INTRODUCTORY CHEMISTRY, ATOMS FIRST FOR FCC

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Introductory Chemistry, Atoms First for FCC

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CHAPTER OVERVIEW

1: Basics of Measurement

Measurements are one of the most important things to understand in chemistry as well as other physical sciences. Measurements are not only important in science, but in many fields of work which depend upon science including agriculture, medicine, and other health related fields. In all of these fields, workers are routinely measuring things and reading measured amounts: the area of a plot of land, the weight of a patient, the concentration of a medication, the volume of a measuring device. Misunderstandings of measurement could result in catastrophe in any of these areas. (in fact, miscalculations related to measurements were responsible for several tragedies including a very expensive Mars mission.) There are several important things to understand related to measurements: what they are, their precision, and how to perform calculations with measured numbers. Section 1.1 discusses measurements in terms of numbers and units. Section 1.2 discusses how we explain precision when we report measurements. Section 1.3 discusses how we can use the units of measurements to correctly perform the types of calculations that will be important in this course, and in applications which you will use in whatever field you go into.

1.1: Taking Measurements- Numbers and Units

Learning Objectives

- Express quantities properly, using a number and a unit.

A coffee maker’s instructions tell you to fill the coffee pot with 4 cups of water and to use 3 scoops of coffee. When you follow these instructions, you are measuring. When you visit a doctor’s office, a nurse checks your temperature, height, weight, and perhaps blood pressure (Figure 1.1.1); the nurse is also measuring.

Figure 1.1.1: Measuring Blood Pressure. A nurse or a doctor measuring a patient’s blood pressure is taking a measurement. (GFDL; Pia von Lützau).

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. The next two sections examine the rules for expressing numbers.

✓ Example 1.1.1

Identify the number and the unit in each quantity.

a. one dozen eggs
b. 2.54 centimeters
c. a box of pencils
d. 88 meters per second

Solution

a. The number is one, and the unit is a dozen eggs.
b. The number is 2.54, and the unit is centimeter.
c. The number 1 is implied because the quantity is only *a* box. The unit is box of pencils.
d. The number is 88, and the unit is meters per second. Note that in this case the unit is actually a combination of two units: meters and seconds.

Key Take Away

- Identify a quantity properly with a number and a unit.

1.1.1: Scientific Notation - Writing Large and Small Numbers

Learning Objectives

- Express a large number or a small number in scientific notation.
- Carry out arithmetical operations and express the final answer in 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

$$N \times 10^n$$

where N is greater than or equal to 1 and less than 10 ($1 \leq N < 10$), and n 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 n. 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 (N). The magnitude of n is then determined as follows:

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

Another way to remember this is to recognize that as the number N decreases in magnitude, the exponent increases and vice versa. The application of this rule is illustrated in Example $1.1.1.1$

Example 1.1.1.1: Expressing Numbers in Scientific Notation

Convert each number to scientific notation.

a. 637.8
b. 0.0479
c. 7.86
d. 12,378
e. 0.00032
f. 61.06700
g. 2002.080
h. 0.01020

Solution

Solutions to Example 2.2.1

	Explanation	Answer
a	To convert 637.8 to a number from 1 to 10, we move the decimal point two places to the left: 637.8 Because the decimal point was moved two places to the left, n = 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: 0.0479 Because the decimal point was moved two places to the right, n = −2.	4.79×10^{-2}
c	This is usually expressed simply as 7.86. (Recall that $10^0 = 1$.)	7.86×10^0

	Explanation	Answer
d	Because the decimal point was moved four places to the left, n = 4.	1.2378×10^4
e	Because the decimal point was moved four places to the right, n = −4.	3.2×10^{-4}
f	Because the decimal point was moved one place to the left, n = 1.	6.106700×10^1
g	Because the decimal point was moved three places to the left, n = 3.	2.002080×10^3
h	Because the decimal point was moved two places to the right, n = -2.	1.020×10^{-2}

Addition and Subtraction

Before numbers expressed in scientific notation can be added or subtracted, they must be converted to a form in which all the exponents have the same value. The appropriate operation is then carried out on the values of N. Example 1.1.1.2illustrates how to do this.

✓ Example 1.1.1.2: Expressing Sums and Differences in Scientific Notation

Carry out the appropriate operation and then express the answer in scientific notation.

a. $(1.36 \times 10^2) + (4.73 \times 10^3)$
b. $(6.923 \times 10^{-3}) - (8.756 \times 10^{-4})$

Solution

Solutions to Example 2.2.2.

	Explanation	Answer
a	Both exponents must have the same value, so these numbers are converted to either $(1.36 \times 10^2) + (47.3 \times 10^2) = (1.36 + 47.3) \times 10^2 = 48.66 \times 10^2$ or $(0.136 \times 10^3) + (4.73 \times 10^3) = (0.136 + 4.73) \times 10^3) = 4.87 \times 10^3$. Choosing either alternative gives the same answer, reported to two decimal places. In converting 48.66 × 10^2 to scientific notation, n has become more positive by 1 because the value of N has decreased.	=$\mathbf{4.87 \times 10^3}$
b	Converting the exponents to the same value gives either $(6.923 \times 10^{-3}) - (0.8756 \times 10^{-3}) = (6.923 - 0.8756) \times 10^{-3}$ or $(69.23 \times 10^{-4}) - (8.756 \times 10^{-4}) = (69.23 - 8.756) \times 10^{-4} = 60.474 \times 10^{-4}$. In converting 60.474 × 10^{-4} to scientific notation, n has become more positive by 1 because the value of N has decreased.	=$\mathbf{6.047 \times 10^{-3}}$

Multiplication and Division

When multiplying numbers expressed in scientific notation, we multiply the values of N and add together the values of n. Conversely, when dividing, we divide N in the dividend (the number being divided) by N in the divisor (the number by which we are dividing) and then subtract n in the divisor from n in the dividend. In contrast to addition and subtraction, the exponents do not have to be the same in multiplication and division. Examples of problems involving multiplication and division are shown in Example 1.1.1.3

✓ Example 1.1.1.3: Expressing Products and Quotients in Scientific Notation

Perform the appropriate operation and express your answer in scientific notation.

a. $(6.022 \times 10^{23})(6.42 \times 10^{-2})$
b. $\dfrac{1.67 \times 10^{-24}}{9.12 \times 10^{-28}}$
c. $\dfrac{(6.63 \times 10^{-34})(6.0 \times 10)}{8.52 \times 10^{-2}}$

Solution

Solution to Example 2.2.3

	Explanation	Answer
a	In multiplication, we add the exponents: $(6.022 \times 10^{23})(6.42 \times 10^{-2}) = (6.022)(6.42) \times 10^{[23+(-2)]} = 38.7 \times 10^{21}$ In converting 38.7×10^{21} to scientific notation, n has become more positive by 1 because the value of N has decreased.	

3.87×10^{22} **b**

In division, we subtract the exponents:

$$\frac{1.67 \times 10^{-24}}{9.12 \times 10^{-28}} = \frac{1.67}{9.12} \times 10^{[-24-(-28)]} = 0.183 \times 10^{4}$$

In converting 0.183×10^{4} to scientific notation, n has become more negative by 1 because the value of N has increased.

1.83×10^{3} **c**

This problem has both multiplication and division:

$$\frac{(6.63 \times 10^{-34})(6.0 \times 10)}{(8.52 \times 10^{-2})} = \frac{39.78}{8.52} \times 10^{[-34+1-(-2)]}$$

4.7×10^{-31}

1.1.2: The Basic Units of Measurement

Learning Objectives

- State the different measurement systems used in chemistry.
- Describe how prefixes are used in the metric system and identify how the prefixes milli-, centi-, and kilo- compare to the base unit.

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).

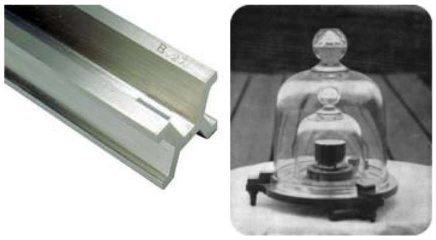


Figure 1.1.2.1: Meter standard (left) and Kilogram standard (right).

SI Base Units

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 very simple. 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 1.1.2.1.

Table 1.1.2.1: SI Base Units of Measurement

Quantity	SI Base Unit	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

The first units are frequently encountered in chemistry. All other measurement quantities, such as volume, force, and energy, can be derived from these seven base units.

Unfortunately, the Metric System is Not Ubiquitous

The map below shows the adoption of the SI units in countries around the world. The United States has legally adopted the metric system for measurements, but does not use it in everyday practice. Great Britain and much of Canada use a combination of metric and imperial units.

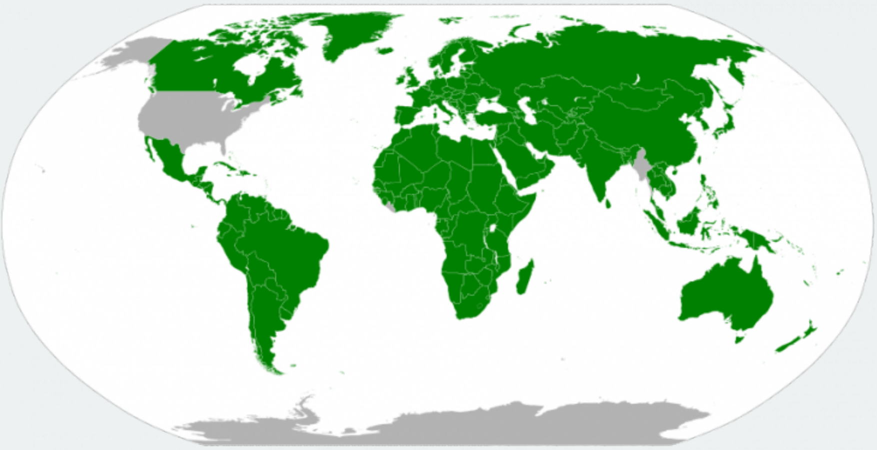


Figure 1.1.2.1: Areas of world using metric system (in green). Only a few countries are slow or resistant to adoption including the United States.

Prefix Multipliers

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. These prefixes all derive from either Latin or Greek terms. For example, *mega* comes from the Greek word $\mu\varepsilon\gamma\alpha\varsigma$, meaning "great". Table 1.1.2.2lists 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.

Table 1.1.2.2: SI Prefixes

Prefix	Unit Abbreviation	Meaning	Example
giga	G	1,000,000,000	1 gigameter $(\mathrm{Gm}) = 10^9\ \mathrm{m}$
mega	M	1,000,000	1 megameter $(\mathrm{Mm}) = 10^6\ \mathrm{m}$
kilo	k	1,000	1 kilometer $(\mathrm{km}) = 1{,}000\ \mathrm{m}$
hecto	h	100	1 hectometer $(\mathrm{hm}) = 100\ \mathrm{m}$
deka	da	10	1 dekameter $(\mathrm{dam}) = 10\ \mathrm{m}$
		1	1 meter (m)
deci	d	1/10	1 decimeter $(\mathrm{dm}) = 0.1\ \mathrm{m}$
centi	c	1/100	1 centimeter $(\mathrm{cm}) = 0.01\ \mathrm{m}$
milli	m	1/1,000	1 millimeter $(\mathrm{mm}) = 0.001\ \mathrm{m}$
micro	μ	1/1,000,000	1 micrometer $(\mu\mathrm{m}) = 10^{-6}\ \mathrm{m}$
nano	n	1/1,000,000,000	1 nanometer $(\mathrm{nm}) = 10^{-9}\ \mathrm{m}$
pico	p	1/1,000,000,000,000	1 picometer $(\mathrm{pm}) = 10^{-12}\ \mathrm{m}$

There are a couple of odd little practices with the use of metric abbreviations. Most abbreviations are lowercase. We use "m" for meter and not "M". However, when it comes to volume, the base unit "liter" is abbreviated as "L" and not "l". So we would write 3.5 milliliters as $3.5\ \mathrm{mL}$.

As a practical matter, whenever possible you should express the units in a small and manageable number. If you are measuring the weight of a material that weighs $6.5\ \mathrm{kg}$, this is easier than saying it weighs $6500\ \mathrm{g}$ or $0.65\ \mathrm{dag}$. All three are correct, but the kg units in this case make for a small and easily managed number. However, if a specific problem needs grams instead of kilograms, go with the grams for consistency.

✓ Example 1.1.2.1: Unit Abbreviations

Give the abbreviation for each unit and define the abbreviation in terms of the base unit.

a. kiloliter
b. microsecond
c. decimeter
d. nanogram

Solutions

Solutions to Example 2.5.1

	Explanation	Answer
a	The prefix kilo means “1,000 ×,” so 1 kL equals 1,000 L.	kL
b	The prefix micro implies 1/1,000,000th of a unit, so 1 µs equals 0.000001 s.	µs
c	The prefix deci means 1/10th, so 1 dm equals 0.1 m.	dm
d	The prefix nano means 1/1000000000, so a nanogram is equal to 0.000000001 g.	ng

? Exercise 1.1.2.1

Give the abbreviation for each unit and define the abbreviation in terms of the base unit.

a. kilometer
b. milligram
c. nanosecond
d. centiliter

(click "answer" below to reveal answer)

Answer a:

km

Answer b:

mg

Answer c:

ns

Answer d:

cL

Summary

- Metric prefixes derive from Latin or Greek terms. The prefixes are used to make the units manageable.
- The SI system is based on multiples of ten. There are seven basic units in the SI system. Five of these units are commonly used in chemistry.

1.2: Significant Figures

In addition to a number and unit, it is also important to consider significant figures when reporting or reading a measurement. Significant figures tell us something about the precision with which a measurement was made. Precision can be very important in some situations, so we like to have a way of knowing how precise a particular measurement was. For example, a parent may pour a glass of water for their child and also pour them some medication. Hopefully the parent is using more precision when measuring the medication compared to measuring the water! Significant figures are how we keep track of this kind of precision in science. We will first discuss how to read the significant figures on a measurement correctly. Then we will discuss how to correctly report the significant figures after perform mathematical operations involving measured numbers.

1.2.1: Significant Figures - Writing Numbers to Reflect Precision

Learning Objectives

- Identify the number of significant figures in a reported value.

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 2.553 cm as there is no possible way that the thousandths digit could be estimated. The 3 is not significant and would not be reported.

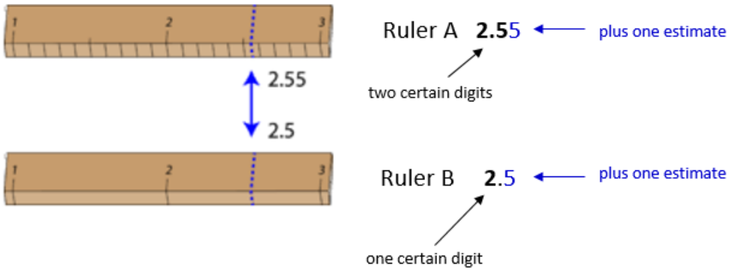


Figure $1.2.1.1$: Measurement with two different rulers.
Ruler A's measurement can be rounded to 2.55, with 2 certain digits, while Ruler B's measurement of 2.5 has 1 certain digit

Measurement Uncertainty

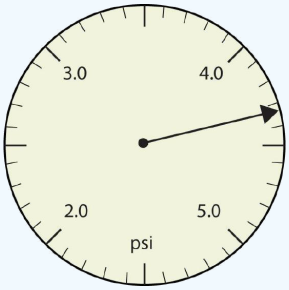
Some error or **uncertainty** always exists in any measurement. The amount of uncertainty depends both upon the skill of the measurer and upon the quality of the measuring tool. While some balances are capable of measuring masses only to the nearest 0.1 g, other highly sensitive balances are capable of measuring to the nearest 0.001 g or even better. Many measuring tools such as rulers and graduated cylinders have small lines which need to be carefully read in order to make a measurement. Figure $1.2.1.1$ shows two rulers making the same measurement of an object (indicated by the blue arrow).

With either ruler, it is clear that the length of the object is between 2 and 3 cm. The bottom ruler contains no millimeter markings. With that ruler, the tenths digit can be estimated and the length may be reported as 2.5 cm. However, another person may judge that the measurement is 2.4 cm or perhaps 2.6 cm. While the 2 is known for certain, the value of the tenths digit is uncertain.

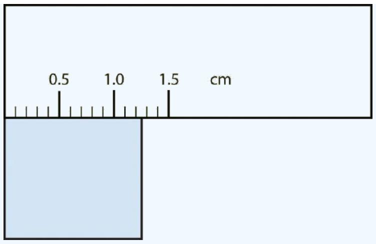
The top ruler contains marks for tenths of a centimeter (millimeters). Now the same object may be measured as 2.55 cm. The measurer is capable of estimating the hundredths digit because he can be certain that the tenths digit is a 5. Again, another measurer may report the length to be 2.54 cm or 2.56 cm. In this case, there are two certain digits (the 2 and the 5), with the hundredths digit being uncertain. Clearly, the top ruler is a superior ruler for measuring lengths as precisely as possible.

✓ Example 1.2.1.1: Reporting Measurements to the Proper Number of Significant Figures

Use each diagram to report a measurement to the proper number of significant figures.

a. 

b.



Ruler measuring a rectangle in units of centimeters, with the rectangle's edge between 1.2 and 1.3 cm marks

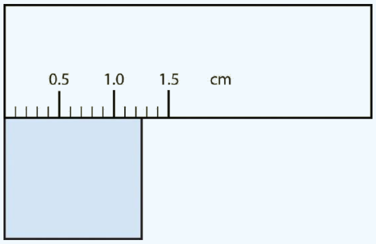
Solutions

Solutions to Example 2.3.1

	Explanation	Answer
a.	The arrow is between 4.0 and 5.0, so the measurement is at least 4.0. The arrow is between the third and fourth small tick marks, so it’s at least 0.3. We will have to estimate the last place. It looks like about one-third of the way across the space, so let us estimate the hundredths place as 3. The symbol psi stands for “pounds per square inch” and is a unit of pressure, like air in a tire. The measurement is reported to three significant figures.	4.33 psi
b.	The rectangle is at least 1.0 cm wide but certainly not 2.0 cm wide, so the first significant digit is 1. The rectangle’s width is past the second tick mark but not the third; if each tick mark represents 0.1, then the rectangle is at least 0.2 in the next significant digit. We have to estimate the next place because there are no markings to guide us. It appears to be about halfway between 0.2 and 0.3, so we will estimate the next place to be a 5. Thus, the measured width of the rectangle is 1.25 cm. The measurement is reported to three significant figures.	1.25 cm

? Exercise 1.2.1.1

What would be the reported width of this rectangle?



Answer

1.25 cm

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.

Table 1.2.1.1: Significant Figure Rules

Rule	Examples
1. All nonzero digits in a measurement are significant.	• 237 has three significant figures. • 1.897 has four significant figures.
2. Zeros that appear between other nonzero digits (middle zeros) are always significant.	• 39,004 has five significant figures. • 5.02 has three significant figures.
3. Zeros that appear in front of all of the nonzero digits are called leading zeros. Leading zeros are never significant.	• 0.008 has one significant figure. • 0.000416 has three significant figures.
4. Zeros that appear after all nonzero digits are called trailing zeros. A number with trailing zeros that lacks a decimal point may or may not be significant. **Use scientific notation to indicate the appropriate number of significant figures.**	• 1400 is ambiguous. ◦ 1.4×10^3 has two significant figures. ◦ 1.40×10^3 three significant figures. ◦ 1.400×10^3 has four significant figures.
5. Trailing zeros in a number with a decimal point are significant. This is true whether the zeros occur before or after the decimal point.	• 620.0 has four significant figures. • 19.000 has five significant figures.

Exact Numbers

Integers obtained either by counting objects or from definitions are exact numbers, which are considered to have infinitely many significant figures. If we have counted four objects, for example, then the number 4 has an infinite number of significant figures (i.e., it represents 4.000…). Similarly, 1 foot (ft) is defined to contain 12 inches (in), so the number 12 in the following equation has infinitely many significant figures:

✓ Example 1.2.1.2

Give the number of significant figures in each. Identify the rule for each.

a. 5.87
b. 0.031
c. 52.90
d. 00.2001
e. 500
f. 6 atoms

Solution

Solution to Example 2.3.2

	Explanation	Answer
a	All three numbers are significant (rule 1).	5.87, three significant figures
b	The leading zeros are not significant (rule 3). The 3 and the 1 are significant (rule 1).	0.031, two significant figures
c	The 5, the 2 and the 9 are significant (rule 1). The trailing zero is also significant (rule 5).	52.90, four significant figures
d	The leading zeros are not significant (rule 3). The 2 and the 1 are significant (rule 1) and the middle zeros are also significant (rule 2).	00.2001, four significant figures
e	The number is ambiguous. It could have one, two or three significant figures.	500, ambiguous
f	The 6 is a counting number. A counting number is an exact number.	6, infinite

Exercise 1.2.1.2

Give the number of significant figures in each.

a. 36.7 m
b. 0.006606 s
c. 2,002 kg
d. 306,490,000 people
e. 3,800 g

Answer a

three significant figures

Answer b

four significant figures

Answer c

four significant figures

Answer d

infinite (exact number)

Answer e

Ambiguous, could be two, three or four significant figures.

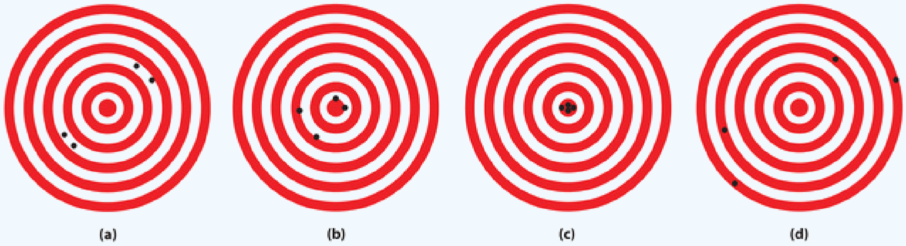
Accuracy and Precision

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.

Video 1.2.1.1: Difference between precision and accuracy.

Example 1.2.1.3

The following archery targets show marks that represent the results of four sets of measurements.



Which target shows

a. a precise, but inaccurate set of measurements?
b. a set of measurements that is both precise and accurate?
c. a set of measurements that is neither precise nor accurate?

Solution

a. Set a is precise, but inaccurate.
b. Set c is both precise and accurate.
c. Set d is neither precise nor accurate.

Summary

Uncertainty exists in all measurements. The degree of uncertainty is affected in part by the quality of the measuring tool. Significant figures give an indication of the certainty of a measurement. Rules allow decisions to be made about how many digits to use in any given situation.

1.2.2: Significant Figures in Calculations

Learning Objectives

- Use significant figures correctly in arithmetical operations.

Rounding

Before dealing with the specifics of the rules for determining the significant figures in a calculated result, we need to be able to round numbers correctly. To **round** a number, first decide how many significant figures the number should have. Once you know that, round to that many digits, starting from the left. If the number immediately to the right of the last significant digit is less than 5, it is dropped and the value of the last significant digit remains the same. If the number immediately to the right of the last significant digit is greater than or equal to 5, the last significant digit is increased by 1.

Consider the measurement 207.518 m Right now, the measurement contains six significant figures. How would we successively round it to fewer and fewer significant figures? Follow the process as outlined in Table $1.2.2.1$.

Table $1.2.2.1$: Rounding examples

Number of Significant Figures	Rounded Value	Reasoning
6	207.518	All digits are significant
5	207.52	8 rounds the 1 up to 2
4	207.5	2 is dropped
3	208	5 rounds the 7 up to 8
2	210	8 is replaced by a 0 and rounds the 0 up to 1
1	200	1 is replaced by a 0

Notice that the more rounding that is done, the less reliable the figure is. An approximate value may be sufficient for some purposes, but scientific work requires a much higher level of detail.

It is important to be aware of significant figures when you are mathematically manipulating numbers. For example, dividing 125 by 307 on a calculator gives 0.4071661238… to an infinite number of digits. But do the digits in this answer have any practical meaning, especially when you are starting with numbers that have only three significant figures each? When performing mathematical operations, there are two rules for limiting the number of significant figures in an answer—one rule is for addition and subtraction, and one rule is for multiplication and division.

> *In operations involving significant figures, the answer is reported in such a way that it reflects the reliability of the **least precise** operation. An answer is no more precise than the least precise number used to get the answer.*

Multiplication and Division

For multiplication or division, the rule is to count the number of significant figures in each number being multiplied or divided and then limit the significant figures in the answer to the lowest count. 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.

Scientific notation provides a way of communicating significant figures without ambiguity. You simply include all the significant figures in the leading number. For example, the number 450 has two significant figures and would be written in scientific notation as 4.5×10^2, whereas 450.0 has four significant figures and would be written as 4.500×10^2. In scientific notation, all significant figures are listed explicitly.

✓ Example 1.2.2.1

Write the answer for each expression using scientific notation with the appropriate number of significant figures.

a. 23.096 × 90.300
b. 125 × 9.000

Solution

a

Explanation	Answer
The calculator answer is 2,085.5688, but we need to round it to five significant figures. Because the first digit to be dropped (in the tenths place) is greater than 5, we round up to 2,085.6.	2.0856×10^3

b

Explanation	Answer
The calculator gives 1,125 as the answer, but we limit it to three significant figures.	1.13×10^3

Addition and Subtraction

How are significant figures handled in calculations? It depends on what type of calculation is being performed. If the calculation is an addition or a subtraction, the rule is as follows: limit the reported answer to the rightmost column that all numbers have significant figures in common. 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.

$$\begin{array}{l} 1.2 \\ \underline{4.41} \\ 5.61 \\ \;\;\uparrow \text{ limit final answer to the tenths column: 5.6} \end{array}$$

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

The dropping of positions in sums and differences 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 if the first dropped digit is less than 5.

$$\begin{array}{l} 77.2 \\ \underline{10.46} \\ 87.66 \\ \;\;\;\uparrow \text{ limit final answer to the tenths column and round up: 87.7} \end{array}$$

✓ Example 1.2.2.2

a. 13.77 + 908.226
b. 1,027 + 611 + 363.06

Solution

a

Explanation	Answer
The calculator answer is 921.996, but because 13.77 has its farthest-right significant figure in the hundredths place, we need to round the final answer to the hundredths position. Because the first digit to be dropped (in the thousandths place) is greater than 5, we round up to 922.00	$922.00 = 9.2200 \times 10^2$

b

Explanation	Answer
The calculator gives 2,001.06 as the answer, but because 611 and 1027 has its farthest-right significant figure in the ones place, the final answer must be limited to the ones position.	$2{,}001.06 = 2.001 \times 10^3$

? Exercise 1.2.2.2

Write the answer for each expression using scientific notation with the appropriate number of significant figures.

a. 217 ÷ 903
b. 13.77 + 908.226 + 515
c. 255.0 − 99
d. 0.00666 × 321

Answer a:

$$0.240 = 2.40 \times 10^{-1}$$

Answer b:

$$1,437 = 1.437 \times 10^3$$

Answer c:

$$156 = 1.56 \times 10^2$$

Answer d:

$$2.14 = 2.14 \times 10^0$$

Remember that calculators do not understand significant figures. *You* are the one who must apply the rules of significant figures to a result from your calculator.

Calculations Involving Multiplication/Division and Addition/Subtraction

In practice, chemists generally work with a calculator and carry all digits forward through subsequent calculations. When working on paper, however, we often want to minimize the number of digits we have to write out. Because successive rounding can compound inaccuracies, intermediate rounding needs to be handled correctly. When working on paper, always round an intermediate result so as to retain at least one more digit than can be justified and carry this number into the next step in the calculation. The final answer is then rounded to the correct number of significant figures at the very end.

Video 1.2.2.1: Significant figures in mixed operations (https://www.youtube.com/watch?v=yBntMndXQWA).

Video 1.2.2.2: https://www.youtube.com/watch?v=__csP0NtlGI

In the worked examples in this text, we will often show the results of intermediate steps in a calculation. In doing so, we will show the results to only the correct number of significant figures allowed for that step, in effect treating each step as a separate calculation. This procedure is intended to reinforce the rules for determining the number of significant figures, but in some cases it may give a final answer that differs in the last digit from that obtained using a calculator, where all digits are carried through to the last step.

✓ Example 1.2.2.3

a. 2(1.008 g) + 15.99 g
b. 137.3 s + 2(35.45 s)
c. $\frac{118.7g}{2} - 35.5g$

Solution

a.

Explanation	Answer

2(1.008 g) + 15.99 g = **Perform multiplication first.** 2 (1.008 g *4 sig figs*) = **2.016 g** *4 sig figs* The number with the least number of significant figures is 1.008 g; *the number 2 is an exact number and therefore has an infinite number of significant figures*. **Then, perform the addition.** **2.016 g** *thousandths place* + 15.99 g *hundredths place (least precise)* = 18.006 g **Round the final answer.** Round the final answer to the hundredths place since 15.99 has its farthest right significant figure in the hundredths place (least precise).	18.01 g (rounding up)

b.

Explanation	Answer
137.3 s + 2(35.45 s) = **Perform multiplication first.** 2(35.45 s *4 sig figs*) = **70.90 s** *4 sig figs* The number with the least number of significant figures is 35.45; *the number 2 is an exact number and therefore has an infinite number of significant figures.* **Then, perform the addition.** 137.3 s *tenths place (least precise)* + **70.90 s** *hundredths place* = 208.20 s **Round the final answer.** Round the final answer to the tenths place based on 137.3 s.	208.2 s

c.

Explanation	Answer
$\frac{118.7g}{2} - 35.5g =$ **Perform division first.** $\frac{118.7g}{2}$ *4 sig figs* = **59.35 g** *4 sig figs* The number with the least number of significant figures is 118.7 g; *the number 2 is an exact number and therefore has an infinite number of significant figures.* **Perform subtraction next.** **59.35 g** *hundredths place* − 35.5 g *tenths place (least precise)* = 23.85 g **Round the final answer.** Round the final answer to the tenths place based on 35.5 g.	23.9 g (rounding up)

? Exercise 1.2.2.3

Complete the calculations and report your answers using the correct number of significant figures.

a. 5(1.008s) - 10.66 s
b. 99.0 cm+ 2(5.56 cm)

Answer a

-5.62 s

Answer b

110.2 cm

Summary

- Rounding
  - If the number to be dropped is greater than or equal to 5, increase the number to its left by 1 (e.g. 2.9699 rounded to three significant figures is 2.97).
  - If the number to be dropped is less than 5, there is no change (e.g. 4.00443 rounded to four significant figures is 4.004).
- The rule in multiplication and division is that the final answer should have the same number of significant figures as there are in the number with the fewest significant figures.
- The rule in addition and subtraction is that the answer is given the same number of decimal places as the term with the fewest decimal places.

1.3: Conversions

Perhaps the most important skill to learn in this class is how to convert between different units of measurement. This skill is not only important in this section, but will continue to come up in almost every chapter of this book. Additionally, this is a skill that is very important for anyone working in a field where you may be providing medication to humans or animals. Even a small mistake on a conversion factor could produce life-threatening results! Please take the time to master the material in this section before moving on to the next chapter. You will need these skills in the next chapter, and several other chapters which follow it.

1.3.1: Problem Solving and Unit Conversions

Learning Objectives

- To convert a value reported in one unit to a corresponding value in a different unit using conversion factors.

During your studies of chemistry (and physics also), you will note that mathematical equations are used in many different applications. Many of these equations have a number of different variables with which you will need to work. You should also note that these equations will often require you to use measurements with their units. Algebra skills become very important here!

Converting Between Units with Conversion Factors

A **conversion factor** is a factor used to convert one unit of measurement into another. A simple conversion factor can convert meters into centimeters, or a more complex one can convert miles per hour into meters per second. Since most calculations require measurements to be in certain units, you will find many uses for conversion factors. Always remember that a conversion factor has to represent a fact; this fact can either be simple or more complex. For instance, you already know that 12 eggs equal 1 dozen. A more complex fact is that the speed of light is 1.86×10^5 miles/sec. Either one of these can be used as a conversion factor depending on what type of calculation you are working with (Table $1.3.1.1$).

Table 1.3.1.1: Conversion Factors from SI units to English Units

English Units	Metric Units	Quantity
1 ounce (oz)	28.35 grams (g)	*mass
1 fluid once (oz)	29.6 mL	volume
2.205 pounds (lb)	1 kilogram (kg)	*mass
1 inch (in)	2.54 centimeters (cm)	length
0.6214 miles (mi)	1 kilometer (km)	length
1 quarter (qt)	0.95 liters (L)	volume

*Pounds and ounces are technically units of force, not mass, but this fact is often ignored by the non-scientific community.

Of course, there are other ratios which are not listed in Table $1.3.1.1$. They may include:

- Ratios embedded in the text of the problem (using words such as *per* or *in each*, or using symbols such as / or %).
- Conversions in the metric system, as covered earlier in this chapter.
- Common knowledge ratios (such as 60 seconds $=$ 1 minute).

If you learned the SI units and prefixes described, then you know that 1 cm is 1/100th of a meter.

$$1 \text{ cm} = \frac{1}{100} \text{ m} = 10^{-2} \text{m}$$

or

$$100 \text{ cm} = 1 \text{ m}$$

Suppose we divide both sides of the equation by 1m (both the number *and* the unit):

$$\frac{100 \text{ cm}}{1 \text{ m}} = \frac{1 \text{ m}}{1 \text{ m}}$$

As long as we perform the same operation on both sides of the equals sign, the expression remains an equality. Look at the right side of the equation; it now has the same quantity in the numerator (the top) as it has in the denominator (the bottom). Any fraction that has the same quantity in the numerator and the denominator has a value of 1:

$$\frac{100 \text{ cm}}{1 \text{ m}} = \frac{1000 \text{ mm}}{1 \text{ m}} = \frac{1 \times 10^6 \mu\text{m}}{1 \text{ m}} = 1$$

We know that 100 cm *is* 1 m, so we have the same quantity on the top and the bottom of our fraction, although it is expressed in different units.

Performing Dimensional Analysis

Dimensional analysis is amongst the most valuable tools that physical scientists use. Simply put, it is the conversion between an amount in one unit to the corresponding amount in a desired unit using various conversion factors. This is valuable because certain measurements are more accurate or easier to find than others. The use of units in a calculation to ensure that we obtain the final proper units is called *dimensional analysis*.

Here is a simple example. How many centimeters are there in 3.55 m? Perhaps you can determine the answer in your head. If there are 100 cm in every meter, then 3.55 m equals 355 cm. To solve the problem more formally with a conversion factor, we first write the quantity we are given, 3.55 m. Then we multiply this quantity by a conversion factor, which is the same as multiplying it by 1. We can write 1 as $\frac{100\text{ cm}}{1\text{ m}}$ and multiply:

$$3.55\text{ m}\times\frac{100\text{ cm}}{1\text{ m}}$$

The 3.55 m can be thought of as a fraction with a 1 in the denominator. Because m, the abbreviation for meters, occurs in both the numerator *and* the denominator of our expression, they cancel out:

$$\frac{3.55\ \cancel{\text{m}}}{1}\times\frac{100\text{ cm}}{1\ \cancel{\text{m}}}$$

The final step is to perform the calculation that remains once the units have been canceled:

$$\frac{3.55}{1}\times\frac{100\text{ cm}}{1}=355\text{ cm}$$

In the final answer, we omit the 1 in the denominator. Thus, by a more formal procedure, we find that 3.55 m equals 355 cm. A generalized description of this process is as follows:

quantity (in old units) × conversion factor = quantity (in new units)

You may be wondering why we use a seemingly complicated procedure for a straightforward conversion. In later studies, the conversion problems you encounter *will not always be so simple*. If you master the technique of applying conversion factors, you will be able to solve a large variety of problems.

In the previous example, we used the fraction $\frac{100\text{ cm}}{1\text{ m}}$ as a conversion factor. Does the conversion factor $\frac{1\text{ m}}{100\text{ cm}}$ also equal 1? Yes, it does; it has the same quantity in the numerator as in the denominator (except that they are expressed in different units). Why did we not use *that* conversion factor? If we had used the second conversion factor, the original unit would not have canceled, and the result would have been meaningless. Here is what we would have gotten:

$$3.55\text{ m}\times\frac{1\text{ m}}{100\text{ cm}}=0.0355\frac{\text{m}^2}{\text{cm}}$$

For the answer to be meaningful, we have to *construct the conversion factor in a form that causes the original unit to cancel out*. Figure $1.3.1.1$shows a concept map for constructing a proper conversion.

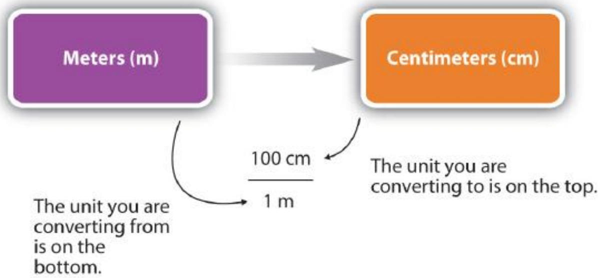


Figure $1.3.1.1$: A Concept Map for Conversions. This is how you construct a conversion factor to convert from one unit to another. Converting meters to centimeters: the unit you are converting is on the bottom of the fraction, and the unit to convert to is on top

General Steps in Performing Dimensional Analysis

1. Identify the "**given**" information in the problem. Look for a number with units to start this problem with.
2. What is the problem asking you to "**find**"? In other words, what unit will your answer have?
3. Use **ratios** and conversion factors to cancel out the units that aren't part of your answer, and leave you with units that are part of your answer.
4. When your units cancel out correctly, you are ready to do the **math**. You are multiplying fractions, so you multiply the top numbers and divide by the bottom numbers in the fractions.

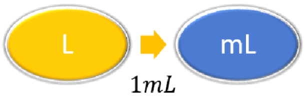
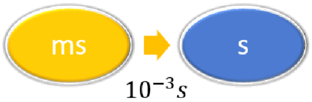
Significant Figures in Conversions

How do conversion factors affect the determination of significant figures?

- Numbers in conversion factors based on prefix changes, such as kilograms to grams, are *not* considered in the determination of significant figures in a calculation because the numbers in such conversion factors are exact.
- Exact numbers are defined or counted numbers, not measured numbers, and can be considered as having an infinite number of significant figures. (In other words, 1 kg is exactly 1,000 g, by the definition of kilo-.)
- Counted numbers are also exact. If there are 16 students in a classroom, the number 16 is exact.
- In contrast, conversion factors that come from measurements (such as density, as we will see shortly) or that are approximations have a limited number of significant figures and should be considered in determining the significant figures of the final answer.

Example 1.3.1.1

Steps for Problem Solving for Example 2.6.1 and 2.6.2

	Example 1.3.1.1	**Example 1.3.1.2**
Steps for Problem Solving	The average volume of blood in an adult male is 4.7 L. What is this volume in milliliters?	A hummingbird can flap its wings once in 18 ms. How many seconds are in 18 ms?
Identify the "given" information and what the problem is asking you to "find."	Given: 4.7 L Find: mL	Given: 18 ms Find: s
List other known quantities.	$1\,mL = 10^{-3}\,L$	$1\,ms = 10^{-3}\,s$
Prepare a concept map and use the proper conversion factor.	 $\frac{1mL}{10^{-3}L}$	 $\frac{10^{-3}s}{1ms}$
Cancel units and calculate.	$4.7\ \cancel{L} \times \frac{1\ \text{mL}}{10^{-3}\ \cancel{L}} = 4{,}700\ \text{mL}$ or $4.7\ \cancel{L} \times \frac{1{,}000\ \text{mL}}{1\ \cancel{L}} = 4{,}700\ \text{mL}$ or 4.7 x 10^3 2SF, not ambiguous	$18\ \cancel{\text{ms}} \times \frac{10^{-3}\ \text{s}}{1\ \cancel{\text{ms}}} = 0.018\ \text{s}$ or $18\ \cancel{\text{ms}} \times \frac{1\ \text{s}}{1{,}000\ \cancel{\text{ms}}} = 0.018\ \text{s}$
Think about your result.	The amount in mL should be 1000 times larger than the given amount in L.	The amount in s should be 1/1000 the given amount in ms.

Exercise 1.3.1.1

Perform each conversion.

a. 101,000 ns to seconds
b. 32.08 kg to grams
c. 1.53 grams to cg

Answer a:

$1.01000x10^{-4}s$

Answer b:

$3.208x10^{4}g$

Answer c:

$1.53x10^{2}cg$

Summary

- Conversion factors are used to convert one unit of measurement into another.
- Dimensional analysis (unit conversions) involves the use of conversion factors that will cancel unwanted units and produce the appropriate units.

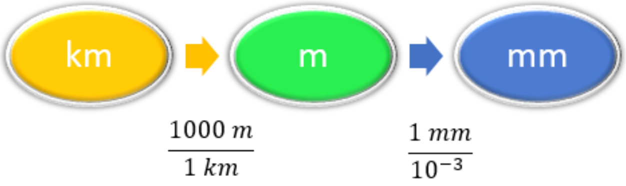
1.3.2: Solving Multi-step Conversion Problems

Multiple Conversions

Sometimes you will have to perform more than one conversion to obtain the desired unit. For example, suppose you want to convert 54.7 km into millimeters. We will set up a series of conversion factors so that each conversion factor produces the next unit in the sequence. We first convert the given amount in km to the base unit, which is meters. We know that 1,000 m =1 km.

Then we convert meters to mm, remembering that 1 $\text{mm} = 10^{-3}$ m.

Concept Map



Convert kilometers to meters to millimeters: use conversion factors 1000 meters per 1 kilometer and 1 millimeter per 0.001 meter

Calculation

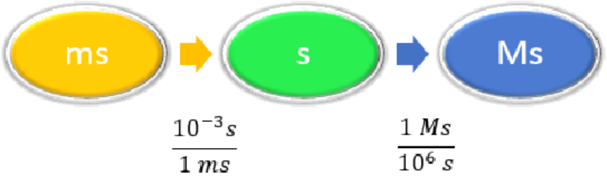
$$54.7\ \cancel{\text{km}} \times \frac{1,000\ \cancel{\text{m}}}{1\ \cancel{\text{km}}} \times \frac{1\ \cancel{\text{mm}}}{10^{-3}\cancel{\text{m}}} = 54,700,000\ \text{mm}$$
$$= 5.47 \times 10^{7}\ \text{mm}$$

> *In each step, the previous unit is canceled and the next unit in the sequence is produced, each successive unit canceling out until only the unit needed in the answer is left.*

✓ Example 1.3.2.1: Unit Conversion

Convert 58.2 ms to megaseconds in one multi-step calculation.

Solution

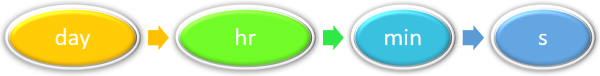
Steps for Problem Solving	Unit Conversion
Identify the "given" information and what the problem is asking you to "find."	Given: 58.2 ms Find: Ms
List other known quantities	$1 ms = 10^{-3} s$ $1 Ms = 10^{6} s$
Prepare a concept map.	 Convert milliseconds to seconds to microseconds: use conversion factors 0.001 second per millisecond and 1 microsecond per 1 million seconds

Steps for Problem Solving	Unit Conversion
Calculate.	$58.2\ \cancel{\text{ms}} \times \frac{10^{-3}\ \cancel{\text{s}}}{1\ \cancel{\text{ms}}} \times \frac{1\ \text{Ms}}{1{,}000{,}000\ \cancel{\text{s}}} = 0.0000000582\ \text{Ms} = 5.82 \times 10^{-8}\ \text{Ms}$ Neither conversion factor affects the number of significant figures in the final answer.

✓ Example 1.3.2.2: Unit Conversion

How many seconds are in a day?

Solution

Steps for Problem Solving	Unit Conversion
Identify the "given" information and what the problem is asking you to "find."	Given: 1 day Find: s
List other known quantities.	1 day = 24 hours 1 hour = 60 minutes 1 minute = 60 seconds
Prepare a concept map.	 $\frac{24\text{hr}}{1\text{ day}}$ $\frac{60\text{min}}{1\text{ hr}}$ $\frac{60\text{ s}}{1\ min}$ Convert day to hour to minute to second: use conversion factors 24 hours per day, 60 minutes per hour, and 60 seconds per minute
Calculate.	$1\text{ d} \times \frac{24\text{ hr}}{1\text{ d}} \times \frac{60\text{ min}}{1\text{ hr}} \times \frac{60\text{ s}}{1\text{ min}} = 86{,}400\text{ s}$

? Exercise 1.3.2.1

Perform each conversion in one multi-step calculation.

a. 43.007 ng to kg
b. 1005 in to ft
c. 12 mi to km

Answer a

$4.3007 \times 10^{-11} kg$

Answer b

$83.75\ ft$

Answer c

$19\ km$

Career Focus: Pharmacist

A pharmacist dispenses drugs that have been prescribed by a doctor. Although that may sound straightforward, pharmacists in the United States must hold a doctorate in pharmacy and be licensed by the state in which they work. Most pharmacy programs require four years of education in a specialty pharmacy school. Pharmacists must know a lot of chemistry and biology so they can understand the effects that drugs (which are chemicals, after all) have on the body. Pharmacists can advise physicians on the selection, dosage, interactions, and side effects of drugs. They can also advise patients on the proper use of their medications, including when and how to take specific drugs properly. Pharmacists can be found in drugstores, hospitals, and other medical facilities. Curiously, an outdated name for pharmacist is *chemist*, which was used when pharmacists formerly did a lot of drug preparation, or *compounding*. In modern times, pharmacists rarely compound their own drugs, but their knowledge of the sciences, including chemistry, helps them provide valuable services in support of everyone’s health.

A woman consulting with a pharmacist. (Public Domain; Rhoda Baer via National Cancer Institute, an agency that is part of the National Institutes of Health.)

Summary

In multi-step conversion problems, the previous unit is canceled for each step and the next unit in the sequence is produced, each successive unit canceling out until only the unit needed in the answer is left.

1.3.3: Units Raised to a Power

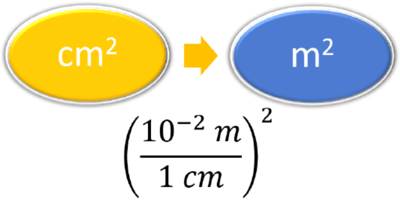
Learning Objectives

- To convert a value reported in one unit raised to a power of 10, to a corresponding value in a different unit raised to the same power of 10, using conversion factors.

Conversion factors for area and volume can also be produced by the dimensional analysis method. Just remember that if a quantity is raised to a power of 10, both the number and the unit must be raised to the same power of 10. For example, to convert 1500 cm^2 to m^2, we need to start with the relationship between centimeter and meter. We know that 1 cm = 10^{-2} m or 100 cm =1 m, but since we are given the quantity in 1500 cm^2, then we have to use the relationship:

$$1\,cm^2 = (10^{-2}\,m)^2 = 10^{-4}\,m^2$$

CONCEPT MAP



$$\left(\frac{10^{-2}\,m}{1\,cm}\right)^2$$

To convert centimeters squared to meters squared, use the conversion factor 0.01 meters per 1 centimeter, squared overall

CALCULATION

$$1500\ \cancel{\text{cm}^2} \times \left(\frac{10^{-2}\ \text{m}}{1\ \cancel{\text{cm}}}\right)^2 = 0.15\ \text{m}^2$$

or

$$1500\ \cancel{\text{cm}^2} \times \left(\frac{1\ \text{m}}{100\ \cancel{\text{cm}}}\right)^2 = 0.15\ \text{m}^2$$

or

$$1500\ \cancel{\text{cm}^2} \times \frac{1\ \text{m}^2}{10,000\ \cancel{\text{cm}^2}} = 0.15\ \text{m}^2$$

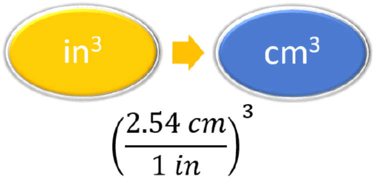
Example 1.3.3.1: Volume of a Sphere

What is the volume of a sphere (radius 4.30 inches) in cubic cm (cm^3)?

Solution

Solution for Example 2.8.1

Steps for Problem Solving	**What is the volume of a sphere (radius 4.30 inches) in cubic cm (cm^3)?**
Identify the "given" information and what the problem is asking you to "find."	Given: radius = 4.30 in Find: cm^3 (volume)
Determine other known quantities.	Volume of a sphere: V = $\frac{4}{3} \times \pi \times r^3$ = $\frac{4}{3} \times 3.1416 \times (4.3\underline{0}in)^3$ = $33\underline{3}.04in^3$

Steps for Problem Solving	**What is the volume of a sphere (radius 4.30 inches) in cubic cm (cm^3)?**
Prepare a concept map.	 To convert inches cubed to centimeters cubed, use conversion factor 2.54 centimeters per 1 inch, cubed overall
Calculate.	$33\underline{3}.04\ \cancel{in^3}\left(\frac{2.54cm}{1\ \cancel{in}}\right)^3 = 5.46\times10^3 cm^3$
Think about your result.	A centimeter is a smaller unit than an inch, so the answer in cubic centimeters is larger than the given value in cubic inches.

? Exercise 1.3.3.1

Lake Tahoe has a surface area of 191 square miles. What is the area in square km (km^2)?

Answer

495 km^2

Contributions & Attributions

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1.4: Density

Learning Objectives

- Define density.
- Use density as a conversion factor.

Density (ρ) is a physical property found by dividing the mass of an object by its volume. Regardless of the sample size, density is always constant. For example, the density of a pure sample of tungsten is always 19.25 grams per cubic centimeter. 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:

$$\text{Density} = \frac{\text{Mass}}{\text{Volume}}$$

or just

$$\rho = \frac{m}{V} \tag{1.4.1}$$

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 $1.4.1$. Notice that corn oil has a lower mass to volume ratio than water. This means that when added to water, corn oil will "float."

Table $1.4.1$: Densities of Common Substances

Substance	Density at 25°C (g/cm3)
blood	1.035
body fat	0.918
whole milk	1.030
corn oil	0.922
mayonnaise	0.910
honey	1.420

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 $1.4.1$: Ethyl Alcohol

Calculate the density of a 30.2 mL sample of ethyl alcohol with a mass of 23.71002 g

Solution

This is a direct application of Equation $1.4.1$:

$$\rho = \frac{23.71002\, g}{30.2\, mL} = 0.785\, g/mL$$

? Exercise $1.4.1$

a. Find the density (in kg/L) of a sample that has a volume of 36.5 L and a mass of 10.0 kg.
b. If you have a 2.130 mL sample of acetic acid with mass 0.002234 kg, what is the density in kg/L?

Answer a

$0.274\, kg/L$

Answer b

$1.049\, kg/L$

Density as a Conversion Factor

Conversion factors can also be constructed for converting between different kinds of units. For example, density can be used to convert between the mass and the volume of a substance. Consider mercury, which is a liquid at room temperature and has a density of 13.6 g/mL. The density tells us that 13.6 g of mercury have a volume of 1 mL. We can write that relationship as follows:

13.6 g mercury = 1 mL mercury

This relationship can be used to construct two conversion factors:

$$\frac{13.6\ g}{1\ mL} = 1$$

and

$$\frac{1\ mL}{13.6\ g} = 1$$

Which one do we use? It depends, as usual, on the units we need to cancel and introduce. For example, suppose we want to know the mass of 2.0 mL of mercury. We would use the conversion factor that has milliliters on the bottom (so that the milliliter unit cancels) and grams on top, so that our final answer has a unit of mass:

$$2.0\ \cancel{\text{mL}} \times \frac{13.6\ \text{g}}{1\ \cancel{\text{mL}}} = 27.2\ \text{g} = 27\ \text{g}$$

In the last step, we limit our final answer to two significant figures because the volume quantity has only two significant figures; the 1 in the volume unit is considered an exact number, so it does not affect the number of significant figures. The other conversion factor would be useful if we were given a mass and asked to find volume, as the following example illustrates.

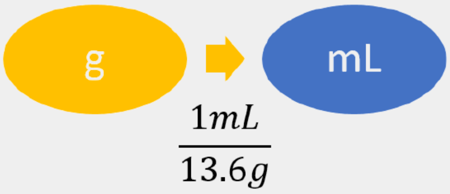
> *Density can be used as a conversion factor between mass and volume.*

✓ Example 1.4.2: Mercury Thermometer Steps for Problem Solving

A mercury thermometer for measuring a patient’s temperature contains 0.750 g of mercury. What is the volume of this mass of mercury?

Solution

Solution to Example 2.9.2

Steps for Problem Solving	**Unit Conversion**
Identify the "given" information and what the problem is asking you to "find."	Given: 0.750 g Find: mL
List other known quantities.	13.6 g/mL (density of mercury)
Prepare a concept map.	
Calculate.	$0.750\ \cancel{\text{g}} \times \frac{1\ \text{mL}}{13.6\ \cancel{\text{g}}} = 0.055147\ldots\ \text{mL} \approx 0.0551\ \text{mL}$ We have limited the final answer to three significant figures.

Exercise 1.4.2

What is the volume of 100.0 g of air if its density is 1.3 g/L?

Answer

$77\ L$

Summary

- Density is defined as the mass of an object divided by its volume.
- Density can be used as a conversion factor between mass and volume.

Contributions & Attributions

1.5: Temperature - Random Motion of Molecules and Atoms

Learning Objectives

- Identify the different between temperature and heat.
- Recognize the different scales used to measure temperature

The concept of temperature may seem familiar to you, but many people confuse temperature with heat. **Temperature** is a measure of how hot or cold an object is relative to another object (its thermal energy content), whereas **heat** is the flow of thermal energy between objects with different temperatures. Temperature is a measure of the average kinetic energy of the particles in matter. In everyday usage, temperature indicates a measure of how hot or cold an object is. Temperature is an important parameter in chemistry. When a substance changes from solid to liquid, it is because there was in increase in the temperature of the material. Chemical reactions usually proceed faster if the temperature is increased. Many unstable materials (such as enzymes) will be viable longer at lower temperatures.

Figure 1.5.1: The glowing charcoal on the left represents high kinetic energy, while the snow and ice on the right are of much lower kinetic energy.

Three different scales are commonly used to measure temperature: Fahrenheit (expressed as °F), Celsius (°C), and Kelvin (K). Thermometers measure temperature by using materials that expand or contract when heated or cooled. Mercury or alcohol thermometers, for example, have a reservoir of liquid that expands when heated and contracts when cooled, so the liquid column lengthens or shortens as the temperature of the liquid changes.

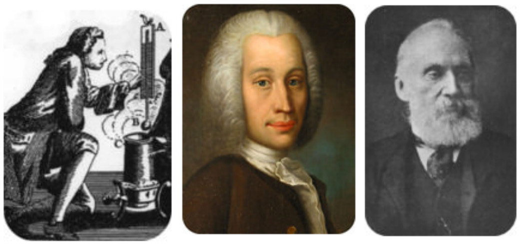


Figure 1.5.2: Daniel Gabriel Fahrenheit (left), Anders Celsius (center), and Lord Kelvin (right).

The Fahrenheit Scale

The first thermometers were glass and contained alcohol, which expanded and contracted as the temperature changed. The German scientist, Daniel Gabriel Fahrenheit used mercury in the tube, an idea put forth by Ismael Boulliau. The Fahrenheit scale was first developed in 1724 and tinkered with for some time after that. The main problem with this scale is the arbitrary definitions of temperature. The freezing point of water was defined as 32^oF and the boiling point as 212^oF. The Fahrenheit scale is typically not used for scientific purposes.

The Celsius Scale

The Celsius scale of the metric system is named after Swedish astronomer Anders Celsius (1701-1744). The Celsius scale sets the freezing point and boiling point of water at 0^oC and 100^oC respectively. The distance between those two points is divided into 100 equal intervals, each of which is one degree. Another term sometimes used for the Celsius scale is "centigrade" because there are 100 degrees between the freezing and boiling points of water on this scale. However, the preferred term is "Celsius".

The Kelvin Scale

The Kelvin temperature scale is named after Scottish physicist and mathematician Lord Kelvin (1824-1907). It is based on molecular motion, with the temperature of 0 K, also known as absolute zero, being the point where all molecular motion ceases. The freezing point of water on the Kelvin scale is 273.15 K, while the boiling point is 373.15 K Notice that there is no "degree" used in the temperature designation. Unlike the Fahrenheit and Celsius scales where temperatures are referred to as "degrees F" or "degrees C", we simply designate temperatures in the Kelvin scale as kelvins.

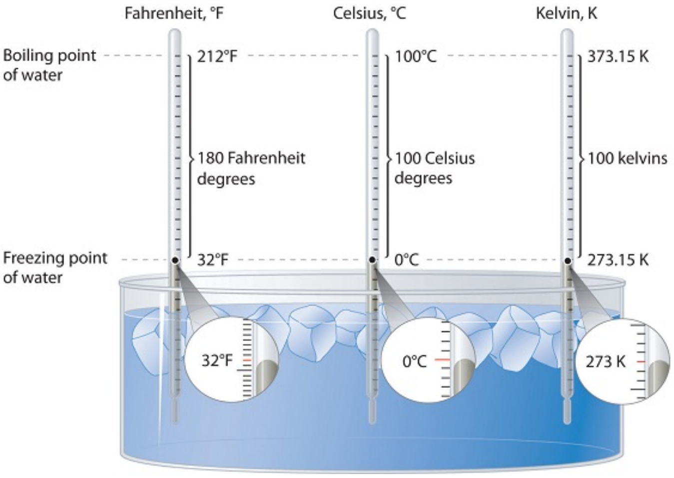


Figure 1.5.1: A Comparison of the Fahrenheit, Celsius, and Kelvin Temperature Scales. Because the difference between the freezing point of water and the boiling point of water is 100° on both the Celsius and Kelvin scales, the size of a degree Celsius (°C) and a kelvin (K) are precisely the same. In contrast, both a degree Celsius and a kelvin are 9/5 the size of a degree Fahrenheit (°F). (CC BY-SA-NC 3.0; anonymous)

Converting Between Scales

The Kelvin is the same size as the Celsius degree, so measurements are easily converted from one to the other. The freezing point of water is 0°C = 273.15 K; the boiling point of water is 100°C = 373.15 K. The Kelvin and Celsius scales are related as follows:

$$T\,(\text{in }^\circ\text{C}) + 273.15 = T\,(\text{in K}) \tag{3.10.1}$$

$$T\ \,(\text{in K}) - 273.15 = T\ (\text{in }^\circ\text{C}) \tag{3.10.2}$$

Degrees on the Fahrenheit scale, however, are based on an English tradition of using 12 divisions, just as 1 ft = 12 in. The relationship between degrees Fahrenheit and degrees Celsius is as follows: where the coefficient for degrees Fahrenheit is exact. (Some calculators have a function that allows you to convert directly between °F and °C.) There is only one temperature for which the numerical value is the same on both the Fahrenheit and Celsius scales: −40°C = −40°F. The relationship between the scales is as follows:

$$^\circ C = \frac{(^\circ F - 32)}{1.8} \tag{3.10.3}$$

$$^\circ F = 1.8 \times (^\circ C) + 32 \tag{3.10.4}$$

✓ Example 1.5.1: Temperature Conversions

A student is ill with a temperature of 103.5°F. What is her temperature in °C and K?

Solution

Converting from Fahrenheit to Celsius requires the use of Equation 3.10.3:

$$\begin{align} ^\circ C &= \frac{(103.5^\circ F - 32)}{1.8} \tag{1.5.1} \\ &= 39.7\,^\circ C \tag{1.5.2} \end{align}$$

Converting from Celsius to Kelvin requires the use of Equation 3.10.1:

$$K = 39.7\,^{\circ}C + 273.15 \tag{1.5.3}$$

$$= 312.9\,K \tag{1.5.4}$$

Exercise 1.5.1

Convert each temperature to °C and °F.

a. the temperature of the surface of the sun (5800 K)
b. the boiling point of gold (3080 K)
c. the boiling point of liquid nitrogen (77.36 K)

Answer (a)

5527 °C, 9980 °F

Answer (b)

2807 °C, 5084 °F

Answer (c)

-195.79 °C, -320.42 °F

Summary

Three different scales are commonly used to measure temperature: Fahrenheit (expressed as °F), Celsius (°C), and Kelvin (K).

Contributions & Attributions

1.E: Measurements (Exercises)

1.1: Expressing Numbers

1. Express these numbers in scientific notation.

   a. 56.9
   b. 563,100
   c. 0.0804
   d. 0.00000667

2. Express these numbers in scientific notation.

   a. −890,000
   b. 602,000,000,000
   c. 0.0000004099
   d. 0.0000000000000011

3. Express these numbers in scientific notation.

   a. 0.00656
   b. 65,600
   c. 4,567,000
   d. 0.000005507

4. Express these numbers in scientific notation.

   a. 65
   b. −321.09
   c. 0.000077099
   d. 0.000000000218

5. Express these numbers in standard notation.

   a. 1.381×10^{5}
   b. 5.22×10^{-7}
   c. 9.998×10^{4}

6. Express these numbers in standard notation.

   a. 7.11×10^{-2}
   b. 9.18×10^{2}
   c. 3.09×10^{-10}

7. Express these numbers in standard notation.

   a. 8.09×10^{0}
   b. 3.088×10^{-5}
   c. -4.239×10^{2}

8. Express these numbers in standard notation.

   a. 2.87×10^{-8}
   b. 1.78×10^{11}
   c. 1.381×10^{-23}

9. These numbers are not written in proper scientific notation. Rewrite them so that they are in proper scientific notation.

   a. 72.44×10^{3}
   b. $9{,}943 \times 10^{-5}$
   c. $588{,}399 \times 10^{2}$

10. These numbers are not written in proper scientific notation. Rewrite them so that they are in proper scientific notation.

    a. 0.000077×10^{-7}
    b. 0.000111×10^{8}
    c. $602{,}000 \times 10^{18}$

11. These numbers are not written in proper scientific notation. Rewrite them so that they are in proper scientific notation.
    a. 345.1×10^{2}
    b. 0.234×10^{-3}
    c. $1{,}800 \times 10^{-2}$
12. These numbers are not written in proper scientific notation. Rewrite them so that they are in proper scientific notation.
    a. $8{,}099 \times 10^{-8}$
    b. 34.5×10^{0}
    c. 0.000332×10^{4}
13. Write these numbers in scientific notation by counting the number of places the decimal point is moved.
    a. 123,456.78
    b. 98,490
    c. 0.000000445
14. Write these numbers in scientific notation by counting the number of places the decimal point is moved.
    a. 0.000552
    b. 1,987
    c. 0.00000000887
15. Use your calculator to evaluate these expressions. Express the final answer in proper scientific notation.
    a. $456 \times (7.4 \times 10^{8}) = ?$
    b. $(3.02 \times 10^{5}) \div (9.04 \times 10^{15}) = ?$
    c. $0.0044 \times 0.000833 = ?$
16. Use your calculator to evaluate these expressions. Express the final answer in proper scientific notation.
    a. $98{,}000 \times 23{,}000 = ?$
    b. $98{,}000 \div 23{,}000 = ?$
    c. $(4.6 \times 10^{-5}) \times (2.09 \times 10^{3}) = ?$
17. Use your calculator to evaluate these expressions. Express the final answer in proper scientific notation.
    a. $45 \times 132 \div 882 = ?$
    b. $[(6.37 \times 10^{4}) \times (8.44 \times 10^{-4})] \div (3.2209 \times 10^{15}) = ?$
18. Use your calculator to evaluate these expressions. Express the final answer in proper scientific notation.
    a. $(9.09 \times 10^{8}) \div [(6.33 \times 10^{9}) \times (4.066 \times 10^{-7})] = ?$
    b. $9{,}345 \times 34.866 \div 0.00665 = ?$

Answers

1. a. 5.69×10^{1}
   b. 5.631×10^{5}
   c. 8.04×10^{-2}
   d. 6.67×10^{-6}

3. a. 6.56×10^{-3}
   b. 6.56×10^{4}
   c. 4.567×10^{6}
   d. 5.507×10^{-6}

5. a. 138,100
   b. 0.000000522
   c. 99,980

7. a. 8.09
   b. 0.00003088
   c. −423.9
9. a. 7.244×10^{4}
   b. 9.943×10^{-2}
   c. 5.88399×10^{7}
11. a. 3.451×10^{4}
   b. 2.34×10^{-4}
   c. 1.8×10^{1}
13. a. 1.2345678×10^{5}
   b. 9.849×10^{4}
   c. 4.45×10^{-7}
15. a. 3.3744×10^{11}
   b. 3.3407×10^{-11}
   c. 3.665×10^{-6}
17. a. 6.7346×10^{0}
   b. 1.6691×10^{-14}

1.2: Expressing Units

1. Identify the unit in each quantity.

- 2 boxes of crayons
- 3.5 grams of gold

2. Identify the unit in each quantity.

- 32 oz of cheddar cheese
- 0.045 cm^3 of water

3. Identify the unit in each quantity.

- 9.58 s (the current world record in the 100 m dash)
- 6.14 m (the current world record in the pole vault)

4. Identify the unit in each quantity.

- 2 dozen eggs
- 2.4 km/s (the escape velocity of the moon, which is the velocity you need at the surface to escape the moon's gravity)

5. Indicate what multiplier each prefix represents.

- k
- m
- M

6. Indicate what multiplier each prefix represents.

- c
- G
- μ

7. Give the prefix that represents each multiplier.

- 1/1,000th ×
- 1,000 ×
- 1,000,000,000 ×

8. Give the prefix that represents each multiplier.

- 1/1,000,000,000th ×

- 1/100th ×
- 1,000,000 ×

a. 9. Complete the following table with the missing information.

Unit	Abbreviation
kilosecond	
	mL
	Mg
centimeter	

b. 10. Complete the following table with the missing information.

Unit	Abbreviation
kilometer per second	
second	
	cm^3
	μL
nanosecond	

11. Express each quantity in a more appropriate unit. There may be more than one acceptable answer.

- 3.44×10^{-6} s
- 3,500 L
- 0.045 m

12. Express each quantity in a more appropriate unit. There may be more than one acceptable answer.

- 0.000066 m/s (Hint: you need consider only the unit in the numerator.)
- 4.66×10^6 s
- 7,654 L

13. Express each quantity in a more appropriate unit. There may be more than one acceptable answer.

- 43,600 mL
- 0.0000044 m
- 1,438 ms

14. Express each quantity in a more appropriate unit. There may be more than one acceptable answer.

- 0.000000345 m^3
- 47,000,000 mm^3
- 0.00665 L

15. Multiplicative prefixes are used for other units as well, such as computer memory. The basic unit of computer memory is the byte (b). What is the unit for one million bytes?

16. You may have heard the terms *microscale* or *nanoscale* to represent the sizes of small objects. What units of length do you think are useful at these scales? What fractions of the fundamental unit of length are these units?

17. Acceleration is defined as a change in velocity per time. Propose a unit for acceleration in terms of the fundamental SI units.

18. Density is defined as the mass of an object divided by its volume. Propose a unit of density in terms of the fundamental SI units.

Answers

1.

- boxes of crayons
- grams of gold

3.

- seconds
- meters

5.

- 1,000 x
- 1/1,000 x
- 1,000,000 x

7.

- milli-
- kilo-
- giga-

9.

a. Unit	Abbreviation
a. kilosecond	a. ks
a. milliliter	a. mL
a. megagram	a. Mg
a. centimeter	a. cm

11.

- 3.44 µs
- 3.5 kL
- 4.5 cm

13.

- 43.6 mL
- 4.4 m
- 1.438 s

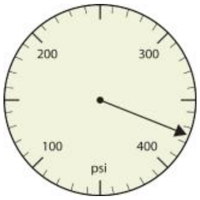
15. megabytes (Mb

17. meters/second^2

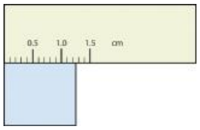
1.3: Significant Figures

1. Express each measurement to the correct number of significant figures.

a.

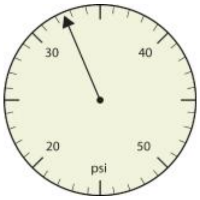


b.

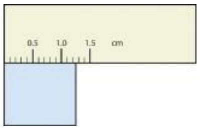


2. Express each measurement to the correct number of significant figures.

a.



b.



3. How many significant figures do these numbers have?

- 23
- 23.0
- 0.00023
- 0.0002302

2. How many significant figures do these numbers have?

- 5.44×10^8
- 1.008×10^{-5}
- 43.09
- 0.0000001381

5. How many significant figures do these numbers have?

- 765,890
- 765,890.0
- 1.2000×10^5
- 0.0005060

6. How many significant figures do these numbers have?

- 0.009
- 0.0000009
- 65,444
- 65,040

7. Compute and express each answer with the proper number of significant figures, rounding as necessary.

- 56.0 + 3.44 = ?
- 0.00665 + 1.004 = ?
- 45.99 − 32.8 = ?
- 45.99 − 32.8 + 75.02 = ?

8. Compute and express each answer with the proper number of significant figures, rounding as necessary.

- 1.005 + 17.88 = ?
- 56,700 − 324 = ?
- 405,007 − 123.3 = ?
- 55.5 + 66.66 − 77.777 = ?

9. Compute and express each answer with the proper number of significant figures, rounding as necessary.

- 56.7 × 66.99 = ?
- ÷ 77 = ?
- ÷ 77.0 = ?
- 6.022 × 1.89 = ?

10. Compute and express each answer with the proper number of significant figures, rounding as necessary.

- 0.000440 × 17.22 = ?
- 203,000 ÷ 0.044 = ?
- 67 × 85.0 × 0.0028 = ?
- 999,999 ÷ 3,310 = ?

11. Write the number 87,449 in scientific notation with four significant figures.

12. Write the number 0.000066600 in scientific notation with five significant figures.

13. Write the number 306,000,000 in scientific notation to the proper number of significant figures.

14. Write the number 0.0000558 in scientific notation with two significant figures.

15. Perform each calculation and limit each answer to three significant figures.

- 67,883 × 0.004321 = ?
- (9.67 × 10^3) × 0.0055087 = ?

16. Perform each calculation and limit each answer to four significant figures.

- 18,900 × 76.33 ÷ 0.00336 = ?
- 0.77604 ÷ 76,003 × 8.888 = ?

Answers

1.

- 375 psi
- 1.25 cm

3.

- two
- three
- two
- four

5.

- five
- seven
- five
- four

7.

- 59.4
- 1.011
- 13.2
- 88.2

9.

- 3.80 × 10^3
- 0.013
- 0.0130
- 11.4

11.

- 8.745×10^4
- 6.6600×10^{-5}

15.

- 293
- 53.3

1.4: Converting Units

1) Write the two conversion factors that exist between the two given units.

1. milliliters and liters
2. microseconds and seconds
3. kilometers and meters

2) Write the two conversion factors that exist between the two given units.

1. kilograms and grams
2. milliseconds and seconds
3. centimeters and meters

3) Perform the following conversions.

1. 5.4 km to meters
2. 0.665 m to millimeters
3. 0.665 m to kilometer

4) Perform the following conversions.

1. 90.6 mL to liters
2. 0.00066 ML to liters
3. 750 L to kiloliters

5) Perform the following conversions.

1. 17.8 µg to grams
2. 7.22×10^2 kg to grams
3. 0.00118 g to nanograms

6) Perform the following conversions.

1. 833 ns to seconds
2. 5.809 s to milliseconds
3. 2.77×10^6 s to megaseconds

7) Perform the following conversions.

1. 9.44 m^2 to square centimeters
2. 3.44×10^8 mm^3 to cubic meters

8) Perform the following conversions.

1. 0.00444 cm^3 to cubic meters
2. 8.11×10^2 m^2 to square nanometers

9) Why would it be inappropriate to convert square centimeters to cubic meters?

10) Why would it be inappropriate to convert from cubic meters to cubic seconds?

11) Perform the following conversions.

a. 45.0 m/min to meters/second
b. 0.000444 m/s to micrometers/second
c. 60.0 km/h to kilometers/second

12) Perform the following conversions.

1. 3.4 × 10^{2} cm/s to centimeters/minute
2. 26.6 mm/s to millimeters/hour
3. 13.7 kg/L to kilograms/milliliters

13) Perform the following conversions.

1. 0.674 kL to milliliters
2. 2.81 × 10^{12} mm to kilometers
3. 94.5 kg to milligrams

14) Perform the following conversions.

1. 6.79 × 10^{-6} kg to micrograms
2. 1.22 mL to kiloliters
3. 9.508 × 10^{-9} ks to milliseconds

15) Perform the following conversions.

1. 6.77 × 10^{14} ms to kiloseconds
2. 34,550,000 cm to kilometers

16) Perform the following conversions.

1. 4.701 × 10^{15} mL to kiloliters
2. 8.022 × 10^{-11} ks to microseconds

17) Perform the following conversions. Note that you will have to convert units in both the numerator and the denominator.

1. 88 ft/s to miles/hour (Hint: use 5,280 ft = 1 mi.)
2. 0.00667 km/h to meters/second

18) Perform the following conversions. Note that you will have to convert units in both the numerator and the denominator.

