Introductory Chemistry

CHEM. 1105

Department of Chemistry

KPU

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Chapter 1 Matters and Measurement

Chemistry is the study of matter—what it consists of, what its properties are, and how it changes. 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.

1.1 What is Matter

The definition of **Matter** is anything that has mass and volume (takes up space). Some things are easily identified as matter—the screen on which you are reading this book, for example. Others are not so obvious. Because we move so easily through air, we sometimes forget that it, too, is matter.

Even though the universe consists of "things" as wildly different as ants and galaxies, the matter that makes up all of these "things" is composed of a very limited number of building blocks. These building blocks are known as **atoms**, and so far, scientists have discovered or created a grand total of 118 different types of atoms. Scientists have given a name to each different type of atom. A substance that is composed of only one type of atom is called an element. At this point, what should amaze you is that all forms of matter in our universe are made with only 118 different building blocks. In some ways, it's sort of like cooking a gourmet, five-course meal using only three ingredients! How is it possible? To answer that question, you have to understand the ways in which different elements are put together to form matter.

The most important method that nature uses to organize atoms into matter is the formation of **molecules**. Molecules are groups of two or more atoms that have been bonded together. There are millions of different ways to bond atoms together, which means that there are millions of different possible molecules. Each of these molecules has its own set of chemical properties, and it's these properties with which chemists are most concerned. You will learn a lot more about atoms and molecules, including how they were discovered, in a later part of the textbook.

1.2 Classifying Matter According to Its State

Matter typically exists in one of three states: **solid**, **liquid**, or **gas**. The most common example is that water can take any of the three forms. At low temperatures (below 0^{o}C), it is a solid. When at "normal" temperatures (between 0^{o}C and 100^{o}C), it is a liquid. While at temperatures above 1100^{o}C, water is a gas (steam).

Figure 1.1 shows the differences among solids, liquids, and gases at the molecular level. A solid has definite volume and shape, a liquid has a definite volume but no definite shape, and a gas has neither a definite volume nor shape.

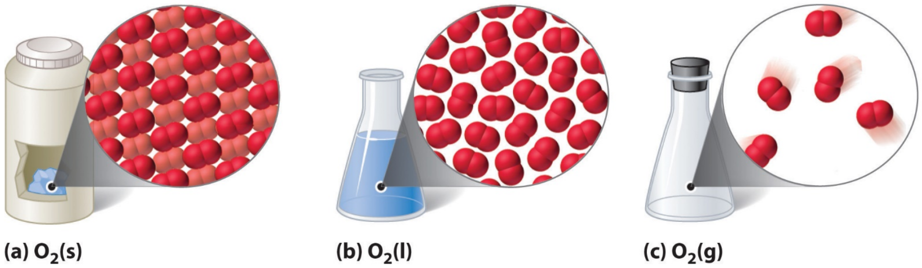


Figure 1.1 A Representation of the Solid, Liquid, and Gas States.

(a) Solid O_2 has a fixed volume and shape, and the molecules are packed tightly together. (b) Liquid O_2 conforms to the shape of its container but has a fixed volume; it contains relatively densely packed molecules. (c) Gaseous O_2 fills its container completely—regardless of the container's size or shape—and consists of widely separated molecules.

Solids

In the solid state, the individual particles of a substance are in fixed positions with respect to each other because there is not enough thermal energy to overcome the intermolecular interactions between the particles. As a result, solids have a definite shape and volume. Most solids are hard, but some (like waxes) are relatively soft. Many solids composed of ions can also be quite brittle.

Solids are defined by the following characteristics:

- Definite shape (rigid)
- Definite volume
- Particles vibrate around fixed axes

If we were to cool liquid mercury to its freezing point of −39^{o}C, and under the right pressure conditions, we would notice all of the liquid particles would go into the solid state. Mercury can be solidified when its temperature is brought to its freezing point. However, when returned to room temperature conditions, mercury does not exist in solid state for long, and returns back to its more common liquid form.

Solids usually have their constituent particles arranged in a regular, three-dimensional array of alternating positive and negative ions called a **crystal**. The effect of this regular arrangement of particles is sometimes visible macroscopically, as shown in Figure 1.2. Some solids, especially those composed of large molecules, cannot easily organize their particles in such regular crystals and exist as amorphous (literally, “without form”) solids. Glass is one example of an amorphous solid.

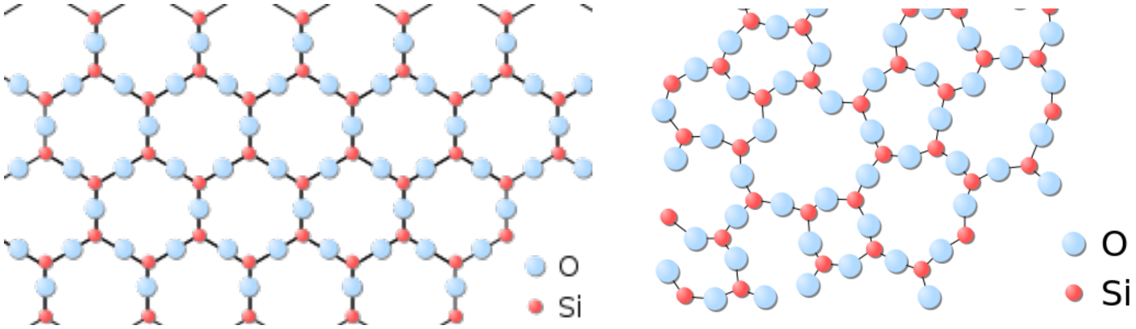


Figure 1.2 (left) The periodic crystalline lattice structure of quartz SiO_2 in two-dimensions. (right) The random network structure of glassy SiO_2 in two-dimensions. Note that, as in the crystal, each Silicon atom is bonded to 4 oxygen atoms, where the fourth oxygen atom is obscured from view in this plane. Images used with permission (public domain).

Liquids

If the particles of a substance have enough energy to partially overcome intermolecular interactions, then the particles can move about each other while remaining in contact. This describes the liquid state. In a liquid, the particles are still in close contact, so liquids have a definite volume. However, because the particles can move about each other rather freely, a liquid has no definite shape and takes a shape dictated by its container.

Liquids have the following characteristics:

- No definite shape (takes the shape of its container).
- Has definite volume.
- Particles are free to move over each other, but are still attracted to each other.

A familiar liquid is mercury metal. Mercury is an anomaly. It is the only metal we know of that is liquid at room temperature. Mercury also has an ability to stick to itself (surface tension)—a property that all liquids exhibit. Mercury has a relatively high surface tension, which makes it very unique.

If we heat liquid mercury to its boiling point of 357°C under the right pressure conditions, we would notice all particles in the liquid state go into the gas state. ***https://youtu.be/0PIZUjhzrKw***

Gases

If the particles of a substance have enough energy to completely overcome intermolecular interactions, then the particles can separate from each other and move about randomly in space. This describes the gas state, which we will consider in more detail elsewhere. Like liquids, gases have no definite shape, but unlike solids and liquids, gases have no definite volume either. The change from solid to liquid usually does not significantly change the volume of a substance. However, the change from a liquid to a gas significantly increases the volume of a substance, by a factor of 1,000 or more. Gases have the following characteristics:

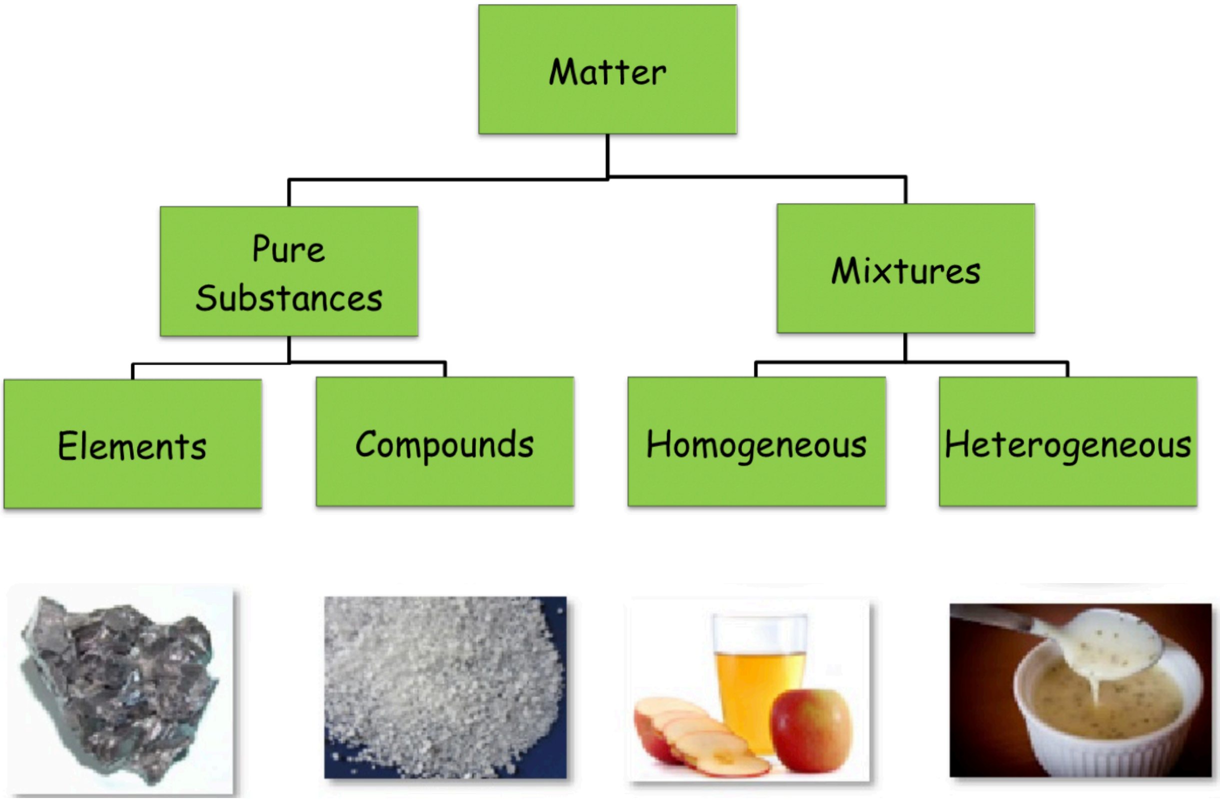
- No definite shape (takes the shape of its container)
- No definite volume
- Particles move in random motion with little or no attraction to each other
- Highly compressible

Figure 1.3 Nitrogen Dioxide Gas

1.3 Classifying Matter According to its Composition

Matter can be classified into two broad categories, pure substances and mixtures, based on the composition (Figure 1.4). A **pure substance** is a form of matter that has a constant composition (meaning that it is the same everywhere) and properties that are constant throughout the sample (meaning that there is only one set of properties such as melting point, color, boiling point, etc. throughout the matter). A material composed of two or more substances is a **mixture**.

Pure substances can be either elements or compounds. A substance that cannot be broken down into chemically simpler components is an **element**. Aluminum, which is used in soda cans, is an element. A substance that can be broken down into chemically simpler components (because it has more than one element) is a **compound**. For example, water is a compound composed of the elements hydrogen and oxygen. Today, there are about 118 elements in the known universe. In contrast, scientists have identified tens of millions of different compounds to date.



iron metal (element)

sodium chloride (compound)

apple juice (homogeneous mixture)

salad dressing (heterogeneous mixture)

Figure 1.4 Relationships between the Types of Matter based on Composition

A **mixture** is a physical blend of two or more components, each of which retains its own identity and properties in the mixture. Only the form of the salt is changed when it is dissolved into water. It retains its composition and properties.

A **homogeneous** mixture is a mixture in which the composition is uniform throughout the mixture. The salt water that is made by dissolving some salt (sodium chloride) in water is a typical example of homogeneous solution. In salt water, the dissolved salt is evenly distributed throughout the entire salt water sample. Often it is easy to confuse a homogeneous mixture with a pure substance because they are both uniform. The difference is that the composition of the pure substance is always the same, while the amount of salt in the salt water can vary from one sample to another. The chemistry term of salt water is **solution**. All solutions are considered homogeneous because the dissolved material is present in the same amount throughout the solution.

A **heterogeneous mixture** is a mixture in which the composition is not uniform throughout the mixture. Vegetable soup is a heterogeneous mixture. Any given spoonful of soup will contain varying amounts of the different vegetables and other components of the soup.

1.4 Changes in Matter — Physical and Chemical Changes

Change is happening all around us all of the time. Just as chemists have classified elements and compounds, they have also classified types of changes. Changes are classified as either **physical** or **chemical changes**.

Physical Change

Physical changes are changes that the identity of the matter does not change. This means that the same types of compounds or elements that were there at the beginning of the change are there at the end of the change. Physical changes involve moving molecules around, but not changing them. Some types of physical changes include:

- Changes of state (changes from a solid to a liquid or a gas and vice versa).
- Separation of a mixture.
- Physical deformation (cutting, denting, stretching).
- Making solutions (special kinds of mixtures).

As an ice cube (water in solid state) melts (Figure 1.5), its shape changes as it acquires the ability to flow. However, its composition, which is still water, does not change. So melting is an example of a physical change. Other changes of state include **vaporization** (liquid to gas), **freezing** (liquid to solid), and **condensation** (gas to liquid), and they are all physical changes. Similarly, if you have a piece of paper, you don't change it into something other than a piece of paper by ripping it up. What was paper before you started tearing is still paper when you are done. Again, this is an example of a physical change.

Figure 1.5 Ice melting is a physical change

When liquid water (H_2O) freezes into a solid state (ice), it appears changed; however, this change is only physical, as the composition of the constituent molecules is the same: 11.19% hydrogen and 88.81% oxygen by mass. (Public Domain; Moussa).

Chemical Change

Chemical changes are the changes that one substance with a certain set of properties (such as melting point, color, taste, etc) is turned into a different substance with different properties.

One good example of a chemical change is burning a candle. The act of burning candle actually results in the formation of new chemicals (carbon dioxide and water) from the burning of the wax. Another example of a chemical change is what occurs when natural gas is burned in your furnace. This time, it is methane, CH_4, burns with oxygen O_2 and produces carbon dioxide and water.

Figure 1.6 Burning of wax to generate water and carbon dioxide is a chemical reaction. (CC-SA-BY-3.0; Andrikkos)

There are some indications in the observations help us to identify whether a change is chemical change. Some of the evidence will involve the energy changes that occur in chemical changes, but some evidence involves the fact that new substances with different properties are formed in a chemical change.

Observations that help to indicate chemical change include:

- Temperature changes (either the temperature increases or decreases).
- Light given off.
- Unexpected color changes (a substance with a different color is made, rather than just mixing the original colors together).
- Bubbles are formed (but the substance is not boiling—you made a substance that is a gas at the temperature of the beginning materials, instead of a liquid).
- Different smell or taste (do not taste your chemistry experiments, though!).
- A solid forms if two clear liquids are mixed (look for *floaties*—technically called a precipitate).

1.5 Measurement: Numbers

Chemists measure the properties of matter and express these measurements as quantities. A quantity is an amount of something and consists of a number and a unit. The number tells us how many (or how much), and the unit tells us what the scale of measurement is. For example, when a distance is reported as “5 kilometers,” we know that the quantity has been expressed in units of kilometers and that the number of kilometers is 5. If you ask a friend how far they walk from home to school, and the friend answers “12” without specifying a unit, you do not know whether your friend walks 12 kilometers, 12 miles, 12 furlongs, or 12 yards. *Both a number and a unit must be included to express a quantity properly.*

To understand chemistry, we need a clear understanding of the units chemists work with and the rules they follow for expressing numbers. In this and next section, we will examine the rules for expressing numbers and units respectively.

Scientific Notation

Chemists often work with numbers that are exceedingly large or small. For example, entering the mass in grams of a hydrogen atom into a calculator would require a display with at least 24 decimal places. A system called **scientific notation** avoids much of the tedium and awkwardness of manipulating numbers with large or small magnitudes. In scientific notation, these numbers are expressed in the form

$$a \times 10^b$$

where **a** is greater than or equal to 1 and less than 10 ($1 \leq a < 10$), and **b** is a positive or negative integer ($10^0 = 1$). The number 10 is called the base because it is this number that is raised to the power **b**. Although a base number may have values other than 10, the base number in scientific notation is always 10.

A simple way to convert numbers to scientific notation is to move the decimal point as many places to the left ***or*** right as needed to give a number from 1 to 10 (**a**). The magnitude of **b** is then determined as follows:

- If the decimal point is moved to the left **b** places, **b** is positive.
- If the decimal point is moved to the right **b** places, **b** is negative.

Another way to remember this is to recognize that as the number **a** decreases in magnitude, the exponent increases and vice versa. The application of this rule is illustrated in examples below.

Example

Express numbers in scientific notation.

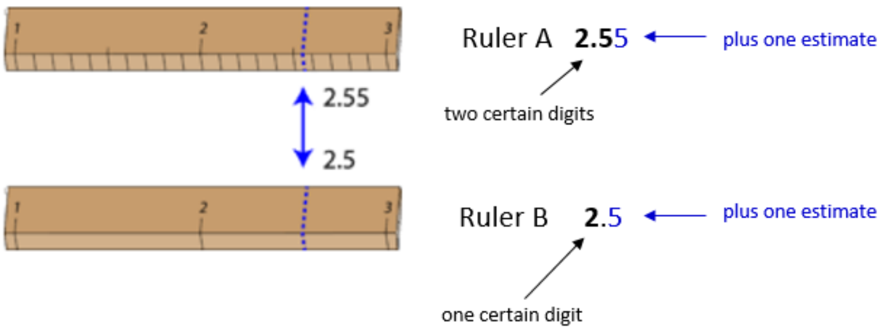
a. 637.8
b. 0.0479
c. 7.86
d. 12,378
e. 0.0003230
f. 616.06700

Solution

	Explanation	Answer
a	To convert 637.8 to a number from 1 to 10, we move the decimal point two places to the left, so 637.8 becomes 6.378 Because the decima point was moved two places to the left, b=2	6.378×10^{2}
b	To convert 0.0479 to a number from 1 to 10, we move the decimal point two places to the right, so 0.0479 becomes 4.79 Because the decima point was moved two places to the right, b = –2	4.79×10^{-2}
c	This is usually expressed simply as 7.86. However if a scientific notation is necessary, then b=0, since no movement of the decimal point needed.	7.86×10^{0}
d	Because the decima point was moved four places to the left, b = 4	1.2378×10^{4}
e	Because the decima point was moved four places to the right, b = –4. Keep all the zeros at the end for sig. fig. reasons (section 2.2)	3.230×10^{-4}
f	Because the decima point was moved two places to the left, b = 2. Keep all the zeros at the end for sig. fig. reasons (section 2.2)	6.1606700×10^{2}

Significant Figures

The **significant figures** in a measurement consist of all the certain digits in that measurement plus one uncertain or estimated digit. In the ruler illustration below, the bottom ruler gave a length with 2 significant figures, while the top ruler gave a length with 3 significant figures. In a correctly reported measurement, the final digit is significant but not certain. Insignificant digits are not reported. With either ruler, it would not be possible to report the length at 2.553cm as there is no possible way that the thousandths digit could be estimated. The 3 is not significant and would not be reported.



Measurement Uncertainty

Some error or **uncertainty** always exists in any measurement. The amount of uncertainty depends mainly upon the quality of the measuring, like the two different rulers in above diagram. While some balances are capable of measuring masses only to the nearest 0.1g, other highly sensitive balances are capable of measuring to the nearest 0.001g or even better.

Many measuring tools such as rulers, graduated cylinders or pipettes have small lines which need to be carefully read in order to make estimation of the last digit. With either ruler, it is clear that the length of the object is between 2 and 3cm. The bottom ruler contains no millimeter markings, therefore the tenths digit can be estimated and the length may be reported as 2.5cm. However, another person may judge that the measurement is 2.4cm or perhaps 2.6cm. All three measurements are reasonable since the estimation of the last digit could be different for different people.

The top ruler contains millimeters markings, so the value of the hundredths digit is uncertain and need estimation. Now the same object may be measured as 2.55cm, 2.54cm or 2.56cm depends on different people. Clearly, the top ruler is a superior ruler with higher precision.

Counting Significant Figures in a Measurement

When you look at a reported measurement, it is necessary to be able to count the number of significant figures. The table below details the rules for determining the number of significant figures in a reported measurement. For the examples in the table, assume that the quantities are correctly reported values of a measured quantity.

Rules	Examples
1. All nonzero digits are significant.	237: three sig. figs. 1.897: four sig. figs.
2. Zeros that appears between nonzero digits are ***always*** significant.	39004: five sig. figs. 5.002: four sig. figs.
3. Zeros that appear in front of the nonzero digits are calling leading zeros. Leading zeros are ***never*** significant.	0.008: one sig. figs. 0.000406: three sig. figs.
4. Zeros that appear after nonzero digits are calling trailing zeros. • Trailing zeros in a number with a decimal point are significant. (This is true whether the zeros occur before or after the decimal point) • Trailing zeros in a number without a decimal point may or may not be significant.	620.0: four sig. figs. 19.000: five sig. figs. 1100: two sig. figs. if it is not exact number 1100: unlimited sig. figs. if it is exact number
5. For scientific notation, a ×10^b, only count the significant number in the part of “a”.	6.30×10^{2}: three sig. figs. 1.0400×10^{-2}: five sig. figs.
6. Exact number has unlimited sig. figs.	

Accuracy and Precision

Measurements may be accurate, meaning that the measured value is the same as the true value; they may be precise, meaning that multiple measurements give nearly identical values (i.e., reproducible results); they may be both accurate and precise; or they may be neither accurate nor precise. The goal of scientists is to obtain measured values that are both accurate and precise. The video below demonstrates the concepts of accuracy and precision.

https://youtu.be/hRAFPdDppzs

Significant Figures in Calculations

- Multiplication and Division

For multiplication or division, the rule is ***the significant figures in the answer is the same as that in the measurement with the least number of significant figures***.

An example is as follows:

$$\underbrace{38.65}_{\text{4 sig figs}} \times \underbrace{105.93}_{\text{5 sig figs}} = \underbrace{4{,}094.1945}_{\text{reduce to 4 sig figs}}$$

The final answer, limited to four significant figures, is **4,094**. The first digit dropped is 1, so we do not round up.

The dropping brings up the topic of rounding. Although there are several conventions, in this text we will adopt the following rule: ***the final answer should be rounded up if the first dropped digit is 5 or greater, and rounded down (keep the same) if the first dropped digit is less than 5.***

Example

Write the answer for each question below.

a. 23.096×90.30
b. 127×9.000

Solution

	Explanation	Answer
a	The calculator answer is 2085.5688, the answer need to be rounded to 4 sig. figs. (limited by 90.30). The first digit to be dropped in 5, so a round up is necessary	2086
b	The calculator answer is 1143, but the answer is limited to 3 sig. figs.	1140

- Addition and Subtraction

If the calculation is an addition or a subtraction, the rule is as follows: ***the answer is limited by the measurement with least number of decimal places.*** For example, if you were to add 1.2 and 4.71, we note that the first number stops its significant figures in the tenths column, while the second number stops its significant figures in the hundredths column. We therefore limit our answer to the tenths column.

$$\begin{array}{l} 1.2 \\ \underline{4.41} \\ 5.61 \end{array}$$

↑ limit final answer to the tenths column: 5.6

We drop the last digit—the 1—because it is not significant to the final answer.

Example

Write the answer for each question below.

a. 13.77 + 908.226
b. 1027.1 + 611 + 363.06

Solution

	Explanation	Answer
a	The calculator answer is $921.9\underline{9}6$, because 13.77 has two least decimal places, that is less than the decimal places in 908.226, the answer need to be rounded to two decimal places. The first digit to be dropped in 6, so a round up is necessary.	922.00
b	The calculator answer is $200\underline{1}.16$, but the answer is limited by 611 that has zero decimal places.	2001

- Mixed Calculations

The video below demonstrates how to keep the proper sig. figs. in mixed calculation. A couple of notes:

– Do calculation by following the proper order: parentheses, exponents, multiplication and division, addition and subtraction.
– Keep extra digits in the intermediate result, and underline the last digit of the sig. figs. the intermediate result should keep as a reminder, and do the rounding off in the last step.

https://youtu.be/yBntMndXQWA

Example

a. 5 ×1.008 – 10.66
b. 99.0 + 2 × 5.56

Solution

In the middle steps of the work, the last digit of the sig. figs. is underlined as reminder.

a. 5 ×1.008 – 10.66
$= \underline{5}.04 - 10.66 = -\underline{5}.62 = -6$

b. 99.0 + 2.01 × 1.56
$= 99.\underline{0} + 3.1\underline{3}56 = 102.\underline{1}356 = 102.1$

1.6 Measurement: Units

How long is a yard? It depends on whom you ask and when you asked the question. Today we have a standard definition of the yard, which you can see marked on every football field. If you move the ball ten yards, you get a first down and it does not matter whether you are playing in Los Angeles, Dallas, or Green Bay. But at one time that yard was arbitrarily defined as the distance from the tip of the king's nose to the end of his outstretched hand. Of course, the problem there is simple: new king, new distance (and then you have to re-mark all of those football fields).

SI Base Unit

All measurements depend on the use of units that are well known and understood. The **English system** of measurement units (inches, feet, ounces, etc.) are not used in science because of the difficulty in converting from one unit to another. The **metric system** is used because all metric units are based on multiples of 10, making conversions easier. The metric system was originally established in France in 1795. **The International System of Units** is a system of measurement based on the metric system. The acronym **SI** is commonly used to refer to this system and stands for the French term, *Le Système International d'Unités*. The SI was adopted by international agreement in 1960 and is composed of seven base units in Table 1.1.

Quantity	SI Base Units	Symbol
Length	meter	m
Mass	kilogram	kg
Temperature	Kelvin	K
Time	second	s
Amount of a Substance	mole	mol
Electric Current	ampere	A
Luminous Intensity	candela	cd

Table 1.1 SI Base Units of Measurement

The first five units are frequently encountered in chemistry.

Prefix

Conversions between metric system units are straightforward because the system is based on powers of ten. For example, meters, centimeters, and millimeters are all metric units of length. There are 10 millimeters in 1 centimeter and 100 centimeters in 1 meter. **Metric prefixes** are used to distinguish between units of different size. Table 1.2 Lists the most common metric prefixes and their relationship to the central unit that has no prefix. Length is used as an example to demonstrate the relative size of each prefixed unit.

Prefix	Abbreviation	Meaning	Example
giga	G	1,000,000,000 *or* 10^9	1 Gm = 10^9 m
mega	M	1,000,000 *or* 10^6	1 Mm = 10^6 m
kilo	k	1000 *or* 10^3	1 km = 1000 m
hecto	h	100 *or* 10^2	1 hm = 100 m
deka	da	10	1 dam = 10 m
		1	1 m
deci	d	0.1	1 dm = 0.1 m
centi	c	0.01 *or* 10^{-2}	1 cm = 0.01 m
milli	m	0.001 *or* 10^{-3}	1 mm = 0.001 m
micro	μ	0.000001 *or* 10^{-6}	1 μm = 10^{-6} m
nano	n	0.000000001 *or* 10^{-9}	1 nm = 10^{-9} m
pico	p	0.000000000001 *or* 10^{-12}	1pm = 10^{-12} m

Table 1.2 SI Prefixes

Combined or Derived Units

All other measurement quantities, such as volume, speed and energy etc., can be derived from these seven base units in Table 1.1.

Speed: The unit of speed could include m/s, km/h, mile/h etc.

Area: Area is the measurement of the size of the surface. Several examples for the unit of area include: m^2, cm^2, km^2, ft^2.

Volume:

Volume is the measure of the amount of space occupied by an object. The standard volume is a cubic meter (m^3), a cube with an edge length of exactly one meter (Figure 1.7). To dispense a cubic meter of water, for example, we could build a cubic box with edge lengths of exactly one meter.

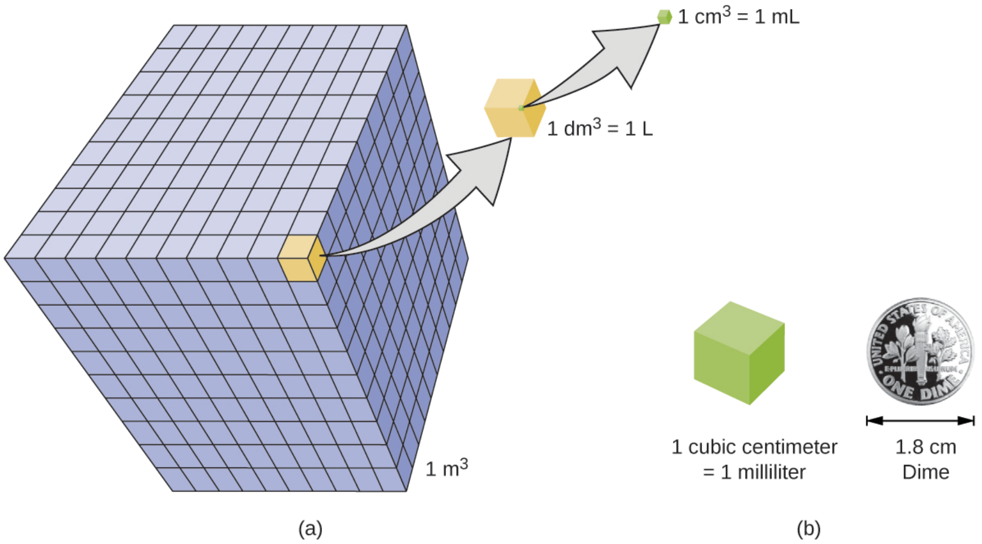


Figure 1.7 (a) The relative volumes are shown for cubes of 1 m^3, 1 dm^3 (1 L), and 1 cm^3 (1 mL) (not to scale). (b) The diameter of a dime is compared relative to the edge length of a 1-cm^3 (1-mL) cube.

A more commonly used unit of volume is derived from the decimeter (0.1 m, or 10 cm). A cube with edge lengths of exactly one decimeter contains a volume of one cubic decimeter (dm^3). A liter (L) is the more common name for the cubic decimeter. A cubic centimeter (cm^3) is the volume of a cube with an edge length of exactly one centimeter.

$$1L = 1\ dm^3 = 1000\ mL = 10^{-3}\ m^3\ ; \quad 1\ mL = 1\ cm^3$$

Example

What is the volume of a cube (cm^3) with an edge length of 0.843 cm?

Solution

V = 0.843 cm × 0.843 cm × 0.843 cm = 0.599 cm^3

Unit Conversions/Dimensional Analysis

In the studies of Chemistry, it is very common that you will need to convert the measurement in one unit to the other unit. Unit conversion, that can also be called dimensional analysis, is the conversion between an amount in one unit to the corresponding amount in a desired unit using various *conversion factors*. Dimensional analysis is amongst the most valuable tools that physical scientists use.

The dimensional analysis (or unit conversion) by using conversion factor can be generally shown as:

$$\text{quantity (in old unit)} \times \text{conversion factor} = \text{quantity (in new units)}$$

Conversion factor is always a fraction that comes from an equivalent statement between old unit and new unit.

Here is a simple example to illustrate this process.

Example

How many cm are there in 3.55 m?

Solution

In this example, m is the old unit and cm is the new unit. We also know the relationship is that 1 m = 100 cm, which can be re-written as two conversion factors:

$$\frac{1\ m}{100\ cm} \text{ or } \frac{1\ 00\ cm}{1\ m}$$

To solving this question, the given quantity 3.55 m should multiple the second conversion factor because then the old unit m, occurs in both the numerator *and* the denominator of our expression, they **cancel out**.

$$3.55\,\cancel{m} \times \frac{100\ \ cm}{1\,\cancel{m}} = 355\ cm$$

Notes for applying conversional factor:

- Conversion factor have to be in fraction format.
- The value of the conversional factor fraction is always 1.
- One equivalent statement leads to two conversion factors. To solve the certain question, choose the proper conversion factor that helps to cancel the old unit.

It seems you can still can solve this simple example without using conversion factor, however, conversion problems you encounter later *will not always be so simple*. The dimensional analysis using conversion factor will have proved to be a powerful tool for more advanced questions.

Solving Multiple-step Conversion Problems

Sometimes you will have to perform more than one conversions to obtain the desired unit. We will set up a series of conversion factors so that each conversion factor produces the next unit in the sequence.

Example
Convert 54.7 km into cm.

Solution

We first convert the given amount in km to the base unit m, then convert from m to mm. Both conversions can be incorporated into one calculation. Also, we also need to apply prefix knowledge that: 1 km = 1000m; 1 cm = 10^{-2} m

$$54.7\ \cancel{km} \times \frac{1000\ \cancel{m}}{1\ \cancel{km}} \times \frac{1\ cm}{10^{-2}\ \cancel{m}} = 5.47 \times 10^{6}\ cm$$

Unit Conversion for Derived or Combined Units

To do unit conversion for unit of area and volume, please keep in mind that the unit is raised to a power of 10, so the conversion factor must be raised to the same power of 10 as well.

Example

Convert 156 cm^3 into $inch^3$, given 1 inch = 2.54 cm.

Solution

$$156\ cm^3 \times \left(\frac{1\ inch}{2.54\ cm}\right)^3 = 156\ \cancel{cm^3} \times \left(\frac{1\ inch}{2.54\ \cancel{cm}}\right) \times \left(\frac{1\ inch}{2.54\ \cancel{cm}}\right) \times \left(\frac{1\ inch}{2.54\ \cancel{cm}}\right) = 9.52\ inch^3$$

For combined unit with expression as a fraction, for example, m/s (the unit of speed), the unit conversion can be carried out by introducing proper conversion factor for top and bottom part of the fraction subsequently.

Example

Convert 100. mile/h into m/s, given 1 mile = 1.6093 km

Solution

In this conversion, we need to convert mile to km, km to m, h to min and min to second. The conversion factors can be included one-by-one in the whole calculation:

$$\frac{100.\ \cancel{mile}}{\cancel{h}} \times \left(\frac{1.6093\ \cancel{km}}{1\ \cancel{mile}}\right) \times \left(\frac{1000\ m}{1\ \cancel{km}}\right) \times \left(\frac{1\cancel{h}}{60\ \cancel{min}}\right) \times \left(\frac{1\ \cancel{min}}{60\ s}\right) = \frac{44.7\ m}{s}$$

1.7 Density

Density (d) is a physical property found by dividing the mass of an object by its volume. Therefore the d has a combined unit of mass/volume. Regardless of the sample size, density is always constant. For example, the density of a pure sample of tungsten is always 19.25 g/cm^3. This means that whether you have one gram or one kilogram of the sample, the density will never vary. The equation, as we already know, is as follows:

$$\text{density} = \frac{mass}{volume} \qquad \text{or} \qquad d = \frac{m}{V}$$

Based on this equation, it's clear that density can, and does, vary from element to element and substance to substance due to differences in the relationship of mass and volume. Pure water, for example, has a density of 0.998 g/cm^3 at 25°C. The average densities of some common substances are in Table 1.3. Notice that corn oil has a lower mass to volume ratio than water. This means that when added to water, corn oil will “float.”

Substance	Density at 25 °C (g/cm^3)
blood	1.035
Body fat	0.918
Whole milk	1.030
Corn oil	0.922
mayonnaise	0.910
honey	1.420

Table 1.3 Density for Common Substances

Density can be measured for all substances—solids, liquids and gases. For solids and liquids, density is often reported using the units of g/cm^3. Densities of gases, which are significantly lower than the densities of solids and liquids, are often given using units of g/L.

Example

Calculate the density of a 30.2mL sample of ethanol with a mass of 23.71002g.

Solution

$$d = \frac{m}{V} = \frac{23.71002\ g}{30.2\ mL} = 0.785\,\frac{g}{mL}$$

Chapter 2 Atoms and Elements

All matter in the universe is made out of tiny building blocks called atoms. All modern scientists accept the concept of the atom, but when the concept of the atom was first proposed about 2,500 years ago, ancient philosophers laughed at the idea. It has always been difficult to convince people of the existence of things that are too small to see. We will spend some time considering the evidence (observations) that convince scientists of the existence of atoms.

2.1 Brief history for the development of Atomic Theory

Democritus and the Greek Philosophers

About 2,500 years ago, early Greek philosophers believed the entire universe was a single, huge, entity. They believed that all objects, all matter, and all substances were connected as a single, big, unchangeable "thing." One of the first people to propose "atoms" was a man known as Democritus. As an alternative to the beliefs of the Greek philosophers, he suggested that **atomos**, or atomon—tiny, indivisible, solid objects—make up all matter in the universe.

Democritus then reasoned that changes occur when the many atomos in an object were reconnected or recombined in different ways. Democritus even extended this theory, suggesting that there were different varieties of atomos with different shapes, sizes, and masses. He thought, however, that shape, size, and mass were the only properties differentiating the different types of atomos. According to Democritus, other characteristics, like color and taste, did not reflect properties of the atomos themselves, but rather, resulted from the different ways in which the atomos were combined and connected to one another.

The early Greek philosophers tried to understand the nature of the world through reason and logic, but not through experiment and observation. As a result, they had some very interesting ideas, but they felt no need to justify their ideas based on life experiences. In a lot of ways, you can think of the Greek philosophers as being "all thought and no action."

Greek philosophers dismissed Democritus' theory entirely. Sadly, it took over two millennia before the theory of atomos (or "atoms," as they are known today) was fully appreciated.

While it must be assumed that many more scientists, philosophers, and others studied composition of matter after Democritus, a major leap forward in our understanding of the composition of matter took place in the 1800's with the work of the British scientists John Dalton. He started teaching school at age twelve, and was primarily known as a teacher. In his twenties, he moved to the growing city of Manchester, where he was able to pursue some scientific studies. His work in several areas of science brought him a number of honors. When he died, over 40,000 people in Manchester marched at his funeral.

Figure 2.1 (left) Democritus by Hendrick ter Brugghen, 1628. Democritus was known as the "laughing philosopher." It was a good thing he liked to laugh, because most other philosophers were laughing at his theories. (right) British physicist and chemist John Dalton (1766-1844). Unlike the Greek philosophers, John Dalton believed in both logical thinking and experimentation.

The modern atomic theory, proposed about 1803 by the English chemist John Dalton, is a fundamental concept that states that all elements are composed of **atoms**. Dalton studied the weights of various elements and compounds. He noticed that matter always combined in fixed ratios based on weight, or volume in the case of gases. Chemical compounds always contain the same proportion of elements by mass, regardless of amount, which provided further support for Proust's law of definite proportions. Dalton also observed that there could be more than one combination of two elements.

The general tenets of Dalton's **atomic theory** were as follows:

- All matter is composed of extremely small particles called atoms.
- Atoms of a given element are identical in size, mass, and other properties. Atoms of different elements differ in size, mass, and other properties.
- Atoms cannot be subdivided, created, or destroyed.
- Atoms of different elements can combine in simple whole number ratios to form chemical compounds.
- In chemical reactions, atoms are combined, separated, or rearranged.

Dalton's atomic theory has been largely accepted by the scientific community, with the exception of three changes. We know now that (1) an atom can be further subdivided, (2) all atoms of an element are not identical in mass, and (3) using nuclear fission and fusion techniques, we can create or destroy atoms by changing them into other atoms.

Electrons and Plums

Dalton's Atomic Theory held up well to a lot of the different chemical experiments that scientists performed to test it. In fact, for almost 100 years, it seemed as if Dalton's Atomic Theory was the whole truth. However, in 1897, a scientist named J. J. Thomson conducted some research that suggested the small, negatively charged particles making up the cathode ray were actually pieces of atoms. He called these pieces "corpuscles," although today we know them as **electrons**. Thanks to his clever experiments and careful reasoning, J. J. Thomson is credited with the discovery of the electron and receive many honors during his lifetime, including being awarded the Nobel Prize in Physics in 1906 and a knighthood in 1908.

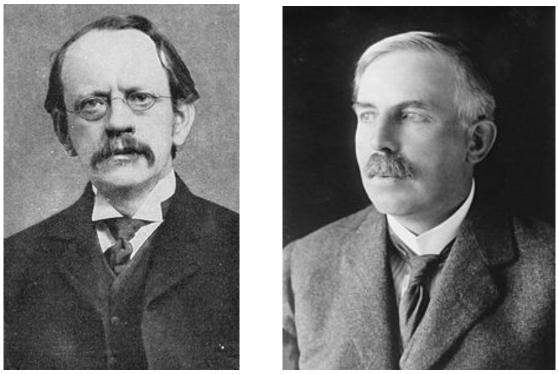


Figure 2.2 (left) J.J. Thomson concluded experiments that suggested that Dalton's (left) atomic theory was not telling the entire story. Ernest Rutherford (right) later built on Thomson's work to argue for the model nuclear atom.

When electron was discovered by J.J. Thomson in 1897, the existence of protons was also known, as was the fact that atoms were neutral in charge. Since the intact atom had no net charge and the electron and proton had opposite charges, the next step after the discovery of these subatomic particles was to figure out how these particles were arranged in the atom. This was a difficult task because of the incredibly small size of the atom. Therefore, scientists set out to design a model of what they believed the atom could look like. The goal of each **atomic model** was to accurately represent all of the experimental evidence about atoms in the simplest way possible.

Following the discovery of the electron, J.J. Thomson developed what became known as the "**plum pudding**" model in 1904. In such model, the electrons were embedded in a uniform sphere of positive charge like plum stuck into pudding. The positive matter was thought to be jelly-like or similar to a thick soup. The electrons were somewhat mobile. As they got closer to the outer portion of the atom, the positive charge in the region was greater than the neighboring negative charges, and the electron would be pulled back more toward the center region of the atom.

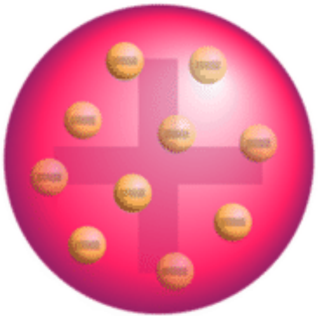


Figure 2.3 The "plum pudding" model of atom

However, this model of the atom soon gave way to a new model developed by New Zealander Ernest Rutherford (1871-1937) about five years later.

Atoms and Gold

In 1911, Rutherford and coworkers initiated a series of ground-breaking experiments that would completely change the accepted model of the atom. They bombarded very thin sheets of gold foil with fast moving **alpha particles**. Alpha particles, a type of natural radioactive particle, are positively charged particles with a mass about four times that of a hydrogen atom.

