as a solid. (s)
Liquid	A reactant or a product is a liquid. (l)
Gas	A reactant is a gas or a product evolves as a gas. (g)
Aqueous	A reactant or a product is soluble in the aqueous solution. (aq)

Consider the following chemical equation.



The way to describe what has happened in this chemical equation is as follows.

Solid calcium carbonate (CaCO_3) was added to an aqueous solution of hydrochloric acid (HCl) which reacted to produce an aqueous solution of calcium chloride (CaCl_2), gaseous carbon dioxide (CO_2), and liquid water (H_2O).

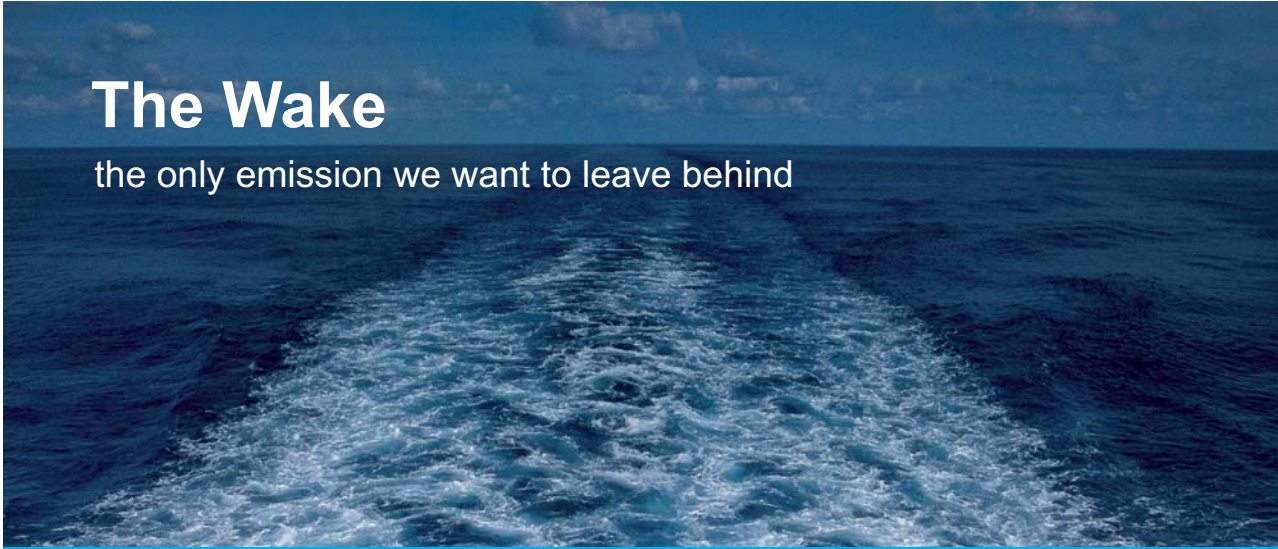
3.4 Naming Chemical Compounds

The rules for naming chemical compounds will be introduced for two main distinctions of these compounds. The two distinctions have already been introduced as *ionic* and *molecular* compounds.

Naming Binary Ionic Compounds

Binary compounds are compounds made up of two types of atoms. In ionic compounds these two types of atoms will almost always be a metal atom followed by a non-metal atom. The rules follow.

- 1) Write the full name of the metal atom.
- 2) Write the stem of the name of the non-metal.
- 3) Finish the name with *-ide*.




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Let's look at naming the compound made of one atom of sodium and one atom of chlorine (NaCl).

- 1) The name starts with *sodium*.
- 2) The name then continues as *sodium chlor*.
- 3) The name is finished as *sodium chloride*.

It should be noted that as a Group IA metal sodium will always have a plus one charge when forming a molecule. As a Group VIIA non-metal chlorine will always have a minus one charge when forming a molecule.

Now let's look at the naming of the compound made of one atom of calcium and two atoms of bromine (CaBr₂).

- 1) The name starts with *calcium*.
- 2) The name then continues as *calcium brom*.
- 3) The name is finished as *calcium bromide*.

It should be noted that as a Group IIA metal, calcium will always have a plus two charge when forming a molecule. As a Group VIIA non-metal, bromine will always have a minus one charge when forming a molecule. Therefore it takes *two atoms of bromine* to neutralize the charge of one atom of calcium. Compounds must *always* have the necessary number of each atom to be *charge neutral*.

Many common ionic compounds are made of metals from Groups IA and IIA combined with non-metals. The charges that exist on these atoms when they form molecules can be characterized by the following:

Group Number	Charge
IA	+1
IIA	+2
VA	-3
VIA	-2
VIIA	-1

Table 3.4.1 Main Group Element Charges

Use the charge numbers listed in Table 3.1.4 and the preceding naming rules to name the following compounds and give their chemical formulae.

Exercise 3.4.1

Name the compound formed by the combination of potassium (K) and oxygen (O) and write its correct chemical formula.

Potassium is in Group IA so +1. Oxygen is in Group VIA so -2.

Potassium Oxide (K_2O)

Exercise 3.4.2

Name the compound formed by the combination of barium (Ba) and sulfur (S) and write its correct chemical formula.

Barium is in Group IIA so +2. Sulfur is in Group VIA so -2.

Barium Sulfide (BaS)

Exercise 3.4.3

Name the compound formed by the combination of strontium (Sr) and nitrogen (N) and write its correct chemical formula.

Strontium is in Group IIA so +2. Nitrogen is in Group VA so -3.

Strontium Nitride (Sr_3N_2)

Note that in the last exercise it took the +6 charge of three strontium atoms to neutralize the -6 charge of two nitrogen atoms.

Also note that the individual ions' charges do not appear in the final chemical formula. This signifies charge neutrality.

Naming Binary Molecular Compounds

Binary molecular compounds are compounds made up of two types of non-metal atoms. Since these compounds are covalently bonded the charges assigned to the several Main Groups in Table 3.4.1 are not used in naming these compounds. Because of this you must be told how many of each atom is present in the molecule. The reason for this will become obvious in the following exercises.

Fortunately, the rules for naming molecular compounds is identical to the rules for naming ionic compounds with one *important addition*.

- 1) Write the full name of the first non-metal atom.
- 2) Write the stem of the name of the second non-metal.
- 3) Finish the name with *-ide*.
- 4) Use *Greek prefixes* to indicate how many of each atom are in the molecule.

Let's look at naming of the compound made up of one carbon (C) atom and two oxygen (O) atoms.

- 1) The name starts with *carbon*.
- 2) The name then continues as *carbon ox*.
- 3) The name is finished with *carbon oxide*.
- 4) The number of oxygen atoms are indicated by the Greek prefix *di*.

Carbon Dioxide (CO₂)

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The following table lists the Greek prefixes for numbers one through six.

Number	Greek Prefix
1	mono
2	di
3	tri
4	tetra
5	penta
6	hexa

Table 3.4.2 Greek Prefixes

Exercise 3.4.4

Name the compound formed by the combination of one carbon (C) and one oxygen (O) and write its correct chemical formula. Remember the Group A charges do not apply for molecular compounds.

The name begins with carbon and ends with oxide with *mon* (rather than mono) in front of the oxide.

Carbon Monoxide (CO)

Exercise 3.4.5

Name the compound formed by the combination of one nitrogen (N) and two sulfurs (S) and write its correct chemical formula.

The name begins with nitrogen and ends with sulfide with *di* in front of the sulfide.

Nitrogen Disulfide (NS₂)

Exercise 3.4.6

Name the compound formed by the combination of two nitrogens (N) and four oxygens (O) and write the correct chemical formula.

The name begins with nitrogen and ends with oxide with *di* in front of the nitrogen and *tetra* in front of the oxide.

Dinitrogen Tetraoxide (N₂O₄)

Trivial Compound Names:

Many compounds have *trivial* names that are used instead of the systematic names just described.

Examples:

H_2O	Water	not Dihydrogenoxide
NH_3	Ammonia	not Nitrogen trihydride

Polyatomic Ions

There are many ionic compounds that are formed by the combination of a *metal cation* (positively charged ion) and a *polyatomic anion* (negatively charged ion made of covalently bonded non-metals).

The following table shows examples of poly atomic ions that should be somewhat familiar.

Ion Formula	Ion Name
OH^-	Hydroxide
NH_4^+	Ammonium
NO_3^-	Nitrate
CN^-	Cyanide
CO_3^{2-}	Carbonate
SO_4^{2-}	Sulfate
PO_4^{3-}	Phosphate

Table 3.4.3 Polyatomic Ions

In each example in the above table the superscript charge number is the charge for the *entire* polyatomic ion.

Naming Polyatomic Ionic Compounds

Even though these are ionic molecules the complexity of the polyatomic anion requires the use of Greek prefixes if the molecule contains *more than one metal atom*.

The naming convention for polyatomic ionic compounds is simply the name of the metal plus the name of the polyatomic ion.

Exercise 3.4.7

Name the compound formed by the combination of sodium (Na) and the phosphate ion (PO_4^{3-}) and write the correct chemical formula.

You are told that the phosphate ion has an overall charge of -3. Sodium is in group IA with a charge of +1. You need three +1 charges to neutralize the -3 charge of phosphate.

Trisodium¹ Phosphate (Na_3PO_4)

With polyatomic ionic compounds, just like binary ionic compounds, the charges of the individual ions do not appear in the final chemical formula (once again indicating charge neutrality).

* Tri is used here to distinguish the name from disodium phosphate.

Exercise 3.4.8

Name the compound formed by the combination of calcium (Ca) and the hydroxide ion (OH^-) and write the correct chemical formula.

You are told that the hydroxide ion has an overall charge of -1. Calcium is in group IIA with a charge of +2. You need two -1 charges to neutralize the +2 charge of calcium.

Calcium Hydroxide ($\text{Ca}(\text{OH})_2$)

Here the OH appears in parentheses so that the subscript two properly indicates that there are two OH groups in calcium hydroxide.

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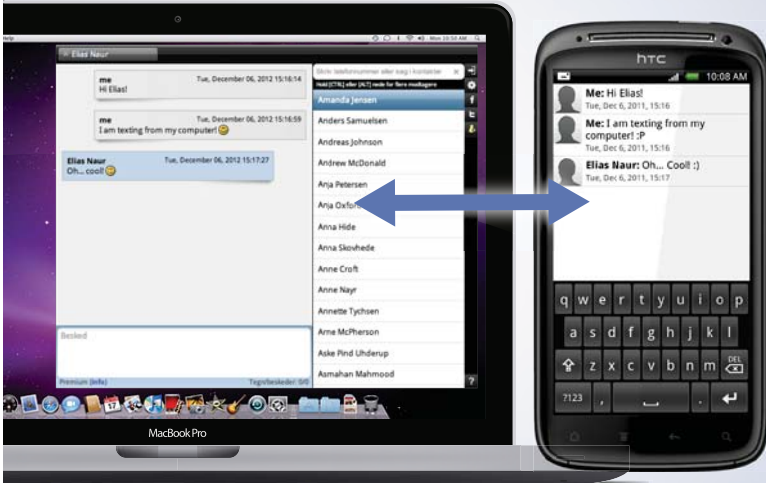
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Exercise 3.4.9

Name the compound formed by the combination of the ammonium ion (NH_4^+) and the nitrate ion (NO_3^-) and write the correct chemical formula.

You are told that the ammonium ion has an overall charge of +1 and that the nitrate ion has an overall charge of -1. One ammonium ion will neutralize one nitrate ion.

Ammonium Nitrate (NH_4NO_3)

Here is a rare example of an ionic compound that contains no metal ions. It is possible because the ammonium is a *cation* and the *nitrate* is an anion.

3.5 Lewis Dot Structures**The Octet Rule**

With a fundamental knowledge of electron configuration we can now look at how different elements bond with one another.

Without fear of anthropomorphizing elements, let's imagine that each element "wishes" it had the stable full electron shells of the Noble Gases.

Remember, at the extreme right hand side of the Periodic Table the Noble Gases exhibit a full *ns2 np6* electron configuration for a valence electron shell containing eight electrons or an *octet*.

The Octet Rule is simply a demonstration of how elements tend toward this full outer electron shell when bonding with other elements.

Example: Let's look at the compound (NaCl).

Sodium (Na)	$1s^2 2s^2 2p^6 3s^1$
Chlorine (Cl)	$1s^2 2s^2 2p^6 3s^2 3p^5$

Na loses one electron for a $2s^2 2p^6$ valence shell and a +1 charge.

Cl gains one electron for a $3s^2 3p^6$ valence shell and a -1 charge.

In these states the two elements are destined to combine to form the *neutrally charged* ionic compound sodium chloride (NaCl).

Example: Let's look at the molecule water (H_2O).

Oxygen (O)	1s ² 2s ² 2p ⁴
Hydrogen (H)	1s ¹

O gains two electrons for a 2s² 2p⁶ valence shell and has a -2 charge.

H loses one electron and has a charge of +1. Remember, hydrogen has only a 1s shell.

Again, these elements are destined to form the *neutrally charged* covalent molecule water.

Lewis Dot Structures

Developed by Gilbert N. Lewis in 1916, Lewis Dot Structures allow one to visualize the electron containing bonds between atoms in ionic compounds or covalent molecules as well as lone electron pairs.

These drawings also reveal compounds with radical (single, non-bonded) electrons as well as resonance structures which we will address in this chapter.

Before we draw any Lewis Dot structures let's start with some simple rules.

Lewis Dot Structure Rules

- 1) Add up all the valence electrons for the atoms in the compound. *Number of valence electrons equals the Group A Number.*
- 2) Select the central atom and bond the outer atoms to it with two electrons each.
- 3) Finish the octets of the outer atoms with the remaining electron pairs.
- 4) Place any remaining electrons on the central atom, in pairs, up to eight electrons around the central atom.
- 5) Finish the octet of the central atom by double or triple bonding with the outer atoms. *Never* double or triple bond to a hydrogen or halogen.
- 6) Compare the finished structure with the electron configuration of the central atom. Make certain the bonding single electrons and lone pairs are predicted by the electron configuration.

Remember, no rules in chemistry are perfect. The octet rule is not always followed. Hydrogen cannot have eight electrons around it. Sulfur can, and will have more than eight electrons around it. By and large the Octet Rule is a *very effective heuristic*.

Exercise 3.5.1

Draw the Lewis Dot Structure for water (H_2O). Confirm that the oxygen exhibits the proper electron structure.

Valence electrons: 2 from 2 H's plus 6 from O = 8

Connect the two H's to the O. **$\text{H}\cdot\text{O}\cdot\text{H}$**

Place remaining electron pairs on O. **$\text{H}\cdot\ddot{\text{O}}\cdot\text{H}$**

All eight valence electrons have been used. O appears to be contributing two single electrons and two lone pairs.

O: **O** $\left(\begin{array}{c} \uparrow\downarrow \\ 1s^2 \end{array}\right)$ $\left(\begin{array}{c} \uparrow\downarrow \\ 2s^2 \end{array}\right)$ $\left(\begin{array}{c} \uparrow\downarrow \\ 2p^4 \end{array}\right)$ $\left(\begin{array}{c} \uparrow \\ 2p^4 \end{array}\right)$ $\left(\begin{array}{c} \uparrow \\ 2p^4 \end{array}\right)$ Which is confirmed here.

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Exercise 3.5.2

Draw the Lewis Dot Structure for carbon dioxide. Confirm that each oxygen exhibits the correct electronic structure.

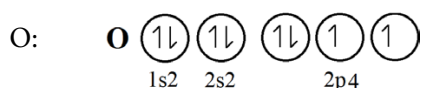
Valence electrons: 12 from two O's plus 4 from C = 16

Connect the two O's to the C. $\text{O}\cdot\cdot\text{C}\cdot\cdot\text{O}$

Complete the octets on the O's. $:\ddot{\text{O}}\cdot\cdot\text{C}\cdot\cdot\ddot{\text{O}}:$

Complete octet on C with double bonds. $:\ddot{\text{O}}::\text{C}::\ddot{\text{O}}:$

Again O is contributing two single electrons and two lone pairs.

**Exercise 3.5.3**

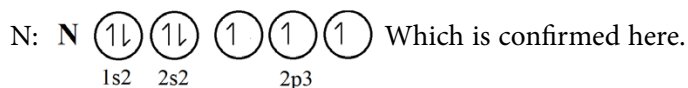
Draw the Lewis Dot Structure for ammonia (NH_3). Confirm that nitrogen exhibits the correct electronic structure.

Valence e's: 3 from 3 H's plus 5 from N = 8

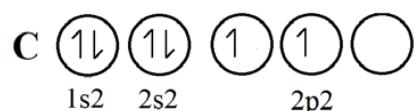
Connect the three H's to the N. $\begin{array}{c} \text{H} \\ \vdots \\ \text{H}\cdot\cdot\text{N}\cdot\cdot\text{H} \end{array}$

Place the remaining electron pair on N. $\begin{array}{c} \text{H} \\ \vdots \\ \text{H}\cdot\cdot\text{N}\cdot\cdot\text{H} \\ \vdots \end{array}$

N is contributing three single electrons and one lone pair.

**The Tetravalent Rule of Carbon**

The electron configuration for carbon appears to show two single electrons and a lone pair.



However, due to hybridized orbitals (not covered in this text) there are actually four equivalent electrons which always lead to carbon being **bonded four times** in any neutral molecule.

Exercise 3.5.4

Draw the Lewis Dot Structure for methane (CH_4). Confirm that the carbon exhibits the correct electronic structure.

Valence e's: 4 from 4 H's plus 4 from C = 8

Connect the four H's to the C with two e's each. $\begin{array}{c} \text{H} \\ \vdots \\ \text{H} \cdot \text{C} \cdot \text{H} \\ \vdots \\ \text{H} \end{array}$

Carbon appears to be contributing four single electrons which is confirmed by the special nature of carbons hybridized orbitals. The drawing above is following the tetravalent rule of carbon.

Exercise 3.5.5

Draw the Lewis Dot Structure for nitrogen oxide (NO). Confirm that the nitrogen exhibits the correct electronic configuration.

Valence e's: 5 from N plus 6 from O = 11

Connect the N and O with one electron pair. $\text{N} \cdot \cdot \text{O}$

Finish the octet on O with three electron pairs. $\text{N} \cdot \cdot \ddot{\text{O}} \cdot \cdot$

Place the remaining "1½" pairs of electrons on N. $\cdot \ddot{\text{N}} \cdot \cdot \ddot{\text{O}} \cdot \cdot$

Finish N's *septet* by double bonding to O. $\cdot \ddot{\text{N}} \cdot \cdot \ddot{\text{O}} \cdot \cdot$
Radical Form

Nitrogen contributes 3 single e's and 1 lone pair.

N: $\left(\uparrow \downarrow \right) \left(\uparrow \downarrow \right) \left(\uparrow \right) \left(\uparrow \right) \left(\uparrow \right)$ Which is confirmed here.
1s² 2s² 2p³

Note that the radical form of nitrogen oxide is an *exception* to the Octet Rule.

Exercise 3.5.6

Draw the Lewis Dot Structure for ozone (O_3). Confirm that each oxygen exhibits the correct electron configuration.

Valence e's: 6 from 3 O's = 18

Connect the three O's with two electron pairs. $\text{O} \cdot \cdot \text{O} \cdot \cdot \text{O}$

Finish the outer O's octets with 6 electron pairs. $:\ddot{\text{O}} \cdot \cdot \text{O} \cdot \cdot \ddot{\text{O}}:$

Place the remaining electron pair on the central O. $:\ddot{\text{O}} \cdot \cdot \ddot{\text{O}} \cdot \cdot \ddot{\text{O}}:$

Finish the inner O's octets by double bonding

"both" outer O's. $:\ddot{\text{O}} \cdot \cdot \ddot{\text{O}} :: \ddot{\text{O}}: \leftrightarrow :\ddot{\text{O}}:: \ddot{\text{O}} \cdot \cdot \ddot{\text{O}}:$
Resonance Form

Both of these drawings, complete with the double headed arrow, constitute the **correct** Lewis Dot Structure for ozone.

The agreement with the correct electron configuration for oxygen is not exhibited in this exercise. The resonance structure of ozone **does not** indicate a rapid oscillation between the two forms. It is drawn as it is because a single drawing is insufficient to describe the molecule.

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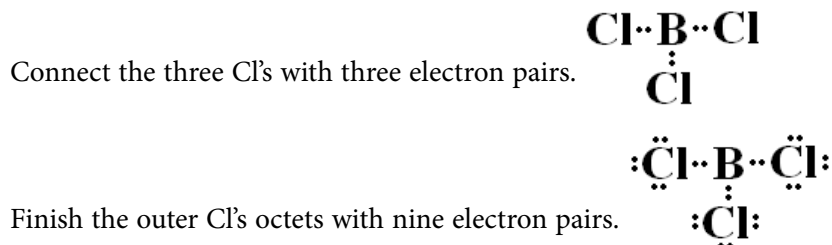
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Exercise 3.5.7

Draw the Lewis Dot Structure for boron trichloride (BCl_3).

Valence e's: 3 from B plus 21 from 3 Cl = 24



You may not finish the octet of electrons on boron because chlorine is a halogen. You *never* double bond to hydrogen or a halogen.

As one can see the Octet Rule is frequently broken. But I hope you can also see that it is a *very useful* tool to use in visualizing the electronic configurations of molecules.

3.6 Polar Molecules

A definite distinction was drawn between ionic and molecular compounds early in the text. You may have been lead to believe that ionic species exhibit charge while molecular species do not.

Certainly an ionic species, like sodium chloride (NaCl), exhibits charge. NaCl dissociates in water into Na^+ and Cl^- ions. Pure, or deionized, water will not conduct electricity. Water with NaCl is an excellent conductor of electricity.

However, it is not entirely accurate to assert that molecular compounds do not exhibit any type of charge or are simply charge free. Some molecular compounds, containing atoms such as oxygen and nitrogen, can develop *centers of apparent charge* within an individual molecule.

Let's look at a model of a molecule of water (H_2O).

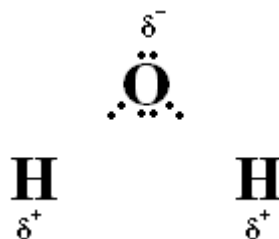


Figure 3.6.1 Water as a Polar Molecule

The oxygen nucleus contains eight positively charged protons. The hydrogen nucleus contains one positively charged proton. For these reasons the oxygen nucleus has more attraction for the single hydrogen electron than does the hydrogen nucleus.

This shift in the position of the hydrogen electron results in a slight positive charge on the hydrogen nucleus and a slight negative charge on the oxygen nucleus. These charges have the symbol “ δ ” and a + charge for hydrogen and a – charge for oxygen.

These centers of **apparent charge** in the water molecule are known as **dipoles**.

Molecules that have dipoles can be attracted to other such molecules only if the molecule is **asymmetrical**. If the molecule is symmetrical the dipoles in the molecule will cancel each other out. In asymmetrical molecules the charge generated by the dipoles is known as the overall **dipole moment** of the molecule.

The SI system unit for dipole moments is the **coulomb meter (Cm)**. The coulomb meter can be a very large number depending upon the molecule. For this reason it is common to see dipole moments expressed in the non-SI system unit **Debye (D)**. The conversion between coulomb meter and Debye is $1 \text{ Cm} = 2.9979 \times 10^{29} \text{ D}$. This conversion results in far easier numbers to cope with when comparing the dipole moment of one molecule to another.

The table below list dipole moments for some common compounds.

Compound Name	Symbol	Debye
Carbon Dioxide	CO ₂	0
Dinitrogen Oxide	N ₂ O	0.316
Ozone	O ₃	0.53
Hydrochloric Acid	HCl	1.08
Ammonia	NH ₃	1.47
Water	H ₂ O	1.85
Hydrogen Cyanide	HCN	2.98
Lithium Hydride	LiH	5.88

Table 3.6.1 Dipole Moments of Common Compounds

Note that carbon dioxide is a completely symmetrical molecule and therefore has a zero Debye value for its overall dipole moment.

Hydrogen Bonding

One of the interesting factors critical to the understanding of chemistry and biochemistry is that of *hydrogen bonding*.

Hydrogen bonding is a phenomenon that arises from the properties of polar molecules. It occurs when the hydrogen center of apparent charge " δ^+ " in a polar molecule is attracted to the negative center of apparent charge " δ^- " in another polar molecule.

Using the same drawing of water as a polar molecule in Figure 3.6.1, it is easy to demonstrate a water molecule hydrogen bonding with another water molecule.

The following figure demonstrates one water molecule being *weakly attracted* to another water molecule as a result of hydrogen bonding.

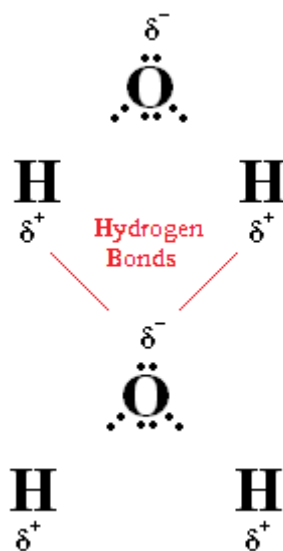


Figure 3.6.2 Hydrogen Bonding

One interesting result of hydrogen bonding in water is the effect it has on the boiling point of water. The following table contrasts the boiling points of several compounds, at or near 100°C , with the molecular masses of those compounds.

Compound	Formula	Mass (amu)	B.P. ($^\circ\text{C}$)
Water	H_2O	18	100
n-Heptane	C_7H_{16}	100	98.4
iso-Octane	C_8H_{18}	114	99
Ethyl Acrylate	$\text{C}_5\text{H}_8\text{O}_2$	100	99.4

Table 3.6.2 Boiling Point versus Molecular Mass

How can water, that has 1/5 to 1/6 times less mass than the other three compounds listed in Table 3.6.2, have a similar boiling points to those compounds?

To boil a liquid you must add sufficient energy to the liquid to overcome any *intermolecular attractions* between individual molecules of the liquid. This will be covered later in the text.

Even though the hydrogen bonding that occurs in water is weaker than the covalent bonds that hold the water molecules together, it still has to be overcome. This then means more energy must be added to the liquid irrespective of the molecular mass of the water molecule.

Water is by no means the only type of molecule that experiences hydrogen bonding. Later in the text, when we study biochemistry, we will see that it is hydrogen bonding between the base pairs in DNA that holds the double helix structure of DNA together.



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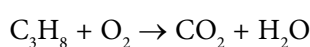
4 Chemical Reactions

4.1 Balancing Chemical Equations

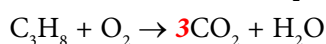
In all chemical equations Dalton's original concept of the *conservation of mass* applies directly. That is to say the mass of the products *must* equal the mass of the reactants.

Later in the text we will learn that mass is not conserved in nuclear reactions.

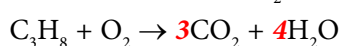
With as few formal rules as possible we will balance the equation for the combustion of propane (C₃H₈).



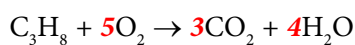
- 1) Place a 3 in front of CO₂ to balance the number of carbons.



- 2) Place a 4 in front of H₂O to balance the number of hydrogens.

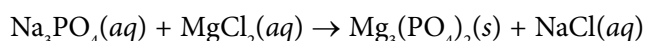


- 3) Place a 5 in front of O₂ to balance the number of oxygens.

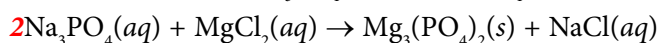


Check: 3 C's, 8 H's, 10 O's → 3 C's, 8 H's, 10 O's

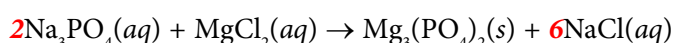
The above combustion reaction is just one type of chemical reaction. Let's look at a *metathesis reaction* sometimes referred to as a double replacement reaction.



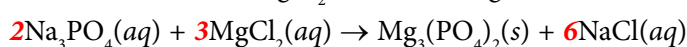
- 1) Place a 2 in front of Na₃PO₄ to balance PO₄.



- 2) Place a 6 in front of NaCl to balance Na.



- 3) Place a 3 in front of MgCl₂ to balance Mg and Cl.

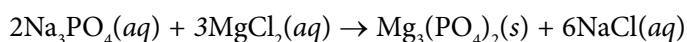


Check: 6 Na's, 2 P's, 8 O's, 3 Mg's, 6 Cl's → 6 Na's, 2 P's, 8 O's, 3 Mg's, 6 Cl's

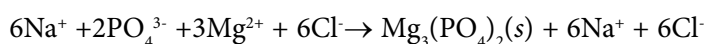
Stages of Chemical Equations

Chemical equations, like the above metatheses reaction, can be expressed in different stages according to different needs.

The above metatheses reaction is stated in the stage known as the **complete chemical equation**. This stage shows all of the compounds present in the reaction in their original states.

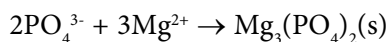


Another stage of the same reaction is the **ionic equation**. In this stage the components of the reaction are shown as they exist in solution.



Please note that the magnesium phosphate ($\text{Mg}_3(\text{PO}_4)_2(\text{s})$) is not in solution. It was **precipitated** in its non-soluble solid state.

A final and simpler stage of this metatheses reaction is known as the **net ionic equation**. In this stage of the chemical equation only the ionic portions of the original compounds that actually undergo metatheses, or a change, are listed.



If you notice, in the ionic equation of the metatheses reaction, there are 6Na^+ and 6Cl^- on both sides of the reaction. They are not taking place in any metatheses and are known as **spectator ions**.

It is not necessary to indicate an aqueous species for an ion showing either a positive or negative charge.

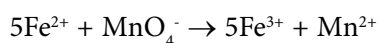
4.2 Reduction-Oxidation (Redox) Reactions

One type of chemical reaction that uses net ionic equations are **reduction-oxidation (redox)** reactions.

In a redox reaction a **balanced transfer of electrons** occurs that changes the oxidation state of some of the components of the reaction. Let's see some examples.

Example 4.2.1

Consider the following net ionic equation.



One can readily see that the iron (Fe) was changed from a 2+ oxidation state in the reactants to a 3+ oxidation state in the products.

One cannot readily see the change of the oxidation state of the manganese (Mn). The individual oxidation state of manganese in the reactants is hidden since the manganese exists in a polyatomic ion. Fortunately the polyatomic ion contains oxygen (O). Since oxygen is a Main Group element you already know it has a charge of 2- from Table 3.4.1.

Set up an equation to solve for the oxidation state of manganese in the reactants as follows:

$Mn + 4(2-) = -1$ where the Mn charge can now be solved for. A simple calculation shows that manganese is in the 7+ oxidation state in the reactants.

The final results of the redox reaction are as follows.

Iron went from 2+ to 3+ by a loss of 1 electron and was **oxidized**. Manganese went from 7+ to 2+ by a gain of 5 electrons and was **reduced**. It gained 1 electron each from the 5 irons.

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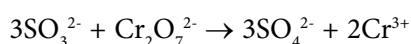
Leo the Lion

A very effective mnemonic device used to remember the direction of electron transfer in redox reactions is **LEO the lion goes GER**.

A **L**oss of **E**lectrons is **O**xidation. A **G**ain of **E**lectrons is **R**eduction.

Example 4.2.2

State which of the elements of sulfur (S) and chromium (Cr) were oxidized and which were reduced in the following reaction. Support your answers with calculations where necessary.



Reactants:

Sulfur: $\text{S} + 3(2-) = -2$ S = +4 Sulfur is in a 4+ oxidation state.

Chromium : $2\text{Cr} + 7(2-) = -2$ Cr = +6 Chromium is in a 6+oxidation state.

Products:

Sulfur: $\text{S} + 4(2-) = -2 \times = +6$ Sulfur is in a 6+ oxidation state.

Chromium is shown in a 3+ oxidation state.

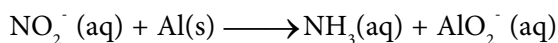
Redox Results:

Sulfur: from 4+ to 6+ is a loss of electrons for **oxidation**.

Chromium: from 6+ to 3+ is a gain of electrons for **reduction**.

Example 4.2.3

State which of the elements of nitrogen (N) and aluminum (Al) were oxidized and which were reduced in the following reaction. Support your answers with calculations where necessary.



Reactants:

Nitrogen: $\text{N} + 2(-2) = -1$ N = +3

Aluminum: Any element in its natural state has a "0" oxidation state.

Products:

Nitrogen: $\text{N} + 3(+1) = 0$ N = -3

Aluminum: $\text{Al} + 2(-2) = -1$ Al = +3

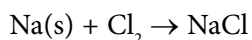
Redox Results:

Nitrogen: from 3+ to 3- is a gain of electrons for **reduction**.

Aluminum: from 0 to 3+ is a loss of electrons for **oxidation**.

Example 4.2.4

State which of the elements of sodium (Na) and chlorine (Cl) were oxidized and which were reduced in the following reaction. Support your answers with calculations where necessary.

*Reactants:*

Sodium: A charge of "0" in its natural state.

Chlorine: A charge of "0" in its natural state.

Products:

Sodium: A Main Group IA charge of 1+.

Chlorine: A Main Group VIIA charge of 1-.

Redox Results:

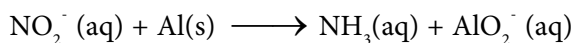
Sodium: from 0 to 1+ is a loss of electrons for **oxidation**.

Chlorine: from 0 to 1- is a gain of electrons for **reduction**.

Some Reasoning Concerning Redox Reactions

The simple arithmetic manipulations shown in the previous examples and the Leo the Lion mnemonic device are very easy to follow. But some sense of what is happening in a redox reaction is in order.

Let's look at the net ionic equation of the redox reaction in Example 4.2.3 again.



In the reactants the species most likely to do the oxidizing is the NO_2^- since it is the species containing oxygen. So it makes sense that the NO_2^- is the oxidizing agent. This then means that the Al is the reducing agent. So the Al is oxidized and the NO_2^- is reduced.

This observation is corroborated by the products. The nitrogen bearing species NH_3 is void of oxygen atoms and the Al bearing species now has two oxygen atoms.

Most redox reactions involve oxygen bearing species. As seen in Example 4.2.4, redox reactions not involving oxygen, the regimen established in this section will still easily show which species was oxidized and which species was reduced.

Here are four important items to remember when considering redox reactions.

- 1) Reduction and oxidation happens as a single reaction. You **cannot** have one without the other.
- 2) The species that is becoming oxidized is reducing the other species and is the **reducing agent**.
- 3) The species that is becoming reduced is oxidizing the other species and is the **oxidizing agent**.
- 4) Close inspection of the redox equation will **always** show a balanced transfer of electrons.

4.3 The Concept of the Mole

Chemistry students often struggle with the concept of a **mole**.

By definition a mole is 6.022×10^{23} of **anything**. It is just another number with a name. Reflect on some common numbers with names and then simply include the mole.

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Name	Number
Dozen	12
Score	20
Gross	144
Google	1×10^{100}
Mole	6.022×10^{23}

Table 4.3.1 Numbers With Names

So why have a name for this huge number? If you look at carbon on the Periodic Table you will see that it has an average atomic weight of 12.011 amu. This in SI units would be approximately 2×10^{-26} kg.

In 1811, an Italian scientist, Amedeo Avogadro established that equal volumes of different gasses at the same temperature had the same number of molecules.

Subsequent research into Avogadro's work resulted in the discovery of a constant relating the mass of a sample containing a pure gas to the number of atoms of the gas in that sample. The constant 6.022×10^{23} was named in honor of Avogadro's original work as *Avogadro's Number*.

The Magic Wand

So what is the practical use of Avogadro's Number? Imagine that your pencil or pen was a *magic wand*. Now approach a Periodic Table and wave the magic wand across the Periodic Table.

You will not actually see anything happen. But now you can read the atomic mass of carbon directly as 12.011 grams per mole. This new and different value cannot have the name atomic mass. The proper name for this new value is *molar mass* with the units of g/mol.

Molar Ratios

It is not an oversimplification to state that the number of moles in a compound occur at the exact same ratios as the number atoms in a molecule.

The subscripts and coefficients in chemical formulae represent the number of atoms in the molecule *and* the number of moles of atoms in a mole of the molecule.

When reading the molecular formula for a certain compound you can now use coefficients and subscripts to assess the number of *moles of atoms* of a certain atom in *one mole of the compound*.

Some examples will clarify this point.

Example 4.3.1

How many moles of H are in one mole of H_2O ?

If there are 2 H atoms in each H_2O molecule then there are 2 moles of H in each mole of H_2O .

Example 4.3.2

How many moles of H are there in 5 moles of C_3H_8 (propane)?

If there are 8 H atoms in each C_3H_8 molecule then there are 8 moles of H in one mole of C_3H_8 and 40 moles H in 5 moles C_3H_8 .

Example 4.3.3

How many moles of H are there in 1 moles of $\text{CO}(\text{NH}_2)_2$ (urea)?

Note that here there are **three multipliers** for H in the chemical formula $1\text{CO}(\text{NH}_2)_2$. You must multiply H by the coefficient 1, the 2 inside the parentheses, and the 2 outside the parentheses.

The single H in the formula multiplied by $1 \times 2 \times 2 = 4$.

There are 4 moles of H in 1 mole of $\text{CO}(\text{NH}_2)_2$.

To make the concept of molar ratios a little clearer, let's look at the number of H atoms in a drawing of the $\text{CO}(\text{NH}_2)_2$ molecule. Remember that this number is also the number of moles of H in 1 mole of $\text{CO}(\text{NH}_2)_2$.

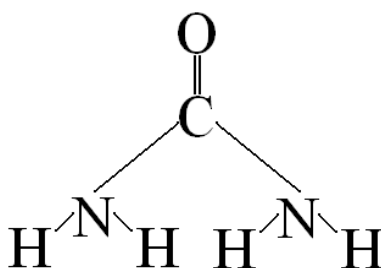


Figure 4.3.1 The Urea Molecule

It is easy to see the 4 H atoms in the drawing of urea in the above figure. This number **must also** be interpreted as the number of moles of H in 1 mole of $\text{CO}(\text{NH}_2)_2$.

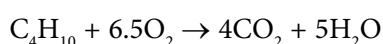
4.4 Stoichiometric Calculations

Stoichiometry is the branch of chemistry that deals with the calculations of amounts of reactants consumed and products formed in a chemical reaction.

The methods used to make these calculations have been being developed all along in the progression of this text. In other words, you are about to see why you were tasked with calculating the number of seconds in a year in Chapter 1 of the text.

Decimal Forms of Coefficients

Consider the following balanced chemical equation for the combustion of butane (C_4H_{10}).



It is *impossible* to have 6.5 molecules of O_2 in the equation of this chemical reaction. However, it is *perfectly acceptable* to have 6.5 moles of O_2 in the equation for this reaction.

The following exercises show some of the unit analyses problems that we prepared for in the exercises of Chapter 1.



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...I finally learned to speak it in just six lessons"
Jane, Chinese architect

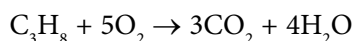
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Exercise 4.4.1

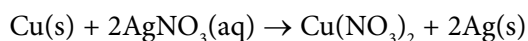
Balance the following chemical equation. Calculate the number of moles of CO_2 generated when 5 moles of propane (C_3H_8) are consumed.



$$\frac{5 \text{ mol C}_3\text{H}_8}{1 \text{ mol C}_3\text{H}_8} \left| \frac{3 \text{ mol CO}_2}{1 \text{ mol C}_3\text{H}_8} \right. = 15 \text{ mol CO}_2$$

Exercise 4.4.2

Balance the following metathesis reaction of silver nitrate (AgNO_3) and copper nitrate ($\text{Cu}(\text{NO}_3)_2$). Calculate how many grams of $\text{Cu}(\text{NO}_3)_2$ are generated when 6 moles of silver (Ag) are generated.



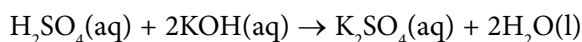
Using the Periodic Table calculate the molar mass of copper nitrate as follows.

$$(1 \times \text{Cu} = 63.55) + (2 \times \text{N} = 28.01) + (6 \times \text{O} = 96.00) = 187.56 \text{ g/mol}$$

$$\frac{6 \text{ mol Ag}}{2 \text{ mol Ag}} \left| \frac{1 \text{ mol Cu}(\text{NO}_3)_2}{1 \text{ mol Cu}(\text{NO}_3)_2} \right. \frac{187.56 \text{ g Cu}(\text{NO}_3)_2}{1 \text{ mol Cu}(\text{NO}_3)_2} = 562.7 \text{ g Cu}(\text{NO}_3)_2$$

Exercise 4.4.3

Balance the following acid-base reaction between sulfuric acid (H_2SO_4) and potassium hydroxide (KOH). Calculate the number of grams of KOH consumed when 348.54 g K_2SO_4 are produced.



$$\frac{348.54 \text{ g K}_2\text{SO}_4}{174.27 \text{ g K}_2\text{SO}_4} \left| \frac{1 \text{ mol K}_2\text{SO}_4}{1 \text{ mol K}_2\text{SO}_4} \right. \frac{2 \text{ mol KOH}}{1 \text{ mol K}_2\text{SO}_4} \left| \frac{56.11 \text{ g KOH}}{1 \text{ mol KOH}} \right. = 224.44 \text{ g KOH}$$

As a matter of review let's look at what was calculated in the three previous exercises. Exercise 4.3.1 was a mole to mole conversion that took one step. Exercise 4.3.2 was a mole to gram conversion that took two steps. Exercise 4.3.3 was a gram to gram conversion that took three steps.

In Exercises 4.3.2 and 4.3.3 it was necessary to calculate the molar masses of molecules by simply summing the molar masses of the constituent atoms in the molecules.

4.5 Limiting Reactants

Up to this point in the text chemical reactions have been represented under ideal conditions. These ideal conditions being as follows.

- 1) Every reaction between two or more atoms, ions, or compounds is a 100% complete reaction.
- 2) Every reaction between two or more atoms, ions, or compounds is irreversible.
- 3) Every reaction between two or more atoms, ions, or compounds occur irrespective of external conditions or catalysts.
- 4) Every atom, ion, or compound in a chemical reaction is present in sufficient quantity to react with the other components of the reaction.

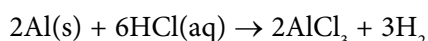
In a literal sense *none of these conditions apply* to any chemical reactions.

The study of chemical reactions rates and contributing factors to those reactions is known as *chemical kinetics* which will not be covered in this text.

We will look at *limiting reactants*. A reactant is limiting if it is not present in sufficient quantity for the reaction to run to completion. Let's look at an example.

Example 4.5.1

Consider the reaction of solid aluminum (Al) with hydrochloric acid (HCl) to produce aluminum chloride (AlCl₃) and hydrogen gas (H₂).



It is understood that there are only 4 moles of Al and 6 moles of HCl available for the reaction.

By looking at the molar ratio of HCl to Al in the reactants (6:2 or 3:1) or the number of chlorides attached to each Al in the products (3) it should become obvious that you need *three times the number of moles of HCl than you need moles of Al*.

Using the molar ratio of HCl to Al in this reaction (3:1) you can calculate the number of moles of HCl needed to completely react 4 moles of Al. You simply multiply the 4 moles of Al by 3 moles HCl per 1 mole Al to get 12 moles HCl. Remember, 12 moles of HCl is the *minimum number of moles* of HCl needed for the reaction to be complete.

To declare what the limiting reacting is ask yourself the question, “What did I run out of?” The 6 moles of HCl available for the reaction was used to react 2 of the 4 moles of Al available. There are still 2 moles of Al left behind because you *ran out of HCl*.

HCl is the limiting reactant!!

There are other reasons than simply not having a sufficient amount of a reactant on hand for a chemical reaction not to go to completion. Some chemical components naturally do not completely react with one another. But again this notion evokes the area of chemical kinetics which we will not cover.

In the previous example we used the molar ratio of the reactants to identify the limiting reactant.

Now let us use the molar ratio of the product to reactant to calculate the *theoretical and percent yields* of the chemical reaction.

Working in moles, the theoretical yield for either the AlCl_3 or the H_2 is simply the coefficients for those components of the reaction from the balanced chemical reaction.

Example 4.5.2

Calculate the theoretical and percent yields for the for the AlCl_3 in the example 4.5.1 in moles.

From the balanced chemical equation the theoretical yield for AlCl_3 is the molar ratio of Al to AlCl_3 which is 2:2 or 1:1. So given that there are 4 moles of Al available for the reaction the theoretical yield of AlCl_3 is 4 moles.

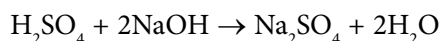
But we know that there were only 2 moles of AlCl_3 produced. The percentage yield is calculated as follows:

$$\text{Percent Yield} = (\text{moles produced} / \text{moles theoretical}) \times 100$$

$$\text{The percent yield of } \text{AlCl}_3 \text{ is } (2 \text{ moles} / 4 \text{ moles}) \times 100 = 50\%$$

In the following exercises balance the chemical equation and identify the limiting reactant based on the given amount of reactants available for the reaction. Identify the percent yield of the identified product.

