INTRODUCTORY CHEMISTRY ONLINE!

Paul R. Young
University of Illinois at Chicago

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University of Illinois at Chicago

Introductory Chemistry Online!

Paul R. Young

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Licensing

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CHAPTER OVERVIEW

1: Measurements and Atomic Structure

Chemistry is the study of matter and the ways in which different forms of matter combine with each other. You study chemistry because it helps you to understand the world around you. Everything you touch or taste or smell is a chemical, and the interactions of these chemicals with each other define our universe. Chemistry forms the fundamental basis for biology and medicine. From the structure of proteins and nucleic acids, to the design, synthesis and manufacture of drugs, chemistry allows you an insight into how things work. Chapter One in this text will introduce you to matter, atoms and their structure. You will learn the basics of scientific measurement and you will gain an appreciation of the scale of chemistry; from the tiniest atom to the incredibly large numbers dealt with in the "mole concept" (Chapter 4). Chapter One lays the foundation on which we will build our understanding.

1.1: Why Study Chemistry
1.2: Organization of the Elements - The Periodic Table
1.3: Scientific Notation
1.4: SI and Metric Units
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1.8: Filling Orbitals with Electrons
1.S: Measurements and Atomic Structure (Summary)

Thumbnail: Two small test tubes held in spring clamps. (CC BY-SA 3.0 Unported; Amitchell125 via Wikipedia)

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1.1: Why Study Chemistry

Chemistry is the branch of science dealing with the structure, composition, properties, and the reactive characteristics of matter. Matter is anything that has mass and occupies space. Thus, chemistry is the study of literally everything around us – the liquids that we drink, the gasses we breathe, the composition of everything from the plastic case on your phone to the earth beneath your feet. Moreover, chemistry is the study of the transformation of matter. Crude oil is transformed into more useful petroleum products such as gasoline and kerosene by the process of refining. Some of these products are further transformed into plastics. Crude metal ores are transformed into metals, that can then be fashioned into everything from foil to automobiles. Potential drugs are identified from natural sources, isolated and then prepared in the laboratory. Their structures are systematically modified to produce the pharmaceuticals that have led to vast advances in modern medicine. Chemistry is at the center of all of these processes and chemists are the people that study the nature of matter and learn to design, predict and control these chemical transformations. Within the branches of chemistry you will find several apparent subdivisions. Inorganic chemistry, historically, focused on minerals and metals found in the earth, while organic chemistry dealt with carbon-containing compounds that were first identified in living things. Biochemistry is an outgrowth of the application of organic chemistry to biology and relates to the chemical basis for living things. In the later chapters of this text we will explore organic and biochemistry in a bit more detail and you will notice examples of organic compounds scattered throughout the text. Today, the lines between the various fields have blurred significantly and a contemporary chemist is expected to have a broad background in all of these areas.

In this chapter we will discuss some of the properties of matter, how chemists measure those properties and we will introduce some of the vocabulary that is used throughout chemistry and the other physical sciences.

Let's begin with matter. **Matter** is defined as any substance that has mass. It's important to distinguish here between weight and mass. Weight is the result of the pull of gravity on an object. On the Moon, an object will weigh less than the same object on Earth because the pull of gravity is less on the Moon. The mass of an object, however, is an inherent property of that object and does not change, regardless of location, gravitational pull, or whatever. It is a property that is solely dependent on the quantity of matter within the object.

Contemporary theories suggests that matter is composed of **atoms**. Atoms themselves are constructed from neutrons, protons and electrons, along with an ever-increasing array of other subatomic particles. We will focus on the neutron, a particle having no charge, the proton, which carries a positive charge, and the electron, which has a negative charge. Atoms are incredibly small. To give you an idea of the size of an atom, a single copper penny contains approximately 28,000,000,000,000,000,000,000 atoms (that's 28 sextillion). Because atoms and subatomic particles are so small, their mass is not readily measured using pounds, ounces, grams or any other scale that we would use on larger objects. Instead, the mass of atoms and subatomic particles is measured using atomic mass units (abbreviated amu). The atomic mass unit is based on a scale that relates the mass of different types of atoms to each other (using the most common form of the element carbon as a standard). The amu scale gives us a convenient means to describe the masses of individual atoms and to do quantitative measurements concerning atoms and their reactions. Within an atom, the neutron and proton both have a mass of one amu; the electron has a much smaller mass (about 0.0005 amu).

Figure 1.2: *Atoms are incredible small. Atoms are incredibly small. To give you an idea of the size of an atom, a single copper penny contains approximately 28,000,000,000,000,000,000,000 atoms (that's 28 sextillion).*

Atomic theory places the neutron and the proton in the center of the atom in the nucleus. In an atom, the nucleus is very small, very dense, carries a positive charge (from the protons) and contains virtually all of the mass of the atom. Electrons are placed in a diffuse cloud surrounding the nucleus. The electron cloud carries a net negative charge (from the charge on the electrons) and in a

neutral atom there are always as many electrons in this cloud as there are protons in the nucleus (the positive charges in the nucleus are balanced by the negative charges of the electrons, making the atom neutral).

An atom is characterized by the number of neutrons, protons and electrons that it possesses. Today, we recognize at least 116 different types of atoms, each type having a different number of protons in its nucleus. These different types of atoms are called elements. The neutral element hydrogen (the lightest element) will always have one proton in its nucleus and one electron in the cloud surrounding the nucleus. The element helium will always have two protons in its nucleus. It is the number of protons in the nucleus of an atom that defines the identity of an element. Elements can, however, have differing numbers of neutrons in their nucleus. For example, stable helium nuclei exists that contain one, or two neutrons (but they all have two protons). These different types of helium atoms have different masses (3 or 4 amu) and they are called isotopes. For any given isotope, the sum of the numbers of protons and neutrons in the nucleus is called the mass number. All elements exist as a collection of isotopes, and the mass of an element that we use in chemistry, the atomic mass, is the average of the masses of these isotopes. For helium, there is approximately one isotope of Helium-3 for every million isotopes of Helium-4, hence the average atomic mass is very close to 4 (4.002602).

As different elements were discovered and named, abbreviations of their names were developed to allow for a convenient chemical shorthand. The abbreviation for an element is called its chemical symbol. A chemical symbol consists of one or two letters, and the relationship between the symbol and the name of the element is generally apparent. Thus helium has the chemical symbol He, nitrogen is N, and lithium is Li. Sometimes the symbol is less apparent but is decipherable; magnesium is Mg, strontium is Sr, and manganese is Mn. Symbols for elements that have been known since ancient times, however, are often based on Latin or Greek names and appear somewhat obscure from their modern English names. For example, copper is Cu (from cuprum), silver is Ag (from argentum), gold is Au (from aurum), and iron is (Fe from ferrum). Throughout your study of chemistry, you will routinely use chemical symbols and it is important that you begin the process of learning the names and chemical symbols for the common elements. By the time you complete General Chemistry, you will find that you are adept at naming and identifying virtually all of the 116 known elements. Table 1.1 contains a starter list of common elements that you should begin learning now!

Table 1.1: Names and Chemical Symbols for Common Elements

Element	Chemical Symbol	Element	Chemical Symbol
Hydrogen	H	Phosphorus	P
Helium	He	Sulfur	S
Lithium	Li	Chlorine	Cl
Beryllium	Be	Argon	Ar
Boron	B	Potassium	K
Carbon	C	Calcium	Ca
Nitrogen	N	Iron	Fe
Oxygen	O	Copper	Cu
Fluorine	F	Zinc	Zn
Neon	Ne	Bromine	Br
Sodium	Na	Silver	Ag
Magnesium	Mg	Iodine	I
Aluminum	Al	Gold	Au
Silicon	Si	Lead	Pb

The chemical symbol for an element is often combined with information regarding the number of protons and neutrons in a particular isotope of that atom to give the atomic symbol. To write an atomic symbol, you begin with the chemical symbol, then

write the atomic number for the element (the number of protons in the nucleus) as a subscript, preceding the chemical symbol. Directly above this, as a superscript, now write the mass number for the isotope, that is, the total number of protons and neutrons in the nucleus. Thus, for helium, the atomic number is 2 and there are two neutrons in the nucleus for the most common isotope making the atomic symbol $^{4}_{2}He$. In the definition of the atomic mass unit, the "most common isotope of carbon", $^{12}_{6}C$, is defined as having a mass of exactly 12 amu and the atomic masses of the remaining elements are based on their masses relative to this isotope. Chlorine (chemical symbol Cl) consists of two major isotopes, one with 18 neutrons (the most common, comprising 75.77% of natural chlorine atoms) and one with 20 neutrons (the remaining 24.23%). The atomic number of chlorine is 17 (it has 17 protons in its nucleus), therefore the chemical symbols for the two isotopes are $^{35}_{17}Cl$ and $^{37}_{17}Cl$.

When data is available regarding the natural abundance of various isotopes of an element, it is simple to calculate the average atomic mass. In the example above, $^{35}_{17}Cl$ was the most common isotope with an abundance of 75.77% and $^{37}_{17}Cl$ had an abundance of the remaining 24.23%. To calculate the average mass, first convert the percentages into fractions; that is, simply divide them by 100. Now, chlorine-35 represents a fraction of natural chlorine of 0.7577 and has a mass of 35 (the mass number). Multiplying these, we get (0.7577 × 35) = 26.51. To this, we need to add the fraction representing chlorine-37, or (0.2423 × 37) = 8.965; adding, (26.51 + 8.965) = 35.48, which is the weighted average atomic mass for chlorine. Whenever we do mass calculations involving elements or compounds (combinations of elements), we always need to use average atomic masses.

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1.2: Organization of the Elements - The Periodic Table

The number of protons in the nucleus of an element is called the atomic number of that element. Chemists typically place elements in order of increasing atomic numbers in a special arrangement that is called the periodic table.

The periodic table is not simply a grid of elements arranged numerically. In the periodic table, the elements are arranged in horizontal rows called periods (numbered in blue) and vertically into columns called groups. These groups are numbered by two, somewhat conflicting, schemes. In the simplest presentation, favored by the International Union of Pure and Applied Chemistry (**IUPAC**), the groups are simply numbered 1-18. The convention in much of the world, however, is to number the first two groups 1A and 2A, the last six groups 3A-8A; the middle ten groups are then numbered 1B-8B (but not in that order!). While the IUPAC numbering appears much simpler, in this text we will use the current USA nomenclature (1A-8A). The reason for this choice will become more apparent in Chapter 3 when we discuss "valence" and electron configuration in more detail. The actual layout of the periodic table is based on the grouping of the elements according to chemical properties. For example, elements in each Group of the periodic table (each vertical column) will share many of the same chemical properties. As we discuss the properties of elements and the ways they combine with other elements, the reasons for this particular arrangement of the periodic table will become more obvious.

As you can see, each element in the periodic table is represented by a box containing the chemical symbol, the atomic number (the number of protons in the nucleus) and the atomic mass of the element. Remember that the atomic mass is the weighted average of the masses of all of the natural isotopes of the particular element.

Periodic tables are often colored, or shaded, to distinguish groups of elements that have similar properties or chemical reactivity. The broadest classification is into metals, metalloids (or semi-metals) and nonmetals. The elements in Groups 1A – 8A are called the representative elements and the elements in Groups 3 - 15 are called the transition metals. the metallic elements are shown in purple. Metals are solids (except for mercury), can conduct electricity and are usually malleable (can be rolled into sheets) and are ductile (can be drawn into wires). Metals are usually separated into the main group metals (the elements colored purple in Groups 1A - 5A) and the transition metals (in Groups 3 – 15). Nonmetals (yellow in the Figure) do not conduct electricity (with the exception of carbon in the form of graphite) and have a variety of physical states (some are solids, some liquids and some gasses). Two important subclasses of nonmetals are the halogens (Group 7A) and the inert gasses (or noble gasses; Group 8A). At the border between metals and nonmetals lie the elements boron, silicon, germanium, astatine, antimony and tellurium. These elements share physical properties of metals and nonmetals and are called metalloids, or semi-metals. The common semiconductors silicon and germanium are in this group and it is their unique electrical properties that make transistors and other solid-state devices possible. Later in this book we will see that the position of elements in the periodic table also correlates with their chemical reactivity.

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1.3: Scientific Notation

In Section 1.1, we stated that a single copper penny contains approximately 28,000,000,000,000,000,000,000 atoms. This is a huge number. If we were to measure the diameter of an atom of hydrogen, it would be about 0.00000000000026 inches across. This is an incredibly small number. Chemists routinely use very large and very small numbers in calculations. In order to allow us to use this range of numbers efficiently, chemists will generally express numbers using exponential, or scientific notation. In scientific notation, a number n is shown as the product of that number and 10, raised to some exponent x; that is, ($n \times 10^x$). The number 10^2 is equal to 100. If we multiply 2×10^2, that is equivalent to multiplying 2 × 100, or 200. Thus 200 can be written in scientific notation as 2×10^2. When we convert a number to scientific notation, we begin by writing a the first (non-zero) digit in the number. If the number contains more than one digit, we write a decimal point, followed by all of the remaining digits. Next we inspect the number to see what power of 10 this decimal must be multiplied by to give the original number. Operationally, what you are doing is moving decimal places. Take the number of atoms in a penny, 28,000,000,000,000,000,000,000. We would begin by writing 2.8. To get the power of 10 that we need, we begin with the last digit in the number and count the number of places that we must move to the left to reach our new decimal point. In this example, we must move 22 places to the left. The number is therefore the product of 2.8 and 10^{22}, and the number is written in scientific notation as 2.8×10^{22}.

Let's look at a very small number; for example, 0.00000000000026 inches, the diameter of a hydrogen atom. We want to place our decimal point between the two and the six. To do this, we have to move the decimal point in our number to the right thirteen places. When you are converting a number to scientific notation and you move the decimal point to the right, the power of 10 must have a negative exponent. Thus our number would be written 2.6×10^{-13} inches. A series of numbers in decimal format and in scientific notation are shown in Table 1.3.1 below.

Table 1.3.1: Examples of Numbers in Decimal Format and in Scientific Notation

Decimal Format	Scientific Notation
274	2.74×10^2
0.0035	3.5×10^{-3}
60221415	6.0221415×10^7
0.125	1.25×10^{-1}
402.5	4.025×10^2
0.0002001	2.001×10^{-4}
10,000	1×10^4

Exercise 1.3.1

Convert the following numbers into scientific notation:

a. 93,000,000
b. 708,010
c. 0.000248
d. 800.0

Exercise 1.3.2

Convert the following numbers from scientific notation into decimal format:

a. 6.02×10^4
b. 6.00×10^{-4}
c. 4.68×10^{-2}
d. 9.3×10^7

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1.4: SI and Metric Units

Within the sciences, we use the system of weights and measures that are defined by the International System of Units which are generally referred to as SI Units. At the heart of the SI system is a short list of base units defined in an absolute way without referring to any other units. The base units that we will use in this text, and later in General Chemistry include the meter (m) for distance, the kilogram (kg) for mass and the second (s) for time. The volume of a substance is a derived unit based on the meter, and a cubic meter (m^3) is defined as the volume of a cube that is exactly 1 meter on all edges.

Because most laboratory work that takes place in chemistry is on a relatively small scale, the mass of a kilogram (about 2.2 pounds) is too large to be convenient and the gram is generally utilized, where a gram (g) is defined as 1/1000 kilograms. Likewise, a volume of one cubic meter is too large to be practical in the laboratory and it is common to use the cubic centimeter to describe volume. A cubic centimeter is a cube that is 1/100 meter on each edge, a teaspoon holds approximately 5 cubic centimeters. For liquids and gasses, chemists will usually describe volume using the liter, where a liter (L) is defined as 1000 cubic centimeters.

SI base units are typically represented using the abbreviation for the unit itself, preceded by a metric prefix, where the metric prefix represents the power of 10 that the base unit is multiplied by. The set of common metric prefixes are shown in Table 1.4.1.

Table 1.4.1: Common Metric Prefixes

Factor	Name	Symbol
10^{-12}	pico	p
10^{-9}	nano	n
10^{-6}	micro	µ
10^{-3}	milli	m
10^{-2}	centi	c
10^{-1}	deci	d
1		none
10^{3}	kilo	k
10^{6}	mega	M
10^{9}	giga	G

Using this Table as a reference, we see the metric symbol “c” represents the factor 10^{-2}; thus writing “cm” is equivalent to writing (10^{-2} × m). Likewise, we could describe 1/1000 of a meter as mm, where the metric symbol “m” represents the factor 10^{-3}. The set of metric prefixes and their symbols that are shown in Table 1.3 are widely used in chemistry and it is important that you memorize them and become adept at relating the prefix (and its’ symbol) to the corresponding factor of 10.

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1.5: Unit Conversion with the Metric System

Because chemists often deal with measurements that are both very small (as in the size of an atom) and very large (as in numbers of atoms), it is often necessary to convert between units of metric measurement. For example, a mass measured in grams may be more convenient to work with if it was expressed in mg (10^{-3} × g). Converting between metric units is an exercise in unit analysis (also called dimensional analysis). Unit analysis is a form of proportional reasoning where a given measurement can be multiplied by a known proportion or ratio to give a result having a different unit, or dimension. For example, if you had a sample of a substance with a mass of 0.0034 grams and you wished to express that mass in mg you could use the following unit analysis:

The given quantity in this example is the mass of 0.0034 grams. The quantity that you want to find is the mass in mg, and the known proportion or ratio is given by the definition of the metric prefix, that is one mg is equal to 10^{-3} grams. Expressing this as a proportion or ratio, you could say there is one mg per 10^{-3} grams, or:

Looking at this expression, the numerator, 1 mg, is equivalent to saying 1 × 10^{-3} g, which is identical to the value in the denominator. This ratio, therefore has a numeric value of one (anything divided by itself is one, by definition). Algebraically, we know that we are allowed to multiply any number by one and that number will be unchanged. If, however, the number has units, and we multiply it by a ratio containing units, the units in the number will multiply and divide by the units of the ratio, giving the original number (remember you are multiplying by one) but with different units. In the present case, if we multiply the given by the known ratio, the unit "g" will cancel, leaving "mg" as the only remaining unit. The original number in grams has therefore been converted to milligrams, the units that you wanted to find.

The method that we used to solve this problem can be generalized as: **given × known ratio = find**. The given is a numerical quantity (with its units), the known ratio is based on the metric prefixes and is set up so that the units in the denominator of the ratio match the units of given and the units in the numerator match those in find. When these are multiplied, the number from given will now have the units of find. In the ratio used in the example, "g" (the units of given) appear in the denominator and "mg" (the units of find) appear in the numerator.

As an example of a case where the units of the known ratio must be inverted, if you wanted to convert 1.3 × 10^{7} µg into grams, the given would be 1.3 × 10^{7} µg, the find would be grams and the known ratio would be based on the definition of µg as one µg per 10^{-6} grams. This ratio must be expressed in the solution with µg (the units of given) in the denominator and g (the units of find) in the numerator.

Note that instead of "one µg per 10^{-6} grams", we must invert the known ratio and state it as either "10^{-6} grams per 1 µg" so that the units of given (µg) will cancel. We can do this inversion because the ratio still has a numeric value of one. Simple ratios like these can also be used to convert English measurements in to their metric equivalents. The ratio relating inches to meters is $\left(\frac{0.0254\ \text{m}}{1\ \text{inch}}\right)$.

? Exercise 1.5.1

Convert the following metric measurements into the indicated units:

a. 9.3 × 10^{-4} g into ng
b. 278 g into mg

? Exercise 1.5.2

Convert the following metric measurements into the indicated units:

a. 2,057 grams - as kg
b. 1.25 × 10^{-7} meters - as µm
c. 6.58 × 10^{4} meters - as km
d. 2.78 × 10^{-1} grams - as mg

In the examples we have done thus far, we have been able to write a known ratio based on the definition of the appropriate metric prefix. But what if we wanted to take a number that was expressed in milligrams and convert it to a number with the units of

nanograms? In a case like this, we need to use two known ratios in sequence; the first with the units of given (mg) in the denominator and the second with the units of find (ng) in the numerator. For example, if we were given 0.00602 mg and asked to find ng, we could set up a ratio based on grams per mg. If we solved the problem at this point, we would have a result with the units of grams. To get a final answer in terms of ng, we would need to multiply this intermediate result (the new given) by a ratio based on nanograms per gram.

In the first two terms, the units of “mg” cancel and in the second two terms, “g” cancels leaving only “ng”, the units of find. One of the reassuring pleasures of doing these types of problems is that, if you set up your problem and the units cancel, leaving only the units of find, you know you have set up the problem correctly! All you have to do is to do the sequential calculations and you know your answer is correct!

? Exercise 1.5.3

Convert the following metric measurements into the indicated units:

a. 2,057 mg - into kg
b. 1.25×10^{-7} km - into µm
c. 9.3×10^{-4} pg - into ng
d. 6.5×10^{4} mm - into km

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1.6: Significant Figures

Experimental work in scientific laboratories will generally involve measurement. Whenever we make a measurement, we always strive to make our value as accurate as possible.

The distance is more than 50 mm, the last numbered digit shown before the second arrow. If we look very carefully, we see that the second arrow is about half-way between the fourth and fifth division following the 50 mm mark. The measurement is therefore greater than 54 mm and less than 55 mm and is about 54.5 mm. The last digit in our measurement is estimated, but the first two digits are exact. In any measurement, like this, the last digit that you report is always an estimated digit. If we were to say that the measurement was 54 mm, that would be incorrect, because we know it's larger. If we were to say the measurement was 54.5567 mm, that would be nonsense because our scale does not show that degree of accuracy. In a measurement in science, the estimated digit is called the least significant digit, and the total number of exact digits plus the estimated digit is called the number of significant figures in the measurement. Thus the measurement in the figure, 54.5, has three significant figures (3 SF). By adhering to this rule, we can look at any measured value and immediately know the accuracy of the measurement that was done. In order to properly interpret the number of significant figures in a measurement, we have to know how to interpret measurements containing zeros. For example, an object is found to have a mass of 602 mg. The last digit (the 2) is estimated and the first two digits are exact. The measurement therefore is accurate to three significant figures. We could also express this measurement in grams using the metric conversion ratio $\left({}^{1\ \mathrm{g}}/_{10^3\ \mathrm{mg}}\right)$, making the measurement 0.00602 g. We now have three additional digits in our number (called leading zeros), but is our number any more accurate? No; in a measurement, leading zeros (zeros that appear before the number) are never significant.

Let's consider another measurement; we are told that a distance is 1700 m. The first thing to notice is that this number does not have a decimal point. What this tells us is that the estimated digit in this number is the 7, and that this number only has two significant figures. The last two zeros in this measurement are called trailing zeros; in numbers without a decimal point, trailing zeros are never significant. If, however, the distance was reported as 1700.00 m, the presence of the decimal point would imply that the last zero was the estimated digit (zeros can be estimated too) and this number would have six significant figures. Stated as a rule, in a number containing a decimal point, trailing zeros are always significant. These simple rules for interpreting zeros in measurements are collected below:

Rules for Handling Zeroes when interpreting Significant Figures

In numbers with a decimal point

- leading zeroes are never significant
- trailing zeroes are always significant

In numbers without a decimal point

- trailing zeroes are never significant

In all numbers

- zeroes which appear between non-zero digits are always significant

Applying these rules to some examples:

- 117.880 m contains six significant figures; the number has a decimal point, so the trailing zero is significant.
- 0.002240 g contains four significant figures; the number has a decimal point so the trailing zero is significant, but the leading zeros are not.
- 1,000,100 contains five significant figures; the number does not have a decimal point, so the trailing zeros are not significant. The zeros between the first and fifth digits, however, are significant.
- 6.022×10^{23} contains four significant figures. In scientific notation, all of the significant figures in a measurement are shown before the exponent. (Remember this when you are converting measurements into scientific notation.)

Exercise 1.6.1

Determine the number of significant figures in each of the following numbers:

a. 2,057,000
b. 1.250600
c. 9.300×10^{-4}
d. 6.05×10^{4}

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1.7: Atomic Structure and Electron Configuration

As we learned in Section 1.1, modern atomic theory places protons and neutrons in the nucleus of an atom and electrons are placed in a diffuse cloud surrounding this nucleus. As chemists and physicists began examining the structure of atoms, however, it became apparent that all of the electrons in atoms were not equivalent. The electrons were not randomly placed in one massive “cloud”, rather they seemed to be arranged in distinct energy levels and energy was required to move electrons from a lower to a higher energy level. A mathematical model of atomic structure was developed in the early nineteenth century that defined these energy levels as quantum levels, and today this description is generally referred to as quantum mechanics.

According to the quantum model of the atom, electron for the known elements can reside in seven different quantum levels, denoted by the principal quantum number *n*, where *n* has a value of one to seven. As the quantum number increases, the average energy of the electrons having that quantum number also increases. Each of the seven rows in the periodic table corresponds to a different quantum number. The first row (n = 1) can only accommodate two electrons. Thus an element in the first row of the periodic table can have no more than two electrons (hydrogen has one, and helium has two). The second row (n = 2) can accommodate eight electrons and an element in the second row of the periodic table will have two electrons in the first level (it is full) and up to eight electrons in the second level.

Quantum theory also tells us that the electrons in a given energy level are not all equivalent. Within an energy level electrons reside within sublevels (or subshells). The sublevels for any given level are identified by the letters, s, p, d and f and the total number of sublevels is also given by the quantum number, *n*. The s sublevel can accommodate two electrons, the p holds six, the d holds 10 and the f can hold 14. The elements in the first row in the periodic table (n = 1) have electrons only in the 1s sublevel (n = 1, therefore there can only be one sublevel). The single electron in hydrogen would be identified as 1s1 and the two electrons in helium would be identified as $1s^2$. Fluorine, in the second row of the periodic table (n = 2), has an atomic number of nine and therefore has nine electrons. The electrons in fluorine are arranged, two in the first level ($1s^2$), two in the 2s suborbital ($2s^2$) and five 2p suborbital ($2p^5$). If we were to write the electron configuration for fluorine, we would write it as $1s^2\ 2s^2\ 2p^5$. Each of the sublevels in an atom is also associated with an orbital, where an orbital is simply a region of space where the electron is likely to be found.

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1.8: Filling Orbitals with Electrons

As stated above, an s sublevel can accommodate two electrons, the p accommodates six, there can be 10 in the d sublevel and 14 in the f. Although there are two electrons in the s sublevel, these electrons are not identical; they differ in the quantum property known as spin. As a simple device to illustrate this, the electrons within a suborbital are often represented as arrows pointing up or down, graphically representing opposite spin axes (↑ and ↓). Electrons are added to sublevels according to Hund's rules which state that every orbital in a subshell is singly occupied with one electron before any one orbital is doubly occupied, and all electrons in singly occupied orbitals have the same spin. When a subshell is doubly occupied, the electrons have opposite spins.

For example, carbon has a filled 1s sublevel, a filled 2s sublevel and two electrons in the 2p sublevel ($2p^2$).

The electron configuration for fluorine is $1s^2\ 2s^2\ 2p^5$.

This sequence continues nicely until the third period; it turns out the 3d orbitals are slightly higher in energy than the 4s orbital, therefore the 4s fills with two electrons, and then the next 10 electrons are placed in the 3d orbital. This is a general trend in the periodic table, and the order of filling can be easily predicted by the scheme where you simply follow the arrows on the diagonal to determine the next orbital to fill.

One of the shortcuts that is often used when writing electron configuration is to show "core" electrons simply as the inert gas from the preceding period. For example, fluorine is in the second period (n = 2). That means that the orbitals associated with the first period are already filled, just like they are in the inert gas, helium (He). Therefore, instead of writing the configuration for fluorine as we did above, we can replace the $1s^2$ with the "helium core".

Calcium is in the fourth period and in Group 2. That means that the first three quantum levels are filled (n = 1, 2 and 3) just like they are in argon.

? Exercise 1.8.1: Electron Configurations

a. Write the complete electron configurations for the elements beryllium and carbon.
b. Identify the elements corresponding to the following electron configurations:
   - $1s^2\ 2s^1$ and $1s^2\ 2s^2\ 2p^6$.

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1.S: Measurements and Atomic Structure (Summary)

- Matter is defined as any substance that has mass. Matter is composed of atoms. that are constructed primarily from neutrons, protons and electrons. Neutrons have no charge, protons, carry a positive charge, and electrons, have a negative charge.
- The mass of atoms and subatomic particles is measured using atomic mass units (abbreviated amu); protons and neutrons have a mass of one amu, and the mass of an electron is negligible.
- The neutron and the proton are in the center of the atom in the nucleus. Virtually all of the mass of the atom resides in the nucleus. Electrons are placed in a diffuse cloud surrounding the nucleus.
- The electron cloud carries a net negative charge and in a neutral atom there are always as many electrons in this cloud as there are protons in the nucleus.
- The identity of an atom is defined by the number of protons in its nucleus; each unique type of atom is called an element. Elements with the same number of protons, but differing numbers of neutrons in their nucleus are called isotopes. The atomic mass of an element is the weighted average of the masses each of these isotopes.
- Each element is referred to using its chemical symbol, which is an abbreviation of its name (many symbols are based on Latin or Greek names).
- The atomic symbol for an element consists of the chemical symbol with the atomic number for the element as a subscript, preceding the chemical symbol, and directly above this, a superscript showing the mass number for the particular isotope of the element.
- The average atomic mass for an element can be calculated as the sum of the fraction of each isotope within the natural abundance, multiplied by the mass number of that isotope; or, average atomic mass = $f_1M_1 + f_2M_2 + f_3M_3 \ldots$
- The number of protons in the nucleus of an element is called the atomic number of that element. Elements are typically arranged in order of increasing atomic numbers in the periodic table. In the periodic table, horizontal rows are called periods and vertical columns are called groups.
- Typically in the sciences, very large or very small numbers are shown using scientific notation (exponential notation) where a number *n* is shown as the product of that number and 10, raised to some exponent x; that is, ($n \times 10^x$).
- In the SI (or metric) system, the unit for distance is the meter (m), kilogram (kg) is used for mass and second (s) for time. The volume of a substance is a derived unit based on the meter, and a cubic meter (m^3) is defined as the volume of a cube that is exactly 1 meter on all edges. Typically, in the laboratory, mass is expressed in grams (g) ($^1/_{1000}$ of a kilogram) and the cubic centimeter (cc) is to describe volume. A cubic centimeter is a cube that is $^1/_{100}$ meter on each edge. For liquids and gasses, volume is usually described using the liter, where a liter (L) is defined as 1000 cubic centimeters.
- SI base units are typically represented using the abbreviation for the unit itself, preceded by a metric prefix, where the metric prefix represents the power of 10 that the base unit is multiplied by.
- When converting between metric units, a simple algorithm involves taking a given measurement and multiplying it by a known proportion or ratio to give a result having the metric unit, or dimension, that you were trying to find.
- In a measurement in science, the last digit that is reported is estimated, and this digit is called the least significant digit; this, along with the total number of exact digits plus the estimated digit is called the number of significant figures in the measurement. When identifying the number of significant figures in a measurement, all leading zeros are excluded. Zeros that are surrounded by non-zero digits are included, and, for numbers with a decimal point, trailing zeros are also included. If a number does not have a decimal point, trailing zeros are not included. A number written in scientific notation includes all significant digits in *n*; ($n \times 10^x$).
- According to the quantum model of the atom, electrons reside in seven different quantum levels, denoted by the principal quantum number n, where n has a value of one to seven, corresponding to the seven rows in the periodic table. The first row (n = 1) can accommodate two electrons; the second row ($n = 2$) can accommodate eight electrons; the third row (n = 3), eighteen, up to a maximum of $2n^2$ for the known elements.
- Quantum theory also tells us that the electrons in a given energy level reside within sublevels (or subshells). The sublevels for any given level are identified by the letters, s, p, d and f and the quantum number for the level, written as $1s^2\ 2s^2\ 2p^5$, etc. Each of the sublevels is also associated with an orbital, where an orbital is simply a region of space where the electron is likely to be found.
- When adding electrons to sublevels, Hund's rules state that every orbital in a subshell is singly occupied with one electron before any one orbital is doubly occupied, and all electrons in singly occupied orbitals have the same spin (shown using "up and

down” arrows). Electrons are added in order of increasing energy of the sublevel, not necessarily in numeric order.

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CHAPTER OVERVIEW

2: The Physical and Chemical Properties of Matter

In chapter one, we defined matter as anything that has mass and occupies space. In this chapter, we will look more closely at matter and break it into sub-classes including pure substances and mixtures. We will look at the physical state that matter can adopt (solids, liquids, and gasses) And we will learned how to characterized these using intensive properties such as density. Finally, we will look at changes in these properties and define them in terms of simple physical changes (such as share of physical state) And chemical changes, where one or more substances combine to make new substances.

2.1: Pure Substances and Mixtures

2.2: The States of Matter

2.3: Density, Proportion and Dimensional Analysis

2.4: Chemical and Physical Properties and Changes

2.5: Conservation of Mass

2.S: The Physical and Chemical Properties of Matter (Summary)

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2.1: Pure Substances and Mixtures

In Chapter 1, we learned that atoms are composed of electrons, protons and neutrons and that the number of protons in the nucleus of an atom (the atomic number) defines the identity of that element. For example, an atom with six protons in its nucleus is a carbon atom; seven protons makes it nitrogen; eight protons makes it oxygen, and so on. The periodic table organizes these elements by atomic number and there are currently over 118 known elements.

Because there are *clearly* more than 118 different *types* of substances in the world around us, we can see that most substances that we encounter are *not* pure elements, but are composed of different elements combined together. In chemistry, we refer to these as **compounds**, which we define as *a substance that results from the combination of two or more elements in a constant ratio.* For example, water is a compound composed of two hydrogen atoms *bonded* to one oxygen atom. We can show the ratio of hydrogen to oxygen in this compound by using subscripts on the chemical symbols for each element. Thus, water (two hydrogens and one oxygen) can be written as H_2O. This shorthand notation for water is called a **chemical formula**. For any compound, the chemical formula tells us the elements that are present and the *ratio* of the elements to each other. Later we will see that water is a member of a special sub-type of compound, called a molecular compound. In a **molecule**, the atoms are not only bonded together in a constant ratio, but they are bonded in a *specific geometric arrangement* as well. In the following chapter, we will look more closely at how elements are bonded together in compounds, but first we will examine some of the properties of chemical substances.

When we speak of a **pure substance**, we are speaking of something that contains only one kind of matter. This can either be one single element or one single compound, but every sample of this substance that you examine must contain exactly the same thing with a fixed, definite set of properties. If we take two or more pure substances and mix them together, we refer to this as a **mixture.** Mixtures can always be separated again into component pure substances,because *bonding* among the atoms of the constituent substances does not occur in a mixture. Whereas a compound may have very different properties from the elements that compose it, in mixtures the substances keep their individual properties. For example sodium is a soft shiny metal and chlorine is a pungent green gas. These two elements can combine to form the compound, sodium chloride (table salt) which is a white, crystalline solid having *none* of the properties of either sodium or chlorine. If, however, you *mixed* table salt with ground pepper, you would still be able to see the individual grains of each of them and, if you were patient, you could take tweezers and carefully separate them back into pure salt and pure pepper.

Mixtures fall into two types, based on the uniformity of their composition. The first, called a **heterogeneous mixture**, is distinguished by the fact that different samples of the mixture may have a different composition. For example, if you open a container of mixed nuts and pull out a series of small samples and examine them, the exact ratio of peanuts-to-almonds in the samples will always be slightly different, no matter how carefully you mix them. Common examples of heterogeneous mixtures include dirt, gravel and vegetable soup.

In a **homogeneous mixture,** on the other hand, any sample that you examine will have exactly the *same* composition as any other sample. Within chemistry, the most common type of homogeneous mixture is a **solution** which is one substance dissolved completely within another. Think of a solution of pure sugar dissolved in pure water. Any sample of the solution that you examine will have *exactly* the same ratio of sugar-to-water, which means that it is a homogeneous mixture. Even in a homogeneous mixture, the properties of the components are generally recognizable. Thus, sugar-water tastes sweet (like sugar) and is wet (like water). Unlike a compound, which has a fixed, definite ratio, in a mixture one can vary the amounts of each component. For example, when you add a little sugar to one cup of tea and a lot of sugar to another, each cup will contain a homogeneous mixture of tea and sugar but they will have a different taste. If you add so much sugar that some does not dissolve and stays on the bottom, however, the mixture is no longer homogeneous, it is heterogeneous;you could easily separate the two components.