1. 3.88 × 10^{2} mm/s to kilometers/hour
2. 1.004 kg/L to grams/milliliter

19) What is the area in square millimeters of a rectangle whose sides are 2.44 cm × 6.077 cm? Express the answer to the proper number of significant figures.

20) What is the volume in cubic centimeters of a cube with sides of 0.774 m? Express the answer to the proper number of significant figures.

21) The formula for the area of a triangle is 1/2 × base × height. What is the area of a triangle in square centimeters if its base is 1.007 m and its height is 0.665 m? Express the answer to the proper number of significant figures.

22) The formula for the area of a triangle is 1/2 × base × height. What is the area of a triangle in square meters if its base is 166 mm and its height is 930.0 mm? Express the answer to the proper number of significant figures.

Answers

a. a. $$\frac{1000mL}{1L} and \frac{1L}{1000mL}$$
   b. $$\frac{1000000\mu s}{1s} and \frac{1s}{1000000\mu s}$$
   c. $$\frac{1000m}{1km} and \frac{1km}{1000m}$$

1. 5,400 m
2. 665 mm
3. 6.65 × 10^{-4} km

-
- 1. 1.78 × 10^{-5} g
  2. 7.22 × 10^{5} g

3. 1.18×10^6 ng

-
- 1. 94,400 cm^2
  2. 0.344 m^3
-

a. One is a unit of area, and the other is a unit of volume.

b.

- a.
  1. 0.75 m/s
  2. 444 µm/s
  3. 1.666×10^{-2} km/s
-
- 1. 674,000 mL
  2. 2.81×10^6 km
  3. 9.45×10^7 mg
-
- 1. 6.77×10^8 ks
  2. 345.5 km
-
- 1. 6.0×10^1 mi/h
  2. 0.00185 m/s
-

a. 1.48×10^3 mm^2

b.

c. 3.35×10^3 cm^2

1.5: Other Units - Temperature and Density

a. Perform the following conversions.
b. 255°F to degrees Celsius
c. −255°F to degrees Celsius
d. 50.0°C to degrees Fahrenheit
e. −50.0°C to degrees Fahrenheit

- a. Perform the following conversions.
- 1,065°C to degrees Fahrenheit
- −222°C to degrees Fahrenheit
- 400.0°F to degrees Celsius
- 200.0°F to degrees Celsius
- a. Perform the following conversions.
- 100.0°C to kelvins
- −100.0°C to kelvins
- 100 K to degrees Celsius
- 300 K to degrees Celsius
- a. Perform the following conversions.
- 1,000.0 K to degrees Celsius
- 50.0 K to degrees Celsius
- 37.0°C to kelvins
- −37.0°C to kelvins

a. Convert 0 K to degrees Celsius. What is the significance of the temperature in degrees Celsius?

b. Convert 0 K to degrees Fahrenheit. What is the significance of the temperature in degrees Fahrenheit?

c. The hottest temperature ever recorded on the surface of the earth was 136°F in Libya in 1922. What is the temperature in degrees Celsius and in kelvins?

d. The coldest temperature ever recorded on the surface of the earth was −128.6°F in Vostok, Antarctica, in 1983. What is the temperature in degrees Celsius and in kelvins?

e. Give at least three possible units for density.

f. What are the units when density is inverted? Give three examples.

g. A sample of iron has a volume of 48.2 cm^3. What is its mass?

h. A sample of air has a volume of 1,015 mL. What is its mass?

i. The volume of hydrogen used by the *Hindenburg*, the German airship that exploded in New Jersey in 1937, was 2.000×10^8 L. If hydrogen gas has a density of 0.0899 g/L, what mass of hydrogen was used by the airship?

j. The volume of an Olympic-sized swimming pool is 2.50×10^9 cm^3. If the pool is filled with alcohol (d = 0.789 g/cm^3), what mass of alcohol is in the pool?

k. A typical engagement ring has 0.77 cm^3 of gold. What mass of gold is present?

l. A typical mercury thermometer has 0.039 mL of mercury in it. What mass of mercury is in the thermometer?

m. What is the volume of 100.0 g of lead if lead has a density of 11.34 g/cm^3?

n. What is the volume of 255.0 g of uranium if uranium has a density of 19.05 g/cm^3?

o. What is the volume in liters of 222 g of neon if neon has a density of 0.900 g/L?

p. What is the volume in liters of 20.5 g of sulfur hexafluoride if sulfur hexafluoride has a density of 6.164 g/L?

17. Which has the greater volume, 100.0 g of iron (d = 7.87 g/cm^3) or 75.0 g of gold (d = 19.3 g/cm^3)?
18. Which has the greater volume, 100.0 g of hydrogen gas (d = 0.0000899 g/cm^3) or 25.0 g of argon gas (d = 0.00178 g/cm^3)?

Answers

1. 124°C
2. −159°C
3. 122°F
4. −58°F

-
- 1. 373 K
  2. 173 K
  3. −173°C
  4. 27°C
-

a. −273°C. This is the lowest possible temperature in degrees Celsius.

b.

c. 57.8°C; 331 K

d.

e. g/mL, g/L, and kg/L (answers will vary)

f.

g. 379 g

h.

i. 1.80×10^7 g

j.

k. 15 g

l.

m. 8.818 cm^3

n.

o. 247 L

p.

q. The 100.0 g of iron has the greater volume

Additional Exercises

a. Evaluate 0.00000000552 × 0.0000000006188 and express the answer in scientific notation. You may have to rewrite the original numbers in scientific notation first.

b. Evaluate 333,999,500,000 ÷ 0.00000000003396 and express the answer in scientific notation. You may need to rewrite the original numbers in scientific notation first.

c. Express the number 6.022×10^{23} in standard notation.

d. Express the number 6.626×10^{-34} in standard notation.

e. When powers of 10 are multiplied together, the powers are added together. For example, $10^2 \times 10^3 = 10^{2+3} = 10^5$. With this in mind, can you evaluate $(4.506 \times 10^4) \times (1.003 \times 10^2)$ without entering scientific notation into your calculator?

f. When powers of 10 are divided into each other, the bottom exponent is subtracted from the top exponent. For example, $10^5/10^3 = 10^{5-3} = 10^2$. With this in mind, can you evaluate $(8.552 \times 10^6) \div (3.129 \times 10^3)$ without entering scientific notation into your calculator?

g. Consider the quantity two dozen eggs. Is the number in this quantity "two" or "two dozen"? Justify your choice.

h. Consider the quantity two dozen eggs. Is the unit in this quantity "eggs" or "dozen eggs"? Justify your choice.

i. Fill in the blank: 1 km = _______________ μm.

j. Fill in the blank: 1 Ms = _______________ ns.

k. Fill in the blank: 1 cL = _______________ ML.

l. Fill in the blank: 1 mg = _______________ kg.

m. Express 67.3 km/h in meters/second.

n. Express 0.00444 m/s in kilometers/hour.

o. Using the idea that 1.602 km = 1.000 mi, convert a speed of 60.0 mi/h into kilometers/hour.

p. Using the idea that 1.602 km = 1.000 mi, convert a speed of 60.0 km/h into miles/hour.

q. Convert 52.09 km/h into meters/second.

r. Convert 2.155 m/s into kilometers/hour.

s. Use the formulas for converting degrees Fahrenheit into degrees Celsius to determine the relative size of the Fahrenheit degree over the Celsius degree.

t. Use the formulas for converting degrees Celsius into kelvins to determine the relative size of the Celsius degree over kelvins.

u. What is the mass of 12.67 L of mercury?

v. What is the mass of 0.663 m^3 of air?

w. What is the volume of 2.884 kg of gold?

x. What is the volume of 40.99 kg of cork? Assume a density of 0.22 g/cm^3.

a. 3.42×10^{-18}
b.
c. 602,200,000,000,000,000,000,000
d.
e. 4.520×10^{6}
f.
g. The quantity is two; dozen is the unit.
h.
i. 1,000,000,000
j.
k. 1/100,000,000
l.
m. 18.7 m/s
n.
o. 96.1 km/h
p.
q. 14.47 m/s
r.
s. One Fahrenheit degree is nine-fifths the size of a Celsius degree.
t.
u. 1.72×10^{5} g
v.
w. 149 mL

CHAPTER OVERVIEW

2: Atomic Structure

2.1: The Scientific Method

Learning Objectives

- To identify the components of the scientific method

Scientists search for answers to questions and solutions to problems by using a procedure called the **scientific method**. This procedure consists of making observations, formulating hypotheses, and designing experiments, which in turn lead to additional observations, hypotheses, and experiments in repeated cycles (Figure $2.1.1$).

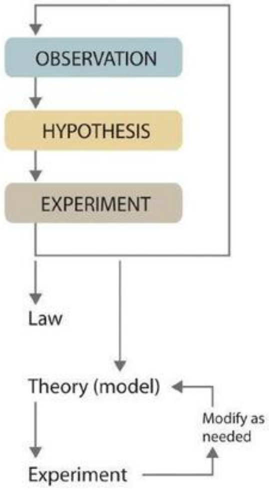


Figure $2.1.1$: The Scientific Method. As depicted in this flowchart, the scientific method consists of making observations, formulating hypotheses, and designing experiments. A scientist may enter the cycle at any point.

Observations can be qualitative or quantitative. Qualitative observations describe properties or occurrences in ways that do not rely on numbers. Examples of qualitative observations include the following: the outside air temperature is cooler during the winter season, table salt is a crystalline solid, sulfur crystals are yellow, and dissolving a penny in dilute nitric acid forms a blue solution and a brown gas. Quantitative observations are measurements, which by definition consist of both a number and a unit. Examples of quantitative observations include the following: the melting point of crystalline sulfur is 115.21 °C, and 35.9 grams of table salt —whose chemical name is sodium chloride—dissolve in 100 grams of water at 20 °C. An example of a quantitative observation was the initial observation leading to the modern theory of the dinosaurs' extinction: iridium concentrations in sediments dating to 66 million years ago were found to be 20–160 times higher than normal. The development of this theory is a good exemplar of the scientific method in action (see Figure $2.1.2$ below).

After deciding to learn more about an observation or a set of observations, scientists generally begin an investigation by forming a **hypothesis**, a tentative explanation for the observation(s). The hypothesis may not be correct, but it puts the scientist's understanding of the system being studied into a form that can be tested. For example, the observation that we experience alternating periods of light and darkness corresponding to observed movements of the sun, moon, clouds, and shadows is consistent with either of two hypotheses:

1. Earth rotates on its axis every 24 hours, alternately exposing one side to the sun, or
2. The sun revolves around Earth every 24 hours.

Suitable experiments can be designed to choose between these two alternatives. For the disappearance of the dinosaurs, the hypothesis was that the impact of a large extraterrestrial object caused their extinction. Unfortunately (or perhaps fortunately), this hypothesis does not lend itself to direct testing by any obvious experiment, but scientists collected additional data that either support or refute it.

After a hypothesis has been formed, scientists conduct experiments to test its validity. **Experiments** are systematic observations or measurements, preferably made under controlled conditions—that is, under conditions in which a single variable changes. For example, in the dinosaur extinction scenario, iridium concentrations were measured worldwide and compared. A properly designed and executed experiment enables a scientist to determine whether the original hypothesis is valid. Experiments often demonstrate that the hypothesis is incorrect or that it must be modified. More experimental data are then collected and analyzed, at which point a scientist may begin to think that the results are sufficiently reproducible (i.e., dependable) to merit being summarized in a **law**, a verbal or mathematical description of a phenomenon that allows for general predictions. A law simply says what happens; it does not address the question of why.

One example of a law, the Law of Definite Proportions, which was discovered by the French scientist Joseph Proust (1754–1826), states that a chemical substance always contains the same proportions of elements by mass. Thus sodium chloride (table salt) always contains the same proportion by mass of sodium to chlorine, in this case 39.34% sodium and 60.66% chlorine by mass, and sucrose (table sugar) is always 42.11% carbon, 6.48% hydrogen, and 51.41% oxygen by mass. Some solid compounds do not strictly obey the law of definite proportions. The law of definite proportions should seem obvious—we would expect the composition of sodium chloride to be consistent—but the head of the US Patent Office did not accept it as a fact until the early 20th century.

Whereas a law states only what happens, a **theory** attempts to explain why nature behaves as it does. Laws are unlikely to change greatly over time unless a major experimental error is discovered. In contrast, a theory, by definition, is incomplete and imperfect, evolving with time to explain new facts as they are discovered. The theory developed to explain the extinction of the dinosaurs, for example, is that Earth occasionally encounters small- to medium-sized asteroids, and these encounters may have unfortunate implications for the continued existence of most species. This theory is by no means proven, but it is consistent with the bulk of evidence amassed to date. Figure 2.1.2 summarizes the application of the scientific method in this case.

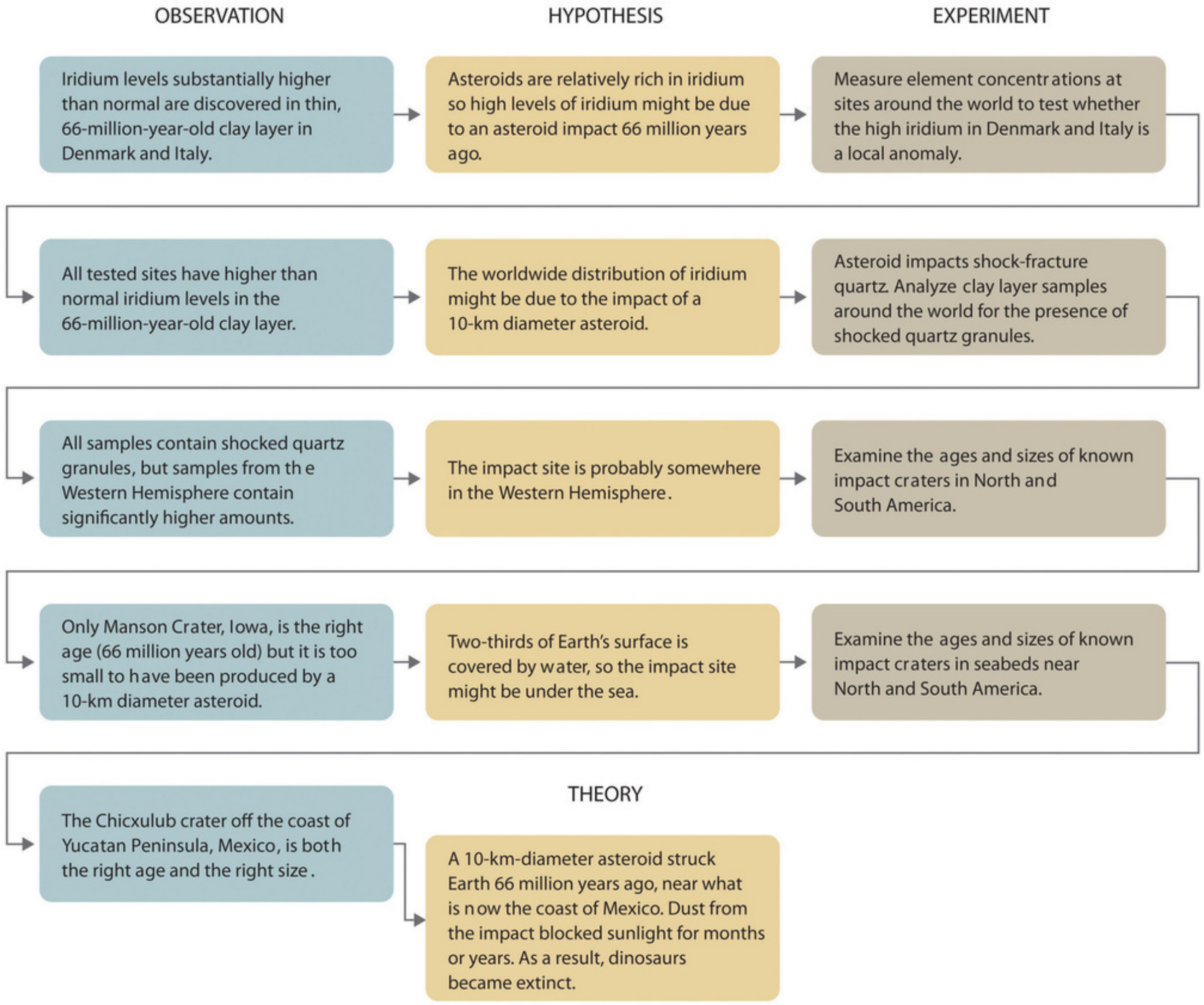


Figure 2.1.2: A Summary of How the Scientific Method Was Used in Developing the Asteroid Impact Theory to Explain the Disappearance of the Dinosaurs from Earth

✓ Example 2.1.1

Classify each statement as a law, a theory, an experiment, a hypothesis, a qualitative observation, or a quantitative observation.

a. Ice always floats on liquid water.
b. Birds evolved from dinosaurs.
c. Hot air is less dense than cold air, probably because the components of hot air are moving more rapidly.
d. When 10 g of ice were added to 100 mL of water at 25 °C, the temperature of the water decreased to 15.5 °C after the ice melted.
e. The ingredients of Ivory soap were analyzed to see whether it really is 99.44% pure, as advertised.

Given: components of the scientific method

Asked for: statement classification

Strategy: Refer to the definitions in this section to determine which category best describes each statement.

Solution

a. This is a general statement of a relationship between the properties of liquid and solid water, so it is a law.
b. This is a possible explanation for the origin of birds, so it is a hypothesis.
c. This is a statement that tries to explain the relationship between the temperature and the density of air based on fundamental principles, so it is a theory.
d. The temperature is measured before and after a change is made in a system, so these are quantitative observations.
e. This is an analysis designed to test a hypothesis (in this case, the manufacturer's claim of purity), so it is an experiment.

? Exercise 2.1.1

Classify each statement as a law, a theory, an experiment, a hypothesis, a qualitative observation, or a quantitative observation.

a. Measured amounts of acid were added to a Rolaids tablet to see whether it really "consumes 47 times its weight in excess stomach acid."
b. Heat always flows from hot objects to cooler ones, not in the opposite direction.
c. The universe was formed by a massive explosion that propelled matter into a vacuum.
d. Michael Jordan is the greatest pure shooter ever to play professional basketball.
e. Limestone is relatively insoluble in water but dissolves readily in dilute acid with the evolution of a gas.
f. Gas mixtures that contain more than 4% hydrogen in air are potentially explosive.

Answer a

experiment

Answer b

law

Answer c

theory

Answer d

hypothesis

Answer e

qualitative observation

Answer f

quantitative observation

Because scientists can enter the cycle shown in Figure 2.1.1 at any point, the actual application of the scientific method to different topics can take many different forms. For example, a scientist may start with a hypothesis formed by reading about work done by others in the field, rather than by making direct observations.

It is important to remember that scientists have a tendency to formulate hypotheses in familiar terms simply because it is difficult to propose something that has never been encountered or imagined before. As a result, scientists sometimes discount or overlook unexpected findings that disagree with the basic assumptions behind the hypothesis or theory being tested. Fortunately, truly important findings are immediately subject to independent verification by scientists in other laboratories, so science is a self-correcting discipline. When the Alvarezes originally suggested that an extraterrestrial impact caused the extinction of the dinosaurs, the response was almost universal skepticism and scorn. In only 20 years, however, the persuasive nature of the evidence overcame the skepticism of many scientists, and their initial hypothesis has now evolved into a theory that has revolutionized paleontology and geology.

Summary

Chemists expand their knowledge by making observations, carrying out experiments, and testing hypotheses to develop laws to summarize their results and theories to explain them. In doing so, they are using the scientific method.

Fundamental Definitions in Chemistry: https://youtu.be/SBwjbkFNkdw

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2.2: Indivisible - The Atomic Theory

Learning Objectives

- Give a short history of the concept of the atom.
- Describe the contributions of Democritus and Dalton to atomic theory.
- Summarize Dalton's atomic theory and explain its historical development.

About 2,500 years ago, early Greek philosophers believed the entire universe was a single, huge, entity. In other words, "everything was one." 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.

Figure 2.2.1: (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.

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." It's truly amazing how much they achieved using their minds, but because they never performed any experiments, they missed or rejected a lot of discoveries that they could have made otherwise. 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.

Greeks: "All Thought and No Action"

Greek philosophers were "all thought and no action" and did not feel the need to test their theories with reality. In contrast, Dalton's efforts were based on experimentation and testing ideas against reality.

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.

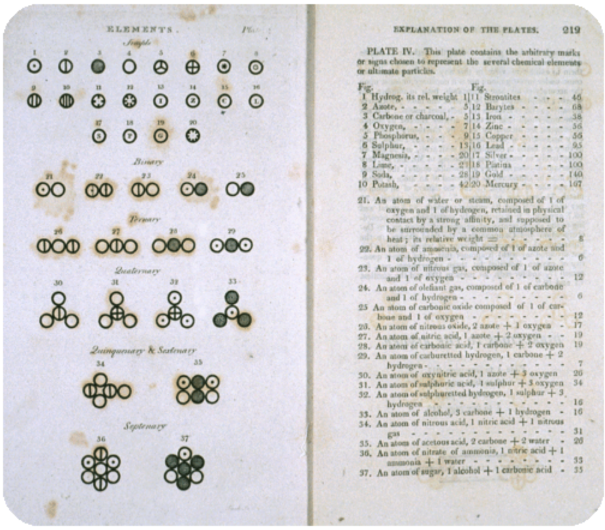
The modern atomic theory, proposed about 1803 by the English chemist John Dalton (Figure 2.2.1), is a fundamental concept that states that all elements are composed of atoms. Previously, we defined an atom as the smallest part of an element that maintains the identity of that element. Individual atoms are extremely small; even the largest atom has an approximate diameter of only 5.4×10^{-10} m. With that size, it takes over 18 million of these atoms, lined up side by side, to equal the width of your little finger (about 1 cm).

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.

From his experiments and observations, as well as the work from peers of his time, Dalton proposed a new theory of the **atom**. This later became known as Dalton's **atomic theory**. The general tenets of this 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.



EXPLANATION OF THE PLATES. 219

PLATE IV. This plate contains the arbitrary marks or signs chosen to represent the several chemical elements or ultimate particles.

Fig.			Fig.		
1	Hydrog. its rel. weight	1	11	Strontites - - - -	46
2	Azote, - - - - - -	5	12	Barytes - - - - -	68
3	Carbone or charcoal, -	5	13	Iron - - - - - -	38
4	Oxygen, - - - - -	7	14	Zinc - - - - - -	56
5	Phosphorus, - - - -	9	15	Copper - - - - -	56
6	Sulphur, - - - - -	13	16	Lead - - - - - -	95
7	Magnesia, - - - - -	20	17	Silver - - - - - -	100
8	Lime, - - - - - -	23	18	Platina - - - - -	100
9	Soda, - - - - - -	28	19	Gold - - - - - -	140
10	Potash, - - - - -	42	20	Mercury - - - - -	167

21. An atom of water or steam, composed of 1 of oxygen and 1 of hydrogen, retained in physical contact by a strong affinity, and supposed to be surrounded by a common atmosphere of heat; its relative weight = - - - - - - 8
22. An atom of ammonia, composed of 1 of azote and 1 of hydrogen - - - - - - - - - - - - 6
23. An atom of nitrous gas, composed of 1 of azote and 1 of oxygen - - - - - - - - - - - 12
24. An atom of olefiant gas, composed of 1 of carbone and 1 of hydrogen - - - - - - - - - - 6
25 An atom of carbonic oxide composed of 1 of carbone and 1 of oxygen - - - - - - - - - - 12
26. An atom of nitrous oxide, 2 azote + 1 oxygen - 17
27. An atom of nitric acid, 1 azote + 2 oxygen - - 19
28. An atom of carbonic acid, 1 carbone + 2 oxygen 19
29. An atom of carburetted hydrogen, 1 carbone + 2 hydrogen - - - - - - - - - - - - - 7
30. An atom of oxynitric acid, 1 azote + 3 oxygen 26
31. An atom of sulphuric acid, 1 sulphur + 3 oxygen 34
32. An atom of sulphuretted hydrogen, 1 sulphur + 3 hydrogen - - - - - - - - - - - - - 16
33. An atom of alcohol, 3 carbone + 1 hydrogen - 16
34. An atom of nitrous acid, 1 nitric acid + 1 nitrous gas - - - - - - - - - - - - - - 31
35. An atom of acetous acid, 2 carbone + 2 water - 26
36. An atom of nitrate of ammonia, 1 nitric acid + 1 ammonia + 1 water - - - - - - - - - 33
37. An atom of sugar, 1 alcohol + 1 carbonic acid - 35

Figure 2.2.2: Dalton's symbols from his text "A New System of Chemical Philosophy."

The evidence for atoms is so great that few doubt their existence. In fact, individual atoms are now routinely observed with state-of-the art technologies. Moreover, they can even be used for making pretty images; or as IBM research demonstrates in Video 2.2.1, control of individual atoms can be use used create animations.

Video 2.2.1: A Boy And His Atom: The World's Smallest Movie.

A Boy and His Atom is a 2012 stop-motion animated short film released by IBM Research. The movie tells the story of a boy and a wayward atom who meet and become friends. It depicts a boy playing with an atom that takes various forms. It was made by moving carbon monoxide molecules viewed with a scanning tunneling microscope, a device that magnifies them 100 million times. These molecules were moved to create images, which were then saved as individual frames to make the film.

Summary

- 2,500 years ago, Democritus suggested that all matter in the universe was made up of tiny, indivisible, solid objects he called "atomos." However, other Greek philosophers disliked Democritus' "atomos" theory because they felt it was illogical.
- Dalton's Atomic Theory is the first scientific theory to relate chemical changes to the structure, properties, and behavior of the atom. The general tenets of this theory are:
  - 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.

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2.3: The Properties of Protons, Neutrons, and Electrons

Learning Objectives

- Describe the locations, charges, and masses of the three main subatomic particles.
- Determine the number of protons and electrons in an atom.
- Define atomic mass unit (amu).

Dalton's Atomic Theory explained a lot about matter, chemicals, and chemical reactions. Nevertheless, it was not entirely accurate, because contrary to what Dalton believed, atoms can, in fact, be broken apart into smaller subunits or subatomic particles. These subatomic particles which are important to understand in chemistry applications are the electron, neutron, and proton. We will discuss the properties of these particles in this section. To know more about the discovery of these particles, you may look here.

Electrons

Electrons are one of three main types of particles that make up atoms. Unlike protons and neutrons, which consist of smaller, simpler particles, electrons are fundamental particles that do not consist of smaller particles. They are a type of fundamental particle called leptons. All leptons have an electric charge of -1 or 0. 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. The figure below is a common way to represent the structure of an atom. It shows the electron as a particle orbiting the nucleus, similar to the way that planets orbit the sun. However, this is an incorrect perspective, as quantum mechanics demonstrates that electrons are more complicated.

Figure 2.3.1: Electrons are much smaller than protons or neutrons. If an electron was the mass of a penny, a proton or a neutron would have the mass of a large bowling ball!

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 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. Unlike protons and electrons, which are electrically charged, neutrons have no charge—they are electrically neutral. That's why the neutrons in the diagram above are labeled n^0. The zero stands for "zero charge". The mass of a neutron is slightly greater than the mass of a proton, which is 1 atomic mass unit (amu). (An atomic mass unit equals about 1.67×10^{-27} kilograms.) A neutron also has about the same diameter as a proton, or 1.7×10^{-15} meters.

As you might have already guessed from its name, the neutron is neutral. In other words, it has no charge whatsoever and is therefore neither attracted to nor repelled from other objects. Neutrons are in every atom (with one exception), and they are bound together with other neutrons and protons in the atomic nucleus.

Before we move on, we must discuss how the different types of subatomic particles interact with each other. When it comes to neutrons, the answer is obvious. Since neutrons are neither attracted to nor repelled from objects, they don't really interact with protons or electrons (beyond being bound into the nucleus with the protons).

Even though electrons, protons, and neutrons are all types of subatomic particles, they are not all the same size. When you compare the masses of electrons, protons, and neutrons, what you find is that electrons have an extremely small mass, compared to either protons or neutrons. On the other hand, the masses of protons and neutrons are fairly similar, although technically, the mass of a neutron is slightly larger than the mass of a proton. Because protons and neutrons are so much more massive than electrons, almost all of the mass of any atom comes from the nucleus, which contains all of the neutrons and protons.

Table 2.3.1: Properties of Subatomic Particles

Particle	Symbol	Mass (amu)	Relative Mass (proton = 1)	Relative Charge	Location
proton	p^+	1	1	+1	inside the nucleus
electron	e^-	5.45×10^{-4}	0.00055	−1	outside the nucleus
neutron	n^0	1	1	0	inside the nucleus

Table 2.3.1 gives the properties and locations of electrons, protons, and neutrons. The third column shows the masses of the three subatomic particles in "atomic mass units." An **atomic mass unit (amu)** is defined as one-twelfth of the mass of a carbon-12 atom. Atomic mass units (amu) are useful, because, as you can see, the mass of a proton and the mass of a neutron are almost exactly 1 in this unit system.

Negative and positive charges of equal magnitude cancel each other out. This means that the negative charge on an electron perfectly balances the positive charge on the proton. In other words, a neutral atom must have exactly one electron for every proton. If a neutral atom has 1 proton, it must have 1 electron. If a neutral atom has 2 protons, it must have 2 electrons. If a neutral atom has 10 protons, it must have 10 electrons. You get the idea. In order to be neutral, an atom must have the same number of electrons and protons.

Summary

- Electrons are a type of subatomic particle with a negative charge.
- Protons are a type of subatomic particle with a positive charge. Protons are bound together in an atom's nucleus as a result of the strong nuclear force.
- Neutrons are a type of subatomic particle with no charge (they are neutral). Like protons, neutrons are bound into the atom's nucleus as a result of the strong nuclear force.
- Protons and neutrons have approximately the same mass, but they are both much more massive than electrons (approximately 2,000 times as massive as an electron).
- The positive charge on a proton is equal in magnitude to the negative charge on an electron. As a result, a neutral atom must have an equal number of protons and electrons.
- The atomic mass unit (amu) is a unit of mass equal to one-twelfth the mass of a carbon-12 atom

Contributions & Attributions

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2.4: Keeping Track of Subatomic Particles

Learning Objectives

- Define atomic number.
- Define mass number.
- Determine the number of protons, neutrons, and electrons in an atom.

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 be 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 2.4.1: 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

Scientists distinguish between different elements by counting the number of protons in the nucleus (Table 2.4.1). If an atom has only one proton, we know that it's a hydrogen atom. An atom with two protons is always a helium atom. If scientists count four protons in an atom, they know it's a beryllium atom. An atom with three protons is a lithium atom, an atom with five protons is a boron atom, an atom with six protons is a carbon atom . . . the list goes on.

Since 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. For example, all helium atoms have two protons, and no other elements have atoms with two protons.

Table 2.4.1: Atoms of the First Six Elements

Name	Protons	Neutrons	Electrons	Atomic Number (Z)	Mass Number (A)
Hydrogen	1	0	1	1	1
Helium	2	2	2	2	4
Lithium	3	4	3	3	7
Beryllium	4	5	4	4	9
Boron	5	6	5	5	11
Carbon	6	6	6	6	12

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.

Neutral Atoms

Atoms are neutral in electrical charge because they have the same number of negative electrons as positive protons (Table $2.4.1$). Therefore, the atomic number of an atom also tells you how many electrons the atom has. This, in turn, determines many of the atom's chemical properties.

Mass Number

The **mass number** (A) of an atom is the total number of protons and neutrons in its nucleus. The mass of the atom is a unit called the atomic mass unit (amu). One atomic mass unit is the mass of a proton, or about 1.67×10^{-27} kilograms, which is an extremely small mass. A neutron has just a tiny bit more mass than a proton, but its mass is often assumed to be one atomic mass unit as well. Because electrons have virtually no mass, just about all the mass of an atom is in its protons and neutrons. Therefore, the total number of protons and neutrons in an atom determines its mass in atomic mass units (Table $2.4.1$).

Consider helium again. Most helium atoms have two neutrons in addition to two protons. Therefore the mass of most helium atoms is 4 atomic mass units ($2\ \mathrm{amu}$ for the protons + $2\ \mathrm{amu}$ for the neutrons). 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, some helium atoms have three neutrons instead of two (these are called isotopes and are discussed in detail later on).

Why do you think that the "mass number" includes protons and neutrons, but not electrons? You know that most of the mass of an atom is concentrated in its nucleus. The mass of an atom depends on the number of protons and neutrons. You have already learned that the mass of an electron is very, very small compared to the mass of either a proton or a neutron (like the mass of a penny compared to the mass of a bowling ball). Counting the number of protons and neutrons tells scientists about the total mass of an atom.

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

An atom's mass number is very easy to calculate, provided that you know the number of protons and neutrons in an atom.

✓ Example 4.5.1

What is the mass number of an atom of helium that contains 2 neutrons?

Solution

$(\text{number of protons})=2$ (Remember that an atom of helium always has 2 protons.)

$(\text{number of neutrons})=2$

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

$$\text{mass number}=\mathbf{2+2=4}$$

A **chemical symbol** is a one- or two-letter designation of an element. Some examples of chemical symbols are O for oxygen, Zn for zinc, and Fe for iron. The first letter of a symbol is always capitalized. If the symbol contains two letters, the second letter is lower case. The majority of elements have symbols that are based on their English names. However, some of the elements that have been known since ancient times have maintained symbols that are based on their Latin names, as shown in Table $2.4.2$.

Table $2.4.2$: *Symbols and Latin Names for Elements*

Chemical Symbol	Name	Latin Name
Na	Sodium	Natrium
K	Potassium	Kalium
Fe	Iron	Ferrum
Cu	Copper	Cuprum
Ag	Silver	Argentum
Sn	Tin	Stannum

Chemical Symbol	Name	Latin Name
Sb	Antimony	Stibium
Au	Gold	Aurum
Pb	Lead	Plumbum

Summary

- Elements are pure substances that make up all matter, so each one is given a unique name.
- The names of elements are also represented by unique one- or two-letter symbols.
- Each element has a unique number of protons. An element's atomic number is equal to the number of protons in the nuclei of any of its atoms.
- The mass number of an atom is the sum of the protons and neutrons in the atom.
- Isotopes are atoms of the same element (same number of protons) that have different numbers of neutrons in their atomic nuclei.

2.5: Looking for Patterns - The Periodic Table

Learning Objectives

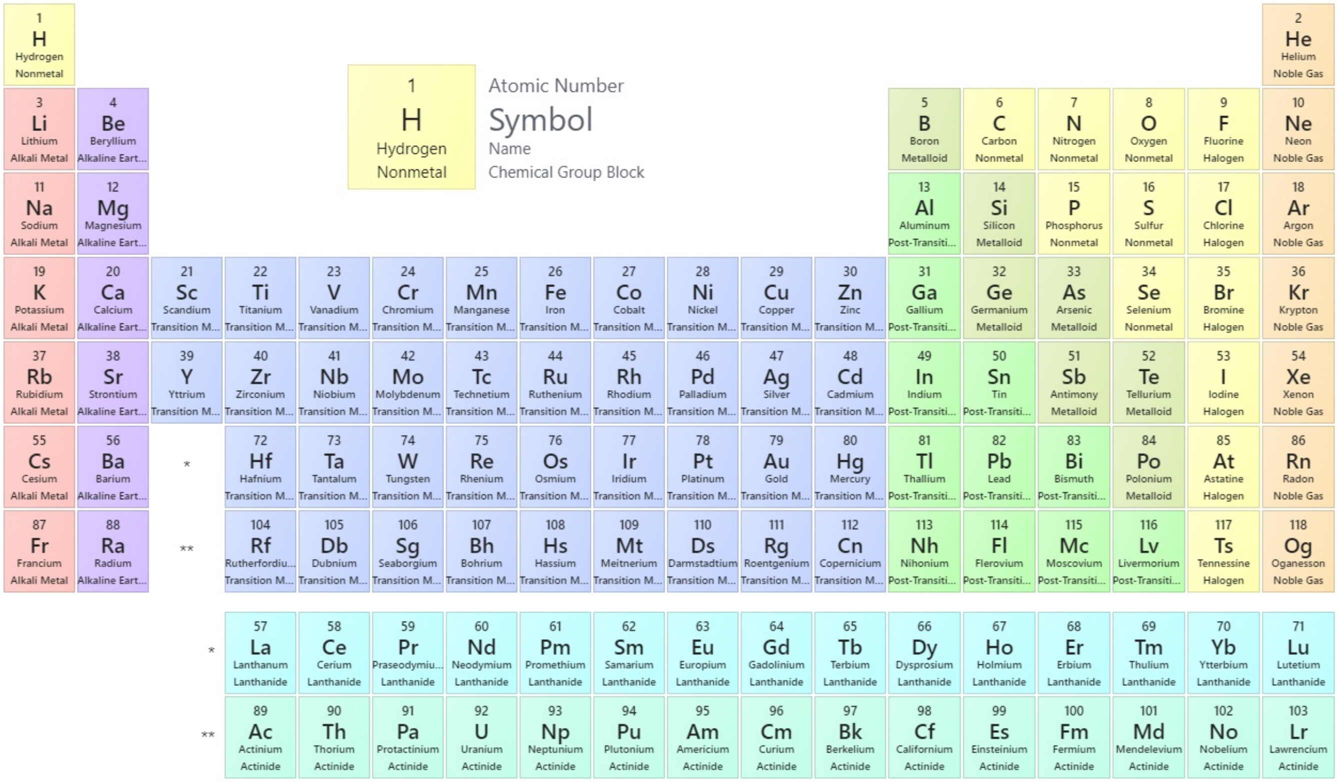
- Explain how elements are organized into the periodic table.
- Describe how some characteristics of elements relate to their positions on the periodic table.

In the 19th century, many previously unknown elements were discovered, and scientists noted that certain sets of elements had similar chemical properties. For example, chlorine, bromine, and iodine react with other elements (such as sodium) to make similar compounds. Likewise, lithium, sodium, and potassium react with other elements (such as oxygen) to make similar compounds. Why is this so?

In 1864, Julius Lothar Meyer, a German chemist, organized the elements by atomic mass and grouped them according to their chemical properties. Later that decade, Dmitri Mendeleev, a Russian chemist, organized all the known elements according to similar properties. He left gaps in his table for what he thought were undiscovered elements, and he made some bold predictions regarding the properties of those undiscovered elements. When elements were later discovered whose properties closely matched Mendeleev's predictions, his version of the table gained favor in the scientific community. Because certain properties of the elements repeat on a regular basis throughout the table (that is, they are periodic), it became known as the periodic table.

> *Mendeleev had to list some elements out of the order of their atomic masses to group them with other elements that had similar properties.*

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 2.5.1. Most periodic tables provide additional data (such as atomic mass) in a box that contains each element's symbol. 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 2.5.1: A Modern Periodic Table. A modern periodic table lists elements left to right by atomic number. An interactive Periodic table can be found Periodic Table of Elements. (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).

> *The word halogen comes from the Greek for "salt maker" because these elements combine with other elements to form a group of compounds called salts.*

To Your Health: Radon

Radon is an invisible, odorless noble gas that is slowly released from the ground, particularly from rocks and soils whose uranium content is high. Because it is a noble gas, radon is not chemically reactive. Unfortunately, it is radioactive, and increased exposure to it has been correlated with an increased lung cancer risk.

Because radon comes from the ground, we cannot avoid it entirely. Moreover, because it is denser than air, radon tends to accumulate in basements, which if improperly ventilated can be hazardous to a building's inhabitants. Fortunately, specialized ventilation minimizes the amount of radon that might collect. Special fan-and-vent systems are available that draw air from below the basement floor, before it can enter the living space, and vent it above the roof of a house.

After smoking, radon is thought to be the second-biggest *preventable* cause of lung cancer in the United States. The American Cancer Society estimates that 10% of all lung cancers are related to radon exposure. There is uncertainty regarding what levels of exposure cause cancer, as well as what the exact causal agent might be (either radon or one of its breakdown products, many of which are also radioactive and, unlike radon, not gases). The US Environmental Protection Agency recommends testing every floor below the third floor for radon levels to guard against long-term health effects.

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 $2.5.2$. 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 $2.5.2$, 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.

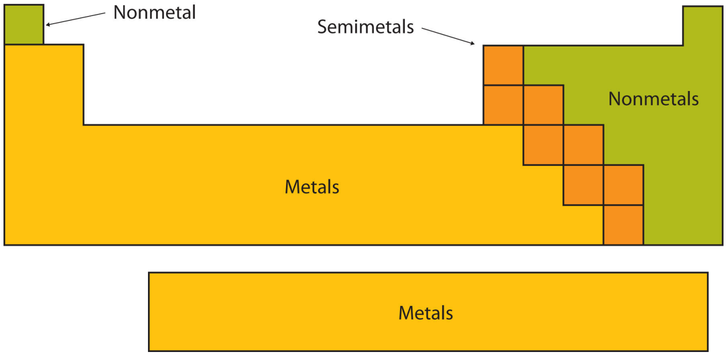


Figure $2.5.2$: Types of Elements. Elements are either metals, nonmetals, or metalloids (or semi metals). Each group is located in a different part of the periodic table. (CC BY-NC-SA; Anonymous by request)

Example $2.5.1$

Based on its position in the periodic table, classify each element below as metal, a nonmetal, or a metalloid.

a. Se

b. Mg
c. Ge

Solution

a. In Figure $2.5.1$, selenium lies above and to the right of the diagonal line marking the boundary between metals and nonmetals, so it should be a nonmetal.
b. Magnesium lies to the left of the diagonal line marking the boundary between metals and nonmetals, so it should be a metal.
c. Germanium lies within the diagonal line marking the boundary between metals and nonmetals, so it should be a metalloid.

? Exercise $2.5.1$

Based on its location in the periodic table, do you expect indium to be a nonmetal, a metal, or a metalloid?

Answer

Indium is a metal.

Another way to categorize the elements of the periodic table is shown in Figure $2.5.3$. The first two columns on the left and the last six columns on the right are called the main group elements. The ten-column block between these columns contains the **transition metals**. The two rows beneath the main body of the periodic table contain the **inner transition metals**. The elements in these two rows are also referred to as, respectively, the **lanthanide metals** and the **actinide metals**.

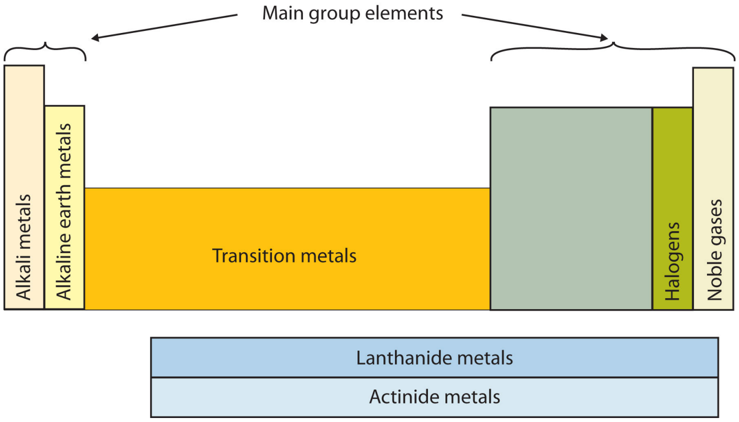


Figure $2.5.3$: Special Names for Sections of the Periodic Table. (CC BY-NC-SA; Anonymous by request)

Sections of period table: Alkali metals, alkaline earth metals, transition metals, halogens, noble gases, lanthanide metals, actinide metals.

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.

✓ Example $2.5.2$: Groups

Provide the family or group name of each element.

a. Li
b. Ar
c. Cl

Solution

a. Lithium is an alkali metal (Group 1)
b. Argon is a noble gas (Group 18)
c. Chlorine is a halogen (Group 17)

? Exercise 2.5.2: Groups

Provide the family or group name of each element.

a. F
b. Ca
c. Kr

Answer a:

Fluorine is a halogen (Group 17).

Answer b:

Calcium is a alkaline earth metal (Group 2).

Answer c:

Krypton is a noble gas (Group 18).

✓ Example 2.5.3: Classification of Elements

Classify each element as metal, non metal, transition metal or inner transition metal.

a. Li
b. Ar
c. Am
d. Fe

Solution

a. Lithium is a metal.
b. Argon is a non metal.
c. Americium is an inner transition metal.
d. Iron is a transition metal.

? Exercise 2.5.3: Classification of Elements

Classify each element as metal, non metal, transition metal or inner transition metal.

a. F
b. U
c. Cu

Answer a:

Fluorine is a nonmetal.

Answer b:

Uranium is a metal (and a inner transition metal too).

Answer c:

Copper is a metal (and a transition metal too).

Summary

The periodic table is an arrangement of the elements in order of increasing atomic number. Elements that exhibit similar chemistry appear in vertical columns called groups (numbered 1–18 from left to right); the seven horizontal rows are called periods. Some of the groups have widely-used common names, including the alkali metals (Group 1) and the alkaline earth metals (Group 2) on the far left, and the halogens (Group 17) and the noble gases (Group 18) on the far right.

The elements can be broadly divided into metals, nonmetals, and semi metals. Semi metals exhibit properties intermediate between those of metals and nonmetals. Metals are located on the left of the periodic table, and nonmetals are located on the upper right. They are separated by a diagonal band of semi metals. Metals are lustrous, good conductors of electricity, and readily shaped (they are ductile and malleable). Solid nonmetals are generally brittle and poor electrical conductors. Other important groupings of elements in the periodic table are the main group elements, the transition metals, and the inner transition metals (the lanthanides, and the actinides).

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2.6: Ions - Losing and Gaining Electrons

Learning Objectives

- Define the two types of ions.

Atoms can gain or lose electrons to become ions. When an atom loses an electron it gains a positive charge and is called a cation. When an atom gains an electron it gains a negative charge and is called an anion. The reasons for gaining and losing electrons involve ideas about electron behavior that we will cover in greater detail in a later chapter. Some of the graphics in this section involve the concept of an electron shell. You do not need to understand this concept now, but hopefully the graphics will help with understanding how gaining or losing electrons result in ions with positive or negative charges.

Cations

A neutral sodium atom is likely to achieve an octet in its outermost shell by losing one electron.

$$\mathrm{Na} \rightarrow \mathrm{Na}^{+} + \mathrm{e}^{-} \tag{2.6.1}$$

The cation produced in this way, Na^+, is called the sodium ion to distinguish it from the element. Figure 2.6.1 is a graphical depiction of this process.

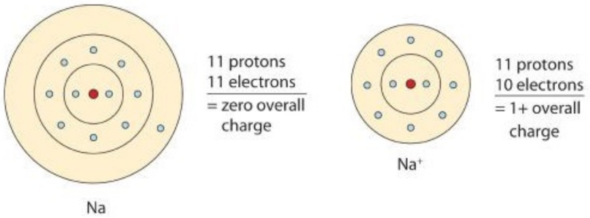

Figure 2.6.1: The Formation of a Sodium Ion. On the left, a sodium atom has 11 electrons. On the right, the sodium ion only has 10 electrons and a 1+ charge.

Anions

Some atoms can gain additional electrons. When these atoms gain electrons, they acquire a negative charge because they now possess more electrons than protons. Negatively charged ions are called **anions**. Most nonmetals become anions when they make ionic compounds.

$$\mathrm{e}^{-} + \mathrm{Cl} \longrightarrow \mathrm{Cl}^{-} \tag{2.6.2}$$

Figure 2.6.2 is a graphical depiction of this process.

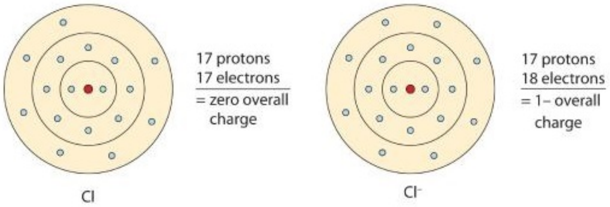

Figure 2.6.2: The Formation of a Chlorine Ion. On the left, the chlorine atom has 17 electrons. On the right, the chloride ion has 18 electrons and has a 1− charge.

> *The names for positive and negative ions are pronounced CAT-eye-ons and ANN-eye-ons, respectively.*

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2.7: Isotopes - When the Number of Neutrons Varies

Learning Objectives

- Explain what isotopes are and how an isotope affects an element's atomic mass.
- Determine the number of protons, electrons, and neutrons of an element with a given mass number.

All atoms of the same element have the same number of protons, but some may have different numbers of neutrons. For example, all carbon atoms have six protons, and most have six neutrons as well. But some carbon atoms have seven or eight neutrons instead of the usual six. Atoms of the same element that differ in their numbers of neutrons are called **isotopes**. Many isotopes occur naturally. Usually one or two isotopes of an element are the most stable and common. Different isotopes of an element generally have the same physical and chemical properties because they have the same numbers of protons and electrons.

An Example: Hydrogen Isotopes

Hydrogen is an example of an element that has isotopes. Three isotopes of hydrogen are modeled in Figure $2.7.1$. 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.

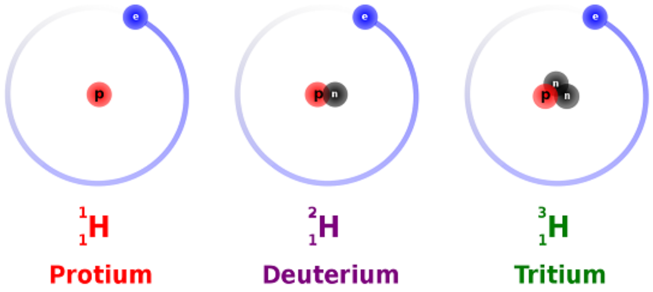


Figure $2.7.1$: The three most stable isotopes of hydrogen: protium (A = 1), deuterium (A = 2), and tritium (A = 3). (CC SA-BY 3.0; Balajijagadesh via Wikipedia).

For most elements other than hydrogen, isotopes are named for their mass number. For example, carbon atoms with the usual 6 neutrons have a mass number of 12 (6 protons + 6 neutrons = 12), so they are called carbon-12. Carbon atoms with 7 neutrons have an atomic mass of 13 (6 protons + 7 neutrons = 13). These atoms are the isotope called carbon-13.

Example 2.7.1: Lithium Isotopes

a. What is the atomic number and the mass number of an isotope of lithium containing 3 neutrons?
b. What is the atomic number and the mass number of an isotope of lithium containing 4 neutrons?

Solution

A lithium atom contains 3 protons in its nucleus irrespective of the number of neutrons or electrons.

a.

$$\begin{aligned} \text{atomic number} = (\text{number of protons}) &= 3 \\ (\text{number of neutrons}) &= 3 \end{aligned}$$

$$\begin{aligned} \text{mass number} &= (\text{number of protons}) + (\text{number of neutrons}) \\ \text{mass number} &= 3 + 3 \\ &= 6 \end{aligned}$$

b.

$$\begin{aligned} \text{atomic number} = (\text{number of protons}) &= 3 \\ (\text{number of neutrons}) &= 4 \end{aligned}$$

$$\begin{aligned}\text{mass number } &= (\text{number of protons}) + (\text{number of neutrons}) \\ \text{mass number } &= 3+4 \\ &= 7\end{aligned}$$

Notice that because the lithium atom always has 3 protons, the atomic number for lithium is always 3. The mass number, however, is 6 in the isotope with 3 neutrons, and 7 in the isotope with 4 neutrons. In nature, only certain isotopes exist. For instance, lithium exists as an isotope with 3 neutrons, and as an isotope with 4 neutrons, but it doesn't exist as an isotope with 2 neutrons or as an isotope with 5 neutrons.

Stability of Isotopes

Atoms need a certain ratio of neutrons to protons to have a stable nucleus. 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.

This whole discussion of isotopes brings us back to Dalton's Atomic Theory. According to Dalton, atoms of a given element are identical. But if atoms of a given element can have different numbers of neutrons, then they can have different masses as well! How did Dalton miss this? It turns out that elements found in nature exist as constant uniform mixtures of their naturally occurring isotopes. In other words, a piece of lithium always contains both types of naturally occurring lithium (the type with 3 neutrons and the type with 4 neutrons). Moreover, it always contains the two in the same relative amounts (or "relative abundance"). In a chunk of lithium, 93% will always be lithium with 4 neutrons, while the remaining 7% will always be lithium with 3 neutrons.

Dalton always experimented with large chunks of an element—chunks that contained all of the naturally occurring isotopes of that element. As a result, when he performed his measurements, he was actually observing the averaged properties of all the different isotopes in the sample. For most of our purposes in chemistry, we will do the same thing and deal with the average mass of the atoms. Luckily, aside from having different masses, most other properties of different isotopes are similar.

There are two main ways in which scientists frequently show the mass number of an atom they are interested in. It is important to note that the mass number is *not* given on the periodic table. These two ways include writing a nuclear symbol or by giving the name of the element with the mass number written.

To write a **nuclear symbol**, the mass number is placed at the upper left (superscript) of the chemical symbol and the atomic number is placed at the lower left (subscript) of the symbol. The complete nuclear symbol for helium-4 is drawn below:

Nuclear symbol for helium-4: The element symbol is He, the mass number to the top left is 4, and the atomic number to the bottom left is 2

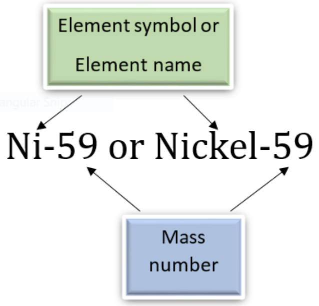
The following nuclear symbols are for a nickel nucleus with 31 neutrons and a uranium nucleus with 146 neutrons.

$$^{59}_{28}\text{Ni}$$

$$^{238}_{92}\text{U}$$

In the nickel nucleus represented above, the atomic number 28 indicates that the nucleus contains 28 protons, and therefore, it must contain 31 neutrons in order to have a mass number of 59. The uranium nucleus has 92 protons, as all uranium nuclei do; and this particular uranium nucleus has 146 neutrons.

Another way of representing isotopes is by adding a hyphen and the mass number to the chemical name or symbol. Thus the two nuclei would be Nickel-59 or Ni-59 and Uranium-238 or U-238, where 59 and 238 are the mass numbers of the two atoms, respectively. Note that the mass numbers (not the number of neutrons) are given to the side of the name.



Example 2.7.2: Potassium-40

How many protons, electrons, and neutrons are in an atom of ${}^{40}_{19}\text{K}$?

Solution

$$\text{atomic number} = (\text{number of protons}) = 19$$

For all atoms with no charge, the number of electrons is equal to the number of protons.

$$\text{number of electrons} = 19$$

The mass number, 40, is the sum of the protons and the neutrons.

To find the number of neutrons, subtract the number of protons from the mass number.

$$\text{number of neutrons} = 40 - 19 = 21.$$

Example 2.7.3: Zinc-65

How many protons, electrons, and neutrons are in an atom of zinc-65?

Solution

$$\text{number of protons} = 30$$

For all atoms with no charge, the number of electrons is equal to the number of protons.

$$\text{number of electrons} = 30$$

The mass number, 65, is the sum of the protons and the neutrons.

To find the number of neutrons, subtract the number of protons from the mass number.

$$\text{number of neutrons} = 65 - 30 = 35$$

Exercise 2.7.3

How many protons, electrons, and neutrons are in each atom?

a. ${}^{60}_{27}\text{Co}$
b. Na-24
c. ${}^{45}_{20}\text{Ca}$
d. Sr-90

Answer a:

27 protons, 27 electrons, 33 neutrons

Answer b:

11 protons, 11 electrons, 13 neutrons

Answer c:

20 protons, 20 electrons, 25 neutrons

Answer d:

38 protons, 38 electrons, 52 neutrons

Summary

- The number of protons is always the same in atoms of the same element.
- The number of neutrons can be different, even in atoms of the same element.
- Atoms of the same element that contain the same number of protons, but different numbers of neutrons, are known as **isotopes**.
- Isotopes of any given element all contain the same number of protons, so they have the same atomic number (for example, the atomic number of helium is always 2).
- Isotopes of a given element contain different numbers of neutrons, therefore, different isotopes have different mass numbers.

2.8: Atomic Mass - The Average Mass of an Element’s Atoms

Learning Objectives

- Explain what is meant by the atomic mass of an element.
- Calculate the atomic mass of an element from the masses and relative percentages of the isotopes of the element.

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 mass of the atoms of an element. The **atomic mass** of an element is the weighted average mass of the atoms in a naturally occurring sample of the element. Atomic mass is typically reported in atomic mass units.

Calculating Atomic Mass

You can calculate the atomic mass (or average mass) of an element provided you know the **relative abundance** (the fraction of an element that is a given isotope), the element's naturally occurring isotopes, and the masses of those different isotopes. We can calculate this by the following equation:

$$\text{Atomic mass} = (\%_1)(\text{mass}_1) + (\%_2)(\text{mass}_2) + \cdots \tag{2.8.1}$$

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

Example 2.8.1: Boron Isotopes

Boron has two naturally occurring isotopes. In a sample of boron, 20% of the atoms are B-10, which is an isotope of boron with 5 neutrons and mass of $10\ \text{amu}$. The other 80% of the atoms are B-11, which is an isotope of boron with 6 neutrons and a mass of $11\ \text{amu}$. What is the atomic mass of boron?

Solution

Boron has two isotopes. We will use the equation:

$$\text{Atomic mass} = (\%_1)(\text{mass}_1) + (\%_2)(\text{mass}_2) + \cdots$$

- Isotope 1: $\%_1 = 0.20$ (Write all percentages as decimals), $\text{mass}_1 = 10$
- Isotope 2: $\%_2 = 0.80$, $\text{mass}_2 = 11$

Substitute these into the equation, and we get:

$$\text{Atomic mass} = (0.20)(10) + (0.80)(11)$$

$$\text{Atomic mass} = 10.8\ \text{amu}$$

The mass of an average boron atom, and thus boron's atomic mass, is $10.8\ \text{amu}$

Example 2.8.2: Neon Isotopes

Neon has three naturally occurring isotopes. In a sample of neon, 90.92% of the atoms are Ne-20, which is an isotope of neon with 10 neutrons and a mass of $19.99\ \text{amu}$ Another 0.3% of the atoms are Ne-21, which is an isotope of neon with 11 neutrons and a mass of $20.99\ \text{amu}$ The final 8.85% of the atoms are Ne-22, which is an isotope of neon with 12 neutrons and a mass of $21.99\ \text{amu}$ What is the atomic mass of neon?

Solution

Neon has three isotopes. We will use the equation:

$$\text{Atomic mass} = (\%_1)(\text{mass}_1) + (\%_2)(\text{mass}_2) + \cdots$$

- Isotope 1: $\%_1 = 0.9092$ (write all percentages as decimals), $\text{mass}_1 = 19.99$

- Isotope 2: $\%_2 = 0.003$, $\text{mass}_2 = 20.99$
- Isotope 3: $\%_3 = 0.0885$, $\text{mass}_3 = 21.99$

Substitute these into the equation, and we get:

$$\text{Atomic mass} = (0.9092)\,(19.99) + (0.003)\,(20.99) + (0.0885)\,(21.99)$$

$$\text{Atomic mass} = 20.17 \text{ amu}$$

The mass of an average neon atom is $\mathbf{20.17}$ amu

The periodic table gives the atomic mass of each element. The atomic mass is a number that usually appears below the element's symbol in each square. Notice that the atomic mass of boron (symbol B) is 10.8, which is what we calculated in Example $2.8.1$, and the atomic mass of neon (symbol Ne) is 20.8, which is what we calculated in Example $2.8.2$. Take time to notice that not all periodic tables have the atomic number above the element's symbol and the mass number below it. If you are ever confused, remember that the atomic number should always be the smaller of the two and will be a whole number, while the atomic mass should always be the larger of the two and will be a decimal number.

? Exercise 2.8.1

Chlorine has two naturally occurring isotopes. In a sample of chlorine, 75.77% of the atoms are Cl-35, with a mass of 34.97 amu Another 24.23% of the atoms are Cl-37, with a mass of 36.97 amu What is the atomic mass of chlorine?

Answer

35.45 amu

Summary

- An element's atomic mass is the weighted average of the masses of the isotopes of an element
- An element's atomic mass can be calculated provided the relative abundance of the element's naturally occurring isotopes and the masses of those isotopes are known.
- The periodic table is a convenient way to summarize information about the different elements. In addition to the element's symbol, most periodic tables will also contain the element's atomic number and the element's atomic mass.

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2.9: Summary of Atomic Theory and the Construction of Atoms

Learning Objectives

- State the modern atomic theory.
- Describe the locations, charges, and masses of the three main subatomic particles.
- Determine the number of protons and electrons in an atom.
- Define atomic number and mass number.
- Determine the number of protons, neutrons, and electrons in an atom.
- Explain how elements are organized into the periodic table.
- Explain what isotopes are and how an isotope affects an element's atomic mass.
- Determine the number of protons, electrons, and neutrons of an element with a given mass number.
- Define the two types of ions.

The smallest piece of an element that maintains the identity of that element is called an atom. Individual atoms are extremely small. It would take about fifty million atoms in a row to make a line that is 1 cm long. The period at the end of a printed sentence has several million atoms in it. Atoms are so small that it is difficult to believe that all matter is made from atoms—but it is.

The concept that atoms play a fundamental role in chemistry is formalized by the modern atomic theory, first stated by John Dalton, an English scientist, in 1808. It consists of three parts:

1. All matter is composed of atoms.
2. Atoms of the same element are the same; atoms of different elements are different.
3. Atoms combine in whole-number ratios to form compounds.

These concepts form the basis of chemistry. Although the word *atom* comes from a Greek word that means "indivisible," we understand now that atoms themselves are composed of smaller parts called *subatomic particles*. The first part to be discovered was the electron, a tiny subatomic particle with a negative charge. It is often represented as e^-, with the right superscript showing the negative charge. Later, two larger particles were discovered. The proton is a more massive (but still tiny) subatomic particle with a positive charge, represented as p^+. The neutron is a subatomic particle with about the same mass as a proton, but no charge. It is represented as either n or n^0. We now know that all atoms of all elements are composed of electrons, protons, and (with one exception) neutrons. Table $2.9.1$ summarizes the properties of these three subatomic particles.

Table $2.9.1$: Properties of the Three Subatomic Particles

Name	Symbol	Mass (approx.; kg)	Charge
Proton	p^+	1.6×10^{-27}	1+
Neutron	n, n^0	1.6×10^{-27}	none
Electron	e^-	9.1×10^{-31}	1−

How are these particles arranged in atoms? They are not arranged at random. Experiments by Ernest Rutherford in England in the 1910s pointed to a nuclear model with atoms that has the protons and neutrons in a central nucleus with the electrons in orbit about the nucleus. The relatively massive protons and neutrons are collected in the center of an atom, in a region called the nucleus of the atom (plural *nuclei*). The electrons are outside the nucleus and spend their time orbiting in space about the nucleus. (Figure $2.9.1$).

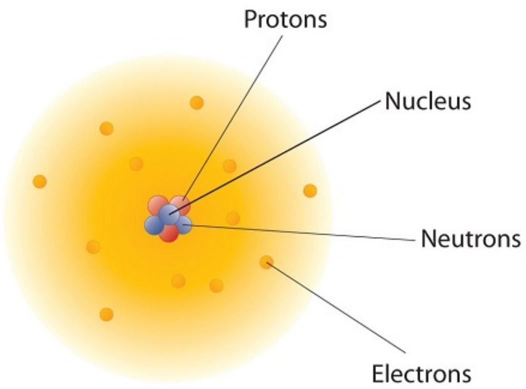


Figure 2.9.1: The Structure of the Atom. Atoms have protons and neutrons in the center, making the nucleus, while the electrons orbit the nucleus.

The modern atomic theory states that atoms of one element are the same, while atoms of different elements are different. What makes atoms of different elements different? The fundamental characteristic that all atoms of the same element share is the *number of protons*. All atoms of hydrogen have one and only one proton in the nucleus; all atoms of iron have 26 protons in the nucleus. This number of protons is so important to the identity of an atom that it is called the atomic number. The number of protons in an atom is the atomic number of the element. Thus, hydrogen has an atomic number of 1, while iron has an atomic number of 26. Each element has its own characteristic atomic number.

Atoms of the same element can have different numbers of neutrons, however. Atoms of the same element (i.e., atoms with the same number of protons) with different numbers of neutrons are called isotopes. Most naturally occurring elements exist as isotopes. For example, most hydrogen atoms have a single proton in their nucleus. However, a small number (about one in a million) of hydrogen atoms have a proton and a neutron in their nuclei. This particular isotope of hydrogen is called deuterium. A very rare form of hydrogen has one proton and two neutrons in the nucleus; this isotope of hydrogen is called tritium. The sum of the number of protons and neutrons in the nucleus is called the mass number of the isotope.

Neutral atoms have the same number of electrons as they have protons, so their overall charge is zero. However, as we shall see later, this will not always be the case.

✓ Example 2.9.1:

a. The most common carbon atoms have six protons and six neutrons in their nuclei. What are the atomic number and the mass number of these carbon atoms?
b. An isotope of uranium has an atomic number of 92 and a mass number of 235. What are the number of protons and neutrons in the nucleus of this atom?

Solution

a. If a carbon atom has six protons in its nucleus, its atomic number is 6. If it also has six neutrons in the nucleus, then the mass number is 6 + 6, or 12.
b. If the atomic number of uranium is 92, then that is the number of protons in the nucleus. Because the mass number is 235, then the number of neutrons in the nucleus is 235 − 92, or 143.

? Exercise 2.9.1

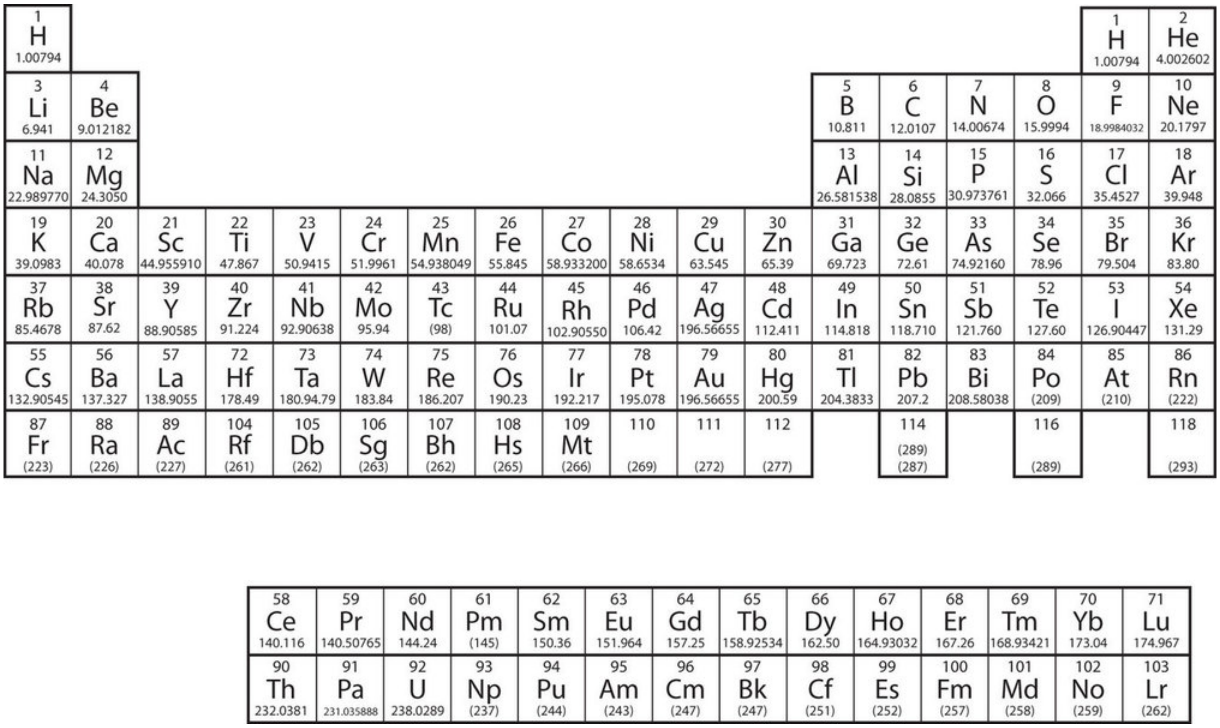
The number of protons in the nucleus of a tin atom is 50, while the number of neutrons in the nucleus is 68. What are the atomic number and the mass number of this isotope?

Answer

Atomic number = 50, mass number = 118

When referring to an atom, we simply use the element's name: the term *sodium* refers to the element as well as an atom of sodium. But it can be unwieldy to use the name of elements all the time. Instead, chemistry defines a symbol for each element. The atomic symbol is a one- or two-letter representation of the name of an element. By convention, the first letter of an element's symbol is always capitalized, while the second letter (if present) is lowercase. Thus, the symbol for hydrogen is H, the symbol for sodium is Na, and the symbol for nickel is Ni. Most symbols come from the English name of the element, although some symbols come from an element's Latin name. (The symbol for sodium, Na, comes from its Latin name, *natrium*.)

The elements are grouped together in a special chart called the periodic table of all the elements. A simple periodic table is shown in Figure $2.9.2$, while one may view a more extensive periodic table from another source. The elements on the periodic table are listed in order of ascending atomic number. The periodic table has a special shape that will become important to us when we consider the organization of electrons in atoms (Chapter 8). One immediate use of the periodic table helps us identify metals and nonmetals. Nonmetals are in the upper right-hand corner of the periodic table, on one side of the heavy line splitting the right-side part of the chart. All other elements are metals.



1 H 1.00794																1 H 1.00794	2 He 4.002602
3 Li 6.941	4 Be 9.012182											5 B 10.811	6 C 12.0107	7 N 14.00674	8 O 15.9994	9 F 18.9984032	10 Ne 20.1797
11 Na 22.989770	12 Mg 24.3050											13 Al 26.581538	14 Si 28.0855	15 P 30.973761	16 S 32.066	17 Cl 35.4527	18 Ar 39.948
19 K 39.0983	20 Ca 40.078	21 Sc 44.955910	22 Ti 47.867	23 V 50.9415	24 Cr 51.9961	25 Mn 54.938049	26 Fe 55.845	27 Co 58.933200	28 Ni 58.6534	29 Cu 63.545	30 Zn 65.39	31 Ga 69.723	32 Ge 72.61	33 As 74.92160	34 Se 78.96	35 Br 79.504	36 Kr 83.80
37 Rb 85.4678	38 Sr 87.62	39 Y 88.90585	40 Zr 91.224	41 Nb 92.90638	42 Mo 95.94	43 Tc (98)	44 Ru 101.07	45 Rh 102.90550	46 Pd 106.42	47 Ag 196.56655	48 Cd 112.411	49 In 114.818	50 Sn 118.710	51 Sb 121.760	52 Te 127.60	53 I 126.90447	54 Xe 131.29
55 Cs 132.90545	56 Ba 137.327	57 La 138.9055	72 Hf 178.49	73 Ta 180.94.79	74 W 183.84	75 Re 186.207	76 Os 190.23	77 Ir 192.217	78 Pt 195.078	79 Au 196.56655	80 Hg 200.59	81 Tl 204.3833	82 Pb 207.2	83 Bi 208.58038	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra (226)	89 Ac (227)	104 Rf (261)	105 Db (262)	106 Sg (263)	107 Bh (262)	108 Hs (265)	109 Mt (266)	110 (269)	111 (272)	112 (277)		114 (289) (287)		116 (289)		118 (293)

58 Ce 140.116	59 Pr 140.50765	60 Nd 144.24	61 Pm (145)	62 Sm 150.36	63 Eu 151.964	64 Gd 157.25	65 Tb 158.92534	66 Dy 162.50	67 Ho 164.93032	68 Er 167.26	69 Tm 168.93421	70 Yb 173.04	71 Lu 174.967
90 Th 232.0381	91 Pa 231.035888	92 U 238.0289	93 Np (237)	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (262)

Figure $2.9.1$: A Simple Periodic Table

There is an easy way to represent isotopes using the atomic symbols. We use the construction:

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

where X is the symbol of the element, A is the mass number, and Z is the atomic number. Thus, for the isotope of carbon that has 6 protons and 6 neutrons, the symbol is:

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

where C is the symbol for the element, 6 represents the atomic number, and 12 represents the mass number.

✓ Example $2.9.2$:

a. What is the symbol for an isotope of uranium that has an atomic number of 92 and a mass number of 235?
b. How many protons and neutrons are in $^{56}_{26}\mathrm{Fe}$

Solution

a. The symbol for this isotope is $^{235}_{92}\mathrm{U}$
b. This iron atom has 26 protons and 56 − 26 = 30 neutrons.

? Exercise 2.9.2

How many protons are in ${}^{23}_{11}\mathrm{Na}$

Answer

11 protons

It is also common to state the mass number after the name of an element to indicate a particular isotope. Atoms of the same element that differ in their numbers of neutrons are called **isotopes**. Different isotopes of an element generally have the same physical and chemical properties because they have the same numbers of protons and electrons. *Carbon-12* represents an isotope of carbon with 6 protons and 6 neutrons, while *uranium-238* is an isotope of uranium that has 146 neutrons.