Exercise 4.5.1



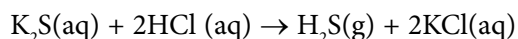
It is given that there are 2 moles of NaOH and 1.5 moles of H_2SO_4 . What is the percent yield of Na_2SO_4 ?

It takes all of the 2 moles of NaOH available to react 1 mole of H_2SO_4 . There will be 0.5 moles of H_2SO_4 left over. All of the NaOH will be used up. NaOH is the limiting reactant.

H_2SO_4 and Na_2SO_4 are in a 1:1 molar ratio. 1.5 moles of H_2SO_4 would theoretically yield 1.5 moles of Na_2SO_4 .

The percent yield would be $(1.5 \text{ moles} / 2 \text{ moles}) \times 100 = 75\%$.

Exercise 4.5.2



It is given that there are 3 moles of K_2S and 3 moles of HCl. What is the percent yield of KCl?

With a 2:1 molar ratio of HCl to K_2S it would take 6 moles HCl to react 3 moles of K_2S . You do not have that much HCl so HCl is the limiting reactant.

With a 2:1 ratio of KCl to HCl the theoretical yield will be 6 moles KCl.

With the limiting amount of 3 moles of HCl 3 moles of KCl will be produced.

The percent yield will then be $(3 \text{ mole} / 6 \text{ moles}) \times 100 = 50\%$

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5 Properties of Gases

5.1 Units of Gas Measurements

Gases are unique in comparison to solids and liquids in that they do not have a fixed volume. Imagine that you are standing in a room holding a balloon. The balloon contains a certain volume of gas. If you pierce the balloon the volume of the gas then becomes the volume of the room.

The following table shows the properties of gases that are measured to help characterize gases.

Measurements	Units	Symbols
Pressure	Pascal	Pa
Temperature	Kelvin	K
Volume	Liter	L
Amount	Moles	n

Table 5.1.1 Measurements of Gases

The Pascal is the SI unit for pressure where $1 \text{ Pa} = 1 \text{ N/m}^2$. However, it is not uncommon to hear the pressure of gases referred to in different units. The following table lists some alternate units for the measurement of gas pressure.

Measurement	Symbol	Equivalence to 1 atm
mm of Mercury	mmHg	760 mmHg
Pounds per Square Inch	lb/in ²	14.7 lb/in ²
Torr	torr	760 torr
Pascal	Pa	101,325 Pa
Atmosphere	atm	1 atm

Table 5.1.2 Alternate Units for Gas Pressure

Example 5.1.1

Convert 745 mmHg to Pascal.

If all of the values in Table 5.1.2 are equivalent to 1 atmosphere then they are all equivalent to one another.

$$745 \text{ mmHg} \times 101,325 \text{ Pa} / 760 \text{ mmHg} = 99,325 \text{ Pa}$$

Example 5.1.2

Convert 1800 torr to pounds per square inch.

$$1800 \text{ torr} \times 14.7 \text{ lb/in}^2 / 760 \text{ torr} = 34.8 \text{ lb/in}^2$$

Example 5.1.3

Convert 450,000 Pa to atmospheres.

$$450,000 \text{ Pa} \times 1 \text{ atm} / 101,325 \text{ Pa} = 4.44 \text{ atm}$$

5.2 The Kinetic-Molecular Gas Theory

Early researchers gathered a series of postulates concerning the nature of gases that are now known as the Kinetic-Molecular Gas Theory.

The following are the postulates of the Kinetic-Molecular Gas Theory:

- 1) Gases are composed of a very large number of particles moving in random directions.
- 2) The particles are so far apart from one another that their aggregate volume, as compared to the volume of the gas, is insignificant.
- 3) The particles travel in straight lines unless they collide with another gas particle or the walls of the container.
- 4) When collisions occur between gas particles or the container walls they always occur in an *elastic* manner.
- 5) There are no attractive forces between different gas particles or the walls of the container.
- 6) The average kinetic energy of a gas is proportional to the temperature of the gas measured in Kelvin.

Elastic and Inelastic Scattering

Elastic scattering is defined as a scattering of particles where the kinetic energy of a particle is always conserved.

If you drop a ball on a flat hard surface you will notice that the ball loses energy on each bounce. This is *inelastic scattering*.

The molecules in a gas lose no energy when they strike another gas molecule. This is *elastic scattering*.

5.3 Basic Gas Laws

Boyle's Law

Boyle's Law states that volume is inversely proportional to pressure at a constant temperature and amount.

$$V \propto 1/P$$

If you press a piston into a cylinder you increase pressure and the volume of the cylinder beneath the piston decreases.

At constant temperature in a closed system the relationship of changing volume and pressure is expressed as follows.

$$P_1V_1 = P_2V_2$$

Where: P is pressure
V is volume

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Exercise 5.3.1

A nitrogen (N_2) gas sample has a volume of 3.0 L and pressure of 1.0 atm. What is the pressure if the volume is decreased to 1.0L?

$$P_2 = \frac{P_1 V_1}{V_2} = \frac{(1 \text{ atm})(3.0 \text{ L})}{(1.0 \text{ L})} = 3 \text{ atm}$$

Exercise 5.3.2

A 4 L sample of air is at 2 atm pressure. What is the volume of the sample when it is at 4 atm pressure?

$$V_2 = \frac{P_1 V_1}{P_2} = \frac{(2 \text{ atm})(4 \text{ L})}{(4 \text{ atm})} = 2 \text{ L}$$

Exercise 5.3.3

What must the pressure be to reduce a 5L volume of oxygen (O_2) at 1 atm to a 2L volume?

$$P_2 = \frac{P_1 V_1}{V_2} = \frac{(1 \text{ atm})(5 \text{ L})}{(2 \text{ L})} = 2.5 \text{ atm}$$

Exercise 5.3.4

What was the original volume of a 2L sample of air at 3 atm when the sample was at 1.5 atm pressure?

$$V_1 = \frac{P_2 V_2}{P_1} = \frac{(3 \text{ atm})(2 \text{ L})}{(1.5 \text{ atm})} = 4 \text{ L}$$

Charles' Law

Charles' Law states that the volume of a gas is directly proportional to temperature, in Kelvin, at constant pressure and amount.

$$V \propto T$$

Think of firing a hot air balloon. As the burner is fired heat is added to the balloon and the volume of the balloon increases.

At constant pressure and number of moles the relationship of changing volume and temperature is expressed as follows.

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

Where V is volume
T is temperature

Exercise 5.3.5

What is the volume of a 1L balloon at 22°C when the temperature is raised to 85°C?

$$T_1 = 273 + 22 = 295\text{K} \quad T_2 = 273 + 85 = 358\text{K}$$

$$V_2 = \frac{V_1 T_2}{T_1} = \frac{(1\text{ L})(358\text{ K})}{295\text{ K}} = 1.21\text{ L}$$

Exercise 5.3.6

What is the temperature, in °C, of a rubber bladder increased in volume from 1.2L, at 25 °C, to 1.5L?

$$T_1 = 273 + 25 = 298\text{ K} \quad T_2 = 373\text{K} - 273\text{K} = 100^\circ\text{C}$$

$$T_2 = \frac{T_1 V_2}{V_1} = \frac{(298\text{ K})(1.5\text{ L})}{1.2\text{ L}} = 373\text{ K}$$

Exercise 5.3.7

What was the original volume of a balloon, in liters, at 20°C if the balloon is at 50°C with a volume of 2L?

$$T_1 = 273 + 20 = 293\text{ K} \quad T_2 = 273 + 50 = 323\text{ K}$$

$$V_1 = \frac{T_1 V_2}{T_2} = \frac{(293\text{ K})(2\text{ L})}{323\text{ K}} = 1.8\text{L}$$

Exercise 5.3.8

A piston causes a volume in a cylinder of 0.15L at 75°. What volume would the piston cause at 30°C?

$$T_1 = 273 + 75 = 348 \text{ K} \quad T_2 = 273 + 30 = 303 \text{ K}$$

$$V_2 = \frac{T_2 V_1}{T_1} = \frac{(303 \text{ K})(0.15 \text{ L})}{348 \text{ K}} = 0.13 \text{ L}$$

Gay-Lussac's Law

Gay-Lussac's law states that the pressure of a gas is directly proportional to temperature, in Kelvin, at a constant volume and amount of gas.

$$P \propto T$$

If you heat a closed container that contains a gas the pressure will increase.



At a constant volume and number of moles the relationship of changing pressure and temperature is as follows.

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$

Where P is pressure
T is temperature

Exercise 5.3.9

A closed container, containing 1 mole of air, is at 25°C and 1 atm pressure. What is the pressure if the container is heated to 150°C?

$$T_1 = 273 + 25 = 298 \text{ K} \quad T_2 = 273 + 150 = 423 \text{ K}$$

$$P_2 = \frac{T_2 P_1}{T_1} = \frac{(423 \text{ K})(1 \text{ atm})}{298 \text{ K}} = 1.42 \text{ atm}$$

Exercise 5.3.10

What was the original temperature, in °C, of a closed container at 1.5 atm if the container is at 1 atm and 25°C?

$$T_2 = 273 + 25 = 298 \text{ K} \quad T_1 = 447 - 273 = 174^\circ\text{C}$$

$$T_1 = \frac{T_2 P_1}{P_2} = \frac{(298 \text{ K})(1.5 \text{ atm})}{1 \text{ atm}} = 447 \text{ K}$$

Exercise 5.3.11

What was the original pressure of a pressure tank at 20°C if it is now at 50°C and 3.8 atmospheres pressure?

$$T_1 = 273 + 20 = 293 \text{ K} \quad T_2 = 273 + 50 = 323 \text{ K}$$

$$P_1 = \frac{T_1 P_2}{T_2} = \frac{(293 \text{ K})(3.8 \text{ atm})}{323 \text{ K}} = 3.4 \text{ atm}$$

Exercise 5.3.12

What is the pressure of a balloon at 1 atmosphere pressure and 30°C if the temperature is raised 75°C?

$$T_1 = 273 + 30 = 303 \text{ K} \quad T_2 = 273 + (30 + 75) = 378 \text{ K}$$

$$P_2 = \frac{T_2 P_1}{T_1} = \frac{(378 \text{ K})(1.0 \text{ atm})}{303 \text{ K}} = 1.2 \text{ atm}$$

Avogadro's Law

Avogadro's Law states that the volume of a gas is directly proportional to the amount of gas, in moles, at a constant pressure and temperature.

$$V \propto n$$

As you add air to a deflated football the volume of the football increases.

At a constant pressure and temperature the relationship of changing volume and number of moles is as follows.

$$\frac{V_1}{n_1} = \frac{V_2}{n_2}$$

Where V is volume and n is number of moles.

Exercise 5.3.13

How many liters of nitrogen (N_2) are there in 50 g of N_2 at STP?

$$\frac{50 \text{ g } N_2}{28 \text{ g } N_2} \left| \frac{1 \text{ mole } N_2}{1 \text{ mole } N_2} \right| \frac{22.4 \text{ L } N_2}{1 \text{ mole } N_2} = 40 \text{ L } N_2$$

Exercise 5.3.14

How many grams of O_2 are there in 89.6 L of O_2 at STP?

$$\frac{89.6 \text{ L } O_2}{22.4 \text{ L } O_2} \left| \frac{1 \text{ mole } O_2}{1 \text{ mole } O_2} \right| \frac{32 \text{ g } O_2}{1 \text{ mole } O_2} = 128 \text{ g } O_2$$

Exercise 5.3.15

The inorganic compound sodium azide (NaN_3) is the gas generating compound in your car's airbag. How many liters of nitrogen (N_2) are produced if 20 g NaN_3 decompose to N_2 at STP?

$$\frac{20 \text{ g NaN}_3}{65 \text{ g NaN}_3} \left| \frac{1 \text{ mole NaN}_3}{1 \text{ mole NaN}_3} \right| \left| \frac{1.5 \text{ moles N}_2}{1 \text{ mole NaN}_3} \right| \left| \frac{22.4 \text{ L N}_2}{1 \text{ mole N}_2} \right| = 10.3 \text{ L N}_2$$

Exercise 5.3.16

Hydrogen for hydrogen balloons was generated by reacting lead with sulfuric acid to form lead sulfate and hydrogen gas according to the following chemical equation. $\text{Pb} + \text{H}_2\text{SO}_4 \rightarrow \text{PbSO}_4 + \text{H}_2$. Calculate the number of liters of H_2 produced if 1 kg Pb was reacted at STP.

$$\frac{1 \text{ kg Pb}}{1 \text{ kg Pb}} \left| \frac{10^3 \text{ g Pb}}{207.2 \text{ g Pb}} \right| \left| \frac{1 \text{ mole Pb}}{1 \text{ mole Pb}} \right| \left| \frac{1 \text{ mole H}_2}{1 \text{ mole Pb}} \right| \left| \frac{22.4 \text{ L H}_2}{1 \text{ mole H}_2} \right| = 108 \text{ L H}_2$$

5.4 The Ideal Gas Law

The most prevalent form of expressing all of the gas laws as a single expression is the *Ideal Gas Law*.

$$PV = nRT$$



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Where “R” is a gas constant and has the same values for all gases. The value for R is 0.082058 L•atm/K•mol or 8.3145 J/K•mol.

Look back at the proportionality statements for the gas laws. You should notice that the values P, V, n, and T have the same relationships to one another in the ideal gas equation as they have in their individual proportionalities.

For example, the statement of the ideal gas equation has the same direct proportionality for P and T as the proportionality statement of Gay-Lussac’s Law (P∝T).

Exercise 5.4.1

Calculate the pressure of a 2L container holding 0.5 moles of oxygen at 25°C.

Calculate the temperature in K.

$$\text{Temperature} = 25 + 273.15 = 298.15 \text{ K}$$

Solve the ideal gas equation for P. $P = nRT/V$

Substitute the values from the statement of the problem.

$$P = \frac{(0.5 \text{ mol})(0.082058 \text{ L}\cdot\text{atm}/\text{K}\cdot\text{mole})(298.15\text{K})}{2\text{L}}$$

Check to see if the units work. K cancels K, mole cancels mole, L cancels L leaving atm.

$$P = 6 \text{ atm}$$

Exercise 5.4.2

The average lung volume of an adult male is 6 L. Calculate the temperature of that adult male (in °C) at 1 atm of pressure and 0.26 moles gas.

Solve the ideal gas equation for T. $T = PV/nR$.

Substitute the values from the statement of the problem.

$$T = \frac{(1 \text{ atm})(6 \text{ L})}{(0.236 \text{ mole})(0.082058 \text{ L}\cdot\text{atm}/\text{K}\cdot\text{mole})} = 310 \text{ K}$$

Note that K and mole are in a denominator of a fraction that is in a denominator of a fraction. K and mole are now in the numerator of the overall fraction. All other units cancel.

$$T_K = 310 \text{ K} \quad T_C = 310 - 273 = 37^\circ\text{C}$$

Obviously this adult male is healthy.

Exercise 5.4.3

Calculate the volume of 1 mole of air in a closed container at 3 atm and 50°C.

Convert 50°C to K. Temperature = 273.15 + 50 = 323.15

Solve ideal gas equation for V. $V = nRT/P$

Substitute the values from the statement of the problem.

$$V = \frac{(1 \text{ mole})(0.082058 \text{ L}\cdot\text{atm}/\text{K}\cdot\text{mole})(323.15 \text{ K})}{3 \text{ atm}} = 8.8 \text{ L}$$

Exercise 5.4.4

Calculate the number of moles of a gas in a closed 2 L container at 1 atm and 20°C.

Solve the ideal gas equation for n. $n = PV/RT$

Convert 20°C to K. Temperature = 273.15 + 20 = 293.15K

Substitute the values from the statement of the problem.

$$n = \frac{(1 \text{ atm})(2 \text{ L})}{(0.082058 \text{ L atm}/\text{K mole})(293.15 \text{ K})} = 0.08$$

5.5 Standard State Conditions and Molar Volume

Using Avogadro's Law we can say that any two gases will have the same volume if they have the same number of moles of gas and the same temperature and pressure.

By using standard values for number of moles, pressure, and temperature the concept of *Standard Temperature and Pressure (STP)* was developed.

One mole of any gas at 1 atm (760 mmHg) pressure and 0°C (273.15K) will occupy a volume of 22.414 liters.

5.6 Partial Pressure of Gas Mixtures

Dalton's Law of Partial Pressure

Dalton's Law states that the pressure of a mixture of gases is the sum of the fractional (or *partial*) pressures of the individual gases that comprise the gas mixture.

$$P_{Total} = P_1 + P_2 + P_3 + \dots$$

The Partial Pressure of Air

The table below lists the partial pressures (in mmHg) for the common components of air. The partial pressures of each component is the component percentage of the gas times 760 mmHg.

Dry Air Components	Percentage of Air %	Partial Pressure (mmHg)
Nitrogen (N ₂)	78.09	593.48
Oxygen (O ₂)	20.95	159.22
Argon (Ar)	0.93	7.07
Carbon Dioxide (CO ₂)	0.039	0.30
Component Totals	760	100

Table 5.6.1 Composition of Dry Air

A Partial Pressure Calculation

A deep sea diver's air tank is a mixture of oxygen and helium. Calculate the partial pressure of helium (He), in atmospheres, if the partial pressure of the oxygen is 1,140 mmHg at a diving pressure of 7.0 atmospheres.

$$P_{Total} = P_{O_2} + P_{He} \text{ so that } P_{He} = P_{Total} - P_{O_2}$$

$$P_{O_2} = 1,140 \text{ mmHg} \times 1 \text{ atm} / 760 \text{ mm Hg} = 1.5 \text{ atm}$$

$$P_{He} = 7.0 \text{ atm} - 1.5 \text{ atm} = 5.5 \text{ atm}$$

6 Chemistry of Solutions

6.1 Types of Homogeneous Mixtures

There are basically three types of **homogeneous mixtures**. This means that the components of the mixtures are evenly dispersed throughout the volume of the mixture.

Solutions

Solutions contain particles in the range of tenths of nanometers (nm) to several nm. A nanometer is 10^{-9} meters. They are transparent and, though they may be colored, do not separate on standing.

Colloids

Colloids, such as homogenized milk and fog, contain particles in the range of hundreds of nanometers. Although they are often murky or opaque to light, they do not separate on standing.

Suspensions

Suspensions are heterogeneous, nonuniform mixtures with particles so large they can be separated by use of filters or semi-permeable membranes.

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6.2 Solution Nomenclature

It is important when discussing solutions that one use the agreed upon terminology that describes the constituents of a solution. Listed below are three very *important* definitions in solution chemistry.

Solution

A homogeneous mixture of molecules or ions.

Solvent

The medium in which the molecules or ions are dissolved.

Solute

Any substance dissolved in a solvent.

Concentration

The ratio of the amount of solute to the amount of solution.

Although we will deal entirely with liquid solutions in this chapter, it should be noted that solutions do exist in all of the three states of matter.

The following table shows examples of solutions in liquid, gaseous, and solid states of matter.

State of Matter	Solvent	Solute	Solution
Liquid	Water	Acetic Acid	Vinegar
Gas	Nitrogen	Oxygen	Air
Solid	Copper	Tin	Bronze

Table 6.2.1 Solutions of Different States of Matter

6.3 Solution Properties

As you may have already noticed, chemistry, like other sciences, can be viewed as a systematic way of observing a component or system of nature. These observations are then recorded, agreed upon, and set down as the *properties* of that component or system.

Listed below are the properties of solutions that you will need to understand the chemistry of solutions.

Solubility

Solubility is the measure of how much of a solute will dissolve in a given amount of solvent. When solubility is measured in g/100 ml the 100 ml is the *given amount*. It has been agreed upon among chemists to measure and record solubilities in this manner using this specific unit.

For example, common table salt (NaCl), has a solubility in water of 39.5 g/100 ml. You could prove this to yourself by measuring out 100 ml of water into a clear glass. Measure out 50 grams of table salt and try to get all of the salt into solution in the 100 ml of water.

The table below lists solubilities of common substances in water at 20°C.

Substance	Formula	Solubility (g/100ml)
Sucrose	$C_{12}H_{22}O_{11}$	200
Potassium Nitrate	KNO_3	47
Sodium Chloride	NaCl	39.5
Sodium Sulfide	Na_2S	1.86
Calcium Hydroxide	$Ca(OH)_2$	0.017

Table 6.3.1 Solubilities in Water at 20°C

Saturation

Saturation is that state of a solution where the amount of solute added to the solvent has exceeded the solubility of that solute.

When excess solute is added to a solvent, that solute will not go into solution. It is common to stir a solution to get solutes into solution. When excess solute is added in this manner, the solution will appear turbid at first due to suspended solutes but will turn clear when the excess solute settles to bottom of the container.

Supersaturation

Supersaturation is the state of a solution when more solute is in solution than the solubility would allow for due to special circumstances.

A sealed bottle of soda is a solution that is supersaturated with carbon dioxide (CO_2) due to the high pressure inside the bottle. When the bottle cap is removed the pressure rapidly decreases releasing the excess CO_2 to the atmosphere.

A rain cloud can be supersaturated with water vapor. In order for the water vapor to coalesce as liquid water it must be supplied with a non-gaseous surface to act as a point of nucleation. Once particles of dust are provided as “cloud seeds” the excess water vapor will quickly coalesce into rain drops.

Miscibility

Miscibility is the property of liquids to combine with one another in all proportions to form homogeneous solutions. In a manner of speaking miscibility is unbounded solubility.

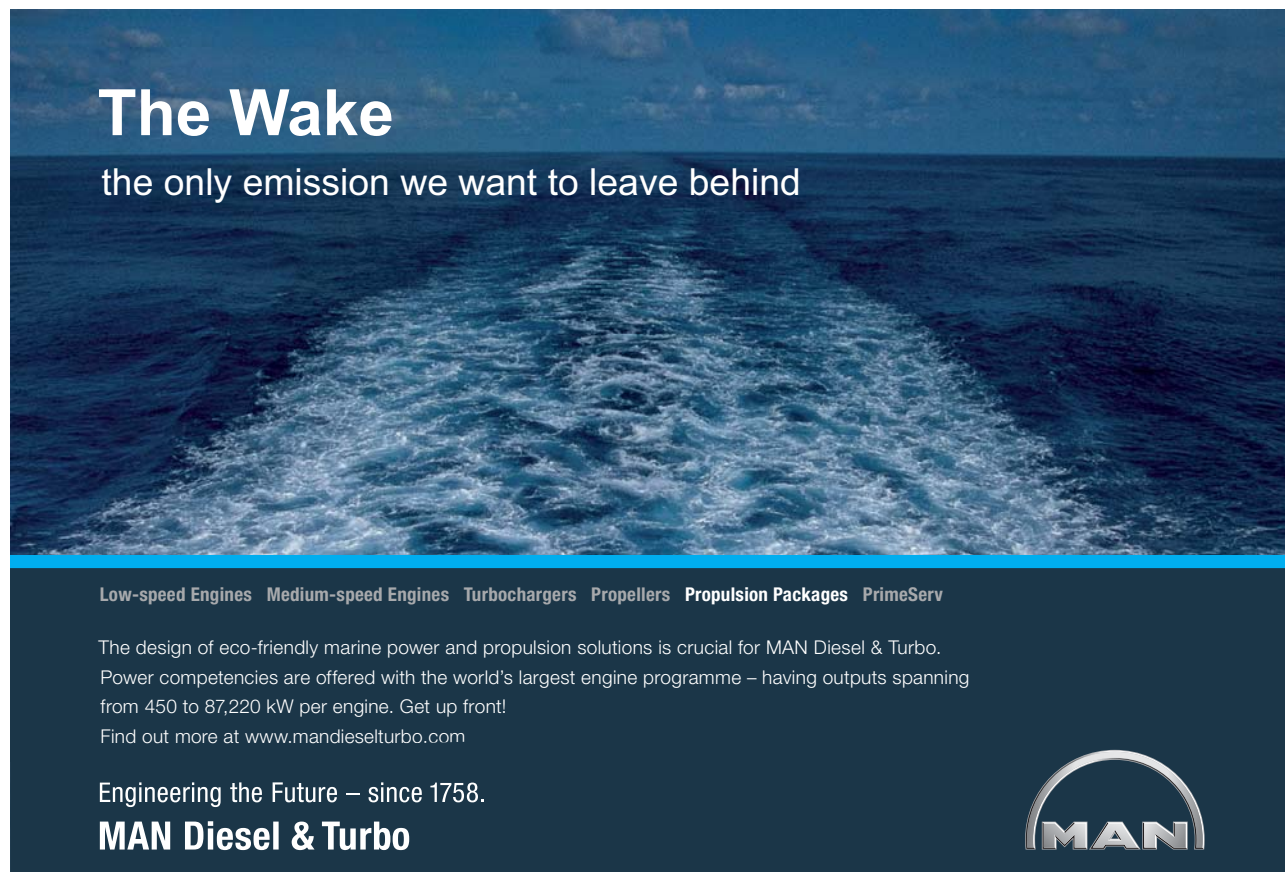
In table 6.3.1, I showed the solubilities of some ionic compounds and a sugar. Had I included acetic acid I would have listed the solubility as *miscible* since it will combine with water at all proportions.

At a range of 4% to 8% acetic acid in water the solution is commonly referred to as *vinegar*.

Concentration

Concentration is the measure of the amount of solute actually dissolved in a solvent.

If you were to return to the experiment of adding 50 g of NaCl to 100 ml of water, under ideal conditions (pure water at 1 atm pressure and 20°C) the *concentration* of the NaCl in the water would be 39.5 g/100 ml. This is due to the limit of the solubility of NaCl in water.




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Staying within the SI system the 39.5 g/100 ml solubility of NaCl in water could be written in other terms of concentration.

The 39.5 g/100 ml could be expressed as 395 g/L, 395 g/kg, 395,000 mg/kg, 395,000 ppm, and **6.76 moles/L**.

6.4 Molarity

In Chapter 4 you were introduced to the concept of the mole. Like other measurements of amount you can convert the mole to concentration by expressing the number of moles per unit volume.

Molarity is the measure of the concentration of a solute in a solvent expressed in terms of the number of moles of that solute in one liter of the solvent.

Symbols and Terms of Molarity

It is important to become familiar with the different symbols and terms used to express molarity.

The symbol for molarity is the upper case letter **M**. However, there are a few different ways you may hear or see molarity expressed.

Here are some examples of the way a solution that contains 1.5×10^{-2} moles of NaCl in one liter of water may be expressed:

- 1) The solution is 1.5×10^{-2} **M** in NaCl.
- 2) The solution has 1.5×10^{-2} **moles/liter** NaCl.
- 3) This is a 1.5×10^{-2} **molar** solution of NaCl.

Just remember that they all mean the number of moles of solute per liter of solvent.

Molarity Calculations

Calculating molarity is a critical skill for many scientific disciplines. Climate scientists will use molarity calculations to estimate the load of carbon being deposited to the Earth's atmosphere.

Pharmaceutical chemists definitely use molarity calculations to determine the correct amounts of the various constituents of a drug product. A nurse could use molarity calculations to determine correct dosage regimens of medicines.

The following exercises may seem a bit extensive. It is my way of stressing how important these calculations are. Molarity calculations are also essential to the calculation of pH coming up in Chapter 8.

Let's do some exercises! I'm still using my problem solving mantra.

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Exercise 6.4.1

What is the molarity of Cl^- in a 1 L solution of water containing 3 moles of NaCl ?

$$\frac{3 \text{ moles NaCl}}{1 \text{ L}} \left| \frac{1 \text{ mole Cl}^-}{1 \text{ mole NaCl}} \right. = \frac{\text{moles Cl}^-}{\text{L}}$$

$$\frac{3 \text{ moles NaCl}}{1 \text{ L}} \left| \frac{1 \text{ mole Cl}^-}{1 \text{ mole NaCl}} \right. = 3 \frac{\text{moles Cl}^-}{\text{L}}$$

Here the molar ratio of Cl^- to NaCl is taken directly from the chemical formula.

Exercise 6.4.2

What is the molarity of OH^- in a 1.5 L solution of water that contains 4 moles of Ca(OH)_2 ?

$$\frac{4 \text{ moles Ca(OH)}_2}{1.5 \text{ L}} \left| \frac{2 \text{ moles OH}^-}{1 \text{ mole Ca(OH)}_2} \right. = \frac{\text{moles OH}^-}{\text{L}}$$

$$\frac{4 \text{ moles Ca(OH)}_2}{1.5 \text{ L}} \left| \frac{2 \text{ moles OH}^-}{1 \text{ mole Ca(OH)}_2} \right. = 5.3 \frac{\text{moles OH}^-}{\text{L}}$$

Here the chemical formula shows that there are 2 moles OH^- for 1 mole of Ca(OH)_2 .

Exercise 6.4.3

What is the molarity of Na^+ in a 0.75 L solution containing 0.35 g of NaBr ?

$$\frac{0.35 \text{ g NaBr}}{0.75 \text{ L}} \left| \frac{\text{moles Na}^+}{\text{L}} \right. =$$

Convert g NaBr to moles NaBr (as shown below) using the periodic table.

The 1 mole of Na^+ in the 1 mole of NaBr has a molar mass of 22.99 g/mol. The 1 mole of Br^- in the 1 mole of NaBr has a molar mass of 79.90 g/mol. Adding them together yields a molar mass for NaBr of 102.9 g/mol.

$$\frac{0.35 \text{ g NaBr}}{0.75 \text{ L}} \left| \frac{1 \text{ mole NaBr}}{102.89 \text{ g NaBr}} \right. = \frac{\text{moles Na}^+}{\text{L}}$$

Once again the molar ratio of Na^+ to NaBr comes directly from the chemical formula.

$$\frac{0.35 \text{ g NaBr}}{0.75 \text{ L}} \times \frac{1 \text{ mole NaBr}}{102.9 \text{ g NaBr}} \times \frac{1 \text{ mole Na}^+}{1 \text{ mole NaBr}} = 4.5 \times 10^{-3} \frac{\text{moles Na}^+}{\text{L}}$$

6.5 Mole Fractions

The Concept of Mole Fraction

Now that we know about both moles and molarity we can embrace the concept of mole fraction.

$$\text{Mole Fraction (X)} = \frac{\text{moles of solute or solvent}}{\text{moles of solution}}$$

A mole fraction can be expressed for either the solute or the solvent. Mole fraction is expressed as a fraction without units.

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If a certain amount of salt (NaCl) is added to a certain volume of pure water (H₂O), you should be able to calculate the mole fraction of Na⁺ ions in that solution. You will need to calculate the number of moles of Na⁺ ions, Cl⁻ ions, and water molecules that exist in that solution. Then the number of moles of Na⁺ ions divided by the number of moles of **all other constituents** in that solution is the mole fraction of Na⁺ ions in that solution.

Exercise 6.5.1

What is the mole fraction of Na⁺ ions in a 1 liter solution of pure water that is 0.1 molar in NaCl? Pure water has a density of 1kg/liter.

$$\frac{1\text{L H}_2\text{O} \left| \frac{1\text{kg H}_2\text{O}}{1\text{L H}_2\text{O}} \right| \frac{1000\text{g}}{1\text{kg}} \left| \frac{1\text{ mol H}_2\text{O}}{18\text{g H}_2\text{O}} \right.}{\left. \right.} = 55.56 \text{ mol H}_2\text{O}$$

Now that we have calculated the number of moles we need to calculate the number of moles Na⁺ and Cl⁻ ions.

$$\frac{0.1 \text{ mol NaCl}}{\text{L}} \left| \frac{1 \text{ mol Na}^+}{1 \text{ mol NaCl}} \right. = 0.1 \text{ mol Na}^+$$

Since Na⁺ and Cl⁻ exist in an equal molar ratio in NaCl there are also be 0.1 moles of Cl⁻ in NaCl. Therefore in the solution there is a total of 55.56 + 0.1 + 0.1 = 55.76 of moles of all constituents.

The mole fraction of Na⁺ ions in the solution is 0.1/ 55.76 or **1/557.6**.

Exercise 6.5.2

What is the mole fraction of Cl⁻ in a 1 liter solution of pure water that has a 1 × 10⁻² molar concentration of CaCl₂? From Exercise 6.5.1 we see that 1 liter of water contains 55.56 moles of water.

$$\frac{0.01 \text{ mol CaCl}_2}{\text{L}} \left| \frac{2 \text{ mol Cl}^-}{1 \text{ mol CaCl}_2} \right. = \frac{0.02 \text{ mol Cl}^-}{\text{L}}$$

If there are 0.02 moles of Cl⁻ in the solution the 1 to 2 molar ratio of Ca²⁺ to Cl⁻ means there are 0.01 moles of Ca²⁺ in the solution. So there are a total of 55.56 + 0.02 + 0.01 = 55.59 moles of all constituents in the solution.

The Cl⁻ mole fraction is 0.02/55.59 = **1/2795**.

6.6 Colligative Properties

Colligative properties are those properties of a solution that are dependent on the amount of a dissolved solute but not on the chemical identity of the solute.

The following four colligative properties will be discussed:

Vapor Pressure Depression

Boiling Point Elevation

Freezing Point Depression

Osmotic Pressure

Vapor Pressure Depression

If the vapor pressure of a solvent is measured and compared with the vapor pressure of the same solvent, under identical conditions, to which a solute has been dissolved *the vapor pressure is lower*.

Raoult's Law states that the vapor pressure of a solution containing a non-volatile solute is equal to the vapor pressure of the pure solvent times the mole fraction of the solvent.

$$P_{soln} = P_{solv} \cdot X_{solv}$$

Boiling Point Elevation

If the vapor pressure of a liquid has been lowered you will need to add more energy to raise the vapor pressure to atmospheric pressure. Therefore, the liquid will *boil at a higher temperature*.

Freezing Point Depression

If a non-volatile solute is dissolved in a pure solvent the freezing point of the solution *will be lower* than the temperature of the pure solvent.

Hint: Think of the salt added to an ice-cream freezer.

Osmotic Pressure

If a vessel contains pure solvent and a solution of the solvent and a non-volatile solute separated by a semi permeable membrane, solvent molecules will migrate through the membrane in both directions. This is the process known as *osmosis*.

Osmotic flow is favored toward the solution side of the vessel according to the *osmotic pressure* (Π) resulting from the solute concentration. Where...

$$\Pi = MRT$$

Π is osmotic pressure, M is solute molarity, R is a gas constant, and T is the temperature in Kelvin.

Osmosis in Blood Cell Biology

Because the cell membranes in biological systems are semipermeable, osmosis is an ongoing process.

Most intravenous solutions are *isotonic* solutions because their osmotic pressure is in equilibrium with the pressure of the body fluids.

For instance, if an isotonic blood cell was placed in pure water, the resulting solution would be of a lower, or *hypotonic*, pressure and water would flow into the cell due to osmosis. This could cause the cell to rupture in a process known as *hemolysis*.

In a concentrated solution, the same blood cell would realize a higher, or *hypertonic*, pressure solution resulting in fluid flowing out of the cell causing cell shrinkage in a process known as *crenation*.

Fractional Distillation

Fractional distillation is a process of separating different components of a gas or liquid due to the fact that these components have different vapor pressures.

The most prevalent use for fractional distillation is the refinement of petroleum products.

Oil in an oil well consists of tens of thousands of different components. Most of these are liquid but many are in a vapor phase above the liquid.

Both the liquids and the gases are extracted and then fractionally distilled to produce the many product streams of the petroleum industry.

These products can vary from light hydrocarbons containing one or two carbons to heavy asphaltene containing hundreds of carbons per compound.

7 Thermochemistry

7.1 The Concepts of Heat and Energy

Energy is defined as the ability to *do work* and *supply heat*.

In general the discussion of energy is divided into the concepts of *kinetic energy* and *potential energy*.

Kinetic Energy

Kinetic energy is the energy an object has due to its motion and is defined by the following formula.

$$KE = \frac{1}{2} mv^2$$

Where KE = kinetic energy
 m = mass in kg
 v = velocity in m/s

The unit of kinetic energy is the *Joule* which is defined as the amount of energy a 2kg object has if it is moving at 1 m/s.

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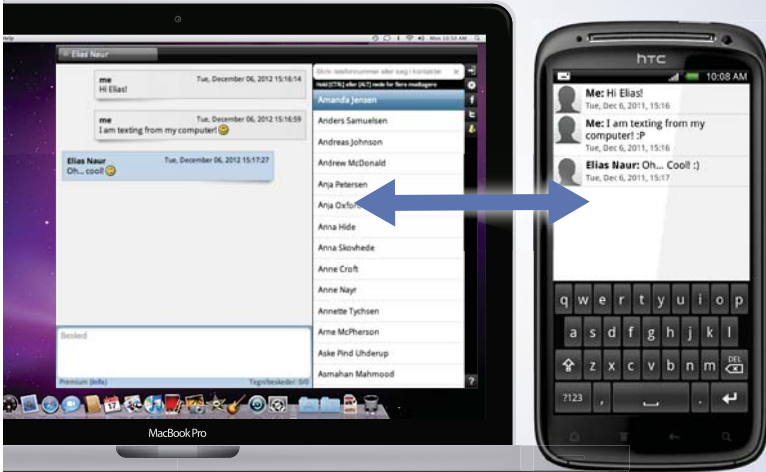
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The units for a Joule come directly from the formula above.

$$\mathbf{KE = \frac{1}{2} (2\text{kg})(1\text{m/s})^2 = kg m^2 s^{-2}}$$

Potential Energy

Potential energy is the energy stored in a stationary object due to its position or condition.

The units of potential energy are the same as those for kinetic energy. If you drop a 2kg object and determine that it achieved 2 Joules of kinetic energy, then it is defined that the object had contained 2 Joules of potential energy.

In the case of potential energy mentioned above it is the Earth's gravity that gives the object its potential energy. Other forces such as electrical, mechanical, and magnetic forces can also give potential energy to objects.

Some Examples of Kinetic and Potential Energy

A boulder at the top of a mountain has *potential* energy. When it begins to roll down the mountain its energy becomes *kinetic*.

The gasoline in your car has *potential* energy that is turned into *kinetic* energy when it is combusted.

If you stretch a rubber band you add *potential* energy to it that becomes *kinetic* energy when it is released.

A snowflake has *kinetic* energy which is converted to *potential* energy when it settles to the ground.

7.2 Calculating Heat Content

Kinetic Energy of a System of Components

Rather than looking at a single object in motion let's look at a system of components, such as atoms or molecules, that are all in motion and colliding with one another.

When we wish to express the kinetic energy realized by these motions and collisions, we refer to it as *heat*.

The unit for heat is the *Joule* just as it is for work. However, a more common unit, the *calorie*, is also used.

The calorie is defined as the amount of energy required to raise one gram of water 1°C and has the symbol "*cal*". A dietary calorie is equal to 1,000 calories and has the symbol "*Cal*".

$$\mathbf{1 \text{ calorie} = 4.184 \text{ Joules}}$$

Let's do some exercises!

Exercise 7.2.1

A 30 g portion of fat contains 1100kJ of energy. How many dietary calories would that be?

$$\frac{1100 \text{ kJ}}{\quad} = \quad \text{Cal}$$

$$\frac{1100 \text{ kJ} | 10^3 \text{ J}}{1 \text{ kJ}} = \quad \text{Cal}$$

Convert kJ to J.

$$\frac{1100 \text{ kJ} | 10^3 \text{ J} | 1 \text{ cal}}{1 \text{ kJ} | 4.181 \text{ J}} = \quad \text{Cal}$$

Convert J to cal.

$$\frac{1100 \text{ kJ} | 10^3 \text{ J} | 1 \text{ cal} | 1 \text{ Cal}}{1 \text{ kJ} | 4.181 \text{ J} | 10^3 \text{ cal}} = 263 \text{ Cal}$$

Convert cal to Cal.

Exercise 7.2.2

A 25 g sample of soda pop contains 2500 kJ of energy. How many Calories does the soda pop contain?

$$\frac{2500 \text{ kJ}}{\quad} = \quad \text{Cal}$$

$$\frac{2500 \text{ kJ} | 10^3 \text{ J}}{1 \text{ kJ}} = \quad \text{Cal}$$

Convert kJ to J.

$$\frac{2500 \text{ kJ} | 10^3 \text{ J} | 1 \text{ cal}}{1 \text{ kJ} | 4.181 \text{ J}} = \quad \text{Cal}$$

Convert from J to cal.

$$\frac{2500 \cancel{\text{kJ}} | 10^3 \cancel{\text{J}} | 1 \cancel{\text{cal}}}{1 \cancel{\text{kJ}} | 4.181 \cancel{\text{J}} | 10^3 \cancel{\text{cal}}} = 598 \text{ Cal}$$

Convert from cal to Cal.

Exercise 7.2.3

How many kilojoules are in a candy bar containing 750 Calories?

$$\frac{750 \text{ Cal}}{1} = \quad \text{kJ}$$

$$\frac{750 \cancel{\text{Cal}} | 10^3 \cancel{\text{cal}}}{1 \cancel{\text{Cal}}} = \quad \text{kJ}$$

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Convert Cal to cal.

$$\frac{750 \cancel{\text{Cal}} | 10^3 \cancel{\text{cal}} | 4.184 \text{ J}}{| 1 \cancel{\text{Cal}} | 1 \cancel{\text{cal}}} = \quad \text{kJ}$$

Convert cal to J.

$$\frac{750 \cancel{\text{Cal}} | 10^3 \cancel{\text{cal}} | 4.184 \text{ J} | 1 \text{ kJ}}{| 1 \cancel{\text{Cal}} | 1 \cancel{\text{cal}} | 10^3 \cancel{\text{J}}} = 3180 \text{ kJ}$$

Convert j to kJ.

Exercise 7.2.4

Calculate the number of kilojoules in a potato containing 105 kilocalories.

$$\frac{105 \text{ kcal}}{\quad} = \quad \text{kJ}$$

$$\frac{105 \cancel{\text{kcal}} | 10^3 \cancel{\text{cal}}}{| 1 \cancel{\text{kcal}} |} = \quad \text{kJ}$$

Convert kcal to cal.

$$\frac{105 \cancel{\text{kcal}} | 10^3 \cancel{\text{cal}} | 4.184 \text{ J}}{| 1 \cancel{\text{kcal}} | 1 \cancel{\text{cal}}} = \quad \text{kJ}$$

Convert cal to J.

$$\frac{105 \cancel{\text{kcal}} | 10^3 \cancel{\text{cal}} | 4.184 \text{ J} | 1 \text{ kJ}}{| 1 \cancel{\text{kcal}} | 1 \cancel{\text{cal}} | 10^3 \cancel{\text{J}}} = 439 \text{ kJ}$$

Convert from j to kJ.

7.3 Exothermic and Endothermic Reactions

When observing the heats of chemical reactions it is important to know which way the heat is flowing in the chemical reaction.

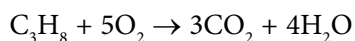
Is the heat being generated by the chemical reaction? Is heat required in order for the chemical reaction to proceed?

The following definitions are agreed upon conventions describing the flow of heat in chemical reactions.

Exothermic Reactions

Chemical reactions that *release heat to the surroundings* are considered to be exothermic reactions.

Let's look at the familiar combustion reaction of propane (C₃H₈).



In truth this reaction is missing one very important product.



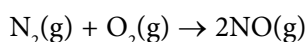
When one mole of propane is burned it releases 2028.8 kJ of heat to the surroundings.

Due to convention the heat of reaction for the combustion of propane is expressed as -2028.8 kJ mol⁻¹. The negative sign is from the perspective of the reactants. The propane and the oxygen *lost heat* as a consequence of the combustion reaction.

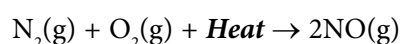
Endothermic Reactions

Chemical reactions that need to *absorb heat from the surroundings* in order to proceed are known as endothermic reactions.

Let's look at the formation of nitrogen monoxide (NO) from nitrogen (N₂) and oxygen (O₂),



Again this chemical equation does not tell the entire story. The reaction will not proceed unless energy, in the form of heat, is added to the reaction.



It is necessary for N_2 and O_2 to absorb $90.37 \text{ kJ mol}^{-1}$ in order to react to form one mole of NO . In the above balanced chemical equation twice that value, 180.74 kJ , were required to form two moles of NO .

By convention the heat of reaction for the formation of NO from N_2 and O_2 is $90.37 \text{ kJ mol}^{-1}$. This number is positive since the N_2 and O_2 are seen to have gained heat.

7.4 Enthalpy Calculations: Hess' Law

When an object or system of objects are heated more is going on than just the heating.

If you heat a beaker of water that is open to ambient pressure the volume of the water will increase. This is a form of work know as $P\Delta v$ work.

Rather than deal with this component of thermochemistry directly, a new value known as *enthalpy* (H) was developed.

Standard enthalpies of formation for many substances were experimentally determined and listed in tables. It is easy to use these listed values to calculate the change in enthalpy for a reaction using the following formula.