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2.2: The States of Matter

As described in Section 2.1, a molecule of water is composed of two atoms of hydrogen bonded to one atom of oxygen(H_2O). All water molecules are exactly the same (same ratio of elements, same geometric bonding pattern), but we encounter water in three different forms in the world around us. At low temperature, water exists as a solid (ice). As the temperature increases, water exists as a liquid, and at high temperature, as water vapor, a gas. These three forms of water represent the three **states of matter**: solids, liquids and gases. States of matter are examples of **physical properties** of a substance. Other physical properties include appearance (shiny, dull, smooth, rough), odor, electrical conductivity, thermal conductivity, hardness and density, to name just a few. We will discuss density in more detail in the next section, but first let's examine the states of matter and how they differ on an atomic level.

If ice, liquid water and water vapor all consist of identical molecules, then what accounts for the difference in their properties? So far, we have talked about molecules as if they were standing still, but in fact, they are always moving. In chemistry, we often explain the states of matter in terms of the **kinetic molecular theory (KMT)**. The word *kinetic* refers to motion and the kinetic molecular theory suggests that atoms and molecules are *always* in motion. The energy associated with this motion is termed *kinetic energy.* The amount of kinetic energy that a particle has is a direct function of temperature, and it is the kinetic energy of the water molecules under different conditions that determines the different properties of the three states of water.

Atoms and molecules move in different ways under different conditions because of the forces attracting them to each other, called **intermolecular forces**. *Intermolecular forces* is a general term describing the fact that all atoms, and molecules share a certain inherent *attraction* for each other. These attractive forces are much weaker than the bonds that hold molecules together, but in a large cluster of atoms or molecules the sum of all of these attractive forces can be quite significant.

Now, consider a group of molecules or atoms clustered together and held in place by these attractive forces. At low temperature, the molecules or atoms will remain stuck together in a *lump* of defined shape and structure, like water in the form of an ice cube. This is referred to as the **solid phase**. At the atomic level, the molecules or atoms in a solid are closely packed, and although they are still all rapidly moving, their movements are so small that they can be thought of as vibrating about a fixed position. As an analogy here, think of a handful of small magnets stuck together in a solid mass. Solids and liquids are the most tightly packed states of matter. Because of the intermolecular forces, solids have a defined shape, which is independent of the container in which they are placed. As energy is added to the system, usually in the form of heat, the individual molecules or atoms acquire enough energy to overcome some of the attractive intermolecular forces between them so that neighboring particles are free to move past or slide over one another. This state of matter is called the **liquid phase**. As in a solid, in a liquid, the attractive forces are strong enough to hold the molecules or atoms close together so they are not easily compressed and have a definite volume. Unlike in a solid, however, the particles will flow (slide over each other) so that they can assume the shape of their container.

Finally, if enough energy is put into the system, the individual molecules or atoms acquire enough energy to totally break all of the attractive forces between them and they are free to separate and rapidly move throughout the entire volume of their container. This is called the **gas phase** and atoms or molecules in the gas phase will totally fill whatever container they occupy, taking on the shape and volume of their container. Because there is so much space between the particles in a gas, a gas is *highly compressible*, which means that the molecules can be forced closer together to fit in a much smaller space. We are all familiar with cylinders of compressed gas, where the compressibility of gasses is exploited to allow a large amount of gas to be transported in a very small space.

Returning to our example of water, at low temperature, water exists as the solid, ice. As the solid is warmed, the water molecules acquire enough energy to overcome the strongest of the attractive forces between them and the ice *melts* to form liquid water. This transition from the solid phase to the liquid phase happens at a fixed temperature for each substance called the **melting point**. The melting point of a solid is one of the physical properties of that solid. If we remove energy from the liquid molecules they will slow down enough for the attractive forces to take hold again and a solid will form. The temperature that this happens is called the **freezing point** and is the same temperature as the melting point.

As more energy is put into the system, the water heats up, the molecules begin moving faster and faster until there is finally enough energy in the system to totally overcome the attractive forces. When this happens, the water molecules are free to fly away from each other, fill whatever container they are occupying and become a gas. The transition from the liquid phase to the gas phase

happens at a fixed temperature for each substance and is called the **boiling point**. Like the melting point, the boiling point is another physical property of a liquid.

Phase transitions for a typical substance can be shown using simple diagram showing the physical states, separated by transitions for melting and boiling points. For example, if you are told that a pure substance is 15˚ C above its boiling point, you can use the diagram to plot the temperature relative to the boiling point. Because you are above the boiling point, the substance will exist in the ***gas phase.***

There are, however, some exceptions to the rules for changes of state that we have just established,. For example, ice is a solid and the molecules in the interior are held together tightly by intermolecular forces. Surface molecules, however, are exposed and they have the opportunity to absorb energy from the environment (think of a patch of snow on a bright sunny day). If some of these surface molecules absorb enough energy, they can break the attractive forces that are holding them and escape as a gas (water vapor) without ever going through the liquid phase. The transition from a solid directly into a gas is called **sublimation**. The reverse process, a direct transition from a gas to a solid, is called **deposition**. Perhaps the most common example of a solid that does not melt, but *only* sublimes, is dry ice (solid carbon dioxide;CO_2). This property of dry ice is what makes it a good refrigerant for shipping perishables. It is quite cold, keeping things well frozen, but does not melt into a messy liquid as it warms during shipment.

Just like surface molecules in solids can move directly into the gas phase, surface molecules in liquids also absorb energy from the environment and move into the gas phase, even though the liquid itself is below the boiling point. This is the process of **vaporization** (evaporation). The reverse process, a transition from a gas to a liquid, is called **condensation**. Liquid substances undergo vaporization and the space above any liquid has molecules of that substance in the gas state. This is called the **vapor pressure** of the liquid, and vapor pressure (at a given temperature) is another of the physical properties of liquid substances.

Summarizing what we know about the different states of matter:

In a **gas**:

- the molecules or atoms are highly separated, making a gas highly compressible,
- attractive forces between the particles are *minimal*, allowing the gas to take on the shape and volume of its container.

In a **liquid**:

- the molecules or atoms are closely spaced, making a liquid much less compressible than a gas,
- attractive forces between the particles are *intermediate*, allowing the molecules or atoms to move past, or slide over one another,
- liquids have a definite volume, but will take on the shape of their container.

In a **solid**:

- the attractive forces are strong, keeping the atoms or molecules in relatively fixed positions,
- the neighboring atoms or molecules are close together, making the solid not compressible and giving it a definite shape that is independent of the shape and size of its container.

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2.3: Density, Proportion and Dimensional Analysis

In the previous section, we have learned about the states of matter. The physical state of a substance at under a defined set of conditions (like temperature and pressure) is an **intensive property** of a substance. An intensive property is defined as a property that is inherent to the substance and is not dependent on the sample size. **Density**, the mass-to-volume ratio of a substance, is another example of an intensive property.

If you picked up equal sized samples of aluminum and gold, you would immediately notice that one was much heavier than the other. The atomic mass of gold is over seven times greater than the atomic mass of aluminum, so although the two samples are the same size, the lump of gold is significantly more massive than the equally sized lump of aluminum. We can say that gold is more *dense* than aluminum.

Making this a quantitative measurement, one cubic centimeter of gold has a mass of 19.3 grams (remember that a cubic centimeter is the volume of a cube that is exactly one cm on each side, and it has the units of cm^3. We defined density as the mass-to-volume ratio of a substance. For gold, the mass is 19.3 grams and the volume is 1 cm^3. The mass-to-volume ratio of gold is and the density (*d*) of gold is written as *d* = 19.3 g/cm^3.

Returning to our block of aluminum;experimentally, one cubic centimeter of aluminum has a mass of 2.70 grams. The mass-to-volume ratio of aluminum is , and the density of aluminum is therefore 2.70 g/cm^3, about 7 times *less* than that of gold.

Density is a physical property that can be measured for all substances, solids, liquids and gasses. For solids and liquids, density is often reported using the units of g/cm^3. Densities of gasses, which are significantly lower than the densities of solids and liquids, are often given using units grams/liter (g/L, remembering from SI and Metric Units" data-cke-saved-href="/Bookshelves/Introductory_Chemistry/Book:_Introductory_Chemistry_Online_(Young)/01:_Measurements_and_Atomic_Structure/1.4:_SI_and_Metric_Units" href="/Bookshelves/Introductory_Chemistry/Book:_Introductory_Chemistry_Online_(Young)/01:_Measurements_and_Atomic_Structure/1.4:_SI_and_Metric_Units" data-quail-id="28">Section 1.4 that a liter is defined as 1000 cm^3).

The definition of density that we used previously was *the mass-to-volume ratio of a substance*. This is also stated as “mass *per* unit volume”. The word *per* in this context implies that a mathematical relationship exists between mass and volume. In this case, the relationship is the ratio of mass-to-volume. Whenever two factors can be related by a *ratio* or fraction we can use *unit analysis* to solve problems relating those factors. For density, the ratio is mass-to-volume. If a sample of iron has a mass of 23.4 grams and a volume of 3.00 cm^3, the density of iron can be calculated as:

$$d = \frac{mass}{volume}$$

$$d = \frac{23.4g}{3.00cm^3} = 7.80\ g/cm^3$$

In this calculation, our two experimental numbers are 23.4 and 3.00. Each of these numbers has *three significant figures* (remember, the trailing zeros in 3.00 are significant because the number has a decimal point). Our answer must therefore *also* be accurate to three significant figures, or 7.80.

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2.4: Chemical and Physical Properties and Changes

A lump of gold can be hammered into a very thin sheet of gold foil (it is the most *malleable* of all of the elements). Nonetheless, the gold in the foil sheet is still just elemental gold;nothing has changed except the physical appearance of the sample. The same is true if you take any solid pure substance and melt it, or convert it to a gas. The atomic or molecular structure of the substance has not changed, it simply has a different physical appearance. Changes in outward appearances that do not alter the chemical nature of the substance and make no new substance are called **physical changes**. Pure carbon, in the form of a briquette, can be smashed to a fine power without changing the fact that it is still just elemental carbon (thus, this is a physical change), but if pure carbon is heated in the presence of oxygen, something else happens. The carbon slowly disappears (often in flames) and the carbon atoms now appear as a compound with oxygen with the formula CO_2. Carbon dioxide is a totally different substance than either the carbon or the oxygen that we started with. For example, carbon is a black solid and carbon dioxide is a colorless gas. You know that a **chemical change** has occurred when the chemical composition of the material changes and a new substance is produced.

Just like we defined a set of physical properties for substances, we can also define a set of **chemical properties**. Chemical properties are simply the set of chemical changes that are possible for that substance. For the element magnesium (Mg), we could say that chemical properties include:

- the reaction with oxygen to form MgO
- the reaction with hydrochloric acid to form $MgCl_2$ and hydrogen gas (H_2)
- the reaction with solid carbon dioxide (dry ice) to form MgO and carbon

Chemical changes can almost always be detected with one of our physical senses. Thus, when magnesium reacts with oxygen (burns in air) a bright white flame is produced, heat is evolved and the shiny metallic magnesium is converted to a crumbly white powder MgO. In the reaction with hydrochloric acid (the molecule HCl dissolved in water), the solid metallic magnesium disappears, bubbles of hydrogen gas (H_2) are evolved, heat is produced, and a clear solution containing $MgCl_2$ is formed. In the reaction with solid carbon dioxide (dry ice), a bright white flame is produced, heat is evolved and the shiny metallic magnesium is converted to a crumbly white powder and solid carbon. In general, when you are trying to identify a chemical change, look for evidence of heat or light, the evolution of a gas, a change in color or the formation of new solid products from otherwise clear solutions.

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2.5: Conservation of Mass

When substances undergo chemical changes their physical state is usually dramatically altered. Despite this dramatic change, however, no matter is lost or created. We can show this with the reaction of magnesium metal with oxygen to form magnesium oxide. Instead of burning the magnesium metal openly in the air, if you were to *seal* the magnesium and air together in a glass vessel, weigh it, heat it to promote reaction, and then weigh the vessel again, you would find that there was *no change* in total mass. The mass of the product, magnesium oxide, would *exactly* equal the masses of the substances that reacted (oxygen gas and magnesium metal).

This is analogous to an experiment performed by the French chemist, Lavoisier, in the 1770s in which he heated metallic tin (Sn) with air in a closed vessel. This, and other experiments of the time, provided the data that led to the **law of mass conservation**. Formally, the law states, *there is no detectable change in the total mass of materials when they react chemically to form new materials*.

Basically, what the *conservation law* says is that whenever a chemical change occurs, the total mass of the substances reacting must equal the total mass of the substances that are produced. Sometimes this is stated as *mass is conserved* or *mass is neither created nor destroyed in a chemical reaction.* For example, when charcoal is burned in oxygen, the mass of the (charcoal + oxygen) must equal the mass of the (carbon dioxide, water vapor and ash) that is produced. The conservation of mass is one of the fundamental principles on which modern chemistry is based.

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2.S: The Physical and Chemical Properties of Matter (Summary)

- A **compound** is defined as a substance that results from the combination of two or more elements in a constant ratio. In a compound such as water, we show the ratio of the elements (hydrogen and oxygen) by using *subscripts* on the chemical symbols for each element. Thus, water (two hydrogens and one oxygen) is written using the **chemical formula** H_2O. In a **molecule**, the atoms are not only bonded together in a constant ratio, but they are also bonded in a *specific geometric arrangement*.
- A **pure substance** contains only one kind of matter;it can be a single element or a single chemical compound. Two or more pure substances mixed together constitute a mixture;you can always separate a mixture by simple physical means.
- A **heterogeneous mixture** is not uniform and different samples of the mixture will have a different compositions. A **homogeneous mixture**, is uniform and any sample that you examine will have *exactly* the same composition as any other sample. Within chemistry, the most common type of homogeneous mixture is a **solution**.
- Any pure substance, under appropriate conditions, can exist in three different **states**: solids, liquids and gases. States of matter are examples of **physical properties** of a substance. Other physical properties include appearance (shiny, dull, smooth, rough), odor, electrical conductivity, thermal conductivity, hardness and density, etc.
- **Solids** have both a definite shape and volume. **Liquids** have a definite volume, but take on the shape of their container. **Gasses** have neither a definite shape nor volume, and both of these are defined by the shape and volume of their container.
- The **kinetic molecular theory (KMT)** is generally used to explain physical states of matter. The KMT suggests that atoms and molecules are *always* in motion and are loosely bound to each other by attractive called **intermolecular forces**. In a **solid**, the kinetic energy (energy of motion) associated with the atoms or molecules is insufficient to break these forces and the particles are essentially fixed in place, adjacent to each other. In a **liquid**, there is enough kinetic energy to break some of the attractive forces, allowing the particles to “slip and slide” next to each other, but there is not enough energy to allow them to escape. In a **gas**, there is sufficient kinetic energy to totally overcome the forces and the particles have no interactions with each other.
- A change of state from a solid to a liquid occurs at a defined temperature (which) called the **melting point** (or freezing point);this temperature is a unique physical property of the substance. The transition from a liquid to a gas, likewise, occurs at the **boiling point**. A direct transition from a solid to a gas is called **sublimation**.
- An **intensive property** is defined as a property that is *inherent* to the substance and is not dependent on the sample size. **Density**, the ratio of mass-to-volume for a substance, is a classic example of an intensive property.
- **Density** is calculated by taking the **mass** of a sample of a substance, and dividing that by the **volume** of that sample. Density for solids is typically expressed using units of grams per cubic centimeter ($g\ cm^{-3}$);liquids as grams per milliliter ($g\ mL^{-1}$) and gasses as grams per liter ($g\ L^{-1}$), although any mixture of mass and volume units may be used. Remember, a mL has the same volume as a cm^3, and a L is simply 1000 mL.
- **Physical changes** are changes in outward appearances that do not alter the chemical nature of the substance and produce no new substance. When a **chemical change** occurs, a new substance is produced. Just like physical properties describe the appearance or intensive properties of a substance, **chemical properties** describe the set of chemical changes that are possible for that substance.
- The **law of mass conservation** (conservation of mass) simply states, that there is no detectable change in the total mass of materials when they react chemically (undergo a chemical change) to form new substances.

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CHAPTER OVERVIEW

3: Chemical Bonding and Nomenclature

When elements combine to make compounds, they form strong chemical bonds to each other so that the compounds now behaves as a single new substance. In this chapter, we will see that there are two ways that atoms bond to each other: either by transferring electrons or by sharing them. These two types of bonding are called ionic and covalent. We will learn to draw Lewis structure for atoms and molecules and see how we can use these to show (and predict) bonding patterns in compounds. Finally, we will learn how to systematically name and classify compounds using simple rules based on the type of bonds used to construct them.

3.1: Compounds, Lewis Diagrams and Ionic Bonds
3.2: Covalent Bonding
3.3: Lewis Representation of Ionic Compounds
3.4: Identifying Molecular and Ionic Compounds
3.5: Polyatomic Ions
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3.S: Chemical Bonding and Nomenclature (Summary)

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3.1: Compounds, Lewis Diagrams and Ionic Bonds

If we take two or more atoms and bond them together chemically so that they now behave as a single substance, we have made a chemical compound. We will see that the process of bonding actually involves either the *sharing*, or the net *transfer*, of electrons from one atom to another. The two types of bonding are **covalent**, for the sharing of electrons between atoms, and **ionic**, for the net transfer of electrons between atoms. Covalent or ionic bonding will determine the *type* of compound that will be formed.

In Chapter 1, we used atomic theory to describe the structure of the fluorine atom. We said that neutral fluorine has nine protons in its nucleus (an atomic number of 9), nine electrons surrounding the nucleus (to make it neutral), and the most common isotope has ten neutrons in its nucleus, for a mass number of 19. Further, we said that the nine electrons exist in two energy levels; the first energy level contains two electrons and is written $1s^2$. The second energy level contains seven electrons, distributed as $2s^2\ 2p^5$. The *outermost* electron level in any atom is referred to as the **valence shell**. For the representative elements (remember, this includes all of the elements except for the transition metals), the number of electrons in the valence shell corresponds to the Group number of the element in the periodic table. Group 1A elements will have one valence electron, Group 6A elements will have six valence electrons, and so on. Fluorine is a Group 7A element and has seven valence electrons. We can show the electron configuration for fluorine using a **Lewis diagram** (or *electron-dot structure*), named after the American chemist G. N. Lewis, who proposed the concepts of electron shells and valence electrons. In a Lewis diagram, the electrons in the valence shell are shown as small "dots" surrounding the atomic symbol for the element.

$$\cdot\ddot{\underset{\cdot\cdot}{F}}\cdot$$

When more than four electrons are present in the valence shell, they are shown as pairs when writing the Lewis diagram (but never more than pairs). Lewis diagrams for the atoms in the second period are shown below:

$$\cdot Li \qquad \cdot Be \cdot \qquad \cdot\dot{B}\cdot \qquad \cdot\dot{\underset{\cdot}{C}}\cdot$$

$$\cdot\ddot{\underset{\cdot}{N}}\cdot \qquad :\ddot{\underset{\cdot}{O}}\cdot \qquad \cdot\ddot{\underset{\cdot\cdot}{F}}\cdot \qquad :\ddot{\underset{\cdot\cdot}{N}}e:$$

As you look at the dot-structures please understand that it makes *no difference* where you place the electrons, or the electron pairs, around the symbol, as long as pairs are shown whenever there are four or more valence electrons.

If you examine the Lewis diagram for neon (Ne) above, you will see that the valence shell is *filled*; that is, there are eight electrons in the valence shell. Elements in Group 8A of the periodic table are called *noble gasses*; they are very stable and do not routinely combine with other elements to form compounds (although today, many compounds containing noble gasses are known). Modern bonding theory tells us that this stability arises because the valence shell in the noble gasses is completely filled. When the valence shell is *not* full, theory suggests that atoms will transfer or share electrons with other atoms in order to achieve a filled valence shell… that is, the electron configuration of the noble gasses. Chemical bonding can then be viewed as a quest by atoms to acquire (or lose) enough electrons so that their valence shells are filled, that is, to achieve a "noble gas configuration". This is often referred to as the "**octet rule**"; the desire for elements to obtain eight electrons in the valence shell (except of course for helium where the noble gas configuration is *two* valence electrons).

Atoms can achieve a noble gas configuration by two methods; the transfer of electrons from their valence shells to another atom, or by sharing electrons with another atom. If you examine the Lewis diagram for lithium (Li), you will see that it has only one valence electron. If lithium was to *transfer* this electron to another atom, it would be left with two electrons in the 1*s*-orbital (denoted as $1s^2$). This is the same electron configuration as helium (He), and so by losing this electron, lithium has achieved a *noble gas configuration*. Because electrons carry a negative charge, the loss of this electron leaves lithium with a single positive charge. This is the **lithium cation** and it is shown as Li^+.

Returning to fluorine (F), in order to achieve the $2s^2\ 2p^6$ configuration of neon (Ne), fluorine needs to *gain* one valence electron. Because fluorine has *gained* one electron, it now has one negative charge. This is the fluoride anion and it is shown as F^-. The transfer of electrons in order to achieve a noble gas configuration is the process known as **ionic bonding**, and this will be covered in more detail later in this chapter.

Exercise 3.1.1

a. Sodium and chlorine are both third-period elements. Draw Lewis diagrams for each of these elements.
b. What number of electrons would chlorine have to gain in order to achieve a “noble gas configuration”? What would be the charge on chlorine?
c. What number of electrons would Na have to lose to obtain the noble gas configuration of Ne with *eight* valence electrons? What charge would Na have?

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3.2: Covalent Bonding

A second method by which atoms can achieve a filled valence shell is by *sharing* valence electrons with another atom. Thus fluorine, with one unpaired valence electron, can share that electron with an unshared electron on another fluorine to form the compound, F_2 in which the two shared electrons form a chemical bond holding the two fluorine atoms together. When you do this, each fluorine now has the equivalent of eight electrons in its valence shell; three unshared pairs and one pair that is *shared* between the two atoms. Note that when you are counting electrons, the electrons that are shared in the covalent bond are counted for each atom, individually. A chemical bond formed by *sharing* electrons between atoms is called a **covalent bond**. When two or more atoms are bonded together utilizing covalent bonds, the compound is referred to as a **molecule**.

There is a simple method, given below, that we can use to construct Lewis diagrams for diatomic and for polyatomic molecules:

- Begin by adding up all of the *valence electrons* in the molecule. For F_2, each fluorine has seven, giving a total of 14 valence electrons.
- Next, draw your *central atom*. For a diatomic molecule like F_2, both atoms are the same, but if several different atoms are present, the *central atom* will be to the *left* (or lower) in the periodic table.
- Next, draw the other atoms around the *central atom*, placing two electrons *between* the atoms to form a covalent bond.
- Distribute the remaining valence electrons, as pairs, around each of the outer atoms, so that they all are surrounded by *eight electrons.*
- Place any remaining electrons on the *central atom.*
- If the central atom is *not* surrounded by an octet of electrons, construct *multiple bonds* with the outer atoms until *all* atoms have a complete octet.
- If there are an *odd number* of valence electrons in the molecule, leave the remaining single electron on the *central atom.*

Let's apply these rules for the Lewis diagram for chlorine gas, Cl_2. There are 14 valence electrons in the molecule. Both atoms are the same, so we draw them next to each other and place two electrons between them to form the covalent bond. Of the twelve remain electrons, we now place six around one chlorine (to give an octet) and then place the other six around the other chlorine (our *central atom*). Checking, we see that each atom is surrounded by an octet of valence electrons, and so our structure is complete.

$$:\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}\cdot\cdot\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}:$$

All of the Group 7A elements (the halogens), have valence shells with seven electrons and all of the common halogens exist in nature as diatomic molecules; fluorine, F_2; chlorine, Cl_2; bromine, Br_2 and iodine I_2 (astatine, the halogen in the sixth period, is a short-lived radioactive element and its chemical properties are poorly understood). Nitrogen and oxygen, Group 5A and 6A elements, respectively, also exists in nature as diatomic molecules (N_2 and O_2). Let's consider **oxygen**; oxygen has six valence electrons (a Group 6A element). Following the logic that we used for chlorine, we draw the two atoms and place one pair of electrons between them, leaving 10 valence electrons. We place three pairs on one oxygen atom, and the remaining two pairs on the second (our *central atom*). Because we only have six valence electrons surrounding the second oxygen atom, we must move one pair from the other oxygen and form a second covalent bond (a **double bond**) between the two atoms. Doing this, each atom now has an octet of valence electrons.

$$:\underset{\cdot\cdot}{O}::\overset{\cdot\cdot}{O}:$$

Nitrogen has five valence electrons. Sharing one on each atom gives the first intermediate where each nitrogen is surrounded by six electrons (not enough!). Sharing another pair, each nitrogen is surrounded by seven electrons, and finally, sharing the third, we get a structure where each nitrogen is surrounded by eight electrons; a noble gas configuration (or the "octet rule"). Nitrogen is a very stable molecule and relatively unreactive, being held together by a strong **triple covalent bond**.

$$:N\vdots\vdots N:$$

As we have constructed Lewis diagrams, thus far, we have strived to achieve an octet of electrons around every element. In nature, however, there are many exceptions to the "octet rule". Elements in the first row of the periodic table (hydrogen and helium) can only accommodate *two* valence electrons. Elements below the second row in the periodic table can accommodate, 10, 12 or even

14 valence electrons (we will see an example of this in the next section). Finally, in many cases molecules exist with single unpaired electrons. A classic example of this is oxygen gas (O_2). We have previously drawn the Lewis diagram for oxygen with an oxygen-oxygen double bond. Physical measurements on oxygen, however, suggest that this picture of bonding is not quite accurate. The magnetic properties of oxygen, O_2, are most consistent with a structure having *two unpaired* electrons in the configuration shown below:

$$:\underset{\cdot}{\ddot{O}}\cdot\cdot\underset{\cdot}{\ddot{O}}:$$

In this Lewis diagram, each oxygen atom is surrounded by *seven* electrons (not eight). This electronic configuration may explain why oxygen is such a *reactive* molecule (reacting with iron, for example, to form rust); the unpaired electrons on the oxygen molecule are readily available to interact with electrons on other elements to form new chemical compounds.

Another notable exception to the "octet rule" is the molecule NO (nitrogen monoxide). Combining one nitrogen (Group 5A) with one oxygen (Group 6A) gives a molecule with *eleven* valence electrons. There is *no way* to arrange eleven electrons without leaving one electron unpaired. Nitric oxide is an extremely reactive molecule (by virtue of its unshared electron) and has been found to play a central role is biochemistry as a reactive, short-lived molecule involved in cellular communication.

$$\cdot\underset{\cdot}{\ddot{N}}\cdot\cdot\underset{\cdot}{\ddot{O}}:$$

As useful as Lewis diagrams can be, chemists tire of drawing little dots and, for a shorthand representation of a covalent bond, a short line (a **line-bond**) is often drawn between the two elements. Whenever you see atoms connected by a line-bond, you are expected to understand that this represents two shared electrons in a covalent bond. Further, the *unshared pairs* of electrons on the bonded atoms are sometimes shown, and sometimes they are omitted. If unshared pairs ore omitted, the chemist reading the structure is assumed to understand that they are present.

$$\underset{\cdot\cdot}{\ddot{F}}\cdot\cdot\underset{\cdot\cdot}{\ddot{F}}:\ or\ :\underset{\cdot\cdot}{\ddot{F}}-\underset{\cdot\cdot}{\ddot{F}}:\ or\ F-F$$

$$:N\vdots N:\ or\ :N\equiv N:\ or\ N\equiv N$$

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3.3: Lewis Representation of Ionic Compounds

As mentioned in Section 3.1, elements can also *transfer* electrons to another element in order to achieve the noble gas configuration. Consider sodium. Sodium (Na) is in Group 3A. Its first energy level is completely filled ($1s^2$), the second energy level is also filled ($2s^2\ 2p^6$) and there is a single electron in the third energy level ($3s^1$). Energetically, the easiest way for sodium to achieve an octet of valence electrons is by *transferring* its valence electron to an acceptor atom. This will leave the sodium atom with the same electron configuration as neon ($1s^2 2s^2\ 2p^6$), and will satisfy the "octet rule". Because sodium *loses* one electron (with its negative charge) the sodium atom must now have a positive charge. Atoms, or covalently bound groups of atoms with a positive charge are called **cations**, and the sodium cation is written as Na^+.

If the acceptor atom in the example above was chlorine, the third valence shell would now be filled, matching the electron configuration of argon. Because the chlorine atom has *accepted* an electron, with its negative charge, the chlorine atom must now have a negative charge. Atoms, or covalently bound groups of atoms with a negative charge are called **anions**, and the chlorine anion is written as Cl^-. Although electron transfer has occurred between the two atoms in this example, there is *no direct bond* holding the sodium cation and the chlorine anion together, other than the simple electrostatic attraction between the two charged atoms. This is the real difference between ionic and covalently bound atoms; covalent molecules are held together in a *specific geometry* which is dictated by the electrons that they share. Ionic compounds are held together by simple electrostatic attraction and, unless these atoms are present in organized crystals, there is no defined geometric order to this attraction. Ionic compounds are often referred to as **salts**.

? Exercise 3.3.1

a. Hydrogen and oxygen react to form water, H_2O. Draw a Lewis diagram for water using the line-bond shorthand.
b. Draw the Lewis diagram for the molecules, hydrogen chloride, BrCl, and hydrogen cyanide (HCN).

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3.4: Identifying Molecular and Ionic Compounds

The tendency for two or more elements to combine and form a molecule that is stabilized by covalent bonds (a molecular compound) can be predicted simply by the location of the various elements on the periodic table. In Chapter 1, we divided the elements in the periodic table into (seemingly) arbitrary groupings; the metals, the non-metals, the semi-metals, and so on. These groupings are not arbitrary, but are largely based on physical properties and on the tendency of the various elements to bond with other elements by forming either an ionic or a covalent bond. As a general rule of thumb, compounds that involve a metal binding with either a non-metal or a semi-metal will display ionic bonding. Compounds that are composed of only non-metals or semi-metals with non-metals will display covalent bonding and will be classified as molecular compounds. Thus, the compound formed from sodium and chlorine will be ionic (a metal and a non-metal). Nitrogen monoxide (NO) will be a covalently bound molecule (two non-metals), silicon dioxide (SiO_2) will be a covalently bound molecule (a semi-metal and a non-metal) and $MgCl_2$ will be ionic (a metal and a non-metal). Later in this chapter we will see that many covalent compounds have bonds that are highly **polarized** with greater electron density around one atom than the other. These compounds are often described as having "ionic character" and these types of covalent bonds can often be readily broken to form sets of ions.

Exercise 3.4.1

a. Determine whether each of the following compounds is likely to exist as a molecule, or as an ionic compound:

i. Hydrogen fluoride; HF
ii. Silicon tetrachloride; $SiCl_4$
iii. Elemental sulfur as S_8
iv. Disodium dioxide; Na_2O
v. PF_3
vi. Be_3N_2
vii. AlP
viii. CBr_4

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3.5: Polyatomic Ions

The compound NaOH has wide industrial use and is the active ingredient in drain cleaners. Based on the discussion in the previous section, we would expect NaOH to be an ionic compound because it contains sodium, a Group 1A metal. Hydrogen and oxygen, however, are nonmetals, and we would expect these to bond together covalently. This compound, called sodium hydroxide, is an example of an ionic compound formed between a metal ion (sodium) and a *polyatomic ion* (HO^-). Charged groups of atoms, like HO^-, that are bonded together covalently are called **polyatomic ions**. Within an ionic compound a polyatomic behaves as a single unit forming salts with other cations or anions.

Using the rules described in Section 3.2, we can draw a Lewis diagram for HO^-. Oxygen has six valence electrons and hydrogen has one, for a total of seven. The central atom in our structure will be hydrogen (it is to the *left* of oxygen in the periodic table). Next, because this is a polyatomic ion with a single negative charge, we add the extra electron to the central atom, pair the electrons and then draw the two atoms bonded together. Next, the six remaining electrons are distributed around the oxygen to form an octet. Finally, the polyatomic ion is enclosed in brackets with the charge as a superscript to show that the ion behaves as a single unit.

Polyatomic ions are very common in chemistry. It is *essential* that you memorize these and be able to correlate the name, the composition and the charge for each of them, as they will be discussed freely throughout the remainder of the course and you will be expected to know these in General Chemistry.

Example 3.5.1:

Construct a Lewis diagram for the polyatomic ion CO_3^{2-}.

Solution

Oxygen has six valence electrons and carbon has four; therefore in CO_3^{2-} there will be a total of 22 valence electrons, plus two additional electrons from the 2- charge. The central atom in our structure will be carbon (it is to the *left* of oxygen in the periodic table). Next, we draw the carbon (our central atom) with its' four electrons and add the additional two electrons from the charge. The three oxygens are placed around the carbon and the electrons are arranged to form the three covalent bonds. Next, the 18 remaining electrons are distributed around the oxygens so that they all have a full octet. The carbon, however, is only surrounded by six electrons. To remedy this, we move one electron pair in to form a double bond to one of the oxygen atoms. Finally, the polyatomic ion is enclosed in brackets with the charge as a superscript.

We need to understand that the process of placing electrons into a particular bond in a compound is an *artificial* aspect of building Lewis diagrams. In fact, the electrons are added to the polyatomic ion, but it is *impossible* to know exactly where they went.

Exercise 3.5.1

a. Draw Lewis diagrams for NO_2^- and NH_4^+.

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3.6: Resonance

In the previous section, we constructed a Lewis diagram for the carbonate anion. Our final structure showed two carbon-oxygen single bonds and one carbon-oxygen double bond. The structure that we drew is shown below, along with two other possible representations for the carbonate anion. These structures differ only in the position of the carbon-oxygen double bond.

So which of these is correct? Actually, they *all* are! These are all “proper” Lewis diagrams for a covalent structure having constant geometry, and the diagrams differ *only* in the manner that we have arbitrarily arranged the electrons. These Lewis diagrams are called **resonance forms**. For the carbonate anion, there are three equivalent resonance forms that can be drawn. It is important to note that the electrons are not “hopping” between the atoms, but that the electrons are spread *evenly* between the carbon and all three oxygens and that each carbon-oxygen bond has a bond-order of 1.33 (one and one-third covalent bonds). A structure such as this is called the **resonance hybrid**, and although it most clearly represents the actual bonding in the compound, it is often difficult to understand the nature of the bonding when structures are represented as resonance hybrids. A full discussion of resonance is beyond the scope of an introductory text and, for structures such as the carbonate anion, we will accept any of the proper resonance forms shown above.

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3.7: Electronegativity and the Polar Covalent Bond

If we were to construct a Lewis diagram for molecular hydrogen (H_2), we would pair the single valence electrons on each atom to make a single covalent bond. Each hydrogen would now have two electrons in its valence shell, identical to helium. The mathematical equations chemists use to describe covalent bonding can be solved to predict the regions of space surrounding the molecule in which these electrons are likely to be found. A particularly useful application of these calculations generates a **molecular surface** that is color coded to show *electron density* surrounding the molecule. This type of molecular surface is called an **electrostatic potential map.** When this type of calculation is done for molecules consisting of two (or more) *different* atoms, the results can be strikingly different. Consider the molecule HF. Hydrogen, with one valance electron, can share that electron with fluorine (with seven valence electrons) to form a single covalent bond.

In this electrostatic potential map, blue is used to indicate low electron density (a relative *positive* charge) and red indicates high electron density (a relative *negative* charge); the colors light blue, green, yellow and orange indicate the increasing charge gradient. The molecule HF is clearly very **polar**, meaning that a significant difference in electron density exists across the length of the molecule. The electrostatic potential map for HF contrasts significantly with that for H_2, where the charge was quite symmetrical (a uniform green color). Hydrogen fluoride (HF) can be described as a very *polar* molecule, while hydrogen (H_2) is *nonpolar*.

The origin of the polarization of the HF covalent bond has to do with *electronegativity*, an inherent property of all atoms. Within the periodic table, there is a trend for atoms to attract electrons towards themselves when they are bonded to another atom (as in HF). Atoms that tend to strongly attract electrons have a high electronegativity, relative to atoms that have a relatively low tendency to attract electrons towards themselves. The modern electronegativity scale was devised by Linus Pauling in 1932 and, in the Pauling scale, atoms in the periodic table vary in electronegativity from a low of 0.8 for cesium to a maximum of 4.0 for fluorine.

In the molecule HF, the electronegativity of the hydrogen is 2.2 and fluorine is 4.0. This difference leads to the profound polarization of the HF covalent bond which is apparent in the electrostatic potential map.