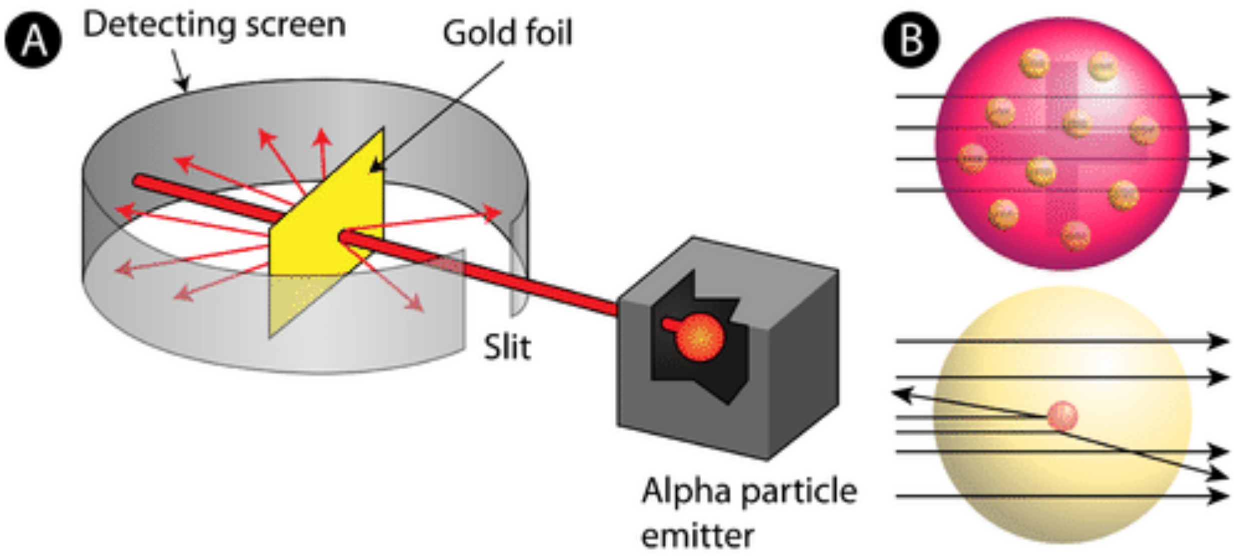


Figure 2.4 (A) The experimental setup for Rutherford's gold foil experiment: A radioactive element that emitted alpha particles was directed toward a thin sheet of gold foil that was surrounded by a screen which would allow detection of the deflected particles. (B) According to the plum pudding model (top), all of the alpha particles should have passed through the gold foil with little or no deflection. Rutherford found that a small percentage of alpha particles were deflected at large angles, which could be explained by an atom with a very small, dense, positively-charged nucleus at its center (bottom).

According to the plum pudding atomic model, in which an atom's mass and charge are uniformly distributed throughout the atom, the scientists expected that all of the alpha particles would pass through the gold foil with only a slight deflection or none at all. Surprisingly, while most of the alpha particles were indeed not deflected, a very small percentage (about 1 in 8000 particles) bounced off the gold foil at very large angles. Some were even redirected back toward the source. In a famous quote, Rutherford exclaimed that it was "as if you had fired a 15-inch [artillery] shell at a piece of tissue and it came back and hit you."

Rutherford came up with an entirely new model of the atom, **nuclear model**, in order to explain his results. In the nuclear model, **nucleus** is the tiny, dense, central core of the atom and is composed of protons and neutrons, and electrons are distributed around the nucleus in the atom. Because most of the atom was empty, so the vast majority of the alpha particles had passed through. For small amount of alpha particles (positively charged) that bombed into the nucleus, they were highly deflected because of the powerful repulsion force of the nucleus with positive charge as well.

It is worth emphasizing just how small the nucleus is compared to the rest of the atom. If we could blow up an atom to be the size of a large professional football stadium, the nucleus would be about the size of a marble.

Nuclear Atomic Model

The **nucleus** (plural, nuclei) is a positively charged region at the center of the atom. It consists of two types of subatomic particles packed tightly together. The particles are protons, which have a positive electric charge, and neutrons, which are neutral in electric charge. Outside of the nucleus, an atom is mostly empty space, with orbiting negative particles called electrons whizzing through it. The figure below shows these parts of the atom.

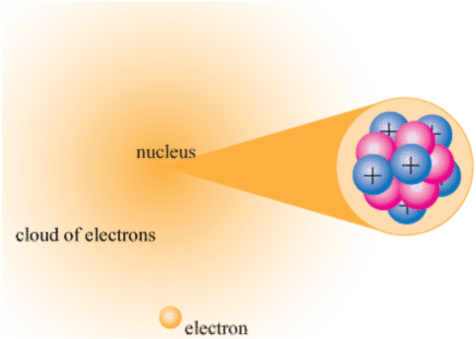


Figure 2.5 The nuclear atomic model

The nucleus of the atom is extremely small. Its radius is only about 1/100,000 of the total radius of the atom. Electrons have virtually no mass, but protons and neutrons have a lot of mass for their size. As a result, the nucleus has virtually all the mass of an atom. Given its great mass and tiny size, the nucleus is very dense. If an object the size of a penny had the same density as the nucleus of an atom, its mass would be greater than 30 million tons!

Protons

A proton is one of three main particles that make up the atom. Protons are found in the nucleus of the atom. This is a tiny, dense region at the center of the atom. Protons have a positive electrical charge of one (+1) and a mass of 1.007 **atomic mass unit (amu)**, which is about 1.67×10^{-27} kilograms. Together with neutrons, they make up virtually all of the mass of an atom.

Neutrons

Atoms of all elements—except for most atoms of hydrogen—have neutrons in their nucleus. As you might have already guessed from its name, neutron is neutral. In other words, neutron has no charge. The mass of a neutron is slightly greater than the mass of a proton, which is 1.0087 atomic mass unit (amu).

Electrons

Electrons are extremely small. The mass of an electron is only about 1/2000 the mass of a proton or neutron, so electrons contribute virtually nothing to the total mass of an atom. Electrons have an electric charge of −1, which is equal but opposite to the charge of a proton, which is +1. All atoms have the same number of electrons as protons, so the positive and negative charges "cancel out", making atoms electrically neutral.

Unlike protons and neutrons, which are located inside the nucleus at the center of the atom, electrons are found outside the nucleus. Because opposite electric charges attract one another, negative electrons are attracted to the positive nucleus. This force of attraction keeps electrons constantly moving through the otherwise empty space around the nucleus.

Particle	Mass (amu)	Relative Charge
proton	1.0073	+1
neutron	1.0087	0
electron	0.00055	–1

Table 2.1 Properties of Subatomic Particles

2.2 Elements, Atomic mass and Isotope

It's important to be able to distinguish atoms of one element from atoms of another element. Elements are pure substances that make up all other matter, so each one is given a unique name. The names of elements are also represented by unique one- or two-letter symbols, such as H for hydrogen, C for carbon, or He for helium. However, it would more powerful if these names could be used to identify the numbers of protons and neutrons in the atoms. That's where atomic number and mass number are useful.

Figure 2.6 It is difficult to find qualities that differ between each element, and to distinguish one element from another. Each element, however, does have a unique number of protons. Sulfur has 16 protons, silicon has 14 protons, and gold has 79 protons. Images used with permission (public domain for sulfur and silicon, gold is licensed by CC-BY-SA-NC-ND; Alchemist-hp).

Atomic Number

An atom of one element can be distinguished from an atom of another element by the number of protons in its nucleus, scientists are always interested in this number, and how this number differs between different elements. The number of protons in an atom is called its **atomic number** (Z). This number is very important because it is unique for atoms of a given element. All atoms of an element have the same number of protons, and every element has a different number of protons in its atoms. In another way, the number of proton (or atomic number) defines the type of element. For example, all helium atoms have two protons, no other elements have atoms with two protons, and an atom with protons is always a helium atom.

Of course, since neutral atoms have to have one electron for every proton, **an element's atomic number also tells you how many electrons are in a neutral atom of that element**. For example, hydrogen has an atomic number of 1. This means that an atom of hydrogen has one proton, and, if it's neutral, one electron as well. Gold, on the other hand, has an atomic number of 79, which means that an atom of gold has 79 protons, and, if it's neutral, 79 electrons as well.

Mass Number and Isotopes

The **mass number** (A) of an atom is the total number of protons and neutrons in its nucleus. The mass of the atom is also in the unit of atomic mass unit (amu). Because electrons have virtually no mass, just about all the mass of an atom comes from protons and neutrons.

$$\text{mass number } A = \text{number of protons} + \text{number of neutrons}$$

Consider helium as an example. Most helium atoms have two neutrons in addition to two protons. Therefore the mass of most helium atoms is 4. However, some helium atoms have more or less than two neutrons. Atoms with the same number of protons but different numbers of neutrons are called **isotopes**. Because the number of neutrons can vary for a given element, the mass numbers of different atoms of an element may also vary. For example, for helium atoms that have three neutrons instead of two, the mass number is 5.

Atomic symbol is the symbol to specify all the above information for an element together:

$$^{A}_{Z}X$$

X: the symbol of the element
A: the mass number (number of protons plus neutrons)
Z: the atomic number (number of protons)

For example, for helium atom with two neutrons, the Atomic/nuclear symbol is: $^{4}_{2}\mathrm{He}$, and this is one isotope of helium element. The other isotope of helium element with three neutrons has the symbol of $^{5}_{2}\mathrm{He}$.

Another common example of isotope is for hydrogen element. Most hydrogen atoms have just one proton, one electron, and lack a neutron. These atoms are just called hydrogen. Some hydrogen atoms have one neutron as well. These atoms are the isotope named deuterium. Other hydrogen atoms have two neutrons. These atoms are the isotope named tritium.

$^{1}_{1}\mathrm{H}$	$^{2}_{1}\mathrm{H}$	$^{3}_{1}\mathrm{H}$
Hydrogen (H)	Deuterium (D)	Tritium (T)

Another way to show isotope of an element is omitting the atomic number, and just use symbol like He-4, H-2. Since all the atoms of helium element have 2 protons (or atomic number is 2), the atomic number can be omitted with element symbol He present.

Many isotopes occur naturally. Different isotopes of an element generally have the same physical and chemical properties because they have the same numbers of protons and electrons. Usually one or two isotopes of an element are the most stable and common. Having too many or too few neutrons relative to protons results in an unstable, or radioactive, nucleus that will sooner or later break down to a more stable form. This process is called radioactive decay. Many isotopes have radioactive nuclei, and these isotopes are referred to as radioisotopes. When they decay, they release particles that may be harmful. This is why radioactive isotopes are dangerous and why working with them requires special suits for protection. The isotope of carbon known as carbon-14 is an example of a radioisotope. In contrast, the carbon isotopes called carbon-12 and carbon-13 are stable.

In chemistry we very rarely deal with only one isotope of an element. We use a mixture of the isotopes of an element in chemical reactions and other aspects of chemistry, because all of the isotopes of an element react in the same manner. That means that we rarely need to worry about the mass of a specific isotope, but instead we need to know the average mass of the atoms of an element. Using the masses of the different isotopes and how abundant each isotope is, we can find the **average atomic mass** of an element. The **average atomic mass** of an element is the weighted average mass of the atoms in a naturally occurring sample of the element. The atomic mass listed in the periodic table is the average atomic mass, with unit of atomic mass unit (amu).

Calculating Average Atomic Mass

To calculate the average atomic mass of an element, two types information are necessary: the **exact mass** of a certain naturally occurring isotope, and the **relative abundance** (the fraction of a given isotope of an element) of that isotope. The average atomic mass can be calculated by the following equation:

Average Atomic Mass = (fraction of isotope 1)(mass of isotope 1)+(fraction of isotope 2)(mass of isotope 2) + fraction of isotope 3)(mass of isotope 3) + ……

Look carefully to see how this equation is used in the following examples.

Example
Magnesium has three naturally occurring isotopes. Mg-24 with mass 23.99amu and a natural abundance of 78.99%, Mg-25 has a mass of 24.99amu and natural abundance 10.00%, and Mg-26 with mass of 25.98amu and a natural abundance of 11.01%. What is the average atomic mass of neon?

Solution
For the three isotopes of magnesium (covert the percent natural abundance to decimal form):

Isotope 1	fraction: 78.99% = 0.7899	mass: 23.99 amu
Isotope 2	fraction: 10.00% = 0.1000	mass: 24.99 amu
Isotope 3	fraction: 11.01% = 0.1101	mass: 25.98 amu

Take these numbers into the equation, **remember to keep all the sig. figs. for each number**:

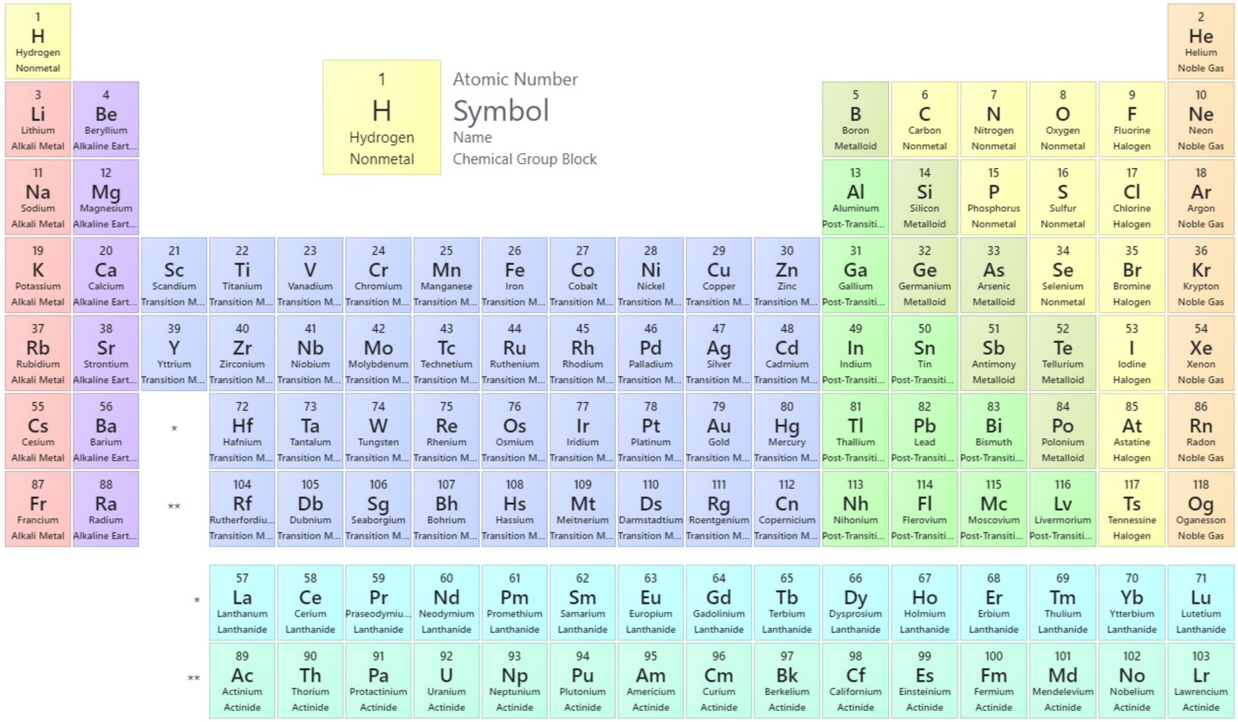
Average atomic mass = 0.7899×23.99 amu + 0.1000×24.99 amu + 0.1101×25.98 amu
= $18.9\underline{4}9$ amu + $2.49\underline{9}$ amu + $2.86\underline{0}4$ amu
= $24.3\underline{0}8$ amu = 24.31 amu

Example Copper has two naturally occurring isotopes, Cu-63 with mass 62.9396 amu and Cu-65 with mass 64.9278 amu. The average atomic mass of copper is 63.55 amu, what is the natural abundance of each isotope for copper?

Answer: 0.6917 for Cu-63 and 0.3083 for Cu-65

2.3 Periodic Table

The periodic table is one of the cornerstones of chemistry because it organizes all of the known elements on the basis of their chemical properties. A modern version is shown in Figure 2.7. The elements are listed in order of atomic number.



1
H
Hydrogen
Nonmetal

Atomic Number
Symbol
Name
Chemical Group Block

1 H Hydrogen Nonmetal																	2 He Helium Noble Gas
3 Li Lithium Alkali Metal	4 Be Beryllium Alkaline Eart...											5 B Boron Metalloid	6 C Carbon Nonmetal	7 N Nitrogen Nonmetal	8 O Oxygen Nonmetal	9 F Fluorine Halogen	10 Ne Neon Noble Gas
11 Na Sodium Alkali Metal	12 Mg Magnesium Alkaline Eart...											13 Al Aluminum Post-Transiti...	14 Si Silicon Metalloid	15 P Phosphorus Nonmetal	16 S Sulfur Nonmetal	17 Cl Chlorine Halogen	18 Ar Argon Noble Gas
19 K Potassium Alkali Metal	20 Ca Calcium Alkaline Eart...	21 Sc Scandium Transition M...	22 Ti Titanium Transition M...	23 V Vanadium Transition M...	24 Cr Chromium Transition M...	25 Mn Manganese Transition M...	26 Fe Iron Transition M...	27 Co Cobalt Transition M...	28 Ni Nickel Transition M...	29 Cu Copper Transition M...	30 Zn Zinc Transition M...	31 Ga Gallium Post-Transiti...	32 Ge Germanium Metalloid	33 As Arsenic Metalloid	34 Se Selenium Nonmetal	35 Br Bromine Halogen	36 Kr Krypton Noble Gas
37 Rb Rubidium Alkali Metal	38 Sr Strontium Alkaline Eart...	39 Y Yttrium Transition M...	40 Zr Zirconium Transition M...	41 Nb Niobium Transition M...	42 Mo Molybdenum Transition M...	43 Tc Technetium Transition M...	44 Ru Ruthenium Transition M...	45 Rh Rhodium Transition M...	46 Pd Palladium Transition M...	47 Ag Silver Transition M...	48 Cd Cadmium Transition M...	49 In Indium Post-Transiti...	50 Sn Tin Post-Transiti...	51 Sb Antimony Metalloid	52 Te Tellurium Metalloid	53 I Iodine Halogen	54 Xe Xenon Noble Gas
55 Cs Cesium Alkali Metal	56 Ba Barium Alkaline Eart...	*	72 Hf Hafnium Transition M...	73 Ta Tantalum Transition M...	74 W Tungsten Transition M...	75 Re Rhenium Transition M...	76 Os Osmium Transition M...	77 Ir Iridium Transition M...	78 Pt Platinum Transition M...	79 Au Gold Transition M...	80 Hg Mercury Transition M...	81 Tl Thallium Post-Transiti...	82 Pb Lead Post-Transiti...	83 Bi Bismuth Post-Transiti...	84 Po Polonium Metalloid	85 At Astatine Halogen	86 Rn Radon Noble Gas
87 Fr Francium Alkali Metal	88 Ra Radium Alkaline Eart...	**	104 Rf Rutherfordiu... Transition M...	105 Db Dubnium Transition M...	106 Sg Seaborgium Transition M...	107 Bh Bohrium Transition M...	108 Hs Hassium Transition M...	109 Mt Meitnerium Transition M...	110 Ds Darmstadtium Transition M...	111 Rg Roentgenium Transition M...	112 Cn Copernicium Transition M...	113 Nh Nihonium Post-Transiti...	114 Fl Flerovium Post-Transiti...	115 Mc Moscovium Post-Transiti...	116 Lv Livermorium Post-Transiti...	117 Ts Tennessine Halogen	118 Og Oganesson Noble Gas
		*	57 La Lanthanum Lanthanide	58 Ce Cerium Lanthanide	59 Pr Praseodymiu... Lanthanide	60 Nd Neodymium Lanthanide	61 Pm Promethium Lanthanide	62 Sm Samarium Lanthanide	63 Eu Europium Lanthanide	64 Gd Gadolinium Lanthanide	65 Tb Terbium Lanthanide	66 Dy Dysprosium Lanthanide	67 Ho Holmium Lanthanide	68 Er Erbium Lanthanide	69 Tm Thulium Lanthanide	70 Yb Ytterbium Lanthanide	71 Lu Lutetium Lanthanide
		**	89 Ac Actinium Actinide	90 Th Thorium Actinide	91 Pa Protactinium Actinide	92 U Uranium Actinide	93 Np Neptunium Actinide	94 Pu Plutonium Actinide	95 Am Americium Actinide	96 Cm Curium Actinide	97 Bk Berkelium Actinide	98 Cf Californium Actinide	99 Es Einsteinium Actinide	100 Fm Fermium Actinide	101 Md Mendelevium Actinide	102 No Nobelium Actinide	103 Lr Lawrencium Actinide

Figure 2.7 A Modern Periodic Table. A modern periodic table lists elements left to right by atomic number. An interactive Periodic table can be found here. (Public Domain; PubChem via NIH)

Features of the Periodic Table

Elements that have similar chemical properties are grouped in columns called **groups** (or families). As well as being numbered, some of these groups have names— for example, *alkali metals* (the first column of elements), *alkaline earth metals* (the second column of elements), *halogens* (the next-to-last column of elements), and *noble gases* (the last column of elements).

Each row of elements on the periodic table is called a **period**. Periods have different lengths; the first period has only 2 elements (hydrogen and helium), while the second and third periods have 8 elements each. The fourth and fifth periods have 18 elements each, and later periods are so long that a segment from each is removed and placed beneath the main body of the table.

Certain elemental properties become apparent in a survey of the periodic table as a whole. Every element can be classified as either a metal, a nonmetal, or a metalloid (or semi metal), as shown in Figure 2.7. A **metal** is a substance that is shiny, typically (but not always) silvery in color, and an excellent conductor of electricity and heat. Metals are also malleable (they can be beaten into thin sheets) and ductile (they can be drawn into thin wires). A **nonmetal** is typically dull and a poor conductor of electricity and heat. Solid nonmetals are also very brittle. As shown in Figure 2.8, metals occupy the left three-fourths of the periodic table, while nonmetals (except for hydrogen) are clustered in the upper right-hand corner of the periodic table. The elements with properties intermediate between those of metals and nonmetals are called **metalloids** (or **semi-metals**). Elements adjacent to the bold line in the right-hand portion of the periodic table have semimetal properties.

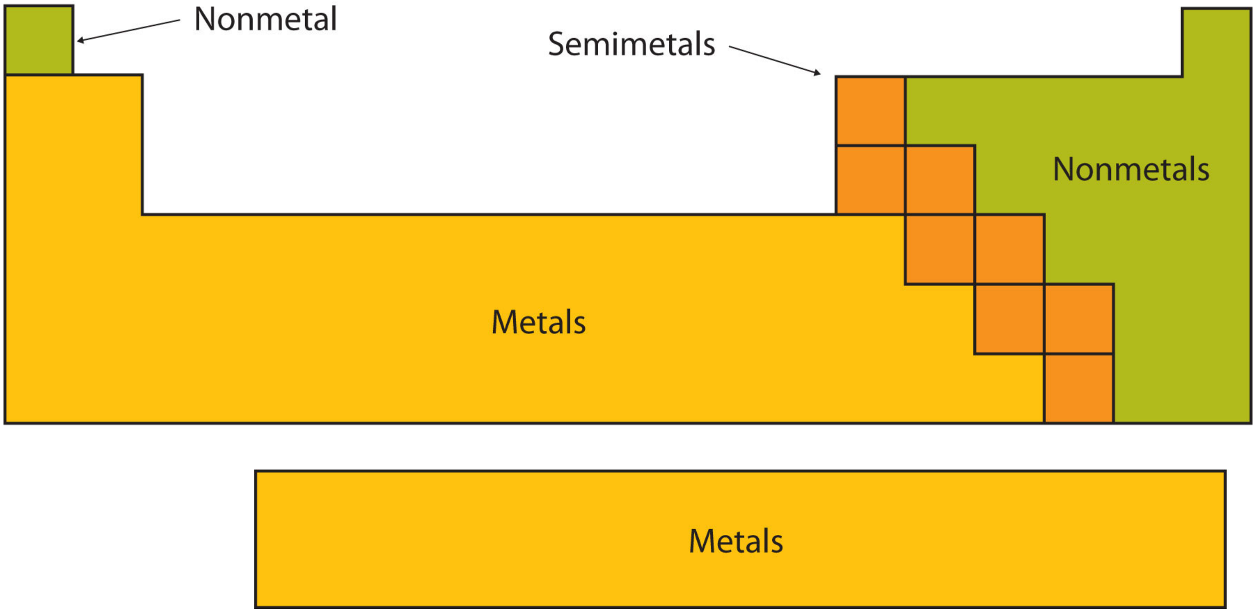


Figure 2.8 Types of Elements. Elements are either metals, nonmetals, or metalloids (or semi metals). Each group is located in a different part of the periodic table. (CC BY-NC-SA; Anonymous by request)

Descriptive Names

As previously noted, the periodic table is arranged so that elements with similar chemical behaviors are in the same group. Chemists often make general statements about the properties of the elements in a group using descriptive names with historical origins.

Group 1: The Alkali Metals

The alkali metals are lithium, sodium, potassium, rubidium, cesium, and francium. Hydrogen is unique in that it is generally placed in Group 1, but it is not a metal.

The compounds of the alkali metals are common in nature and daily life. One example is table salt (sodium chloride); lithium compounds are used in greases, in batteries, and as drugs to treat patients who exhibit manic-depressive, or bipolar, behavior. Although lithium, rubidium, and cesium are relatively rare in nature, and francium is so unstable and highly radioactive that it exists in only trace amounts, sodium and potassium are the seventh and eighth most abundant elements in Earth's crust, respectively.

Video: Alkali metals in water - Chemical elements: properties and reactions. (The Open University via https://youtu.be/6ZY6d6jrq-0)

Group 2: The Alkaline Earth Metals

The alkaline earth metals are beryllium, magnesium, calcium, strontium, barium, and radium. Beryllium, strontium, and barium are rare, and radium is unstable and highly radioactive. In contrast, calcium and magnesium are the fifth and sixth most abundant elements on Earth, respectively; they are found in huge deposits of limestone and other minerals.

Group 17: The Halogens

The halogens are fluorine, chlorine, bromine, iodine, and astatine. The name halogen is derived from the Greek words for "salt forming," which reflects that all of the halogens react readily with metals to form compounds, such as sodium chloride and calcium chloride (used in some areas as road salt).

Compounds that contain the fluoride ion are added to toothpaste and the water supply to prevent dental cavities. Fluorine is also found in Teflon coatings on kitchen utensils. Although chlorofluorocarbon propellants and refrigerants are believed to lead to the depletion of Earth's ozone layer and contain both fluorine and chlorine, the latter is responsible for the adverse effect on the ozone layer. Bromine and iodine are less abundant than chlorine, and astatine is so radioactive that it exists in only negligible amounts in nature.

Group 18: The Noble Gases

The noble gases are helium, neon, argon, krypton, xenon, and radon. Because the noble gases are composed of only single atoms, they are called monatomic. At room temperature and pressure, they are unreactive gases. Because of their lack of reactivity, for many years they were called inert gases or rare gases. However, the first chemical compounds containing the noble gases were prepared in 1962. Although the noble gases are relatively minor constituents of the atmosphere, natural gas contains substantial amounts of helium. Because of its low reactivity, argon is often used as an unreactive (inert) atmosphere for welding and in light bulbs. The red light emitted by neon in a gas discharge tube is used in neon lights.

When building a house, the starting point is a blueprint of what the house will look like. The plan states how many windows and what kind, how many doors and what style, how many rooms and what type (bedroom, kitchen, other). The blueprint shows how the different pieces will go together to make the house. As long as the blueprint is followed and exactly the same items are used, the house will be identical to its blueprint.

Chapter 3 Formula and Names

In chapter 1, we have learned that pure substance can be categorized as element or compounds. Here we will take a look at chemical formula and naming of substance.

3.1 Elements

Elements can be either **atomic elements** or **molecular elements**. The elements exist with individual atoms as their basic unit are atomic elements. For example: all the metals (Fe, Cu, Mg, etc.), noble gases. It is assumed that there is only one atom in a formula if there is no numerical subscript on the right side of an element's symbol.

There are other substances that exist as two or more atoms connected together so strongly that they behave as a single particle. These multi-atom combinations are called **molecules**. A molecule is the smallest part of a substance that has the physical and chemical properties of that substance. In some respects, a molecule is similar to an atom. A molecule, however, is composed of more than one atom.

Some elements exist *naturally* as molecules. For example, hydrogen gas (H_2) and oxygen gas (O_2) exist as diatomic molecules. Other elements also exist naturally as diatomic molecules—a molecule with only two atoms (Table 3.1). As with any molecule, these elements are labeled with a **molecular formula**, a formal listing of *what* and *how many* atoms are in a molecule. For example, the molecular formula for elemental hydrogen is H_2, with H being the symbol for hydrogen and the subscript 2 implying that there are two atoms of this element in the molecule. Other diatomic elements have similar formulas: O_2, N_2, and so forth.

Hydrogen (H_2)	Oxygen (O_2)	Nitrogen (N_2)	Fluorine (F_2)	Chlorine (Cl_2)	Bromine (Br_2)	Iodine (I_2)

Table 3.1 Elements That Exist Naturally as Diatomic Molecules

Other elements exist as molecules—for example, sulfur normally exists as an eight-atom molecule, S_8, while phosphorus exists as a four-atom molecule, P_4 (Fig. 3.1).

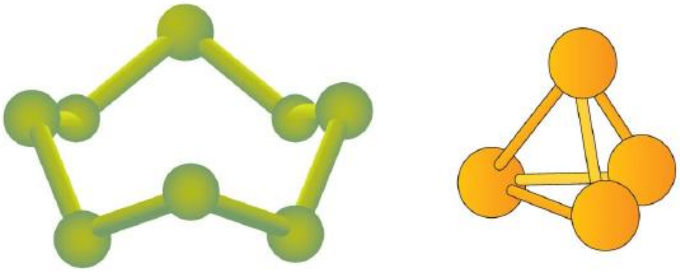


Figure 3.1 Molecular Model of S_8 (left) and P_4 Molecules (right)

3.2 Compounds

A **compound** is a substance that contains two or more elements chemically combined in a fixed proportion.

Recall that the components of a mixture can be separated from one another by physical means. This is not true for a compound. Table salt is a compound consisting of equal parts of the elements sodium and chlorine. Salt cannot be separated into its two elements by filtering, distillation, or any other physical process. Salt and other compounds can only be decomposed into their elements by a chemical process.

The properties of compounds are generally very different than the properties of the elements from which the compound is formed. Sodium is an extremely reactive soft metal that cannot be exposed to air or water. Chlorine is a deadly gas. The compound sodium chloride is a white solid which is essential for all living things (see below).

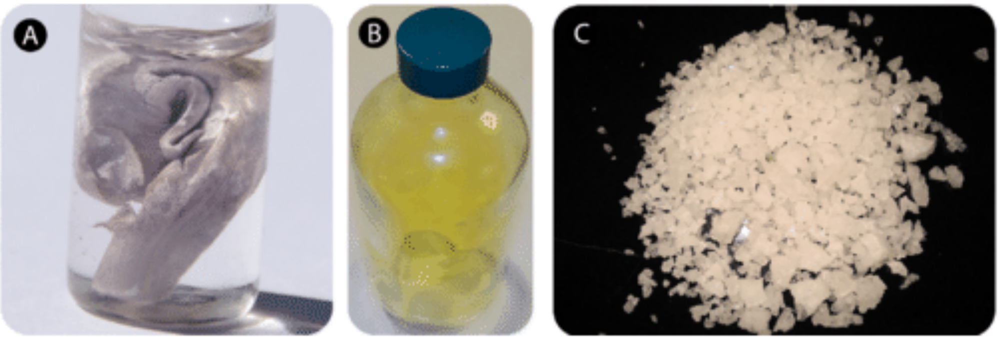


Figure 3.2 (A) Sodium is so reactive that it must be stored under oil. (B) Chlorine is a poisonous yellow-green gas. (C) Salt crystals, a compound of sodium and chlorine.

The two major types of compounds are ionic compounds and molecular compounds.

Ionic Compounds

The elements in the periodic table are divided into specific groupings; the metals, the non-metals, the semi-metals, and so on. These groupings 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 a non-metal (or a semi-metal) will display ionic bonding. Thus, the compound formed from sodium and chlorine will be ionic (a metal and a non-metal). The basic unit of ionic compounds is the **formula unit**.

Please note that Ionic compounds do not exist as molecules.

Molecular Compounds

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. Nitrogen monoxide (NO) will be a covalently bound molecule (two non-metals) and silicon dioxide (SiO_2) will also be a covalently bound molecule (a semi-metal and a non-metal). The basic unit of molecular compounds is the **molecule**.

Molecular Formula

A **molecular formula** is a chemical formula of a molecular compound that shows the kinds and numbers of atoms present in a molecule of the compound. Ammonia is a compound with one nitrogen atom bonded with three hydrogen atoms, with the formula of: NH_3.

Empirical Formula

An **empirical formula** is a formula that shows the elements in a compound in their lowest whole-number ratio. Glucose is an important simple sugar that cells use as their primary source of energy. Its molecular formula is $C_6H_{12}O_6$. Since each of the subscripts is divisible by 6, the empirical formula for glucose is CH_2O. When chemists analyze an unknown compound, often the first step is to determine its empirical formula. The relationship between empirical formula (EF) and molecular formula (MF) is :

$$\mathrm{MF} = (\mathrm{EF})_n \quad (n = 1, 2, 3 \ldots \text{etc})$$

For glucose, n is 6. There are a great many compounds whose molecular and empirical formulas are the same, or n = 1. If the molecular formula cannot be simplified into a smaller whole-number ratio, as in the case of H_2O or P_2O_5, then the empirical formula is also the molecular formula.

3.3: Ionic compounds: Formulas and Names

Ions - Losing and Gaining Electrons

Ions are formed when neutral atoms lose or gain electrons. Positively charged ions are called **cations.** Cation is formed when an atom loses electrons. For example:

$$Na \rightarrow Na^+ + e^-$$

Sodium atom is neutral because charge balanced with the same number of protons and electrons. In the case that sodium atom loses one electron, the resulting species has 10 electrons and 11 protons, so it has a positive charge. Such ion is called sodium ion (or sodium cation) and shown as Na^+.

On the other hand, negatively charged ions are called **anions.** Anion is formed when an atom gains electrons. For example:

$$Cl + e^{-} \rightarrow Cl^{-}$$

Chlorine atom is neutral because charge balanced with the same number of protons and electrons. In the case that chlorine atom gains one electron, the resulting species has 18 electrons and 17 protons, so it has a negative charge. Such ion is called chloride ion and shown as Cl^{-}. Please note the slight change in the suffix of the name of anion, the suffix *-ide* is used to replace the suffix -*ine in the name of atom.*

Element	**Symbol of Anion**	**Anion Name**
Fluorine	F^{-}	fluoride
Chlorine	Cl^{-}	chloride
Bromine	Br^{-}	bromide
Iodine	I^{-}	iodide
Oxygen	O^{2-}	oxide
Sulfur	S^{2-}	sulfide
Nitrogen	N^{3-}	nitride
Phosphorus	P^{3-}	phosphide

Table 3.2 Names of Some Monatomic Anions

Usually, metals become cations when they make ionic compounds, and non-metals become anions.

In many cases, elements that belong to the same group (vertical column) on the periodic table form ions with the same charge because they have similar properties. Thus, the periodic table becomes a tool for remembering the charges on many ions. For example, all ions made from alkali metals, the first column on the periodic table, have a 1+ charge. Ions made from alkaline earth metals, the second group on the periodic table, have a 2+ charge. The calcium cation is written Ca^{2+}, not Ca^{+2}. On the other side of the periodic table, the next-to-last column, the halogens, form ions having a 1− charge. Figure 3.3 shows how the charge on many ions can be predicted by the location of an element on the periodic table. Note the convention of first writing the number and then the sign on a ion with multiple charges.

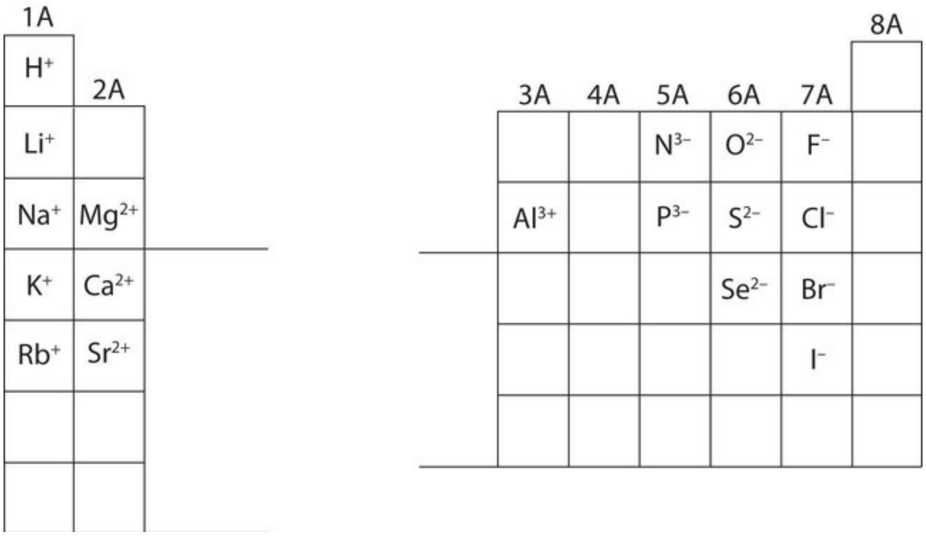


Figure 3.3 Predicting Ionic Charges. The charge that an atom acquires when it becomes an ion is related to the structure of the periodic table. Within a group (family) of elements, atoms form ions of a certain charge.

Writing Formula for Ionic Compounds

In the solid state, ionic compounds are in crystal lattice containing many ions each of the cation and anion. The formula of an ionic compound, like NaCl, is an empirical formula. This formula merely indicates that sodium chloride is made of an equal number of sodium and chloride ions. Another ionic compound, sodium sulfide, has the formula Na_2S that indicates it is made up of twice as many sodium ions as sulfide ions.

Since ionic compounds are charge neutral, the formulas for binary ionic compounds can be deducted from their constituent elements.

For example, the formula of compound composed on calcium and chlorine should be $CaCl_2$ because Ca always forms 2+ cations and Cl always form 1- anions. In order for this compound to be charge neutral, it must contain one Ca^{2+} to every two Cl^{-} anions.

Example

Write the formula for ionic compound that forms between aluminum and oxygen.

Solution

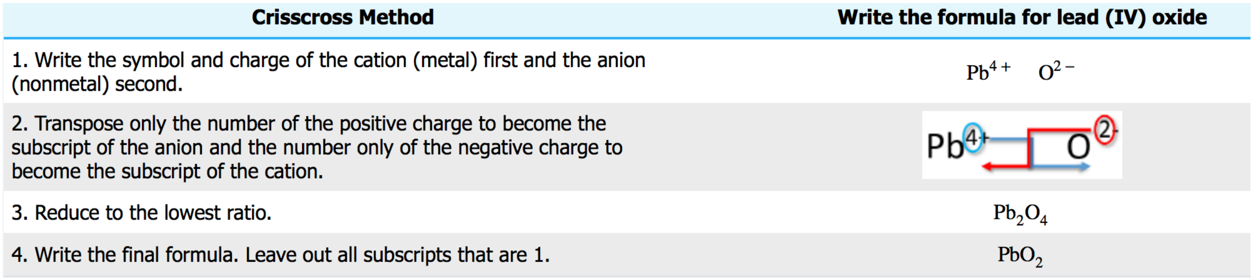
1. Write the symbol and charge of the cation and anion involved	Al^{3+} O^{2-}
2. Use a multiplier to make the total charge of the cations and anions equal to each other.	total charge of cations = total charge of anions 2 (3+) = 3 (2-) +6 = -6
3. Use the multipliers as subscript for each ion	Al_2O_3
4. Write the final formula. Leave out the charges and subscripts that are 1.	Al_2O_3

An alternative way to writing a correct formula for an ionic compound is to use the **crisscross method**. In this method, the numerical value of each of the ion charges is crossed over to become the subscript of the other ion. Signs of the charges are dropped.

Example

Write the formula for ionic compound that forms between Pb^{4+} and oxygen.

Solution



Crisscross Method	Write the formula for lead (IV) oxide
1. Write the symbol and charge of the cation (metal) first and the anion (nonmetal) second.	Pb^{4+} O^{2-}
2. Transpose only the number of the positive charge to become the subscript of the anion and the number only of the negative charge to become the subscript of the cation.	Pb^{4+} O^{2-}
3. Reduce to the lowest ratio.	Pb_2O_4
4. Write the final formula. Leave out all subscripts that are 1.	PbO_2

Naming Binary Ionic Compounds Containing a Metal that Forms only one type of cation

A **binary** ionic compound is a compound composed of a mono-atomic metal **cation** and a mono-atomic nonmetal **anion**. To name such compound, the metal cation is named first, followed by the name of the nonmetal anion, as illustrated in Figure 3.4 for the compound $BaCl_2$. The word *ion* is dropped from both parts.

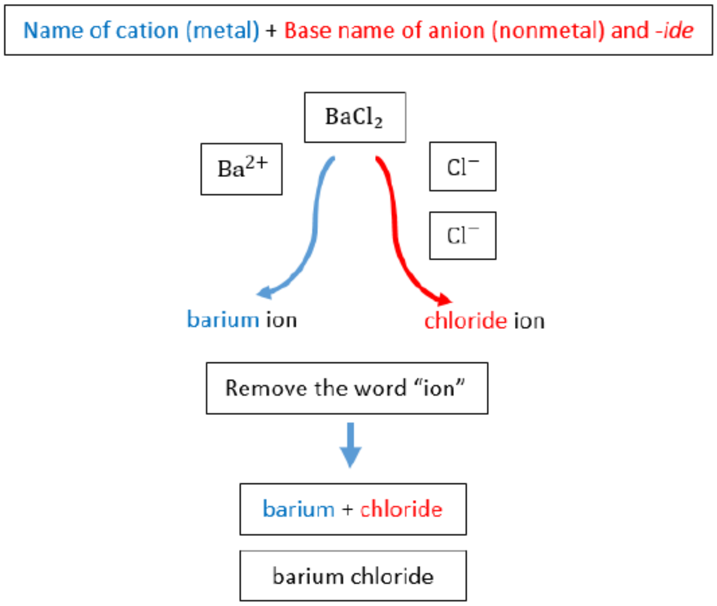


Figure 3.4 Naming $BaCl_2$

Naming Binary Ionic Compounds Containing a Metal that Forms more than one type of cation

For main group metals, they can only form cation with one possible charge (Figure 3.3). For transition metals, however, they can form cations with more than one possible charge. To name such ionic compounds, we must first determine the charge on the cation in this compound, and then show the charge of the cation as Roman numeral in parenthesis in the name.

For example, name $FeCl_2$ and $FeCl_3$, the two ionic compounds that can be formed between iron and chlorine.

In $FeCl_2$, the iron ion has a 2+ charge (to balance the total charges of two Cl^- ions that is 2-), it can be named as iron (II), with the charge shown as Roman numerals in parentheses. So the name of this compound is: iron (II) chloride.