So far, we have discussed elements and compounds that are electrically neutral. They have the same number of electrons as protons, so the negative charges of the electrons are balanced by the positive charges of the protons. However, this is not always the case. Electrons can move from one atom to another; when they do, species with overall electric charges are formed. Such species are called ions. Species with overall positive charges are termed **cations**, while species with overall negative charges are called **anions**. Remember that ions are formed only when *electrons* move from one atom to another; a proton never moves from one atom to another.

Key Takeaways

- Chemistry is based on the modern atomic theory, which states that all matter is composed of atoms.
- Atoms themselves are composed of protons, neutrons, and electrons.
- Each element has its own atomic number, which is equal to the number of protons in its nucleus.
- Isotopes of an element contain different numbers of neutrons.
- Elements are represented by an atomic symbol.
- The periodic table is a chart that organizes all the elements.
- Ions form when atoms lose or gain electrons.

2.E: Atomic Structure (Exercises)

2.1-2.4: Basic Atomic Theory

1. List the three statements that make up the modern atomic theory.

2. Explain how atoms are composed.

3. Which is larger, a proton or an electron?

4. Which is larger, a neutron or an electron?

5. What are the charges for each of the three subatomic particles?

6. Where is most of the mass of an atom located?

7. Sketch a diagram of a boron atom, which has five protons and six neutrons in its nucleus.

8. Sketch a diagram of a helium atom, which has two protons and two neutrons in its nucleus.

9. Define *atomic number*. What is the atomic number for a boron atom?

10. What is the atomic number of helium?

11. Define *isotope* and give an example.

12. What is the difference between deuterium and tritium?

13. Which pair represents isotopes?

a.
$$^{4}_{2}\text{He} \; and \; ^{3}_{2}\text{He} \tag{2.E.1}$$

b.
$$^{56}_{26}\text{Fe} \; and \; ^{56}_{25}\text{Mn} \tag{2.E.2}$$

c.
$$^{28}_{14}\text{Si} \; and \; ^{31}_{15}\text{P} \tag{2.E.3}$$

14. Which pair represents isotopes?

a.
$$^{40}_{20}\text{Ca} \; and \; ^{40}_{19}\text{K} \tag{2.E.4}$$

b.
$$^{56}_{26}\text{Fe} \; and \; ^{56}_{28}\text{Fe} \tag{2.E.5}$$

c.
$$^{238}_{92}\text{U} \; and \; ^{235}_{92}\text{U} \tag{2.E.6}$$

15. Give complete symbols of each atom, including the atomic number and the mass number.

a. an oxygen atom with 8 protons and 8 neutrons
b. a potassium atom with 19 protons and 20 neutrons
c. a lithium atom with 3 protons and 4 neutron

16. Give complete symbols of each atom, including the atomic number and the mass number.

a. a magnesium atom with 12 protons and 12 neutrons
b. a magnesium atom with 12 protons and 13 neutrons
c. a xenon atom with 54 protons and 77 neutron

17. Americium-241 is an isotope used in smoke detectors. What is the complete symbol for this isotope?

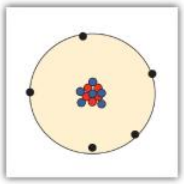
18. Carbon-14 is an isotope used to perform radioactive dating tests on previously living material. What is the complete symbol for this isotope?

19. Give atomic symbols for each element.

a. sodium
b. argon
c. nitrogen
d. radon

20. Give atomic symbols for each element.
    a. silver
    b. gold
    c. mercury
    d. iodine
21. Give the name of the element.
    a.Si
    b. Mn
    c. Fe
    d. Cr
22. Give the name of the element.
    a. F
    b. Cl
    c. Br
    d. I

Answers

1. All matter is composed of atoms; atoms of the same element are the same, and atoms of different elements are different; atoms combine in whole-number ratios to form compounds.
2.
3. A proton is larger than an electron.
4. proton: 1+; electron: 1−; neutron: 0
5.
6. In the nucleus of the atom
7. 
8.
9. The atomic number is the number of protons in a nucleus. Boron has an atomic number of five.
10.
11. Isotopes are atoms of the same element but with different numbers of neutrons.

$$^{1}_{1}\mathrm{H}\, and\ ^{2}_{1}\mathrm{H} \tag{2.E.7}$$

12.
13.

    a. isotopes
    b. not isotopes
    c. not isotopes

14.
15.

    a. $$^{16}_{8}\mathrm{O} \tag{2.E.8}$$
    b. $$^{39}_{19}\mathrm{K} \tag{2.E.9}$$
    c. $$^{7}_{3}\mathrm{Li} \tag{2.E.10}$$

16.

17. $$^{241}_{95}\text{Am} \tag{2.E.11}$$

18.

19. a. Na
    b. Ar
    c. N
    d. Rn

20.

21. a. silicon
    b. manganese
    c. iron
    d. chromium

2.5-2.7: Ions and Groups on the Periodic Table

1. How many protons and electrons are in each of the following atoms or ions?

   a. Mg
   b. Mg^{2+}
   c. P
   d. P^{3-}

2. Explain how an ion is formed. How can you know the charge of an ion?

3. For each of the following determine if it is a metal or non-metal?

   a. Oxygen, O
   b. Sodium, Na
   c. Phosphorus, P
   d. Potassium, K

4. What is the name of the periodic table "Group" for each of the following elements?

   a. Chlorine, Cl
   b. Argon, Ar
   c. Sodium, Na
   d. Potassium, K

Answers

1.

   a. Mg, 12 protons, 12 electrons
   b. Mg^{2+}, 12 protons, 10 electrons
   c. P, 15 protons, 15 electrons
   d. P^{3-}, 15 protons, 18 electrons

2. Please explain in your own words.

3. a. non-metal

   b. metal

   c. non-metal

   d. metal

4. a. Halogen

   b. Noble Gas

c. Alkali Metals

d. Alkali Metals

2.8-2.9: Masses of Atoms and Molecules

1. Define *atomic mass unit*. What is its abbreviation?
2. Estimate the mass, in whole numbers, of each isotope.
    a. hydrogen-1
    b. hydrogen-3
    c. iron-56
3. Estimate the mass, in whole numbers, of each isotope.
    a. phosphorus-31
    b. carbon-14
    c. americium-241
4. Determine the atomic mass of each element, given the isotopic composition.
    a. lithium, which is 92.4% lithium-7 (mass 7.016 u) and 7.60% lithium-6 (mass 6.015 u)
    b. oxygen, which is 99.76% oxygen-16 (mass 15.995 u), 0.038% oxygen-17 (mass 16.999 u), and 0.205% oxygen-18 (mass 17.999 u)
5. Determine the atomic mass of each element, given the isotopic composition.
    a. neon, which is 90.48% neon-20 (mass 19.992 u), 0.27% neon-21 (mass 20.994 u), and 9.25% neon-22 (mass 21.991 u)
    b. uranium, which is 99.27% uranium-238 (mass 238.051 u) and 0.720% uranium-235 (mass 235.044 u)
6. How far off would your answer be from Exercise 5a if you used whole-number masses for individual isotopes of lithium?
7. How far off would your answer be from Exercise 6b if you used whole-number masses for individual isotopes of uranium?
8. a. What is the atomic mass of an oxygen atom?
    b. What is the molecular mass of oxygen in its elemental form?
9. a. What is the atomic mass of bromine?
    b. What is the molecular mass of bromine in its elemental form?
10. Determine the mass of each substance. (Add the masses of the individual elements.)
    a. F_2
    b. CO
    c. CO_2
11. Determine the mass of each substance.
    a. Kr
    b. KrF_4
    c. PF_5
12. Determine the mass of each substance. (Add the masses of the individual elements.)
    a. Na
    b. B_2O_3
    c. S_2Cl_2
13. Determine the mass of each substance.
    a. IBr_3
    b. N_2O_5
    c. CCl_4
14. Determine the mass of each substance.
    a. GeO_2
    b. IF_3
    c. XeF_6
15. Determine the mass of each substance.
    a. NO

   b. N_2O_4
   c. Ca

Answers

1. The atomic mass unit is defined as one-twelfth of the mass of a carbon-12 atom. Its abbreviation is u.
2. a. 1
   b. 3
   c. 56
3.
4. a. 6.940 u
   b. 16.000 u
5.
6. We would get 6.924 u.
7.
8. a. 15.999 u
   b. 31.998 u
9.
10. a. 37.996 u
    b. 28.010 u
    c. 44.009 u
11.
12. a. 22.990 u
    b. 69.617 u
    c. 135.036 u
13.
14. a. 104.64 u
    b. 183.898 u
    c. 245.281 u

Additional Exercises

1. How many electrons does it take to make the mass of one proton?
2. How many protons does it take to make the mass of a neutron?
3. Dalton’s initial version of the modern atomic theory says that all atoms of the same element are the same. Is this actually correct? Why or why not?
4. How are atoms of the same element the same? How are atoms of the same element different?
5. Give complete atomic symbols for the three known isotopes of hydrogen.
6. A rare isotope of helium has a single neutron in its nucleus. Write the complete atomic symbol of this isotope.
7. Use its place on the periodic table to determine if indium, In, atomic number 49, is a metal or a nonmetal.
8. Only a few atoms of astatine, At, atomic number 85, have been detected. On the basis of its position on the periodic table, would you expect it to be a metal or a nonmetal?
9. Americium-241 is a crucial part of many smoke detectors. How many neutrons are present in its nucleus?
10. Potassium-40 is a radioactive isotope of potassium that is present in the human body. How many neutrons are present in its nucleus?
11. Determine the atomic mass of ruthenium from the given abundance and mass data.

Ruthenium-96	5.54%	95.907 u
Ruthenium-98	1.87%	97.905 u
Ruthenium-99	12.76%	98.906 u
Ruthenium-100	12.60%	99.904 u

Ruthenium-101	17.06%	100.906 u
Ruthenium-102	31.55%	101.904 u
Ruthenium-104	18.62%	103.905 u

12. Determine the atomic mass of tellurium from the given abundance and mass data.

Tellurium-120	0.09%	119.904 u
Tellurium-122	2.55%	121.903 u
Tellurium-123	0.89%	122.904 u
Tellurium-124	4.74%	123.903 u
Tellurium-125	7.07%	124.904 u
Tellurium-126	18.84%	125.903 u
Tellurium-128	31.74%	127.904 u
Tellurium-130	34.08%	129.906 u

13. One atomic mass unit has a mass of 1.6605×10^{-24} g. What is the mass of one atom of sodium?
14. One atomic mass unit has a mass of 1.6605×10^{-24} g. What is the mass of one atom of uranium?

- One atomic mass unit has a mass of 1.6605×10^{-24} g. What is the mass of one molecule of H_2O?
- One atomic mass unit has a mass of 1.6605×10^{-24} g. What is the mass of one molecule of PF_5?
- From their positions on the periodic table, will Cu and I form a molecular compound or an ionic compound?

18. From their positions on the periodic table, will N and S form a molecular compound or an ionic compound?
19. Mercury is an unusual element in that when it takes a 1+ charge as a cation, it always exists as the diatomic ion.
    a. Propose a formula for the mercury(I) ion.
    b. What is the formula of mercury(I) chloride?
20. Propose a formula for hydrogen peroxide, a substance used as a bleaching agent. (Curiously, this compound does not behave as an acid, despite its formula. It behaves more like a classic nonmetal-nonmetal, molecular compound.)
21. The uranyl cation has the formula UO_2^{2+}. Propose formulas and names for the ionic compounds between the uranyl cation and F^-, SO_4^{2-}, and PO_4^{3-}.
22. The permanganate anion has the formula MnO_4^-. Propose formulas and names for the ionic compounds between the permanganate ion and K^+, Ca^{2+}, and Fe^{3+}.

Answers

1. about 1,800 electrons
2.
3. It is not strictly correct because of the existence of isotopes.
4.
5.

$$ {}^{1}_{1}\mathrm{H},\ {}^{2}_{1}\mathrm{H},\ and\ {}^{3}_{1}\mathrm{H} \tag{2.E.12}$$

6.
7. It is a metal.
8.
9. 146 neutrons
10.
11. 101.065 u
12.

13. 3.817×10^{-23} g
14.
15. 2.991×10^{-23} g
16.
17. ionic
18.
19.
    a. $Hg_2{}^{2+}$
    b. Hg_2Cl_2
20.
21. uranyl fluoride, UO_2F_2; uranyl sulfate, UO_2SO_4; uranyl phosphate, $(UO_2)_3(PO_4)_2$

CHAPTER OVERVIEW

3: Light, Electrons, and the Periodic Table

3.1: Light is Visible Electromagnetic Radiation

Learning Objectives

- Define the terms wavelength and frequency with respect to wave-form energy.
- State the relationship between wavelength and frequency with respect to electromagnetic radiation.

During the summer, almost everyone enjoys going to the beach. Beach-goers can swim, have picnics, and work on their tans. But if a person gets too much sun, they can burn. A particular set of solar wavelengths are especially harmful to the skin. This portion of the solar spectrum is known as UV B, with wavelengths of $280\text{-}320 \text{ nm}$. Sunscreens are effective in protecting skin against both the immediate skin damage and the long-term possibility of skin cancer.

Waves

Waves are characterized by their repetitive motion. Imagine a toy boat riding the waves in a wave pool. As the water wave passes under the boat, it moves up and down in a regular and repeated fashion. While the wave travels horizontally, the boat only travels vertically up and down. The figure below shows two examples of waves.

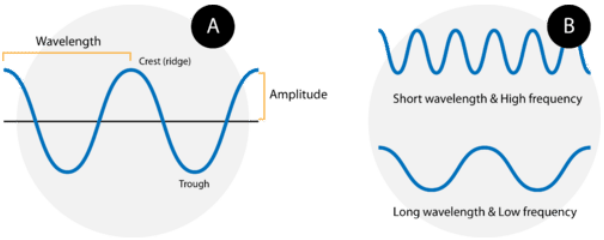


Figure $3.1.1$: (A) A wave consists of alternation crests and troughs. The wavelength (λ) is defined as the distance between any two consecutive identical points on the waveform. The amplitude is the height of the wave. (B) A wave with a short wavelength (top) has a high frequency because more waves pass a given point in a certain amount of time. A wave with a longer wavelength (bottom) has a lower frequency.

A wave cycle consists of one complete wave—starting at the zero point, going up to a wave **crest**, going back down to a wave **trough**, and back to the zero point again. The **wavelength** of a wave is the distance between any two corresponding points on adjacent waves. It is easiest to visualize the wavelength of a wave as the distance from one wave crest to the next. In an equation, wavelength is represented by the Greek letter lambda (λ). Depending on the type of wave, wavelength can be measured in meters, centimeters, or nanometers $\left(1 \text{ m} = 10^9 \text{ nm}\right)$. The **frequency**, represented by the Greek letter nu (ν), is the number of waves that pass a certain point in a specified amount of time. Typically, frequency is measured in units of cycles per second or waves per second. One wave per second is also called a Hertz (Hz) and in SI units is a reciprocal second $\left(\text{s}^{-1}\right)$.

Figure B above shows an important relationship between the wavelength and frequency of a wave. The top wave clearly has a shorter wavelength than the second wave. However, if you picture yourself at a stationary point watching these waves pass by, more waves of the first kind would pass by in a given amount of time. Thus the frequency of the first wave is greater than that of the second wave. Wavelength and frequency are therefore inversely related. As the wavelength of a wave increases, its frequency decreases. The equation that relates the two is:

$$c = \lambda \nu$$

The variable c is the speed of light. For the relationship to hold mathematically, if the speed of light is used in m/s, the wavelength must be in meters and the frequency in Hertz.

Example 3.1.1: Orange Light

The color orange within the visible light spectrum has a wavelength of about 620 nm. What is the frequency of orange light?

Solution

Solutions to Example 9.2.1

Steps for Problem Solving	Example $3.1.1$

Steps for Problem Solving	Example 3.1.1
Identify the "given" information and what the problem is asking you to "find."	Given : - Wavelength $(\lambda) = 620 \text{ nm}$ - Speed of light $(c) = 3.00 \times 10^8 \text{ m/s}$ Find: Frequency (Hz)
List other known quantities.	$1 \text{ m} = 10^9 \text{ nm}$
Identify steps to get the final answer.	1.Convert the wavelength to m. 2. Apply the equation $c = \lambda\nu$ and solve for frequency. Dividing both sides of the equation by λ yields: $\nu = \frac{c}{\lambda}$
Cancel units and calculate.	$620 \text{ nm} \times \left(\frac{1 \text{ m}}{10^9 \text{ nm}}\right) = 6.20 \times 10^{-7} \text{ m}$ $\nu = \frac{c}{\lambda} = \frac{3.0 \times 10^8 \text{ m/s}}{6.20 \times 10^{-7}} = 4.8 \times 10^{14} \text{ Hz}$
Think about your result.	The value for the frequency falls within the range for visible light.

? Exercise 3.1.1

What is the wavelength of light if its frequency is $1.55 \times 10^{10} \text{ s}^{-1}$?

Answer

0.0194 m, or 19.4 mm

Summary

All waves can be defined in terms of their frequency and intensity. $c = \lambda\nu$ expresses the relationship between wavelength and frequency.

3.1.1: The Electromagnetic Spectrum

Learning Objectives

- Know the properties of different types of electromagnetic radiation.

Electromagnetic waves have an extremely wide range of wavelengths, frequencies, and energies. The highest energy form of electromagnetic waves are gamma (γ) rays and the lowest energy form are radio waves.

The figure below shows the **electromagnetic spectrum**, which is all forms of electromagnetic radiation. On the far left of Figure 3.1.1.1are the highest energy electromagnetic waves. These are called **gamma rays** and can be quite dangerous, in large numbers, to living systems. The next lower energy form of electromagnetic waves are called **x-rays**. Most of you are familiar with the penetration abilities of these waves. They can also be dangerous to living systems. Humans are advised to limit as much as possible the number of medical x-rays they have per year. Next lower, in energy, are **ultraviolet rays**. These rays are part of sunlight and the upper end of the ultraviolet range can cause sunburn and perhaps skin cancer. The tiny section next in the spectrum is the **visible range of light**. The visible light spectrum has been greatly expanded in the bottom half of the figure so that it can be discussed in more detail. The visible range of electromagnetic radiation are the frequencies to which the human eye responds. Lower in the spectrum are infrared rays and radio waves.

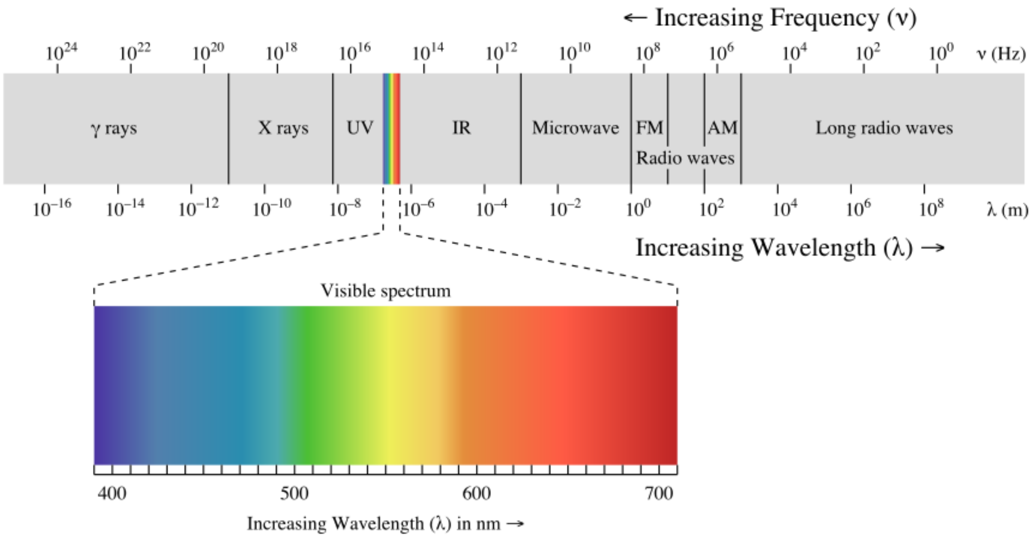


Figure 3.1.1.1: The electromagnetic spectrum, with its various regions labeled. The borders of each region are approximate. (CC BY-NC-SA; anonymous by request).

The light energies that are in the visible range are electromagnetic waves that cause the human eye to respond when those frequencies enter the eye. The eye sends a signal to the brain and the individual "sees" various colors. The highest energy waves in the visible region cause the brain to see violet and as the energy decreases, the colors change to blue, green, yellow, orange, and red. When the energy of the wave is above or below the visible range, the eye does not respond to them. When the eye receives several different frequencies at the same time, the colors are blended by the brain. If all frequencies of light strike the eye together, the brain sees white. If there are no visible frequencies striking the eye, the brain sees black. The objects that you see around you are light absorbers—that is, the chemicals on the surface of the object will absorb certain frequencies and not others. Your eyes detect the frequencies that strike your eye. Therefore, if your friend is wearing a red shirt, it means the dye in that shirt absorbs every frequency except red and the red frequencies are reflected. If your only light source was one exact frequency of blue light and you shined it on a shirt that was red in sunlight, the shirt would appear black because no light would be reflected. The light from fluorescent types of lights do not contain all the frequencies of sunlight and so clothes inside a store may appear to be a slightly different color when you get them home.

Summary

- Electromagnetic radiation has a wide spectrum, including gamma rays, X-rays, UV rays, visible light, IR radiation, microwaves, and radio waves.
- The different colors of light differ in their frequencies (or wavelengths).

3.2: Models of Electron Behavior

Scientists observed the ways in which light interacted with matter and proposed models to try to explain this behavior. Much of this behavior was very unexpected and sometimes appeared to defy logic. There were many intense arguments among the scientists about which models were correct and how to interpret their meaning. Some of these arguments are still unresolved. Creating these models required a lot of detailed math which we will not get into in this textbook. However, we will provide a brief overview of some of the highlights of these models within this section. In the following sections, we will show how these models predict electron behavior and thereby the chemical bonding behaviors of atoms.

3.2.1: The Bohr Model - Atoms with Orbits

Learning Objectives

- Define an energy level in terms of the Bohr model.
- Discuss how the Bohr model can be used to explain atomic spectra.

Electric light bulbs contain a very thin wire in them that emits light when heated. The wire is called a filament. The particular wire used in light bulbs is made of tungsten. A wire made of any metal would emit light under these circumstances, but tungsten was chosen because the light it emits contains virtually every frequency and therefore, the light emitted by tungsten appears white. A wire made of some other element would emit light of some color that was not convenient for our uses. Every element emits light when energized by heating or passing electric current through it. Elements in solid form begin to glow when they are heated sufficiently, and elements in gaseous form emit light when electricity passes through them. This is the source of light emitted by neon signs and is also the source of light in a fire.

Figure 3.2.1.1: Human/Need/Desire. Neon sculpture by Bruce Nauman (1983), who has been characterized as a conceptual artist.

Each Element Has a Unique Spectrum

The light frequencies emitted by atoms are mixed together by our eyes so that we see a blended color. Several physicists, including Angstrom in 1868 and Balmer in 1875, passed the light from energized atoms through glass prisms in such a way that the light was spread out so they could see the individual frequencies that made up the light. The **emission spectrum** (or **atomic spectrum**) of a chemical element is the unique pattern of light obtained when the element is subjected to heat or electricity.

Figure 3.2.1.2: Atomic Emission Spectrum of Hydrogen.

When hydrogen gas is placed into a tube and electric current passed through it, the color of emitted light is pink. But when the color is spread out, we see that the hydrogen spectrum is composed of four individual frequencies. The pink color of the tube is the result of our eyes blending the four colors. Every atom has its own characteristic spectrum; no two atomic spectra are alike. The image below shows the emission spectrum of iron. Because each element has a unique emission spectrum, elements can be defined using them.

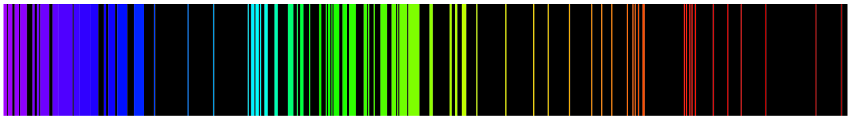


Figure 3.2.1.3: Atomic Emission Spectrum of Iron.

You may have heard or read about scientists discussing what elements are present in the sun or some more distant star, and after hearing that, wondered how scientists could know what elements were present in a place no one has ever been. Scientists determine what elements are present in distant stars by analyzing the light that comes from stars and finding the atomic spectrum of elements in that light. If the exact four lines that compose hydrogen's atomic spectrum are present in the light emitted from the star, that element contains hydrogen.

Bohr's Model of the Atom

By 1913, the concept of the atom had evolved from Dalton's indivisible spheres idea, to J. J. Thomson's plum pudding model, and then to Rutherford's nuclear atom theory. Rutherford, in addition to carrying out the brilliant experiment that demonstrated the presence of the atomic nucleus, also proposed that the electrons circled the nucleus in a planetary type motion. The solar system or planetary model of the atom was attractive to scientists because it was similar to something with which they were already familiar, namely the solar system.

Figure 3.2.1.3: Niels Bohr with Albert Einstein at Paul Ehrenfest's home in Leiden (December 1925).

Unfortunately, there was a serious flaw in the planetary model. It was already known that when a charged particle (such as an electron) moves in a curved path, it gives off some form of light and loses energy in doing so. This is, after all, how we produce TV signals. If the electron circling the nucleus in an atom loses energy, it would necessarily have to move closer to the nucleus as it loses energy, and would eventually crash into the nucleus. Furthermore, Rutherford's model was unable to describe how electrons give off light forming each element's unique atomic spectrum. These difficulties cast a shadow on the planetary model and indicated that, eventually, it would have to be replaced.

In 1913, the Danish physicist Niels Bohr proposed a model of the electron cloud of an atom in which electrons orbit the nucleus and were able to produce atomic spectra. Understanding Bohr's model requires some knowledge of electromagnetic radiation (or light).

Energy Levels

Bohr's key idea in his model of the atom is that electrons occupy definite orbitals that require the electron to have a specific amount of energy. In order for an electron to be in the electron cloud of an atom, it must be in one of the allowable orbitals and it must have the precise energy required for that orbit. Orbits closer to the nucleus would require smaller amounts of energy for an electron, and orbits farther from the nucleus would require the electron to have a greater amount of energy. The possible orbits are known as **energy levels**. One of the weaknesses of Bohr's model was that he could not offer a reason why only certain energy levels or orbits were allowed.

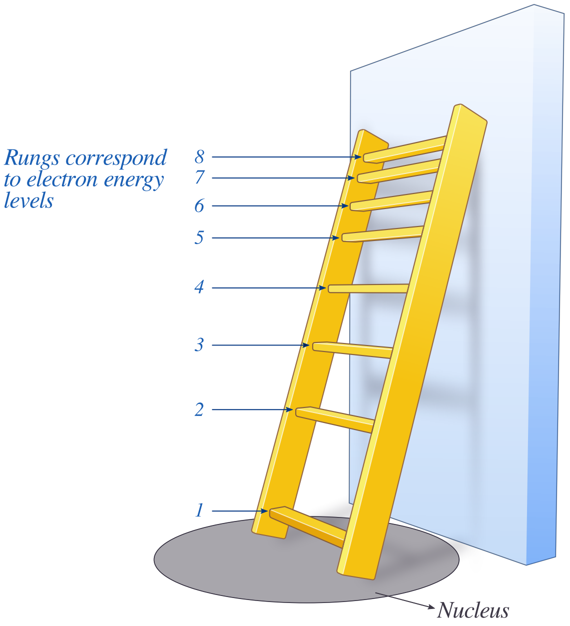


Figure 3.2.1.4: The energy levels of the electrons can be viewed as rungs on a ladder. Note that the spacing between rungs gets smaller at higher energies (CC BY-NC; Ümit Kaya)

Bohr hypothesized that the only way electrons could gain or lose energy would be to move from one energy level to another, thus gaining or losing precise amounts of energy. The energy levels are **quantized**, meaning that only specific amounts are possible. It would be like a ladder that had rungs only at certain heights. The only way you can be on that ladder is to be on one of the rungs, and the only way you could move up or down would be to move to one of the other rungs. Suppose we had such a ladder with 10 rungs. Other rules for the ladder are that only one person can be on a rung in the normal state, and the ladder occupants must be on the lowest rung available. If the ladder had five people on it, they would be on the lowest five rungs. In this situation, no person could move down because all of the lower rungs are full. Bohr worked out rules for the maximum number of electrons that could be in each energy level in his model, and required that an atom in its normal state (ground state) had all electrons in the lowest energy levels available. Under these circumstances, no electron could lose energy because no electron could move down to a lower energy level. In this way, Bohr's model explained why electrons circling the nucleus did not emit energy and spiral into the nucleus.

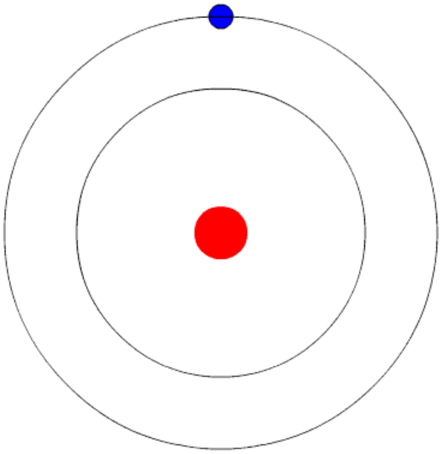


Figure 3.2.1.5: In Bohr's Model of the atom, electrons absorb energy to move to a higher level and release energy to move to lower levels. (CC BY-SA 3.0; Kurzon).

Bohr's Model and Atomic Spectra

The evidence used to support Bohr's model came from the atomic spectra. He suggested that an atomic spectrum is made by the electrons in an atom moving energy levels. The electrons typically have the lowest energy possible, called the **ground state**. If the electrons are given energy (through heat, electricity, light, etc.) the electrons in an atom could absorb energy by jumping to a higher energy level, or **excited state**. The electrons then give off the energy in the form of a piece of light—called a **photon**—that they had absorbed, to fall back to a lower energy level. The energy emitted by electrons dropping back to lower energy levels will always be precise amounts of energy, because the differences in energy levels are precise. This explains why you see specific lines of light when looking at an atomic spectrum—each line of light matches a specific "step down" that an electron can take in that atom. This also explains why each element produces a different atomic spectrum. Because each element has different acceptable energy levels for its electrons, the possible steps each element's electrons can take differ from all other elements.

Summary

- Bohr's model suggests each atom has a set of unchangeable energy levels, and electrons in the electron cloud of that atom must be in one of those energy levels.
- Bohr's model suggests that the atomic spectra of atoms is produced by electrons gaining energy from some source, jumping up to a higher energy level, then immediately dropping back to a lower energy level and emitting the energy difference between the two energy levels.
- The existence of the atomic spectra is support for Bohr's model of the atom.
- Bohr's model was only successful in calculating energy levels for the hydrogen atom.

Vocabulary

- **Emission spectrum** (or **atomic spectrum**) - The unique pattern of light given off by an element when it is given energy.
- **Energy levels** - Possible orbits that an electron can have in the electron cloud of an atom.
- **Ground state** - To be in the lowest energy level possible.
- **Excited state** - To be in a higher energy level.
- **Photon** - A piece of electromagnetic radiation, or light, with a specific amount of energy.
- **Quantized** - To have a specific amount.

3.2.2: The Quantum-Mechanical Model- Atoms with Orbitals

Learning Objectives

- Define quantum mechanics
- Differentiate between an orbit and an orbital.

How do you study something that seemingly makes no sense? We talk about electrons being in orbits and it sounds like we can tell where that electron is at any moment. We can draw pictures of electrons in orbit, but the reality is that we don't know exactly where they are. We are going to take a look at an area of science that even leaves scientists puzzled. When asked about quantum mechanics, Niels Bohr (who proposed the Bohr model of the atom) said: "Anyone who is not shocked by quantum theory has not understood it". Richard Feynman (one of the founders of modern quantum theory) stated: "I think I can safely say that nobody understands quantum theory." So, let's take a short trip into a land that challenges our everyday world.

Quantum Mechanics

The study of motion of large objects such as baseballs is called mechanics, or more specifically, classical mechanics. Because of the quantum nature of the electron and other tiny particles moving at high speeds, classical mechanics is inadequate to accurately describe their motion. **Quantum mechanics** is the study of the motion of objects that are atomic or subatomic in size and thus demonstrate wave-particle duality. In classical mechanics, the size and mass of the objects involved effectively obscures any quantum effects, so that such objects appear to gain or lose energies in any amounts. Particles whose motion is described by quantum mechanics gain or lose energy in small pieces called **quanta**.

One of the fundamental (and hardest to understand) principles of quantum mechanics is that the electron is both a particle and a wave. In the everyday macroscopic world of things we can see, something cannot be both. But this duality can exist in the quantum world of the submicroscopic on the atomic scale.

At the heart of quantum mechanics is the idea that we cannot accurately specify the location of an electron. All we can say is that there is a probability that it exists within this certain volume of space. The scientist Erwin Schrödinger developed an equation that deals with these calculations, which we will not pursue at this time.

Erwin Schrödinger.

Recall that in the Bohr model, the exact path of the electron was restricted to very well-defined circular **orbits** around the nucleus. An **orbital** is the quantum mechanical refinement of Bohr's orbit. In contrast to his concept of a simple circular orbit with a fixed radius, orbitals are mathematically derived regions of space with different *probabilities* of having an electron.

Summary

Quantum mechanics involves the study of material at the atomic level. This field deals with probabilities, since we cannot definitely locate a particle. Orbitals are mathematically derived regions of space with different *probabilities* of having an electron.

- **9.5: The Quantum-Mechanical Model- Atoms with Orbitals** by Henry Agnew, Marisa Alviar-Agnew is licensed CK-12. Original source: https://www.ck12.org/c/chemistry/.

3.3: Quantum-Mechanical Orbitals and Electron Configurations

Learning Objectives

- Represent the organization of electrons by an electron configuration and orbital diagram.

You now know that the periodic table is arranged in groups and periods (columns and rows) based on chemical and physical properties of the different elements. The first element, hydrogen (Z=1) has one proton and one electron and as you move right across the rows, each subsequent element has one additional proton and electron. You may have asked yourself, why are periodic trends observed across the rows and down the groups? Or, why do the rows have different numbers of elements, giving the table a unique shape?

These questions can be answered by learning more about the electrons in atoms. Although we have discussed the general arrangement of subatomic particles in atoms, we have said little about how electrons occupy the space around the nucleus. Do they move around the nucleus at random, or do they exist in some ordered arrangement?

In 1913, the Danish scientist Niels Bohr suggested that the electron in a hydrogen atom could not have any random energy, having *only* certain fixed values of energy that were indexed by the number n (now called a **quantum number**). Bohr suggested that the energy of the electron in hydrogen was **quantized** because it was in a specific orbit; much like the steps on a staircase does not have half or quarter stairs or the keys on a piano don't have notes in between, there are no energy levels in between each orbit. Figure

shows a model of the hydrogen atom based on Bohr's ideas.

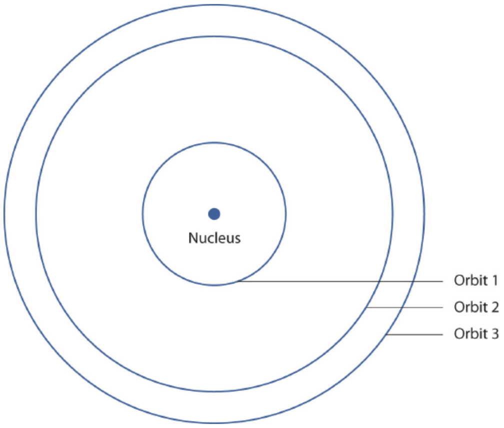


Figure 3.3.1: Bohr's Model of the Hydrogen Atom. Bohr's description of the hydrogen atom had specific orbits for the electron, which had quantized energies.

Bohr's ideas were useful, but were applicable only to the hydrogen atom. However, later researchers generalized Bohr's ideas into a new theory called **quantum mechanics**, which explains the behavior of electrons as if they were acting as a wave, not as particles. Quantum mechanics predicts two major things: quantized energies for electrons of all atoms (not just hydrogen) and an organization of electrons within atoms. Electrons are no longer thought of as being randomly distributed around a nucleus or restricted to certain orbits (in that regard, Bohr was wrong). Instead, electrons are collected into groups (*shells*) and subgroups (*subshells*) that explain much about the chemical behavior of the atom.

In the quantum-mechanical model of an atom, which is the modern and currently accepted model, the location of electrons in the atom are described by four **quantum numbers**, not just the one predicted by Bohr. Much like your home address can be used to locate you in a specific state, city, street, and house number, the first three quantum numbers identify approximately where electrons are in an atom. The fourth quantum number describes the electron and whether it is spin up or down (clockwise or counterclockwise). The theory and mathematics behind these four quantum numbers are well beyond the scope of this textbook, however, it is useful to learn some of the basics in order to understand how atoms behave and interact with (react) with other atoms.

Electron Arrangements: Shells, Subshells, and Orbitals

Electrons are organized according to their energies into sets called **shells** (labeled by the principle quantum number, ***n***). Generally the higher the energy of a shell, the farther it is (on average) from the nucleus. Shells do not have specific, fixed distances from the nucleus, but an electron in a higher-energy shell will spend more time farther from the nucleus than does an electron in a lower-energy shell.

Shells are further divided into subsets of electrons called **subshells**, labeled by type as *s*, *p*, *d*, or *f*. The first shell has only one subshell, *s*. The second shell has two subshells, *s* and *p;* the third shell has three subshells, *s*, *p*, and *d*, and the fourth shell has four subshells, *s*, *p*, *d*, and *f*. Within each subshell, electrons are arranged into different numbers of **orbitals**, an *s* subshell is made up of one *s* orbital, a *p* subshell has two *p* orbitals, a *d* subshell, five *d* orbitals, and an *f* subshell, seven *f* orbitals. Each orbital has a different shape and orientation around the nucleus (Figure

, however, rather than representing an orbit, as the name suggests, orbitals define a boundary for the region of space where a given electron is most likely to be found. Lastly, a single orbital can hold up to two electrons each with a different **spin**.

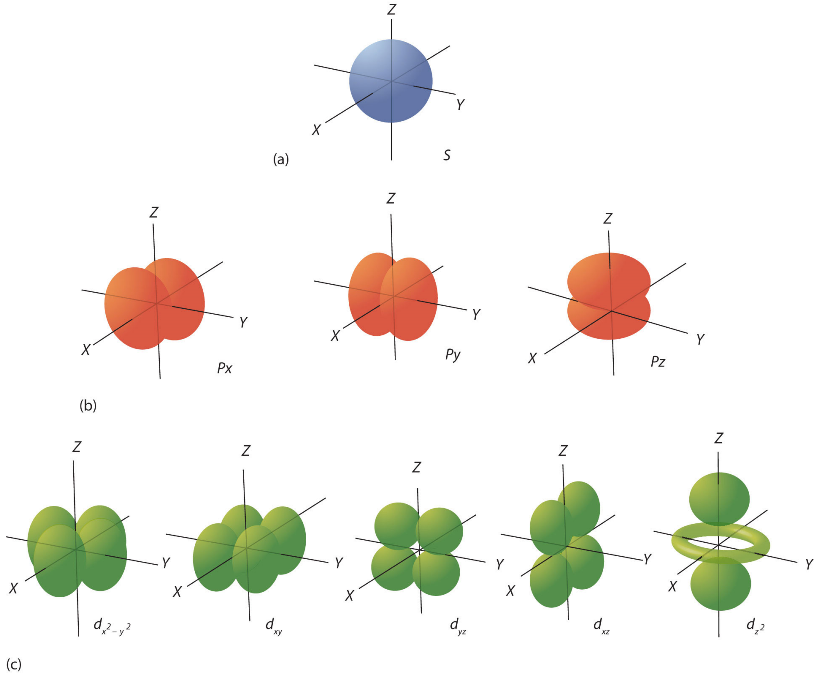


Figure $3.3.2$: Electron Orbitals. (a) The lone *s* orbital in an *s* subshell is spherical in distribution. (b) The three *p* orbitals have two lobes, shaped kind of like dumbbells, each is oriented around the nucleus along a different axis. (c) The five *d* orbitals have four lobes, except for the orbital, which is a "dumbbell + torus" combination. They are all oriented in different directions.

It is important to note that according to quantum theory, there are specific *allowed* combinations of quantum numbers and others that are not allowed. For example, shell two can only have two subshells, *s* with one orbital and *p* with 3 orbitals, therefore, this shell can hold a maximum of eight electrons (four orbitals times two electrons each). It takes practice to learn the allowed combinations as shown in Table $3.3.1$ but it is helpful to visualize the atom as a sphere with the nucleus in the center. Close to the nucleus, there is a smaller amount of space for electrons – a smaller shell. As the number of electrons increases, the shells that hold the electrons get larger and thus further away from the nucleus.

Table $3.3.1$: Atomic shell and subshell structure with the number of electrons in each

Shell	Number of Subshells	Names of Subshells	Number of Orbitals (*per Subshell*)	Number of Electrons (*per Subshell*)	Total Electrons (*per Shell*)
1	1	*1s*	1	2	2

Shell	Number of Subshells	Names of Subshells	Number of Orbitals (*per Subshell*)	Number of Electrons (*per Subshell*)	Total Electrons (*per Shell*)
2	2	*2s* and *2p*	1, 3	2, 6	8
3	3	*3s*, *3p*, and *3d*	1, 3, 5	2, 6, 10	18
4	4	*4s*, *4p*, *4d*, and *4f*	1, 3, 5, 7	2, 6, 10, 14	32

All of this information about the shell, subshell, and orbital is put together to make up the "address" for an electron and all of the addresses for all the electrons in an atom make up the **electron configuration**, which is described more later.

Electron Configurations

Can you name one thing that easily distinguishes you from the rest of the world? And we're not talking about DNA—that's a little expensive to sequence. For many people, it is their email address. Your email address allows people all over the world to contact you. It does not belong to anyone else, but serves to identify you. Electrons also have a unique set of identifiers in the quantum numbers that describe their location and spin. Chemists use an **electronic configuration** to represent the organization of electrons in shells and subshells in an atom. An electron configuration simply lists the shell and subshell labels, with a right superscript giving the number of electrons in that subshell. The shells and subshells are listed in the order of filling. Electrons are typically organized around an atom by starting at the lowest possible quantum numbers first, which are the shells-subshells with lower energies.

For example, an H atom has a single electron in the 1s subshell. Its electron configuration is

H, $1s^1$

He has two electrons in the 1s subshell. Its electron configuration is

He, $1s^2$

The three electrons for Li are arranged in the 1s subshell (two electrons) and the 2s subshell (one electron). The electron configuration of Li is

Li, $1s^2 2s^1$

Be has four electrons, two in the 1s subshell and two in the 2s subshell. Its electron configuration is

Be, $1s^2 2s^2$

Now that the 2s subshell is filled, electrons in larger atoms must go into the 2p subshell, which can hold a maximum of six electrons. The next six elements progressively fill up the 2p subshell:

- B: $1s^2 2s^2 2p^1$
- C: $1s^2 2s^2 2p^2$
- N: $1s^2 2s^2 2p^3$
- O: $1s^2 2s^2 2p^4$
- F: $1s^2 2s^2 2p^5$
- Ne: $1s^2 2s^2 2p^6$

Now that the 2p subshell is filled (all possible subshells in the n = 2 shell), the next electron for the next-larger atom must go into the n = 3 shell, s subshell.

Second Period Elements

Periods refer to the horizontal rows of the periodic table. Looking at a periodic table you will see that the first period contains only the elements hydrogen and helium. This is because the first principal energy level consists of only the *s* sublevel and so only two electrons are required in order to fill the entire principal energy level. Each time a new principal energy level begins, as with the third element lithium, a new period is started on the periodic table. As one moves across the second period, electrons are successively added. With beryllium (Z=4), the 2s sublevel is complete and the 2p sublevel begins with boron (Z=5). Since there are three 2p orbitals and each orbital holds two electrons, the 2p sublevel is filled after six elements. Table $3.3.2$ shows the electron configurations of the elements in the second period.

Table $3.3.3$: Electron Configurations of Second-Period Elements

Element Name	Symbol	Atomic Number	Electron Configuration
Lithium	Li	3	$1s^2\ 2s^1$
Beryllium	Be	4	$1s^2\ 2s^2$
Boron	B	5	$1s^2\ 2s^2\ 2p^1$
Carbon	C	6	$1s^2\ 2s^2\ 2p^2$
Nitrogen	N	7	$1s^2\ 2s^2\ 2p^3$
Oxygen	O	8	$1s^2\ 2s^2\ 2p^4$
Fluorine	F	9	$1s^2\ 2s^2\ 2p^5$
Neon	Ne	10	$1s^2\ 2s^2\ 2p^6$

Aufbau Principle

Construction of a building begins at the bottom. The foundation is laid and the building goes up step by step. You obviously cannot start with the roof since there is no place to hang it. The building goes from the lowest level to the highest level in a systematic way. In order to create ground state electron configurations for any element, it is necessary to know the way in which the atomic sublevels are organized in order of increasing energy. Figure $3.3.4$ shows the order of increasing energy of the sublevels.

The lowest energy sublevel is always the $1s$ sublevel, which consists of one orbital. The single electron of the hydrogen atom will occupy the $1s$ orbital when the atom is in its ground state. As we proceed with atoms with multiple electrons, those electrons are added to the next lowest sublevel: $2s$, $2p$, $3s$, and so on. The **Aufbau principle** states that an electron occupies orbitals in order from lowest energy to highest. The Aufbau (German: "building up, construction") principle is sometimes referred to as the "building up" principle. It is worth noting that in reality atoms are not built by adding protons and electrons one at a time, and that this method is merely an aid for us to understand the end result.

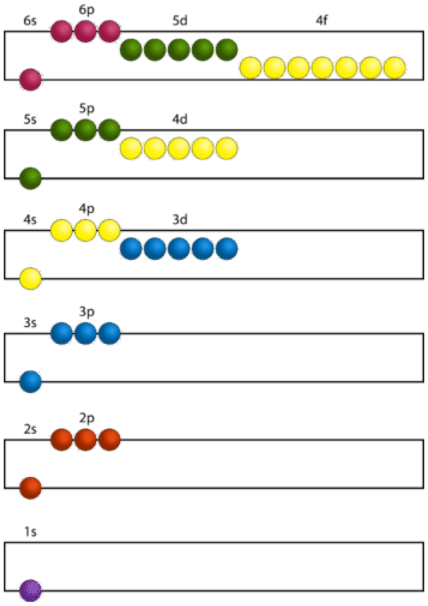


Figure $3.3.5$: Electrons are added to atomic orbitals in order from low energy (bottom of the graph) to high (top of the graph) according to the Aufbau principle. Principle energy levels are color coded, while sublevels are grouped together and each circle represents an orbital capable of holding two electrons.

As seen in the figure above, the energies of the sublevels in different principal energy levels eventually begin to overlap. After the $3p$ sublevel, it would seem logical that the $3d$ sublevel should be the next lowest in energy. However, the $4s$ sublevel is slightly lower in energy than the $3d$ sublevel and thus fills first. Following the filling of the $3d$ sublevel is the $4p$, then the $5s$ and the $4d$. Note that the $4f$ sublevel does not fill until just after the $6s$ sublevel. Figure $3.3.6$ is a useful and simple aid for keeping track of the order of fill of the atomic sublevels.

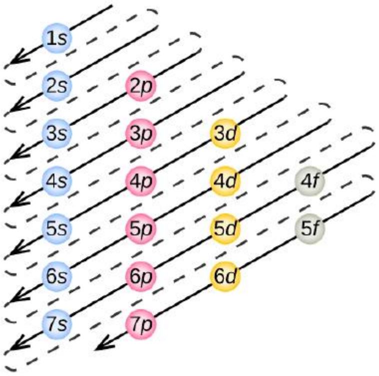


Figure $3.3.6$: The arrow leads through each subshell in the appropriate filling order for electron configurations. This chart is straightforward to construct. Simply make a column for all the s orbitals with each n shell on a separate row. Repeat for p, d, and f. Be sure to only include orbitals allowed by the quantum numbers (no 1p or 2d, and so forth). Finally, draw diagonal lines from top to bottom as shown.

Video $3.3.1$: Energy levels, sublevels and orbitals.

✓ Example $3.3.1$: Nitrogen Atoms

Nitrogen has 7 electrons. Write the electron configuration for nitrogen.

Solution:

Take a close look at Figure $3.3.5$, and use it to figure out how many electrons go into each sublevel, and also the order in which the different sublevels get filled.

1. Begin by filling up the 1*s* sublevel. **This gives $1s^2$**. Now all of the orbitals in the red *n* = 1 block are filled.

Since we used 2 electrons, there are 7 − 2 = **5 electrons left**

2. Next, fill the 2*s* sublevel. This gives **$1s^2 2s^2$**. Now all of the orbitals in the *s* sublevel of the orange *n* = 2 block are filled.

Since we used another 2 electrons, there are 5 − 2 = **3 electrons left**

3. Notice that we haven't filled the entire *n* = 2 block yet… there are still the *p* orbitals!

The final 3 electrons go into the 2*p* sublevel. This gives **$1s^2 2s^2 2p^3$**

The overall electron configuration is: $\mathbf{1s^22s^22p^3}$.

✓ Example 3.3.2: Potassium Atoms

Potassium has 19 electrons. Write the electron configuration code for potassium.

Solution

This time, take a close look at Figure 3.3.5.

1. Begin by filling up the 1*s* sublevel. **This gives** $\mathbf{1s^2}$. Now the *n* = 1 level is filled.

   Since we used 2 electrons, there are 19 − 2 = **17 electrons left**

2. Next, fill the 2*s* sublevel. **This gives** $\mathbf{1s^22s^2}$

   Since we used another 2 electrons, there are 17 − 2 = **15 electrons left**

3. Next, fill the 2*p* sublevel. **This gives** $\mathbf{1s^22s^22p^6}$**.** Now the *n* = 2 level is filled.

   Since we used another 6 electrons, there are 15 − 6 = **9 electrons left**

4. Next, fill the 3*s* sublevel. **This gives** $\mathbf{1s^22s^22p^63s^2}$

   Since we used another 2 electrons, there are 9 − 2 = **7 electrons left**

5. Next, fill the 3*p* sublevel. **This gives** $\mathbf{1s^22s^22p^63s^23p^6}$

   Since we used another 6 electrons, there are 7 − 6 = **1 electron left**

Here's where we have to be careful – right after $\mathbf{3p^6}$**!**

   Remember, 4*s* comes before 3*d*

6. The final electron goes into the 4*s* sublevel. **This gives** $\mathbf{1s^22s^22p^63s^23p^64s^1}$

The overall electron configuration is: $\mathbf{1s^22s^22p^63s^23p^64s^1}$

? Exercise 3.3.1: Magnesium and Sodium Atoms

What is the electron configuration for Mg and Na?

Answer Mg

Mg: $1s^22s^22p^63s^2$

Answer Na

Na: $1s^22s^22p^63s^1$

Pauli Exclusion Principle

When we look at the orbital possibilities for a given atom, we see that there are different arrangements of electrons for each different type of atom. Since each electron must maintain its unique identity, we intuitively sense that the four quantum numbers for any given electron must not match up exactly with the four quantum numbers for any other electron in that atom.

For the hydrogen atom, there is no problem since there is only one electron in the H atom. However, when we get to helium we see that the first three quantum numbers for the two electrons are the same: same energy level, same spherical shape. What differentiates the two helium electrons is their spin. One of the electrons has a $+\frac{1}{2}$ spin while the other electron has a $-\frac{1}{2}$ spin. So the two electrons in the $1s$ orbital are each unique and distinct from one another because their spins are different. This observation leads to the **Pauli exclusion principle**, which states that no two electrons in an atom can have the same set of four quantum numbers. The energy of the electron is specified by the principal, angular momentum, and magnetic quantum numbers. If those three numbers are identical for two electrons, the spin numbers must be different in order for the two electrons to be differentiated from one another. The two values of the spin quantum number allow each orbital to hold two electrons. Figure $3.3.7$ shows how the electrons are indicated in a diagram.

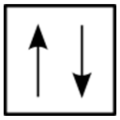


Figure $3.3.7$: In an orbital filling diagram, a square represents an orbital, while arrows represent electrons. An arrow pointing upward represents one spin direction, while an arrow pointing downward represents the other spin direction.

Hund's Rule

The last of the three rules for constructing electron arrangements requires electrons to be placed one at a time in a set of orbitals within the same sublevel. This minimizes the natural repulsive forces that one electron has for another. **Hund's rule** states that orbitals of equal energy are each occupied by one electron before any orbital is occupied by a second electron and that each of the single electrons must have the same spin. The figure below shows how a set of three p orbitals is filled with one, two, three, and four electrons.

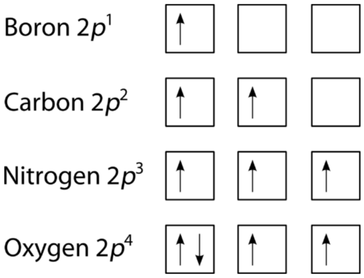


Figure $3.3.8$: The $2p$ sublevel, for the elements boron $(Z = 5)$, carbon $(Z = 6)$, nitrogen $(Z = 7)$, and oxygen $(Z = 8)$. According to Hund's rule, as electrons are added to a set of orbitals of equal energy, one electron enters each orbital before any orbital receives a second electron.

Orbital Filling Diagrams

An **orbital filling diagram** is the more visual way to represent the arrangement of all the electrons in a particular atom. In an orbital filling diagram, the individual orbitals are shown as circles (or squares) and orbitals within a sublevel are drawn next to each other horizontally. Each sublevel is labeled by its principal energy level and sublevel. Electrons are indicated by arrows inside of the circles. An arrow pointing upwards indicates one spin direction, while a downward pointing arrow indicates the other direction. The orbital filling diagrams for hydrogen, helium, and lithium are shown in the figure below.

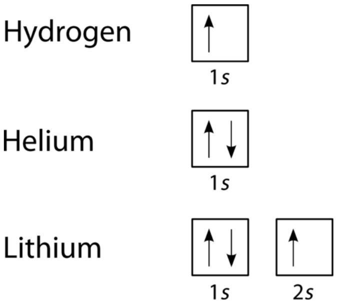


Figure $3.3.9$: Orbital filling diagrams for hydrogen, helium, and lithium.

According to the Aufbau process, sublevels and orbitals are filled with electrons in order of increasing energy. Since the s sublevel consists of just one orbital, the second electron simply pairs up with the first electron as in helium. The next element is lithium and necessitates the use of the next available sublevel, the $2s$.

The filling diagram for carbon is shown in Figure $3.3.10$. There are two $2p$ electrons for carbon and each occupies its own $2p$ orbital.

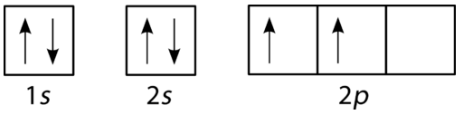


Figure 3.3.10: Orbital filling diagram for carbon.

Oxygen has four $2p$ electrons. After each $2p$ orbital has one electron in it, the fourth electron can be placed in the first $2p$ orbital with a spin opposite that of the other electron in that orbital.

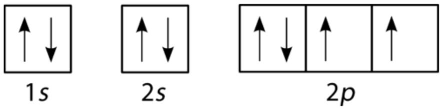


Figure 3.3.11: Orbital filling diagram for oxygen.

If you keep your papers in manila folders, you can pick up a folder and see how much it weighs. If you want to know how many different papers (articles, bank records, or whatever else you keep in a folder), you have to take everything out and count. A computer directory, on the other hand, tells you exactly how much you have in each file. We can get the same information on atoms. If we use an orbital filling diagram, we have to count arrows. When we look at electron configuration data, we simply add up the numbers.

Example 3.3.3: Carbon Atoms

Draw the orbital filling diagram for carbon and write its electron configuration.

Solution

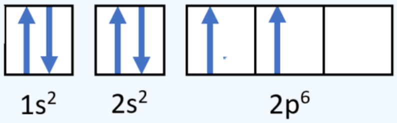
Step 1: List the known quantities and plan the problem.

Known

- Atomic number of carbon, Z=6

Use the order of fill diagram to draw an orbital filling diagram with a total of six electrons. Follow Hund's rule. Write the electron configuration.

Step 2: Construct the diagram.



Orbital filling diagram for carbon.

Electron configuration $1s^22s^22p^2$

Step 3: Think about your result.

Following the 2s sublevel is the 2p, and p sublevels always consist of three orbitals. All three orbitals need to be drawn even if one or more is unoccupied. According to Hund's rule, the sixth electron enters the second of those p orbitals and has the same spin as the fifth electron.

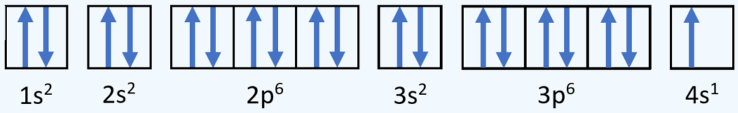
Exercise 3.3.2: Electronic Configurations

Write the electron configurations and orbital diagrams for

a. Potassium atom: K
b. Arsenic atom: As
c. Phosphorus atom: P

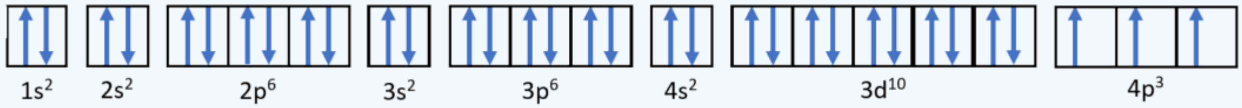
Answer a:

Potassium: $1s^22s^22p^63s^23p^64s^1$



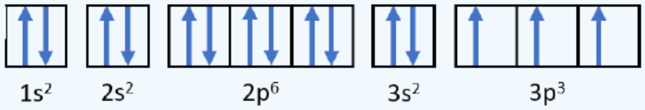
Answer b:

Arsenic: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^3$



Answer c:

Phosphorus $1s^2 2s^2 2p^6 3s^2 3p^3$



Summary

There are four different classes of electron orbitals. These orbitals are determined by the value of the angular momentum quantum number ℓ. An orbital is a wave function for an electron defined by the three quantum numbers, n, ℓ and m_ℓ. Orbitals define regions in space where you are likely to find electrons. *s* orbitals ($\ell = 0$) are spherical shaped. *p* orbitals ($\ell = 1$) are dumb-bell shaped. The three possible *p* orbitals are always perpendicular to each other.

Electron configuration notation simplifies the indication of where electrons are located in a specific atom. Superscripts are used to indicate the number of electrons in a given sublevel. The Aufbau principle gives the order of electron filling in an atom. It can be used to describe the locations and energy levels of every electron in a given atom. Hund's rule specifies the order of electron filling within a set of orbitals. Orbital filling diagrams are a way of indicating electron locations in orbitals. The Pauli exclusion principle specifies limits on how identical quantum numbers can be for two electrons in the same atom.

Vocabulary

principal quantum number (*n*)

Defines the energy level of the wave function for an electron, the size of the electron's standing wave, and the number of nodes in that wave.

quantum numbers

Integer numbers assigned to certain quantities in the electron wave function. Because electron standing waves must be continuous and must not "double over" on themselves, quantum numbers are restricted to integer values.

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3.4: Core and Valence Electrons

Learning Objectives

- Identify valence electrons using the periodic table and electron configuration.
- Define core and valence electrons.

Valence Electrons

In the study of chemical reactivity, we will find that the electrons in the outermost principal energy level are very important and so they are given a special name. **Valence electrons** are the electrons in the highest occupied principal energy level of an atom.

In the second period elements, the two electrons in the $1s$ sublevel are called **inner-shell electrons** and are not involved directly in the element's reactivity or in the formation of compounds. Lithium has a single electron in the second principal energy level and so we say that lithium has one valence electron. Beryllium has two valence electrons. How many valence electrons does boron have? You must recognize that the second principal energy level consists of both the $2s$ and the $2p$ sublevels and so the answer is three. In fact, the number of valence electrons goes up by one for each step across a period until the last element is reached. Neon, with its configuration ending in $2s^2 2p^6$, has eight valence electrons.

The alkali metal sodium (atomic number 11) has one more electron than the neon atom. This electron must go into the lowest-energy subshell available, the 3s orbital, giving a $1s^22s^22p^63s^1$ configuration. The electrons occupying the outermost shell orbital(s) (highest value of n) are called valence electrons, and those occupying the inner shell orbitals are called **core electrons** (Figure \PageIndex4). Since the core electron shells correspond to noble gas electron configurations, we can abbreviate electron configurations by writing the noble gas that matches the core electron configuration, along with the valence electrons in a condensed format. For our sodium example, the symbol [Ne] represents core electrons, ($1s^22s^22p^6$) and our abbreviated or condensed configuration is [Ne]$3s^1$.

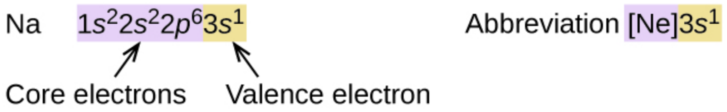


Figure 3.4.1: A core-abbreviated electron configuration (right) replaces the core electrons with the noble gas symbol whose configuration matches the core electron configuration of the other element.

Similarly, the abbreviated configuration of lithium can be represented as [He]$2s^1$, where [He] represents the configuration of the helium atom, which is identical to that of the filled inner shell of lithium. Writing the configurations in this way emphasizes the similarity of the configurations of lithium and sodium. Both atoms, which are in the alkali metal family, have only one electron in a valence *s* subshell outside a filled set of inner shells.

$$\mathrm{Li}:[\mathrm{He}]\,2s^1$$
$$\mathrm{Na}:[\mathrm{Ne}]\,3s^1$$

A chemical reaction results from electron removal, electron addition, or electron sharing of the valence electrons of the different atoms. The path a specific element will take depends on where the electrons are in the atom and how many there are. Thus, it is convenient to separate electrons into two groups. Valence shell electrons (or, more simply, the *valence electrons*) are the electrons in the highest-numbered shell, or valence shell, while core electrons are the electrons in lower-numbered shells. We can see from the electron configuration of a carbon atom—$1s^22s^22p^2$—that it has 4 valence electrons ($2s^22p^2$) and 2 core electrons ($1s^2$). You will see in the next chapters that the chemical properties of elements are determined by the number of valence electrons.

Example 3.4.3

Examine the electron configuration of neutral phosphorus atoms in Example 3.4.1, $1s^22s^22p^63s^23p^3$ and write the abbreviated notation.

Solution

Phosphorus has electron configuration, $1s^22s^22p^63s^23p^3$.

The highest-numbered shell is the third shell ($3s^23p^3$): **2 electrons** in the 3*s* subshell and **3 electrons** in the 3*p* subshell. That gives a total of **5 valence electrons**.

The 10 inner shell (core) electrons, $1s^22s^22p^6$ can be replaced by [Ne] (see Figure 3.4.3). Abbreviated notation is : $[Ne]3s^23p^3$

? Exercise 3.4.3

Examine the electron configuration of neutral calcium atom (Exercise 3.4.2), $1s^22s^22p^63s^23p^64s^2$, and write the abbreviated notation.

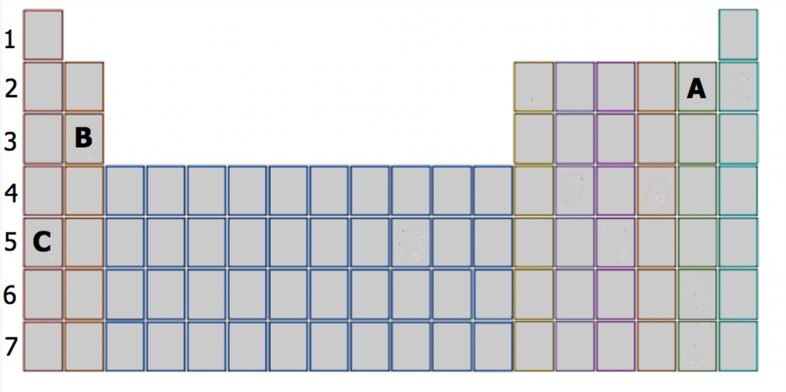
Answer

The highest-numbered shell is the fourth shell $4s^2$, which has **2 electrons** in the *4s* subshell. Hence, Calcium has **2 valence electrons**.

The 18 inner-shell (core) electrons, $1s^22s^22p^63s^23p^6$, can be replaced by [Ar], see Figure 3.4.3 The abbreviated notation is: $[Ar]4s^2$

✓ Example 3.4.4

Based on their respective locations in the periodic table (use Figure 3.4.3), determine the number of valence electrons and the valence shell configuration of elements A, B and C.



Solution

Element A is located in Period 2, the *5th position* in *2p*-block. Before the electrons are placed in *2p* subshell, the *2s* subshell must be filled first. This means that A has ***two valence electrons*** in 2s (**$2s^2$**) and ***five valence electrons*** in 2p (**$2p^5$**). Answer: **$2s^22p^5$.** It has ***2 + 5 = 7*** **valence electrons.**

Element B is located in Period 3, the *2nd position* in *3s*-block. This means that B has ***two valence electrons*** in 3s (**$3s^2$**). Answer: **$3s^2$.**

Element C is located in Period 5, the *1st position* in *5s*-block). This means that there is only **one valence electron** in 5s (**$5s^1$**). Answer: **$5s^1$**.

rcise

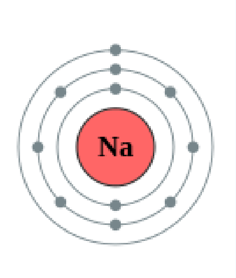
Using the location of Na is the periodic table (Figure 3.4.3), draw the shell diagram of sodium atom.

Answer

Sodium (Na) is the first element in the 3rd row (Period 3) in the periodic table. This means that the first shell and second shells of Na atom are filled to the maximum number of electrons.

The first shell **(1s)** *is filled with* ***2 electrons***. The second shell (2s and 2p) has a **total of *8 electrons***. And, the third (last) shell has ***1 electron***.

The shell diagram of the Na atom is shown below. The shell nearest the nucleus (first shell) has 2 electrons (2 dots), the second shell has 8 electrons and the last (outermost) shell has 1 electron. (**2.8.1**)



Concept Review Exercises

1. What is the difference between core electrons and valence electrons?

Answers

1. Electrons are organized into shells and subshells around nuclei.
2. The electron configuration states the arrangement of electrons in shells and subshells.
3. Valence electrons are in the highest-numbered shell; all other electrons are core electrons.

Key Takeaway

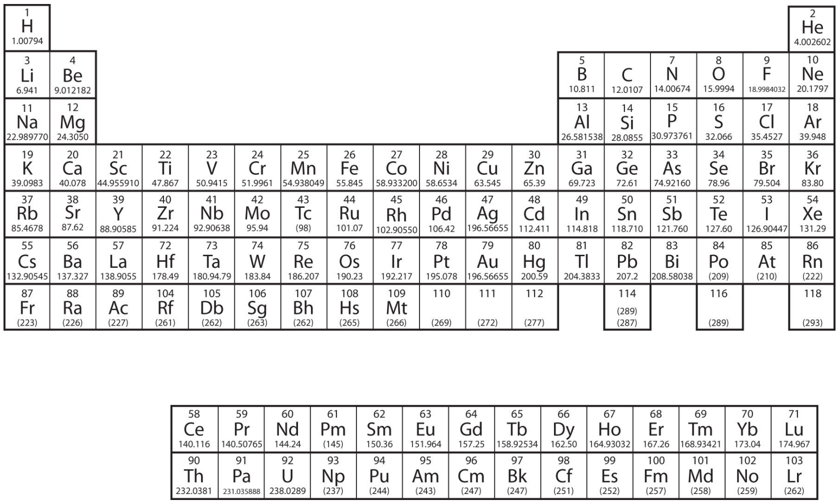
- Electrons are organized into shells and subshells about the nucleus of an atom.
- The valence electrons determine the reactivity of an atom.

3.5: Electron Configurations and the Periodic Table

Learning Objectives

- Relate the electron configurations of the elements to the shape of the periodic table.
- Determine the expected electron configuration of an element by its place on the periodic table.

Previously, we introduced the periodic table as a tool for organizing the known chemical elements. A periodic table is shown in Figure 3.5.1. The elements are listed by atomic number (the number of protons in the nucleus), and elements with similar chemical properties are grouped together in columns.



1 H 1.00794																	2 He 4.002602
3 Li 6.941	4 Be 9.012182											5 B 10.811	C 12.0107	7 N 14.00674	8 O 15.9994	9 F 18.9984032	10 Ne 20.1797
11 Na 22.989770	12 Mg 24.3050											13 Al 26.581538	14 Si 28.0855	15 P 30.973761	16 S 32.066	17 Cl 35.4527	18 Ar 39.948
19 K 39.0983	20 Ca 40.078	21 Sc 44.955910	22 Ti 47.867	23 V 50.9415	24 Cr 51.9961	25 Mn 54.938049	26 Fe 55.845	27 Co 58.933200	28 Ni 58.6534	29 Cu 63.545	30 Zn 65.39	31 Ga 69.723	32 Ge 72.61	33 As 74.92160	34 Se 78.96	35 Br 79.504	36 Kr 83.80
37 Rb 85.4678	38 Sr 87.62	39 Y 88.90585	40 Zr 91.224	41 Nb 92.90638	42 Mo 95.94	43 Tc (98)	44 Ru 101.07	45 Rh 102.90550	46 Pd 106.42	47 Ag 196.56655	48 Cd 112.411	49 In 114.818	50 Sn 118.710	51 Sb 121.760	52 Te 127.60	53 I 126.90447	54 Xe 131.29
55 Cs 132.90545	56 Ba 137.327	57 La 138.9055	72 Hf 178.49	73 Ta 180.94.79	74 W 183.84	75 Re 186.207	76 Os 190.23	77 Ir 192.217	78 Pt 195.078	79 Au 196.56655	80 Hg 200.59	81 Tl 204.3833	82 Pb 207.2	83 Bi 208.58038	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra (226)	89 Ac (227)	104 Rf (261)	105 Db (262)	106 Sg (263)	107 Bh (262)	108 Hs (265)	109 Mt (266)	110 (269)	111 (272)	112 (277)		114 (289) (287)		116 (289)		118 (293)

58 Ce 140.116	59 Pr 140.50765	60 Nd 144.24	61 Pm (145)	62 Sm 150.36	63 Eu 151.964	64 Gd 157.25	65 Tb 158.92534	66 Dy 162.50	67 Ho 164.93032	68 Er 167.26	69 Tm 168.93421	70 Yb 173.04	71 Lu 174.967
90 Th 232.0381	91 Pa 231.035888	92 U 238.0289	93 Np (237)	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (262)

Figure 3.5.1: The Periodic Table

Why does the periodic table have the structure it does? The answer is rather simple, if you understand electron configurations: the shape of the periodic table mimics the filling of the subshells with electrons.

> *The shape of the periodic table mimics the filling of the subshells with electrons.*

Let us start with H and He. Their electron configurations are $1s^1$ and $1s^2$, respectively; with He, the $n = 1$ shell is filled. These two elements make up the first row of the periodic table (Figure 3.5.2)

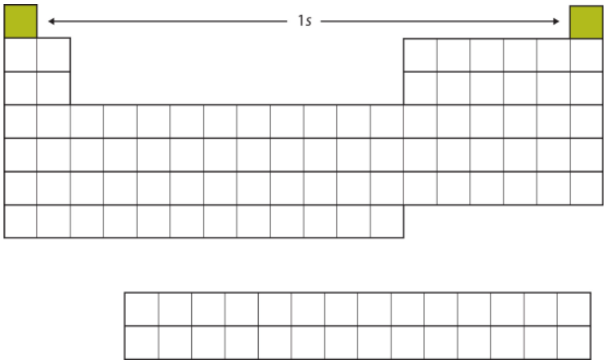


Figure 3.5.2: The 1*s* Subshell. H and He represent the filling of the 1*s* subshell.

The next two electrons, for Li and Be, would go into the 2*s* subshell. Figure 3.5.3 shows that these two elements are adjacent on the periodic table.

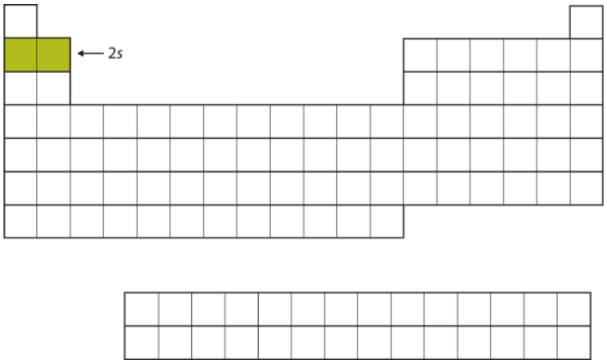


Figure 3.5.3: The 2s Subshell. In Li and Be, the 2*s* subshell is being filled.

For the next six elements, the 2*p* subshell is being occupied with electrons. On the right side of the periodic table, these six elements (B through Ne) are grouped together (Figure 3.5.4).