Polarizations of covalent bonds also occur in more complex molecules. In water, the oxygen has an electronegativity of 3.5; hydrogen is 2.2. Because of this, each of the H-O bonds is polarized with greater electron density towards the oxygen. Within the molecule, H_2O, the effect of this polarization becomes apparent in the electrostatic potential map, as shown in Figure 3.18. The end of the molecule with the oxygen has a high electron density and the hydrogen ends are electron deficient. We will see in later chapters that the polarization of water, caused by the difference in electronegativities, gives water the special properties that allows it to dissolve ionic compounds, and basically support life as we know it. Within organic chemistry (the study of carbon-containing molecular compounds), you will appreciate that the relative reactivity of organic molecules with each other is largely dependent on the polarization of covalent bonds in these molecules.

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3.8: Exceptions to the Octet Rule

Returning briefly to classical Lewis diagrams. Consider the diagram shown below for the molecule SF_4. In constructing this diagram, six valence electrons are placed around the sulfur and seven valence electrons are placed around each fluorine. As we attempt to pair these to form covalent bonds, we note that there are "too many" electrons on the sulfur! We clearly cannot form a covalent bond using three electrons, so we *split* one pair, move the single electrons into bonding position and form bonds with the remaining two fluorines. The "extra pair" of electrons just *sits there* on the sulfur and does not participate directly in the bonding.

This is an example of **valence expansion**. In general, elements *below* the second period in the periodic table (S, Se, Te, etc.) will commonly have 10 – 12 electrons in their valence shells. As in SF_4, these electrons are not directly involved in the formation of covalent bonds, but they affect the overall reactivity of the particular molecule.

In general, all molecular compounds containing elements that appear below the second row in the periodic table are capable of valence expansion and you need to be very careful when you are drawing Lewis diagrams for these compounds. As we saw in Section 3.1 for the molecule nitrogen oxide (NO), stable molecules also exist in which atoms are *not* surrounded by an octet of electrons. Another example of this is the molecule BF_3, which is shown in the following example.

Example 3.8.1: Boron Trifluoride

Construct a Lewis diagram for the molecule BF_3.

Solution

Boron has three valence electrons and fluorine has seven. The central atom in our structure will be boron (it is to the *left* of fluorine in the periodic table). Next, we draw the boron (our central atom) with its' three electrons and place the three fluorines around the boron with the electrons arranged to form the three covalent bonds. Each of the fluorines have a full octet. The boron, however, is only surrounded by six electrons. Because of this, the boron in BF_3 is a powerful *electron acceptor* and forms strong complexes with electrons from other compounds. In Chapter 8 we will see that this property is called Lewis acidity and BF_3 is a very powerful Lewis acid.

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3.9: Common Valence States and Ionic Compounds

In an ionic compound the total number of charges on the cations must equal the total number of charges on the anions; that is, the compound must be *neutral*. In Section 3.2 we described how a sodium atom can donate an electron to another atom in order to form an ion with a full octet of electrons in its outermost electron shell (the same electron configuration as Ne). The charge on the sodium atom, when this happens, is now 1+, because it has eleven protons in its nucleus, but is only surrounded by 10 electrons. Lithium, likewise, can lose one electron to form Li^{1+} and be left with the same electron configuration as He. In fact, all of the Group 1A metals can lose a single electron to form 1+ ions. Elements in Group 2A can each lose *two* electrons to form 2+ ions and achieve a noble gas configuration. In fact, the group that a main-group element is associated with in the periodic table will dictate the valence (or charge) of its corresponding ion. Metals in Groups 1A, 2A and 3A will form ions with 1+, 2+ and 3+ charges, respectively.

Main-group nonmetals can easily achieve an octet of valence electrons by accepting electrons from other elements. Thus Group 5A elements can accept three electrons to form 3- ions, Group 6A elements accept two electrons to form 2- ions and Group 7A elements (the halogens) accept one electron to form 1- ions. For example, oxygen (Group 6A) needs to accept two electrons to achieve the electron configuration of neon. This gives oxygen a total of 10 electrons, but it only has eight protons in its nucleus (its atomic number is 8), therefore, the oxygen ion has a net charge of 2- (O^{2-}).

To write a formula for an ionic compound composed of main group elements (or containing polyatomic ions) you need to adjust the ratio of anions and cations so that the resulting molecule is electrically neutral. For example, consider an ionic compound containing sodium and chlorine. Lithium is a Group 1A element and will form a 1+ ion; fluorine is a Group 7A element and will form a 1- ion. Neutrality is achieved when one lithium is paired with one fluorine, or LiF. For a compound composed of calcium and chlorine, the Group 2A calcium will form a 2+ ion while chlorine forms a 1- ion. To achieve neutrality, there must be *two* chlorines for every calcium, and the formula must be as $CaCl_2$. Aluminum (Group 3A) will form a 3+ ion. If this was paired with oxygen (Group 6A) which forms a 2- ion neutrality would only be achieved if *two* Al^{3+} ions (for a total of six positive charges) were paired with *three* O^{2-} ions (a total of six negative charges).

Consider a compound consisting of sodium and the polyatomic ion sulfate (SO_4^{2-}). Sodium (Group 1A) yields a 1+ cation and so there must be *two* sodiums in the compound for every sulfate (which has a 2- charge), or Na_2SO_4. For a compound containing calcium (Group 2A) and nitrate (NO_3^-), *two* nitrate anions must be present for every calcium 2+ cation. In a compound containing multiple copies of a polyatomic ion, the entire ion is enclosed in parenthesis with a subscript to indicate the number of units. Thus the compound from calcium and nitrate would be written as $Ca(NO_3)_2$.

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3.10: Nomenclature of Ionic Compounds

The simplest ionic compounds consist of a single type of cation associated with a single type of anion. Nomenclature for these compounds is trivial; the cation is named first, followed by the anion. If the anion is a single element, the suffix *ide* is added to the root name of the element.

When you are constructing names for ionic compounds, you do not use "multipliers" to indicate how many cations or anions are present in the compound. For example NaI is named *sodium iodide;* Na_2S is named *sodium sulfide;* $CaCl_2$ is named *calcium chloride.* The chemist reading the name is assumed to have sufficient knowledge to pair the elements properly based on their common valence states. There are exceptions to this simple nomenclature, however. Many transition metals exist as more than one type of cation. Thus, iron exists as Fe^{2+} and Fe^{3+} cations (they are referred to as "oxidation states", and will be covered in detail in Chapter 5). When you are naming an ionic compound containing iron, it is necessary to indicate which oxidation state the metal has. For metals, the oxidation state is the same as the charge. Thus Fe^{2+} in a compound with chloride would have a formula $FeCl_2$ and would be named iron (II) chloride, with the oxidation state (the charge on the iron) appearing as a Roman numeral in parenthesis after the cation. The cation Fe^{3+} paired with oxygen would have the formula Fe_2O_3 and would have the name iron (III) oxide.

The procedure for naming ionic compounds contain polyatomic ions is identical to that described above for simple ions. Thus, $CaCO_3$ is named *calcium carbonate;* Na_2SO_4 is named *sodium sulfate;* $(NH_4)_2HPO_4$ (a compound with two polyatomic ions) is named *ammonium hydrogen phosphate;* and Pb^{2+} paired with SO_4^{2-}, $PbSO_4$ is named *lead (II) sulfate.*

Example 3.10.1:

Write a correct chemical formula for each of the following ionic compounds:

a. Calcium bromide
b. Aluminum oxide
c. Copper (II) chloride
d. Iron (III) oxide

Solution

a. Calcium is 2+, bromide is 1-; $CaBr_2$.
b. Aluminum is 3+, oxide is 2-; Al_2O_3.
c. From the oxidation state that is given, copper is 2+, chloride is 1-; $CuCl_2$.
d. From the oxidation state, iron is 3+, oxide is 2-; Fe_2O_3.

Example 3.10.1:

Write a proper chemical name for each of the following ionic compounds:

a. Li_2S
b. CaO
c. $NiCl_2$
d. FeO

Solution

a. We don't use multipliers, so this is simply lithium sulfide.
b. This is simply calcium oxide.
c. We don't have to specify an oxidation state for nickel, so this is nickel chloride.
d. We must specify that iron is 2+ in this compound; iron (II) oxide.

Exercise 3.10.1

Write a correct chemical formula for each of the following ionic compounds:

a. Sodium phosphide
b. Iron (II) nitrite
c. Calcium hydrogen phosphate
d. Chromium (III) oxide

Exercise 3.10.1

Write a proper chemical name for each of the following ionic compounds:

a. NaBr
b. $CuCl_2$
c. $Fe(NO_3)_3$
d. $(NH_4)_3PO_4$

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3.11: Nomenclature of Molecular Compounds

The nomenclature of simple binary molecular compounds (covalently bonded compounds consisting of only two elements) is slightly more complicated than the nomenclature of ionic compounds because *multipliers* must be used to indicate the ratio of the elements in the molecule; the multiplier *mono* is only used for the second element in a compound.

Further, when you are naming a molecular compound, you must also decide which element should be listed first. In general, elements appearing to the *left* or *lower* in the periodic table are listed first in the name. Once you have decided on the order, the second element is named using the element root and *ide*, just like in ionic compounds. Thus, for CCl_4, carbon is to the *left* of chlorine (Group 4A *vs.* Group 5A), so it is listed first. There are four chlorines, so the multiplier *tetra* is used, and the name is **carbon tetrachloride**. Compounds containing hydrogen are generally an exception, and the hydrogen is listed as the first element in the name. Thus, H_2S would be named using the multiplier *di* to indicate that there are two hydrogens and *mono* to indicate that there is only one sulfur, or, dihydrogen monosulfide.

For the molecule SO_2; they are both Group 6A elements, but sulfur is *lower* in the periodic table (Row 3 *vs.* Row 2) so it is *first* in the name. There are two oxygens, so the multiplier is *di* and the name is **sulfur dioxide**.

For the molecule NO; nitrogen is to the *left* of oxygen (Group 6A *vs.* Group 5A) so it is *first* in the name. There is one oxygen, so the multiplier is *mono* and, following the rules, the name would be "nitrogen mon**oo**xide". In this case, however, the second "o" in the name is *dropped* (to allow for easier pronunciation) and the name is shortened to **nitrogen monoxide**. Distinguish this from another oxide of nitrogen, N_2O_4. Again nitrogen is first and needs the multiplier *di*. There are four oxygens, so the multiplier is *tetra*, but once again the multiplier is shortened (again, the "a" is dropped) and the name is **dinitrogen tetroxide**.

Example 3.11.1:

Write a correct chemical formula for each of the following molecular compounds:

a. Chlorine monofluoride
b. Dihydrogen monosulfile
c. Carbon tetrabromide
d. Bromine

Solution

a. ClF
b. H_2S
c. CBr_4
d. Br_2

Example 3.11.1:

Write a proper chemical name for each of the following molecular compounds:

a. IF
b. PCl_3
c. I_2
d. N_2F_2

Solution

a. Iodine monofluoride
b. Phosphorus trichloride
c. Iodine
d. Dinitrogen difluoride

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3.S: Chemical Bonding and Nomenclature (Summary)

- In **covalent bonding**, electrons are *shared* between atoms. In **ionic bonding**, electrons are transferred from one atom to another. Compounds that are formed using only covalent bonds are termed **molecular compounds**.
- The *outermost* electron level in any atom is referred to as the **valence shell**. The electron configuration of the valence shell of an atom can be shown graphically using a **Lewis diagram** (or *electron-dot structure*). The arrangement of "dots" around the chemical symbol for the element are shown singly up through four electrons, and then paired until eight electrons are present.
- To form ions from individual elements, electrons are added or subtracted from the valence shell in order to completely fill the shell with eight electrons (the **octet rule**). The charge on the ion reflects the electrons added or removed. Representative elements through Group IIIA will lose electrons to form cations, while those in groups IVA – VIIA will gain electrons and form anions.
- A **covalent bond** is constructed in a Lewis diagram by pairing a set of unpaired electrons from two different atoms. For the purposes of the "octet rule", a pair of shared electrons is counted as two electrons for each atom. Multiple covalent bonds (**double bonds** and **triple bonds**) are used, if necessary, to give each bonded atom a full octet (except, of course, for helium and hydrogen). When two or more atoms are bonded together utilizing covalent bonds, the compound is referred to as a **molecule**.
- As a rule of thumb, **ionic** bonds will be formed whenever the compound contains a **metal**. **Covalent** bonding will be observed in compounds containing only **semimetals** or **nonmetals**.
- Groups of covalently bonded semimetals or nonmetals which are charged are called **polyatomic ions**. Common examples include sulfate dianion, nitrate anion, phosphate trianion, etc. These polyatomic ions are commonly paired with metals forming ionic compounds.
- Many (but not all) polyatomic ions can be drawn in two or more equivalent Lewis representations. These are called **resonance forms** of the ion. The actual electronic structure of the ion is a combination of these Lewis structures and is called the **resonance hybrid**.
- The **electronegativity** of an element is a measure of the tendency of that element to attract electrons towards itself. Electronegativities range from 0.6 to 4.0, with fluorine as the most electronegative element (a value of 4.0). The general trend in the periodic table is for electronegativity to increase from the lower left-hand corner (Fr) to the upper right-hand corner (F).
- Covalent bonds formed between atoms with different electronegativity will be **polarized** with the greatest electron density localized around the most electronegative atom. The effect of electronegativity on electron distribution within a molecule can be shown using a computer-calculated **electrostatic potential map** where colors are used to represent electron density.
- Elements in periods 3 – 7 can accommodate more that eight electrons in there valence shells. This phenomena is called **valence shell expansion** and molecules involving these elements may have 10 – 14 valence electrons in properly drawn Lewis diagrams. Exceptions to the "octet rule" also exist where the valence shell contains less than eight electrons, or contains unpaired electrons.
- When naming simple, binary **ionic** compounds, the cation is named first using the name of the element, followed by the anion, where the suffix *ide* is added to the root name of the element. Multipliers are **not used**. For transition metals in which the metal can assume a variety of oxidation states (different positive charges), the charge of the metal ion is shown in the name using Roman numerals, in parenthesis, following the name of the element (i.e., iron (III) chloride).
- When naming simple binary **molecular** compounds (compounds containing only covalent bonds) the *least electronegative* element is (generally) named first, followed by the second element, where the suffix *ide* is again added to the root name of the element. In molecular compounds multipliers are used to indicate the number of each atom present (mono-, di-, tri-, tetra-, etc.) with the exception that *mono* is not used for the first element in the compound.

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CHAPTER OVERVIEW

4: The Mole and Measurements in Chemistry

In the preceding chapters, you should have gained an appreciation of the scale of chemistry, with regard to the physical size and mass of individual atoms and compounds. Because a typical samples of a substance (such as a copper penny) contains so many atoms, chemistry have defined a unit by which we can easily county these large numbers; this units is called a mole. However, we will see that a mole is more than a just a large number; a mole is also directly related to the atomic weight of atoms and compounds and the mole concept will give us the tools to consider chemical reactions in a quantitative manner. This chapter serves as an introduction to the concepts and we will continues to build upon this foundation when we consider stoichiometry in the following chapters.

4.1: Measurement and Scale - The Mole Concept

4.2: Molar Mass

4.3: Mole-Mass Conversions

4.4: Percentage Composition

4.5: Empirical and Molecular Formulas

4.S: The Mole and Measurements in Chemistry (Summary)

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4.1: Measurement and Scale - The Mole Concept

One of the important concepts to grasp in chemistry is *scale*. Atoms and molecules are very small. A single atom of hydrogen has a mass of about 1.67 x 10^{-24} grams (that's 0.000000000000000000000000167 grams). One cubic centimeter of water (one mL) contains about 3.3 x 10^{22} water molecules (that's 33 sextillion molecules). Because chemists routinely use numbers that are both incredibly small and incredibly large, unique units of measurement have been developed to simplify working with these numbers. As we learned in Chapter 1, the atomic mass unit (amu) helps us talk about the mass of atoms on a scale appropriate to atoms (one grams is about 600 sextillion amu). In this chapter, we will introduce the concept of a mole to help us talk about numbers of atoms on a scale appropriate to the size of a sample we could work with in a laboratory (for example, in grams). The **mole** is defined as the number of atoms contained in *exactly* 12 grams of carbon-12 (the isotope $^{12}_{6}C$). Chemist have measured this number and it turns out to be 6.0221415 x 10^{23}. We can think of the term *mole* as a number, just like the word *dozen* represents the number 12. We will use the mole to represent this very large number (a *chemist's dozen*) and we will see that there is a special relationship between a mole of a pure substance and the mass of the substance measured in amu.

The origin of the mole concept is generally attributed to the Italian chemical physicist, Amadeo Avogadro. In 1811, Avogadro published an important article that drew a distinction between atoms and molecules (although these terms were not in use at the time). As part of his explanation of the behavior of gasses, he suggested *that equal volumes of all gases at the same temperature and pressure contained the same number of molecules*. This statement is referred to as **Avogadro's Hypothesis** and today we commonly refer to the number of *things* in a mole, (6.0221415 x 10^{23}) as **Avogadro's number** (this is rounded to 6.02 x 10^{23} for most calculations). Because a mole can be thought of as a *number*, you can convert any number to moles by dividing that number by 6.02 x 10^{23}. For example, at the time of this writing, the national debt of the United States is about 7.9 trillion dollars (7.9 x 10^{12} dollars). This could be expressed as *moles of dollars* as shown below:

$$(7.9 \times 10^{12} dollars)\left(\frac{1\ mol\ dollars}{6.02 \times 10^{23} dollars}\right) = 1.3 \times 10^{-11}\ mol\ dollars$$

The ratio of any number to the number of things in a mole is often referred to as a **mole fraction**.

Exercise 4.1.1

a. It is estimated there are 7 x 10^{22} stars in the universe. How many moles of stars is this?
b. It is estimated there are 7.5 x 10^{18} grains of sand on the earth. How many moles of sand grains is this?
c. You have 0.0555 moles of jelly donuts. What number of donuts would that be?
d. You drink a small bottle of drinking water that contains 13 moles of water. What is the number of molecules of water you drank?

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4.2: Molar Mass

As we described in Section 4.1, in chemistry, the term **mole** can be used to describe a particular number. The number of things in a mole is large, *very* large (6.0221415×10^{23}). We are all familiar with common copy-machine paper that comes in 500 sheet reams. If you stacked up 6.02×10^{23} sheets of this paper, the pile would reach from the earth to the moon **80 billion times**! The mole is a *huge* number, and by appreciating this, you can also gain an understanding of how *small* molecules and atoms really are.

Chemists work simultaneously on the level of individual atoms, and on the level of samples large enough to work with in the laboratory. In order to go back and forth between these two scales, they often need to know how many atoms or molecules there are in the sample they're working with. The concept that allows us to bridge these two scales is **molar mass**. Molar mass is defined **as the mass in grams of one mole of a substance**. The units of molar mass are grams *per* mole, abbreviated as **g/mol**.

The mass of a single isotope of any given element (the **isotopic atomic mass**) is a value relating the mass of that isotope to the mass of the isotope carbon-12 ($^{12}_{6}C$); a carbon atom with six proton and six neutrons in its' nucleus, surrounded by six electrons. The **atomic mass** of an element is the relative average of *all* of the naturally occurring isotopes of that element and atomic mass is the number that appears in the periodic table. We have defined a mole based on the isotopic atomic mass of carbon-12. By definition, the *molar mass* of carbon-12 is numerically the same, and is therefore *exactly* 12 grams. Generalizing this definition, **the molar mass of any substance in grams *per* mole is numerically equal to the mass of that substance expressed in atomic mass units**. For example, the *atomic mass* of an oxygen atom is 16.00 amu; that means the *molar mass* of an oxygen atom is 16.00 g/mol. Further, if you have 16.00 grams of oxygen atoms, you know from the definition of a mole that your sample contains 6.022×10^{23} oxygen atoms.

The concept of molar mass can also be applied to compounds. For a molecule (for example, nitrogen, N_2) the mass of molecule is the sum of the atomic masses of the two nitrogen atoms. For nitrogen, the mass of the N_2 molecule is simply (14.01 + 14.01) = 28.02 amu. This is referred to as the **molecular mass** and the molecular mass of any molecule is simply the sum of the atomic masses of all of the elements in that molecule. The molar mass of the N_2 molecule is therefore 28.02 g/mol. For compounds that are *not molecular* (ionic compounds), it is improper to use the term "molecular mass" and "**formula mass**" is generally substituted. This is because there are no individual molecules in ionic compounds. However when talking about a mole of an ionic compound we will still use the term molar mass. Thus, the *formula* mass of calcium hydrogen carbonate is 117.10 amu and the *molar* mass of calcium hydrogen carbonate is 117.10 grams per mole (g/mol).

? Exercise 4.2.1

Find the molar mass of each of the following compounds:

- Sand - silicon dioxide (SiO_2)
- Draino - sodium hydroxide (NaOH)
- Nutrasweet - Aspartame ($C_{14}H_{18}N_2O_5$)
- Bone phosphate - calcium phosphate $Ca_3(PO_4)_2$

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4.3: Mole-Mass Conversions

As described in the previous section, molar mass is expressed as "grams *per* mole". The word *per* in this context implies a mathematical relationship between grams and mole. Think of this as a ratio. The fact that a *per* relationship, ratio, exists between grams and moles implies that you can use dimensional analysis to interconvert between the two. For example, if we wanted to know the mass of 0.50 mole of molecular hydrogen (H_2) we could set up the following equations:

The ***known*** molar mass of H_2 is:

$$\left(\frac{2.06g\ H_2}{1\ mol\ H_2}\right)$$

We are ***given*** that we have 0.50 moles of H_2 and we want to ***find*** the number of grams of H_2 that this represents. To perform the dimensional analysis, we arrange the *known* and the *given* so that the units cancel, leaving only the units of the item we want to *find*.

$$(0.5mol\ H_2) \times \left(\frac{2.06g\ H_2}{1\ mol\ H_2}\right) = x\ g\ H_2 = 1.0g\ H_2$$

? Exercise 4.3.1

a. Determine the mass of 0.752 mol of H_2 gas.
b. How many *moles* of molecular hydrogen are present in 6.022 grams of H_2?
c. If you have 22.414 grams of Cl_2, how many *moles* of molecular chlorine do you have?

We can also use what is often called a *per* relationship (really just a **ratio**) to convert between number of *moles* and the number to *things* (as in 6.02 x 10^{23} *things per mole*). For example, if we wanted to know how many *molecules* of H_2 are there in 3.42 moles of H_2 gas we could set up the following equations:

The ***known*** ratio of molecules *per* mole is :

$$\left(\frac{6.02 \times 10^{23} molecules\ H_2}{1\ mol\ H_2}\right)$$

We are ***given*** that we have 3.42 moles of H_2 and we want to ***find*** the number of molecules of H_2 that this represents. To perform the dimensional analysis, we arrange the *known* and the *given* so that the units cancel, leaving only the units of the item we want to *find*.

$$(3.42mol\ H_2) \times \left(\frac{6.02 \times 10^{23} molecules\ H_2}{1\ mol\ H_2}\right) = x\ molecules\ H_2 = 2.06 \times 10^{24}\ molecules\ H_2$$

And finally, we can combine these two operations and use the *per* relationships to convert between *mass* and the *number* of atoms or molecules. For example, if we wanted to know how many *molecules* of H_2 are there in 6.022 *grams* of H_2 gas we could set up the following series of equations:

The ***known*** molar mass of H_2 is

$$\left(\frac{2.016gH_2}{1molH_2}\right)$$

The ***known*** ratio of molecules *per* mole is

$$\left(\frac{6.02 \times 10^{23} molecules\ H_2}{1\ mol\ H_2}\right)$$

We are ***given*** that we have 6.022 grams of H_2 and we want to ***find*** the number of molecules of H_2 that this represents. As always, to perform the dimensional analysis, we arrange the *known* ratios and the *given* so that the units cancel, leaving only the units of the item we want to *find*.

$$(6.022gH_2) \times \left(\frac{1molH_2}{2.016gH_2}\right) \times \left(\frac{6.02 \times 10^{23} molecules\ H_2}{1\ mol\ H_2}\right) = x\ molecules\ H_2 = 1.80 \times 10^{24}$$

? Exercise 4.3.1

a. A sample of molecular chlorine is found to contain 1.0 x 10^{20} molecules of Cl_2. What is the *mass* (in grams) of this sample?

b. How many moles of sand, silicon dioxide (SiO_2), and how many molecules of sand are found in 1.00 pound (454g) of sand?

c. You add 2.64 x 10^{23} molecules of sodium hydroxide (Drano™; NaOH), to your drain. How many moles are this and how many grams?

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4.4: Percentage Composition

We are all familiar with the term *percentage*. We take an exam that is worth 100 points, we get 96 correct and we describe our score as 96%. We arrive at 96% by first taking our score and dividing it by the total number of points to get the *fraction* that we got correct. To convert the fraction to a *percentage*, we multiply the fraction by 100.

$$\left(\frac{96\ points}{100\ points\ total}\right) \times 100 = 96\%$$

Applying this concept to molecules, we could describe HCl as consisting of one atom of hydrogen and one atom of chlorine. Likewise, we could use *mole* nomenclature and say that one *mole* of the molecule consists of one *mole* of hydrogen and one *mole* of chlorine, and that one *mole* of HCl has a mass of 36.46 grams. These descriptions, however, tell us nothing about how much of this mass is attributable to the hydrogen and how much comes from the chlorine. In order to do this, we need to speak of the **percentage composition** of a molecule, that is, what percent of the total mass arises from each element. These calculations are simple and involve taking the atomic mass of the element in question and dividing by the molar mass of the molecule.

For HCl, the *fraction* of hydrogen in HCl is given by the molar mass of hydrogen divided by the molar mass of HCl:

$$\frac{1.008\frac{g}{mol}}{36.46\frac{g}{mol}}$$

and the *percentage* of hydrogen in HCl is obtained by multiplying the *fraction* by 100:

$$0.02765 \times 100 = 2.765\%$$

Combining the steps, the *percentage* of chlorine in HCl can be calculated by dividing the molar mass of chlorine by the molar mass of HCl and multiplying by 100:

$$\frac{1.008\frac{g}{mol}}{36.46\frac{g}{mol}} = 0.02765$$

? Exercise 4.4.1

a. Find the percentage of fluorine in calcium fluoride (CaF_2).

These types of problems can also be presented as mass calculations. For example, determine the mass of calcium in 423.6 grams of CaF_2. Collecting our known, given and find values:

The known molar mass of Ca is

$$\frac{40.08g\ Ca}{1mol\ Ca}$$

The known molar mass of CaF_2 is

$$\frac{78.08g\ CaF_2}{1mol\ Cl_2}$$

We are given that we have a sample of CaF_2 with a mass of 423.6 grams and we want to find the mass of Ca in this sample. We could find the mass of Ca if we knew the fraction of Ca in CaF_2. We could then multiply this fraction by the known mass of CaF_2 to obtain the mass of calcium in the sample. The fraction of Ca in CaF_2 is the ratio of the two known molar masses (the percentage, before you multiply by 100). As always, to perform the dimensional analysis, we arrange the known and the given so that the units cancel, leaving only the units of the item we want to find.

$$(423.6g\ CaF_2) \times \left(\frac{1mol}{78.08g\ CaF_2}\right) \times \left(\frac{40.08g\ Ca}{1mol\ Ca}\right) = x\ g\ Ca = 217.4\ g\ Ca$$

Note that in this example, you want to use the fraction of Ca in CaF2, not the percentage; if you used percentage, you would have to divide your answer by 100 to get the proper number of grams of Ca in the sample.

Exercise 4.4.1

a. A sample of CaF_2 is known to contain 18.00 grams of calcium; what mass of fluorine is contained in this sample?
b. Carbon dioxide is a green house gas produced in combustion. What is the percentage of oxygen in CO_2?
c. Barium sulfate is use when x-raying the gastrointestinal track. Determine the mass of barium in 523 grams of $BaSO_4$.
d. Sulfuric acid, H_2SO_4 is the most used chemical in industrial processes. If a sample of sulfuric acid contained 3.67 g of hydrogen how many grams of sulfur would it contain?

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4.5: Empirical and Molecular Formulas

In Chapter 2, we introduced the concept of a chemical compound as a substance that results from the combination of two or more atoms, in such a way that the atoms are bonded together in a constant ratio. We represented that ratio using the symbols for the atoms in the molecule, with subscripts to indicate the fixed ratios of the various atoms. The result is a molecular formula, and in Chapter 3, we used molecular formulas to devise chemical names for both molecular and ionic compounds. As we have seen in this chapter, molecular formulas can be used to directly calculate the molar mass of a compound.

Many of the methods, however, that chemists use in the laboratory to determine the composition of compounds do not give the molecular formula of the compound directly, but instead simply yield the *lowest whole-number ratio* of the elements in the compound. A formula such as this is called an **empirical formula**. For example, the molecular formula for glucose is $C_6H_{12}O_6$, but the simplest whole-number ratio of the elements in glucose is CH_2O; if you multiply each element in (CH_2O) by *six*, you obtain the molecular formula for glucose. An empirical formula cannot be converted into a molecular formula unless you know the molar mass of the compound. For example, the empirical formula for acetic acid (the acidic component in vinegar) is identical to that for glucose (CH_2O). If you analyzed these two compounds and determined only an empirical formula, you could not identify which compound you had.

Conversion of an empirical formula into a molecular formula requires that you know the molar mass of the compound in question. Knowing this, you can calculate a molecular formula based on the fact that an empirical formula can always be multiplied by an integer *n* to yield a molecular formula. Thus, some value of *n*, multiplying each element in CH_2O will yield the molecular formula of acetic acid. The value of *n* can be determined as follows:

$$n \times (CH_2O),\ where\ n = \frac{molar\ mass\ of\ the\ compound}{molar\ mass\ of\ the\ empirical\ formula}$$

For acetic acid, the molar mass is 60.05 g/mol, and the molar mass of the empirical formula CH_2O is 30.02 g/mol. The value of the integer *n* for acetic acid is therefore,

$$n = \frac{60.05\ g/mol}{30.02\ g/mol} = 2$$

And the molecular formula is $\mathbf{C_2H_4O_2}$.

Note that *n* must be an integer and that your calculation should always yield a whole number (or very close to one).

? Exercise 4.5.1

a. A compound is determined to have a molar mass of 58.12 g/mol and an empirical formula of C_2H_5; determine the molecular formula for this compound.
b. Benzene is an intermediate in the production of many important chemicals used in the manufacture of plastics, drugs, dyes, detergents and insecticides. Benzene has an empirical formula of CH. It has a molar mass of 78.11 g/mol.What is the molecular formula?

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4.S: The Mole and Measurements in Chemistry (Summary)

- The **mole** is defined as the number of atoms contained in *exactly* 12 grams of carbon-12 (the isotope). There are 6.0221415 x 10^{23} particles in a mole. Remember, a *mole* is just a number (like *dozen*) and you can have a mole of *anything.*
- The concept of a mole is based on **Avogadro's Hypothesis** (*equal volumes of all gases at the same temperature and pressure contained the same number of molecules*) and the number of particles in a mole (6.0221415 x 10^{23}) is commonly referred to as **Avogadro's number** (typically rounded to 6.02 x 10^{23} for most calculations).
- Because atomic masses, and the number of particles in a mole, are both based on the isotopic atomic mass of the isotope carbon-12, **the mass of any substance expressed in atomic mass units is numerically equal to the *molar mass* of the substance in grams *per* mole**. Thus, *exactly* 12 grams of carbon-12 contains *exactly* a mole of carbon atoms; likewise, 31.9988 grams of O_2 contains 6.02214 x 10^{23} oxygen molecules (note, *six* significant figures), etc.
- To convert the number of **moles** of a substance into the **mass** of a substance, you simply need to multiply (**moles** x **molar mass**).
- To convert the **mass** of a substance into the number of **moles**, you simply need to *divide* the **mass** by the **molar mass**.
- To convert the number of **moles** of a substance into the number of **particles** of that substance, you simply need to multiply (**moles** x **Avogadro's number**).
- The **percentage composition** of a compound, simply tells us what *percent* of the total mass arises from each element in the compound. To do the calculation, simply take the atomic mass of the element in question and divide it by the molar mass of the molecule.
- The **empirical formula** for a compound is the *lowest whole-number ratio* of the elements in that compound. For example, the molecular formula for glucose is $C_6H_{12}O_6$, but the simplest whole-number ratio of the elements in glucose is CH_2O.

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CHAPTER OVERVIEW

5: Chemical Reactions

In Chapter 2, we learned that chemical changes result in the transformation of one chemical substance into a different substance having a new set of chemical and physical properties. The transformation of one substance into another is called a *chemical reaction* and is described using a *chemical equation*. In this chapter we will learn how to write and balance simple chemical equations. We will learn the basic *types* of chemical reactions and we will learn how to predict the products that are likely to be formed when these reactions occur. We will examine a special type of chemical reaction in which one of the products has low solubility in water and *precipitates* from solution. Understanding the basic rules of solubility is simple and again will allow us to predict when this type of reaction is likely to be observed. Finally, we will address the *energetics* of chemical reactions, laying a fundamental background for the study of reaction rates and equilibrium later in the course.

5.1: Chemical Changes and Chemical Reactions
5.2: Chemical Equations
5.3: Balancing Chemical Equations
5.4: Classifying Chemical Reactions
5.5: Oxidation and Reduction Reactions
5.6: Predicting Products from Chemical Reactions
5.7: Predicting Solubility Trends
5.8: The Energetics of Chemical Reactions
5.S: Chemical Reactions (Summary)

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5.1: Chemical Changes and Chemical Reactions

In Chapter 2, we classified changes in our environment utilizing the concepts of *physical* and *chemical changes*. We said that a **physical change** alters the *appearance* of a substance without changing its molecular structure. Ice melts, water evaporates and mountains are slowly weathered into dust. All of these change the *characteristics* of substances, but they do not alter its basic structure. A **chemical change**, however, results in the transformation of one molecular substance into another. Gasoline burns, reacting with oxygen in the atmosphere, generating light, heat, and converting the carbon-based molecules into carbon dioxide gas and water vapor. When substances combine like this and undergo chemical changes, we say that a **chemical reaction** has occurred. Some chemical reactions are quite evident, like the burning of gasoline, and involve the production of **heat** or **light**. In other types of chemical reactions, **gases** are evolved, **color changes** occur and clear solutions become cloudy, with the ultimate formation of an insoluble substance (a **precipitate**). Chemical changes can also be quite obscure and their occurrence can only be detected by sophisticated chemical analysis.

Sometimes chemical changes occur spontaneously, others require the input of energy (heat) in order to occur. Chemical reactions can occur rapidly, like the explosive reaction of sodium metal in the presence of water, and others occur very slowly, like the rusting of iron or the tarnish that slowly develops on some metal surfaces exposed to air. In this chapter we will learn to represent chemical reactions using **chemical equations**. We will learn to **balance** these equations, explore **types** of reactions and learn to **predict products** from simple reactions. Central to all of this is the concept of the *chemical equation*.

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5.2: Chemical Equations

The processes that occur during a chemical change can be represented using a **chemical equation**. In a chemical equation, the chemical formulas for the substance or substances that *undergo* the chemical reaction (the **reactants**) and the formulas for the new substance or substances that are formed (the **products**) are both shown, and are linked by an **arrow**. The arrow in a chemical equation has the properties of an "equals sign" in mathematics, and because of this, ***in a chemical equation, there must be the same number and types of atoms on each side of the arrow.***

Reactants → Products

As an example of a chemical reaction, consider the reaction between solid carbon and oxygen gas to form carbon dioxide gas. This chemical equation for this reaction can be written as shown below.

$$\mathbf{C}\ \boldsymbol{(s)} + \mathbf{O_2}\ \boldsymbol{(g)} \rightarrow \mathbf{CO_2}\ \boldsymbol{(g)}$$

In this equation, we have used ***(s)*** and ***(g)*** to represent the physical state of the reactants at the time of the reaction (solid and gas). Other abbreviations that are often used include ***(l)*** for liquid and ***(aq)*** to indicate that the reactant or product is dissolved in aqueous solution.

As we inspect this equation we see that there is one carbon atom on each side of the arrow and that there are two oxygen atoms on each side. An equation in which there are the same number and types of atoms on both sides of the arrow is referred to as **balanced**. As you write chemical equations, it is important to remember those elements that naturally occur as diatomic molecules (Table 1.1). Remember that when you include these as reactants or products, remember to indicate that they are diatomic by using the subscript "2".

Table 1.1 Common Diatomic Elements

Element	Chemical Formula
Hydrogen	H_2
Oxygen	O_2
Nitrogen	N_2
Fluorine	F_2
Chlorine	Cl_2
Bromine	Br_2
Iodine	I_2

? Exercise 5.2.1

a. Write a chemical equation for the reaction of solid iron with solid sulfur to form solid iron(II) sulfide.
b. Write a chemical equation for the reaction of solid carbon with solid magnesium oxide to form carbon monoxide gas and magnesium metal.