In $FeCl_3$, the iron ion has a 3+ charge (to balance the total charges of three Cl^- ions that is 3-), it can be named as iron (III). So the name of this compound is: iron (III) chloride.

Example Name each ionic compound.

a. Co_2O_3
b. $CuCl_2$
c. MnO_2

Solution

a. cobalt (III) oxide; b: copper (II) chloride; c: manganese (IV) oxide

Naming Ionic Compounds Containing Polyatomic Ions

Some ions consist of groups of atoms bonded together and have an overall electric charge. Because these ions contain more than one atom, they are called polyatomic ions. Polyatomic ions have characteristic formulas, names, and charges that should be memorized (Table 3.3). For example, NO_3^- is the nitrate ion; it has one nitrogen atom and three oxygen atoms and an overall 1− charge. Most polyatomic ions are anions, with only one cation NH_4^+.

Name	Formula	Name	Formula
ammonium	NH_4^+	nitrate	NO_3^-
acetate	$C_2H_3O_2^-$ (also written as $CH_3CO_2^-$)	nitrite	NO_2^-
carbonate	CO_3^{2-}	permanganate	MnO_4^-
hydrogen carbonate	HCO_3^-	phosphate	PO_4^{3-}
hypochlorite	$HClO^-$	hydrogen phosphate	HPO_4^{2-}
chlorite	$HClO_2^-$	dihydrogen phosphate	$H_2PO_4^-$
chlorate	$HClO_3^-$	sulfate	SO_4^{2-}
perchlorate	$HClO_4^-$	sulfite	SO_3^{2-}
chromate	CrO_4^{2-}	hydrogen sulfate	HSO_4^-
dichromate	$Cr_2O_7^{2-}$	hydrogen sulfite	HSO_3^-
hydroxide	OH^-	cyanide	CN^-

Table 3.3 Some Common Polyatomic Ions

The rule for constructing formulas for ionic compounds containing polyatomic ions is the same as for formulas containing monatomic (single-atom) ions: the positive and negative charges must balance. If more than one of a particular polyatomic ion is needed to balance the charge, the *entire formula* for the polyatomic ion must be enclosed in parentheses, and the numerical subscript is placed *outside* the parentheses. This is to show that the subscript applies to the entire polyatomic ion. An example is $Ba(NO_3)_2$.

The process of naming ionic compounds with polyatomic ions is the same as naming binary ionic compounds. The cation is named first, followed by the anion. The name of $Ba(NO_3)_2$, as an example, is barium nitrate.

Example Write the proper name for each ionic compound.

a. $(NH_4)_2S$
b. $AlPO_4$
c. $Fe_3(PO_4)_2$

Solution

a. ammonium sulfide; b. aluminum phosphate; c. iron(II) phosphate

Hydrated Ionic Compounds

Some ionic compounds contain a specific number of water molecules associate with each formula unit, they are called hydrates. An example is Epson salt that has the formula of $MgSO_4 \cdot 7H_2O$. Hydrates are named in the similar way as other ionic compounds, but with the additional name "*prefix*hydrate" at the end, where the prefix indicates the number of water molecules associate with each formula unit (see Table 3.4 in next section for details of prefix).

So the name of Epson salt is magnesium sulfate heptahydrate.

Waters of hydration can usually be removed by heating the compound. The hydrate and anhydrous format of the ionic compound usually show different color.

Example

Name the following hydrates.

a. $CoCl_2 \cdot 6H_2O$
b. $CuSO_4 \cdot 5H_2O$

Solution

a. cobalt(II) chloride hexahydrate; b. coper(II) sulfate pentahydrate

3.4: Naming Binary Molecular compounds

Recall that a molecular formula shows the number of atoms of each element that a molecule contains. A molecule of water contains two hydrogen atoms and one oxygen atom, so its formula is H_2O. A molecule of octane, which is a component of gasoline, contains 8 atoms of carbon and 18 atoms of hydrogen. The molecular formula of octane is C_8H_{18}.

Naming *binary* (two-element) molecular compounds is similar to naming simple ionic compounds. The first element in the formula is simply listed using the name of the element. The second element is named by taking the stem of the element name and adding the suffix ***-ide***. A system of numerical prefixes is used to specify the number of atoms in a molecule. Table 3.4 lists these numerical prefixes.

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

Table 3.4 Numerical Prefix

Notes of prefix in naming binary molecular compounds:

- **Such prefix only apply to molecular compound, not ionic compound**.
- The *a* or *o* at the end of a prefix is usually dropped from the name when the name of the element begins with a vowel. As an example, four oxygen atoms, is tetr**o**xide instead of tetr**ao**xide.
- The prefix is "mono" is not added to the first element's name if there is only one atom of the first element in a molecule.

Examples: Name the following compounds.

a. NO
b. N_2O
c. CCl_4
d. Cl_2O_7

Answers:

a. nitrogen monoxide
b. dinitrogen monoxide
c. carbon tetrachloride
d. dichlorine heptoxide

Simple Molecular Compounds with Common Names

For some simple covalent compounds, we use common names rather than systematic names. We have already encountered these compounds, but we list them here explicitly:

- H_2O: water
- NH_3: ammonia
- CH_4: methane
- H_2O_2: hydrogen peroxide

Methane is the simplest organic compound. Organic compounds are compounds with carbon atoms and are named by a separate nomenclature system.

3.5: Naming Acids

An **acid** can be defined in several ways. The most straightforward definition is that an acid is a molecular compound that contains one or more hydrogen atoms and produces hydrogen ions (H^+) when dissolved in water.

Figure 3.5 (A) Vinegar comes in a variety of types, but all contain acetic acid. (B) Citrus fruits like grapefruit contain citric and ascorbic acids.

This is a different type of compound than the others we have seen so far. Acids are molecular, which means that in their pure state they are individual molecules and do not adopt the extended three-dimensional structures of ionic compounds like NaCl. However, when these molecules are dissolved in water, the chemical bond between the hydrogen atom and the rest of the molecule breaks, leaving a positively-charged hydrogen ion and an anion. This can be symbolized in a chemical equation:

$$HCl \rightarrow H^+ + Cl^-$$

Since acids produce H^+ cations upon dissolving in water, the H of an acid is written first in the formula of an inorganic acid. The remainder of the acid (other than the H) is the anion after the acid dissolves. Organic acids are also an important class of compounds, but will not be discussed here.

Naming Acids

Since all acids contain hydrogen, the name of an acid is based on the anion that goes with it. These anions can either be monatomic or polyatomic.

Naming Binary acids

A **binary acid** is an acid that consists of hydrogen and one other element. The most common binary acids contain a halogen. The acid name begins with the prefix *hydro-*, followed by the base name of the anion, followed by the suffix *-ic acid.*

Hydro- and Base name of Non metal and *-ic + acid*

Example: $HCl_{(aq)}$

Cl^-, chloride ion

↓

hydrochloric acid

Base name of non metal for binary acid:

Cl^- = chlor; F^- = fluor; Br^- = brom; I^- = iod; CN^- = cyan; S^{2-} = sulfur

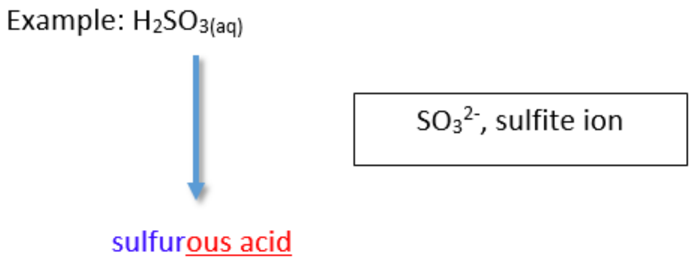
Naming Oxyacids

An **oxyacid** is an acid that consists of hydrogen, oxygen, and a third element. The third element is usually a nonmetal.

a. Oxyanions with *-ite* ending.

The name of the acid is the root of the anion followed by the suffix *-ous*. There is no prefix.

Base name of oxyanion and -*ous+ acid*


Example: $H_2SO_{3(aq)}$

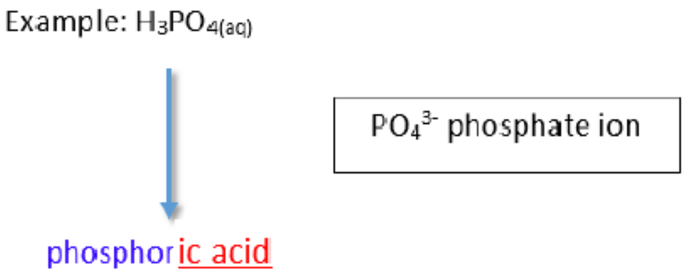
SO_3^{2-}, sulfite ion

sulfurous acid

b. Oxyanions with -*ate* ending.

The name of the acid is the root of the anion followed by the suffix -*ic*. There is no prefix.

Base name of oxyanion and -*ic+ acid*


Example: $H_3PO_{4(aq)}$

PO_4^{3-} phosphate ion

phosphoric acid

Example

Name the following acids:

a. HI(aq)
b. H_2SO_4(aq)
c. $HClO_2$(aq)

Solution

a. hydroiodic acid; b. sulfuric acid; c. chlorous acid

Chapter 4 Chemical Composition and Chemical Equations

4.1: Mole Concept (for Compounds): Counting Atoms/Molecules by the Gram

When objects are very small, it is often inconvenient, inefficient, or even impossible to deal with the objects one at a time. For these reasons, we often deal with very small objects in groups, and have even invented names for various numbers of objects. The most common of these is "dozen" which refers to 12 objects. We frequently buy objects in groups of 12, like doughnuts or pencils. Even smaller objects such as straight pins or staples are usually sold in boxes of 144, or a dozen dozen. A group of 144 is also called a "gross".

Avogadro's Number and Mole

This problem of dealing with things that are too small to operate with as single items also occurs in chemistry. Atoms and molecules are too small to see, let alone to count or measure. Chemists have selected a number of particles with which to work that is convenient. Since molecules are extremely small, you may suspect this number is going to be very large, and you are right. The number of particles in this group is 6.02×10^{23} particles and the name of this group is the **mole** (with abbreviation and unit as ***mol***). One mole of any object is 6.02×10^{23} of those objects.

The **mole** (symbol: **mol**) is the base unit of amount of substance ("number of substance") in the International System of Units or System International (SI), defined as exactly 6.02214076×10^{23} particles, e.g., atoms, molecules, ions or electrons. The current definition was adopted in November 2018, revising its old definition based on the number of atoms in 12 grams of carbon-12 (^{12}C) (the isotope of carbon with relative atomic mass 12 Daltons, by definition). For most purposes, 6.022×10^{23} provides an adequate number of significant figures. Just as 1 mole of atoms contains 6.022×10^{23} atoms, 1 mole of eggs contains 6.022×10^{23} eggs. This number is called Avogadro’s number, after the 19th-century Italian scientist who first proposed a relationship between the volumes of gases and the numbers of particles they contain.

Converting between Number of Atoms to Moles and Vice Versa

We can use Avogadro's number as a conversion factor, or ratio, in dimensional analysis problems. If we are given the number of atoms of an element *X*, we can convert it into moles by using the relationship

1 mol $X = 6.022\times10^{23}$ X atoms

Example
How many moles of carbon atoms is 4.72×10^{24} atoms of carbon?

Solution

1 mol X = 6.022×10^{23} X atoms can be re-written as two conversion factors:

$$\frac{1\, mol}{6.022\times 10^{23}} \quad \text{or} \quad \frac{6.022\times 10^{23}}{1\, mol}$$

For this question, we will need to convert from # of atoms to # of moles, so it is reasonable to use the **first** conversion factor, and the # of atom could be cancelled as a result.

$$4.72 \times 10^{24}\, \cancel{carbon\ atoms}\, \frac{1\, mol}{6.022 \times 10^{23}\, \cancel{carbon\ atoms}} = 7.84\, mol$$

Think about the meaning of the result: The given number of carbon atoms was greater than Avogadro's number, so the number of moles of carbon atoms is greater than 1 mol, and the answer makes sense.

Example

How many mole of Al atoms in 0.78 mol of aluminum?

Solution

$$0.78\, \cancel{mol}\, \frac{6.022 \times 10^{23}\, atoms}{1\, \cancel{mol}} = 4.70 \times 10^{23}\, atoms$$

4.2: Molar Mass

Molar mass is defined as the mass of one mole of a substance.

For the atomic element, we can conclude the molar mass by looking at a periodic table. The number listed in the periodic table for each element with multiple decimal places is the value of the molar mass of that element, with unit of g/mol (grams per mole). For example, the molar mass of element lithium is 6.94 g/mol, the molar mass of zinc is 65.38 g/mol. Each of these quantities contains 6.022×10^{23} atoms of that particular element.

For molecular or ionic compounds, the molar mass is the sum of molar masses of the atoms in the formula of that substance. It is calculated by adding together the atomic molar masses in the substance, each multiplied by its subscript (written or implied) in the formula, with units of g/mol as well.

Example

Calculate the molar mass of ethanol C_2H_5OH.

Solution

Obtain the atomic molar mass of element C, H and O from the periodic table. Multiple the molar mass of certain element with its subscript and add them together.

12.0×2 + 1.0×6 + 16.0×1 = 46.0 g/mol

Example

Calculate the molar mass of ethanol $Ca_3(PO_4)_2$.

Solution

40.1×3 + 31.0×2 + 16.0×8 = 310.3 g/mol

Note: there are total 8 oxygen atoms in one formula unit of this compound.

Converting Between Mass and Moles

The molar mass of any substance is the mass in grams of one mole of representative particles of that substance. The representative particles can be atoms, molecules, ion, or formula units of ionic compounds. This relationship is frequently used in the laboratory. Suppose that for a certain experiment you need 3.00 moles of calcium chloride ($CaCl_2$). Since calcium chloride is a solid, it would be convenient to use a balance to measure the mass that is needed. Dimensional analysis will allow you to calculate the mass of $CaCl_2$ that you should measure as shown in next Example.

Example
Calculate the mass of 3.00 moles of calcium chloride.

Solution
First get the MM of $CaCl_2$ = 40.1 + 35.5×2 = 111.1 g/mol
The MM can be used as conversion factor, choose the proper one for different question

$$\frac{111.1\ g}{1..0\ \ mol} \text{ or } \frac{1.0\ mol}{111.1\ g}$$

To calculate the mass of 3.00 mol of $CaCl_2$ we should choose the first conversion factor
mass of 3.00 mol of $CaCl_2$ = 3.00 mol $\times \frac{111.1\ g}{1.0\ mol} = 333.3\ g$

Example
How many moles of water molecules are present in 100.0g of water? How many moles of hydrogen atoms are present in the same amount of water?

Solution

In this example, pay attention to the relationship between hydrogen atom to water molecule as shown in Figure 4.1. In the formula of H_2O, the subscript also means the mole ratio, that is there are two moles of hydrogen atoms in each mole of water molecules.

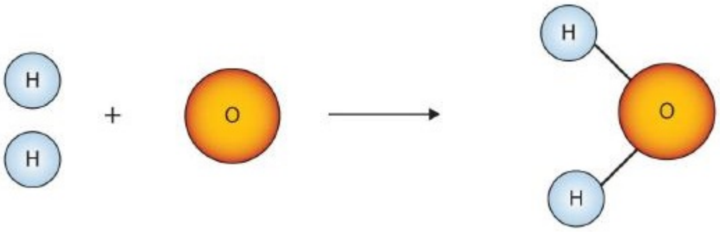


Figure 4.1 Element composition of water molecule

1 H_2O molecule has	2 H atoms
1 **mole** of H_2O molecule has	2 **mole** of H atoms

MM of water = 18.0g/mol

# of mole of <u>water molecules</u> in 100.0g of water = 100.0g $\times \frac{1.0\ mol}{18.0\ g}$ = 5.55 mol

# of mole of <u>hydrogen atoms</u> in 100.0g of water = 100.0g $\times \frac{1.0\ mol}{18.0\ g} \times \frac{2\ mol\ H\ atoms}{1\ mol\ H2O}$ = 11.1 mol

The application of conversion between mass and mole is of particular importance in stoichiometry in Chapter 5.

Conversions Between Mass and Number of Particles

In "Conversions Between Moles and Mass", you learned how to convert back and forth between moles and the number of representative particles. Now you have seen how to convert back and forth between moles and mass of a substance in grams. We can combine the two types of problems into one. Mass and number of particles are both related to moles. To convert from mass to number of particles or vice-versa, it will first require a conversion to moles as shown in following examples.

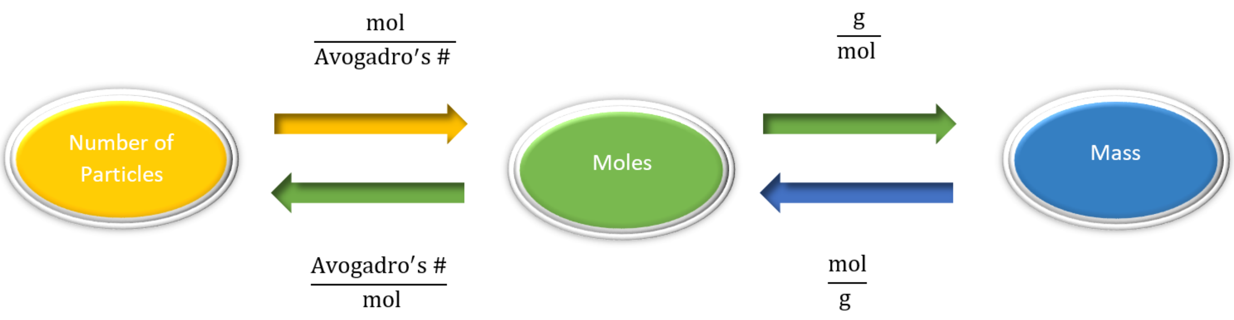


Figure 4.2 Conversion from number of particles to mass, or from mass to number of particles, requires two steps.

Example

What is the number of chlorine molecules in 20.0g of chlorine gas (Cl_2)? What is the number of chlorine atoms in the same amount of sample?

Solution

MM of Cl_2 is $35.5 \times 2 = 71.0$ g/mol

of <u>Cl_2 molecules</u> in 20.0g of Cl_2 $=20.0\text{g} \times \frac{1.0\ mol}{71.0\ g} \times \frac{6.022\times10^{23}\ molecules}{1.0\ mol} = 1.70 \times 10^{23}\ Cl_2$ molecules

of <u>chlorine atoms</u> in 20.0g of $Cl_2 = 1.70 \times 10^{23}\ Cl_2$ molecule$\times \frac{2\ Cl\ atoms}{1\ Cl2\ molecule} = 3.4 \times 10^{23}$ Cl atoms

4.3: Mass Percent Composition of Compounds

Packaged foods that you eat typically have nutritional information provided on the label. The label on a jar of peanut butter reveals that one serving size is considered to be 32g. The label also gives the masses of various types of compounds that are present in each serving: 7g of protein, 15g of fat, and 3g of sugar etc. To figure out the mass percent of protein in peanut butter, we can calculate as: $\frac{7\ g\ protein}{32\ \text{g peanut butter}} \times 100\ \% = 21.9\ \%$

Chemists often need to know what elements are present in a compound and in what percentage. The **percent composition** is the percent by mass of each element in a compound. It is calculated in a similar way to that of the composition of the peanut butter.

$$\%\text{ by mass}=\frac{mass\ of\ element}{\text{mass of compound}} \times 100\ \%$$

With the formula of a compound provided, the percent composition can be calculated by comparing the molar mass of an element verse the molar mass of the compound as shown in the example below.

Example

What is the percent composition of each element in sulfuric acid H_2SO_4?

Solution

% by mass of H element = $\frac{molar\ mass\ of\ H}{\text{molar mass of H2SO4}} \times 100\ \%$

$$= \frac{2\ \times\ 1.0}{2 \times 1.0 + 32.0 + 4 \times 16.0} \times 100\ \% = \frac{2.0}{98.0} \times 100\ \%$$

$$= 0.0204 \times 100\ \% = 2.04\ \%$$

% by mass of S element = $\frac{molar\ mass\ of\ S}{\text{molar mass of H2SO4}} \times 100\ \%$

$$= \frac{32.0}{98.0} \times 100\ \% = 0.3265 \times 100\ \% = 32.7\%$$

% by mass of O element = $\frac{molar\ mass\ of\ O}{\text{molar mass of H2SO4}} \times 100\ \%$

$$= \frac{4\ \times\ 16.0}{98.0} \times 100\ \% = \frac{64.0}{98.0} \times 100\ \%$$

$$= 0.653 \times 100\ \% = 65.3\ \%$$

Example

What is the percent composition of water in Epson salt $MgSO_4 \cdot 7H_2O$?

Solution

$$H_2O\ \% = \frac{7 \times MM_{H_2O}}{MM_{MgSO_4 \cdot 7H_2O}} \times 100\%$$

$$= \frac{7 \times 18.0}{246.3} \times 100\% = 51.2\ \%$$

4.4: Determining a Chemical Formula from Mass Percent or other Experimental Data

In the early days of chemistry, there were few tools for the detailed study of compounds. Much of the information regarding the composition of compounds came from the elemental analysis of materials. This method is particularly useful for determining the formula of new compounds.

Determining Empirical Formula

An empirical formula tells us the smallest ratios of different atoms in a compound. The ratios hold true on the *molar* level as well. Thus, H_2O is composed of two atoms of hydrogen and 1 atom of oxygen. Likewise, **1.0 mole of H_2O** is composed **of 2.0 moles of hydrogen** and **1.0 mole of oxygen**. We can also work backwards from molar ratios because *if we know the molar amounts of each element in a compound, we can determine the empirical formula*.

In a procedure called elemental analysis, an unknown compound can be analyzed in the laboratory in order to determine the percentages of each element contained within it. These percentages can be transformed into the mole ratio of the elements, which leads to the empirical formula.

Steps to determine **empirical formula** with given mass percent composition:

1. Assume a 100g sample of the compound so that the given percentages can be directly converted into grams.
2. Use each element's molar mass to convert the grams of each element to moles.
3. In order to find a whole-number ratio, divide the moles of each element by whichever of the moles from step 2 is the smallest.
4. If all the moles at this point are whole numbers (or very close), the empirical formula can be written with the moles as the subscript of each element.
5. In some cases, one or more of the moles calculated in step 3 will not be whole numbers. Multiply each of the moles by the smallest whole number that will convert each into a whole number. Write the empirical formula.

Example

A compound of iron and oxygen is analyzed and found to contain 69.94% iron and 30.06% oxygen. Find the empirical formula of the compound.

Solution

step 1	Assume a 100 g sample, there are 69.96 g Fe and 30.06 g O.
step 2	Convert mass to mol: 69.96 g Fe $\times \frac{1\text{mol Fe}}{55.85\text{ g}} = 1.252\text{ mol Fe}$ 30.03 g O $\times \frac{1\text{mol O}}{16.0\text{ g}} = 1.879\text{ mol O}$
step 3	Divide both moles by the smallest result, which is 1.252 for here: Fe: $\frac{1.252\text{ mol}}{1.252} = 1$ O: $\frac{1.879\text{ mol}}{1.252} = 1.5$ **(note: 1.5 *can't* be round to either 1 or 2)**
step 4 and 5	Multiple each of the moles by the smallest whole number that will convert each into a whole number: Multiple both 1 and 1.5 by 2 for here, to get the whole number mole ratio as 2:3, and the empirical formula of the compound is Fe_2O_3.

Determining Molecular Formula

Below, we see two carbohydrates: glucose and sucrose. Sucrose is almost exactly twice the size of glucose, although their empirical formulas are very similar. Some people can distinguish them on the basis of taste, but it's not a good idea to go around tasting chemicals. The best way to tell glucose and sucrose apart is to determine the molar masses—this approach allows you to easily tell which compound is which.

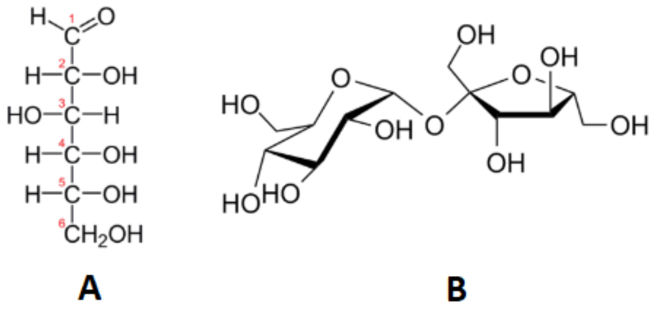


Figure 4.3 (A) the molecular structure of glucose and (B) the molecular structure of sucrose.

Molecular formulas give the actual kind and number of atoms of each element present in the molecular compound. The molecular formula will always be some *integer multiple* (n) of the empirical formula (i.e. integer multiples of the subscripts of the empirical formula).

$$\text{Molecular Formula} = (\text{Empirical formula})_n$$

therefore

$$n = \frac{Molecular\ Formula}{Empirical\ Formula} = \frac{Molar\ Mass}{Empirical\ Formula\ Molar\ Mass}$$

For the case that n=1, the molecular formula is the same as the empirical formula.

The integer multiple, n, can also be obtained by dividing the molar mass, MM, of the compound by the empirical formula mass, EFM (the molar mass represented by the empirical formula).

$$n = \frac{Molar\ Mass}{Empirical\ Formula\ Molar\ Mass}$$

Table 4.1 shows the comparison between the empirical and molecular formula of methane, acetic acid, and glucose, and the different values of n.

Compound	Molecular Formula	Empirical Formula	n
water	H_2O	H_2O	1
acetic acid	$C_2H_4O_2$	CH_2O	2
glucose	$C_6H_{12}O_6$	CH_2O	6

Table 4.1 Molecular Formula vs Empirical Formula of Various Compounds.

The molecular formula of water is H_2O and because it contains only one oxygen atom, that is also its empirical formula. Sometimes, however, the molecular formula is a simple whole number multiple of the empirical formula. Acetic acid is an organic acid that is the main component of vinegar. Its molecular formula is $C_2H_4O_2$. Glucose is a simple sugar that cells use as a primary source of energy. Its molecular formula is $C_6H_{12}O_6$. They are very different compounds, yet both have the same empirical formula of CH_2O.

Empirical formulas can be determined from the percent composition of a compound as discussed earlier in this section. In order to determine its molecular formula, it is necessary to know the molar mass of the compound. In order to go from the empirical formula to the molecular formula, follow these steps:

1. Calculate the empirical formula molar mass.
2. Divide the given molar mass of the compound by the empirical formula molar mass. The result should be a whole number or very close to a whole number.

3. Multiply all the subscripts in the empirical formula by the whole number found in step 2. The result is the molecular formula.

Example

The empirical formula of a compound of boron and hydrogen is BH_3. The molar mass of this compound is 27.7 g/mol. Determine the molecular formula of the compound.

Solution

empirical formula mass = 10.8 + 3×1.0 = 13.8 g/mol

$$n = \frac{Molar\ Mass}{Empirical\ Formula\ Molar\ Mass} = \frac{27.7}{13.8} = 2$$

The molecular formula of the compound is $(BH_3)_2$ or B_2H_6

Combustion Analysis

This section is adapted from https://chem.libretexts.org/Bookshelves/General_Chemistry/Chemistry_(OpenSTAX)/04%3A_Stoichiometry_of_Chemical_Reactions/4.5%3A_Quantitative_Chemical_Analysis by LibreText

The elemental composition of compounds may be determined via a gravimetric method known as combustion analysis. In a combustion analysis, a weighed sample of the compound is heated to a high temperature under a stream of oxygen gas, resulting in its complete combustion to yield gaseous products of known identities. The complete combustion of some organic compounds, for example, will yield carbon dioxide and water as the only products. The gaseous combustion products are swept through separate, pre-weighed collection devices containing compounds that selectively absorb each product (Figure 4.4). The mass increase of each device corresponds to the mass of the absorbed product and may be used in an appropriate stoichiometric calculation to derive the mass of the relevant element.

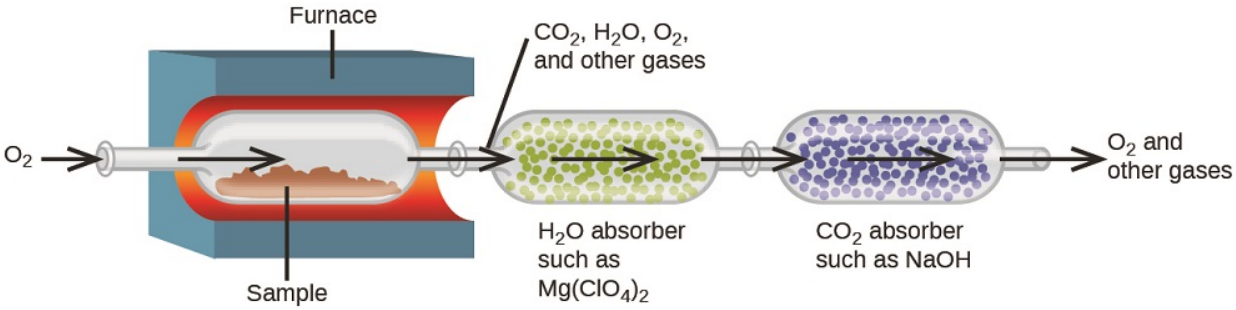


Figure 4.4 This schematic diagram illustrates the basic components of a combustion analysis device

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Example

Vitamin C contains only C, H and O. Combustion of 1.000 g of pure vitamin C produced 1.502 g CO_2 and 0.409 g H_2O. A different experiment determined that the molar mass of vitamin C is 176.12 g/mol. Determine the molecular formula and empirical formula of Vitamin C.

Solution

Step 1: determine the mass of each element from combustion analysis data:

mass of C = 1.502 g $CO_2 \times \frac{12.0\text{ g C}}{44.0\text{ g CO2}} = 0.4096$ g

mass of H =1.502 g $H_2O \times \frac{2.0\text{ g H}}{18.0\text{ g H2O}} = 0.0454$ g

mass of O = mass of sample - mass of C - mass of H = 1.000g – 0.4096g – 0.0454g=0.545 g

Step 2: determine the EF

mol of C = 0.4096g $\times \frac{1\text{ mol C}}{12.0\text{ g}}$ = 0.0341 mol

mol of H = 0.0454g $\times \frac{1\text{ mol H}}{1.0\text{ g}}$ = 0.0454 mol

mol of O = 0.545g $\times \frac{1\text{ mol O}}{16.0\text{ g}}$ = 0.0341 mol

Divide all the mol numbers by the smallest result, which is 0.0341 for here, so

mol of C $= \frac{0.0341}{0.0341} = 1\text{mol}$

mol of H = $\frac{0.0454}{0.0341} = 1.3\text{mol}$

mol of O = $\frac{0.0341}{0.0341} = 1\text{mol}$

multiple all the mol numbers by 3, to convert to the smallest whole number, so the EF is:

$(CH_{1.3}O)_3 = C_3H_4O_3$

Step 3: determine the MF

$$n = \frac{Molar\ Mass}{Empirical\ Formula\ Molar\ Mass} = \frac{176.12}{MM\ of\ C3H4O3} = \frac{176.12}{88} = 2$$

So the MF is $(C_3H_4O_3)_2$ or $C_6H_8O_6$

Chapter 5 Quantities in Chemical Reactions

5.1 Writing and Balancing Chemical Equations

In a chemical change, new substances are formed. In order for this to occur, the chemical bonds of the substances break, and the atoms that compose them separate and rearrange themselves into new substances with new chemical bonds. When this process occurs, we call it a chemical reaction. A **chemical reaction** is the process in which one or more substances are changed into one or more new substances.

Writing Chemical Equations

To describe a chemical reaction, we need to indicate what substances are present at the beginning and what substances are present at the end. The substances that are present at the beginning are called **reactants** and the substances present at the end are called **products**.

In chemical reactions, the reactants are found before the symbol "→" and the products are found after the symbol "→". The general equation for a reaction is:

$$\text{Reactants} \rightarrow \text{Products}$$

When sulfur dioxide is added to oxygen, sulfur trioxide is produced. Sulfur dioxide and oxygen, $SO_2 + O_2$, are reactants and sulfur trioxide, SO_3, is the product.

$$\underbrace{2SO_2(g) + O_2(g)}_{\textbf{reactants}} \rightarrow \underbrace{2SO_3(g)}_{\textbf{products}}$$

In the symbolic equation, chemical formulas are used instead of chemical names for reactants and products. The phase of each substance is indicated by different symbol: (g) is for gas, (l) is for liquid, (s) is for solid and (aq.) is for aqueous solution. It should be apparent that the chemical shorthand method is the quickest and clearest method for writing chemical equations.

To turn word equations into symbolic equations, we need to follow the given steps:

1. Identify the reactants and products. This will help you know which symbols go on each side of the arrow and where the + signs go.
2. Write the correct formulas for all compounds. (Apply the rules we learned in Chapter 3).
3. Write the correct formulas for all elements. Usually this is given straight off of the periodic table. However, there are seven elements that are diatomic molecules, meaning that they are always found in pairs in nature. These elements as diatomic molecules are H_2, N_2, O_2, F_2, Cl_2, Br_2, I_2. These list is also available in section 3.1 of Chapter 3.

Example

Write chemical equation for the reaction that solid copper reacts with an aqueous solution of silver nitrate to produce a solution of copper (II) nitrate with solid silver.

Solution

$Cu(s) + AgNO_3(aq) \rightarrow Cu(NO_3)_2(aq) + Ag(s)$

Balance Chemical Equations

In chemical reactions, atoms are never created or destroyed. The same atoms that were present in the reactants are present in the products—they are merely reorganized into different arrangements. That means atoms are **conserved** in a chemical reaction, there must be the same number of each type of atom on both sides of the equation. So a complete chemical equation must be a balanced chemical equation.

The chemical equation can be balanced by adjusting the **coefficients. Coefficients** are the smallest integers (whole numbers) in front of the substance in a chemical equation, they indicate indicate the number (and the number of moles) of each substance involved in the reaction. It is important to distinguish between coefficient in a chemical equation and subscript in a chemical formula. The **subscripts** are part of the formulas and once the formulas for the reactants and products are determined, the subscripts ***can not*** be changed. ***Only coefficients can be modified in order to balance the equation.***

The simplest and most generally useful method for balancing chemical equations is “inspection,” better known as trial and error. The following is an efficient approach to balancing a chemical equation using this method.

Steps in Balancing a Chemical Equation

1. Identify the most complex substance.
2. Beginning with that substance, choose an element(s) that appears in only one reactant and one product, if possible. Adjust the coefficients to obtain the same number of atoms of this element(s) on both sides.
3. Balance polyatomic ions (if present on both sides of the chemical equation) as a unit.
4. Balance the remaining atoms, usually ending with the least complex substance and using fractional coefficients if necessary. If a fractional coefficient has been used, multiply both sides of the equation by the denominator to obtain whole numbers for the coefficients.
5. Count the numbers of atoms of each kind on both sides of the equation to be sure that the chemical equation is balanced.

Example

Balance the chemical equation for the combustion of heptane C_7H_{16}:

$$C_7H_{16}\ (l) + O_2\ (g) \rightarrow CO_2\ (g) + H_2O\ (l)$$

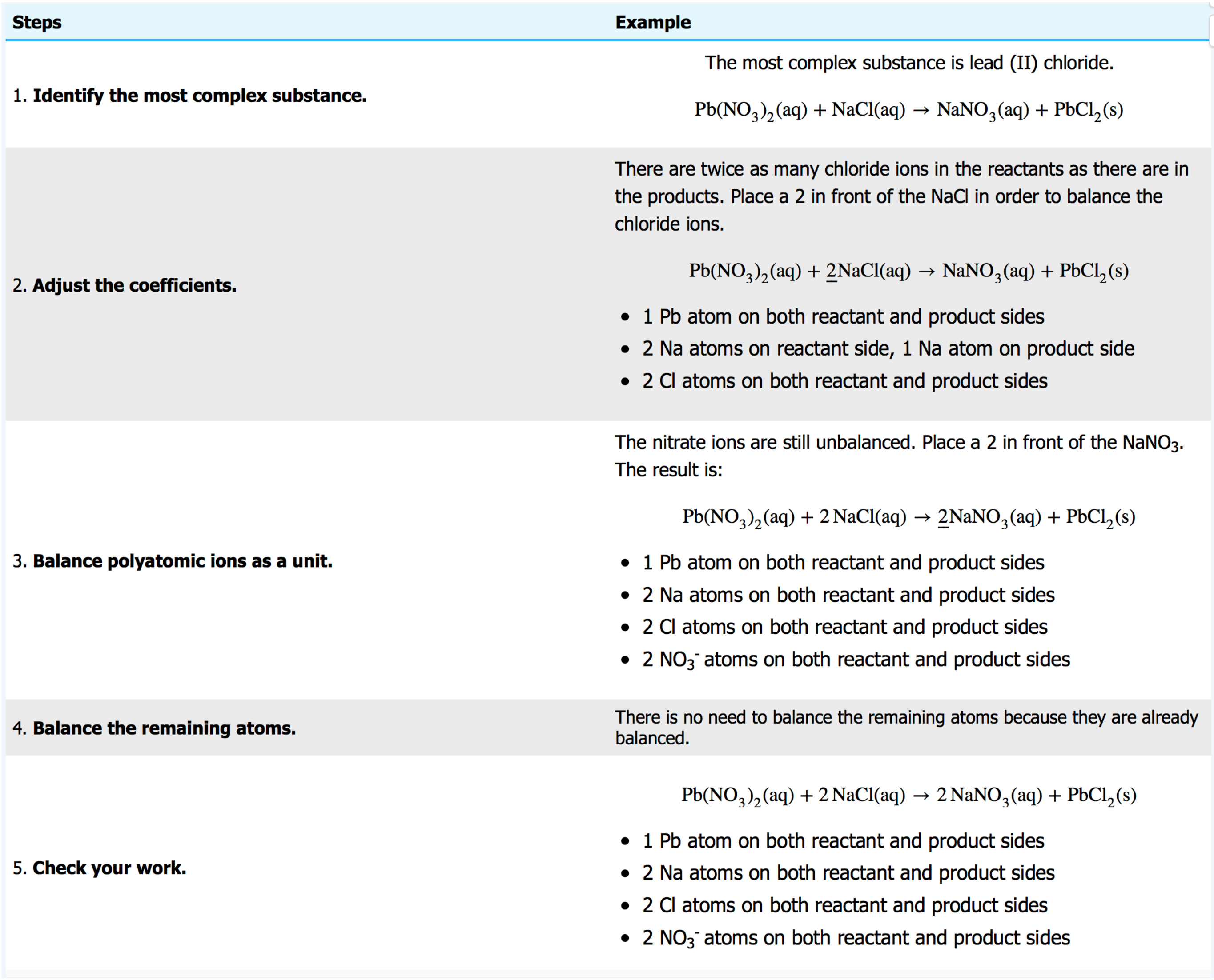
Solution

1. Identify the most complex substance.	The most complex substance is the one with the largest number of different atoms, which is C_7H_{16}. We will assume initially that the final balance equation contains 1 mol of this substance
2. Adjust the coefficients	a. Because one molecule of n-heptane contains 7 carbon atoms, we need 7 CO_2 molecules, each of which contains 1 carbon atom, on the right side: $C_7H_{16}\ (l) + O_2\ (g) \rightarrow \underline{\mathbf{7}}\ CO_2\ (g) + H_2O\ (l)$ • 7 carbon atoms on both reactant and product sides b. Because one molecule of n-heptane contains 16 hydrogen atoms, we need 8 H_2O molecules, each of which contains 2 hydrogen atoms, on the right side: $C_7H_{16}\ (l) + O_2\ (g) \rightarrow 7\ CO_2\ (g) + \underline{\mathbf{8}}\ H_2O\ (l)$ • 16 hydrogen atoms on both reactant and product sides
3. Balance the polyatomic ions.	There are no polyatomic ions in this reaction.
4. Balance the remaining atoms	The carbon and hydrogen atoms are now balances, but we have 22 oxygen atoms on the right side any only 2 oxygen atoms on the left side. The oxygen atoms can be balanced by adjusting the coefficient in front of the least complex substance O_2. $C_7H_{16}\ (l) + \underline{\mathbf{11}}\ O_2\ (g) \rightarrow 7\ CO_2\ (g) + 8\ H_2O\ (l)$
5. Check your work	The equation is now balanced. $C_7H_{16}\ (l) + 11\ O_2\ (g) \rightarrow 7\ CO_2\ (g) + 8\ H_2O\ (l)$

Example

Balance the chemical equation: $Pb(NO_3)_2\ (aq) + NaCl\ (aq) \rightarrow NaNO_3\ (aq) + PbCl_2\ (s)$

Solution



Steps	Example
1. **Identify the most complex substance.**	The most complex substance is lead (II) chloride. $Pb(NO_3)_2(aq) + NaCl(aq) \rightarrow NaNO_3(aq) + PbCl_2(s)$
2. **Adjust the coefficients.**	There are twice as many chloride ions in the reactants as there are in the products. Place a 2 in front of the NaCl in order to balance the chloride ions. $Pb(NO_3)_2(aq) + \underline{2}NaCl(aq) \rightarrow NaNO_3(aq) + PbCl_2(s)$ • 1 Pb atom on both reactant and product sides • 2 Na atoms on reactant side, 1 Na atom on product side • 2 Cl atoms on both reactant and product sides
3. **Balance polyatomic ions as a unit.**	The nitrate ions are still unbalanced. Place a 2 in front of the $NaNO_3$. The result is: $Pb(NO_3)_2(aq) + 2\,NaCl(aq) \rightarrow \underline{2}NaNO_3(aq) + PbCl_2(s)$ • 1 Pb atom on both reactant and product sides • 2 Na atoms on both reactant and product sides • 2 Cl atoms on both reactant and product sides • 2 NO_3^- atoms on both reactant and product sides
4. **Balance the remaining atoms.**	There is no need to balance the remaining atoms because they are already balanced.
5. **Check your work.**	$Pb(NO_3)_2(aq) + 2\,NaCl(aq) \rightarrow 2\,NaNO_3(aq) + PbCl_2(s)$ • 1 Pb atom on both reactant and product sides • 2 Na atoms on both reactant and product sides • 2 Cl atoms on both reactant and product sides • 2 NO_3^- atoms on both reactant and product sides

Example

Balance the following chemical equations.

a. $N_2(g) + O_2(g) \rightarrow NO_2(g)$

b. $Pb(NO_3)_2(aq) + FeCl_3(aq) \rightarrow Fe(NO_3)_3(aq) + PbCl_2(s)$

c. $C_2H_5OH(l) + O_2(g) \rightarrow CO_2(g) + H_2O(g)$

Solutions

a. $N_2(g) + 2O_2(g) \rightarrow 2NO_2(g)$

b. $3Pb(NO_3)_2(aq) + 2FeCl_3(aq) \rightarrow 2Fe(NO_3)_3(aq) + 3PbCl_2(s)$

c. $C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(g)$

5.2: Stoichiometry

You have learned that chemical equations provide us with information about the types of particles that react to form products. Chemical equations also provide us with the relative number of particles and moles that react to form products. In this section you will explore the quantitative relationships that exist between the quantities of reactants and products in a balanced equation. This is known as **stoichiometry**.