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Hess' Law

Hess' Law uses standardized enthalpies of formations for reactants and products in order to calculate the change in enthalpy for a chemical reaction.

$$\Delta H_{\text{rxn}} = \sum H^{\circ}_{\text{form-prod}} - \sum H^{\circ}_{\text{form-react}}$$

Where “Δ” signifies a change in
 “Σ” signifies a summation of
 “°” signifies a standardized value
 “rxn” signifies the chemical reaction

Hess' Law simply states that if you subtract the standard energies (enthalpies) of formation of the reactants from the standard energies of formation of the products that whatever is left is the energy change for that reaction.

If the value is negative, that means that energy is released to the surroundings and the reaction is *exothermic*.

If the value is positive, that means that the energy is absorbed from the environment and the reaction is *endothermic*.

The following table lists standard enthalpies of formations for some compounds. This table can be used to work the exercises that follow.

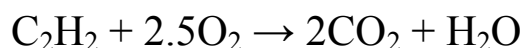
Substance	Formula	ΔH_{rxn} (kJ mol ⁻¹)
Water – liquid	H ₂ O(l)	-284.83
Water – gas	H ₂ O(g)	-241.816
Carbon Dioxide	CO ₂	-393.5
Carbon Monoxide	CO	-110.525
Ammonia	NH ₃	-80.8
Ammonium Chloride	NH ₄ Cl	-314.55
Oxygen	O ₂	0
Nitrogen	N ₂	0
Hydrogen Chloride	HCl	-167.2
Methane	CH ₄	-17.9
Ethane	C ₂ H ₆	-20.0
Acetylene	C ₂ H ₂	+54.2
Propane	C ₃ H ₈	-25.0

Table 7.4.1 Enthalpies of Formation for Selected Substances

Now that we are familiar with Hess' Law and have some standard enthalpies of formation, we can do some problems.

Exercise 7.4.1

Balance the combustion reaction for acetylene (C_2H_2) and calculate the change in enthalpy for the reaction.

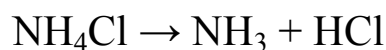


$$\begin{aligned}\Delta H_{\text{rxn}} &= \sum H_{\text{form-prod}}^{\circ} - \sum H_{\text{form-react}}^{\circ} \\ &= [2(-393.5) + (-241.816)] - [(54.2) + 2.5(0)] \\ &= -787 - 241.816 - 54.2 \\ &= -1083 \text{ kJ mol}^{-1}\end{aligned}$$

A negative value indicates an exothermic reaction. It's on fire!

Exercise 7.4.2

Calculate the change in enthalpy for the dissociation of ammonium chloride (NH_4Cl) to ammonia (NH_3) and hydrogen chloride (HCl).



$$\begin{aligned}\Delta H_{\text{rxn}} &= \sum H_{\text{form-prod}}^{\circ} - \sum H_{\text{form-react}}^{\circ} \\ &= [(-80.8) + (-167.2)] - [-314.55] \\ &= -248 + 314.55 \\ &= 66.6 \text{ kJ mol}^{-1}\end{aligned}$$

A positive value indicates an endothermic reaction. Energy is required for the reaction to occur.

In fact if you were holding a beaker or test tube where this reaction was occurring you would not only smell the ammonia but the reaction vessel would feel cool.

7.5 States of Matter

The three principle states of matter are **solid**, **liquid**, and **gas**. Below are listed the basic definitions that differentiate these three states of matter from one another.

Solids

Solids are materials that have a definite shape and volume. The arrangement of atoms or molecules in a solid are fixed. The movement of the atoms or molecules in a solid are very slow.

Liquids

Liquids are materials that have a definite volume but an indefinite shape. The arrangement of liquid atoms or molecules is random. The shape of a liquid is determined by the container holding the liquid. The movement of atoms and molecules in a liquid is faster than they are in a solid.

Gases

Gases are materials that have an indefinite shape and volume. Both the shape and the volume of a gas are determined by the shape and the volume of the container holding the gas. The arrangement of atoms or molecules in a gas is random. The movement of atoms or molecules in a gas is very rapid.



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Changes of States in Matter

Figure 7.5.1 indicates the six changes of state for matter

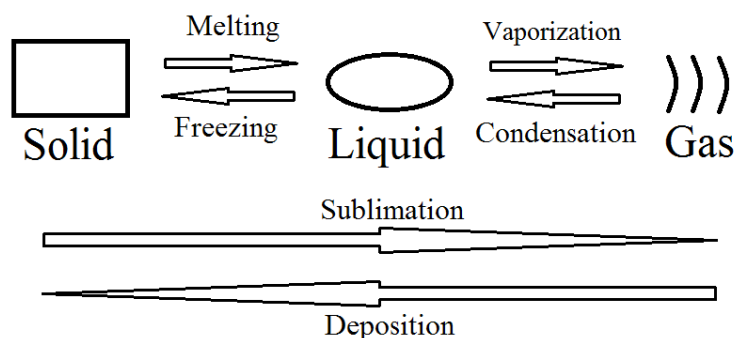


Figure 7.5.1 Changes of State For Matter

Melting

Melting is the change of state of a substance when that substance changes from a **solid to a liquid**. This conversion from solid to liquid is dependent on the amount of energy the substance must gain to allow freedom of movement of the molecules or atoms of that substance.

The **melting point** of a substance is that temperature at which the solid and liquid phases of the substance exist in equilibrium.

Freezing

Freezing is the change of state of a substance when that substance changes from a **liquid to a solid**. This conversion from liquid to solid is dependent on the amount of energy the substance must lose to prohibit freedom of movement of the molecules or atoms of that substance.

The **freezing point** of a substance is the same as the melting point of that substance in nearly all substances. Since some substances have the ability to supercool, the melting point is considered a more valid property of a substance than the freezing point.

Vaporization

Vaporization is the change of state of a substance when that substance changes from a **liquid to a gas**. Molecules at the surface of a liquid can have enough energy to escape the liquid and exist in a **vapor or gas phase** just above the surface of the liquid. Molecules in the vapor phase of a liquid can lose enough energy to return to liquid phase.

The pressure at which the number of molecules or atoms of a liquid are at equilibrium, as many entering the vapor phase as leaving it, is known as the *vapor pressure* of the liquid.

When enough energy is added to a liquid to increase the vapor pressure to ambient pressure the liquid is said to have reached its *boiling point*.

Condensation

Condensation is the change of state of a substance when that substance changes from a *gas to a liquid*. Condensation, obviously the reverse of evaporation, occurs in the vapor phase of a liquid when vapor molecules or atoms return to the liquid phase.

Sublimation

Sublimation is the change of state of a substance when that substance changes from a *solid to a gas*. A good example of sublimation is the reduction in size of an icicle hanging from the eave of your house. The icicle reduces in size without being broken or melting. Where did the missing ice go? It was converted, using the energy of the sun, directly from a solid to a gas.



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Deposition

Deposition is the change of state of a substance when that substance changes from a *gas to a solid*. Everyone, in cold climates, has had to clean ice and/or snow from the windscreen of their car at sometime or other. The hardest of these to remove from your windscreen is the very thin layer of ice that appeared when there was no snow, no freezing rain or mist, and no freezing fog. Where did that ice come from? It was *deposited* as a solid on your windscreen from the gaseous molecules of water in the air.

7.6 Phase Diagrams

After the description of the states of matter and the changes of states of matter, it is appropriate to view all of this information in a single form.

The *phase diagram* of a substance shows graphically, as a function of temperature and pressure, all of the states and changes of states for that substance.

Figure 7.6.1 is the phase diagram for water.

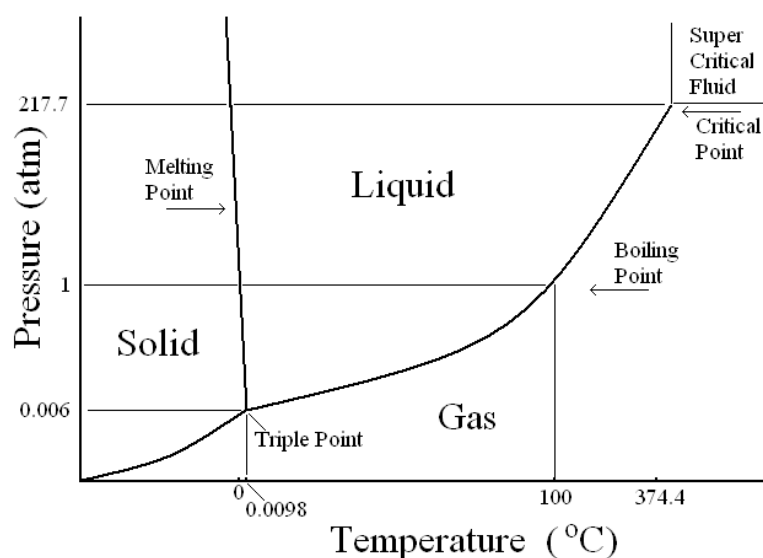


Figure 7.6.1 The Phase Diagram for Water

The phase diagram has three areas delineating the three states of matter.

Solid is above the curved line and to the left of the melting point line.

Liquid is above the curved line and to the right of the melting point line.

Gas is below the curved line.

Other features of the phase diagram are listed below.

Melting Point is all along its vertical line as a function of pressure.

Boiling Point is all along its curved line as a function of pressure.

Triple Point, the point at which all three phases of matter are at equilibrium, is at 0.0098°C and 0.006 atmospheres.

Critical Point, the point at which a gas and liquid are indistinguishable due to high temperature and pressure, is at 374.4°C and 217.7 atmospheres.

When a substance is above both the critical temperature and critical pressure it is considered a **supercritical fluid**.

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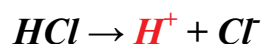
8 The Chemistry of Water: Acids and Bases

8.1 Acid – Base Theories

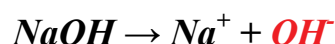
The Nature of Acids and Bases

In water chemistry the use of the terms *acids* and *bases* are used to distinguish the presence of H^+ and OH^- ions in solution, respectively.

A common acid is hydrochloric, or stomach, acid (HCl) which dissociates in water as follows:



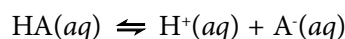
A common base is lye (NaOH), which dissociates in water as follows:



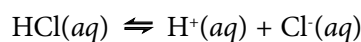
The Arrhenius Acid-Base Theory

The Arrhenius acid-base theory states that an *acid* is any substance that dissolves in water and *yields the H^+ ion*.

The generalized equation for an Arrhenius acid follows:

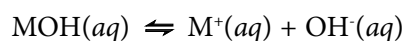


A specific example would be hydrochloric acid (HCl).



The Arrhenius acid-base theory states that a *base* is any substance that dissolves in water to *yield the OH^- ion*.

The generalized equation for an Arrhenius base follows:



A specific example would be sodium hydroxide (NaOH).



The Brønsted-Lowry Acid-Base Theory

The Brønsted-Lowry acid-base theory defines an **acid** as any compound that can **donate H^+** . It also defines a **base** as any compound that can **accept H^+** .

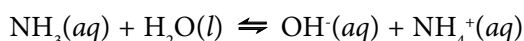
The generalized acid-base equilibrium equation for two acid-base **pairs** is as follows:



Where HA and A^- is one **conjugate acid-base pair**,

and B and BH^+ is the **other conjugate acid-base pair**.

Perhaps an example would be in order. When the base ammonia (NH_3) reacts with water, the water is acting as an acid.

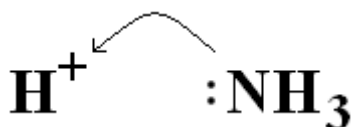


The NH_3 and NH_4^+ are a Brønsted-Lowry conjugate acid-base pair **because** the NH_3 is able to accept an H^+ and the NH_4^+ is able to donate an H^+ .

Inspection of the H_2O and OH^- reveals the opposite, establishing the **other** conjugate acid-base pair.

The Lewis Acid-Base Theory

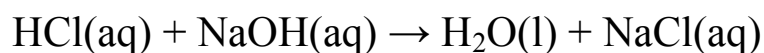
In the previous example of a Brønsted-Lowry acid-base pair, the ammonia (NH_3) was said to be accepting an H^+ ion. It could also be said the NH_3 was donating its lone pair of electrons to form a covalent bond with the H^+ ion.



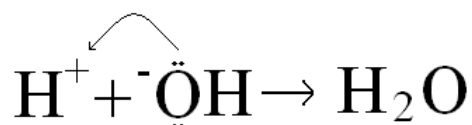
A **Lewis acid** is a substance that **accepts an electron pair**.

A **Lewis base** is a substance that **donates an electron pair**.

A reaction example would be the Lewis Acid-Base Theory interpretation of the following acid base reaction.

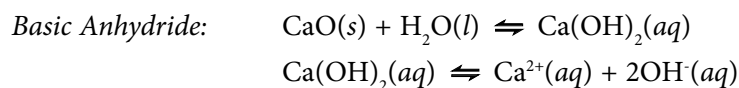
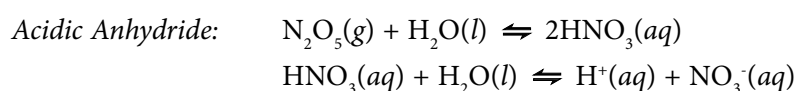


Without regard to the yielding or donating of H^+ or OH^- , the Lewis Acid-base Theory would interpret the previous reaction as the oxygen of the OH^- ion donating a pair of electrons to the H^+ ion to form water.



Acid and Base Anhydrides

Anhydrides are compounds that react with water to “form” H^+ ions or OH^- ions rather than “releasing” them.



It should be noted that the Arrhenius acid-base theory *fails to explain* acid and base anhydrides.

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...I finally learned to speak it in just six lessons”
Jane, Chinese architect

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8.2 Naming Acids and Bases

Acids Without Oxygen in the Anion

If an acid is simply a combination of H^+ and a non-metallic anion that does not contain oxygen use the prefix *hydro-* and replace the *-ide* portion of the anionic species with *-ic acid*.

Acids With Oxygen in the Anions

Naming an acid with polyatomic anions that do contain oxygen requires knowing the name of the polyatomic ion.

If the name of the polyatomic anion ends with *-ate* replace the *-ate* with *-ic acid*.

If the name of the polyatomic anion ends with *-ite* replace the *-ite* with *-ous acid*.

Ion Formula	Ion name	Ion Formula	Ion Name
SO_4^{2-}	sulfate	CO_3^{2-}	carbonic
SO_3^{2-}	sulfite	PO_4^{3-}	phosphate
NO_3^-	nitrate	$C_2H_3O_2^-$	acetate
NO_2^-	nitrite	CN^-	cyanide

Table 8.2.1 Names of Polyatomic Anions

Basic Compounds

Basic compounds are named as metal hydroxides. For example $Ca(OH)_2$ would simply be named *calcium hydroxide*.

Exercise 8.2.1

Name and give the proper formula for the neutral acid containing the phosphate ion.

Phosphoric acid H_3PO_4

The neutral acid requires three H^+ ions to equal the 3- charge of the phosphate ion.

Exercise 8.2.2

Name and give the proper formula for the neutral acid containing the sulfite ion.

Sulfurous acid H_2SO_3

The acid requires two H^+ ions to equal the 2- charge of the sulfite ion.

Exercise 8.2.3

Name and give the proper formula for the neutral acid containing the sulfate ion.

Sulfuric acid H_2SO_4

The acid requires two H^+ ions to equal the 2- charge of the sulfate ion.

Exercise 8.2.4

Name and give the proper formula for the neutral acid containing the chloride ion.

Hydrochloric acid HCl

The acid requires one H^+ ion to equal the 1- charge of the sulfite ion.chloride ion.

Exercise 8.2.5

Name and give the proper formula for the neutral acid containing the acetate ion.

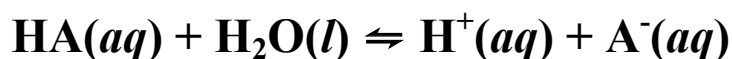
Acetic acid $\text{HC}_2\text{H}_3\text{O}_2$

The acid requires one H^+ ions to equal the 1- charge of the acetate ion

8.3 Strengths of Acids and Bases

Strengths of Acids

The strength of an acid is essentially a measurement of the acids ability to dissociate in an aqueous solution.

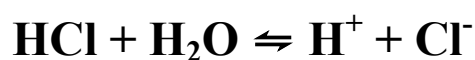


A **strong acid** will dissociate almost completely in water or almost **fully to the right**.

A **weak acid** will dissociate only **partially to the right** leaving most of the acid molecules in tact.

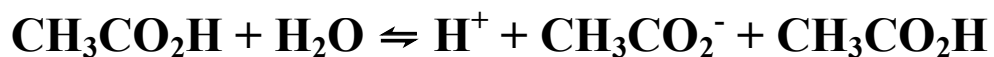
Examples

The **strong** acid hydrochloric acid will dissociate as follows:



Here, essentially, **none** of the original HCl remains.

The *weak* acid acetic acid will dissociate as follows:



Here, *most* of the $\text{CH}_3\text{CO}_2\text{H}$ remains.

Strengths of Bases

Unsurprisingly, the strength of a base is the measurement of how well the base dissociates in water.



A *strong base* will dissociate completely in water or *fully to the right*.

A *weak base* will dissociate only *partially to the right* leaving most of the base molecules intact.

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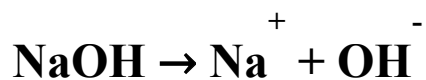
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Examples

The **strong base** sodium hydroxide will dissociate as follows.



Here, essentially **none** of the NaOH remains.

The **weak base** ammonia will dissociate as follows.



Here, **most** of the NH_3 remains.

Figure 8.3.1 shows the relative strengths of some acids and bases. Remember, the strengths of acids and bases are a consequence of their individual abilities to dissociate.

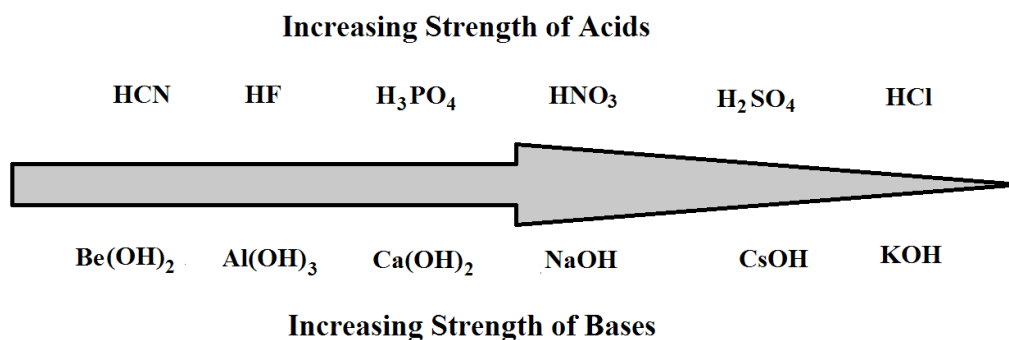
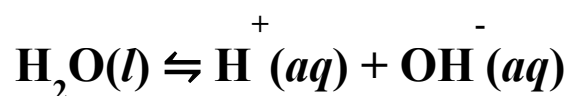


Figure 8.3.1 Relative Strengths of Acids and Bases

8.4 Calculation of pH

So far we have discussed the equilibria of strong and weak acids and bases in water, or their **aqueous equilibria**. But what about water itself? Is it an acid or a base?

Water is **both an acid and a base**. That is to say that there is a very small amount of dissociation of water to H^+ and OH^- .



The dissociation constant for water (K_w) expresses this small degree of the dissociation of water.

$$K_w = [H^+][OH^-] = (1 \times 10^{-7})(1 \times 10^{-7}) = 1 \times 10^{-14}$$

The 1×10^{-14} dissociation constant of water shows that water dissociates very little. Scientists often use logarithms to reference very large or very small numbers.

In the case of the very small amounts of H^+ and OH^- ions in pure water, logarithms are used to express their concentrations.

The H^+ and OH^- concentrations are viewed as the antilog of their concentration exponents. These values are expressed as *pH* and *pOH*.

In both cases the *p* stands for the potential (from the original concept in German as “Potenz”) of the H^+ and OH^- concentrations respectively.

Acid-Base Concentration Formulae

The values of *pH* and *pOH* are simply logarithmic scales reflecting the concentration of H^+ ions and OH^- ions, respectively, in moles per liter.

$$pH = -\log \text{mol } H^+ / L \text{ and } pOH = -\log \text{mol } OH^- / L$$

Applying this math to the dissociation constant (K_w) yields the following:

$K_w = [H^+][OH^-] = 10^{-14}$ so that $[H^+] = 10^{-14}/[OH^-]$
and $[OH^-] = 10^{-14}/[H^+]$ or logarithmically as...

$$pH = 14 - pOH \text{ and } pOH = 14 - pH$$

Strong Acid and Base pH Calculations

Strong acids and bases dissociate at what is essentially 100%. For this reason there is no consideration given to chemical equilibria in these calculations.

Example Calculate the pH of a 0.02 molar solution of hydrochloric acid (HCl).

Since HCl is a *monoprotic* acid, the solution is also 0.02 molar in H⁺.

$$\text{pH} = -\log \text{ mol H}^+/\text{L} = -\log (0.02) = -(-1.7) = 1.7$$

Note: A hydrogen atom without an electron is nothing but a proton.

Example What is the pH of a solution that is 0.02 molar in sodium hydroxide (NaOH)?

Without knowing the [H⁺], simply calculate the pOH and then convert the value to pH.

There is 1 mole of OH⁻ for every 1 mole of NaOH.

Therefore, the following calculation applies:

$$\text{pOH} = -\log \text{ mol OH}^-/\text{L} = -\log(0.02) = 1.7$$

Since $\text{pH} = 14 - \text{pOH}$ the following conversion applies:

$$\text{pH} = 14 - 1.7 = 12.3$$

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Since we have already studied stoichiometric calculations we should be able to calculate the pH of a single solution containing specific masses of acid or base.

Exercise 8.4.1

What is the pH of a 1.5 liter solution containing 0.03g sulfuric acid (H_2SO_4)?

Let's return to the problem solving *mantra* introduced in the first chapter.

$$\frac{0.03\text{g H}_2\text{SO}_4}{1.5\text{L}} \left| \frac{\quad}{\quad} \right| = \frac{\text{mol H}^+}{\text{L}}$$

Here we have used all of the information given in the statement of the problem *and* established the final units for the calculation.

By using the molar masses of the atoms in the sulfuric acid (H_2SO_4) we can calculate the mass of one mole of sulfuric acid.

$$\text{H: } 2 \times 1 = 2 \text{ g/mol S: } 1 \times 32 = 32 \text{ g/mol O: } 4 \times 16 = 64 \text{ g/mol}$$

The molar mass of sulfuric acid is 98 g/mol.

$$\frac{0.03\text{g H}_2\text{SO}_4}{1.5\text{L}} \left| \frac{1 \text{ mole H}_2\text{SO}_4}{98\text{g H}_2\text{SO}_4} \right| = \frac{\text{mol H}^+}{\text{L}}$$

By looking at the formula H_2SO_4 it should become obvious that there are 2 moles of H^+ in every 1 mole of H_2SO_4 .

$$\frac{0.03\text{g H}_2\text{SO}_4}{1.5\text{L}} \left| \frac{1 \text{ mole H}_2\text{SO}_4}{98\text{g H}_2\text{SO}_4} \right| \left| \frac{2 \text{ moles H}^+}{1 \text{ mole H}_2\text{SO}_4} \right| = 4.1 \times 10^{-4} \frac{\text{mol H}^+}{\text{L}}$$

$$\text{The pH} = -\log 4.1 \times 10^{-4} \text{ mol H}^+/\text{L} = 3.4$$

Exercise 8.4.2

What is the pH of a 0.75L solution containing 0.025g $\text{Ca}(\text{OH})_2$?

We know that we have to first calculate the moles OH^-/L and pOH in order to convert to pH.

$$\frac{0.025 \text{ g Ca}(\text{OH})_2}{0.75 \text{ L}} \Bigg| \frac{\text{mol OH}^-}{\text{L}} =$$

Ca: $1 \times 40 = 40 \text{ g/mol}$ O: $2 \times 16 = 32 \text{ g/mol}$ H: $2 \times 1 = 2$

The molar mass of $\text{Ca}(\text{OH})_2$ is 74 g/mol.

$$\frac{0.025 \text{ g Ca}(\text{OH})_2}{0.75 \text{ L}} \Bigg| \frac{1 \text{ mole Ca}(\text{OH})_2}{74 \text{ g Ca}(\text{OH})_2} = \frac{\text{mol OH}^-}{\text{L}}$$

There are 2 moles of OH^- in every mole of $\text{Ca}(\text{OH})_2$.

$$\frac{0.025 \text{ g Ca}(\text{OH})_2}{0.75 \text{ L}} \Bigg| \frac{1 \text{ mole Ca}(\text{OH})_2}{74 \text{ g Ca}(\text{OH})_2} \Bigg| \frac{2 \text{ moles OH}^-}{1 \text{ mole Ca}(\text{OH})_2} = 9.0 \times 10^{-4} \frac{\text{mol OH}^-}{\text{L}}$$

The pOH = $-\log 9.0 \times 10^{-4} \text{ mol OH}^-/\text{L} = 3.1$

The pH = $14 - 3.1 = 11$

Exercise 8.4.3

What is the pH of a 1.75 liter solution containing 0.035g phosphoric acid (H_3PO_4)?

$$\frac{0.035 \text{ g H}_3\text{PO}_4}{1.75 \text{ L}} = \frac{\text{moles H}^+}{\text{L}}$$

$$\frac{0.035 \text{ g H}_3\text{PO}_4}{1.75 \text{ L}} \Bigg| \frac{1 \text{ mole H}_3\text{PO}_4}{98 \text{ g H}_3\text{PO}_4} = \frac{\text{moles H}^+}{\text{L}}$$

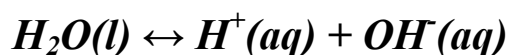
$$\frac{0.035 \text{ g H}_3\text{PO}_4}{1.75 \text{ L}} \Bigg| \frac{1 \text{ mole H}_3\text{PO}_4}{98 \text{ g H}_3\text{PO}_4} \Bigg| \frac{3 \text{ moles H}^+}{1 \text{ mole H}_3\text{PO}_4} = 6.1 \times 10^{-4} \frac{\text{moles H}^+}{\text{L}}$$

The pH = $-\log 6.1 \times 10^{-4} \text{ mol H}^+/\text{L} = 3.2$

8.5 Neutralization Reactions

It is important to remember that when we are talking about the pH of a solution we are by necessity talking about an *aqueous* solution.

We have learned that water, or the water in an aqueous solution, will slightly dissociate to H^+ and OH^- according to the following reaction.



It is important to note that the above chemical equation describes an equilibrium reaction. In other words, the reaction arrows point both right and left.

If an acidic solution containing a certain concentration of H^+ is added to a basic solution containing a certain concentration of OH^- , the H^+ and OH^- ions will react to form H_2O which is the right to left reaction in the above chemical equation. These ions will have been said to have *neutralized* each other.

If the H^+ and OH^- concentrations of the two solutions being combined are identical, the solution will be absent of acid and base concentration (excepting the 10^{-14} molar concentrations of pure water) and will have a $pH = 7.00$.



If the H^+ and OH^- concentrations of the two solutions being combined are not identical the pH can be calculated by the remaining H^+ or OH^- concentration after neutralization has occurred.

Example What is the pH of a 0.5L solution that is 0.005 molar in H^+ when it is added to a 0.5L solution that is 0.004 molar in OH^- ?

The total volume of the solution is 1.0L. In the one liter of solution the 0.004 moles of OH^- will neutralize 0.004 moles of H^+ leaving 0.001 moles H^+ in one liter of solution.

$$\text{So the pH} = -\log 0.001 \text{ mol H}^+/\text{L} = 3$$

Example The following shows the calculation of the pH of a 1 liter solution containing 0.001 g HCl and 0.001 g NaOH.

M OH^-

$$\frac{0.001\text{g NaOH}}{1 \text{ liter}} \left| \frac{1 \text{ mole NaOH}}{40 \text{ g NaOH}} \right| \frac{1 \text{ mole OH}^-}{1 \text{ mole NaOH}} = 2.5 \times 10^{-5} \text{ M OH}^-$$

M H^+

$$\frac{0.001\text{g HCl}}{1 \text{ liter}} \left| \frac{1 \text{ mole HCl}}{36.5 \text{ g HCl}} \right| \frac{1 \text{ mole H}^+}{1 \text{ mole HCl}} = 2.7 \times 10^{-5} \text{ M H}^+$$

With a 0.2×10^{-5} excess of H^+ the $\text{pH} = -\log 0.2 \times 10^{-5} = 5.7$

This then is an example of a **neutralization** of an acid and base in solution.

Exercise 8.5.1

What is the pH of a 1 liter solution of 0.04 molar hydrochloric acid (HCl) to which 0.02 g sodium hydroxide (NaOH) has been added? If you know you have 1 liter of HCl that is 0.04 moles per liter then you have 0.04 mole HCl as well as 0.04 moles H^+ per liter.

Calculate the moles OH^- per liter.

$$\frac{0.02 \text{ g NaOH}}{1 \text{ L}} = \frac{\text{moles OH}^-}{\text{L}}$$

$$\frac{0.02 \text{ g NaOH}}{1 \text{ L}} \left| \frac{1 \text{ mole NaOH}}{40 \text{ g NaOH}} \right. = \frac{\text{moles OH}^-}{\text{L}}$$

$$\frac{0.02 \text{ g NaOH}}{1 \text{ L}} \left| \frac{1 \text{ mole NaOH}}{40 \text{ g NaOH}} \right| \frac{1 \text{ mole OH}^-}{1 \text{ mole NaOH}} = 5.0 \times 10^{-4} \frac{\text{moles OH}^-}{\text{L}}$$

The number of H^+ moles left per liter after neutralization is $0.04 - 5.0 \times 10^{-4} = 3.95 \times 10^{-2}$ moles per liter.

The $\text{pH} = -\log 3.95 \times 10^{-2} \text{ M H}^+ = 1.4$

Exercise 8.5.2

Calculate the pH of a 2 liter aqueous solution to which were added 0.025g lithium hydroxide (LiOH) and 0.018g nitric acid (HNO_3).

M OH^-

$$\frac{0.025 \text{ g LiOH}}{2 \text{ L}} = \frac{\text{moles OH}^-}{\text{L}}$$

$$\frac{0.025 \text{ g LiOH}}{2 \text{ L}} \left| \frac{1 \text{ mole LiOH}}{23.94 \text{ g LiOH}} \right. = \frac{\text{moles OH}^-}{\text{L}}$$

$$\frac{0.025 \text{ g LiOH}}{2 \text{ L}} \left| \frac{1 \text{ mole LiOH}}{23.94 \text{ g LiOH}} \right| \frac{1 \text{ mole OH}^-}{1 \text{ mole LiOH}} = 5.2 \times 10^{-4} \frac{\text{moles OH}^-}{\text{L}}$$

M H⁺

$$\frac{0.018\text{g HNO}_3}{2\text{L}} = \frac{\text{moles H}^+}{\text{L}}$$

$$\frac{0.018\text{g HNO}_3}{2\text{L}} \left| \frac{1 \text{ mole HNO}_3}{63\text{g HNO}_3} \right| = \frac{\text{moles H}^+}{\text{L}}$$

$$\frac{0.018\text{g HNO}_3}{2\text{L}} \left| \frac{1 \text{ mole HNO}_3}{63\text{g HNO}_3} \right| \left| \frac{1 \text{ mole H}^+}{1 \text{ mole HNO}_3} \right| = 1.4 \times 10^{-4} \frac{\text{moles H}^+}{\text{L}}$$

The amount of OH⁻ not neutralized is $5.2 \times 10^{-4} - 1.4 \times 10^{-4} = 3.8 \times 10^{-4}$ M OH⁻.

The pOH = $-\log 3.8 \times 10^{-4}$ M OH⁻ = 3.4

The pH = $14 - 3.4 = 10.6$

Exercise 8.5.3

Calculate the pH of a 1.5 liter aqueous solution to which were added 0.035g calcium hydroxide (Ca(OH)₂) and 0.047g sulfuric acid (H₂SO₄).

M OH⁻

$$\frac{0.035\text{g Ca(OH)}_2}{1.5\text{L}} = \frac{\text{moles OH}^-}{\text{L}}$$

$$\frac{0.035\text{g Ca(OH)}_2}{1.5\text{L}} \left| \frac{1 \text{ mole Ca(OH)}_2}{74\text{g Ca(OH)}_2} \right| = \frac{\text{moles OH}^-}{\text{L}}$$

$$\frac{0.035\text{g Ca(OH)}_2}{1.5\text{L}} \left| \frac{1 \text{ mole Ca(OH)}_2}{74\text{g Ca(OH)}_2} \right| \left| \frac{2 \text{ moles OH}^-}{1 \text{ mole Ca(OH)}_2} \right| = 6.3 \times 10^{-4} \frac{\text{moles OH}^-}{\text{L}}$$

M H⁺

$$\frac{0.047\text{g H}_2\text{SO}_4}{1.5\text{L}} = \frac{\text{moles H}^+}{\text{L}}$$

$$\frac{0.047\text{g H}_2\text{SO}_4}{1.5\text{L}} \left| \frac{1 \text{ mole H}_2\text{SO}_4}{98\text{g H}_2\text{SO}_4} \right. = \frac{\text{moles H}^+}{\text{L}}$$

$$\frac{0.047\text{g H}_2\text{SO}_4}{1.5\text{L}} \left| \frac{1 \text{ mole H}_2\text{SO}_4}{98\text{g H}_2\text{SO}_4} \right| \frac{2 \text{ moles H}^+}{1 \text{ mole H}_2\text{SO}_4} = 6.4 \times 10^{-4} \frac{\text{moles H}^+}{\text{L}}$$

The amount of H⁺ not neutralized is $6.4 \times 10^{-4} - 6.3 \times 10^{-4} = 0.1 \times 10^{-4}$ M H⁺.

The pH is $-\log 0.1 \times 10^{-4}$ M OH = 5.0

8.6 Buffer Solutions

A *buffer* solution is a solution that resists changes in pH.

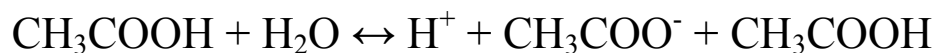
This resistance is accomplished by a phenomenon known as the *common-ion effect* where more of an ion involved in the aqueous equilibrium of a solution is added from another source.

The common-ion effect is a prime example of *Le Châtelier's Principle*.

Le Châtelier's Principle: If the equilibrium of a reaction is stressed a reaction will occur that relieves that stress.

In pH buffer solutions the common-ion effect is between a weak acid and its conjugate base or a weak base and its conjugate acid.

Let's look at the example of the weak acid acetic acid (CH₃COOH).



If a strong acid is added to a solution of acetic acid the pH would rapidly decrease.

If sodium acetate (CH₃COONa) were added to the solution the concentration of the conjugate base acetate ion (CH₃COO⁻) would increase and neutralize the acid added to the solution.

The solution would be said to be *buffered* against a decrease in pH.

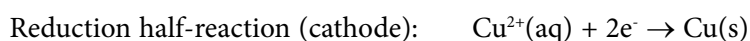
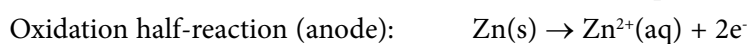
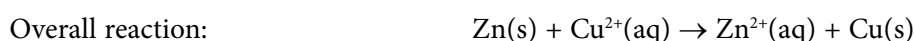
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9 Electrochemistry

9.1 The Galvanic Cell

If you immerse two dissimilar metals into an electrolytic or ionic solution, a reduction oxidation reaction will occur that will result in a transfer of electrons between the two metals. This results in a potential difference or voltage between the two metals. You will then have created a **galvanic cell** more commonly known as a battery.

The Daniell cell is a type of galvanic cell that utilizes the oxidation of zinc metal (Zn) to zinc ions (Zn^{2+}) and the reduction of copper ions (Cu^{2+}) to copper metal (Cu).



Remember that **oxidation** is a **loss of electrons** and **reduction** is a **gain of electrons**.

As seen in the above half-reactions, **oxidation** occurs at the **anode** and **reduction** occurs at the **cathode**.



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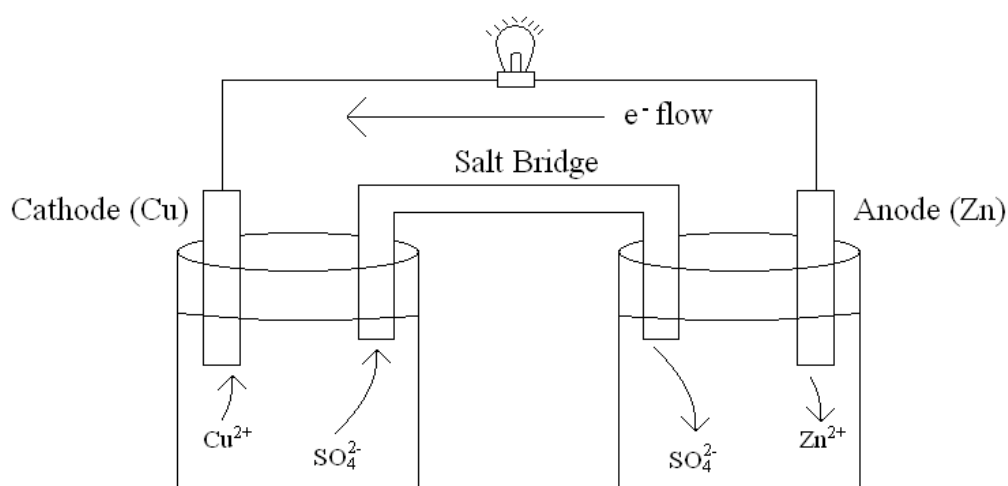
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A Daniell cell can easily be constructed. Into two beakers containing a solution of sodium sulfate (Na_2SO_4), insert copper and zinc strips. Prepare a salt bridge between the two beakers. Wire the two metal strips in series with a test lamp. The lamp will glow with the current flow from the potential difference between the two metals.

Figure 9.1.1 Shows a typical Daniell cell.



The Daniell Cell

Figure 9.1.1 A Typical Daniell Cell

I'm sure everyone has seen the popular novelty toy where a fruit or vegetable is used as an electrolytic source to light a small light bulb.

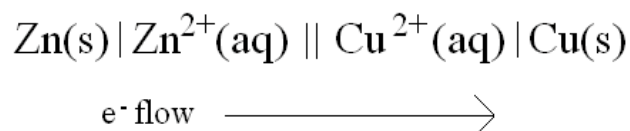
Two wires of dissimilar metals, such as copper and zinc, are wired in series with the light bulb. The ends of the wires are inserted into the fruit or vegetable and a current sufficient to light the bulb is generated.

In the fruit or vegetable both the electrons and ionic species are free to flow in what is essentially a completed circuit.

The purpose of the salt bridge in the Daniell cell is to bridge the two separate containers to complete the electrical circuit.

Shorthand Notation for Daniell Cells

The following shorthand notation has been adopted for Daniell cells, once again using the copper-zinc cell for demonstration.



The single vertical lines represent phase boundaries and the double vertical lines represent the salt bridge.

What's Going On in a Typical Battery?

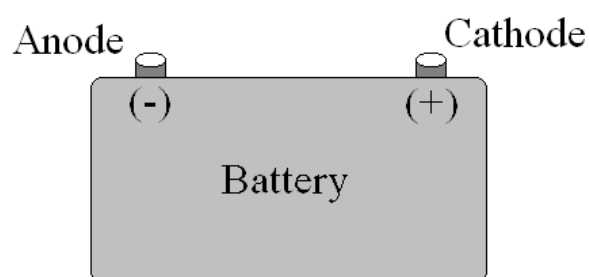


Figure 9.1.1 A Typical Daniell Cell

Let's break down the reduction oxidation chemistry between the electrodes.

The Anode

Oxidation occurs at the anode. Since oxidation is a loss of electrons it is at the anode that electrons are generated. Therefore, the anode has a negative sign.

The Cathode

Reduction occurs at the cathode. Since reduction is a gain of electrons it is to the cathode that electrons flow. Therefore, the cathode is positive.

9.2 Standard Reduction Potentials

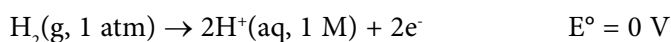
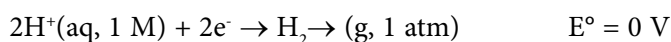
It must first be noted that neither a reduction potential or an oxidation potential can be measured on a single electrode. Potentials can only be measured *between two electrodes*.

Early chemists decided that these potentials would be measured against an arbitrary standard electrode and recorded as *reduction potentials*.

The Standard Hydrogen Electrode (S.H.E.)

The *standard hydrogen electrode* is defined as platinum (Pt) in contact with hydrogen (H_2) gas, at 1 atmosphere, being bubbled through an aqueous solution that is 1 molar in hydrogen ions (H^+) at 25°C .

In either direction the reaction is viewed the electric potential of the cell was arbitrarily standardized as exactly zero volts.



With this standardization accomplished the standard reduction potentials of half cell reactions could then be compared to one another.

Table 9.2.1 is a listing of the standard reduction potentials of some half cell reactions held relative to the standard hydrogen electrode.

Reduction Half Reactions	E° (V)
$\text{F}_2(\text{g}) + 2\text{e}^- \rightarrow 2\text{F}^-(\text{aq})$	2.87
$\text{MnO}_4^- + 8\text{H}^+(\text{aq}) + 5\text{e}^- \rightarrow \text{Mn}^{2+}(\text{aq}) + 4\text{H}_2\text{O}(\text{l})$	1.51
$\text{Cl}_2(\text{g}) + 2\text{e}^- \rightarrow 2\text{Cl}^-(\text{aq})$	1.36
$\text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}(\text{l})$	1.23
$\text{Ag}^+(\text{aq}) + \text{e}^- \rightarrow \text{Ag}(\text{s})$	0.80
$\text{O}_2(\text{g}) + 2\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{H}_2\text{O}_2(\text{aq})$	0.70
$\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cu}(\text{s})$	0.34
$\text{Sn}^{4+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Sn}^{2+}(\text{aq})$	0.15
$2\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{H}_2(\text{g})$	0
$\text{Pb}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Pb}(\text{s})$	- 0.13
$\text{Cd}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cd}(\text{s})$	- 0.40
$\text{Fe}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Fe}(\text{s})$	- 0.45
$\text{Zn}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Zn}(\text{s})$	- 0.76
$\text{Al}^{3+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Al}(\text{s})$	- 1.66
$\text{Mg}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Mg}(\text{s})$	- 2.37
$\text{Na}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{Na}(\text{s})$	- 2.71
$\text{Li}^+(\text{aq}) + \text{e}^- \rightarrow \text{Li}(\text{s})$	- 3.04

Table 9.2.1 Standard Reduction Potentials (25°C)

Electric Cell Potentials

Now that we have established standardized half-cell potentials it should be relatively easy to calculate the potential of a complete cell. The following equation establishes the potential for a Daniell cell.

$$E^{\circ}_{cell} = E^{\circ}_{oxidation} + E^{\circ}_{reduction}$$

Doing cell potential calculations comes with one very important caveat. The half-cell potential of the species being oxidized in the cell's oxidation-reduction reaction is viewed as the *negative value* of that half-cell's listed standard reduction potential.

Example

Calculate the cell potential for the copper-zinc (Cu-Zn) cell that we have looked at in the beginning of this section.

The copper (Cu) is being reduced with a standard reduction potential of 0.34 V. (It is above the Zn in table 9.2.1.)

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The zinc (Zn) is being oxidized with a standard reduction potential of -0.76 V. It is below the Cu in Table 9.1.2.)

$$E_{\text{cell}}^{\circ} = E_{\text{oxidation}}^{\circ} + E_{\text{reduction}}^{\circ}$$
$$E_{\text{cell}}^{\circ} = -(-0.76 \text{ V}) + 0.34 \text{ V} = 1.10 \text{ V}$$

Exercise 9.2.1

Calculate the cell potential of a copper-cadmium (Cu-Cd) cell.

The copper (Cu) is being reduced with a standard reducing potential of 0.34 V.

The cadmium (Cd) is being oxidized with a standard reduction potential of -0.40 V.

$$E_{\text{cell}}^{\circ} = -(-0.40) + 0.34 \text{ V} = 0.74 \text{ V}$$

Exercise 9.2.2

Calculate the cell potential of a chlorine-iron (Cl-Fe) cell.

The chlorine (Cl) is being reduced with a standard reducing potential of 1.36 V.

The iron (Fe) is being oxidized with a standard reduction potential of -0.45 V.

$$E_{\text{cell}}^{\circ} = -(-0.45) + 1.36 \text{ V} = 1.81 \text{ V}$$

Exercise 9.2.3

Calculate the cell potential of a silver-aluminum (Ag-Al) cell.