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5.3: Balancing Chemical Equations

In another example of a chemical reaction, sodium metal reacts with chlorine gas to form solid sodium chloride. An equation describing this process is shown below.

$$\mathbf{Na}\ \textit{(s)} + \mathbf{Cl_2}\ \textit{(g)} \rightarrow \mathbf{NaCl}\ \textit{(s)}$$

Inspection of this equation, however, shows that, while there is one sodium atom on each side of the arrow, there are two chlorine atoms in the reactants and only one in the products. This equation is **not balanced**, and is therefore *not* a valid chemical equation. In order to balance this equation, we must insert **coefficients** (not *subscripts*) in front of the appropriate reactants or products so that *the same number and types of atoms appear on both sides of the equation.* Because chlorine is diatomic, there are two chlorines in the reactants and there must also be two chlorines in the products. In order to accomplish this, we place the coefficient "2" in front of the product, NaCl. Now we are balanced for chlorine, but there are two atoms of sodium in the products and only one shown in the reactants. To resolve this, we need to place the coefficient "2" in front of the sodium in the reactant, to give the equation shown below.

$$\mathbf{2\ Na}\ \textit{(s)} + \mathbf{Cl_2}\textit{(g)} \rightarrow \mathbf{2\ NaCl}\ \textit{(s)}$$

In this equation, there are two sodiums in the reactants, two sodiums in the products, two chlorines in the reactants and two chlorines in the products; **the equation is now balanced**.

There are many different strategies that people use in order to balance chemical equations. The simplest methods, where you examine and modify coefficients in some systematic order, is generally called "balancing by inspection". These methods are generally useful for most simple chemical equations, although mathematical algorithms are often necessary for highly complex reactions. One version of the "inspection" method that we will use in this section can be called the "**odd-even**" approach. Looking at the first equation that we wrote for the sodium-chlorine reaction, we note that there are an **odd** number of chlorines in the products and an **even** number of chlorines in the reactants. The first thing we did in balancing this equation was to insert the multiplier "2" in front of the product (NaCl) so that there were now an *even* number of chlorines on both sides of the equation. Once we did that, we simply had to balance the other element (Na) which was "odd" on both sides, and the equation was easily balanced. When you are using this approach with more complicated equations, it is often useful to begin by balancing the **most complex molecule** in the equation first (the one with the most atoms), and focus on the element in this compound that is present in the **greatest amount**.

Another example where the "odd-even" approach works well is the decomposition of hydrogen peroxide to yield water and oxygen gas, as shown below.

$$\mathbf{H_2O_2}\ \textit{(aq)} \rightarrow \mathbf{O_2}\ \textit{(g)} + \mathbf{H_2O}\ \textit{(l)}$$

As we inspect this equation, we note that there are an even number of oxygen atoms in the reactants and an odd number of oxygens in the products. Specifically, water has only one oxygen (in the products) and the number of oxygen atoms in the products can be made "even" by inserting the coefficient "2" in front of H_2O. Doing this (shown below) we note that we now have four hydrogens in the products and only two in the reactants.

$$\mathbf{H_2O_2}\ \textit{(aq)} \rightarrow \mathbf{O_2}\ \textit{(g)} + \mathbf{2\ H_2O}\ \textit{(l)}$$

Balancing the hydrogens by inserting "2" in front of H_2O_2 in the reactants gives us an equation with four hydrogens on both sides on four oxygens on both sides; **the equation is now balanced**.

$$\mathbf{2\ H_2O_2}\ \textit{(aq)} \rightarrow \mathbf{O_2}\ \textit{(g)} + \mathbf{2\ H_2O}\ \textit{(l)}$$

? Exercise 5.3.1

Write a **balanced chemical equation** for the reactions given below:

a. When hydrogen gas reacts is combined with oxygen gas and the mixture ignited with a spark, water is formed in a violent reaction.
b. Lead (IV) oxide reacts with HCl to give lead (II) chloride, chlorine gas and water.
c. Solid potassium chlorate decomposes on heating to form solid KCl and oxygen gas.

d. An aqueous solution of barium chloride reacts with an aqueous solution of sodium sulfate to form solid barium sulfate and a solution of sodium chloride.

e. Hydrogen reacts with nitrogen to give ammonia, according to the equation shown below; **balance this equation**.
_____H_2 *(g)* + _____N_2 *(g)* → _____NH_3 *(g)*

f. Zinc metal reacts with aqueous HCl to give hydrogen gas and zinc chloride, according to the equation shown below; **balance this equation**.
_____Zn *(s)* + _____HCl *(aq)* → _____H_2 *(g)* + _____$ZnCl_2$ *(aq)*

g. Iron(III) oxide reacts with chlorine gas to give iron(III) chloride and oxygen gas, according to the equation shown below; **balance this equation**.
_____Fe_2O_3 *(s)* + _____Cl_2 *(g)* → _____$FeCl_3$ *(s)* + _____O_2 *(g)*

h. Sodium metal reacts with ammonia to give sodium amide and hydrogen gas, according to the equation shown below; **balance this equation**.
_____Na *(s)* + _____NH_3 *(l)* → _____H_2 *(g)* + _____$NaNH_2$ *(s)*

i. Ethane reacts with oxygen gas to give carbon dioxide and water vapor, according to the equation shown below; **balance this equation**.
_____C_2H_6 *(g)* + _____O_2 *(g)* → _____CO_2 *(g)* + _____H_2O *(g)*

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5.4: Classifying Chemical Reactions

The reactions we have examined in the previous sections can be classified into a few simple types. Organizing reactions in this way is useful because it will assist us in predicting the products of unknown reactions. There are many different classifications of chemical reactions, but here we will focus on the following types: **synthesis**, **decomposition**, **single replacement** and **double replacement**. In addition, we will see that some of these reactions involve changes in the oxidation numbers of the reactants and products; these will be referred to as **oxidation-reduction**, or "**redox**" reactions.

The first type of reaction we will consider is a **synthesis** reaction (also called a *combination* reaction). In a synthesis reaction, elements or compounds undergo reaction and combine to form a single new substance. The reaction of sodium metal with chlorine gas to give sodium chloride is an example of a synthesis reaction where both reactants are elements.

$$\mathbf{2\ Na}\ \boldsymbol{(s)} + \mathbf{Cl_2}\ \boldsymbol{(g)} \rightarrow \mathbf{2\ NaCl}\ \boldsymbol{(s)}$$

In this reaction, sodium metal and chlorine gas have *combined* to yield (synthesize) the more complex molecule, sodium chloride. Another example of a synthesis reaction, where compounds are involved as reactants, is the reaction of the *organic* molecule ethene (a carbon-based molecule – covered in more depth in Chapter 14) with HBr to yield the organic molecule bromoethane.

In this example, two molecular compounds (the organic compound, **ethene**, and hydrogen bromide) have combined to yield (synthesize) the new molecule, **bromoethane**. In a similar manner, synthesis reaction can also involve elements reacting with compounds.

In **decomposition** reactions, a single compound will break down to form two or more new substances. The substances formed can be elements, compounds, or a mixture of both elements and compounds. Two simple examples of decomposition reactions are shown below.

$$\mathbf{Cu_2S}\ \boldsymbol{(s)} \rightarrow \mathbf{2\ Cu}\ \boldsymbol{(s)} + \mathbf{S}\ \boldsymbol{(s)}$$

$$\mathbf{CaCO_3}\ \boldsymbol{(s)} \rightarrow \mathbf{CaO}\ \boldsymbol{(s)} + \mathbf{CO_2}\ \boldsymbol{(g)}$$

In a **single-replacement reaction** (also called a single-displacement reaction) an element and a compound will react so that their elements are switched. In other words, an element will typically displace another element from within a compound. As a general rule, **metals** will replace **metals** in compounds and **non-metals** will typically replace **non-metals**. An example of a single replacement reaction is shown below.

$$\mathbf{Zn}\ \boldsymbol{(s)} + \mathbf{CuCl_2}\ \boldsymbol{(s)} \rightarrow \mathbf{ZnCl_2}\ \boldsymbol{(s)} + \mathbf{Cu}\ \boldsymbol{(s)}$$

In this example, elemental zinc has *displaced* the metal, copper, from copper(II) chloride to form zinc chloride and elemental copper. In the reactants, zinc was elemental and in the products, it is present within the compound, zinc chloride. Likewise, copper was present in a compound in the reactants and is elemental in the products.

In another example, iron metal will react with an aqueous solution of copper sulfate to give copper metal and iron(II) sulfate.

$$\mathbf{Fe}\ \boldsymbol{(s)} + \mathbf{CuSO_4}\ \boldsymbol{(aq)} \rightarrow \mathbf{Cu}\ \boldsymbol{(s)} + \mathbf{FeSO_4}\ \boldsymbol{(aq)}$$

In this reaction, elemental iron replaces copper in a compound with sulfate anion and elemental copper metal is formed; metal replaces metal. The tendency of metals to replace other metals in single-replacement reactions is often referred to as an activity series. In the activity series shown below, any metal will replace any other metal which is to the right of itself in the series. Thus, iron will replace copper, as shown above, but copper metal would not replace iron from iron sulfate (iron is more active than copper). The activity series is useful in predicting whether a given single-replacement reaction will occur or not. Note that hydrogen is also included in the table, although it is not generally considered a "metal". Within this table, metals which occur before hydrogen will react with acids to form hydrogen gas and metal salts. Copper, silver, mercury and gold are less active than hydrogen and will not liberate hydrogen from simple acids. The metals in Groups I & II of the periodic table (Li, Na, K, Rb, Cs, Ca, Sr and Ba) are so reactive that they will directly react with water to liberate hydrogen gas and form metal hydroxides. These are generally referred to as "**active metals**".

The activity series is useful in predicting whether a given single-replacement reaction will occur or not. Note that hydrogen is also included in the table, although it is not generally considered a "metal". Within this table, metals which occur before hydrogen will react with acids to form hydrogen gas and metal salts. Copper, silver, mercury and gold are less active than hydrogen and will not

liberate hydrogen from simple acids. The metals in Groups I & II of the periodic table (Li, Na, K, Rb, Cs, Ca, Sr and Ba) are so reactive that they will directly react with water to liberate hydrogen gas and form metal hydroxides. These are generally referred to as "**active metals**".

A **double-replacement** reaction (or double-displacement) two ionic compounds in aqueous solution switch anions and form two new compounds. In order for a chemical reaction to occur in a double-replacement reaction, one of the new compounds that is formed must be *insoluble* in water, forming a solid **precipitate** (or a gas, to be covered in Chapter 6). If both of the new compounds which are formed are water-soluble, then no reaction has occurred. In the reactants, there were two cations and two anions in solution, and in the products there are the *same* two cations and two anions, in the *same* solution; nothing has happened. An example of a double-replacement reaction is shown below.

$$\mathbf{BaCl_2}\ \boldsymbol{(aq)} + \mathbf{Na_2SO_4}\ \boldsymbol{(aq)} \rightarrow \mathbf{BaSO_4}\ \boldsymbol{(s)} + \mathbf{2\ NaCl}\ \boldsymbol{(aq)}$$

In this reaction, solid barium sulfate is formed as a precipitate. This is a chemical change and this is a valid chemical reaction. In order to predict whether a double-replacement reaction will occur or not you need to understand rules for predicting solubility of ionic compounds. These rules will be covered in a later section, but are not related to the activity series discussed above.

Table 5.2 Activity Series for Common Metals

Li >	K >	Ba >	Sr >	Ca >
Na >	Mg >	Al >	Mn >	Zn >
Fe >	Cd >	Co >	Ni >	Sn >
Pb >	H >	Cu >	Ag >	Hg >
Au				

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5.5: Oxidation and Reduction Reactions

The **oxidation number** of an element represents the total number of electrons which have been *removed* (a positive oxidation state) or *added* (a negative oxidation state) to get the element into its present state. The term **oxidation** describes the *loss* of electrons by an element and an *increase* in oxidation state; the term **reduction** describes the *gain* of electrons and a *decrease* in oxidation state. Oxidation numbers for elements in compounds can be calculated using a simple set of rules, which are reproduced below in Table 5.3.

Table 5.3 Rules for Assigning Oxidation Numbers

Table 5.3 Rules for Assigning Oxidation Numbers
1. The oxidation number of an element in the free state is **zero**.
2. A monoatomic ion will have an oxidation number that is equal to its charge.
3. In compounds with metals, hydrogen will be **–1**, otherwise it will always be **+1**.
4. Oxygen, within a compound, will generally have an oxidation number of **–2**.
5. Halogens will be **–1**, except in compounds with oxygen.
6. Sulfur will generally be **–2**, except in compounds with oxygen.
7. In a molecular compound, the most electronegative element is assigned a negative oxidation number

In many chemical reactions, the oxidation number of elements change. Consider the synthesis reaction shown below. In the reactants, carbon and oxygen are both elements and their oxidation numbers are zero (Rule 1). In the product, oxygen will have an oxidation number of –2 (Rule 4), therefore, carbon in CO_2 must have an oxidation number of +4 in order to balance the four negative charges on the oxygens. During this reaction, the oxidation number of carbon has changed from zero in the reactants to +4 in the products and the oxidation number of oxygen has changed from zero to –2. This is an example of a **redox reaction**; **a chemical reaction in which the oxidation numbers of elements change on going from reactants to products.**

$$\mathbf{C}\ (s) + \mathbf{O_2}\ (g) \rightarrow \mathbf{CO_2}\ (g)$$

In a redox reaction, the element that "**loses electrons**" is said to be **oxidized** and will have *an increase in its oxidation number*. In the example above, the oxidation number of carbon *increases* from zero to +4; it has "lost electrons" and has been **oxidized**. The element that "**gains electrons**" in a redox reaction is said to be **reduced** and will have a *decrease in its oxidation number*. In the reaction above, the oxidation number of oxygen has *decreased* from zero to –2; it has "gained electrons" and has been **reduced**.

? Exercise 5.5.1

Arsonic and nitric acids react to form nitrogen monoxide, arsenic acid and water according to the equation shown below. Is this an example of a redox reaction?

$2\ HNO_3\ (aq) + 3\ H_3AsO_3\ (aq) \rightarrow 2\ NO\ (g) + 3\ H_3AsO_4\ (aq) + H_2O\ (l)$

? Exercise 5.5.1

For each of the reactions given below, calculate the oxidation number of each of the elements in the reactants and the products and determine if the reaction involves oxidation-reduction. If it is a redox reaction, identify the elements that have been oxidized and reduced.

a. $Cu_2S \rightarrow 2\ Cu + S$
   Reactants: Cu _____ S _____
   Products: Cu _____ S _____
   Element oxidized: _____ Element Reduced _____

b. $CaCO_3 \rightarrow CaO + CO_2$
Reactants: Ca _____ C _____ O _____
Products: Ca _____ C _____ O _____
Element oxidized: _____ Element Reduced _____

c. $Fe_2O_3 + 3\ H_2 \rightarrow 2\ Fe + 3\ H_2O$
Reactants: Fe _____ O _____ H _____
Products: Fe _____ O _____ H _____
Element oxidized: _____ Element Reduced _____

d. $AgNO_3 + NaCl \rightarrow AgCl\ (s) + NaNO_3$
Reactants: Ag _____ N _____ O _____ Na _____ Cl _____
Products: Ag _____ N _____ O _____ Na _____ Cl _____
Element oxidized: _____ Element Reduced _____

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5.6: Predicting Products from Chemical Reactions

Part of the lure of chemistry is that things don't always work out the way you expect. You plan a reaction, anticipate the products and, quite often, the results astound you! The exercise, then, is trying to figure out what was formed, why, and whether your observation leads to other useful generalizations. The first step in this process of discovery is anticipating or predicting the products which are likely to be formed in a given chemical reaction. The guidelines we describe here will accurately predict the products of most classes of simple chemical reactions. As your experience in chemistry grows, however, you will begin to appreciate the unexpected!

In simple **synthesis** reactions involving reaction of elements, such as aluminum metal reacting with chlorine gas, the product will be a simple compound containing both elements. In this case, it is easiest to consider the common charges that the elements adopt as ions and build your product accordingly. Aluminum is a Group III element and will typically form a +3 ion. Chlorine, being Group VII, will accept one electron and form a monoanion. Putting these predictions together, the product is likely to be **$AlCl_3$**. In fact, if aluminum metal and chlorine gas are allowed to react, solid $AlCl_3$ is the predominant product.

$$\mathbf{2\ Al}\ \textit{(s)} + \mathbf{3\ Cl_2}\ \textit{(g)} \rightarrow \mathbf{2\ AlCl_3}\ \textit{(s)}$$

The **synthesis** reaction involving the non-metals hydrogen gas and bromine can be approached similarly. The product will contain both elements. Hydrogen, Group I, has one valence electron and will form one covalent bond. Bromine, Group VII, has seven valence electrons and will form one covalent bond. The likely product is therefore **HBr**, with one covalent bond between the hydrogen and the bromine.

$$\mathbf{H_2}\ \textit{(g)} + \mathbf{Br_2}\ \textit{(g)} < \rightarrow \mathbf{2\ HBr}\ \textit{(g)}$$

For a **single-replacement** reaction, recall that (in general) metals will replace metals and non-metals will replace non-metals. For the reaction between lead(IV) chloride and fluorine gas, the fluorine will replace the chlorine, leading to a compound between lead and fluorine and the production of **elemental chlorine**. The lead can be viewed as a "spectator" in the reaction and the product is likely to be **lead(IV) fluoride**. The complete equation is shown below.

$$\mathbf{PbCl_4}\ \textit{(s)} + \mathbf{2\ F_2}\ \textit{(g)} \rightarrow \mathbf{PbF_4}\ \textit{(s)} + \mathbf{2\ Cl_2}\ \textit{(g)}$$

In single-replacement reactions in which metals (or carbon or hydrogen) are expected to replace metals, first you should check the activity series to see if any reaction is anticipated. Remember that metals can only replace metals that are *less active* than themselves (to the right in the Table). If the reaction is predicted to occur, use the same general guidelines that we used above. For example, solid iron reacting with aqueous sulfuric acid (H_2SO_4). In this reaction the question is whether iron will displace hydrogen and form hydrogen gas. Consulting the activity series, we see that hydrogen is to the *right* of iron, meaning that the reaction is expected to occur. Next, we reason that iron will replace hydrogen, leading to the formation of iron sulfate, where the sulfate is the "spectator" ion. The formation of hydrogen gas requires a change in oxidation number in the hydrogen of +1 to zero. Two hydrogen atoms must therefore be **reduced** (a *decrease* in oxidation number) and the two electrons required for the reduction must come from the iron. The charge on the iron is therefore most likely to be +2 (it starts off at zero and donates two electrons to the hydrogens). The final product is therefore most likely **iron(II) sulfate**. The complete equation is shown below.

$$\mathbf{Fe}\ \textit{(s)} + \mathbf{H_2SO_4}\ \textit{(aq)} \rightarrow \mathbf{FeSO_4}\ \textit{(aq)} + \mathbf{H_2}\ \textit{(g)}$$

Decomposition reactions are the most difficult to predict, but there are some general trends that are useful. For example, most **metal carbonates** will decompose on heating to yield the **metal oxide** and **carbon dioxide**.

$$\mathbf{NiCO_3}\ \textit{(s)} \rightarrow \mathbf{NiO}\ \textit{(s)} + \mathbf{CO_2}\ \textit{(g)}$$

Metal hydrogen carbonates also decompose on heating to give the **metal carbonate**, **carbon dioxide** and **water**.

$$\mathbf{2\ NaHCO_3}\ \textit{(s)} \rightarrow \mathbf{Na_2CO_3}\ \textit{(s)} + \mathbf{H_2O}\ \textit{(g)} + \mathbf{CO_2}\ \textit{(g)}$$

Finally, many **oxygen-containing compounds** will decompose on heating to yield **oxygen gas** and "other compounds". Identifying these compounds and building an understanding of why and how they are formed is one of the challenges of chemistry. Some examples:

$$\mathbf{H_2O_2}\ \textit{(aq)} \rightarrow \mathbf{O_2}\ \textit{(g)} + \mathbf{H_2O}\ \textit{(l)}$$

$$2\ HgO\ (s) \rightarrow O_2\ (g) + 2\ Hg\ (l)$$

$$2\ KClO_3\ (s) \rightarrow 3\ O_2\ (g) + 2\ KCl\ (s)$$

The potential products in **double-replacement** reactions are simple to predict; the anions and cations simply exchange. Remember, however, that one of the products must **precipitate**, otherwise no chemical reaction has occurred. For the reaction between lead(II) nitrate and potassium iodide, the products are predicted to be lead(II) iodide and potassium nitrate. No redox occurs, and the product, lead iodide, precipitates from the solution as a bright yellow solid. The question of how do you predict this type of solubility trend is addressed in the next section.

$$Pb(NO_3)_2\ (aq) + 2\ KI(aq) < \rightarrow PbI_2\ (s) + 2\ KNO_3\ (aq)$$

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5.7: Predicting Solubility Trends

The solubility of many simple ionic compounds can be predicted by applying the set of rules shown below.

1. Salts of the alkali metal ions and the ammonium ion, Li^+, Na^+, K^+, and NH_4^+ are almost always **soluble**.
2. Virtually all metal **nitrates** and metal **acetates** are soluble.
3. Metal **halides** are generally **soluble**, *except* for salts of Ag^+, Pb^{2+}, Cu^+ and Hg^+.
4. Metal **sulfates** are generally **soluble**, *except* for salts of Ba^{2+}, Pb^{2+} and Ca^{2+}.
5. With exception of the alkali metal ions and ammonium (*Rule 1*), the following salts are generally **insoluble**: metal carbonates (CO_3^{2-}), metal phosphates (PO_4^{3-}) and metal chromates (CrO_4^{2-}).
6. Metal hydroxides and metal sulfides are generally **insoluble**, except for those covered by *Rule 1* and Ca^{2+}, Sr^{2+} and Ba^{2+}.

Applying these rules to the reaction between lead nitrate and potassium iodide, the reactants are both **soluble** (Rule 1 and Rule 2). In the products, potassium nitrate will be soluble (Rule 2) and lead iodide will be **insoluble**, based on Rule 3.

? Exercise 5.7.1

Mixing each of the following salt solutions results in the formation of a precipate. In each case, identify the insoluble salt.

a. $NaCl + Pb(NO_3)_2$
b. $Fe(C_2H_3O_2)_3 + KOH$
c. $Ca(NO_3)_2 + K_2SO_4$
d. $Li_2S + CuSO_4$
e. $Co(C_2H_3O_2)_2 + LiOH$

? Exercise 5.7.2

For each of the ionic compounds given below, determine whether or not the compound will be soluble in water, according to the trends given above.

a. $AgNO_3$ ☐ soluble ☐ insoluble
b. $MgCl_2$ ☐ soluble ☐ insoluble
c. Na_2SO_4 ☐ soluble ☐ insoluble
d. $AgCl$ ☐ soluble ☐ insoluble
e. $Ba(NO_3)_2$ ☐ soluble ☐ insoluble
f. PbI_2 ☐ soluble ☐ insoluble
g. $Mg(NO_3)_2$ ☐ soluble ☐ insoluble
h. $BaSO_4$ ☐ soluble ☐ insoluble
i. $FeCl_3$ ☐ soluble ☐ insoluble
j. $Pb(CH_3COO)_2$ ☐ soluble ☐ insoluble

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5.8: The Energetics of Chemical Reactions

Many of the chemical reactions that we have discussed in this chapter occur with the generation of significant amounts of light and heat. A prime example is the synthesis reaction between zinc and sulfur, described by the equation shown below.

$$\mathbf{Zn}\ \boldsymbol{(s)} + \mathbf{S}\ \boldsymbol{(s)} \rightarrow \mathbf{ZnS}\ \boldsymbol{(s)}$$

Initially, both elements are present as fine powders. They are mixed (carefully) and the mixture is stable sitting of the laboratory bench. When the mixture is touched with a heated metal rod, however, a violent reaction occurs (the reaction is termed ***exothermic***; producing heat) and zinc sulfide is formed as the product. The reaction is obviously favorable, so why does it need heat to start the reaction? This concept can be understood by considering a **reaction coordinate diagram** for a simple one-step reaction.

In a reaction coordinate diagram, the y-axis corresponds to energy. The initial and final "energy wells" represent the ground-state energies of the reactants and products, and the path connecting them describes the energy changes that occur in the course of the reaction.

Looking at the reaction coordinate diagram for the zinc sulfide reaction, the reactants sit at an initial energy level that is characteristic and unique for each element or compound. Likewise, zinc sulfide sits at a lower overall energy level; that means that the conversion from the elements to the compound is **favorable** and that heat is *liberated* during the reaction. If the energy level of the products was *higher* than the reactants, the reaction would be *unfavorable* and heat would be *absorbed* during the reaction (the reaction is said to be **endothermic**; consuming heat).

Why, then, does the zinc sulfide reaction need energy input before the reaction begins? The answer lies in the curved path that connects the reactants and products in the reaction coordinate diagram. In order for the zinc-sulfur mixture to react, enough energy must be put *into* the system so that the energy level of the reactants equals the highest hill in the diagram. Once that point is reached, the reactants can "tumble down" the energy hill and form the more stable products (with the evolution of all of the excess energy as heat, light, etc.).

The top of the energy hill in a reaction coordinate diagram is called the **transition state** (or activated complex). In modern chemical theory, the transition state is the energy maximum corresponding to the processes of bond-making and bond-breaking. The energy required to go from the reactants to the transition state is the **activation energy**. Reactions that occur with little requirement for heat simply have a small activation energy. The magnitude of the activation energy controls the *rate* of a reaction and the *difference* in energy between the reactants and the products controls the equilibrium distribution of the products and reactants in a reversible reaction. We will return to these concepts when we address reaction rates and equilibrium later in the book.

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5.S: Chemical Reactions (Summary)

- The processes that occur during a chemical change can be represented using a **chemical equation**. In a chemical equation, the chemical formulas for the substance or substances that *undergo* the chemical reaction (the **reactants**) and the formulas for the new substance or substances that are formed (the **products**) are both shown, and are linked by an **arrow**. The arrow in a chemical equation has the properties of an "equals sign" in mathematics, and because of this, ***in a chemical equation, there must be the same number and types of atoms on each side of the arrow.***
- A chemical equation in which the same number and types of atoms appear on each side of the arrow is called balanced. In order to balance an equation, insert **coefficients** in front of the appropriate reactants or products until there are the same number and types of atoms on both sides of the arrow.
- In a **synthesis reaction'**, ***elements or compounds undergo reaction and combine to form a*** *single new substance.*
- In a **decomposition'** ***reaction, a single compound will break down to form two or more new substances. The substances formed can be elements, compounds, or a mixture of both.***
- In a **single-replacement'** ***(single-displacement)*** *reaction,* ***an element and a compound will react so that their elements are switched. As a general rule,*** *metals* ***will replace*** *metals* ***in compounds and*** *non-metals* ***will typically replace*** *non-metals.*
- A **double-replacement'** ***(double-displacement) reaction, two ionic compounds in aqueous solution switch anions and form two new compounds. In order for a chemical reaction to occur, one of the new compounds that is formed must be*** **insoluble** ***in water, forming a solid*** *precipitate* ***or a gas.***
- The **oxidation number'** ***of an element represents the total number of electrons which have been*** **removed** ***(a positive oxidation state) or*** **added** ***(a negative oxidation state) to get the element into its present state. The term*** *oxidation* ***describes the*** **loss** ***of electrons by an element and an*** **increase** ***in oxidation state; the term*** *reduction* ***describes the*** **gain** ***of electrons and a*** **decrease** ***in oxidation state.***
- A chemical reaction in which oxidation numbers undergo a change is called a **redox reaction**. In a redox reaction, the element that "**loses electrons**" is said to be **oxidized** and will have *an increase in its oxidation number*. The element that "**gains electrons**" in a redox reaction is said to be **reduced** and will have a *decrease in its oxidation number*.
- In a simple **synthesis reaction** involving reaction of elements, the product will be a compound containing both elements. Write the product considering the common charges that the elements adopt as ions or the number of bonds that the elements typically form in molecules.
- In a simple **single-replacement** reaction, (in general) *metals* (including **carbon** and **hydrogen**) will tend to replace *metals* and that *non-metals* will replace *non-metals*.
- In a **double-replacement** reaction, the anions and cations simply of the two compounds simply exchange. In order for a reaction to occur, one of the products must **precipitate**, otherwise no chemical reaction has occurred. Changes in oxidation numbers do not occur in double-replacement reactions.
- Solubility trends can be predicted using a simple set of rules shown in Table 5.5; you should review there rules, remembering to apply them *in order*.
- The energy required to initiate a chemical reaction is called the **activation energy**. The greater the activation energy, the slower, or less favorable a reaction will be. The magnitude of the activation energy is directly linked to the *rate* of a chemical reaction.

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CHAPTER OVERVIEW

6: Quantitative Relationships in Chemistry

With the background that we have built in this course, thus far, we can now approach a more quantitative view of chemistry. While the notion of chemistry and math (together in the same room) may make you want to scream, we will see in this chapter that concepts such as chemical stoichiometry and mass balance are not overwhelming and can be approached using the same problem-solving algorithms that we have mastered in previous chapters. Once the concept of stoichiometric balance has been mastered, we will finally tackle limiting reactants. Limiting reactant problems may appear challenging, but we will see it is the same calculation that we do routinely… we simply have to do the calculations twice.

6.1: An Introduction to Stoichiometry
6.2: Molar Stoichiometry in Chemical Equations
6.3: Mass Calculations
6.4: Percentage Yield
6.5: Limiting Reactants
6.S: Quantitative Relationships in Chemistry (Summary)

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6.1: An Introduction to Stoichiometry

Stoichiometry… what a wonderful word! It sounds so complex and so *chemical*. In fact, it's a fairly simple concept; **stoichiometry** is the relationship between the molar masses of chemical reactants and products in a given chemical reaction. In Chapter 5 we learned to balance chemical equations by inserting numerical coefficients in front of reactants or products so that there were the same number and types of atoms on each side of the equation. Thus, in the reaction between sodium metal and chlorine gas, the balanced chemical equation is:

$$2\,\mathrm{Na}\,(\mathrm{s}) + \mathrm{Cl_2}\,(\mathrm{g}) \;\rightarrow 2\,\mathrm{NaCl}\,(\mathrm{s})$$

This equation tells us that two atoms of sodium react with one molecule of chlorine gas to give two sodium chlorides. The coefficients in front of the sodium and the sodium chloride are called the **stoichiometric coefficients** for this reaction. If we were to totally react a single molecule of chlorine gas in this reaction, this stoichiometry tells us that two atoms of sodium (atomic mass 22.99) having a total mass of 45.98 amu, would react with one molecule of chlorine gas (having a mass 70.90 amu) to give two sodium chlorides (formula mass 137.94), for a total of 275.9 amu of product. Because chemists usually don't speak of chemical reactions in terms of individual atoms or molecules, it is much more common to describe the stoichiometry of a reaction in terms of grams of reactants and products, or more conveniently in terms of moles. **Molar stoichiometry** is simply the expression of the coefficients of a reaction in terms of moles of reactants and products.

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6.2: Molar Stoichiometry in Chemical Equations

If we were to describe the reaction of sodium metal with chlorine gas in molar terms, we would say that two *moles* of sodium metal combine with one *mole* of Cl_2 to give two *moles* of sodium chloride. In terms of mass, two moles of sodium, having a total mass of 45.98 grams, would react with one mole of chlorine gas (a mass 70.90 grams) to give two moles of sodium chloride, for a total of 275.9 grams of product. Likewise, the molar stoichiometry for the decomposition of hydrogen peroxide (H_2O_2) to form oxygen and water, can be described simply as *two moles of H_2O_2 decompose to form one mole of oxygen gas and two moles of water.*

$$2H_2O_2(aq) \rightarrow O_2(g) + 2H_2O(l)$$

The stoichiometric coefficients for this reaction gives us the key information about the relationship between molar quantities of reactants and products, but in the real world, we will not always be working with exactly two moles of hydrogen peroxide. What if you want to know how much oxygen gas will be formed when 0.28 moles of H_2O_2 decompose? One way to solve this type of problem is to utilize a tool that we will call a *reaction pathway*. The reaction pathway is a kind of simple map of the stoichiometry of a reaction, which uses arrows to show the relationship between reactants and products.

Using the ***given-find-ratio*** algorithm that we introduced back in Chapter 1, if we were given *mol reactant* and we wanted to find *mol product*, we could set up a simple equation as follows:

$$(\text{mol product}) = \cancel{(\text{mol reactant})}\left(\frac{\text{mol product}}{\cancel{\text{mol reactant}}}\right)$$

The units *mol reactant* cancel to give the solution in *mol product*. If we were given *mol product* and we wanted to find *mol reactant*, we would set up the equation as follows in order for the units to properly cancel:

$$(\text{mol reactant}) = \cancel{(\text{mol product})}\left(\frac{\text{mol reactant}}{\cancel{\text{mol product}}}\right)$$

This basic approach can be used to solve for any molar (mass, or gas) conversion based on a balanced chemical equation, as long as you are careful to set up the ratios so that the units cancel, giving you the desired solution with the proper units. As an example, return to the question of the decomposition of H_2O_2. If 0.28 moles of H_2O_2 decompose, according to the equation given below, how many moles of oxygen gas (O_2) will be formed?

$$\left(\frac{1\ mol\ O_2}{2\ mol\ H_2O_2}\right)$$

We set up the problem to solve for mol product; the general equation is:

$$(molproduct) = (molreactant)\left(\frac{molproduct}{molreactant}\right)$$

The stoichiometric mole ratio is set up so that *mol reactant* will cancel, giving a solution in *mol product*. Substituting,

$$(x\, molO_2) = (0.28\, mol\ H_2O_2) \times \left(\frac{1\ mol\ O_2}{2\ mol\ H_2O_2}\right) = 0.14\, mol\ O_2$$

Thus, the decomposition of 0.28 mol of H_2O_2 will produce 0.14 mol of the product, oxygen gas (O_2).

? Exercise 6.2.1

a. Iron (III) oxide reacts with hydrogen gas to form elemental iron and water, according to the balanced equation shown below. How many moles of iron will be formed from the reduction of excess iron (III) oxide by 0.58 moles of hydrogen gas?
b. When an impure sample containing an unknown amount of Fe_2O_3 is reacted with *excess* hydrogen gas, 0.16 moles of solid Fe are formed. How many moles of Fe_2O_3 were in the original sample?

Exercise 6.2.2

Ammonia is produced industrially from nitrogen and hydrogen according to the equation:

$$N_2 + 3H_2 \rightarrow 2NH_3$$

a. If you are given 6.2 moles of nitrogen how many mole of ammonia could you produce?
b. How many moles of hydrogen would you need to fully react with 6.2 moles of nitrogen?
c. If you wished to produce 11 moles of ammonia how many moles of nitrogen would you need to start with?

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6.3: Mass Calculations

The methods described in the previous section allow us to express reactants and products in terms of moles, but what if we wanted to know how many *grams* of a reactant would be required to produce a given number of *grams* of a certain product? This logical extension is, of course, trivial! In Chapter 4, we learned to express molar quantities in terms of the *masses* of reactants or products. For example, the reduction of iron (III) oxide by hydrogen gas, produces metallic iron and water. If we were to ask how many grams of elemental iron will be formed by the reduction of 1.0 grams of iron (III) oxide, we would simply use the molar stoichiometry to determine the number of moles of iron that would be produced, and then convert moles into grams using the known molar mass. For example, one gram of Fe_2O_3 can be converted into mol Fe_2O_3 by remembering that moles of a substance is equivalent to grams of that substance divided by the molar mass of that substance:

$$moles = \left(\frac{grams}{molar\ mass}\right) = \left(\frac{grams}{grams/mol}\right) = (grams) \times (mol/grams)$$

Using this approach, the mass of a reactant can be inserted into our reaction pathway as the ratio of mass-to-molar mass. This is shown here for the reduction of 1.0 gram of Fe_2O_3.

$$Given: \left(\frac{1.0g\ Fe_2O_3}{159.70\frac{g\ Fe_2O_3}{mol\ Fe_2O_3}}\right) \quad Find: x\ mol\ Fe$$

We set up the problem to solve for *mol product*; the general equation is:

$$(molproduct) = (molreactant) \times \left(\frac{molproduct}{molreactant}\right)$$

The stoichiometric mole ratio is set up so that mol reactant will cancel, giving a solution in *mol product*. Substituting,

$$x\ mol\ Fe = \left(\frac{1.0g\ Fe_2O_3}{159.70\frac{g\ Fe_2O_3}{mol\ Fe_2O_3}}\right) \times \left(\frac{2\ mol\ Fe}{1\ mol\ Fe_2O_3}\right)$$

It is often simpler to express the ratio (mass)/(molar mass) as shown below,

$$\left(\frac{1.0g\ Fe_2O_3}{159.70\frac{g\ Fe_2O_3}{mol\ Fe_2O_3}}\right) = (1.0g\ Fe_2O_3) \times \left(\frac{1\ mol\ Fe_2O_3}{159.70\ g\ Fe_2O_3}\right)$$

Doing this, and rearranging,

$$x\ mol\ Fe = (1.0g\ Fe_2O_3) \times \left(\frac{1\ mol\ Fe_2O_3}{159.70\ g\ Fe_2O_3}\right) \times \left(\frac{2\ mol\ Fe}{1\ mol\ Fe_2O_3}\right) = 0.013\ mol$$

That is, the reduction of 1.0 grams of Fe_2O_3 by excess hydrogen gas will produce 0.013 moles of elemental iron. All of these calculations are good to two significant figures based on the mass of iron (III) oxide in the original problem (1.0 grams). Note that we have *two* conversion factors (ratios) in this solution; one from mass to molar mass and the second, the stoichiometric mole ratio from the balanced chemical equation. Knowing that we have 0.013 moles of Fe, we could now convert that into grams by knowing that one mole of Fe has a mass of 55.85 grams; the yield would be 0.70 grams.