Stoichiometry, by definition, is the calculation of the quantities of reactants or products in a chemical reaction using the relationships found in the balanced chemical equation.

Interpreting Chemical Equations

The mole, as you remember, is a quantitative measure that is equivalent to Avogadro's number of particles. So how does this relate to the chemical equation? Look at the chemical equation below (the phases of the substances are skipped here).

$$2CuSO_4 + 4KI \rightarrow 2CuI + 2K_2SO_4 + I_2$$

The coefficients used, as we have learned, tell us the relative amounts of each substance in the equation. So for every 2 units of copper (II) sulfate (CuSO4) we have, we need to have 4 units of potassium iodide (KI). Because the unit "mole" is also a counting unit, we can interpret this equation in terms of moles, as well: For every **2 moles** of copper (II) sulfate, we need **4 moles** potassium iodide.

Consider another simple chemical equation:

$$2H_2 + O_2 \rightarrow 2H_2O$$

We see that 2 molecule of hydrogen reacts with 1 molecules of oxygen to form 2 molecules of water. This is the smallest possible relative amount of the reactants and products. To consider larger relative amounts, each coefficient can be multiplied by the same number. For example, 20 molecules of hydrogen would react with 10 molecules of oxygen to produce 20 molecules of water.

The most useful quantity for counting particles is the mole. So if each coefficient is multiplied by a mole, the balanced chemical equation tells us that 2 mole of hydrogen reacts with 1 moles of oxygen to produce 2 moles of water. This is the conventional way to interpret any balanced chemical equation.

$$2\text{mol } H_2 + 1\text{mol } O_2 \rightarrow 2\text{mol } H_2O$$

Now we interpret the coefficients as referring to **mole** amounts, not individual molecules.

Mole-to-Mole conversions

By interpreting the coefficients as mole amounts, the mole amount relationship between any two substances in the above balanced equation can be established. For example, the mole relationship between hydrogen and oxygen is:

$$2\text{mol } H_2 = 1\text{mol } O_2$$

The "=" sign here means that in the formation of water reaction equation, every two moles of hydrogen react with 1 mol of oxygen. Such relationship can also be rewritten the format of mole ratio:

$$\frac{2 \text{ mol } H_2}{1 \text{ mol } O_2} \text{ or } \frac{1 \text{ mol } O_2}{2 \text{ mol } H_2}$$

The ratios between any two other substances in the above equation can also be constructed as:

$$\frac{2 \text{ mol } H_2O}{1 \text{ mol } O_2} \text{ or } \frac{1 \text{ mol } O_2}{2 \text{ mol } H_2O} \quad \frac{2 \text{ mol } H_2}{2 \text{ mol } H_2O} \text{ or } \frac{2 \text{ mol } H_2O}{2 \text{ mol } H_2}$$

We can use these mole ratios as conversion factors to determine what amount of a substance, in moles, will react with or produce a given number of moles of a different substance. As mentioned earlier, this is called *stoichiometry*.

Example

How many moles of oxygen is required to produce 27.6 mol of H_2O?

Solution

Steps	
1.Balanced equation:	$2H_2 + O_2 \rightarrow 2H_2O$
2.Identify the "given" information and the "unknown"	"given": mol of H_2O "unknown": mol of O_2
3.List the mole relation between "given" and "unknown"	$1\text{mol } O_2 = 2\text{mol } H_2O$
4.Rewrite as mole ratio	$\frac{2 \text{ mol } H_2O}{1 \text{ mol } O_2}$ or $\frac{1 \text{ mol } O_2}{2 \text{ mol } H_2O}$
5.Use the proper mole ratio to calculate the "unknown"	$27.6\text{mol } \cancel{H_2O} \times \frac{1 mol\ O_2}{2\ mol\ \cancel{H_2O}} = 13.8 \text{ mol } O_2$ required

Example

Balance the following equation and determine how many moles of water are prepared when 1.65mol of NH_3 react. $NH_3 + O_2 \rightarrow N_2 + H_2O$

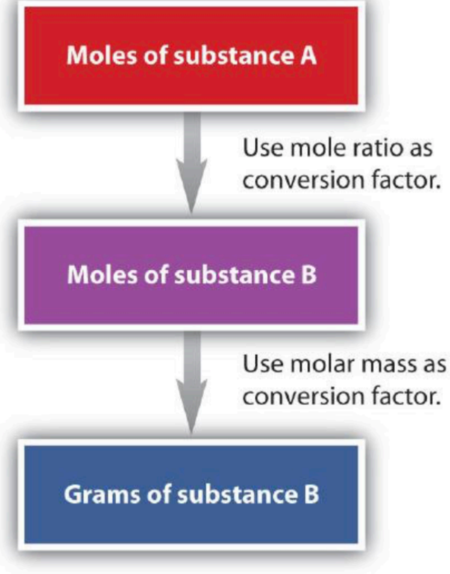
Solution

The balanced equation is: $4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O$

$1.65\text{mol } NH_3 \times \frac{6\ mol\ H_2O}{4\ mol\ \cancel{HN_3}} = 2.48 \text{ mol } H_2O$ are prepared.

Mole-to-Mass Conversions

We have learned how to use mole ratio as conversion factor to answer stoichiometric questions—such as how many moles of substance A react with so many moles of reactant B. We can extend this technique even further to mass, with the involvement of molar mass. We can use that relation to answer stoichiometry questions in terms of the masses of a particular substance, in addition to moles. We do this using the following sequence:



Example

Consider the balanced chemical equation: $Fe_2O_3 + 3SO_3 \rightarrow Fe_2(SO_4)_3$

If we have 3.59 mol of Fe_2O_3, how many grams of SO_3 required to react with it?

Solution

As usual, we start with the quantity were given, and calculate the mole of SO_3:

$$3.59\ \cancel{\text{mol Fe}_2\text{O}_3} \times \left(\frac{3\ \text{mol SO}_3}{1\ \cancel{\text{mol Fe}_2\text{O}_3}}\right) = 10.77\ \text{mol SO}_3$$

Now, we take this answer and convert it to grams of SO_3, using the molar mass of SO_3 as the conversion factor:

$$10.77\ \cancel{\text{mol SO}_3} \times \left(\frac{80.06\ \text{g SO}_3}{1\ \cancel{\text{mol SO}_3}}\right) = 862\ \text{g SO}_3$$

Usually, the two steps can be combined in a single line, rather than as two separate steps, as follows:

$$3.59\ \cancel{mol\ Fe_2O_3} \times \underbrace{\left(\frac{3\ \cancel{mol\ SO_3}}{1\ \cancel{mol\ Fe_2O_3}}\right)}_{\text{converts to moles of SO}_3} \times \underbrace{\left(\frac{80.06\ g\ SO_3}{1\ \cancel{mol\ SO_3}}\right)}_{\text{converts to grams of SO}_3} = 862\ g\ SO_3$$

Example

How many moles of HCl will be produced when 249 g of $AlCl_3$ are reacted according to this chemical equation? $2AlCl_3 + 3H_2O \rightarrow Al_2O_3 + 6HCl$

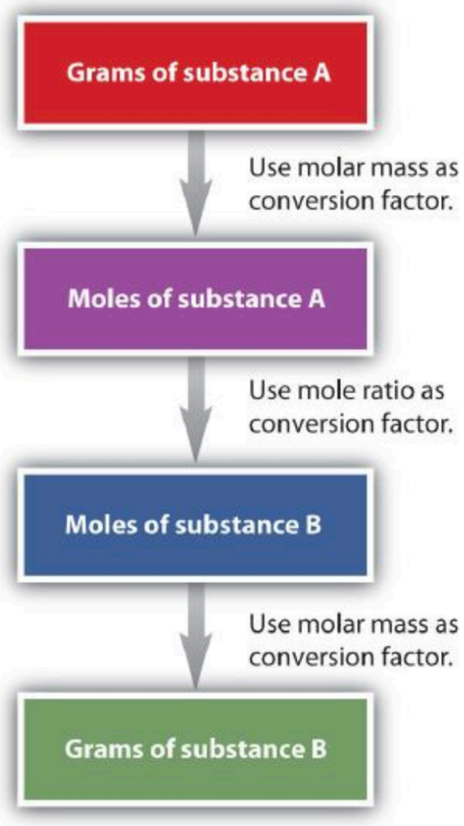
Solution

$$249\ \cancel{g\,AlCl_3} \times \frac{1\ \cancel{mol\,AlCl_3}}{133.33\ \cancel{g\,AlCl_3}} \times \frac{6\,mol\,HCl}{2\ \cancel{mol\,AlCl_3}} = 5.60\,mol\,HCl$$

Mass-to-Mass Conversions

The most common situation we have for stoichiometry, however, is the mass-to-mass conversion. This is because that mass is the amount that can be measured conveniently in real practice, not mole.

If we start with a known mass of one substance A in a chemical reaction, we can calculate the corresponding masses of another substance B in the reaction, by following a three-step sequence:



This three-step process can be carried out in three discrete steps or combined into a single calculation that contains three conversion factors. The latter way is used more commonly because of its convenience.

Make sure you understand and double check each conversion factor carefully when put them together.

Example

Ammonium nitrate decomposes to dinitrogen monoxide and water according to the following equation. $NH_4NO_3(s) \rightarrow N_2O(g) + 2H_2O(l)$

In a certain experiment, 45.7g of ammonium nitrate is decomposed. Find the mass of each of the products formed.

Solution

Step 1. Preparation: determine the molar mass of each substance:

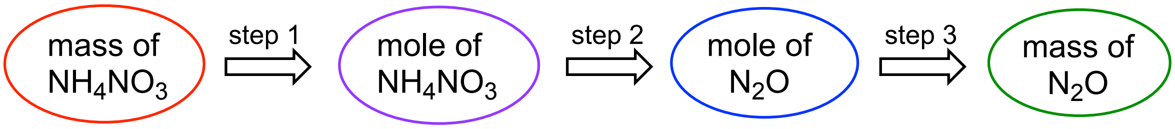
MM of NH_4NO_3: 80.06 g/mol

MM of N_2O: 44.02 g/mol

MM of H_2O: 18.02 g/mol

Step 2. To solve the amount of product $N_2O(g)$:

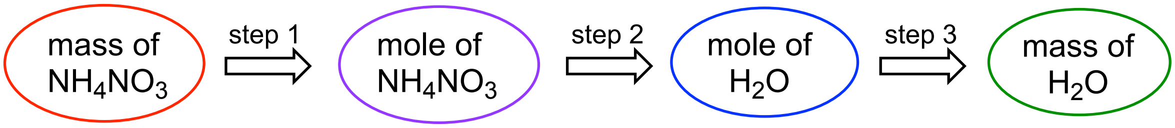
The concept map of the three-step process is:



Calculation:

$$45.7 \text{ g NH}_4\text{NO}_3 \times \frac{1 \text{ mol NH}_4\text{NO}_3}{80.06 \text{ g NH}_4\text{NO}_3} \times \frac{1 \text{ mol N}_2\text{O}}{1 \text{ mol NH}_4\text{NO}_3} \times \frac{44.02 \text{ g N}_2\text{O}}{1 \text{ mol N}_2\text{O}} = 25.1 \text{ g N}_2\text{O}$$

Step 3. To solve the amount of product $H_2O(l)$:



Calculation:

$$45.7\ \text{g NH}_4\text{NO}_3 \times \frac{1\ \text{mol NH}_4\text{NO}_3}{80.06\ \text{g NH}_4\text{NO}_3} \times \frac{2\ \text{H}_2\text{O}}{1\ \text{mol NH}_4\text{NO}_3} \times \frac{18.02\ \text{g H}_2\text{O}}{1\ \text{mol H}_2\text{O}} = 20.6\ \text{g H}_2\text{O}$$

Example

Methane can react with chlorine to make carbon tetrachloride (CCl_4). The balanced chemical equation is as follows: $CH_4\ (g) + 4Cl_2\ (g) \rightarrow CCl_4\ (l) + 4HCl\ (l)$

How many grams of HCl are produced by the reaction of 100.0g of CH_4 with enough chlorine?

Solution

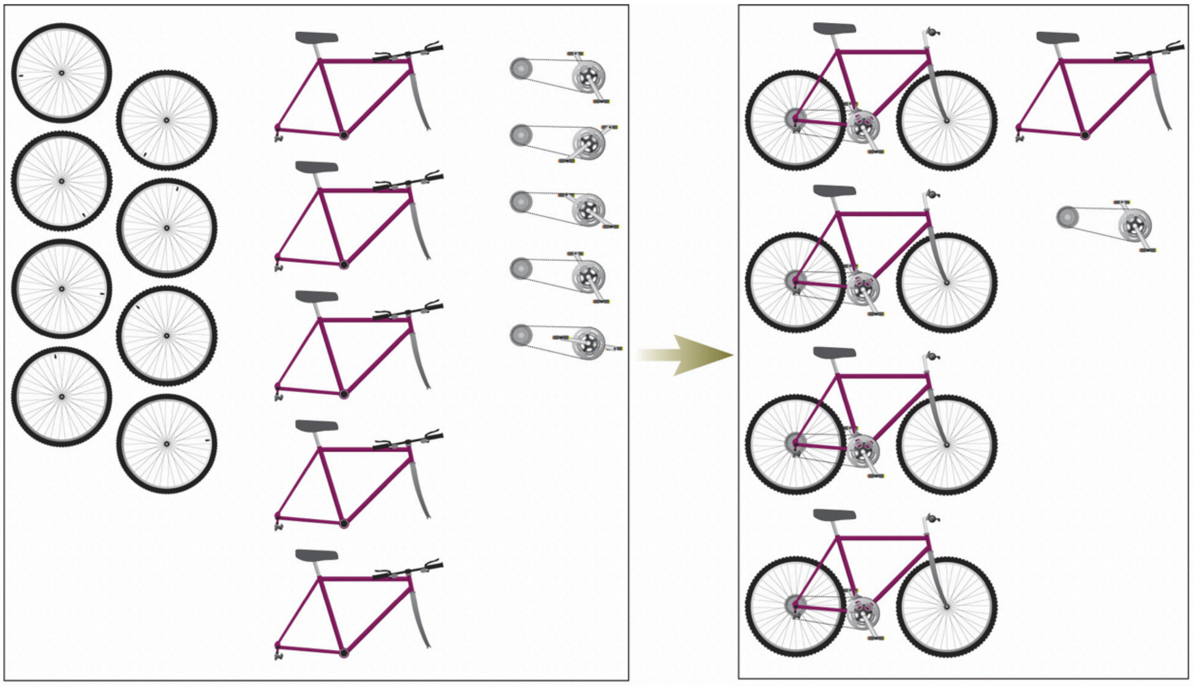
MM of CH_4 is 16.0g/mol; MM of HCl is 36.5g/mol

$$100.0\text{g}\ \cancel{\text{CH}_4} \times \frac{1\ \cancel{mol\ CH4}}{16.0g\ \cancel{CH4}} \times \frac{4\ \cancel{mol\ HCl}}{1\ \cancel{mol\ CH4}} \times \frac{36.5g\ HCl}{1\ \cancel{mol\ HCl}} = 912.5g\ \text{HCl}$$

5.3: Limiting Reagent

In all examples discussed thus far, the reactants were assumed to be present in stoichiometric quantities. Consequently, none of the reactants were left over at the end of the reaction. This is often desirable—as in the case of a space shuttle—where excess oxygen or hydrogen is not only extra freight to be hauled into orbit, but also an explosion hazard. More often, however, reactants are present in mole ratios that are not the same as the ratio of the coefficients in the balanced chemical equation. As a result, one or more of them will not be used up completely, but will be left over when the reaction is completed. In this situation, the amount of product that can be obtained is limited by the amount of only one of the reactants. The reactant that restricts the amount of product obtained is called the **limiting reagent (or limiting reactant)**. The reactant that remains after a reaction has gone to completion is **in excess**.

Consider a nonchemical example. Assume you work in a bicycle factory and assemble bicycles. There are 8 wheels, 5 frames and 5 chains in the stock, how many bicycles can you make?



2 wheels + 1 frame + 1 chain → bicycle

8 wheels + 5 frames + 5 chains → 4 bicycle + 1 frames + 1 chains

The answer seems obvious for this example. To make one bicycle, 2 wheels, 1 frame and 1 chain are required. Therefore 4 bicycles can be made with the available stock, and 1 frame and 1 chain will be left. Because the wheels are used up first, and the amount of bicycle is limited by the amount of wheels, so "8 wheels" is the "**limiting reagent**" for this example.

How to Identify Limiting Reagent

Consider this concept now with regard to a chemical process, the Haber process to produce ammonia:

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

When 1.5mol of H_2 and 1.0mol of N_2 are combined, which is the limiting reagent and how many moles of NH_3 is produced?

An approach to identifying the limiting reactant involves comparing the amount of product expected for the complete reaction of each reactant. Each reactant amount is used to separately calculate the amount of product that would be formed per the reaction's stoichiometry. The reactant yielding the **lesser amount** of product is the **limiting reactant**. Just like in the bicycle example, that 8 wheels give 4 bicycles, and 5 frames produce 5 bicycles. So 8 wheels is the "limiting" part.

For the Haber process example, we need to compare between the following two situations:

- Complete reaction of the available hydrogen would yield:

$$\text{mol of } NH_3 \text{ produced} = 1.\cancel{5\,mol\,H_2} \times \frac{2\,mol\,NH_3}{3\cancel{mol\,H_2}} = 1.0 mol\ NH_3$$ **(less amount)**

- Complete reaction of the available nitrogen would yield:

$$\text{mol of } NH_3 \text{ produced} = 1.0\cancel{mol\,N_2} \times \frac{2\,mol\,NH_3}{1\cancel{mol\,N_2}} = 2.0 mol\ NH_3$$

If all the available hydrogen H_2 will be completely consumed, 1.0 moles of NH_3 will be produced, which is **less** than the amount of NH_3 would be produced if all the available N_2 have been produced. ***The reactant that produces less amount of the product is the limiting reagent (L.R.).*** Hydrogen H_2, therefore, is the limiting reactant and nitrogen N_2 is the excess reactant. And the amount of the produce is also determined (or limited) by the amount of L.R., there are 1.0mol of NH_3 produced for this example. Meanwhile there will be non-reacted nitrogen N_2 remaining once this reaction is complete.

Usually the amounts of reactants will be given by mass, so the mass-to-mole conversion is necessary as part of the comparison step. The steps to identify the Limiting Reagent are summarized below.

Find the limiting reactant by calculating and comparing the amount of product that each reactant will produce:

1. Balance the chemical equation for the chemical reaction.
2. Convert the given information into moles.
3. Use stoichiometry for each individual reactant to find the mass of product produced.
4. The reactant that produces a **lesser** amount of product is the limiting reactant.
5. The reactant that produces a larger amount of product is the excess reactant.
6. To find the amount of remaining excess reactant, subtract the mass of excess reactant consumed from the total mass of excess reactant given.

Note: The smaller amount (mass or mole) of reactant is *not* necessarily the limiting reagent. Like in the bicycle example, the limiting reagent is "8 wheels" instead not "5 frames". The key to recognizing which reactant is the limiting reactant is based on a mole-mass or mass-mass calculation: **whichever reactant gives the *lesser* amount of product is the limiting reactant.** So what we need to do is determine an amount of one product (either moles or mass) assuming all of each reactant reacts. It does not matter which product we use, as long as we use the same one each time. It does not matter whether we determine the number of moles or grams of that product; however, we will see shortly knowing that the final mass of product can be useful.

Example

In the reaction of magnesium metal and oxygen, calculate the mass of magnesium oxide that can be produced if 2.40g Mg reacts with 10.0g O_2. Also determine the leftover amount of excess reactant. $2Mg(s) + O_2(g) \rightarrow 2MgO(s)$

Solution

Step 1: Balance the chemical equation: as given above.

Step 2: Convert mass to moles and do stoichiometry.

$$2.40\ \cancel{\text{g Mg}} \times \frac{1\ \cancel{\text{mol Mg}}}{24.31\ \cancel{\text{g Mg}}} \times \frac{2\ \cancel{\text{mol MgO}}}{2\ \cancel{\text{mol Mg}}} \times \frac{40.31\ \text{g MgO}}{1\ \cancel{\text{mol MgO}}} = 3.98\ \text{g MgO} \qquad \textbf{(less amount)}$$

$$10.0\ \cancel{\text{g O}_2} \times \frac{1\ \cancel{\text{mol O}_2}}{32.00\ \cancel{\text{g O}_2}} \times \frac{2\ \cancel{\text{mol MgO}}}{1\ \cancel{\text{mol O}_2}} \times \frac{40.31\ \text{g MgO}}{1\ \cancel{\text{mol MgO}}} = 25.2\ \text{g MgO}$$

Step 3: Determine the limiting reagent by comparing the numbers in step 2.

2.40g Mg produces ***less*** MgO than does 10.0g O_2, therefore **2.40g Mg is the limiting reagent** in this reaction.

Step 5: 10.0g O_2 is the excess reactant in this reaction, and $O_{2\ \text{leftover}} = O_{2\ \text{total}} - O_{2\ \text{used}}$

The amount of O_2 used can be calculated using the amount of limiting reagent:

$$2.40\ \cancel{\text{g Mg}} \times \frac{1\ \cancel{\text{mol Mg}}}{24.31\ \cancel{\text{g Mg}}} \times \frac{1\ \cancel{\text{mol O}_2}}{2\ \cancel{\text{mol Mg}}} \times \frac{32.00\ \text{g O}_2}{1\ \cancel{\text{mol O}_2}} = 1.58\ \text{g O}_2$$

So, $O_{2\ \text{leftover}} = O_{2\ \text{total}} - O_{2\ \text{used}} = 10.0\text{g} - 1.58\text{g} = 8.4\text{g}\ O_2$ leftover

Example

1. What is the limiting reactant if 78.0 grams of Na_2O_2 were reacted with 29.4 grams of H_2O? The unbalanced chemical equation is: $Na_2O_2(s) + H_2O(l) \rightarrow NaOH(aq) + H_2O_2(l)$

2. 5.00 g quantity of Rb is combined with 3.44 g of $MgCl_2$ according to this chemical reaction:

$2Rb(s) + MgCl_2(s) \rightarrow Mg(s) + 2RbCl(s)$

What mass of Mg is formed, and what mass of excess reactant is left over?

Solution

1.

Step 1: Balance the reaction equation: $Na_2O_2(s) + 2H_2O(l) \rightarrow 2NaOH(aq) + H_2O_2(l)$

Step 2: Convert mass to moles and do stoichiometry.

MM of Na_2O_2 is: 82.0 g/mol; MM of H_2O is 18.0 g/mol

$$78.0\text{g } \cancel{Na_2O_2} \times \frac{\cancel{1\, mol\, Na_2O_2}}{\cancel{82.0g\, Na_2O_2}} \times \frac{2\, mol\, NaOH}{1\, \cancel{mol\, Na_2O_2}} = 1.90\, mol\, NaOH$$

$$29.4\text{g } \cancel{H_2O} \times \frac{1\, \cancel{mol\, H_2O}}{18.0g\, \cancel{H_2O}} \times \frac{2\, mol\, NaOH}{2\cancel{mol\, H_2O}} = 1.63\, mol\, NaOH$$

Step 3: Determine the limiting reagent by comparing the numbers in step 2.

78.0g of Na_2O_2 produces ***less*** amount of product than does 29.4g H_2O, therefore **78.0g of Na_2O_2 is the limiting reagent** in this reaction.

2.

Step 1: Convert mass to moles and do stoichiometry.

MM of Rb is: 85.5 g/mol; MM of $MgCl_2$ is 95.2 g/mol

$$5.0\text{g } \cancel{Rb} \times \frac{1\, \cancel{mol\, Rb}}{85.5g\, \cancel{Rb}} \times \frac{1\, \cancel{mol\, Mg}}{2\, \cancel{mol\, Rb}} \times \frac{24.3g\, Mg}{1\, \cancel{mol\, Mg}} = 0.71g\, Mg$$

$$3.44\text{g } \cancel{MgCl_2} \times \frac{1\, \cancel{mol\, MgCl_2}}{95.2g\, \cancel{MgCl_2}} \times \frac{1\, \cancel{mol\, Mg}}{1\, \cancel{mol\, MgCl_2}} \times \frac{24.3g\, Mg}{1\, \cancel{mol\, Mg}} = 0.88g\, Mg$$

Step 3: Determine the limiting reagent by comparing the numbers in step 2.

5.0g of Rb produces ***less*** amount of product than does 3.44g $MgCl_2$, therefore **5.0g of Rb is the limiting reagent** in this reaction, and **0.71g of Mg(s) product** is formed.

Step 4: Determine the left over amount of excess reactant.

$MgCl_{2\ \text{leftover}} = MgCl_{2\ \text{total}} - MgCl_{2\ \text{used}}$

$$= 3.44\text{g} - 5.0\text{g}\ \cancel{\text{Rb}} \times \frac{1\ \cancel{mol\ Rb}}{85.5g\ \cancel{Rb}} \times \frac{1\ \cancel{mol\ MgCl2}}{2\ \cancel{mol\ Rb}} \times \frac{95.2g}{1\ \cancel{mol\ MgCl2}}$$

$$= 3.44\text{g} - 2.78\text{g} = 0.66\text{g}\ MgCl_{2\ \text{leftover}}$$

5.4: Theoretical Yield and Percent Yield

Chemical reactions in the real world don't always go exactly as planned on paper. In the course of an experiment, many things will contribute to the formation of less product than predicted. Besides spills and other experimental errors, there are usually losses due to an incomplete reaction, undesirable side reactions, etc. Chemists need a measurement that indicates how successful a reaction has been. This measurement is called the percent yield.

To compute the percent yield, it is first necessary to determine how much of the product should be formed based on stoichiometry. This is called the **theoretical yield**, the maximum amount of product that can be formed from the given amounts of reactants. The amount of product that was calculated with limiting reagent in the previous section is also the theoretical yield. The **actual yield** is the amount of product that is actually formed when the reaction is carried out in the laboratory. The **percent yield** is the ratio of the actual yield to the theoretical yield, expressed as a percentage.

$$\text{percent yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100\%$$

Percent yield is very important in the manufacture of products. Much time and money is spent improving the percent yield for chemical production. When complex chemicals are synthesized by many different reactions, one step with a low percent yield can quickly cause a large waste of reactants and unnecessary expense.

Typically, percent yields are understandably less than 100% because of the reasons indicated earlier.

Example

Potassium chlorate decomposes upon slight heating in the presence of a catalyst, according to the reaction below: $2KClO_3(s) \rightarrow 2KCl(s) + 3O_2(g)$

In a certain experiment, 40.0g $KClO_3$ is heated until it completely decomposes and 14.9g oxygen gas is collected.

a. What is the theoretical yield of oxygen gas?
b. What is the percent yield for the reaction?

Solution

MM of $KClO_3$ = 122.55 g/mol; MM of O_2 = 32.0 g/mol

a. Apply stoichiometry to convert from the mass of $KClO_3$ to the mass of product O_2, that is the theoretical yield of O_2:

$$40.0\ \cancel{\text{g KClO}_3} \times \frac{1\ \cancel{\text{mol KClO}_3}}{122.55\ \cancel{\text{g KClO}_3}} \times \frac{3\ \cancel{\text{mol O}_2}}{2\ \cancel{\text{mol KClO}_3}} \times \frac{32.00\ \text{g O}_2}{1\ \cancel{\text{mol O}_2}} = 15.7\ \text{g O}_2$$

b. The given amount of 14.9g O_2 is the actual yield, use the theoretical yield obtained in part a, work out the percent yield:

$$\text{percent yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100\% = \frac{14.9\text{ g}}{15.7\text{ g}} \times 100\% = 94.9\ \%$$

5.5 Percent Purity

In all the examples so far, we always assume that all the reagents are completely pure, however this may not be case for most practical situations. If a sample is not pure, that is congaing certain percentage of inactive impurity (the impurity does not takes in part of the reaction), then this factor need to be accounted in for the stoichiometry calculation.

The percent purity of a reagent is defined as:

$$\text{percent purity} = \frac{\text{mass of pure compound}}{\text{total mass of the impure sample}} \times 100\%$$

Example

A sample of 12.0 g of impure Zn metal (mixed with inactive impurity) is added to excess amount of HCl, and 0.222 g of H_2 gas is formed by reaction:

$$Zn + 2HCl \rightarrow ZnCl_2 + H_2$$

Determine the percent purity of zinc in the mixture.

Solution

The amount of pure Zn metal can be calculated from the amount of H_2 gas produced:

$$0.222\text{g } \cancel{H_2} \times \frac{1\ \cancel{mol\ H_2}}{2.0g\ \cancel{H_2}} \times \frac{1\ \cancel{mol\ Zn}}{1\ \cancel{mol\ H_2}} \times \frac{65.4g\ Zn}{1\ \cancel{mol\ Zn}} = 7.26g\ \text{Zn}$$

$$\text{percent purity} = \frac{\text{mass of pure compound}}{\text{total mass of the impure sample}} \times 100\%$$

$$= \frac{7.26\ g\ Zn}{12.0\ g\ total\ sample} \times 100\% = 60.5\%$$

Chapter 6 Different Types of Chemical Reactions

6.1 Aqueous Solutions

When some substances are dissolved in water, they undergo a physical change that yields ions in solution. These substances constitute an important class of compounds called electrolytes. Substances that do not yield ions when dissolved are called nonelectrolytes. If the physical process that generates the ions is essentially 100% efficient (all of the dissolved compound yields ions), then the substance is known as a strong electrolyte. If only a relatively small fraction of the dissolved substance undergoes the ion-producing process, it is called a weak electrolyte.

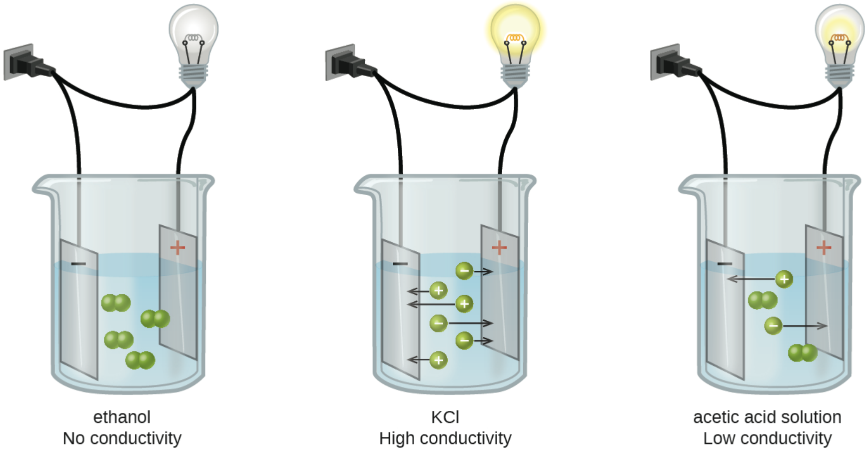


Figure 6.1 Solutions of nonelectrolytes (ethanol), strong electrolyte (KCl) and weak electrolyte (acetic acid)

Water and other polar molecules are attracted to ions, as shown in Figure 6.2. The electrostatic attraction between an ion and a molecule with a dipole is called an ion-dipole attraction. These attractions play an important role in the dissolution of ionic compounds in water.

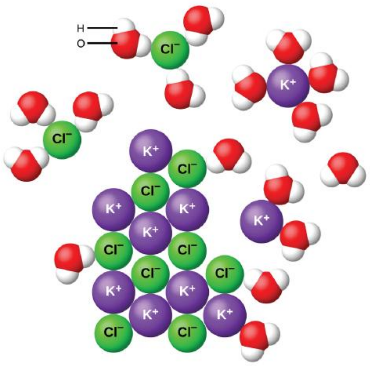


Figure 6.2 As potassium chloride (KCl) dissolves in water, the ions are surrounded by water molecules by ion-dipole interaction

When ionic compounds like KI dissolve in water, the ions in the solid separate and disperse uniformly throughout the solution because water molecules surround and solvate the ions by ion-dipole attraction. This process represents a physical change known as **dissociation**. Under most conditions, ionic compounds will dissociate nearly completely when dissolved, and so they are classified as strong electrolytes. As shown in Figure 6.2, the dissociation of solid KI in aqueous solution can be shown by chemical equation:

$$\text{KI (aq)} \rightarrow \text{K}^{+}\text{ (aq)} + \text{I}^{-}\text{ (aq)}$$

Example: Show chemical equation for the dissociation of following compounds in aqueous solution.

a. $CaCl_2$
b. Na_3PO_4
c. $(NH_4)_2SO_4$

Answers:

a. $CaCl_2\text{ (aq)} \rightarrow Ca^{2+}\text{ (aq)} + 2Cl^{-}\text{ (aq)}$
b. $Na_3PO_4\text{ (aq)} \rightarrow 3Na^{+}\text{ (aq)} + (PO_4)^{3-}\text{ (aq)}$
c. $(NH_4)_2SO_4 \rightarrow 2NH_4^{+}\text{ (aq)} + (SO_4)^{2-}\text{ (aq)}$

Note:

- For the ions on product side, make sure the proper charge of the ion is give, for example Ca^{2+}, $(PO_4)^{3-}$.
- Pay attention to the coefficient of the ions, which is consistent to the subscript in the formula of ionic compound.

Not all ionic compounds dissociate completely in aqueous solution. In other cases, the ion-dipole attractive forces between the ions and water molecules are not strong enough to separate the ions, and the solid is insoluble. More discussions for insoluble solid in **section 6.3**. Such is the case for compounds such as calcium carbonate (limestone), calcium phosphate (the inorganic component of bone), and iron oxide (rust).

Solution Concentration: Molarity

Solutions play a very important role in many biological, laboratory, and industrial applications of chemistry. Of particular importance are solutions involving substances dissolved in water, or aqueous solutions. Quantitative measurements of solutions are another key component of this chapter. Solutions can involve all physical states—gases dissolved in gases (the air around us), solids dissolved in solids (metal alloys), and liquids dissolved in solids (amalgams—liquid mercury dissolved in another metal such as silver, tin or copper). This chapter is almost exclusively concerned with aqueous solutions, substances dissolved in water. Water is called solvent, and the substances dissolved is called solute.

One way of expressing concentration of a solution is to give the number of moles of solute per unit volume of solution. Of all the quantitative measures of concentration, molarity is the one used most frequently by chemists. **Molarity** is defined as the number of moles of solute per liter of solution.

$$\text{Molarity} = \frac{\text{number of moles of solute}}{\text{volume of solution in Liter}}$$

$$\text{M} = \frac{\text{mol}}{\text{V}} \qquad \text{or} \qquad \text{M} = \frac{\text{mol}}{\text{L}}$$

The symbol for molarity is M or moles/liter. Chemists also use square brackets to indicate a reference to the molarity of a substance. For example, the expression [Ag^+] refers to the molarity of the silver ion in solution. Solution concentrations expressed in molarity are the easiest to perform calculations with, but the most difficult to make in the lab. Such concentration units are useful for discussing chemical reactions in which a solute is a product or a reactant. Molar mass can then be used as a conversion factor to convert amounts in moles to amounts in grams.

It is important to remember that "mol" in this expression refers to **moles of solute** and that "L" refers to **liters of solution**. For example, if you have 1.5 mol of NaCl dissolved in 0.500 L of solution, its molarity is:

$$\frac{1.5 \text{ mol NaCl}}{0.5000 \text{ L solution}} = 3.0\text{M}$$

Sometimes (aq) is added when the solvent is water, as in "3.0 M NaCl (aq)." This is read as "a 3.00 ***molar*** sodium chloride solution," meaning that there are 3.00 moles of NaOH dissolved per one liter of solution.

If the quantity of the solute is given in mass units, you must convert mass units to mole units before using the definition of molarity to calculate concentration.

Example

What is the molar concentration of a solution of 22.4 g of HCl dissolved in 1.56 L?

Solution

1. Convert the mass of solute to moles using the molar mass of HCl (36.5 g/mol):

$$22.4\text{g HCl} \times \frac{1\text{mol HCl}}{36.5 \text{ g}} = 0.614\text{mol}$$

2. Use the definition of molarity to determine a concentration:

$$\mathrm{M} = \frac{0.614\mathrm{mol\ HCl}}{1.56\mathrm{L}} = 0.394\ \mathrm{M}$$

Example

A solution is prepared by dissolving 42.23g of NH_4Cl (MM: 53.5g/mol) into enough water to make 500.0mL of solution. Calculate its molarity.

Solution

$$42.23\mathrm{g\ HCl} \times \frac{1\mathrm{mol\ NH_4Cl}}{53.5\ \mathrm{g}} = 0.789\ \mathrm{mol}$$

$$\mathrm{M} = \frac{0.789\mathrm{mol\ HCl}}{0.5000\mathrm{L}} = 1.58\ \mathrm{M}$$

Video: How to prepare solution https://youtu.be/0_CsM6br4PI

Using Molarity in Calculations

Molarity concentration can be a conversion factor between the amount of solute and the volume of solution. As such, concentrations can be useful in a variety of stoichiometry problems.

A simple example of using a concentration unit as a conversion factor is one in which we use the definition of the concentration unit and rearrange; we can also do the calculation again as a unit conversion, rather than as a definition. The calculations involve the following categories.

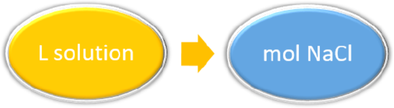
1. Determining amount (mol and mass) of solute, given the concentration and volume of a solution

Example

How many moles of solute are present in 0.108 L of a 0.887 M NaCl solution.

Solution

Because 0.887 M means **0.887 mol/L**, we can use this second expression for the concentration as a conversion factor:



$$\frac{.887\ mol\ NaCl}{1\ L\ solution}$$

$$0.108\cancel{\text{L}}\ \text{NaCl solution} \times \frac{0.887mol}{\cancel{1\ L\ solution}} = 0.0958\text{mol NaCl}$$

If we used the definition approach, we get the same answer, but now we are using conversion factor skills. Like any other conversion factor that relates two different types of units, the reciprocal of the concentration can be also used as a conversion factor.

In a laboratory situation, a chemist must frequently prepare a given volume of solutions of a known molarity. The task is to calculate the mass of the solute that is necessary. The molarity equation can be rearranged to solve for moles, which can then be converted to grams. The following example illustrates this.

Example

A chemist needs to prepare 3.00L of a 0.250M solution of potassium permanganate ($KMnO_4$, MM = 158.0 g/mol). What mass of $KMnO_4$ does he need to make the solution?

Solution

Solve the mol of $KMnO_4$ in the solution, then convert it to grams. The two steps can be combined.

$$3.00\cancel{\text{L solution}} \times \frac{0.250\cancel{mol\ KMnO4}}{\cancel{1\ L\ solution}} \times \frac{158.0\ g}{\cancel{1mol\ KMnO4}} = 119.0\text{g } KMnO_4$$

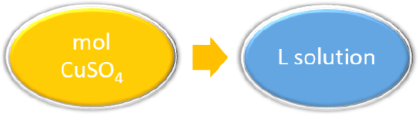
2. Determining volume of a solution, given the concentration and moles of solute

Example

How many liters of 2.35M $CuSO_4$ solution contain 4.88mol of $CuSO_4$?

Solution

This is a one-step conversion, but the concentration must be written as the reciprocal for the units to work out:



$$\frac{1\ L\ solution}{2.35\ mol\ CuSO_4}$$

$$4.88\cancel{\text{mol}}\ \text{CuSO}_4 \times \frac{1\ L}{2.35\ \cancel{mol}} = 2.08\text{L of solution}$$

Other than using molarity as a conversion factor, we can also focus on the definition of molarity, and do proper rearrangement to calculate other variable. Because M = $\frac{\text{mol}}{\text{V}}$, the rearrangement gives:

mole of solute is: mol = M×V

volume of the solution is: V = $\frac{\text{mol}}{\text{M}}$

The relationship of mol = M×V is used very often in the solution stoichiometry (**section 6.2**).

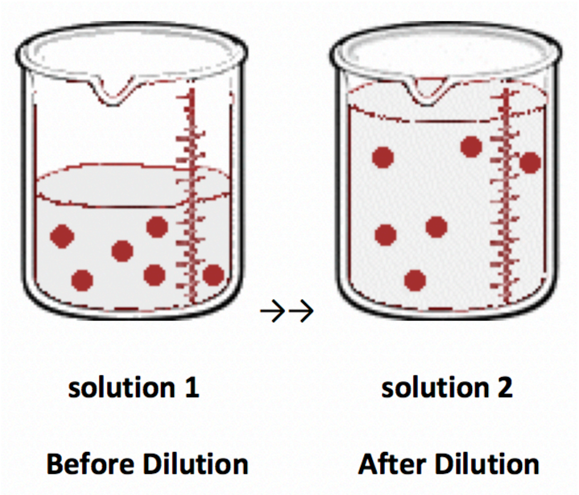
Dilution

We are often concerned with how much solute is dissolved in a given amount of solution. We will begin our discussion of solution concentration with two related and relative terms: **dilute** and **concentrated**.

- A **dilute** solution is one in which there is a relatively small amount of solute dissolved in the solution.
- A **concentrated** solution contains a relatively large amount of solute.

These two terms do not provide any quantitative information (actual numbers), but they are often useful in comparing solutions in a more general sense.

Imagine we have a salt water solution with a certain concentration. That means we have a certain amount of salt (a certain mass or a certain number of moles) dissolved in a certain volume of solution. Next, we will dilute this solution. This is done by ***adding more water***, not more salt, as shown below:



The mole of salt in solution 1 is: $mole_1 = M_1V_1$

and mole of salt in solution 2 is: $mole_2 = M_2V_2$

By adding more water, we changed the volume of the solution. Doing so also changed its concentration. **However, the number of moles of solute did *not* change.** So,

$$mole_1 = mole_2$$

Therefore for dilution,

$$M_1V_1 = M_2V_2$$

where

- M_1 and M_2 are the concentrations of the original and diluted solutions
- V_1 and V_2 are the volumes of the two solutions

6.2 Solution Stoichiometry in Acid-base Titration

This section is adapted from
https://chem.libretexts.org/Bookshelves/General_Chemistry/Map%3A_Chemistry_-_The_Central_Science_(Brown_et_al.)/04._Reactions_in_Aqueous_Solution/4.6%3A_Solution_Stoichiometry_and_Chemical_Analysis by LibreText

To determine the amounts or concentrations of substances present in a sample, chemists use a combination of chemical reactions and stoichiometric calculations in a methodology called quantitative analysis. Suppose, for example, we know the identity of a certain compound in a solution but not its concentration. If the compound reacts rapidly and completely with another reactant, we may be able to use the reaction to determine the concentration of the compound of interest. In a **titration**, a carefully measured volume of a solution of known concentration, called the titrant, is added to a measured volume of a solution containing a compound whose concentration is to be determined (the unknown). The reaction used in a titration can be an acid–base reaction, a precipitation reaction, or an oxidation–reduction reaction. Here we will focus on the acid-base titration. In all cases, the reaction chosen for the analysis must be fast, complete, and specific; that is, only the compound of interest should react with the titrant. The **equivalence point** is reached when a stoichiometric amount of the titrant has been added—the amount required to react completely with the unknown (A full in-depth discussion on this topic is in Chapter 10).