The silver (Ag) is being reduced with a standard reduction potential of 0.80 V.

The aluminum (Al) is being oxidized with a standard reduction potential of -1.66 V.

$$E_{\text{cell}}^{\circ} = -(-1.66) + 0.80 \text{ V} = 2.46 \text{ V}$$

Exercise 9.2.4

Calculate the cell potential of a hydrogen ion-lithium (H⁺-Li) cell.

The hydrogen ion (H⁺) is being reduced with a standard reducing potential of 0 V.

The lithium (Li) is being oxidized with a standard reduction potential of -3.04 V.

$$E_{\text{cell}}^{\circ} = -(-3.04) + 0 \text{ V} = 3.04 \text{ V}$$

9.3 Electrolysis

Up to this point, in this chapter, we have discussed only the galvanic cell. In a galvanic cell spontaneous chemical reactions occur which, through oxidation-reduction, result in a potential.

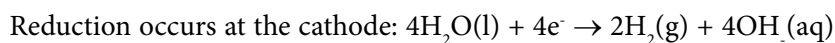
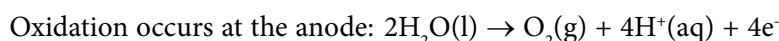
But what if you wanted to accomplish a nonspontaneous reaction for a specific purpose? You could power a cell with an external source of electricity to force the nonspontaneous reaction to occur. This would then be an *electrolytic cell* accomplishing *electrolysis*.

This happens every time you start your car. With the car not running the battery provides electrical power to the starter to start the engine. This is done through the use of a galvanic cell. Once the engine is running the alternator uses the battery as an electrolytic cell to run the galvanic reaction backwards and charge the battery.

Electrolysis of Water

Electrolysis of water is used to produce hydrogen gas (H_2) and oxygen gas (O_2).

The following chemical equations describe the electrolysis of water:



Electroplating

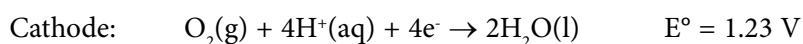
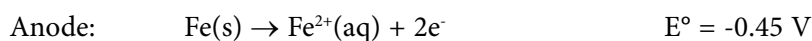
Electroplating is an electrolysis based technique that deposits one metal on the surface of another. Silver can be electroplated onto steel to form a silver-plated steel object.

9.4 Corrosion

Corrosion, by definition, is the oxidative decomposition of a metal. But as we all should know, oxidation cannot exist without reduction. Let's look at the most well known occurrence of corrosion the rusting of iron. The corrosion of iron will only occur in the presence of oxygen (O_2) and water (H_2O).

When water is in contact with iron (Fe), in the presence of oxygen (O_2), a galvanic cell is formed where oxidation occurs at an anodic portion of the surface that is shielded from oxygen (O_2) and oxygen (O_2) is reduced at a nearby cathodic region of the surface.

The following oxidation-reduction equations apply:



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Protection from Corrosion

To protect iron surfaces from corrosion it is common to connect a *sacrificial anode* to the iron (Fe).

The choice of the material to protect iron (Fe) simply needs to be a metal that is more readily oxidized than iron (Fe).

Ships at sea will attach large blocks of zinc (Zn) to the iron (Fe) of the ship to act as sacrificial anodes to protect the iron (Fe).

Steel is often dipped in molten zinc (Zn) to prevent corrosion in a process known as *galvanization*.

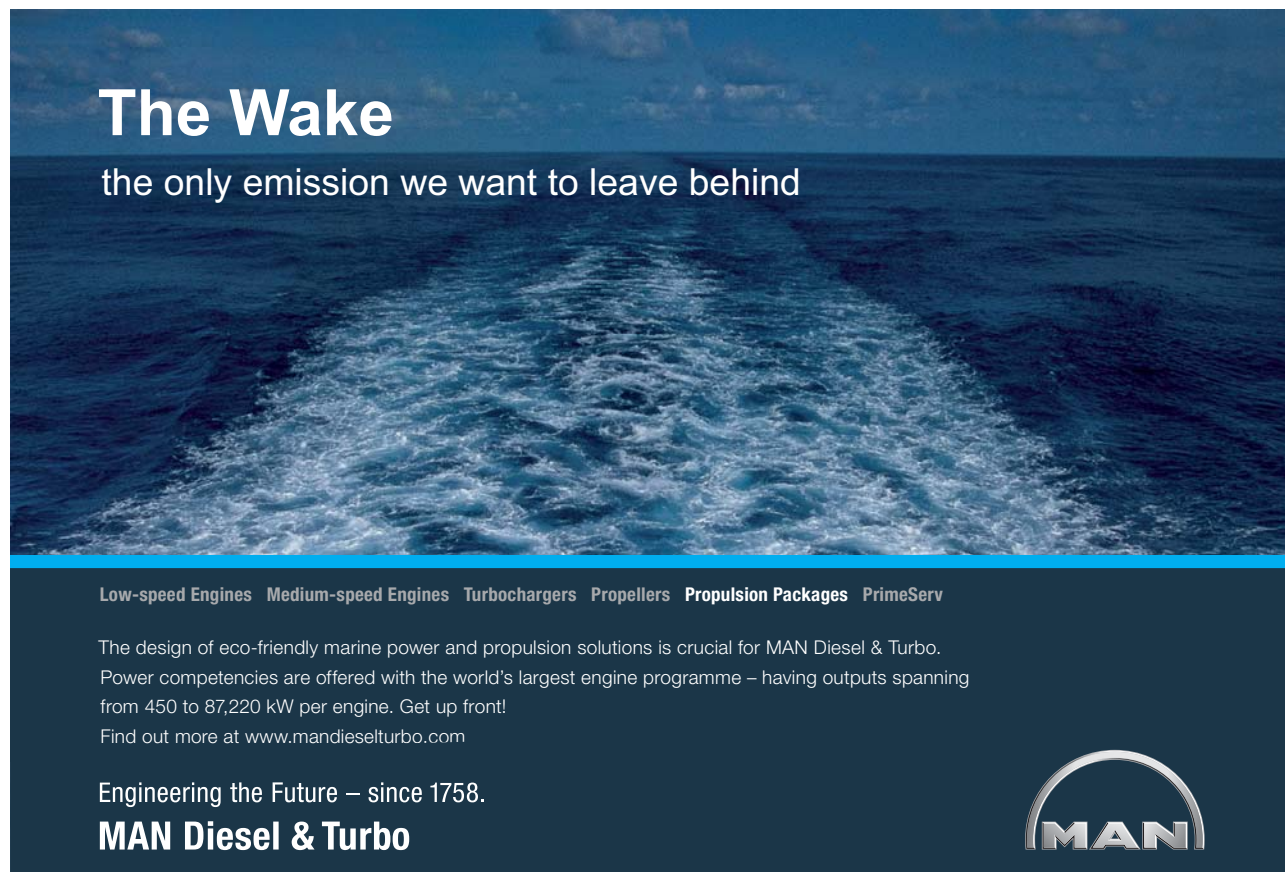
9.5 Batteries

This section will present the oxidation-reduction chemistry of batteries that are common in everyday use.

Dry Cell Batteries

A conventional dry cell battery consists of a zinc (Zn) can acting as an anode and a graphite rod acting as a cathode. The graphite rod is coated with a manganese oxide (MnO_2) and carbon black paste.

The electrolyte is a damp paste consisting of ammonium chloride (NH_4Cl) and zinc chloride (ZnCl_2).




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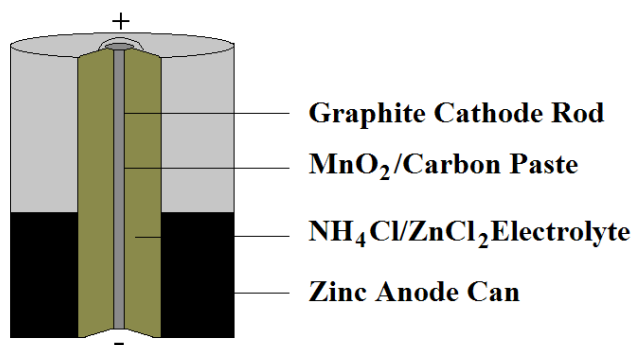
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A dry cell is not actually dry. It is called dry because the electrolyte exists as damp and viscous paste. Figure 9.5.1 shows a diagram of a typical dry cell battery.



A Dry Cell Battery

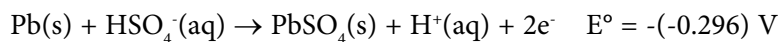
Figure 9.5.1 A Dry Cell Battery

Lead Storage Batteries

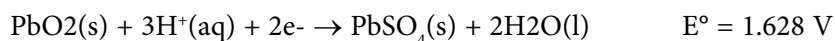
Your car battery is a lead storage battery. In fact it is actually six galvanic cells, producing 1.924 V each, connected in series to produce nearly twelve volts.

Lead ($\text{Pb}(s)$) is oxidized at the anode into lead sulfate $\text{PbSO}_4(s)$. Lead oxide ($\text{PbO}_2(s)$) is reduced at the cathode to lead sulfate $\text{PbSO}_4(s)$.

Anode



Cathode



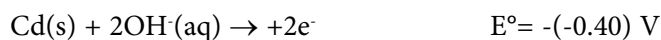
The total cell voltage is 1.924 V. The total voltage of the battery is 11.544 V.

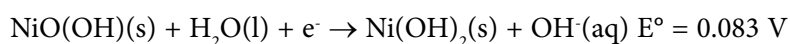
Nickel-Cadmium Batteries

Nickel-cadmium (or ni-cad) batteries are of popular use as dry cell batteries because they are rechargeable.

Cadmium ($\text{Cd}(s)$) is oxidized at the anode. Nickeloxyhydroxide ($\text{NiO}(\text{OH})$) is reduced at the cathode.

Anode

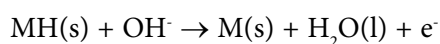
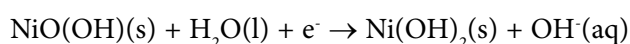


Cathode

The total voltage for a nickel-cadmium battery is 1.23 V.

Nickel-Hydride Batteries

Cadmium is very expensive and a toxic heavy metal. Nickel-hydride batteries present a more economical and environmentally safe alternative to cadmium batteries. A metal hydride (MH(s)) is oxidized at the anode. Nickeloxyhydroxide is reduced at the cathode.

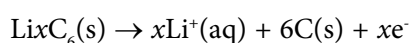
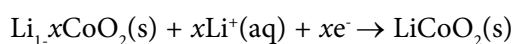
Anode*Cathode*

The nickel-hydride battery produces approximately the same 1.2 volts as the nickel-cadmium battery.

Lithium-Ion Batteries

Since lithium is both a light weight metal and a very strong reducing agent, lithium-ion batteries are light weight and can produce just over 3 volts per cell.

The lithium-ion battery contains no lithium metal (Li(s)) as such. The anode is graphite that has been impregnated with lithium ions, $\text{Li}_x\text{C}_6\text{(s)}$. The cathode is cobalt oxide also containing lithium ions, $\text{Li}_{1-x}\text{CoO}_2\text{(s)}$.

Anode*Cathode***9.6 Fuel Cells**

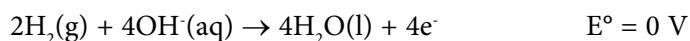
A fuel cell, like other batteries, is a galvanic cell with one distinct difference. The cell does not contain the reactants for the oxidation-reduction reaction.

The reactants of a fuel cell are fed to the cell on a continuous basis while the products of this reaction are channeled out of the cell.

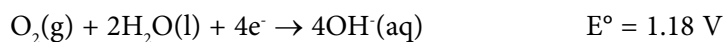
The chemical process of a hydrogen-oxygen fuel cell, as shown in Figure 9.6.1, is essentially the reaction of converting hydrogen (H_2) and oxygen (O_2) to water (H_2O).

Hydrogen is oxidized at the anode. Oxygen is reduced at the cathode. A hot solution of potassium hydroxide (KOH) acts as the electrolyte.

Anode



Cathode



Of course the standard reduction potential of hydrogen (H_2) held in reference to the standard hydrogen electrode is 0 V. The total potential is the standard reduction potential of oxygen (O_2) of 1.18 V.

It should be noted that the hydrogen-oxygen fuel cell is considerably eco-friendly. Consider that the “exhausts” of the cell are water and excess oxygen.

Figure 9.6.1 shows a diagram of a hydrogen-oxygen fuel cell.

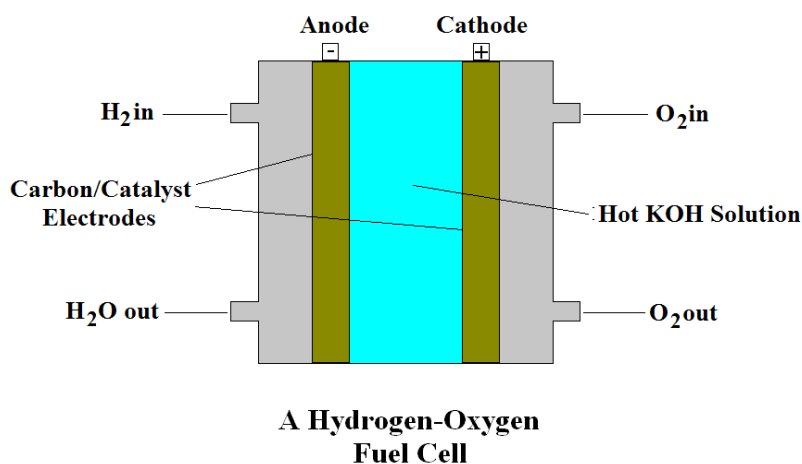


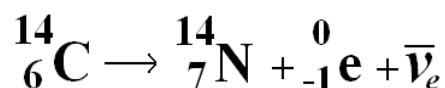
Figure 9.6.1 A Hydrogen-Oxygen Fuel Cell

10 Nuclear Chemistry

Nuclear Reactions

A nuclear reaction is a reaction where a change in the identity of the nucleus has occurred.

Look at the following reaction of carbon-14 in the atmosphere when exposed to cosmic radiation.



Here one of the neutrons of carbon-14 has been changed into a proton through the ejection of an electron and an antineutrino.

Distinctions of Nuclear Reactions

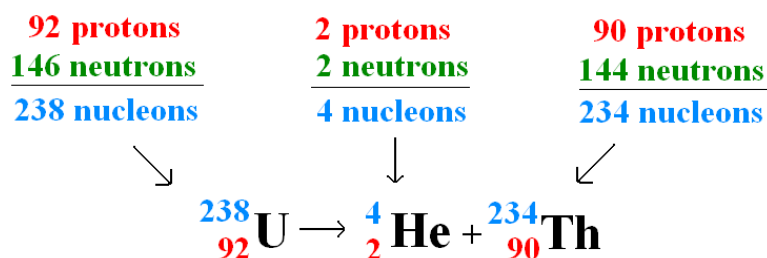
1. The nucleus is altered.
2. Different isotopes behave differently.
3. Reaction rate is unaffected by temperature, pressure, or the addition of a catalyst.
4. The reaction is the same whether the atom is uncombined or combined in a molecule.
5. The energy change is much greater than that of a chemical reaction.

10.1 Types of Radiation

Alpha (α) Radiation

The first of the four major types of radiation to be described is *alpha* (α) radiation.

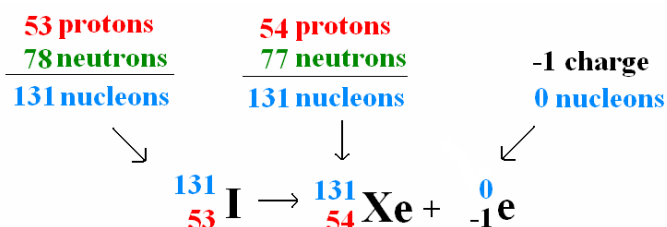
The alpha *particle* is essentially the nucleus of the helium atom. A decay of uranium-238 may be described by the following nuclear reaction equation.



Beta (β) Radiation

The second type of radiation to be described is **beta (β)** radiation. Beta particles are essentially electrons and have the symbol indicating a charge but no (appreciable) mass.

During the radioactive decay of iodine (I) to xenon (Xe) a neutron decays to a proton and emits an electron.



Gamma (γ) Radiation

The third type of radiation is **gamma (γ)** radiation. Gamma radiation is simply very high electromagnetic radiation. It is unaffected by magnetic fields and has no mass.

Gamma radiation often accompanies the emission of β and α radiation as a release of energy.

Gamma radiation is nearly always omitted when writing nuclear equations because it changes neither the mass number nor the atomic number of the product nuclei.

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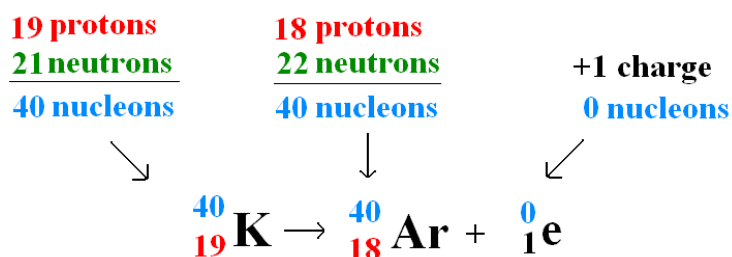
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Positron (β^+) Radiation

A fourth type of radiation is *positron* (β^+) emission.

A positron is essentially a *positively charged electron*.

During the natural decay of potassium (K) to argon (Ar) a proton is converted to a neutron and ejects a positron.



10.2 Measurement of Radiation and Radioactive Dose

A *radiation measurement* is a measure of the rate of radiation emission from a radioactive source.

A *radiation dose measurement* is a measure of biological effect on soft human or mammal tissue.

Radiation Measurement Units

Radiation is measured in Becquerel (Bq) and Curie (Ci).

A Becquerel (Bq) is defined as one event of radiation emission per second.

The Curie (Ci), a vastly larger number, is equal to 37,000 megaBq.

Radiation Dose Measurement Units

The SI unit for radiation dose is the *Gray (Gy)* and is equal to the absorbed dose of 1 Joule per kilogram.

Another common unit of radiation dose is the *rad* and is equal to the absorbed dose of 0.01 Joule per kilogram or 0.01 Gy.

A *dose equivalent* is a special measurement of radiation dose that has been multiplied by special quality factors to account for different types of radiation and different parts of the body.

Radiation Dose Equivalent Measurement Units

The *Sievert (Sv)* is the SI unit of dose equivalence and is equal to the absorbed dose in Gy multiplied by special factors.

Another unit of dose equivalence is the *rem* and is equal to the absorbed dose in rad multiplied by special factors. One rem is equal to 0.01 Sv.

Table 10.2.1 lists the quality factors (Q) of different types of radiation.

Radiation Type	Q-Factor	Dose Equivalent
Alpha	20	0.05
Beta	1	1
Gamma	1	1
Neutron	10	0.1

Table 10.2.1 Q-Factors for Different Radiation Types

Body Part	Q-Factor	Dose Equivalent
Bladder	25	0.04
Bone Marrow	8.33	0.12
Bone Surface	100	0.01
Brain	100	0.01
Breasts	8.33	0.12
Colon	8.33	0.12
Esophagus	25	0.04
Gonads	12.5	0.08
Liver	25	0.04
Lungs	8.33	0.12
Salivary Glands	100	0.01
Skin	100	0.01
Stomach	8.33	0.12
Thyroid	25	0.04
Rest of the body	8.33	0.12
Total		1.00

Table 10.2.3 Q-Factors for Different Body Parts

Body Burden Limits

A **body burden limit** is a regulatory limit on the amount of radiation dose different types of people are **generally** allowed.

Table 10.2.3 lists the body burden limits for a variety of radiation workers and the ordinary citizen.

Person Type	Body Part	Body Burden Limit (mrem/yr)
Radiation Worker	Whole Body	5,000
Minor (<18 yrs)	Whole Body	500
Radiation Worker's Unborn Child	Whole Body	500
General Public	Whole Body	100
Radiation Worker	Eye Lens	15,000
Radiation Worker	Hands, Wrists, Feet, Ankles	50,000
Radiation Worker	Skin	50,000
Radiation Worker	Thyroid	50,000

Table 10.2.3 Body Burden Limits

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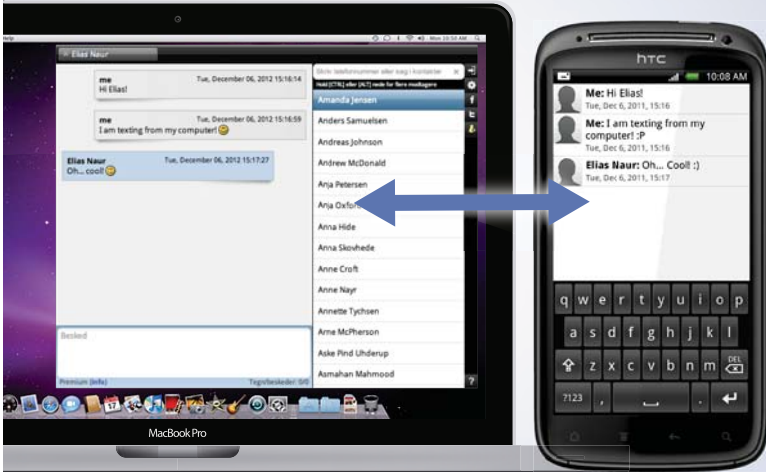
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10.3 Radioactive Decay

Radioactive Decay Rates

Just like all other processes in chemistry if the rate can be characterized or calculated it will be.

Radioactive decay is a *first order process* whose rate is proportional to the number of radioactive nuclei (N) in a sample.

The decay rate is characterized by the following.

$$\text{Decay Rate} = k \times N$$

Where k is a rate constant called the *decay constant*.

Half-Life

Like all first-order processes, radioactive decay is characterized by a half-life ($t_{1/2}$), the time required for the number of radioactive nuclei to drop to half of the original value.

A general formula for half-life is calculated by assuming that $N = \frac{1}{2} N_0$. $\ln(\frac{1}{2}N_0/N_0) = -k/t_{1/2}$ then $\ln\frac{1}{2} = -\ln 2 = -kt_{1/2}$ therefore

$$t_{1/2} = \ln 2/k.$$

Table 10.3.1 lists half-lives for some radioactive isotopes.

Radioisotope	Half-life
Uranium-238	4.5×10^9 yr
Potassium-40	1.3×10^9 yr
Carbon-14	5.7×10^3 yr
Radium-226	1.6×10^3 yr
Iron-59	46 dy
Iodine-131	8 dy

Table 10.3.1 Half-lives of Radioactive Isotopes

Note that the large number for carbon-14 is why it is so good at dating carbonaceous materials. Also, the immensely large number for uranium-238 is why the nuclear waste problem is so immense.

Let's look more closely at the radioactive decay of carbon-14. Used in carbon dating of carbonaceous material it must stick around awhile in order to date very old material.

Figure 10.3.1 is a graph of the radioactive decay of 100 grams of carbon-14 over ten half-lives of the isotope.

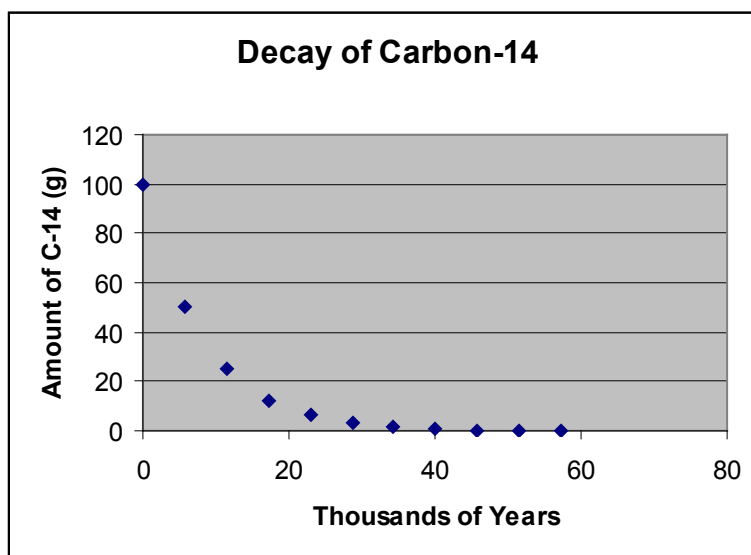


Figure 10.3.1 Decay of Carbon-14

After ten half-lives (57,300 years) less than one tenth of the original 100 grams of carbon-14 remains radioactive.

Also note the logarithmic shape of the graph. Remember the formula for half-life is $t_{1/2} = \ln 2/K$. The natural logarithm (\ln) results in a logarithmic shape.

Let's do some problems.

Exercise 10.3.1

What is the half-life of a radioactive isotopes with a K value of 0.0812 hr^{-1} ?

Remember that the decay constant (K) is always in units of reciprocal time. This way when you divided the unitless numerator by reciprocal time you get units of time.

$$t_{1/2} = \ln 2 / 0.0812 \text{ hr}^{-1} = 0.693 / 0.0812 \text{ hr}^{-1} = 8.5 \text{ hr}$$

Exercise 10.3.2

What is the decay constant of a radioactive isotope that has a half-life of 25 days?

$$\text{If } t_{1/2} = \ln 2 / K \text{ then } K = \ln 2 / t_{1/2}$$

$$K = 0.693 / 25 \text{ dy} = 0.028 \text{ dy}^{-1}$$

Exercise 10.3.3

Starting with 50 g of a radioactive isotope, how many grams are left after 2 half-lives if the isotope has a decay constant (K) of 0.00135 years?

Don't over think this problem! After one *half*-life there will be 25 grams of product left. After the second *half*-life there will be **12.5 grams** of the isotope left.

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10.4 Fission

Mass Defects and Binding Energy

Binding energy (ΔE) is the energy that holds a nucleus together. If we force that nucleus apart (*fission*) there is a noticeable mass defect (Δm) that relates to the energy released according to the following formula.

$$\Delta E = \Delta mc^2$$

This now famous formula was what drove the scientists in the Manhattan Project forward to obtain the massive amounts of energy when the “missing” mass in the fission reaction was converted to energy.

Example

Let's look at a typical fission of uranium-235.

Subtract the accurate masses of the products from the reactants.

$$\text{U-235} = 235.0439 \text{ amu}$$

$$\text{Kr-91} = 90.9234 \text{ amu}$$

$$\text{Ba-142} = 141.9164 \text{ amu}$$

$$n = 1.00865 \text{ amu}$$

$$(235.0439 + 1.00865) - (90.9234 + 141.9164 + 3.02595) = 0.1868 \text{ amu}$$

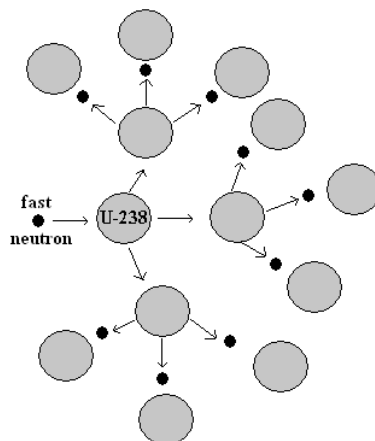
Atomic masses directly predict molar masses. Therefore, the molar mass is 0.1868 g/mole.

$$\Delta E = \Delta mc^2 = (0.1868 \text{ g/mol})(10^{-3} \text{ kg/g})(3.00 \times 10^8 \text{ m/s})^2 =$$

$$1.68 \times 10^{13} \text{ kg}\cdot\text{m}^2/(\text{s}^2\cdot\text{mol}) = \mathbf{1.68 \times 10^{13} \text{ J/mol}}$$

This massive amount of energy per mole of material absolutely dwarves the amount of energy per mole you could get out of combusting 0.1868 grams of combustible material.

In Figure 10.4.1 a fast neutron fissions with an atom of U-238 which gives birth to, among other radioactive isotopes, approximately three fast neutrons per fission.



Fission of U-238

Figure 10.4.1 Fission of U-238

Since U-238 needs fast neutrons to fission and gives birth to fast neutrons, the uncontrollable nuclear fission reaction can take place.

U-235, on the other hand, requires a thermal (or slowed) neutron in order to fission yet it also gives birth to approximately three fast neutrons per fission.

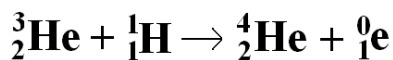
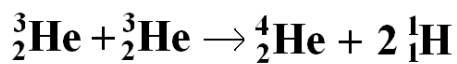
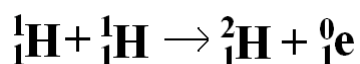
The way the fast neutrons of U-235 are slowed down is by letting them collide with things that are nearly identical in size in a process known as inelastic scattering.

The particles used to effect the inelastic scattering of the fast neutrons are the hydrogen (H) atoms in a water (H_2O) molecule. With each collision between a fast neutron and a hydrogen (H) atom the momentum of the fast neutron is decreased. When the fast neutron has lost sufficient momentum it can then fission with a U-235 atom. For this reason the water is considered to be a *moderator*.

10.5 Fusion

Nuclear Fusion

Just as heavy atoms, such as uranium, release vast amounts of energy when they undergo fission, very light atoms, such as the isotopes of hydrogen, also release enormous amounts of energy when they are forced together (*fusion*). It is believed that helium is formed in the sun through the following reactions.



One problem with utilizing fusion is the 4×10^7 Kelvin needed to initiate the process.

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11 Basic Organic Chemistry

Organic Molecules

Organic molecules are those molecules made up primarily of carbon and hydrogen.

Known as *hydrocarbons*, only a molecule consisting exclusively of carbon and hydrogen would be considered a pure hydrocarbon.

Methane (or natural gas) is the simplest hydrocarbon.



Heteroatomic Hydrocarbons

Other atoms are formed along with carbon and hydrogen into organic molecules. Examples of these would be nitrogen (N), oxygen (O), sulfur (S), phosphorus (P), and others.

These non-carbon, non-hydrogen atoms are then referred to as *heteroatoms*.

Formaldehyde is a good example of a heteroatomic hydrocarbon.



Organic Compound Families

The organic compounds presented in this chapter will be divided into two major groups.

Pure hydrocarbons and their different families

For these compounds you will be expected to know *family names, structures, and carbon to hydrogen ratio formulae*.

Heteroatomic hydrocarbons and their different families

For these compounds you will be expected to know *family names and functional groups*.

11.1 The Alkanes

The first and the simplest of the pure hydrocarbons are the *alkanes*.

The alkanes are characterized by all single carbon to carbon covalent bonds.

The restriction to only single carbon to carbon bonds in a pure hydrocarbon results in alkanes having the maximum number of hydrogen atoms attached.

When a hydrocarbon has the maximum number of hydrogen atoms attached it is said to be *saturated* with hydrogen.

Examples of Alkanes

Here are shown the alkanes with the carbon numbers 1,2,3, and 4.

C1,C2, and C3 hydrocarbons cannot have isomers. The C4 hydrocarbon has one isomer.

The carbon to hydrogen ratio formula for alkanes is C_nH_{2n+2} .

Figure 11.1.1 shows structures and formulae for the first four alkanes.

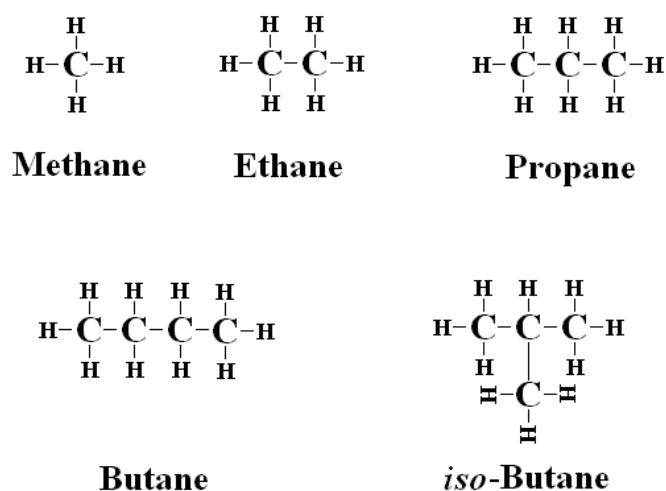


Figure 11.1.1 The C1, C2, C3, and C4 Alkanes

Notice that even though butane and *iso*-butane are different compounds they both have the same formula of C_4H_{10} .

They are *structural isomers* of one another.

Every alkane from butane up will have an increasing number of isomers of the straight chained version of the alkane.

Decane, the C₁₀ alkane, has 75 structural isomers.

Instruction in this chapter is fairly well limited to compounds with ten or less carbon atoms.

Naming Alkanes

We will deal with alkanes that contain no more than 10 carbon atoms. *Know these empirical formulae and names.*

Table 11.1.1 shows the formulae and names for the first ten unbranched alkanes.

C#	Structure	Name
1	CH ₄	Methane
2	CH ₃ CH ₃	Ethane
3	CH ₃ CH ₂ CH ₃	Propane
4	CH ₃ CH ₂ CH ₂ CH ₃	Butane
5	CH ₃ CH ₂ CH ₂ CH ₂ CH ₃	Pentane
6	CH ₃ CH ₂ CH ₂ CH ₂ CH ₂ CH ₃	Hexane
7	CH ₃ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₃	Heptane
8	CH ₃ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₃	Octane
9	CH ₃ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₃	Nonane
10	CH ₃ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₃	Decane



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Naming Alkanes

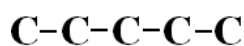
The alkanes listed in Table 11.1.1 are all straight chained alkanes. That is to say there are no branches in their structures. These type of alkanes are referred to as *normal alkanes*.

The symbol for this is the lower case “n”. If you were referring to pentane and wanted to be sure you stressed the straight chained isomer you would refer to it as *n-pentane*.

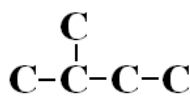
All n-alkanes from butane up have branched isomers. These compounds are referred to as *branched alkanes*.

Using “hydrogen suppressed” drawings the following diagrams show the three isomers of pentane (C_5H_{12}).

n-Pentane



2-Methylbutane



2,2-Dimethylpropane

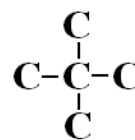


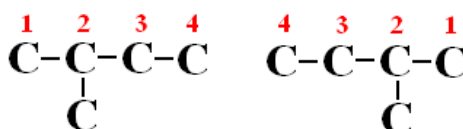
Figure 11.1.2 The Three Isomers of Pentane

The following rules were applied to naming the pentane isomers in Figure 11.1.2.

- 1) Each name was written as a continuous word and contained the name of the longest chain.
- 2) Each substituent was named by replacing the *-ane* of the alkane name with *-yl*.
- 3) The number of each substituent was assigned by numbering the longest chain to result in substituents with the smallest numbers.
- 4) Multiple substituents were named using the Greek prefixes.

Please note the two drawings of 2-methylbutane below.

Both of these drawings are of the same isomer of pentane and are numbered correctly.

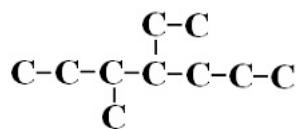


Just because an isomer is drawn to the opposite hand does not make it a unique isomer.

Using the four rules listed previously and adding a fifth rule, the following branched alkane can be named.

- 5) Different substituents on an alkane chain appear in the name alphabetically.

Figure 11.1.3 shows 4-ethyl-3-methylheptane since “e” comes before “m” in the alphabet.



4-Ethyl-3-methylheptane

Figure 11.1.3 4-Ethyl-3-methylheptane

Cycloalkanes

If you can imagine bringing the two ends of hexane together to form a ring, do so with one important rule in mind:

The Tetravalent Rule of Carbon

Carbon must always be bonded four times in a neutral molecule.

By following the tetravalent rule of carbon two hydrogens were given up in order to form the ring.

Figure 11.1.4 shows the cyclohexane molecule.

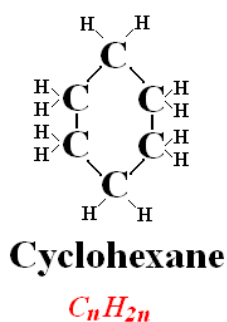


Figure 11.1.4 Cyclohexane

Those two hydrogens are known as *1 point of unsaturation*.

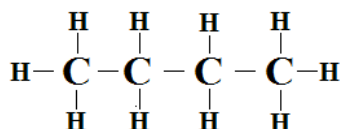
A Review of Rules for Naming Alkanes

- 1) Each name was written as a continuous word and contained the name of the longest chain.
- 2) Each substituent was named by replacing the *-ane* of the alkane name with *-yl*.
- 3) The number of each substituent was assigned by numbering the longest chain to result in substituents with the smallest numbers.
- 4) Multiple substituents were named using the Greek prefixes.
- 5) Different substituents on an alkane chain appear in the name alphabetically.
- 6) Use the prefix *"cyclo"* to indicate a non-aromatic ring.

Drawing Conventions for Organic Molecules

Several different conventions for drawing organic molecules are in force today. Consider the following drawings of butane.

- 1) A full structural drawing with all atoms and bonds.



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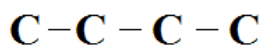
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2) A full structural drawing with the hydrogen molecules suppressed.



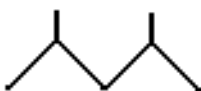
3) A hydrogen suppressed graphical form where each vertex is a carbon and each edge is a bond.



Let's do some naming exercises!

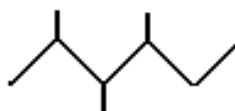
Using the six rules previously listed and the concept of hydrogen suppressed graphical forms name the following compounds.

Exercise 11.1.1



The longest chain is 5 so *pentane*. There are 2 methyl groups attached so *dimethyl*. The lowest numbering is 2,4 so *2,4-Dimethylpentane*.

Exercise 11.1.2

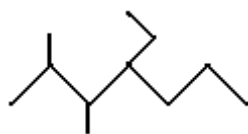


The longest chain is 6 so *hexane*. There are 3 methyl groups attached so *trimethyl*. The lowest numbering is 2,3,4 so *2,3,4-Trimethylhexane*.

Exercise 11.1.3



The molecule is cyclic so *cyclo*. There are 5 carbons so *cyclopentane*. There are 2 methyl groups attached so *dimethylcyclopentane*. The lowest numbering is 1,3 so *1,3-Dimethylcyclopentane*.

Exercise 11.1.4

The longest chain is 7 so *heptane*. There are 2 methyl groups so *dimethylheptane*. There is an ethyl group so *ethyl dimethylheptane*. The lowest numbers are 2,3,4 so *4-Ethyl-2,3-dimethylheptane*.

Now let's switch from naming a hydrogen suppressed graphical representation of an alkane to drawing that same hydrogen suppressed representation if you are given a valid compound name.

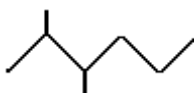
Exercise 11.1.5

Draw 2,3-Dimethylhexane.

First draw a six (hex=6) carbon chain.



Attach methyl groups to carbons 2 and 3.

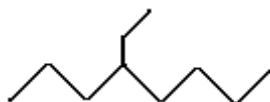
**Exercise 11.1.6**

Draw 4-Ethyl-3-methyl octane.

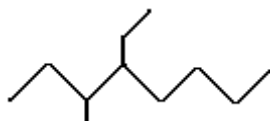
First draw an eight (oct=8) carbon chain.



Attach an ethyl group to carbon 4.



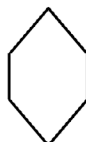
Attach a methyl group to carbon 3.



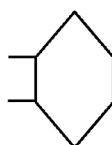
Exercise 11.1.7

Draw 1,2-Dimethylcyclohexane.

Draw a cyclohexane ring.



Attach two methyl groups adjacent to each other starting with any carbon.

**Exercise 11.1.8**

Draw 1,3-Dimethylcyclobutane.

First draw 4 (but=4) carbon ring.



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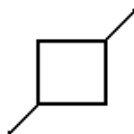
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Attach two methyl groups at opposing corners of the ring.



Properties of Alkanes

Solubility – Alkanes are nonpolar and insoluble in water. They are soluble in other nonpolar solvents.
(Fuel and water do not mix.)

Density – Alkanes have densities from 0.62 g/ml to 0.79 g/ml. (Fuel floats on water.)

Combustibility – All alkanes will burn readily in oxygen. (Fuel burns.)

Combustion of Alkanes

When alkanes undergo complete combustion in oxygen they do so according to the following formula:



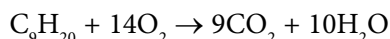
Write and balance the combustion reaction for propane.

- 1) We know propane has 3 carbons and $(2 \times 3) + 2 = 8$ hydrogens.
- 2) So the combustion reaction $\text{C}_3\text{H}_8 + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O}$
- 3) Balance C products to reactants. $\text{C}_3\text{H}_8 + \text{O}_2 \rightarrow 3 \text{CO}_2 + \text{H}_2\text{O}$
- 4) Balance H products to reactants. $\text{C}_3\text{H}_8 + \text{O}_2 \rightarrow 3 \text{CO}_2 + 4 \text{H}_2\text{O}$
- 5) Balance O reactants to products. $\text{C}_3\text{H}_8 + 5 \text{O}_2 \rightarrow 3 \text{CO}_2 + 4 \text{H}_2\text{O}$

Let's do some combustion reaction exercises!

Exercise 11.1.10

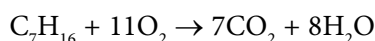
Write and balance the combustion reaction for 2,3 dimethylheptane. heptane = 7 C's and $(2 \times 9) + 2 = 20$ H's



Exercise 11.1.11

Write and balance the combustion equation for the following compound.

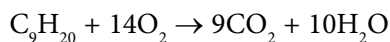
7 C's and $(2 \times 7) + 2 = 16$ H's



Exercise 11.1.12

Write and balance the combustion reaction for 4-ethyl-2-methylhexane.

Carbons = 6 (hexane) + 2 (ethyl) + 1 (methyl) for a total of 9 carbons. Hydrogens = $(2 \times 9) + 2$ for 20 hydrogens

**11.2 The Alkenes, Alkynes, and Aromatics****Alkenes**

Alkenes are essentially alkanes that contain one or more double bonds (also a point of unsaturation). The compound 1-hexene is a straight chain of six carbon atoms with a double bond between the first and second carbons.

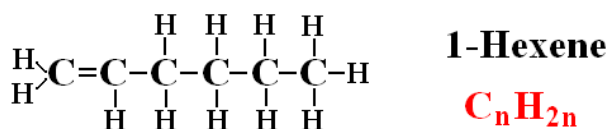


Figure 11.2.1 1-Hexene

All single bonds between carbon atoms are referred to as *sigma (σ) bonds*. An additional bond between two carbon atoms is referred to as a *pi (π) bond*.

If the alkene has two double bonds it is referred to as a *diene*.

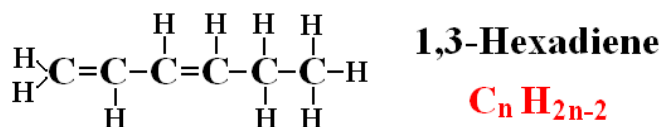


Figure 11.2.2 1,3-Hexadiene

The every other carbon π -bond configuration is known as a *conjugated π -bond system*. Conjugated π -bond systems are often responsible for color and odor in organic molecules.

Alkynes

Alkynes are essentially alkanes that contain one or more triple bonds between carbon atoms.

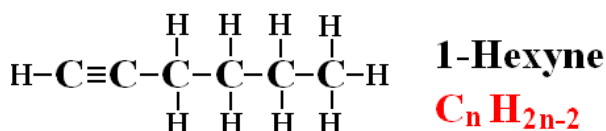


Figure 11.2.3 1-Hexyne

The triple bond is a bond consisting of two σ -electrons and four π -electrons. Alkynes are essential in the make up of the planet. A simpler way of stating that is that it takes alkynes to make a world.

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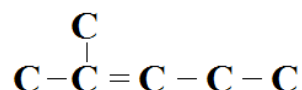
Nomenclature Update

The nomenclature rules previously listed in this chapter apply to alkenes, and alkynes with the following addenda.

7. Alkenes end with *-ene*
8. Alkynes end with *-yne*
9. Both use the same lowest carbon number scheme to indicate the positions of multiple bonds. (In numbering schemes double bonds take precedence over substituents.)
10. Both use Greek prefixes to indicate more than one of the same type of multiple bond.

Exercise 11.2.1

Name the following compound.



A double bond so *ene*. 5 carbons for the longest chain so *pentene*.

Double Bond originates at #2 C so *2-pentene*.

A methyl group on #2 carbon so *2-methyl-2-pentene*

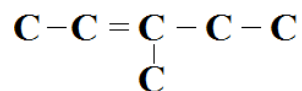
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Exercise 11.2.2

Name the following compound.



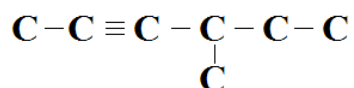
A double bond so *ene*. 5 carbons for longest chain so *pentene*.

Double bond originates at #2 C so *2-pentene*.

A methyl group on #3 C so *3-methyl-2-pentene*.