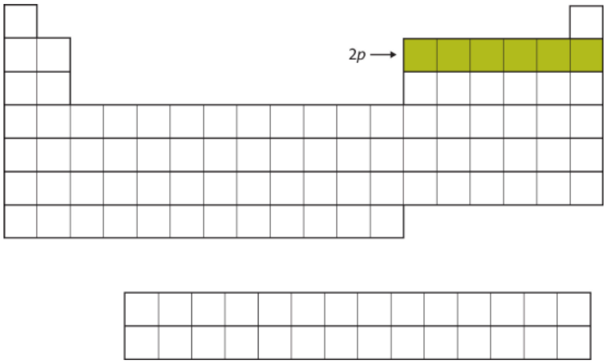


Figure 3.5.4: The 2*p* Subshell. For B through Ne, the 2*p* subshell is being occupied.

The next subshell to be filled is the 3*s* subshell. The elements when this subshell is being filled, Na and Mg, are back on the left side of the periodic table (Figure 3.5.5).

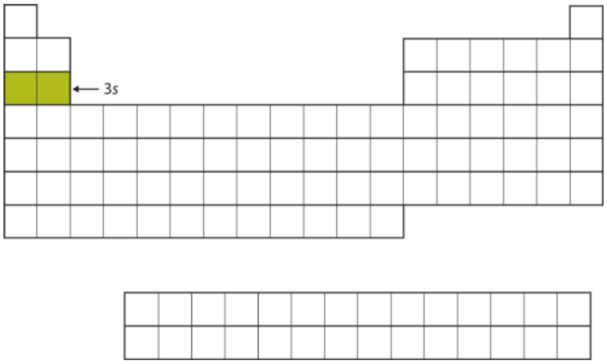


Figure 3.5.5: The 3*s* Subshell. Now the 3*s* subshell is being occupied.

Next, the 3*p* subshell is filled with the next six elements (Figure 3.5.6).

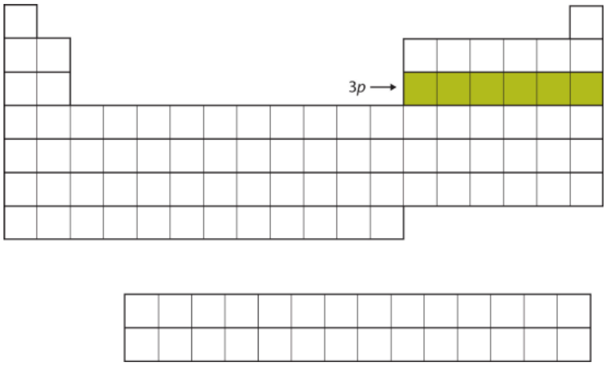


Figure 3.5.6: The 3*p* Subshell. Next, the 3*p* subshell is filled with electrons.

Instead of filling the 3*d* subshell next, electrons go into the 4*s* subshell (Figure 3.5.7).

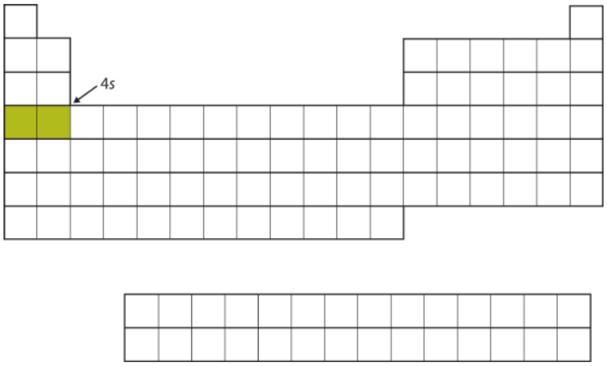


Figure 3.5.7: The 4*s* Subshell. The 4*s* subshell is filled before the 3*d* subshell. This is reflected in the structure of the periodic table.

After the 4*s* subshell is filled, the 3*d* subshell is filled with up to 10 electrons. This explains the section of 10 elements in the middle of the periodic table (Figure 3.5.8).

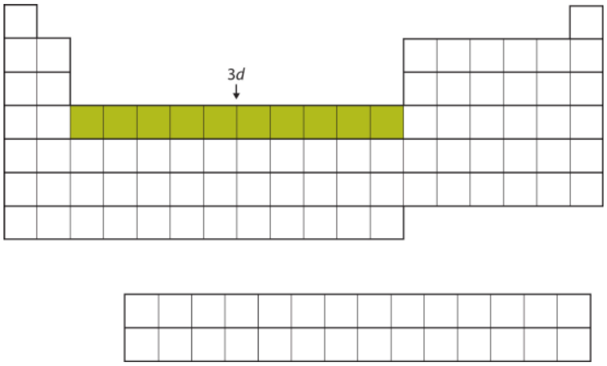


Figure 3.5.8: The 3*d* Subshell. The 3*d* subshell is filled in the middle section of the periodic table.

...And so forth. As we go across the rows of the periodic table, the overall shape of the table outlines how the electrons are occupying the shells and subshells.

The first two columns on the left side of the periodic table are where the *s* subshells are being occupied. Because of this, the first two rows of the periodic table are labeled the **s block**. Similarly, the **p block** are the right-most six columns of the periodic table, the **d block** is the middle 10 columns of the periodic table, while the **f block** is the 14-column section that is normally depicted as detached from the main body of the periodic table. It could be part of the main body, but then the periodic table would be rather long and cumbersome. Figure 3.5.9 shows the blocks of the periodic table.

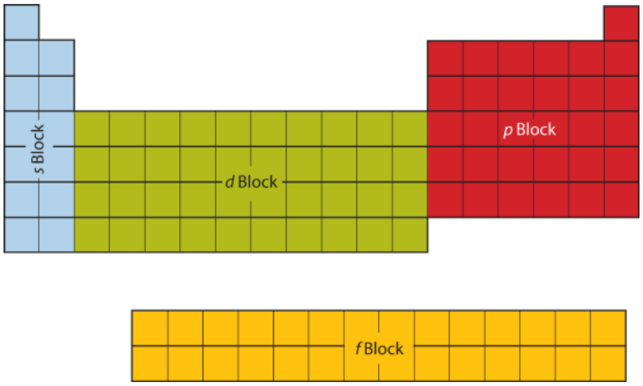


Figure 3.5.9: Blocks on the Periodic Table. The periodic table is separated into blocks depending on which subshell is being filled for the atoms that belong in that section.

The electrons in the highest-numbered shell, plus any electrons in the last unfilled subshell, are called **valence electrons**; the highest-numbered shell is called the **valence shell**. (The inner electrons are called *core electrons*.) The valence electrons largely control the chemistry of an atom. If we look at just the valence shell's electron configuration, we find that in each column, the valence shell's electron configuration is the same. For example, take the elements in the first column of the periodic table: H, Li, Na, K, Rb, and Cs. Their electron configurations (abbreviated for the larger atoms) are as follows, with the valence shell electron configuration highlighted:

Electrons, electron configurations, and the valence shell electron configuration highlighted.

H:	$1s^{\mathbf{1}}$
Li:	$1s^{2}2s^{\mathbf{1}}$
Na:	$[Ne]3s^{\mathbf{1}}$
K:	$[Ar]4s^{\mathbf{1}}$
Rb:	$[Kr]5s^{\mathbf{1}}$
Cs:	$[Xe]6s^{\mathbf{1}}$

They all have a similar electron configuration in their valence shells: a single *s* electron. Because much of the chemistry of an element is influenced by valence electrons, we would expect that these elements would have similar chemistry—*and they do*. The organization of electrons in atoms explains not only the shape of the periodic table, but also the fact that elements in the same column of the periodic table have similar chemistry.

The same concept applies to the other columns of the periodic table. Elements in each column have the same valence shell electron configurations, and the elements have some similar chemical properties. This is strictly true for all elements in the *s* and *p* blocks. In the *d* and *f* blocks, because there are exceptions to the order of filling of subshells with electrons, similar valence shells are not absolute in these blocks. However, many similarities do exist in these blocks, so a similarity in chemical properties is expected.

Similarity of valence shell electron configuration implies that we can determine the electron configuration of an atom solely by its position on the periodic table. Consider Se, as shown in Figure 3.5.10. It is in the fourth column of the *p* block. This means that its electron configuration should end in a p^4 electron configuration. Indeed, the electron configuration of Se is $[Ar]4s^{2}3d^{10}4p^{4}$, as expected.

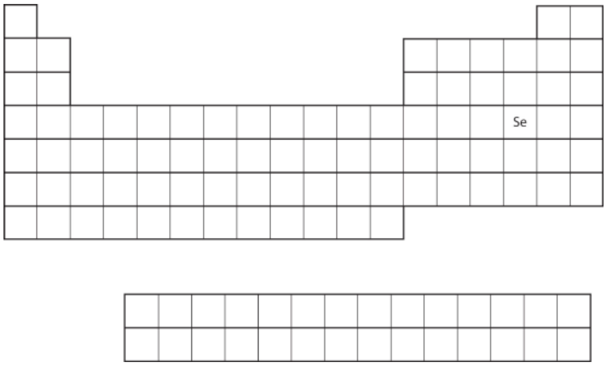


Figure 3.5.10: Selenium on the Periodic Table

Example 3.5.1: Predicting Electron Configurations

From the element's position on the periodic table, predict the valence shell electron configuration for each atom (Figure 3.5.11).

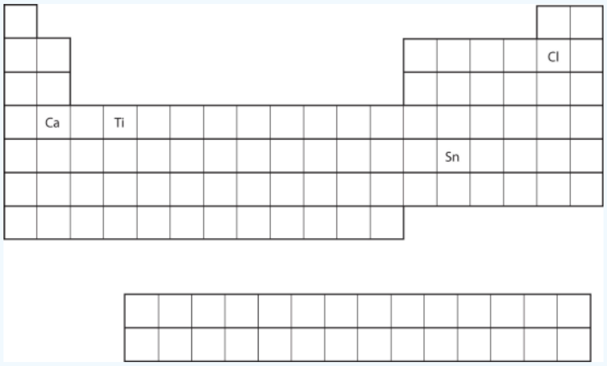


Figure 3.5.11: Various Elements on the Periodic Table

a. Ca
b. Sn

Solution

a. Ca is located in the second column of the *s* block. We expect that its electron configuration should end with s^2. Calcium's electron configuration is $[\text{Ar}]4s^2$.
b. Sn is located in the second column of the *p* block, so we expect that its electron configuration would end in p^2. Tin's electron configuration is $[\text{Kr}]5s^2 4d^{10} 5p^2$.

Exercise 3.5.1

From the element's position on the periodic table, predict the valence shell electron configuration for each atom. Figure 3.5.11

a. Ti
b. Cl

Answer a

$[\text{Ar}]4s^2 3d^2$

Answer b

$[\text{Ne}]3s^2 3p^5$

Summary

The arrangement of electrons in atoms is responsible for the shape of the periodic table. Electron configurations can be predicted by the position of an atom on the periodic table.

3.5.1: The Explanatory Power of the Quantum-Mechanical Model

Learning Objectives

- Give the name and location of specific groups on the periodic table, including alkali metals, alkaline earth metals, noble gases, halogens, and transition metals.
- Explain the relationship between the chemical behavior of families in the periodic table and their electron configurations.
- Identify elements that will have the most similar properties to a given element.

The chemical behavior of atoms is controlled by their electron configuration. Since the families of elements were organized by their chemical behavior, it is predictable that the individual members of each chemical family will have similar electron configurations.

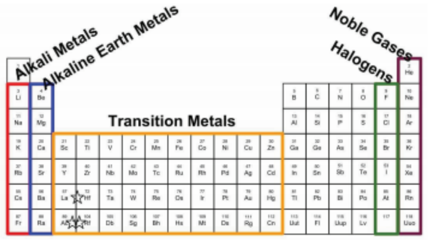
Families of the Periodic Table

Remember that Mendeleev arranged the periodic table so that elements with the most similar properties were placed in the same group. A **group** is a vertical column of the periodic table. All of the 1A elements have one valence electron. This is what causes these elements to react in the same ways as the other members of the family. The elements in 1A are all very reactive and form compounds in the same ratios with similar properties with other elements. Because of their similarities in their chemical properties, Mendeleev put these elements into the same group. Group 1A is also known as the **alkali metals**. Although most metals tend to be very hard, these metals are actually soft and can be easily cut.

Group 2A is also called the **alkaline earth metals**. Once again, because of their similarities in electron configurations, these elements have similar properties to each other. The same pattern is true of other groups on the periodic table. Remember, Mendeleev arranged the table so that elements with the most similar properties were in the same group on the periodic table.

It is important to recognize a couple of other important groups on the periodic table by their group name. Group 7A (or 17) elements are also called **halogens**. This group contains very reactive nonmetal elements.

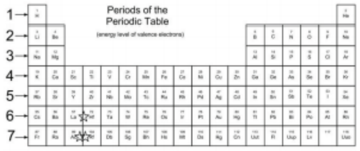
The **noble gases** are in group 8A. These elements also have similar properties to each other, the most significant property being that they are extremely unreactive, rarely forming compounds. The reason for this will be communicated later, when we discuss how compounds form. The elements in this group are also gases at room temperature.



Families of the periodic table.
CC – Tracy Poulsen

An alternate numbering system numbers all of the s, p, and d block elements from 1-18. In this numbering system, group 1A is group 1; group 2A is group 2; the halogens (7A) are group 17; and the noble gases (8A) are group 18. You will come across periodic tables with both numbering systems. It is important to recognize which numbering system is being used, and to be able to find the number of valence electrons in the main block elements, regardless of which numbering system is being used.

Periods of the Periodic Table



CC – Tracy Poulsen

If you can locate an element on the Periodic Table, you can use the element's position to figure out the energy level of the element's valence electrons. A **period** is a horizontal row of elements on the periodic table. For example, the elements sodium (Na) and magnesium (Mg) are both in period 3. The elements astatine (At) and radon (Rn) are both in period 6.

Summary

- The vertical columns on the periodic table are called groups or families because of their similar chemical behavior.
- All the members of a family of elements have the same number of valence electrons and similar chemical properties.
- The horizontal rows on the periodic table are called periods.

Vocabulary

- **Group (family)** - A vertical column of the periodic table.
- **Alkali metals** - Group 1A of the periodic table.
- **Alkaline earth metals** - Group 2A of the periodic table.
- **Halogens** - Group 7A of the periodic table.
- **Noble gases** - Group 8A of the periodic table.
- **Transition elements** - Groups 3 to 12 of the periodic table.

3.6: Periodic Trends - Atomic Size, Ionization Energy, and Metallic Character

Learning Objectives

- Be able to state how certain properties of atoms vary based on their relative position on the periodic table.

One of the reasons the periodic table is so useful is because its structure allows us to qualitatively determine how some properties of the elements vary versus their position on the periodic table. The variations of properties versus positions on the periodic table are called **periodic trends**. There is no other tool in science that allows us to judge relative properties of a class of objects like this, which makes the periodic table a very useful tool. Many periodic trends are general. There may be a few points where an opposite trend is seen, but there is an overall trend when considered across a whole row or down a whole column of the periodic table.

The first periodic trend we will consider is atomic radius. The **atomic radius** is an indication of the size of an atom. Although the concept of a definite radius of an atom is a bit fuzzy, atoms behave as if they have a certain radius. Such radii can be estimated from various experimental techniques, such as the x-ray crystallography of crystals.

As you go down a column of the periodic table, the atomic radii increase. This is because the valence electron shell is getting larger and there is a larger principal quantum number, so the valence shell lies physically farther away from the nucleus. This trend can be summarized as follows:

$$as \downarrow PT, atomic\ radius \uparrow \tag{3.6.1}$$

where PT stands for periodic table. Going across a row on the periodic table, left to right, the trend is different. Even though the valence shell maintains the same principal quantum number, the number of protons—and hence the nuclear charge—is increasing as you go across the row. The increasing positive charge casts a tighter grip on the valence electrons, so as you go across the periodic table, the atomic radii decrease. Again, we can summarize this trend as follows:

$$as \rightarrow PT, atomic\ radius \downarrow \tag{3.6.2}$$

Figure $3.6.1$ shows spheres representing the atoms of the *s* and *p* blocks from the periodic table to scale, showing the two trends for the atomic radius.

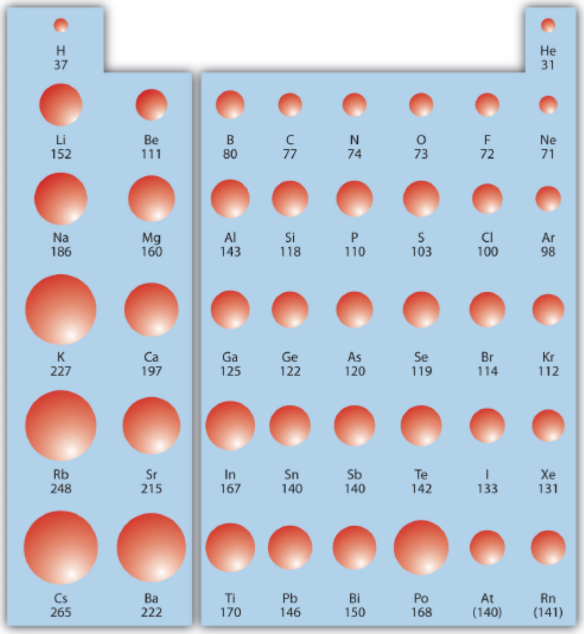


Figure $3.6.1$: Atomic Radii Trends on the Periodic Table. Although there are some reversals in the trend (e.g., see Po in the bottom row), atoms generally get smaller as you go across the periodic table and larger as you go down any one column. Numbers are the radii in pm.

Example 3.6.1: Atomic Radii

Referring only to a periodic table and not to Figure 3.6.1, which atom is larger in each pair?

a. Si or S
b. S or Te

Solution

a. Si is to the left of S on the periodic table; it is larger because as you go across the row, the atoms get smaller.
b. S is above Te on the periodic table; Te is larger because as you go down the column, the atoms get larger.

Exercise 3.6.1: Atomic Radii

Referring only to a periodic table and not to Figure 3.6.1, which atom is smaller, Ca or Br?

Answer

Br

Ionization energy (IE) is the amount of energy required to remove an electron from an atom in the gas phase:

$$A(g) \rightarrow A^{+}(g) + e^{-} \qquad \Delta H \equiv IE \tag{3.6.3}$$

IE is usually expressed in kJ/mol of atoms. It is always positive because the removal of an electron always requires that energy be put in (i.e., it is endothermic). IE also shows periodic trends. As you go down the periodic table, it becomes easier to remove an electron from an atom (i.e., IE decreases) because the valence electron is farther away from the nucleus. Thus,

$$as \downarrow PT,\ IE \downarrow \tag{3.6.4}$$

However, as you go across the periodic table and the electrons get drawn closer in, it takes more energy to remove an electron; as a result, IE increases:

$$as \rightarrow PT,\ IE \uparrow \tag{3.6.5}$$

Figure 3.6.2 shows values of IE versus position on the periodic table. Again, the trend is not absolute, but the general trends going across and down the periodic table should be obvious.

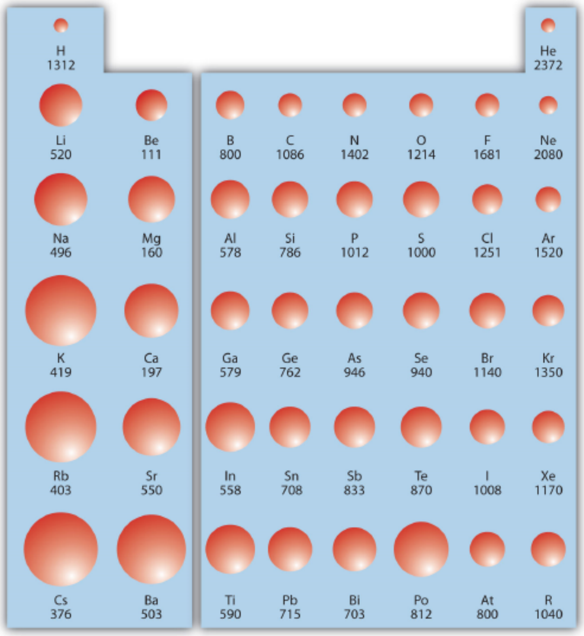


Figure 3.6.2: Ionization Energy on the Periodic Table. Values are in kJ/mol.

IE also shows an interesting trend within a given atom. This is because more than one IE can be defined by removing successive electrons (if the atom has them to begin with):

- First Ionization Energy (IE_1):

$$A(g) \rightarrow A^+(g) + e^- \tag{3.6.6}$$

- Second Ionization Energy (IE_2):

$$A^+(g) \rightarrow A^{2+}(g) + e^- \tag{3.6.7}$$

- Third Ionization Energy (IE_3):

$$A^{2+}(g) \rightarrow A^{3+}(g) + e^- \tag{3.6.8}$$

and so forth.

Each successive IE is larger than the previous because an electron is being removed from an atom with a progressively larger positive charge. However, IE takes a large jump when a successive ionization goes down into a new shell. For example, the following are the first three IEs for Mg, whose electron configuration is $1s^22s^22p^63s^2$:

- First Ionization Energy (IE_1) = 738 kJ/mol:

$$Mg(g) \rightarrow Mg^+(g) + e^- \tag{3.6.9}$$

- Second Ionization Energy (IE_2) = 1,450 kJ/mol:

$$Mg^+(g) \rightarrow Mg^{2+}(g) + e^- \tag{3.6.10}$$

- Third Ionization Energy (IE_3) = 7,734 kJ/mol:

$$Mg^{2+}(g) \rightarrow Mg^{3+}(g) + e^- \tag{3.6.11}$$

The second IE is twice the first, which is not a surprise: the first IE involves removing an electron from a neutral atom, while the second one involves removing an electron from a positive ion. The third IE, however, is over *five times* the previous one. Why is it so much larger? Because the first two electrons are removed from the 3*s* subshell, but the third electron has to be removed from the $n = 2$ shell (specifically, the 2*p* subshell, which is lower in energy than the $n = 3$ shell). Thus, it takes much more energy than just overcoming a larger ionic charge would suggest. It is trends like this that demonstrate that electrons within atoms are organized in groups.

✓ Example 3.6.2: Ionization Energies

Which atom in each pair has the larger first ionization energy?

a. Ca or Sr
b. K or K^+

Solution

a. Because Sr is below Ca on the periodic table, it is easier to remove an electron from it; thus, Ca has the higher IE.
b. Because K^+ has a positive charge, it will be harder to remove another electron from it, so its IE is larger than that of K. Indeed, it will be significantly larger because the next electron in K^+ to be removed comes from another shell.

? Exercise 3.6.2: Ionization Energies

Which atom has the lower ionization energy, C or F?

Answer

C

The opposite of IE is described by **electron affinity (EA),** which is the energy change when a gas-phase atom accepts an electron:

$$A(g) + e^- \rightarrow A^-(g) \qquad \Delta H \equiv EA \tag{3.6.12}$$

EA is also usually expressed in kJ/mol. EA also demonstrates some periodic trends, although they are less obvious than the other periodic trends discussed previously. Generally, as you go across the periodic table, EA increases its magnitude:

$$as \rightarrow PT,\ EA\uparrow \tag{3.6.13}$$

There is not a definitive trend as you go down the periodic table; sometimes EA increases, sometimes it decreases. Figure 3.6.3 shows EA values versus position on the periodic table for the *s*- and *p*-block elements. The trend is not absolute, especially considering the large positive EA values for the second column. However, the general trend going across the periodic table should be obvious.

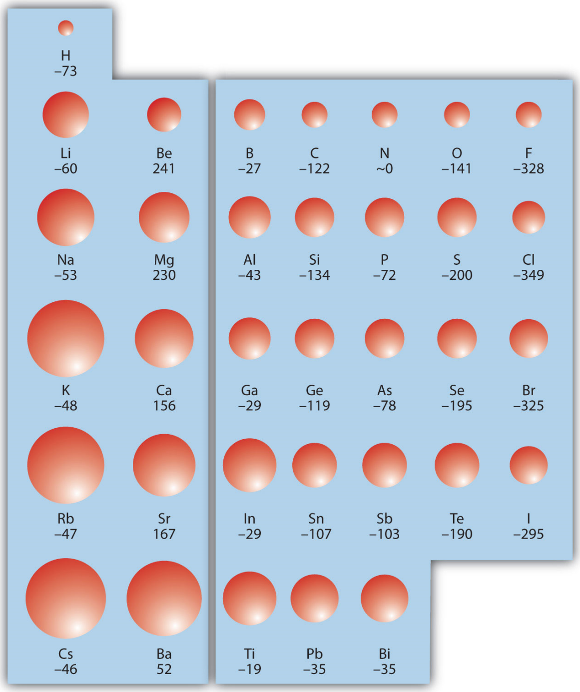


Figure 3.6.3: Electron Affinity on the Periodic Table. Values are in kJ/mol.

Example 3.6.3: Electron Affinities

Predict which atom in each pair will have the highest magnitude of Electron Affinity.

a. C or F
b. Na or S

Solution

a. C and F are in the same row on the periodic table, but F is farther to the right. Therefore, F should have the larger magnitude of EA.
b. Na and S are in the same row on the periodic table, but S is farther to the right. Therefore, S should have the larger magnitude of EA.

Exercise 3.6.3: Electron Affinities

Predict which atom will have the highest magnitude of Electron Affinity: As or Br.

Answer

Br

Metallic Character

The metallic character is used to define the chemical properties that metallic elements present. Generally, metals tend to lose electrons to form cations. Nonmetals tend to gain electrons to form anions. They also have a high oxidation potential—therefore they are easily oxidized and are strong reducing agents. Metals also form basic oxides; the more basic the oxide, the higher the metallic character.

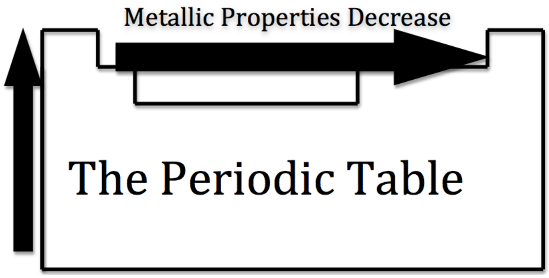


Figure 3.6.4: Courtesy of Jessica Thornton (UCD)

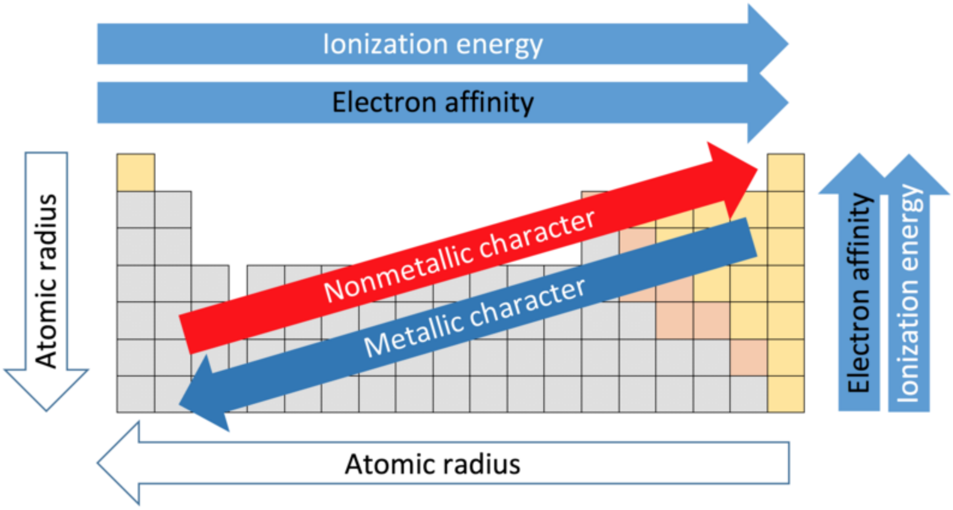
As you move across the table from left to right, the metallic character decreases, because the elements easily accept electrons to fill their valance shells. Therefore, these elements take on the nonmetallic character of forming anions. As you move up the table, the metallic character decreases, due to the greater pull that the nucleus has on the outer electrons. This greater pull makes it harder for the atoms to lose electrons and form cations.

Uses of the Periodic Properties of Elements

1. Predict greater or smaller atomic size and radial distribution in neutral atoms and ions.
2. Measure and compare ionization energies.
3. Compare electron affinities and electronegativities.
   - Predict redox potential.
   - Compare metallic character with other elements; ability to form cations.
   - Predict reactions that may or may not occur due to the trends.
   - Determine greater cell potential (sum of oxidation and reduction potential) between reactions.
   - Complete chemical reactions according to trends.

Summary

- Certain properties—notably atomic radius, ionization energies, and electron affinities—can be qualitatively understood by the positions of the elements on the periodic table. The major trends are summarized in the figure below.
- There are three factors that help in the prediction of the trends in the Periodic Table: number of protons in the nucleus, number of shells, and shielding effect.



Various periodic trends (CC BY-SA 4.0; Sandbh via Wikipedia)

Contributions & Attributions

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3.E: Electronic Structure (Exercises)

3.1: Light

**Read about light here and here.*

1. Describe the characteristics of a light wave.
2. What is the frequency of light if its wavelength is 7.33×10^{-5} m?
3. What is the frequency of light if its wavelength is 733 nm?
4. What is the wavelength of light if its frequency is $8.19 \times 10^{14}\ s^{-1}$?
5. Place the following in order of increasing energy.

   visible light, microwaves, radio waves, gamma radiation, x-rays, infrared light, ultraviolet light

6. "5G" cell phone signal uses electromagnetic radiation (light) with wavelengths of 0.001 m - 0.01 m. What category (see the previous question) does this fall into?

Answers:

1. Light has a wavelength and a frequency.
2. $4.09 \times 10^{12}\ s^{-1}$
3. $4.09 \times 10^{14}\ s^{-1}$
4. 3.66×10^{-7} m
5. radio waves < microwaves< infrared < visible < ultraviolet < x-rays < gamma
6. microwave

3.2: Electron Behaviour

1. Which of the following electron transitions would result in emission of light? ("n" is the shell)

   a. n=1 → n=3

   b. n=2 → n=1

   c. n=2 → n=5

   d. n=1 → n=7

2. Which of the following electron transitions would result in absorption of light? ("n" is the shell)

   a. n=5 → n=3

   b. n=2 → n=1

   c. n=2 → n=5

   d. n=7 → n=6

3. The hydrogen atom only has one electron. What shell represents the "ground state" for that electron?
4. The hydrogen atom only has one electron. What shell(s) represents an "excited state" for that electron?

Answers

1. Which of the following electron transitions would result in emission of light? ("n" is the shell)

   b. n=2 → n=1

2. Which of the following electron transitions would result in absorption of light? ("n" is the shell)

   c. n=2 → n=5

3. n = 1
4. n = 2 through n = ∞

3.3 - 3.5: Electron Configurations

1. How many subshells are completely filled with electrons for Na? How many subshells are unfilled?
2. What is the maximum number of electrons in the entire $n = 2$ shell?
3. Write the complete electron configuration for each atom.

    a. Si, 14 electrons
    b. Sc, 21 electron

4. Write the complete electron configuration for each atom.

    a. Cd, 48 electrons
    b. Mg, 12 electrons

5. Write the noble gas abbreviated electron configuration for each atom in question 3.

Answers

1. Three subshells ($1s$, $2s$, $2p$) are completely filled, and one shell ($3s$) is partially filled.
2. 8 electrons
3. a. $1s^2 2s^2 2p^6 3s^2 3p^2$, b. $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^1$
4. a. $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10}$, $1s^2 2s^2 2p^6 3s^2$
5. a. $[\mathrm{Ne}]3s^2 3p^2$, $[\mathrm{Ar}]4s^2 3d^1$

3.6: Periodic Trends

1. State the trends in atomic radii as you go across (right) and down the periodic table.
2. State the trends in IE as you go across and down the periodic table.
3. Which atom of each pair is larger?

    a. Na or Cs
    b. N or Bi
    c. C or Ge
    d. C or B

4. Which atom has the higher IE?

    a. Na or S
    b. Cl or Br

5. Which atom has the greater magnitude of EA?

    a. Cl or F
    b. Al or Cl

Answers

1. Across (right) = smaller radius/size, down = larger radius/size
2. Across (right) = higher IE, down = lower IE
3. Which atom of each pair is larger?

    a. Cs
    b. Bi
    c. Ge
    d. B

4. Which atom has the higher IE?

    a. S
    b. Cl

5. Which atom has the greater magnitude of EA?

    a. F
    b. Cl

CHAPTER OVERVIEW

4: Compounds and Chemical Bonds

4.1: Properties and Changes of Matter

In addition to discussing the categories of matter, we can also discuss both its properties and ways in which it may change. Both properties and changes may be categorized as either physical or chemical. Understanding the differences between physical and chemical properties or changes requires an understanding of how matter behaves on the level of atoms and molecules. We are able to discuss each of these in broad terms now, but will continue to sharpen our perspective on this by learning more about the behavior of atoms and molecules in the chapters to come. Regardless of the change, it is also important to understand that matter itself is essentially permanent, and it does not go away even if our senses can't detect it in the same way that they did before. These concepts will be explored in the subsections of this section.

4.1.1: Differences in Matter- Physical and Chemical Properties

Learning Objectives

To separate physical from chemical properties.

All matter has physical and chemical properties. Physical properties are characteristics that scientists can measure without changing the composition of the sample under study, such as mass, color, and volume (the amount of space occupied by a sample). Chemical properties describe the characteristic ability of a substance to react to form new substances; they include its flammability and susceptibility to corrosion. All samples of a pure substance have the same chemical and physical properties. For example, pure copper is always a reddish-brown solid (a physical property) and always dissolves in dilute nitric acid to produce a blue solution and a brown gas (a chemical property).

Physical Property

A *physical property* is a characteristic of a substance that can be observed or measured without changing the identity of the substance. Silver is a shiny metal that conducts electricity very well. It can be molded into thin sheets, a property called malleability. Salt is dull and brittle and conducts electricity when it has been dissolved into water, which it does quite easily. Physical properties of matter include color, hardness, malleability, solubility, electrical conductivity, density, melting point, and boiling point.

For the elements, color does not vary much from one element to the next. The vast majority of elements are colorless, silver, or gray. Some elements do have distinctive colors: sulfur and chlorine are yellow, copper is (of course) copper-colored, and elemental bromine is red. However, density can be a very useful parameter for identifying an element. Of the materials that exist as solids at room temperature, iodine has a very low density compared to zinc, chromium, and tin. Gold has a very high density, as does platinum. 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 4.1.1.1. Notice that corn oil has a lower mass to volume ratio than water. This means that when added to water, corn oil will “float.”

Table 4.1.1.1: Densities of Common Substances

Substance	Density at 25°C (g/cm3)
blood	1.035
body fat	0.918
whole milk	1.030
corn oil	0.922
mayonnaise	0.910
honey	1.420

Hardness helps determine how an element (especially a metal) might be used. Many elements are fairly soft (silver and gold, for example) while others (such as titanium, tungsten, and chromium) are much harder. Carbon is an interesting example of hardness. In graphite, (the "lead" found in pencils) the carbon is very soft, while the carbon in a diamond is roughly seven times as hard.

Figure 4.1.1.1: Pencil (left) and Diamond ring (right). Both are a form of carbon, but exhibit very different physical properties.

Melting and boiling points are somewhat unique identifiers, especially of compounds. In addition to giving some idea as to the identity of the compound, important information can be obtained about the purity of the material.

Chemical Properties

Chemical properties of matter describe its potential to undergo some chemical change or reaction by virtue of its composition. The elements, electrons, and bonds that are present give the matter potential for chemical change. It is quite difficult to define a chemical property without using the word "change". Eventually, after studying chemistry for some time, you should be able to look at the formula of a compound and state some chemical property. For example, hydrogen has the potential to ignite and explode given the right conditions—this is a chemical property. Metals in general have the chemical property of reacting with an acid. Zinc reacts with hydrochloric acid to produce hydrogen gas—this is a chemical property.

Figure 4.1.1.2: Heavy rust on the links of a chain near the Golden Gate Bridge in San Francisco; it was continuously exposed to moisture and salt spray, causing surface breakdown, cracking, and flaking of the metal. (CC BY-SA 3.0; Marlith).

A chemical property of iron is its capability of combining with oxygen to form iron oxide, the chemical name of rust (Figure 4.1.1.2). The more general term for rusting and other similar processes is corrosion. Other terms that are commonly used in descriptions of chemical changes are burn, rot, explode, decompose, and ferment. Chemical properties are very useful in identifying substances. However, unlike physical properties, chemical properties can only be observed as the substance is in the process of being changed into a different substance.

Table 4.1.1.2: Contrasting Physical and Chemical Properties

Physical Properties	Chemical Properties
Gallium metal melts at 30 ^{o}C.	Iron metal rusts.
Mercury is a very dense liquid.	A green banana turns yellow when it ripens.
Gold is shiny.	A dry piece of paper burns.

✓ Example 4.1.1.1

Which of the following is a chemical property of iron?

a. Iron corrodes in moist air.
b. Density = 7.874 g/cm^3
c. Iron is soft when pure.
d. Iron melts at 1808 K.

Solution

"Iron corrodes in moist air" is the only chemical property of iron from the list.

? Exercise $4.1.1.1A$

Which of the following is a physical property of matter?

a. corrosiveness
b. pH (acidity)
c. density
d. flammability

Answer

c

? Exercise $4.1.1.1B$

Which of the following is a chemical property?

a. flammability
b. melting point
c. boiling point
d. density

Answer

a

Summary

A physical property is a characteristic of a substance that can be observed or measured without changing the identity of the substance. Physical properties include color, density, hardness, and melting and boiling points. A chemical property describes the ability of a substance to undergo a specific chemical change. To identify a chemical property, we look for a chemical change. A chemical change always produces one or more types of matter that differ from the matter present before the change. The formation of rust is a chemical change because rust is a different kind of matter than the iron, oxygen, and water present before the rust formed.

4.1.2: Changes in Matter - Physical and Chemical Changes

Learning Objectives

- Label a change as chemical or physical.
- List evidence that can indicate a chemical change occurred.

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. Chemists learn a lot about the nature of matter by studying the changes that matter can undergo. Chemists make a distinction between two different types of changes that they study—physical changes and chemical changes.

Physical Change

Physical changes are changes in which no bonds are broken or formed. 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. Because the ending materials are the same as the beginning materials, the properties (such as color, boiling point, etc.) will also be the same. 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 melts, its shape changes as it acquires the ability to flow. However, its composition does not change. Melting is an example of a physical change. A physical change is a change to a sample of matter in which some properties of the material change, but the identity of the matter does not. When liquid water is heated, it changes to water vapor. However, even though the physical properties have changed, the molecules are exactly the same as before. We still have each water molecule containing two hydrogen atoms and one oxygen atom covalently bonded. When you have a jar containing a mixture of pennies and nickels and you sort the mixture so that you have one pile of pennies and another pile of nickels, you have not altered the identity of the pennies or the nickels—you've merely separated them into two groups. This would be an example of a physical change. 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 4.1.2.1: 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).

Physical changes can further be classified as reversible or irreversible. The melted ice cube may be refrozen, so melting is a reversible physical change. Physical changes that involve a change of state are all reversible. Other changes of state include **vaporization** (liquid to gas), **freezing** (liquid to solid), and **condensation** (gas to liquid). Dissolving is also a reversible physical change. When salt is dissolved into water, the salt is said to have entered the aqueous state. The salt may be regained by boiling off the water, leaving the salt behind.

Chemical Change

Chemical changes occur when bonds are broken and/or formed between molecules or atoms. This means 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. Chemical changes are frequently harder to reverse than physical changes.

One good example of a chemical change is burning a candle. The act of burning paper 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, on the left there is a molecule of methane, CH_4, and two molecules of oxygen, O_2; on the right are two molecules of water, H_2O, and one molecule of carbon dioxide, CO_2. In this case, not only has the appearance changed, but the structure of the molecules has also changed. The new substances do not have the same chemical properties as the original ones. Therefore, this is a chemical change.

Figure 4.1.2.2: Burning of wax to generate water and carbon dioxide is a chemical reaction. (CC-SA-BY-3.0; Andrikkos)

We can't actually see molecules breaking and forming bonds, although that's what defines chemical changes. We have to make other observations to indicate that a chemical change has happened. Some of the evidence for chemical change 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).

✓ Example 4.1.2.1

Label each of the following changes as a physical or chemical change. Give evidence to support your answer.

a. Boiling water.
b. A nail rusting.
c. A green solution and colorless solution are mixed. The resulting mixture is a solution with a pale green color.
d. Two colorless solutions are mixed. The resulting mixture has a yellow precipitate.

Solution

a. Physical: boiling and melting are physical changes. When water boils, no bonds are broken or formed. The change could be written: $H_2O\,(l) \rightarrow H_2O\,(g)$
b. Chemical: The dark grey nail changes color to form an orange flaky substance (the rust); this must be a chemical change. Color changes indicate chemical change. The following reaction occurs: $Fe + O_2 \rightarrow Fe_2O_3$

c. Physical: because none of the properties changed, this is a physical change. The green mixture is still green and the colorless solution is still colorless. They have just been spread together. No color *change* occurred or other evidence of chemical change.
d. Chemical: the formation of a precipitate and the color change from colorless to yellow indicate a chemical change.

? Exercise 4.1.2.1

Label each of the following changes as a physical or chemical change.

a. A mirror is broken.
b. An iron nail corroded in moist air
c. Copper metal is melted.
d. A catalytic converter changes nitrogen dioxide to nitrogen gas and oxygen gas.

Answer a:

physical change

Answer b:

chemical change

Answer c:

physical change

Answer d:

chemical change

Separating Mixtures Through Physical Changes

Homogeneous mixtures (solutions) can be separated into their component substances by physical processes that rely on differences in some physical property, such as differences in their boiling points. Two of these separation methods are distillation and crystallization. Distillation makes use of differences in volatility, a measure of how easily a substance is converted to a gas at a given temperature. A simple distillation apparatus for separating a mixture of substances, at least one of which is a liquid. The most volatile component boils first and is condensed back to a liquid in the water-cooled condenser, from which it flows into the receiving flask. If a solution of salt and water is distilled, for example, the more volatile component, pure water, collects in the receiving flask, while the salt remains in the distillation flask.

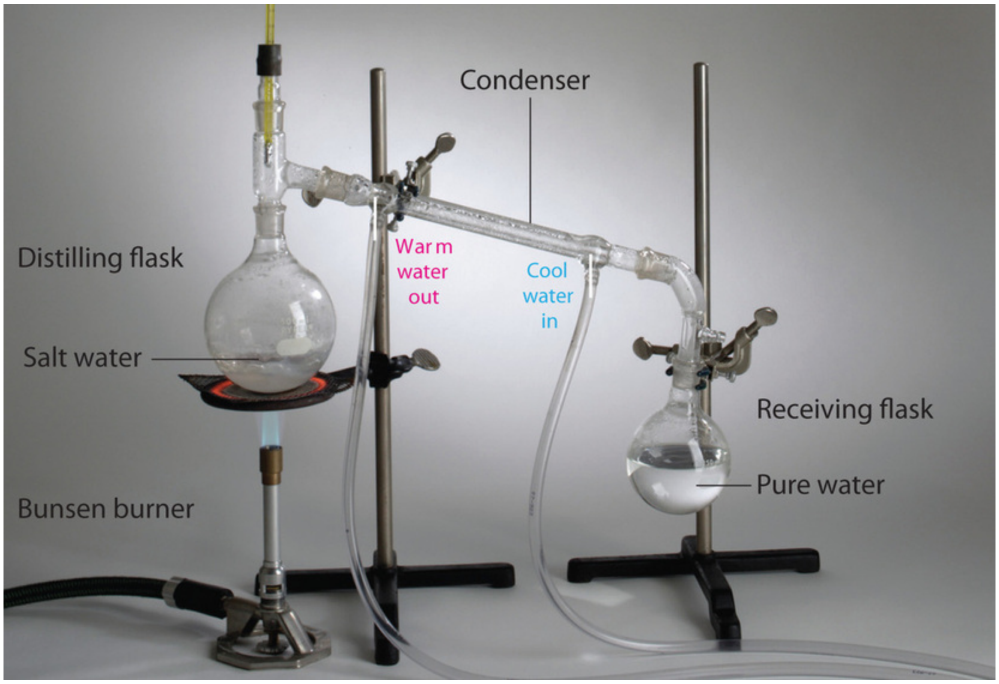

Figure 4.1.2.3: *The Distillation of a Solution of Table Salt in Water. The solution of salt in water is heated in the distilling flask until it boils. The resulting vapor is enriched in the more volatile component (water), which condenses to a liquid in the cold condenser and is then collected in the receiving flask.*

Parts of a distillation setup: Bunsen burner, salt water in distilling flask, condenser with cool water in and warm water out, pure water in receiving flask

Mixtures of two or more liquids with different boiling points can be separated with a more complex distillation apparatus. One example is the refining of crude petroleum into a range of useful products: aviation fuel, gasoline, kerosene, diesel fuel, and lubricating oil (in the approximate order of decreasing volatility). Another example is the distillation of alcoholic spirits such as brandy or whiskey. This relatively simple procedure caused more than a few headaches for federal authorities in the 1920s during the era of Prohibition, when illegal stills proliferated in remote regions of the United States.

Another example for using physical properties to separate mixtures is filtration (Figure 4.1.2.4). Filtration is any mechanical, physical or biological operation that separates solids from fluids (liquids or gases) by adding a medium through which only the fluid can pass. The fluid that passes through is called the filtrate. There are many different methods of filtration; all aim to attain the separation of substances. Separation is achieved by some form of interaction between the substance or objects to be removed and the filter. The substance that is to pass through the filter must be a fluid, i.e. a liquid or gas. Methods of filtration vary depending on the location of the targeted material, i.e. whether it is dissolved in the fluid phase or suspended as a solid.

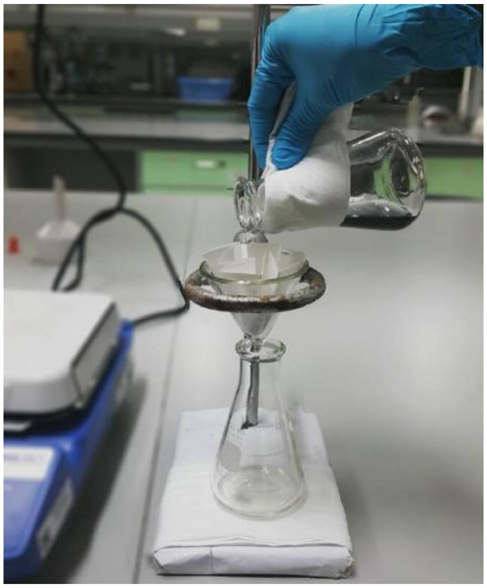

Figure 4.1.2.4: *Filtration for the separation of solids from a hot solution. (CC BY-SA 4.0; Suman6395).*

Summary

- Chemists make a distinction between two different types of changes that they study—physical changes and chemical changes.
- Physical changes are changes that do not alter the identity of a substance.
- Chemical changes are changes that occur when one substance is turned into another substance.
- Chemical changes are frequently harder to reverse than physical changes. Observations that indicate a chemical change has occurred include color change, temperature change, light given off, formation of bubbles, formation of a precipitate, etc.

Contributions & Attributions

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- Boundless (www.boundless.com)

4.1.3: Conservation of Mass - There is No New Matter

It may seem as though burning destroys matter, but the same amount, or mass, of matter still exists after a campfire as before. Look at Figure 4.1.3.1below. It shows that when wood burns, it combines with oxygen and changes not only to ashes, but also to carbon dioxide and water vapor. The gases float off into the air, leaving behind just the ashes. Suppose you had measured the mass of the wood before it burned and the mass of the ashes after it burned. Also suppose you had been able to measure the oxygen used by the fire and the gases produced by the fire. What would you find? The total mass of matter after the fire would be the same as the total mass of matter before the fire.

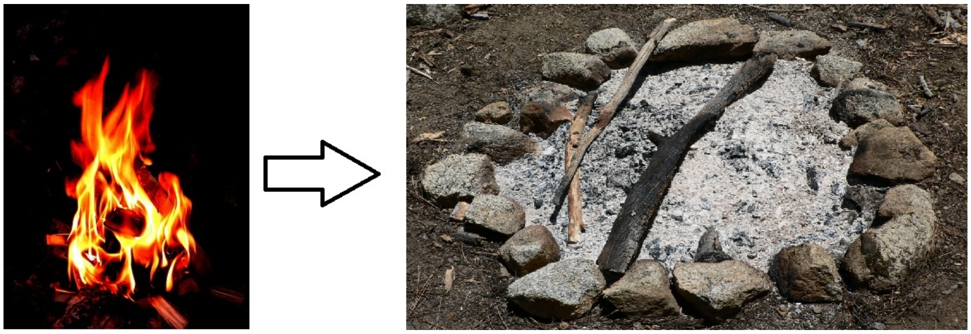

Figure 4.1.3.1: Burning is a chemical process. The flames are caused as a result of a fuel undergoing combustion (burning). (CC BY-SA 2.5; Einar Helland Berger for fire and Walter Siegmund for ash).

Law of Conservation of Mass

The law of conservation of mass was created in 1789 by a French chemist, Antoine Lavoisier. The **law of conservation of mass** states that matter cannot be created or destroyed in a chemical reaction. For example, when wood burns, the mass of the soot, ashes, and gases equals the original mass of the charcoal and the oxygen when it first reacted. So the mass of the product equals the mass of the reactant. A reactant is the chemical reaction of two or more elements to make a new substance, and a product is the substance that is formed as the result of a chemical reaction (Video 4.1.3.1). Matter and its corresponding mass may not be able to be created or destroyed, but can change forms to other substances like liquids, gases, and solids.

Video 4.1.3.1: This is a nice little demonstration showing the Conservation of Mass in action.

If you witness a 300 kg tree burn to the ground, there are only ashes left after the burn, and all of them together weigh 10 kg. It may make you wonder where the other 290 kg went. The missing 290 kg was released into the atmosphere as smoke, so the only thing left that you can see is the 10 kg of ash. If you know the law of conservation of mass, then you know that the other 290 kg has to go somewhere, because it has to equal the mass of the tree before it burnt down.

✓ Example 4.1.3.1

If heating 10.0 grams of calcium carbonate ($CaCO_3$) produces 4.4 g of carbon dioxide (CO_2) and 5.6 g of calcium oxide (CaO), show that these observations are in agreement with the law of conservation of mass.

Solution

$$\text{Mass of the reactants} = \text{Mass of the products}$$

$$10.0 \text{ g of } CaCO_3 = 4.4 \text{ g of } CO_2 + 5.6 \text{ g of } CaO$$

$$10.0 \text{ g of reactant} = 10.0 \text{ g of products}$$

Because the mass of the reactant is equal to the mass of the products, the observations are in agreement with the law of conservation of mass.

? Exercise 4.1.3.1

Potassium hydroxide (KOH) readily reacts with carbon dioxide (CO_2) to produce potassium carbonate (K_2CO_3) and water (H_2O). How many grams of potassium carbonate are produced if 224.4 g of KOH reacts with 88.0 g of CO_2? The reaction also produces 36.0 g of water.

Answer

276.4 g of potassium carbonate

The Law is also applicable to both chemical and physical changes. For example, if you have an ice cube that melts into a liquid and you heat that liquid up, it becomes a gas. It will appear to have disappeared, but is still there.

Summary

- Burning and other changes in matter do not destroy matter.
- The mass of matter is always the same before and after the changes occur.
- The law of conservation of mass states that matter cannot be created or destroyed.

Contributions & Attributions

- Binod Shrestha (University of Lorraine)

4.2: Summary of Matter and Changes

Learning Objective

- Learn the basic terms used to describe matter

The definition of chemistry—the study of the interactions of matter with other matter and with energy—uses some terms that should also be defined. We start the study of chemistry by defining basic terms.

Matter

Matter is anything that has mass and takes up space. A book is matter, a computer is matter, food is matter, and dirt in the ground is matter. Sometimes matter may be difficult to identify. For example, air is matter, but because it is so thin compared to other matter (e.g., a book, a computer, food, and dirt), we sometimes forget that air has mass and takes up space. Things that are not matter include thoughts, ideas, emotions, and hopes.

Example 4.2.1

Which of the following is matter and not matter?

a. a hot dog
b. love
c. a tree

Solution

a. A hot dog has mass and takes up space, so it is matter.
b. Love is an emotion, and emotions are not matter.
c. A tree has mass and takes up space, so it is matter.

Exercise 4.2.1

Which of the following is matter and not matter?

a. the moon
b. an idea for a new invention

Answer a

The moon is matter.

Answer b

The invention itself may be matter, but the idea for it is not.

To understand matter and how it changes, we need to be able to describe matter. There are two basic ways to describe matter: physical properties and chemical properties.

Physical properties

Physical properties are characteristics that describe matter as it exists. Some physical characteristics of matter are shape, color, size, and temperature. An important physical property is the **phase** (or **state**) of matter. The three fundamental phases of matter are solid, liquid, and gas (Figure 4.2.1).

Figure 4.2.1: The Phases of Matter. Chemistry recognizes three fundamental phases of matter: solid (left), liquid (middle), and gas (right). (CC BY-SA 3.0; Spirit469)

The solid state depicted is an ice sculpture of an angel, the liquid state is a drop of water, and the gas is clouds made of water vapor.

Chemical Properties

Chemical properties are characteristics of matter that describe how matter changes form in the presence of other matter. Does a sample of matter burn? Burning is a chemical property. Does it behave violently when put in water? This reaction is a chemical property as well (Figure 4.2.2). In the following chapters, we will see how descriptions of physical and chemical properties are important aspects of chemistry.

Figure 4.2.2: Chemical Properties. The fact that this match burns is a chemical property of the match. (Sebastian Ritter (Rise0011)).

Physical Change

A physical change occurs when a sample of matter changes one or more of its physical properties. For example, a solid may melt (Figure 4.2.3), or alcohol in a thermometer may change volume as the temperature changes. A physical change does not affect the chemical composition of matter.

Figure 4.2.2: Physical Changes: The solid ice melts into liquid water—a physical change. A time-lapse animation of ice cubes melting in a glass over 50 minutes. (Public Domain; Moussa).

Chemical Change

Chemical change is the process of demonstrating a chemical property, such as the burning match in Figure 4.2.2 "Chemical Properties". As the matter in the match burns, its chemical composition changes, and new forms of matter with new physical properties are created. Note that chemical changes are frequently accompanied by physical changes, as the new matter will likely have different physical properties from the original matter.

Example 4.2.2

Describe each process as a physical change or a chemical change.

a. Water in the air turns into snow.
b. A person's hair is cut.
c. Bread dough becomes fresh bread in an oven.

Solution

a. Because the water is going from a gas phase to a solid phase, this is a physical change.
b. Your long hair is being shortened. This is a physical change.
c. Because of the oven's temperature, chemical changes are occurring in the bread dough to make fresh bread. These are chemical changes. (In fact, a lot of cooking involves chemical changes.)

Exercise 4.2.2

Identify each process as a physical change or a chemical change.

a. A fire is raging in a fireplace.
b. Water is warmed to make a cup of coffee.

Answer a

chemical change

Answer b

physical change

Substance

A sample of matter that has the same physical and chemical properties throughout is called a substance. Sometimes the phrase *pure substance* is used, but the word *pure* isn't needed. The definition of the term *substance* is an example of how chemistry has a specific definition for a word that is used in everyday language with a different, vaguer definition. Here, we will use the term *substance* with its strict chemical definition.

> *Chemistry recognizes two different types of substances: elements and compounds.*

Element

An element is the simplest type of chemical substance; it cannot be broken down into simpler chemical substances by ordinary chemical means. There are 118 elements known to science, of which 80 are stable. (The other elements are radioactive, a condition we will consider in Chapter 15.) Each element has its own unique set of physical and chemical properties. Examples of elements include iron, carbon, and gold.

Compound

A compound is a combination of more than one element. The physical and chemical properties of a compound are different from the physical and chemical properties of its constituent elements; that is, it behaves as a completely different substance. There are over 50 million compounds known, and more are being discovered daily. Examples of compounds include water, penicillin, and sodium chloride (the chemical name for common table salt).

Mixtures

Physical combinations of more than one substance are called mixtures. Elements and compounds are not the only ways in which matter can be present. We frequently encounter objects that are physical combinations of more than one element or compound—mixtures. There are two types of mixtures.

Heterogeneous Mixture

A heterogeneous mixture is a mixture composed of two or more substances. It is easy to tell, sometimes by the naked eye, that more than one substance is present.

Homogeneous Mixture/ Solution

A homogeneous mixture is a combination of two or more substances that is so intimately mixed, that the mixture behaves as a single substance. Another word for a homogeneous mixture is a solution. Thus, a combination of salt and steel wool is a heterogeneous mixture because it is easy to see which particles of the matter are salt crystals and which are steel wool. On the other hand, if you take salt crystals and dissolve them in water, it is very difficult to tell that you have more than one substance present just by looking—even if you use a powerful microscope. The salt dissolved in water is a homogeneous mixture, or a solution (Figure $4.2.3$).

Figure $4.2.3$: Types of Mixtures © Thinkstock. On the left, the combination of two substances is a heterogeneous mixture because the particles of the two components look different. On the right, the salt crystals have dissolved in the water so finely that you cannot tell that salt is present. The homogeneous mixture appears like a single substance.

✓ Example $4.2.3$

Identify the following combinations as heterogeneous mixtures or homogenous mixtures.

a. soda water (carbon dioxide is dissolved in water)
b. a mixture of iron metal filings and sulfur powder (both iron and sulfur are elements)

Solution

a. Because carbon dioxide is dissolved in water, we can infer from the behavior of salt crystals dissolved in water that carbon dioxide dissolved in water is (also) a homogeneous mixture.
b. Assuming that the iron and sulfur are simply mixed together, it should be easy to see what is iron and what is sulfur, so this is a heterogeneous mixture.

? Exercise $4.2.3$

a. the human body
b. an amalgam, a combination of some other metals dissolved in a small amount of mercury

Answer a

heterogeneous mixture

Answer b

homogeneous mixture

There are other descriptors that we can use to describe matter, especially elements. We can usually divide elements into metals and nonmetals, and each set shares certain (but not always all) properties.

Metal

A metal is an element that conducts electricity and heat well and is shiny, silvery, solid, ductile, and malleable. At room temperature, metals are solid (although mercury is a well-known exception). A metal is ductile because it can be drawn into thin wires (a property called *ductility*); and malleable because it can be pounded into thin sheets (a property called *malleability*).

Nonmetal

A non-metal is an element that is brittle when solid, and does not conduct electricity or heat very well. Non-metals cannot be made into thin sheets or wires (Figure $4.2.4$). Nonmetals also exist in a variety of phases and colors at room temperature.

Semi-metals

Some elements have properties of both metals and nonmetals and are called semi-metals (or metalloids). We will see later how these descriptions can be assigned rather easily to various elements.

Figure $4.2.4$: Semimetals © Thinkstock. On the left is some elemental mercury, the only metal that exists as a liquid at room temperature. It has all the other expected properties of a metal. On the right, elemental sulfur is a yellow nonmetal that usually is found as a powder.

Describing Matter Flowchart

"Describing Matter" is a flowchart of the relationships among the different ways of describing matter.

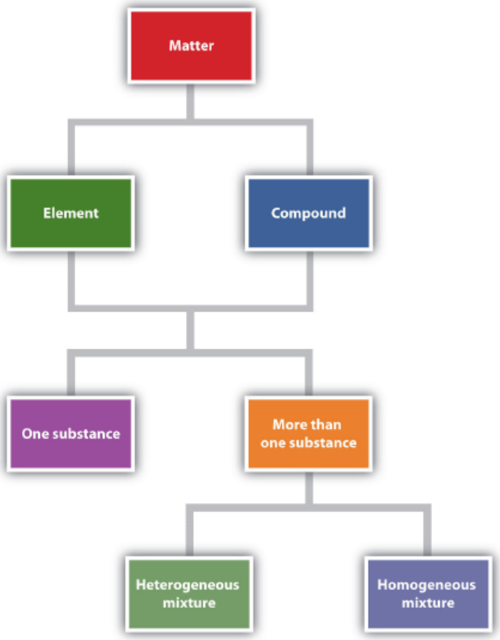

Figure 4.2.5: Describing Matter. This flowchart shows how matter can be described.

Matter forks into element & compound which fork into 1 substance & more than 1 substance. More than 1 substance is homogenous or heterogenous.

✓ Example 4.2.1: Chemistry is Everywhere: In the Morning

Most people have a morning ritual, a process that they go through every morning to get ready for the day. Chemistry appears in many of these activities.

- If you take a shower or bath in the morning, you probably use soap, shampoo, or both. These items contain chemicals that interact with the oil and dirt on your body and hair to remove them and wash them away. Many of these products also contain chemicals that make you smell good; they are called *fragrances*.
- When you brush your teeth in the morning, you usually use toothpaste, a form of soap, to clean your teeth. Toothpastes typically contain tiny, hard particles called *abrasives* that physically scrub your teeth. Many toothpastes also contain fluoride, a substance that chemically interacts with the surface of the teeth to help prevent cavities.
- Perhaps you take vitamins, supplements, or medicines every morning. Vitamins and other supplements contain chemicals your body needs in small amounts to function properly. Medicines are chemicals that help combat diseases and promote health.
- Perhaps you make some fried eggs for breakfast. Frying eggs involves heating them enough so that a chemical reaction occurs to cook the eggs.
- After you eat, the food in your stomach is chemically reacted so that the body (mostly the intestines) can absorb food, water, and other nutrients.
- If you drive or take the bus to school or work, you are using a vehicle that probably burns gasoline, a material that burns fairly easily and provides energy to power the vehicle. Recall that burning is a chemical change.

These are just a few examples of how chemistry impacts your everyday life. And we haven't even made it to lunch yet!

Figure 4.2.6: Chemistry in Real Life © Thinkstock. Examples of chemistry can be found everywhere—in personal hygiene products, food, and motor vehicles.

Personal hygiene products (left), food (middle), and motor vehicles (right) images next to one another.

Key Takeaways

- Chemistry is the study of matter and its interactions with other matter and energy.
- Matter is anything that has mass and takes up space.
- Matter can be described in terms of physical properties and chemical properties.
- Physical properties and chemical properties of matter can change.
- Matter is composed of elements and compounds.
- Combinations of different substances are called mixtures.
- Elements can be described as metals, nonmetals, and semi-metals.

4.3: Compounds

Compounds were first introduced in a previous chapter, and will be discussed in more detail throughout the rest of this chapter. A **compound** is a substance that contains two or more elements chemically combined in a fixed proportion. The elements carbon and hydrogen combine to form many different compounds. One of the simplest is called methane, in which there are always four times as many hydrogen particles as carbon particles. Methane is a pure substance because it always has the same composition. However, it is not an element because it can be broken down into simpler substances—carbon and hydrogen.

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. A **chemical change** is a change that produces matter with a different composition. Many compounds can be decomposed into their elements by heating. When sugar is heated, it decomposes into carbon and water. Water is still a compound, but one which cannot be broken down into hydrogen and oxygen by heating. Instead, the passage of an electrical current through water will produce hydrogen and oxygen gases.

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).

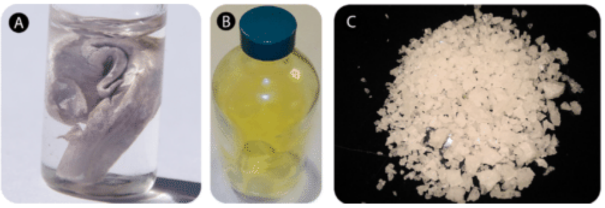

Figure 4.3.1: (A) Sodium is so reactive that it must be stored under oil. (B) Chlorine is a poisonous yellow-green gas. (C) Salt crystals, a compound of sodium and chlorine.

Summary

- A compound is a substance that contains two or more elements chemically combined in a fixed proportion.
- A chemical change is a change that produces matter with a different composition.

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4.3.1: Chemical Formulas - How to Represent Compounds

Learning Objectives

- Determine the number of different atoms in a formula.
- Define chemical formula, molecular formula, and empirical formula.

A **chemical formula** is an expression that shows the elements in a compound and the relative proportions of those elements. Water is composed of hydrogen and oxygen in a 2:1 ratio. The chemical formula for water is H_2O. Sulfuric acid is one of the most widely produced chemicals in the United States and is composed of the elements hydrogen, sulfur, and oxygen. The chemical formula for sulfuric acid is H_2SO_4.

Certain groups of atoms are bonded together to form what is called a polyatomic ion that acts as a single unit. Polyatomic ions are discussed in greater detail later in this chapter. Polyatomic ions are enclosed in parenthesis followed by a subscript if more than one of the same ion exist in a chemical formula. The formula $Ca_3(PO_4)_2$ represents a compound with the following:

3 Ca atoms + 2 PO_4^{3-} ions

To count the total number of atoms for formulas with polyatomic ions enclosed in parenthesis, use the subscript as a multiplier for each atom or number of atoms.

$$Ca_3(PO_4)_2$$

$$3\text{ Ca} + 2 \text{ x}1\text{ P} + 2\text{ x }4\text{ O} = 3\text{ Ca atoms} + 2\text{ P atoms} + 8\text{ O atoms}$$

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 of nitrogen and hydrogen as shown below:

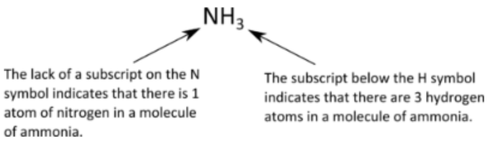


Figure 4.3.1.1: The molecular formula for ammonia. NH3. There is one atom of nitrogen and 3 atoms of hydrogen in a molecule of ammonia.

Note from the example that there are some standard rules to follow in writing molecular formulas. The arrangements of the elements depend on the particular structure, which is not of concern at this point. The number of atoms of each kind is indicated by a subscript following the atom. If there is only one atom, no number is written. If there is more than one atom of a specific kind, the number is written as a subscript following the atom. We would not write N_3H for ammonia, because that would mean that there are three nitrogen atoms and one hydrogen atom in the molecule, which is incorrect.

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.

- molecular formula: $C_6H_{12}O_6$
- empirical formula: CH_2O

There are a great many compounds whose molecular and empirical formulas are the same. 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.

Summary

- A chemical formula is an expression that shows the elements in a compound and the relative proportions of those elements.
- If only one atom of a specific type is present, no subscript is used.
- For atoms that have two or more of a specific type of atom present, a subscript is written after the symbol for that atom.
- Polyatomic ions in chemical formulas are enclosed in parentheses followed by a subscript if more than one of the same type of polyatomic ion exist.
- Molecular formulas do not indicate how the atoms are arranged in the molecule.
- The empirical formula tells the lowest whole-number ratio of elements in a compound. The empirical formula does not show the actual number of atoms.

4.4: A Molecular View of Elements and Compounds

Learning Objectives

- Classify substances as atomic elements, molecular elements, molecular compounds, or ionic compounds.

Atomic Elements

Most elements exist with **individual atoms** as their basic unit. 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.

Molecular Elements

There are many 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.

Table 4.4.1: Elements That Exist as Diatomic Molecules

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

Some elements exist naturally as molecules. For example, hydrogen and oxygen exist as two-atom molecules. Other elements also exist naturally as diatomic molecules—a molecule with only two atoms (Table 4.4.1). 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. (Sometimes only the word *formula* is used, and its meaning is inferred from the context.) 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. 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 (Figure 4.4.1).

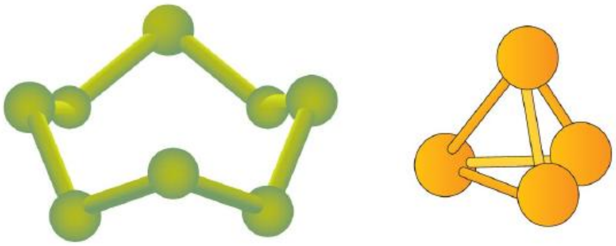


Figure 4.4.1: Molecular Art of S_8 and P_4 Molecules. If each green ball represents a sulfur atom, then the diagram on the left represents an S_8 molecule. The molecule on the right shows that one form of elemental phosphorus exists, as a four-atom molecule.

Figure 4.4.1 shows two examples of how molecules will be represented in this text. An atom is represented by a small ball or sphere, which generally indicates where the nucleus is in the molecule. A cylindrical line connecting the balls represents the connection between the atoms that make this collection of atoms a molecule. This connection is called a chemical bond.

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 either 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**.

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**.

✓ Example 4.4.1

Provide the classification (i.e. atomic element, molecular element, molecular compound, or ionic compound) of each substance.

a. Fe
b. PCl_3
c. LiBr
d. P_4
e. oxygen gas

Solution

a. **Fe** (iron) is an element that is represented with no subscript, so it is an **atomic element**.
b. **PCl_3** is made up of two nonmetals, so it is a **molecular compound**.
c. **LiBr** is made up of lithium, a metal, and bromine, a nonmetal, so it is an **ionic compound**.
d. **P_4** is a substance that is made up of four atoms of the same element, so it is a **molecular element**.
e. The formula for **oxygen gas** is **O_2** so it is a molecular element.

? Exercise 4.4.1

Provide the classification (i.e. atomic element, molecular element, molecular compound, or ionic compound) of each substance.

a. I_2
b. He
c. H_2O
d. Al
e. CuCl

Answer a:

molecular element

Answer b:

atomic element

Answer c:

molecular compound

Answer d:

atomic element

Answer e:

ionic compound

4.5: Ionic Compounds

Ionic compounds are formed by balancing charges of ions. In order to determine the formulas of ionic compounds, we need to understand the charges of ions as well as how to balance them when they come together. In a later chapter we will learn why the charges are what they are (in some cases), but for now we want to understand how to determine those charges from some portions of the periodic table, and recognize when a group of atoms has a charge (which is called a polyatomic ion). And for any ionic compound, how to determine the correct formula once you know what the charges are.

4.5.1: Ions - Monatomic and Polyatomic

Learning Objectives

Most atoms do not have eight electrons in their valence electron shell. Some atoms have only a few electrons in their outer shell, while some atoms lack only one or two electrons to have an octet. In cases where an atom has three or fewer valence electrons, the atom may lose those valence electrons quite easily until what remains is a lower shell that contains an octet. Atoms that lose electrons acquire a positive charge as a result because they are left with fewer negatively charged electrons to balance the positive charges of the protons in the nucleus. Positively charged ions are called **cations**. Most metals become cations when they make ionic compounds.

Cations

A neutral sodium atom is likely to achieve an octet in its outermost shell by losing its one valence electron.

$$\mathrm{Na} \rightarrow \mathrm{Na^+} + \mathrm{e^-} \tag{4.5.1.1}$$

The cation produced in this way, Na^+, is called the sodium ion to distinguish it from the element. The outermost shell of the sodium ion is the second electron shell, which has eight electrons in it. The octet rule has been satisfied. Figure $4.5.1.1$ is a graphical depiction of this process.

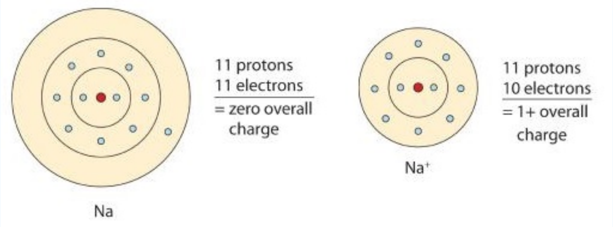


Figure 4.5.1.1: The Formation of a Sodium Ion. On the left, a sodium atom has 11 electrons. On the right, the sodium ion only has 10 electrons and a 1+ charge.

Anions

Some atoms have nearly eight electrons in their valence shell and can gain additional valence electrons until they have an octet. When these atoms gain electrons, they acquire a negative charge because they now possess more electrons than protons. Negatively charged ions are called **anions**. Most nonmetals become anions when they make ionic compounds.

A neutral chlorine atom has seven electrons in its outermost shell. Only one more electron is needed to achieve an octet in chlorine's valence shell. (In table salt, this electron comes from the sodium atom.)

$$\mathrm{e^-} + \mathrm{Cl} \longrightarrow \mathrm{Cl^-} \tag{4.5.1.2}$$

In this case, the ion has the same outermost shell as the original atom, but now that shell has eight electrons in it. Once again, the octet rule has been satisfied. The resulting anion, Cl^-, is called the chloride ion; note the slight change in the suffix (*-ide* instead of *-ine*) to create the name of this anion. Figure $4.5.1.2$ is a graphical depiction of this process.

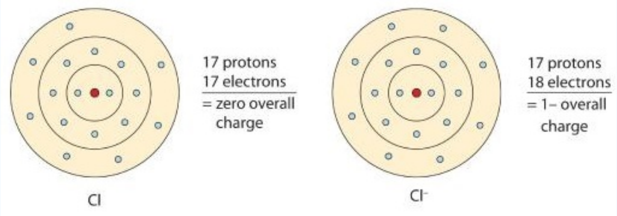


Figure 4.5.1.2: The Formation of a Chlorine Ion. On the left, the chlorine atom has 17 electrons. On the right, the chloride ion has 18 electrons and has a 1− charge.