Acid-base reaction

According to Brønsted-Lowry definition, acid is the substance that donate H^+, and base is the substance that accept H^+. The common strong acids include: HCl, HBr, HI, HNO_3, H_2SO_4 etc. The examples of common strong bases are: M(OH) and $M(OH)_2$ (M: Group I or Group II metal, except Mg).

In the reaction between strong acid and strong base, water is formed, that is the driving force for such acid-base reaction. For examples:

$HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$

$H_2SO_4(aq) + 2NaOH(aq) \rightarrow Na_2SO_4(aq) + 2H_2O(l)$

The following example illustrates how to determine the concentration of an unknown solution using an acid-base titration:

Example

Suppose 15.66 mL of 0.1078 M NaOH was used to titrate 15.00 mL of an unknown HCl sample. What was the concentration of unknown HCl solution?

Solution

Step 1: determine the mole of NaOH used.

mol = $M \times V$, so mol of NaOH = $0.1078\ M \times 0.01566\ L = 0.0016881$ mol

Step 2: determine the mole of HCl based on the mole ratio between NaOH and HCl in the reaction.

mol of HCl = mol of NaOH$\times\frac{1\ \mathrm{mol\ HCl}}{1\mathrm{mol\ NaOH}}$ = 0.0016881 mol

Step 3: determine the concentration of HCl.

$M = \frac{\text{mol}}{\text{V}} = \frac{0.0016881\text{mol HCl}}{0.01500\text{ L}}$ = 0.1125 M (answer)

The first and last step of the titration calculation here involves the concepts of molarity, and the 2nd step is the stoichiometry. That is how the stoichiometry applies in the solution reaction.

Example

28.38 mL of 0.1078 M NaOH was used to titrate 15.00 mL of an unknown H_2SO_4 sample. What was the concentration of unknown H_2SO_4 solution?

Solution

Step 1: determine the mole of NaOH used.

mol = M×V, so mol of NaOH = 0.1078 M × 0.02838 L = 0.0030594 mol

Step 2: determine the mole of HCl based on the mole ratio between NaOH and HCl in the reaction.

mol of HCl = mol of NaOH × $\frac{1\text{ mol H2SO4}}{2\text{mol NaOH}}$ = 0.0015297 mol

Step 3: determine the concentration of HCl.

$M = \frac{\text{mol}}{\text{V}} = \frac{0.0015297\text{mol HCl}}{0.01500\text{ L}}$ = 0.1020 M (answer)

Note: the mole ratio between H_2SO_4 and NaOH is $\frac{1\text{ mol H2SO4}}{2\text{mol NaOH}}$

6.3: Precipitation Reactions

Precipitation reaction is a reaction that yields an insoluble product—a precipitate—when two solutions are mixed. When a colorless solution of silver nitrate is mixed with a yellow-orange solution of potassium dichromate, a reddish precipitate of silver dichromate is produced. https://youtu.be/Gv-WsSpZpMs

$$AgNO_3(aq) + K_2Cr_2O_7(aq) \rightarrow Ag_2Cr_2O_7(s) + KNO_3(aq)$$

A precipitate is the compound that is insoluble in aqueous solution. The precipitate, or insoluble compound, barely dissociates in aqueous solution, and still mainly maintain as solid phase.

Because both components of each compound change partners, such reactions are sometimes called **double-displacement reactions**. Precipitation reactions are used to isolate metals that have been extracted from their ores, and to recover precious metals for recycling.

Some combinations of aqueous reactants result in the formation of a solid precipitate as a product. However, some combinations will not produce such a product. If solutions of sodium nitrate and ammonium chloride are mixed, no reaction occurs. One could write a molecular equation showing a double-replacement reaction, but both "products", sodium chloride and ammonium nitrate, are soluble and would remain in the solution as ions, and then no net reaction occurred.

$$NaNO_3(aq) + NH_4Cl\ (aq) \rightarrow \text{no reaction}$$

It is useful to be able to predict when a precipitate will occur in a reaction. To do so, you can use a set of guidelines called the **solubility rules** (Tables 6.1).

IONS	**RULES**
Group IA , NH_4^+	All compounds in which the cation is a group IA element or NH_4^+ are *soluble*
$C_2H_3O_2^-$, NO_3^-	All acetates and nitrates are *soluble*.
Cl^-, Br^-, I^-	Most chlorides, bromides and iodides are *soluble*, **except** those of Ag^+, Pb^{2+}, Hg^{2+} and Hg_2^{2+}.
SO_4^{2-}	Most sulfates are *soluble* **except** $CaSO_4$, $SrSO_4$, $BaSO_4$, $PbSO_4$, Hg_2SO_4 and Ag_2SO_4
CO_3^{2-}, PO_4^{3-}, S^{2-}	Most carbonates, phosphates and sulfides are *insoluble* **except** those of Group IA or NH_4^+
OH^-	Most hydroxides are *insoluble* **except** those of Group IA hydroxide and $Ca(OH)_2$, $Sr(OH)_2$, and $Ba(OH)_2$.

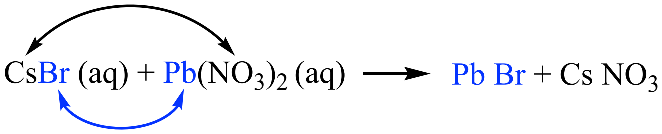
Table 6.1 Solubility Rules

As an **example** on how to use the solubility rules, predict if a precipitate will form when solutions of cesium bromide CsBr and lead (II) nitrate $Pb(NO_3)_2$ are mixed.

$CsBr\ (aq) + Pb(NO_3)_2 \rightarrow ???$

Solution

Step1: Change the partners of the anions and cations on the reactant side to form new compounds (products):



Step2: Correct the formulas of the products based on the charges of the ions.

$PbBr_2$ and $CsNO_3$

Step3: Refer to the solubility rules table to determine **insoluble** products which will therefore form a precipitate.

The potential precipitates from a double-replacement reaction are cesium nitrate and lead (II) bromide. According to the solubility rules table (Tables 6.1), cesium nitrate is soluble because all compounds containing the nitrate ion, as well as all compounds containing the alkali metal ions, are soluble. Most compounds containing the bromide ion are soluble, but lead (II) is an exception. Therefore, the cesium and nitrate ions are spectator ions and the lead (II) bromide is a **precipitate**. The is balanced reaction equation is:

$$2CsBr\ (aq) + Pb(NO_3)_2\ (aq) \rightarrow PbBr_2(\mathbf{s}) + 2CsNO_3\ (aq)$$

Note: The phase of precipitate must be shown as **(s)** in the reaction equation.

Example

Predict what will happen when the two aqueous solutions are mixed. Show the balanced chemical equation if reaction occurs.

a. rubidium hydroxide and cobalt(II) chloride

b. $SrBr_2\ (aq) + Al(NO_3)_3\ (aq) \rightarrow$

c. An aqueous solution of strontium hydroxide is added to an aqueous solution of iron(II) chloride.

d. Aqueous solutions of calcium bromide and cesium carbonate are mixed.

Solution

a. $2RbOH\ (aq) + CoCl_2\ (aq) \rightarrow Co(OH)_2\ (s) + 2RbCl\ (aq)$

b. $SrBr_2\ (aq) + Al(NO_3)_3\ (aq) \rightarrow$ no reaction

c. $3Sr(OH)_2\ (aq) + 2FeCl_3\ (aq) \rightarrow 2Fe(OH)_3\ (s) + 3SrCl_2\ (aq)$

d. $CaBr_2\ (aq) + Cs_2CO_3\ (aq) \rightarrow CaCO_3\ (s) + 2CsBr\ (aq)$

Representing Aqueous Reactions: Molecular, Complete Ionic and Net Ionic Equations

The equation above to show the precipitation reaction when solutions of cesium bromide CsBr and lead (II) nitrate $Pb(NO_3)_2$ are mixed, is called the **molecular equation**. The molecular equation describes what happens with the complete chemical formula involved for all the substances.

Molecular Equation:

$$2CsBr\ (aq) + Pb(NO_3)_2\ (aq) \rightarrow PbBr_2(\mathbf{s}) + 2CsNO_3\ (aq)$$

However, molecular equation does not really represent the microscopic particles (that is, the ions) present in the solution. Below is the complete ionic equation:

Complete Ionic Equation:

$$\underbrace{2Cs^{+}(aq)}_{\text{spectator}} + 2Br^{-}(aq) + Pb^{2+}(aq) + \underbrace{2NO_3^{-}(aq)}_{\text{spectator}} \longrightarrow PbBr_2(s) + \underbrace{2Cs^{+}(aq)}_{\text{spectator}} + \underbrace{2NO_3^{-}(aq)}_{\text{spectator}}$$

In **complete ionic equation**, all soluble compounds are shown as ions because they dissociate completely to ions in aqueous solution. However, since the precipitate (insoluble salt) does not dissociate, it can only be shown with the complete chemical formula with (s) as the phase.

The complete ionic equation is rather cumbersome and includes so many different ions that it may be confusing. In any case, we are often interested in the independent behavior of ions, not the specific compound from which they came. A precipitate of $PbBr_2(s)$ will form when *any* solution containing $Pb^{2+}(aq)$ is mixed with *any* solution containing $2NO_3^-$ (aq). This happens independently of the $Cs^+(aq)$ and $Br^-(aq)$ ions in equation. These ions are called **spectator ions** because they do not participate in the reaction. When we want to emphasize the independent behavior of ions, a **net ionic equation** is written, omitting the spectator ions. For precipitation of $PbBr_2(s)$ the net ionic equation is:

Net Ionic Equation:

$$Pb^{2+}(aq) + 2Br^-(aq) \rightarrow PbBr_2(\mathbf{s})$$

Example

Write three equations (molecular equation, complete ionic equation, and net ionic equation) for the reaction when $AgNO_3$ solution and $CaCl_2$ solution are mixed insoluble AgCl precipitates.

Solution

Molecular Equation:

$$2AgNO_3\ (aq) + CaCl_2\ (aq) \rightarrow 2AgCl\ (s) + Ca(NO_3)_2\ (aq)$$

Complete Ionic Equation:

$$2Ag^+(aq) + 2NO_3^-(aq) + Ca^{2+}(aq) + 2Cl^-(aq) \longrightarrow 2AgCl\ (s) + Ca^{2+}(aq) + 2NO_3^-(aq)$$

Net Ionic Equation:

$$2Ag^+(aq) + 2Cl^-(aq) \longrightarrow 2AgCl\ (s)$$

6.4: Single Displacement Reaction: Activity Series

Single-replacement reactions only occur when the element that is doing the replacing is more reactive than the element that is being replaced. Therefore, it is useful to have a list of elements in order of their relative reactivity. The **activity series** is a list of elements in decreasing order of their reactivity. The diagram below is an activity series of most common metals.

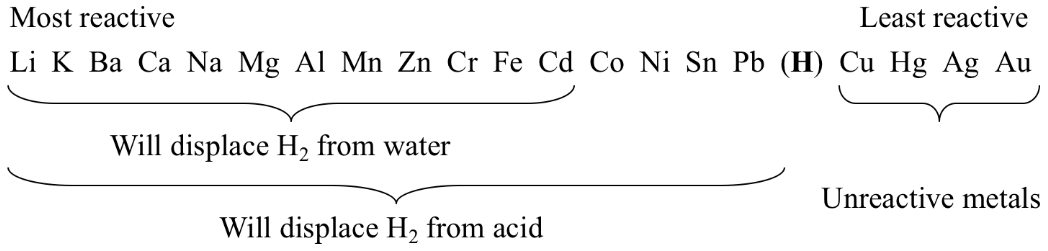


Figure 6.3 Activity Series of Metals

There are two types of single displacement reactions need our attention.

1. Metal Displacement Reaction:

The metal that is more reactive is able to replace the other less reactive metal from its compound. Suppose that small pieces of the metal nickel were placed into two separate aqueous solutions: one of iron (III) nitrate and one of lead (II) nitrate. Looking at the activity series, we see that nickel is below iron, but above lead. Therefore, the nickel metal will be capable of replacing the lead in a reaction, but will not be capable of replacing iron.

$$Ni(s) + Pb(NO_3)_2(aq) \rightarrow Ni(NO_3)_2(aq) + Pb(s)$$

$$Ni(s) + Fe(NO_3)_3(aq) \rightarrow \text{no reaction}$$

2. Hydrogen Displacement Reaction:

The metals that above H in the activity series can replace hydrogen from strong acid to produce hydrogen gas H_2. An example is:

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

Practice

Use the activity series to predict if the following reactions will occur. If not, write NR. If the reaction does occur, write the balanced molecular equation.

a. $Al(s) + Zn(NO_3)_2(aq) \rightarrow$
b. $Fe (s) + ZnCl_2 (aq) \rightarrow$
c. $Mg(s) + HCl(aq) \rightarrow$
d. $H_2SO_4(aq)+ Au(s) \rightarrow$

Answers

a. $2Al(s) + 3Zn(NO_3)_2(aq) \rightarrow 2Al(NO_3)_3(aq) + 3Zn(s)$

b. $Fe (s) + ZnCl_2 (aq) \rightarrow$ no reaction

c. $Mg(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2(g)$

d. $H_2SO_4(aq) + Au(s) \rightarrow$ no reaction

6.5: Oxidation-Reduction Reactions

In the course of a chemical reaction between a metal and a nonmetal, electrons are transferred from the metal atoms to the nonmetal atoms. For example, when zinc metal is mixed with sulfur and heated, the compound zinc sulfide is produced. Two electrons from each zinc atom are transferred to each sulfur atom.

$$Zn (s) + S (s) \rightarrow ZnS (s)$$

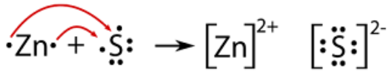


Figure 6.4 Electron transfer between zinc and sulfur

Since the zinc is losing electrons in the reaction, it is being oxidized. The sulfur is gaining electrons and is thus being reduced. An **oxidation-reduction reaction** is a reaction that involves the full or partial transfer of electrons from one reactant to another. **Oxidation** is the loss of electrons, and **reduction** is the gain of electrons. A **redox reaction** is another term for an oxidation-reduction reaction.

Each of these processes can be shown in a separate equation called a half-reaction. A **half-reaction** is an equation that shows either the oxidation or the reduction reaction that occurs during a redox reaction.

oxidation half-reaction: $Zn \rightarrow Zn^{2+} + 2e^{-}$

reduction half-reaction: $S + 2e^{-} \rightarrow S^{2-}$

It is important to remember that the two half-reactions occur simultaneously. The resulting ions that are formed are then attracted to one another in an ionic bond.

Oxidation Number

Redox reactions require that we keep track of the electrons assigned to each atom in a chemical reaction. How do we do that? We use **oxidation numbers** to keep track of electrons in atoms. Oxidation numbers are assigned to atoms based on the rules we will see below. Oxidation numbers are not necessarily equal to the charge on the atom (although sometimes they can be); we must keep the concepts of charge and oxidation numbers separate.

Keeping track and comparing oxidation number also helps to identify a reaction is redox reaction or not.

The rules for assigning oxidation numbers to atoms are as follows:

1. Atoms in their elemental state are assigned an oxidation number of 0.

- For elements like Na(s), Fe(s), He(g), the oxidation number is 0
- For elements as diatomic molecules, such as O_2, H_2, Cl_2, the oxidation number is 0.

2. In compound, metal atoms as monoatomic (i.e., one-atom) ions are assigned an oxidation number equal to their charge. (Oxidation numbers are usually written with the sign first, then the magnitude, to differentiate them from charges.)

- For species like Cu^+, Ca^{2+}, the oxidation number is the same as charge.
- Group I metals always have an oxidation number of +1.
- Group II metals always have an oxidation number of +2.
- The oxidation number of transition metal depends on its charge in the compound, for example:

$$\overset{+2}{\mathrm{Fe}}\mathrm{Cl_2} \qquad \qquad \overset{+3}{\mathrm{Fe}}\mathrm{Cl_3}$$

3. In compounds, the rules for oxidation number of non-metals are:

- Fluorine is *always* assigned a −1 oxidation number;
- Oxygen is *usually* assigned a −2 oxidation number, except in peroxide compounds (for example H_2O_2, the oxidation number of oxygen is −1) and in binary compounds with fluorine (in F_2O, the oxidation number of oxygen is +2);

$$\mathrm{H_2}\overset{-2}{\mathrm{O}} \qquad \qquad \mathrm{H_2}\overset{-1}{\mathrm{O}}\mathrm{_2} \qquad \qquad \mathrm{F_2}\overset{+2}{\mathrm{O}}$$

- Hydrogen is *usually* assigned a +1 oxidation number, except when it exists as the hydride ion (for example NaH, the oxidation number of hydrogen is -1).

$\overset{+1}{H}_2O$ $\qquad$ $Ca\overset{-1}{H}_2$

- Halogen (Cl, Br, I) is usually assigned a −1 oxidation number, except when it exist in compound with F or O.

$H\overset{-1}{Cl}$ $\qquad$ $\overset{+2}{Cl}F_2$ $\qquad$ $\overset{+4}{Cl}O_2$

4. In compounds, all other atoms are assigned an oxidation number so that the sum of the oxidation numbers on all the atoms in the species equals the charge on the species (which is zero if the species is neutral molecule).

$\overset{+4}{S}\overset{-2}{O}_2$ $\qquad$ $(\overset{+5}{Cl}\overset{-2}{O}_3)^-$

In SO_2, each O atom has an oxidation number of −2; for the sum of the oxidation numbers to equal the charge on the species (which is zero), the S atom is assigned an oxidation number of +4. Does this mean that the sulfur atom has a 4+ charge on it? No, it means only that the S atom is assigned a +4 oxidation number by our rules of apportioning electrons among the atoms in a compound.

In chlorate anion $(ClO_3)^-$, the total charge is -1, the oxidation number of O atom is -2, with the calculation $x+3(-2) = -1$; $x = +5$. So the oxidation number of Cl atom is +5.

Examples

Assign oxidation numbers to the atoms in each substance.

a. Cl_2
b. GeO_2
c. $Ca(NO_3)_2$

Solution

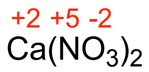
a. Cl_2 is the elemental form of chlorine. Rule 1 states that each atom has an oxidation number of 0.

$\overset{0}{Cl}_2$

b. By rule 3, oxygen is normally assigned an oxidation number of −2. For the sum of the oxidation numbers to equal the charge on the species (zero), the Ge atom is assigned an oxidation number of +4.

$\overset{+4}{Ge}\overset{-2}{O}_2$

c. $Ca(NO_3)_2$ can be separated into two parts: the Ca^{2+} ion and the NO_3^- ion. Considering these separately, the Ca^{2+} ion has an oxidation number of +2 by rule 2. For NO_3^- ion, oxygen is assigned an oxidation number of −2, and there are three of them. According to rule 4, the sum of the oxidation numbers on all atoms must equal the charge on the species, so the simple algebraic calculation gives: $x+3(-2) = -1$; $x = +5$



$$\overset{+2}{Ca}(\overset{+5}{N}\overset{-2}{O}_3)_2$$

Identifying Redox Reaction

All redox reactions occur with a simultaneous change in the oxidation numbers of some atoms. In the redox reaction, **at least two elements must change their oxidation numbers**.
When an oxidation number of an atom is *increased* in the course of a redox reaction, that atom is being *oxidized*. When an oxidation number of an atom is *decreased* in the course of a redox reaction, that atom is being *reduced*. Thus oxidation and reduction can also be defined in terms of increasing or decreasing oxidation numbers, respectively.

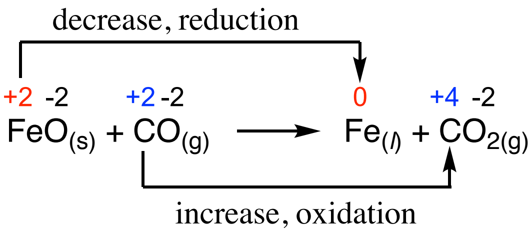
Example

Determine whether the following reaction is redox reaction or not.

a. $FeO_{(s)} + CO_{(g)} \rightarrow Fe_{(l)} + CO_{2(g)}$
b. $FeCO_{3(s)} \rightarrow FeO_{(s)} + CO_{2(g)}$

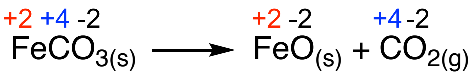
Solution

a. The oxidation number of iron atom decrease from +2 to 0, Fe is reduced. The oxidation number of carbon atom increase from +2 to +4, C is oxidized. The overall reaction is a redox reaction.



$$\overset{+2}{Fe}\overset{-2}{O}_{(s)} + \overset{+2}{C}\overset{-2}{O}_{(g)} \longrightarrow \overset{0}{Fe}_{(l)} + \overset{+4}{C}\overset{-2}{O}_{2(g)}$$

b. The oxidation number of all the elements remain the same, the reaction is **not** a redox reaction.



$$\overset{+2}{Fe}\overset{+4}{C}\overset{-2}{O}_{3(s)} \longrightarrow \overset{+2}{Fe}\overset{-2}{O}_{(s)} + \overset{+4}{C}\overset{-2}{O}_{2(g)}$$

Oxidizing agent and reducing agent

For redox reactions, other than identify oxidation and reduction half-reactions, we also need to be able to tell oxidizing agent and reducing agent.

Reducing agent (RA) is the agent that reduce other species, and reducing agent itself is oxidized (undergoes oxidation reaction).

Oxidizing agent (OA) is the agent that oxidize other species, and oxidizing agent itself is reduced (undergoes reduction reaction).

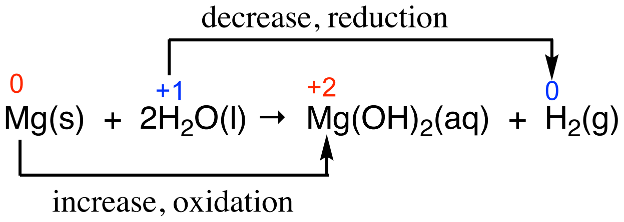
For example, in the reaction Zn(s) + S(s) → ZnS(s), zinc metal is the reducing agent, and Zn(s) is oxidized (lose 2e to become Zn^{2+}); sulfur is the oxidizing agent, and S(s) is reduced (gain 2e to become S^{2-})

Example

Identify the oxidation and reduction half-reactions, oxidizing agent and reducing agent for following reaction.

$Mg(s) + 2H_2O(l) \rightarrow Mg(OH)_2(aq) + H_2(g)$

Solution



Mg(s) is oxidized, and Mg(s) is the reducing agent. The H in water is reduced, and H in water is the oxidizing agent (usually it can be said that water is the reducing agent).

Balance Redox Reaction

To balance redox reactions, both elements and the number of electrons transferred need to be balanced. We can balance redox reaction occurring in aqueous reaction by using a procedure called the **half-reaction method**. In this method, we separate the overall reaction into two half-reactions: one for oxidation and one for reduction. Each half reaction is balanced individually and then add together. The steps are summarized as below.

Procedures for balancing redox reaction:

1. Divide the reaction into a reduction half-reaction and oxidation half-reaction.
2. Balance the half reactions separately, following the four-step procedure:
    a) Balance all elements except oxygen and hydrogen
    b) Balance oxygen using H_2O where necessary
    c) Balance hydrogen with H^+
    d) Balance net charge with electrons
3. Equalize the number of electrons gained and lost in both half reactions by multiplying each half-reaction by a whole number
4. Add the half-reactions together and cancel duplicated species
5. In basic solution, convert H^+ to H_2O by adding equal number of OH^- on both sides, Cancel the H_2O that occur on both sides.

Example

Balance the following redox reactions in acidic solution:

a. $Al(s) + Cu^{2+}(aq) \rightarrow Al^{3+}(aq) + Cu(s)$

b. $Fe^{2+}(aq) + MnO_4^-(aq) \rightarrow Fe^{3+}(aq) + Mn^{2+}(aq)$

Solution

Reaction a:	
1. Divide the reaction into a reduction half-reaction and oxidation half-reaction	$Al(s) \rightarrow Al^{3+}(aq)$ $Cu^{2+}(aq) \rightarrow Cu(s)$
2. Balance the half reactions separately, following the four-step procedure	All elements are balanced, step 2a)- 2c) can be skipped, only need to balance the charges. Electron has "-" charge, so proper # of electrons should be added to the side with more "+" charges. $Al(s) \rightarrow Al^{3+}(aq) + 3e^-$ $2e^- + Cu^{2+}(aq) \rightarrow Cu(s)$
3. Equalize the number of electrons gained and lost in both half reactions by multiplying each half-reaction by a whole number	$[\, Al(s) \rightarrow Al^{3+}(aq) + 3e^- \,] \times 2$ $3\times [\, 2e^- + Cu^{2+}(aq) \rightarrow Cu(s) \,]$

4. Add the half-reactions together and cancel duplicated species	$2Al(s) + 3Cu^{2+}(aq) \rightarrow 2Al^{3+}(aq) + 3Cu(s)$ **Note**: electrons should be completely cancelled and not shown in the overall balanced redox reaction.

Reaction b:	
1. Divide the reaction into a reduction half-reaction and oxidation half-reaction	$Fe^{2+}(aq) \rightarrow Fe^{3+}(aq)$ $MnO_4^-(aq) \rightarrow Mn^{2+}(aq)$
2. Balance the half reactions separately, following the four-step procedure	element balanced for this half: $Fe^{2+}(aq) \rightarrow Fe^{3+}(aq)$ add e^- to balance charge: $Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^-$ add H_2O to balance O: $MnO_4^-(aq) \rightarrow Mn^{2+}(aq) + 4H_2O$ add H^+ to balance H: $8H^+ + MnO_4^-(aq) \rightarrow Mn^{2+}(aq) + 4H_2O$ add e^- to balance charge: $5e^- + 8H^+ + MnO_4^-(aq) \rightarrow Mn^{2+}(aq) + 4H_2O$
3. Equalize the number of electrons gained and lost in both half reactions by multiplying each half-reaction by a whole number	$[\ Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^-\ ] \times 5$ $1\times [\ 5e^- + 8H^+ + MnO_4^-(aq) \rightarrow Mn^{2+}(aq) + 4H_2O\ ]$
4. Add the half-reactions together and cancel duplicated species	$5Fe^{2+}(aq) + 8H^+ + MnO_4^-(aq) \rightarrow 5Fe^{3+}(aq) + Mn^{2+}(aq) + 4H_2O$

Example

Balance the following redox reactions in basic solution:

$I^-(aq) + MnO_4^-(aq) \rightarrow I_2(aq) + MnO_2(s)$

Solution

If the redox reaction occurs in basic solution, the step 5 in the procedure is required.

1. Divide the reaction into a reduction half-reaction and oxidation half-reaction	$I^- (aq) \rightarrow I_2 (aq)$ $MnO_4^- (aq) \rightarrow MnO_2 (s)$
2. Balance the half reactions separately, following the four-step procedure	balance element: $2I^- (aq) \rightarrow I_2 (aq)$ add e^- to balance charge: $2I^- (aq) \rightarrow I_2 (aq) + 2e^-$ add H_2O to balance O: $MnO_4^- (aq) \rightarrow MnO_2 (s) + 2H_2O$ add H^+ to balance H: $4H^+ + MnO_4^- (aq) \rightarrow MnO_2 (s) + 2H_2O$ add e^- to balance charge: $3e^- + 4H^+ + MnO_4^- (aq) \rightarrow MnO_2 (s) + 2H_2O$
3. Equalize the number of electrons gained and lost in both half reactions by multiplying each half-reaction by a whole number	$[2I^- (aq) \rightarrow I_2 (aq) + 2e^-] \times 3$ $2\times [3e^- + 4H^+ + MnO_4^- (aq) \rightarrow MnO_2 (s) + 2H_2O]$
4. Add the half-reactions together and cancel duplicated species	$6I^- (aq) + 8H^+ + 2MnO_4^- (aq) \rightarrow 3I_2 (aq) + 2MnO_2 (s) + 4H_2O$
5. In basic solution, convert H^+ to H_2O by adding equal number of OH^- on both sides, Cancel the H_2O that occur on both sides	There are $8H^+$, so $8OH^-$ required for both sides: $8OH^- + 6I^- (aq) + 8H^+ + 2MnO_4^- (aq) \rightarrow 3I_2 (aq) + 2MnO_2 (s) + 4H_2O + 8OH^-$ Becomes: $6I^- (aq) + 8H_2O + 2MnO_4^- (aq) \rightarrow 3I_2 (aq) + 2MnO_2 (s) + 4H_2O + 8OH^-$ Cancel the duplicate H_2O, the final balanced equation is: $6I^- (aq) + 4H_2O + 2MnO_4^- (aq) \rightarrow 3I_2 (aq) + 2MnO_2 (s) + 8OH^-$

Chapter 7 Gases

7.1 Kinetic Molecular Theory: A Model for Gases

Gases were among the first substances studied in terms of the modern scientific method, which was developed in the 1600s. It did not take long to recognize that gases all shared certain physical behaviors, suggesting that all gases could be described by one all-encompassing theory. Today, that theory is the **kinetic theory of gases**. It is based on the following statements:

1. Gases consist of tiny particles of matter that are in constant motion.
2. Gas particles are constantly colliding with each other and the walls of a container. These collisions are elastic, that is, there is no net loss of energy from the collisions.
3. Gas particles are separated by large distances, with the size of a gas particle tiny compared to the distances that separate them.
4. There are no interactive forces (i.e., attraction or repulsion) between the particles of a gas.
5. The average speed of gas particles is dependent on the temperature of the gas.

Figure 7.1 shows a representation of how we mentally picture the gas phase.

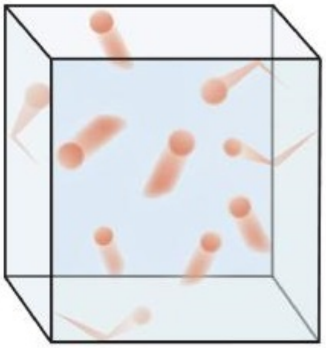


Figure 7.1 The Kinetic Theory of Gases. The kinetic theory of gases describes this state of matter as composed of tiny particles in constant motion with a lot of distance between the particles.

This model of gases explains some of the physical properties of gases. Because most of a gas is empty space, a gas has a low density and can expand or contract under the appropriate influence. The fact that gas particles are in constant motion means that two or more gases will always mix, as the particles from the individual gases move and collide with each other.

An **ideal gas** is a gas that exactly follows the statements of the kinetic theory. Although real gases are not ideal, many gases just deviate slightly from agreeing perfectly with the kinetic theory of gases. However, most gases adhere to the statements so well that the kinetic theory of gases is well accepted by the scientific community.

7.2 Pressure

The kinetic theory of gases indicates that gas particles are always in motion and are colliding with other particles and the walls of the container holding them. Although collisions with container walls are elastic (i.e., there is no net energy gain or loss because of the collision), a gas particle does exert a force on the wall during the collision. The accumulation of all these forces distributed over the area of the walls of the container causes something we call pressure. **Pressure** (P) is defined as the force of all the gas particle/wall collisions divided by the area of the wall:

$$\text{pressure} = \frac{\text{force}}{\text{area}}$$

All gases exert pressure; it is one of the fundamental measurable quantities of this phase of matter. For example our atmosphere exerts pressure—in this case, the gas is being “held in” by the earth’s gravity, rather than the gas being in a container. The pressure of the atmosphere is about 14.7 pounds of force for every square inch of surface area: 14.7 lb/in^2.

Pressure has a variety of units. The formal, SI-approved unit of pressure is the *pascal* (Pa), which is defined as 1 N/m^2 (one newton of force over an area of one square meter). However, this is usually too small in magnitude to be useful. A common unit of pressure is the **atmosphere** (atm), which was originally defined as the average atmospheric pressure at sea level.

However, “average atmospheric pressure at sea level” is difficult to pinpoint because of atmospheric pressure variations. A more reliable and common unit is **millimeters of mercury** (mmHg), which is the amount of pressure exerted by a column of mercury exactly 1 mm high. An equivalent unit is the **torr**, which equals 1 mmHg. (The torr is named after Evangelista Torricelli, a seventeenth-century Italian scientist who invented the mercury barometer.) With these definitions of pressure, the atmosphere unit is redefined: 1 atm is defined as exactly 760 mmHg, or 760 torr. We thus have the following equivalents:

$$1 \text{ atm} = 760 \text{ mmHg} = 760 \text{ torr}$$

We can use these equivalents as with any equivalence—to perform conversions from one unit to another. Relating these to the formal SI unit of pressure:

$$1 \text{ atm} = 760 \text{ mmHg} = 760 \text{ torr} = 101{,}325 \text{ Pa}$$

Examples

a) How many atmospheres are there in 595 torr?
b) How many mmHg are there in 2.02 atm?

c) The atmosphere on Mars is largely CO_2 at a pressure of 6.01 mmHg. What is this pressure in atm and Pa?

Solution

a) 595 torr × $\frac{1\ atm}{760\ torr} = 0.783\ atm$

b) 2.02 atm × $\frac{760\ mmHg}{1\ atm} = 1535\ mmHg$

c) 6.01 mmHg × $\frac{1\ atm}{760\ mmHg} = 0.00791\ atm$

6.01 mmHg × $\frac{1\ atm}{760\ mmHg} \times \frac{101325\ Pa}{1\ atm} = 801\ Pa$

7.3 Gas Laws

Boyle's Law – Pressure and Volume

When seventeenth-century scientists began studying the physical properties of gases, they noticed some simple relationships between some of the measurable properties of the gas. Take pressure (*P*) and volume (*V*), for example. Scientists noted that for a given amount of a gas (usually expressed in units of moles [*n*]), if the temperature (*T*) of the gas was kept constant, pressure and volume were related: as one increases, the other decreases. As one decreases, the other increases. This means that pressure and volume are *inversely related*.

There is more to it, however: pressure and volume of a given amount of gas at constant temperature are *numerically* related. If you take the pressure value and multiply it by the volume value, the product is a constant for a given amount of gas at a constant temperature:

$$P \times V = \text{constant (at constant n and T)}$$

If either volume or pressure changes while amount and temperature stay the same, then the other property must change so that the product of the two properties still equals that same constant. That is, if the original conditions are labeled P_1 and V_1 and the new conditions are labeled P_2 and V_2, we have

$$P_1V_1=\text{constant}=P_2V_2$$

where the properties are assumed to be multiplied together. Leaving out the middle part, we have simply:

$$P_1V_1 = P_2V_2 \text{ at constant n and T}$$

This equation is an example of a gas law. A **gas law** is a simple mathematical formula that allows you to model, or predict, the behavior of a gas. This particular gas law is called **Boyle's Law**, after the English scientist Robert Boyle, who first announced it in 1662. Figure 7.2 shows two representations of how Boyle's Law works.

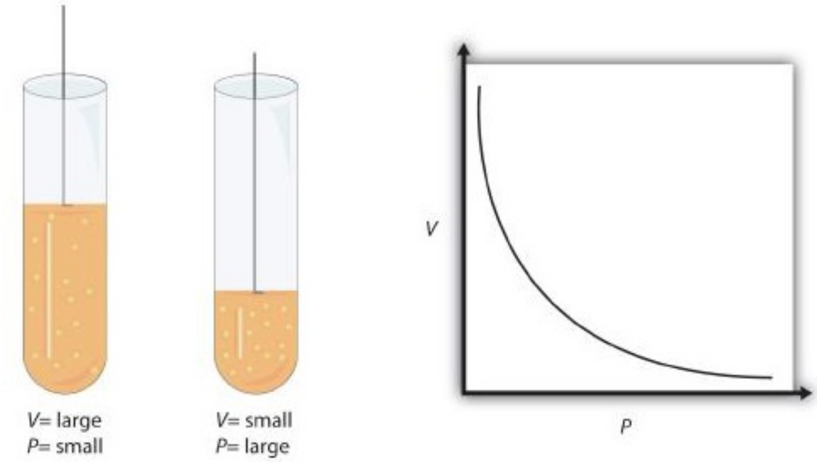


Figure 7.2 Boyle's Law. A piston having a certain pressure and volume (left piston) will have half the volume when its pressure is twice as much (right piston). One can also plot *P* versus *V* for a given amount of gas at a certain temperature; such a plot will look like the graph on the right.

Charles's Law – Volume and Temperature

French physicist Jacques Charles (1746-1823) studied the effect of temperature on the volume of a gas at constant pressure. **Charles's Law** states that the volume of a given mass of gas varies directly with the absolute temperature of the gas when pressure is kept constant. The absolute temperature is temperature measured with the Kelvin scale. The Kelvin scale must be used because zero on the Kelvin scale corresponds to a complete stop of molecular motion.

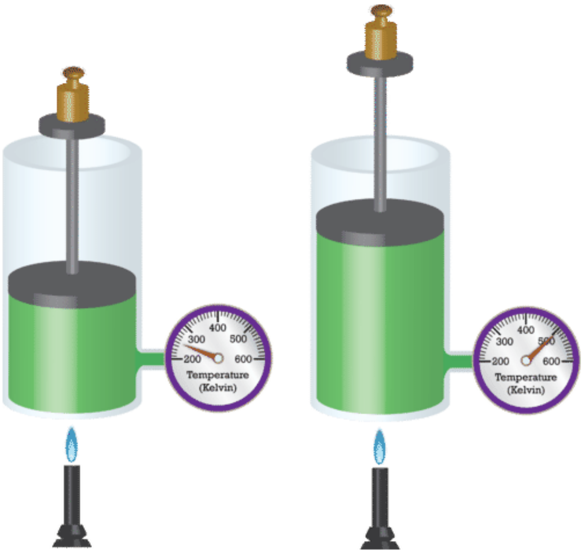


Figure 7.3 As a container of confined gas is heated, its molecules increase in kinetic energy and push the movable piston outward, resulting in an increase in volume.

Mathematically, the direct relationship of Charles's Law can be represented by the following equation:

$$\frac{V}{T} = \text{constant}$$

The table below shows temperature and volume data for a set amount of gas at a constant pressure. The third column is the constant for this particular data set and is always equal to the volume divided by the Kelvin temperature.

Temperature (K)	**Volume** (mL)	***V/T*= constant** (mL/K)
50	20	0.40
100	40	0.40
150	60	0.40
200	80	0.40
300	120	0.40
500	200	0.40
1000	400	0.40

When this data is graphed, the result is a straight line, indicative of a direct relationship, shown in the figure below.

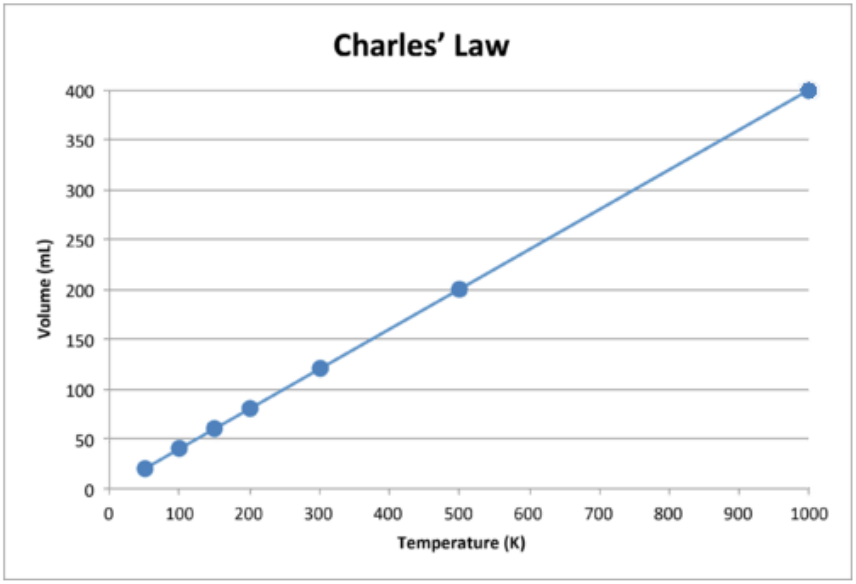


Figure 7.4 The volume of a gas increases as the Kelvin temperature increases.

Notice that the line goes exactly toward the origin, meaning that as the absolute temperature of the gas approaches zero, its volume approaches zero. However, when a gas is brought to extremely cold temperatures, its molecules would eventually condense into the liquid state before reaching absolute zero.

Charles's Law can also be used to compare changing conditions for a gas. Now we use V_1 and T_1 to stand for the initial volume and temperature of a gas, while V_2 and T_2 stand for the final volume and temperature. The mathematical relationship of Charles's Law becomes:

$$V_1T_1 = V_2T_2$$

This equation can be used to calculate any one of the four quantities if the other three are known. The direct relationship will only hold if the temperatures are expressed in Kelvin. Temperatures in Celsius will not work. Recall the relationship that K = °C + 273

Avogadro's Law

A flat tire is not very useful. It does not cushion the rim of the wheel and creates a very uncomfortable ride. When air is added to the tire, the pressure increases as more molecules of gas are forced into the rigid tire. How much air should be put into a tire depends on the pressure rating for that tire. Too little pressure and the tire will not hold its shape. Too much pressure and the tire could burst.

Avogadro's Law states that the volume of a gas is directly proportional to the number of moles (or number of particles) of gas when the temperature and pressure are held constant. The mathematical expression of Avogadro's Law is:

$$\frac{V}{n} = \text{constant}$$

or

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

where n is the number of moles of gas. Avogadro's Law is in evidence whenever you blow up a balloon. The volume of the balloon increases as you add moles of gas to the balloon by blowing it up.

Ideal Gas Law

The Combined Gas Law shows that the pressure of a gas is inversely proportional to volume and directly proportional to temperature. Avogadro's Law shows that volume or pressure is directly proportional to the number of moles of gas. Putting these together leaves us with the following equation:

$$\frac{P\,V}{n\,T} = \text{constant}$$

The **Ideal Gas Law** is a single equation which relates the pressure, volume, temperature, and number of moles of an ideal gas. If we substitute in the variable R for the constant, the equation becomes:

$$\frac{P\,V}{n\,T} = \text{R}$$

The Ideal Gas Law is conveniently rearranged to look this way, with the multiplication signs omitted:

$$\text{PV} = \text{nRT}$$

The variable R in the equation is called the **ideal gas constant**.

The value of R, the ideal gas constant, depends on the *units* chosen for pressure, temperature, and volume in the ideal gas equation. It is necessary to use Kelvin for the temperature and mole for the amount n. However, the units of pressure and volume could be varied and R could have different values as a result

The table below shows a summary of commonly applied values of R. It is important to choose the correct value of R to use for a given problem.