We could also modify our basic set-up so that we could find the number of *grams* of iron directly.

Here we have simply substituted the quantity (*moles molar mass*) to get mass of iron that would be produced. Again, we set up the problem to solve for *mol product*;

$$(molproduct) = (molreactant) \times \left(\frac{molproduct}{molreactant}\right)$$

In place of *mol product* and *mol reactant*, we use the expressions for *mass* and *molar mass*, as shown in the scheme above. The stoichiometric mole ratio is set up so that *mol reactant* (the ***given***) will cancel, giving a solution in *mol product*. Substituting,

$$x\ mol\ Fe\left(\frac{55.85g\ Fe}{mol\ Fe}\right) = (1.0g\ Fe_2O_3) \times \left(\frac{1\ mol\ Fe_2O_3}{159.70\ g\ Fe_2O_3}\right) \times \left(\frac{2\ mol\ Fe}{1\ mol\ Fe_2O_3}\right)$$

Rearranging and canceling units,

$$x\ g\ Fe = \left(\frac{55.85 g\ Fe}{mol\ Fe}\right)\left(\frac{1\ g\ Fe_2O_3 \times mol\ Fe_2O_3}{159.70\ g\ Fe_2O_3}\right) \times \left(\frac{2\ mol\ Fe}{1\ mol\ Fe_2O_3}\right) = 0.70g$$

Exercise 6.3.1

Aqueous solutions of silver nitrate and sodium chloride react in a double-replacement reaction to form a precipitate of silver chloride, according to the balanced equation shown below.

$$AgNO_3\ (aq) + NaCl\ (aq) \rightarrow AgCl\ (s) + NaNO_3\ (aq)$$

If 3.06 grams of solid AgCl are recovered from the reaction mixture, what mass of $AgNO_3$ was present in the reactants?

Exercise 6.3.2

Aluminum and chlorine gas react to form aluminum chloride according to the balanced equation shown in below.

$$2\ Al\ (s) + 3\ Cl_2\ (g) \rightarrow 2\ AlCl_3\ (s)$$

If 17.467 grams of chlorine gas are allowed to react with excess Al, what mass of solid aluminum chloride will be formed?

Exercise 6.3.3

Ammonia, NH_3, is also used in cleaning solutions around the house and is produced from nitrogen and hydrogen according to the equation:

$$N_2 + 3\ H_2 \rightarrow 2\ NH_3$$

a. If you have 6.2 moles of nitrogen what mass of ammonia could you hope to produce?
b. If you have 6.2 grams of nitrogen how many grams of hydrogen would you need?

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6.4: Percentage Yield

When we use stoichiometric calculations to predict quantities in a reaction, our results are based on the assumption that everything happens in reality exactly as described by the chemical equation. Unfortunately, that is not always the case. When you work in the laboratory, things often go wrong. When you are weighing out reactants and transferring the materials to reaction vessels, some material will often remain on the spatula or in the weighing vessel. As you collect product, some may spill, or in a vigorous reaction, material may escape from the reaction vessel. Stoichiometric calculations will give you a **theoretical yield** for a reaction; the yield that you should obtain assuming that the reaction proceeds with 100% efficiency and that no material is lost in handling. The amount of material that you isolate from a given reaction is called the **actual yield** and it is always less than the theoretical yield. The *percentage* of the theoretical yield that you actually isolate is called the **percentage yield**.

Consider the reaction between silver nitrate and sodium chloride to form solid silver chloride. If we react 10.00 grams silver nitrate with excess sodium chloride, we would predict that we would obtain:

We set up the problem to solve for mol product; the general equation is:

$$(molproduct) = (molreactant) \times \left(\frac{molproduct}{molreactant}\right)$$

For *mol product* and *mol reactant*, we use the expressions for (mass)/(molar mass), as shown in the scheme above. The stoichiometric mole ratio is set up so that mol reactant will cancel, giving a solution in mol product. Substituting,

$$(x\ g\ AgCl)\left(\frac{1\ mol\ AgCl}{143.32\ g\ AgCl}\right) = (10.00\ g\ AgNO_3)\left(\frac{1\ mol\ AgNO_3}{169.88\ g\ AgNO_3}\right) \times \left(\frac{1\ mol\ AgCl}{1\ mol\ AgNO_3}\right)$$

$$(x\ g\ AgCl)$$

$$= (10.00\ g\ AgNO_3)\left(\frac{1\ mol\ AgNO_3}{169.88\ g\ AgNO_3}\right) \times \left(\frac{1\ mol\ AgCl}{1\ mol\ AgNO_3}\right) \times \left(\frac{143.32\ g\ AgCl}{1\ mol\ AgCl}\right) = 8.440\ g$$

This mass, calculated from the masses of starting materials and the stoichiometry of the equation is the theoretical yield. Because the silver chloride is a precipitate from an aqueous solution, however, we must filter it, dry it, transfer it to our balance and weigh it, before we can measure how much product we obtain as our actual yield. As we filter it, a small amount of solid is likely to remain stuck to the sides of the flask. When it is dry and we transfer it to the balance, some solid will remain on the filter paper, some on the spatula, and (most likely) your lab partner will sneeze at an inopportune moment and blow some of it all over the desktop. Considering all of this, it is very unlikely that we will end up with an actual yield of 8.044 grams of solid AgCl.

Let's assume that we have done all of these operations (including the sneeze) and when we weigh our solid AgCl, we actually obtain 7.98 grams of solid. We know that we obtain 7.98 grams of product (our actual yield) and we calculated that we should obtain 8.440 grams of product (the theoretical yield). The percentage of the theoretical yield that we obtain is called the **percentage yield**, and is calculated as (actual yield)/(theoretical yield) 100. In the present case:

$$\left(\frac{7.98g}{8.440g}\right) \times 100 = 94.5\%$$

The percentage yield of solid AgCl that we obtained in this reaction is therefore 94.5% (not bad, actually, considering your lab partner). The concept of percentage yield is generally applied to all experimental work in chemistry.

? Exercise 6.4.1

Powdered zinc and solid sulfur combine explosively to form zinc sulfide. You and your lab partner carefully mix 0.010 mole of solid zinc powder with exactly 0.010 mole of powdered sulfur in a small porcelain crucible. Knowing your lab partner, you allow your instructor to ignite the mixture. The explosion forms a cloud of ZnS, scatters some all over the ground, and leaves a crusty pile of product in the crucible. You transfer this and determine that 0.35 grams of solid product has been recovered. Calculate the percentage yield.

Exercise 6.4.2

The Harber process is used making ammonia from nitrogen and hydrogen according to the equation shown below. The yield of the reaction, however, is not 100%.

$$N_2 + 3\ H_2 \rightarrow 2\ NH_3$$

a. Suppose you end up with 6.2 moles of ammonia, but the reaction stoichiometry predicts that you should have 170.0 grams of ammonia. What is the percent yield for this reaction?
b. If you started with 6.2 grams of nitrogen and you produce 6.2 grams of ammonia what would be the percent yield?

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6.5: Limiting Reactants

Gloves will typically come is right- and left-handed models. In order to make a *pair* of gloves, you need one that is designed to fit each hand. If you had a box containing 50 left-handed gloves and another box containing 40 right-handed gloves, you could make 40 proper pairs and you would have ten left-handed gloves left over. The number of pairs of gloves that you could assemble is *limited* by the glove in the smallest number (the right-handed glove). The other glove in this example, the left, is present in *excess*.

The same sort of logic applies to chemical reactions in which there are two or more reactants. In Example 6.4, we carefully weighed out 0.010 mole of solid zinc and solid sulfur in order to react them to form 0.010 mole of the product, ZnS. If instead, we had reacted 0.010 mole of Zn with 0.020 moles of sulfur, how much ZnS would have (theoretically) formed? The answer is still 0.010 mole of ZnS. What happens to the leftover sulfur? It just sits there! When the reaction is complete, there is (theoretically) 0.010 mole of ZnS mixed with the remaining 0.010 mole of sulfur. 10 atoms of Zn reacting with 20 atoms of S yield 10 molecules of ZnS with 10 atoms of S remaining.

You may have noticed that, in many of the problems in this chapter, we stated that one reactant reacted with an *excess* of a second reactant. In all of these cases, the theoretical yield of product is determined by the limiting reactant in the reaction, and some of the excess reactant is left over. If aluminum and chlorine gas, a diatomic gas, react to form aluminum chloride according to the equation shown below,

$$\mathbf{2\ Al}\ \boldsymbol{(s)} + \mathbf{3\ Cl_2}\ \boldsymbol{(g)} \rightarrow \mathbf{2\ AlCl_3}\ \boldsymbol{(s)}$$

and there are 2.0 moles of aluminum and 14 moles of chlorine present, two moles of aluminum chloride are formed and 11 moles of chlorine gas remain in excess. Our stoichiometry is:

$$\left(\frac{3\ mol\ Cl_2}{2\ mol\ AlCl_3}\right)$$

If three moles of chlorine gas are used in the reaction, (14 – 3) = 11 moles of chlorine must remain. When a problem is presented and one reactant is labeled as excess, the theoretical yield of product is equal to the moles of the limiting reagent, adjusted for the stoichiometry of the reaction.

Although it would be easier if reactants were routinely labeled as “limiting” or “excess”, more commonly problems are written in such a way that it is not always trivial to identify the limiting reactant. For example, if you were told that 6.0 grams of aluminum was reacted with 3.8 grams of chlorine gas and you were asked to calculate the mass of $AlCl_3$ that would be formed, there would be no simple way to identify the limiting- and excess reactants. In a case like this what you want to do is to simply solve the problem *twice*. First you would calculate the number of moles of aluminum in 6.0 grams, and then calculate how many moles of $AlCl_3$ could be formed. Next, you calculate how many moles of chlorine are present in 3.8 grams of chlorine gas and again, calculate how many moles of $AlCl_3$ could be formed. Whichever reagent produces the *smallest number of moles of product* must be *limiting* and the other reagent must be in *excess*.

Find: *x* moles of $AlCl_3$

We set up the problem to solve for *mol product* for *each* reactant. The general equation is:

$$(molproduct) = (molreactant) \times \left(\frac{molproduct}{molreactant}\right)$$

The solutions for both reactants are:

$$x\ mol\ AlCl_3 = (6.0\ g\ Al)\left(\frac{1\ mol\ Al}{26.98\ g\ Al}\right)\left(\frac{1\ mol\ AlCl}{1\ mol\ Al}\right)$$

$$x\ mol\ AlCl_3 = (3.8\ g\ Cl_2)\left(\frac{1\ mol\ Cl_2}{70.90\ g\ Cl_2}\right)\left(\frac{2\ mol\ AlCl}{3\ mol\ Cl_2}\right)$$

Solving these equations, we see that, beginning with 6.0 grams of aluminum, **0.22 moles** of $AlCl_3$ can be formed, and that, beginning with 3.8 grams of chlorine, **0.036 moles** of $AlCl_3$ can be formed.

Keeping score, 6.0 grams of Al yields 0.22 moles of $AlCl_3$, and 3.8 grams of chlorine gas yields 0.036 moles of $AlCl_3$. The *lowest* yield comes from the chlorine gas, therefore it must be *limiting* and aluminum must be in excess. The reaction in the problem will

therefore produce 0.036 moles of product, which is equivalent to:

$$0.036\ mol\ AlCl_3(133.33\ g/mol) = 4.8\ g\ AlCl_3$$

Exercise 6.5.1

Lead (IV) chloride reacts with fluorine gas to give lead (IV) fluoride and Cl_2. If 0.023 moles of fluorine gas reacts with 5.3 grams of lead (IV) chloride, what mass of lead (IV) fluoride will be formed?

Although "limiting reactant problems" may be *tedious*, they are not difficult. When you are faced with a limiting reactant problem, just remember, you do the simple molar yield calculations *twice*, one for each reactant. The reactant that yields the *lowest* molar quantity is your limiting reagent and the molar value you calculate determines the theoretical yield in the problem.

Exercise 6.5.2

Ammonia, which is the active ingredient in "smelling salts", is prepared from nitrogen and hydrogen according to the equation shown below.

$$\mathbf{N_2 + 3\ H_2 \rightarrow 2\ NH_3}$$

a. If you mix 5.0 mol of nitrogen and 10.0 moles of hydrogen how many moles of ammonia would you produce? Which reactant is in excess?
b. If you have 6.2 grams of nitrogen and you react it with 6.2 grams of hydrogen how many grams of ammonia would you produce? Which reactant is the limiting reactant?

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6.S: Quantitative Relationships in Chemistry (Summary)

- **Stoichiometry** is the relationship between the masses of chemical reactants and products in a given chemical reaction. The coefficients placed in a chemical equation in order to balance it are called the **stoichiometric coefficients**. **Molar stoichiometry** is simply the expression of the coefficients of a reaction in terms of moles of reactants and products.
- In order to find the number of **moles of a product** that is produced in a chemical reaction when you are *given* **moles of reactant**, simply multiply the moles of reactant by the *stoichiometric ratio* relating that reactant and the desired product; i.e.,

$$(molreactant) \times \left(\frac{molproduct}{molreactant}\right)$$

- In order to find the number of **moles of a product** that are produced in a chemical reaction when you are *given* **mass of reactant**, simply *divide* the mass of reactant by the **molar mass** (to get *moles reactant*) and then *multiply* by the *stoichiometric ratio* relating that reactant and the desired product; i.e.,

$$\left(\frac{grams}{grams/mol}\right) \times \left(\frac{molproduct}{molreactant}\right)$$

- Always remember, **mass divided by molar mass equals moles**;

$$\left(\frac{grams}{grams/mol}\right) = mol$$

- The *mass* or the *number of moles* that you calculate for a product based on reaction stoichiometry is called the **theoretical yield** for the reaction. The amount of material that you actually isolate from a given reaction is called the **actual yield** and it is always less than the theoretical yield. The ratio of the actual and theoretical yields, expressed as a *percentage* is called the **percentage yield**.
- ***If*** a reaction requires more than one reactant and ***if*** you are given the mass, or the number of moles of *each* reactant, you must approach the calculation as a **limiting reactant problem**. To solve a limiting reactant problem, simply perform the standard mass calculation for *each* reactant, noting the mass (or number of moles) of product formed in each calculation. The reactant that yields the *smallest* amount or product from these calculations is called the **limiting reactant**. Reactants that yield *larger* amounts of products in these calculations are called **excess reactants**. The theoretical yield in the reaction will be based *solely* on the calculated amount for the limiting reactant.
- If a reactant in a chemical reaction is said to be “in excess”, you assume that you have *unlimited* amount of the reactant, and that it will never be the limiting reactant.

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CHAPTER OVERVIEW

7: Aqueous Solutions

Water is the most remarkable solvent! The O—H bonds in water are *polarized* due to the differences in electronegativity between hydrogen and oxygen. When this uneven charge distribution is coupled with the fact that water has a “bent” molecular geometry, the two covalent bond dipoles combine to form a molecular dipole (shown in the electrostatic potential map on the right. This molecular dipole allows water to surround and stabilize ions in solution, making water a powerful solvent for the dissolution of polar and ionic compounds. If we know the *amount* of solute that we have dissolved in a given *volume* of solvent, we can define the term molarity, as the *number of moles of solute in each liter of solution*. Finally, by combining the concept of molarity with what we have learned about simple stoichiometric calculations, we can now approach quantitative chemical calculations in solution.

7.1: Hydrogen Bonding and the Properties of Water

7.2: Molecular Dipoles

7.3: Dissolution of Ionic Compounds

7.4: Concentration and Molarity

7.5: Solution Stoichiometry

7.6: Dilution of Concentrated Solutions

7.S: Aqueous Solutions (Summary)

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7.1: Hydrogen Bonding and the Properties of Water

Water is an amazing solvent, and has remarkable physical and chemical properties that make it the essential ingredient to life as we know it. The special properties of water come from the fact that the elements hydrogen and oxygen have differing electronegativities. In Chapter 3 we learned that covalent bonds formed between atoms of differing electronegativity are polarized. Because electronegativity is a measure of how strongly a given atom attracts electrons to itself, the atom in the covalent bond with the highest electronegativity will tend to draw the bonding electrons towards itself, resulting in a bond that is electron-rich on one end and electron-poor on the other. Covalent bonds that are polarized are said to have a **dipole**, where the term **dipole moment** refers to the direction and magnitude of the charge separation.

Consider water. The electronegativities of hydrogen and oxygen are 2.20 and 3.44, respectively. That means that in each covalent bond, the electrons will be attracted towards the oxygen, leaving the hydrogen electron-poor. In Chapter 3, we used a calculated electrostatic potential map to visualize the electron density around molecules. The map for water is shown to the left and is colored using red to indicate a high electron density and blue to show electron-poor regions. Because electrons carry a negative charge, this also means that the red regions of the molecule are anionic (negative) and that the blue regions are cationic (positive).

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7.2: Molecular Dipoles

Electrostatic potential maps are useful because they clearly show the electron distribution around covalent bonds within molecules. They must be calculated, however, using sophisticated computer programs, and then rendered in color for visualization. Because of this, the polarization of covalent bonds is typically shown using a special arrow (a dipole arrow) to indicate the direction in which the bond is polarized. A **dipole arrow** is crossed at the beginning (as in a plus sign) and points in the direction of the greatest electron density. Thus for hydrogen fluoride, the electronegativities are 2.20 and 3.98 for the hydrogen and fluorine, respectively. We would predict that the H—F bond would be polarized with the greatest electron density towards the fluorine.

A molecule such as water, with two covalent bonds, will have *two* local dipoles, each oriented along the covalent bonds, as shown below. Because water is asymmetric (it has a bend structure) both of these local dipoles point in the same direction, generating a **molecular dipole**, in which the entire molecule has a charge imbalance, with the "oxygen end" being anionic and the "hydrogen end" being cationic.

Molecules with local dipoles do not necessarily possess a molecular dipole. Consider the molecule boron trihydride (BH_3). The BH_3 molecule is planar with all three hydrogens spaced evenly surrounding the boron (trigonal planar). The electronegativities of boron and hydrogen are 2.04 and 2.20, respectively. The bonds in BH_3 will therefore be somewhat polarized, with the local dipoles oriented towards the hydrogen atoms, as shown below. But because the molecule is *symmetrical*, the three dipole arrows cancel and, as a *molecule*, BH_3 has no net molecular dipole.

? Exercise 7.2.1

For each of the molecules of NH_3 and CO_2 indicate whether a molecular dipole exists. If a dipole does exist, use a dipole arrow to indicate the direction of the molecular dipole.

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7.3: Dissolution of Ionic Compounds

A simple ionic compound, such as sodium chloride (NaCl) consists of a sodium cation and a chloride anion. Because these are oppositely charge ions, they are strongly attracted to each other. This attraction is non-specific and the sodium cation would also be strongly attracted to *any* anion. When an ionic compound dissolves in water, the individual cations and anions are completely surrounded by water molecules, but these water molecules are not randomly oriented. A sodium cation in water will be surrounded by water molecules oriented so that the negative end of the molecular dipole is in contact with the sodium cation. Likewise, the waters surrounding the chloride anion are oriented so that the positive end of the molecular dipole contacts the anion.When arranged like this, the charged poles of the water molecules *neutralize*, and thus *stabilize* the charges on the ions.

The ability of water to interact with and stabilize charge particles goes well beyond the water molecules that actually touch the ion. Surrounding the inner water shell is another shell of waters that will orient themselves so that their dipoles bind to the exposed dipoles from the inner shell. As the subsequent layers of water surround each other, the positive charge from the cation is *dispersed* or spread out over the whole group of interacting molecules. The cluster then becomes effectively *neutral* allowing the charged ion to exist free in solution, removed from its counter-ion (the chloride). The dynamic collection of water molecules surrounding an ion in solution is referred to as the **solvation shell** and it is the ability of water to solvate and stabilize ions that makes water such an important solvent, both in chemistry and in biology.

In addition to ionic compounds, water will also dissolve and stabilize most molecules that are polar, that is, if they possess a molecular dipole. The organic compound, methyl propionate, contains a highly polar carbon-oxygen double bond. The electrostatic potential map in the figure clearly shows the resulting molecular dipole and methyl propionate is quite soluble in water; 6.2 grams of methyl propionate will dissolve in 100 mL of water. The organic molecule propane, does not possess a significant molecular dipole and is only very slightly soluble in water.

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7.4: Concentration and Molarity

As described in the previous section, sodium chloride is quite soluble in water. At 25 ˚C (about room temperature), 359 grams of sodium chloride will dissolve in one liter of water. If you were to add more sodium chloride to the solution, it would not dissolve, because a given volume of water can only dissolve, disperse and stabilize a fixed amount of solute (the stuff that dissolves). This amount is different for every compound and it depends on the structure of the particular compound and how that structure interacts with the solvation shell. When a substance is dissolved in water to the point that no more will go into solution, we say the solution is **saturated**. For most compounds, heating the solution will allow more of the substance to dissolve, hence it is important to note the temperature when you are speaking of the solubility of a particular compound.

If we had a saturated solution of sodium chloride at 25 ˚C, we could quote the concentration as 359 grams/L, but because we know the molar mass of sodium chloride (58.44 grams/mole), we could also express our concentration as:

$$\left(\frac{(359\,g)\times\frac{1\,mole}{58.44\,g}}{1\,L}\right)=6.14\,moles/L$$

In chemistry, the units of moles/L are called **molarity**, with the abbreviation M. Thus we could say that our saturated solution of sodium chloride was **6.14 molar**, or **6.14 M**.

The advantage of expressing concentrations in terms of molarity is that these solutions can now be used in chemical reactions of known stoichiometry because any volume of the solution corresponds directly to a known number of moles of a particular compound. For example, the molar mass of potassium bromide is 119.0 g/mole. If we dissolved 119.0 grams of KBr in 1.000 L of water, the concentration would be 1.000 mole/L, or 1.000 M. If we now took half o this solution (0.500 L) we know that we would also have 0.500 moles of KBr.

We can determine the concentration of a solution using the problem-solving algorithm we introduced back in Chapter 1. For example, if you wan to find the molarity of a solution containing 42.8 grams of KBr in 1.00 L of water, you would identify the *given* and 42.8 g, your *ratio* is the molar mass (119 g/mole) and you want to *find* molarity (or moles/L). Remembering to set the equation up so that the units of *given* appear in the denominator of the *ratio*, the number of moles is:

$$42.8\,g)\times\left(\frac{1\,mole}{119\,g}\right)=0.360\,moles$$

and, the molarity is:

$$\left(\frac{0.360\,mole}{1.00\,L}\right)=0.360\,moles/L\ or\ 0.360\,M$$

When you become comfortable with the simple two-step method, you can combine steps and simply divide your given mass by the given volume to get the result directly. Thus, if you had 1.73 grams of KBr in 0.0230 L of water, your concentration would be:

$$\left(\frac{(1.73\,g)\times\frac{1\,mole}{119\,g}}{0.0230\,L}\right)=6.32\,moles/L\ or\ 0.632\,M$$

We can also solve these problems *backwards*, that is, convert molarity into mass. For example; determine the number of grams of KBr that are present in 72.5 mL of a 1.05 M solution of KBr. Here we are given a volume of 0.0725 L and our ratio is the molarity, or (1.05 moles/L). We first solve for moles,

$$0.0725\,L\times\left(\frac{1.05\,mole}{1.00\,L}\right)=0.0761\,moles$$

and then convert to mass using:

$$0.0761\,moles\times\left(\frac{119\,grams}{1\,mole}\right)=9.06\,grams\,of\,KBr$$

Exercise 7.4.1

A sample of 12.7 grams of sodium sulfate (Na_2SO_4) is dissolved in 672 mL of distilled water.

a. What is the molar concentration of sodium sulfate in the solution?
b. What is the concentration of sodium ion in the solution?

Exercise 7.4.1

Calculate the mass of sodium chloride required to make 125.0 mL of a 0.470 M NaCl solution. If you dissolve 5.8g of NaCl in water and then dilute to a total of 100.0 mL, what will be the molar concentration of the resulting sodium chloride solution?

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7.5: Solution Stoichiometry

As we learned in Chapter 5, double replacement reactions involve the reaction between ionic compounds in solution and, in the course of the reaction, the ions in the two reacting compounds are "switched" (they *replace* each other). As an example, silver nitrate and sodium chloride react to form sodium nitrate and the *insoluble* compound, silver chloride.

$$\mathrm{AgNO_3\,(aq) + NaCl\,(aq) \longrightarrow AgCl\,(s) + NaNO_3\,(aq)}$$

Because these reactions occur in aqueous solution, we can use the concept of molarity to directly calculate the number of moles of products that will be formed, and hence the mass of precipitates. In the reaction shown above, if we mixed 123 mL of a 1.00 M solution of NaCl with 72.5 mL of a 2.71 M solution of AgNO3, we could calculate the moles (and hence, the mass) of AgCl that will be formed as follows:

First, we must examine the reaction stoichiometry. In this reaction, one mole of AgNO3 reacts with one mole of NaCl to give one mole of AgCl. Because our ratios are one, we don't need to include them in the equation. Next, we need to calculate the number of moles of each reactant:

$$0.123L \times \left(\frac{1.00\,mole}{1.00\,L}\right) = 0.123\,moles\,NaCl$$

$$0.0725L \times \left(\frac{2.71\,mole}{1.00\,L}\right) = 0.196\,moles\,AgNO_3$$

Because this is a *limiting reactant* problem, we need to recall that the moles of product that can be formed will equal the *smaller* of the number of moles of the two reactants. In this case, NaCl is limiting and AgNO3 is in excess. Because our stoichiometry is one-to-one, we will therefore form 0.123 moles of AgCl. Finally, we can convert this to mass using the molar mass of AgCl:

$$0.0725L \times \left(\frac{2.71\,mole}{1.00\,L}\right) = 0.196\,moles\,AgNO_3$$

In a reaction where the stoichiometry is not one-to-one, you simply need to include the stoichiometric ratio in you equations. Thus, for the reaction between lead (II) nitrate and potassium iodide, two moles of potassium iodide are required for every mole of lead (II) iodide that is formed.

\[\ce{Pb(NO3)2 (aq) + 2 KI (aq) → PbI2 (s) + 2 KNO3 (aq)} \nonumber \] For example: 1.78 grams of lead (II) nitrate are dissolved in 17.0 mL of water and then mixed with 25.0 mL of 2.5 M potassium iodide solution. What *mass* of lead (II) iodide will be formed and what will be the *final concentration* of potassium nitrate in the solution? Again, we need to look at this as a limiting reactant problem and first calculate the number of moles of each reactant:

$$1.78\,g \times \left(\frac{1.00\,mole}{331.2\,g}\right) = 5.37 \times 10^{-3}\,moles\,Pb(NO_3)_2$$

$$0.0025\,L \times \left(\frac{2.50\,mole}{1.00\,L}\right) = 6.25 \times 10^{-3}\,moles\,KI$$

The stoichiometry of this reaction is given by the ratios:

$$\left(\frac{1\,mole\,PbI_2}{2\,mole\,KI}\right)\ and\ \left(\frac{1\,mole\,PbI_2}{1\,mole\,Pb(NO_3)_2}\right)$$

so the number of moles of product that would be formed from each reactant is calculated as:

$$\left(\frac{1\,mole\,PbI_2}{1\,mole\,Pb(NO_3)_2}\right)$$

$$6.25 \times 10^{-3}\,moles\,KI \times \left(\frac{1\,mole\,PbI_2}{2\,moles\,KI}\right) = 3.12 \times 10^{-3}\,moles\,PbI_2$$

Potassium iodide produces the smaller amount of PbI2 and hence, is *limiting* and lead (II) nitrate is in *excess*. The mass of lead (II) iodide that will be produced is then calculated from the number of moles and the molar mass:

$$3.12 \times 10^{-3}\ moles\ \times \left(\frac{461\ grams}{1\ mole}\right) = 1.44\ grams\ PbI_2$$

To determine the concentration of potassium nitrate in the final solution, we need to note that two moles of potassium nitrate are formed for every mole of PbI_2, or a stoichiometric ratio of

$$\left(\frac{2\ moles\ KNO_3}{1\ mole\ PbI_2}\right)$$

Our final volume is (17.0 + 25.0) = 42.0 mL, and the concentration of potassium nitrate is calculated as:

$$\frac{3.12 \times 10^{-3}\ moles\ PbI_2 \times \left(\frac{2\ moles\ KNO_3}{1\ mole\ PbI_2}\right)}{0.0420\ L} = 0.148\ moles\ KNO_3/L\ or\ 0.148\ M$$

? Exercise 7.5.1

1. A sample of 12.7 grams of sodium sulfate (Na_2SO_4) is dissolved in 672 mL of distilled water.
   a. What is the molar concentration of sodium sulfate in the solution?
   b. What is the concentration of sodium ion in the solution?
2. How many moles of sodium sulfate must be added to an aqueous solution that contains 2.0 moles of barium chloride in order to precipitate 0.50 moles of barium sulfate?
3. If 1.0 g of NaN_3 reacts with 25 mL of 0.20 M $NaNO_3$ according to the reaction shown below, how many moles of N_2*(g)* are produced?

$$5NaN3(s) + NaNO3(aq) \rightarrow 3Na2O(s) + 8N2(g)$$

- Paul R. Young, Professor of Chemistry, University of Illinois at Chicago, Wiki: AskTheNerd; PRY@askthenerd.com - pyoung@uic.edu; ChemistryOnline.com

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7.6: Dilution of Concentrated Solutions

In the laboratory, a chemist will often prepare solutions of known concentration beginning with a standard stock solution. A stock solution is generally concentrated and, of course, the molar concentration of the solute must be known. To perform a reaction, a measured amount of this stock solution will be withdrawn and added to another reactant, or will be diluted into a larger volume for some other use. The calculations involved in these dilutions are trivial and simply involve calculating the number of moles transferred and dividing this by the final volume. For example, 15.0 mL of a stock solution of 1.00 M hydrochloric acid (HCl) is withdrawn and diluted into 75 mL of distilled water; what is the final concentration of hydrochloric acid?

First, the number of moles of HCl is calculated from the volume added and the concentration of the stock solution:

$$0.0150L \times \left(\frac{1.00\,moles}{1\,L}\right) = 0.0150\,moles\,HCl$$

We have diluted this number of moles into (15.0 + 75.0) = 90.0 mL, therefore the final concentration of HCl is given by:

$$\left(\frac{0.0150\,moles\,HCl}{0.0900\,L}\right) = (0.167\,moles\,HCl/L)\;or\;0.167\,M$$

An even simpler way to approach these problems is to multiply the initial concentration of the stock solution by the *ratio* of the aliquot (the amount withdrawn from the stock solution) to the final volume, using the equation below:

$$(stock\;concentration) \times \left(\frac{volume\;of\;the\;aliquot}{final\;volume}\right) = final\;concentration$$

Using this method on the previous problem,

$$(1.00\,M) \times \left(\frac{15.0\,ml}{90.0\,ml}\right) = 0.167\,M$$

Note that we did not have to convert our volumes (15.0 and 90.0 mL) into L when we use this approach because the units of volume cancel in the equation. If the units that are given for the aliquot and the final volume are different, a metric conversion ratio may be required. For example, 10.0 µL of a 1.76 M solution of HNO_3 (nitric acid) are diluted into 10.0 mL of distilled water; what is the final concentration of nitric acid?

In this problem, we need to convert µL and mL into a common unit. We can do this using the ratios,

$$\left(\frac{10^{-6}L}{1\mu L}\right)\;and\;\left(\frac{10^{-3}L}{1\,mL}\right)$$

We need to multiply each of our volumes by the appropriate factor to get our volumes in terms of liters, and then simply multiply by the initial concentration. Thus,

$$1.76\,M \times \left\{\frac{10.0\mu L\left(\frac{10^{-6}L}{1\mu L}\right)}{10.0\,mL\left(\frac{10^{-3}L}{1\,mL}\right)}\right\} = 1.76 \times 10^{-3}M$$

The final volume in this problem is actually (1.00×10^{-2} L) + (1.00×10^{-5} L) = 1.001×10^{-2} L, but because our calculation is only accurate to three significant figures, the volume of the aliquot is not significant and the final volume has been rounded.

The standard method we have used here can also be adapted to the type of problem in which you need to find the volume of a stock solution that must be diluted to a certain volume in order to produce a solution of a given concentration. For example, what volume of 0.029 M $CaCl_2$ must be diluted to exactly 0.500 L in order to give a solution that is 50.0 µM?

In order to solve this problem in the simplest of terms, we should re-examine the above equation:

$$(stock\;concentration) \times \left(\frac{volume\;of\;the\;aliquot}{final\;volume}\right) = final\;concentration$$

This equation can be re-written as:

$$\left(\frac{volume\;of\;the\;aliquot}{final\;volume}\right) = \left(\frac{final\;concentration}{stock\;concentration}\right)$$

Or

$$\left(\frac{V}{V_f}\right) = \left(\frac{C_f}{C_i}\right)$$

where C_i and C_f are the *stock* and *final* concentrations, respectively, V is the volume of the aliquot and V_f is the final volume of the solution. Stated another way, this is simply a set of ratios; *aliquot* to *final volume*, and *final concentration* to *initial concentration* (operationally, these ratios will always be "*small value/larger value*"). Working with this set of ratios, we can directly solve this type of problem as follows:

First, we need to convert our final concentration (50.0 µM) into M, to match the units of our stock solution. The metric multiplier for µ is 10^{-6}, making our final concentration 50.0×10^{-6} M, or more properly, 5.00×10^{-5} M. Our equation is therefore:

$$\left(\frac{V}{0.500L}\right) = \left(\frac{5.00\times10^{-5}M}{0.029M}\right)$$

$$V = \left(\frac{5.00\times10^{-5}M}{0.029M}\right)\times 0.500L$$

The volume of the aliquot, V, is 8.62×10^{-4} L, or using the conversion factor

$$\left(\frac{10^3 mL}{1L}\right)$$

the required volume is 0.86 mL (there are only two significant figures in the concentration of the stock solution, 0.029 M).

Dilution problems can be solved directly using the above equation, or, as you become more comfortable with the math, using the initial and final ratios like we did in this problem (remember, the numbers in the two ratios are "*smaller/larger*").

? Exercise 7.6.1

1. A 1.50 mL aliquot of a 0.177 M solution of sulfuric acid (H_2SO_4) is diluted into 10.0 mL of distilled water, to give solution **A**. A 10.0 mL aliquot of **A** is then diluted into 50.0 mL of distilled water, to give solution **B**. Finally, 10.0 mL of **B** is diluted into 900.0 mL of distilled water to give solution **C**. Additional distilled water is then added to **C** to give a final volume of 1.0000 L. What is the final concentration of sulfuric acid in solution **C**?
2. A solution was prepared by mixing 250 mL of 0.547 M NaOH with 50.0 mL of 1.62 M NaOH and then diluting to a final volume of 1.50 L. What is the molarity of Na^+ in this solution? To what final volume should 75.00 mL of 0.889 M HCl(aq) be diluted to prepare 0.800 M HCl(aq)?