> *The names for positive and negative ions are pronounced CAT-eye-ons and ANN-eye-ons, respectively.*

> 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 the same number of valence electrons. 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. On the other side of the periodic table, the next-to-last column, the halogens, form ions having a 1− charge. Figure 4.5.1.3 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. The barium cation is written Ba^{2+}, not Ba^{+2}.

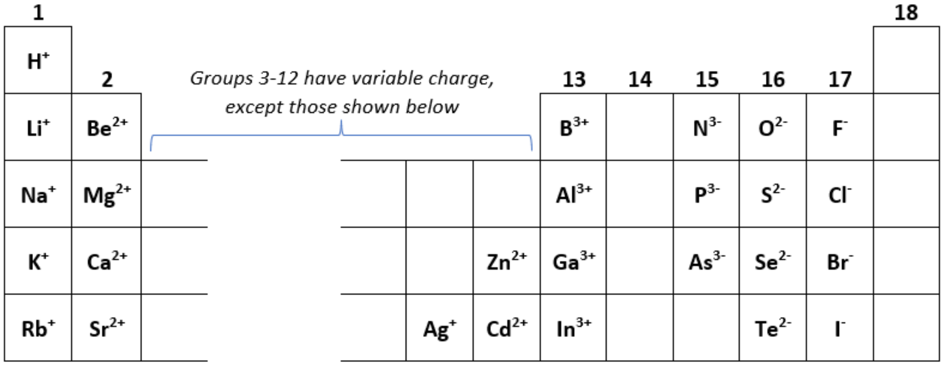
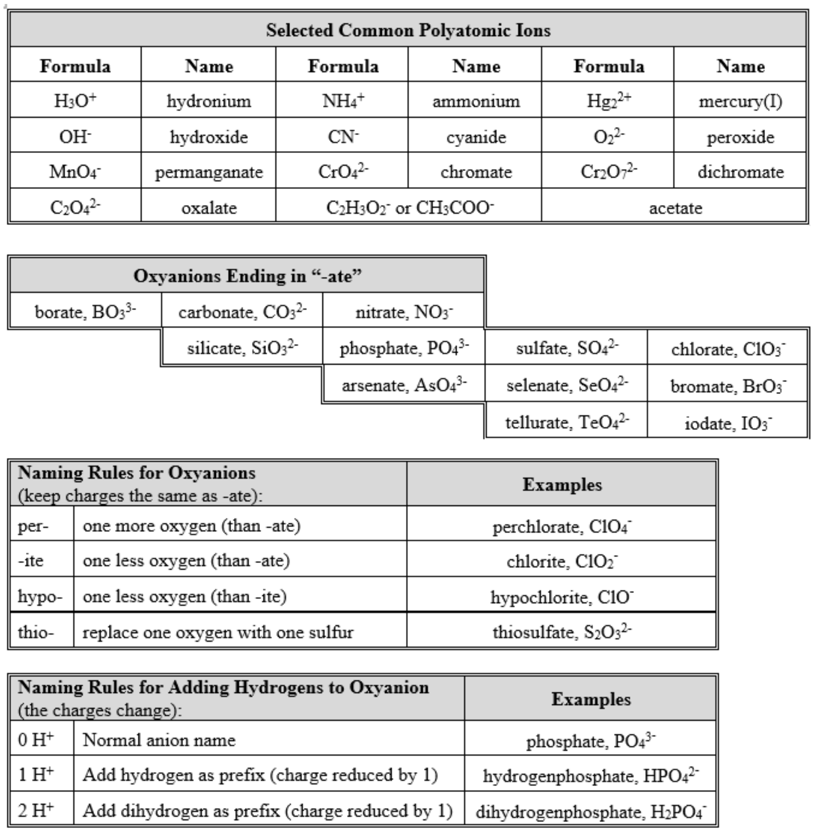


Figure 4.5.1.3: Predicting Ionic Charges. The charge that an atom acquires when it becomes an ion is related to the structure of the periodic table. Within a group (family) of elements, atoms form ions of a certain charge.

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. For example, NO_3^- is the nitrate ion; it has one nitrogen atom and three oxygen atoms and an overall 1− charge. Table 4.5.1.1 lists the most common polyatomic ions.



Selected Common Polyatomic Ions					
Formula	**Name**	**Formula**	**Name**	**Formula**	**Name**
H_3O^+	hydronium	NH_4^+	ammonium	Hg_2^{2+}	mercury(I)
OH^-	hydroxide	CN^-	cyanide	O_2^{2-}	peroxide
MnO_4^-	permanganate	CrO_4^{2-}	chromate	$Cr_2O_7^{2-}$	dichromate
$C_2O_4^{2-}$	oxalate	$C_2H_3O_2^-$ or CH_3COO^-		acetate	

Oxyanions Ending in "-ate"				
borate, BO_3^{3-}	carbonate, CO_3^{2-}	nitrate, NO_3^-		
	silicate, SiO_3^{2-}	phosphate, PO_4^{3-}	sulfate, SO_4^{2-}	chlorate, ClO_3^-
		arsenate, AsO_4^{3-}	selenate, SeO_4^{2-}	bromate, BrO_3^-
			tellurate, TeO_4^{2-}	iodate, IO_3^-

Naming Rules for Oxyanions (keep charges the same as -ate):		**Examples**
per-	one more oxygen (than -ate)	perchlorate, ClO_4^-
-ite	one less oxygen (than -ate)	chlorite, ClO_2^-
hypo-	one less oxygen (than -ite)	hypochlorite, ClO^-
thio-	replace one oxygen with one sulfur	thiosulfate, $S_2O_3^{2-}$

Naming Rules for Adding Hydrogens to Oxyanion (the charges change):		**Examples**
0 H^+	Normal anion name	phosphate, PO_4^{3-}
1 H^+	Add hydrogen as prefix (charge reduced by 1)	hydrogenphosphate, HPO_4^{2-}
2 H^+	Add dihydrogen as prefix (charge reduced by 1)	dihydrogenphosphate, $H_2PO_4^-$

Figure 4.5.1.3: Common Polyatomic Ion Charges

Here's a simple method for memorizing oxyanions ending in "-ate".

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- Henry Agnew (UC Davis)

4.5.2: Writing Formulas for Ionic Compounds

Learning Objectives

- Write the correct formula for an ionic compound.
- Recognize polyatomic ions in chemical formulas.

Ionic compounds do not exist as molecules. In the solid state, ionic compounds are in crystal lattice containing many ions each of the cation and anion. An ionic formula, like $NaCl$, is an empirical formula. This formula merely indicates that sodium chloride is made of an equal number of sodium and chloride ions. Sodium sulfide, another ionic compound, has the formula Na_2S. This formula indicates that this compound is made up of twice as many sodium ions as sulfide ions. This section will teach you how to find the correct ratio of ions, so that you can write a correct formula.

If you know the name of a binary ionic compound, you can write its **chemical formula**. Start by writing the metal ion with its charge, followed by the nonmetal ion with its charge. Because the overall compound must be electrically neutral, decide how many of each ion is needed in order for the positive and negative charges to cancel each other out.

✓ Example 4.5.2.1: Aluminum Nitride and Lithium Oxide

Write the formulas for aluminum nitride and lithium oxide.

Solution

	Write the formula for aluminum nitride	**Write the formula for lithium oxide**
1. Write the symbol and charge of the cation (metal) first and the anion (nonmetal) second.	$Al^{3+}\quad N^{3-}$	$Li^{+}\quad O^{2-}$
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 1(3+) = 1(3-) +3 = -3	total charge of cations = total charge of anions 2(1+) = 1(2-) +2 = -2
3. Use the multipliers as subscript for each ion.	Al_1N_1	Li_2O_1
4. Write the final formula. Leave out all charges and all subscripts that are 1.	AlN	Li_2O

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 4.5.2.2: The Crisscross Method for Lead (IV) Oxide

Write the formula for lead (IV) oxide.

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.	$Pb^{4+}\quad O^{2-}$
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.	
3. Reduce to the lowest ratio.	Pb_2O_4

Crisscross Method	Write the formula for lead (IV) oxide
4. Write the final formula. Leave out all subscripts that are 1.	PbO_2

? Exercise 4.5.2.2

Write the chemical formula for an ionic compound composed of each pair of ions.

a. the calcium ion and the oxygen ion
b. the 2+ copper ion and the sulfur ion
c. the 1+ copper ion and the sulfur ion

Answer a:

CaO

Answer b:

CuS

Answer c:

Cu_2S

> *Be aware that ionic compounds are empirical formulas and so must be written as the lowest ratio of the ions.*

✓ Example 4.5.2.3: Sulfur Compound

Write the formula for sodium combined with sulfur.

Solution

Crisscross Method	Write the formula for sodium combined with sulfur
1. Write the symbol and charge of the cation (metal) first and the anion (nonmetal) second.	Na^+ S^{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.	
3. Reduce to the lowest ratio.	This step is not necessary.
4. Write the final formula. Leave out all subscripts that are 1.	Na_2S

? Exercise 4.5.2.3

Write the formula for each ionic compound.

a. sodium bromide
b. lithium chloride
c. magnesium oxide

Answer a:

$NaBr$

Answer b:

$LiCl$

Answer c:

MgO

Writing Formulas for Ionic Compounds Containing Polyatomic Ions

Polyatomic ions were introduced in a previous subsection. It is important to understand the relationship between the name, formula, and charge of polyatomic ions before beginning to use them within ionic compounds.

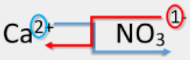
The rule for constructing formulas for ionic compounds containing polyatomic ions is the same as for formulas containing monatomic (single-atom) ions: the positive and negative charges must balance. If more than one of a particular polyatomic ion is needed to balance the charge, the *entire formula* 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 $Ba(NO_3)_2$.

Writing a formula for ionic compounds containing polyatomic ions also involves the same steps as for a binary ionic compound. Write the symbol and charge of the cation followed by the symbol and charge of the anion.

Example 4.5.2.4: Calcium Nitrate

Write the formula for calcium nitrate.

Solution

Crisscross Method	Write the formula for calcium nitrate
1. Write the symbol and charge of the cation (metal) first and the anion (nonmetal) second.	$Ca^{2+} \quad NO_3^-$
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.	
3. Reduce to the lowest ratio.	$Ca_1(NO_3)_2$
4. Write the final formula. Leave out all subscripts that are 1. If there is only 1 of the polyatomic ion, leave off parentheses.	$Ca(NO_3)_2$

Example 4.5.2.5

Write the chemical formula for an ionic compound composed of the potassium ion and the sulfate ion.

Solution

Explanation	Answer
Potassium ions have a charge of 1+, while sulfate ions have a charge of 2−. We will need two potassium ions to balance the charge on the sulfate ion, so the proper chemical formula is K_2SO_4.	K_2SO_4

? Exercise 4.5.2.5

Write the chemical formula for an ionic compound composed of each pair of ions.

a. the magnesium ion and the carbonate ion
b. the aluminum ion and the acetate ion

Answer a:

$MgCO_3$

Answer b:

$Al(CH_3COO)_3$

Recognizing Ionic Compounds

There are two ways to recognize ionic compounds. First, compounds between metal and nonmetal elements are usually ionic. For example, $CaBr_2$ contains a metallic element (calcium, a group 2 [or 2A] metal) and a nonmetallic element (bromine, a group 17 [or 7A] nonmetal). Therefore, it is most likely an ionic compound. (In fact, it *is* ionic.) In contrast, the compound NO_2 contains two elements that are both nonmetals (nitrogen, from group 15 [or 5A], and oxygen, from group 16 [or 6A]. It is not an ionic compound; it belongs to the category of covalent compounds discussed elsewhere. Also note that this combination of nitrogen and oxygen has no electric charge specified, so it is *not* the nitrite ion.

Second, if you recognize the formula of a polyatomic ion in a compound, the compound is ionic. For example, if you see the formula $Ba(NO_3)_2$, you may recognize the "NO_3" part as the nitrate ion, NO_3^-. (Remember that the convention for writing formulas for ionic compounds is not to include the ionic charge.) This is a clue that the other part of the formula, Ba, is actually the Ba^{2+} ion, with the 2+ charge balancing the overall 2− charge from the two nitrate ions. Thus, this compound is also ionic.

✓ Example 4.5.2.6

Identify each compound as ionic or not ionic.

a. Na_2O
b. PCl_3
c. NH_4Cl
d. OF_2

Solution

Explanation	Answer
a. Sodium is a metal, and oxygen is a nonmetal. Therefore, Na_2O is expected to be ionic.	Na_2O, ionic
b. Both phosphorus and chlorine are nonmetals. Therefore, PCl_3 is not ionic.	PCl_3, not ionic
c. The NH_4 in the formula represents the ammonium ion, NH_4^+, which indicates that this compound is ionic.	NH_4Cl, ionic
d. Both oxygen and fluorine are nonmetals. Therefore, OF_2 is not ionic.	OF_2, not ionic

? Exercise 4.5.2.6

Identify each compound as ionic or not ionic.

a. N_2O
b. $FeCl_3$
c. $(NH_4)_3PO_4$
d. $SOCl_2$

Answer a:

not ionic

Answer b:

ionic

Answer c:

ionic

Answer d:

not ionic

Summary

Formulas for ionic compounds contain the symbols and number of each atom present in a compound in the lowest whole number ratio.

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4.6: How to Name Compounds

Knowing how to name a compound correctly is an important skill both for the remainder of this course, and as you move into other fields. Many compounds have long names which differ only by a single letter. But that single letter makes a big difference in the properties of those compounds. For example, sodium chloride is something that you might use in food preparation, but sodium chlorite might explode if mixed with certain foods! Likewise, in the medical fields there are many drugs with long and sometimes similar names. Being able to distinguish between different chemical names is a safety issue.

In history, the first names for a particular element or compound was generally invented by whomever discovered it. As you can imagine, as many more compounds were discovered, this became a bit confusing. In 1787, Antoine Lavoisier tried to improve the situation by publishing a book of "New Chemical Nomenclature", which attempted to bring all chemical names into a common system of naming, that could be consistent and more easily learned. Today, this is primarily done by a group called the International Union of Pure and Applied Chemists (IUPAC). Their naming recommendations relevant to introductory and general chemistry are recorded in what they call the "Red Book", which can be accessed at the IUPAC website. Modern day chemists and students primarily follow these rules, but if you look and listen closely, you may find that even chemistry professors and chemical industry suppliers are slow to adopt modern recommendations.

The most important step in naming a chemical is determining which category that chemical belongs in. As you read the sections on how to name different types of chemicals, please recognize the importance of these chemical classifications. A previous section in this chapter discussed how we categorize compounds. These are the same categories we will be using as we name compounds. Pay attention to these categories as you're naming chemicals.

4.6.1: Naming Ionic Compounds

Learning Objectives

- To use the rules for naming ionic compounds.

After learning a few more details about the names of individual ions, you will be one step away from knowing how to name ionic compounds. This section begins the formal study of nomenclature, the systematic naming of chemical compounds.

Naming Ions

Monatomic cations can be separated into two categories.

Type I- Ions whose charge does not vary.

Ions like Na^+, Al^{3+}, Ca^{2+} only form ions of a single charge magnitude. So, it is unambiguous and simplest to refer to them by their name, simply adding the word "ion". So a sodium ion is Na^+, an aluminum ion is Al^{3+}, etc.

Type II- Ions whose charge does vary.

Some elements lose different numbers of electrons, producing ions of different charge magnitude (Figure 3.3). Iron, for example, can form two cations, each of which, when combined with the same anion, makes a different compound with unique physical and chemical properties. Thus, we need a different name for each iron ion to distinguish Fe^{2+} from Fe^{3+}. The same issue arises for other ions with more than one possible charge. The International Union of Pure and Applied Chemists (IUPAC) dictates that an ion's positive charge is indicated in parentheses after the element name, followed by the word *ion*. This can be done with either arabic numerals for charge (e.g. Iron (3+) ion) or roman numerals for oxidation state (e.g. Iron (III) ion). In this case, either would be correct, but many textbooks and instructors continue to use only roman numerals, so we will adopt the same convention for cations with variable charge for the sake of consistency.

Sodium forms only a 1+ ion, so there is no ambiguity about the name *sodium ion*.

*Refer to section IR-5.3.2-3 of the IUPAC Red Book for more on cation and anion naming conventions.

Table 4.6.1.1: The Modern and Common System of Cation Names

Element	Charge	Name
iron	2+	iron(II) ion
	3+	iron(III) ion
copper	1+	copper(I) ion
	2+	copper(II) ion
tin	2+	tin(II) ion
	4+	tin(IV) ion
lead	2+	lead(II) ion
	4+	lead(IV) ion
chromium	2+	chromium(II) ion
	3+	chromium(III) ion
gold	1+	gold(I) ion
	3+	gold(III) ion

Monatomic Anions

Like, type I cations, monatomic anions generally form ions of a single charge magnitude. To avoid confusion with cations, the ending of the element's name is changed to "-ide", before addition of the word anion. See the table below for examples.

Table 4.6.1.2: Some Monatomic Anions

Ion	Name
F^-	fluoride ion
Cl^-	chloride ion
Br^-	bromide ion
I^-	iodide ion
O^{2-}	oxide ion
S^{2-}	sulfide ion
P^{3-}	phosphide ion
N^{3-}	nitride ion

✓ Example 4.6.1.1

Name each ion.

a. Ca^{2+}
b. S^{2-}
c. $SO_3{}^{2-}$
d. $NH_4{}^+$
e. Cu^+

Solution

a. the calcium ion
b. the sulfide ion
c. the sulfite ion
d. the ammonium ion
e. the copper(I) ion

? Exercise 4.6.1.1

Name each ion.

a. Fe^{2+}
b. Fe^{3+}
c. $SO_4{}^{2-}$
d. Ba^{2+}
e. $HCO_3{}^-$

Answer a:

iron(II) ion

Answer b:

iron(III) ion

Answer c:

sulfate ion

Answer d:

barium ion

Answer e:

hydrogencarbonate ion or bicarbonate ion

✓ Example 4.6.1.2

Write the formula for each ion.

a. the bromide ion
b. the phosphate ion
c. the copper(II) ion
d. the magnesium ion

Solution

a. $Br^−$
b. $PO_4{}^{3−}$
c. Cu^{2+}
d. Mg^{2+}

? Exercise 4.6.1.2

Write the formula for each ion.

a. the fluoride ion
b. the carbonate ion
c. the tin(II) ion
d. the potassium ion

Answer a:

F^-

Answer b:

$CO_3{}^{2-}$

Answer c:

$Sn^{\ 2+}$

Answer d:

K^+

Naming Binary Ionic Compounds with a Metal that Forms Only One Type of Cation

A **binary** ionic compound is a compound composed of a **monatomic** metal **cation** and a monatomic nonmetal **anion**. The metal cation is named first, followed by the nonmetal anion as illustrated in Figure 4.6.1.1 for the compound $BaCl_2$. The word *ion* is dropped from both parts.

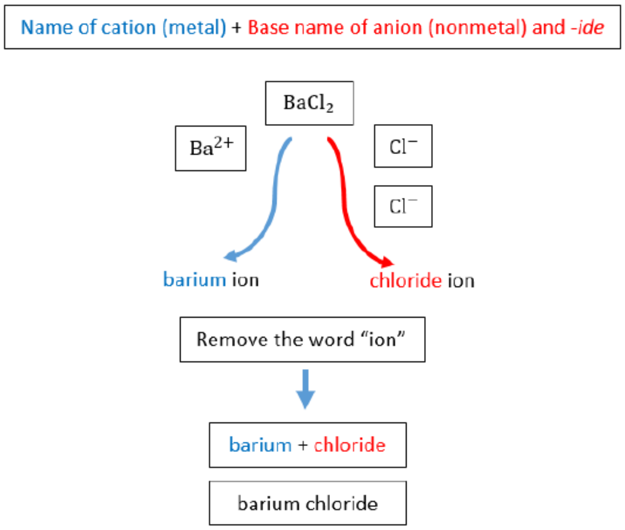


Figure 4.6.1.1: Naming $BaCl_2$
Naming formula: Name of metal cation + base
name of nonmetal anion + suffix -ide. BaCl2 is named as barium chloride.

Subscripts in the formula do not affect the name.

✓ Example 4.6.1.3: Naming Ionic Compounds

Name each ionic compound.

a. $CaCl_2$
b. AlF_3
c. KCl

Solution

a. Using the names of the ions, this ionic compound is named calcium chloride.
b. The name of this ionic compound is aluminum fluoride.
c. The name of this ionic compound is potassium chloride

? Exercise 4.6.1.3

Name each ionic compound.

a. AgI
b. MgO
c. Ca_3P_2

Answer a:

silver iodide

Answer b:

magnesium oxide

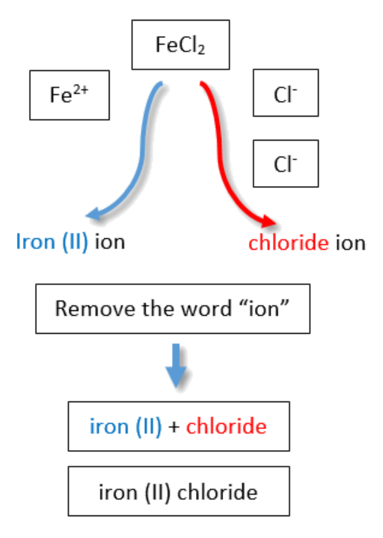
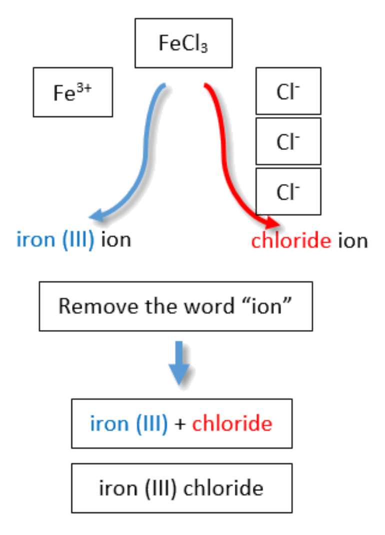
Answer c:

calcium phosphide

Naming Binary Ionic Compounds with a Metal That Forms More Than One Type of Cation

If you are given a formula for an ionic compound whose cation can have more than one possible charge, you must first determine the charge on the cation before identifying its correct name. For example, consider $FeCl_2$ and $FeCl_3$. In the first compound, the iron ion has a 2+ charge because there are two Cl^- ions in the formula (1− charge on each chloride ion). In the second compound, the iron ion has a 3+ charge, as indicated by the three Cl^- ions in the formula. These are two different compounds that need two different names. By the Stock system, the names are iron(II) chloride and iron(III) chloride (Figure $4.6.1.2$).

Table $4.6.1.3$: Naming the $FeCl_2$ and $FeCl_3$ Compounds in the Modern/Stock System.

Name of cation (metal) + (Roman Numeral in parenthesis) + Base name of anion (nonmetal) and *-ide*	
	

Example $4.6.1.4$:

Name each ionic compound.

a. Co2O3
b. FeCl2

Solution

Solutions to Example 5.7.4

	Explanation	Answer
a	We know that cobalt can have more than one possible charge; we just need to determine what it is. • Oxide always has a 2− charge, so with three oxide ions, we have a total negative charge of 6−. • This means that the two cobalt ions have to contribute 6+, which for two cobalt ions means that each one is 3+. • Therefore, the proper name for this ionic compound is cobalt(III) oxide.	cobalt(III) oxide

	Explanation	Answer
b	Iron can also have more than one possible charge. • Chloride always has a 1− charge, so with two chloride ions, we have a total negative charge of 2−. • This means that the one iron ion must have a 2+ charge. • Therefore, the proper name for this ionic compound is iron(II) chloride.	iron(II) chloride

Exercise 4.6.1.4

Name each ionic compound.

a. $AuCl_3$
b. PbO_2
c. CuO

Answer a:

gold(III) chloride

Answer b:

lead(IV) oxide

Answer c:

copper(II) oxide

Naming Ionic Compounds with Polyatomic Ions

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. One example is the ammonium sulfate compound in Figure 4.6.1.6

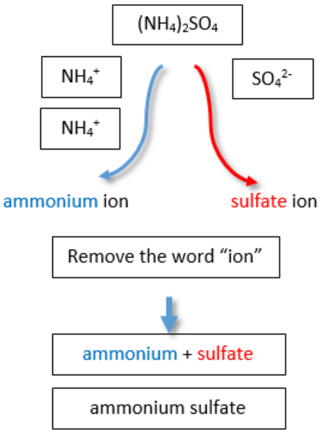


Figure 4.6.1.2: Naming Ionic Compounds with Polyatomic Ions

Example 4.6.1.5: Naming Ionic Compounds

Write the proper name for each ionic compound.

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

Solution

Solutions to Example 5.7.5

Explanation	Answer
a. The ammonium ion has a 1+ charge and the sulfide ion has a 2− charge. Two ammonium ions need to balance the charge on a single sulfide ion. The compound’s name is ammonium sulfide.	ammonium sulfide
b. The ions have the same magnitude of charge, one of each (ion) is needed to balance the charges. The name of the compound is aluminum phosphate.	aluminum phosphate
c. Neither charge is an exact multiple of the other, so we have to go to the least common multiple of 6. To get 6+, three iron(II) ions are needed, and to get 6−, two phosphate ions are needed . The compound’s name is iron(II) phosphate.	iron(II) phosphate

Exercise 4.6.1.5A

Write the proper name for each ionic compound.

a. $(NH_4)_3PO_4$
b. $Co(NO_2)_3$

Answer a:

ammonium phosphate

Answer b:

cobalt(III) nitrite

Figure 4.6.1.1is a synopsis of how to name simple ionic compounds.

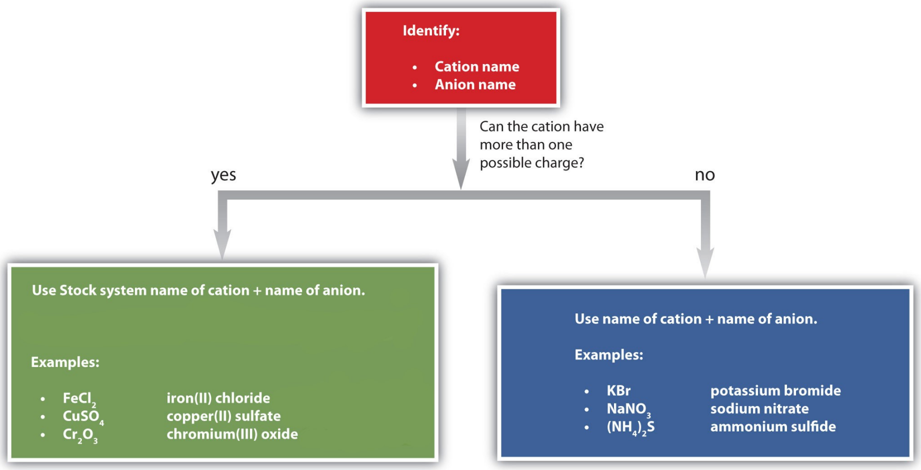


Figure 4.6.1.3: A Guide to Naming Simple Ionic Compounds.

Exercise 4.6.1.5B

Name each ionic compound.

a. $ZnBr_2$
b. Al_2O_3

c. $(NH_4)_3PO_4$
d. AuF_3
e. AgF

Answer a:

zinc bromide

Answer b:

aluminum oxide

Answer c:

ammonium phosphate

Answer d:

gold(III) fluoride or auric fluoride

Answer e:

silver fluoride

Summary

- Ionic compounds are named by stating the cation first, followed by the anion.
- Positive and negative charges must balance.
- Some anions have multiple forms and are named accordingly with the use of roman numerals in parentheses.
- Ternary compounds are composed of three or more elements.

4.6.2: Naming Molecular Compounds

Learning Objectives

- Determine the name of a simple molecular compound from its chemical formula.

Molecular Compounds

Molecular compounds are inorganic compounds that take the form of discrete **molecules**. Examples include such familiar substances as water (H_2O) and carbon dioxide (CO_2). These compounds are very different from ionic compounds like sodium chloride $(NaCl)$. Ionic compounds are formed when metal atoms lose one or more of their electrons to nonmetal atoms. The resulting cations and anions are electrostatically attracted to each other.

So what holds the atoms of a molecule together? Rather than forming ions, the atoms of a molecule share their **electrons** in such a way that a **bond** forms between a pair of atoms. In a carbon dioxide molecule, there are two of these bonds, each occurring between the carbon atom and one of the two oxygen atoms.

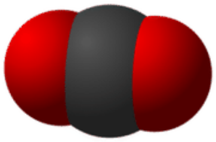


Figure 4.6.2.1: Carbon dioxide molecules consist of a central carbon atom bonded to 2 oxygen atoms.

Larger molecules can have many, many bonds that serve to keep the molecule together. In a large sample of a given molecular compound, all of the individual molecules are identical.

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}.

Figure 4.6.2.2: Nitrogen dioxide (NO_2) is a reddish-brown toxic gas that is a prominent air pollutant produced by internal combustion engines.

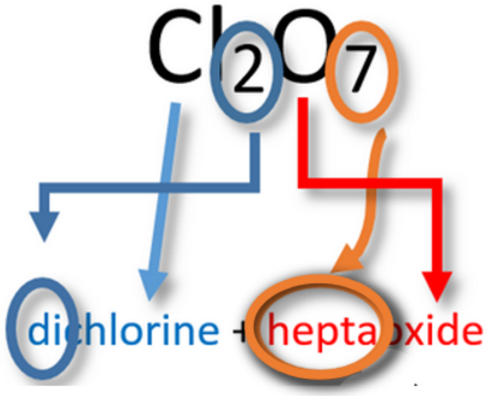
Naming *binary* (two-element) molecular compounds is similar to naming simple ionic compounds. The first element in the formula is simply listed using the name of the element. The second element is named by taking the stem of the element name and adding the suffix *-ide*. A system of numerical prefixes is used to specify the number of atoms in a molecule. Table 4.6.2.1 lists these numerical prefixes.

Table 4.6.2.1: Numerical Prefixes for Naming Binary Covalent Compounds

Number of Atoms in Compound	Prefix on the Name of the Element
1	mono-*
2	di-
3	tri-
4	tetra-
5	penta-
6	hexa-

Number of Atoms in Compound	Prefix on the Name of the Element
7	hepta-
8	octa-
9	nona-
10	deca-

*May be omitted for the first element’s name.



dichlorine heptaoxide

Note

- Generally, the less electronegative element is written first in the formula, though there are a few exceptions. Carbon is always first in a formula and hydrogen is after nitrogen in a formula such as NH_3. The order of common nonmetals in binary compound formulas is $C, P, N, H, S, I, Br, Cl, O, F$.
- Although older naming schemes allowed for removal of letters (elisions), modern IUPAC nomenclature rules do not recommend this. (Except that an allowance is made for removing one of the double o's in "monooxide", to get "monoxide".) See section IR-2.7 of the IUPAC Red Book for more information.
- The prefix is "mono" may be left off of the first element’s name if there is only one atom of the first element in a molecule.

Some examples of molecular compounds are listed in Table 4.6.2.2

Table 4.6.2.2

Formula	Name
NO	mononitrogen monooxide (or nitrogen monoxide)
N_2O	dinitrogen monooxide (or dinitrogen monoxide)
S_2Cl_2	disulfur dichloride
Cl_2O_7	dichlorine heptaoxide
SI_2	monosulfur diiodide (or sulfur diiodide)

Exercise 4.6.2.1

Write the name for each compound.

a. CF_4
b. $SeCl_2$
c. SO_3

Answer a:

carbon tetrafluoride (or monocarbon tetrafluoride)

Answer b:

selenium dichloride (or monoselenium dichloride)

Answer c:

sulfur trioxide (or monosulfur trioxide)

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.

Some Compounds Have Both Covalent and Ionic Bonds

If you recall the introduction of polyatomic ions, you will remember that the bonds that hold the polyatomic ions together are covalent bonds. Once the polyatomic ion is constructed with covalent bonds, it reacts with other substances as an ion. The bond between a polyatomic ion and another ion will be ionic. An example of this type of situation is in the compound sodium nitrate. Sodium nitrate is composed of a sodium ion and a nitrate ion. The nitrate ion is held together by covalent bonds and the nitrate ion is attached to the sodium ion by an ionic bond.

Summary

- A molecular compound is usually composed of two or more nonmetal elements.
- Molecular compounds are named with the first element first and then the second element by using the stem of the element name plus the suffix -ide. Numerical prefixes are used to specify the number of atoms in a molecule.

4.6.3: Naming Acids

A spot test for gold has been in use for decades. The sample is first treated with nitric acid. Other metals may react or dissolve in this acid, but gold will not. Then the sample is added to a mixture of nitric acid and hydrochloric acid. Gold will only dissolve in this mixture. The term "acid test" arose from the California gold rush in the late 1840's when this combination was used to test for the presence of real gold. It has since come to mean, "tested and approved" in a number of fields.

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 $\left(\mathrm{H}^{+}\right)$ when dissolved in water.

Figure 4.6.3.1: (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:

$$\mathrm{HCl} \rightarrow \mathrm{H}^{+}+\mathrm{Cl}^{-}$$

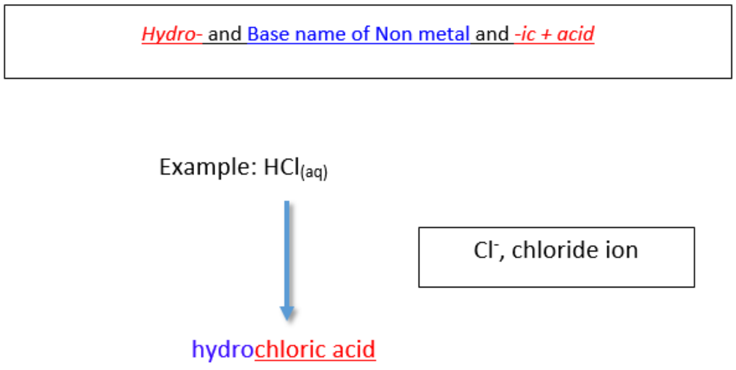
Since acids produce H^{+} cations upon dissolving in water, the H of an acid is written first in the formula of an inorganic acid. The remainder of the acid (other than the H) is the anion after the acid dissolves. Organic acids are also an important class of compounds, but will not be discussed here.

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 (in aqueous form)

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*.



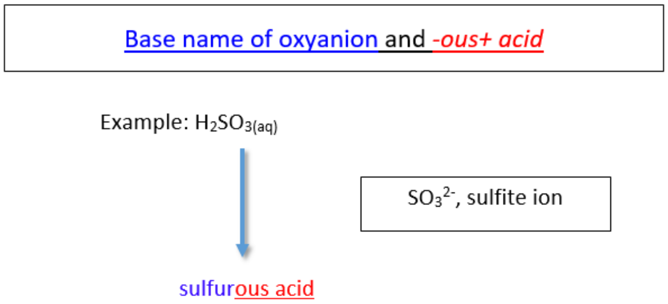
Formula for naming acids: Hydro- and Base name of nonmetal and -ic + acid. Example: HCl is hydrochloric acid.

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.

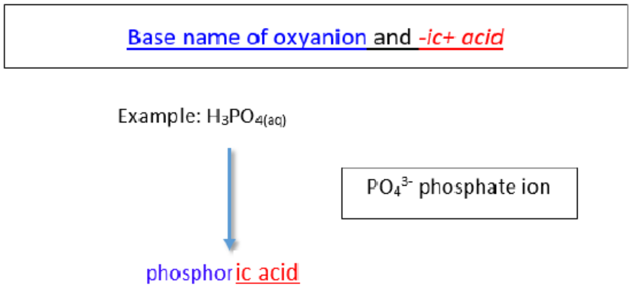
The name of the acid is the root of the anion followed by the suffix ***-ous***. There is no prefix.



Formula for naming oxyanions with -ite ending: Base name of oxyanion and -ous + acid. Example: H2SO3 is 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.



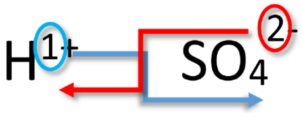
Formula for naming oxyanions with -ate ending: Base name of oxyanion and -ic + acid. Example: H3PO4 is phosphoric acid.

Note

The base name for sulfur containing oxyacid is ***sulfur-*** instead of just ***sulf-***. The same is true for a phosphorus containing oxyacid. The base name is ***phosphor-*** instead of simply ***phosph-***.

Writing Formulas for Acids

Like other compounds that we have studied, acids are electrically neutral. Therefore, the charge of the anion part of the formula must be exactly balanced out by the H^+ ions. Another way to think about writing the correct formula is to utilize the crisscross method, shown below for sulfuric acid.



H2SO4: H has +1 charge and SO4 has -2 charge, so there must be 2 H+ and 1 SO4 for the charges to balance out.

Formula: H_2SO_4

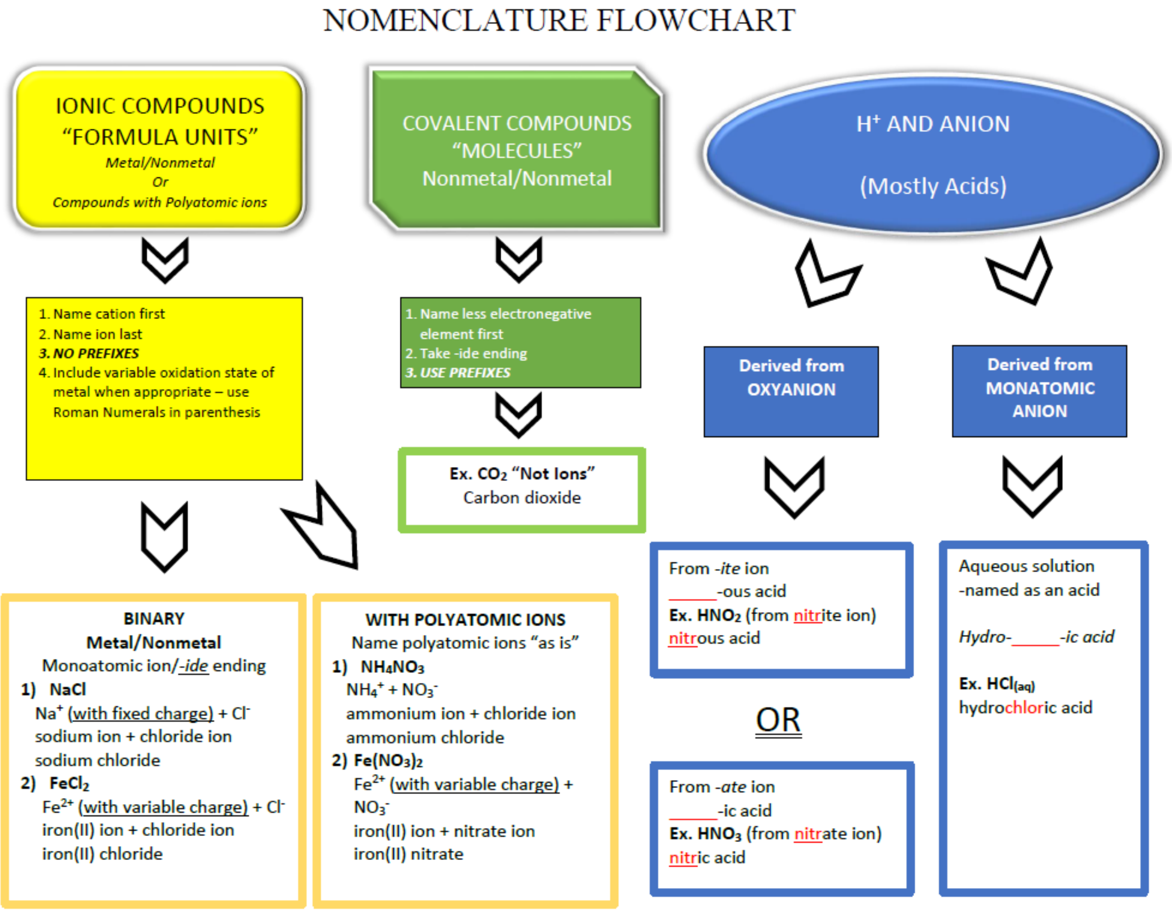
Figure 4.6.3.2: *Crisscross approach to writing formula for sulfuric acid.*

Summary

- Acids are molecular compounds that release hydrogen ions.
- A binary acid consists of hydrogen and one other element.
- Oxyacids contain hydrogen, oxygen, and one other element.
- The name of the acid is based on the anion attached to the hydrogen.

4.6.4: Nomenclature Summary

The most important step in naming a chemical is determining which category that chemical belongs in. There are several categories of chemicals, but we have discussed 3 of them in this section: ionic, covalent, and acids. When you begin to name a compound, the first thing you should do is decide which of these 3 categories that compound fits into. Ionic compounds usually contain a metal and a nonmetal (any exceptions would involve polyatomic ions instead of a metal.) Covalent compounds will only contain nonmetals. Acids will start with hydrogen. Decide on which of these categories the compound fits into, and then name it using the appropriate system. The flow chart below summarizes many of the details about naming these compounds.



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4.7: Atoms, Molecules, and Ions (Exercises)

The following questions are related to the material covered in this chapter. Answers to selected questions, only.

4.1-4.2 Matter and Changes

1. Match the following terms with their meaning.

Terms	Definitions
(a) Mass	a. a measure of the total quantity of matter in an object
(b) Volume	b. a measure of how strongly gravity pulls on an object
(c) Weight	c. a measure of the space occupied by an object

2. Identify each as either matter or not matter.
   - a book
   - hate
   - light
   - a car
   - a fried egg

3. Give an example of matter in each phase: solid, liquid, or gas.

4. Does each statement represent a physical property or a chemical property?

- Sulfur is yellow.
- Steel wool burns when ignited by a flame.
- A gallon of milk weighs over eight pounds.

5. Does each statement represent a physical property or a chemical property?

- A pile of leaves slowly rots in the backyard.
- In the presence of oxygen, hydrogen can interact to make water.
- Gold can be stretched into very thin wires.

6. Does each statement represent a physical change or a chemical change?

- Water boils and becomes steam.
- Food is converted into usable form by the digestive system.
- The alcohol in many thermometers freezes at about −40 degrees Fahrenheit.

7. Does each statement represent a physical change or a chemical change?

- Graphite, a form of elemental carbon, can be turned into diamond, another form of carbon, at very high temperatures and pressures.
- The house across the street has been painted a new color.
- The elements sodium and chlorine come together to make a new substance called sodium chloride.

8. Distinguish between an element and a compound. About how many of each are known?

9. What is the difference between a homogeneous mixture and a heterogeneous mixture?

10. Identify each as a heterogeneous mixture or a homogeneous mixture.

- Salt is mixed with pepper.
- Sugar is dissolved in water.
- Pasta is cooked in boiling water.

11. Identify each as a heterogeneous mixture or a homogeneous mixture.

- air
- dirt
- a television set

Answers

2.
    1. matter
    2. not matter
    3. not matter
    4. matter
    5. matter

8. An element is a fundamental chemical part of a substance; there are about 115 known elements. A compound is a combination of elements that acts as a different substance ; there are over 50 million known substances.

11.
    1. homogeneous
    2. heterogeneous
    3. heterogeneous

Molecules and Molecular Compounds

1. Which of these formulas represent molecules? State how many atoms are in each molecule.
    - a. Fe
    - b. PCl_3
    - c. P_4
    - d. Ar
2. Which of these formulas represent molecules? State how many atoms are in each molecule.
    - a. I_2
    - b. He
    - c. H_2O
    - d. Al
3. What is the difference between CO and Co?
4. What is the difference between H_2O and H_2O_2 (hydrogen peroxide)?
5. Give the proper formula for each diatomic element.
6. In 1986, when Halley's comet last passed the earth, astronomers detected the presence of S_2 in their telescopes. Why is sulfur not considered a diatomic element?
7. What is the stem of fluorine used in molecule names? CF_4 is one example.
8. What is the stem of selenium used in molecule names? $SiSe_2$ is an example.
9. Give the proper name for each molecule.
    - a. PF_3
    - b. $TeCl_2$
    - c. N_2O_3
10. Give the proper name for each molecule.
    - a. NO
    - b. CS_2
    - c. As_2O_3
11. Give the proper name for each molecule.
    - a. XeF_2
    - b. O_2F_2
    - c. SF_6
12. Give the proper name for each molecule.
    - a. P_4O_{10}
    - b. B_2O_3
    - c. P_2S_3
13. Give the proper name for each molecule.
    - a. N_2O
    - b. N_2O_4

   - c. N_2O_5
14. Give the proper name for each molecule.
    - a. SeO_2
    - b. Cl_2O
    - c. XeF_6
15. Give the proper formula for each name.
    - a. dinitrogen pentoxide
    - b. tetraboron tricarbide
    - c. phosphorus pentachloride
16. Give the proper formula for each name.
    - a. nitrogen triiodide
    - b. diarsenic trisulfide
    - c. iodine trichloride
17. Give the proper formula for each name.
    - a. dioxygen dichloride
    - b. dinitrogen trisulfide
    - c. xenon tetrafluoride
18. Give the proper formula for each name.
    - a. chlorine dioxide
    - b. selenium dibromide
    - c. dinitrogen trioxide
19. Give the proper formula for each name.
    - a. iodine trifluoride
    - b. xenon trioxide
    - c. disulfur decafluoride
20. Give the proper formula for each name.
    - a. germanium dioxide
    - b. carbon disulfide
    - c. diselenium dibromide

Answers

1. a. not a molecule
   b. a molecule; four atoms total
   c. a molecule; four atoms total
2.
3. CO is a compound of carbon and oxygen; Co is the element cobalt.
4.
5. H_2, O_2, N_2, F_2, Cl_2, Br_2, I_2
6.
7. *fluor-*
8.
9. a. phosphorus trifluoride
   b. tellurium dichloride
   c. dinitrogen trioxide
10.
11. a. xenon difluoride
    b. dioxygen difluoride
    c. sulfur hexafluoride
12.

13. a. dinitrogen monoxide
    b. dinitrogen tetroxide
    c. dinitrogen pentoxide

14.

15. a. N_2O_5
    b. B_4C_3
    c. PCl_5

16.

17. a. O_2Cl_2
    b. N_2S_3
    c. XeF_4

18.

19. a. IF_3
    b. XeO_3
    c. S_2F_{10}

Ions and Ionic Compounds

1. Explain how cations form.
2. Explain how anions form.
3. Give the charge each atom takes when it forms an ion. If more than one charge is possible, list both.
    a. K
    b. O
    c. Co
4. Give the charge each atom takes when it forms an ion. If more than one charge is possible, list both.
    a. Ca
    b. I
    c. Fe
5. Give the charge each atom takes when it forms an ion. If more than one charge is possible, list both.
    a. Ag
    b. Au
    c. Br
6. Give the charge each atom takes when it forms an ion. If more than one charge is possible, list both.
    a. S
    b. Na
    c. H
7. Name the ions from Exercise 3.
8. Name the ions from Exercise 4.
9. Name the ions from Exercise 5.
10. Name the ions from Exercise 6.
11. Give the formula and name for each ionic compound formed between the two listed ions.
    a. Mg^{2+} and Cl^{-}
    b. Fe^{2+} and O^{2-}
    c. Fe^{3+} and O^{2-}
12. Give the formula and name for each ionic compound formed between the two listed ions.
    a. K^{+} and S^{2-}
    b. Ag^{+} and Br^{-}
    c. Sr^{2+} and N^{3-}
13. Give the formula and name for each ionic compound formed between the two listed ions.
    a. Cu^{2+} and F^{-}

   - b. Ca^{2+} and O^{2-}
   - c. K^{+} and P^{3-}
14. Give the formula and name for each ionic compound formed between the two listed ions.
   - a. Na^{+} and N^{3-}
   - b. Co^{2+} and I^{-}
   - c. Au^{3+} and S^{2-}
15. Give the formula and name for each ionic compound formed between the two listed ions.
   - a. K^{+} and $SO_4{}^{2-}$
   - b. $NH_4{}^{+}$ and S^{2-}
   - c. $NH_4{}^{+}$ and $PO_4{}^{3-}$
16. Give the formula and name for each ionic compound formed between the two listed ions.
   - a. Ca^{2+} and $NO_3{}^{-}$
   - b. Ca^{2+} and $NO_2{}^{-}$
   - c. Sc^{3+} and $C_2H_3O_2{}^{-}$
17. Give the formula and name for each ionic compound formed between the two listed ions.
   - a. Pb^{4+} and $SO_4{}^{2-}$
   - b. Na^{+} and $I_3{}^{-}$
   - c. Li^{+} and $Cr_2O_7{}^{2-}$
18. Give the formula and name for each ionic compound formed between the two listed ions.
   - a. $NH_4{}^{+}$ and N^{3-}
   - b. Mg^{2+} and $CO_3{}^{2-}$
   - c. Al^{3+} and OH^{-}
19. Give the formula and name for each ionic compound formed between the two listed ions.
   - a. Ag^{+} and $SO_3{}^{2-}$
   - b. Na^{+} and $HCO_3{}^{-}$
   - c. Fe^{3+} and $ClO_3{}^{-}$
20. Give the formula and name for each ionic compound formed between the two listed ions.
   - a. Rb^{+} and $O_2{}^{2-}$
   - b. Au^{3+} and $HSO_4{}^{-}$
   - c. Sr^{2+} and $NO_2{}^{-}$
21. What is the difference between SO_3 and $SO_3{}^{2-}$?
22. What is the difference between NO_2 and $NO_2{}^{-}$?

Answers

1. Cations form by losing electrons.
2.
3.
   - a. 1+
   - b. 2−
   - c. 2+, 3+
4.
5.
   - a. 1+
   - b. 1+, 3+
   - c. 1−
6.
7.
   - a. the potassium ion
   - b. the oxide ion
   - c. the cobalt(II) and cobalt(III) ions, respectively
8.

9. a. the silver ion
   b. the gold(I) and gold(III) ions, respectively
   c. the bromide ion
10.
11. a. magnesium chloride, $MgCl_2$
    b. iron(II) oxide, FeO
    c. iron(III) oxide, Fe_2O_3
12.
13. a. copper(II) fluoride, CuF_2
    b. calcium oxide, CaO
    c. potassium phosphide, K_3P
14.
15. a. potassium sulfate, K_2SO_4
    b. ammonium sulfide, $(NH_4)_2S$
    c. ammonium phosphate, $(NH_4)_3PO_4$
16.
17. a. lead(IV) sulfate, $Pb(SO_4)_2$
    b. sodium triiodide, NaI_3
    c. lithium dichromate, $Li_2Cr_2O_7$
18.
19. a. silver sulfite, Ag_2SO_3
    b. sodium hydrogen carbonate, $NaHCO_3$
    c. iron(III) chlorate, $Fe(ClO_3)_3$
20.
21. SO_3 is sulfur trioxide, while SO_3^{2-} is the sulfite ion.

Acids

1. Give the formula for each acid.
   a. perchloric acid
   b. hydriodic acid
2. Give the formula for each acid.
   a. hydrosulfuric acid
   b. phosphorous acid
3. Name each acid.
   a. HF(aq)
   b. HNO_3(aq)
   c. $H_2C_2O_4$(aq)
4. Name each acid.
   a. H_2SO_4(aq)
   b. H_3PO_4(aq)
   c. HCl(aq)
5. Name an acid found in food.
6. Name some properties that acids have in common.

Answers

1. a. $HClO_4$(aq)
   b. HI(aq)
2.
3. a. hydrofluoric acid

   b. nitric acid
   c. oxalic acid
4.
5. oxalic acid (answers will vary)

CHAPTER OVERVIEW

5: The Mole and Chemical Formulas

The mole concept is central to any chemistry calculation based on experimental results. The mole is how we relate the unbelievably small atoms and molecules that make something up to the measurable properties such as mass which we may observe in a laboratory setting. A proper understanding of the mole concept is essential in order to do any calculations on experimental data. The mole concept is introduced in this chapter, and will appear again in many of the forthcoming chapters. Mastering the concepts in those later chapters is dependent upon mastering the mole concept in this chapter. This might be the most important chapter in the textbook!

Because of the centrality of the mole concept throughout this textbook, here are a few guidelines you might want to consider as you begin studying this chapter:

- Refresh your understanding of conversion factors by reviewing the appropriate section of this textbook. Conversion factors are necessary in order to do all of the mole calculations introduced in this chapter.
- Master each section of this chapter before moving on to the next section. Perhaps more so than in any chapter we have looked at so far, the sections of this chapter build on each other. You might imagine it like a staircase, where you have to step on the first step before you can move on to the next one.
- Do additional homework problems if you are struggling to understand the concepts. The exercise section of this chapter includes links to additional homework sets and answer keys that you may practice if necessary.

5.1: Avogadro's Number

Figure 5.1.1 (Credit: User:OSX/Wikimedia Commons; Source: http://commons.wikimedia.org/wiki/File:1983-1988_Toyota_Hilux_4-door_utility_01.jpg(opens in new window); License: Public Domain)

Is there an easier way to load this truck?

When the weather is nice, many people begin to work on their yards and homes. For many projects, sand is needed as a foundation for a walk or to add to other materials. You could order up twenty million grains of sand and have people really stare at you. You could order by the pound, but that takes a lot of time weighing out. The best bet is to order by the yard, meaning a cubic yard. The loader can easily scoop up what you need and put it directly in your truck.

Avogadro's Number

It certainly is easy to count objects such as bananas, or something as large as elephants (as long as you stay out of their way). However, counting grains of sugar from a sugar canister would take a long, long time. Atoms and molecules are extremely small—far, far smaller than grains of sugar. Counting atoms or molecules is not only unwise, it is absolutely impossible. One drop of water contains about 10^{22} molecules of water. If you counted 10 molecules every second for 50 years, without stopping, you would have counted only 1.6×10^{10} molecules. Put another way, at that counting rate, it would take you over 30 trillion years to count the water molecules in one tiny drop.

Chemists of the past needed a name that could stand for a very large number of items. Amadeo Avogadro (1776-1856), an Italian scientist, provided such a number. He is responsible for the counting unit of measure called the mole. A **mole** (mol) is the amount of a substance that contains 6.022×10^{23} representative particles of that substance. The mole is the SI unit for amount of a substance. Just like the dozen and the gross, it is a name that stands for a number. There are therefore 6.022×10^{23} water molecules in a mole of water molecules. There also would be 6.022×10^{23} bananas in a mole of bananas, if such a huge number of bananas ever existed.

Figure 5.1.2: Italian scientist Amadeo Avogadro, whose work led to the concept of the mole as a counting unit in chemistry. (Credit: C. Sentier; Source: http://commons.wikimedia.org/wiki/File:Amedeo_Avogadro2.jpg(opens in new window); License: Public Domain)

The number 6.022×10^{23} is called **Avogadro's number**, the number of representative particles in a mole. It is an experimentally determined number. A **representative particle** is the smallest unit in which a substance naturally exists. For the majority of elements, the representative particle is the atom. Iron, carbon, and helium consist of iron atoms, carbon atoms, and helium atoms, respectively. Seven elements exist in nature as diatomic molecules and they are $\mathrm{H_2}$, $\mathrm{N_2}$, $\mathrm{O_2}$, $\mathrm{F_2}$, $\mathrm{Cl_2}$, $\mathrm{Br_2}$, and $\mathrm{I_2}$. The representative particle for these elements is the molecule. Likewise, all molecular compounds such as $\mathrm{H_2O}$ and $\mathrm{CO_2}$ exist as molecules and so the molecule is their representative particle. For ionic compounds such as NaCl and $\mathrm{Ca(NO_3)_2}$, the representative particle is the formula unit. A mole of any substance contains Avogadro's number $\left(6.022 \times 10^{23}\right)$ of representative particles.

Figure 5.1.3: The animal mole is very different than the counting unit of the mole. Chemists nonetheless have adopted the mole as their unofficial mascot. National Mole Day is a celebration of chemistry that occurs on October 23rd (10/23) of each year. (Credit: Left: Michael David Hill, 2005 (Mikiwikipikidikipedia); Right: chrisbb@prodigy.net;(left) Michael David Hill, 2005 (Mikiwikipikidikipedia); (right) chrisbb@prodigy.net; Source: Left: http://commons.wikimedia.org/wiki/File:Close-up_of_mole.jpg(opens in new window); Right: http://www.flickr.com/photos/chrisbrenschmidt/436990097/(opens in new window); (left) http://commons.wikimedia.org/wiki/File:Close-up_of_mole.jpg(opens in new window); (right) http://www.flickr.com/photos/chrisbrenschmidt/436990097/(opens in new window); License: (left) CC-BY 2.5; (right) CC-BY 2.0)

Summary

- A mole of any substance contains Avogadro's number $\left(6.022 \times 10^{23}\right)$ of representative particles.

Review

1. What is the SI unit for amount of a substance?
2. What is the representative particle for an element?
3. The formula unit is the representative particle for what?

5.2: Conversions Between Moles and Atoms

Figure 5.2.1 (Credit: Courtesy of Diane A. Reid/National Cancer Institute; Source: http://commons.wikimedia.org/wiki/File:Man_responds_to_telephone_call.jpg(opens in new window); License: Public Domain)

Big numbers or little numbers?

Do you hate to type subscripts and superscripts? Even with a good word-processing program, having to click on an icon to get a superscript and then remembering to click off after you type the number can be a real hassle. If we did not know about moles and just knew about numbers of atoms or molecules (those big numbers that require lots of superscripts), life would be much more complicated and we would make many more typing errors.

Conversions Between Moles and Atoms

Conversions Between Moles and Number of Particles

Using our unit conversion techniques, we can use the mole label to convert back and forth between the number of particles and moles.

5.2.1 Example : Converting Number of Particles to Moles

The element carbon exists in two primary forms: graphite and diamond. How many moles of carbon atoms is 4.72×10^{24} atoms of carbon?

Solution

Step 1: List the known quantities and plan the problem.

Known

- number of C atoms $= 4.72 \times 10^{24}$
- $1 \text{ mole} = 6.022 \times 10^{23}$ atoms

Unknown

- 4.72×10^{24} = ? mol C

One conversion factor will allow us to convert from the number of C atoms to moles of C atoms.

Step 2: Calculate.

$$4.72 \times 10^{24} \text{ atoms C} \times \frac{1 \text{ mol C}}{6.022 \times 10^{23} \text{ atoms C}} = 7.84 \text{ mol C}$$

Step 3: Think about your result.

The given number of carbon atoms was greater than Avogadro's number, so the number of moles of C atoms is greater than 1 mole. Since Avogadro's number is a measured quantity with three significant figures, the result of the calculation is rounded to three significant figures.

Suppose that you want to know how many hydrogen atoms are in a mole of water molecules. First, you need to know the chemical formula for water, which is H_2O. There are two atoms of hydrogen in each molecule of water. How many atoms of hydrogen are in two water molecules? There are $2 \times 2 = 4$ hydrogen atoms. How about in a dozen? In that case, a dozen is 12; so $12 \times 2 = 24$ hydrogen atoms in a dozen water molecules. To get the answers (4 and 24), you multiply the given number of molecules by two atoms of hydrogen per molecule. So, to find the number of hydrogen atoms in a mole of water molecules, the problem can be solved using conversion factors:

$$1 \text{ mol } H_2O \times \frac{6.022 \times 10^{23} \text{ molecules } H_2O}{1 \text{ mol } H_2O} \times \frac{2 \text{ atoms H}}{1 \text{ molecule } H_2O} = 1.20 \times 10^{24} \text{ atoms H}$$

The first conversion factor converts from moles of particles to the number of particles. The second conversion factor reflects the number of atoms contained within each molecule.

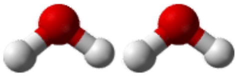

Figure 5.2.2: Two water molecules contain 4 hydrogen atoms and 2 oxygen atoms. A mole of water molecules contains 2 moles of hydrogen atoms and 1 mole of oxygen atoms. (Credit: Ben Mills (Wikimedia: Benjah-bmm27); Source: http://commons.wikimedia.org/wiki/File:Water-3D-balls-A.png(opens in new window); License: Public Domain)

5.2.2 Example : Atoms, Molecules, and Moles

Sulfuric acid has the chemical formula H_2SO_4. A certain quantity of sulfuric acid contains 4.89×10^{25} atoms of oxygen. How many moles of sulfuric acid is the sample?

Solution:

Step 1: List the known quantities and plan the problem.

Known

- $4.89 \times 10^{25} = \text{O atoms}$
- $1 \text{ mole} = 6.022 \times 10^{23} \text{ molecules } H_2SO_4$

Unknown

- mol of H_2SO_4 molecules

Two conversion factors will be used. First, convert atoms of oxygen to molecules of sulfuric acid. Then, convert molecules of sulfuric acid to moles of sulfuric acid.

Step 2: Calculate.

$$4.89 \times 10^{25} \text{ atoms O} \times \frac{1 \text{ molecule } H_2SO_4}{4 \text{ atoms O}} \times \frac{1 \text{ mol } H_2SO_4}{6.022 \times 10^{23} \text{ molecules } H_2SO_4} = 20.3 \text{ mol } H_2SO_4$$

Step 3: Think about your result.

The original number of oxygen atoms was about 80 times larger than Avogadro's number. Since each sulfuric acid molecule contains 4 oxygen atoms, there are about 20 moles of sulfuric acid molecules.

Summary

- Methods are described for conversions between moles, atoms, and molecules.

Review

1. What conversion factor would we need to convert moles of helium to atoms of helium?
2. I want to convert atoms to moles. My friend tells me to multiply the number of atoms by 6.022×10^{23} atoms/mole. Is my friend correct?
3. Why do you need to know the formula for a molecule in order to calculate the number of moles of one of the atoms?
4. How many atoms of fluorine are in 5.6×10^{22} molecules of MgF_2?

5.3: Molar Mass

Figure 5.3.1 (Credit: Ben Mills (Wikimedia: Benjah-bmm27); Source: http://commons.wikimedia.org/wiki/File:Potassium-dichromate-sample.jpg(opens in new window); License: Public Domain)

When creating a solution, how do I know how much of each substance to put in?

I want to make a solution that contains 1.8 moles of potassium dichromate. You do not have a balance calibrated in moles, but you do have one calibrated in grams. If you know the relationship between moles and the number of grams in a mole, you can use your balance to measure out the needed amount of material.

Molar Mass

Molar mass is defined as the mass of one mole of representative particles of a substance. By looking at a periodic table, we can conclude that the molar mass of lithium is 6.94 g, the molar mass of zinc is 65.38 g, and the molar mass of gold is 196.97 g. Each of these quantities contains 6.02×10^{23} atoms of that particular element. The units for molar mass are grams per mole, or g/mol.

Molar Masses of Compounds

The molecular formula of the compound carbon dioxide is CO_2. One molecule of carbon dioxide consists of 1 atom of carbon and 2 atoms of oxygen. We can calculate the mass of one molecule of carbon dioxide by adding together the masses of 1 atom of carbon and 2 atoms of oxygen:

$$12.01 \text{ amu} + 2\,(16.00 \text{ amu}) = 44.01 \text{ amu}$$

The **molecular mass** of a compound is the mass of one molecule of that compound. The molecular mass of carbon dioxide is 44.01 amu.

The molar mass of any compound is the mass in grams of one mole of that compound. One mole of carbon dioxide molecules has a mass of 44.01 g, while one mole of sodium sulfide formula units has a mass of 78.04 g. The molar masses are 44.01 g/mol and 78.04 g/mol respectively. In both cases, that is the mass of 6.02×10^{23} representative particles. The representative particle of CO_2 is the molecule, while for Na_2S it is the formula unit.

5.3.1 Example : Molar Mass of a Compound

Calcium nitrate, $Ca(NO_3)_2$, is used as a component in fertilizer. Determine the molar mass of calcium nitrate.

Solution

Step 1: List the known and unknown quantities and plan the problem.

Known

- $\text{Formula} = Ca(NO_3)_2$
- $\text{Molar mass Ca} = 40.08 \text{ g/mol}$
- $\text{Molar mass N} = 14.01 \text{ g/mol}$
- $\text{Molar mass O} = 16.00 \text{ g/mol}$

Unknown

- molar mass $Ca(NO_3)_2$

First we need to analyze the formula. Since the Ca lacks a subscript, there is one Ca atom per formula unit. The 2 outside the parentheses means that there are two nitrate ions per formula unit and each nitrate ion consists of one nitrogen atom and three oxygen atoms per formula unit. Thus, 1 mol of calcium nitrate contains 1 mol of Ca atoms, 2 mol of N atoms, and 6 mol of O atoms.

Step 2: Calculate

Use the molar masses of each atom together with the number of atoms in the formula and add together.

$$1 \text{ mol Ca} \times \frac{40.08 \text{ g Ca}}{1 \text{ mol Ca}} = 40.08 \text{ g Ca}$$

$$2 \text{ mol N} \times \frac{14.01 \text{ g N}}{1 \text{ mol N}} = 28.02 \text{ g N}$$

$$6 \text{ mol O} \times \frac{16.00 \text{ g O}}{1 \text{ mol O}} = 96.00 \text{ g O}$$

$$\text{Molar mass of } \mathrm{Ca(NO_3)_2} = 40.08 \text{ g} + 28.02 \text{ g} + 96.00 \text{ g} = 164.10 \text{ g/mol}$$

Summary

- Calculations are described for the determination of molar mass of an atom or a compound.

Review

1. What is the molar mass of Pb?
2. Where do you find the molar mass of an element?
3. How many moles of Cl are in one mole of the $CaCl_2$?
4. How many moles of H are in one mole of the compound $(NH_4)_3PO_4$?
5. Calculate the molar mass of $CaCl_2$.

5.4: Conversions Between Moles and Mass

Figure 5.4.1 (Credit: User:Estormiz/Wikimedia Commons; Source: http://commons.wikimedia.org/wiki/File:Fermion_Plant_Oulu_2007_01_20.JPG(opens in new window); License: Public Domain)

How can we get more product?

Chemical manufacturing plants are always seeking to improve their processes. One way that improvement comes about is through measuring the amount of material produced in a reaction. By knowing how much is made, the scientists and engineers can try different ways of getting more product at less cost.

Conversions Between Moles and Mass

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, 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 $\left(\mathrm{CaCl_2}\right)$. Since calcium chloride is a solid, it would be convenient to use a balance to measure the mass that is needed. The molar mass of $\mathrm{CaCl_2}$ is $110.98 \mathrm{~g/mol}$ The conversion factor that can be used is then based on the equality that $1 \mathrm{~mol} = 110.98 \mathrm{~g~CaCl_2}$. Dimensional analysis will allow you to calculate the mass of $\mathrm{CaCl_2}$ that you should measure.

$$3.00 \mathrm{~mol~CaCl_2} \times \frac{110.98 \mathrm{~g~CaCl_2}}{1 \mathrm{~mol~CaCl_2}} = 333 \mathrm{~g~CaCl_2}$$

When you measure the mass of $333 \mathrm{~g}$ of $\mathrm{CaCl_2}$, you are measuring 3.00 moles of $\mathrm{CaCl_2}$.

Figure 5.4.2: Calcium chloride is used as a drying agent and as a road deicer. (Credit: Martin Walker (User:Walkerma/Wikimedia Commons); Source: http://commons.wikimedia.org/wiki/File:Calcium_chloride.jpg(opens in new window); License: Public Domain)

5.4.1 Example : Converting Moles to Mass

Chromium metal is used for decorative electroplating of car bumpers and other surfaces. Find the mass of 0.560 moles of chromium.

Solution

Step 1: List the known quantities and plan the problem.

Known

- Molar mass of $\mathrm{Cr} = 52.00 \mathrm{~g/mol}$
- $0.560 \mathrm{~mol~Cr}$

Unknown

- 0.560 mol Cr= ? g

One conversion factor will allow us to convert from the moles of Cr to mass.

Step 2: Calculate.

$$0.560 \text{ mol Cr} \times \frac{52.00 \text{ g Cr}}{1 \text{ mol Cr}} = 29.1 \text{ g Cr}$$

Step 3: Think about your result.

Since the desired amount was slightly more than one half of a mole, the mass should be slightly more than one half of the molar mass. The answer has three significant figures because of the 0.560 mol

A similar conversion factor utilizing molar mass can be used to convert from the mass of a substance to moles. In a laboratory situation, you may perform a reaction and produce a certain amount of a product which can be massed. It will often then be necessary to determine the number of moles of the product that was formed. The next problem illustrates this situation.

5.4.2 Example : Converting Mass to Moles

A certain reaction produces 2.81 g of copper (II) hydroxide, $\mathrm{Cu(OH)_2}$. Determine the number of moles produced in the reaction.

Step 1: List the known quantities and plan the problem.

Known

- mass = 2.81g

Unknown

- mol $\mathrm{Cu(OH)_2}$

One conversion factor will allow us to convert from mass to moles.

Step 2: Calculate.

First, it is necessary to calculate the molar mass of $\mathrm{Cu(OH)_2}$ from the molar masses of Cu, O, and H. The molar mass is 97.57 g/mol

$$2.81 \text{ g } \mathrm{Cu(OH)_2} \times \frac{1 \text{ mol } \mathrm{Cu(OH)_2}}{97.57 \text{ g } \mathrm{Cu(OH)_2}} = 0.0288 \text{ mol } \mathrm{Cu(OH)_2}$$

Step 3: Think about your result.

The relatively small mass of product formed results in a small number of moles.

Summary

- Calculations involving conversions between moles of a material and the mass of that material are described.

Review

1. You have 19.7 grams of a material and wonder how many moles were formed. Your friend tells you to multiply the mass by grams/mole. Is your friend correct?
2. How many grams of MgO are in 3.500 moles?
3. How many moles of H_2O are in 15.2 grams of pure ice?

5.5: Conversions Between Mass and Number of Particles

Avogadro theorized that equal volumes of gases under the same conditions contained the same number of particles. Other researchers studied how many gas particles were in specific volumes of gases. Eventually, scientists were able to develop the relationship between number of particles and mass, using the idea of moles.

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 the 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 grams. In order to convert from mass to number of particles or vice-versa, a conversion to moles is required.

Figure 5.5.1: Conversion from number of particles to mass, or from mass to number of particles requires two steps.

Example 5.5.1

How many molecules is 20.0 g of chlorine gas, Cl_2?

Solution

Step 1: List the known quantities and plan the problem.

Known

- Molar mass $\text{Cl}_2 = 70.90\text{ g/mol}$
- 20.0 g Cl_2

Unknown

Use two conversion factors. The first converts grams of Cl_2 to moles. The second converts moles of Cl_2 to the number of molecules.

Step 2: Calculate.

$$20.0\text{ g Cl}_2 \times \frac{1\text{ mol Cl}_2}{70.90\text{ g Cl}_2} \times \frac{6.022 \times 10^{23}\text{ molecules Cl}_2}{1\text{ mol Cl}_2} = 1.70 \times 10^{23}\text{ molecules Cl}_2 \tag{5.5.1}$$

The problem is done using two consecutive conversion factors. There is no need to explicitly calculate the moles of Cl_2.

Step 3: Think about your result.

Since the given mass is less than half of the molar mass of chlorine, the resulting number of molecules is less than half of Avogadro's number.

Summary

- Mass and number of particles are both related to grams.
- In order to convert from mass to number of particles or vice-versa, a conversion to moles is required.
- Calculations are illustrated for conversions between mass and number of particles.

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5.6: Percent Composition

Nutrition Facts

Serv. Size 2 tbsp (32g)
Servings about 16

Calories 180
Fat Cal.130

*Percent Daily Values (DV) are based on a 2,000 calorie diet.

Amount Per Serving	% DV*	Amount Per Serving	% DV*
Total Fat 15g	23%	**Total Carbohydrate** 8g	3%
Saturated Fat 2g	10%	Dietary Fiber 2g	8%
Trans Fat 0g		Sugars 3g	
Cholesterol 0mg	0%	**Protein** 7g	
Sodium 140mg	6%		

Vitamin A 0% • Vitamin C 0% • Calcium 2% • Iron 4%

INGREDIENTS: PEANUTS, SUGAR, HYDROGENATED VEGETABLE OIL (RAPESEED, COTTONSEED, OYBEAN), SALT, MOLASSES.

Figure 5.6.1 (Credit: Joy Sheng; Source: CK-12 Foundation; License: CC BY-NC 3.0(opens in new window))

Is there anything healthy in this jar?

Packaged foods that you eat typically have nutritional information provided on the label. The label on a jar of peanut butter (shown above) reveals that one serving size is considered to be 32 g. The label also gives the masses of various types of compounds that are present in each serving. One serving contains 7 g of protein, 15 g of fat, and 3 g of sugar. By calculating the fraction of protein, fat, or sugar in one serving size of peanut butter and converting to percent values, we can determine the composition of peanut butter on a percent by mass basis.

Percent Composition

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 what was just indicated for the peanut butter.

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

Percent Composition from Mass Data

The sample problem below shows the calculation of the percent composition of a compound based on mass data.

5.6.1 Example : Percent Composition from Mass

A certain newly synthesized compound is known to contain the elements zinc and oxygen. When a 20.00 g sample of the compound is decomposed, 16.07 g of zinc remains. Determine the percent composition of the compound.