Unit of ***P***	Unit of ***V***	Unit of ***n***	Unit of ***T***	Value and Unit of ***R***
Pa	m^3	mol	K	$8.314\,\frac{J}{mol{\cdot}K}$
kPa	L	mol	K	$8.314\,\frac{J}{mol{\cdot}K}$
atm	L	mol	K	$0.08206\,\frac{L{\cdot}atm}{mol\,{\cdot}K}$

Table 7.1 Values of the Ideal Gas Constant

Example

A 4.22 mol sample of Ar has a pressure of 1.21 atm and a temperature of 34°C. What is its volume?

Solution

Convert temperature to Kelvin, K = 273 + 34^{o}C = 307K

Because PV = nRT , V $= \frac{n\times R\times T}{P} = \frac{4.22\ mol \times 0.08206\frac{atm\ L}{mol\ K}\times 307\ K}{1.21\ atm} = 87.9\ L$

Example

The volume of 3.76g of oxygen gas is 3.23L at a temperature of 19^{o}C? What is the pressure of the gas in Pa.

Solution

Convert temperature to Kelvin, K = 273 + 19^{o}C = 292K
Convert mass of oxygen gas to mol of oxygen: n_{O2} = 3.76g $\times \frac{1\ mol\ O2}{32.0\ g} = 0.1175\ mol$

Because PV = nRT , P $= \frac{n\times R\times T}{V} = \frac{0.1175\ mol \times 8.314\frac{J}{mol\ K}\times 292\ K}{3.23\ L} = 88.3\ kPa$

Convert the pressure to Pa, that is 88300 Pa.

A very important note for using the ideal gas law is that make sure all the variables are in the value with proper units that match with the R value applied.

Application of the Ideal Gas Law: Density and Molar Mass of Gas

The ideal-gas equation can be manipulated to solve a variety of different types of problems, for example to determine the molar mass (MM) or density (d) of a gas.

Based on PV = nRT, if the n(mol) is replaced by n = $\frac{m}{MM}$, then the ideal gas law can be rewritten as:

$$PV = \frac{m}{MM}RT \quad \text{(m: mass ; MM: molar mass)}$$

Make rearrangement to move "V" to the other side,

$$P = \frac{m}{V \times MM}RT$$

Because $\frac{m}{V} = d$, the density is introduced:

$$P = \frac{d}{MM}RT$$

Therefore, the equation for density is:

$$d = \frac{P \times MM}{RT}$$

The equation for molar mass (MM) is:

$$MM = \frac{d \times R \times T}{P} = \frac{m \times R \times T}{P \times V}$$

Density of a gas is generally expressed in g/L.

Example

What is the density of nitrogen gas (N_2) at 248.0 Torr and 18°C?

Solution

P = 248.0 Torr × $\frac{1atm}{760\ Torr}$ = 0.3263 atm;

MM of N_2 gas = 28.0 g/mol

$$d = \frac{P \times MM}{RT} = \frac{0.3263\ atm \times 28.0\ g/mol}{0.08206\ \frac{atm\ L}{mol\ K} \times (273+18)K} = 0.383\ \frac{g}{L}$$

Example

Calculate the molar mass of a gas if 1.50g of the gas in a 670 mL container has a pressure of 0.950 atm at 27.0 °C

Solution

$$MM = \frac{m \times R \times T}{P \times V} = \frac{1.50\ g \times 0.08206\ \frac{atm\ L}{mol\ K} \times (273+27)K}{0.950\ atm \times 0.670\ L} = 58.0\ \frac{g}{mol}$$

7.4 Mixture of Gas and Partial Pressures

The mixture of gas contains two or more gas components mixed together. Because the particles in a gas do not interact, each component in a gas mixture acts independently of the others. John Dalton, the English chemist who proposed the atomic theory, also studied mixtures of gases. He found that each gas in a mixture exerts a pressure independently of every other gas in the mixture. For example, our atmosphere is composed of about 78% nitrogen and 21% oxygen, with smaller amounts of several other gases making up the rest. Since nitrogen makes up 78% of the gas particles in a given sample of air, it exerts 78% of the pressure. If the overall atmospheric pressure is 1.00atm, then the pressure of just the nitrogen in the air is 0.78atm. The pressure of the oxygen in the air is 0.21atm.

The **partial pressure** of a gas is the contribution that gas makes to the total pressure when the gas is part of a mixture. The partial pressure of nitrogen is represented by P_{N2}. **Dalton's Law of Partial Pressures** states that the total pressure of a mixture of gases is equal to the sum of all of the partial pressures of the component gases. Dalton's Law can be expressed with the following equation:

$$P_{total} = P_1 + P_2 + P_3 + \cdots$$

The figure below shows two gases that are in separate, equal-sized containers at the same temperature. Each exerts a different pressure, P1 and P2, reflective of the number of particles in the container. On the right, the two gases are combined into the same container, with no volume change. The total pressure of the gas mixture is equal to the sum of the individual pressures. If P_1 = 300mmHg and P_2 = 500mmHg, then P_{total} = 800mmHg.

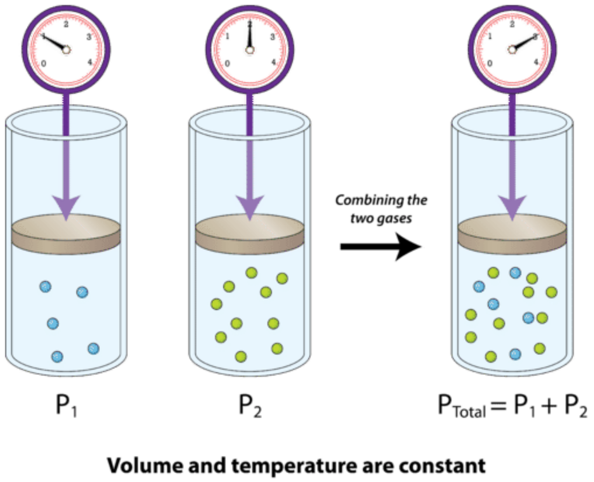


Figure 7.5 Dalton's Law states that the pressure of a gas mixture is equal to the partial pressures of the combining gases.

Since each component in a gas mixture acts independently of the others, the partial pressure of each component can be calculated from the ideal gas law, that is:

$$P_1 = \frac{n_1\,RT}{V};\ P_2 = \frac{n_2\,RT}{V};\ P_3 = \frac{n_3\,RT}{V};\ \ldots$$

Therefore, the total pressure can also be written as:

$$P_{total} = P_1 + P_2 + P_3 + \cdots$$

$$P_{total} = \frac{n_1\,RT}{V} + \frac{n_2\,RT}{V} + \frac{n_3\,RT}{V} + \cdots$$

$$P_{total} = (n_1 + n_2 + n_3 + \cdots)\frac{RT}{V} = n_{total}\frac{RT}{V}$$

If we divide P_1 by P_{total}, we will get the following result:

$$\frac{P_1}{P_{total}} = \frac{n_1\cancel{\frac{RT}{V}}}{n_{total}\cancel{\frac{RT}{V}}} = \frac{n_1}{n_{total}}$$

The quantity $\frac{n_1}{n_{total}}$, the number of moles of a component in a mixture divided by the total number of moles in the mixture, is the mole fraction of that component (X_1)

$$X_1 = \frac{n_1}{n_{total}}$$

Rearrange the above equation also gives: $P_1 = X_1\,P_{total}$, that means the partial pressure of a gas component can also be obtained if the total pressure and the mole fraction of the component available.

Example

A 5.00L gas tank contains 80.0 g of O_2 and 20.0 g of He at 298 K. Determine:

a) The partial pressure for each gas.
b) The total pressure of the mixture.
c) The mole fraction of each gas.

Solution

First of all, we need to convert the mass of each gas component to the mole (n) of each gas:

$n_{O2} = 80.0\text{g} \times \frac{1\,mol\,O2}{32.0\,g} = 2.50\,mol$

$n_{He} = 20.0\text{g} \times \frac{1\,mol\,He}{4.0\,g} = 5.00\,mol$

a) $P_{O2} = \frac{n_{O2}\,RT}{V} = \frac{2.50\,mol \times 0.08206\,\frac{atm\,L}{mol\,K} \times 298\,K}{5.00\,L} = 12.2\text{ atm}$

$P_{He} = \frac{n_{O2}\,RT}{V} = \frac{5.00\,mol \times 0.08206\,\frac{atm\,L}{mol\,K} \times 298\,K}{5.00\,L} = 24.4\text{ atm}$

b) $P_{total} = P_{O2} + P_{He} = 12.2\text{ atm} + 24.4\text{ atm} = 36.6\text{ atm}$

P_{total} can also calculated as $= \frac{n_{total}\,RT}{V} = \frac{(2.50+5.00)mol \times 0.08206\,\frac{atm\,L}{mol\,K} \times 298\,K}{5.00\,L} = 36.6\text{ atm}$

c) $X_{O2} = \frac{n_{O2}}{n_{total}} = \frac{2.50\,mol}{(2.50+5.00)mol} = \frac{1}{3}$

$X_{He} = \frac{n_{He}}{n_{total}} = \frac{5.00\,mol}{(2.50+5.00)mol} = \frac{2}{3}$

Gas Collection by Water Displacement

Gases that are produced in laboratory experiments are often collected by a technique called **water displacement** (Figure 7.6). A glass tube (or bottle) is filled with water and placed upside-down in a container of water. The reaction flask is fitted with rubber tubing, which is then fed under the bottle of water. As the gas is produced in the reaction flask, it exits through the rubber tubing and displaces the water in the glass tube or bottle. When the bottle is full of the gas, it can be sealed with a lid.

Figure 7.6 A gas produced in a chemical reaction can be collected by water displacement.

Because the gas is collected over water, it is not pure, but is mixed with vapor from the evaporation of the water. Dalton's Law can be used to calculate the pressure of the desired gas by subtracting the contribution of the water vapor.

$$P_{total} = P_{gas} + P_{H2O}$$

$P_{gas} = P_{total} – P_{H2O}$ (P_{gas} is the pressure of the desired gas)

In order to solve a problem, it is necessary to know the vapor pressure of water at the temperature of the reaction (see table below). The sample problem illustrates the use of Dalton's Law when a gas is collected over water.

Temp (°C)	**0**	**5**	**10**	**15**	**20**	**25**	**30**
Water Vapor Pressure (mmHg)	4.58	6.54	9.21	12.79	17.54	23.76	31.82
Temp (°C)	**35**	**40**	**45**	**50**	**55**	**60**	
Water Vapor Pressure (mmHg)	42.18	55.32	71.88	92.51	118.04	149.38	

Table 7.2 Vapor Pressure of Water (mmHg) at Selected Temperatures (°C)

Example

A certain experiment generates 2.58L of hydrogen gas, which is collected over water. The temperature is 20°C and the atmospheric pressure is 98.60kPa. How many grams of hydrogen gas collected?

Solution

Based on Dalton’s Law, $P_{gas} = P_{total} – P_{H2O,}$ unit conversion is necessary to make P_{total} and P_{H2O} in the same unit.

P_{total} = 98.60 kPa = 9.860×10^4 Pa = 9.860×10^4 Pa× $\frac{1atm}{101325\ Pa} = 0.973$ atm

P_{H2O} = 17.54 mmHg × $\frac{1atm}{760\ mmHg} = 0.0231\ atm$

P_{gas} = P_{total} – P_{H2O} = 0.973 – 0.0231 atm = 0.950 atm

From ideal gas law: PV = nRT, $n_{H2} = \frac{PV}{RT} = \frac{0.950\ atm \times 2.58\ L}{0.08206\frac{atm\ L}{mol\ K}\times(273+20)K} = 0.102\ mol$

So the mass of H_2 gas = 0.102 mol× $\frac{2.0\ g}{1\ mol\ H2} = 0.204$ g

7.5 Gas Stoichiometry

This section is adapted from https://chem.libretexts.org/Bookshelves/General_Chemistry/Map%3A_General_Chemistry_(Petrucci_et_al.)/06%3A_Gases/6.5%3A_Gases_in_Chemical_Reactions by LibreTexts

Many reactions that are carried out in the laboratory involve the formation or reaction of a gas, so chemists must be able to quantitatively treat gaseous products and reactants as readily as they quantitatively treat solids or solutions. Furthermore, many, if not most, industrially important reactions are carried out in the gas phase for practical reasons that gases mix readily, are easily heated or cooled, and can be transferred from one place to another in a manufacturing facility via simple pumps and plumbing.

Since stoichiometry is based on mole ratio, we can use the ideal gas law to figure out the relationship between the amounts of gases (in moles) and their volumes, pressure and temperature.

Example

Sulfuric acid, the industrial chemical produced in greatest quantity (almost 45 million tons per year in the United States alone), is prepared by the combustion of sulfur in air to give SO_2, followed by the reaction of SO_2 with O_2 in the presence of a catalyst to give SO_3, which reacts with water to give H_2SO_4. The overall chemical equation is as follows:

$$2S(s) + 3O_2(g) + 2H_2O(l) \rightarrow 2H_2SO_4(aq)$$

What volume of O_2 (in liters) at 22°C and 745 mmHg pressure is required to produce 1.00 ton (907.18 kg) of H_2SO_4?

Solution

Step 1: Calculate the number of moles of H_2SO_4 in 1.00 ton. From the stoichiometric coefficients in the balanced chemical equation, calculate the number of moles of O_2 required.

$$\frac{907.18 \times 10^3 \text{ g } \mathrm{H_2SO_4}}{(2 \times 1.008 + 32.06 + 4 \times 16.00) \text{ g/mol}} = 9250 \text{ mol } \mathrm{H_2SO_4}$$

$$9250 \text{ mol } \mathrm{H_2SO_4} \times \frac{3\text{mol } \mathrm{O_2}}{2\text{mol } \mathrm{H_2SO_4}} = 1.389 \times 10^4 \text{ mol } \mathrm{O_2}$$

Step 2: Use the ideal gas law to determine the volume of O_2 required under the given conditions. Be sure that all quantities are expressed in the appropriate units.

$$V = \frac{nRT}{P} = \frac{1.389 \times 10^4 \text{ mol} \times 0.08206 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \times (273 + 22) \text{ K}}{745 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}}} = 3.43 \times 10^5 \text{ L}$$

The answer means that more than 300,000 L of oxygen gas are needed to produce 1 ton of sulfuric acid. These numbers may give you some appreciation for the magnitude of the engineering and plumbing problems faced in industrial chemistry.

Example

Sodium azide (NaN_3) decomposes to form sodium metal and nitrogen gas according to the following balanced chemical equation:

$$2NaN_3 \rightarrow 2Na(s) + 3N_2(g)$$

This reaction is used to inflate the air bags that cushion passengers during automobile collisions. The reaction is initiated in air bags by an electrical impulse and results in the rapid evolution of gas. If the N_2 gas that results from the decomposition of a 5.00 g sample of NaN_3 could be collected by displacing water from an inverted flask, what volume of gas would be produced at 20°C and 762 mmHg?

Solution

This question involves the gas stoichiometry and collecting gas over water (in section 7.2).

Step 1. Calculate the number of moles of N_2 gas produced according to the amount of NaN_3 provided.

$$\frac{5.00\ \text{g NaN}_3}{(22.99 + 3 \times 14.01)\ \text{g/mol}} \times \frac{3\text{mol N}_2}{2\text{mol NaN}_3} = 0.115\ \text{mol N}_2$$

Step 2. From the data in Table 7.3, determine the partial pressure of N_2 gas in the flask.

$P_{N2} = P_{total} – P_{H2O} = 762 – 17.54 = 744.5$ mmHg

$P_{N2} = 744.5\ \text{mmHg} \times \frac{1atm}{760\ mmHg} = 0.980\ \text{atm}$

Step 3. Use the ideal gas law to find the volume of N_2 gas produced.

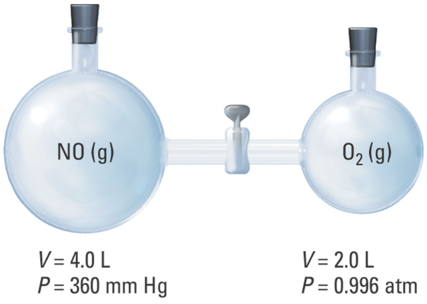
$$V = \frac{nRT}{P} = \frac{0.115\ mol \times 0.08206\ \frac{atm\ L}{mol\ K} \times (273+20)K}{0.950\ atm} = 2.91\ L$$

Limiting Reagent and Gas Reaction

Example

NO(g) and O_2(g) are kept in separate containers as shown below. When the valve is opened, the reaction proceeds to completion at constant temperature of 25 °C.

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$



a) What gases remain at the end of the reaction, and how many moles of each of them is present?
b) What are their partial pressures, and what is the total pressure in the system at the end of the reaction?

Solution

This is a question involves stoichiometry, limiting reagent and gas mixture.

Analysis: With two gases phase reactants react, one of it will be the limiting reagent (L.R.), the other one is in excess. The L.R. reacts completely and has nothing left, while the excess reagent has leftover at the end. So at the end of the reaction, there will be the product (the amount of is determined by the L.R) and the leftover of the excess reagent present in the system.

So first of all, we need to determine the L.R.

Step 1: Determining the L.R and then answer part a).

$$n_{NO} = \frac{PV}{RT} = \frac{360\ mmHg \times \frac{1\ atm}{760\ mmHg} \times 4.0\ L}{0.08206\ \frac{atm\ L}{mol\ K} \times (273+25)K} = 0.0775\ mol$$

$$n_{O2} = \frac{PV}{RT} = \frac{0.996\ atm \times 2.0\ L}{0.08206\ \frac{atm\ L}{mol\ K} \times (273+25)K} = 0.08146\ mol$$

If all the NO gas reacts, gives $0.0775\ mol$ NO $\times \frac{2\ mol\ NO2}{2\ mol\ NO} = 0.0775\ mol\ NO_2$ (this is also the yield of NO_2 product)

If all the O_2 gas reacts, gives $0.08146\ mol$ O_2 $\times \frac{2\ mol\ NO2}{1\ mol\ O2} = 0.163\ mol\ NO_2$

NO gas gives less amount of product, so it is the L.R., O_2 gas is the excess reagent.

$O_{2\ leftover}$ = $O_{2\ total}$ - $O_{2\ reacted}$ = 0.08146 mol - $0.0775\ mol$ NO $\times \frac{1\ mol\ O2}{2\ mol\ NO}$ = 0.0427 mol $O_{2\ leftover}$

Part a): At the end of the reaction, there are: 0.0775 mol NO_2 gas product and 0.0427 mol O_2 gas leftover present in the system.

Step 2: calculate partial pressure and total pressure

Part b):

$$P_{O2} = \frac{n_{O2}RT}{V} \frac{0.0427\ mol \times 0.08206\ \frac{atm\ L}{mol\ K} \times (273+25)K}{6.0\ L} = 0.174\ atm$$

$$P_{NO2} = \frac{n_{NO2}RT}{V} \frac{0.0775\ mol \times 0.08206\ \frac{atm\ L}{mol\ K} \times (273+25)K}{6.0\ L} = 0.316\ atm$$

Chapter 8 Thermochemistry

Chapter 8 was adapted
from https://chem.libretexts.org/Bookshelves/General_Chemistry/Map%3A_Chemistry_-_The_Central_Science_(Brown_et_al.)/05%3A_Thermochemistry by LibreText.

This chapter introduces you to **thermochemistry**, a branch of chemistry that describes the energy changes that occur during chemical reactions. In some situations, the energy produced by chemical reactions is actually of greater interest to chemists than the material products of the reaction. For example, the controlled combustion of organic molecules, primarily sugars and fats, within our cells provides the energy for physical activity, thought, and other complex chemical transformations that occur in our bodies. Similarly, our energy-intensive society extracts energy from the combustion of fossil fuels, such as coal, petroleum, and natural gas, to manufacture clothing and furniture, heat your home in winter and cool it in summer, and power the car or bus that gets you to class and to the movies.

8.1 The Nature of Energy

In this section, we describe the forms of energy and discuss the relationship between energy, heat, and work.

Forms of Energy

The forms of energy include thermal energy, radiant energy, electrical energy, nuclear energy, and chemical energy (Figure 8.1). Thermal energy results from atomic and molecular motion; the faster the motion, the greater the thermal energy. The temperature of an object is a measure of its thermal energy content. Radiant energy is the energy carried by light, microwaves, and radio waves. Objects left in bright sunshine or exposed to microwaves become warm because much of the radiant energy they absorb is converted to thermal energy. Electrical energy results from the flow of electrically charged particles. When the ground and a cloud develop a separation of charge, for example, the resulting flow of electrons from one to the other produces lightning, a natural form of electrical energy. Nuclear energy is stored in the nucleus of an atom, and chemical energy is stored within a chemical compound because of a particular arrangement of atoms.

(a) Thermal energy **(b) Radiant energy**

(c) Electrical energy **(d) Nuclear energy** **(e) Chemical energy**

Figure 8.1 Forms of Energy.

(a) *Thermal energy* results from atomic and molecular motion; molten steel at 2000°C has a very high thermal energy content. (b) *Radiant energy* (e.g., from the sun) is the energy in light, microwaves, and radio waves. (c) Lightning is an example of *electrical energy*, which is due to the flow of electrically charged particles. (d) *Nuclear energy* is released when particles in the nucleus of the atom are rearranged. (e) *Chemical energy* results from the particular arrangement of atoms in a chemical compound; the heat and light produced in this reaction are due to energy released during the breaking and reforming of chemical bonds.

Electrical energy, nuclear energy, and chemical energy are different forms of **potential energy** (**PE**), which is energy stored in an object because of the relative positions or orientations of its components. A brick lying on the windowsill of a 10th-floor office has a great deal of potential energy, but until its position changes by falling, the energy is contained. In contrast, **kinetic energy** (**KE**) is energy due to the motion of an object. When the brick falls, its potential energy is transformed to kinetic energy, which is then transferred to the object on the ground that it strikes. The electrostatic attraction between oppositely charged particles is a form of potential energy, which is converted to kinetic energy when the charged particles move toward each other.

Energy can be converted from one form to another (Figure 8.2) or, as we saw with the brick, transferred from one object to another. For example, when you climb a ladder to a high diving board, your body uses chemical energy produced by the combustion of organic molecules. As you climb, the chemical energy is converted to *mechanical work* to overcome the force of gravity. When you stand on the end of the diving board, your potential energy is greater than it was before you climbed the ladder: the greater the distance from the water, the greater the potential energy. When you then dive into the water, your potential energy is converted to kinetic energy as you fall, and when you hit the surface, some of that energy is transferred to the water, causing it to splash into the air. Chemical energy can also be converted to radiant energy; one common example is the light emitted by fireflies, which is produced from a chemical reaction.

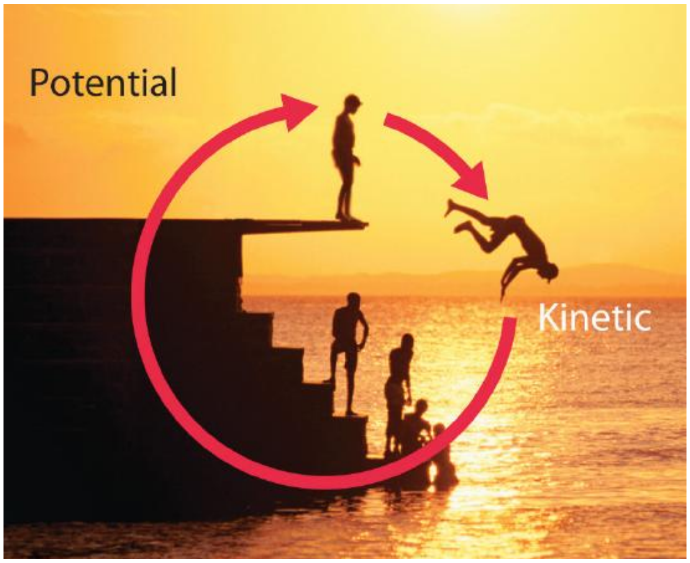


Figure 8.2 Interconversion of Forms of Energy.

When a swimmer steps off the platform to dive into the water, potential energy is converted to kinetic energy. As the swimmer climbs back up to the top of the diving platform, chemical energy is converted to mechanical work.

Although energy can be converted from one form to another, *the total amount of energy in the universe remains constant*. This is known as the **law of conservation of energy**: *Energy cannot be created or destroyed.*

Energy, Heat, and Work

One definition of energy is the capacity to do work. The easiest form of work to visualize is mechanical work (Figure 8.3), which is the energy required to move an object a distance d when opposed by a force F, such as gravity:

$$\text{work} = \text{force x distance}$$

$$w = F \times d$$

Recall from that weight is a force caused by the gravitational attraction between two masses, such as you and Earth.

Consider the mechanical work required for you to travel from the first floor of a building to the second. Whether you take an elevator or an escalator, trudge upstairs, or leap up the stairs two at a time, energy is expended to overcome the force of gravity. The amount of work done (*w*) and thus the energy required depends on three things:

a) the height of the second floor (the distance *d*);
b) your mass, which must be raised that distance against the downward acceleration due to gravity; and
c) your path.

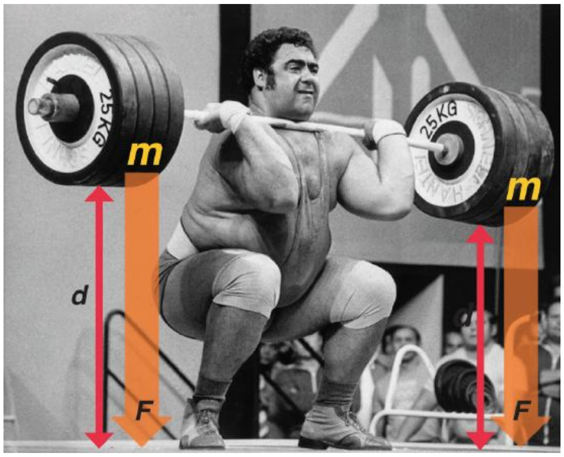


Figure 8.3 An Example of Mechanical Work

In contrast, heat (*q*) is thermal energy that can be transferred from an object at one temperature to an object at another temperature. The net transfer of thermal energy stops when the two objects reach the same temperature.

Energy is an *extensive* property of matter—for example, the amount of **thermal energy** in an object is proportional to both its mass and its temperature. A water heater that holds 150 L of water at 50°C contains much more thermal energy than does a 1 L pot of water at 50°C. Similarly, a bomb contains much more chemical energy than does a firecracker.

Units of Energy

The units of energy are the same for all forms of energy. The SI unit of energy, the joule (J), is named after the British physicist James Joule. Joule is defined as 1 $kg{\cdot}m^2/s^2$. Because a joule is such a small quantity of energy, chemists sometimes express energy in kilojoules (1 kJ = 10^3 J)

Energy can also be expressed in the non-SI units of calories (cal), where 1 cal was originally defined as the amount of energy needed to raise the temperature of exactly 1 g of water from 14.5°C to 15.5°C. We specify the exact temperatures because the amount of energy needed to raise the temperature of 1 g of water 1°C varies slightly with elevation. The name is derived from the Latin *calor*, meaning “heat.” Although energy may be expressed as either calories or joules, calories were defined in terms of heat, whereas joules were defined in terms of motion. Because calories and joules are both units of energy, however, the calorie is now defined in terms of the joule:

$$1\ cal = 4.184\ J \text{ exactly}$$

8.2 The First Law of Thermodynamics

To study the flow of energy during a chemical reaction, we need to distinguish between a **system**, the small, well-defined part of the universe in which we are interested (such as a chemical reaction), and its **surroundings**, the rest of the universe, including the container in which the reaction is carried out (Figure 8.4). In the discussion that follows, the mixture of chemical substances that undergoes a reaction is always the system, and the flow of heat can be from the system to the surroundings or vice versa.

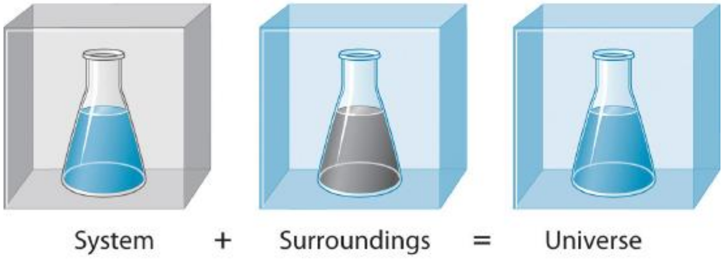


Figure 8.4 A System and Its Surroundings
The system is that part of the universe we are interested in studying, such as a chemical reaction inside a flask. The surroundings are the rest of the universe, including the container in which the reaction is carried out.

Three kinds of systems are important in chemistry. An **open system** can exchange both matter and energy with its surroundings. A pot of boiling water is an open system because a burner supplies energy in the form of heat, and matter in the form of water vapor is lost as the water boils. A **closed system** can exchange energy but not matter with its surroundings. The sealed pouch of a ready-made dinner that is dropped into a pot of boiling water is a closed system because thermal energy is transferred to the system from the boiling water but no matter is exchanged (unless the pouch leaks, in which case it is no longer a closed system). An **isolated system** exchanges neither energy nor matter with the surroundings. A truly isolated system does not actually exist. An insulated thermos containing hot coffee, for example, approximates an isolated system with energy exchange with its surroundings take place very slowly (eventually the coffee cools as heat is transferred to the surroundings). In all cases, the amount of heat lost by a system is equal to the amount of heat gained by its surroundings and vice versa. That is, *the total energy of a system plus its surroundings is constant*, which must be true if *energy is conserved*.

The state of a system is a complete description of a system at a given time, including its temperature and pressure, the amount of matter it contains, its chemical composition, and the physical state of the matter. A **state function** is a property of a system whose magnitude depends on only the present state of the system, not its previous history. Temperature, pressure, volume, and potential energy are all state functions.

Heat and work, on the other hand, are **path functions** because they are *path dependent*. For example, a car sitting on the top level of a parking garage has the *same potential energy* whether it was lifted by a crane, set there by a helicopter, driven up, or pushed up by a group of students (Figure 8.5). The *amount of work* expended to get it there, however, can differ greatly depending on the path chosen. If the students decided to carry the car to the top of the ramp, they would perform a great deal more work than if they simply pushed the car up the ramp. The potential energy of the car is the same, however, no matter which path they choose.

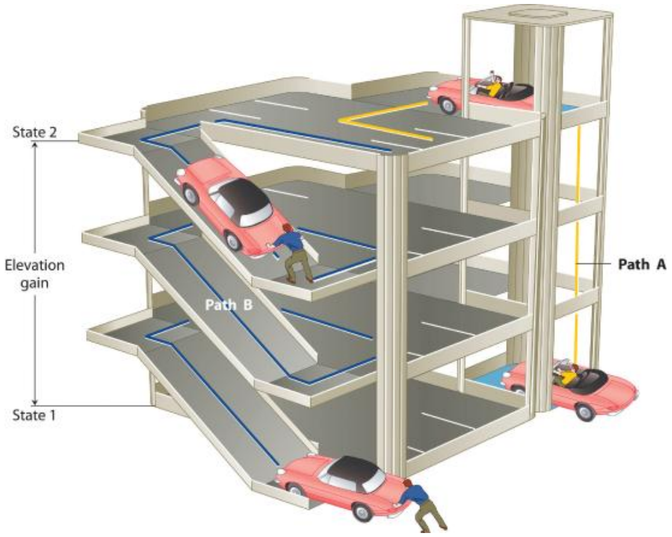


Figure 8.5 Elevation as an Example of a State Function.
The change in elevation between state 1 (at the bottom of the parking garage) and state 2 (at the top level of the parking garage) is the same for both paths A and B; it does not depend on which path is taken from the bottom to the top. In contrast, the distance traveled and the work needed to reach the top do depend on which path is taken. Elevation is a state function, but distance and work are *path* functions.

The First Law of Thermodynamics

The relationship between the energy change of a system and that of its surroundings is given by the **first law of thermodynamics**, which states that the energy of the universe is constant. We can express this law mathematically as follows:

$$\Delta E_{univ} = \Delta E_{sys} + \Delta E_{surr} = 0$$
$$\Delta E_{sys} = -\Delta E_{surr}$$

where the subscripts univ, sys, and surr refer to the universe, the system, and the surroundings, respectively. Thus the change in energy of a system is identical in magnitude but opposite in sign to the change in energy of its surroundings.

Because heat and work are the only two ways in which energy can be transferred between a system and its surroundings, any change in the internal energy of the system is the sum of the heat transferred (q) and the work done (w):

$$\Delta E_{sys} = q + w$$

Because we focus almost exclusively on the changes in the energy of a system, we will not use "sys" as a subscript unless we need to distinguish explicitly between a system and its surroundings.

Thus, because of the first law, we can determine ΔE for any process if we can measure both q and w. Heat, q, may be calculated by measuring a change in temperature of the surroundings (more discussion in section 8.6). Work, w, may come in different forms, but it too can be measured. One important form of work for chemistry is *pressure-volume work* done by an expanding gas. At a constant external pressure (for example, atmospheric pressure),

$$w = -P\Delta V$$

The negative sign associated with PV work done indicates that the system loses energy when the volume increases. That is, an expanding gas does work on its surroundings, while a gas that is compressed has work done on it by the surroundings.

8.3 Enthalpy and Thermochemical Equations

Enthalpy as a Composite Function

For chemistry processes that occurs in an open system, the pressure of the system equals to the atmospheric pressure all the time, as a result the process is a constant-pressure process. If it is assumed that PV work is the only kind of work possible for the system, we can get:

$$\Delta E = q + w = q + (-P\Delta V)$$

(ΔE is for system, where the subscripts have been deleted)

With rearrangement, $q = \Delta E - (-P\Delta V) = \Delta E + P\Delta V$

Because reactions here are under constant pressure, the heat flow under such condition is given the symbol of q_p, means the heat flow for constant-pressure process.

$$q_p = \Delta E + P\Delta V \quad \text{(for constant pressure)}$$

Thus, at constant pressure, the heat flow for any process is equal to the change in the internal energy of the system plus the PV work done.

Because conditions of constant pressure are so important in chemistry, a new state function called **enthalpy** (**H**) is defined as

$$H = E + PV$$

At constant pressure, the change in the enthalpy of a system is as follows:

$$\Delta H = \Delta E + \Delta(PV) = \Delta E + P\Delta V$$

Comparing the previous two equations shows that at constant pressure, the change in the enthalpy of a system is equal to the heat flow: $\Delta H = q_p$. This expression is consistent with our definition of enthalpy, where we stated that enthalpy is the heat absorbed or produced during any process that occurs at constant pressure.

At constant pressure, the change in the enthalpy of a system is equal to the heat flow: $\Delta H = q_p$

Just as with ΔE, because enthalpy is a state function, the magnitude of ΔH depends on only the initial and final states of the system, not on the path taken.

Enthalpy of Reaction

When we study energy changes in chemical reactions, the most important quantity is usually the enthalpy of reaction (ΔH_{rxn}), the change in enthalpy that occurs during a reaction (such as the dissolution of a piece of copper in nitric acid). If heat flows from a system to its surroundings, the enthalpy of the system decreases, so ΔH_{rxn} is negative "–" . Conversely, if heat flows from the surroundings to a system, the enthalpy of the system increases, so ΔH_{rxn} is positive "+". Thus:

- $\Delta H_{rxn} < 0$ for an *exothermic reaction*,
- $\Delta H_{rxn} > 0$ for an *endothermic reaction*.

In chemical reactions, bond breaking requires an input of energy and is therefore an endothermic process, whereas bond making releases energy, which is an exothermic process. The sign conventions for heat flow and enthalpy changes are summarized in the following table:

Reaction Type	**q**	**ΔH_{rxn}**	**Sign of ΔH_{rxn}**
exothermic	< 0	< 0 (heat flows from a system to its surroundings)	–
endothermic	> 0	> 0 (heat flows from the surroundings to a system)	+

If ΔH_{rxn} is negative, then the enthalpy of the products is less than the enthalpy of the reactants; that is, *an exothermic reaction is energetically downhill* (Figure 8.6a). Conversely, if ΔH_{rxn} is positive, then the enthalpy of the products is greater than the enthalpy of the reactants; thus, *an endothermic reaction is energetically uphill* (Figure 8.6b).

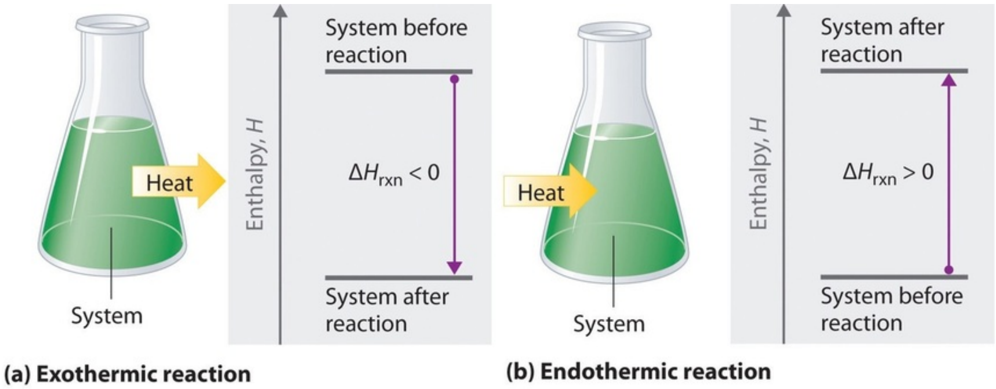


Figure 8.6 The Enthalpy of Reaction

Energy changes in chemical reactions are usually measured as changes in enthalpy. (a) If heat flows from a system to its surroundings, the enthalpy of the system decreases, ΔH_{rxn} is negative, and the reaction is exothermic; it is energetically downhill. (b) Conversely, if heat flows from the surroundings to a system, the enthalpy of the system increases, ΔH_{rxn} is positive, and the reaction is endothermic; it is energetically uphill. (CC BY-NC-SA; anonymous)

Thermochemical Equation

When the specific value of ΔH_{rxn} (enthalpy of reaction or heat of reaction) is combined with the balanced chemical equation, the equation is the thermochemical equation. A few examples here:

$C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2\ g) + 4H_2O(g)$ $\Delta H_{rxn} = -2044$ kJ

$H_2(g) + ½\ O_2(g) \rightarrow H_2O(g)$ $\Delta H_{rxn} = -241.8$ kJ

Several important characteristics of enthalpy and changes in enthalpy are summarized in the following discussion.

- **Reversing a reaction or a process changes the sign of Δ*H*.**

  Formation of water releases heat, while the decomposition of water absorbs heat.

  $H_2(g) + ½\ O_2(g) \rightarrow H_2O(g)$ $\Delta H_{rxn} = -241.8$ kJ
  $H_2O(g) \rightarrow H_2(g) + ½\ O_2(g)$ $\Delta H_{rxn} = +241.8$ kJ

  In both cases, the *magnitude* of the enthalpy change is the same; but the *sign* is opposite.

- **Enthalpy is an extensive property (like mass).** The magnitude of ΔH for a reaction is proportional to the amounts of the substances that react, so **if the equation is multiplied by a factor, ΔH is also multiplied by the same factor.** For the above reaction example, 241.8 kJ of heat is released for the formation of 1 mol of $H_2O(g)$. When 2 mol of $H_2O(g)$ is formed, the amount of heat released will be doubled, that is 483.6 kJ.

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(g) \qquad \Delta H_{rxn} = -483.6 \text{ kJ}$$

- **The magnitude of Δ*H*** *depends on the states of substances as well. For example, the formation of* $H_2O(l)$ releases more heat than the formation of $H_2O(g)$.

$$H_2(g) + \tfrac{1}{2} O_2(g) \rightarrow H_2O(l) \qquad \Delta H_{rxn} = -285.8 \text{ kJ}$$

According to thermochemical reaction, the amount of heat relates to the amount (mole) of substances involved in the reaction, like 1mol $H_2O(g)$ = -241.8 kJ. Such relationship can be used as conversion factor to calculate how much heat involved for certain mass of substance in a reaction, in the way of calculation that is similar to the stoichiometry we usually do.

Example

For following thermite reaction, when 3.0g of Al(s) reacts with enough amount of $Fe_2O_3(s)$, how much heat will be released?

$$2Al(s) + Fe_2O_3(s) \rightarrow 2Fe(s) + Al_2O_3(s) \qquad \Delta H = -851.5\text{kJ}$$

Solution

The correlation between aluminum and heat is: 2mol Al(s) = −851.5kJ

So, to do the calculation, we first of all need to convert the mass of Al(s) to the mole, and then use the conversion factor between mol of Al(s) with heat, in the similar way as stoichiometry:

$$3.0\text{g Al} \times \frac{1\text{mol}}{27.0\text{g Al}} \times \frac{-851.5 \text{ kJ}}{2\text{mol Al}} = -94.6 \text{ kJ}$$

Example

Ethanol (C_2H_5OH) can be used as a fuel based on the following thermochemical equation. Calculate the mass of ethanol you would need to provide 425 kJ of heat.

$$C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l) \qquad \Delta H = -1366.8 \text{ kJ}$$

Solution

425kJ of heat is provided by the reaction, so the heat should have "-" sign in the calculation.

$$-425\text{ kJ} \times \frac{1\ mol\ C2H5OH}{-1366.8\ kJ} \times \frac{46.0\ g}{1\ mol\ C2H5OH} = 14.3\text{g } C_2H_5OH \text{ required}$$

8.4 Enthalpies of Formation

Enthalpy of formation (ΔH_f) is the enthalpy change for the formation of 1 mol of a compound from its component elements in the most stable state. The formation of any chemical can be as a reaction from the corresponding elements.

For example, consider the combustion of carbon with oxygen to form carbon dioxide:

$$C(s) + O_2(g) \longrightarrow CO_2(g)$$

then

$$\Delta H_{rxn} = \Delta H_{f\ (CO2(g))}$$

The sign convention for ΔH_f is the same as for any enthalpy change: $\Delta H_f < 0$ if heat is released when elements combine to form a compound, and $\Delta H_f > 0$ if heat is absorbed.

Standard Enthalpies of Formation

The magnitude of ΔH for a reaction depends on the physical states of the reactants and the products (gas, liquid, solid, or solution), the pressure of any gases present, and the temperature at which the reaction is carried out. To avoid confusion caused by differences in reaction conditions and ensure uniformity of data, the scientific community has selected a specific set of conditions under which enthalpy changes are measured. These **standard conditions** serve as a reference point for measuring differences in enthalpy, much as sea level is the reference point for measuring the height of a mountain or for reporting the altitude of an airplane.

The **standard conditions** for which most thermochemical data are tabulated are: a *pressure* of 1 atmosphere (atm) for all gases, a *concentration* of 1 M for all species in solution (1 mol/L). In addition, each pure substance must be in its standard state, which is usually its most stable form at a pressure of 1 atm at a specified temperature. We usually assume a temperature of 25°C (298 K) for all enthalpy changes given, unless otherwise indicated.