Exercise 11.2.3

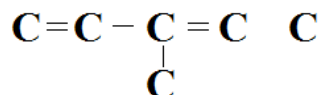
Name the following compound.



A triple bond so *yne*. Longest chain of 6 C's so *hexyne*. Triple bond originates at #2 C so *2-hexyne*. A methyl group on #4 C so *4-methyl-2-hexyne*.

Exercise 11.2.4

Name the following compound.



Two double bonds so *diene*. Longest chain of 5 C's so *pentadiene*.

Double bonds originating at #1 C and #3 C so *1,3-pentadiene*.

A methyl group on #3 C so *3-methyl-1,3-pentadiene*.

Exercise 11.2.5

Name the following compound.



A 6 carbon cycle with a double bond so *cyclohexene*.

Double bond originates at #1 C so still *cyclohexene* due to symmetry.

A methyl group on #4 C so *4-methylcyclohexene*.

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Exercise 11.2.6

Name the following compound.



Two double bonds so *diene*. Double bonds originating at #1 C and #3 C so *1,3-diene*. 6 C ring so *cyclohexa-1,3-diene*. A methyl group so *methylcyclohexa-1,3-diene*. Methyl group at #1 C so *1-methylcyclohexa-1,3-diene*.

cis – trans Isomers

Unlike single bonds, double bonds are “rigid” and do not allow substituents to rotate freely about the bond. Because of this it matters which direction a substituent “approaches” the double bond.

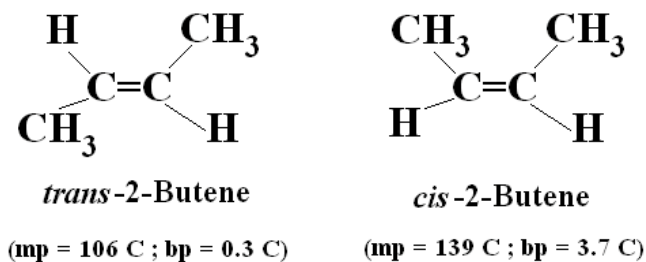
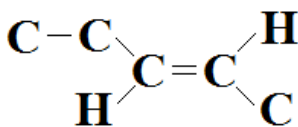


Figure 11.2.4 cis-trans Isomers of 2-Butene

Exercise 11.2.7

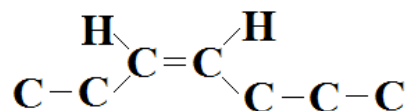
Name the following compound.



A double bond so *ene*. 5 carbons so *pentene*. Double bond originates from #2 C (from the right) so *2-pentene*. Hydrogens are opposite each other so *trans-2-pentene*.

Exercise 11.2.8

Name the following compound.



A double bond so *ene*. 7 carbons so *heptene*. Double bond originates from #3 C (from the left) so *3-heptene*. Hydrogens are on the same side so *cis-3-heptene*.

Addition Reactions with Double Bonds

There are three common types of addition reactions that occur with or “*across*” double bonds. In this case the double bond is taken away.

- 1) *Hydrogenation* – the addition of hydrogen
- 2) *Hydration* – the addition of water
- 3) *Polymerization* – the addition of a monomer unit

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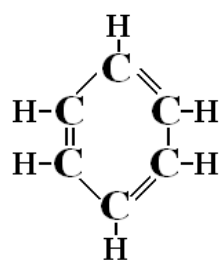
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Aromatic Compounds

Aromatics are compounds consisting of one or more six carbon rings that contain systems of conjugated (every other carbon) π -bond electrons.

In the drawing of benzene, the simplest aromatic compound, there are three double bonds and a ring for a total of four points of unsaturation.

The general formula for all single ring aromatics is C_nH_{2n-6m} where “n” is the number of carbons and “m” is the number of aromatic rings.



Benzene

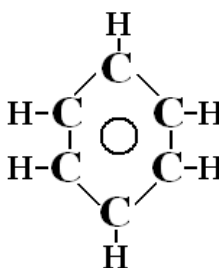
Figure 11.2.8 Benzene

The True Aromatic Ring Structure

The structure shown in Figure 11.2.8, for benzene, was envisioned by the German organic chemist Friedrich August Kekule von Stradonitz in the late 1800s.

With modern analytical techniques, capable of mapping electrostatic charges, it was determined that the Kekule structure was not entirely correct.

The extra electrons shown in the double bonds of the Kekule structure are actually π electrons but they exist as a *cloud* of π electrons around the benzene ring, which is represented as a circle in the center of the six carbon ring.



Benzene

Figure 11.29 Benzene's True Structure

Aromatic Nomenclature

I prefer to use the line drawing method for ring structures but not for the substituents attached to the ring.

For example, the second drawing below is seen more often for the molecule methylbenzene (aka, toluene).

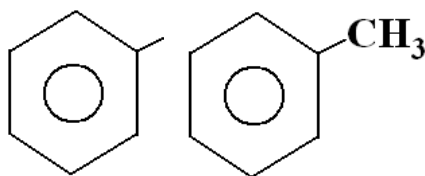


Figure 11.2.10 Benzene Drawings

Naming Aromatic Compounds

- 1) Single ring aromatic compounds with a single substituent are named as benzene derivatives. However, trivial names generally dominate.

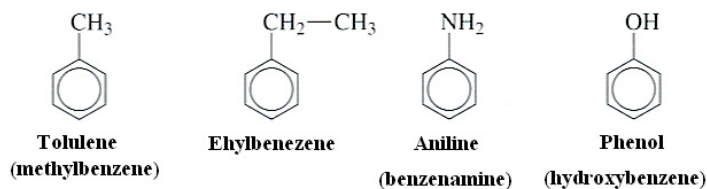


Figure 11.2.11 Benzene Derivatives

2) When benzene is used as a substituent (C_6H_5-), it is named as a phenyl group.

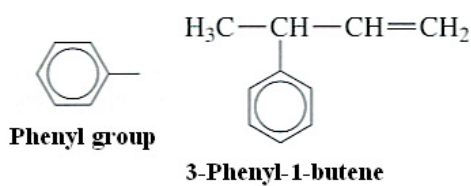


Figure 11.2.12 Benzene Substituents

3) When two or more substituents are present, they are numbered with the lowest numbers.

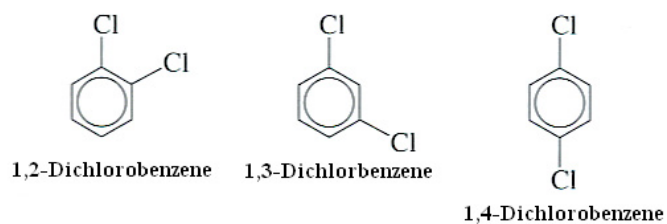


Figure 11.2.13 Benzene Substituent Numbering

4) When trivial names are used, the carbon attached to the group inherent to the trivial name is numbered as carbon 1.

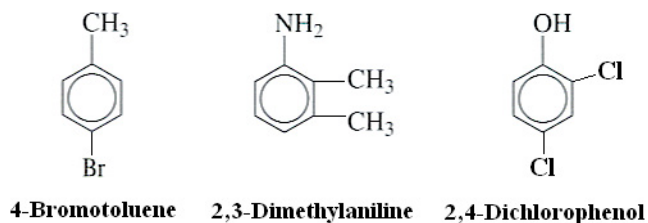


Figure 11.2.14 Trivial Benzene Substituent Names

5) Substituents to a benzene ring are named alphabetically.

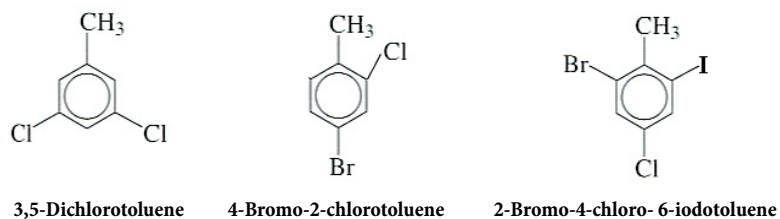


Figure 11.2.15 Benzene Substituent Priorities

Exercise 11.2.9

Name the following aromatic compound as a derivative of toluene.



The benzene ring carbon with the CH₃ group is #1 C because the compound is named as a toluene. So **4-chlorotoluene**.

Exercise 11.2.10

Name the following aromatic compound as a derivative of phenol.



The benzene ring carbon with the OH group is #1 C. So **3-bromophenol**

Exercise 11.2.11

Name the following aromatic compound as a derivative of benzene.



Number the bottom Br as 1 and the top Br as 2 so that the methyl group has a lowest number. So **1,2-dibromo-4-methylbenzene**.

Exercise 11.2.12

Name the following aromatic compound as a derivative of phenol.



The carbon with the OH attached is #1 C. Br is #2 C and CH₃ is #4 C. So **2-bromo-4-methylphenol**.

11.3 Functional Groups: Alcohols, Ethers, Aldehydes, and Ketones

Organic Functional Groups

The notion of functional groups in organic molecules and the notion of heteroatoms in organic molecules are one in the same.

All functional groups contain at least one heteroatom.

Oxygen plays a prominent role in organic functional groups. In fact, seven of eight functional groups you will be responsible for contain oxygen.

Actually, these eight oxygen containing functional groups could be looked at as differing degrees of oxidation of hydrocarbons

Alcohols

Alcohols are hydrocarbons where a hydrogen has apparently been replaced with an **-OH** group.

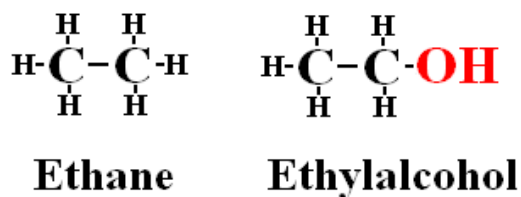


Figure 11.3.1 Alcohol

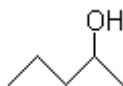
An alcohol could also be viewed as an organic derivative of water where one hydrogen has been replaced with an organic substituent.

Naming Alcohols

- 1) For alkane alcohols, replace the -e in the name of the longest chain containing the -OH group with **-ol**.
- 2) Number the chain starting at the end closest to the -OH group.
- 3) Name and number all other substituents relative to the -OH group.
- 4) For cyclic alkane alcohols, replace the -e in the cyclic alkane name with **-ol**.
- 5) The IUPAC name for the alcohol of benzene is **phenol**.

Exercise 11.3.1

Name this alcohol compound

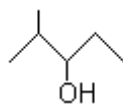


2-Pentanol

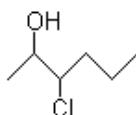
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Exercise 11.3.2

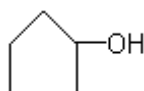
Name this alcohol compound.

*2-Methyl-3-pentanol***Exercise 11.3.3**

Name this alcohol compound.

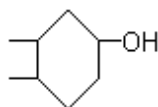
*3-Chloro-2-hexanol***Exercise 11.3.4**

Draw the alcohol compound cyclopentanol.

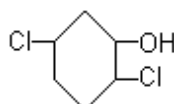


Exercise 11.3.5

Draw the alcohol compound 3,4-dimethylphenol.

**Exercise 11.3.6**

Draw the alcohol compound 2,5-dichlorophenol.

**Classification of Alcohols**

Alcohols are classified as primary (1°), secondary (2°), or tertiary (3°) depending on the number of carbon groups attached to the carbon that is attached to the alcohol group.

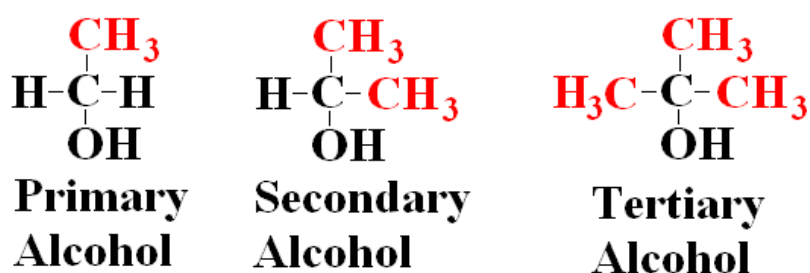


Figure 11.3.2 Classification of Alcohols

Ethers

Ethers can be viewed as derivatives of water where both hydrogens have been replaced with organic substituents.

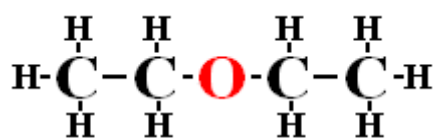
**Diethylether**

Figure 11.3.3 Ethers

The most common ether, diethylether, was used as an anesthetic gas until safer, nonflammable alternatives were developed.

Naming Ethers

Since the oxygen of an ether molecule cannot be terminal on the molecule, the rest of the molecule is named as constituents (in alphabetical order) to the ether oxygen. Look at the diethylether above.

When ethers become more complicated the ether portion of the name is dropped. Below are some ether molecules used as anesthetics.

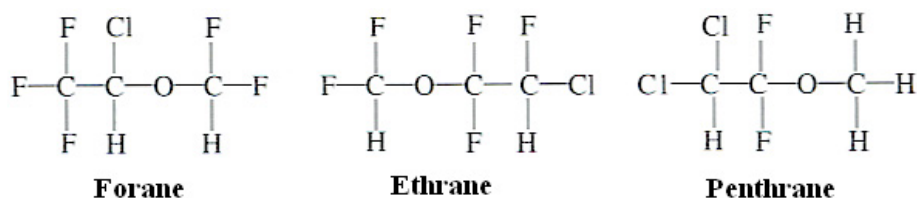


Figure 11.3.4 Trivial names of Ethers

Properties of Alcohols and Ethers

Table 11.3.1 shows some properties of an alcohol and an ether of identical molar mass. These properties are compared to a pure hydrocarbon of similar mass.

Compound	Empirical Formula	Molar Mass (g/mol)	Boiling Point (°C)	Solubility (g/L)
1-Butanol	$\text{C}_4\text{H}_{10}\text{O}$	74	118	74
Diethylether	$\text{C}_4\text{H}_{10}\text{O}$	74	35	69
n-Pentane	C_5H_{12}	72	36	Insol.

Table 11.3.1 Properties of an Alcohol and Ether

Given the boiling point of the n-pentane of 36°C, ask these two questions:

Why does the n-butanol have a much higher boiling point than the n-pentane? The answer is its ability to hydrogen bond.

Why does the diethylether have a boiling point nearly identical to the n-pentane? The answer is its inability to hydrogen bond.

Of course the pentane would be insoluble in water. Oil and water don't mix.

Reactions of Alcohols

Figure 11.3.5 shows the dehydration of an alcohol to form an alkene.

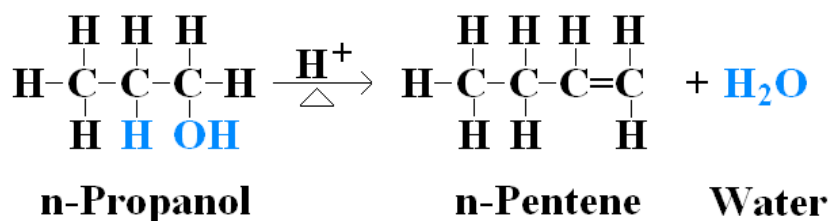


Figure 11.3.5 Dehydration of Alcohol

The triangle underneath the arrow represents the use of heat.

In organic chemistry water is known as a very good *leaving group*.

Oxidation of Alcohols

An alcohol is formed by the chemical oxidation, with the symbol [O], of an alkane. This reaction is not to be confused with combustion which is also an oxidative process.

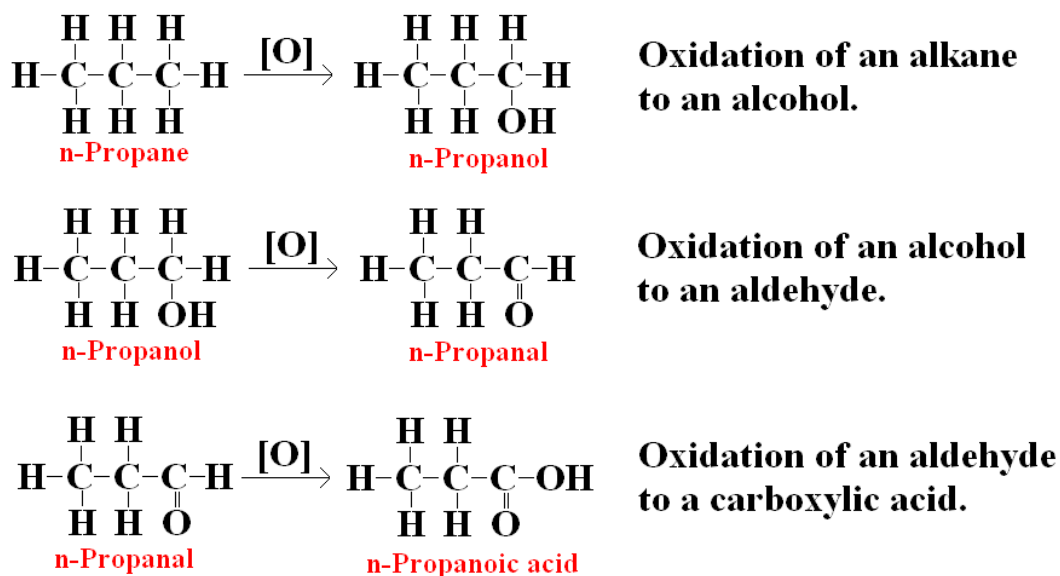


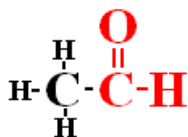
Figure 11.3.6 Chemical Oxidation of Alcohol

Please note that in the oxidation equations above that there is one carbon to oxygen bond in the alcohol, two carbon to oxygen bonds in the aldehyde, and three carbon to oxygen bonds in the carboxylic acid.

Not every concept introduced in this text makes sense right away. But it should be intuitive that the more times a carbon atom is bonded to an *oxygen* the more *oxidized* that atom (and hence the molecule) becomes.

Aldehydes

Aldehydes are characterized by a carbonyl group with *at least* one hydrogen atom attached to the carbonyl carbon. If the compound in Figure 11.3.7 had two hydrogens so attached, it would be formaldehyde.



Ethanal (Acetaldehyde)

Figure 11.3.7 Ethanal



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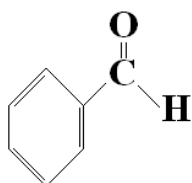
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Naming Aldehydes

- 1) Name the longest carbon chain containing the carbonyl group by replacing the -e with **-al**.

IUPAC specifies that the aldehyde of benzene is named **benzaldehyde**.



Benzaldehyde

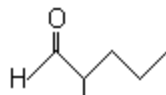
- 2) Name and number any substituents on the carbon chain by counting the carbonyl carbon as carbon #1.

Some common or trivial names of aldehydes persist. The aldehyde of methane, **methanal**, is more commonly named **formaldehyde**. The aldehyde of ethane, **ethanal**, is more commonly named **acetaldehyde**.

The following exercises are for naming and drawing aldehydes.

Exercise 11.3.7

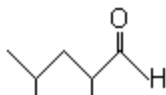
Name this aldehyde compound.



2-Methylpentanal

Exercise 11.3.8

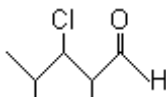
Name this aldehyde compound.



2,4-Dimethylpentanal

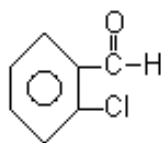
Exercise 11.3.9

Draw the aldehyde compound **3-Chloro-2,4-dimethylpentanal**.



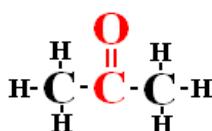
Exercise 11.3.10

Draw the aldehyde compound *2-Chlorobenzaldehyde*.

**Ketones**

Ketones are characterized by two carbon atoms bonded to a carbonyl group.

Ketones, like aldehydes, are very often referred to by trivial names.



Propanone
(Acetone)

Figure 11.3.8 Propanone

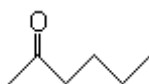
Naming Ketones

- 1) Name the longest carbon chain containing the carbonyl group by replacing the -e with **-one**.
- 2) Number the main chain by starting from the end nearest to the carbonyl group,
- 3) Name and number any substituents on the carbon chain.
- 4) Name the carbon chain opposite the main chain as a substituent.
- 5) For cyclic ketones the term **cyclo** is used in front of the ketone name.

The following exercises are for naming and drawing ketones.

Exercise 11.3.11

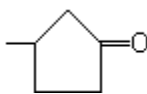
Name this ketone compound.



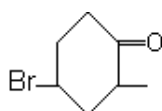
Methylbutylketone

Exercise 11.3.12

Name this ketone compound.

*3-Methylcyclopentanone***Exercise 11.3.13**

Draw the ketone compound 4-bromo-2-methylcyclohexanone.



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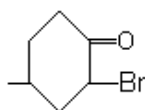
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Exercise 11.3.14

Draw the ketone compound 2-bromo-4-methylcyclohexanone.

**Properties of Aldehydes and Ketones**

The **boiling point** of aldehydes and ketones and the other functional compounds we have studied depends largely on the ability of their molecules to undergo **dipole-dipole** interactions with one another.

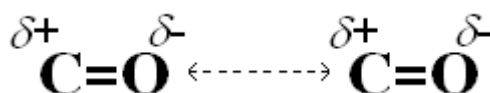


Figure 11.3.9 Dipole-Dipole Interactions

Remember that hydrogen bonding is just one type of dipole-dipole interaction. The figure above shows a dipole-dipole interaction between the carbonyl oxygen of one molecule to the carbonyl carbon of another of the same type molecule.

The following table, which is an expansion of Table 11.3.1, lists five hydrocarbon compounds of similar molar mass by their ascending values of boiling point.

Compound Name	Compound Family	Compound Formula	Molar Mass (g/mol)	Boiling Point (°C)
Diethylether	Ether	C ₄ H ₁₀ O	74	35
n-Pentane	Alkane	C ₅ H ₁₂	72	36
1-Butanal	Aldehyde	C ₄ H ₈ O	72	75
1-Butanol	Alcohol	C ₄ H ₁₀ O	74	138
Propanoic Acid	Carboxylic Acid	C ₃ H ₆ O ₂	74	141

Table 11.3.2 Dipole-Dipole Effects on Boiling Point

Listed this way two things should become apparent.

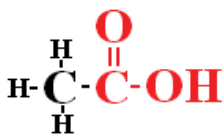
First, the first two compounds are not capable of dipole-dipole interactions. They show similarly low boiling points for similar molar masses.

Second, the remainder of the compounds show increasing boiling points as a result of ever increasing capability for dipole-dipole interactions.

11.4 Functional Groups: Carboxylic Acids, Esters, Amines, and Amides

Carboxylic Acids

Carboxylic acids are characterized by a carbon atom and an -OH group attached to the carbonyl carbon. The hydrogen on the -OH group is known as an *acidic hydrogen*.



Ethanoic acid (Acetic acid)

Figure 11.4.1 Ethanoic Acid

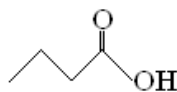
Naming Carboxylic Acids

- 1) Identify the longest carbon chain containing the carbonyl group, and replace the -e of the alkane name with *-oic acid*.
- 2) Number the carbon chain, beginning with the carboxyl carbon as carbon #1.
- 3) Number and name any substituents on the carbon chain in reference to the #1 carbon.
- 4) IUPAC specifies that the carboxylic acid of benzene is named *benzoic acid*.
- 5) Start numbering substituents on any ringed carboxylic acid at the carbon attached to the carbonyl carbon.

The following exercises are for naming carboxylic acids.

Exercise 11.4.1

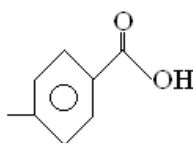
Name this carboxylic acid.



Butanoic acid

Exercise 11.4.2

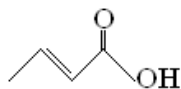
Name this carboxylic acid.



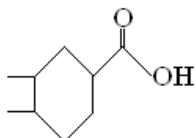
4-Methylbenzoic acid

Exercise 11.4.3

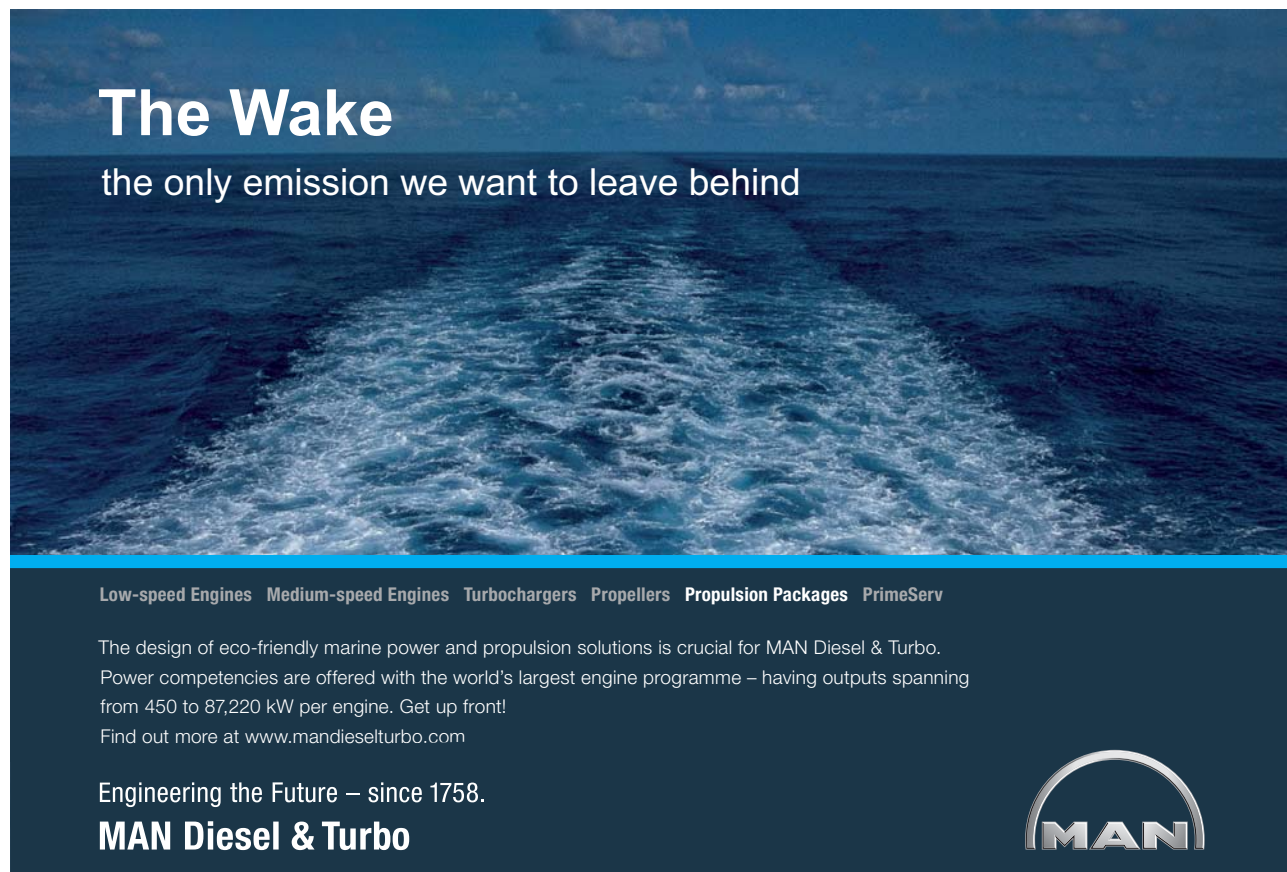
Name this carboxylic acid.

*2-Butenoic acid***Exercise 11.4.4**

Name this carboxylic acid.

*3,4-Dimethylcyclohexanoic acid*

The following exercises are for the drawing of carboxylic acids.



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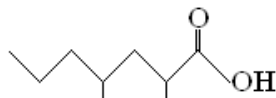
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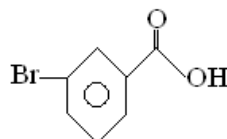


Exercise 11.4.5

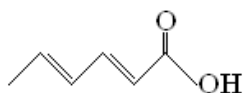
Draw the molecule 2,4-dimethylheptanoic acid.

**Exercise 11.4.6**

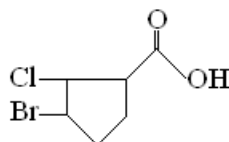
Draw the molecule 3-bromobenzoic acid.

**Exercise 11.4.7**

Draw the molecule 2,4-hexadienoic acid.

**Exercise 11.4.8**

Draw the molecule 3-bromo-2-chlorocyclopentanoic acid.



Carboxylic acids are among the most polar of hydrocarbons since they contain two polar groups in each molecule. Consider the structure of propanoic acid.

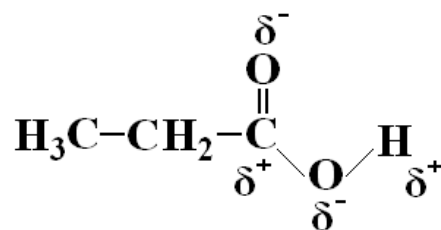
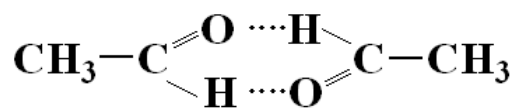
**Propanoic Acid**

Figure 11.4.2 Propanoic Acid

Because of the two polar groups, it is possible for one acid molecule to bond to another. Consider the dimer of two ethanoic acid molecules



Ethanoic Acid Dimer

Figure 11.4.3 Ethanoic Acid Dimer

Properties of Carboxylic Acids

Table 11.3.2, which includes a carboxylic acid, shows the effect of dipole-dipole interactions on the boiling points of compounds with similar molar masses.

Reactions of Carboxylic Acids

The *esterification* of a carboxylic acid with an alcohol is a *condensation* reaction.

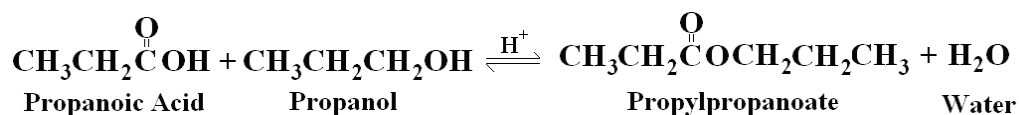


Figure 11.4.4 Esterification of Propanoic Acid

Notice the occurrence of water in the products of the reaction. Remember, this is a *condensation* reaction.

The *neutralization* of a carboxylic acid occurs when the acid is reacted with a basic compound.

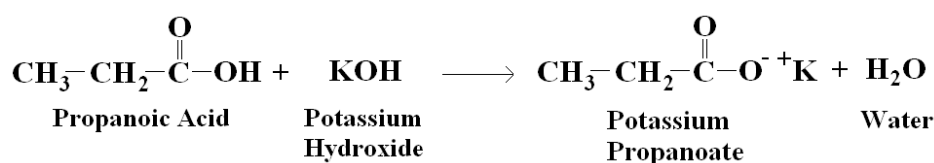


Figure 11.4.5 Neutralization of Propanoic Acid

The *ionization* of a carboxylic acid in an aqueous solution is the manner in which the compound acts as an acid.

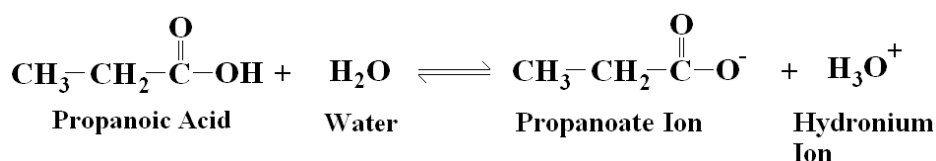
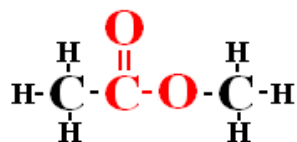


Figure 11.4.6 Ionization of Propanoic Acid

Esters

Esters are characterized by a carbon atom group replacing the acidic hydrogen of the corresponding carboxylic acid.



Methylethanoate (Methlyacetate)

Figure 11.4.7 Methylethanoate

Naming Esters

- 1) Name the carbonyl side of the ester by replacing -oic acid with *-oate*.
- 2) Name the oxygen side of the ester as the alkane substituent.
- 3) IUPAC specifies the name of the ester of benzene as *benzoate*.
- 4) Start numbering on any ringed esters at the carbon attached to the carbonyl carbon.

The following exercises deal with naming and drawing ester compounds.

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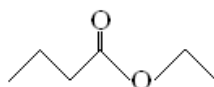
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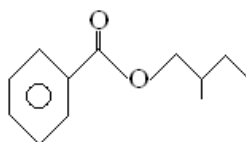


Exercise 11.4.9

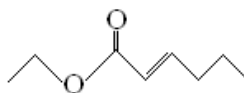
Name this ester compound.

*Ethylbutanoate***Exercise 11.4.10**

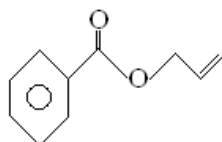
Name this ester compound.

*2-Methylbutylbenzoate***Exercise 11.4.11**

Draw Ethyl-2-hexenoate.

**Exercise 11.4.12**

Draw 2-Propenylbenzoate.



In the chemistry of plants, esters play a major role in generating the characteristic odors and flavors of the plants.

Odor/Flavor	Common Name	IUPAC Name
Banana	<i>iso</i> -Amylacetate	3-Methylbutylethanoate
Wintergreen	Methylsalicylate	Methyl-2-hydroxybenzoate
Pineapple	Ethylbutyrate	Ethylbutanoate
Cherry	Benzylbutyrate	Benzylbutanoate
Peach	Benzylacetate	Benzylethanoate
Apple	Methylbutyrate	Methylbutanoate
Pear	<i>n</i> -Propylacetate	<i>n</i> -Propylethanoate

Table 11.4.3 Ester Odors and Flavors

Table 11.4.4 compares the boiling point and water solubility of an ester, alcohol, and two acids all near the same molecular weight.

Compound	Molar Mass (g/mol)	Boiling Point (°C)	Aqueous Solubility
Methylethanoate	74	57	moderate
1-Butanol	74	118	complete
Propanoic Acid	74	141	complete
Ethanoic Acid	60	118	complete

Table 11.4.4 Comparison of Ester Properties

Ethanoic acid was included in this table to compare only to methylethanoate.

If the acidic hydrogen of a carboxylic acid is replaced with a methyl group through esterification, the boiling point goes down while the molar mass goes up. Hydrogen bonding is no longer possible.

Once again, the effect of the dipole-dipole interaction of hydrogen bonding on boiling points and solubilities is reaffirmed.

Reactions of Esters

The *acid hydrolysis* of an ester is merely the *reverse reaction* of the esterification of a carboxylic acid as shown above.

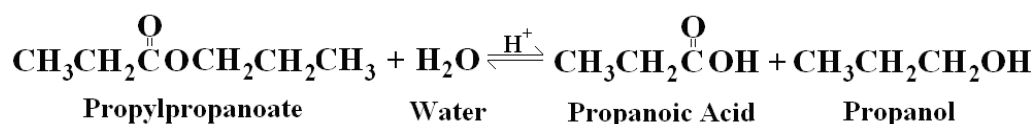


Figure 11.4.8 Acid Hydrolysis of an Ester

The **base hydrolysis** of an ester is analogous to the neutralization of a carboxylic acid (both reactions for a metal ion ester). The base hydrolysis forms an alcohol rather than a water as in the neutralization of a carboxylic acid.

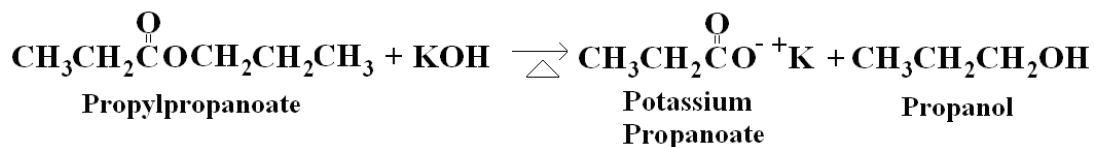


Figure 11.4.9 Base Hydrolysis of an Ester

Amines

Amines are organic derivatives of ammonia in the same way as alcohols and ethers are organic derivatives of water.

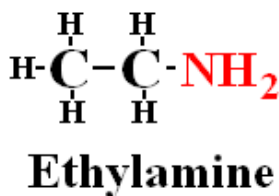


Figure 11.4.10

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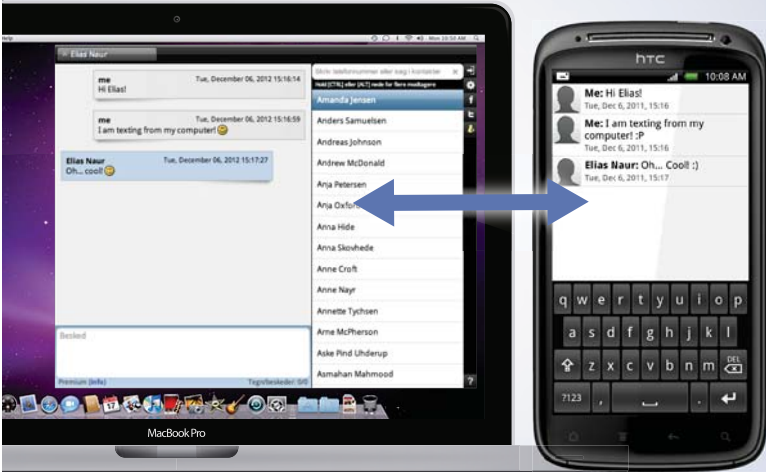
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One distinction of amines is that whether one or all of the ammoniacal hydrogens are replaced with organic substituents the compound is still an amine.

Amines are characterized by the number of carbon atoms attached to the nitrogen atom as follows.

One carbon atom attached makes a *primary amine*.

Two carbon atoms attached make a *secondary amine*.

Three carbon atoms attached makes a *tertiary amine*.

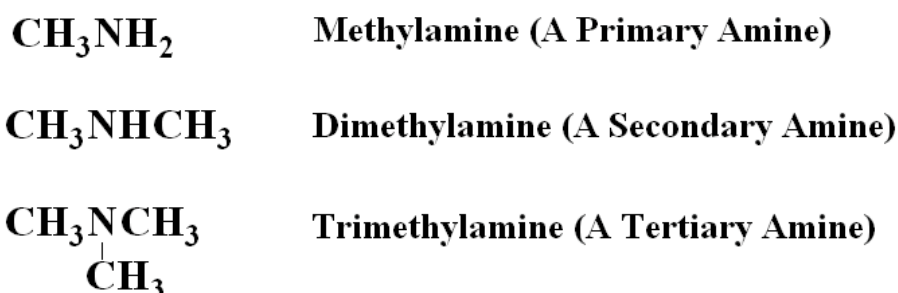


Figure 11.4.11 Primary (1°), Secondary (2°), and Tertiary (3°) Amines

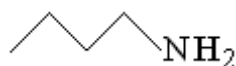
Naming Amines

- 1) Everything attached to the nitrogen is named as a substituent.
- 2) A carbon connected to a nitrogen is carbon #1. Name and number substituents “to a substituent” in reference to the #1 carbon.
- 3) The prefixes *di* and *tri* are used to identify two or three identical groups attached to the nitrogen.
- 4) IUPAC specifies that the amine of benzene is named *aniline*.
- 5) Substituents to the nitrogen of an amine are prefaced with *N*.

The following exercises are for naming amines.

Exercise 11.4.13

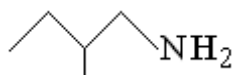
Name this amine compound.



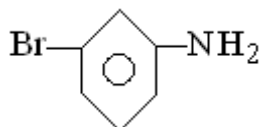
Butylamine

Exercise 11.4.14

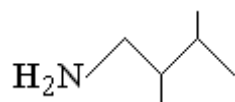
Name this amine compound.

***2-Methylbutylamine*****Exercise 11.4.15**

Name this amine compound.

***3-Bromoaniline*****Exercise 11.4.15**

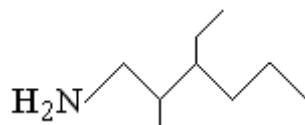
Name this amine compound.

***2,3-Dimethylbutylamine***

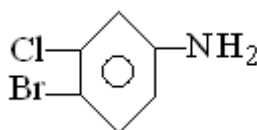
The following exercises are for the drawing of amines.

Exercise 11.4.16

Draw 3-Ethyl-2-methylhexylamine.

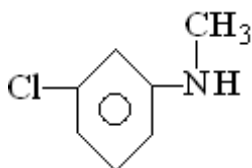
**Exercise 11.4.17**

Draw 4-Bromo-3-chloroaniline.

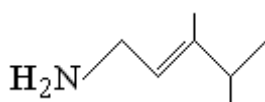


Exercise 11.4.18

Draw N-Methyl-3-chloroaniline.

**Exercise 11.4.19**

Draw 3,4-Dimethyl-2-pentenylamine.

**Properties of Amines**

Amines have **higher boiling points** than hydrocarbons of similar mass since the polar N-H bond facilitates hydrogen bonding.

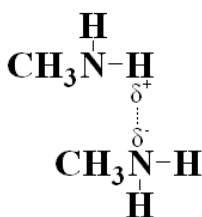


Figure 11.4.12 Hydrogen Bonding in Amines

Of course hydrogen bonding cannot occur in tertiary amines since there are no N-H bonds.

There is another consideration, besides hydrogen bonding, that effects the boiling points of organic molecules.

When organic molecules lay next to one another, it is less likely that intermolecular forces will hold them together the more they are branched. This effect is known as **steric hindrance**.

Observe the boiling points of the three amines in Figure 11.4.13. Note that each of these amines has the empirical formula $C_4H_{11}N$.



n-Butylamine (1°) bp = 78°C



N-Methylpropylamine (2°) bp = 62°C



N,N-Dimethylethylamine (3°) bp = 36°C

Figure 11.4.13 Steric Hindrance Effects on the Boiling Points of Amines

Due to the hydrogen bonding in amines they are more *water soluble* than similar weight compounds that are incapable of hydrogen bonding.

If there are more than six carbons in the amine molecule, the alkyl portion of the molecule will diminish the water solubility afforded by the hydrogen bonding.

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Amines act as *Lewis bases* in that they donate an electron pair. In Figure 11.4.14 the dimethylamine donates its electron pair to form the dimethylammonium ion and a hydroxide ion.

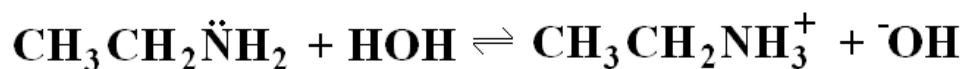
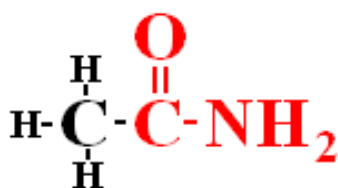


Figure 11.4.14 Dimethylamine as a Lewis Base

Amides

Amides are characterized by a carbon atom and an amine group attached to the carbonyl carbon.



Ethanamide (Acetamide)

Figure 11.4.15 Ethanamide

The same primary, secondary, and tertiary considerations of amines apply to amides.

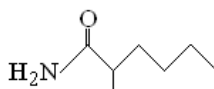
Naming Amides

- 1) Drop the -ic acid or -oic acid from the carboxylic acid name and add the suffix *amide*.
- 2) Name and number the amide from the carboxylic carbon.
- 3) IUPAC specifies that the amide of benzene is named *benzamide*.
- 4) Name and number substituents on any ringed amide starting from the carbon connected to the carbonyl carbon.
- 5) Substituents to the amide nitrogen are preceded by *N*.

The following exercises are for the naming and drawing amides.

Exercise 11.4.20

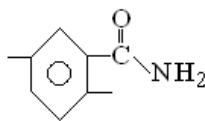
Name this amide compound.



2-Methylhexanamide

Exercise 11.4.21

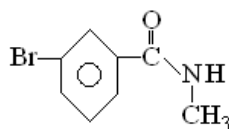
Name this amide compound.



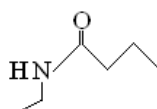
2,5-Dimethylbenzamide

Exercise 11.4.22

Draw N-Methyl-3-bromobenzamide.

**Exercise 11.4.23**

Draw N-Ethylbutanamide.

**Properties of Amides**

Amides *do not have the basic* properties of amines. Only methanamide is liquid at room temperature.

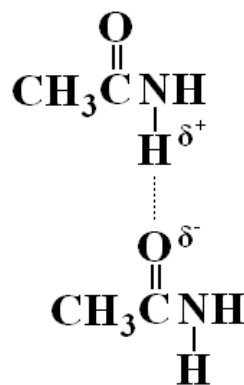


Figure 11.4.16 Hydrogen Bonding in Amides

Primary amides have higher *melting points* than the other amides due to the ability of an amide molecule to hydrogen bond with other amide molecules. Note that this an example of *polymerization* in a hydrocarbon.