Solution

Step 1: List the known quantities and plan the problem.

Known

- Mass of compound $= 20.00 \text{ g}$
- Mass of $\text{Zn} = 16.07 \text{ g}$

Unknown

- Percent $\text{Zn} = ?\%$
- Percent $\text{O} = ?\%$

Subtract to find the mass of oxygen in the compound. Divide each element's mass by the mass of the compound to find the percent by mass.

Step 2: Calculate.

$$\text{Mass of oxygen} = 20.00 \text{ g} - 16.07 \text{ g} = 3.93 \text{ g O}$$

$$\% \text{ Zn} = \frac{16.07 \text{ g Zn}}{20.00 \text{ g}} \times 100\% = 80.35\% \text{ Zn}$$

$$\% \text{ O} = \frac{3.93 \text{ g O}}{20.00 \text{ g}} \times 100\% = 19.65\% \text{ O}$$

Step 3: Think about your result.

The calculations make sense because the sum of the two percentages adds up to 100%. By mass, the compound is mostly zinc.

Percent Composition from a Chemical Formula

The percent composition of a compound can also be determined from the formula of the compound. The subscripts in the formula are first used to calculate the mass of each element in one mole of the compound. That is divided by the molar mass of the compound and multiplied by 100%.

$$\% \text{ by mass} = \frac{\text{mass of element in 1 mol}}{\text{molar mass of compound}} \times 100\%$$

The percent composition of a given compound is always the same as long as the compound is pure.

5.6.2 Example : Percent Composition from Chemical Formula

Dichlorineheptoxide $\left(\mathrm{Cl_2O_7}\right)$ is a highly reactive compound used in some organic synthesis reactions. Calculate the percent composition of dichlorineheptoxide.

Solution

Step 1: List the known quantities and plan the problem.

Known

- Mass of Cl in $1 \text{ mol } \mathrm{Cl_2O_7} = 70.90 \text{ g}$
- Mass of O in $1 \text{ mol } \mathrm{Cl_2O_7} = 112.00 \text{ g}$
- Molar mass of $\mathrm{Cl_2O_7} = 182.90 \text{ g/mol}$

Unknown

- Percent $\mathrm{Cl} = ?\%$
- Percent $\mathrm{O} = ?\%$

Calculate the percent by mass of each element by dividing the mass of that element in 1 mole of the compound by the molar mass of the compound and multiplying by 100%.

Step 2: Calculate.

$$\%\mathrm{Cl} = \frac{70.90 \text{ g Cl}}{182.90 \text{ g}} \times 100\% = 38.76\% \text{ Cl}$$

$$\% \text{ O} = \frac{112.00 \text{ g O}}{182.90 \text{ g}} \times 100\% = 61.24\% \text{ O}$$

Step 3: Think about your result.

The percentages add up to 100%.

Percent composition can also be used to determine the mass of a certain element that is contained in any mass of a compound. In the previous sample problem, it was found that the percent composition of dichlorine heptoxide is $38.76\% \text{ Cl}$ and $61.24\% \text{ O}$. Suppose that you need to know the masses of chlorine and oxygen present in a 12.50 g sample of dichlorine heptoxide. You can set up a conversion factor based on the percent by mass of each element:

$$12.50 \text{ g } \mathrm{Cl_2O_7} \times \frac{38.76 \text{ g Cl}}{100 \text{ g } \mathrm{Cl_2O_7}} = 4.845 \text{ g Cl}$$

$$12.50 \text{ g } \mathrm{Cl_2O_7} \times \frac{61.24 \text{ g O}}{100 \text{ g } \mathrm{Cl_2O_7}} = 7.655 \text{ g O}$$

The sum of the two masses is 12.50 g the mass of the sample size.

Science Friday: Stained Glass Conservation

Stained glass from the Middle Ages is often hundreds of years old. Unfortunately, many of these relics are in need of cleaning and maintenance. In this video by Science Friday, conservator Mary Higgins discusses the methods used to protect the stained glass.

Summary

- Processes are described for calculating the percent composition of a material based on mass or on chemical composition.

Review

1. What is the formula for calculating percent composition?
2. What information do you need to calculate percent composition by mass?
3. What do subscripts in a chemical formula tell you?

5.7: Determining Empirical Formulas

Figure 5.7.1 (Credit: Harriet Moore; Source: http://commons.wikimedia.org/wiki/File:M_Faraday_Lab_H_Moore.jpg(opens in new window); License: Public Domain)

What is occuring in this picture?

In the early days of chemistry, there were few tools available for the detailed study of compounds. Much of the information regarding the composition of compounds came from the elemental analysis of inorganic materials. The "new" field of organic chemistry (the study of carbon compounds) faced the challenge of not being able to characterize a compound completely. The relative amounts of elements could be determined, but many of these materials had carbon, hydrogen, oxygen, and possibly nitrogen in simple ratios. Chemists had no way to determine the exact amounts of these atoms that were contained in specific molecules.

Determining Empirical Formulas

An **empirical formula** is one that shows the lowest whole-number ratio of the elements in a compound. Because the structure of ionic compounds is an extended three-dimensional network of positive and negative ions, all formulas of ionic compounds are empirical. However, we can also consider the empirical formula of a molecular compound. Ethene is a small hydrocarbon compound with the formula C_2H_4 (see figure below). While C_2H_4 is its molecular formula and represents its true molecular structure, it has an empirical formula of CH_2. The simplest ratio of carbon to hydrogen in ethene is 1:2. There are two ways to view that ratio. Considering one molecule of ethene, the ratio is 1 carbon atom for every 2 atoms of hydrogen. Considering one mole of ethene, the ratio is 1 mole of carbon for every 2 moles of hydrogen. So, the subscripts in a formula represent the mole ratio of the elements in that formula.

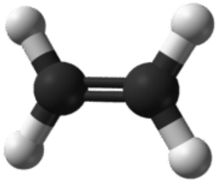

Figure 5.7.2: Ball-and-stick model of ethene, C_2H_4. (Credit: Ben Mills (Wikimedia: Benjah-bmm27); Source: http://commons.wikimedia.org/wiki/File:Ethylene-CRC-MW-3D-balls.png(opens in new window); License: Public Domain)

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. The steps to be taken are outlined below.

1. Assume a 100 g 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.

5.7.1 Example : Determining the Empirical Formula of a Compound

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: List the known quantities and plan the problem.

Known

- $\%$ of $\mathrm{Fe} = 69.94\%$
- $\%$ of $\mathrm{O} = 30.06\%$

Unknown

- Empirical formula = $Fe_?O_?$

Steps to follow are outlined in the text.

Step 2: Calculate.

1. Assume a 100 g sample.

$$69.94 \text{ g Fe}$$

$$30.06 \text{ g O}$$

2. Convert to moles.

$$69.94 \text{ g Fe} \times \frac{1 \text{ mol Fe}}{55.85 \text{ g Fe}} = 1.252 \text{ mol Fe}$$

$$30.06 \text{ g O} \times \frac{1 \text{ mol O}}{16.00 \text{ g O}} = 1.879 \text{ mol O}$$

3. Divide both moles by the smallest of the results.

$$\frac{1.252 \text{ mol Fe}}{1.252} = 1 \text{ mol Fe} \quad \frac{1.879 \text{ mol O}}{1.252} = 1.501 \text{ molO}$$

4/5. Since the moles of O is still not a whole number, both moles can be multiplied by 2, while rounding to a whole number.

$$1 \text{ mol Fe} \times 2 = 2 \text{ mol Fe} \quad 1.501 \text{ mol O} \times 2 = 3 \text{ mol O}$$

The empirical formula of the compound is $\mathrm{Fe_2O_3}$.

Step 3: Think about your result.

The subscripts are whole numbers and represent the mole ratio of the elements in the compound. The compound is the ionic compound iron (III) oxide.

Summary

- A process is described for the calculation of the empirical formula for a compound based on the percent composition of that compound.

Review

1. What is an empirical formula?
2. What does an empirical formula tell you?
3. What does it not tell you?

5.8: Percent of Water in a Hydrate

Figure 5.8.1 (Credit: Doug Smith (Wikimedia: Xsmith); Source: http://commons.wikimedia.org/wiki/File:CurrituckSoundMap.png(opens in new window); License: Public Domain)

Why does the color change?

If you look at a typical bottle of copper sulfate, it will be a bluish-green. If someone were to tell you that copper sulfate is white, you likely would not believe them. However, it turns out that you are both right; it just depends on the copper sulfate. Your blue-green copper sulfate has several water molecules attached to it, while your friend's copper sulfate is anhydrous (no water attached). Why the difference? The water molecules interact with some of the d electrons in the copper ion and produce the color. When the water is removed, the electron configuration changes and the color disappears.

Percent of Water in a Hydrate

Many ionic compounds naturally contain water as part of the crystal lattice structure. A **hydrate** is a compound that has one or more water molecules bound to each formula unit. Ionic compounds that contain a transition metal are often highly colored. Interestingly, it is common for the hydrated form of a compound to be of a different color than the **anhydrous** form, which has no water in its structure. A hydrate can usually be converted to the anhydrous compound by heating. For example, the anhydrous compound cobalt (II) chloride is blue, while the hydrate is a distinctive magenta color.

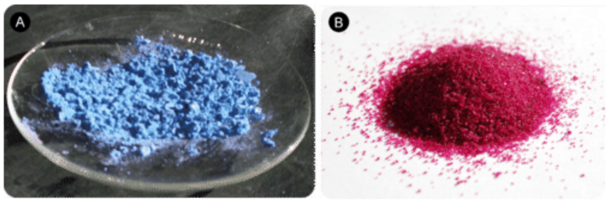

Figure 5.8.2: On the left is anhydrous cobalt (II) chloride, $\mathrm{CoCl_2}$. On the right is the hydrated form of the compound called cobalt (II) chloride hexahydrate, $\mathrm{CoCl_2 \cdot 6H_2O}$. (Credit: (A) Martin Walker (Wikimedia: Walkerma); (B) Ben Mills (Wikimedia: Benjah-bmm27); Source: (A) http://commons.wikimedia.org/wiki/File:Cobalt%2528II%2529_chloride.jpg(opens in new window); (B) http://commons.wikimedia.org/wiki/File:Cobalt%2528II%2529-chloride-hexahydrate-sample.jpg(opens in new window); License: Public Domain)

The hydrated form of cobalt (II) chloride contains six water molecules in each formula unit. The name of the compound is cobalt (II) chloride hexahydrate and its formula is $\mathrm{CoCl_2 \cdot 6H_2O}$. The formula for water is set apart at the end of the formula with a dot, followed by a coefficient that represents the number of water molecules per formula unit.

It is useful to know the percent of water contained within a hydrate. The sample problem below demonstrates the procedure.

5.8.1 Example : Percent of Water in a Hydrate

Find the percent water in cobalt (II) chloride hexahydrate, $\mathrm{CoCl_2 \cdot 6H_2O}$.

Solution

Step 1: List the known quantities and plan the problem.

The mass of water in the hydrate is the coefficient (6) multiplied by the molar mass of $\mathrm{H_2O}$. The molar mass of the hydrate is the molar mass of the $\mathrm{CoCl_2}$ plus the mass of water.

Known

- Mass of H_2O in $1 \text{ mol hydrate} = 108.12 \text{ g}$
- Molar mass of hydrate $= 237.95 \text{ g/mol}$

Unknown

- percent H_2O = ?%

Calculate the percent by mass of water by dividing the mass of H_2O in 1 mole of the hydrate by the molar mass of the hydrate and multiplying by 100%.

Step 2: Calculate.

$$\% \text{ H}_2\text{O} = \frac{108.12 \text{ g H}_2\text{O}}{237.95 \text{ g}} \times 100\% = 45.44\% \text{ H}_2\text{O}$$

Step 3: Think about your result.

Nearly half of the mass of the hydrate is composed of water molecules within the crystal.

Summary

- The process of calculating the percent water in a hydrate is described.

Review

1. What is a hydrate?
2. How can you convert a hydrate to an anhydrous compound?
3. What does hexahydrate mean?

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5.9: Determining Molecular Formulas

Below are two carbohydrates: glucose and sucrose. Sucrose is almost exactly twice the size of glucose, although their empirical formulas are very similar. Some people could distinguish them on the basis of taste, but it's not a good idea to go around tasting chemicals. The best way is to determine the molecular weights—this approach makes the compounds easily distinguishable.

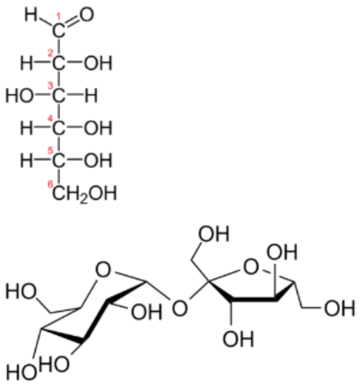


Figure 5.9.1: On top, the molecular structure of glucose. Below, the molecular structure of sucrose. please note: you do not need to understand the meaning of these structures at this point in the course.

Molecular Formulas

Molecular formulas give the kind and number of atoms of each element present in a molecular compound. In many cases, the molecular formula is the same as the empirical formula. The molecular formula of methane is CH_4 and because it contains only one carbon 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 $C_6H_{12}O_6$. The structures of both molecules are shown in the figure below. They are very different compounds, yet both have the same empirical formula of CH_2O.

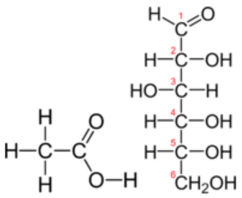


Figure 5.9.2: Acetic acid (left) has a molecular formula of $C_2H_4O_2$, while glucose (right) has a molecular formula of $C_6H_{12}O_6$. Both have the empirical formula CH_2O.

Empirical formulas can be determined from the percent composition of a compound. In order to determine its molecular formula, it is necessary to know the molar mass of the compound. Chemists use an instrument called a mass spectrometer to determine the molar mass of compounds. In order to go from the empirical formula to the molecular formula, follow these steps:

1. Calculate the **empirical formula mass (EFM)**, which is simply the molar mass represented by the empirical formula.
2. Divide the molar mass of the compound by the empirical formula 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 5.9.1

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

Solution

Step 1: List the known quantities and plan the problem.

Known

- Empirical formula $= \mathrm{BH_3}$
- Molar mass $= 27.7 \mathrm{~g/mol}$

Unknown

Steps to follow are outlined in the text.

Step 2: Calculate.

$$\text{Empirical formula mass (EFM)} = 13.84 \mathrm{~g/mol} \tag{5.9.1}$$

$$\frac{\text{molar mass}}{\text{EFM}} = \frac{27.7}{13.84} = 2 \tag{5.9.2}$$

$$\mathrm{BH_3} \times 2 = \mathrm{B_2H_6} \tag{5.9.3}$$

The molecular formula of the compound is $\mathrm{B_2H_6}$.

Step 3: Think about your result.

The molar mass of the molecular formula matches the molar mass of the compound.

Summary

- Molecular formulas give the kind and number of atoms of each element present in a molecular compound.
- A procedure is described for the calculation of the exact molecular formula of a compound.

5.10: Mole Road Map

If you want to visit the town of Manteo, North Carolina, out on the coast, you need a map to get there. You may have a printed map or may download directions from the internet, but need something to steer you in the right direction. Chemistry road maps serve the same purpose. How do you handle a certain type of calculation? There is a process and a set of directions to help.

Mole Road Map

The mole concept is central to any chemistry calculation based on experimental results. The mole is how we relate the unbelievably small atoms and molecules that make something up to the measurable properties such as mass which we may observe in a laboratory setting. In this chapter, we have limited our discussion on the mole concept to the measurable property of masses of pure substances. However, this is not the only type of matter that exists. In later chapters, we will need to consider how to find the moles of a portion of matter which may not be a pure substance, or may be difficult to mass. Or we may need to find how the amount of substance changes as a result of a chemical change. Having a way to map conversion factors between moles and various properties becomes important as we introduce these other ways of measuring matter.

The following diagram shows a mole map which includes one additional measurable property (the volume of the gas at STP). You do not need to understand the meaning of STP at the moment, and we will explore gas properties in more detail in a later chapter. However, you should be able to look at the diagram and see how the mole concept is central. As additional conversions between moles and measurable properties are introduced in later chapters, please take a moment to create your own mole map showing how those properties relate to the mole concept via a conversion factor.

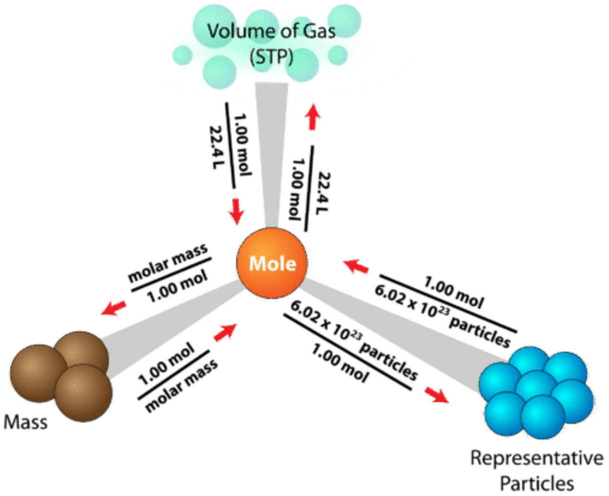


Figure 5.10.1: The mole road map shows the conversion factors needed to interconvert mass, number of particles, and volume of a gas.

The mole is at the center of any calculation involving amount of a substance. The sample problem below is one of many different problems that can be solved using the mole road map.

Example 5.10.1

What is the volume of $79.3\ \text{g}$ of neon gas at STP?

Solution

Step 1: List the known quantities and plan the problem.

Known

- $\text{Ne} = 20.18\ \text{g/mol}$
- $1\ \text{mol} = 22.4\ \text{L}$

Unknown

The conversion factors will be grams $\rightarrow$ moles $\rightarrow$ gas volume.

Step 2: Calculate.

$$79.3 \text{ g Ne} \times \frac{1 \text{ mol Ne}}{20.18 \text{ g Ne}} \times \frac{22.4 \text{ L Ne}}{1 \text{ mol Ne}} = 88.0 \text{ L Ne} \tag{5.10.1}$$

Step 3: Think about your result.

The given mass of neon is equal to about 4 moles, resulting in a volume that is about 4 times larger than molar volume.

Summary

5.E: The Mole Concept (Exercises)

5.1-5.5: Avogadro's Number, Molar Mass and the Mole

Conceptual Problems

Please be sure you are familiar with the topics discussed in Essential Skills 2 before proceeding to the Conceptual Problems.

1. Describe the relationship between an atomic mass unit and a gram.
2. Is it correct to say that ethanol has a formula mass of 46? Why or why not?
3. If 2 mol of sodium reacts completely with 1 mol of chlorine to produce sodium chloride, does this mean that 2 g of sodium reacts completely with 1 g of chlorine to give the same product? Explain your answer.
4. Construct a flowchart to show how you would calculate the number of moles of silicon in a 37.0 g sample of orthoclase ($KAlSi_3O_8$), a mineral used in the manufacture of porcelain.
5. Construct a flowchart to show how you would calculate the number of moles of nitrogen in a 22.4 g sample of nitroglycerin that contains 18.5% nitrogen by mass.

Numerical Problems

Please be sure you are familiar with the topics discussed in Essential Skills 2 before proceeding to the Numerical Problems.

1. Derive an expression that relates the number of molecules in a sample of a substance to its mass and molecular mass.

2. Calculate the molecular mass or formula mass of each compound.

a. KCl (potassium chloride)
b. NaCN (sodium cyanide)
c. H_2S (hydrogen sulfide)
d. NaN_3 (sodium azide)
e. H_2CO_3 (carbonic acid)
f. K_2O (potassium oxide)
g. $Al(NO_3)_3$ (aluminum nitrate)
h. $Cu(ClO_4)_2$ [copper(II) perchlorate]

3. Calculate the molecular mass or formula mass of each compound.

a. V_2O_4 (vanadium(IV) oxide)
b. $CaSiO_3$ (calcium silicate)
c. BiOCl (bismuth oxychloride)
d. CH_3COOH (acetic acid)
e. Ag_2SO_4 (silver sulfate)
f. Na_2CO_3 (sodium carbonate)
g. $(CH_3)_2CHOH$ (isopropyl alcohol)

8. Calculate the number of molecules or formula units in 5.00×10^2 g of each substance. (Remember that a basic unit of a molecular compound is called a "molecule", while it is called a "Formula Unit" for an ionic compound.)

a. CaO (lime)

b. $CaCO_3$(chalk)

c. $C_{12}H_{22}O_{11}$ [sucrose (cane sugar)]

d. NaOCl (bleach)

e. CO_2 (dry ice)

9. Calculate the mass in grams of each sample.

a. 0.520 mol of N_2O_4

b. 1.63 mol of $C_6H_4Br_2$

c. 4.62 mol of $(NH_4)_2SO_3$

10. Give the number of molecules or formula units in each sample.

a. 1.30×10^{-2} mol of SCl_2

b. 1.03 mol of N_2O_5

c. 0.265 mol of $Ag_2Cr_2O_7$

11. Give the number of moles in each sample.

a. 9.58×10^{26} molecules of Cl_2

b. 3.62×10^{27} formula units of KCl

c. 6.94×10^{28} formula units of $Fe(OH)_2$

12. Solutions of iodine are used as antiseptics and disinfectants. How many iodine atoms correspond to 11.0 g of molecular iodine (I_2)?

13. What is the total number of atoms in each sample?

a. 0.431 mol of Li

b. 2.783 mol of methanol (CH_3OH)

c. 0.0361 mol of $CoCO_3$

d. 1.002 mol of $SeBr_2O$

14. What is the total number of atoms in each sample?

a. 0.980 mol of Na

b. 2.35 mol of O_2

c. 1.83 mol of Ag_2S

d. 1.23 mol of propane (C_3H_8)

15. What is the total number of atoms in each sample?

a. 2.48 g of HBr

b. 4.77 g of CS_2

c. 1.89 g of NaOH

d. 1.46 g of SrC_2O_4

16. Decide whether each statement is true or false and explain your reasoning.

a. There are more molecules in 0.5 mol of Cl_2than in 0.5 mol of H_2.
b. One mole of H_2 has 6.022×10^{23} hydrogen atoms.
c. The molecular mass of H_2O is 18.0 amu.
d. The formula mass of benzene is 78 amu.

17. Complete the following table.

Substance	Mass (g)	Number of Moles	Number of Molecules or Formula Units	Number of Atoms or Ions
$MgCl_2$	37.62	a.	b.	c.
$AgNO_3$	d.	2.84	e.	f.
NH_4Cl	g.	h.	8.93×10^{25}	i.
K_2S	j	k.	l.	7.69×10^{26}
H_2SO_4	m.	1.29	n.	o.

Substance	Mass (g)	Number of Moles	Number of Molecules or Formula Units	Number of Atoms or Ions
C_6H_{14}	11.84	p.	q.	r.
$HClO_3$	s.	t.	2.45×10^{26}	u.

18. Give the formula mass or the molecular mass of each substance.

a. $PbClF$
b. $Cu_2P_2O_7$
c. $BiONO_3$
d. Tl_2SeO_4

19. Give the formula mass or the molecular mass of each substance.

a. $MoCl_5$
b. B_2O_3
c. UO_2CO_3
d. $NH_4UO_2AsO_4$

Conceptual Answers

1. While both are units of mass, a gram is Avogadro's number of atomic mass units so you would multiply the number of amu by 6.022x10^23 to find total number of grams
2. The correct way to state formula mass of ethanol is to show the units of mass which is amu.
3. No because moles and weight operate on different set of standards meaning that they're not equal to each other. This means that moles of different compounds contain different weights. For example, 2 moles of Na = 2 x 22.989 g = 45.98g while 1 mole of Cl = 1 x 35.453 g = 35.453 g Cl. This makes the sodium react completely with chlorine. 2g of sodium would react with = (35.453/45.978) x 2 = 1.542 g Cl
4. Construct a flowchart to show how you would calculate the number of moles of silicon in a 37.0 g sample of orthoclase ($KAlSi_3O_8$), a mineral used in the manufacture of porcelain
   1. . $$\frac{given\ mass}{molar\ mass\ of\ KAlSi3O8} x \frac{(3\ moles\ of\ Si)}{(1\ mole\ of\ KAlSi3O8)} = \frac{37\ mol}{278\ mol} x \frac{(3\ moles\ of\ Si)}{(1\ mole\ of\ KAlSi3O8)} = 0.4\ moles$$
5. Construct a flowchart to show how you would calculate the number of moles of nitrogen in a 22.4 g sample of nitroglycerin that contains 18.5% nitrogen by mass.
   1. $$\frac{given\ mass\ of\ nitroglycerin}{molar\ mass\ of\ nitroglcerin} x \frac{(3\ moles\ of\ Si)}{(1\ mole\ of\ KAlSi3O8)} = \frac{22.4\ g}{227.0\ \ g/mol} = 0.099\ mole \rightarrow \frac{4.14\ (mass\ of\ nitrogen)}{14\ (molar\ atomic\ mass\ of\ nitrogen)} = 0.296\ moles$$
6. The information required to determine the mass of the solute would be the molarity of the solution because once that is achieved, volume of the solution and molar mass of the solute can be used to calculate the total mass. A derivatization that achieves this goes as: Molarity = moles of solute / volume of solution in liter -> Moles = molarity x volume in liter -> Mass= moles x molar mass.

Numerical Answers

1. Derive an expression that relates the number of molecules in a sample of a substance to its mass and molecular mass.

$$1\ mole = 6.022x10^{23} mol = NA\ (Avogadro's\ Number)$$

$$mole = \frac{mass}{molecular\ mass}$$

$$Number\ of\ molecules = moles\ x\ NA \rightarrow \frac{mass}{molecular\ mass} xNA$$

2. Calculate the molecular mass or formula mass of each compound.

   a. 74.55 amu

b. 49.01 amu
c. 34.08 amu
d. 65.01 amu
e. 62.02 amu
f. 94.20 amu
g. 213.00 amu
h. 262.45 amu

3. Calculate the molecular mass or formula mass of each compound.

a. 165.88 amu
b. 116.16 amu
c. 260.43 amu
d. 60.05 amu
e. 311.80 amu
f. 105.99 amu
g. 60.10 amu

4. Calculate the molar mass of each compound.

a. 153.82 g/mol

b. 80.06 g/mol

c. 92.01 g/mol

d. 70.13 g/mol

e. 74.12 g/mol

5. Calculate the molar mass of each compound.

a. 92.45 g/mol

b. 135.04 g/mol

c. 44.01 g/mol

d. 40.06 g/mol

6. For each compound, write the condensed formula, name the compound, and give its molar mass.

a. $C_5H_{10}O_2$, Valeric Acid, 102.13 g/mol

b. $H_3PO_{3,}$ Phosphorous acid, 82 g/mol

7. For each compound, write the condensed formula, name the compound, and give its molar mass.

a. $C_2H_5NH_{2,}$ Ethylamine, 45.08 g/mol

b. $HIO_{3,}$ Iodic acid, 175.91 g/mol

8. Calculate the number of moles in 5.00×10^2 g of each substance. How many molecules or formula units are present in each sample?

a. 5.37×10^{24} molecules

b. 3.01×10^{24} formula units

c. 8.80×10^{23} molecules

d. 4.04×10^{24} formula units

e. 6.84×10^{24} molecules

9. Calculate the mass in grams of each sample.

a. 47.9 grams

b. 384 grams

c. 537 grams

10. Give the number of molecules or formula units in each sample.

a. 7.83×10^{21} molecules

b. 6.20×10^{23} molecules

c. 1.60×10^{23} molecules

11. Give the number of moles in each sample.

a. 1590 moles

b. 6010 moles

c. 1.15×10^{5} moles or 115000 moles

12. Solutions of iodine are used as antiseptics and disinfectants. How many iodine atoms correspond to 11.0 g of molecular iodine (I_2)?

2.61×10^{22} molecules

13. What is the total number of atoms in each sample?

a. 2.60×10^{23} atoms

b. 1.006×10^{25} atoms

c. 1.09×10^{23} atoms

d. 2.41×10^{24} atoms

14. What is the total number of atoms in each sample?

a. 5.9×10^{23} atoms

b. 2.8×10^{24} atoms

c. 3.31×10^{24} atoms

d. 8.15×10^{24} atoms

15. What is the total number of atoms in each sample?

a. 3.69×10^{22} atoms

b. 1.13×10^{23} atoms

c. 8.54×10^{22} atoms

d. 3.50×10^{23} atoms

16.

a. False, the number of molecules in 0.5 mol Cl2 are the same amount of molecules in H2

b. False, the number of molecules in H2 is 2 x (6.022 x10^23) H atoms

c. True, 2 H (1.01 amu) + 1 O (16.01) = 18.0 amu

d. True, C6H6 -> 12(6) + 1(6) = 78 amu

17. Complete the following table

a. 0.39

b. 2.36x10^23

c. 7.08x10^23

d. 482.8

e. 1.71x10^24

f. 8.55x10^24

g. 7932.7

h. 148.3

i. 5.36x10^26

j. 46938.5

k. 425.7

l. 1276.98

m. 126.5

n. 7.77x10^23

o. 5.44x10^24

p. 0.14

q. 8.27x10^22

r. 1.65x10^24

s. 34358

t. 406.8

u. 1.23x10^2

18. Give the formula mass or the molecular mass of each substance.

   a. 261.67 amu
   b. 301.04 amu
   c. 286.98 amu
   d. 551.73 amu

19. Give the formula mass or the molecular mass of each substance.

   a. 273.21 amu
   b. 69.62 amu
   c. 330.04 amu
   d. 426.99 amu

5.6-5.9: Percent Composition, Empirical Formula, and Molecular Formula

Conceptual Problems

1. What is the relationship between an empirical formula and a molecular formula
2. Construct a flowchart showing how you would determine the empirical formula of a compound from its percent composition.

Numerical Problems

1. What is the mass percentage of water in each hydrate?

   a. $H_3AsO_4 \cdot 5H_2O$

   b. $NH_4NiCl_3 \cdot 6H_2O$

   c. $Al(NO_3)_3 \cdot 9H_2O$

2. What is the mass percentage of water in each hydrate?

   a. $CaSO_4 \cdot 2H_2O$

   b. $Fe(NO_3)_3 \cdot 9H_2O$

   c. $(NH_4)_3ZrOH(CO_3)_3 \cdot 2H_2O$

3. Which of the following has the greatest mass percentage of oxygen—$KMnO_4$, $K_2Cr_2O_7$, or Fe_2O_3?

4. Which of the following has the greatest mass percentage of oxygen—$ThOCl_2$, $MgCO_3$, or NO_2Cl?

5. Calculate the percent composition of the element shown in bold in each compound.

a. $Sb\mathbf{Br}_3$

b. $\mathbf{As}_2I_4$

c. $Al\mathbf{P}O_4$

d. $\mathbf{C}_6H_{10}O$

6. Calculate the percent composition of the element shown in bold in each compound.

a. $H\mathbf{Br}O_3$

b $\mathbf{Cs}ReO_4$

c. $\mathbf{C}_3H_8O$

d. $Fe\mathbf{S}O_4$

7. A sample of a chromium compound has a molar mass of 151.99 g/mol. Elemental analysis of the compound shows that it contains 68.43% chromium and 31.57% oxygen. What is the identity of the compound?

8. The percentages of iron and oxygen in the three most common binary compounds of iron and oxygen are given in the following table. Write the empirical formulas of these three compounds.

Compound	% Iron	% Oxygen	Empirical Formula
1	69.9	30.1	
2	77.7	22.3	
3	72.4	27.6	

9. What is the mass percentage of water in each hydrate?

a. $LiCl·H_2O$

b. $MgSO_4·7H_2O$

c. $Sr(NO_3)_2·4H_2O$

10. What is the mass percentage of water in each hydrate?

a. $CaHPO_4·2H_2O$

b. $FeCl_2·4H_2O$

c. $Mg(NO_3)_2·4H_2O$

11. Two hydrates were weighed, heated to drive off the waters of hydration, and then cooled. The residues were then reweighed. Based on the following results, what are the formulas of the hydrates?

Compound	Initial Mass (g)	Mass after Cooling (g)
$NiSO_4·xH_2O$	2.08	1.22
$CoCl_2·xH_2O$	1.62	0.88

12. Which contains the greatest mass percentage of sulfur—FeS_2, $Na_2S_2O_4$, or Na_2S?

13. Given equal masses of each, which contains the greatest mass percentage of sulfur—$NaHSO_4$ or K_2SO_4?

14. Calculate the mass percentage of oxygen in each polyatomic ion.

a. bicarbonate

b. chromate

c. acetate

d. sulfite

15. Calculate the mass percentage of oxygen in each polyatomic ion.

a. oxalate

b. nitrite

c. dihydrogen phosphate

d. thiocyanate

16. The empirical formula of garnet, a gemstone, is $Fe_3Al_2Si_3O_{12}$. An analysis of a sample of garnet gave a value of 13.8% for the mass percentage of silicon. Is this consistent with the empirical formula?

17. A compound has the empirical formula C_2H_4O, and its formula mass is 88 g. What is its molecular formula?

18. Mirex is an insecticide that contains 22.01% carbon and 77.99% chlorine. It has a molecular mass of 545.59 g. What is its empirical formula? What is its molecular formula?

27. Calculate the formula mass or the molecular mass of each compound.

a. $MoCl_5$

b. B_2O_3

c. bromobenzene

d. cyclohexene

e. phosphoric acid

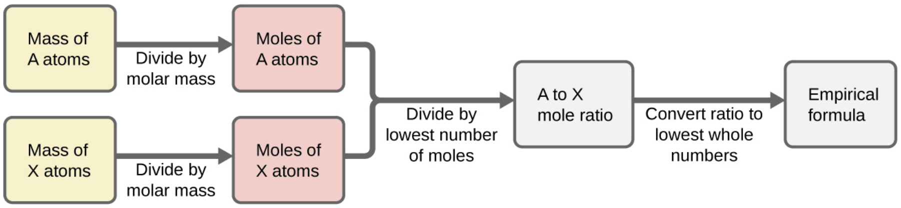
f. ethylamine

Conceptual Answers

1) What is the relationship between an empirical formula and a molecular formula

- An empirical formula refers to the simplest ratio of elements that is obtained from a chemical formula while a molecular formula is calculated to show the actual formula of a molecular compound.

2) Construct a flowchart showing how you would determine the empirical formula of a compound from its percent composition.



Numerical Answers

a. What is the formula mass of each species?

a. 53.49146 amu

b. 49.0072 amu

c. 58.3197 amu

d. 310.177 amu

e. 73.891 amu

f. 81.07 amu

b. What is the molecular or formula mass of each compound?

a.158.034 amu

   - b. 142.04 amu
   - c. 27.0253 amu
   - d. 97.181 amu
   - e. 124.1 amu
   - f. 65.99 amu

1. To two decimal places, the percentages are:
   - a. 5.97%
   - b. 37.12%
   - c. 43.22%
2. Percentage of Oxygen in each hydrates are:
   - a. 20.93%
   - b. 40.13%
   - c. 9.52%
3. % oxygen: $KMnO_4$, 40.50%; $K_2Cr_2O_7$, 38.07%; Fe_2O_3, 30.06%
4. % oxygen: ThOCl2, 5.02%; MgCO3, 56.93%; NO2Cl, 39.28%
5. To two decimal places, the percentages are:
   - a. 66.32% Br
   - b. 22.79% As
   - c. 25.40% P
   - d. 73.43% C
6.
   - a. 61.98% Br
   - b. 34.69% Cs
   - c. 59.96% C
   - d. 21.11% S
7. Cr_2O_3.
8. Empirical Formulas
   1. Fe_2O_3
   2. Fe_4O_4
   3. Fe_6O_8
9. To two decimal places, the percentages are:
   - a. 29.82%
   - b. 51.16%
   - c. 25.40%
10. What is the mass percentage of water in each hydrate?
    - a. 20.94%
    - b. 36.25%
    - c. 32.70%
11. $NiSO_4 \cdot 6H_2O$ and $CoCl_2 \cdot 6H_2O$

12. FeS_2

13. $NaHSO_4$

14. Calculate the mass percentage of oxygen in each polyatomic ion.

   a. 78.66%

   b. 55.17%

   c. 54.19%

   d. 59.95%

15.

   a. 72.71%

   b. 69.55%

   c. 65.99%

   d. 0%

16. The empirical formula of garnet, a gemstone, is $Fe_3Al_2Si_3O_{12}$. An analysis of a sample of garnet gave a value of 13.8% for the mass percentage of silicon. Is this consistent with the empirical formula?

No, the calculated mass percentage of silicon in garnet is 16.93%

17. $C_4H_8O_2$

18.

Empirical Formula: $C_{10}Cl_{12}$

Molecular Formula: $C_{10}Cl_{12}$

19. How many moles of CO_2 and H_2O will be produced by combustion analysis of 0.010 mol of styrene?

Moles of CO2: 0.08 mol CO_2

Moles of H2O: 0.04 mol H_2O

20. How many moles of CO_2, H_2O, and N_2 will be produced by combustion analysis of 0.0080 mol of aniline?

Mole of CO2: 0.048 mol CO_2

Mole of H2O: 0.028 mol H_2O

Mole of N2: 0.004 mol N_2

21. How many moles of CO_2, H_2O, and N_2 will be produced by combustion analysis of 0.0074 mol of aspartame?

Mole of CO2: 0.104 mol CO_2

Mole of H2O: 0.666 mol H_2O

Mole of N2: 0.0074 mol N_2

22. How many moles of CO_2, H_2O, N_2, and SO_2 will be produced by combustion analysis of 0.0060 mol of penicillin G?

Mole of CO2: 0.096 mol CO_2

Mole of H2O: 0.054 mol H_2O

Mole of N2: 0.060 mol N_2

Mole of SO2: 0.060 mol SO_2

23.

   a. 27.6 mg C and 1.98 mg H

   b. 5.2 mg O

c. 15%

d. C_7H_6O

e. C_7H_6O

24. Salicylic acid is used to make aspirin. It contains only carbon, oxygen, and hydrogen. Combustion of a 43.5 mg sample of this compound produced 97.1 mg of CO_2 and 17.0 mg of H_2O.

a. What is the mass of oxygen in the sample?

70.4mg

b. What is the mass percentage of oxygen in the sample?

61.70%

c. What is the empirical formula of salicylic acid?

$C_7H_6O_3$

d. The molar mass of salicylic acid is 138.12 g/mol. What is its molecular formula?

$C_7H_6O_3$

25. hydrocyanic acid, HCN

26. Calculate the formula mass or the molecular mass of each compound.

a. 130.1849 amu

b. 60.1 amu

c. 158.034 amu

d. 323.4 amu

e. 82.07 amu

f. 106.17 amu

27. To two decimal places, the values are:

a. 273.23 amu

b. 69.62 amu

c. 157.01 amu

d. 82.14 amu

e. 98.00 amu

f. 45.08 amu

28. Cyclobutene

29. Urea

CHAPTER OVERVIEW

6: Lewis Structures, Shapes, and Intermolecular Forces

6.1: The Octet Rule

In the previous section, we established a direct link between electron configurations, the periodic table, and the similarities of the elements within groups of the periodic table. We can generalize some of the ways in which many compounds and molecules form based on these trends. This generalization is called the octet rule. According to **the octet rule**, atoms will tend to lose, gain, or share electrons such that their valence electron shell resembles that of a noble gas. In most cases, the noble gas has 8 electrons in his valence shell, hence the word octet to describe the number 8.

When ions form, they conform to the **octet rule** by either losing or gaining electrons in order to achieve the electron configuration of the nearest noble gas. You can confirm this by looking at the trends of ion formation that we established in an earlier chapter. The reason why the periodic table is so good at predicting these trends in ion formation is because they result in filled valence electron shells.

In a similar way, nonmetal atoms share electrons in the formation of a covalent bond in such a way that each of the atoms involved in the bond can attain a noble-gas electron configuration. The shared electrons are "counted" for each of the atoms involved in the sharing. For hydrogen $(\mathrm{H_2})$, the shared pair of electrons means that each of the atoms is able to attain the electron configuration of helium, the noble gas with two electrons. For atoms other than hydrogen, the sharing of electrons will usually provide each of the atoms with eight valence electrons. We will explore this concept more within the subsections here using a concept called Lewis structures.

When we first introduced the idea of compounds, we emphasized the difference between ionic and molecular compounds. In fact, it was the most important thing to consider when naming compounds! We can now discuss the reason for that difference: it is because the octet rule is satisfied in different ways in the formation of these compounds. In ionic compounds electrons are lost or gained. In molecular compounds, electrons are shared. It is because of this difference, that we must use different naming conventions for ionic compounds and molecules. Each electron that is lost by a metal will be gained by a nonmetal with forming an ionic compound. In contrast, there are multiple ways to share electrons in molecules as we will see. This difference is why it was necessary to use a different naming convention for ionic compounds compared to molecules.

Summary

- The octet rule is followed when an atom achieves the electron configuration of the nearest noble gas.
- When ions form, they conform to the octet rule by either losing or gaining electrons.
- When molecules form, they conform to the octet rule by sharing electrons.

6.1.1: Representing Valence Electrons with Dots

Learning Objective

- Draw a Lewis electron dot diagram for an atom or a monatomic ion.

In almost all cases, chemical bonds are formed by interactions of valence electrons in atoms. To facilitate our understanding of how valence electrons interact, a simple way of representing those valence electrons would be useful.

A **Lewis electron dot diagram** (or electron dot diagram, or a Lewis diagram, or a Lewis structure) is a representation of the valence electrons of an atom that uses dots around the symbol of the element. The number of dots equals the number of valence electrons in the atom. These dots are arranged to the right and left and above and below the symbol, with no more than two dots on a side. (The order in which the positions are used does not matter.) For example, the Lewis electron dot diagram for hydrogen is simply

$$\mathbf{H}\cdot$$

Because the side is not important, the Lewis electron dot diagram could also be drawn as follows:

$$\dot{\mathbf{H}}\ \ \textit{or}\ \cdot\mathbf{H}\ \ \ \textit{or}\ \ \ \underset{\cdot}{\mathbf{H}}$$

The electron dot diagram for helium, with two valence electrons, is as follows:

$$\mathbf{He}\!:$$

By putting the two electrons together on the same side, we emphasize the fact that these two electrons are both in the 1s subshell; this is the common convention we will adopt, although there will be exceptions later. The next atom, lithium, has an electron configuration of $1s^22s^1$, so it has only one electron in its valence shell. Its electron dot diagram resembles that of hydrogen, except the symbol for lithium is used:

$$\mathbf{Li}\cdot$$

Beryllium has two valence electrons in its 2s shell, so its electron dot diagram is like that of helium:

$$\cdot\mathbf{Be}\cdot$$

The next atom is boron. Its valence electron shell is $2s^22p^1$, so it has three valence electrons. The three electrons will go on separate sides of the symbol:

$$\cdot\dot{\mathbf{B}}\cdot$$

Again, it does not matter on which sides of the symbol the electron dots are positioned.

For carbon, there are four valence electrons, two in the 2s subshell and two in the 2p subshell. As usual, we will draw the electrons on different sides. As such, the electron dot diagram for carbon is as follows:

$$\cdot\underset{\cdot}{\dot{\mathbf{C}}}\cdot$$

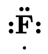
With N, which has two s and three p electrons, we put a single dot on each of the four sides, then the fifth electron is shown paired with an electron on any one of the sides:

$$\cdot\underset{\cdot}{\dot{\mathbf{N}}}\!:$$

For oxygen, which has two s and four p electrons, we now have to start doubling up on the dots on one other side of the symbol. When doubling up electrons, make sure that each side has no more than two electrons.

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

Fluorine and neon have seven and eight dots, respectively:



$:\overset{\cdot\cdot}{\underset{\cdot}{\mathbf{F}}}:$

$:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathbf{Ne}}}:$

With the next element, sodium, the process starts over with a single electron because sodium has a single electron in its highest-numbered shell, the *n* = 3 shell. By going through the periodic table, we see that the Lewis electron dot diagrams of atoms will never have more than eight dots around the atomic symbol.

✓ Example 6.1.1.1: Lewis Dot Diagrams

What is the Lewis electron dot diagram for each element?

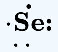
a. aluminum
b. selenium

Solution

a. The valence electron configuration for aluminum is $3s^2 3p^1$. So it would have three dots around the symbol for aluminum, two of them paired to represent the 3*s* electrons:

$\cdot\overset{\cdot}{\mathbf{Al}}\cdot$

2. The valence electron configuration for selenium is $4s^2 4p^4$. In the highest-numbered shell, the *n* = 4 shell, there are six electrons. Its electron dot diagram is as follows:



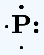
$\cdot\overset{\cdot}{\underset{\cdot\cdot}{\mathbf{Se}}}:$

? Exercise 6.1.1.1

What is the Lewis electron dot diagram for each element?

a. phosphorus
b. argon

Answer a



$\cdot\overset{\cdot}{\underset{\cdot}{\mathbf{P}}}:$

Answer b

$:\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathbf{Ar}}}:$

Summary

- Lewis electron dot diagrams use dots to represent valence electrons around an atomic symbol.
- Lewis electron dot diagrams for ions have less (for cations) or more (for anions) dots than the corresponding atom.

6.1.2: Lewis Structures of Ionic Compounds- Electrons Transferred

Learning Objectives

- State the octet rule.
- Define *ionic bond*.
- Draw Lewis structures for ionic compounds.

In a previous section, we demonstrated that ions are formed by losing electrons to make cations, or by gaining electrons to form anions. The astute reader may have noticed something: many of the ions that form have eight electrons in their valence shell. Either atoms gain enough electrons to have eight electrons in the valence shell and become the appropriately charged anion, or they lose the electrons in their original valence shell; the *lower* shell, now the valence shell, has eight electrons in it, so the atom becomes positively charged. For whatever reason, having eight electrons in a valence shell is a particularly energetically stable arrangement of electrons. The **octet rule** explains the favorable trend of atoms having eight electrons in their valence shell. When atoms form compounds, the octet rule is not always satisfied for all atoms at all times, but it is a very good rule of thumb for understanding the kinds of bonding arrangements that atoms can make.

It is not impossible to violate the octet rule. Consider sodium: in its elemental form, it has one valence electron and is stable. It is rather reactive, however, and does not require a lot of energy to remove that electron to make the Na^+ ion. We *could* remove another electron by adding even more energy to the ion, to make the Na^{2+} ion. However, that requires much more energy than is normally available in chemical reactions, so sodium stops at a 1+ charge after losing a single electron. It turns out that the Na^+ ion has a complete octet in its new valence shell, the *n* = 2 shell, which satisfies the octet rule. The octet rule is a result of trends in energies and is useful in explaining why atoms form the ions that they do.

Now consider an Na atom in the presence of a Cl atom. The two atoms have these Lewis electron dot diagrams and electron configurations:

$$\mathbf{Na}\cdot \qquad \cdot\underset{\cdot\cdot}{\ddot{\mathbf{Cl}}}\mathbf{:} \tag{6.1.2.1}$$

$$[Ne]\,3s^1 \qquad [Ne]\,3s^2 3p^5 \tag{6.1.2.2}$$

For the Na atom to obtain an octet, it must lose an electron; for the Cl atom to gain an octet, it must gain an electron. An electron transfers from the Na atom to the Cl atom:

$$\mathbf{Na}\cdot \curvearrowright \cdot\underset{\cdot\cdot}{\ddot{\mathbf{Cl}}}\mathbf{:} \tag{6.1.2.3}$$

resulting in two ions—the Na^+ ion and the Cl^- ion:

$$\mathbf{Na}^+ \qquad \mathbf{:}\underset{\cdot\cdot}{\ddot{\mathbf{Cl}}}\mathbf{:}^- \tag{6.1.2.4}$$

$$[Ne] \qquad [Ne]\,3s^2 3p^6 \tag{6.1.2.5}$$

Both species now have complete octets, and the electron shells are energetically stable. From basic physics, we know that opposite charges attract. This is what happens to the Na^+ and Cl^- ions:

$$\mathbf{Na}^+ + \mathbf{:}\underset{\cdot\cdot}{\ddot{\mathbf{Cl}}}\mathbf{:}^- \rightarrow Na^+Cl^- \;\; or \;\; NaCl \tag{6.1.2.6}$$

where we have written the final formula (the formula for sodium chloride) as per the convention for ionic compounds, without listing the charges explicitly. The attraction between oppositely charged ions is called an **ionic bond,** and it is one of the main types of chemical bonds in chemistry. Ionic bonds are caused by electrons *transferring* from one atom to another.

In electron transfer, the number of electrons lost must equal the number of electrons gained. We saw this in the formation of NaCl. A similar process occurs between Mg atoms and O atoms, except in this case two electrons are transferred:

The two ions each have octets as their valence shell, and the two oppositely charged particles attract, making an ionic bond:

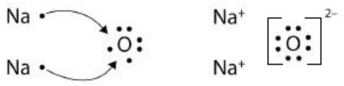
$$\mathbf{Mg}^{2+} + \left[\mathbf{:\ddot{O}:}\right]^{2-} \quad Mg^{2+}O^{2-} \textit{ or } MgO \tag{6.1.2.7}$$

Remember, in the final formula for the ionic compound, we do not write the charges on the ions.

What about when an Na atom interacts with an O atom? The O atom needs two electrons to complete its valence octet, but the Na atom supplies only one electron:

$$\mathbf{Na}\cdot \curvearrowright \cdot\mathbf{\ddot{O}}\mathbf{:} \tag{6.1.2.8}$$

The O atom still does not have an octet of electrons. What we need is a second Na atom to donate a second electron to the O atom:



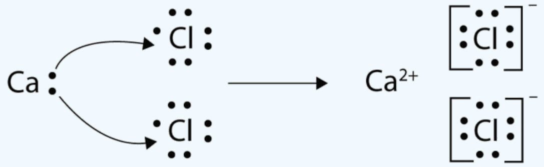
These three ions attract each other to give an overall neutral-charged ionic compound, which we write as Na_2O. The need for the number of electrons lost being equal to the number of electrons gained explains why ionic compounds have the ratio of cations to anions that they do. This is required by the law of conservation of matter as well.

Example 6.1.2.1: Synthesis of Calcium Chloride from Elements

With arrows, illustrate the transfer of electrons to form calcium chloride from Ca atoms and Cl atoms.

Solution

A Ca atom has two valence electrons, while a Cl atom has seven electrons. A Cl atom needs only one more to complete its octet, while Ca atoms have two electrons to lose. Thus we need two Cl atoms to accept the two electrons from one Ca atom. The transfer process looks as follows:

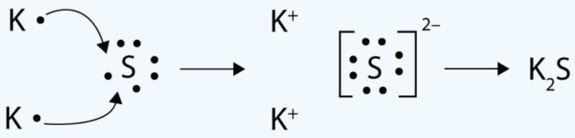


The oppositely charged ions attract each other to make $CaCl_2$.

Exercise 6.1.2.1

With arrows, illustrate the transfer of electrons to form potassium sulfide from K atoms and S atoms.

Answer



Summary

- The tendency to form species that have eight electrons in the valence shell is called the octet rule.
- The attraction of oppositely charged ions caused by electron transfer is called an ionic bond.
- The strength of ionic bonding depends on the magnitude of the charges and the sizes of the ions.

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6.1.3: Covalent Lewis Structures- Electrons Shared

Learning Objectives

- Define *covalent bond*.
- Illustrate covalent bond formation with Lewis electron dot diagrams.

Ionic bonding typically occurs when it is easy for one atom to lose one or more electrons and another atom to gain one or more electrons. However, some atoms won't give up or gain electrons easily. Yet they still participate in compound formation. How? There is another mechanism for obtaining a complete valence shell: *sharing* electrons. When electrons are shared between two atoms, they make a bond called a **covalent bond**.

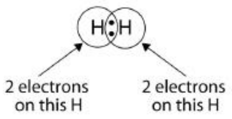
Let us illustrate a covalent bond by using H atoms, with the understanding that H atoms need only two electrons to fill the 1*s* subshell. Each H atom starts with a single electron in its valence shell:

$$\mathbf{H\cdot \quad \cdot H}$$

The two H atoms can share their electrons:

$$\mathbf{H:H}$$

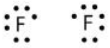
We can use circles to show that each H atom has two electrons around the nucleus, completely filling each atom's valence shell:



Because each H atom has a filled valence shell, this bond is stable, and we have made a diatomic hydrogen molecule. (This explains why hydrogen is one of the diatomic elements.) For simplicity's sake, it is not unusual to represent the covalent bond with a dash, instead of with two dots:

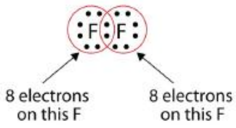
H–H

Because two atoms are sharing one pair of electrons, this covalent bond is called a **single bond**. As another example, consider fluorine. F atoms have seven electrons in their valence shell:

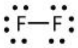


These two atoms can do the same thing that the H atoms did; they share their unpaired electrons to make a covalent bond.

Note that each F atom has a complete octet around it now:

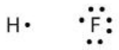


We can also write this using a dash to represent the shared electron pair:

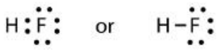


There are two different types of electrons in the fluorine diatomic molecule. The **bonding electron pair** makes the covalent bond. Each F atom has three other pairs of electrons that do not participate in the bonding; they are called **lone pair electrons**. Each F atom has one bonding pair and three lone pairs of electrons.

Covalent bonds can be made between different elements as well. One example is HF. Each atom starts out with an odd number of electrons in its valence shell:



The two atoms can share their unpaired electrons to make a covalent bond:



We note that the H atom has a full valence shell with two electrons, while the F atom has a complete octet of electrons.

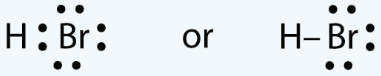
✓ Example 6.1.3.1:

Use Lewis electron dot diagrams to illustrate the covalent bond formation in HBr.

Solution

HBr is very similar to HF, except that it has Br instead of F. The atoms are as follows:

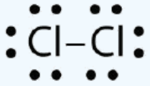
The two atoms can share their unpaired electron:



? Exercise 6.1.3.1

Use Lewis electron dot diagrams to illustrate the covalent bond formation in Cl_2.

Answer



When working with covalent structures, it sometimes looks like you have leftover electrons. You apply the rules you learned so far, and there are still some electrons that remain unattached. You can't just leave them there. So where do you put them?

Multiple Covalent Bonds

Some molecules are not able to satisfy the octet rule by making only single covalent bonds between the atoms. Consider the compound ethene, which has a molecular formula of C_2H_4. The carbon atoms are bonded together, with each carbon also bonded to two hydrogen atoms.

$$\text{two C atoms} = 2 \times 4 = 8 \;\text{ valence electrons}$$

$$\text{four H atoms} = 4 \times 1 = 4 \;\text{ valence electrons}$$

$$\text{total of 12 valence electrons in the molecule}$$

If the Lewis electron dot structure was drawn with a single bond between the carbon atoms and with the octet rule followed, it would look like this:

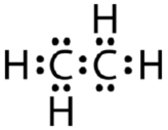


Figure 6.1.3.1: Incorrect dot structure of ethene. (CK12 License)

This Lewis structure is incorrect because it contains a total of 14 electrons. However, the Lewis structure can be changed by eliminating the lone pairs on the carbon atoms and having to share two pairs instead of only one pair.

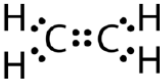


Figure 6.1.3.2: Correct dot structure for ethene. (CK12 License)

A **double covalent bond** is a covalent bond formed by atoms that share two pairs of electrons. The double covalent bond that occurs between the two carbon atoms in ethane can also be represented by a structural formula and with a molecular model as shown in the figure below.

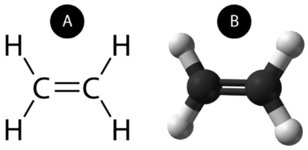


Figure 6.1.3.3: (A) The structural model for C_2H_4 consists of a double covalent bond between the two carbon atoms and single bonds to the hydrogen atoms. (B) Molecular model of C_2H_4.

A **triple covalent bond** is a covalent bond formed by atoms that share three pairs of electrons. The element nitrogen is a gas that composes the majority of Earth's atmosphere. A nitrogen atom has five valence electrons, which can be shown as one pair and three single electrons. When combining with another nitrogen atom to form a diatomic molecule, the three single electrons on each atom combine to form three shared pairs of electrons.

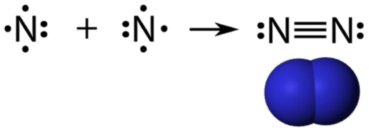


Figure 6.1.3.4: Triple bond in N_2.

Each nitrogen atom follows the octet rule with one lone pair of electrons, and six electrons that are shared between the atoms.

Summary

- Covalent bonds are formed when atoms share electrons.
- Lewis electron dot diagrams can be drawn to illustrate covalent bond formation.
- Double bonds or triple bonds between atoms may be necessary to properly illustrate the bonding in some molecules.

Contributions & Attributions

-
- Anonymous by request

6.2: Writing Lewis Structures for Covalent Compounds

Learning Objectives

- Draw Lewis structures for covalent compounds.

We have established that molecules form by sharing electrons in covalent bonds. Also, that there are several ways in which these electrons could be shared. However, there is a little bit involved in determining how electrons are shared in a particular molecule. We will go through a series of steps in this section which will help determine the correct sharing of electrons in most molecules. Prior to starting on this section, it is important that you know how to determine the number of valence electrons of any element.

Additional ideas related to Lewis structures for molecules will be discussed in the 2 subsections. We will discuss additional considerations for some molecules when more than one Lewis structure might be possible. We will also mention some exceptions to the octet rule.

The following procedure can be used to construct Lewis electron structures for more complex molecules and ions.

How-to: Constructing Lewis electron structures

1. Determine the total number of valence electrons in the molecule or ion.

- Add together the valence electrons from each atom. (Recall that the number of valence electrons is indicated by the position of the element in the periodic table.)

For OF_2, for example, the oxygen has 6 electrons and each of the 2 fluorines has 7 electrons for a total of 20 electrons.

- If the species is a polyatomic ion, remember to add or subtract the number of electrons necessary to give the total charge on the ion.

  For CO_3^{2-}, for example, we add two electrons to the total because of the −2 charge.

2. Arrange the atoms to show specific connections.

- To begin with, we will consider molecules that have only one central atom along with 2 or more terminal atoms. When we say an atom is central in the molecule, that means each of the other atoms is connected to that central atom. When we say an atom is terminal in the molecule, that means the atom is connected only to the central atom and not to other atoms. (If the molecule has only 2 atoms in it, the distinction between central and terminal doesn't mean anything.)
- When there is a central atom, chemists usually list this central atom first in the chemical formula (as in CCl_4 and CO_3^{2-}, which both have C as the central atom).
- Hydrogen is always connected to only one other atom, so it is always *terminal* rather than central even if it is first in the formula.

3. Place a bonding pair of electrons between each pair of adjacent atoms to give a single bond.

- In H_2O, for example, there is a bonding pair of electrons between oxygen and each hydrogen.

4. Beginning with the terminal atoms, add enough electrons to each atom to give each atom an octet (two for hydrogen).

- These added electrons will usually be lone pairs.
- Remember to count the bonding electrons on these terminal atoms while determining if they have enough electrons to satisfy the octet rule.

5. If any electrons are left over, place them on the central atom.

- Determine the number of left over electrons by counting all of the electrons that have already been added (either as lone pairs or in each of the single bonds) and comparing it to the total number of electrons that you counted in the first step. If they are the same, then there are no leftover electrons. If you had more electrons in the first step, then you are able to add the difference between that amount and the amount you have here.
- We will explain later that some atoms are able to accommodate more than eight electrons.

6. If the central atom has fewer electrons than an octet, use lone pairs from terminal atoms to form multiple (double or triple) bonds to the central atom to achieve an octet.

- This will not change the number of electrons on the terminal atoms, as you are moving the electrons when you do this.

7. Final check

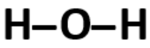
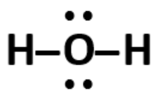
- Always make sure all valence electrons are accounted for. This means that the number of electrons you counted in step one is the same as the number of electrons you can count in step six.
- Each atom has an octet of electrons, except for hydrogen (with two electrons).

Now let's apply this procedure to some particular compounds, beginning with one we have already discussed.

✓ Example 6.2.1: Water

Write the Lewis Structure for H_2O.

Solution

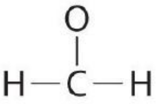
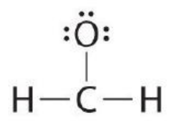
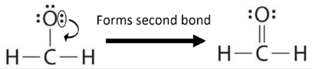
Steps for Writing Lewis Structures	Example 6.2.1
1. Determine the total number of valence electrons in the molecule or ion.	Each H atom (group 1) has 1 valence electron, and the O atom (group 16) has 6 valence electrons, for a total of <u>8 valence electrons.</u>
2. Arrange the atoms to show specific connections.	H O H Because H atoms are always terminal, the arrangement within the molecule must be <u>HOH.</u>
3. Place a bonding pair of electrons between each pair of adjacent atoms to give a single bond. 4. Beginning with the terminal atoms, add enough electrons to each atom to give each atom an octet (two for hydrogen).	Placing one bonding pair of electrons between the O atom and each H atom gives  with 4 electrons left over. Each H atom has a full valence shell of 2 electrons.
5. If any electrons are left over, place them on the central atom.	Adding the remaining 4 electrons to the oxygen (as two lone pairs) gives the following structure: 
6. If the central atom has fewer electrons than an octet, use lone pairs from terminal atoms to form multiple (double or triple) bonds to the central atom to achieve an octet.	Not necessary.
7. Final check.	The Lewis structure gives oxygen an octet and each hydrogen 2 electrons.

✓ Example 6.2.2

Write the Lewis structure for the CH_2O molecule

Solution

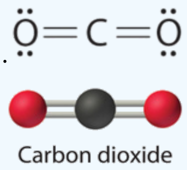
Steps for Writing Lewis Structures	Example 6.2.2
1. Determine the total number of valence electrons in the molecule or ion.	Each hydrogen atom (group 1) has 1 valence electron, carbon (group 14) has 4 valence electrons, and oxygen (group 16) has 6 valence electrons, for a total of [(2)(1) + 4 + 6] = <u>12 valence electrons.</u>

Steps for Writing Lewis Structures	Example 6.2.2
2. Arrange the atoms to show specific connections.	 Because carbon is first in the formula, we make it the central atom. We are assuming each of the other atoms is a terminal atom connected to the central carbon.
3. Place a bonding pair of electrons between each pair of adjacent atoms to give a single bond.	Placing a bonding pair of electrons between each pair of bonded atoms gives the following:  6 electrons are used, and 6 are left over.
4. Beginning with the terminal atoms, add enough electrons to each atom to give each atom an octet (two for hydrogen).	Adding all 6 remaining electrons to oxygen (as three lone pairs) gives the following:  Although oxygen now has an octet and each hydrogen has 2 electrons, carbon has only 6 electrons.
5. If any electrons are left over, place them on the central atom.	Not necessary. There are no electrons left to place on the central atom.
6. If the central atom has fewer electrons than an octet, use lone pairs from terminal atoms to form multiple (double or triple) bonds to the central atom to achieve an octet.	To give carbon an octet of electrons, we use one of the lone pairs of electrons on oxygen to form a carbon–oxygen double bond: 
7. Final check	The total number of electrons in the final structure is 12, which matches the total number of electrons we counted in step one. Both the oxygen and the carbon now have an octet of electrons, the O has two bonding pairs and two lone pairs, and C has four bonding pairs. Because both of these requirements have been met, this is an acceptable Lewis electron structure.

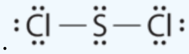
? Exercise 6.2.1

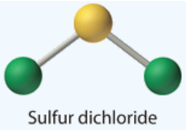
Write Lewis electron structures for CO_2 and SCl_2, a vile-smelling, unstable red liquid that is used in the manufacture of rubber.

Answer CO_2



Answer SCl_2





Writing Lewis Structures for Polyatomic Ions

Recall that a polyatomic ion is a group of atoms that are covalently bonded together and which carry an overall electrical charge. The ammonium ion, NH_4^+, is formed when a hydrogen ion $\left(H^+\right)$ attaches to the lone pair of an ammonia $\left(NH_3\right)$ molecule in a coordinate covalent bond.

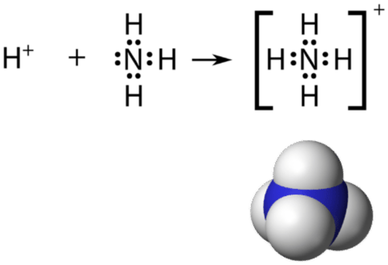


Figure 6.2.3: The ammonium ion.

When drawing the Lewis structure of a polyatomic ion, the charge of the ion is reflected in the number of total valence electrons in the structure. In the case of the ammonium ion:

$$1 \text{ N atom} = 5 \text{ valence electrons}$$

$$4 \text{ H atoms} = 4 \times 1 = 4 \text{ valence electrons}$$

$$\text{subtract } 1 \text{ electron for the } 1+ \text{ charge of the ion}$$

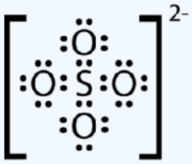
$$\text{total of } 8 \text{ valence electrons in the ion}$$

It is customary to put the Lewis structure of a polyatomic ion into a large set of brackets, with the charge of the ion as a superscript outside of the brackets.

✓ Exercise 6.2.2

Draw the Lewis electron dot structure for the sulfate ion.

Answer



Summary

Lewis dot symbols provide a simple rationalization of why elements form compounds with the observed formulas. In Lewis electron structures, we encounter **bonding pairs**, which are shared by two atoms, and **lone pairs**, which are not shared between atoms. A process for creating the correct Lewis structures involves 2 criteria: (1) making sure the total number of valence electrons is the same in the molecule as in the sum of the individual atoms which make it up, and (2) making sure that each atom in the structure follows the octet rule. Lewis structures for polyatomic ions follow the same rules as those for other covalent compounds.

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- Henry Agnew (UC Davis)

6.2.1: Resonance - Equivalent Lewis Structures for the Same Molecule

Learning Objectives

- Explain the concept of resonance and how it works with within molecules.

Resonance

There are some cases in which more than one viable Lewis structure can be drawn for a molecule. An example is the ozone $\left(O_3\right)$ molecule in Figure $6.2.1.1$. There are a total of 18 electrons in the structure and so the following two structures are possible.

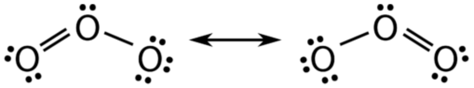


Figure $6.2.1.1$: Resonance forms of ozone. Note the use of the double-headed arrow.

The structure on the left ($6.2.1.1$) can be converted to the structure on the right by a shifting of electrons without altering the positions of the atoms.

It was once thought that the structure of a molecule such as O_3 consisted of one single bond and one double bond which then shifted back and forth as shown above. However, further studies showed that the two bonds are identical. Any double covalent bond between two given atoms is typically shorter than a single covalent bond. Studies of the O_3 and other similar molecules showed that the bonds were identical in length. Interestingly, the length of the bond is in between the lengths expected for an $O-O$ single bond and a double bond.

Resonance is the use of two or more Lewis structures to represent the covalent bonding in a molecule. One of the valid structures is referred to as a resonance structure. It is now understood that the true structure of a molecule which displays resonance is that of an average or a hybrid of all the resonance structures. In the case of the O_3 molecule, each of the covalent bonds between O atoms are best thought of as being "one and a half" bonds, as opposed to either a pure single bond or a pure double bond. This "half-bond" can be shown as a dotted line in both the Lewis structure and the molecular model (Figure $6.2.1.2$).

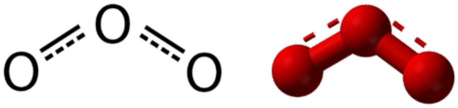


Figure $6.2.1.2$: "Half-bond" model of ozone molecule. This is a better description of the electronic structure of ozone than either of the resonance structures in Figure $6.2.1.1$.

Many polyatomic ions also display resonance. In some cases, the true structure may be an average of three valid resonance structures, as in the case of the nitrate ion, NO_3^- in Figure $6.2.1.3$.

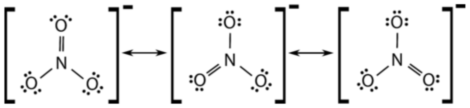


Figure $6.2.1.3$: Resonance structure of nitrate anion.

The bond lengths between the central N atom and each O atom are identical and the bonds can be approximated as being equal to one and one-third bonds.

Summary

- Resonance structures are averages of different Lewis structure possibilities.
- Bond lengths are intermediate between covalent bonds and covalent double bonds.

6.2.2: Exceptions to the Octet Rule

Learning Objectives

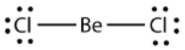
- Recognize when there is an exception to the octet rule.

As important and useful as the octet rule is in chemical bonding, there are some well-known violations. This does not mean that the octet rule is useless—quite the contrary. As with many rules, there are exceptions.

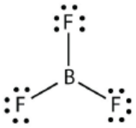
There are three violations to the octet rule. Odd-electron molecules represent the first violation to the octet rule. Although they are few, some stable compounds have an odd number of electrons in their valence shells. With an odd number of electrons, at least one atom in the molecule will have to violate the octet rule. Examples of stable odd-electron molecules are NO, NO_2, and ClO_2. The Lewis electron dot diagram for NO is as follows:

Although the O atom has an octet of electrons, the N atom has only seven electrons in its valence shell. Although NO is a stable compound, it is very chemically reactive, as are most other odd-electron compounds.

Electron-deficient molecules represent the second violation to the octet rule. These stable compounds have less than eight electrons around an atom in the molecule. The most common examples are the covalent compounds of beryllium and boron. For example, beryllium can form two covalent bonds, resulting in only four electrons in its valence shell:



Boron commonly makes only three covalent bonds, resulting in only six valence electrons around the B atom. A well-known example is BF_3:



The third violation to the octet rule is found in those compounds with more than eight electrons assigned to their valence shell. These are called expanded valence shell molecules. Such compounds are beyond the scope of this book, but should be covered in general chemistry textbooks.

Summary

There are three exceptions to the octet rule: odd-electron molecules, electron-deficient molecules, and expanded valence shell molecules.

Contributions & Attributions

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- Henry Agnew (UC Davis)

6.3: Predicting the Shapes of Molecules

Learning Objective

- Determine the shape of simple molecules.

Molecules have shapes. There is an abundance of experimental evidence to that effect—from their physical properties to their chemical reactivity. Small molecules—molecules with a single central atom—have shapes that can be easily predicted. The basic idea in molecular shapes is called **valence shell electron pair repulsion (VSEPR).** VSEPR says that electron pairs, being composed of negatively charged particles, repel each other to get as far away from one another as possible. VSEPR makes a distinction between *electron group geometry*, which expresses how electron groups (bonds and nonbonding electron pairs) are arranged, and *molecular geometry*, which expresses how the atoms in a molecule are arranged. However, the two geometries are related.

There are two types of **electron groups**: any type of bond—single, double, or triple—and lone electron pairs. When applying VSEPR to simple molecules, the first thing to do is to count the number of electron groups around the central atom. Remember that a multiple bond counts as only *one* electron group.

Any molecule with only two atoms is linear. A molecule whose central atom contains only two electron groups orients those two groups as far apart from each other as possible—180° apart. When the two electron groups are 180° apart, the atoms attached to those electron groups are also 180° apart, so the overall molecular shape is linear. Examples include BeH_2 and CO_2:

Figure 6.3.1: Beryllium hydride and carbon dioxide bonding.

The two molecules, shown in the figure below in a "ball and stick" model.

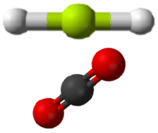


Figure 6.3.2: Beryllium hydride and carbon dioxide models. (CK12 Licence)

A molecule with three electron groups orients the three groups as far apart as possible. They adopt the positions of an equilateral triangle—120° apart and in a plane. The shape of such molecules is *trigonal planar*. An example is BF_3:

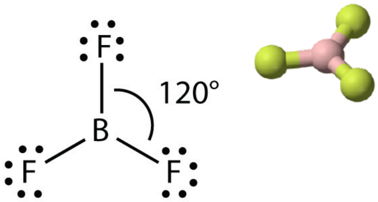


Figure 6.3.3: Boron trifluoride bonding. (CK12 Licence)

Some substances have a trigonal planar electron group distribution but have atoms bonded to only two of the three electron groups. An example is GeF_2:

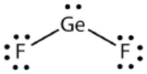


Figure 6.3.4: Germanium difluoride bonding.

From an electron group geometry perspective, GeF_2 has a trigonal planar shape, but its real shape is dictated by the positions of the atoms. This shape is called *bent* or *angular*.

A molecule with four electron groups about the central atom orients the four groups in the direction of a tetrahedron, as shown in Figure 6.3.1 Tetrahedral Geometry. If there are four atoms attached to these electron groups, then the molecular shape is also *tetrahedral*. Methane (CH_4) is an example.