Enthalpies of formation measured under these conditions are called **standard enthalpies of formation** (ΔH_f°), that is the enthalpy change for the formation of 1 mol of a compound from its component elements when the component elements are each in their standard states.

The standard enthalpy of formation of any element in its standard state is zero by definition.

For example, although oxygen can exist as ozone (O_3), atomic oxygen (O), and molecular oxygen (O_2), O_2 is the most stable form at 1 atm pressure and 25°C. Similarly, hydrogen is H_2(g), not atomic hydrogen (H). Graphite and diamond are both forms of elemental carbon, but because graphite is more stable at 1 atm pressure and 25°C, the standard state of carbon is graphite (Figure 8.7). Therefore, O_2(g), H_2(g), and graphite have ΔH_f° values of zero.

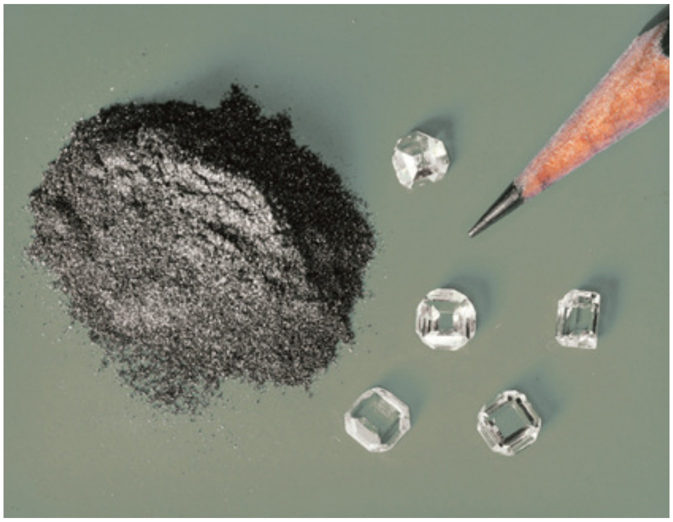


Figure 8.7 Elemental Carbon

Although graphite and diamond are both forms of elemental carbon, graphite is slightly more stable at 1 atm pressure and 25°C than diamond is, and is defined as the standard state of element carbon.

Example

For the formation of each compound, write a balanced chemical equation corresponding to the standard enthalpy of formation of each compound.

a. HCl(g)
b. $MgCO_3$(s)
c. CH_3CO_2H (l) (*acetic acid*)

Solution

a. ½ H_2(g) + ½ Cl_2(g) ⟶ HCl(g)

b. Mg(s) + C(s,graphite) + 3/2 O_2(g) ⟶ $MgCO_3$(s)

c. 2C(s,graphite) + O_2(g) + 2 H_2(g) ⟶ CH_3CO_2H (l)

Standard Enthalpies of Reaction

Tabulated values of standard enthalpies of formation can be used to calculate enthalpy changes for *any* reaction involving substances whose ΔH°_{f} values are known. The standard enthalpy of reaction ΔH°_{rxn} is the enthalpy change that occurs when a reaction is carried out with all reactants and products in their standard states. Consider the general reaction:

$$aA + bB \longrightarrow cC + dD$$

The magnitude of ΔH°_{rxn} is the sum of the standard enthalpies of formation of the products, each multiplied by its appropriate coefficient, minus the sum of the standard enthalpies of formation of the reactants, also multiplied by their coefficients:

$$\Delta H^{o}_{rxn} = \underbrace{\left[c\Delta H^{o}_{f}\,(C) + d\Delta H^{o}_{f}\,(D)\right]}_{\text{products}} - \underbrace{\left[a\Delta H^{o}_{f}\,(A) + b\Delta H^{o}_{f}\,(B)\right]}_{\text{reactants}}$$

More generally, we can write

$$\Delta H^{o}_{rxn} = \sum m\Delta H^{o}_{f}\,(products) - \sum n\Delta H^{o}_{f}\,(reactants)$$

where the symbol ∑ means "sum of" and m and n are the stoichiometric coefficients of each of the products and the reactants, respectively.

Example

Calculate ΔH° for the combustion of glucose, the reaction that provides energy for your brain:

$$C_6H_{12}O6(s) + 6O_2(g) \longrightarrow 6CO_2(g) + 6H_2O(l)$$

Given: $\Delta H^{\circ}_{f(C6H12O6(s))}$ = -1273.3 kJ
$\Delta H^{\circ}_{f(CO2(g))}$ = -393.5 kJ
$\Delta H^{\circ}_{f(H2O(l))}$ = -285.8 kJ

Solution

$$\Delta H^{o}_{rxn} = \sum m\Delta H^{o}_{f}\,(products) - \sum n\Delta H^{o}_{f}\,(reactants)$$

$$= 6 \times \Delta H^{\circ}_{f(CO2(g))} + 6 \times \Delta H^{\circ}_{f(H2O(l))} - (\Delta H^{\circ}_{f(C6H12O6(s))} + 6 \times \Delta H^{\circ}_{f(O2(g))})$$

$$= 6 \times (-393.5) + 6 \times (-285.8) - ((-1273.3) + 0) = -\,2802.5\ \text{kJ}$$

8.5 Calorimetry

Thermal energy itself cannot be measured easily, but the temperature change caused by the flow of thermal energy between objects or substances can be measured. **Calorimetry** describes a set of techniques employed to measure enthalpy changes in chemical processes using devices called *calorimeters*. To have any meaning, the quantity that is actually measured in a calorimetric experiment, the change in the temperature of the device, must be related to the heat evolved or consumed in a chemical reaction. We begin this section by explaining how the flow of heat affects the temperature of an object.

Heat Capacity

We have seen that the temperature of an object changes when it absorbs or loses thermal energy. The *magnitude* of the temperature change depends on both the *amount* of thermal energy transferred (q) and the *heat capacity* of the object. Heat capacity (C) is the amount of energy needed to raise the temperature of the object exactly 1°C. The unit of C is joules per degree Celsius (J/°C). Note that a degree Celsius is exactly the same as a Kelvin, so the heat capacities can be expresses equally well, as joules per Kelvin, J/K.

The heat capacity of an object depends on both its *mass* and its *composition*. For example, doubling the mass of an object doubles its heat capacity. Consequently, the amount of substance must be indicated when the heat capacity of the substance is reported. The specific heat (C_s) is the amount of heat needed to increase the temperature of 1 g of a substance by 1°C; its units are thus J/(g•°C).

Therefore, the amount of heat transferred relates to the mass of a substance, its specific heat capacity and the temperature change via the equation:

$$q = mC_s\Delta T$$

where m is the mass of substance in grams, and C_s is the specific heat. ΔT is the temperature change, that is *always* written as the final temperature minus the initial temperature:

$$\Delta T = T_{final} - T_{initial}$$

The specific heats of some common substances are given in Table 8.1. Note that the specific heat values of most solids are less than 1 J/(g•°C), whereas those of most liquids are about 2 J/(g•°C). Water in its solid and liquid states is an exception. The heat capacity of ice is twice as high as that of most solids; the heat capacity of liquid water, 4.184 J/(g•°C), is one of the highest known.

Compound	Specific Heat [J/(g•°C)]	Compound	Specific Heat [J/(g•°C)]
H_2O (s)	2.108	Al(s)	0.897
H_2O (l)	4.184	Fe(s)	0.449
H_2O (g)	2.062	Cu(s)	0.385
CH_3OH (methanol)	2.531	Au(s)	0.129
CH_3CH_2OH (ethanol)	2.438	Hg(l)	0.140
n-C_6H_{14} (*n*-hexane)	2.270	NaCl(s)	0.864
C_6H_6 (benzene)	1.745	MgO(s)	0.921
C(s) (graphite)	0.709	SiO_2(s) (quartz)	0.742
C(s) (diamond)	0.509	$CaCO_3$(s) (calcite)	0.915

Table 8.1 Specific Heats of Selected Substances at 25°C

The high specific heat of liquid water has important implications for life on Earth. A given mass of water releases more than five times as much heat for a 1°C temperature change as does the same mass of limestone or granite. Consequently, coastal regions of our planet tend to have less variable climates than regions in the center of a continent. After absorbing large amounts of thermal energy from the sun in summer, the water slowly releases the energy during the winter, thus keeping coastal areas warmer than otherwise would be expected. Moreover, because the human body is about 70% water by mass, a great deal of energy is required to change its temperature by even 1 °C. Consequently, the mechanism for maintaining our body temperature at about 37 °C does not have to be as finely tuned as would be necessary if our bodies were primarily composed of a substance with a lower specific heat.

Example

To heat up the water in a 60L water tank from 25 °C to 80 °C, how much heat will be required? (The density of water is 1.0 g/mL)

Solution

The mass of water is: m = 60 L × $\frac{1000\,mL}{L} \times 1.0\frac{g}{mL} = 60000\ g$

The temperature change $\Delta T = T_{final} - T_{initial} = 80 - 25 = 55$ °C

Heat required: $q = mC_s\Delta T = 60000\text{ g} \times 4.184\,\frac{J}{g\,°C} \times 55°C = 1.38 \times 10^7$ J

Heat Transfer Process between Hot Metal and Cold water

For an example: If a 30.0 g piece of hot copper at 80.0 °C is placed in 100.0 g of water at 27.0 °C, what is the final temperature? Assume that copper and water are kept in a thermal container and no heat is transferred to the surroundings.

When two objects at different temperatures are placed in contact, heat flows from the warmer object to the cooler one **until the temperature of both objects is the same**. Since such process is carried out in a container that no heat is lost to the surroundings, the law of conservation of energy says that the total energy doesn't change during this process:

$$q_{cold} + q_{hot} = 0$$

The equation implies that the amount of heat that flows *from* a warmer object is the same as the amount of heat that flows *into* a cooler object. Because the direction of heat flow is opposite for the two objects, the sign of the heat flow values must be opposite:

$$q_{cold} = -q_{hot}$$

Thus heat is conserved in any such process, consistent with the law of conservation of energy.

For this specific example, it can be written as:

$$q_{water} = -q_{copper}$$

Substituting for *q* from equation $q = mC_s\Delta T$, gives:

$$(mC_s\Delta T)_{water} = -(mC_s\Delta T)_{copper}$$

Solution

Mass of both water and copper are given in the question, Cs can be obtained from the Table 8.1. However, ΔT is unknown for both because the T_{final} is what we want to solve (keep in mind that water and copper reaches the same T_{final}).

$$(mC_s\Delta T)_{water} = -(mC_s\Delta T)_{copper}$$

$$100.0\ \text{g} \times 4.184\ \frac{J}{g\ {}^\circ\text{C}} \times (T_{final} - 27.0){}^\circ\text{C} = -(30.0\ \text{g} \times 0.385\ \frac{J}{g\ {}^\circ\text{C}} \times (T_{final} - 80.0){}^\circ\text{C})$$

$$418.4\ (T_{final} - 27.0) = -11.55\ (T_{final} - 80.0)$$

$$418.4\ T_{final} - 11296.8 = -11.55\ T_{final} + 924$$

$$429.95\ T_{final} = 11220.8$$

$$T_{final} = 28.4\ {}^\circ\text{C}$$

Coffer-Cup Calorimeter

Because ΔH is defined as the heat flow at constant pressure, measurements made using a constant-pressure calorimeter (a device used to measure enthalpy changes in chemical processes at constant pressure) give ΔH values directly. This device is particularly well suited to studying reactions carried out in solution at a constant atmospheric pressure. A "student" version, called a *coffee-cup calorimeter* (Figure 8.8), is often encountered in general chemistry laboratories. Because the heat released or absorbed at constant pressure is equal to ΔH, the relationship between heat and ΔH_{rxn} is

$$\Delta H_{rxn} = q_{rxn} = -q_{\text{solution in calorimater}} = -mCs\Delta T$$

The use of a constant-pressure calorimeter is illustrated in next example.

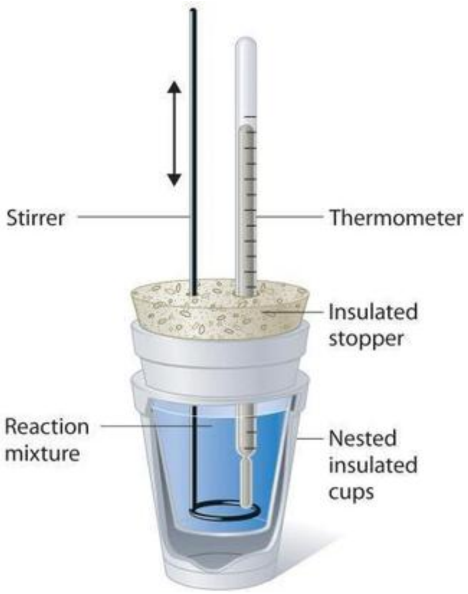


Figure 8.8 A Coffee-Cup Calorimeter

This simplified version of a constant-pressure calorimeter consists of two Styrofoam cups nested and sealed with an insulated stopper to thermally isolate the system (the solution being studied) from the surroundings (the air and the laboratory bench). Two holes in the stopper allow the use of a thermometer to measure the temperature and a stirrer to mix the reactants.

Coffee-cup Calorimeter Example

Calculate ΔH for the reaction based on the following experiment:

$NaOH(aq) + HCl(aq) \rightarrow NaCl(aq) + H_2O(l)$

50.0 mL of 0.500 *M* NaOH and 25.0 mL of 0.500 *M* HCl were placed in a coffee-cup calorimeter at 25.00 ^{o}C. After reaction, the final temperature is 27.21 ^{o}C. Assume that the total volume of the mixture is the sum of the individual volumes, and the final solution has the same density and specific heat capacity as water (Cs_{water} = 4.184 J/g ^{o}C, d_{water}= 1.00 g/mL), and the calorimeter absorbs a negligible amount of heat because of the large volume of solution., i.e., ***heat capacity of the coffee cup is negligible.***

Strategy

Step 1: Apply mCsΔT to calculate the heat q evolved in this experiment with given amount of reactants.

Step 2: ΔH is the heat of reaction for 1mol of reaction based on balanced equation, but the q calculated in step 1 is for the amounts in that experiment, *not* one mole of reaction. So ΔH need to be calculated by ΔH = $\frac{q}{mol}$

Solution

Step 1

$q_{rxn} = -q_{\text{solution in calorimater}} = -mCs\Delta T$

m = (50.0 + 25.0) mL × $1.0\frac{g}{mL} = 75.0\ g$

$\Delta T = T_{final} - T_{initial} = 27.21\ ^{o}C - 25.00\ ^{o}C = 2.21^{o}C$

$q_{rxn} = -mCs\Delta T = -(75.0\ g \times 4.184\ \frac{J}{g\ ^{\circ}C} \times 2.21\ ^{o}C) = -\ 693.5\ J$

This experiment tells us that when 0.01250mol NaOH reacts with 0.01250mol HCl, 695.5J of heat is released. Because q has "-" sign, the neutralization reaction is exothermic.

Step 2

Determine the mole of reaction with given amounts of reactants:

mol of NaOH = 0.0500 L × 0.500 M = 0.0250 mol

mol of HCl = 0.0250 L × 0.500 M = 0.01250 mol

HCl is the limiting reagent, the mole of the reaction is determined by the L.R., that is 0.01250 mol.

$\Delta H = \frac{q}{mol} = \frac{-693.5\ J}{0.01250} = -55480\ J/mol$

8.6 Hess's Law

Because enthalpy is a state function, the enthalpy change for a reaction depends on only two things: (1) the masses of the reacting substances and (2) the physical states of the reactants and products. It does **not** depend on the path by which reactants are converted to products. If you climbed a mountain, for example, the altitude change would not depend on whether you climbed the entire way without stopping or you stopped many times to take a break. If you stopped often, the overall change in altitude would be the sum of the changes in altitude for each short stretch climbed. Similarly, when we add two or more balanced chemical equations to obtain a net chemical equation, ΔH for the net reaction is the sum of the ΔH values for the individual reactions. This principle is called Hess's law, after the Swiss-born Russian chemist Germain Hess (1802–1850), a pioneer in the study of thermochemistry. Hess's law allows us to calculate ΔH values for reactions that are difficult to carry out directly by adding together the known ΔH values for individual steps that give the overall reaction, even though the overall reaction may not actually occur via those steps.

***Hess's Law** argues that ΔH for the net reaction is the sum of the ΔH values for the individual reactions.*

We can illustrate Hess's law using the formation reaction of CO, carbon monoxide. The overall reaction can be viewed as occurring in two distinct steps with known ΔH values.

As shown in Figure 8.9, the first reaction produces 1 mol of CO_2 with the enthalpy change for this reaction is −393.1 kJ/mol of CO_2. The second reaction is the decomposition of 1 mol CO_2 to CO and ½ mol of O_2, and the enthalpy change for this reaction is +282.7/mol of CO_2. As you can see in Figure 8.8, the overall reaction is given by the red arrow, which is the sum of the two blue arrow reactions.

Overall (net) reaction: $C\ (s) + \frac{1}{2}\ O_2\ (g) \rightarrow CO\ (g)$ $\Delta H = ?$

Step 1: $C\ (s) + O_2\ (g) \rightarrow CO_2\ (g)$ $\Delta H_1 = -393.1\ kJ$

Step 2: $CO_2\ (g) \rightarrow CO\ (g) + \frac{1}{2}\ O_2\ (g)$ $\Delta H_2 = +282.7\ kJ$

By Hess's law, the enthalpy change for the net reaction is the sum of the enthalpy changes for parts step 1 and step 2. In essence, Hess's law enables us to calculate the enthalpy change for the sum of a series of reactions without having to draw a diagram like that in.

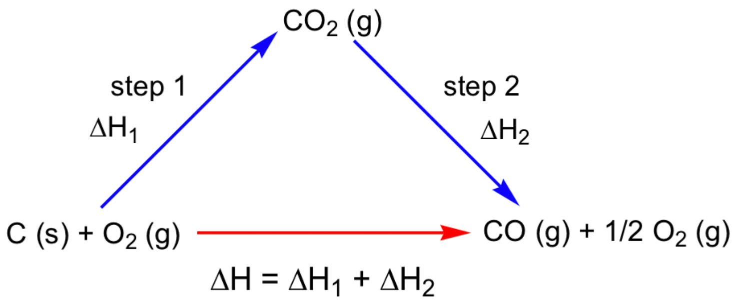


Figure 8.9 Illustration of Hess's Law

Solution

Overall (net) reaction: $C\ (s) + \frac{1}{2}\ O_2\ (g) \rightarrow CO\ (g)$

$\Delta H = \Delta H_1 + \Delta H_2 = -393.1\ \text{kJ} + 282.7\ \text{kJ} = -110.4\ \text{kJ}$

When using Hess's law to calculate the value of ΔH for a reaction, follow this procedure:

1. Identify the equation whose ΔH value is unknown and individual reactions with known ΔH given.
2. Arrange the individual reactions with known ΔH so that the reaction of interest is the sum of the individual reactions. Using the reaction of interest as reference, for example, a certain compound in the reaction of interest is on which side, with what coefficient, to decide how to arrange the individual reactions.
3. If a reaction must be reversed, change the sign of ΔH for that reaction. Additionally, if a reaction must be multiplied by a factor to obtain the correct number of moles of a substance, multiply its ΔH value by that same factor.
4. Add together the individual reactions and their corresponding ΔH values to obtain the reaction of interest and the unknown ΔH.

Example

Determine the enthalpy change for the reaction $C_2H_{6(g)} \rightarrow C_2H_{4(g)} + H_{2(g)}$ $\Delta H = ?$
from the following data:

$2C_2H_{6(g)} + 7O_{2(g)} \rightarrow 4CO_{2(g)} + 6H_2O_{(l)}$ $\Delta H = -3119.4\ \text{kJ}$

$C_2H_{4(g)} + 3O_{2(g)} \rightarrow 2CO_{2(g)} + 2H_2O_{(l)}$ $\Delta H = -1410.9\ \text{kJ}$

$2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(l)}$ $\Delta H = -571.66\ \text{kJ}$

Solution

rxn 1 ÷ 2 $C_2H_{6(g)} + 7/2\ O_{2(g)} \rightarrow 2CO_{2(g)} + 3H_2O_{(l)}$ $\Delta H = (-3119.4) \div 2\ \text{kJ}$

rxn 2 reversed $2CO_{2(g)} + 2H_2O_{(l)} \rightarrow C_2H_{4(g)} + 3O_{2(g)}$ $\Delta H = +1410.9\ \text{kJ}$

rxn 3 reversed, then ÷ 2 $H_2O_{(l)} \rightarrow H_{2(g)} + 1/2\ O_{2(g)}$ $\Delta H = (+571.66) \div 2\ \text{kJ}$ add up

gives overall reaction: $C_2H_{6(g)} \rightarrow C_2H_{4(g)} + H_{2(g)}$

For overall reaction, $\Delta H = (-3119.4) \div 2 + (1410.9) + (571.66) \div 2 = 137.0\ \text{kJ}$

Chapter 9 Chemical Equilibrium

9.1 Dynamic Chemical Equilibrium

Reactions do not always proceed all the way from start to finish. You may have reactions that (1) go to completion so that at the end, the reaction vessel contains all products and only products. Some reactions (2) may not start at all, so at the end the reaction vessel contains all reactants and only reactants. And some reactions (3) may start but not go to completion, that is, the reaction might start but not go completely to products. In this last case, the reaction vessel would contain some reactants and some products. In this section, we are going to take a closer look at the third type of reaction.

Reversible Reactions and Equilibrium

Consider the hypothetical reaction:

$$A + B \rightarrow C + D$$

If we looked at this reaction using what we have learned, this reaction will keep going, forming C and D until A and B run out. This is what we call an "irreversible reaction" or a "reaction that goes to completion".

Some reactions, however, are **reversible**, meaning the reaction can go backwards in which products react to form reactants, so that: $A + B \leftarrow C + D$. The direction of the arrow shows that C and D are reacting to form A and B. What if the two reactions, the forward reaction and the reverse reaction, were occurring at the same time? What would this look like? If you could peer into the reaction, you would be able to find A, B, C, and D particles. A and B would react to form C and D at the same time that C and D are reacting to form A and B.

If the forward and reverse reactions are happening at the same rate, the reaction is said to be at **equilibrium** or **dynamic equilibrium**. At this point, the concentrations of A, B, C, and D are not changing (or, are constant) and we would see no difference in our reaction container, but reactions are still occurring in both directions. It is important to point out that having constant amounts of reactants and products does NOT mean that the concentration of the reactants is equal to the concentration of the products. **It means they are not changing**. There are no net changes for the concentration of all substances with the reactions still running.

Chemists use a double-headed arrow, $\rightleftharpoons$, to show that a reaction is at equilibrium. We would write the example reaction as:

$$A + B \rightleftharpoons C + D$$

The arrow indicates that both directions of the reaction are happening.

Equilibrium Constant

In the previous section, you learned about reactions that can reach a state of equilibrium, in which the concentration of reactants and products aren't changing. If these amounts are changing, we should be able to make a relationship between the amount of product and reactant when a reaction reaches equilibrium.

Equilibrium reactions are those that do not go to completion, but are in a state where the reactants are reacting to yield products and the products are reacting to produce reactants. In a reaction at equilibrium, the equilibrium concentrations of all reactants and products can be measured. The **equilibrium constant (K_{eq})** is a mathematical relationship that shows how the concentrations of the products over the concentration of the reactants when a reaction reaches equilibrium. Sometimes, subscripts are added to the equilibrium constant symbol K, K_c, K_p, K_a, K_b etc. These are all equilibrium constants and are subscripted to indicate special types of equilibrium reactions. K_c, is the equilibrium constant in terms of concentration, is also the most common applied version of equilibrium constant. The K_p, equilibrium constant in terms of partial pressure, will be introduced later in this chapter.

Please note that equilibrium constant K has no unit!

For the hypothetic reaction, expression of K_c is:

$$aA + bB \rightleftharpoons cD + dD$$

$$K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

[ ]: molarity concentration of substance at equilibrium

There are some rules about writing equilibrium constant expressions that need to be learned:

1. Concentrations of products are multiplied on the top of the expression. Concentrations of reactants are multiplied together on the bottom.
2. Coefficients in the equation become ***exponents*** in the equilibrium constant expression.
3. Pure solids, liquids, and solvents are assigned a value of 1, so their concentrations do not affect the value of K_c.

Example

Write the K_c expression for following reactions.

a) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

b) $CaO(s) + CO_2(g) \rightleftharpoons CaCO_3(s)$

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

Solution

a) $K_c = \frac{[NH_3]^2}{[N_2]\ \ [H_2]^3}$

b) $K_c = \frac{1}{1 \times [CO_2]}$

c) $K_c = \frac{[ZnCl_2]\ \ [H_2]}{[HCl]^2}$

Meaning of Equilibrium Constant Value

The equilibrium constant value is the ratio of the concentrations of the products over the reactants. This means that we can use the value of K to predict whether there are more products or reactants at equilibrium for a given reaction. What can the value of K_{eq} tell us about a reaction?

- **If K_{eq} is very large**, the concentration of the products is much greater than the concentration of the reactants. The reaction essentially "goes to completion"; all, or most of, the reactants are used up to form the products.
- **If K_{eq} is very small**, the concentration of the reactants is much greater than the concentration of the products. The reaction does not occur to any great extent—most of the reactants remain unchanged, and there are few products produced.
- **When K_{eq} is not very large or very small** (close to a value of 1) then roughly equal amounts of reactants and products are present at equilibrium.

Here are some examples to consider:

Reaction	Equilibrium Constant
$2O_3(g) \rightleftharpoons 3O_2(g)$	$K_{eq} = 2.0 \times 10^{57}$ K_{eq} is very large, indicating that mostly O_2 is present in an equilibrium system, with very little O_3.
$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$	$K_{eq} = 1.0 \times 10^{-25}$ Very little NO is produced by this reaction; N_2 and O_2 do not react readily to produce NO (this is lucky for us—otherwise we would have little oxygen to breath in our atmosphere!).
$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$	$K_{eq} = 5.09$ The concentrations of the reactants are very close to the concentrations of the products at equilibrium.

If the equilibrium constant is 1 or nearly 1, it indicates that the molarities of the reactants and products are about the same. If the equilibrium constant value is a large number, like 100, or a very large number, like 1×10^{15}, it indicates that the products (numerator) are a great deal larger than the reactants. This means that at equilibrium, the great majority of the material is in the form of products and it is said that the "products are strongly favored". If the equilibrium constant is small, like 0.10, or very small, like 1×10^{-12}, it indicates that the reactants are much larger than the products and the reactants are strongly favored. With large K values, most of the material at equilibrium is in the form of products and with small K values, most of the material at equilibrium is in the form of the reactants.

The equilibrium constant expression is an equation that we can use to solve for K or for the concentration of a reactant or product.

Relationship between the Equilibrium Constant and the Chemical Equation

If a chemical reaction is modified in some way, then the equilibrium constant for the equation must be changed to reflect the modification. Here are examples for common modifications.

1. If the reaction is reversed, the equilibrium constant is inverted.
   - $K_{\text{reverse}} = \frac{1}{K_{forward}}$
2. If the reaction coefficients multiplied by a factor of n, raise the power of the equilibrium constant by the same factor.
   - $K_{\text{new}} = (K_{\text{old}})^n$
3. If two equations are added together, multiply the corresponding equilibrium constant by each other to obtain the overall equilibrium constant.
   - $K_{\text{overall}} = K_1 \times K_2$

Example

The reaction A (g) $\rightleftharpoons$ 2B (g) has an equilibrium constant of K = 0.010. What is the equilibrium constant for the reaction of 2B (g) $\rightleftharpoons$ A (g)

Solution

The reaction is reversed, so the equilibrium constant should be inverted:

$$K_{reverse} = \frac{1}{K} = \frac{1}{0.010} = 100$$

Example

Consider the equilibrium constant for the synthesis of ammonia:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g), \quad K = 3.7\times10^8$$

What is the equilibrium constant for the following reaction: $NH_3(g) \rightleftharpoons \frac{1}{2} N_2(g) + \frac{3}{2} H_2(g)$

Solution

The reaction is reversed, and the coefficients are multiplied by ½. To get the new equilibrium constant, the old one should be inverted, and also raised to the power of ½.

$$K_{reverse} = \frac{1}{K} = \frac{1}{3.7\times10^8}$$

$$K' = (K_{reverse})^{1/2} = \left(\frac{1}{3.7\times10^8}\right)^{1/2} = 5.2\times10^{-5}$$

Example

Given the equilibrium constants for the first two reactions, predict the equilibrium constant for the last reaction:

$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$ $\quad K_1 = 1.0\times10^5$

$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$ $\quad K_2 = 1.0\times10^7$

$CO_2(g) + 3H_2(g) \rightleftharpoons CH_3OH(g) + H_2O(g)$ $\quad K_3 = ?$

Solution

Equation 3 is obtained by reversing equation 1 and then add to equation 2. So:

$K_3 = (\frac{1}{K1}) \times K_2 = \frac{1}{1.0\times10^5} \times 1.0\times10^7 = 1.0\times10^2$

9.2: Calculating the Equilibrium Constants

The most direct way to obtain an experimental value of the equilibrium constant of a reaction is to measure the concentration of all reactants and products at equilibrium.

Consider the following **example**:

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

Suppose the reaction is allowed to come to equilibrium at 445 °C, and the measured equilibrium concentrations are $[H_2] = 0.11M$, $[I_2] = 0.11M$ and $[HI] = 0.78M$. What is the K_c of the reaction at this temperature?

Solution

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{(0.78)^2}{0.11 \times 0.11} = 5.0$$

For most cases, however, we only need to know the initial concentration of the reactants and the equilibrium concentration of any one reactant or product. The other equilibrium concentrations can be deduced from the stoichiometry of the reaction. To solve Kc for such situation, a specific strategy by summarizing the initial concentrations, the changes and the equilibrium conditions in a table, ICE table, is often applied.

Example

Consider the following reaction:

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$$

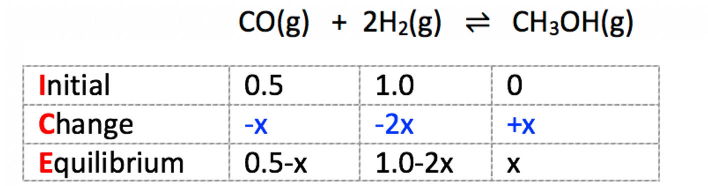
Suppose 1.0mol of CO and 2.0mol H_2 are placed in a 2.0L reaction flask at 780 °C. When the reaction equilibrium is approached, the concentration of CO is found to be 0.15M. What is the equilibrium constant?

Solution

Step 1: calculate the initial concentrations of reactants

[CO] = 1.0mol / 2.0L = 0.5M;
$[H_2]$ = 2.0mol / 2.0L = 1.0M

Step 2: Set up the ICE table:



$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$$

Initial	0.5	1.0	0
Change	-x	-2x	+x
Equilibrium	0.5-x	1.0-2x	x

In ICE table, the change amount of each substance is unknown so it is set up as *n*x, with *n* as the coefficient for each substance based on the balanced equation. Meanwhile, initially there are only reactants present in the reaction mixture, the reaction must proceed to the right to approach the equilibrium. So the sign of x for reactants are "-" (consumed) and the sign of product is "+" to (produced).

Step 3: Solving x based on the given information.

It was mentioned in the question, the [CO] = 0.15M at equilibrium, that means:
0.5 – x = 0.15; so x = 0.35

Step 4: Solving the equilibrium concentration of the other substances:

$[H_2]$ = 1.0 – 2x = 1.0 – 2 x 0.35 = 0.30 M
$[CH_3OH]$ = x = 0.35M

Step 5: Calculate the equilibrium constant K_c

$$K_c = \frac{[CH_3OH]}{[H_2]^2[CO]} = \frac{0.35}{(0.30)^2 \times 0.15} = 26$$

9.3: Determining the Reaction Direction: Reaction Quotient

In the previous example, the reaction start with the mixture of only reactants so it must proceed to right side to reach equilibrium. However, for the mixture that containing both reactants and products to start the reaction, it is hard to predict which way the reaction proceed for equilibrium without a qualitative proof.

To predict the progress of a reaction with respect to equilibrium, we use a quantity called the **reaction quotient,** Q_c. **Reaction quotient** is in the same for as the definition of equilibrium constant, except that the reaction is **not** at equilibrium. For general reaction:

$$\mathrm{aA + bB \rightleftharpoons cD + dD}$$

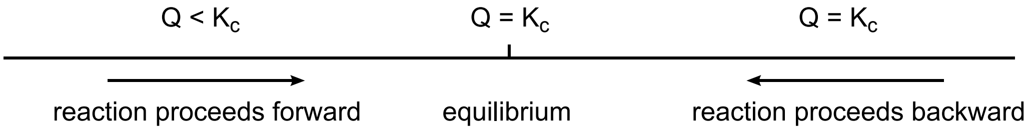
$$Q_c = \frac{[\mathrm{C}]^{\mathrm{c}}[\mathrm{D}]^{\mathrm{d}}}{[\mathrm{A}]^{\mathrm{a}}[\mathrm{B}]^{\mathrm{b}}}$$

[ ]: molarity concentration of substance

For a given reaction under certain temperature, equilibrium constant K_c is a fixed value. However, the reaction quotient Q_c will have many different values depends on the specific state of the reaction. The value of Q_c also changes as the reaction proceed.

A comparison of Q with K indicates which way the reaction shifts and which side of the reaction is favored:

- If Q >K, then the reaction favors the reactants. This means that in the Q equation, the ratio of the numerator (the concentration or pressure of the products) to the denominator (the concentration or pressure of the reactants) is larger than that for K, indicating that more products are present than there would be at equilibrium. Because reactions always tend toward equilibrium, the reaction produces more reactants from the excess products, therefore causing the system to shift to the **LEFT.** This allows the system to reach equilibrium.
- If Q<K, then the reaction favors the products. The ratio of products to reactants is less than that for the system at equilibrium—the concentration or the pressure of the reactants is greater than the concentration or pressure of the products. Because the reaction tends toward reach equilibrium, the system shifts to the **RIGHT** to make more products.
- If Q=K, then the reaction is already at equilibrium. There is no tendency to form more reactants or more products at this point. No side is favored and no shift occurs.



Example

What is the Q value for this reaction when the initial concentration of the substance are: [CO_2(g)]= 2.0 M, [H_2(g)]= 2.0 M, [CO(g)]= 1.0 M, [H_2O(g)]= 1.0 M? Which direction will the reaction proceed?

Given: $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$ $K_c = 1.0$

Solution

$$Q_c = \frac{[CO_2][H_2]}{[CO][H_2O]} = \frac{[2.0][2.0]}{[1.0][1.0]} = 4$$

$Q_c > K_c$, so the reaction proceed to the left (reactant) side.

9.4 Determining the equilibrium concentration

Generally, with the equilibrium constant K_c available, together with other information, the equilibrium concentration of the reactants and products can be obtained. These kinds of calculations are important because they allow us to calculate how much of the products forms when the reaction reaches equilibrium. These type of problems can be divided into two categories:

1. Finding the equilibrium concentration of one substance with K_c and the equilibrium concentrations of all other substances given
2. Finding the equilibrium concentration with K_c and initial concentrations given

Type 1: Finding the equilibrium concentration of one substance with K_c and the equilibrium concentrations of all other substances given

Example

In a study of the conversion of methane (CH_4) to other fuels, a chemist examed the following reaction in a 0.32 L flask at 1200 K.

$CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$

At equilibrium, the flask contains 0.26 mol of CO, 0.091 mol of H_2 and 0.041 mol of CH_4. What is concentration of H_2O at equilibrium? $K_C = 0.26$ for the reaction at 1200K.

Solution

The equilibrium concentration of other reactants and products can be solved with M = $\frac{\text{mol}}{\text{V}}$
So at equilibrium,

$$[CO] = \frac{\text{mol}}{\text{V}} = \frac{0.26\text{ mol}}{0.32\text{ L}} = 0.813\text{ M}$$

$$[H_2] = \frac{\text{mol}}{\text{V}} = \frac{0.091\text{ mol}}{0.32\text{ L}} = 0.284\text{ M}$$

$$[CH_4] = \frac{\text{mol}}{\text{V}} = \frac{0.041\text{ mol}}{0.32\text{ L}} = 0.128\text{ M}$$

Since $K_C = \frac{[CO]\,[H_2]^3}{[CH_4]\,[H_2O]} = 0.26$, and the concentration of three substances are known, the last one can be solved.

$$[H_2O] = \frac{[CO]\,[H_2]^3}{K_c \times [CH_4]} = \frac{0.813 \times (0.284)^3}{0.26 \times 0.128} = \frac{0.0186}{0.03328} = 0.56\text{ M}$$

Type 2: Finding the equilibrium concentration with K_c and initial concentrations given

Example

Consider the reaction:

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g) \qquad K_c = 0.10 \text{ at } 2000\ {}^\circ\text{C}$$

A reaction mixture initially contains $[N_2]$ = 0.20M and $[O_2]$ = 0.20M. Find the concentration of all the substances when reaction approach equilibrium at this temperature.

Solution

Step 1: set up the ICE table

	$N_2(g)$	+	$O_2(g)$	⇌	$2NO(g)$
Initial	0.20		0.20		0
Change	-x		-x		+2x
Equilibrium	0.20-x		0.20-x		2x

Step 2: solve x

$$K_c = \frac{[\mathrm{NO}]^2}{[\mathrm{N_2}][\mathrm{O_2}]} = \frac{(2\mathrm{x})^2}{(0.20-\mathrm{x})(0.20-\mathrm{x})} = \frac{(2\mathrm{x})^2}{(0.20-x)^2} = 0.10$$

Taking the square root of both side of the expression to solve for x is an easier way for such perfect square situation.

$$\sqrt{\frac{(2\mathrm{x})^2}{(0.20-x)^2}} = \sqrt{0.10}$$

$$\frac{2\mathrm{x}}{0.20-\mathrm{x}} = 0.316$$

2x = 0.316 × (0.20-x)

2x = 0.063 – 0.316x

2x + 0.316x = 0.063

2.316 x = 0.063

x = 0.0273 M

Step 3: Taking the value of x into the ICE table, to get the equilibrium concentration for all substances:

$[N_2] = [O_2] = 0.20 - x = 0.20 - 0.0273 = 0.17$ M

$[NO] = 2x = 2 \times 0.0273 = 0.0546$ M

9.5: Equilibrium Constant in Terms of Partial Pressure K_p

For reactions that include gases, the partial pressure of a gas is proportional to its concentration. Therefore, we can also express the equilibrium constant in terms of *partial pressure* of the reactants and products, and it is the K_p. For example, consider the gaseous reaction:

$2CO\,(g) + O_2(g) \rightleftharpoons 2CO_2(g)$

The expression of K_p takes the same form as the expression for K_c, except that the partial pressure of each gas is used in place of its concentration. For the above reaction, K_p can be expressed as:

$$K_p = \frac{P_{CO_2}{}^2}{P_{CO}{}^2\, P_{O_2}}$$

From the ideal gas law, we can derive the relationship between the partial pressure and molarity concentration, and then the relationship between K_p and K_c.

Because PV = nRT, the molarity concentration of a gas [ ] = n/V = P/RT, so P = [ ] × RT

Taking this relationship to the expression of K_p for above reaction:

$$K_p = \frac{P_{CO_2}{}^2}{P_{CO}{}^2\, P_{O_2}} = \frac{([CO_2]RT)^2}{([CO]RT)^2([O_2]RT)} = \frac{([CO_2])^2(RT)^2}{([CO])^2(RT)^2([O_2])RT} = K_c \times \frac{(RT)^2}{(RT)^3}$$

As a general way, the relationship between K_p and K_c can be summarized as:

$$K_p = K_c\,(RT)^{\Delta n}$$

and the meaning of Δn is:

Δn = sum of coefficients of the ***gaseous products*** - sum of coefficients of the ***gaseous reactants***

Example

Consider the following reaction: $2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$ $K_c = 4.02\times10^{-2}$ at 298K

What is the value of K_p at this temperature?

Solution

$K_p = K_c\,(RT)^{\Delta n} = 4.02\times10^{-2}\,(RT)^{3-2} = 4.02\times10^{-2}\,(RT) = 4.02\times10^{-2} \times 0.08206 \times 298 = 0.983$

9.6: Disturbing a Reaction at Equilibrium – Le Châtelier's Principle

When a reaction has reached equilibrium with a given set of conditions, if the conditions are not changed, the reaction will remain at equilibrium forever.

It is possible, however, to disturb that equilibrium by changing conditions. For example, you could increase the concentration of one of the products, or decrease the concentration of one of the reactants, or change the temperature. When a change of this type is made within a reaction at equilibrium, the reaction is no longer in equilibrium. When you alter something in a reaction at equilibrium, chemists say that **stress (or disturbance)** is applied on the equilibrium. When this occurs, the reaction will no longer be in equilibrium and the reaction itself will begin changing the concentrations of reactants and products until the reaction comes to a new position of equilibrium. How a reaction will change when a stress is applied can be explained and predicted by Le Châtelier's Principle.

Le Châtelier's Principle states that when a stress is applied to a system at equilibrium, the equilibrium will shift in a direction to partially **counteract (or offset) the stress** and once again reach equilibrium. Le Châtelier's principle is not an explanation of what happens on the molecular level to cause the equilibrium shift, it is simply a quick way to *determine* which way the reaction will run in response to a stress applied to the system at equilibrium.

Equilibrium is all about rates—the rate of the forward reaction is equal to the rate of the reverse reaction. External stresses are factors that will cause the rate of either the forward or reverse reaction to change, throwing the system out of balance. Le Chatelier's Principle allows us to predict how this will affect our system.

In the discussions we examined the following factors that influenced reaction rates:

- Concentration
- Volume and Pressure
- Temperature

Effect of Concentration Changes on Equilibrium

If a stress is applied by increasing the concentration of a reactant, the reaction will adjust in such a way that the reactants and products can get back to equilibrium. In the case of too much reactant, the reaction will use up some of the reactant to make more product. It is said in this scenario that the reaction "shifts to the products" or "shifts to the right". If the concentration of a product is increased, there is an opposite effect. The reaction will use up some of the product to make more reactant. The reaction "shifts to the reactants" or "shifts to the left". Decreasing the concentration of reactant or product will have just the opposite effect. As a summary:

- Increase the concentration of reactant, reaction shift to the product/right side;
- Decrease the concentration of reactant, reaction shift to the reactant/left side;
- Increase the concentration of product, reaction shift to the reactant/left side;
- Decrease the concentration of product, reaction shift to the product/right side.

For the example of ammonia synthesis reaction: $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

- When more N_2 (or H_2) added to the equilibrium system, the reaction shifts to the product/right side, that is to produce more NH_3.
- When more NH_3 is added to the equilibrium system, the reaction shift to the left side that produces more N_2 and H_2.

Effect of Pressure and Volume Changes on Equilibrium

Changing the pressure or volume of a container enclosing an equilibrium system will only affect the reaction if gases are present.

How does changing pressure and volume affect equilibrium systems?