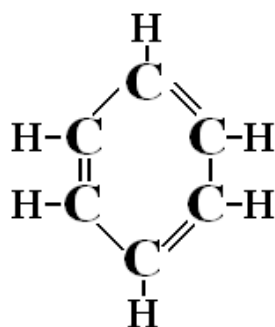
The bond in this polymer formation is called an *amide link* by a chemist and a *peptide link* by a biochemist or biologist. The two terms are entirely synonymous.

11.5 The Concept of Aromaticity

Aromaticity is the occurrence of delocalization of what appears to be a conjugated system of π electrons in a cyclic structure. The cyclic structure will be more stable than what could be normally attributed to conjugation alone.

Aromatics

Aromatics are compounds consisting of one or more six carbon rings that contain systems of conjugated π -bond electrons.



Benzene

Figure 11.5.1 An Aromatic Molecule

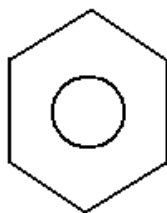
In Figure 11.5.1, benzene appears to have three double bonds for a total of six π electrons.

The structure shown for benzene was “envisioned” by the German organic chemist Friedrich August Kekule von Stradonitz in the late 1800s.

With modern analytical techniques, capable of mapping electrostatic charges, it was determined that the Kekule structure was not entirely correct.

The extra electrons shown in the double bonds of the Kekule structure are actually π electrons existing as a **cloud** of π electrons around the benzene ring.

Figure 11.5.2 shows a modified representation of the benzene molecule using a circle inside the ring to represent the cloud of π electrons.



Benzene

Figure 11.5.2 A Simplified Aromatic Ring Structure

Even though this structure is a more “honest” representation of the simplest aromatic molecule, most drawings of aromatic molecules that you will see in chemical literature still use the Kekule structure.

Aromatic Nomenclature

The benzene molecule is a perfectly symmetrical molecule. For this reason the number one carbon is not established until a substituent is added to the ring.

The IUPAC name for the six-member aromatic ring is *benzene*.

All nomenclature rules you have learned so far still apply to aromatic molecules.

The following exercises will illustrate the ease of naming and drawing aromatic compounds.



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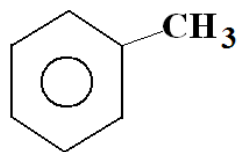
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Exercise 11.5.1

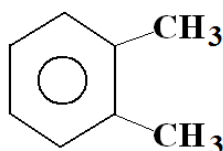
Name the aromatic compound.



Methylbenzene (aka. toluene)

Exercise 11.5.2

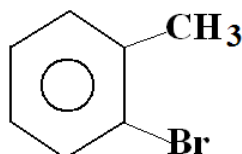
Name the aromatic compound.



1,2-Dimethylbenzene (Note that either of the substituted carbons can be the number one carbon.)

Exercise 11.5.3

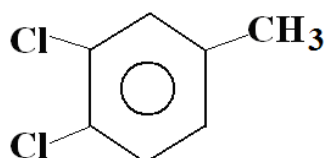
Name the aromatic compound.



1-Bromo-2-methylbenzene (The carbon with the Br must be number one due to alphabetical consideration.)

Exercise 11.5.4

Draw *1,2-Dichloro-4-methylbenzene*.

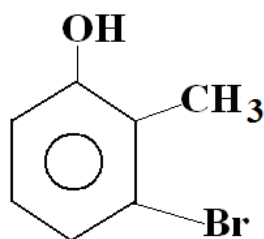


Here only the bottom carbon with an attached chlorine can be the number one carbon to allow the methyl group to be attached to the number four carbon.

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Exercise 11.5.5

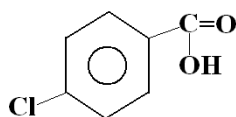
Draw *3-Bromo-2-methylphenol*.



IUPAC states that this compound must be named as a phenol. Therefore, the carbon attached to the alcohol group is automatically designated as the number one carbon.

Exercise 11.5.6

Draw *4-Chlorobenzoic acid*.



IUPAC states that this compound must be named as a benzoic acid. Therefore, the carbon attached to the carbonyl is automatically the number one carbon.

11.6 The Concepts of Saturation and Unsaturation

Everyone has heard the term *saturated fat*. So what does the term saturation or unsaturation mean? First, one must understand what a point of unsaturation in an organic molecule actually means.

Remembering the fact that the term *hydrocarbon* means a compound made up of, at least, hydrogen and carbon and that each carbon in a neutral hydrocarbon molecule must always be bonded four times.

The degree of unsaturation in an organic molecule, as compared to a completely saturated analog, then becomes an accounting of the overall amount of hydrogen attached to that molecule.

If you recall when we studied the pure hydrocarbons at the beginning of this chapter, I gave you a general formula for each of the pure hydrocarbon families.

Table 11.6.1 is a recap of those general formulae.




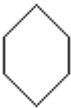
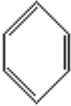
Family Name	Compound Name	Structure	General Formula
Alkane	n-Hexane		$C_n H_{2n+2}$
Alkene	2-Hexene		$C_n H_{2n}$
Alkyne	2-Hexyne		$C_n H_{2n-2}$
Cycloalkane	Cyclohexane		$C_n H_{2n}$
Aromatic	Benzene		$C_n H_{2n-6m}^*$

Table 11.6.1 General Formulae for Pure Hydrocarbons

* The "m" in the general formula for aromatics signifies the number of rings in the aromatic compound.

The drawings in table 11.6.1 are hydrogen suppressed graphical representations of each compound.

Using the general formulae for each compound we should be able to calculate the number of hydrogens for each compound.

The n-hexane compound has six carbons so its actual formula should be $C_6 H_{(2 \times 6) + 2}$ which is $C_6 H_{14}$.

Looking at the hydrogen suppressed graphical drawing of n-hexane and remembering the tetravalent nature of carbon it should be obvious that the two terminal carbons are CH_3 groups and the four internal carbons are CH_2 groups. This adds up to 14 hydrogens or $C_6 H_{14}$. The utility of a general formula is that, in this case, every member of the alkane family will adhere to the $C_n H_{2n+2}$ general formula. So the general formula for alkanes *mathematically describes* the entire alkane family of compounds.

The alkene and cycloalkane families each have the general formula $C_n H_{2n}$. Simple arithmetic reveals that alkenes and cycloalkanes each have *two fewer hydrogens* than their alkane analogs.

The 2-hexene compound has two fewer hydrogens than the n-hexane compound because of the presence of a double bond.

The cyclohexane compound has two fewer hydrogens than the n-hexane compound because of the presence of a ringed structure.

Both the 2-hexene compound and the cyclohexane compound are then said to have **one point of unsaturation**. In each case this is in comparison to the **fully saturated** n-hexane molecule.

It is well established that points of unsaturation are an accounting system of hydrogen in organic compounds where each point of unsaturation represents **two hydrogens**. The summation of all this is a very simple formula.

Points of Unsaturation = # Double Bonds + # Rings



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12 Complex Organic Molecules

12.1 Carbohydrates: Sugars to Polysaccharides

Carbohydrates were originally thought to be a hydrated form of carbon. Early researchers were able to arrive at an empirical formula of $C_6H_{12}O_6$ for common glucose. They then interpreted this to be in the form of $C_6(H_2O)_6$.

Even though the true structures of sugars and other carbohydrates are known, the term carbohydrate is still used.

Types of Carbohydrates

There are three basic types of carbohydrates:

- 1) Monosaccharides: The basic $C_6H_{12}O_6$ unit.
- 2) Disaccharides: Two monosaccharide units.
- 3) Polysaccharides: Many monosaccharide units.

Monosaccharides

There are two basic monosaccharide structures.

Aldose:

The carbonyl group is on the first carbon to form an aldehyde (-CHO) group.

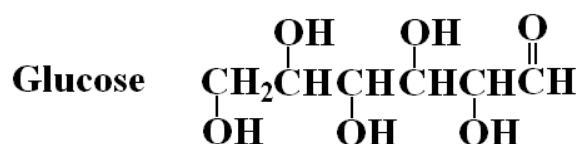


Figure 12.1.1 Glucose

Glucose is an *aldose* monosaccharide.

Ketose:

The carbonyl carbon is on the second carbon to form a ketone (-CO) group.

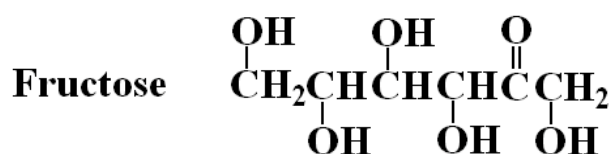


Figure 12.1.2

Fructose is *ketose* monosaccharide.

Fischer Projections of Monosaccharides

It actually matters which side of the fifth carbon of the fructose or glucose molecule that the -OH group is attached.

If a carbon atom in an organic molecule can have four distinctly different groups attached to it, it is said to be a *chiral* atom.

Chirality is a notion of left or right handedness in a molecule. Any organic compound that has a chiral center will have left and right handed molecules known as stereoisomers.

Looking at the drawing of glucose in Figure 12.1.1, it appears that the fifth carbon (actually second from the right) has the following four distinct groups attached: A hydrogen, -OH, CH₂OH, and the rest of the molecule. Therefore, carbon five is chiral.

It is difficult to tell left from right in the above drawings. If you draw glucose from Figure 12.1.1 vertically with the aldehyde at the top, the fifth carbon will be second from the bottom.

This vertical drawing is known as a *Fischer projection*. If the -OH group on carbon number five is on the right, the stereoisomer is known as D-glucose. If the -OH group is on the left, the stereoisomer is known as L-glucose.

D and L are simply the first letters of the Latin words for right and left *dextro* and *levo*.

Figure 12.1.3 compares the D and L stereoisomers of glucose.

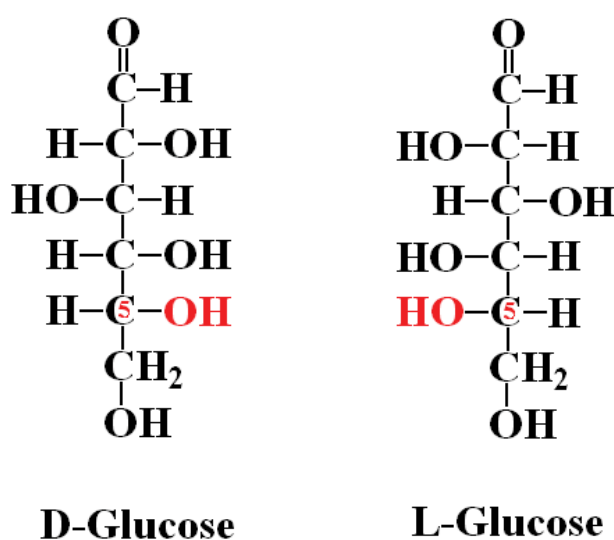


Figure 12.1.3 D and L Stereoisomers of Glucose

The D stereoisomers of glucose, fructose, and galactose (another monosaccharide) are more prevalent in nature and more easily used by the body.

Ring Structures of Monosaccharides

So far the monosaccharides listed have been described as open chained molecules.

The carbonyl group of a particular monosaccharide can react with an alcohol group in the same molecule to form a ring structure.

Figure 12.1.4 shows the comparison of the open chained structure and the ring structure of D-glucose.

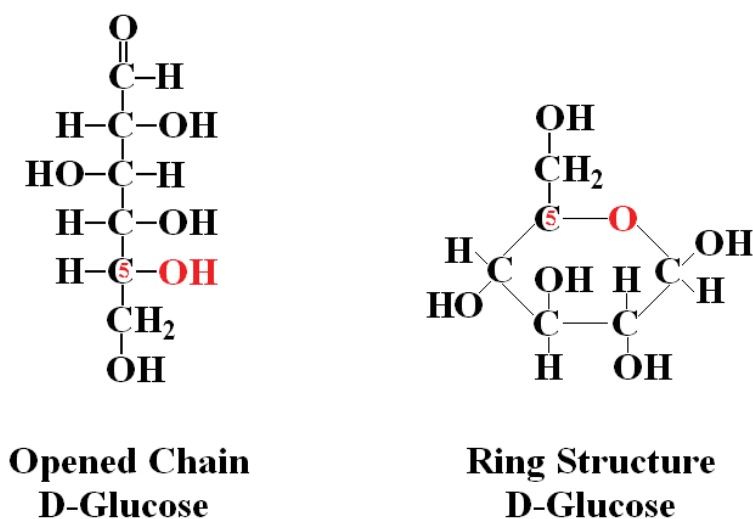


Figure 12.1.4 Opened Chain and Ring Structure for D-Glucose

It should be noted here that the chemical formula for the ring structure of D-glucose is still $C_6H_{12}O_6$. There is no additional point of unsaturation in the ring structure. The double bond of the carbonyl carbon in the open chained structure was sacrificed for a single ring.

Haworth Structures of Monosaccharides

The number one carbon in the ring structure of D-glucose has been rendered *chiral*. In order to distinguish whether the -OH group on that carbon is *pointing downward* (α) or *pointing upward* (β) we embrace the Haworth structures.

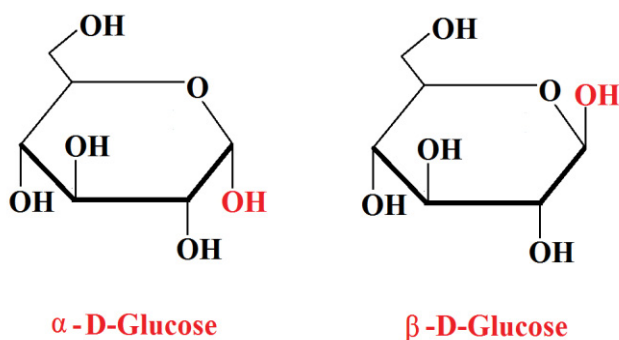


Figure 12.1.5 Hawthorn Structures of D-Glucose

The oxygen atom in the ring is still attached to the number five carbon. It is still on the right hand side of the number five carbon which establishes it as D-glucose.

Disaccharides

α -Maltose

When the 1 and 4 position alcohols on two α -D-glucose molecules bond in a downward (α) position, α -maltose is formed.

Figure 12.1.6 shows the formation of α -maltose from two α -D-glucose molecules.

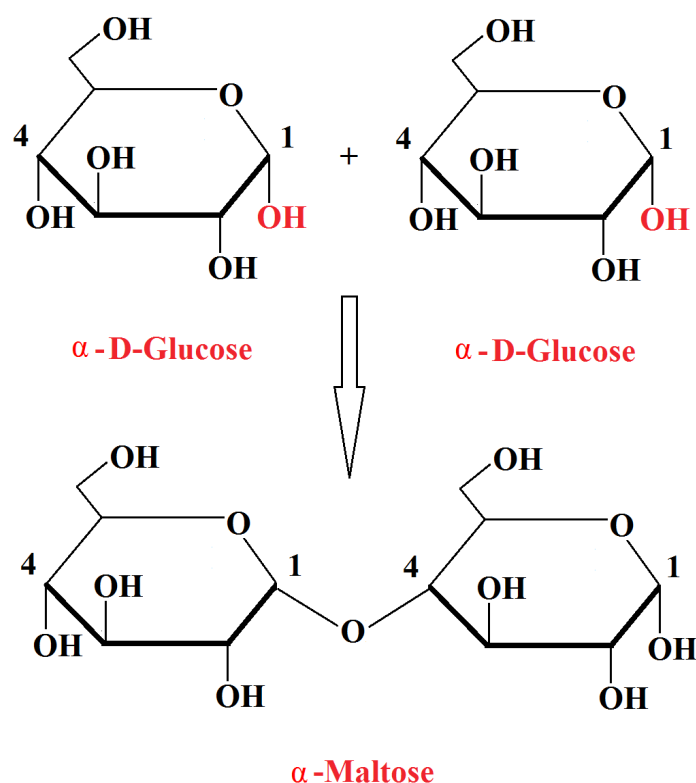


Figure 12.1.6 Formation of α -Maltose

The bond between the two rings is in a downward or α position between the number one carbon on one of the α -D-glucose rings and the number four carbon on the other α -D-glucose ring. Therefore, it is an **α -1,4-glycosidic bond**.

α -Lactose

When the 1 position alcohol of β -D-galactose and the 4 position alcohol of α -D-glucose bond in an upward (β) position, α -lactose is formed.

Figure 12.1.7 shows the formation of α -lactose.

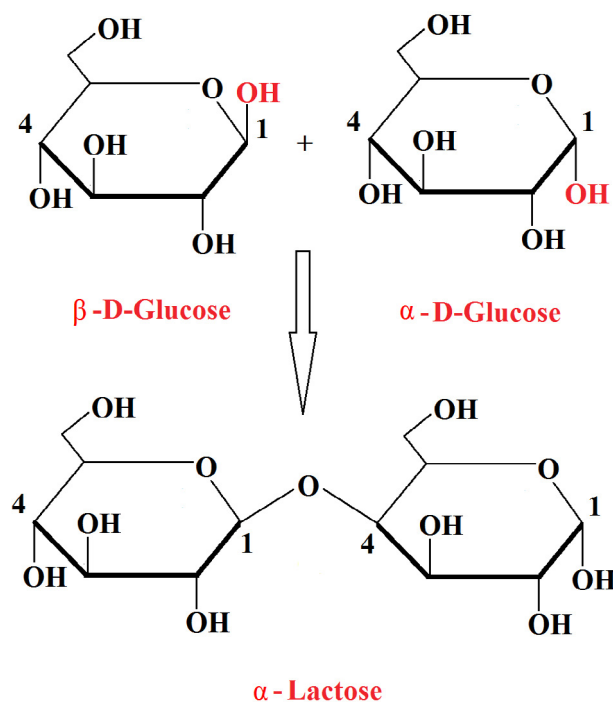


Figure 12.1.7 Formation of α -Lactose

It is the -OH closest to the (previously) carbonyl oxygen that determines α , β orientation. Note the **β -1,4-glycosidic bond**.

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Sucrose

When the 1 position alcohol in α -D-glucose and the 2 position alcohol in β -D-fructose are joined by an α,β -glycosidic bond, sucrose is formed.

Figure 12.1.8 shows the formation of sucrose.

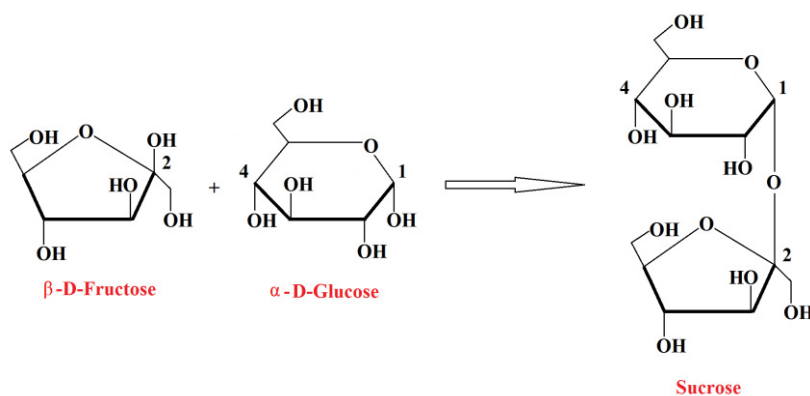


Figure 12.1.8 Formation of Sucrose

Note that where the oxygen connects the two monosaccharides is a **α,β -1,2-glycosidic bond**. Sucrose is a nonreducing sugar since its glycosidic bond cannot open to an aldehyde.

Polysaccharides

Polysaccharides can be viewed as polymers of many monosaccharides bonded together. The position of their glycosidic bonds can result in profound differences between molecules.

Four biologically important polysaccharides are *amylose*, *amylopectin*, *cellulose*, and *glycogen*.

Starch is composed of about 20% *amylose* and about 80% *amylopectin*. Both of these polysaccharides are characterized by **α -1,4-glycosidic** bonds.

Figure 12.1.9 shows an unbranched chain of amylose.

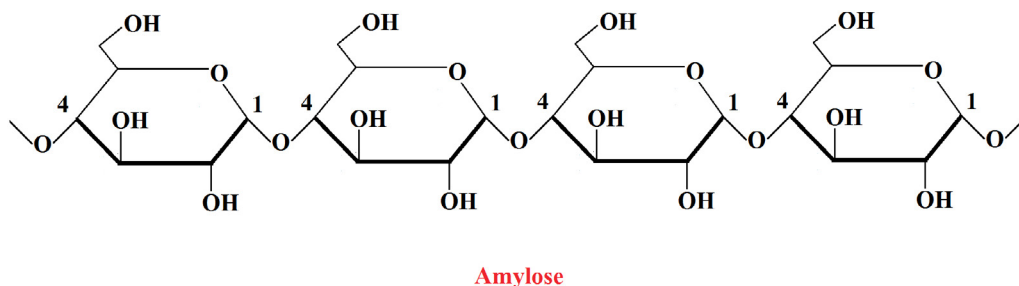
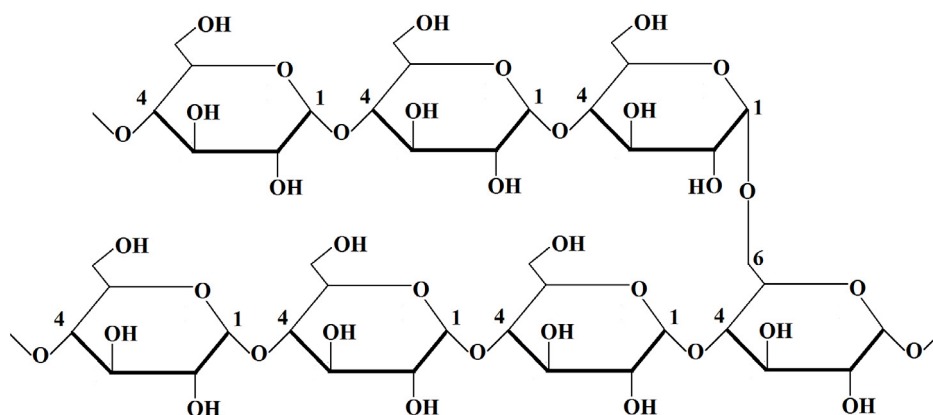


Figure 12.1.9 An Unbranched Chain of Amylose

Note that each pair of monosaccharides are bonded between position 1 and 4 carbons in a downward direction. This establishes the 1,4- α -glycosidic bonds.

Figure 12.1.10 shows a branched chain of amylopectin.



Amylopectin

Figure 12.1.10 A Branched Chain of Amylopectin

Take note of the 1,6- α -glycosidic bond that connects the branched parts of the amylopectin.

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12.2 Carbohydrates: Cellulose and Glycogen

Cellulose

Cellulose is a polymer of glucose characterized by **β -1,4-glycosidic bonds**.

Cellulose is the principle structural material in plants such as the wooden or leafy portions of the plant. Cotton is nearly pure cellulose.

Figure 12.2.1 shows unbranched cellulose with its β -1,4-glycosidic bonds.

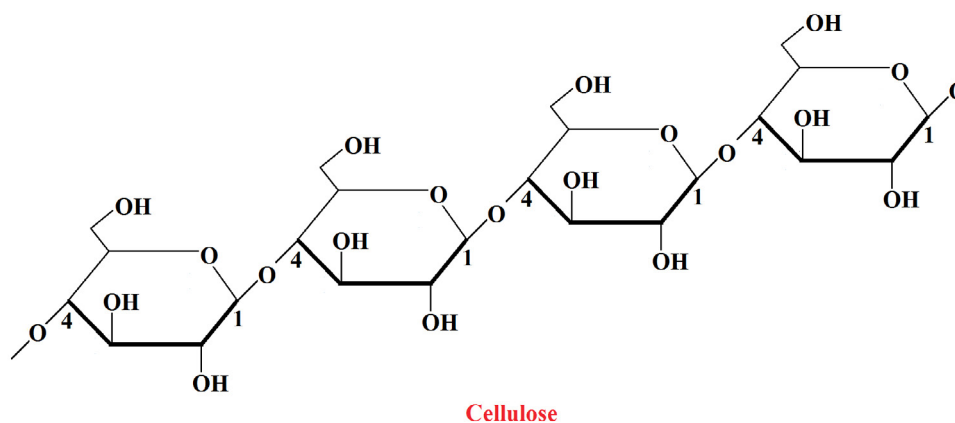


Figure 12.2.1 A Branched Cellulose Chain

Glycogen

Glycogen, also a polymer of glucose, is characterized by **α -1,4-glycosidic bonds**.

Glycogen, or animal starch, is stored in the muscles and liver of animals. Glycogen is hydrolyzed in the cells to help maintain blood glucose levels

Figure 12.2.2 shows an unbranched glycogen chain.

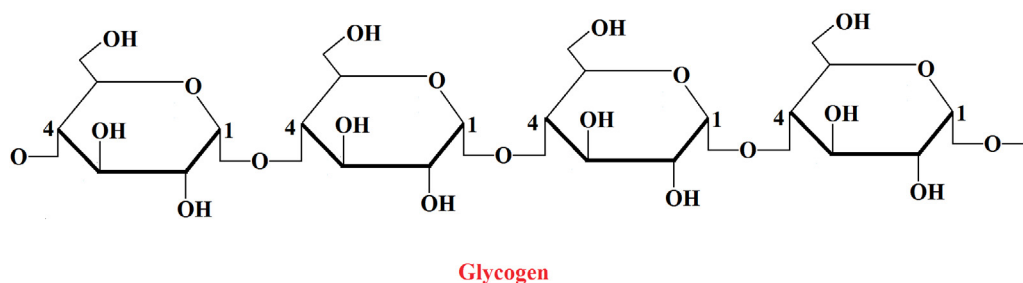


Figure 12.2.2 An Unbranched Glycogen Chain

12.3 Lipids: Fatty Acids and Waxes

Lipids

Lipids are a family of biomolecules that are insoluble in water and soluble in organic solvents.

The different types of lipids are characterized in the organizational chart in Figure 12.3.1.

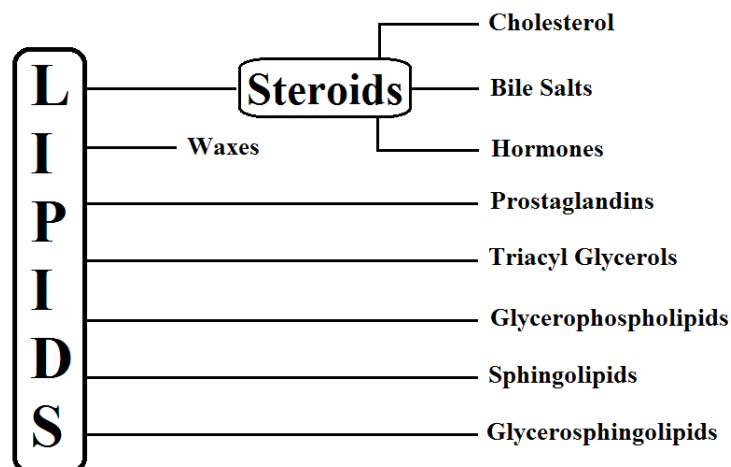


Figure 12.3.1 Lipids

Fatty Acids

The simplest of lipids, fatty acids, are comprised of long unbranched carbon chains terminating in a carboxylic acid groups.

Table 12.3.1 shows some common saturated fatty acids. The trivial and IUPAC names for each fatty acid is listed. The carbon number, common source, melting point, and graphical drawing is listed for each fatty acid.

Trivial Name	IUPAC Name	C#	Common Source	mp °C	Graphical Drawing
Capric Acid	Decanoic Acid	10	Coconut	32	
Lauric Acid	Dodecanoic Acid	12	Coconut	43	
Myristic Acid	Tetradecanoic Acid	14	Nutmeg	54	
Palmitic Acid	Hexadecanoic Acid	16	Palm	63	
Stearic Acid	Octadecanoic Acid	18	Animal	70	

Table 12.3.1 Saturated Fatty Acids

Monounsaturated fatty acids (MUFA) are those containing one carbon to carbon double bond.

Table 12.3.2 shows two common monounsaturated fatty acids.


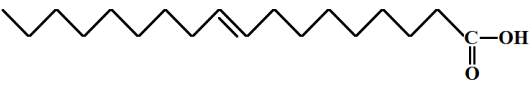
Trivial Name	IUPAC Name	Source	MP °C	Graphical Drawing
Palmitoleic Acid	9-Hexadeceneoic Acid	Butter	0	
Oleic Acid	9-Octadeceneoic Acid	Olive	43	

Table 12.3.2 Monounsaturated Fatty Acids

Polyunsaturated fatty acids are fatty acids with two or more carbon to carbon double bonds.

Table 12.3.3 show polyunsaturated fatty acids of contemporary interest.

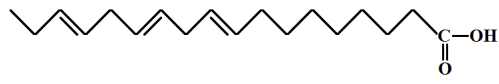
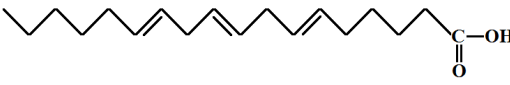
Trivial Name	IUPAC Name	Type	C#	Graphical Drawing
Alpha-Linolenic Acid	<i>all-cis</i> 9,12,15 Octadecatrienoic Acid	Omega-3	18	
Gamma-Linolenic Acid	<i>all-cis</i> 6,9,12 Octadecatrienoic Acid	Omega-6	18	

Table 12.3.3 Polyunsaturated Fatty Acids

The fatty acids in Table 12.3.3 are depicted by trivial name, IUPAC names, and their drawings. The important thing to note is the *all-cis* part of the IUPAC nomenclature.

Any fatty acid molecule is characterized by a carbonyl (acid group) end and a methylene (CH₃) end. The omega designation is assigned by how many carbons the nearest double bond is from the methylene carbon.

cis and *trans* Isomerization of Fatty Acids

When a carbon to carbon bond contains only one set of sigma electrons, the carbons can rotate freely about the bond. When there are additional pi bonds, as in the case of double bonds, the bond then becomes rigid.

If the bond is rigid it then becomes significant which way the atoms of the molecule are situated around the double bond.

In Figure 12.3.2 the stark difference between the shapes of *cis*-oleic acid and *trans*-oleic acid are shown.

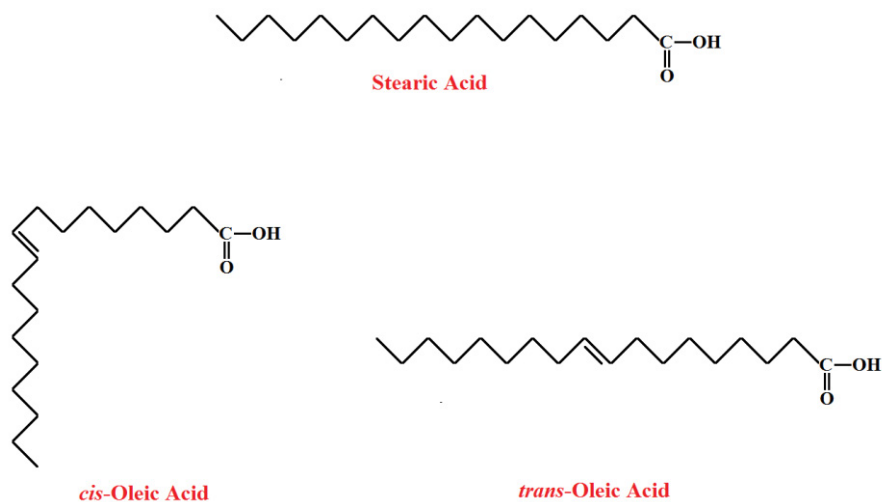


Figure 12.3.2 *cis* and *trans* Isomers of A Fatty Acid

The important thing to note from Figure 12.3.2 is that the *trans*-oleic acid has not been changed in shape from fully saturated analog stearic acid.

The melting point of *trans*-oleic acid is 44.5°C. The melting point of *cis*-oleic acid is 13.4°C.

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This difference is due to what is known as a **steric differences** between the two molecules. Molecules of *trans*-oleic acid can lay close to one another more easily than molecules of *cis*-oleic acid.

Because of this, molecules of *trans*-oleic acid are more prone to be attracted to one another by intermolecular forces and will require more energy to melt and, thus a higher melting point.

Waxes

Most waxes are esters of saturated fatty acids and a long chained alcohol. Paraffin wax is comprised of long chained alkane hydrocarbons ranging from 20 to 40 carbons long.

Table 12.3.4 lists eight waxes in increasing order of melting points and lists the type and source of the waxes.

Wax	Type	Source	mp (°C)
Jojoba Oil	Plant	Jojoba Plant	7–11
Paraffin Wax	Hydrocarbon	Petroleum	37
Lanolin	Animal	Sheep's Wool	38
Spermaceti	Animal	Sperm Whale Oil	50
Beeswax	Animal	Bees	62–64
Candelilla	Plant	Candelilla Plant	69–73
Carnauba Wax	Plant	Brazilian Palm	82–85
Montan Wax	Hydrocarbon	Lignite Coal	82–95

Table 12.3.4 Types and Source of Waxes

12.4 Lipids: Triacylglycerols to Glycerophospholipids

Triacylglycerols: Fats and Oils

Fatty acids are stored in the body as triacylglycerols, also known as triglycerides. These compounds are triesters of glycerol (a trihydroxy alcohol) and fatty acids.

Triacylglycerols have the general formulation shown in Figure 12.4.1.

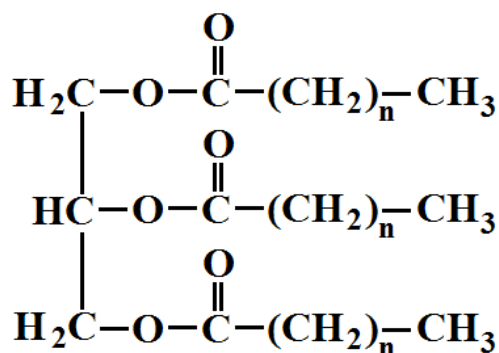


Figure 12.4.1 A Triacylglycerol

In the drawing in Figure 12.4.1 the “n” represent the number of CH_2 groups in the long chain of the fatty acid.

If the value of “n” were 16 in the triacylglycerides in Figure 12.4.1 the triacylglyceride would have been formed from glycerol and three molecules of stearic acid.

Fatty Acid Content of Fats and Oils

A **fat** is a triacylglycerol that is solid at room temperature and usually comes from animal sources. Some examples are lard, butter, and cheese.

An **oil** is a triacylglycerol that is liquid at room temperature and usually comes from plant sources. Some examples are peanut, safflower, and corn oils.

Table 12.4.1 lists saturated fatty acids (SFA), monounsaturated fatty acids (MUFA), polyunsaturated (PUFA) fatty acids content of some common fats and oils in descending order of percent MUFA content.

Fat or Oil	% SFA	% MUFA	% PUFA
Olive	16	76	8
Safflower	12	75	13
Canola	6	62	32
Peanut	18	49	33
Beef Tallow	52	44	4
Soybean	14	40	46
Milk Butterfat	66	30	4
Walnut	13	25	62
Corn	17	24	59
Cottonseed	25	23	52
Palm Kernel	85	13	2
Coconut	91	6	3

Table 12.4.1 Fatty Acid Content of Fats and Oils

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The entries in Table 12.4.1 were listed in descending order of percent MUFA in order to list what this author considers the healthier oils first.

Effects on Melting Points of Fats and Oils

There are two major effects on the melting points of fats and oils. The first effect is the *shape* of the molecule. Notice the difference in the shapes and the melting points of the *cis* and *trans* isomers of oleic acid.

The *cis* isomer is unable to lay in next to other *cis* isomers therefore reducing the effects of intermolecular forces that act to hold *trans* isomers together.

Figure 12.4.2 shows the *cis* and *trans* isomers of oleic acid and their melting points.

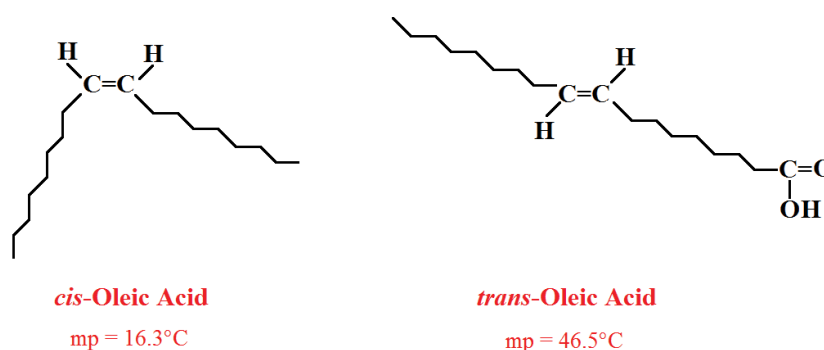


Figure 12.4.2 *cis* and *trans* Isomers of Oleic Acid

Note that the more linear *trans* isomer has the higher melting point.

The second effect is the *degree of saturation* in the fat or oil molecule. Notice the difference in the number of points of unsaturation and melting points of linoleic and stearic acid. Each molecule has the same number of carbon atoms.

Since linoleic acid has four less hydrogens than the stearic there is a pronounced effect on the amount of intermolecular forces and melting points of the two molecules.

Figure 12.4.3 shows the degrees of unsaturation and melting points for linoleic acid and stearic acid.

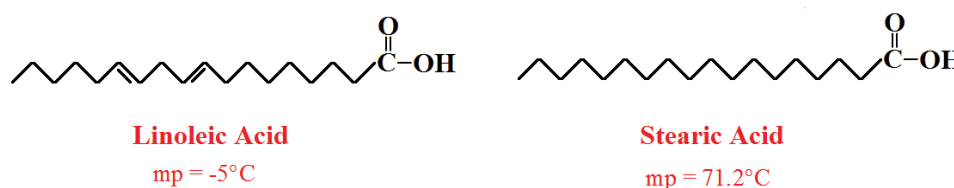


Figure 12.4.3 Linoleic Acid and Stearic Acid

Hydrogenation of Triacylglycerols

The **hydrogenation** of an unsaturated fat is accomplished by bubbling hydrogen gas through the fat in the presence of nickel.

Figure 12.4.4 shows glyceryltriolate being converted to glyceryl tristearate, a totally saturated fat.

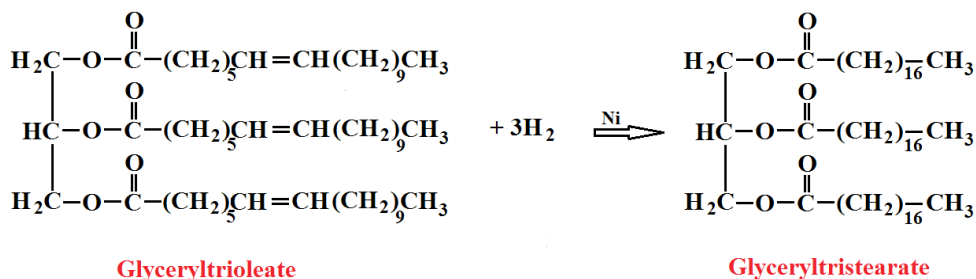


Figure 12.4.4 Hydrogenation of Glyceryltriolate

Hydrolysis of Triacylglycerols

Triacylglycerols are **hydrolyzed** in the presence of strong acids or digestive enzymes called **lipases**. The resulting products are the original glycerol and the three original fatty acids.

Figure 12.4.5 shows the hydrolysis of glyceryl tristearate to glycerol and three stearic acid molecules.

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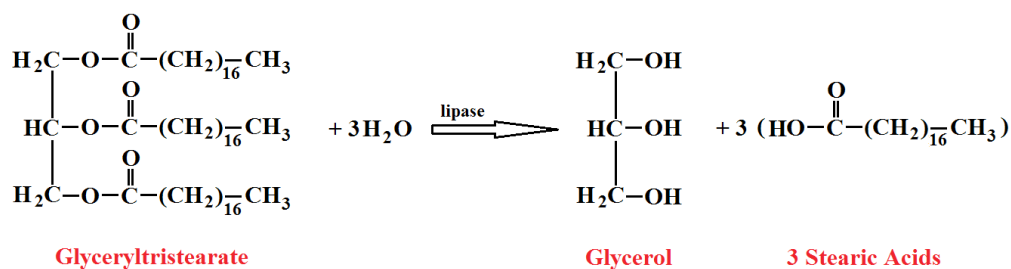


Figure 12.4.5 Hydrolysis of Glyceryltristearate

Saponification

When a fat is heated with a strong base such as sodium hydroxide (NaOH), **saponification** of the fat occurs yielding the original glycerol and three sodium esters of the original three fatty acids or **soap**.

Figure 12.4.6 shows the saponification of glyceryltristearate to glycerol and three sodium stearate molecules.

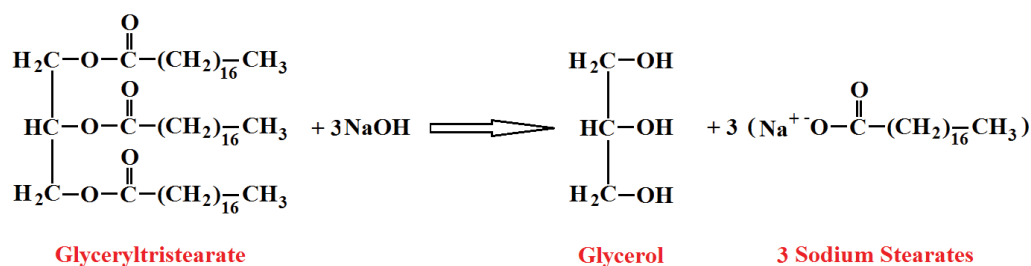


Figure 12.4.6 Saponification of Glyceryltristearate

Properties of Soaps

The soap product in the saponification reaction of Figure 12.4.6 would literally be your great grandparents' "lye soap".

If the sodium hydroxide (NaOH) in the reaction is replaced with potassium hydroxide (KOH) a softer soap would result. Polyunsaturated oils also produce softer soaps.

If you see products such as "coconut or avocado" shampoos, you know the source of the oils used to make the soaps.

Glycerophospholipids

Glycerophospholipids are a family of lipids similar to triacylglycerols except that one of the fatty acid groups on the triacylglycerol has been replaced by the ester of phosphoric acid and an alcoholic amine.

Lecithins and **cephalins** are two types of glycerophospholipids that are abundant in brain and nerve tissue as well as the yolks of eggs. Lecithin contains the alcoholic amine **choline**. Cephalin contains the alcoholic amine **ethanolamine** and sometimes **serine**.

Figure 12.4.7 shows the glycerophospholipids lecithin and cephalin.

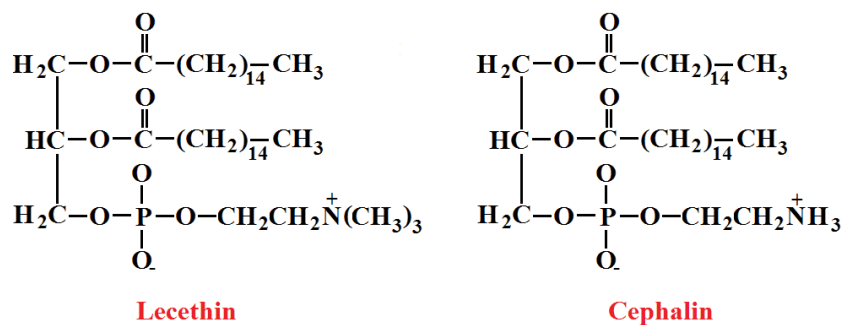


Figure 12.4.7 Lecithin and Cephalin

Biological Properties of Glycerophospholipids

Glycerophospholipids are the most abundant lipids in cell membranes.

Because they have both a polar (the ionized alcohol and phospho group) "head" and a nonpolar (fatty acid) "tail", they are able to "solubilize" the barely water soluble triglycerides and cholesterol and aid in their transport through the body.

Glycerophospholipids make up much of the myelin sheaths that protects nerve cells.

12.5 Steroids

Steroids are compounds comprising the steroid backbone which is composed of three fused cyclohexane rings fused to a cyclopentane ring.

Figure 12.5.1 shows the steroid backbone with the carbon numbering convention as well as individual ring designations.

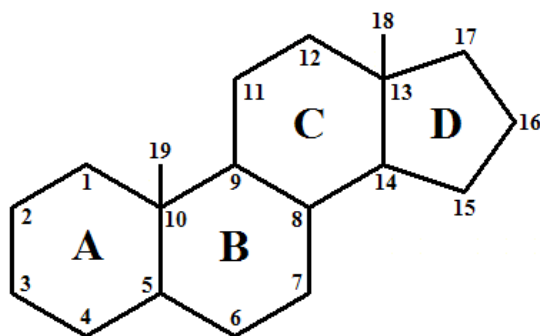
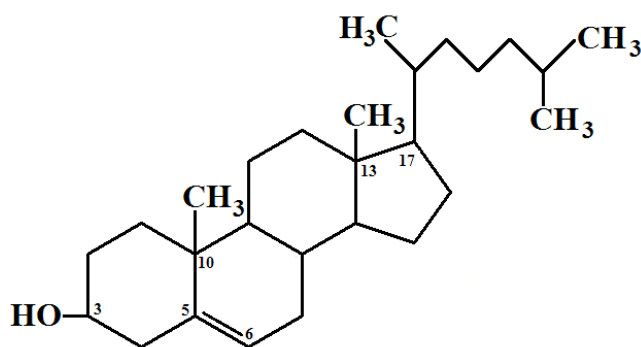


Figure 12.5.1 Steroid Backbone

Cholesterol

Cholesterol is a steroid referred to as a **sterol** due to the alcohol group on carbon 3. The methyl groups on carbons 10 and 13, the double bond between carbons 5 and 6, and the carbon chain on carbon 17 are typical of most steroids.