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7.S: Aqueous Solutions (Summary)

- Covalent bonds formed between atoms of differing electronegativity are *polarized*, resulting in a bond that is electron-rich on one end and electron-poor on the other. Covalent bonds that are polarized are said to have a **dipole**, where the term **dipole moment** refers to the direction and magnitude of the charge separation.
- If a molecule is *asymmetric* (such as a molecule with a bend structure) local dipoles along covalent bonds can combine, generating a **molecular dipole**, in which the entire molecule has an imbalance with regard to electron distribution. This can be shown with an dipole arrow (with a positive end) indicating the direction of the charge separation in the molecule.
- If a molecule is symmetrical (such as BH_3, which is trigonal planar), the individual dipoles associated with the covalent bonds cancel, leaving a molecule with no molecular dipole.
- Water has a significant molecular dipole, allowing it to strongly interact with other polar molecules and with individual ions from ionic compounds. Because of this, water is able to break the electrostatic attraction between ions in compounds and to move the ions into solution. In solution, cations will be surrounded by a **solvation shell** where the water molecules are oriented so that the *negative* end of the water molecule interacts with the *cation*. Likewise, the *cationic* end of water will surround and solvate *anions*.
- **Molarity** is simply defined as the *number of moles of a solute* dissolved in *one liter of solvent*, or (**moles/L**). The abbreviation for molarity is the **uppercase M**.
- You should remember that **concentration** multiplied by **volume** gives the number of **moles** of solute; (**moles/L**)×**L=moles.**
- When you are given the amount of solute in grams, remember, **mass** divided by **molar mass** gives **moles**. Dividing this by **volume** (in liters) gives **molarity**;

$$\frac{\left(\frac{grams}{grams/mole}\right)}{L} = molarity$$

- In a **standard solution**, we simply know the *molarity* of the solute(s). Because *concentration* (the molarity) multiplied by *volume* gives us *moles*, we can calculate the number of moles in given volume and use this value in standard stoichiometric calculations.
- A sample of a solution of known volume is called an aliquot. When an aliquot of a solution is diluted into a larger volume, the final concentration can be calculated as:

$$\left(\frac{volume\ of\ the\ aliquot}{final\ volume}\right) = \left(\frac{final\ concentration}{stock\ concentration}\right)$$

or

$$\left(\frac{V}{V_f}\right) = \left(\frac{C_f}{C_i}\right)$$

where C_i and C_f are the *stock* and *final* concentrations, respectively, V is the volume of the aliquot and V_f is the final volume of the solution. This relationship is also often stated as $V_1C_1 = V_2C_2$, where the subscripts refer to the initial and final concentrations and volumes.

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CHAPTER OVERVIEW

8: Acids, Bases and pH

We have all heard of acids… *acid indigestion*, the acid content of *vinegars* and *cheap wines*, vats of *sulfuric acid* and arch villains. In the last chapter we learned about the molecular dipole in water and how water molecules form hydrogen bonds among themselves, and to other polar molecules. In this chapter we will see that this hydrogen bonding can be strong enough to actually break the O—H bonds in water and in other hydrogen bonded molecules, transferring the proton to water to form the hydronium ion, H_3O^+. In its simplest sense, the formation of the hydronium ion is the "acidity" that we are all familiar with. We will see how we measure this acidity (the pH scale). We will get an introduction to the concept of equilibrium and you will finally come to appreciate the utility of the *log* and *anti-log* buttons on your scientific calculator!

8.1: Hydrogen Bonding

8.2: Ionization of Acids in Solution

8.3: Conjugate Acid-Base Pairs

8.4: Acids-Bases Reactions: Neutralization

8.5: The Meaning of Neutrality - The Autoprotolysis of Water

8.6: pH Calculations

8.7: Titrations - Neutralization and Stoichiometry

8.S: Acids, Bases and pH (Summary)

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8.1: Hydrogen Bonding

In Chapter 7, we explored the unique properties of water that allow it to serve as a powerful solvent with the ability to dissolve both ionic compounds, as well as polar molecular compounds. We attributed this to the ability of water molecules to align themselves so that the polarized hydrogen-oxygen bonds could stabilize cations, anions, and virtually any compound that also contained a significantly polarized covalent bond. By this logic, it is not at all surprising that water can also react strongly with itself, and indeed water exists as a vast network of molecules aligned so that their positive and negative dipoles interact with each other. A bond that is formed from a hydrogen atom, which is part of a polar covalent bond (such as the O—H bond) to another, more electronegative atom (that has at least one unshared pair of electrons in its valence shell) is called a **hydrogen bond**. Recall that oxygen has two unshared pairs in its valence shell, and the hydrogen-oxygen interaction in water is the classic example of a hydrogen bond. Hydrogen bonds are weak, relative to covalent bonds. The energy required to break the O—H covalent bond (the **bond dissociation energy**) is about 111 kcal/mole, or in more proper *SI* units, 464 kJ/mole. The energy required to break an O—H••••O hydrogen bond is about 5 kcal/mole (21 kJ/mole), or less than 5% of the energy of a "real" covalent bond. Even though hydrogen bonds are relatively weak, if you consider that every water molecule is participating in a least four hydrogen bonds, the total energy of hydrogen bonding interactions can rapidly become significant. Hydrogen bonding is generally used to explain the high boiling point of water (100 ˚C). For many compounds which do not possess highly polarized bonds, boiling points parallel the molar mass of the compound. Methane, CH_4, has a molar mass of 16 and a boiling point of –164 ˚C. Water, with a molar mass of 18, has a boiling point of +100 ˚C. Although these two compounds have similar molar masses, a significant amount of energy must be put into the polar molecule, water, in order to move into the gas phase, relative to the non-polar methane. The extra energy that is required is necessary to break down the hydrogen bonding network.

Hydrogen bonding is also important is DNA. According to the Watson-Crick model, the double helix of DNA is assembled and stabilized by hydrogen pairing between matching "bases". The hydrogen bonds are formed between the oxygen atoms (red) and the adjacent N—H bonds, and between the central nitrogen (blue) and the adjacent N—H bond. It is suggested that the precise alignment of these hydrogen bonds contributes to stability of the double helix and ensures the proper alignment of the corresponding base pairs.

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8.2: Ionization of Acids in Solution

In general, acids can be thought of as molecular compounds containing at least one hydrogen which is covalently bonded to a more electronegative atom. As an example, consider the compound hydrogen fluoride (HF). As we discussed in Chapter 7, the electronegativities of hydrogen and fluorine are 2.1 and 4.0, respectively, and the hydrogen-fluoride covalent bond is very highly polarized.

Because of this, when hydrogen fluoride is dissolved in water, water molecules orient themselves around HF so that the water dipoles interact with, and stabilize, the highly polarized H—F bond. Important to this stabilization is the hydrogen bond that is formed between the hydrogen of HF and the oxygen of an adjacent water. This hydrogen bond not only stabilizes the HF molecular dipole, but it also *weakens* the H—F covalent bond. As a result of this weakening, the H—F bond stretches (the bond length increases) and then fully breaks. The hydrogen that was hydrogen-bonded to the water molecule now becomes *fully* bonded to the oxygen, forming the species H_3O^+ (the **hydronium ion**) and the fluorine now exists as a fluoride anion. This is known as the process of **acid dissociation.**

The chemical equation describing the acid dissociation reaction of HF is given in Equation 8.2**a**. The products of the reaction, fluoride anion and the hydronium ion, are oppositely charged ions, and it is reasonable to assume that they will be attracted to each other. If they *do* come in contact, it is also reasonable to suggest that the process of hydrogen transfer that we described above can also happen *in reverse*. That is, H_3O^+ can hydrogen bond to the fluoride ion and the hydrogen can be transferred back, to form HF and water. The chemical equation describing this process is shown in Equation 8.2**b**. In fact, these two reaction do occur simultaneously (and very rapidly) in solution. When we speak of a set of forward- and back-reactions that occur together on a *very fast* time-scale, we describe the set of reactions as an **equilibrium** and we use a special double arrow in the chemical reaction to show this (Equation 8.2**c**). Equation 8.2**c** can be said to represent the *equilibrium dissociation of HF in water.*

$$\mathbf{HF}\ \boldsymbol{(aq)} + \mathbf{H_2O}\boldsymbol{(l)} \rightarrow \mathbf{H_3O^+}\ \boldsymbol{(aq)} + \mathbf{F^-}\ \boldsymbol{(aq)}\ \textbf{Eq. 8.2a}$$

$$\mathbf{HF}\ \boldsymbol{(aq)} + \mathbf{H_2O}\boldsymbol{(l)} \leftarrow \mathbf{H_3O^+}\ \boldsymbol{(aq)} + \mathbf{F^-}\ \boldsymbol{(aq)}\ \textbf{Eq. 8.2b}$$

$$\mathbf{HF}\ \boldsymbol{(aq)} + \mathbf{H_2O}\boldsymbol{(l)} \rightleftarrows \mathbf{H_3O^+}\ \boldsymbol{(aq)} + \mathbf{F^-}\ \boldsymbol{(aq)}\ \textbf{Eq. 8.2c}$$

For any equilibrium, an **equilibrium constant** can be written that describes whether the *products* or the *reactants* will be the predominant species in solution. We will address this fully in Chapter 10, but according to the *Law of Mass Action*, the equilibrium constant, *K* for this reaction, is simply given by the ratio of the activities of the products and reactants. To simplify the calculations, the activities of the **solutes** are approximated by the concentration in units of molarity. Note that **any solid or liquid reactants or products**, **or solvents** (such as water) are considered to be pure substances, and so have an activity that is equal to 1. Thus for the ionization of HF

$$K_a = \frac{a_{H_3O^+} \cdot a_{OH^-}}{a_{HF} \cdot a_{H_2O}} \approx \frac{[H_3O^+][F^-]}{[HF](1)} = \frac{[H_3O^+][F^-]}{[HF]}$$

When you are dealing with acids, the equilibrium constant is generally called an **acid dissociation constant**, and is written as K_a. The larger the value of K_a, the greater the extent of ionization and the and the higher the resulting concentration of the hydronium ion. Because the concentration of the hydronium ion is directly correlated with acidity, acids with a large value of K_a are termed **strong acids**. We will introduce “weak acids” in Chapter 10, but for now the important thing to remember is that strong acids are virtually 100% ionized in solution. That doesn’t mean that the back-reaction does not occur, is simply means that much more favorable and that 99.9999999999% of the acid is present in its ionized form. Because this exceeds the number of significant figures that we typically work with, strong acids are generally described as 100% ionized in solution. Table 8.1 lists the common strong acids that we will study in this text.

Table 8.1. Common Strong Acids

Table 8.1 Common Strong Acids

HCl	hydrochloric acid
HNO_3	nitric acid
H_2SO_4	sulfuric acid
HBr	hydrobromic acid
HI	hydroiodic acid
$HClO_4$	perchloric acid

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8.3: Conjugate Acid-Base Pairs

Acid dissociation reactions are often described in terms of the concepts of conjugate acids and their corresponding conjugate bases. The description of "acids and bases" that we will deal with in this text will be limited to simple dissociation reactions, like those shown above, where a hydronium ion is produced. This description is referred to as the **Brønsted-Lowery Acid-Base Theory**, and in the Brønsted theory, the **conjugate acid** is defined as the species that *donates* a hydrogen in the forward reaction, and the **conjugate base** is the species that *accepts* a hydrogen the reverse reaction. Thus for the ionization of HCl, HCl is the conjugate acid and Cl^- is the conjugate base.

$$\mathbf{HCl}\ \boldsymbol{(aq)} + \mathbf{H_2O} \rightleftarrows \mathbf{H_3O^+}\ \boldsymbol{(aq)} + \mathbf{Cl^-}\ \boldsymbol{(aq)}$$

In the discussion of Brønsted acid-base behavior, the hydrogen atom that is transferred is generally referred to as a **proton**, because it is transferred as a hydrogen atom without its electron. Thus for the ionization of HCl, HCl (the conjugate acid) is a *proton donor* and Cl^- (the conjugate base) is a *proton acceptor.* In General Chemistry you will learn that acid-base behavior can also be described in terms of electron donors and electron acceptors (the **Lewis Acid-Base Theory** in which an *acid* is an electron acceptor and a *base* is an electron donor), but here we will limit our discussion to simple, strong, Brønsted acids and bases.

? Exercise 8.3.1

For each of the reactions given below, identify the conjugate acid and the conjugate base. For example (d), also identify the conjugate acid and the conjugate base in the reverse reaction.

a. $HClO_4\ (aq) + H_2O \rightleftarrows H_3O^+\ (aq) + ClO_4^-\ (aq)$
b. $H_2SO_4\ (aq) + H_2O \rightleftarrows H_3O^+\ (aq) + HSO_4^-\ (aq)$
c. $HSO_4^-\ (aq) + H_2O \rightleftarrows H_3O^+\ (aq) + SO_2^{2-}\ (aq)$
d. $HNO_3\ (aq) + NH_3 \rightleftarrows NH_4^+\ (aq) + NO_3^-\ (aq)$
e. $H_2PO_4^- + H_3O^+ \rightleftarrows H_2O + H_3PO_4$
f. $NH_3(g) + H_2O \rightleftarrows NH_4^+(aq) + OH^-(aq)$
g. $H_2O(l) + HNO_2(aq) \rightleftarrows H_3O^+(aq) + NO_2^-(aq)$

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8.4: Acids-Bases Reactions: Neutralization

In Chapter 5, we examined a special case of a double replacement reaction in which an acid reacted with a base to give water and a pair of ions in solution. In the context of the Brønsted Theory, a base can be thought of as an ionic compound that produces the hydroxide anion in solution. Thus, sodium hydroxide, NaOH, ionizes to form the sodium cation and the hydroxide anion ($\mathrm{OH^-}$).

$$\mathrm{NaOH\,(aq) \longrightarrow Na^+\,(aq) + OH^-\,(aq)}$$

We have written this equation using a single arrow because sodium hydroxide is a *strong base* and is essentially 100% ionized in solution. The hydroxide anion ($\mathrm{OH^-}$) reacts with the hydronium ion ($\mathrm{H_3O^+}$) to form two moles of water, as shown in the equation given below.

$$\mathrm{H_3O^+ + OH^- \longrightarrow 2\,H_2O}$$

Thus, if you have aqueous solutions of HCl and NaOH, the following process occur:

- HCl ionizes to form the hydronium ion:

$$\mathrm{HCl\,(aq) + H_2O \longrightarrow H_3O^+\,(aq) + Cl^-\,(aq)}$$

- NaOH ionizes to form the hydroxide anion:

$$\mathrm{NaOH\,(aq) \longrightarrow Na^+\,(aq) + OH^-\,(aq)}$$

- $\mathrm{OH^-}$ reacts with $\mathrm{H_3O^+}$ to form *two* moles of water:

$$\mathrm{H_3O^+ + OH^- \longrightarrow 2\,H_2O}$$

If we add up the set of three equations, we see that hydronium and hydroxide ions appear on both sides of the arrow and cancel, leaving:

$$\mathrm{HCl\,(aq) + NaOH\,(aq) \longrightarrow H_2O + NaCl\,(aq)} \tag{8.4.1}$$

In Equation 8.4.1, we have not shown the additional water from the hydronium ion and we have grouped the sodium and chloride ions as NaCl *(aq)*, with the understanding that it will be fully ionized in aqueous solution. This is an example of a **neutralization reaction**; an *acid* and a *base* have reacted to form *water*. When we write neutralization equations we generally do not show hydronium or hydroxide ions and we generally show ionic species as distinct compounds. Neutralization equations therefore look very much like the other double replacements that we studied in Chapter 5.

? Exercise 8.4.1

For each of the following, write a balanced neutralization equation:

a. The reaction of calcium hydroxide with hydrochloric acid.
b. The reaction of sodium hydroxide with sulfuric acid (both ionizations).
c. The reaction of barium hydroxide with nitric acid.

? Exercise 8.4.2

Write a balanced neutralization equation for the reaction of calcium hydroxide with sulfuric acid

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8.5: The Meaning of Neutrality - The Autoprotolysis of Water

In the previous section, we described the reaction of an acid and a base to form water. When all of the acid and base have been consumed, we are left with water and an aqueous solution containing an ionic compound. Another way to think of this would be to say that, the acid we began with had a high concentration of hydronium cations (H_3O^+), the base had a high concentration of hydroxide anions (HO^-) and the neutral solution contains only water. This, however, is a little too simplistic. Just like water can promote the ionization of acids, water can also promote the ionization of *itself*. Picture two water molecules sharing a hydrogen bond. Just like for HF , the partially bonded hydrogen can transfer *along* the hydrogen bond to form a hydronium cation and a hydroxide anion. This process occurs very rapidly in pure water, thus, any sample of pure water will *always* contain a small concentration of hydronium and hydroxide ions. How small is "small"? Very small! In pure water at 25 ^oC, the concentration of hydronium ions ($[H_3O^+]$) and hydroxide ions ($[HO^-]$) will both be equal to exactly 1×10^{-7} M. Based on this, we can expand upon our definitions of acidic, basic and neutral solutions:

- A solution is **acidic** if $[H_3O^+] > 1 \times 10^{-7}$ M.
- A solution is **basic** if $[H_3O^+] < 1 \times 10^{-7}$ M.
- A solution is **neutral** if $[H_3O^+] = 1 \times 10^{-7}$ M.

Working with these definitions, if you have a solution with $[H_3O^+] = 4.5 \times 10^{-4}$ M, it will be *acidic* ($4.5 \times 10^{-4} > 1 \times 10^{-7}$). If you have a solution with $[H_3O^+] = 1 \times 10^{-4}$ M, it will be *basic* ($1 \times 10^{-4} < 1 \times 10^{-7}$). Finally, a *neutral* solution is one in which $[H_3O^+]$ and $[HO^-]$ are *both* 1×10^{-7} M.

Recalling our discussion of acid dissociation constants from Section 8.2, we can write the ionization equilibrium for water

$$2\,H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + OH^-\,(aq)$$

and the expression for the dissociation constant, K_a, as shown below:

$$\begin{aligned} K_a &= \frac{a_{H_3O^+} \cdot a_{OH^-}}{a^2_{H_2O}} \\ &\approx \frac{[H_3O^+][HO^-]}{(1)^2} \\ &= [H_3O^+][HO^-] \end{aligned}$$

where a is the activity of a species. Because water is the solvent, and the solution is assumed to be dilute, the activity of the water is approximated by the activity of pure water, which is defined as having a value of 1. The activity of each of the solutes is approximated by the molarity of the solute. In this reaction, one water molecule acts as an acid and one water molecule acts as a base. Thus, this reaction actually can be designated as the K_a of water and the K_b of water. It is most common, however, to designate this reaction and the associated law of mass action as the K_w of water:

$$K_w = [H_3O^+][HO^-]$$

At neutrality and 25 ^oC, $[H_3O^+]$ and $[HO^-]$ are *both* 1×10^{-7} M, therefore:

$$K_w = [1 \times 10^{-7}][1 \times 10^{-7}] = 1 \times 10^{-14}$$

This simple relationship is actually quite powerful. Because K_W is a constant, if we know *either* a hydronium ion or a hydroxide ion concentration, we can directly calculate the concentration of the other species. For example, if you are *given* that $[H_3O^+]$ is 1×10^{-4} M, $[HO^-]$ can be calculated as:

$$\begin{aligned} K_w &= [H_3O^+][HO^-] \\ &= 1 \times 10^{-14} \\ &= [1 \times 10^{-4}][HO^-] \end{aligned}$$

$$[HO^-] = \frac{1 \times 10^{-14}}{1 \times 10^{-4}} = 1 \times 10^{-10} M$$

Exercise 8.5.1: Calculating hydronium and hydroxide concentrations

A solution at 25 ^{o}C, is known to have a hydronium ion concentration of 4.5×10^{-5} M; what is the concentration of hydroxide ion in this solution?

Exercise 8.5.2: Calculating hydronium and hydroxide concentrations

A solution at 25 ^{o}C, is known to have a hydroxide ion concentration of 7.5×10^{-2} M; what is the concentration of hydronium ion in this solution?

Exercise 8.5.3: Calculating hydronium and hydroxide concentrations

A solution is known to have a hydronium ion concentration of 9.5×10^{-8} M; what is the concentration of hydroxide ion in this solution?

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8.6: pH Calculations

One thing that you should notice about the numbers in the previous examples is that they are *very small*. In general, chemists find that working with large negative exponents like these (very small numbers) is cumbersome. To simplify the process, calculations involving hydronium ion concentrations are generally done using *logarithms*. Recall that a **logarithm** is simply the exponent that some base number needs to be raised to in order to generate a given number. In these calculations, we will use a base of 10. A number such as 10,000 can be written as 10^4, so by the definition, the logarithm of 10^4 is simply 4. For a small number such as 10^{-7}, the logarithm is again simply the exponent, or -7. Before calculators became readily available, taking the logarithm of a number that was *not* an integral power of 10 meant a trip to "log tables" (or even worse, using a slide rule). Now, pushing the LOG button on an a scientific calculator makes the process trivial. For example, the logarithm of 14,283 (with the push of a button) is 4.15482. If you are paying attention, you should have noticed that the logarithm contains *six* digits, while the original number (14,283) only contains *five* significant figures. This is because a logarithm consists of two sets of numbers; the digits to the left of the decimal point (called the **characteristic**) simply reflect the integral power of 10, and are *not included* when you count significant figures. The numbers *after* the decimal (the **mantissa**) should have the same significance as your experimental number, thus a logarithm of 4.15482 actually represents *five* significant figures.

There is one other convention that chemists apply when they are dealing with logarithms of hydronium ion concentrations, that is, the logarithm is multiplied by (-1) to change its sign. Why would we do this? In most aqueous solutions, $[H_3O^+]$ will vary between 10^{-1} and 10^{-13} M, giving logarithms of –1 to –13. To make these numbers easier to work with, we take the *negative* of the logarithm ($-\log[H_3O^+]$) and call it a ***p*H** value. The use of the lower-case "*p*" reminds us that we have taken the *negative* of the logarithm, and the upper-case "H" tells us that we are referring to the *hydronium ion concentration.* Converting a hydronium ion concentration to a *p*H value is simple. Suppose you have a solution where $[H_3O^+] = 3.46 \times 10^{-4}$ M and you want to know the corresponding *p*H value. You would enter 3.46×10^{-4} into your calculator and press the LOG button. The display should read "-3.460923901". First, we multiply this by (-1) and get 3.460923901. Next, we examine the number of significant figures. Our experimental number, 3.46×10^{-4} has three significant figures, so our mantissa must have three digits. We round our answer and express our result as, *p*H = 3.461.

The reverse process is equally simple. If you are given a *p*H value of 7.04 and are asked to calculate a hydronium ion concentration, you would first multiply the *p*H value by (-1) to give –7.04. Enter this in your calculator and then press the key (or key combination) to calculate "10^x"; your display should read "9.120108×10^{-8}". There are only two digits in our original mantissa (7.**04**) so we must round this to *two* significant figures, or $[H_3O^+] = 9.1 \times 10^{-8}$.

? Exercise 8.6.1

Calculating $[H_3O^+]$ and pH Values

1. A solution is known to have a hydronium ion concentration of 4.5×10^{-5} M; what is the *p*H this solution?
2. A solution is known to have a *p*H of 9.553; what is the concentration of hydronium ion in this solution?
3. A solution is known to have a hydronium ion concentration of 9.5×10^{-8} M; what is the *p*H this solution?
4. A solution is known to have a pH of 4.57; what is the hydronium ion concentration of this solution?

There is another useful calculation that we can do by combining what we know about *p*H and expression

$$K_W = [H_3O^+][HO^-]$$

We know that $K_W = 10^{-14}$ and we know that ($-\log [H_3O^+]$) is *p*H. If we define ($-\log [HO^-]$) as *p*OH, we can take our expression for K_W and take the (-log) of both sides (remember, algebraically you can perform the same operation on both sides of an equation) we get:

$$K_W = 10^{-14} = [H_3O^+][HO^-]$$

$$-\log(10^{-14}) = (-\log[H_3O^+]) + (-\log[HO^-])$$

$$14 = pH + pOH$$

Which tells us that the values of *p*H and *p*OH must always add up to give 14! Thus, if the *p*H is 3.5, the *p*OH must be 14 – 3.5 = 11.5. This relationship is quite useful as it allows you to quickly convert between *p*H and *p*OH, and therefore between $[H_3O^+]$ and $[HO^-]$.

We can now re-address *neutrality* in terms of the *p*H scale:

- A solution is **acidic** if *p*H < 7.
- A solution is **basic** if *p*H > 7.
- A solution is **neutral** if *p*H = 7.

The simplest way to determine the *p*H of a solution is to use an electronic *p*H meter. A *p*H meter is actually a sensitive millivolt meter that measures the potential across a thin, sensitive glass electrode that is immersed in the solution. The voltage that develops is a direct function of the *p*H of the solution and the circuitry is calibrated so that the voltage is directly converted into the equivalent of a *p*H value. You will most likely use a simple *p*H meter in the laboratory. The thing to remember is that the sensing electrode has a very thin, fragile, glass membrane and is somewhat expensive to replace. Be careful!

A simple way to estimate the *p*H of a solution is by using an *indicator.* A ***p*H indicator** is a compound that undergoes a change in color at a certain *p*H value. For example, phenolphthalein is a commonly used indicator that is *colorless* at *p*H values below 9, but is *pink* at *p*H 10 and above (at very high *p*H it becomes colorless again). In the laboratory, a small amount of phenolphthalein is added to a solution at low *p*H and then a base is slowly added to achieve neutrality. When the phenolphthalein changes from colorless to pink, you know that enough base has been added to neutralize all of the acid that is present. In reality, the transition occurs at *p*H 9.2, not *p*H 7, so the resulting solution is actually slightly alkaline, but the additional hydroxide ion concentration at pH 9 (10^{-5} M) is generally insignificant relative to the concentrations of the solutions being tested.

A convenient way to estimate the *p*H of a solution is to use *p*H paper. This is simply a strip of paper that has a mixture of indicators embedded in it. The indicators are chosen so that the paper takes on a slightly different color over a range of *p*H values. The simplest *p*H paper is *litmus paper* that changes from pink to blue as a solution goes from acid to base. Other *p*H papers are more exotic. In the laboratory, you will use both indicators, like phenolphthalein, and *p*H papers in neutralization experiments called *titrations* as described in section 8.7.

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8.7: Titrations - Neutralization and Stoichiometry

One of the standard laboratory exercises in General Chemistry is an **acid-base titration**. In order to perform an acid-base titration, you must have a solution of acid or base with a known concentration. You then slowly add a known volume of this solution, using a volumetric **burette**, to an acid or base solution with an *unknown* concentration until neutrality has been achieved. At that point, you know the volume and concentration of the reactant you have added, which means that you can calculate the number of *moles* that you added. Based on the stoichiometry of your neutralization reaction, you then know how many moles of acid or base were in the unknown sample. How do you know when you have reached neutrality? Generally an indicator or a *p*H meter is used (as described in Section 8.5). For example, if we had a solution of NaOH that was exactly 0.100 M and we had a beaker containing an *unknown* concentration of HCl. To perform the titration we would add a few drops of a stock phenolphthalein solution to our HCl, and then slowly add a measured amount of the NaOH solution until all of the acid had been consumed and the indicator changed from colorless to pink.

$$\mathbf{HCl}\ \boldsymbol{(aq)} + \mathbf{NaOH}\ \boldsymbol{(aq)} \rightarrow \mathbf{NaCl}\ \boldsymbol{(aq)} + \mathbf{H_2O}$$

Working with the above example, if the volume of base that we added (as measured on the buret) was 12.6 mL, we could calculate the number of moles present in the unknown acid solution. This is equal to the known concentration of our NaOH (0.100 M) multiplied by the volume required for neutrality (0.0126 L), or:

$$(0.100 moles/L)(0.0126 L) = 1.26 \times 10^{-3} moles$$

If we had used exactly 100.0 mL of our unknown acid in our titration, the concentration of our acid would be:

$$\frac{(1.26 \times 10^{-3} moles)}{(0.1000 L)} = 1.26 \times 10^{-2} M$$

? Exercise 8.7.1

1. You are given a solution containing an unknown concentration of HCl. You carefully measure 50.0 mL of this solution into a flask and then add a few drops of phenolphthalein solution. You prepare a buret containing 0.055 M NaOH and note that the initial level of the solution in the buret is 12.6 mL. You slowly add the NaOH solution to the acid until the color change *just* occurs (as evidence of the color change becomes visible, you carefully stir the solution after each drop has been added). When the acid solution turns (and remains) pink, you note that the volume in the buret is now 28.9 mL. What is the concentration of the unknown acid solution?
2. If 25.00 mL of HCl solution with a concentration of 0.1234 M is neutralized by 23.45 mL of NaOH, what is the concentration of the base?

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8.S: Acids, Bases and pH (Summary)

- A bond that is formed from a hydrogen atom, which is part of a polar covalent bond (such as the O—H bond) to another, more electronegative atom (that has at least one unshared pair of electrons in its valence shell) is called a **hydrogen bond**. Hydrogen bonds are *weak*, partially covalent bonds. The **bond dissociation energy** of the O—H covalent bond 464 kJ/mole; the bond dissociation energy an O—H••••O hydrogen bond is about 21 kJ/mole.
- Even though hydrogen bonds are relatively weak, the *vast network* of hydrogen bonds in water makes the energy significant, and hydrogen bonding is generally used to explain the high boiling point of water (100 ˚C), relative to molecules of similar mass that *cannot* hydrogen bond. The extra energy represents the energy required to break down the hydrogen bonding network.
- Polar molecules, such as **acids**, strongly hydrogen bond to water. This hydrogen bonding not only *stabilizes* the molecular dipoles, but also *weakens* the H—**A** covalent bond (**A** represents the acid molecule). As a result of this weakening, the H—**A** bond in these acids stretches (the bond length increases) and then fully breaks. The hydrogen that was hydrogen-bonded to the water molecule now becomes *fully* bonded to the oxygen, forming the species H_3O^+ (the **hydronium ion**) and the acid now exists as an anion (A^-); this is the process of **acid dissociation**.
- The hydronium ion and the acid anion that are formed in an acid dissociation can react to re-form the original acid. This represents a set of forward- and back-reactions that occur together on a *very fast* time-scale; this type of a set of reactions is called an **equilibrium** and a double arrow is used in the chemical reaction to show this. This type of reaction is referred to as an **acid dissociation equilibrium**. **HA *(aq)* + H_2O ⇄ H_3O^+ *(aq)* + A^- *(aq)***
- For any equilibrium, an **equilibrium constant** can be written that describes whether the *products* or the *reactants* will be the predominant species in solution. For the dissociation of the simple acid, HA, the equilibrium constant, K_a, is simply given by the ratio of the concentrations of the products and the reactants, **remembering that the molarity of the solutes have been used to approximate their activity, and that solvents, such as water, have an activity of 1**. Thus for the ionization of HA;

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

- According to the **Brønsted Acid-Base Theory**, any substance that ionizes in water to form hydronium ions (a **proton donor**) is called an **acid**; any substance that *accepts* a proton from a hydronium ion is a **base**. In an acid-base equilibrium, the **conjugate acid** is defined as the species that *donates* a hydrogen (a proton) in the *forward* reaction, and the **conjugate base** is the species that *accepts* a hydrogen (a proton) the *reverse* reaction. Thus for the ionization of HCl, HCl is the conjugate acid and Cl^- is the conjugate base. HCl ***(aq)*** **+ H_2O ⇄ H_3O^+ *(aq)* + Cl^- *(aq)***
- Metal hydroxides, such as NaOH, dissolve in water to form metal cations and hydroxide anion. Hydroxide anion is a strong **Brønsted base** and, therefore, hydroxide anion accepts a proton from the hydronium ion to form *two moles of water*. The reaction of a Brønsted acid with a Brønsted base to form water is the process of **neutralization**.
- Just like water can promote the ionization of acids, water can also promote the ionization of *itself*. This equilibrium process occurs very rapidly in pure water and any sample of pure water will *always* contain a small concentration of hydronium and hydroxide ions. In pure water, at 25 ^oC, the concentration of hydronium ions ($[H_3O^+]$) and hydroxide ions ($[HO^-]$) will both be equal to exactly **1×10^{-7} M**. This is referred to as the **autoprotolysis** of water.
- The equilibrium for the autoprotolysis of water is defined as K_W, according to the equation shown below:

$$K_W = [H_3O^+][HO^-]$$

and at neutrality, $[H_3O^+]$ and $[HO^-]$ are *both* 1×10^{-7} M, making the value of K_W

$$K_W = [1 \times 10^{-7}][1 \times 10^{-7}] = 1 \times 10^{-14}$$

- Based on the autoprotolysis equilibrium, acidic, basic and neutral solutions can be defined as:
  - A solution is **acidic** if $[H_3O^+] > 1 \times 10^{-7}$ M.
  - A solution is **basic** if $[H_3O^+] < 1 \times 10^{-7}$ M.
  - A solution is **neutral** if $[H_3O^+] = 1 \times 10^{-7}$ M.
- A ***pH*** value is simply the *negative* of the logarithm of the hydronium ion concentration ($-\log[H_3O^+]$).
- Remember that a logarithm consists of two sets of numbers; the digits to the left of the decimal point (the **characteristic**) reflect the integral power of 10, and are *not included* when you count significant figures. The numbers *after* the decimal (the **mantissa**)

have the same significance as your experimental number, thus a logarithm of 4.15482 represents *five* significant figures.

- In an **acid-base titration** a solution of acid or base with a known concentration is slowly add to an acid or base solution with an *unknown* concentration, using a volumetric **burette**, to until neutrality has been achieved. Typically an indicator or a pH meter is used to signify neutrality.
- At neutrality, the *volume* and *concentration* of the reactant you have added is known, which means that you can calculate the number of *moles* that you added (remember, **concentration × volume = moles**). Based on the stoichiometry of your neutralization reaction, you then know how many moles of acid or base were in the unknown sample.

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CHAPTER OVERVIEW

9: The Gaseous State

Some of the first real breakthroughs in the study of chemistry happened in the study of the gaseous state. In gases, the volume of the actual gas particles is but a tiny fraction of the total volume that the gas occupies. This allowed early chemists to relate parameters such as volume and the number of gas particles, leading to the development of the mole concept. As we have seen in previous chapters, the notion of a chemical mole allows us to do quantitative chemistry and lead us to the point where we can routinely address reaction stoichiometry, etc. In this chapter, we will visit some of the early observations that lead to our current understand of gasses and how they behave. We will see how the relationships between pressure and volume; volume and temperature and volume and moles lead to the ideal gas laws and how these simple rules can allow us to do quantitative calculations in the gas phase.

9.1: Gasses and Atmospheric Pressure

9.5: The Ideal Gas Law

9.6: Combining Stoichiometry and the Ideal Gas Laws

9.S: The Gaseous State (Summary)

9.2: The Pressure-Volume Relationship: Boyle's Law

9.3: The Temperature-Volume Relationship: Charles's Law

9.4: The Mole-Volume Relationship - Avogadro's Law

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9.1: Gasses and Atmospheric Pressure

In Chapter 2, we learned about the three principle states of matter; solids, liquids and gasses. We explained the properties of the states of matter using the *kinetic molecular theory* (KMT). Substances in the gaseous state, according to the KMT, have enough kinetic energy to break *all* of the attractive forces between the individual gas particles and are therefore free to separate and rapidly move throughout the entire volume of their container. Because there is so much space between the particles in a gas, a gas is *highly compressible*. High compressibility and the ability of gases to take on the shape and volume of its container are two of the important physical properties of gasses.

The gas that we are all most familiar with is the mixture of elements and compounds that we call the "atmosphere". The air that we breath is mostly nitrogen and oxygen, with much smaller amounts of water vapor, carbon dioxide, noble gasses and the organic compound, methane (Table 9.1).

Table 9.1. Approximate Composition of the Atmosphere

Table 9.1 Approximate Composition of the Atmosphere

Gas	Concentration, Parts per Billion	Percentage
N_2	7.8×10^8	78%
O_2	2.0×10^8	20%
H_2O	About $10^6 – 10^7$	< 1%
Ar	9.3×10^6	< 1%
CO_2	3.5×10^5	< 0.05%
Ne	1.8×10^4	*trace*
He	5.2×10^3	*trace*
CH_4	1.6×10^3	*trace*

A gas that is enclosed in a container exerts a *pressure* on the inner walls of that container. This pressure is the result of the countless collisions of the gas particles with the container wall. As each collision occurs, a small amount of energy is transferred, generating a net pressure. Although we are generally unaware of it, the gasses in the atmosphere generate a tremendous pressure on all of us. At sea level, atmospheric pressure is equal to 14.7 pounds per square inch. Putting this in perspective, for a person of average height and build, the total pressure from the atmosphere pressing on their body is about 45,000 pounds! Why aren't we squashed? Remember, we also have air *inside* our bodies and the pressure from the inside balances the pressure outside, keeping us nice and firm, not squishy!