- If the pressure of a system at equilibrium is increased by reducing the volume of the container, the stress will be reduced by reaction shifting to the side with the ***fewest*** moles of gas, since fewer moles of gas will bring the pressure backdown and to offset the disturbance.
- Conversely, if the pressure of a system is decreased by increasing the volume of the container, equilibrium will shift to the side with the ***most*** moles of gas, since more moles of gas will increase the pressure and to offset the disturbance.
- If both sides of the equation have the same number of moles of gas, then there will be no change in the position of equilibrium.
- If the pressure of a system at equilibrium is increased by adding inert gases (N_2 or Noble gases), there will be no change in the position of equilibrium.

When considering the effect of changing volume or pressure on equilibrium systems, be sure to only count the number of moles of **gases** on each side of the equation. Solids, liquids, and aqueous solutions will not be affected by changing pressure and volume.

For the example of ammonia synthesis reaction: $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

- If the pressure of the system is increased by reducing the volume of the contain, the reaction shifts to the side with less moles of gas, and it is the product/right side for this reaction (right side has 2moles of gas and left side has 4moles of gases).
- If the pressure of the system is decreased by increasing the volume of the contain, the reaction shifts to the side with more moles of gas, and it is the reactant/left side for this reaction.

Effect of Temperature Changes on Equilibrium

When temperature is the stress that affects a system at equilibrium, there are two important consequences:

- Increase in temperature will shift the reaction to the direction that ***absorbs*** heat (i.e. the **endothermic** reaction); decrease in in temperature will shift the reaction to the direction that ***releases*** heat (i.e. the **exothermic** reaction);
- The value of K_{eq} will change as well.

Consider the following equilibrium system:

$N_2O_4(g) \rightleftharpoons 2NO_2(g)$ $\Delta H^\circ = 58{\cdot}0\text{kJ}$

With the positive sign of ΔH°, we can tell that the forward reaction is endothermic, that is heat is absorbed when the reaction proceeds to the product/right side.

By adding more heat (increase temperature), reaction will shift to use up the additional heat, thus favoring this forward (endothermic) direction. Oppositely, when temperature decreased (heat removed from the system), reaction will shift to produce more heat, thus favoring this backwards (exothermic) direction.

For a given reaction, equilibrium constant K_{eq} has nothing to do with the concentration, pressure and volume changes. **However, K_{eq} does depend on the temperature**.

When temperature changes cause an equilibrium to shift, one entire side of the reaction equation is favored over the other side. Mathematically, this will alter the value of K_{eq} as follows:

If the **forward** reaction is favored by temperature change	more products are produced; fewer reactants	K_{eq} **increase**
if the **backward** reaction is favored by temperature change	fewer products are produced; more reactants	K_{eq} **decrease**

So as a general trend, increasing the temperature increase the K_{eq} of endothermic reaction, decreasing the temperature increase the K_{eq} of exothermic reaction.

Example

1. In which direction the equilibrium is going to shift if an increase in pressure is obtained by decreasing the volume:
    a) $CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g)$
    b) $2H_2S(g) \rightleftharpoons 2H_2(g) + S_2(g)$
    c) $C(graphite) + S_2(g) \rightleftharpoons CS_2(g)$

2. Sodium bicarbonate undergoes decomposition according to the reaction:
   $2NaHCO_3(s) \rightleftharpoons Na_2CO_3(s) + CO_2(g) + H_2O(g)$
   The reaction is *endothermic*. How does the equilibrium position shift as a result of each of the following disturbances?

   a) 0.20 atm of argon gas is added.

   b) $NaHCO_3(s)$ is added.

   c) $Mg(ClO_4)_2(s)$ is added as a drying agent to remove H_2O.

   d) Decrease the temperature by cooling with dry ice.

Solution

1. Pressure increase due to decreasing the volume shifts the reaction to the side with fewer moles of gases, so:
   a) shift to right side
   b) shift to left side
   c) no shift (both left side and right side has the same moles of gases)

2.
   a) no shift
   b) no shift
   c) shift to right side
   d) shift to left side

Chapter 10 Acids and Bases

Acids are very common in some of the foods that we eat. Citrus fruits such as oranges and lemons contain citric acid and ascorbic acid, which is better known as vitamin C. Carbonated sodas contain phosphoric acid. Vinegar contains acetic acid. Your own stomach utilizes hydrochloric acid to digest food. Bases are less common as foods, but they are nonetheless present in many household products. Many cleaners contain ammonia, a base. Sodium hydroxide is found in drain cleaner. Antacids, which combat excess stomach acid, are comprised of bases such as magnesium hydroxide or sodium hydrogen carbonate.

10.1 Definitions of Acids and Bases

The Arrhenius Theory of Acids and Bases

In 1884, the Swedish chemist Svante Arrhenius proposed two specific classifications of compounds, termed acids and bases. When dissolved in an aqueous solution, certain ions were released into the solution. An **Arrhenius acid** is a compound that increases the concentration of **H^+** ions that are present when added to water. These H^+ ions form the hydronium ion (H_3O^+) when they combine with water molecules. This process is represented in a chemical equation by adding H_2O to the reactants side.

$$HCl(aq) \rightarrow H^+(aq) + Cl^-(aq)$$

In this reaction, hydrochloric acid (HCl) dissociates completely into hydrogen (H^+) and chlorine (Cl^-) ions when dissolved in water, thereby releasing H^+ ions into solution. Formation of the hydronium ion equation:

$$HCl(aq) + H_2O(l) \rightarrow H_3O^+(aq) + Cl^-(aq)$$

An **Arrhenius base** is a compound that increases the concentration of **OH^-** ions that are present when added to water. The dissociation is represented by the following equation:

$$NaOH(aq) \rightarrow Na^+(aq) + OH^-(aq)$$

In this reaction, sodium hydroxide (NaOH) disassociates into sodium (Na^+) and hydroxide (OH^-) ions when dissolved in water, thereby releasing OH^- ions into solution.

Arrhenius acids are substances which produce hydrogen ions H^+ in solution;

Arrhenius bases are substances which produce hydroxide ions OH^- in solution.

The Brønsted-Lowry Theory of Acids and Bases

In 1923, Danish chemist Johannes Brønsted and English chemist Thomas Lowry independently proposed new definitions for acids and bases, ones that focus on proton transfer.

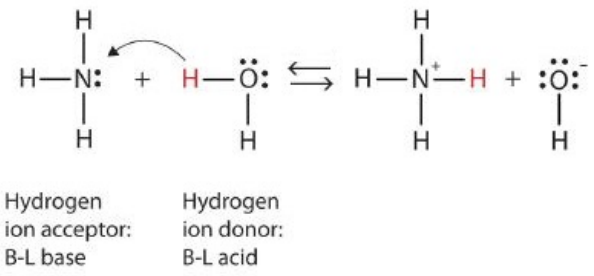
A **Brønsted-Lowry acid** is any species that can donate a proton (H^+) to another molecule. A **Brønsted-Lowry base** is any species that can accept a proton from another molecule.

In short, ***a Brønsted-Lowry acid is a proton donor***, while ***a Brønsted-Lowry base is a proton acceptor***.

Let us use the reaction of ammonia in water to demonstrate the Brønsted-Lowry definitions of an acid and a base. Ammonia and water molecules are reactants, while the ammonium ion and the hydroxide ion are products:

$$NH_3(aq) + H_2O(\ell) \rightleftharpoons NH_4^+ (aq) + OH^-(aq)$$

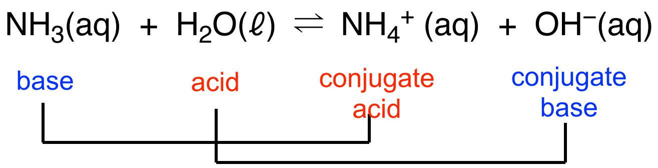
What has happened in this reaction is that the original water molecule has donated a hydrogen ion to the original ammonia molecule, which in turn has accepted the hydrogen ion. We can illustrate this as follows:



Because the water molecule donates a hydrogen ion to the ammonia, it is the Brønsted-Lowry acid, while the ammonia molecule—which accepts the hydrogen ion—is the Brønsted-Lowry base. Thus, ammonia acts as a base in both the Arrhenius sense and the Brønsted-Lowry sense.

Conjugate Acid and Base Pair

In above reaction, base NH_3 becomes the acid NH_4^+ after accepting the proton, and acid H_2O becomes the base OH^- after donating the proton. NH_4^+ and NH_3 are a conjugate acid-base pair, so are H_2O and OH^-.



$$NH_3(aq) + H_2O(\ell) \rightleftharpoons NH_4^+ (aq) + OH^-(aq)$$

For definition:

- **A base accepts a proton and becomes a conjugate acid;**
- **An acid donates a proton and becomes a conjugate base.**

Example

Identify the conjugate acid and the conjugate base for H_2O, HCO_2H, and $H_2PO_4^-$.

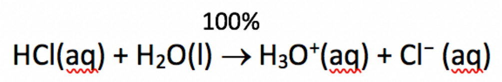
Solution

	conjugate acid	conjugate base
H_2O	H_3O^+	OH^-
HCO_2H	$HCO_2H_2^+$	HCO_2^-
$H_2PO_4^-$	H_3PO_4	HPO_4^{2}

10.2 Strong and Weak Acids and Bases

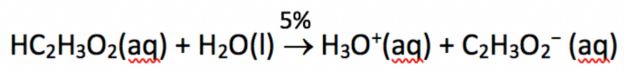
Strong and Weak Acids

Except for their names and formulas, so far we have treated all acids as equals, especially in a chemical reaction. However, acids can be very different in a very important way. Consider HCl(aq), when HCl is dissolved in H_2O, it completely dissociates into H_3O^+(aq) and Cl^-(aq) ions; all the HCl molecules become ions:



$$HCl(aq) + H_2O(l) \xrightarrow{100\%} H_3O^+(aq) + Cl^- (aq)$$

Any acid that dissociates completely (or 100%) into ions is called a **strong acid**. If it just dissociate partially, it is a **weak acid**. Acetic acid, $HC_2H_3O_2$, is an example of a weak acid:



$$HC_2H_3O_2(aq) + H_2O(l) \xrightarrow{5\%} H_3O^+(aq) + C_2H_3O_2^- (aq)$$

As it turns out, there are very few strong acids, which are given in Table 10.1. If an acid is not listed here, it is a weak acid, that dissociates partially.

Any acid that dissociates completely (or 100%) into ions is called a strong acid. If it does not dissociate completely, it is a weak acid.

Strong Acids	Strong Bases
HCl	LiOH
HBr	NaOH
HI	KOH
HNO_3	RbOH
H_2SO_4	CsOH
$HClO_4$	$Ca(OH)_2$
	$Sr(OH)_2$
	$Ba(OH)_2$

Table 10.1 Strong Acids and Bases

Ionization Constant K_a of Weak Acid

Because ionization reaction of weak acid does not go to completion, it is more appropriate to use the equilibrium arrow in the reaction equation, to indicate the partial ionization. The example below is for the ionization equilibrium for acetic acid.

$$HC_2H_3O_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + C_2H_3O_2^-\ (aq)$$

The equilibrium constant of the above ionization reaction indicate the relative strength of weak acids, and is called the **acid ionization constant, K_a**. For the following general reaction of weak acid HA,

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-\ (aq)$$

the acid ionization constant is:

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

The value of K_a indicates the extend for the ionization reaction of acid, therefore the smaller the K_a, the less the acid ionizes, the weaker the acid. On the other side, the larger the value of K_a, the stronger the acid.

Strong and Weak Bases

The issue is similar with bases: a **strong base** is a base that is 100% ionized in solution. If it is less than 100% ionized in solution, it is a **weak base**. There are very few strong bases (**Table 10.1**); any base not listed is a weak base. All strong bases are hydroxide compounds. So a base based on some other mechanism, such as NH_3 (which does not contain OH^- ions as part of its formula), will be a weak base.

Ionization Constant K_b of Weak Base

A weak base is analogous to a weak acid. Other than strong base that contain OH^- and dissociates completely in water, the most common weak bases produce OH^- by accepting a H^+ from water, as shown by the general equation below:

$$B(aq) + H_2O(l) \rightleftharpoons BH^+(aq) + OH^- (aq)$$

Again, the ionization process for weak base does not go to completion, and the equilibrium constant of the above reaction indicate the relative strength of weak bases, and is called the **base ionization constant, K_b**, with the expression of:

$$K_b = \frac{[BH^+][OH^-]}{[B\}}$$

By analogy with K_a, the smaller the value of K_b, the weaker the base; and the larger the value of K_b, the stronger the base.

Example

Identify each acid or base as strong or weak:

a. HCl
b. $Ba(OH)_2$
c. C_5H_5N
d. RbOH
e. HNO_2

Solution

a. HCl, strong acid
b. $Ba(OH)_2$, strong base
c. C_5H_5N, weak base
d. RbOH, strong base
e. HNO_2, weak acid

10.3 Water – Acid and Base in One

We have already seen that water can act as an acid or a base:

$$\underbrace{NH_3}_{\text{base}} + \underbrace{H_2O}_{\text{acid}} \rightleftharpoons NH_4^+ + OH^-$$

where H_2O acts as an acid (in red).

$$\underbrace{HCl}_{\text{acid}} + \underbrace{H_2O}_{\text{base}} \longrightarrow H_3O^+ + Cl^-$$

where H_2O acts as an base (in blue).

It may not surprise you to learn, then, that within any given sample of water, some H_2O molecules are acting as acids, and other H_2O molecules are acting as bases. The chemical equation is as follows:

$$\underbrace{H_2O}_{\text{acid}} + \underbrace{H_2O}_{\text{base}} \rightleftharpoons H_3O^+ + OH^-$$

This occurs only to a very small degree: only about 6 in 10^8 H_2O molecules are participating in this process, which is called the **autoionization (self-ionization) of water**.

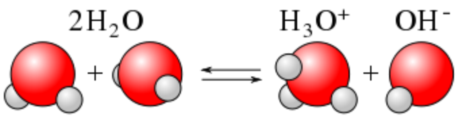


Figure 10.1 Autoionization of water, resulting in hydroxide and hydronium ions

The autoionization of water can be quantified with the equilibrium constant, **that is the ion product constant for water, K_w**. At 25°C, $K_w = 1.0 \times 10^{-14}$.

$$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14}$$

In pure water, H_2O is the only source of these ions, the concentration of H_3O^+ and OH^- are equal, that is:

$$[H_3O^+] = [OH^-] = \sqrt{K_w} = 10^{-7}\text{ M (in pure water)}$$

Note: In this chapter, the temperature is always assumed to be 25°C for this course purpose.

In any aqueous solution, both H_3O^+ and OH^- always exist, and the product of the two concentration $[H_3O^+][OH^-]$ always equals to 1.0×10^{-14}. This also implies that as one concentration goes up, the other must go down to compensate so that their product always equals the value of K_w.

As a result, according to the relative amount between the two ions in a solution, solutions can be categorized as acidic, basic or neutral:

- For neutral solution, $[H_3O^+] = [OH^-] = 10^{-7}$ M
- For acidic solution, $[H_3O^+] > [OH^-]$
- For basic solution, $[H_3O^+] < [OH^-]$

Since the product of the two concentrations—$[H_3O^+][OH^-]$ is always equal to1.0×10^{-14}, if you know $[H_3O^+]$ for a solution, you can calculate what $[OH^-]$, and or if you know $[OH^-]$), you can calculate $[H_3O^+]$.

Example

What is $[OH^-]$ of an aqueous solution with $[H_3O^+]$ of 0.020M?

Solution

Because $K_w = [H_3O^+][OH^-]$, so $[OH^-] = \frac{K_W}{[H_3O^+]} = \frac{1\times 10^{-14}}{0.02} = 5.0 \times 10^{-13}$M

10.4 The pH and pOH Scales

As we have seen, $[H_3O^+]$ and $[OH^-]$ values can be markedly different from one aqueous solution to another. So chemists defined a new scale that succinctly indicates the concentrations of either of these two ions.

pH is a negative logarithmic function of $[H_3O^+]$: $\mathrm{pH} = -\log[H_3O^+]$

Because hydrogen ion concentrations are generally less than one (for example 1.3×10^{-3}M), the log of the number will be a negative number. To make pH even easier to work with, pH is defined as the ***negative* log of** $[H_3O^+]$, which will give a positive value for pH.

pH is *usually* (but not always) between 0 and 14.

Example

Calculate the pH of the neutral solution.

Solution

From previous discussion, it is mentioned that $[H_3O^+] = 10^{-7}$ M for neutral solution. Therefor the pH is:

$$pH = -\log[H_3O^+] = -\log(10^{-7}) = 7$$

Knowing the pH of neutral solution, also the dependence of pH on $[H_3O^+]$, we can summarize as follows:

- For neutral solution, pH = 7
- For acidic solution, pH < 7
- For basic solution, pH > 7

The pH scale is the range of values from 0 to 14 that describes the acidity or basicity of a solution. You can use pH to make a quick determination whether a given aqueous solution is acidic, basic, or neutral. Figure 10.2 illustrates this relationship, along with some examples of various solutions.

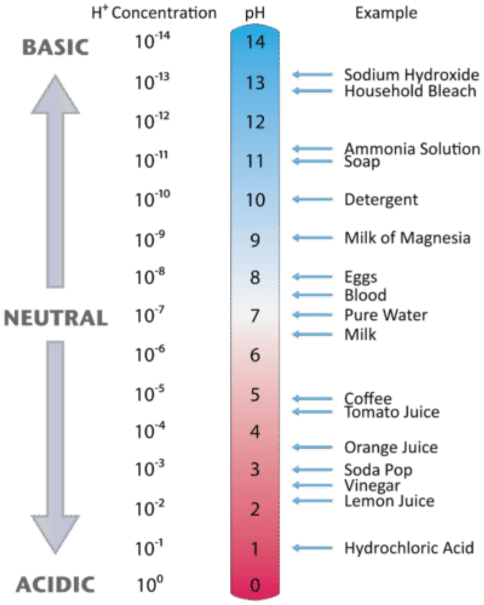


Figure 10.2 The pH values for several common materials.

Calculating pH from Hydronium Concentration

The pH of solutions can be determined directly if the concentration of hydronium ion is known.

Example

What is the pH of the 1.2×10^{-3}M HCl solution?

Solution

HCl is strong acid that dissociates completely, $HCl(aq) + H_2O(l) \rightarrow H_3O^+(aq) + Cl^-(aq)$

so for strong acid, $[H_3O^+] = [HCl]$

$$pH=-\log[H_3O^+]=-\log(1.2\times10^{-3})=-(-2.92)=2.92$$

As the general trend, the concentration of H_3O^+ in a strong acid solution can be derived directly from the concentration of the strong acid.

Calculating Hydronium Concentration from pH

Sometimes you need to work "backwards"—you know the pH of a solution and need to find $[H_3O^+]$. How do you do that? To convert pH into $[H_3O^+]$ we need to take the antilog (or inverse log) of the negative value of pH. The log for pH calculation has the base of 10, so:

$$[H_3O^+]=10^{-pH}$$

As mentioned above, different calculators work slightly differently—make sure you can do the following calculations using ***your*** calculator.

Example

What is the $[H_3O^+]$ for the solution with pH = 3.56?

Solution

$[H_3O^+]=10^{-pH} = 10^{-3.56} = 0.000275$M

The pOH scale

As with the hydronium ion concentration, the concentration of the hydroxide ion can be expressed logarithmically by the pOH.

pOH is the negative logarithm of the $[OH^-]$: $pOH=-\log[OH^-]$

Example

What is the pOH of the 1.20×10^{-3}M HCl solution?

Solution

For strong acid HCl, $[H_3O^+] = [HCl] = 1.20\times10^{-3}$M

$[OH^-] = \frac{K_w}{[H_3O^+]} = \frac{1\times 10^{-14}}{1.20\times10^{-3}} = 8.33 \times 10^{-12}$M; pOH=$-\log[OH^-] = -\log(8.33 \times 10^{-12}) = 11.1$

The relation between the pH and pOH is easily derived from the K_w expression:

$$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14}$$

$$-\log K_w = -\log([H_3O^+][OH^-]) = -\log[H_3O^+] + (-\log[OH^-])$$

$-\log K_w$ is also a “p”scale, that is called pK_w

$$pK_w = pH + pOH$$

At 25 °C, the value of K_w is 1.0×10^{-14}, so: $pK_w = 14$

$$\text{So, } 14 = pH + pOH$$

The diagram below shows all of the interrelationships between $[H_3O^+]$, $[OH^-]$, pH, and pOH.

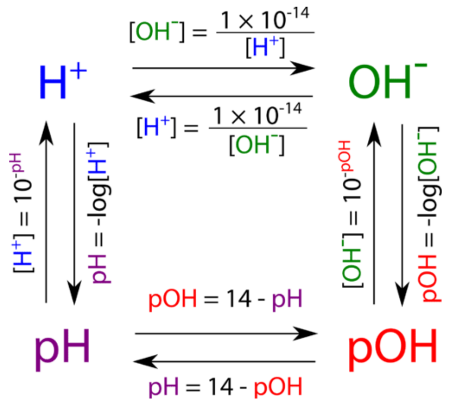


Figure 10.3 Relationships between hydrogen ion concentration, hydroxide ion concentration, pH and pOH.

Example

For 0.1M $Ca(OH)_2$ solution, what is $[H_3O^+]$, $[OH^-]$, pH, and pOH?

Solution

$Ca(OH)_2$ is strong base that dissociates completely, the mol ratio between $Ca(OH)_2$ and OH^- is 1:2

$$Ca(OH)_2(aq) \rightarrow Ca^{2+}(aq) + 2OH^-(aq)$$

so $[OH^-] = 2 \times [Ca(OH)_2] = 2 \times 0.1M = 0.2M$;

$$[H_3O^+] = \frac{K_w}{[OH^-]} = \frac{10^{-14}}{0.2} = 5.0\times10^{-14}\ M$$

$$pH = -\log(5.0\times10^{-14}) = 13.3$$

$$pOH = 14 - 13.3 = 0.70$$

10.5 Finding $[H_3O^+]$ and pH of Weak Acid and Weak Base

Finding the pH of a weak acid solution is more complicated, because weak acid dissociates partially, and the concentration of hydronium is not equal to the molarity concentration of the weak acid. The same problem applies to weak base.

Weak Acid

Calculating the $[H_3O^+]$ formed by the ionization of a weak acid requires solving an equilibrium problem similar to those introduced in Ch. 9. Let's consider a solution of a generic weak acid HA (concentration is [HA]), with an acid ionization constant K_a. The H_3O^+ is produced by partial ionization of the acid, and can be determined by working on the following equilibrium.

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq) \qquad K_a \text{ is given}$$

The ICE table can be set up:

	[HA]	$[H_3O^+]$	$[A^-]$
Initial	[HA]	0	0
Change	-x	+x	+x
Equilibrium	[HA]- x	x	x
	$x \ll [HA]$	x	x
approximation	$[HA] - x \approx [HA]$		

The variable x represent the amount of HA ionizes, so x = $[H_3O^+]$, therefore the key step here is to solve x.

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} = \frac{x \cdot x}{[HA]-x} = \frac{x^2}{[HA]-x}$$

With known value of K_a, soling x involves the quadratic equation. For many cases, the value of x is a very small value (see next example), and it is much smaller than initial concentration of HA that is 0.1M for this case. So an approximation can be applied: with **$x \ll [HA]$, $[HA] - x \approx [HA]$**. The calculation can be simplified with such approximation as:

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} = \frac{x^2}{[HA]-x} \approx \frac{x^2}{[HA]}$$

$$x = [H_3O^+] = \sqrt{K_a[HA]}$$

Another way to evaluate the extend of ionization of a weak acid is to check the percent ionization, which is defined as:

$$\text{percent ionization} = \frac{[H_3O^+]}{[HA]} \times 100\%$$

Example

Find the pH and percent ionization of 0.200M HNO_2 solution. K_a of HNO_2 is 4.6×10^{-4}.

Solution

The ionization reaction equation is:

$$HNO_2(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + NO_2^-(aq)$$

Set up the ICE table:

	$[HNO_2]$	$[H_3O^+]$	$[NO_2^-]$
Initial	0.200	0	0
Change	$-x$	$+x$	$+x$
Equilibrium	$0.200 - x$	x	x
	$x \ll 0.200$	x	x
approximation	$0.200 - x \approx 0.200$		

$$x = [H_3O^+] = \sqrt{K_a[HA]} = \sqrt{(4.6 \times 10^{-4}) \times 0.200} = 9.6 \times 10^{-3}\,\text{M}$$

$$\text{pH} = -\log[H_3O^+] = -\log(9.6 \times 10^{-3}) = 2.02$$

$$\text{percent ionization} = \frac{[H_3O^+]}{[HA]} \times 100\% = \frac{9.6 \times 10^{-3}}{0.200} \times 100\% = 4.8\%$$

Weak Base

Finding the $[OH^-]$ and pH of a weak base solution is analogous to finding the $[H_3O^+]$ and pH of a weak acid. Please not that ***because OH^- is the majority species in basic solution, so the work is based on $[OH^-]$ and K_b***. See following example for details.

Example

Find the $[OH^-]$ and pH of a 0.100M NH_3 solution. K_b of NH_3 is 1.76×10^{-5}.

Solution

The ionization reaction equation is:

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

Set up the ICE table:

	$[NH_3]$	$[NH_4^+]$	$[OH^-]$
Initial	0.100	0	0
Change	-x	+x	+x
Equilibrium	0.100 - x	x	x
	x << 0.100	x	x
approximation	0.100 -x ≈ 0.100		

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = \frac{x^2}{0.100-x}$$

With assumption, 0.100 – x ≈ 0.100, above equation can be simplified as:

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = \frac{x^2}{0.100-x} \approx \frac{x^2}{0.100} = 1.76\times10^{-5}$$

To solve x:

$$x = [OH^-] = \sqrt{K_b[B]} = \sqrt{(1.76 \times 10^{-4}) \times 0.100} = 1.33\times10^{-3}\text{ M}$$

Pay attention that the x solved here is $[OH^-]$, the pH will be obtained by one more step conversion:

$$[H_3O^+] = \frac{K_w}{[OH^-]} = \frac{10^{-14}}{1.33 \times 10^{-3}} = 7.52\times10^{-12}\ M$$

$$pH = -\log\,[H_3O^+] = -\log\,(7.52\times10^{-12}) = 11.1$$

10.6 Acid-base Properties of Salts

Ionic compounds are also called salts. Ionic compounds, or salts, dissociate to cations and anions. Here we will look in general the acid-base properties of salts and the ions they contain. Some salts are pH-neutral when dissolved in water, others are acidic, and still others are basic, depending on their constituent cations and anions. In general, cations tend to form either acidic or neutral solutions, while anions tend to form either basic or neutral solutions.

Anions as Weak Bases

In general, the anion A^- is conjugate base of the acid HA. Consider the following anions and their conjugate acids.

This anion	is the conj. base of	this acid
Cl^-		HCl
F^-		HF
NO_3^-		HNO_3
$C_2H_3O_2^-$		$HC_2H_3O_2$

Since virtually any anion can be regarded as the conjugate base of an acid, the anion may itself act as a base. However, whether an anion acts as the base depends on the strength of the corresponding acid. In general:

- ***An anion that is the conj. base of a weak acid is itself a weak base;***
- ***An anion that is the conj. base of a strong acid is pH-neutral (neither acidic nor basic).***

For example, the Cl^- is the conjugate base of HCl, a strong acid, therefore the Cl^- anion is pH-neutral. The F^- anion, however is the conjugate base of HF, a weak acid. Therefore F^- ion is itself a weak base. When F^- ion reacts with water, OH^- is released so the solution is basic.

$$F^-\,(aq) + H_2O\,(l) \rightleftharpoons HF\,(aq) + OH^-\,(aq)$$

Cations as Weak Acids

In contrast to anions, which in some cases acts as weak bases, cations can in some cases act as weak acids. Cations and their properties have the general trend as:

- ***Cation that is counterion of strong bases is itself pH-neutral***. Example: Na^+, K^+, Ca^{2+} are pH-neutral.

- ***Cation that is the conj. acid of a weak acid is itself weak acid***. Example: NH_4^+, $CH_3NH_3^+$ are weak acid.

Strong bases such as NaOH or $Ca(OH)_2$ dissociate completely in solution, to form $OH^-(aq)$ and the counterions Na^+ and Ca^{2+}. These counterions, Na^+, Ca^{2+} etc., do not ionize water and they don't contribute to the acidity or basicity of the solution.

The cation, for example $CH_3NH_3^+$, is conjugate acid of a weak base (NH_3), and it ionizes water and produces H_3O^+, so it is weak acid.

$$CH_3NH_3^+ (aq) + H_2O (l) \rightleftharpoons CH_3NH_2 (aq) + H_3O^+ (aq)$$

In general, the acid-base properties of salts can be summarized as:

Cations	Anions	
	conj. base of a strong acid example: Cl^-, Br^-, I^-, NO_3^- SO_4^{2-}, ClO_4^-	***conj. base of a weak acid*** example: F^-, $C_2H_3O_2^-$, NO_2^- ClO^-, CN^- , etc.
counterion of strong bases example: Na^+, K^+, Ca^{2+}, Ba^{2+} etc.	**neutral** example : NaCl, KI, $Ca(NO_3)_2$, Li_2SO_4 , etc.	**basic** example: KF, NaCN, $Ca(ClO)_2$, Li_2SO_3 , etc.
conj. acid of a weak acid example: NH_4^+, $CH_3NH_3^+$ etc.	**acidic** example NH_4Cl, $(NH_4)_2SO_4$, CH_3NH_3Br, etc	

10.7 Buffers

Weak acids are relatively common, even in the foods we eat. But we occasionally come across a strong acid or base, such as stomach acid, that has a strongly acidic pH of 1~2. By definition, strong acids and bases can produce a relatively large amount of hydrogen or hydroxide ions and, as a consequence, have marked chemical activity. In addition, very small amounts of strong acids and bases can change the pH of a solution very quickly. If 1 mL of stomach acid (which we will approximate as 0.05 M HCl(aq)) is added to the bloodstream, and if no correcting mechanism is present, the pH of the blood would go from about 7.4 to about 4.9 — a pH that is not conducive to life. Fortunately, the body has a mechanism for minimizing such dramatic pH changes.

How Does Buffer Work

This mechanism involves a **buffer**, a solution that resists dramatic changes in pH. Buffers do so by being composed of certain pairs of solutes: either a weak acid *plus* a salt contains the anion that is conjugate base of that weak acid, or a weak base *plus* a salt that contains the cation that is conjugate acid of that weak base.

For example, a buffer can be composed of dissolved acetic acid ($HC_2H_3O_2$, a weak acid) and sodium acetate ($NaC_2H_3O_2$, dissociates to form $C_2H_3O_2^-$ anion that is the conjugate base of acetic acid). Another example of a buffer is a solution containing ammonia (NH_3, a weak base) and ammonium chloride (NH_4Cl, NH_4^+ cation is the conjugate acid of ammonia).

Let us use an acetic acid — sodium acetate buffer to demonstrate how buffers work. If a strong base, a source of OH^- ions, is added to the buffer solution, those hydroxide ions will be neutralized by the acetic acid in an acid-base reaction:

$$HC_2H_3O_2(aq) + OH^-(aq) \rightarrow H_2O(l) + C_2H_3O_2^-(aq)$$

Rather than changing the pH dramatically by making the solution basic, the added hydroxide ions are neutralized to make water, and the pH does not change much.

If a strong acid, a source of H^+ ions, is added to the buffer solution, the H^+ ions will be neutralized by $C_2H_3O_2^-$, the anion that is the weak acid.

$$H^+(aq) + C_2H_3O_2^-(aq) \rightarrow HC_2H_3O_2(aq)$$

Rather than changing the pH dramatically and making the solution acidic, the added hydrogen ions are neutralized to make molecules of weak acid. Figure 10.4 illustrates both actions of a buffer.

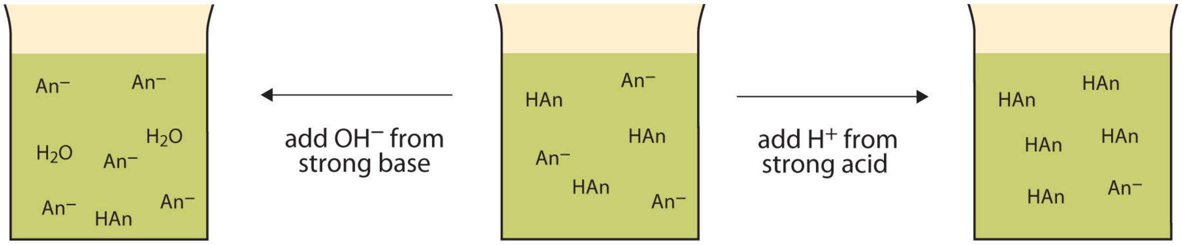


Figure 10.4 The Action of Buffers. Buffers can react with both strong acids and strong bases to minimize large changes in pH.

Buffers made from weak bases and salts of weak bases act similarly. For example, in a buffer containing NH_3 and NH_4Cl, ammonia molecules can react with any excess hydrogen ions introduced by strong acids:

$$NH_3(aq) + H^+(aq) \rightarrow NH_4^+(aq)$$

while the ammonium ion ($NH_4^+(aq)$) can react with any hydroxide ions introduced by strong bases:

$$NH_4^+(aq) + OH^-(aq) \rightarrow NH_3(aq) + H_2O(l)$$

Example

Which solute combinations can make a buffer solution? Assume that all are aqueous solutions.

a. $HCHO_2$ and $NaCHO_2$
b. HCl and NaCl
c. CH_3NH_2 and CH_3NH_3Cl
d. NH_3 and NaOH

Solution

a. Formic acid ($HCHO_2$) is a weak acid, while $NaCHO_2$ is the salt made from the anion of the weak acid—the formate ion (CHO_2^-). The combination of these two solutes would make a buffer solution.
b. Hydrochloric acid (HCl) is a strong acid, not a weak acid, so the combination of these two solutes would not make a buffer solution.
c. Methylamine (CH_3NH_2) is like ammonia with one of its hydrogen atoms substituted with a CH_3 (methyl) group. Because it is not on our list of strong bases, we can assume that it is a weak base. The compound CH_3NH_3Cl is a salt made from that weak base, so the combination of these two solutes would make a buffer solution.
d. Ammonia (NH_3) is a weak base, but NaOH is a strong base. The combination of these two solutes would not make a buffer solution.

pH of Buffer

Finding the pH of a buffer solution can be simplified if we derive an equation that relates the pH of the solution to the initial concentration of the buffer components. Consider a buffer containing the generic weak acid HA and its conjugate base A^-.

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$$

The ICE table can be set up for buffer:

	$[HA]$	$[H_3O^+]$	$[A^-]$
Initial	$[HA]$	0	$[A^-]$
Change	$-x$	$+x$	$+x$
Equilibrium	$[HA]- x$	x	$[A^-] + x$
	$x \ll [HA]$	x	$x \ll [A^-]$
approximation	$[HA] -x \approx [HA]$		$[A^-] + x \approx [A^-]$

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

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

The pH of the buffer can then be calculated with the $[H_3O^+]$.

Since both components are in the same buffer mixture, the <u>concentration ratio</u> is the same as the <u>mol ratio</u>, and the $[H_3O^+]$ can be calculated by another version formula in terms of mol ratio.

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

Example

Calculate the pH of the a buffer solution prepared by mixing 100.0mL 0.50 M acetic acid ($HC_2H_3O_2$) and 100.0mL 0.60 M sodium acetate ($NaC_2H_3O_2$). K_a for acetic acid is 1.8×10^{-5}.

Solution

Since the buffer solution is prepared by mixing two solutions together, so the concentration of both components changes after the mixing. Therefore it is more convenient to use the 2nd formula.

$mol_{HA} = 0.50 \text{ M} \times 0.1000 \text{ L} = 0.050 \text{ mol}$
$mol_{A^-} = 0.60 \text{ M} \times 0.1000 \text{ L} = 0.060 \text{ mol}$

$$[H_3O^+] = \frac{K_a\, mol_{HA}}{mol_{A^-}} = 1.8 \times 10^{-5} \times \frac{0.050}{0.060} = 1.5 \times 10^{-5}$$

$\text{pH} = -\log[H_3O^+] = -\log(1.5\times10^{-5}) = 4.8$

Example

Calculate the pH of the a buffer solution prepared by mixing 100.0mL 0.125M benzoic acid ($HC_7H_5O_2$) and 2.53g of sodium benzoate ($NaC_7H_5O_2$, MM is 144.1g/mol). K_a for benzoic acid is 6.5 x 10^{-5}.

Solution

$mol_{HA} = 0.125\text{ M} \times 0.1000\text{ L} = 0.0125\text{ mol}$

$mol_{A^-} = 2.53\text{g} \times \frac{1mol\ \text{NaC7H5O2}}{144.1\ g} = 0.01756\text{ mol}$

$[H_3O^+] = \frac{K_a\ mol_{HA}}{mol_{A^-}} = 6.5 \times\ 10^{-5}\ \times\ \frac{0.0125}{0.01756} = 4.49\ \times\ 10^{-5}$

$\text{pH} = -\log(4.49 \times 10^{-5}) = 4.35$

Buffer Prepared by Reaction between Strong Base and Excess Weak Acid

Buffer must have two components: weak acid and its conjugate base. Rather than mixing the two components directly as in previous examples, buffer can also be generated indirectly from reactions between weak acid and appropriate amount of strong base. Let's explain the process with following example.

Example

For the reaction of 25.0mL of 0.100M acetic acid with 15.0mL of 0.100M NaOH solution, calculation the pH at the end of reaction. K_a for acetic acid is 1.8 x 10^{-5}.

Solution

First of all, we need to understand how the reaction proceed. Acetic acid, a weak acid, is neutralized when reacting with strong base NaOH, and the product is sodium acetate ($NaC_2H_3O_2$), the conjugate base of acetic acid, as shown in the above reaction equation.

Secondly, let's work out the amount of each reactant and product. The amounts given for $HC_2H_3O_2$ and NaOH in this example are not in stoichiometric ratio, instead that NaOH is the L.R (0.00150mol) and $HC_2H_3O_2$ (0.00250mol) is in excess. At the end of the reaction, all NaOH consumed, there are certain amount of $HC_2H_3O_2$ leftover (0.00100mol) together with certain amount of product $NaC_2H_3O_2$ (0.00150mol) in the mixture. **The mixture is now a buffer!**

The amount of each substance before and after reaction is summarized in the table:

mol	$HC_2H_3O_2(aq) + NaOH(aq) \rightarrow NaC_2H_3O_2(aq) + H_2O(l)$			
initial	0.00250	0.00150	0	
reacted/produced	-0.00150	-0.00150	+0.00150	
at the end	0.00100	0	0.00150	

Recognizing the mixture at the end of this reaction is a buffer is the most critical point for such questions. The weak acid component ($HC_2H_3O_2$) is the leftover from the reaction, the conjugate base component ($NaC_2H_3O_2$) is the product from the reaction, and this is how buffer can be prepared indirectly.

The last step is then to calculate pH of the buffer according to the formula:

$$[H_3O^+] = K_a \frac{mol_{HA}}{mol_{A^-}} = 1.8 \times 10^{-5} \times \frac{0.00100}{0.00150} = 1.2 \times 10^{-5}$$

$$pH = -\log[H_3O^+] = -\log(1.2\times10^{-5}) = 4.9$$

10.8 Acids and Bases Titration Curve

In an acid-base titration, a solution of unknown concentration reacts with another solution of known concentration. With the solution with known solution is added slowly to the unknown solution, the pH of the mixture keep on changing. A plot of the pH of the vs the volume of the known solution added is known as a titration curve.

A pH curve for the titration of HCl with NaOH is shown below.

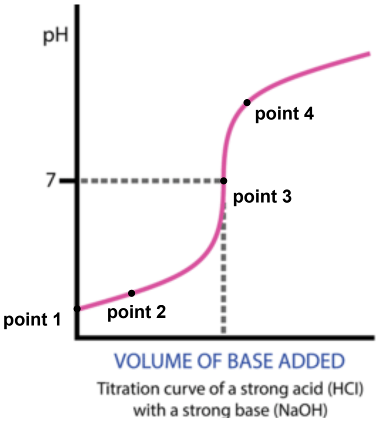


Figure 10.5 A titration curve of HCl with NaOH, with base is being added to acid. This diagram is fromhttps://chem.libretexts.org/Bookshelves/Introductory_Chemistry/Introductory_Chemistry_(CK-12)/21%3A_Acids_and_Bases/21.19%3A_Titration_Curves and modified

Consider the titration of 25.0mL of 0.100M HCl with 0.100M NaOH. We will study several important points on the titration curve, to further understand the titration process.

Point 1: V_{NaOH} = 0 mL

Before base is added, the solution is 0.100M HCl, with $[H_3O^+]$ = 0.100M, pH = -log(0.100) = 1

Point 2: V_{NaOH} = 10.0mL

At this point, the mol of NaOH added is: 0.100M × 0.0100L = 0.00100mol NaOH

Total mole of HCl is: 0.100M × 0.0250L = 0.00250mol HCl

So the amount of NaOH is the L.R, is all consumed; and the amount of HCl is in excess, with some leftover.

HCl leftover = 0.00250mol - 0.00100mol = 0.001500mol

The amount of each substance before and after reaction is summarized in the table:

mol	$HCl(aq)$	$+ NaOH(aq)$	$\rightarrow NaCl(aq)$	$+ H_2O(l)$
initial	0.002500	0.00100	0	
reacted/produced	-0.00100	-0.00100	+0.00100	
at the end	0.001500	0	0.00100	

The solution at this point is the mixture of 0.001500mol HCl and 0.00100mol NaCl. Since NaCl is the neutral salt, it does not affect pH, the mixture is just the strong acid HCl solution. The molarity concentration of HCl = $\frac{0.001500\ mol}{(0.0250+0.0100)\ L} = 0.0429M$

pH = -log (0.0429) = 1.37

Point 3: V_{NaOH} = 25.0mL

At this point, the amount of NaOH added equals exactly to the amount of HCl, both acid and base just react completely, the point is the equivalent point. At equivalent point, neither NaOH nor HCl present, the solution only contains the neutral salt NaCl. So the pH of the solution is 7.

Point 4: V_{NaOH} = 30.0mL

At this point, the amount of NaOH added is more than the amount required at equivalent point, that is in excess. All the HCl has been reacted, the solution contains neutral salt NaCl and leftover amount of NaOH, and pH is determined by the concentration of NaOH.

mol	$HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$			
initial	0.002500	0.00300	0	
reacted/produced	-0.002500	-0.00250	+0.00250	
at the end	0	0.0005	0.00250	

The molarity concentration of NaOH = $\frac{0.002500\ mol}{(0.0250+0.0300)\ L} = 0.00455M$

pOH = -log (0.00455)= 2.34

pH = 14 – pOH = 11.66