Figure 12.5.2 shows the cholesterol molecule.



Cholesterol

Figure 12.5.2 Cholesterol



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The Role of Cholesterol in the Body

Cholesterol is a component of cell membranes, myelin sheath, and brain and nerve tissue. It is also found in the liver, bile salts, and skin.

If the diet is high in cholesterol then the liver produces less cholesterol.

The American Heart Association recommends that we consume no more than 300 mg cholesterol per day.

Table 12.5.1 lists some common foodstuffs and their cholesterol content in mg cholesterol per 100 g of the foodstuff.

Foodstuff	mg/100 g Cholesterol
Eggs	1436
Butter	250
Cream Cheese	110
Animal Fat	95
Beef	72
Chicken	64
Whole Milk	11
Skim Milk	4
Fruits	0
Egg Whites	0
Grains	0
Nuts	0

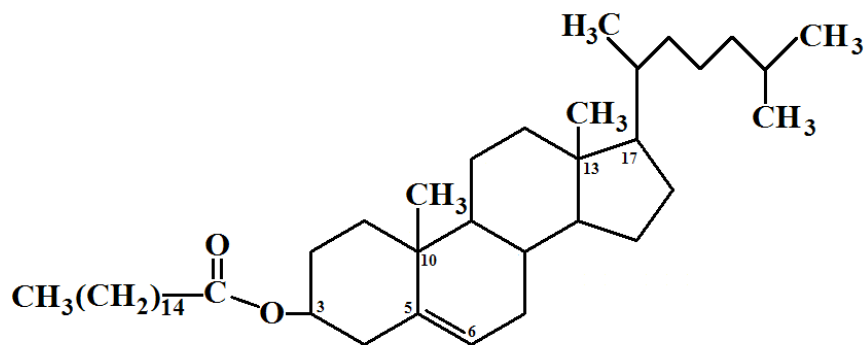
Table 12.5.1 Cholesterol Content of Common Foodstuffs

Lipoproteins

Lipoproteins are spherical particles with a surface of polar proteins and glycerophospholipids surrounding hundreds of nonpolar triacylglycerols and cholesterol esters, the prevalent form of cholesterol in the blood.

Their function in the bloodstream is to **transport lipids** that are nonpolar and insoluble in the aqueous environment of the blood.

Figure 12.5.3 shows the structure of a lipoprotein.

**Lipoprotein****Figure 12.5.3** A Lipoprotein

Take note of the esterification of cholesterol (at carbon #3) that this lipoprotein represents.

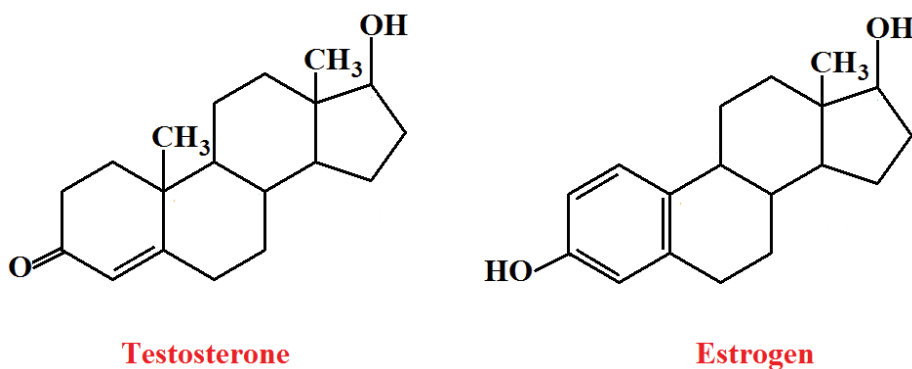
Steroid Hormones

In the body hormones serve as a sort of communication system from one part of the body to another.

Steroid hormones include the sex hormones and adrenocortical hormones.

The sex hormones and adrenocortical hormones are closely related in structure to cholesterol and depend on cholesterol for their synthesis.

Figure 12.5.4 shows the structures of testosterone and estrogen.

**Testosterone****Estrogen****Figure 12.5.4** Testosterone and Estrogen

Notice how the term testosterone reflects the presence of a ketone group in the molecule.

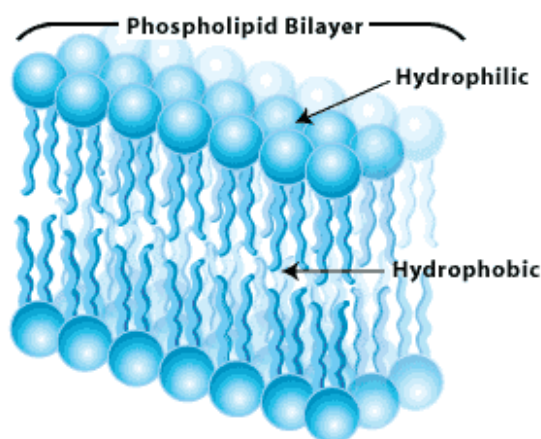
The Lipid Bilayer of Cell Membranes

In a cell membrane two layers of glycerophospholipids are arranged like a sandwich.

Their nonpolar tails (which are *hydrophobic* or “water-fearing”) are aligned to the center of the cell membrane while their polar heads (which are *hydrophilic* or “water-loving”) are aligned to the outside of the cell membrane.

The hydrophobic layer aligns with the nonpolar contents of the cell while the hydrophilic layer aligns with the aqueous environment on the outer surface of the cell membrane in what is known as a *lipid bilayer*.

Figure 12.5.5 shows a cross section of a lipid bilayer.



(1)

Figure 12.5.5 A Lipid Bilayer

13 Basic Biological Chemistry

13.1 Amino Acids and Proteins

If you only remember one thing from this section of Chapter 13, please let it be this:

Proteins are polymers of amino acids.

Amino Acids

An amino acid, surprisingly enough, contains an amine ($-\text{NH}_2$) group and an acid ($-\text{COOH}$) group.

There are a total of 20 amino acids found in human proteins. Each of these proteins have an amine group, an acid group, and a hydrogen attached to the central, or **alpha** (α), carbon. The remaining non-functional, side chain is generally referred to as the **R-group**.

Think of the **R-group** as the **Rest** of the molecule



It is convenient to draw an amino acid as a neutral molecule. However, in aqueous media, they exist as a dipolar ion known as a **zwitterion** as shown in Figure 13.1.1.

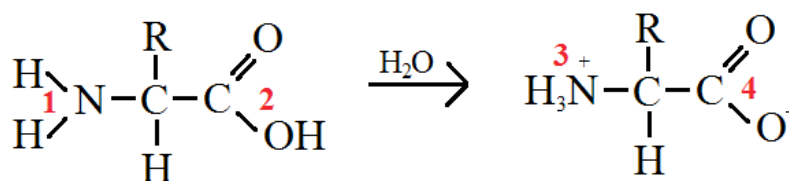


Figure 13.1.1 The General Structure of Amino Acids

The functional portions of the amino acid in Figure 13.1.1 are numbered in red and are as follows:

- 1) Amine group
- 2) Acid group
- 3) Positively charged **ammonium** group
- 4) Negatively charged **carboxylate** group

The molecule on the right in Figure 13.1.1 is the **zwitterion** configuration of an amino acid as it exists in aqueous solution.

Remember, there is not an ammonium or carboxylate **ion** present in the zwitterion of an amino acid – no matter how much there appears to be.

Note that the carbon of the amino acid drawn in Figure 13.1.1 is the **chiral** carbon of the molecule.

In Figure 13.1.2 the R group is defined as a methyl group to represent the amino acid **alanine**.

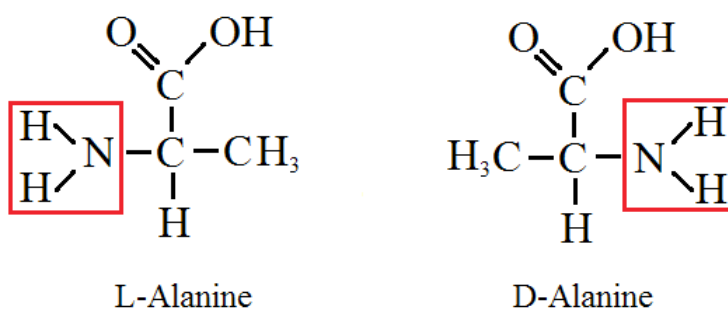


Figure 13.1.2 Stereoisomers of Alanine

Of the twenty amino acids found in proteins all have stereoisomers except the one where the R group is defined as hydrogen. This is the amino acid glycine.

Classifications of Amino Acids

The following tables lists the twenty amino acids found in proteins by their classification, name, symbol, and the structures of their individual R groups. Remember, the drawings in these tables are not amino acids. They are substituent groups for amino acids.

Name	Symbol	R Group Structure
Glycine	Gly	H
Alanine	Ala	CH_3
Valine	Val	$\begin{array}{c} \text{H}_3\text{C} \quad \text{CH}_3 \\ \quad \diagdown \quad / \\ \quad \text{CH} \\ \quad \\ \quad \text{H} \end{array}$
Leucine	Leu	$\begin{array}{c} \text{H}_3\text{C} \quad \text{CH}_3 \\ \quad \diagdown \quad / \\ \quad \text{CH} \\ \quad \\ \quad \text{CH}_2 \end{array}$
Isoleucine	Ile	$\text{H}_3\text{C}-\text{CH}_2\text{CH}_2\text{CH}_3$
Proline	Pro	$\begin{array}{c} \text{H} \quad \text{H} \\ \quad \diagdown \quad / \\ \quad \text{C} \\ \quad / \quad \diagdown \\ \text{H}_2\text{C} \quad \text{CH}_2 \end{array}$
Methionine	Met	$\begin{array}{c} \text{CH}_3 \\ \\ \text{S} \\ \\ \text{CH}_2 \\ \\ \text{CH}_2 \end{array}$

Table 13.1.1 Nonpolar Amino Acids


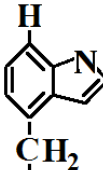
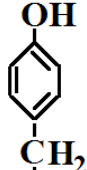
Name	Symbol	R Group Structure
Phenylalanine	Phe	
Tryptophan	Trp	
Tyrosine	Tyr	

Table 13.1.2 Aromatic Amino Acids

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Name	Symbol	R Group Structure
Serine	Ser	$\begin{array}{c} \text{OH} \\ \\ \text{CH}_2 \\ \end{array}$
Threonine	Thr	$\begin{array}{c} \text{CH}_3 \\ \\ \text{H}-\text{C}=\text{O} \\ \end{array}$
Cysteine	Cys	$\begin{array}{c} \text{SH} \\ \\ \text{CH}_2 \\ \end{array}$
Asparagine	Asn	$\begin{array}{c} \text{O} \\ \\ \text{H}_2\text{N}-\text{C} \\ \\ \text{CH}_2 \\ \end{array}$
Glutamine	Gln	$\begin{array}{c} \text{O} \\ \\ \text{H}_2\text{N}-\text{C} \\ \\ \text{CH}_2 \\ \\ \text{CH}_2 \\ \end{array}$

Table 13.1.3 Polar Amino Acids

Name	Symbol	R Group Structure
Aspartic Acid	Asp	$\begin{array}{c} \text{O} \\ \\ \text{C}-\text{OH} \\ \\ \text{CH}_2 \\ \end{array}$
Glutamic Acid	Glu	$\begin{array}{c} \text{O} \\ \\ \text{C}-\text{OH} \\ \\ \text{CH}_2 \\ \\ \text{CH}_2 \\ \end{array}$

Table 13.1.4 Acidic Amino Acids

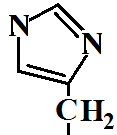
Name	Symbol	R Group Structure
Histidine	His	
Lysine	Lys	$\begin{array}{c} \text{NH}_2 \\ \\ \text{CH}_2 \\ \\ \text{CH}_2 \\ \\ \text{CH}_2 \\ \\ \text{CH}_2 \\ \\ \text{CH}_2 \end{array}$
Arginine	Arg	$\begin{array}{c} \text{NH}_2 \\ \\ \text{C}=\text{NH} \\ \\ \text{NH} \\ \\ \text{CH}_2 \\ \\ \text{CH}_2 \\ \\ \text{CH}_2 \end{array}$

Table 13.1.5 Basic Amino Acids



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Notes: The unattached bond lines in Tables 13.1.1 through 13.1.5 are where the R groups bond to the common amino acid base.

The unattached bond line on the left of the proline R group, in Table 13.1.1, attaches to the N of the amine group of the amino acid structure.

Isoelectric Point

The perfectly balanced charged of the zwitterion shown in Figure 13.1.1 is not the only charge condition that an amino acid can be in.

In fact, the amino acid is only in the perfectly balanced charge state when the solution the amino acid is in has a certain pH that is known as the *isoelectric point (pI)* for that amino acid.

Table 13.1.6 shows the three possible charge conditions for an amino acid in relation to solution pH.

pH vs. pI	Charged Groups Charges	$\Delta[\text{H}^+]$	Amino Acid Charge
pH > pI	$-\text{COO}^-$, $-\text{NH}_2$	↓	1-
pH = pI	$-\text{COO}^-$, NH_3^+	↔	0
pH < pI	$-\text{COOH}$, $-\text{NH}_3^+$	↓	1+

Table 13.1.6 pH vs. pI for Amino Acids

Note: In chemistry the symbol “ Δ ” means “change in” and the symbols [] mean “concentration of”.

Formation of Peptides

The linking of two or more amino acids forms a *peptide*. A peptide has an *amide* bond formed between the $-\text{COO}^-$ group of one amino acid to the $-\text{NH}_3^+$ group of another amino acid. The $-\text{NH}_3^+$ group is called the *N terminal* and the $-\text{COO}^-$ group is called the *C terminal*.



Figure 13.1.3 The Formation of a Peptide

The blue numbered areas in Figure 13.1.3 are significant as follows:

- 1) A positively charged amino group and the N terminal
- 2) A negatively charged carboxylate group and the C terminal
- 3) The formation of a *peptide bond*
- 4) The formation of water in a condensation reaction

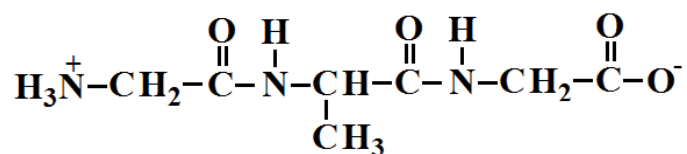
Naming Peptides

The naming of a peptide starts from the N terminal amino acid where the -ine, -an, or -ic on the N terminal, and successive amino acids, is replaced with *-yl* and the C terminal acid's full name is used.

The peptide in Figure 13.1.3 is *glycylglycine* with the shorthand notation (*Gly-Gly*).

Exercise 13.1.1

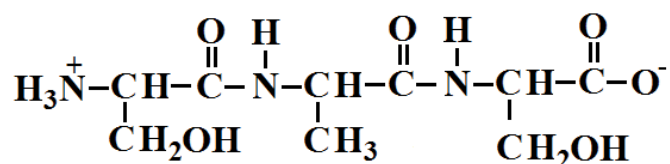
Name the peptide and give its shorthand notation.



Glycylalanylglycine (Gly-Ala-Gly)

Exercise 13.1.2

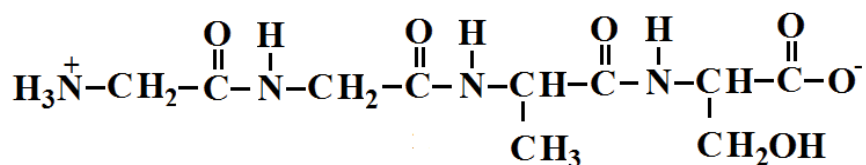
Name the peptide and give its shorthand notation.



Serylalanylserine (Ser-Ala-Ser)

Exercise 13.1.3

Name the peptide and give its shorthand notation.



Glycylglycylalanylserine (Gly-Gly-Ala-Ser)

In the drawings of peptides above it is easy to see the peptide bonds stick up. If you count n peptide bonds then the peptide is constructed of $n + 1$ amino acids. Therefore the name should have $n + 1$ parts.

Levels of Protein Structure

The **primary structure** of a protein is the type of structures we have seen so far. Simply line structures with elemental symbols and bonds. The drawing below is the primary structure of arginylhistidinyllysine (Arg-His-Lys).

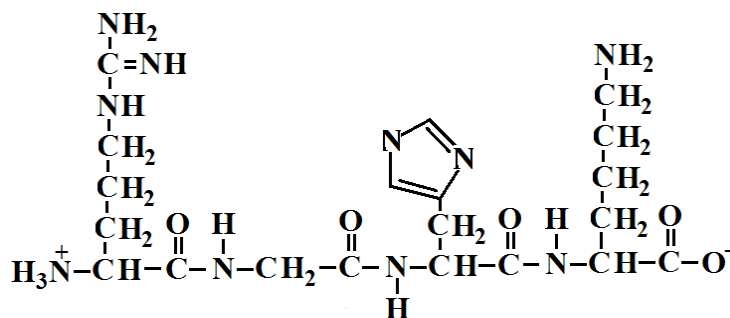


Figure 13.1.4 A Primary Protein Structure

The **secondary structure** of a protein is that structure formed when two proteins are linked to one another through **hydrogen bonding**.

The best example of this intermolecular bonding is the bonds between the two helices in the double helix structure of DNA.

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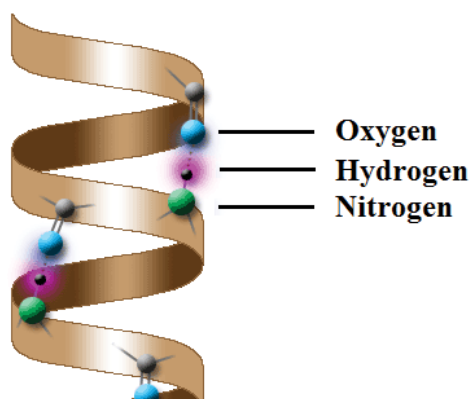
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Figure 13.1.5 shows a representation of a strand of DNA. Hydrogen bonding between a hydrogen on an amine group and an oxygen on a carboxylate group is what holds the two helices of DNA together.

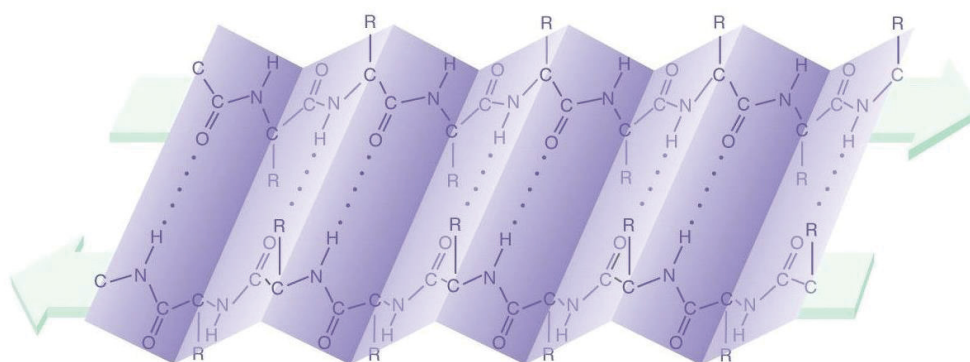


(2)

Figure 13.1.5 A Secondary Protein Structure

The need for a secondary structure is that there is a way to view the structure of a molecule. The helical shape of DNA is evident in Figure 13.1.5.

Figure 13.1.6 shows another secondary structure evident in DNA as the *beta - pleated sheet*.



Beta - Pleated Sheet

(3)

Figure 13.1.6 The Beta - Pleated Sheet

The very long peptide chains of proteins are capable of *intramolecular interactions*, of which hydrogen bonding is only one example.

These interactions along the peptide chain result in a certain three dimensional shape for the protein.

Figure 13.1.7 shows a tertiary form of a protein with four distinct intramolecular interactions.

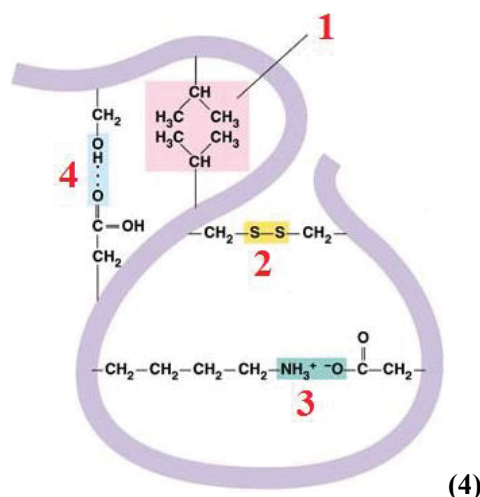


Figure 13.1.7 A Tertiary Protein Structure

The distinctions of the four intramolecular interactions are as follows:

- 1) A hydrophobic (water fearing) reaction resulting in a van der Waals attraction
- 2) A disulfide bond
- 3) An ionic bond
- 4) A hydrogen bond

When a biologically active protein consists of two or more polypeptide subunits, the structural level is referred to as a *quaternary structure*.

Hemoglobin is a globular protein consisting of four polypeptide chains, two α -chains and two β -chains. The subunits are held together by the same interactions that stabilize tertiary protein structures.

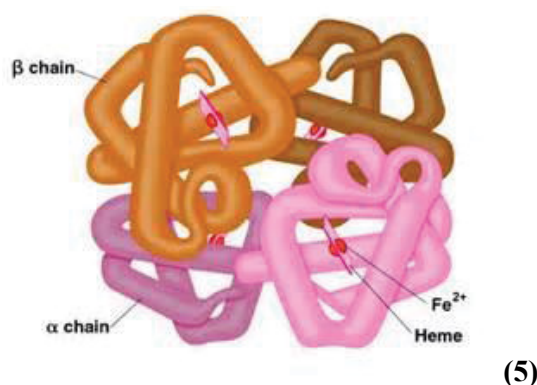


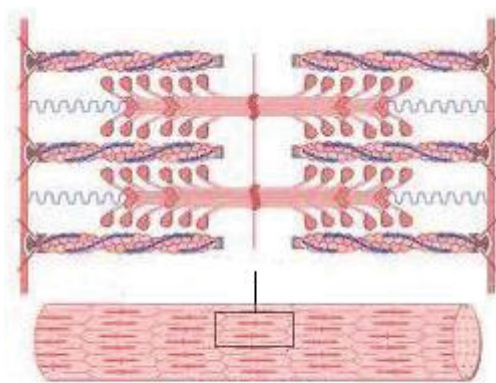
Figure 13.1.8 A Quaternary Protein Structure

Hemoglobin is known as a *globular protein*. Globular proteins are roughly spherical in shape because the peptide chains fold over each other.

Fibrous Proteins

The **fibrous proteins** are proteins that consist of long, thin, fiber-like shapes. The α -keratins are fibrous proteins that make up hair, wool, skin, and nails.

The α -helices of the protein twist together to form **fibrils**. These fibrils twist together to form hair or wool as shown in the figure 13.1.9.



Fibrill

(6)

Figure 13.1.9 Fibrous Protein

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Denaturation of Proteins

Denaturation of proteins occurs when there are disruptions of any of the bonds that establish the secondary, tertiary, or quaternary structures of a protein.

The following list the effects of certain conditions and chemicals on the internal bonds of proteins.

Excessive **heat**, in excess of 50°C, can disrupt hydrogen bonding as well as the hydrophobic attraction between nonpolar side chains.

Acids and **bases** disrupt hydrogen bonding in polar side chains. They can also disrupt the bonding in salt bridges.

Organic compounds can disrupt the hydrophobic interactions between nonpolar side chains.

Heavy metals, such as silver and lead, can disrupt disulfide bonds through the formation of ionic bonds with the sulfur.

13.2 Enzymes

Enzymes are the biological catalysts needed for most of the chemical reactions taking place in the body.

In general they act to lower the activation energy for a particular reaction. Enzymes are named by replacing the end of the reaction or reacting compound with **-ase**.

Figure 13.2.1 shows the lower activation energy for a reaction made possible by the presence of an enzyme catalyst.

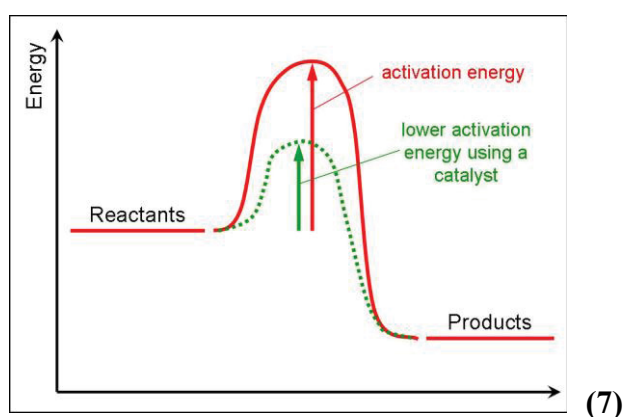
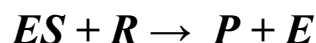
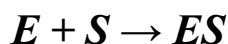


Figure 13.2.1 Enzyme Catalyst

The following is a representation of the basic enzyme catalyzed reaction. An enzyme (E) will form with a substrate (S) to form an enzyme substrate complex (ES). The enzyme substrate (ES) complex will react with reactant (R) to form a product (P) and the enzyme.



Enzyme Action

Nearly all enzymes are globular proteins. Each has a unique shape that recognizes and binds a small group of molecules, called *substrates*.

In this way, the tertiary structure of enzymes play an important role in catalysis reactions.

Figure 13.2.2 is a graphic representation of an enzyme catalyzed reaction.

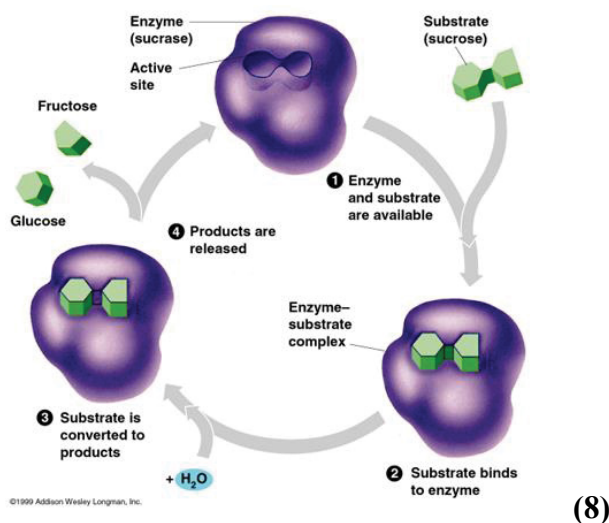


Figure 13.2.2 An Enzyme Catalyzed Reaction

Here *sucrose* is catalytically separated into *fructose* and *glucose* through a *sucrase* catalyzed reaction.

The Induced Fit Model

The positioning of the sucrose molecule onto the sucrose enzyme is what is known as the *lock and key model*; where the sucrose molecule is the key and sucrose enzyme is the lock.

In the theory of the induced fit model it is believed that an active site in the enzyme is able to adjust to better accommodate the reaction.

Figure 13.2.3 is a graphic demonstration of the induced fit model.

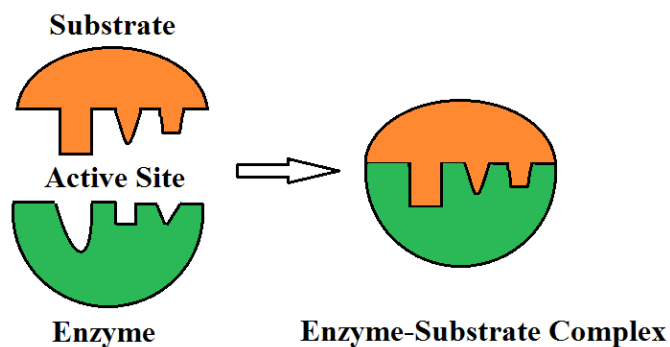


Figure 13.2.3 The Induced Fit Model

Enzyme Inhibitors

Enzyme inhibitors cause enzymes to lose catalytic activity. The two kinds of enzyme inhibitors are the **competitive inhibitor** and the **noncompetitive inhibitor**.

In the Figure 13.2.4, below, a competitive inhibitor is preventing the binding of a substrate.

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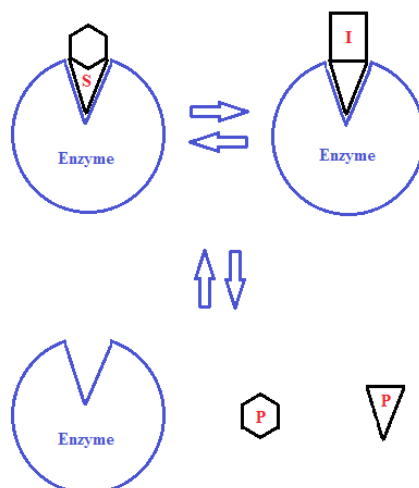


Figure 13.2.4 A Competitive Enzyme Inhibitor

Factors Affecting Enzyme Activity

It should be evident that among the factors affecting the activity of an enzyme are the *concentration of the enzyme*, the *concentration of the substrate*, and the presence of any *enzyme inhibitors*.

Two remaining factors that affect the activity of enzymes are *pH* and *temperature*.

Most enzymes are at optimal activity at 37°C or human body temperature.

The pH for the optimal activities of different enzymes varies widely.

Table 13.2.1 lists the optimal activity pH for some common enzymes.

Enzyme	Optimal pH
Pepsin	1.5–1.6
Lipase (stomach)	4.0–5.0
Invertase	4.5
Amylase (malt)	4.6–5.2
Lipase (castor oil)	4.7
Maltase	6.1–6.8
Amylase (pancreas)	6.7–7.0
Catylase	7.0
Urease	7.0
Trypsin	7.8–8.7
Lipase (pancreas)	8.0

Table 13.2.1 pH for Optimal Enzyme Activity

Enzyme Cofactors

A simple enzyme consists of only proteins. However, many enzymes require small molecules or metal ions, known as **cofactors**, to properly catalyze reactions. The table below lists a series of metal ions used as cofactors. When organic molecules are used as cofactors they are known as **coenzymes**.

Table 13.2.2 lists some metal ions, and vitamins with their enzymes and their functions.

Cofactor	Coenzyme/Enzyme	Function
niacin	nicotinamide adenine dinucleotide (NAD ⁺)	oxidation or hydrogen transfer
riboflavin	flavin adenine dinucleotide (FAD)	oxidation or hydrogen transfer
pantothenic acid	coenzyme A (CoA)	acetyl group carrier
vitamin B-12	coenzyme B-12	transfers methyl groups
vitamin B-1 (thiamin)	thiaminpyrophosphate (TPP)	transfers aldehyde groups
Cu ²⁺	cytochrome oxidase	oxidation-reduction
Fe ²⁺	catalase	oxidation-reduction
Fe ³⁺	cytochrome oxidase	oxidation-reduction
Mg ²⁺	glucose-6 phosphate	phosphate ester hydrolyzation
Mn ²⁺	arginase	electron removal
Ni ²⁺	Urease	amide hydrolyzation

Table 13.2.2 Metal Ions and Vitamins Enzyme Cofactors

13.3 Nucleic Acids: DNA and RNA

Components of Nucleic Acids

Two closely related types of nucleic acids, **deoxyribonucleic acid (DNA)** and **ribonucleic acid (RNA)** are both unbranched polymers of repeating monomer units known as **nucleotides**.

DNA molecules contain up to several million nucleotides and RNA molecules contain several thousand nucleotides. These nucleotides are all made up of a **base**, a **five-carbon sugar**, and a **phosphate group**.

The Five Bases of DNA and RNA

The five bases found in nucleic acids are of two types: pyrimidines and purines. The three pyrimidines used in the construction of nucleic acids are **cytosine**, **thymine**, and **uracil**.

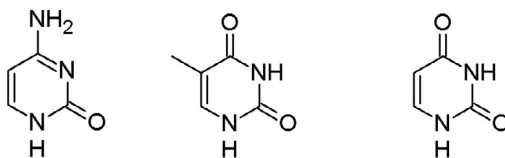
The two purines used in the construction of nucleic acids are **adenine** and **guanine**.

Figure 13.3.1 shows the structures of the five bases used to construct the nucleic acids in DNA and RNA.

It is essential to remember that **thymine is unique to DNA** and **uracil is unique to RNA**.

That is to say, you will never see an RNA molecule containing thymine. Likewise, you will never see a DNA molecule containing uracil.

Pyrimidines

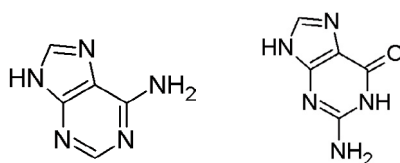


Cytosine

Thymine

Uracil

Purines



Adenine

Guanine

Figure 13.3.1 The Fives Bases of DNA and RNA

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The Two Sugars of DNA and RNA

The two sugars used in the construction of DNA and RNA are deoxyribose and ribose.

Figure 13.3.2 shows the structure of ribose followed by the structure of deoxyribose where there is clearly a hydroxide group missing in comparison to the ribose structure.

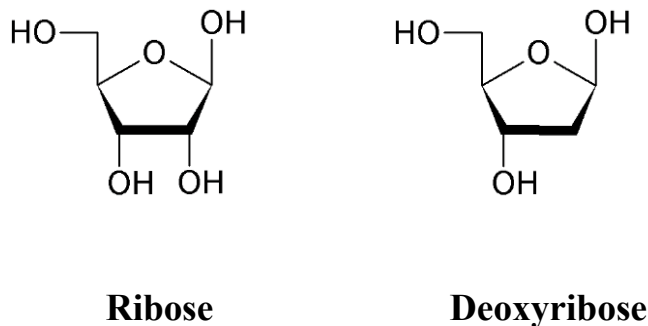


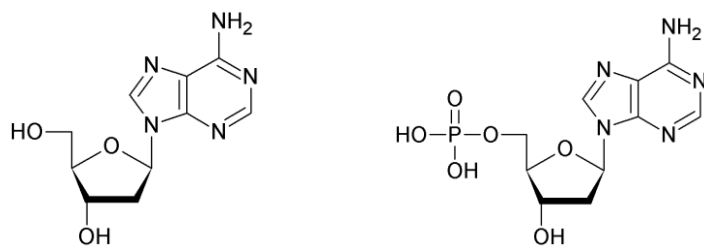
Figure 13.3.2 The Two Sugars of DNA and RNA

Nucleosides and Nucleotides

A **nucleoside** is the term used when a base forms a bond with the C1 carbon in the sugar.

A **nucleotide** is the term used when the nucleoside bonds a phosphate group to the C5 -OH group on the sugar.

The example of each are shown in Figure 13.3.3



A Deoxyribonucleoside

A Deoxyribonucleotide

Figure 13.3.3 A Nucleoside and A Nucleotide

Naming Nucleosides and Nucleotides

Nucleosides and nucleotides containing purine end with **-osine**. Nucleosides and nucleotides containing pyrimidine end with **-ine**. **Deoxy** is added to the front of all DNA nucleosides and nucleotides.

Table 13.3.1 lists the four nucleosides and the four nucleotides of DNA and RNA.

The Bases	The Nucleosides	The Nucleotides
Deoxyribonucleic Acids (DNA)		
Adenine (A)	Deoxyadenosine (A)	Deoxyadenosine 5'-monophosphate (dAMP)
Guanine (G)	Deoxyguanosine (G)	Deoxyguanosine 5'-monophosphate (dGMP)
Cytosine (C)	Deoxycytidine (C)	Deoxycytidine 5'-monophosphate (dCMP)
Thymine (T)	Deoxythymidine (D)	Deoxythymidine 5'-monophosphate (dUMP)
Ribonucleic Acids (RNA)		
Adenine (A)	Adenosine (A)	Adenosine 5'-monophosphate (AMP)
Guanine (G)	Guanosine (G)	Guanosine 5'-monophosphate (GMP)
Cytosine (C)	Cytidine (C)	Cytidine 5'-monophosphate (CMP)
Uracil (U)	Uridine (U)	Uridine 5'-monophosphate (UMP)

Table 13.3.1 Nucleosides and Nucleotides of DNA and RNA

Primary Structure of Nucleic Acids

The nucleic acids consist of polymers of many nucleotides in which the 3'-OH group in the sugar of one nucleotide is bonded, through the phosphate group, to the 5'-carbon atom of the sugar of another nucleotide in what is known as the **phosphodiester bond**.

Figure 13.3.4 shows a phosphodiester bond between adenosine 5'-monophosphate (AMP) and guanosine 5'-monophosphate (GMP).

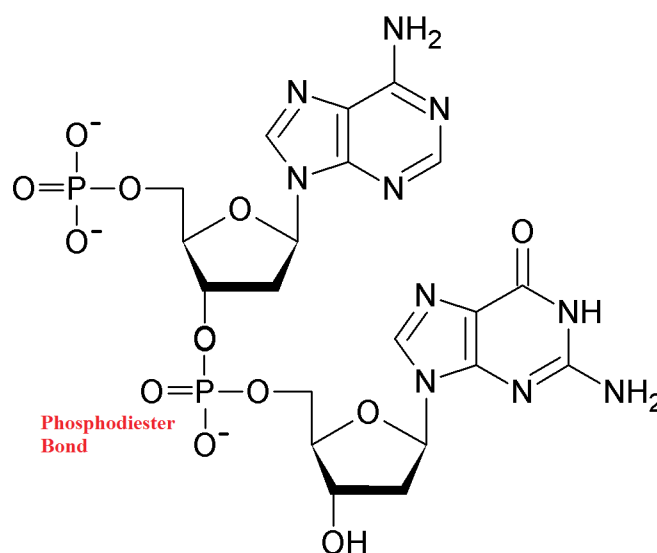


Figure 13.3.4 Phosphodiester Bond Between AMP and GMP

The DNA Double Helix

The double helix of the DNA molecule is formed like a spiral staircase. The sugar-phosphate backbones form the railing while the steps are formed by hydrogen bonding of the bases in the two helices.

These hydrogen bonded bases are known as *complimentary base pairs*.

The base pairs formed are exclusive to *adenine to thymine* by two hydrogen bonds and *guanine to cytosine* by three hydrogen bonds.

Figure 13.3.5 shows the double helical shape of DNA



(9)

Figure 13.3.5 The DNA Double Helix

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Please note the restriction to hydrogen bonding between adenine and thymine and between cytosine and guanine.

Let us take a closer look at hydrogen bonding that occurs between the complementary base pairs in the DNA molecule.

Figure 13.3.6 shows an expansion of the “ladder like” construction of the DNA molecule in between the two helices.

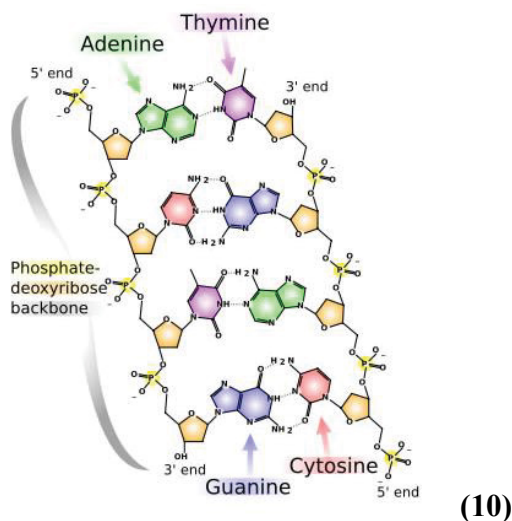


Figure 13.3.6 Hydrogen Bonding in DNA Base Pairs

DNA Replication

In DNA replication, the separate strands of the parent DNA are the templates for the synthesis of complimentary strands, which produce two exact copies of the parent DNA.

Figure 13.3.7 shows the replication of a DNA strand.

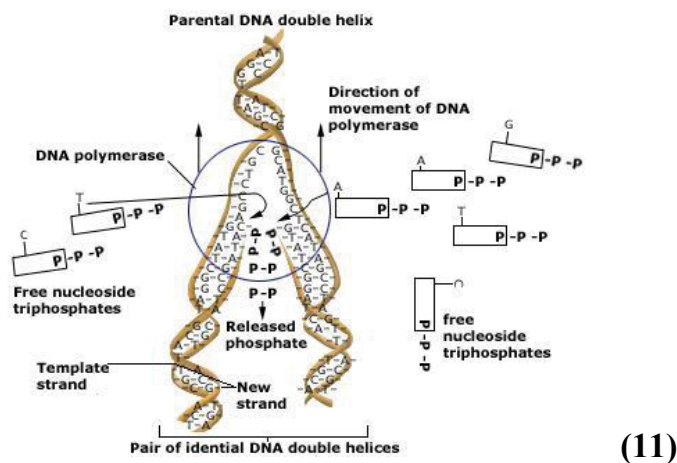


Figure 13.3.7 DNA Replication

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13.4 Protein Synthesis

RNA and the Genetic Code

There are three major types of RNA in the cells of the body.

Ribosomal RNA (rRNA): rRNA serves as the sites for the synthesis of proteins.

Messenger RNA (mRNA): mRNA carries protein synthesis information from the DNA to the ribosomes in the cell cytoplasm.

Transfer RNA (tRNA): tRNA interprets genetic information in mRNA and provides amino acid specific information for protein synthesis.

RNA and Protein Synthesis

Transcription is the process where information from a gene in the DNA is copied to mRNA for the synthesis of a protein.

Translation is the process where tRNA converts the information in the mRNA into the proper sequence of amino acids needed for protein synthesis.

Figure 13.4.1 shows the progression from DNA through messenger RNA to the synthesis of a protein.

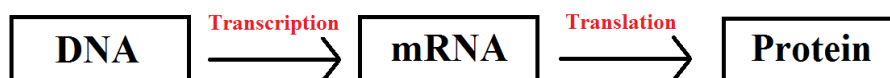


Figure 13.4.1 Protein Synthesis

The Genetic Code

The genetic code consists of series of three nucleotides (triplets) in the mRNA known as **codons**.

An example codification is a triplet of uracil (UUU) which produces a peptide that contains only phenylalanine.

A total of 64 codons are possible from the combinations of adenine (A), guanine (G), cytosine (C), and uracil (U).

1 st * 3 rd Letters	Second Letters (Symbol)			
	U	C	A	G
U * U	UUU (Phe)	UCU (Ser)	UAU (Tyr)	UGU (Cys)
U * C	UUC (Phe)	UCC (Ser)	UAC (Tyr)	UGC (Cys)
U * A	UUA (Leu)	UCA (Ser)	UAA (Stop)	UGA (Stop)
U * G	UUG (Leu)	UCG (Ser)	UAG (Stop)	UGG (Trp)
C * U	CUU (Leu)	CCU (Pro)	CAU (His)	CGU (Arg)
C * C	CUC (Leu)	CCC (Pro)	CAC (His)	CGC (Arg)
C * A	CUA (Leu)	CCA (Pro)	CAA (Gln)	CGA (Arg)
C * G	CUG (Leu)	CCG (Pro)	CAG (Gln)	CGG (Arg)
A * U	AUU (Ile)	ACU (Thr)	AAU (Asn)	AGU (Ser)
A * C	AUC (Ile)	ACC (Thr)	AAC (Asn)	AGC (Ser)
A * A	AUA (Ile)	ACA (Thr)	AAA (Lys)	AGA (Arg)
A * G	AUG (Start)	ACG (Thr)	AAG (Lys)	AGG (Arg)
G * U	GUU (Val)	GCU (Ala)	GAU (Asp)	GGU (Gly)
G * C	GUC (Val)	GCC (Ala)	GAC (Asp)	GGC (Gly)
G * A	GUA (Val)	GCA (Ala)	GAA (Glu)	GGA (Gly)
G * G	GUG (Val)	GCG (Ala)	GAG (Glu)	GGG (Gly)

Table 13.4.1 mRNA Codons and Resultant Amino Acids

The Start and Stop results for certain of the codons in Table 13.4.1 are for starting and stopping protein sequences.

Table 13.4.2 gives the names of the amino acids in parentheses in Table 13.4.1.