The proper SI unit for pressure is the Pascal (Pa), where 1 Pa = 1 kg m^{-1} s^{-2}. In chemistry, however, it is more common to measure pressure in terms of atmospheres (atm) where 1 atm is atmospheric pressure at sea level, or 1 atm = 14.7 pounds per square inch (1 atm = 101,325 Pa). Atmospheric pressure is typically measured using a device called a *barometer*. A simple mercury barometer (also called a *Torricelli barometer*, after its inventor) consists of a glass column, about 30 inches high, closed at one end and filled with mercury. The column is inverted and placed in an open, mercury-filled reservoir. The weight of the mercury in the tube causes the column to drop to the point that the mass of the mercury column matches the atmospheric pressure exerted on the mercury in the reservoir. The atmospheric pressure is then read as the *height* of the mercury column. Again, working at sea level, 1 atmosphere is *exactly* equal to a column height of 760 mm of mercury. The units for the conversion are 1 atm = 760 mm Hg, and this is an *exact* relationship with regard to significant figures. The unit *torr* (after Torricelli) is sometimes used in place of mm Hg.

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9.5: The Ideal Gas Law

The three gas laws that we covered in Section 9.2, 9.3, 9.4 and 9.5 describe the effect of pressure, temperature and the number of moles of a gas on volume. The three independent gas laws are:

- ***Boyle's law:*** $V \propto 1/P$
- ***Charles's law:*** $V \propto T$
- ***Avogadro's law:*** $V \propto n$

If volume (V) is proportion to each of these variables, it must also be proportional to their product:

$$V \propto \frac{nT}{P}$$

If we replace the proportionality symbol with a constant (let's just choose ***R*** to represent our constant), we can re-write the equation as:

$$V = R\left(\frac{nT}{P}\right)$$

or

$$PV = nRT$$

Example 9.5.1:

The value of the proportionality constant R, can be calculated from the fact that exactly one mole of a gas at exactly 1 atm and at 0 ˚C (273 K) has a volume of 22.414 L.

Solution

Substituting in the equation:

$$PV = nRT \;\; or \;\; R = \frac{PV}{nT}$$

$$R = \frac{(1\ atm)(22.414\ L)}{(1\ mole)(273\ K)} = 0.082057\ L\ atm\ mol^{-1}\ K^{-1}$$

The uncomfortable and somewhat obnoxious constant is called the **universal gas constant**, and you will need to know it (or look it up) whenever you solve problems using the combined ideal gas law.

Exercise 9.5.1

What volume will 17.5 grams of N_2 occupy at a pressure of 876 mm Hg and at 123 ˚C?

Many of the problems that you will encounter when dealing with the gas laws can be solved by simply using the "two-state" approach. Because ***R*** is a constant, we can equate an initial and a final state as:

$$R = \frac{P_1V_1}{n_1T_1} \;\; for\ the\ initial\ state$$

$$R = \frac{P_2V_2}{n_2T_2} \;\; for\ the\ final\ state$$

$$\frac{P_1V_1}{n_1T_1} = \frac{P_2V_2}{n_2T_2}$$

Using this equation, you can solve for multiple variables within a single problem.

Exercise 9.5.1

A sample of oxygen occupies 17.5 L at 0.75 atm and 298 K. The temperature is raised to 303 K and the pressure is increased to 0.987 atm. What is the final volume of the sample?

If you noticed, we calculated the value of the proportionality constant *R* based on the fact that *exactly* one mole of a gas at *exactly* 1 atm and at 0 ˚C (273 K) has a volume of 22.414 L. This is one of the "magic numbers in chemistry; *exactly* one mole of *any* gas under these conditions will occupy a volume of 22.414 L. The conditions, 1 atm and 0 ˚C, are called **standard temperature and pressure**, or **STP**. The fact that all gases occupy this same molar volume can be rationalized by realizing that 99.999% of a gas is empty space, so it really doesn't matter what's in there, it all occupies the same volume. This realization is attributed to Amedeo Avogadro and **Avogadro's hypothesis**, published in 1811, suggested that *equal volumes of all gases at the same temperature and pressure contained the same number of molecules.* This is the observation that led to the measurement of Avogadro's number (6.0221415×10^{23}), the number of *things* in a mole. The importance of the "magic number" of 22.414 L per mole (at STP) is that, when combined with the ideal gas laws, any volume of a gas can be easily converted into the number of moles of that gas.

Exercise 9.5.1

1. A sample of methane has a volume of 17.5 L at 100.0 ˚C and 1.72 atm. How many moles of methane are in the sample?
2. A 0.0500 L sample of a gas has a pressure of 745 mm Hg at 26.4˚ C. The temperatureis now raised to 404.4 K and the volume is allowed to expand until a final pressure of 1.06 atm is reached. What is the final volume of the gas?
3. When 128.9 grams of cyclopropane (C_3H_6) are placed into an 8.00 L cylinder at 298 K, the pressure is observed to be 1.24 atm. A piston in the cylinder is now adjusted so that the volume is now 12.00 L and the pressure is 0.88 atm. What is the final temperature of the gas?

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9.6: Combining Stoichiometry and the Ideal Gas Laws

With an understanding of the ideal gas laws, it is now possible to apply these principles to chemical stoichiometry problems. For example, zinc metal and hydrochloric acid (hydrogen chloride dissolved in water) react to form zinc (II) chloride and hydrogen gas according to the equation shown below:

$$2\ HCl\ (aq) + Zn\ (s) \rightarrow ZnCl_2\ (aq) + H_2\ (g)$$

Example 9.6.1:

A sample of pure zinc with a mass of 5.98 g is reacted with excess hydrochloric acid and the (dry) hydrogen gas is collected at 25.0 ˚C and 742 mm Hg. What *volume* of hydrogen gas would be produced?

Solution

This is a "single state" problem, so we can solve it using the ideal gas law, $PV = nRT$. In order to find the volume of hydrogen gas (V), we need to know the number of *moles* of hydrogen that will be produced by the reaction. Our stoichiometry is simply *one mole of hydrogen per mole of zinc*, so we need to know the number of moles of zinc that are present in 5.98 grams of zinc metal. The temperature is given in centigrade, so we need to convert into Kelvin, and we also need to convert mm Hg into atm.

Conversions:

$$25.0\ C + 273 = 298\ K$$

$$(742\ mm\ Hg) \times \left(\frac{1\ atm}{760\ mm\ Hg}\right) = 0.976\ atm$$

$$(5.98\ g\ Zn) \times \left(\frac{1.00\ mol}{65.39\ g\ Zn}\right) = 0.0915\ mol$$

Substituting:

$$PV = nRT$$

$$(0.976\ atm) \times V = (0.0915\ mol)(0.0821\ L\ atm\ mol^{-1}K^{-1})(298\ K)$$

$$V = \frac{(0.0915\ mol)(0.0821\ L\ atm\ mol^{-1}K^{-1})(298\ K)}{(0.976\ atm)} = 2.29\ L$$

We can also use the fact that one mole of a gas occupies 22.414 L at STP in order to calculate the number of moles of a gas that is produced in a reaction. For example, the organic molecule ethane (CH_3CH_3) reacts with oxygen to give carbon dioxide and water according to the equation shown below:

$$2\ CH_3CH_3\ (g) + 7\ O_2\ (g) \rightarrow 4\ CO_2\ (g) + 6\ H_2O\ (g)$$

Example 9.6.1:

An unknown mass of ethane is allowed to react with excess oxygen and the carbon dioxide produced is separated and collected. The carbon dioxide collected is found to occupy 11.23 L at STP; what mass of ethane was in the original sample?

Solution

Because the volume of carbon dioxide is measured at STP, the observed value can be converted directly into *moles of carbon dioxide* by dividing by 22.414 L mol^{-1}. Once moles of carbon dioxide are known, the stoichiometry of the problem can be used to directly give moles of ethane (molar mass 30.07 g mol^{-1}), which leads directly to the *mass* of ethane in the sample.

$$(11.23\ L\ CO_2) \times \left(\frac{1\ mol}{22.414\ L}\right) = 0.501\ mol\ CO_2$$

Reaction stoichiometry:

$$(0.501\ mol\ CO_2) \times \left(\frac{2\ mol\ CH_3CH_3}{4\ mol\ CO_2}\right) = 0.250\ mol\ CH_3CH_3$$

The ideal gas laws allow a quantitative analysis of whole spectrum of chemical reactions. When you are approaching these problems, remember to *first* decide on the *class* of the problem:

- If it is a "single state" problem (a gas is produced at a single, given, set of conditions), then you want to use *PV* = *nRT*.
- If it is a "two state" problem (a gas is changed from one set of conditions to another) you want to use

$$\frac{P_1V_1}{n_1T_1} = \frac{P_2V_2}{n_2T_2}$$

- If the volume of gas is quoted at STP, you can quickly convert this volume into moles with by dividing by 22.414 L mol^{-1}.

Once you have isolated your approach ideal gas law problems are no more complex that the stoichiometry problems we have addressed in earlier chapters.

? Exercise 9.6.1

1. An automobile air bag requires about 62 L of nitrogen gas in order to inflate. The nitrogen gas is produced by the decomposition of sodium azide, according to the equation shown below

$$\mathbf{2\ NaN_3}\ \textit{(s)} \rightarrow \mathbf{2\ Na}\ \textit{(s)} + \mathbf{3\ N_2}\ \textit{(g)}$$

What mass of sodium azide is necessary to produce the required volume of nitrogen at 25 ˚C and 1 atm?

2. When Fe_2O_3 is heated in the presence of carbon, CO_2 gas is produced, according to the equation shown below. A sample of 96.9 grams of Fe_2O_3 is heated in the presence of excess carbon and the CO_2 produced is collected and measured at 1 atm and 453 K. What volume of CO_2 will be observed?

$$\mathbf{2\ Fe_2O_3}\textit{(s)} + \mathbf{3\ C}\ \textit{(s)} \rightarrow \mathbf{4\ Fe}\ \textit{(s)} + \mathbf{3\ CO_2}\ \textit{(g)}$$

3. The reaction of zinc and hydrochloric acid generates hydrogen gas, according to the equation shown below. An unknown quantity of zinc in a sample is observed
to produce 7.50 L of hydrogen gas at a temperature of 404 K and a pressure of 1.75 atm. How many moles of zinc were in the sample?

$$\mathbf{Zn}\ \textit{(s)} + \mathbf{2\ HCl}\ \textit{(aq)} \rightarrow \mathbf{ZnCl_2}\ \textit{(aq)} + \mathbf{H_2}\ \textit{(g)}$$

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9.S: The Gaseous State (Summary)

- Gasses are *compressible* because there is so much space between individual gas particles. Energy transferred from the collision of gas particles with their container exerts a *gas pressure*. In chemistry, we typically measure gas pressure using units of *atmospheres* (atm) or in *mm Hg* (also referred to as torr). One atmosphere of pressure equals exactly 760 mm Hg.
- The volume of a gas varies *inversely* with the applied pressure; the greater the pressure, the smaller the volume. This is relationship is referred to as *Boyles's Law*. For a two-state system where the number of moles of gas and the temperature remain constant, Boyle's Law can be expressed as

$$P_1V_1 = P_2V_2$$

- The volume of a gas varies *directly* with the absolute temperature; the higher the temperature, the larger the volume. This is relationship is referred to as *Charles's Law*. For a two-state system where the number of moles of gas and the pressure remain constant, Charles's Law can be expressed as:

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

- In this equation, the *absolute temperature* in Kelvin (K) must be used. Kelvin is defined as (degrees centigrade + 273.15). Zero degrees Kelvin is referred to as "absolute zero" and it is the temperature at which (theoretically) all molecular motion would cease.
- The volume of a gas varies *directly* with the number of moles of the gas that are present; the greater the number of moles, the larger the volume. This is relationship is referred to as *Avogadro's Law*. For a two-state system where the temperature and the pressure of a gas remain constant, Avogadro's Law can be expressed as:

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

- Because the volume of a gas varies directly with the number of moles of the gas that are present and with the absolute temperature (in Kelvin), and inversely with the pressure, the gas laws can be combined into a single proportionality;

$$V \propto \left(\frac{nT}{P}\right)$$

- This proportionality can be converted to an equality by inserting the proportionality constant *R* (the universal gas constant), where *R* = 0.082057 L atm mol^{-1} K^{-1}, and can be re-written as:

$$V = R\left(\frac{nT}{P}\right) \quad or \quad PV = nRT$$

- This is referred to as the Ideal *Gas Law* and is valid for most gasses at low concentrations. For a two-state system where the identity of the gas does not change, the Ideal Gas Law can be expressed as:

$$\frac{P_1V_1}{n_1T_1} = \frac{P_2V_2}{n_2T_2}$$

- The gas constant *R*, is calculated based on the experimental observation that *exactly* one mole of any gas at *exactly* 1 atm and at 0 ˚C (273 K) has a volume of **22.414 L**. The conditions, 1 atm and 0 ˚C, are called standard temperature and pressure, or *STP*.
- The ideal gas laws allow a quantitative analysis of whole spectrum of chemical reactions involving gasses. When you are approaching these problems, remember to *first* decide on the *class* of the problem:
  - If it is a "single state" problem (a gas is produced at a single, given, set of conditions), then you want to use *PV* = *nRT*.
  - If it is a "two state" problem (a gas is changed from one set of conditions to another) you want to use

$$\frac{P_1V_1}{n_1T_1} = \frac{P_2V_2}{n_2T_2}$$

  - If the volume of gas is quoted at STP, you can quickly convert this volume into moles with by dividing by 22.414 L mol^{-1}.

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9.2: The Pressure-Volume Relationship: Boyle's Law

The kinetic molecular theory is useful when we are trying to understand the properties and behaviors of gases. The KMT (and related theories) tell us that:

- There is a tremendous amount of distance between individual particles in the gas phase.
- Gas particles move randomly at various speeds and in every possible direction.
- Attractive forces between individual gas particles are negligible.
- Collisions between gas particles are fully elastic.
- The average kinetic energy of particles in the gas phase is proportional to the temperature of the gas.

In reality, these predictions only apply to "ideal gases". An ideal gas has perfectly elastic collisions and has no interactions with its neighbors or with the container. Real gases deviate from these predictions, but at common temperatures and pressures, the deviations are generally small and in this text we will treat all gases as if they were "ideal".

Because there is so much empty space between gas molecules, it is easy to see why a gas is so compressible. If you have a container filled with a gas, you can *squeeze* it down to a smaller volume by applying pressure. The harder you squeeze (the more pressure you apply) the smaller the resulting volume will be. Imagine a bicycle pump compressing air into a tire. As pressure is applied to the pump, the same number of gas molecules are squeezed into a smaller volume.

The dependence of volume on pressure is not linear. In 1661, Robert Boyle systematically studied the compressibility of gasses in response to increasing pressure. Boyle found that the dependence of volume on pressure was *non-linear* but that a linear plot could be obtained if the volume was plotted against the *reciprocal* of the pressure, 1/*P*. This is stated as **Boyle's law**.

Boyle's law

The volume (*V*) of an ideal gas varies *inversely* with the applied pressure (*P*) when the temperature (*T*) and the number of moles (*n*) of the gas are constant.

Mathematically, Boyle's law can be stated as:

$$V \propto \frac{1}{P} \quad at\ constant\ T\ and\ n$$

$$V = constant\left(\frac{1}{P}\right) \quad or \quad PV = constant$$

We can use Boyle's law to predict what will happen to the volume of a sample of gas as we change the pressure. Because *PV* is a constant for any given sample of gas (at constant *T*), we can imagine two states; an initial state with a certain pressure and volume (P_1V_1), and a final state with different values for pressure and volume (P_2V_2). Because *PV* is always a constant, we can equate the two states and write:

$$P_1V_1 = P_2V_2$$

Example 9.2.1:

Now imagine that we have a container with a piston that we can use to compress the gas inside. You are told that, initially, the pressure in the container is 765 mm Hg and the volume is 1.00 L. The piston is then adjusted so that the volume is now 0.500 L; what is the final pressure?

Solution

We substitute into our Boyle's law equation:

$$P_1V_1 = P_2V_2$$

$$(765\ mm\ Hg)(1.00\ L) = P_2(0.500\ L)$$

$$P_2 = \left(\frac{(765\ mm\ Hg)(1.00\ L)}{(0.500\ L)}\right) = 1530\ mm\ Hg$$

Exercise 9.2.1

1. A container with a piston contains a sample of gas. Initially, the pressure in the container is exactly 1 atm, but the volume is unknown. The piston is adjusted so that the volume is 0.155 L and the pressure is 956 mm Hg; what was the initial volume?
2. The pressure of 12.5 L of a gas is 0.82 atm. If the pressure changes to 1.32 atm, what will the final volume be? A sample of helium gas has a pressure of 860.0 mm Hg. This gas is transferred to a different container having a volume of 25.0 L; in this new container, the pressure is determined to be 770.0 mm Hg. What was the initial volume of the gas?

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9.3: The Temperature-Volume Relationship: Charles's Law

A fun laboratory demonstration in which a fully inflated balloon is placed in liquid nitrogen (at a temperature of –196 ˚C) and it shrinks to about 1/1000th of its former size. If the balloon is carefully removed and allowed to warm to room temperature, it will again be fully inflated.

This is a simple demonstration of the effect of temperature on the volume of a gas. In 1787, Jacques Charles performed a systematic study of the effect of temperature on gases. Charles took samples of gases at various temperatures, but at the same pressure, and measured their volumes.

The first thing to note is that the plot is *linear*. When the pressure is constant, volume is a direct linear function of temperature. This is stated as **Charles's law.**

Charles's law

The volume (*V*) of an ideal gas varies *directly* with the temperature of the gas (*T*) when the pressure (*P*) and the number of moles (*n*) of the gas are constant.

We can express this mathematically as:

$$V \propto T \;\; at\ constant\ P\ and\ n$$

$$V = constant(T)\ or\ \frac{V}{T} = constant$$

The data for three different samples of the same gas is as follows: 0.25 moles, 0.50 moles and 0.75 moles. All of these samples behave as predicted by Charles's law (the plots are all linear), but , if you extrapolate each of the lines back to the *y*-axis (the temperature axis), all three lines intersect at the same point! This point, with a temperature of –273.15 ˚C, is the theoretical point where the samples would have "zero volume". This temperature, -273.15 ˚C, is called **absolute zero**. An even more intriguing thing is that the value of absolute zero is independent of the nature of the gas that is used. Hydrogen, oxygen, helium, argon, (or whatever), all gases show the same behavior and *all* intersect at the same point.

The temperature of this intersection point is taken as "zero" on the Kelvin temperature scale. The abbreviation used in the Kelvin scale is **K** (no degree sign) and there are *never* negative values in degrees Kelvin. The size of the degree increment in Kelvin is identical to that in Centigrade and Kelvin and centigrade scales are related by the simple conversion:

$$Kelvin = Centigrade + 273.15$$

Note

Please note that whenever you work gas law problems where temperature is one variable, you MUST use the Kelvin scale.

Just like we did for pressure-volume problems, we can use Charles's law to predict what will happen to the volume of a sample of gas as we change the temperature. Because V/T is a constant for any given sample of gas (at constant *P*), we can again imagine two states; an initial state with a certain temperature and volume (V_1/T_1), and a final state with different values for pressure and volume ([V_2/T_2). Because V/T is always a constant, we can equate the two states and write:

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

Example 9.3.1:

We have a container with a piston that we can use to adjust the pressure on the gas inside. You are told that, initially, the temperature of the gas in the container is 175 K and the volume is 1.50 L. The temperature is changed to 76 K and the piston is then adjusted so that the pressure is identical to the pressure in the initial state; what is the final volume?

Solution

We substitute into our Charles's law equation:

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

$$\frac{1.50\ L}{175\ K} = \frac{V_2}{76\ K}$$

$$V_2 = \left(\frac{(76\ K)(1.50\ L)}{175\ K}\right) = 0.65\ L$$

Exercise 9.3.1

1. A container with a piston contains a sample of gas. Initially, the pressure in the container is exactly 1 atm, the temperature is 14.0 ˚C and the volume is 997 mL.
   The temperature is raised to 100.0 ˚C and the piston is adjusted so that the pressure is again exactly 1 atm What is the final volume?
2. A 50.0 mL sample of gas at 26.4˚ C, is heated at constant pressure until its volume is 62.4 mL . What is the final temperature of the gas? A sample container of carbon monoxide occupies a volume of 435 mL at a temperature of 298 K. What would its temperature be if the pressure remained constant and the volume was changed to 265 mL? (182 K)

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9.4: The Mole-Volume Relationship - Avogadro's Law

A plot of the effect of temperature on the volume of a gas at constant pressure shows that the volume of a gas is directly proportional to the number of moles of that gas. This is stated as **Avogadro's law.**

Avogadro's law

The volume (V) of an ideal gas varies *directly* with the number of moles of the gas (n) when the pressure (P) and the number of temperature (T) are constant.

We can express this mathematically as:

$$V \propto n \;\; at \;\; constant \; P \; and \; T$$

$$V = constant \times (n) \;\; or \;\; \frac{V}{n} = constant$$

As before, we can use Avogadro's law to predict what will happen to the volume of a sample of gas as we change the number of moles. Because V/n is a constant for any given sample of gas (at constant P and T), we can again imagine two states; an initial state with a certain number of moles and volume (V_1/n_1), and a final state with values for a different number of moles and volume (V_2/n_2). Because V/n is always a constant, we can equate the two states and write:

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

Example 9.4.1

We have a container with a piston that we can use to adjust the pressure on the gas inside, and we can control the temperature. You are told that, initially, the container contains 0.20 moles of hydrogen gas and 0.10 mole of oxygen in a volume is 2.40 L. The two gases are allowed to react (a spark ignites the mixture) and the piston is then adjusted so that the pressure is identical to the pressure in the initial state and the container is cooled to the initial temperature; what is the final volume of the product of the reaction?

Solution

First, we need to look at the reaction involved. Hydrogen and oxygen react to form water. Two moles of hydrogen react with one mole of oxygen to give two moles of water, as shown below:

$$2\,\mathrm{H_2\,(g)} + \mathrm{O_2\,(g)} \longrightarrow 2\,\mathrm{H_2O\,(g)}$$

Initially we have three moles of gas and, after reaction, we have two moles. We can now substitute into Avogadro's law:

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

$$\frac{2.40\ L}{3\ moles} = \frac{V_2}{2\ moles}$$

$$V_2 = \left(\frac{(2.40\ L)(2\ moles)}{3\ moles}\right) = 1.60\ L$$

Thus we have described the dependence of the volume of a gas on the pressure (Boyle's law), the temperature (Charles's law) and the number of moles of the gas (Avogadro's law). In the following section, we will combine these to generate the Ideal Gas Law, in which all three variables (pressure, temperature and number of moles) can vary independently.

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CHAPTER OVERVIEW

10: Principles of Chemical Equilibrium

As we have studied chemical reactions in this course, we have used a “reaction arrow” to indicate the process of reactants being converted into products. The implication here is that the reaction is “irreversible”, proceeding in the direction of the arrow. Many simple reactions that we encounter in chemistry, however, are *not* irreversible, but proceed in *both* directions with products readily be converted back into reactants. When a set of reactions, such as this, proceed so that the *rate* of conversion in one direction equals the *rate* of conversion in the other, we say the reactions are in equilibrium. An equilibrium system is shown by using a set of double arrows, proceeding in opposite directions. An understanding of equilibrium is essential to an appreciation of the concepts behind acid-base behavior, solubility phenomena, etc.

10.1: The Concept of Equilibrium Reactions
10.2: The Equilibrium Constant
10.3: Calculating Equilibrium Values
10.4: Using Molarity in Equilibrium Calculations
10.5: Equilibria involving Acids and Bases
10.6: The pH of Weak Acid Solutions
10.7: Solubility Equilibria
10.8: Study Points

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10.1: The Concept of Equilibrium Reactions

Pure dinitrogen tetroxide (N_2O_4) is a colorless gas that is widely used as a rocket fuel. Although N_2O_4 is colorless, when a container is filled with pure N_2O_4, the gas rapidly begins to turn a dark brown. A chemical reaction is clearly occurring, and indeed, chemical analysis tells us that the gas in the container is no longer pure N_2O_4, but has become a mixture of dinitrogen tetroxide and nitrogen dioxide; N_2O_4 is undergoing a *decomposition reaction* to form NO_2. If the gaseous mixture is cooled, it again turns colorless and analysis tells us that it is again, almost pure N_2O_4; this means that the NO_2 in the mixture can also undergo a *synthesis reaction* to re-form N_2O_4. Initially, only N_2O_4 is present. As the reaction proceeds, the concentration of N_2O_4 decreases and the concentration of NO_2 increases. However, if you examine the figure, after some time, the concentrations of N_2O_4 and NO_2 have *stabilized* and, as long as the temperature is not changed, the relative concentrations of the two gasses remain constant.

The reversible reaction of one mole of N_2O_4, forming two moles of NO_2, is a classic example of a **chemical equilibrium**. We encountered the concept of equilibrium in Chapter 9 when we dealt with the autoprotolysis of water to form the hydronium and hydroxide ions, and with the dissociation of weak acids in aqueous solution.

$$2\,H_2O \rightleftharpoons H_3O^+ + HO^-$$

When we wrote these chemical equations, we used a **double arrow** to signify that the reaction proceeded in both directions. Using this convention, the dissociation of dinitrogen tetroxide to form two molecules of nitrogen dioxide can be shown as:

$$N_2O_4 \rightleftarrows 2\,NO_2$$

If the temperature of our gas mixture is again held constant and the total pressure of the gas in the container is varied, analysis shows that the partial pressure of N_2O_4 varies as the *square* of the partial pressure of NO_2. The Ideal Gas Laws tell us that the partial pressure of a gas, P_{gas}, is directly proportional to the *concentration* of that gas in the container). Mathematically, the relationship between the partial pressures of the two gasses can be expressed by the equation below:

$$\frac{(P_{NO_2})^2}{P_{N_2O_4}} = K$$

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10.2: The Equilibrium Constant

The constant in the equation in section 10.1 is called the **equilibrium constant** for the reaction. What the equilibrium constant for this reaction tells us is that, regardless of pressures (or concentrations), a mixture of the two gasses will undergo reaction such that the ratios of the partial pressures reach a constant value, given by the equilibrium constant, *K*. Once this constant ratio has been reached does this mean the reactions stop? Of course not. In the region of the plot where the concentrations of N_2O_4 and NO_2 are constant (the lines are level) N_2O_4 is still decomposing to form two molecules of NO_2 and two molecules of NO_2 are still reacting to synthesize a molecule of N_2O_4, but the lines are level because the **rates** of the two chemical reactions have become constant; N_2O_4 is decomposing at the same *rate* as two molecules of NO_2 are reacting to form N_2O_4.

In theory, *all* chemical reactions are equilibria. In practice, however, most reactions are so slow in the reverse direction that they are considered "irreversible". When a reaction evolves a gas, forms a precipitate or proceeds with the generation of a large amount of heat or light (for example, combustion) the reaction is essentially irreversible. Many chemical reactions are, however, readily reversible and for these reactions the mathematical expression for the equilibrium constant can be written using a simple set of rules.

1. Partial pressures (or molar concentrations) of products are written in the numerator of the expression and the partial pressures (or concentrations) of the reactants are written in the denominator.
2. If there is more that one reactant or more that one product, the partial pressures (or concentrations) are multiplied together.
3. The partial pressure (or concentration) of each reactant or product is then raised to the power that numerically equals the stoichiometric coefficient appearing with that term in the balanced chemical equation.
4. Reactants or products that are present as solids or liquids or solvents *have a defined activity of 1*. Therefore, although their activity **does** formally appear in the equilibrium expression, they do not affect the value of the equilibrium constant, and so are often not written in the expression.

Thus, for the reaction of nitrogen with hydrogen gas to form ammonia:

$$N_2\ (g) + 3\ H_2\ (g) \rightleftarrows 2\ NH_3\ (g)$$

The expression for the equilibrium constant will have the partial pressure of ammonia in the numerator, and it will be *squared*, corresponding to the coefficient "2" in the balanced equation; $(P_{NH_3})^2$. Because there are two reactants, the partial pressures for nitrogen and hydrogen will be *multiplied* in the denominator. The partial pressure of nitrogen will be raised to the "first power" (which is not shown) and the partial pressure of hydrogen will be *cubed*, corresponding to the coefficient "3"; $(P_{N_2})(P_{H_2})^3$. The final expression for the equilibrium constant is given in the equation below:

$$\frac{(P_{NH_3})^2}{PN_2(P_{H_2})^3} = K$$

? Exercise 10.2.1

For the chemical reactions shown below, write an expression for the equilibrium constant in terms of the partial pressures of the reactants and products.

1. $PCl_5\ (g) \rightleftarrows PCl_3\ (g) + Cl_2\ (g)$
2. $2\ NOCl\ (g) \rightleftarrows 2\ NO\ (g) + Cl_2\ (g)$
3. $PCl_3\ (g) + 3\ NH_3\ (g) \rightleftarrows P(NH_2)_3\ (g) + 3\ HCl\ (g)$

- ContribEEWikibooks
- Tom Neils (Grand Rapids Community College)

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10.3: Calculating Equilibrium Values

The numeric value of the equilibrium constant tells us something about the *ratio* of the reactants and products in the final equilibrium mixture. Likewise, the magnitude of the equilibrium constant tells us about the actual composition of that mixture.

In the three equilibrium systems, the first depicts a reaction in which the ratio of products to reactants is very *small*. Because the expression for the equilibrium constant is given by the pressure (or concentration) of products divided by the pressure (or concentration) of reactants, the equilibrium constant, *K*, for this system is also small. In the second example, the concentrations of reactants and products are shown to be *equal*, making the ratio (the equilibrium constant) equal to "1". In the last example, the products are shown to dominate the equilibrium mixture, making the ratio $(P_{Products})/(P_{Reactants})$ very large. In these examples, the stoichiometric ratios of the reactants and products are one and there is only one reactant and only one product; if multiple reactants or products are involved, the relationship between their concentrations would be more complex, but that ratio is always given by the expression for *K*. This fact allows us to take data for an equilibrium reaction and, if *K* is known, calculate concentrations for reactants and products. Likewise, if all of the equilibrium concentrations are known, we can use these to calculate a value for the equilibrium constant.

In these types of problems, an *ICE* table is often useful. This table has entries for *Initial* concentrations (or pressures), *Equilibrium* concentrations and any *Change* between the initial and equilibrium states. For example, consider the reaction between carbon monoxide and chlorine to form phosgene, a deadly compound that was used as a gas warfare agent in World War I.

$$\mathbf{CO}\ (g) + \mathbf{Cl_2}\ (g) \rightleftarrows \mathbf{COCl_2}\ (g)$$

Example 10.3.1:

A mixture of CO and Cl_2 has initial partial pressures of 0.60 atm for CO and 1.10 atm for Cl_2. After the mixture reaches equilibrium, the partial pressure of $COCl_2$ is 0.10 atm. Determine the value of *K*.

Solution

The initial pressures for carbon monoxide and chlorine are placed in the first row and the equilibrium pressure for phosgene is placed in the last row. ***Initially***, the pressure of phosgene was zero, so that goes in the first row; the change for phosgene is therefore "+ 0.10 atm".

Solutions to Example 10.3.1

	P_{CO}	P_{Cl_2}	P_{COCl_2}
=== Initial ===	0.60 atm	1.10 atm	0 atm
Change			

+ 0.10 atm

Equilibrium

0.10 atm

Because one mole of CO is required to make one mole of $COCl_2$ the partial pressure of CO must have dropped by 0.10 atm (the ***Change***) in order to make $COCl_2$ with a partial pressure of 0.10 atm, giving a final (***Equilibrium***) pressure of 0.50 atm for carbon monoxide. Likewise, one mole of chlorine is required to make one mole of $COCl_2$ making the ***Change*** for chlorine 0.10 atm and the ***Equilibrium*** partial pressure 1.00 atm. The completed table is shown below:

Solutions to Example 10.3.1

	P_{CO}	P_{Cl_2}	P_{COCl_2}
=== Initial ===	0.60 atm	1.10 atm	0 atm
Change	-0.10 atm	-0.10 atm	+ 0.10 atm
Equilibrium	0.50 atm	1.00 atm	0.10 atm

The equilibrium expression for the phosgene-forming reaction is given by the following equation:

$$\frac{P_{COCl_2}}{P_{CO}P_{Cl_2}} = K$$

Substituting the values from the Table into this equation:

$$\frac{P_{COCl_2}}{P_{CO}P_{Cl_2}} = \frac{(0.10)}{(0.50)(1.00)} = 0.20$$

Notice that equilibrium constants for gas phase reactions are not typically written with units, although units are sometimes used in equilibrium constants calculated from molar concentrations. Many textbooks differentiate between equilibrium constants calculated from partial pressures and molar concentrations by affixing subscripts; K_P and K_C. In this book, we will simply use K and K_C to represent the two; a value for K will always denote a constant calculated from partial pressure data.

? Exercise 10.3.1

1. For the reaction shown below, all four gasses are introduced into a vessel, each with an initial partial pressure of 0.500 atm, and allowed to come to equilibrium; at equilibrium, the partial pressure of SO_3 is found to be 0.750 atm. Determine the value of K.

$$\mathbf{SO_2}\ \boldsymbol{(g)} + \mathbf{NO_2}\ \boldsymbol{(g)} \rightleftarrows \mathbf{SO_3}\ \boldsymbol{(g)} + \mathbf{NO}\ \boldsymbol{(g)}$$

2. For the reaction shown above, the initial partial pressures of SO_3 and NO are 0.500 atm under conditions where the equilibrium constant is, K = 9.00. The equilibrium partial pressure for SO_2 is found to be 0.125 atm. Calculate the equilibrium partial pressure for SO_3.

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10.4: Using Molarity in Equilibrium Calculations

As we have pointed out several times in the preceding sections, the Ideal Gas Laws (Chapter 10) tell us that the **partial pressure** of a gas and the **molar concentration** of that gas are directly proportional. We can show this simply by beginning with the combined gas law:

$$P_{gas}V = nRT$$

If we divide both sides by the volume, *V*, and state that *V* must be expressed in liters, the right side of the equation now contains the term (n/V_{liters}). Realizing that the number of moles of gas (*n*) divided by the volume in liters is equal to *molarity*, *M*, this expression can be re-written as:

\[P_{gas}=MRT \nonumber \]

Using this expression, molar concentrations can easily be substituted for partial pressures, and *visa versa*.

? Exercise 10.4.1

1. For the reaction shown below, if the molar concentrations of SO_3, NO and SO_2 are all 0.100 *M*, what is the equilibrium concentration of NO_2?
2. For the reaction between carbon monoxide and chlorine to form phosgene, the equilibrium constant calculated from partial pressures is $K = 0.20$. How does this value relate to the equilibrium constant, K_C, under the same conditions, calculated from molar concentrations?

$$\mathbf{CO}\ (g) + \mathbf{Cl_2}\ (g) \rightleftarrows \mathbf{COCl_2}\ (g)$$

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10.5: Equilibria involving Acids and Bases

Consider a simple chemical system that is at equilibrium, such as dinitrogen tetroxide: nitrogen dioxide. The Law of Mass Action states that when this system reaches equilibrium, the ratio of the products and reactants (at a given temperature) will be defined by the equilibrium constant, *K*. Now imagine that, after equilibrium has been reached, *more* dinitrogen tetroxide is introduced into the container. In order for the ratio to remain constant (as defined by *K*) some of the N_2O_4 that you added must be converted to NO_2. The addition of reactants or products to a system at equilibrium is commonly referred to as a "stress". The response of the system to this stress is dictated by **Le Chatelier's Principle.**

Le Chatelier's Principle

Le Chatelier's Principle states that, if a "stress" is applied to a chemical reaction at equilibrium, the system will readjust in the direction that best *reduces* the stress imposed on the system. Again, *stress* refers to a change in **concentration**, a change in **pressure** or a change in **temperature**, depending on the system being examined. If pressure or temperature are changed, the numeric value *K* will change; **if only concentration changes are involved, *K* does *not* change**.

We will consider temperature and pressure effects in General Chemistry, but for now, remember; in a reaction at equilibrium, the introduction of more products will shift the mass balance towards more reactants, but the ratio of *Products/Reactants* (as defined by the equilibrium expression) does *not* change, hence, *K* is unchanged.