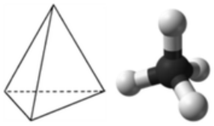


Figure 6.3.5: Tetrahedral structure of methane. (CK12 Licence)

This diagram of CH_4 illustrates the standard convention of displaying a three-dimensional molecule on a two-dimensional surface. The straight lines are in the plane of the page, the solid wedged line is coming out of the plane toward the reader, and the dashed wedged line is going out of the plane away from the reader.

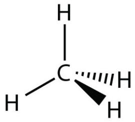


Figure 6.3.6: Methane bonding. (CK12 Licence)

NH_3 is an example of a molecule whose central atom has four electron groups, but only three of them are bonded to surrounding atoms.

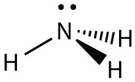


Figure 6.3.7: Ammonia bonding. (CK12 Licence)

Although the electron groups are oriented in the shape of a tetrahedron, from a molecular geometry perspective, the shape of NH_3 is *trigonal pyramidal*.

H_2O is an example of a molecule whose central atom has four electron groups, but only two of them are bonded to surrounding atoms.

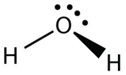


Figure 6.3.8: Water bonding.

Although the electron groups are oriented in the shape of a tetrahedron, the shape of the molecule is *bent* or *angular*. A molecule with four electron groups about the central atom, but only one electron group bonded to another atom, is linear because there are only two atoms in the molecule.

Double or triple bonds count as a single electron group. The Lewis electron dot diagram of formaldehyde (CH_2O) is shown in Figure 6.3.9.

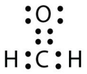


Figure 6.3.9: Lewis Electron Dot Diagram of Formaldehyde.

The central C atom has three electron groups around it because the double bond counts as one electron group. The three electron groups repel each other to adopt a trigonal planar shape.

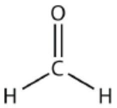
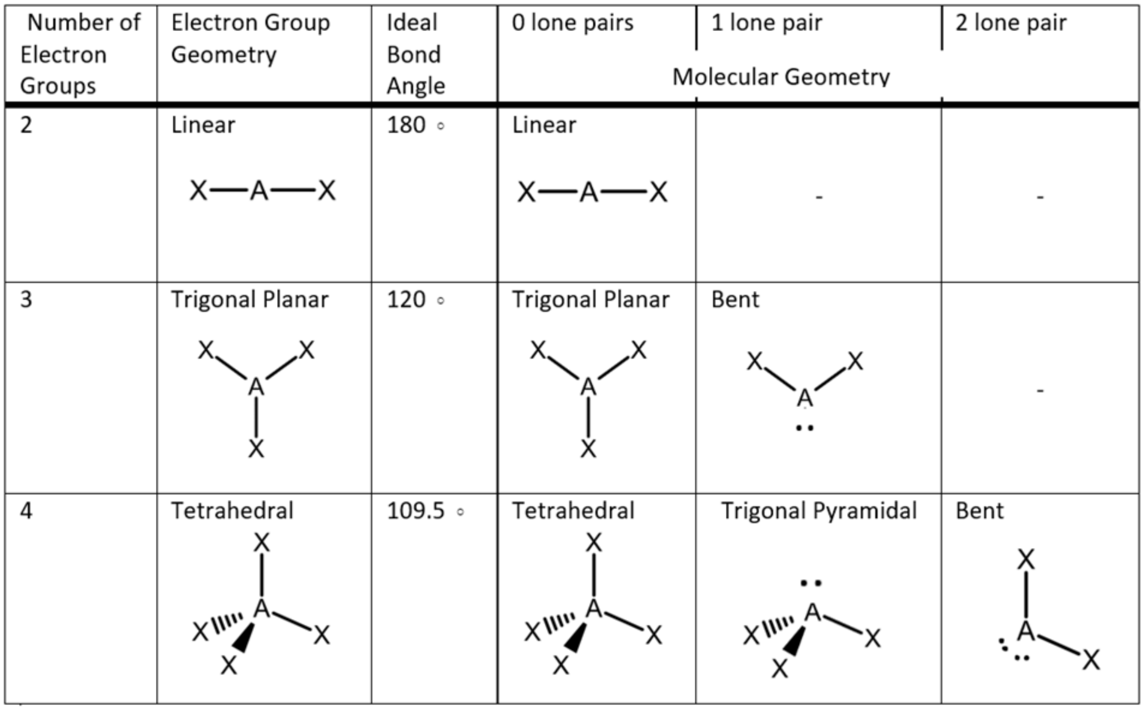


Figure 6.3.10: Formaldehyde bonding.

(The lone electron pairs on the O atom are omitted for clarity.) The molecule will not be a perfect equilateral triangle because the C–O double bond is different from the two C–H bonds, but both planar and triangular describe the appropriate approximate shape of this molecule.



Number of Electron Groups	Electron Group Geometry	Ideal Bond Angle	0 lone pairs	1 lone pair	2 lone pair
			Molecular Geometry		
2	Linear X—A—X	180 °	Linear X—A—X	-	-
3	Trigonal Planar	120 °	Trigonal Planar	Bent	-
4	Tetrahedral	109.5 °	Tetrahedral	Trigonal Pyramidal	Bent

Figure 6.3.11: Electron and Molecule Shapes

Example 6.3.1

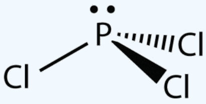
What is the approximate shape of each molecule?

a. PCl_3
b. NOF

Solution

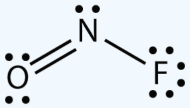
The first step is to draw the Lewis structure of the molecule.

For PCl_3, the electron dot diagram is as follows:



The lone electron pairs on the Cl atoms are omitted for clarity. The P atom has four electron groups with three of them bonded to surrounding atoms, so the molecular shape is trigonal pyramidal.

The electron dot diagram for NOF is as follows:



The N atom has three electron groups on it, two of which are bonded to other atoms. The molecular shape is bent.

Exercise 6.3.1

What is the approximate molecular shape of CH_2Cl_2?

Answer

Tetrahedral

Exercise 6.3.2

Ethylene (C_2H_4) has two central atoms. Determine the geometry around each central atom and the shape of the overall molecule. (Hint: hydrogen is a terminal atom.)

Answer

Trigonal planar about both central C atoms.

Summary

The approximate shape of a molecule can be predicted from the number of electron groups and the number of surrounding atoms.

6.4: Electronegativity and Polarity

Learning Objectives

- Explain how polar compounds differ from nonpolar compounds.
- Determine if a molecule is polar or nonpolar.
- Given a pair of compounds, predict which would have a higher melting or boiling point.

Bond Polarity

The ability of an atom in a molecule to attract shared electrons is called **electronegativity**. When two atoms combine, the difference between their electronegativities is an indication of the type of bond that will form. If the difference between the electronegativities of the two atoms is small, neither atom can take the shared electrons completely away from the other atom, and the bond will be covalent. If the difference between the electronegativities is large, the more electronegative atom will take the bonding electrons completely away from the other atom (electron transfer will occur), and the bond will be ionic. This is why metals (low electronegativities) bonded with nonmetals (high electronegativities) typically produce ionic compounds.

A bond may be so polar that an electron actually transfers from one atom to another, forming a true ionic bond. How do we judge the degree of polarity? Scientists have devised a scale called **electronegativity**, a scale for judging how much atoms of any element attract electrons. Electronegativity is a unitless number; the higher the number, the more an atom attracts electrons. A common scale for electronegativity is shown in Figure 6.4.1.

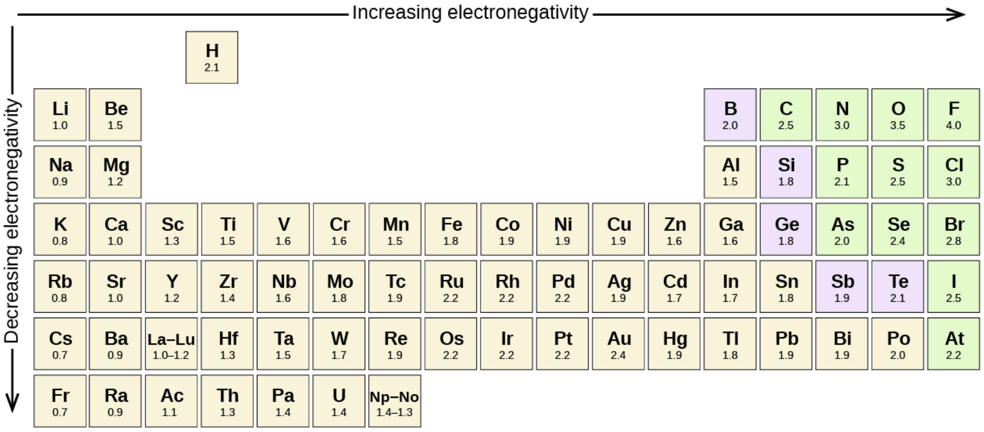


Figure 6.4.1: Electronegativities of the Elements. Electronegativities are used to determine the polarity of covalent bonds.

The polarity of a covalent bond can be judged by determining the *difference* of the electronegativities of the two atoms involved in the covalent bond, as summarized in the following table:

difference of the electronegativities of the two atoms involved in the covalent bond

Electronegativity Difference	Bond Type
0–0.4	pure covalent
0.5–2.0	polar covalent
>2.0	likely ionic

Nonpolar Covalent Bonds

A bond in which the electronegativity difference is less than 1.9 is considered to be mostly covalent in character. However, at this point we need to distinguish between two general types of covalent bonds. A **nonpolar covalent bond** is a covalent bond in which the bonding electrons are shared equally between the two atoms. In a nonpolar covalent bond, the distribution of electrical charge is balanced between the two atoms.

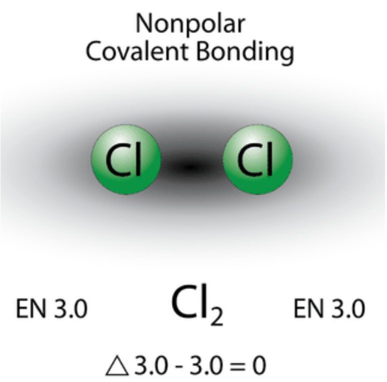


Figure 6.4.2: A nonpolar covalent bond is one in which the distribution of electron density between the two atoms is equal.

The two chlorine atoms share the pair of electrons in the single covalent bond equally, and the electron density surrounding the $\mathrm{Cl_2}$ molecule is symmetrical. Also note that molecules in which the electronegativity difference is very small (<0.5) are also considered nonpolar covalent. An example would be a bond between chlorine and bromine ($\Delta\mathrm{EN} = 3.0 - 2.8 = 0.2$).

Polar Covalent Bonds

A bond in which the electronegativity difference between the atoms is between 0.5 and 2.0 is called a polar covalent bond. A **polar covalent bond** is a covalent bond in which the atoms have an unequal attraction for electrons and so the sharing is unequal. In a polar covalent bond, sometimes simply called a polar bond, the distribution of electrons around the molecule is no longer symmetrical.

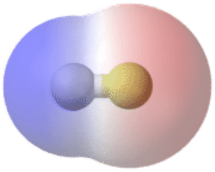


Figure 6.4.3: In the polar covalent bond of HF, the electron density is unevenly distributed. There is a higher density (red) near the fluorine atom, and a lower density (blue) near the hydrogen atom.

An easy way to illustrate the uneven electron distribution in a polar covalent bond is to use the Greek letter delta (δ).

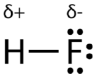


Figure 6.4.4: Use of δ to indicate partial charge.

The atom with the greater electronegativity acquires a partial negative charge, while the atom with the lesser electronegativity acquires a partial positive charge. The delta symbol is used to indicate that the quantity of charge is less than one. A crossed arrow can also be used to indicate the direction of greater electron density.

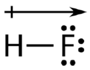


Figure 6.4.5: Use of crossed arrow to indicate polarity.

Electronegativity differences in bonding using Pauling scale. Differences in electronegativity classify bonds as covalent, polar covalent, or ionic.

✓ Example 6.4.1: Bond Polarity

What is the polarity of each bond?

a. C–H
b. O–H

Solution

Using Figure 6.4.1, we can calculate the difference of the electronegativities of the atoms involved in the bond.

a. For the C–H bond, the difference in the electronegativities is 2.5 − 2.1 = 0.4. Thus we predict that this bond will be nonpolar covalent.
b. For the O–H bond, the difference in electronegativities is 3.5 − 2.1 = 1.4, so we predict that this bond will be polar covalent.

? Exercise 6.4.1

What is the polarity of each bond?

a. Rb–F
b. P–Cl

Answer a

likely ionic

Answer b

polar covalent

Molecular Polarity

To determine if a molecule is polar or nonpolar, it is generally useful to look at Lewis structures. **Nonpolar compounds** will be symmetric, meaning all of the sides around the central atom are identical—bonded to the same element with no unshared pairs of electrons. **Polar molecules** are asymmetric, either containing lone pairs of electrons on a central atom or having atoms with different electronegativities bonded. This works pretty well, as long as you can visualize the molecular geometry. That's the hard part. To know how the bonds are oriented in space, you have to have a strong grasp of Lewis structures and VSEPR theory. Assuming that you do, you can look at the structure of each one and decide if it is polar or not, *whether or not you know the individual atom's electronegativity*. This is because you know that all bonds between dissimilar elements are polar, and in these particular examples, it doesn't matter which direction the dipole moment vectors are pointing (out or in).

A **polar molecule** is a molecule in which one end of the molecule is slightly positive, while the other end is slightly negative. A diatomic molecule that consists of a polar covalent bond, such as HF, is a polar molecule. The two electrically charged regions on either end of the molecule are called poles, similar to a magnet having a north and a south pole. A molecule with two poles is called a **dipole** (see figure below). Hydrogen fluoride is a dipole.

Figure 6.4.6: A dipole is any molecule with a positive end and a negative end, resulting from unequal distribution of electron density throughout the molecule.

For molecules with more than two atoms, the molecular geometry must also be taken into account when determining if the molecule is polar or nonpolar. The figure below shows a comparison between carbon dioxide and water. Carbon dioxide $(\mathrm{CO_2})$ is a linear molecule. The oxygen atoms are more electronegative than the carbon atom, so there are two individual dipoles pointing outward from the C atom to each O atom. However, since the dipoles are of equal strength and are oriented this way, they cancel out and the overall molecular polarity of $\mathrm{CO_2}$ is zero.

Water is a bent molecule because of the two lone pairs on the central oxygen atom. The individual dipoles point from the H atoms toward the O atom. Because of the shape, the dipoles do not cancel each other out and the water molecule is polar. In the figure below, the net dipole is shown in blue and points upward.

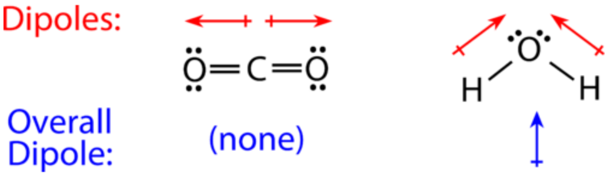


Figure 6.4.7: The molecular geometry of a molecule affects its polarity. Each CO bond has a dipole moment, but they point in opposite directions so that the net CO2 molecule is nonpolar. In contrast, water is polar because the OH bond moments do not cancel out.

Some other molecules are shown in the figure below. Notice that a tetrahedral molecule such as $\mathrm{CH_4}$ is nonpolar. However, if one of the peripheral H atoms is replaced with another atom that has a different electronegativity, the molecule becomes polar. A trigonal planar molecule $(\mathrm{BF_3})$ may be nonpolar if all three peripheral atoms are the same, but a trigonal pyramidal molecule $(\mathrm{NH_3})$ is polar.

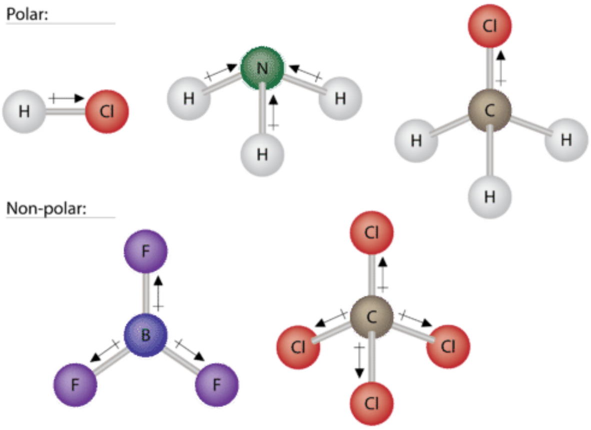


Figure 6.4.8: Some examples of polar and nonpolar molecules based on molecular geometry.

To summarize, to be polar, a molecule must:

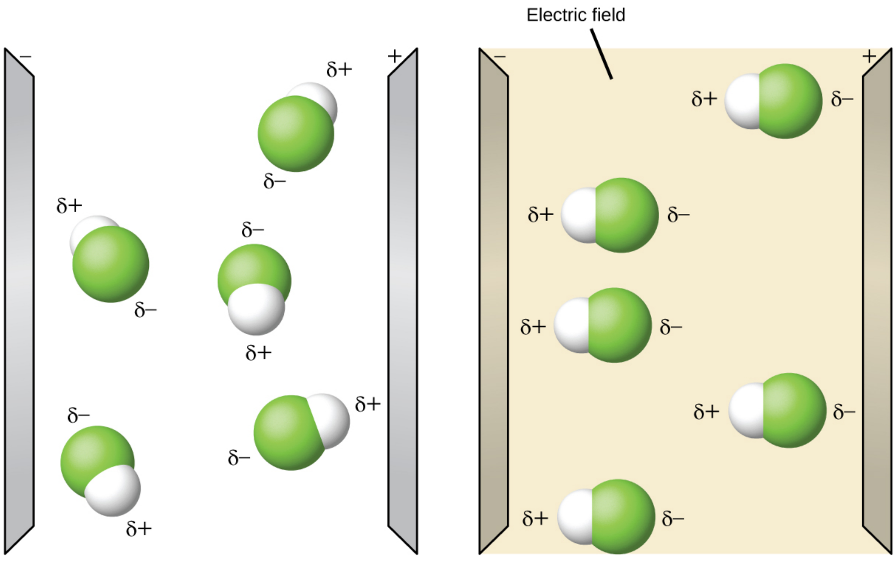
1. Contain at least one polar covalent bond.
2. Have a molecular shape that is unbalanced/unsymmetrical. (This is generally a molecule with different atoms or a lone pair around the central atom.)

Steps to Identify Polar Molecules

1. Draw the Lewis structure.
2. Figure out the molecular shape/geometry (using VSEPR theory).
3. Look up the electronegativity values of each element.
4. If it meets both of the above criteria (polar bond and unbalanced shape), it is polar.
5. If not, it is non-polar.

Properties of Polar Molecules

Polar molecules tend to align when placed in an electric field with the positive end of the molecule oriented toward the negative plate and the negative end toward the positive plate (Figure 6.4.14). We can use an electrically charged object to attract polar molecules, but nonpolar molecules are not attracted. Also, polar solvents are better at dissolving polar substances, and nonpolar solvents are better at dissolving nonpolar substances.



(a) (b)

Figure 6.4.9: (a) Molecules are always randomly distributed in the liquid state in the absence of an electric field. (b) When an electric field is applied, polar molecules like HF will align to the dipoles with the field direction. (OpenStax CC-BY-SA);

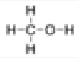
While molecules can be described as "pure covalent" or "polar covalent", it must be noted that this is often a relative term, with one molecule simply being *more polar* or *less polar* than another. However, the following properties are typical of such molecules. Polar molecules tend to:

- have higher melting points than nonpolar molecules
- have higher boiling points than nonpolar molecules
- be more soluble in water (dissolve better) than nonpolar molecules
- have lower vapor pressures than nonpolar molecules

Example 6.4.2:

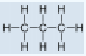
Label each of the following as polar or nonpolar.

a. Water, H_2O: 

b. Methanol, CH_3OH: 

c. Hydrogen Cyanide, HCN: 

d. Oxygen, O_2: 

e. Propane, C_3H_8: 

Solution

a. Water is polar. Any molecule with lone pairs of electrons around the central atom is polar.
b. Methanol is polar. This is not a symmetric molecule. The $-\mathrm{OH}$ side is different from the other 3 $-\mathrm{H}$ sides.
c. Hydrogen cyanide is polar. The molecule is not symmetric. The nitrogen and hydrogen have different electronegativities, creating an uneven pull on the electrons.
d. Oxygen is nonpolar. The molecule is symmetric. The two oxygen atoms pull on the electrons by exactly the same amount.
e. Propane is nonpolar, because it is symmetric, with H atoms bonded to every side around the central atoms and no unshared pairs of electrons.

Exercise 6.4.2

Label each of the following as polar or nonpolar.

a. SO_3
b. NH_3

Answer a

nonpolar

Answer b

polar

Contributions & Attributions

- StackExchange (thomij).

6.5: Intermolecular Forces- Dispersion, Dipole–Dipole, Hydrogen Bonding

Learning Objectives

- To describe the intermolecular forces.

In contrast to *intra*molecular forces, such as the covalent bonds that hold atoms together in molecules and polyatomic ions, *inter*molecular forces hold molecules together in a liquid or solid. Intermolecular forces are generally much weaker than covalent bonds. For example, it requires 927 kJ to overcome the intramolecular forces and break both O–H bonds in 1 mol of water, but it takes only about 41 kJ to overcome the intermolecular attractions and convert 1 mol of liquid water to water vapor at 100°C. (Despite this seemingly low value, the intermolecular forces in liquid water are among the strongest such forces known!) Given the large difference in the strengths of intra- and intermolecular forces, changes between the solid, liquid, and gaseous states almost invariably occur for molecular substances *without breaking covalent bonds*.

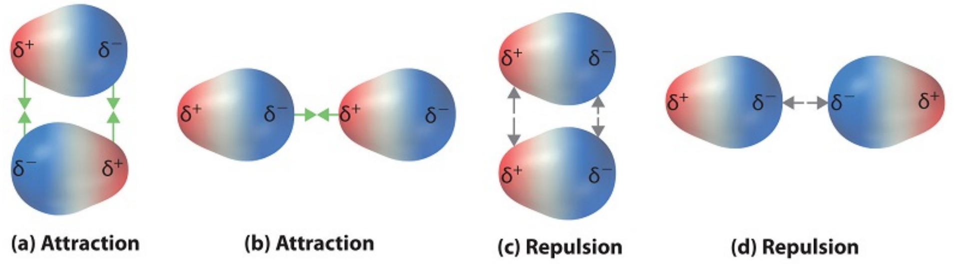
> *The properties of liquids are intermediate between those of gases and solids, but are more similar to solids.*

Intermolecular forces determine bulk properties, such as the melting points of solids and the boiling points of liquids. Liquids boil when the molecules have enough thermal energy to overcome the intermolecular attractive forces that hold them together, thereby forming bubbles of vapor within the liquid. Similarly, solids melt when the molecules acquire enough thermal energy to overcome the intermolecular forces that lock them into place in the solid.

Intermolecular forces are electrostatic in nature; that is, they arise from the interaction between positively and negatively charged species. Like covalent and ionic bonds, intermolecular interactions are the sum of both attractive and repulsive components. Because electrostatic interactions fall off rapidly with increasing distance between molecules, intermolecular interactions are most important for solids and liquids, where the molecules are close together. These interactions become important for gases only at very high pressures, where they are responsible for the observed deviations from the ideal gas law at high pressures.

Dipole–Dipole Interactions

Polar covalent bonds behave as if the bonded atoms have localized fractional charges that are equal but opposite (i.e., the two bonded atoms generate a *dipole*). If the structure of a molecule is such that the individual bond dipoles do not cancel one another, then the molecule has a net dipole moment. Molecules with net dipole moments tend to align themselves so that the positive end of one dipole is near the negative end of another and vice versa, as shown in Figure $6.5.1a$.



(a) Attraction **(b) Attraction** **(c) Repulsion** **(d) Repulsion**

Figure $6.5.1$: Attractive and Repulsive Dipole–Dipole Interactions. (a and b) Molecular orientations in which the positive end of one dipole (δ^+) is near the negative end of another (δ^-) (and vice versa) produce attractive interactions. (c and d) Molecular orientations that juxtapose the positive or negative ends of the dipoles on adjacent molecules produce repulsive interactions.

These arrangements are more stable than arrangements in which two positive or two negative ends are adjacent (Figure $6.5.1c$). Hence dipole–dipole interactions, such as those in Figure $6.5.1b$, are *attractive intermolecular interactions*, whereas those in Figure $6.5.1d$ are *repulsive intermolecular interactions*. Because molecules in a liquid move freely and continuously, molecules always experience both attractive and repulsive dipole–dipole interactions simultaneously, as shown in Figure $6.5.2$. On average, however, the attractive interactions dominate.

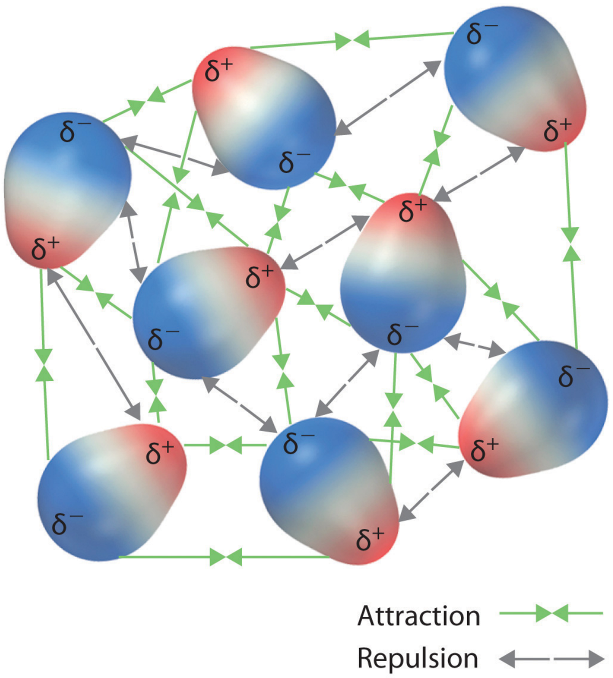


Figure 6.5.2: Both attractive and repulsive dipole–dipole interactions occur in a liquid sample with many molecules.

Because each end of a dipole possesses only a fraction of the charge of an electron, dipole–dipole interactions are substantially weaker than the interactions between two ions, each of which has a charge of at least ±1, or between a dipole and an ion, in which one of the species has at least a full positive or negative charge. In addition, the attractive interaction between dipoles falls off much more rapidly with increasing distance than do the ion–ion interactions. Thus a substance such as HCl, which is partially held together by dipole–dipole interactions, is a gas at room temperature and 1 atm pressure. Conversely, NaCl, which is held together by interionic interactions, is a high-melting-point solid. Within a series of compounds of similar molar mass, the strength of the intermolecular interactions increases as the dipole moment of the molecules increases, as shown in Table 6.5.1.

Table 6.5.1: Relationships Between the Dipole Moment and the Boiling Point for Organic Compounds of Similar Molar Mass

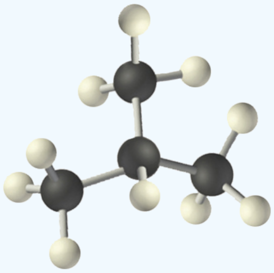
Compound	**Molar Mass (g/mol)**	**Dipole Moment (D)**	**Boiling Point (K)**
C_3H_6 (cyclopropane)	42	0	240
CH_3OCH_3 (dimethyl ether)	46	1.30	248
CH_3CN (acetonitrile)	41	3.9	355

> *The following video contains some examples of determining whether a molecule can have dipole intermolecular forces. It includes some review of when we first introduced the idea of molecular polarity.*

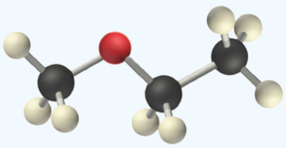
Video Discussing Dipole Intermolecular Forces. Source: https://youtu.be/ACq_95SIBck

✓ Example 6.5.1

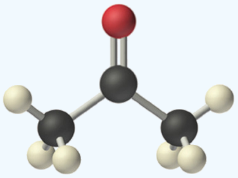
Arrange ethyl methyl ether ($CH_3OCH_2CH_3$), 2-methylpropane [isobutane, $(CH_3)_2CHCH_3$], and acetone (CH_3COCH_3) in order of increasing boiling points. Their structures are as follows:



2-Methylpropane



Ethyl methyl ether



Acetone

Given: compounds.

Asked for: order of increasing boiling points.

Strategy:

Compare the molar masses and the polarities of the compounds. Compounds with higher molar masses and that are polar will have the highest boiling points.

Solution:

The three compounds have essentially the same molar mass (58–60 g/mol), so we must look at differences in polarity to predict the strength of the intermolecular dipole–dipole interactions and thus the boiling points of the compounds.

The first compound, 2-methylpropane, contains only C–H bonds, which are not very polar because C and H have similar electronegativities. It should therefore have a very small (but nonzero) dipole moment and a very low boiling point.

Ethyl methyl ether has a structure similar to H_2O; it contains two polar C–O single bonds oriented at about a 109° angle to each other, in addition to relatively nonpolar C–H bonds. As a result, the C–O bond dipoles partially reinforce one another and generate a significant dipole moment that should give a moderately high boiling point.

Acetone contains a polar C=O double bond oriented at about 120° to two methyl groups with nonpolar C–H bonds. The C–O bond dipole therefore corresponds to the molecular dipole, which should result in both a rather large dipole moment and a high boiling point.

Thus we predict the following order of boiling points:

$$\text{2-methylpropane} < \text{ethyl methyl ether} < \text{acetone}$$

This result is in good agreement with the actual data: 2-methylpropane, boiling point = −11.7°C, and the dipole moment (μ) = 0.13 D; methyl ethyl ether, boiling point = 7.4°C and μ = 1.17 D; acetone, boiling point = 56.1°C and μ = 2.88 D.

? Exercise 6.5.1

Arrange carbon tetrafluoride (CF_4), ethyl methyl sulfide ($CH_3SC_2H_5$), dimethyl sulfoxide [$(CH_3)_2S{=}O$], and 2-methylbutane [isopentane, $(CH_3)_2CHCH_2CH_3$] in order of decreasing boiling points.

Answer

dimethyl sulfoxide (boiling point = 189.9°C) > ethyl methyl sulfide (boiling point = 67°C) > 2-methylbutane (boiling point = 27.8°C) > carbon tetrafluoride (boiling point = −128°C)

London Dispersion Forces

Thus far, we have considered only interactions between polar molecules. Other factors must be considered to explain why many nonpolar molecules, such as bromine, benzene, and hexane, are liquids at room temperature; why others, such as iodine and naphthalene, are solids. Even the noble gases can be liquefied or solidified at low temperatures, high pressures, or both (Table 6.5.2).

What kind of attractive forces can exist between nonpolar molecules or atoms? This question was answered by Fritz London (1900–1954), a German physicist who later worked in the United States. In 1930, London proposed that temporary fluctuations in the electron distributions within atoms and nonpolar molecules could result in the formation of short-lived instantaneous dipole moments, which produce attractive forces called London dispersion forces between otherwise nonpolar substances.

Table 6.5.2: Normal Melting and Boiling Points of Some Elements and Nonpolar Compounds

Substance	Molar Mass (g/mol)	Melting Point (°C)	Boiling Point (°C)
Ar	40	−189.4	−185.9
Xe	131	−111.8	−108.1
N_2	28	−210	−195.8
O_2	32	−218.8	−183.0
F_2	38	−219.7	−188.1
I_2	254	113.7	184.4
CH_4	16	−182.5	−161.5

Consider a pair of adjacent He atoms, for example. On average, the two electrons in each He atom are uniformly distributed around the nucleus. Because the electrons are in constant motion, however, their distribution in one atom is likely to be asymmetrical at any given instant, resulting in an instantaneous dipole moment. As shown in part (a) in Figure 6.5.3, the instantaneous dipole moment on one atom can interact with the electrons in an adjacent atom, pulling them toward the positive end of the instantaneous dipole or repelling them from the negative end. The net effect is that the first atom causes the temporary formation of a dipole, called an induced dipole, in the second. Interactions between these temporary dipoles cause atoms to be attracted to one another. These attractive interactions are weak and fall off rapidly with increasing distance.

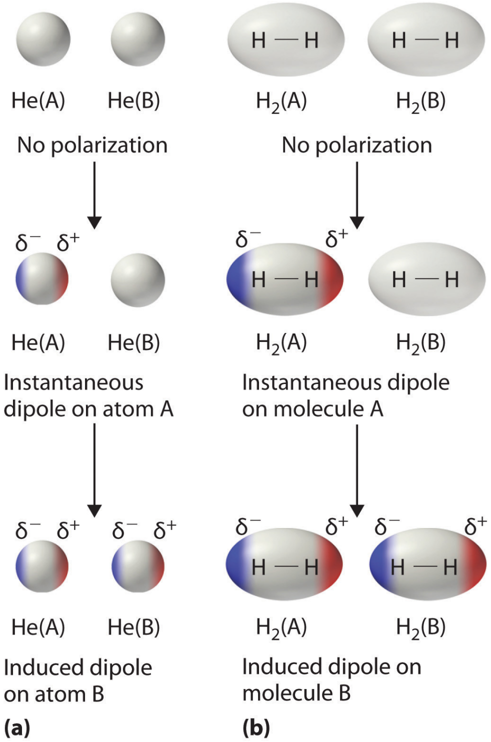


Figure 6.5.3: Instantaneous Dipole Moments. The formation of an instantaneous dipole moment on one He atom (a) or an H_2 molecule (b) results in the formation of an induced dipole on an adjacent atom or molecule.

Instantaneous dipole–induced dipole interactions between nonpolar molecules can produce intermolecular attractions just as they produce interatomic attractions in monatomic substances like Xe. This effect, illustrated for two H_2 molecules in part (b) in Figure 6.5.3, tends to become more pronounced as atomic and molecular masses increase (Table 6.5.2). For example, Xe boils at −108.1°C, whereas He boils at −269°C. The reason for this trend is that the strength of London dispersion forces is related to the ease with which the electron distribution in a given atom can be perturbed. In small atoms such as He, the two 1*s* electrons are held close to the nucleus in a very small volume, and electron–electron repulsions are strong enough to prevent significant asymmetry in their distribution. In larger atoms such as Xe, however, the outer electrons are much less strongly attracted to the nucleus because of filled intervening shells. As a result, it is relatively easy to temporarily deform the electron distribution to generate an instantaneous or induced dipole. The ease of deformation of the electron distribution in an atom or molecule is called its polarizability. Because the electron distribution is more easily perturbed in large, heavy species than in small, light species, we say that heavier substances tend to be much more *polarizable* than lighter ones.

> *For similar substances, London dispersion forces get stronger with increasing molecular size.*

The polarizability of a substance also determines how it interacts with ions and species that possess permanent dipoles. Thus, London dispersion forces are responsible for the general trend toward higher boiling points with increased molecular mass and greater surface area in a homologous series of compounds, such as the alkanes (part (a) in Figure 6.5.4). The strengths of London dispersion forces also depend significantly on molecular shape because shape determines how much of one molecule can interact with its neighboring molecules at any given time. For example, part (b) in Figure 6.5.4 shows 2,2-dimethylpropane (neopentane) and *n*-pentane, both of which have the empirical formula C_5H_{12}. Neopentane is almost spherical, with a small surface area for intermolecular interactions, whereas *n*-pentane has an extended conformation that enables it to come into close contact with other *n*-pentane molecules. As a result, the boiling point of neopentane (9.5°C) is more than 25°C lower than the boiling point of *n*-pentane (36.1°C).

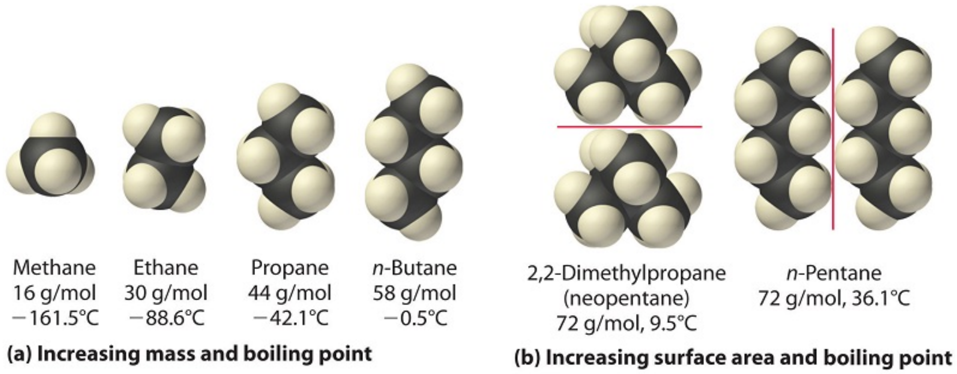


Figure 6.5.4: Mass and Surface Area Affect the Strength of London Dispersion Forces. (a) In this series of four simple alkanes, larger molecules have stronger London forces between them than smaller molecules do, and consequently have higher boiling points. (b) Linear *n*-pentane molecules have a larger surface area and stronger intermolecular forces than spherical neopentane molecules. As a result, neopentane is a gas at room temperature, whereas *n*-pentane is a volatile liquid.

All molecules, whether polar or nonpolar, are attracted to one another by London dispersion forces in addition to any other attractive forces that may be present. In general, however, dipole–dipole interactions in small polar molecules are significantly stronger than London dispersion forces, so the former predominate.

Video Discussing London/Dispersion Intermolecular Forces. Source: https://youtu.be/RCRTcIEQ-Hk

✓ Example 6.5.2

Arrange *n*-butane, propane, 2-methylpropane [isobutene, $(CH_3)_2CHCH_3$], and *n*-pentane in order of increasing boiling points.

Given: compounds

Asked for: order of increasing boiling points

Strategy:

Determine the intermolecular forces in the compounds, and then arrange the compounds according to the strength of those forces. The substance with the weakest forces will have the lowest boiling point.

Solution:

The four compounds are alkanes and nonpolar, so London dispersion forces are the only important intermolecular forces. These forces are generally stronger with increasing molecular mass, so propane should have the lowest boiling point and *n*-pentane should have the highest, with the two butane isomers falling in between. Of the two butane isomers, 2-methylpropane is more compact, and *n*-butane has the more extended shape. Consequently, we expect intermolecular interactions for *n*-butane to be stronger due to its larger surface area, resulting in a higher boiling point. The overall order is thus as follows, with actual boiling points in parentheses: propane (−42.1°C) < 2-methylpropane (−11.7°C) < *n*-butane (−0.5°C) < *n*-pentane (36.1°C).

? Exercise 6.5.2

Arrange GeH_4, $SiCl_4$, SiH_4, CH_4, and $GeCl_4$ in order of decreasing boiling points.

Answer

$GeCl_4$ (87°C) > $SiCl_4$ (57.6°C) > GeH_4 (−88.5°C) > SiH_4 (−111.8°C) > CH_4 (−161°C)

Hydrogen Bonds

Molecules with hydrogen atoms bonded to electronegative atoms such as O, N, and F (and to a much lesser extent, Cl and S) tend to exhibit unusually strong intermolecular interactions. These result in much higher boiling points than are observed for substances in which London dispersion forces dominate, as illustrated for the covalent hydrides of elements of groups 14–17 in Figure 6.5.5. Methane and its heavier congeners in group 14 form a series whose boiling points increase smoothly with increasing molar mass. This is the expected trend in nonpolar molecules, for which London dispersion forces are the exclusive intermolecular forces. In contrast, the hydrides of the lightest members of groups 15–17 have boiling points that are more than 100°C greater than predicted on the basis of their molar masses. The effect is most dramatic for water: if we extend the straight line connecting the points for H_2Te and H_2Se to the line for period 2, we obtain an estimated boiling point of −130°C for water! Imagine the implications for life on Earth if water boiled at −130°C rather than 100°C.

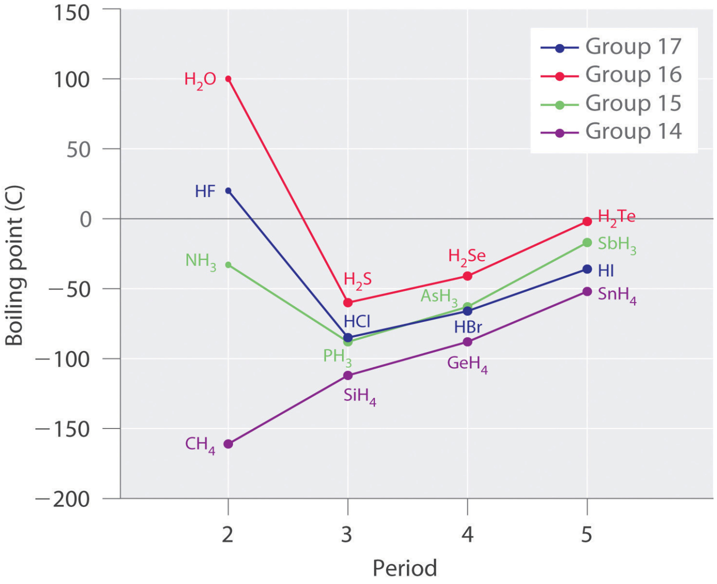


Figure 6.5.5: The Effects of Hydrogen Bonding on Boiling Points. These plots of the boiling points of the covalent hydrides of the elements of groups 14–17 show that the boiling points of the lightest members of each series for which hydrogen bonding is possible (HF, NH_3, and H_2O) are anomalously high for compounds with such low molecular masses.

Why do strong intermolecular forces produce such anomalously high boiling points and melting points? The answer lies in the highly polar nature of the bonds between hydrogen and very electronegative elements such as O, N, and F. The large difference in electronegativity results in a large partial positive charge on hydrogen and a correspondingly large partial negative charge on the O, N, or F atom. Consequently, H–O, H–N, and H–F bonds have very large bond dipoles that can interact strongly with one another. Because a hydrogen atom is so small, these dipoles can also approach one another more closely than most other dipoles. The combination of large bond dipoles and short dipole–dipole distances results in very strong dipole–dipole interactions called hydrogen bonds, as shown for ice in Figure 6.5.6. A hydrogen bond is usually indicated by a dotted line between the hydrogen atom attached to O, N, or F (the *hydrogen bond donor*) and the atom that has the lone pair of electrons (the *hydrogen bond acceptor*). Because each water molecule contains two hydrogen atoms and two lone pairs, a tetrahedral arrangement maximizes the number of hydrogen bonds that can be formed. In the structure of ice, each oxygen atom is surrounded by a distorted tetrahedron of hydrogen atoms that form bridges to the oxygen atoms of adjacent water molecules. The bridging hydrogen atoms are *not* equidistant from the two oxygen atoms they connect, however. Instead, each hydrogen atom is 101 pm from one oxygen and 174 pm from the other. In contrast, each oxygen atom is bonded to two H atoms at the shorter distance and two at the longer distance, corresponding to two O–H covalent bonds and two O⋯H hydrogen bonds from adjacent water molecules, respectively. The resulting open, cagelike structure of ice means that the solid is actually slightly less dense than the liquid, which explains why ice floats on water, rather than sinks.

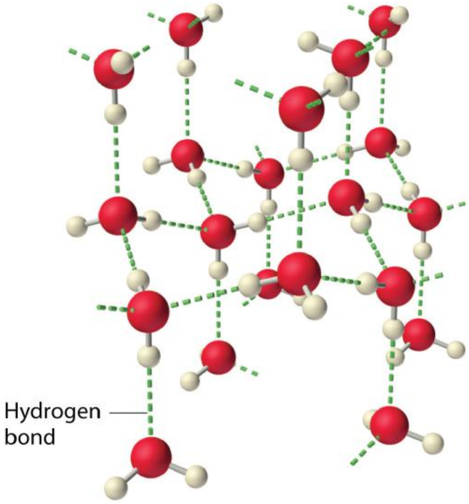


Figure 6.5.6: The Hydrogen-Bonded Structure of Ice

Each water molecule accepts two hydrogen bonds from two other water molecules and donates two hydrogen atoms to form hydrogen bonds with two more water molecules, producing an open, cagelike structure. The structure of liquid water is very similar, but in the liquid, the hydrogen bonds are continually broken and formed because of rapid molecular motion.

> *Hydrogen bond formation requires both a hydrogen bond donor and a hydrogen bond acceptor.*

Because ice is less dense than liquid water, rivers, lakes, and oceans freeze from the top down. In fact, the ice forms a protective surface layer that insulates the rest of the water, allowing fish and other organisms to survive in the lower levels of a frozen lake or sea. If ice were denser than the liquid, the ice formed at the surface in cold weather would sink as fast as it formed. Bodies of water would freeze from the bottom up, which would be lethal for most aquatic creatures. The expansion of water when freezing also explains why automobile or boat engines must be protected by “antifreeze” and why unprotected pipes in houses break if they are allowed to freeze.

Video Discussing Hydrogen Bonding Intermolecular Forces. Source: https://youtu.be/92rbjSpHbr0

✓ Example 6.5.3

Considering CH_3OH, C_2H_6, Xe, and $(CH_3)_3N$, which can form hydrogen bonds with themselves? Draw the hydrogen-bonded structures.

Given: compounds

Asked for: formation of hydrogen bonds and structure

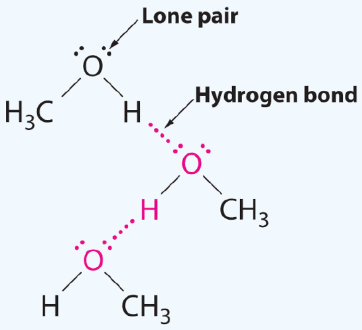
Strategy:

A. Identify the compounds with a hydrogen atom attached to O, N, or F. These are likely to be able to act as hydrogen bond donors.
B. Of the compounds that can act as hydrogen bond donors, identify those that also contain lone pairs of electrons, which allow them to be hydrogen bond acceptors. If a substance is both a hydrogen donor and a hydrogen bond acceptor, draw a structure showing the hydrogen bonding.

Solution:

A. Of the species listed, xenon (Xe), ethane (C_2H_6), and trimethylamine [$(CH_3)_3N$] do not contain a hydrogen atom attached to O, N, or F; hence they cannot act as hydrogen bond donors.

B. The one compound that can act as a hydrogen bond donor, methanol (CH_3OH), contains both a hydrogen atom attached to O (making it a hydrogen bond donor) and two lone pairs of electrons on O (making it a hydrogen bond acceptor); methanol can thus form hydrogen bonds by acting as either a hydrogen bond donor or a hydrogen bond acceptor. The hydrogen-bonded structure of methanol is as follows:



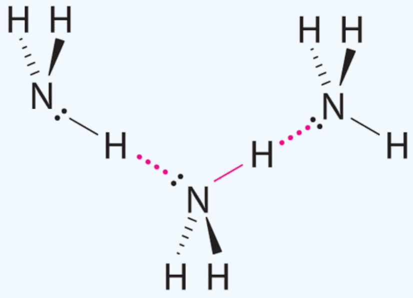
Hydrogen bonding in methanol

Exercise 6.5.3

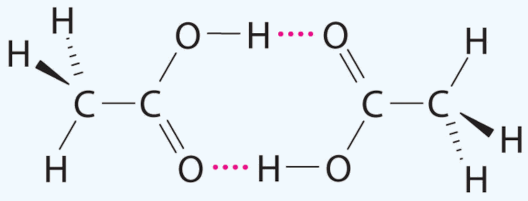
Considering CH_3CO_2H, $(CH_3)_3N$, NH_3, and CH_3F, which can form hydrogen bonds with themselves? Draw the hydrogen-bonded structures.

Answer

CH_3CO_2H and NH_3;



Hydrogen bonding in ammonia



Hydrogen bonding in acetic acid

Although hydrogen bonds are significantly weaker than covalent bonds, with typical dissociation energies of only 15–25 kJ/mol, they have a significant influence on the physical properties of a compound. Compounds such as HF can form only two hydrogen bonds at a time as can, on average, pure liquid NH_3. Consequently, even though their molecular masses are similar to that of water, their boiling points are significantly lower than the boiling point of water, which forms *four* hydrogen bonds at a time.

✓ Example 6.5.4: Buckyballs

Arrange C_{60} (buckminsterfullerene, which has a cage structure), NaCl, He, Ar, and N_2O in order of increasing boiling points.

Given: compounds.

Asked for: order of increasing boiling points.

Strategy:

Identify the intermolecular forces in each compound and then arrange the compounds according to the strength of those forces. The substance with the weakest forces will have the lowest boiling point.

Solution:

Electrostatic interactions are strongest for an ionic compound, so we expect NaCl to have the highest boiling point. To predict the relative boiling points of the other compounds, we must consider their polarity (for dipole–dipole interactions), their ability to form hydrogen bonds, and their molar mass (for London dispersion forces). Helium is nonpolar and by far the lightest, so it should have the lowest boiling point. Argon and N_2O have very similar molar masses (40 and 44 g/mol, respectively), but N_2O is polar while Ar is not. Consequently, N_2O should have a higher boiling point. A C_{60} molecule is nonpolar, but its molar mass is 720 g/mol, much greater than that of Ar or N_2O. Because the boiling points of nonpolar substances increase rapidly with molecular mass, C_{60} should boil at a higher temperature than the other nonionic substances. The predicted order is thus as follows, with actual boiling points in parentheses:

$$\text{He } (-269°\text{C}) < \text{Ar } (-185.7°\text{C}) < N_2O\ (-88.5°\text{C}) < C_{60}\ (>280°\text{C}) < \text{NaCl } (1465°\text{C}).$$

? Exercise 6.5.4

Arrange 2,4-dimethylheptane, Ne, CS_2, Cl_2, and KBr in order of decreasing boiling points.

Answer

KBr (1435°C) > 2,4-dimethylheptane (132.9°C) > CS_2 (46.6°C) > Cl_2 (−34.6°C) > Ne (−246°C)

✓ Example 6.5.5:

Identify the most significant intermolecular force in each substance.

a. C_3H_8
b. CH_3OH
c. H_2S

Solution

a. Although C–H bonds are polar, they are only minimally polar. The most significant intermolecular force for this substance would be dispersion forces.

b. This molecule has an H atom bonded to an O atom, so it will experience hydrogen bonding.

c. Although this molecule does not experience hydrogen bonding, the Lewis electron dot diagram and VSEPR indicate that it is bent, so it has a permanent dipole. The most significant force in this substance is dipole-dipole interaction.

? Exercise 6.5.6

Identify the most significant intermolecular force in each substance.

a. HF
b. HCl

Answer a

hydrogen bonding

Answer b

dipole-dipole interactions

Summary

Intermolecular forces are electrostatic in nature and include van der Waals forces and hydrogen bonds. Molecules in liquids are held to other molecules by intermolecular interactions, which are weaker than the intramolecular interactions that hold the atoms together within molecules and polyatomic ions. Transitions between the solid and liquid, or the liquid and gas phases, are due to changes in intermolecular interactions, but do not affect intramolecular interactions. The three major types of intermolecular interactions are dipole–dipole interactions, London dispersion forces (these two are often referred to collectively as **van der Waals forces**), and hydrogen bonds. **Dipole–dipole interactions** arise from the electrostatic interactions of the positive and negative ends of molecules with permanent dipole moments. **London dispersion forces** are due to the formation of **instantaneous dipole moments** in polar or nonpolar molecules as a result of short-lived fluctuations of electron charge distribution, which in turn cause the temporary formation of an **induced dipole** in adjacent molecules. Larger atoms tend to be more **polarizable** than smaller ones, because their outer electrons are less tightly bound and are therefore more easily perturbed. **Hydrogen bonds** are especially strong dipole–dipole interactions between molecules that have hydrogen bonded to a highly electronegative atom, such as O, N, or F. The resulting partially positively charged H atom on one molecule (the *hydrogen bond donor*) can interact strongly with a lone pair of electrons of a partially negatively charged O, N, or F atom on adjacent molecules (the *hydrogen bond acceptor*). Because of strong O⋯H hydrogen bonding between water molecules, water has an unusually high boiling point, and ice has an open, cagelike structure that is less dense than liquid water.

6.E: Electrons and Chemical Bonds (Exercises)

6.1.1: Lewis Electron Dot Diagrams

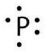
1. Explain why the first two dots in a Lewis electron dot diagram are drawn on the same side of the atomic symbol.
2. Is it necessary for the first dot around an atomic symbol to go on a particular side of the atomic symbol?
3. What column of the periodic table has Lewis electron dot diagrams with two electrons?
4. What column of the periodic table has Lewis electron dot diagrams that have six electrons in them?
5. Draw the Lewis electron dot diagram for each element.
    a. strontium
    b. silicon
6. Draw the Lewis electron dot diagram for each element.
    a. krypton
    b. sulfur
7. Draw the Lewis electron dot diagram for each element.
    a. titanium
    b. phosphorus
8. Draw the Lewis electron dot diagram for each element.
    a. bromine
    b. gallium
9. Draw the Lewis electron dot diagram for each ion.
    a. Mg^{2+}
    b. S^{2-}
10. Draw the Lewis electron dot diagram for each ion.
    a. In^{+}
    b. Br^{-}
11. Draw the Lewis electron dot diagram for each ion.
    a. Fe^{2+}
    b. N^{3-}
12. Draw the Lewis electron dot diagram for each ion.
    a. H^{+}
    b. H^{-}

Answers

1. The first two electrons in a valence shell are *s* electrons, which are paired.
2.
3. the second column of the periodic table
4.
5. a. 

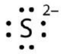
    b. 

6.
7. a. 

b. 

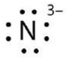
8.

9. a. Mg^{2+}

b. 

10.

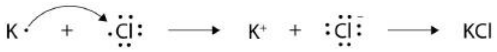
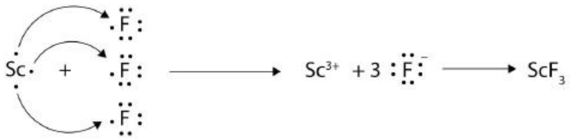
11. a. Fe^{2+}

b. 

6.1.2: Electron Transfer - Ionic Bonds

1. Comment on the possible formation of the K^{2+} ion. Why is its formation unlikely?
2. Comment on the possible formation of the Cl^{2-} ion. Why is its formation unlikely?
3. How many electrons does a Ba atom have to lose to have a complete octet in its valence shell?
4. How many electrons does a Pb atom have to lose to have a complete octet in its valence shell?
5. How many electrons does an Se atom have to gain to have a complete octet in its valence shell?
6. How many electrons does an N atom have to gain to have a complete octet in its valence shell?
7. With arrows, illustrate the transfer of electrons to form potassium chloride from K atoms and Cl atoms.
8. With arrows, illustrate the transfer of electrons to form magnesium sulfide from Mg atoms and S atoms.
9. With arrows, illustrate the transfer of electrons to form scandium fluoride from Sc atoms and F atoms.
10. With arrows, illustrate the transfer of electrons to form rubidium phosphide from Rb atoms and P atoms.
11. Which ionic compound has the higher lattice energy—KI or MgO? Why?
12. Which ionic compound has the higher lattice energy—KI or LiF? Why?
13. Which ionic compound has the higher lattice energy—BaS or MgO? Why?

Answers

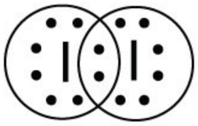
1. The K^{2+} ion is unlikely to form because the K^{+} ion already satisfies the octet rule and is rather stable.
2.
3. two
4.
5. two
6.
7. 
8.
9. 
10.
11. MgO because the ions have a higher magnitude charge
12.
13. MgO because the ions are smaller

6.2: Covalent Bonds

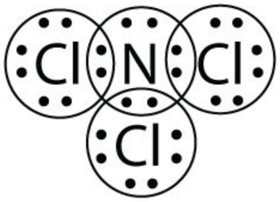
1. How many electrons will be in the valence shell of H atoms when it makes a covalent bond?
2. How many electrons will be in the valence shell of non-H atoms when they make covalent bonds?
3. What is the Lewis electron dot diagram of I_2? Circle the electrons around each atom to verify that each valence shell is filled.
4. What is the Lewis electron dot diagram of H_2S? Circle the electrons around each atom to verify that each valence shell is filled.
5. What is the Lewis electron dot diagram of NCl_3? Circle the electrons around each atom to verify that each valence shell is filled.
6. What is the Lewis electron dot diagram of SiF_4? Circle the electrons around each atom to verify that each valence shell is filled.
7. Draw the Lewis electron dot diagram for each substance.
    a. SF_2
    b. BH_4^-
8. Draw the Lewis electron dot diagram for each substance.
    a. PI_3
    b. OH^-
9. Draw the Lewis electron dot diagram for each substance.
    a. GeH_4
    b. ClF
10. Draw the Lewis electron dot diagram for each substance.
    a. AsF_3
    b. NH_4^+
11. Draw the Lewis electron dot diagram for each substance. Double or triple bonds may be needed.
    a. SiO_2
    b. C_2H_4 (assume two central atoms)
12. Draw the Lewis electron dot diagram for each substance. Double or triple bonds may be needed.
    a. CN^-
    b. C_2Cl_2 (assume two central atoms)
13. Draw the Lewis electron dot diagram for each substance. Double or triple bonds may be needed.
    a. CS_2
    b. NH_2CONH_2 (assume that the N and C atoms are the central atoms)
14. Draw the Lewis electron dot diagram for each substance. Double or triple bonds may be needed.
    a. POCl (This is phosphorus, oxygen, and chlorine)
    b. HCOOH (assume that the C atom and one O atom are the central atoms)

Answers

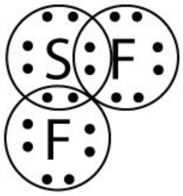
1. two
2.



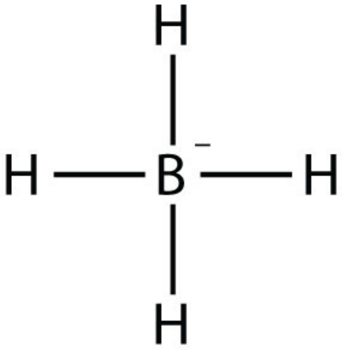
3.
4.



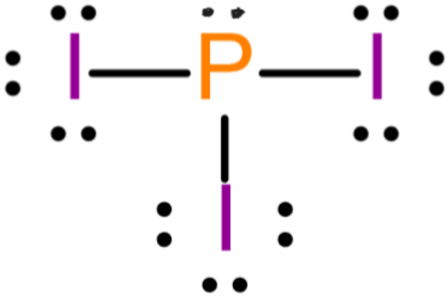
5.
6.



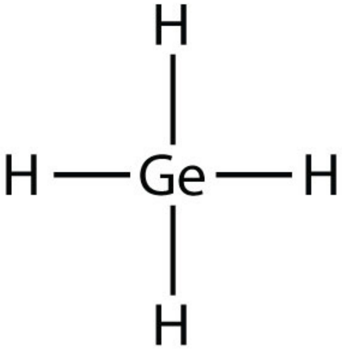
7. a.



b.



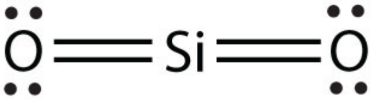
8. a.



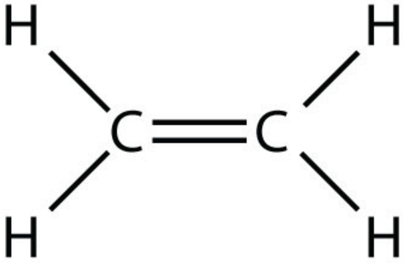
9. a.

b.

10.

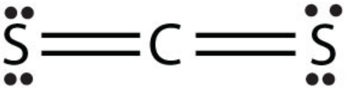


11. a.

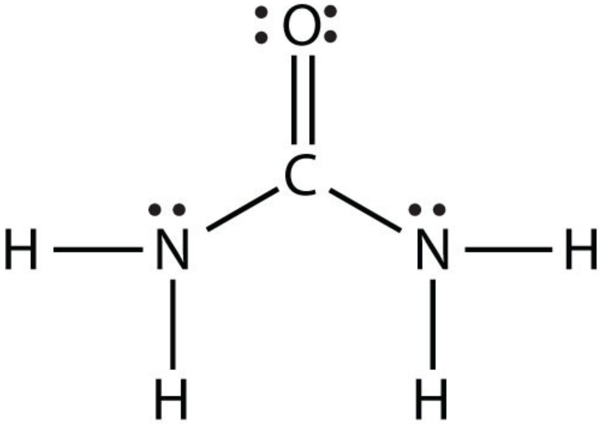


b.

12.



13. a.



b.

6.2.1: Other Aspects of Covalent Bonds

1. Give an example of a nonpolar covalent bond. How do you know it is nonpolar?
2. Give an example of a polar covalent bond. How do you know it is polar?
3. How do you know which side of a polar bond has the partial negative charge? Identify the negatively charged side of each polar bond.

   a. H–Cl
   b. H–S
4. How do you know which side of a polar bond has the partial positive charge? Identify the positively charged side of each polar bond.
   a. H–Cl
   b. N-F
5. Label the bond between the given atoms as nonpolar covalent, slightly polar covalent, definitely polar covalent, or likely ionic.
   a. H and C
   b. C and F
   c. K and F
6. Label the bond between the given atoms as nonpolar covalent, slightly polar covalent, definitely polar covalent, or likely ionic.
   a. S and Cl
   b. P and O
   c. Cs and O
7. Which covalent bond is stronger—a C–C bond or a C–H bond?
8. Which covalent bond is stronger—an O–O double bond or an N–N double bond?
9. Estimate the enthalpy change for this reaction: $N_2 + 3H_2 \rightarrow 2NH_3$ .Start by drawing the Lewis electron dot diagrams for each substance.
10. Estimate the enthalpy change for this reaction. Start by drawing the Lewis electron dot diagrams for each substance: HN=NH + $2H_2 \rightarrow 2NH_3$
11. Estimate the enthalpy change for this reaction. Start by drawing the Lewis electron dot diagrams for each substance: CH_4 + $2O_2 \rightarrow CO_2 + 2H_2O$
12. Estimate the enthalpy change for this reaction. Start by drawing the Lewis electron dot diagrams for each substance: $4NH_3$ + $3O_2 \rightarrow 2N_2 + 6H_2O$

Answers

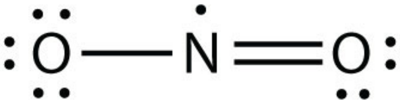
1. H–H; it is nonpolar because the two atoms have the same electronegativities (answers will vary).
2.
3. a. Cl side
   b. S side
4.
5. a. slightly polar covalent
   b. definitely polar covalent
   c. likely ionic
6.
7. C–H bond
8.
9. −80 kJ
10.
11. −798 kJ

6.2.2: Violations of the Octet Rule

1. Why can an odd-electron molecule not satisfy the octet rule?
2. Why can an atom in the second row of the periodic table not form expanded valence shell molecules?
3. Draw an acceptable Lewis electron dot diagram for these molecules that violate the octet rule.
   a. NO_2
4. Draw an acceptable Lewis electron dot diagram for these molecules that violate the octet rule.
   a. BCl_3
   b. ClO_2
5. Draw an acceptable Lewis electron dot diagram for these molecules that violate the octet rule.

  a. BeH_2

Answers

1. There is no way all electrons can be paired if there are an odd number of them.
2. 
3. a.
4.

6.3: Molecular Shapes

1. What is the basic premise behind VSEPR?
2. What is the difference between the electron group geometry and the molecular geometry?
3. Identify the electron group geometry and the molecular geometry of each molecule.
    a. H_2S
4. Identify the electron group geometry and the molecular geometry of each molecule.
    a. CS_2
    b. H_2S
5. Identify the electron group geometry and the molecular geometry of each molecule.
    a. HCN
    b. CCl_4
6. Identify the electron group geometry and the molecular geometry of each molecule.
    a. BI_3
    b. PH_3
7. What is the geometry of each species?
    a. CN^-
    b. PO_4^{3-}
8. What is the geometry of each species?
    a. PO_3^{3-}
    b. NO_3^-
9. What is the geometry of each species?
    a. COF_2
    b. C_2Cl_2 (both C atoms are central atoms and are bonded to each other)
10. What is the geometry of each species?
    a. CO_3^{2-}
    b. N_2H_4 (both N atoms are central atoms and are bonded to each other)

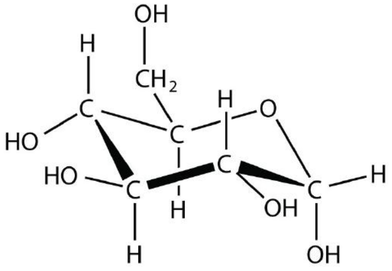
Answers

1. Electron pairs repel each other.
2.
3. a. electron group geometry: tetrahedral; molecular geometry: bent
4.
5. a. electron group geometry: linear; molecular geometry: linear
    b. electron group geometry: tetrahedral; molecular geometry: tetrahedral
6.

7. a. linear
   b. tetrahedral
8.
9. a. trigonal planar
   b. linear and linear about each central atom

6.4 - 6.5: Intermolecular Forces

1. What type of intermolecular force do all substances have?
2. What is necessary for a molecule to experience dipole-dipole interactions?
3. What is necessary for a molecule to experience hydrogen bonding?
4. How does varying the temperature change the preferred phase of a substance?
5. Identify the strongest intermolecular force present in each substance.
   a. He
   b. $CHCl_3$ (this is carbon, hydrogen, and 3 chlorine atoms)
   c. HOF
6. Identify the strongest intermolecular force present in each substance.
   a. CH_3OH
   b. $(CH_3)_2CO$
   c. N_2
7. Identify the strongest intermolecular force present in each substance.
   a. HBr
   b. $C_6H_5NH_2$
   c. CH_4
8. Identify the strongest intermolecular force present in each substance.
   a. $C_{10}H_{22}$
   b. HF
   c. glucose



Answers

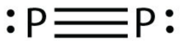
1. dispersion force
2.
3. An H atom must be bonded to an N, O, or F atom.
4.
5. a. dispersion forces
   b. dipole-dipole interactions
   c. hydrogen bonding
6.
7. a. dipole-dipole interactions
   b. hydrogen bonding
   c. dispersion forces

6.7 Additional Exercises

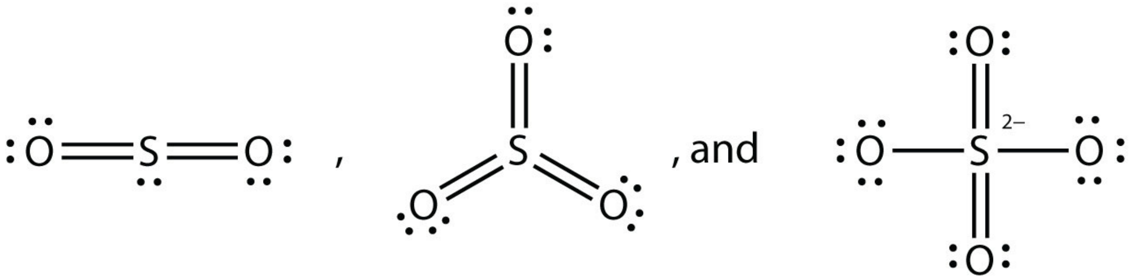
1. Explain why iron and copper have the same Lewis electron dot diagram when they have different numbers of electrons.
2. Name two ions with the same Lewis electron dot diagram as the Cl^- ion.
3. Based on the known trends, what ionic compound from the first column of the periodic table and the next-to-last column of the periodic table should have the highest lattice energy?
4. Based on the known trends, what ionic compound from the first column of the periodic table and the next-to-last column of the periodic table should have the lowest lattice energy?
5. P_2 is not a stable form of phosphorus, but if it were, what would be its likely Lewis electron dot diagram?
6. Se_2 is not a stable form of selenium, but if it were, what would be its likely Lewis electron dot diagram?
7. What are the Lewis electron dot diagrams of SO_2, SO_3, and SO_4^{2-}?
8. What are the Lewis electron dot diagrams of PO_3^{3-} and PO_4^{3-}?
9. Which bond do you expect to be more polar—an O–H bond or an N–H bond?
10. Which bond do you expect to be more polar—an O–F bond or an S–O bond?
11. Use bond energies to estimate the energy change of this reaction. $C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O$
12. Use bond energies to estimate the energy change of this reaction. $N_2H_4 + O_2 \rightarrow N_2 + 2H_2O$
13. Ethylene (C_2H_4) has two central atoms. Determine the geometry around each central atom and the shape of the overall molecule.
14. Hydrogen peroxide (H_2O_2) has two central atoms. Determine the geometry around each central atom and the shape of the overall molecule.

Answers

1. Iron has *d* electrons that typically are not shown on Lewis electron dot diagrams.
2.
3. LiF
4.
5. It would be like N_2:



6.



7.
8.
9. an O–H bond
10.
11. −2,000 kJ
12.
13. trigonal planar about both central C atoms

CHAPTER OVERVIEW

7: Solids, Liquids, and Phase Changes

In previous chapters we discussed the properties of gases. In this chapter, we consider some properties of liquids and solids. As a review, the table below lists some general properties of the three phases of matter.

Phase	Shape	Density	Compressibility
Gas	fills entire container	low	high
Liquid	fills a container from bottom to top	high	low
Solid	rigid	high	low

7.1: Properties of Liquids and Solids

Learning Objectives

- Describe the solid and liquid phases.

Solids and liquids are collectively called *condensed phases* because their particles are in virtual contact. The two states share little else, however.

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.

Figure $7.1.1$: A crystalline arrangement of quartz crystal cluster. Some large crystals look the way they do because of the regular arrangement of atoms (ions) in their crystal structure. (Source: Wikipedia.)

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 $7.1.1$. 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.

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.

Figure $7.1.2$: The formation of a spherical droplet of liquid water minimizes the surface area, which is the natural result of surface tension in liquids. (Source: Wikipedia.)

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. Like liquids, gases have no definite shape, but unlike solids and liquids, gases have no definite volume either.

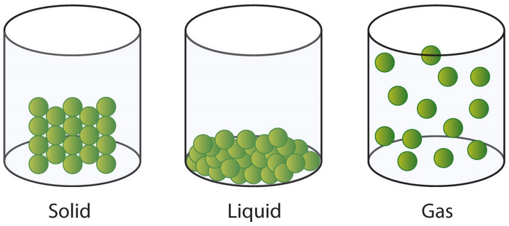


Figure $7.1.3$: A Representation of the Solid, Liquid, and Gas States. A solid has definite volume and shape, a liquid has a definite volume but no definite shape, and a gas has neither a definite volume nor shape.

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. Figure $7.1.3$ shows the differences among solids, liquids, and gases at the molecular level, while Table $7.1.1$ lists the different characteristics of these states.

Table $7.1.1$: Characteristics of the Three States of Matter

Characteristic	Solid	Liquid	Gas
shape	definite	indefinite	indefinite
volume	definite	definite	indefinite
relative intermolecular interaction strength	strong	moderate	weak
relative particle positions	in contact and fixed in place	in contact but not fixed	not in contact, random positions

✓ Example $7.1.1$

What state or states of matter does each statement describe?

a. This state has a definite volume.
b. This state has no definite shape.
c. This state allows the individual particles to move about while remaining in contact.

Solution

a. This statement describes either the liquid state or the solid state.
b. This statement describes either the liquid state or the gas state.
c. This statement describes the liquid state.

? Exercise $7.1.1$

What state or states of matter does each statement describe?

a. This state has individual particles in a fixed position with regard to each other.
b. This state has individual particles far apart from each other in space.
c. This state has indefinite shape.

Answer a

solid

Answer b

gas

Answer c

liquid or gas

Looking Closer: Water, the Most Important Liquid

Earth is the only known body in our solar system that has liquid water existing freely on its surface; life on Earth would not be possible without the presence of liquid water.

Water has several properties that make it a unique substance among substances. It is an excellent solvent; it dissolves many other substances and allows those substances to react when in solution. In fact, water is sometimes called the *universal solvent* because of this ability. Water has unusually high melting and boiling points (0°C and 100°C, respectively) for such a small molecule. The boiling points for similar-sized molecules, such as methane (BP = −162°C) and ammonia (BP = −33°C), are more than 100° lower. Though a liquid at normal temperatures, water molecules experience a relatively strong intermolecular interaction that allows them to maintain the liquid phase at higher temperatures than expected.

Unlike most substances, the solid form of water is less dense than its liquid form, which allows ice to float on water. In colder weather, lakes and rivers freeze from the top, allowing animals and plants to continue to live underneath. Water also requires an unusually large amount of energy to change temperature. While 100 J of energy will change the temperature of 1 g of Fe by 230°C, this same amount of energy will change the temperature of 1 g of H_2O by only 100°C. Thus, water changes its temperature slowly as heat is added or removed. This has a major impact on weather, as storm systems like hurricanes can be impacted by the amount of heat that ocean water can store.

Water’s influence on the world around us is affected by these properties. Isn’t it fascinating that such a small molecule can have such a big impact?

Key Takeaway

- Solids and liquids are phases that have their own unique properties.

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- Henry Agnew (UC Davis)

7.2: Intermolecular Forces in Action- Surface Tension, Viscosity, and Capillary Action

Learning Objectives

- To describe the unique properties of liquids.

Although you have been introduced to some of the interactions that hold molecules together in a liquid, we have not yet discussed the consequences of those interactions for the bulk properties of liquids. We now turn our attention to three unique properties of liquids that intimately depend on the nature of intermolecular interactions:

- surface tension,
- capillary action, and
- viscosity.