Symbol	Amino Acid Name	Codons
Ala	Alanine	GCU, GCC, GCA, GCG
Arg	Arginine	CGU, CGC, CGA, CGG, AGA, AGG
Asn	Asparagine	AAU, AAC
Asp	Aspartic Acid	GAU, GAC
Cys	Cysteine	UGU, UGC
Gln	Glutamine	CAA, CAG
Glu	Glutamic Acid	GAA, GAG
Gly	Glycine	GGU, GGC, GGA, GGG
His	Histidine	CAU, CAC
Ile	Isoleucine	AUU, AUC, AUA
Leu	Leucine	UUA, UUG, CUU, CUC, CUA, CUG
Lys	Lysine	AAA, AAG
Phe	Phenylalanine	UUU, UUC
Pro	Proline	CCU, CCC, CCA, CCG
Ser	Serine	AGU, AGC
Thr	Threonine	ACU, ACC, ACA, ACG
Trp	Tryptophan	UGG
Tyr	Tyrosine	UUA, UUC
Val	Valine	GUU, GUC, GUA, GUG

Table 13.4.2 mRNA Amino Acid Names

Translation of mRNA by tRNA

Each tRNA contains a loop called an *anticodon*, which is a triplet of bases that complements a codon in an mRNA.

tRNA is activated for protein synthesis by the tRNA synthetase enzyme. The synthetase uses the anticodons to attach the correct amino acid to the tRNA stem.

Figure 13.4.2 shows the anticodon loop of tRNA.

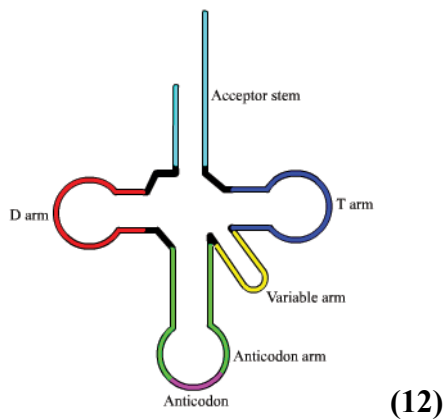


Figure 13.4.2 tRNA Anticodon Loop

Genetic Mutations

A **mutation** is a change in the DNA nucleotide sequence that alters the sequence of amino acids, which may alter the structure and function of a protein.

A **substitution** mutation occurs when one base in the coding strand of DNA is replaced with another.

A **frame shift** mutation occurs when a base is added or deleted from the coding strand of the DNA.

Figure 13.4.3 shows a graphic demonstration of substitution and both addition and deletion mutations.

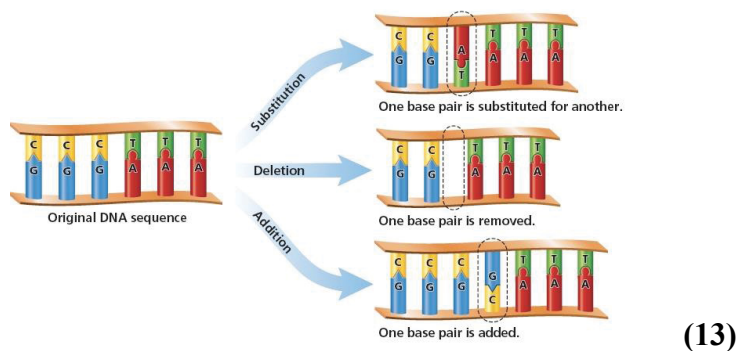


Figure 13.4.3 Genetic Mutations

13.5 Metabolism and Energy Production

Types of Metabolism

The term **metabolism** refers to all the chemical reactions that provide the energy and materials necessary for cell growth. There are two types of metabolic reactions.

In **catabolic reactions** complex molecules are broken down into smaller ones resulting in a release of energy.

Anabolic reactions utilize available energy in cells to produce larger molecules from smaller ones.

Stages of Metabolism

There are three stages of metabolism.

In Stage 1, the processes of **digestion** break down larger macromolecules into smaller units.

In Stage 2, these molecules are further broken down to 2 and 3 carbon species, such as pyruvate and acetyl coenzyme A (CoA), through the processes of **oxidation** and **hydrolysis**.

In Stage 3, the **oxidation** of materials to CO₂ and H₂O provides energy for adenosine triphosphate (ATP) synthesis.

Figure 13.5.1 shows all of the intricacies of metabolism. Most of these will be covered in the ensuing pages.

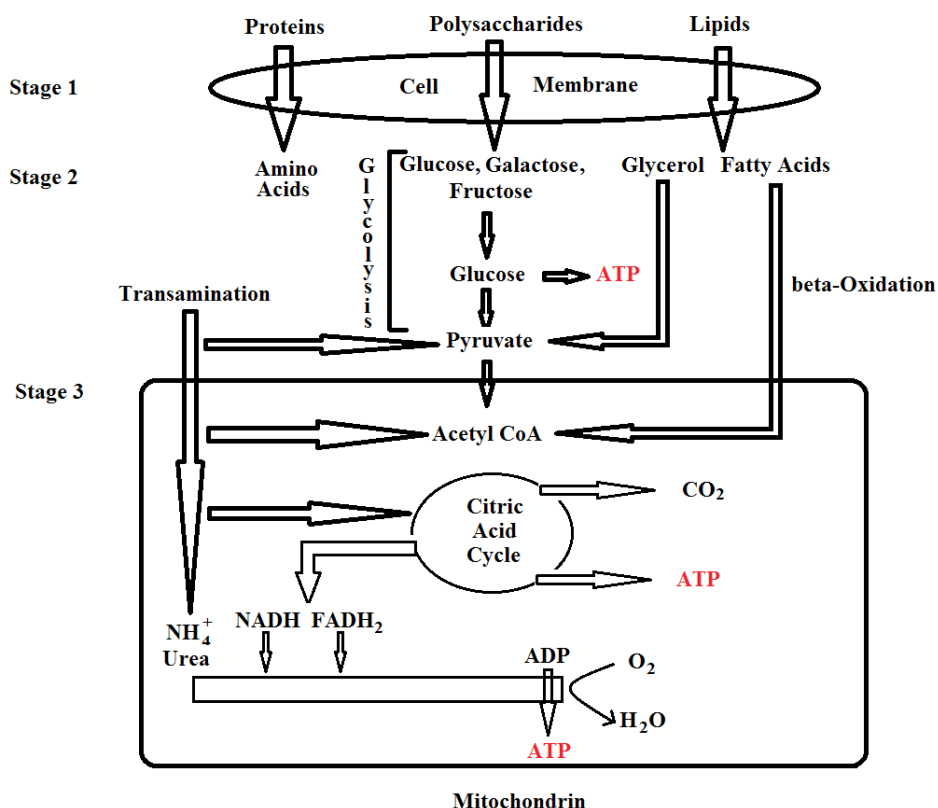


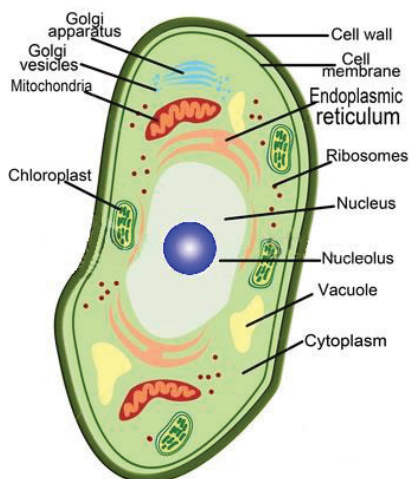
Figure 13.5.1 Stages of Metabolism

The Structure of a Cell

The **nucleus** of the cell contains the genes that control replication of DNA and protein synthesis.

The **cytoplasm** contains a aqueous solution (cytosol) that contains the electrolytes and enzymes that catalyze many of the cell's chemical reactions.

Figure 13.5.2 shows the cut away structure of a cell.



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Figure 13.5.2 Cut Away Structure of A Cell

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ATP and Energy

When the food we eat is metabolized, the energy released from the oxidation process is stored in the **adenosine triphosphate (ATP)** molecule. When ATP is hydrolyzed the products of the reaction are adenosine diphosphate (ADP), a phosphate group, and **7.3 kcal** per mole of ATP.

Figure 13.5.3 shows the molecular structure of adenosine triphosphate (ATP).

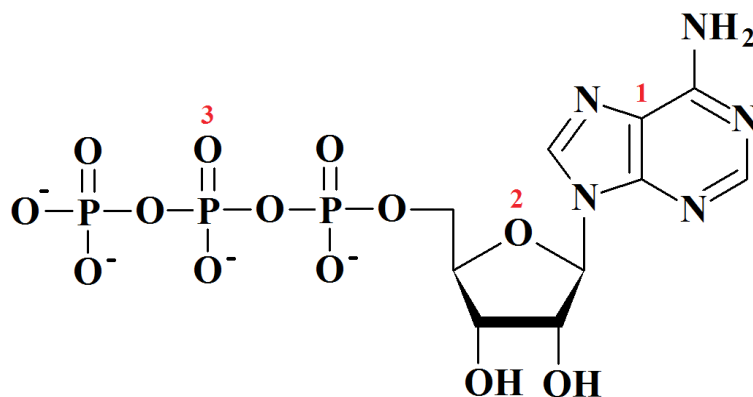


Figure 13.5.3 Adenosine Triphosphate (ATP)

As a point of review, let's interpret the red numbers from Figure 13.5.3.

1. The adenine molecule
2. The ribose molecule (Together 1 and 2 comprise the adenosine molecule.)
3. The ionic triphosphate chain

All together these components make adenosine triphosphate.

Digestion of Carbohydrates

The salivary enzyme **amylase** hydrolyzes α -glycosidic bonds in amylose and amylopectin to produce maltose, glucose, and the smaller polysaccharides dextrins.

In the small intestines, at a pH of around 8, an α -amylase (produced in the pancreas) hydrolyzes the remaining polysaccharides to maltose and glucose.

Enzymes produced in the mucosal cells of the small intestines can hydrolyze maltose, glucose, and sucrose.

Figure 13.5.5 shows the digestion of carbohydrates from ingestion to the deposit of glucose into the bloodstream.

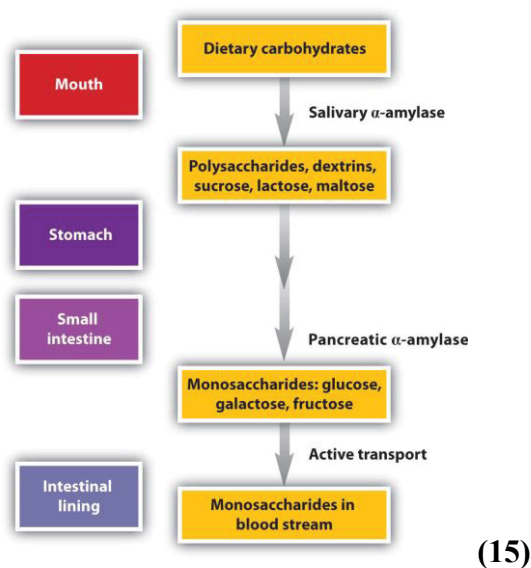


Figure 13.5.5 Digestion of Carbohydrates

Maintaining Blood Glucose Levels

After eating, the blood *glucose* level is elevated. The pancreas secretes the hormone *insulin* which increases the flow of glucose into muscle and adipose tissue. There the insulin converts the glucose to *glycogen* which is stored in the liver.

When you are fasting throughout the night, blood glucose levels drop. This stimulates the pancreas to secrete another hormone *glucagon*, which stimulates the breakdown of glycogen in the liver in order to secrete glucose.

Digestion of Triacylglycerols

In the small intestines, a process known as *emulsification* uses bile salts from the gall bladder to form fat micelles. Then *lipases* produced in the pancreas hydrolyze the micelle fat to form free fatty acids and a monoacylglycerol.

These products are reformed in the intestinal lining to triacylglycerols coated with proteins to form lipoproteins known as *chylomicrons*. In the cells, enzymes hydrolyze the triacylglycerides to glycerol and free fatty acids.

Digestion of Proteins

In the stomach, hydrochloric acid (HCl), at pH=2, denatures proteins and activates enzymes, such as *pepsin*, that begin to hydrolyze peptide bonds.

The polypeptides move from the stomach into the small intestines where the enzymes *trypsin* and *chymotrypsin* complete the hydrolysis of the peptides into amino acids. These amino acids are then absorbed through the intestinal walls into the bloodstream for transport to the cells.

Metabolic Pathway Coenzymes

Before we look at some important coenzymes, let's review the concepts of *oxidation* and *reduction*.

Oxidation is a loss of H and electrons. When an enzyme catalyzes oxidation hydrogen atoms and electrons are removed from a substrate.

Reduction is a gain of H and electrons. When hydrogen atoms and electrons are picked up by a coenzyme, it is reduced.

Nicotinamide adenine dinucleotide (**NAD⁺**) is an important coenzyme formed by the nicotinamide group from the vitamin niacin, which is bonded to adenosine phosphate.

NAD⁺ participates in producing C=O bonds through the oxidation of alcohols to aldehydes and ketones. Note that Figure 13.5.6 shows the conversion of NAD⁺ to NADH is a reduction for the coenzyme.

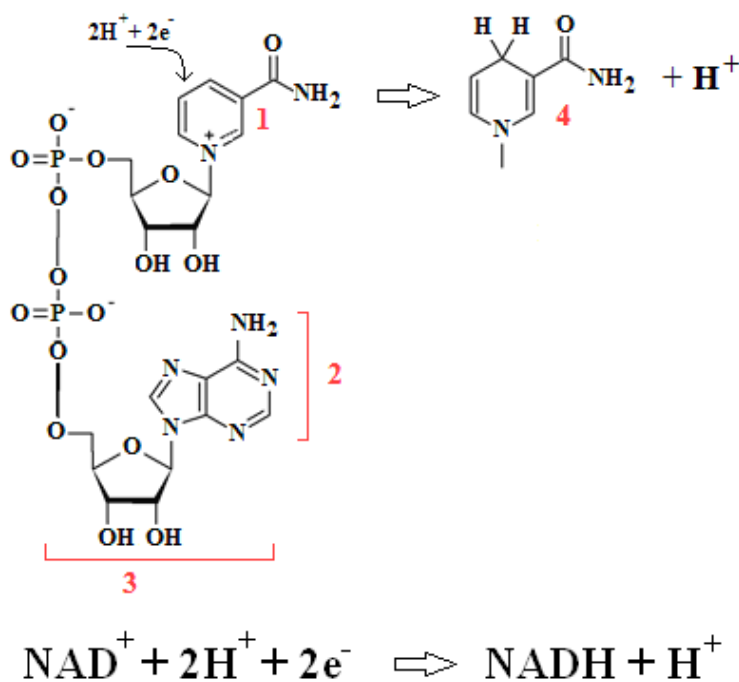


Figure 13.5.6 NAD⁺ Conversion to NADH

Let's interpret the red numbers from Figure 13.5.6:

1. The nicotinamide from the niacin molecule
2. Adenosine diphosphate (ADP)
3. The NAD^+ ion
4. The NADH molecule

Flavin adenine dinucleotide (**FAD**) is a coenzyme containing riboflavin (vitamin B_2) and adenosine diphosphate (ADP).

Riboflavin consists of a sugar alcohol (ribitol) and flavin. Two nitrogen atoms in the FAD receive hydrogens and are reduced to FADH_2 .

Figure 13.5.7 shows the conversion of FAD to FADH_2 .



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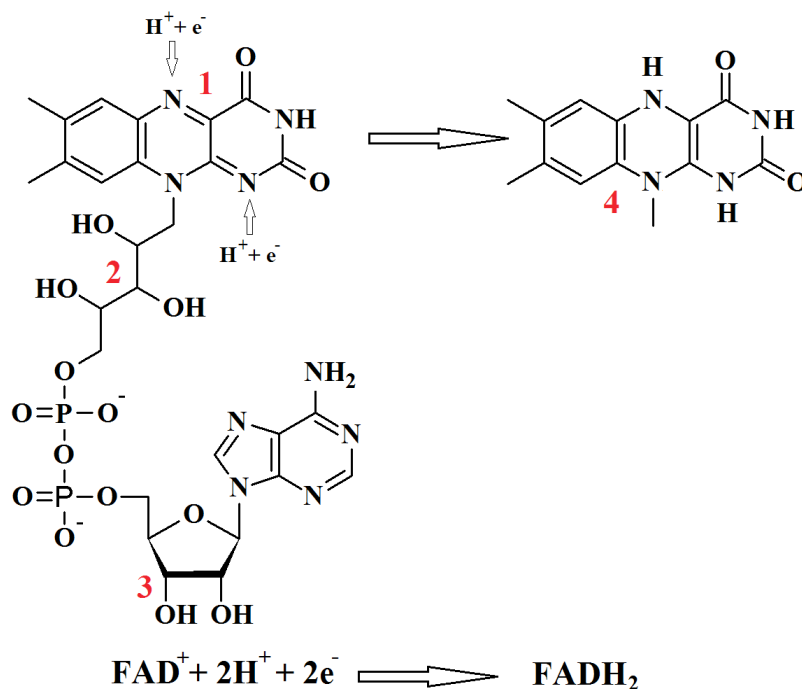


Figure 13.5.7 FAD Conversion to FADH₂

Let's interpret the red numbers from Figure 13.5.7:

1. The flavin molecule
2. The ribitol molecule
3. The ADP ion
4. The FADH₂ molecule

Coenzyme A (CoA) is made up of pantothenic acid (vitamin B₅) adenosine diphosphate (ADP) and aminoethanethiol. CoA prepares small groups like the acetyl group for enzyme action.

Figure 13.5.8 shows the structure of Coenzyme A (CoA).

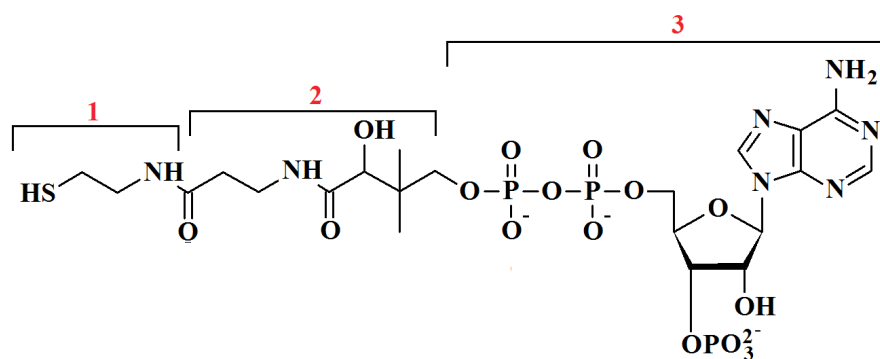


Figure 13.5.8 Coenzyme A (CoA)

Let's interpret the red numbers from Figure 13.5.8:

1. The molecule aminoethanethiol
2. The molecule pantothenic acid
3. The ion phosphorylated ADP

Glycolysis, an anaerobic process (no oxygen required), is a Stage 2 process where a six carbon glucose is broken down into two three carbon molecules such as pyruvate.

Figure 13.5.9 shows the overall process of the conversion of glucose to NADH in three distinct stages.

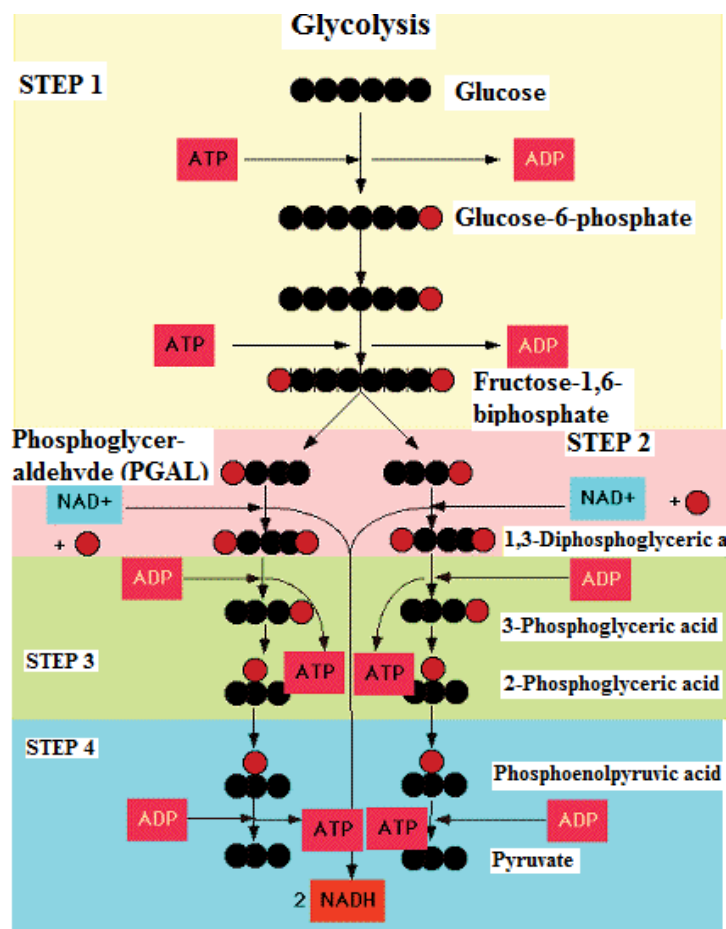


Figure 13.5.9 Stages of Glycolysis

Figures 13.5.10 and 13.5.11 show the ten chemical reactions in the conversion of glucose to pyruvate. These reactions are labeled alphabetically A through J in red. The product(s) of each reaction are labeled numerically 1 through 10 in red.

Table 13.5.1 lists the starting chemical in each reaction, additional reactants and processes, and products.

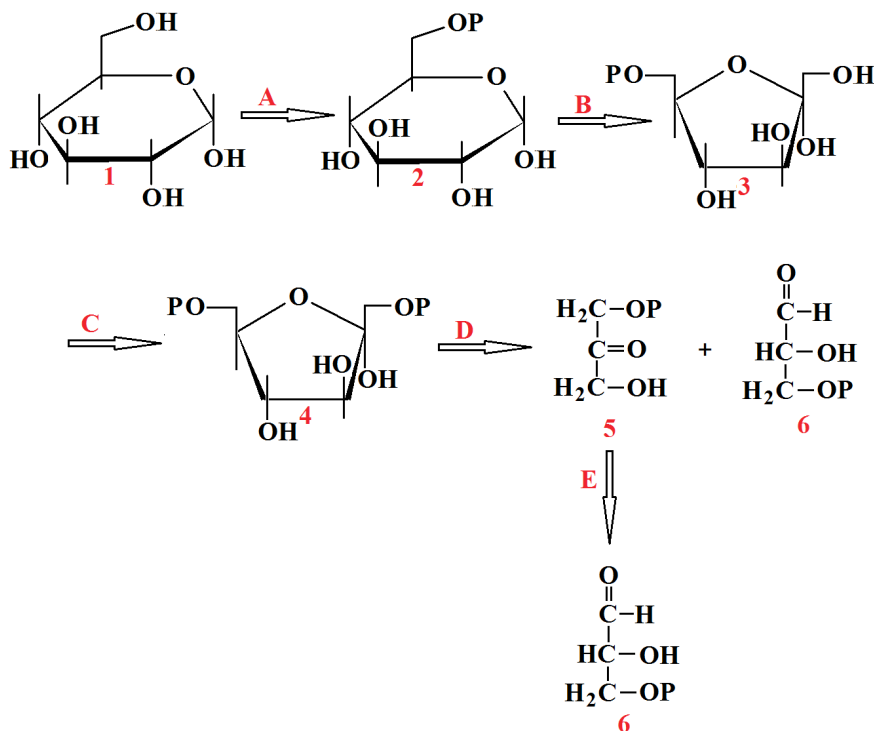


Figure 13.5.10 Glycolysis Reactions 1 through 5

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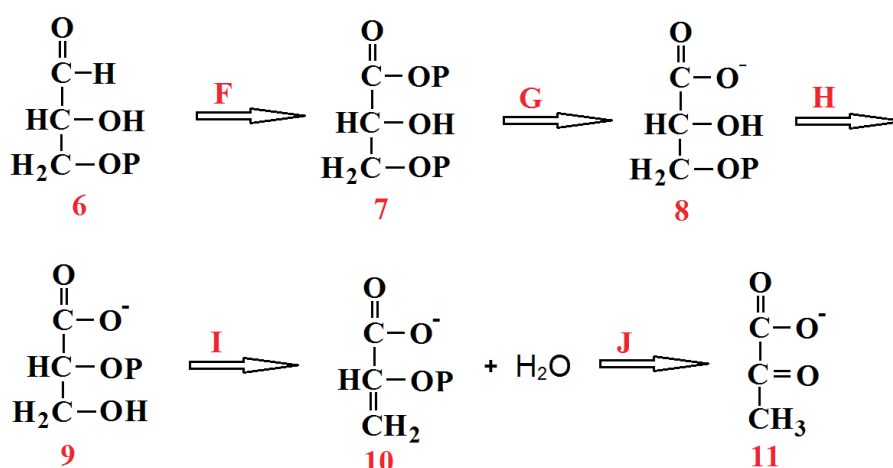


Figure 13.5.11 Glycolysis Reactions 6 through 10

Starting Compound		Additional Reactants/Processes	Final Compound	
A	Glucose	Hexokinase (ATP → ADP)	1	Glucose-6-phosphate
B	Glucose-6-phosphate	Phosphogluco-isomerase	2	Fructose-6-phosphate
C	Fructose-6-phosphate	Phosphofruktokinase (ATP → ADP)	3	Fructose-1,6-biphosphate
D	Fructose-1,6-biphosphate	Fructose-1,6-biphosphate adolase	4	Dihydroxyacetone phosphate Glyceraldehyde-3-phosphate
E	Dihydroxyacetone phosphate	Triosephosphate isomerase	5	Glyceraldehyde-3-phosphate
F	Glyceraldehyde-3-phosphate	Glyceraldehyde-3-phosphate dehydrogenase (P+NAD ⁺ →NADH+H ⁺)	6	1,3-Biphospho-glycerate
G	1,3-Biphospho-glycerate	Phosphoglycerate kinase (ADP→ATP)	7	3-Phosphoglycerate
H	3-Phosphoglycerate	Phosphoglycerate mutase	8	2-Phophoglycerate
I	2-Phophoglycerate	Enolase	9	Phosphoenolpyruvate Water
J	Phosphoenolpyruvate	Pyruvate kinase	10	Pyruvate

Table 13.5.1 Glycolysis of Glucose to Pyruvate

After an exhausting coverage of the conversion of glucose to pyruvate, let's look briefly at the *aerobic* (with oxygen) and the *anaerobic* (without oxygen) conversions of pyruvate.

Aerobic conditions exist in the cell's *mitochondria* (cell's energy converters).

Figure 13.5.12 shows the aerobic conversion of pyruvate to lactate.

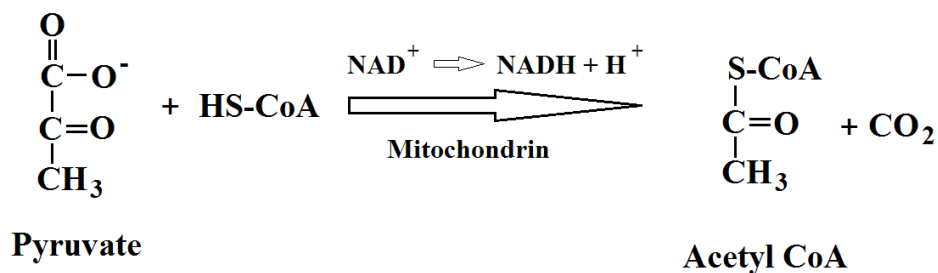


Figure 13.5.12 Aerobic Conversion of Pyruvate to CoA

Anaerobic conditions exist in the cell's *cytosol* (intercellular fluid).

Figure 13.5.13 shows the anaerobic conversion of pyruvate to lactate.

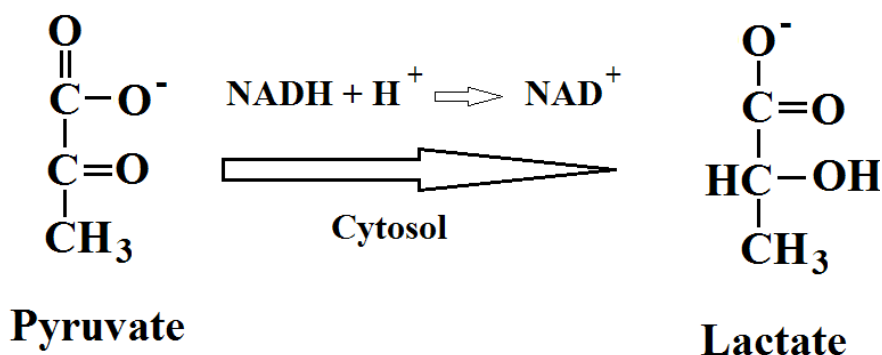


Figure 13.5.13 Conversion of Pyruvate to Lactate

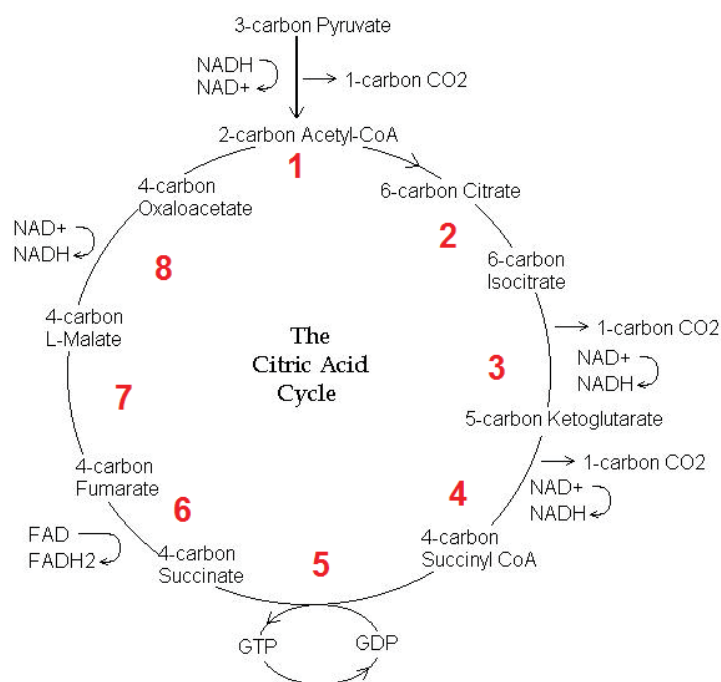
Now that we have traversed from glucose to CoA through forests of complicated chemical reactions, we should be able to simplify things a bit.

You would think that's true but unfortunately it is not. Welcome to the *Citric Acid Cycle*!

Also known as the *Krebs Cycle*, it covers the conversion of acetyl CoA to NADH.

Figure 13.5.14 covers the eight steps of the Citric Acid Cycle.

Explanations for each step follow the figure.



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Figure 13.5.14 The Citric Acid Cycle

Reaction 1 Acetyl CoA bonds with oxaloacetate to yield citrate and CoA.

Reaction 2 Citrate is isomerized to isocitrate. Only the secondary hydroxyl group in isocitrate can be oxidized.

Reaction 3 Oxidative decarboxylation is accomplished as follows.

1. Hydroxyl group (OH^-) is oxidized to a ketone ($\text{C}=\text{O}$).
2. NAD^+ is reduced to yield NADH .
3. A carboxylate group (COO^-) is removed as CO_2 .

Reaction 4 Oxidative decarboxylation is accomplished as follows:

1. A second carbon is removed as CO_2 .
2. NAD^+ is reduced to yield NADH .

Reaction 5 Energy released by hydrolysis of succinyl CoA used to add phosphate group (P_i) to guanosine diphosphate (GDP) to form the high energy compound (GTP).

The hydrolysis of GDP is used to add a phosphate group to ADP. This is the only example of direct substrate phosphorylation in the citric acid cycle.

Reaction 6 Two hydrogen atoms are removed from the succinate to produce fumarate through the reduction of FAD to FADH₂.

Reaction 7 In a hydration reaction, water adds to the double bond of fumarate to form malate.

Reaction 8 The hydroxyl group (OH⁻) in malate is oxidized to yield oxaloacetate. The coenzyme NAD⁺ is reduced to NADH + H⁺.

The chemical reactions and systems in the human body can be chiefly described as *electrochemical* in nature.

So what are the electricity producing reactions inside or outside the human body?

The following are four types of systems in the human body that are used to transfer electrons. Be sure you notice that each of them are reversible redox reactions.

The Iron-Sulfur (Fe-S) System

Figure 13.5.15 shows a simple reduction of an iron(III) sulfur cluster to an iron(II) sulfur cluster by the gaining of an electron.

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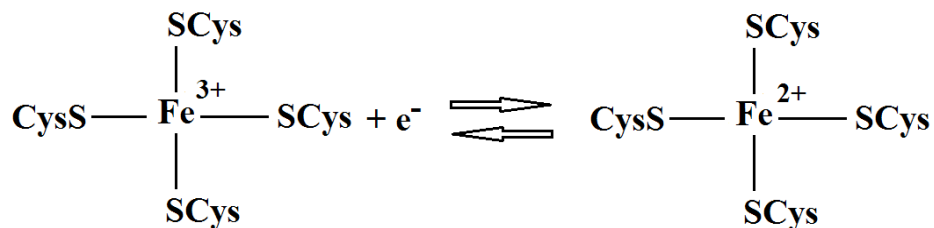


Figure 13.5.15 An Iron-Sulfur Cluster Reduction

The Flavin Mononucleotide (FMN) Coenzyme System

FMN (flavin mononucleotide) is a coenzyme derived from riboflavin (vitamin B₂). In riboflavin, the flavin is connected to ribitol (the sugar alcohol of ribose). Here FMN is reduced to FMNH₂.

Figure 13.5.16 shows the reduction of FMN to FMNH₂.

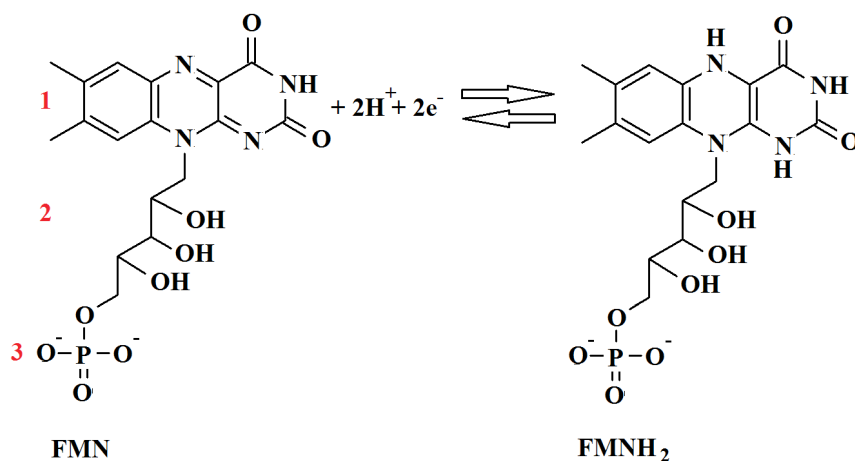


Figure 13.5.16 A Flavin Mononucleotide Reduction

Some constituent identifications for Figure 13.5.16 follow.

1. The flavin molecule
2. The ribitol molecule
3. The riboflavin phosphate ion

The Coenzyme Q (CoQ) System

Coenzyme Q (Q or CoQ) is derived from quinone as seen below. When the two ketone groups accept hydrogens and electrons they are reduced to alcohols.

Figure 13.5.17 shows the reduction of CoQ.

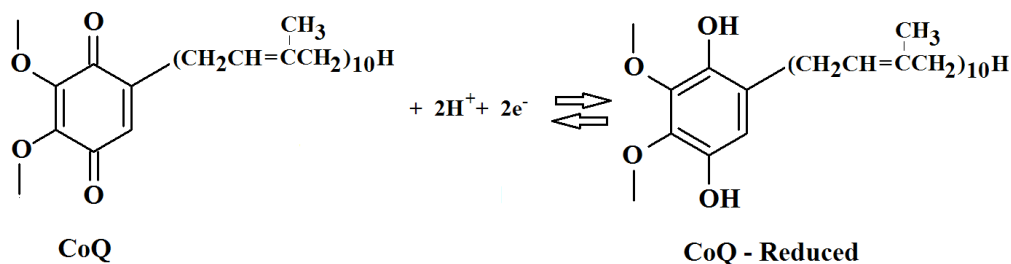


Figure 13.5.17 A Coenzyme Q Reduction

The Cytochrome (cyt) System

Cytochromes (cyt) are proteins that carry an iron in a heme group. In each of the cytochromes (cyt b, cyt c₁, cyt c, cyt a, and cyt a₃) Fe²⁺ is oxidized back to Fe³⁺ through the loss of an electron.

Figure 13.5.18 shows the reduction of cytochrome c (cyt c).

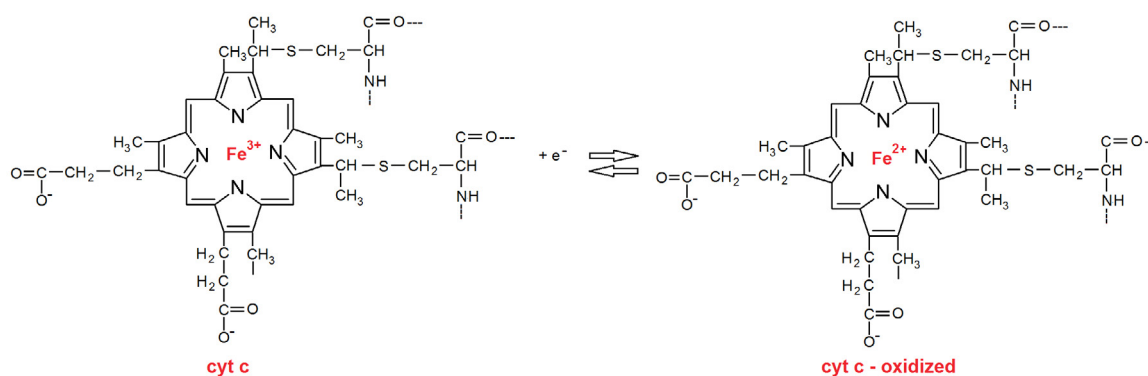
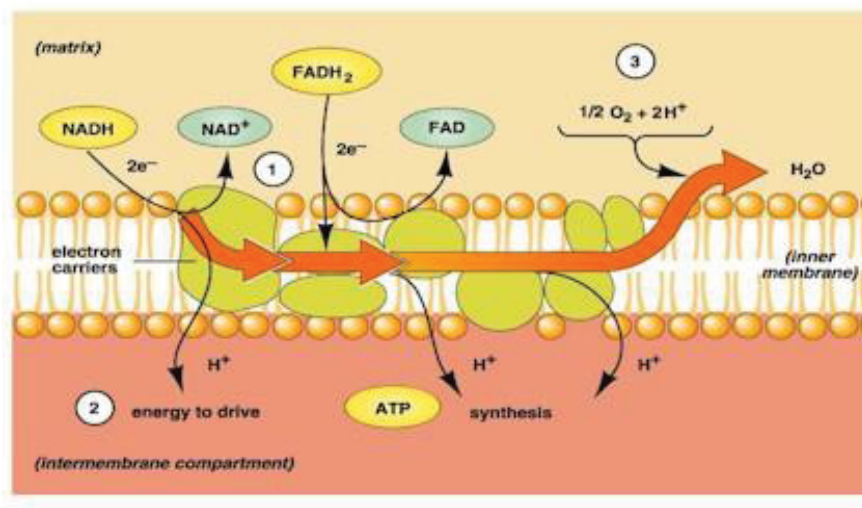


Figure 12.5.18 A Cytochrome c Reduction

In the inner membrane of the mitochondria, **CoQ** and **cyt c** are not firmly attached to the membrane. As such they are considered as mobile carriers that transfer electrons between protein complexes.

Figure 13.5.19 shows the direction of electron transfer in the inner mitochondrial membrane.



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Figure 13.5.19 Inner Mitochondrial Electron Transfer

Oxidative Phosphorylation and ATP

Oxidative phosphorylation is the process of using the energy of the electrons from the oxidation of substrates to produce ATP in the cell. The process occurs in the intermitochondrial membrane of the cell.

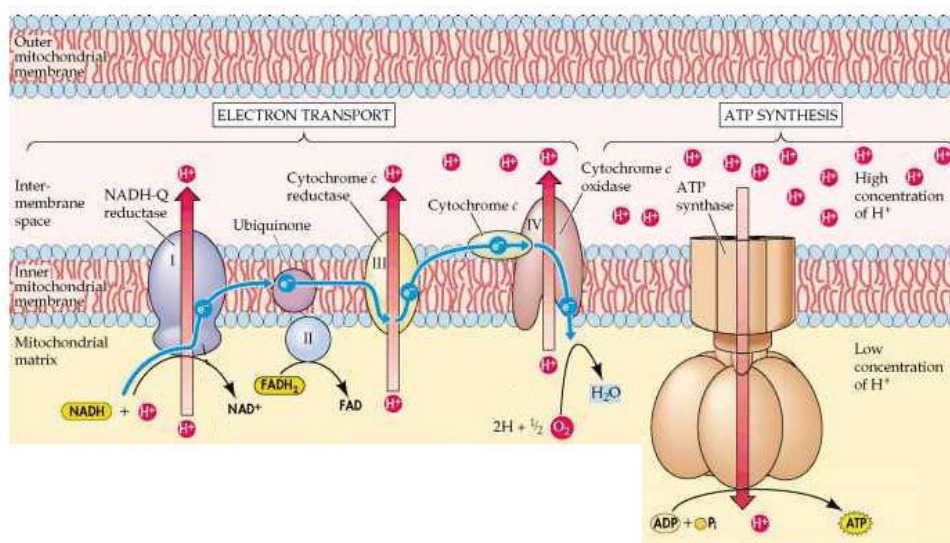
“I studied English for 16 years but...
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Figure 13.5.20 shows the synthesis of adenosine triphosphate (ATP) through the process of oxidative phosphorylation.



(19)

Figure 13.5.20 ATP Synthesis by Oxidative Phosphorylation

Oxidation of Fatty Acids

A large amount of energy is obtained by the oxidation of fatty acids in the mitochondria. These fatty acids undergo ***β-oxidation*** and yield acetyl CoA. This process continues, removing two carbons at a time to make more acetyl CoA, until the fatty acid is completely degraded. The acetyl CoA that is produced can then enter the citric acid cycle

Figure 13.5.21 shows the fatty acid stearic acid (animal fat). It should be obvious by now that the “important” part of the molecule is the carboxylic acid group.

That being said, the numbering of atoms in the molecule starts with the carbonyl carbon as number 1. Rather than referring to the carbon just to the left of the carbonyl carbon as one away from the carbonyl carbon it is referred to as ***alpha (α)*** to the carbonyl carbon. The next carbon to the left is then referred to as ***beta (β)*** to the carbonyl carbon.

The oxidation of the stearic acid in Figure 13.5.21 occurs at the carbon ***beta*** to the carbonyl carbon.

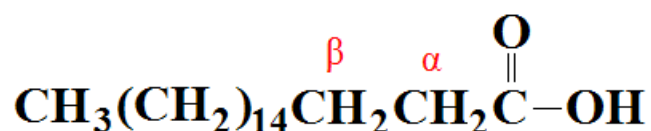


Figure 13.5.21 Beta Oxidation of Stearic Acid

When **fatty acid activation** occurs, in the cytosol of the cell, an acyl group is added to the fatty acid. This activation process combines a fatty acid and CoA to yield fatty acyl CoA. The energy for this process comes from hydrolysis of ATP to produce adenosine monophosphate (AMP) and two inorganic phosphorous atoms.

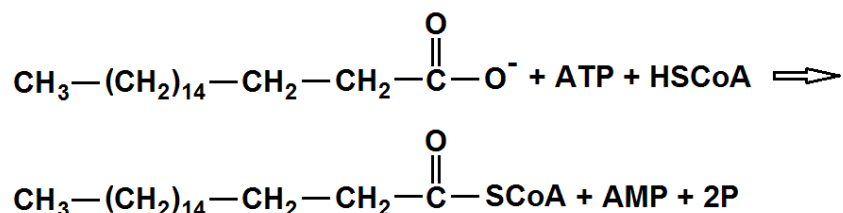


Figure 13.5.21 Fatty Acid Activation

Urea Cycle

The final product of amino acid degradation is NH_4^+ . NH_4^+ is toxic if it is allowed to accumulate in the body. Through a series of reactions known as the **urea cycle**, the NH_4^+ is detoxified and converted to urea which is removed from the body by urine.

If urea is not removed from your body, as measured by blood urea nitrogen (BUN) procedures as extreme as hemodialysis may be required.

Figure 13.5.22 shows the reaction of the ammonium ion (NH_4^+).

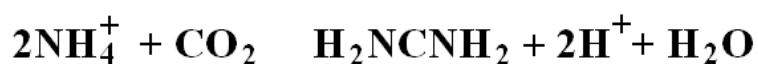


Figure 13.5.22 Reaction of CO_2 with NH_4^+

Website References for Free Clipart

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