In Chapter 8, we learned that a "weak acid" was only partially dissociated in solution, while a "strong acid" was fully dissociated. Now that we better understand the concept of equilibrium, these two classes of Brønsted acids can simply be differentiated based on their equilibrium constants. For an acid, BH, that dissociates in water to form B^- and hydronium ion:

$$\mathrm{BH\,(aq) + H_2O\,(l) \rightleftharpoons B^-\,(aq) + H_3O^+\,(aq)}$$

we can write a simple equilibrium expression, as follows:

$$K_C = \frac{[H_3O^+][B^-]}{[BH]} ='' K_a''$$

You should note two things in this equation. Because the activity of water, as the solvent, is defined to have a value of 1, the activity for water does not affect the value of the equilibrium constant (remember, solids and liquids and solvents all have an activity of 1, and so do not affect the value of K) and the equilibrium constant for K_C is written as $\boldsymbol{K_a}$ to denote that this is an *acid dissociation equilibrium.* Now, as we learned in Chapter 8, a strong acid is "fully dissociated", which simply means that [BH] is very, very small, thus K_a for a strong acid is very, very large. A weak acid is only "partially dissociated" which means that there are significant concentrations of both BH and B^- in solution, thus K_a for a weak acid is "small". For most common weak acids, the values for K_a will be in the range of 10^{-3} to 10^{-6}.

Example 10.5.1:

Consider acetic acid (the acidic component of vinegar) where $K_a = 1.8 \times 10^{-5}$.

$$\mathrm{CH_3COOH\,(aq) + H_2O\,(l) \rightleftharpoons CH_3COO^-\,(aq) + H_3O^+\,(aq)}$$

Solution

$$K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]} = 1.8 \times 10^{-5}$$

Exercise 10.5.1

1. A series of acids have the following *K*a values: rank these in descending order from the *strongest* acid to the *weakest* acid.

   A. 6.6×10^{-4} **B**. 4.6×10^{-4} **C**. 9.1×10^{-8} **D**. 3.0×10^{2}

2. At 25.0 ^{o}C, the concentrations of H_3O^+ and OH^- in pure water are both 1.00×10^{-7} M, making $K_C = 1.00 \times 10^{-14}$ (recall that this equilibrium constant is generally referred
to as K_W). At 60.0^{o} C, K_W *increases* to 1.00×10^{-13}. What is the *p*H of a sample of pure water at 60.0^{o} C?

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10.6: The pH of Weak Acid Solutions

For a solution of a strong acid, calculating the $[H_3O^+]$ concentration is simple; because the acid is 100% dissociated, the concentration of hydronium ions is equal to the molar concentration of the strong acid (this is, of course, only true for a monoprotic acid such as HCl or HNO_3; for H_2SO_4, $[H_3O^+] = 2 \times [H_2SO_4]$, etc.). For a weak acid, however, the hydronium ion concentration will be much, much less than the molar concentration of the acid and $[H_3O^+]$ must be calculated using the value of K_a. We can approach this using an *ICE* table, like we did for previous equilibrium problems. If we prepared a solution of acetic acid that was exactly 0.50 M, then *initially* $[CH_3COOH]$ is 0.50 M and both $[CH_3COO^-]$ and $[H_3O^+]$ are zero. A small amount of CH_3COOH will ionize; let's call this *x*, making the *change* for $[CH_3COOH]$ "-*x*", increasing both $[CH_3COO^-]$ and $[H_3O^+]$ by the amount "+*x*". Finally, the *equilibrium* concentration of $[CH_3COOH]$ will be (0.50 M – *x)* and both $[CH_3COO^-]$ and $[H_3O^+]$ will be *x*. The completed table is shown below.

	$[CH_3COOH]$	**$[CH_3COO^-]$**	**$[H_3O]^+$**
=== Initial ===	0.50 M	0	0
Change	- *x*	+ *x*	+ *x*
Equilibrium	0.50 M - *x*	*x*	*x*

The expression for K_a for acetic acid is given in equation in section 10.5. Substituting for our equilibrium values:

$$K_a = 1.8 \times 10^{-5} = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]} = \frac{x^2}{0.50 - x}$$

$$x^2 + 9.0 \times 10^{-6}x - 1.8 \times 10^{-5} = 0$$

The above equation is a quadratic equation and we could solve it using the standard quadratic formula. This is not necessary, however, because acetic acid is a *weak acid* and by definition, very little of the dissociated form will exist in solution, making the quantity *x* very, very small. If *x* is much, much less than 0.50 M (our initial concentration of acetic acid), then (0.50 M – *x)* ▯ 0.50 M and the equation simplifies to:

$$K_a = 1.8 \times 10^{-5} = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]} = \frac{x^2}{0.50}$$

$$x = [H_3O^+] = \sqrt{(1.8 \times 10^{-5}) \times 0.50} = 3.0 \times 10^{-3} M$$

We can test our assumption by substituting for *x*; (0.50 – 0.0030*)* = 0.497, which rounds to 0.50 to two significant figures. Because the concentration of hydronium ion is very small for a weak acid, for most typical solutions, the concentration of hydronium ion can be estimated simply as:

$$[H_3O^+] = \sqrt{(K_a \times C_0}$$

where C_0 is the initial molar concentration of the weak acid.

? Exercise 10.6.1

1. Nitrous acid (HNO_2) is a weak acid with a K_a of 4.3×10^{-4}. Estimate the hydronium ion concentration and the *p*H for a 0.50 M solution of nitrous acid in distilled water.
2. Acetic acid is a weak acid with $K_a = 1.8 \times 10^{-5}$. For a solution of acetic acid in water, the $[H_3O^+]$ is found to be 4.2×10^{-3} M. What is the concentration of *unionized* acetic acid in this solution?

$$CH_3COOH\,(aq) + H_2O\,(l) \rightleftharpoons CH_3COO^-\,(aq) + H_3O^+\,(aq)$$

3. A solution is prepared in which acetic acid is 0.700 M and its conjugate base, acetate anion is 0.600 M. As shown above, the K_a of acetic acid is 1.8 x 10^{-5}; what will the *p*H of this solution be?

4. What concentration of the weak acid, acetic acid ($K_a = 1.8 \times 10^{-5}$) must you have in pure water in order for the final pH to be 2.38?

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10.7: Solubility Equilibria

In Chapter 5 we learned about a class of reactions that involved the formation of a solid that was "insoluble" in water, and precipitated from the solution. In these "precipitation reactions", one ionic salt was described as "insoluble", driving the reaction towards the formation of products. Silver chloride is a classic example of this. If you mix silver nitrate (almost *all* nitrate salts are "soluble" in water) with sodium chloride, a copious white precipitate of silver chloride formed and the silver nitrate was deemed "insoluble".

Nonetheless, if you took the clear solution from above the silver chloride precipitate and did a chemical analysis, there will be sodium ions, nitrate ions, and *traces* of chloride ions and silver ions. The concentrations of silver and chloride ions would be about 1.67×10^{-5} M, far below the concentrations we typically work with, hence we say that silver chloride is "insoluble in water". That, of course, is not true. Solubility is an equilibrium in which ions leave the solid surface and go into solution at the same time that ions are re-deposited on the solid surface. For silver chloride, we could write the equilibrium expression as:

$$\mathrm{AgCl\,(s) + H_2O\,(l) \rightleftharpoons Ag^+\,(aq) + Cl^-\,(aq)}$$

In order to write the expression for the equilibrium constant for this solubility reaction, we need to recall the rules stated in Section 10.2 of this chapter; Rule #4 states, "Reactants or products that are present as solids or liquids or the solvent, all have an activity value of 1, and so they do not affect the value of the equilibrium expression." Because silver chloride is a solid, and water is the solvent, the expression for the equilibrium constant is simply,

$$K_{sp} = [Ag^+][Cl^-]$$

Note that we have denoted the equilibrium constant as K_{sp}, where "sp" refers to solubility equilibrium, or "solubility product" (the product of the concentrations of the ions). We can calculate the value of K_{sp} for silver chloride from the analytical data that we cited above; an aqueous solution above solid silver chloride has a concentration of silver and chloride ions of 1.67×10^{-5} M, at 25° C. Because the concentrations of silver and chloride ions are both 1.67×10^{-5} M, the value of K_{sp} under these conditions must be:

$$K_{sp} = [Ag^+][Cl^-] = (1.67 \times 10^{-5})^2 = 2.79 \times 10^{-10}$$

This is very small, considering that K_{sp} for sodium chloride is about 29!

For a salt such as PbI_2 chemical analysis tells us that the lead concentration in a saturated solution (the maximum equilibrium solubility under a specified set of conditions, such as temperature, pressure, etc.) is about 1.30×10^{-3} M. In order to calculate K_{sp} for lead (II) iodide, you must first write the chemical equation and then the equilibrium expression for K_{sp} and then simply substitute for the ionic concentrations.

$$\mathrm{PbI_2\,(s) \rightleftharpoons Pb^{2+}\,(aq) + 2\,I^-\,(aq)}$$

As you do this, remember that there are *two* iodide ions for every lead ion, therefore the concentrations for lead (II) and iodide are 1.30×10^{-3} M and 2.60×10^{-3} M, respectively.

$$K_{sp} = [Pb^{2+}][I^-]^2 = (1.30 \times 10^{-3})(2.60 \times 10^{-3})^2 = 8.79 \times 10^{-9}$$

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10.8: Study Points

- If two opposing chemical reactions proceed simultaneously *at the same rate*, the processes are said to be in **equilibrium**. The two opposing reactions are shown linked with a double arrow (⇄). An example of opposing chemical reactions and their equilibrium expressions are:

$$\mathrm{N_2\,(g) + 3\,H_2\,(g) \longrightarrow 2\,NH_3\,(g)} \tag{10.8.1}$$

and

$$\mathrm{2\,NH_3\,(g) \longrightarrow N_2\,(g) + 3\,H_2\,(g)} \tag{10.8.2}$$

The equilibrium would be written as:

$$\mathrm{N_2\,(g) + 3\,H_2\,(g) \rightleftharpoons 2\,NH_3\,(g)} \tag{10.8.3}$$

- An equilibrium constant (*K*) is a numerical value that relates the concentrations of the **products** and **reactants** for a chemical reaction that is at equilibrium. The numeric value of an equilibrium constant is **independent of the initial concentrations of reactants**, but *is* dependent on the **temperature**. Equilibrium constants are *generally* not written with units (although they may be).
- Because equilibrium constants are written as the concentrations (or partial pressures) of **products** divided by the concentrations (or partial pressures) of **reactants**, a *large* value of *K* means that there are more products in the equilibrium mixture than there are products. Likewise, a *small* value of *K* means that, at equilibrium, there are more reactants than products.
- Equilibrium constants that are based on **partial pressures** are often written as K_P, while equilibrium constants based on **molar concentrations** are written as K_C.
- An expression for an equilibrium constant can be written from a balanced chemical equation for the reaction. **The Law of Mass Action** states the following regarding equilibrium expressions:
  - Partial pressures (or molar concentrations) of **products** are written in the **numerator** of the expression and the partial pressures (or concentrations) of the **reactants** are written in the **denominator**.
  - If there is more that one reactant or more that one product, the partial pressures (or concentrations) are *multiplied* together.
  - The partial pressure (or concentration) of each reactant or product is then **raised to the power** that numerically equals the **stoichiometric coefficient** appearing with that term in the balanced chemical equation.
  - Reactants or products that are present as **solids** or **liquids** *do not appear* in the equilibrium expression.
- As an example of an equilibrium expression, consider the reaction of nitrogen and hydrogen to form ammonia. The partial pressure of ammonia will be in the numerator, and it will be *squared*. Because there are two reactants, the partial pressures for nitrogen and hydrogen will be *multiplied* in the denominator. The partial pressure of nitrogen will be raised to the "first power" (which is not shown) and the partial pressure of hydrogen will be *cubed*.

$$\mathrm{N_2\,(g) + 3\,H_2\,(g) \rightleftharpoons 2\,NH_3\,(g)} \tag{10.8.4}$$

$$\frac{(P_{NH_3})^2}{P_{N_2}(P_{H_2})^3} = K$$

- If equilibrium values for a given reaction are known, the equilibrium constant can be calculated simply by substituting those values in the equilibrium expression. Quite often, however, initial and equilibrium values are only given for selected reactants and products. In these cases, *initial* and *equilibrium* values are arranged in an ***ICE* Table**, and the *changes* between initial and equilibrium states are calculated based on reaction stoichiometry.
- Because the **partial pressure** of a gas and the **molar concentration** of that gas are directly proportional, the ideal gas law can be rearranged as follows, to give an expression relating molarity and partial pressure of a gas.

$$P_{gas}V = nRT$$

Dividing by the volume in **liters** gives the term (n/V_{liters}) which is equivalent to *molarity*, ***M*.**

\[P_{gas}=MRT \nonumber \]

- Le Chatelier's Principle states that, if a "stress" is applied to a chemical reaction at equilibrium, the system will readjust in the direction that best reduces the stress imposed on the system. In this context, *stress* refers to a change in **concentration**, a change in **pressure** or a change in **temperature**, although only concentration is considered here. If pressure or temperature are changed, the numeric value *K* will change; **if only concentration changes are involved, *K* does *not* change**. In a reaction at equilibrium, the introduction of more products will shift the mass balance towards more reactants, and the introduction of more reactants will lead to the formation of more products, but the *ratio* of *Products/Reactants* (as defined by the equilibrium expression) does *not* change, hence, *K* is unchanged.
- For a **weak acid**, dissociating in water to form it's **conjugate base** and **hydronium** ion, the equilibrium constant is referred to as K_a. Because a weak acid is only "partially dissociated", the concentration of BH in solution is large, thus K_a for a weak acid is "small" (in the range of 10^{-3} to 10^{-6}). For example, acetic acid (the acidic component of vinegar), has an acid dissociation constant of $K_a = 1.8 \times 10^{-5}$.

$$\mathbf{CH_3COOH}\boldsymbol{(aq)} + \mathbf{H_2O}\boldsymbol{(l)} \rightleftarrows \mathbf{CH_3COO^-}\boldsymbol{(aq)} + \mathbf{H_3O^+}\boldsymbol{(aq)}$$

- For a solution of a *weak acid* in water, the concentration of hydronium ion will be *very small.* If the concentration of the weak acid is fairly large (typically > 0.01 M) the concentration of the undissociated acid will be much larger than $[H_3O^+]$. Because of this, the hydronium ion concentration (hence, the pH) can be fairly accurately estimated from the K_a of the weak acid and the initial concentration of the acid (C_o), by the equation:

$$[H_3O^+] = \sqrt{K_a \times C_0}$$

- The equilibrium constant defining the solubility of an ionic compound with low solubility is defined as K_{sp}, where “sp” refers to “solubility product”. Because reactants or products that are present as solids or liquids *do not appear* in equilibrium expressions, for silver chloride, the expression K_{sp} will be written as:

$$\mathbf{AgCl}\boldsymbol{(s)} \rightleftarrows \mathbf{Ag^+}\boldsymbol{(aq)} + \mathbf{Cl^-}\boldsymbol{(aq)}$$

$$K_{sp} = [Ag^+][Cl^-]$$

- For silver chloride, the **solubility** at 25 ^oC is 1.67×10^{-5} M. That means the concentrations of silver and chloride ions in solution are *each* 1.67×10^{-5} M, making the value of K_{sp} under these conditions:

$$K_{sp} = [Ag^+][Cl^-] = (1.67 \times 10^{-5})^2 = 2.79 \times 10^{-10}$$

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CHAPTER OVERVIEW

11: Nuclear Chemistry

In today's society, the term *radioactivity* conjures up a variety of images. Nuclear power plants producing hydrocarbon-free energy, but with potentially deadly by-products that are difficult to store safely. Bombs that use nuclear reactions to produce devastating explosions with horrible side effects on the earth as we know it and on the surviving populations that would inhabit it. Medical technology that utilizes nuclear chemistry to peer inside living things to detect disease and the power to irradiate tissues to potentially cure these diseases. Fusion reactors that hold the promise of limitless energy with few toxic side products. Radioactivity has a colorful history and clearly presents a variety of social and scientific dilemmas. In this chapter we will introduce the basic concepts of radioactivity, nuclear equations and the processes involved in nuclear fission and nuclear fusion.

11.1: Radioactivity
11.2: The Nuclear Equation
11.3: Beta Particle Emission
11.4: Positron Emission
11.5: Radioactive Half-Life
11.6: Nuclear Fission
11.7: Nuclear Fusion
11.S: Nuclear Chemistry (Summary)

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11.1: Radioactivity

The actual discovery of radioactivity is generally attributed to the French scientist, Henri Becquerel in 1896. As with most discoveries, he was working on something else. In this case it was the nature of phosphorescence; the property of some substances to “glow in the dark” after being exposed to light. In the course of his work, he allowed photographic plates to come in contact with uranium salts, only to find out that the uranium had “fogged” the unexposed plates. Further work by Becquerel and others (including Marie Curie) led to the realization that certain elements spontaneously produced a variety of particles, some of which were charged (both positive and negative) and one class that was of higher energy, but appeared to be neutral. The three basic classes of particles were characterized and identified as “alpha”, “beta”, and “gamma” particles. Alpha particles were positive, relatively massive and, subsequent work showed that they were identical to the nucleus of the helium atom, containing two protons and two neutrons. Beta particles had a very small mass. They were of higher energy and they carried a negative charge; equivalent in mass and charge to an electron. Gamma particles (actually referred to as gamma rays) were much more energetic, appeared to be neutral and were comparable to a high-energy photon of light. Although it was not apparent immediately, one of the most surprising observations regarding radioactive elements was that as they emitted particles, the identity of the element slowly changed; uranium, for example, slowly became enriched with lead.

When alpha, beta or gamma particles collides with a target, some of the energy in the particle is transferred to the target, typically resulting in the promotion of an electron to an “excited state”. In many “targets”, especially gasses, this results in *ionization*, and alpha, beta and gamma radiation is broadly referred to as **ionizing radiation**. A **Geiger counter** (or Geiger-Müller counter) takes advantage of this in order to detect these particles. In a Geiger tube, the electron produced by ionization of a captive gas travels to the anode and the change in voltage is detected by the attached circuitry. Most counters of this type are designed to emit an audible “click” in response to the change in voltage, and to also show it on a digital or analog meter.

Today, we recognize that radioactive decay is actually quite complex, but the basic principles and patterns that were established over 100 years ago still stand. The three basic subatomic particles that occur in radioactive decay are the alpha particle, the beta particle and the gamma ray. The gamma ray is of highest energy (and perhaps the greatest ultimate danger), but from a chemistry standpoint, the alpha and beta particles are of the greatest interest. An alpha particle consists of two protons and two neutrons. It has a mass of four amu and a charge of +2. It is identical with the helium nucleus, and when a radioactive element emits an alpha particle, it loses four amu from its nucleus, including two protons. Because the number of protons in a nucleus define the identity of the element, the atomic number of the element decreases by two when it loses an alpha particle; thus uranium ($^{238}_{92}\mathrm{U}$) loses an alpha particle and becomes an atom of thorium ($^{234}_{90}\mathrm{Th}$); we will discuss this process further in the following section. In order for a beta particle (an electron) to emerge from the nucleus, it must be formed by the decomposition of a neutron (on a very simple scale, think of a neutron as being composed of a positive proton bound to a negative electron). When a neutron decays and emits a beta particle, it leaves behind the newly formed proton. Again, this changes the identity of the element in question.

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11.2: The Nuclear Equation

In Chapter 1, we described the meaning of the atomic symbol for an element. In the atomic symbol, the atomic number (the number of protons in the nucleus) appears as a subscript preceding the symbol for the element. The mass number appears as a superscript, also preceding the symbol. Thus for uranium (atomic number 92) with a mass of 238, the symbol is $^{238}_{92}\mathrm{U}$. To show radioactive decay in a chemical equation, you need to use atomic symbols. Thus, for the loss of an alpha particle from $^{238}_{92}\mathrm{U}$, you need to show uranium on the "reactant" side of the equation and thorium and the alpha particle on the "product" side. Just like any other chemical equation, a nuclear equation must **balance**. The sum of the mass numbers on the reactant side must equal the sum of the mass numbers on the product side. Because we started with uranium-238 and lost four mass units in the alpha particle, the product (or products) of the decay must have a total mass of (238 – 4) = **234**. We have also removed two protons from the uranium nucleus, dropping the atomic number by two. The newly formed element is therefore thorium-234.

$$^{238}_{92}\mathrm{U} \rightarrow ^{4}_{2}\mathrm{He} + ^{234}_{90}\mathrm{Th}$$

In this equation, we have shown the alpha particle using the atomic symbol for helium ($^{4}_{2}\mathrm{He}$), but this is often shown using the symbol $^{4}_{2}\alpha$. Compounds that emit alpha particles are *very* toxic, in spite of the poor penetrating ability of the particle. This is especially true if the emitting element is inhaled or ingested. The toxic dose of the alpha-emitter $^{210}\mathrm{Po}$ in a 175-pound person has been estimated to be about one microgram (1×10^{-6} g).

? Exercise 11.2.1

Thorium-230 and **polonium-210** both undergo loss of an alpha particle to form different elements. For each of these radioactive decay processes, write the appropriate nuclear equation and show the nature of the elements that are formed.

? Exercise 11.2.2

Radium-226 and polonium-214 both undergo loss of an alpha particle to form different elements. For each of these radioactive decay processes, write the appropriate nuclear equation and show the nature of the elements that are formed.

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11.3: Beta Particle Emission

In an element with an “excess” of neutrons, one of these neutrons can break down to form an electron and a proton. In this process, an *antinutrino* is also produced, but because it has no mass, it is generally ignored in this process. The nuclear equation for the decomposition of a neutron can be written:

$$ {}^{1}_{0}\mathrm{n} \longrightarrow {}^{0}_{-1}\beta^{+}_{1} \quad {}^{1}\mathrm{p} $$

where the neutron has the symbol, ${}^{1}_{0}\mathrm{n}$, the proton has the symbol, ${}^{1}_{1}\mathrm{p}$, and the electron that is produced is called a beta particle, with the symbol ${}^{0}_{-1}\beta$. Because the nuclear equation must balance for mass and atomic numbers, the “atomic number” of the beta particle must be –1. Adding the atomic numbers on the right side of the equation shown above gives {(-1) + (+1) = 0}; identical to the “atomic number” in the neutron (${}^{1}_{0}\mathrm{n}$); (even though a neutron can break down to produce a proton, there are no actual protons in a neutron, hence its atomic number is zero). Likewise, the “mass number” of the beta particle must be zero because the proton (the product) and the neutron (the reactant) each have a mass of one. Therefore, when a nucleus loses a beta particle, the number of neutrons in the nucleus decreases by one, but the mass number does not change; the neutron is converted into a proton, also having a mass number of one. Because the neutron is converted into a proton, the atomic number of the element increases by one unit, changing the identity of the element to the next highest in the periodic table. For example, thorium-234 undergoes loss of a beta particle to form protactinium-234 by the equation shown below:

$$ {}^{234}_{90}\mathrm{Th} \rightarrow +{}^{0}_{-1}\beta + {}^{234}_{91}Pa $$

Again, with a beta-particle emission, the mass number does not change, but the atomic number *increases* by one unit.

Exercise 11.3.1: Beta-Particle Emission

Bismuth-210 and **lead-214** both undergo loss of a beta particle to form different elements. For each of these radioactive decay processes, write the appropriate nuclear equation and show the nature of the elements that are formed.

Exercise 11.3.2: Beta-Particle Emission

Chlorine-39 and strontium-90 both undergo loss of a beta particle to form different elements. For each of these radioactive decay processes, write the appropriate nuclear equation and show the nature of the elements that are formed.

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11.4: Positron Emission

A **positron**, also called an **antielectron**, is an exotic bit of matter, or more correctly, an example of **antimatter**. A positron is the antimatter equivalent of an electron. It has the mass of an electron, but it has a charge of +1. Positrons are formed when a proton sheds its positive charge and becomes a neutron, as shown below:

$$^{1}_{1}\rho \rightarrow +^{0}_{+1}\beta +^{1}_{0} n$$

Again, in the nuclear equation for positron emission, the sum of protons (atomic numbers) on the right equals the number of protons on the left and the masses all equal one. When an element emits a positron, the identity of the element changes to the one having one fewer protons on the periodic table. An example of a nuclear equation showing positron emission is shown below:

$$^{11}_{6}C \rightarrow +^{0}_{+1}\beta +^{11}_{5} B$$

Boron has one fewer protons in its nucleus than carbon, but the mass is unchanged because the proton has been replaced by a neutron.

$$^{18}_{9}F \rightarrow +^{0}_{+1}\beta +^{18}_{8} O$$

Positron emission from Fluorine-18, as shown above , has become an important medical diagnostic tool; Positron Emission Tomography (a *PET* scan). The heart of this technique is based on the fact that positrons undergo instant annihilation when they collide with an electron (an example of *matter-antimatter annihilation*). When this occurs, two high-energy gamma rays are produced and exit the scene of the annihilation in exactly opposite directions. During a PET scan, a patient is given an injection containing fluorodeoxyglucose (FDG), a sugar analog. The glucose analog is absorbed by metabolically active cells, where the FDG accumulates and undergoes positron decay. After a short waiting period, the patient is *scanned* using a circular array of gamma-radiation detectors. The fact that the gamma rays are emitted in opposite directions allows the attached computer to “draw a line” through the patient, where the line passes through the point of annihilation. Because this occurs through many directions, the exact location of the emission can be accurately calculated and then imaged as a three-dimensional picture showing the intensity of the emission.

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11.5: Radioactive Half-Life

Elements such as $^{238}_{92}U$ that emit radioactive particles do so at rates that are *constant* and *unique* for each element. The rate at which an radioactive element decays is measured by its **half-life**; the time it takes for one half of the radioactive atoms to decay, emitting a particle and forming a new element. Half-lives for elements vary widely, from billions of years to a few microseconds. On a simple, intuitive level, if you begin with 1.00 gram of a radioactive element, after one half-life there will be 0.500 grams remaining; after two half-lives, half of this has decayed, leaving 0.250 grams of the original element; after three half-lives, 0.125 grams would remain, etc. For those that prefer equations, the amount remaining after *n* half-lives can be calculated as follows:

$$R = I\left(\frac{1}{2}\right)^n$$

where ***I*** represents the initial mass of the element and ***R*** represents the mass remaining.

Example 11.5.1:

The half-life of Actinium-225 is 10.0 days. If you have a 1.00 gram sample of Actinium-225, how much is remaining after 60.0 days?

Solution

The number of half-lives is 6.00 (that is *n*) and I = 1.00 gram. Substituting:

$$R = (1.00\ gram)\left(\frac{1}{2}\right)^{6.00} = (1.00\ gram)(0.0156) = 0.0156\ gram$$

Exercise 11.5.1

The half-life of Antimony-124 is 60.20 days. If you have a 5.00 gram sample of Actinium, how much is remaining after 5.0 half-lives?

One of the interesting uses for half-life calculations involves radiocarbon dating, where the content of carbon-14 in organic (formally living matter) is used to calculate the age of a sample. The process begins in the upper atmosphere, where nitrogen is bombarded constantly by high-energy neutrons from the sun. Occasionally, one of these neutrons collides with a nitrogen nucleus and the isotope that is formed undergoes the following nuclear equation:

$$^{1}_{0}n + ^{14}_{7}N \rightarrow ^{1}_{1}\rho + ^{14}_{6}C$$

Plants take up atmospheric carbon dioxide by photosynthesis, and are ingested by animals, so every living thing is constantly exchanging carbon-14 with its environment as long as it lives. Once it dies, however, this exchange stops, and the amount of carbon-14 gradually decreases through radioactive decay with a half-life of about 5,730 years, following the nuclear equation shown below:

$$^{14}_{6}C \rightarrow ^{0}_{-1}\beta + ^{14}_{7}N$$

Thus, by measuring the carbon-14/carbon-12 ratio in a sample and comparing it to the ratio observed in living things, the number of half-lives that have passed since new carbon-14 was absorbed by the object can be calculated.

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11.6: Nuclear Fission

The process by which nitrogen is converted to carbon-14 is an example of *neutron capture*, in which particles are absorbed by the nucleus of another atom to form a new element. These types of reactions are actually quite common in nuclear chemistry. A uranium-235 nucleus captures a “slow-moving” neutron, just like nitrogen captures a neutron, leading to the formation of carbon-14. Initially, uranium-236 is formed, but this nucleus has a neutron-to-proton ratio that makes it exceptionally unstable. The unstable nucleus instantaneously breaks apart (undergoes **fission**) to form lighter elements and to release additional free neutrons. As the nucleus breaks apart, a significant amount of energy is also released. A nuclear equation showing a typical fission of uranium-235 is shown below:

$$^{235}_{92}U +^{1}_{0} n \rightarrow^{141}_{56} Ba +^{92}_{36} Kr + 3^{1}_{0}n$$

The three neutrons that are released are now speeding through the mass of uranium. If these are captured by another nucleus, the process happens again and three more neutrons are released. This represents a *chain reaction*, and in order to sustain a chain reaction like this, the mass or uranium must be large enough so that the probability of every released neutron being captured by another uranium is high. The mass of uranium (or other fissile element) that is required in order to sustain a chain reaction is called the **critical mass**.

The process of nuclear fission is best known within the context of fission bombs and as the process that operates within nuclear power plants. Designing a workable fission bomb presents many technical challenges. A mass of fissile material that exceeds the critical mass is unstable, so you must begin with a smaller, non-critical mass and somehow create one within a few microseconds. In the original design, this was accomplished by taking two non-critical pieces and forcing them together (very rapidly). This is typically referred to as a “gun assembly”, in which one piece of fissile uranium is fired at a fissile uranium target at the end of the weapon, similar to firing a bullet down a gun barrel.

Each of the uranium fragments are less than a critical mass, but when they collide, they form a mass capable of sustaining the nuclear chain reaction. The assembly stays together for a few microseconds before the energy released from the fission blows it to pieces. The trick is designing nuclear devices like this is to keep them together long enough so that enough energy is released. Neutron reflectors and “boosters” are generally used to accomplish this, nonetheless, this basic type of weapon is inefficient, although easy to design and incredibly deadly. A critical mass of uranium-235 is a sphere that is slightly less than 7 inches in diameter.

A much more efficient fission bomb is based on achieving a critical mass of fissile material, not by combining smaller fragments, but by increasing the density of a sub-critical mass to the point that the rate of neutron capture sustains the chain reaction. This design is called the “implosion” bomb and it basically consists of a sphere of fissile material surrounded by shaped explosives that must be detonated simultaneously. The resulting shock wave compresses the fissile material, allowing the chain reaction to occur. This type of design requires much less fissile material, but is technically challenging. Modern devices have neutron reflectors, “neutron initiators”, etc., and sophisticated bombs can be efficient, have a high yield and a relatively small physical size.

In a nuclear reactor designed to heat water, produce steam and electrical power, the chemistry is the same, but *control rods* are introduced between the pieces of fissile material to absorb some of the neutrons that are produced so that a critical mass is never achieved and the chain reaction can be controlled. In this set-up, as the control rods are withdrawn, the chain reaction speeds up, and as they are inserted, the reaction slows down. Even under “meltdown” conditions, where control rods fail, the critical mass of fissile material would be formed slowly. The resulting explosion would be a bad thing, but would not compare with the energy released from a well-designed fission weapon.

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11.7: Nuclear Fusion

As we saw in the preceding section, when the nuclei of heavy atoms split, energy is released. For light atoms, the opposite is true; when these nuclei combine (fuse together), energy is released. This is the process of nuclear fusion. Fusion of light elements, mostly hydrogen, is the force that powers energy release in the sun and in sun-like stars. Imagine the sun as a huge sphere of hydrogen. Because a star is so massive, the gravitation pull on the hydrogen atoms is sufficient to overcome the repulsion between the two nuclei to force them together to form an unstable $^{2}_{2}He$ nucleus. This immediately ejects a positron, leaving deuterium, $^{2}_{1}H$, and releasing a significant amount of energy. In the cascade of reactions deuterium fuses with another hydrogen to give $^{3}_{2}He$, and two of these combine to form helium, ejecting two high-energy protons in the process.

In stars that are larger and heavier than our sun, the “triple alpha process” is the dominant nuclear reaction. In this, helium nuclei fuse to eventually form carbon, releasing significant energy in the process.

One of the great challenges in physics and engineering today is to replicate fusion of this sort under controlled conditions, harvesting the energy released and converting it, indirectly, into electrical power. The extremely high temperatures and pressures that are required to initiate and sustain fusion reactions thwarted, thus far, attempts to build a fusion reactor that is “break even” in terms of the energy released relative to the energy required to produce the fusion events. Uncontrolled fusion is certainly possible, and fusion bombs exist, but these typically use an advanced fission bomb to create the temperatures and pressures necessary to promote the fusion of the lighter elements. Clearly, this approach does not work in the laboratory! Work on fusion reactors continues at a fast pace and includes novel approaches such as *aneutronic* fusion reactions that utilize proton-boron fusion to produce charged particles rather than a barrage of neutrons. The advantage here is that few neutrons are produced, reducing the need for shielding, and the charged particles formed can potentially be captured *directly* as electricity.

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11.S: Nuclear Chemistry (Summary)

- In most atoms, a nucleus containing an “excess” of neutrons (more neutrons than protons) is unstable and the nucleus will decompose by **radioactive decay**, in which particles are emitted until a stable nucleus is achieved. Common particles emitted during radioactive decay include:
  - **Alpha particles**, consist of *two protons* and *two neutrons.* This is equivalent to a *helium nucleus* and an alpha particle has a charge of **2+**. Because it is positive, it will be attracted towards a negative charge in an electric field. The atomic symbol for an alpha particle is ${}^{4}_{2}He$, or sometimes ${}^{4}_{2}\alpha$. Alpha particles are slow-moving and are easily absorbed by air or a thin sheet of paper. When an element ejects an alpha particle, the identity of the element changes to the element with an atomic number that is *two less* than the original element. The mass number of the element *decreases by four units.*
  - **Beta particles** are electrons, are considered to have negligible mass and have a *single negative charge.* They will be attracted towards a *positive* charge in an electric field. The atomic symbol for a beta particle is ${}^{0}_{-1}\beta$, or sometimes ${}^{0}_{-1}e$. Beta particles have “intermediate” energy and typically require thin sheets of metal for shielding. A beta particle is formed in the nucleus when a neutron “ejects” its negative charge (the beta particle) leaving a *proton* behind. When an element ejects a beta particle, the identity of the element changes to the *next higher atomic number*, but the mass number does not change.
  - **Gamma particles** (gamma rays) are high-energy photons. They have no mass and can be quite energetic, requiring thick shielding.
  - **Positrons** are anti-electrons, are considered to have negligible mass and have a *single positive charge.* They will be attracted towards a *negative* charge in an electric field. The atomic symbol for a positron is symbol ${}^{0}_{+1}\beta$. Positrons have “intermediate” energy and typically require thin sheets of metal for shielding. A positron is formed in the nucleus when a proton “ejects” its positive charge (the positron) leaving a *neutron* behind. When an element ejects a positron, the identity of the element changes to the *next lower atomic number*, but the mass number does not change.
- In a **nuclear equation**, elements and sub-atomic particles are shown linked by a reaction arrow. When you balance a nuclear equation, the sums of the mass numbers and the atomic numbers on each side must be the same.
- Radioactive elements decay at rates that are *constant* and *unique* for each element. The rate at which an radioactive element decays is measured by its **half-life**; the time it takes for one half of the radioactive atoms to decay, emitting a particle and forming a new element. The amount of an original element remaining after *n* half-lives can be calculated using the equation:

$$R = I\left(\frac{1}{2}\right)^{n}$$

  where ***I*** represents the initial mass of the element and ***R*** represents the mass remaining.
- In nuclear **fission**, a nucleus captures a *neutron* to form an unstable intermediate nucleus, which then splits (undergoes fission) to give nuclei corresponding to lighter elements. Typically, *neutrons* are also ejected in the process. For heavy isotopes, the process of fission also releases a significant amount of energy. A nuclear equation for a classical fission reaction is shown below:

$${}^{235}_{92}U +{}^{1}_{0} n \rightarrow{}^{141}_{56} Ba +{}^{92}_{36} Kr + 3{}^{1}_{0}n$$

- In nuclear **fusion**, nuclei *combine* to form a new element. For light isotopes, the process of fusion also releases a significant amount of energy. A nuclear equation for the fusion cascade that typically occurs in stars the size of our sun is shown below:

$$2{}^{1}_{1}\rho \rightarrow{}^{0}_{+1} \beta +{}^{3}_{2} He$$

$$2{}^{3}_{2}He \rightarrow 2{}^{1}_{1}\rho +{}^{4}_{2} He$$

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