Surface Tension

If liquids tend to adopt the shapes of their containers, then why do small amounts of water on a freshly waxed car form raised droplets instead of a thin, continuous film? The answer lies in a property called *surface tension*, which depends on intermolecular forces. Surface tension is the energy required to increase the surface area of a liquid by a unit amount and varies greatly from liquid to liquid based on the nature of the intermolecular forces, e.g., water with hydrogen bonds has a surface tension of 7.29 x 10^{-2} J/m^2 (at 20°C), while mercury with metallic bonds has as surface tension that is 15 times higher: 4.86 x 10^{-1} J/m^2 (at 20°C).

Figure $7.2.1$ presents a microscopic view of a liquid droplet. A typical molecule in the *interior* of the droplet is surrounded by other molecules that exert attractive forces from all directions. Consequently, there is no *net* force on the molecule that would cause it to move in a particular direction. In contrast, a molecule on the *surface* experiences a net attraction toward the drop because there are no molecules on the outside to balance the forces exerted by adjacent molecules in the interior. Because a sphere has the smallest possible surface area for a given volume, intermolecular attractive interactions between water molecules cause the droplet to adopt a spherical shape. This maximizes the number of attractive interactions and minimizes the number of water molecules at the surface. Hence raindrops are almost spherical, and drops of water on a waxed (nonpolar) surface, which does not interact strongly with water, form round beads. A dirty car is covered with a mixture of substances, some of which are polar. Attractive interactions between the polar substances and water cause the water to spread out into a thin film instead of forming beads.

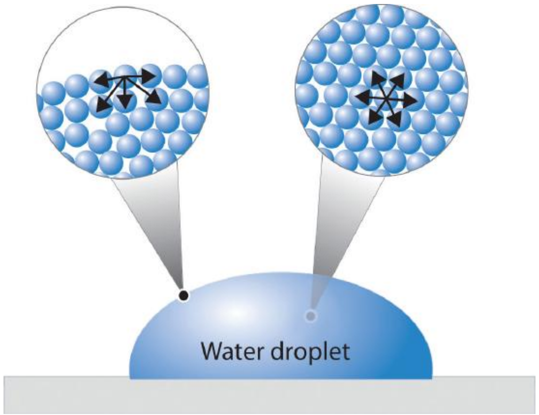


Figure $7.2.1$: A Representation of Surface Tension in a Liquid. Molecules at the surface of water experience a net attraction to other molecules in the liquid, which holds the surface of the bulk sample together. In contrast, those in the interior experience uniform attractive forces.

The same phenomenon holds molecules together at the surface of a bulk sample of water, almost as if they formed a skin. When filling a glass with water, the glass can be overfilled so that the level of the liquid actually extends *above* the rim. Similarly, a sewing needle or a paper clip can be placed on the surface of a glass of water where it “floats,” even though steel is much denser than water. Many insects take advantage of this property to walk on the surface of puddles or ponds without sinking. This is even observable in the zero gravity conditions of space as shown in Figure $7.2.2$ (and more so in the video link) where water wrung from a wet towel continues to float along the towel's surface!

Figure 7.2.2: The Effects of the High Surface Tension of Liquid Water. The full video can be found at www.youtube.com/watch?v=9jB7rOC5kG8.

Such phenomena are manifestations of surface tension, which is defined as the energy required to increase the surface area of a liquid by a specific amount. Surface tension is therefore measured as energy per unit area, such as joules per square meter (J/m^2) or dyne per centimeter (dyn/cm), where 1 dyn = 1×10^{-5} N. The values of the surface tension of some representative liquids are listed in Table 7.2.1. Note the correlation between the surface tension of a liquid and the strength of the intermolecular forces: the stronger the intermolecular forces, the higher the surface tension. For example, water, with its strong intermolecular hydrogen bonding, has one of the highest surface tension values of any liquid, whereas low-boiling-point organic molecules, which have relatively weak intermolecular forces, have much lower surface tensions. Mercury is an apparent anomaly, but its very high surface tension is due to the presence of strong metallic bonding.

Table 7.2.1: Surface Tension, Viscosity, Vapor Pressure (at 25°C Unless Otherwise Indicated), and Normal Boiling Points of Common Liquids

Substance	Surface Tension ($\times 10^{-3}$ J/m^2)	Viscosity (mPa•s)	Vapor Pressure (mmHg)	Normal Boiling Point (°C)
Organic Compounds				
diethyl ether	17	0.22	531	34.6
n-hexane	18	0.30	149	68.7
acetone	23	0.31	227	56.5
ethanol	22	1.07	59	78.3
ethylene glycol	48	16.1	~0.08	198.9
Liquid Elements				
bromine	41	0.94	218	58.8
mercury	486	1.53	0.0020	357
Water				
0°C	75.6	1.79	4.6	—
20°C	72.8	1.00	17.5	—
60°C	66.2	0.47	149	—
100°C	58.9	0.28	760	—

Adding soaps and detergents that disrupt the intermolecular attractions between adjacent water molecules can reduce the surface tension of water. Because they affect the surface properties of a liquid, soaps and detergents are called surface-active agents, or surfactants. In the 1960s, US Navy researchers developed a method of fighting fires aboard aircraft carriers using "foams," which are aqueous solutions of fluorinated surfactants. The surfactants reduce the surface tension of water below that of fuel, so the fluorinated solution is able to spread across the burning surface and extinguish the fire. Such foams are now used universally to fight large-scale fires of organic liquids.

Capillary Action

Intermolecular forces also cause a phenomenon called capillary action, which is the tendency of a polar liquid to rise against gravity into a small-diameter tube (a *capillary*), as shown in Figure 7.2.3. When a glass capillary is placed in liquid water, water rises up into the capillary. The height to which the water rises depends on the diameter of the tube and the temperature of the water but *not* on the angle at which the tube enters the water. The smaller the diameter, the higher the liquid rises.

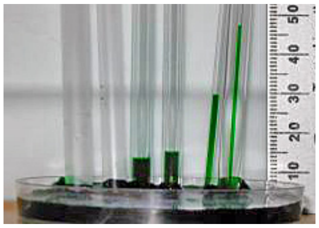


Figure 7.2.3: The Phenomenon of Capillary Action. Capillary action seen as water climbs to different levels in glass tubes of different diameters. Credit: Dr. Clay Robinson, PhD, West Texas A&M University.

> - Cohesive forces bind molecules of the same type together
> - Adhesive forces bind a substance to a surface

Capillary action is the net result of two opposing sets of forces: cohesive forces, which are the intermolecular forces that hold a liquid together, and adhesive forces, which are the attractive forces between a liquid and the substance that composes the capillary. Water has both strong adhesion to glass, which contains polar SiOH groups, and strong intermolecular cohesion. When a glass capillary is put into water, the surface tension due to cohesive forces constricts the surface area of water within the tube, while adhesion between the water and the glass creates an upward force that maximizes the amount of glass surface in contact with the water. If the adhesive forces are stronger than the cohesive forces, as is the case for water, then the liquid in the capillary rises to the level where the downward force of gravity exactly balances this upward force. If, however, the cohesive forces are stronger than the adhesive forces, as is the case for mercury and glass, the liquid pulls itself down into the capillary below the surface of the bulk liquid to minimize contact with the glass (Figure 7.2.4). The upper surface of a liquid in a tube is called the meniscus, and the shape of the meniscus depends on the relative strengths of the cohesive and adhesive forces. In liquids such as water, the meniscus is concave; in liquids such as mercury, however, which have very strong cohesive forces and weak adhesion to glass, the meniscus is convex (Figure 7.2.4).

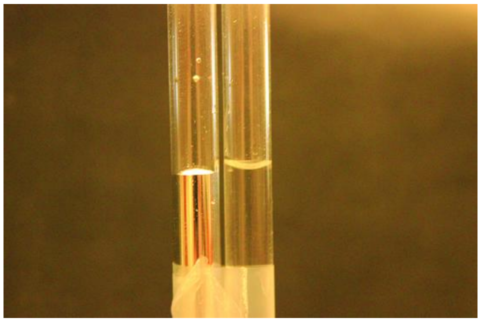


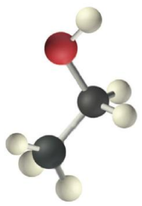
Figure 7.2.4: The Phenomenon of Capillary Action. Capillary action of water compared to mercury, in each case with respect to a polar surface such as glass. Differences in the relative strengths of cohesive and adhesive forces result in different meniscus shapes for mercury (left) and water (right) in glass tubes. (credit: Mark Ott)

> Polar substances are drawn up a glass capillary and generally have a concave meniscus.

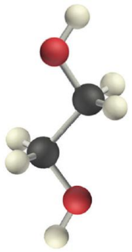
Fluids and nutrients are transported up the stems of plants or the trunks of trees by capillary action. Plants contain tiny rigid tubes composed of cellulose, to which water has strong adhesion. Because of the strong adhesive forces, nutrients can be transported from the roots to the tops of trees that are more than 50 m tall. Cotton towels are also made of cellulose; they absorb water because the tiny tubes act like capillaries and "wick" the water away from your skin. The moisture is absorbed by the entire fabric, not just the layer in contact with your body.

Viscosity

Viscosity (η) is the resistance of a liquid to flow. Some liquids, such as gasoline, ethanol, and water, flow very readily and hence have a *low viscosity*. Others, such as motor oil, molasses, and maple syrup, flow very slowly and have a *high viscosity*. The two most common methods for evaluating the viscosity of a liquid are (1) to measure the time it takes for a quantity of liquid to flow through a narrow vertical tube and (2) to measure the time it takes steel balls to fall through a given volume of the liquid. The higher the viscosity, the slower the liquid flows through the tube and the steel balls fall. Viscosity is expressed in units of the poise (mPa•s); the higher the number, the higher the viscosity. The viscosities of some representative liquids are listed in Table 11.3.1 and show a correlation between viscosity and intermolecular forces. Because a liquid can flow only if the molecules can move past one another with minimal resistance, strong intermolecular attractive forces make it more difficult for molecules to move with respect to one another. The addition of a second hydroxyl group to ethanol, for example, which produces ethylene glycol ($HOCH_2CH_2OH$), increases the viscosity 15-fold. This effect is due to the increased number of hydrogen bonds that can form between hydroxyl groups in adjacent molecules, resulting in dramatically stronger intermolecular attractive forces.



Ethanol



Ethylene glycol

There is also a correlation between viscosity and molecular shape. Liquids consisting of long, flexible molecules tend to have higher viscosities than those composed of more spherical or shorter-chain molecules. The longer the molecules, the easier it is for them to become “tangled” with one another, making it more difficult for them to move past one another. London dispersion forces also increase with chain length. Due to a combination of these two effects, long-chain hydrocarbons (such as motor oils) are highly viscous.

> *Viscosity increases as intermolecular interactions or molecular size increases.*

Video Discussing Surface Tension and Viscosity. Video Link: Surface Tension, Viscosity, & Melting Point, YouTube(opens in new window) [youtu.be]

Application: Motor Oils

Motor oils and other lubricants demonstrate the practical importance of controlling viscosity. The oil in an automobile engine must effectively lubricate under a wide range of conditions, from subzero starting temperatures to the 200°C that oil can reach in an engine in the heat of the Mojave Desert in August. Viscosity decreases rapidly with increasing temperatures because the kinetic energy of the molecules increases, and higher kinetic energy enables the molecules to overcome the attractive forces that prevent the liquid from flowing. As a result, an oil that is thin enough to be a good lubricant in a cold engine will become too “thin” (have too low a viscosity) to be effective at high temperatures.

Figure $7.2.5$: Oil being drained from a car

The viscosity of motor oils is described by an SAE (Society of Automotive Engineers) rating ranging from SAE 5 to SAE 50 for engine oils: the lower the number, the lower the viscosity (Figure $7.2.5$). So-called *single-grade oils* can cause major problems. If they are viscous enough to work at high operating temperatures (SAE 50, for example), then at low temperatures, they can be so viscous that a car is difficult to start or an engine is not properly lubricated. Consequently, most modern oils are *multigrade*, with designations such as SAE 20W/50 (a grade used in high-performance sports cars), in which case the oil has the viscosity of an SAE 20 oil at subzero temperatures (hence the W for winter) and the viscosity of an SAE 50 oil at high temperatures. These properties are achieved by a careful blend of additives that modulate the intermolecular interactions in the oil, thereby controlling the temperature dependence of the viscosity. Many of the commercially available oil additives “for improved engine performance” are highly viscous materials that increase the viscosity and effective SAE rating of the oil, but overusing these additives can cause the same problems experienced with highly viscous single-grade oils.

✓ Example $7.2.1$

Based on the nature and strength of the intermolecular cohesive forces and the probable nature of the liquid–glass adhesive forces, predict what will happen when a glass capillary is put into a beaker of SAE 20 motor oil. Will the oil be pulled up into the tube by capillary action or pushed down below the surface of the liquid in the beaker? What will be the shape of the meniscus (convex or concave)? (Hint: the surface of glass is lined with Si–OH groups.)

Given: substance and composition of the glass surface

Asked for: behavior of oil and the shape of meniscus

Strategy:

A. Identify the cohesive forces in the motor oil.
B. Determine whether the forces interact with the surface of glass. From the strength of this interaction, predict the behavior of the oil and the shape of the meniscus.

Solution

A Motor oil is a nonpolar liquid consisting largely of hydrocarbon chains. The cohesive forces responsible for its high boiling point are almost solely London dispersion forces between the hydrocarbon chains.

B Such a liquid cannot form strong interactions with the polar Si–OH groups of glass, so the surface of the oil inside the capillary will be lower than the level of the liquid in the beaker. The oil will have a convex meniscus similar to that of mercury.

? Exercise $7.2.1$

Predict what will happen when a glass capillary is put into a beaker of ethylene glycol. Will the ethylene glycol be pulled up into the tube by capillary action or pushed down below the surface of the liquid in the beaker? What will be the shape of the meniscus (convex or concave)?

Answer

Capillary action will pull the ethylene glycol up into the capillary. The meniscus will be concave.

Summary

Surface tension, capillary action, and viscosity are unique properties of liquids that depend on the nature of intermolecular interactions. **Surface tension** is the energy required to increase the surface area of a liquid by a given amount. The stronger the intermolecular interactions, the greater the surface tension. **Surfactants** are molecules, such as soaps and detergents, that reduce the surface tension of polar liquids like water. **Capillary action** is the phenomenon in which liquids rise up into a narrow tube called a capillary. It results when **cohesive forces**, the intermolecular forces in the liquid, are weaker than **adhesive forces**, the attraction between a liquid and the surface of the capillary. The shape of the **meniscus**, the upper surface of a liquid in a tube, also reflects the balance between adhesive and cohesive forces. The **viscosity** of a liquid is its resistance to flow. Liquids that have strong intermolecular forces tend to have high viscosities.

7.3: Types of Crystalline Solids

Learning Objectives

- Identify different types of solid substances.

As a society, we sometimes take things for granted. For example, it is often assumed that we will get electric power when we connect a plug to an electrical outlet. The wire that comprises that outlet is almost always copper, a material that conducts electricity well. The unique properties of the solid copper allow electrons to flow freely through the wire and into whatever device we connect it to. Then we can enjoy music, television, computer work, or whatever other activity we want to undertake. However, these activities—and the miracle of electricity itself—would not be possible without that copper wire!

Classes of Crystalline Solids

Crystalline substances can be described by the types of particles in them and the types of chemical bonding that take place between the particles. There are four types of crystals: (1) **ionic**, (2) **metallic**, (3) **covalent network**, and (4) **molecular**. Properties and several examples of each type are listed in the following table and are described in the table below. The bonding responsible for ionic solids and molecular solids have each been discussed earlier in this book. The other two bonding types have not been discussed yet.

Table 7.3.1: Crystalline Solids: Melting and Boiling Points

Type of Crystalline Solid	Examples (formulas)	Melting Point (°C)	Normal Boiling Point (°C)
Ionic	$NaCl$	801	1413
	CaF_2	1418	1533
Metallic	Hg	-39	630
	Na	371	883
	Au	1064	2856
	W	3410	5660
Covalent Network	B	2076	3927
	C (diamond)	3500	3930
	SiO_2	1600	2230
Molecular	H_2	-259	-253
	I_2	114	184
	NH_3	-78	-33
	H_2O	0	100

Ionic crystals - The ionic crystal structure consists of alternating positively-charged cations and negatively-charged anions (see figure below). The ions may either be monatomic or polyatomic. Generally, ionic crystals form from a combination of Group 1 or 2 metals and Group 16 or 17 nonmetals or nonmetallic polyatomic ions. Ionic crystals are hard and brittle and have high melting points. Ionic compounds do not conduct electricity as solids, but do conduct electricity when molten or in aqueous solution.

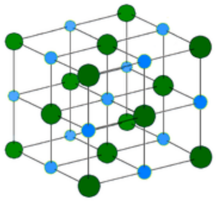


Figure 7.3.1: $NaCl$ crystal.

Metallic crystal - Metallic crystals consist of metal cations surrounded by a "sea" of mobile valence electrons (see figure below). These electrons, also referred to as delocalized electrons, do not belong to any one atom, but are capable of moving through the entire crystal. As a result, metals are good conductors of electricity. As seen in the table above, the melting points of metallic crystals span a wide range.

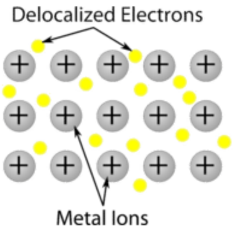


Figure $7.3.2$: Metallic crystal lattice with free electrons able to move among positive metal atoms.

Covalent network crystals - A covalent network crystal consists of atoms at the lattice points of the crystal, with each atom being covalently bonded to its nearest neighbor atoms (see figure below). The covalently bonded network is three-dimensional and contains a very large number of atoms. Network solids include diamond, quartz, many metalloids, and oxides of transition metals. Network solids are hard and brittle, with extremely high melting and boiling points. Being composed of atoms rather than ions, they do not conduct electricity in any state.

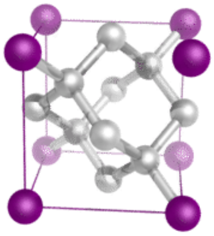


Figure $7.3.3$: Diamond is a network solid and consists of carbon atoms covalently bonded to one another in a repeating three-dimensional pattern. Each carbon atom makes for single covalent bonds in a tetrahedral geometry.

Molecular crystals - Molecular crystals typically consist of molecules at the lattice points of the crystal, held together by relatively weak intermolecular forces (see figure below). The intermolecular forces may be dispersion forces in the case of nonpolar crystals, or dipole-dipole forces in the case of polar crystals. Some molecular crystals, such as ice, have molecules held together by hydrogen bonds. When one of the noble gases is cooled and solidified, the lattice points are individual atoms rather than molecules. In all cases, the intermolecular forces holding the particles together are far weaker than either ionic or covalent bonds. As a result, the melting and boiling points of molecular crystals are much lower. Lacking ions or free electrons, molecular crystals are poor electrical conductors.

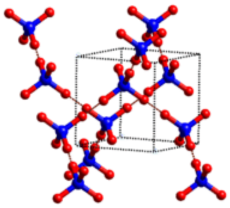


Figure $7.3.4$: Ice crystal structure.

Some general properties of the four major classes of solids are summarized in Table $7.3.2$.

Table $7.3.2$: Properties of the Major Classes of Solids

Ionic Solids	Molecular Solids	Covalent Solids	Metallic Solids
poor conductors of heat and electricity	poor conductors of heat and electricity	poor conductors of heat and electricity*	good conductors of heat and electricity
relatively high melting point	low melting point	high melting point	melting points depend strongly on electron configuration
*Many exceptions exist. For example, graphite has a relatively high electrical conductivity within the carbon planes, and diamond has the highest thermal conductivity of any known substance.			

Ionic Solids	Molecular Solids	Covalent Solids	Metallic Solids
hard but brittle; shatter under stress	soft	very hard and brittle	easily deformed under stress; ductile and malleable
relatively dense	low density	low density	usually high density
dull surface	dull surface	dull surface	lustrous
*Many exceptions exist. For example, graphite has a relatively high electrical conductivity within the carbon planes, and diamond has the highest thermal conductivity of any known substance.			

✓ Example 7.3.1

Classify Ge, RbI, $C_6(CH_3)_6$, and Zn as ionic, molecular, covalent, or metallic solids and arrange them in order of increasing melting points.

Given: compounds

Asked for: classification and order of melting points

Strategy:

A. Locate the component element(s) in the periodic table. Based on their positions, predict whether each solid is ionic, molecular, covalent, or metallic.
B. Arrange the solids in order of increasing melting points based on your classification, beginning with molecular solids.

Solution:

A. **Germanium** lies in the p block just under Si, along the diagonal line of semi-metallic elements, which suggests that elemental Ge is likely to have the same structure as Si (the diamond structure). Thus Ge is probably a **covalent solid**.

RbI contains a metal from group 1 and a nonmetal from group 17, so it is **an ionic solid** containing Rb^+ and I^- ions.

The compound $C_6(CH_3)_6$ is a hydrocarbon (hexamethylbenzene), which consists of isolated molecules that stack to form **a molecular solid** with no covalent bonds between them.

Zn is a d-block element, so it is **a metallic solid**.

B. Arranging these substances in order of increasing melting points is straightforward, with one exception. We expect $C_6(CH_3)_6$ to have the lowest melting point and Ge to have the highest melting point, with RbI somewhere in between. The melting points of metals, however, are difficult to predict based on the models presented thus far. Because Zn has a filled valence shell, it should not have a particularly high melting point, so a reasonable guess is

$$\mathbf{C_6(CH_3)_6 < Zn \sim RbI < Ge.}$$

The actual melting points are $C_6(CH_3)_6$, 166°C; Zn, 419°C; RbI, 642°C; and Ge, 938°C. This agrees with our prediction.

? Exercise 7.3.1

Classify CO_2, $BaBr_2$, GaAs, and AgZn as ionic, covalent, molecular, or metallic solids and then arrange them in order of increasing melting points.

Answer

CO_2 (molecular) < AgZn (metallic) ~ $BaBr_2$ (ionic) < GaAs (covalent).

The actual melting points are: CO_2, about -15.6°C; AgZn, about 700°C; $BaBr_2$, 856°C; and GaAs, 1238°C.

Summary

- Ionic crystals are composed of alternating positive and negative ions.
- Metallic crystals consist of metal cations surrounded by a "sea" of mobile valence electrons.
- Covalent crystals are composed of atoms which are covalently bonded to one another.

- Molecular crystals are held together by weak intermolecular forces.

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7.4: Temperature, Heat, and Energy

Terms such as energy, heat, and temperature are sometimes used somewhat interchangeably although they mean very different things. In this section, we will define these terms based on how they are used in science. We will also introduce some units and conversions for each of them.

7.4.1: Energy and Chemical and Physical Change

Learning Objectives

- Define endothermic and exothermic reactions.
- Describe how heat is transferred in endothermic and exothermic reactions.
- Determine whether a reaction is endothermic or exothermic through observations, temperature changes, or an energy diagram.

So far, we have talked about how energy exists as either *kinetic energy* or *potential energy* and how energy can be transferred as either *heat* or *work*. While it's important to understand the difference between kinetic energy and potential energy and the difference between heat and work, the truth is, energy is constantly changing. Kinetic energy is constantly being turned into potential energy, and potential energy is constantly being turned into kinetic energy. Likewise, energy that is transferred as work might later end up transferred as heat, while energy that is transferred as heat might later end up being used to do work.

Even though energy can change form, it must still follow one fundamental law: *Energy cannot be created or destroyed, it can only be changed from one form to another*. This law is known as the **Law of Conservation of Energy**. In a lot of ways, energy is like money. You can exchange quarters for dollar bills and dollar bills for quarters, but no matter how often you convert between the two, you will not end up with any more or any less money than you started with. Similarly, you can transfer (or spend) money using cash, or transfer money using a credit card; but you still spend the same amount of money, and the store still makes the same amount of money.

A campfire is an example of basic thermochemistry. The reaction is initiated by the application of heat from a match. The reaction converting wood to carbon dioxide and water (among other things) continues, releasing heat energy in the process. This heat energy can then be used to cook food, roast marshmallows, or just keep warm when it's cold outside.

An image of a campfire with colored flames, made by the burning of a garden hose in a copper pipe. (CC SA-BY 3.0; Jared)

Exothermic and Endothermic Processes

When physical or chemical changes occur, they are generally accompanied by a transfer of energy. The **law of conservation of energy** states that in any physical or chemical process, energy is neither created nor destroyed. In other words, the entire energy in the universe is conserved. In order to better understand the energy changes taking place during a reaction, we need to define two parts of the universe: *the system* and *the surroundings*. The **system** is the specific portion of matter in a given space that is being studied during an experiment or an observation. The **surroundings** are everything in the universe that is not part of the system. In practical terms for a laboratory chemist, the system is the particular chemicals being reacted, while the surroundings are the immediate vicinity within the room. During most processes, energy is exchanged between the system and the surroundings. If the system loses a certain amount of energy, that same amount of energy is gained by the surroundings. If the system gains a certain amount of energy, that energy is supplied by the surroundings.

A chemical reaction or physical change is **endothermic** if heat is absorbed by the system from the surroundings. In the course of an endothermic process, the system gains heat from the surroundings and so the temperature of the surroundings decreases. The quantity of heat for a process is represented by the letter q. The sign of q for an endothermic process is positive because the system is gaining heat. A chemical reaction or physical change is **exothermic** if heat is released by the system into the surroundings. Because the surroundings are gaining heat from the system, the temperature of the surroundings increases. The sign of q for an exothermic process is negative because the system is losing heat.

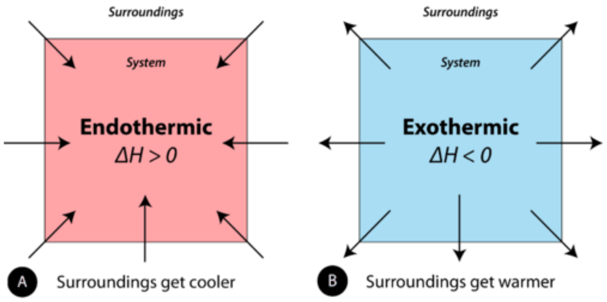

Figure 7.4.1.1: (A) Endothermic reaction. (B) Exothermic reaction.

Endothermic reaction: surroundings get cooler and delta H is greater than 0, Exothermic reaction: surroundings get warmer and delta H is less than 0

During phase changes, energy changes are usually involved. For example, when solid dry ice vaporizes (physical change), carbon dioxide molecules absorb energy. When liquid water becomes ice, energy is released. Remember that all chemical reactions involve a change in the bonds of the reactants. The bonds in the reactants are broken and the bonds of the products are formed. Chemical bonds have **potential energy** or "stored energy". Because we are changing the bonding, this means we are also changing how much of this "stored energy" there is in a reaction.

Energy changes are frequently shown by drawing an energy diagram. Energy diagrams show the stored/hidden energy of the reactants and products as well as the activation energy. If, on an energy diagram, the products have more stored energy than the reactants started with, the reaction is endothermic. You had to give the reaction energy. If, on the energy diagram, the products have less stored energy than the reactants started with, the reaction is exothermic.

Example 7.4.1.1

Label each of the following processes as endothermic or exothermic.

a. water boiling
b. gasoline burning
c. ice forming on a pond

Solution

a. Endothermic—you must put a pan of water on the stove and give it heat in order to get water to boil. Because you are adding heat/energy, the reaction is endothermic.
b. Exothermic—when you burn something, it feels hot to you because it is giving off heat into the surroundings.
c. Exothermic—think of ice forming in your freezer instead. You put water into the freezer, which takes heat out of the water, to get it to freeze. Because heat is being pulled out of the water, it is exothermic. Heat is leaving.

Exercise 7.4.1.1

Label each of the following processes as endothermic or exothermic.

a. water vapor condensing
b. gold melting

Answer (a)

exothermic

Answer (b)

endothermic

Summary

Phase changes involve changes in energy. All chemical reactions involve changes in energy. This may be a change in heat, electricity, light, or other forms of energy. Reactions that absorb energy are endothermic. Reactions that release energy are exothermic.

7.4.3: Energy

Learning Objectives

- Define heat and work.
- Distinguish between kinetic energy and potential energy.
- State the law of conservation of matter and energy.

Just like matter, energy is a term that we are all familiar with and use on a daily basis. Before you go on a long hike, you eat an *energy* bar; every month, the *energy* bill is paid; on TV, politicians argue about the *energy* crisis. But what is energy? If you stop to think about it, energy is very complicated. When you plug a lamp into an electric socket, you see energy in the form of light, but when you plug a heating pad into that same socket, you only feel warmth. Without energy, we couldn't turn on lights, we couldn't brush our teeth, we couldn't make our lunch, and we couldn't travel to school. In fact, without energy, we couldn't even wake up because our bodies require energy to function. We use energy for every single thing that we do, whether we are awake or asleep.

Ability to Do Work or Produce Heat

When we speak of *using* energy, we are really referring to *transferring* energy from one place to another. When you use energy to throw a ball, you transfer energy from your body to the ball, and this causes the ball to fly through the air. When you use energy to warm your house, you transfer energy from the furnace to the air in your home, and this causes the temperature in your house to rise. Although energy is used in many kinds of different situations, all of these uses rely on energy being transferred in one of two ways. Energy can be transferred as *heat* or as *work*.

When scientists speak of ***heat***, they are referring to energy that is transferred from an object with a higher temperature to an object with a lower temperature, as a result of the temperature difference. Heat will "flow" from the hot object to the cold object until both end up at the same temperature. When you cook with a metal pot, you witness energy being transferred in the form of heat. Initially, only the stove element is hot—the pot and the food inside the pot are cold. As a result, heat moves from the hot stove element to the cold pot. After a while, enough heat is transferred from the stove to the pot, raising the temperature of the pot and all of its contents (Figure $7.4.3.1$).

Figure $7.4.3.1$: Energy is transferred as heat from the hot stove element to the cooler pot until the pot and its contents become just as hot as the element. The energy that is transferred into the pot as heat is then used to cook the food.

Heat is only one way in which energy can be transferred. Energy can also be transferred as **work**. The scientific definition of work is *force (any push or pull) applied over a distance*. When you push an object and cause it to move, you do work, and you transfer some of *your* energy to the object. At this point, it's important to warn you of a common misconception. Sometimes we think that the amount of work done can be measured by the amount of effort put in. This may be true in everyday life, but it is not true in science. By definition, scientific work requires that force be applied *over a distance*. It does not matter how hard you push or how hard you pull. If you have not moved the object, you haven't done any work.

So far, we've talked about the two ways in which energy can be transferred from one place, or object, to another. Energy can be transferred as heat, and energy can be transferred as work. But the question still remains—*what IS energy*?

Kinetic Energy

Machines use energy, our bodies use energy, energy comes from the sun, energy comes from volcanoes, energy causes forest fires, and energy helps us to grow food. With all of these seemingly different types of energy, it's hard to believe that there are really only two different *forms* of energy: kinetic energy and potential energy. **Kinetic energy** is energy associated with motion. When an object is moving, it has kinetic energy. When the object stops moving, it has no kinetic energy. While all moving objects have kinetic energy, not all moving objects have the same amount of kinetic energy. The amount of kinetic energy possessed by an object is determined by its mass and its speed. The heavier an object is and the faster it is moving, the more kinetic energy it has.

Kinetic energy is very common, and it's easy to spot examples of it in the world around you. Sometimes we even try to capture kinetic energy and use it to power things like our home appliances. If you are from California, you might have driven through the Tehachapi Pass near Mojave or the Montezuma Hills in Solano County and seen the windmills lining the slopes of the mountains (Figure $7.4.3.2$). These are two of the larger wind farms in North America. As wind rushes along the hills, the kinetic energy of the moving air particles turns the windmills, trapping the wind's kinetic energy so that people can use it in their houses and offices.

Figure $7.4.3.2$: A wind farm in Solano County harnesses the kinetic energy of the wind. (CC BY-SA 3.0 Unported; BDS2006 at Wikipedia)

Potential Energy

Potential energy is *stored* energy. It is energy that remains available until we choose to use it. Think of a battery in a flashlight. If left on, the flashlight battery will run out of energy within a couple of hours, and the flashlight will die. If, however, you only use the flashlight when you need it, and turn it off when you don't, the battery will last for days or even months. The battery contains a certain amount of energy, and it will power the flashlight for a certain amount of time, but because the battery stores *potential* energy, you can choose to use the energy all at once, or you can save it and only use a small amount at a time.

Any stored energy is potential energy. There are a lot of different ways in which energy can be stored, and this can make potential energy very difficult to recognize. In general, an object has potential energy because of its *position relative to another object*. For example, when a rock is held above the earth, it has potential energy because of its position relative to the ground. This is *potential energy* because the energy is *stored* for as long as the rock is held in the air. Once the rock is dropped, though, the stored energy is released as kinetic energy as the rock falls.

Chemical Energy

There are other common examples of potential energy. A ball at the top of a hill stores potential energy until it is allowed to roll to the bottom. When two magnets are held next to one another, they store potential energy too. For some examples of potential energy, though, it's harder to see how "position" is involved. In chemistry, we are often interested in what is called **chemical potential energy**. Chemical potential energy is energy stored in the atoms, molecules, and chemical bonds that make up matter. How does this depend on position?

As you learned earlier, the world, and all of the chemicals in it are made up of atoms and molecules. These store potential energy that is dependent on their positions relative to one another. Of course, you can't see atoms and molecules. Nevertheless, scientists do know a lot about the ways in which atoms and molecules interact, and this allows them to figure out how much potential energy is stored in a specific quantity (like a cup or a gallon) of a particular chemical. *Different chemicals have different amounts of potential energy* because they are made up of different atoms, and those atoms have different positions relative to one another.

> Since different chemicals have different amounts of potential energy, scientists will sometimes say that potential energy depends not only on ***position***, but also on ***composition***. Composition affects potential energy because it determines which

> molecules and atoms end up next to one another. For example, the total potential energy in a cup of pure water is different than the total potential energy in a cup of apple juice, because the cup of water and the cup of apple juice are *composed* of different amounts of different chemicals.

At this point, you may wonder just how useful chemical potential energy is. If you want to release the potential energy stored in an object held above the ground, you just drop it. But how do you get potential energy out of chemicals? It's actually not difficult. Use the fact that different chemicals have *different amounts of potential energy*. If you start with chemicals that have a lot of potential energy and allow them to react and form chemicals with less potential energy, all the extra energy that was in the chemicals at the beginning, but not at the end, is released.

Units of Energy

Energy is measured in one of two common units: the calorie and the joule. The joule (J) is the SI unit of energy. The calorie is familiar because it is commonly used when referring to the amount of energy contained within food. A **calorie** (cal) is the quantity of heat required to raise the temperature of 1 gram of water by 1^oC. For example, raising the temperature of 100 g of water from 20^oC to 22^oC would require $100 \times 2 = 200 \text{ cal}$.

Calories contained within food are actually kilocalories (kcal). In other words, if a certain snack contains 85 food calories, it actually contains 85 kcal or $85,000 \text{ cal}$ In order to make the distinction, the dietary calorie is written with a capital C.

$$1 \text{ kilocalorie} = 1 \text{ Calorie} = 1000 \text{ calories}$$

To say that the snack "contains" 85 Calories means that 85 kcal of energy are released when that snack is processed by your body.

Heat changes in chemical reactions are typically measured in joules rather than calories. The conversion between a joule and a calorie is shown below.

$$1 \text{ J} = 0.2390 \text{ cal or } 1 \text{ cal} = 4.184 \text{ J}$$

We can calculate the amount of heat released in kilojoules when a 400 Calorie hamburger is digested.

$$400 \text{ Cal} = 400 \text{ kcal} \times \frac{4.184 \text{ kJ}}{1 \text{ kcal}} = 1.67 \times 10^3 \text{ kJ}$$

Summary

- Any time we use energy, we transfer energy from one object to another.
- Energy can be transferred in one of two ways: as heat, or as work.
- Heat is the term given to energy that is transferred from a hot object to a cooler object due to the difference in their temperatures.
- Work is the term given to energy that is transferred as a result of a force applied over a distance.
- Energy comes in two fundamentally different forms: kinetic energy and potential energy.
- Kinetic energy is the energy of motion.
- Potential energy is stored energy that depends on the position of an object relative to another object.
- Chemical potential energy is a special type of potential energy that depends on the positions of different atoms and molecules relative to one another.
- Chemical potential energy can also be thought of according to its dependence on chemical composition.
- Energy can be converted from one form to another. The total amount of mass and energy in the universe is conserved.

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7.5: Heat Capacity

In the previous section, we introduced the ideas of temperature, heat, and energy. We will build on those ideas in this section by looking at how we can measure properties of a substance to determine how much heat is gained or lost from that substance when the temperature changes.

7.5.1: Energy and Heat Capacity Calculations

Learning Objectives

- To relate heat transfer to temperature change.

Heat is a familiar manifestation of transferring energy. When we touch a hot object, energy flows from the hot object into our fingers, and we perceive that incoming energy as the object being “hot.” Conversely, when we hold an ice cube in our palms, energy flows from our hand into the ice cube, and we perceive that loss of energy as “cold.” In both cases, the temperature of the object is different from the temperature of our hand, so we can conclude that differences in temperatures are the ultimate cause of heat transfer.

The specific heat of a substance can be used to calculate the temperature change that a given substance will undergo when it is either heated or cooled. The equation that relates heat (q) to specific heat (c_p), mass (m), and temperature change (ΔT) is shown below.

$$q = c_p \times m \times \Delta T$$

The heat that is either absorbed or released is measured in joules. The mass is measured in grams. The change in temperature is given by $\Delta T = T_f - T_i$, where T_f is the final temperature and T_i is the initial temperature.

Every substance has a characteristic specific heat, which is reported in units of cal/g•°C or cal/g•K, depending on the units used to express Δ*T*. The specific heat of a substance is the amount of energy that must be transferred to or from 1 g of that substance to change its temperature by 1°. Table $7.5.1.1$lists the specific heats for various materials.

Table $7.5.1.1$: *Specific Heats of Some Common Substances*

Substance	**Specific Heat** $(\mathrm{J/g^oC})$
Water (l)	4.18
Water (s)	2.06
Water (g)	1.87
Ammonia (g)	2.09
Ethanol (l)	2.44
Aluminum (s)	0.897
Carbon, graphite (s)	0.709
Copper (s)	0.385
Gold (s)	0.129
Iron (s)	0.449
Lead (s)	0.129
Mercury (l)	0.140
Silver (s)	0.233

The *direction* of heat flow is not shown in heat = *mc*Δ*T*. If energy goes into an object, the total energy of the object increases, and the values of heat Δ*T* are positive. If energy is coming out of an object, the total energy of the object decreases, and the values of heat and Δ*T* are negative.

Example 7.5.1.1

A 15.0 g piece of cadmium metal absorbs 134 J of heat while rising from 24.0^oC to 62.7^oC. Calculate the specific heat of cadmium.

Solution

Step 1: List the known quantities and plan the problem.

Known

- $\text{Heat} = q = 134 \text{ J}$
- $\text{Mass} = m = 15.0 \text{ g}$
- $\Delta T = 62.7^\circ\text{C} - 24.0^\circ\text{C} = 38.7^\circ\text{C}$

Unknown

- c_p of cadmium $= ? \text{ J/g}^\text{o}\text{C}$

The specific heat equation can be rearranged to solve for the specific heat.

Step 2: Solve.

$$c_p = \frac{q}{m \times \Delta T} = \frac{134 \text{ J}}{15.0 \text{ g} \times 38.7^\circ\text{C}} = 0.231 \text{ J/g}^\text{o}\text{C}$$

Step 3: Think about your result.

The specific heat of cadmium, a metal, is fairly close to the specific heats of other metals. The result has three significant figures.

Since most specific heats are known (Table $7.5.1.1$), they can be used to determine the final temperature attained by a substance when it is either heated or cooled. Suppose that a 60.0 g of water at 23.52°C was cooled by the removal of 813 J of heat. The change in temperature can be calculated using the specific heat equation:

$$\Delta T = \frac{q}{c_p \times m} = \frac{813 \text{ J}}{4.18 \text{ J/g}^\text{o}\text{C} \times 60.0 \text{ g}} = 3.24^\text{o}\text{C}$$

Since the water was being cooled, the temperature decreases. The final temperature is:

$$T_f = 23.52^\circ\text{C} - 3.24^\circ\text{C} = 20.28^\circ\text{C}$$

✓ Example 7.5.1.2

What quantity of heat is transferred when a 150.0 g block of iron metal is heated from 25.0°C to 73.3°C? What is the direction of heat flow?

Solution

We can use heat = $mc\Delta T$ to determine the amount of heat, but first we need to determine ΔT. Because the final temperature of the iron is 73.3°C and the initial temperature is 25.0°C, ΔT is as follows:

$$\Delta T = T_\text{final} - T_\text{initial} = 73.3°\text{C} - 25.0°\text{C} = 48.3°\text{C}$$

The mass is given as 150.0 g, and Table 7.3 gives the specific heat of iron as 0.108 cal/g•°C. Substitute the known values into heat = $mc\Delta T$ and solve for amount of heat:

$$\text{heat} = (150.0 \text{ g})\left(0.108 \frac{\text{cal}}{\text{g} \cdot {}^\circ\text{C}}\right)(48.3^\circ\text{C}) = 782 \text{ cal}$$

Note how the gram and °C units cancel algebraically, leaving only the calorie unit, which is a unit of heat. Because the temperature of the iron increases, energy (as heat) must be flowing *into* the metal.

? Exercise 7.5.1.1

What quantity of heat is transferred when a 295.5 g block of aluminum metal is cooled from 128.0°C to 22.5°C? What is the direction of heat flow?

Answer

Heat leaves the aluminum block.

✓ Example 7.5.1.2

A 10.3 g sample of a reddish-brown metal gave off 71.7 cal of heat as its temperature decreased from 97.5°C to 22.0°C. What is the specific heat of the metal? Can you identify the metal from the data in Table 7.5.1.1?

Solution

The question gives us the heat, the final and initial temperatures, and the mass of the sample. The value of ΔT is as follows:

$$\Delta T = T_{\text{final}} - T_{\text{initial}} = 22.0°\text{C} - 97.5°\text{C} = -75.5°\text{C}$$

If the sample gives off 71.7 cal, it loses energy (as heat), so the value of heat is written as a negative number, −71.7 cal. Substitute the known values into heat = $mc\Delta T$ and solve for c:

$$-71.7\text{ cal} = (10.3\text{ g})(c)(-75.5°\text{C})$$

$$c = \frac{-71.7\text{ cal}}{(10.3\text{ g})(-75.5°\text{C})}$$

$$c = 0.0923\text{ cal/g}\bullet°\text{C}$$

This value for specific heat is very close to that given for copper in Table 7.3.

? Exercise 7.5.1.2

A 10.7 g crystal of sodium chloride (NaCl) has an initial temperature of 37.0°C. What is the final temperature of the crystal if 147 cal of heat were supplied to it?

Answer

Summary

Specific heat calculations are illustrated.

7.5.2: Temperature Changes - Heat Capacity

If a swimming pool and wading pool, both full of water at the same temperature, were subjected to the same input of heat energy, the wading pool would certainly rise in temperature more quickly than the swimming pool. The heat capacity of an object depends on both its mass and its chemical composition. Because of its much larger mass, the swimming pool of water has a larger heat capacity than the wading pool.

Heat Capacity and Specific Heat

Different substances respond to heat in different ways. If a metal chair sits in the bright sun on a hot day, it may become quite hot to the touch. An equal mass of water in the same sun will not become nearly as hot. We would say that water has a high **heat capacity** (the amount of heat required to raise the temperature of an object by 1^oC). Water is very resistant to changes in temperature, while metals in general are not. The **specific heat** of a substance is the amount of energy required to raise the temperature of 1 gram of the substance by 1^oC. The symbol for specific heat is c_p, with the p subscript referring to the fact that specific heats are measured at constant pressure. The units for specific heat can either be joules per gram per degree $\left(\text{J/g}^\text{o} \text{C} \right)$ or calories per gram per degree $\left(\text{cal/g}^\text{o} \text{C} \right)$ (Table $7.5.2.1$). This text will use $\text{J/g}^\text{o} \text{C}$ for specific heat.

$$\text{specific heat} = \frac{\text{heat}}{\text{mass} \times \text{cal/g}^\text{o} \text{C}}$$

Notice that water has a very high specific heat compared to most other substances.

Table $7.5.2.1$: Specific Heat Capacities

Substance	Specific Heat Capacity at 25°C in J/g °C	Substance	Specific Heat Capacity at 25°C in J/g °C
H_2 gas	14.267	steam @ 100°C	2.010
He gas	5.300	vegetable oil	2.000
$H_2O(l)$	4.184	sodium	1.23
lithium	3.56	air	1.020
ethyl alcohol	2.460	magnesium	1.020
ethylene glycol	2.200	aluminum	0.900
ice @ 0°C	2.010	concrete	0.880
steam @ 100°C	2.010	glass	0.840

Water is commonly used as a coolant for machinery because it is able to absorb large quantities of heat (see table above). Coastal climates are much more moderate than inland climates because of the presence of the ocean. Water in lakes or oceans absorbs heat from the air on hot days and releases it back into the air on cool days.

Figure $7.5.2.1$: This power plant in West Virginia, like many others, is located next to a large lake so that the water from the lake can be used as a coolant. Cool water from the lake is pumped into the plant, while warmer water is pumped out of the plant and back into the lake.

Summary

- Heat capacity is the amount of heat required to raise the temperature of an object by 1^oC).
- The specific heat of a substance is the amount of energy required to raise the temperature of 1 gram of the substance by 1^oC.

7.6: Phase Transitions

Learning Objective

- Describe what happens during a phase change.

Substances can change phase—often because of a temperature change. At low temperatures, most substances are solid; as the temperature increases, they become liquid; at higher temperatures still, they become gaseous.

The process of a solid becoming a liquid is called **melting**. The opposite process, a liquid becoming a solid, is called **freezing**. For any pure substance, the temperature at which melting occurs—known as the **melting point**—is a characteristic of that substance. It requires energy for a solid to melt into a liquid. Generally, the temperature at which something freezes is the same as its melting point. But melting point is how it is generally tabulated. During melting, energy goes exclusively to changing the phase of a substance; it does not go into changing the temperature of a substance. Hence melting is an **isothermal** process because a substance stays at the same temperature. Only when all of a substance is melted does additional energy go to changing its temperature.

What happens when a solid becomes a liquid? In a solid, individual particles are stuck in place because the intermolecular forces cannot be overcome by the energy of the particles. When more energy is supplied (e.g., by raising the temperature), there comes a point at which the particles have enough energy to move around, but not enough energy to separate. This is the liquid phase: particles are still in contact, but are able to move around each other. This explains why liquids can assume the shape of their containers: the particles move around and, under the influence of gravity, fill the lowest volume possible (unless the liquid is in a zero-gravity environment—see Figure 7.6.1.

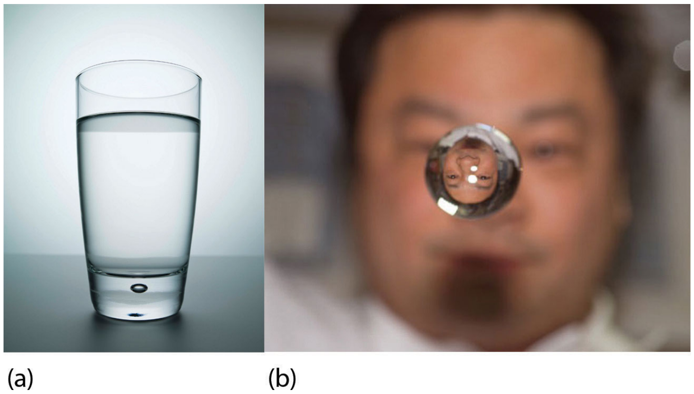

Figure 7.6.1: Liquids and Gravity. (a) A liquid fills the bottom of its container as it is drawn downward by gravity and the particles slide over each other. (b) A liquid floats in a zero-gravity environment. The particles still slide over each other because they are in the liquid phase, but now there is no gravity to pull them down. Source: Photo on the left © Thinkstock. Photo on the right courtesy of NASA, http://www.nasa.gov/mission_pages/st...image_009.html.

The phase change between a liquid and a gas has some similarities to the phase change between a solid and a liquid. At a certain temperature, the particles in a liquid have enough energy to become a gas. The process of a liquid becoming a gas is called **boiling (or vaporization)**, while the process of a gas becoming a liquid is called **condensation**. However, unlike the solid/liquid conversion process, the liquid/gas conversion process is noticeably affected by the surrounding pressure on the liquid because gases are strongly affected by pressure. This means that the temperature at which a liquid becomes a gas, the **boiling point**, can change with surrounding pressure. In fact, it is possible for this phase change to occur at temperatures below the boiling point through a process called **evaporation**.

What happens when a liquid becomes a gas? We have already established that a liquid is composed of particles in contact with each other. When a liquid becomes a gas, the particles separate from each other, with each particle going its own way in space. This is how gases tend to fill their containers. Indeed, in the gas phase most of the volume is empty space; only about 1/1,000th of the volume is actually taken up by matter (Figure 7.6.1). It is this property of gases that explains why they can be compressed, a fact that is considered in a previous chapter.

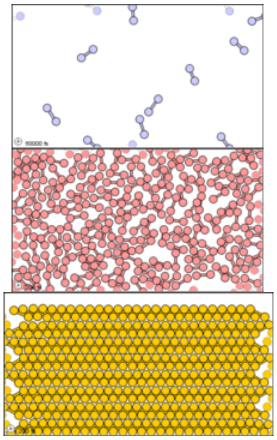

Figure 7.6.2: Sub-microscopic view of the diatomic molecules of the element bromine (a) in the gaseous state (above 58°C); (b) in liquid form (between -7.2 and 58.8°C); and (c) in solid form (below -7.2°C). As a solid, the molecules are fixed, but fluctuate. As a liquid, the molecules are in contact but are also able to move around each other. As a gas, most of the volume is actually empty space. The particles are not to scale; in reality, the dots representing the particles would be about 1/100th of the size depicted.

There is also a phase change where a solid goes directly to a gas:

$$\text{solid} \rightarrow \text{gas} \tag{7.6.1}$$

This phase change is called **sublimation.** Each substance has a characteristic heat of sublimation associated with this process. For example, the heat of sublimation (ΔH_{sub}) of H_2O is 620 cal/g.

Chemical equations can be used to represent a phase change. In such cases, it is crucial to use phase labels on the substances. For example, the chemical equation for the melting of ice to make liquid water is as follows:

$$H_2O(s) \rightarrow H_2O(\ell)$$

No chemical change is taking place; however, a physical change is taking place.

The details of these phase changes are outlined within the subsections of this section. Phase changes between solids and other physical states are discussed in 9.3.1. Phase changes between liquids and gases are discussed in 9.3.2. Calculations for any of these phase changes are discussed in 9.3.3. And finally, we will look at how to graphically show the relationship between energy transfer and changes in physical state and temperature in 9.3.4.

Summary

- Phase changes can occur between any two phases of matter.
- All phase changes occur with a simultaneous change in energy.
- All phase changes are isothermal.

7.6.1: Melting, Freezing, and Sublimation

Learning Objectives

- Define melting, freezing, and sublimation.

A phase change is a physical process in which a substance goes from one phase to another. In this subsection, we will be focusing on the transitions between liquids and solids, as well as between solids and gases. The process of a solid becoming a liquid is called **melting** (an older term that you may see sometimes is *fusion*). The opposite process, a liquid becoming a solid, is called **freezing** (some textbooks also use the word *solidification* for this process). Although we associate the term freezing with low temperatures and melting with high temperatures, the temperature at which these changes occur depends upon the substance. For example, bacon grease becomes solid at room temperature; we could say that it freezes even though we do not experience that temperature as being "cold." Even more extreme, many metals freeze at temperatures greater than 1000°C! (And based on what we have already covered related to crystalline solids, hopefully you can predict that metals will freeze at much higher temperatures than water.)

Usually the phase change occurs when adding or removing heat at a particular temperature, known as the melting point or the boiling point of the substance. The melting point is the temperature at which the substance goes from a solid to a liquid (or from a liquid to a solid). The boiling point is the temperature at which a substance goes from a liquid to a gas (or from a gas to a liquid). The nature of the phase change depends on the direction of the heat transfer. Heat going *into* a substance changes it from a solid to a liquid, or a liquid to a gas. Removing heat *from* a substance changes a gas to a liquid, or a liquid to a solid.

Two key points are worth emphasizing. First, at a substance's melting point or boiling point, two phases can exist simultaneously. Take water (H_2O) as an example. On the Celsius scale, H_2O has a melting point of 0°C and a boiling point of 100°C. At 0°C, both the solid and liquid phases of H_2O can coexist. However, if heat is added, some of the solid H_2O will melt and turn into liquid H_2O. If heat is removed, the opposite happens: some of the liquid H_2O turns into solid H_2O. A similar process can occur at 100°C: adding heat increases the amount of gaseous H_2O, while removing heat increases the amount of liquid H_2O (Figure $7.6.1.1$).

Figure $7.6.1.1$: The Boiling Point of Water. Nucleate boiling of water over a kitchen stove burner. (Source: Wikipedia). *Water is a good substance to use as an example because many people are already familiar with it. Other substances have melting points and boiling points as well.*

Second, the temperature of a substance does not change as the substance goes from one phase to another. In other words, phase changes are isothermal (isothermal means "constant temperature"). Again, consider H_2O as an example. Solid water (ice) can exist at 0°C. If heat is added to ice at 0°C, some of the solid changes phase to make liquid, which is also at 0°C. Remember, the solid and liquid phases of H_2O can coexist at 0°C. Only after all of the solid has melted into liquid does the addition of heat change the temperature of the substance.

For each phase change of a substance, there is a characteristic quantity of heat needed to perform the phase change per gram (or per mole) of material. The heat of fusion (ΔH_{fus}) is the amount of heat per gram (or per mole) required for a phase change that occurs at the melting point. Calculations related to the heat of fusion will be covered in a later subsection.

Melting Point

Solids are similar to liquids in that both are condensed states, with particles that are far closer together than those of a gas. However, while liquids are fluid, solids are not. The particles of most solids are packed tightly together in an orderly arrangement. The motion of individual atoms, ions, or molecules in a solid is restricted to **vibrational motion** about a fixed point. Solids are almost completely **incompressible** and are the most dense of the three states of matter.

As a solid is heated, its particles vibrate more rapidly as the solid absorbs kinetic energy. Eventually, the organization of the particles within the solid structure begins to break down and the solid starts to melt. The **melting point** is the temperature at which a solid changes into a liquid. At its melting point, the disruptive vibrations of the particles of the solid overcome the attractive forces operating within the solid. As with boiling points, the melting point of a solid is dependent on the strength of those attractive forces. Sodium chloride (NaCl) is an ionic compound that consists of a multitude of strong ionic bonds. Sodium chloride melts at $801^{\mathrm{o}}\mathrm{C}$. Ice (solid $\mathrm{H_2O}$) is a molecular compound composed of molecules that are held together by hydrogen bonds. Though hydrogen bonds are the strongest of the intermolecular forces, the strength of hydrogen bonds is much less than that of ionic bonds. The melting point of ice is $0^{\mathrm{o}}\mathrm{C}$.

The melting point of a solid is the same as the freezing point of the liquid. At that temperature, the solid and liquid states of the substance are in equilibrium. For water, this equilibrium occurs at $0^{\mathrm{o}}\mathrm{C}$.

$$\mathrm{H_2O}\,(s) \rightleftharpoons \mathrm{H_2O}\,(l) \tag{7.6.1.1}$$

We tend to think of solids as those materials that are solid at room temperature. However, all materials have melting points of some sort. Gases become solids at extremely low temperatures, and liquids will also become solid if the temperature is low enough. The table below gives the melting points of some common materials.

Table 7.6.1.2: Melting Points of Common Materials

Materials	Melting Point (°C)
Hydrogen	-259
Oxygen	-219
Diethyl ether	-116
Ethanol	-114
Water	0
Pure silver	961
Pure gold	1063
Iron	1538

? Exercise 7.6.1.2

a. Explain what happens when heat flows into or out of a substance at its melting point or boiling point.
b. How does the amount of heat required for a phase change relate to the mass of the substance?

Answer a

The energy goes into changing the phase, not the temperature.

Answer b

The amount of heat is a constant per gram of substance.

Sublimation

Under some circumstances, the solid phase can transition directly to the gas phase without going through a liquid phase, and a gas can directly become a solid. The solid-to-gas change is called **sublimation**, while the reverse process is called **deposition.** Sublimation is isothermal, like the other phase changes. There is a measurable energy change during sublimation—this energy change is called the **enthalpy of sublimation**, represented as ΔH_{sub}. The relationship between the ΔH_{sub} and the other enthalpy changes is as follows:

$$\Delta H_{sub} = \Delta H_{fus} + \Delta H_{vap}$$

As such, ΔH_{sub} is not always tabulated because it can be simply calculated from ΔH_{fus} and ΔH_{vap}.

There are several common examples of sublimation. A well-known product, dry ice, is actually solid CO_2. Dry ice is dry because it sublimes, with the solid bypassing the liquid phase and going straight to the gas phase. The sublimation occurs at temperature of $-77°C$, so it must be handled with caution. If you have ever noticed that ice cubes in a freezer tend to get smaller over time, it is because the solid water is very slowly subliming. "Freezer burn" isn't actually a burn; it occurs when certain foods, such as meats, slowly lose solid water content because of sublimation. The food is still good, but looks unappetizing. Reducing the temperature of a freezer will slow the sublimation of solid water.

Figure 7.6.1.3: Freezer burn on a piece of beef. (Public Domain; RolloM.)

Summary

- There is an energy change associated with any phase change.
- Sublimation is the change of state from a solid to a gas, without passing through the liquid state.
- Deposition is the change of state from a gas to a solid.
- Carbon dioxide is an example of a material that easily undergoes sublimation.
- The melting point is the temperature at which a solid changes into a liquid.
- Intermolecular forces have a strong influence on melting point.

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7.6.2: Boiling, Evaporation and Condensation

Learning Objectives

- Explain how intermolecular forces affect rates of vaporization, evaporation, and condensation.

On the roof of the house in the picture below is a device known as a "swamp cooler". This piece of equipment traces its origin back to the ancient Egyptians who hung wet blankets across the doors of their homes. As the warm air passed through the blankets, water would evaporate and cool the air. The royalty went one step further and had servants fan wet cloths over jugs of water to get more evaporation and cooling.

Figure $7.6.2.1$: A home with a swamp cooler attached to the roof.

The origin of the term "swamp cooler" is not known - they certainly don't work in a swamp. Best conditions for cooling include a high temperature (over $80^{\circ}F$) and a low humidity (preferably less than 30%). These coolers work well in desert areas, but don't provide any cooling in the humid areas of the country.

Evaporation

A puddle of water left undisturbed eventually disappears. The liquid molecules escape into the gas phase, becoming water vapor. **Vaporization** is the process in which a liquid is converted to a gas. **Evaporation** is the conversion of a liquid to its vapor below the boiling temperature of the liquid. If the water is instead kept in a closed container, the water vapor molecules do not have a chance to escape into the surroundings and so the water level does not change. As some water molecules become vapor, an equal number of water vapor molecules condense back into the liquid state. **Condensation** is the change of state from a gas to a liquid.

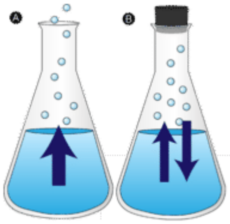

Figure $7.6.2.2$: Evaporation (A) and condensation (B).

In order for a liquid molecule to escape into the gas state, the molecule must have enough kinetic energy to overcome the intermolecular attractive forces in the liquid. Recall that a given liquid sample will have molecules with a wide range of kinetic energies. Liquid molecules that have this certain threshold kinetic energy escape the surface and become vapor. As a result, the liquid molecules that remain now have lower kinetic energy. As evaporation occurs, the temperature of the remaining liquid decreases. You have observed the effects of evaporative cooling. On a hot day, the water molecules in your perspiration absorb body heat and evaporate from the surface of your skin. The evaporating process leaves the remaining perspiration cooler, which in turn absorbs more heat from your body.

A given liquid will evaporate more quickly when it is heated. This is because the heating process results in a greater fraction of the liquid's molecules having the necessary kinetic energy to escape the surface of the liquid. The figure below shows the kinetic energy distribution of liquid molecules at two temperatures. The numbers of molecules that have the required kinetic energy to evaporate are shown in the shaded area under the curve at the right. The higher temperature liquid (T_2) has more molecules that are capable of escaping into the vapor phase than the lower temperature liquid (T_1).

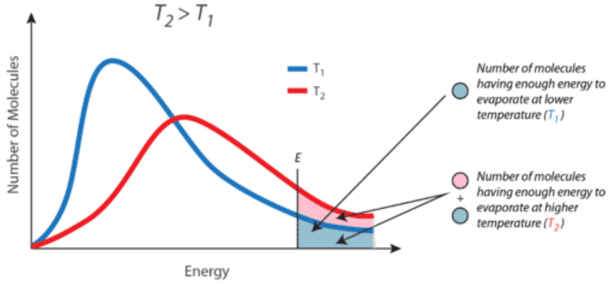

Figure 7.6.2.3: Kinetic energy distribution curves for a liquid at two temperatures T_1 and T_2. The shaded area represents the molecules with enough kinetic energy to escape the liquid and become vapor.

At 29,029 feet (8848 m), Mount Everest in the Himalayan range on the border between China and Nepal is the highest point on the earth. Its altitude presents many practical problems to climbers. The oxygen content of the air is much lower than at sea level, making it necessary to bring oxygen tanks along (although a few climbers have reached the peak without oxygen). One other problem is that of boiling water for cooking food. Although water boils at 100^oC at sea level, the boiling point on top of Mount Everest is only about 70^oC. This difference makes it very difficult to get a decent cup of tea (which definitely frustrated some of the British climbers).

Boiling

As a liquid is heated, the average kinetic energy of its particles increases. The rate of evaporation increases as more and more molecules are able to escape the liquid's surface into the vapor phase. Eventually a point is reached when the molecules all throughout the liquid have enough kinetic energy to **vaporize**. At this point the liquid begins to boil. The **boiling point** is the temperature at which the vapor pressure of a liquid is equal to the external pressure. The figure below illustrates the boiling of liquid.

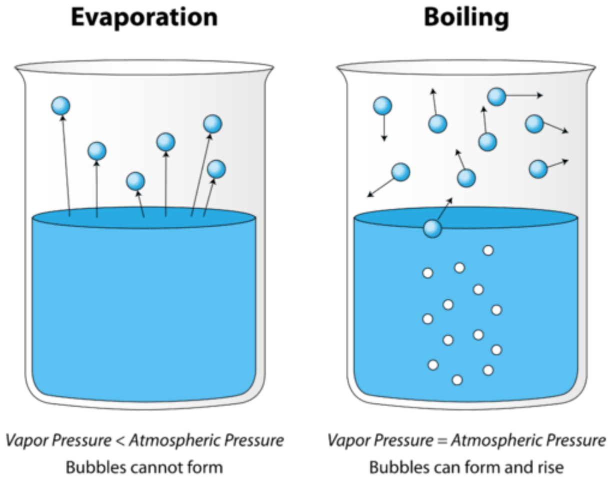

Figure 7.6.2.4: Comparison between evaporation and boiling.

In the picture on the left, the liquid is below its boiling point, yet some of the liquid evaporates. On the right, the temperature has been increased until bubbles begin to form in the body of the liquid. When the vapor pressure inside the bubble is equal to the external atmospheric pressure, the bubbles rise to the surface of the liquid and burst. The temperature at which this process occurs is the boiling point of the liquid.

The normal boiling point is the temperature at which the vapor pressure of the liquid is equal to standard pressure. Because atmospheric pressure can change based on location, the boiling point of a liquid changes with the external pressure. The normal boiling point is a constant because it is defined relative to the standard atmospheric pressure of 760 mm Hg (or 1 atm or 101.3 kPa).

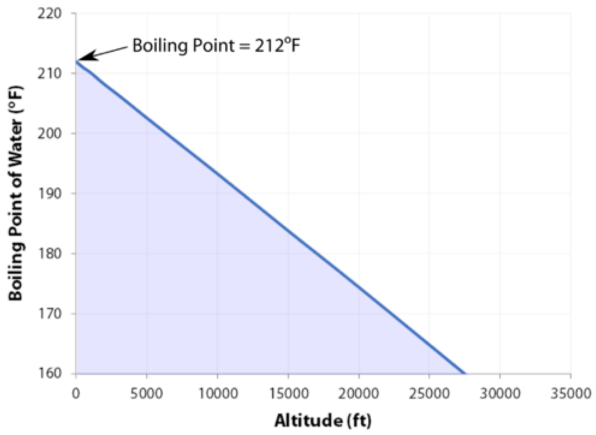

Figure 7.6.2.5: Influence of altitude on the boiling point of water.

Summary

- The boiling point is the temperature at which the vapor pressure of a liquid is equal to the external pressure.
- As the altitude increases, the boiling point decreases.
- Evaporation is the conversion of a liquid to its vapor below the boiling temperature of the liquid.
- Condensation is the change of state from a gas to a liquid.
- As the temperature increases, the rate of evaporation increases.

7.6.3: Calculations for Phase Changes

Learning Objectives

- Calculate the energy change needed for a phase change.

For each phase change of a substance, there is a characteristic quantity of heat needed to perform the phase change per gram (or per mole) of material. The heat of fusion (ΔH_{fus}) is the amount of heat per gram (or per mole) required for a phase change that occurs at the melting point. The heat of vaporization (ΔH_{vap}) is the amount of heat per gram (or per mole) required for a phase change that occurs at the boiling point. If you know the total number of grams or moles of material, you can use the ΔH_{fus} or the ΔH_{vap} to determine the total heat being transferred for melting or solidification using these expressions:

$$\text{heat} = n \times \Delta H_{fus} \tag{7.6.3.1}$$

where n is the number of moles and ΔH_{fus} is expressed in energy/mole or

For the boiling or condensation, use these expressions:

$$\text{heat} = n \times \Delta H_{vap} \tag{7.6.3.2}$$

where n is the number of moles) and ΔH_{vap} is expressed in energy/mole or

Remember that a phase change depends on the direction of the heat transfer. If heat transfers in, solids become liquids, and liquids become solids at the melting and boiling points, respectively. If heat transfers out, liquids solidify, and gases condense into liquids.

Some ΔH_{fus} values are listed in Table 7.6.3.1; it is assumed that these values are for the melting point of the substance. Note that the unit of ΔH_{fus} is kilojoules per mole, so we need to know the quantity of material to know how much energy is involved. The ΔH_{fus} is always tabulated as a positive number. However, it can be used for both the melting and the freezing processes, minding that melting is always endothermic (so ΔH will be positive), while freezing is always exothermic (so ΔH will be negative).

Table 7.6.3.1: Enthalpies of Fusion for Various Substances

Substance (Melting Point)	ΔH_{fus} (kJ/mol)
Water (0°C)	6.01
Aluminum (660°C)	10.7
Benzene (5.5°C)	9.95
Ethanol (−114.3°C)	5.02
Mercury (−38.8°C)	2.29

Example 7.6.3.1

What is the energy change when 45.7 g of H_2O melt at 0°C?

Solution

The ΔH_{fus} of H_2O is 6.01 kJ/mol. However, our quantity is given in units of grams, not moles, so the first step is to convert grams to moles using the molar mass of H_2O, which is 18.0 g/mol. Then we can use ΔH_{fus} as a conversion factor. Because the substance is melting, the process is endothermic, so the energy change will have a positive sign.

$$45.7\ g\ \cancel{H_2O} \times \frac{1\ mol\ \cancel{H_2O}}{18.0\ \cancel{g}} \times \frac{6.01 kJ}{\cancel{mol}} = 15.3\ kJ$$

Without a sign, the number is assumed to be positive.

Exercise 7.6.3.1

What is the energy change when 108 g of C_6H_6 freeze at 5.5°C?

Answer

−13.8 kJ

Like the solid/liquid phase change, the liquid/gas phase change involves energy. The amount of energy required to convert a liquid to a gas is called the **enthalpy of vaporization** (or heat of vaporization), represented as ΔH_{vap}. Some ΔH_{vap} values are listed in Table $7.6.3.2$; it is assumed that these values are for the normal boiling point temperature of the substance, which is also given in the table. The unit for ΔH_{vap} is also kilojoules per mole, so we need to know the quantity of material to know how much energy is involved. The ΔH_{vap} is also always tabulated as a positive number. It can be used for both the boiling and the condensation processes as long as you keep in mind that boiling is always endothermic (so ΔH will be positive), while condensation is always exothermic (so ΔH will be negative).

Table $7.6.3.1$: Enthalpies of Vaporization for Various Substances

Substance (Normal Boiling Point)	ΔH_{vap} (kJ/mol)
Water (100°C)	40.68
Bromine (59.5°C)	15.4
Benzene (80.1°C)	30.8
Ethanol (78.3°C)	38.6
Mercury (357°C)	59.23

✓ Example 7.6.3.2

What is the energy change when 66.7 g of $Br_2(g)$ condense to a liquid at 59.5°C?

Solution

The ΔH_{vap} of Br_2 is 15.4 kJ/mol. Even though this is a condensation process, we can still use the numerical value of ΔH_{vap} as long as we realize that we must take energy out, so the ΔH value will be negative. To determine the magnitude of the energy change, we must first convert the amount of Br_2 to moles. Then we can use ΔH_{vap} as a conversion factor.

$$66.7\ g\ \cancel{Br_2} \times \frac{1\ mol\ \cancel{Br_2}}{159.8\ \cancel{g}} \times \frac{15.4 kJ}{\cancel{mol}} = 6.43\ kJ$$

Because the process is exothermic, the actual value will be negative: $\Delta H = -6.43$ kJ.

Exercise 7.6.3.2

What is the energy change when 822 g of $C_2H_5OH(\ell)$ boil at its normal boiling point of 78.3°C?

Answer

689 kJ

As with melting, the energy in boiling goes exclusively to changing the phase of a substance; it does not go into changing the temperature of a substance. So boiling is also an isothermal process. Only when all of a substance has boiled does any additional energy go to changing its temperature.

Summary

Contributions & Attributions

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7.6.4: Heating Curve for Water

Freezing, condensation, and deposition, which are the reverse of fusion, sublimation, and vaporization—are exothermic. Thus heat pumps that use refrigerants are essentially air-conditioners running in reverse. Heat from the environment is used to vaporize the refrigerant, which is then condensed to a liquid in coils within a house to provide heat. The energy changes that occur during phase changes can be quantified by using a heating or cooling curve.

Heating Curves

Figure $7.6.4.3$ shows a heating curve, a plot of temperature versus heating time, for a 75 g sample of water. The sample is initially ice at 1 atm and −23°C; as heat is added, the temperature of the ice increases linearly with time. The slope of the line depends on both the mass of the ice and the specific heat (C_s) of ice, which is the number of joules required to raise the temperature of 1 g of ice by 1°C. As the temperature of the ice increases, the water molecules in the ice crystal absorb more and more energy and vibrate more vigorously. At the melting point, they have enough kinetic energy to overcome attractive forces and move with respect to one another. As more heat is added, the temperature of the system does *not* increase further but remains constant at 0°C until all the ice has melted. Once all the ice has been converted to liquid water, the temperature of the water again begins to increase. Now, however, the temperature increases more slowly than before because the specific heat capacity of water is *greater* than that of ice. When the temperature of the water reaches 100°C, the water begins to boil. Here, too, the temperature remains constant at 100°C until all the water has been converted to steam. At this point, the temperature again begins to rise, but at a *faster* rate than seen in the other phases because the heat capacity of steam is *less* than that of ice or water.

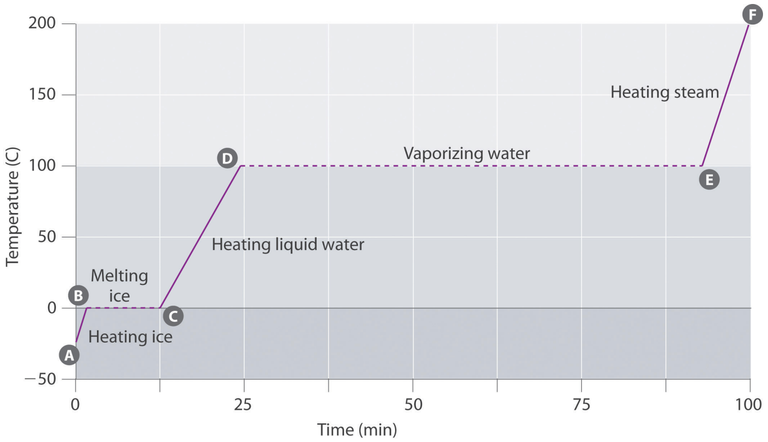

Figure $7.6.4.1$: A Heating Curve for Water. This plot of temperature shows what happens to a 75 g sample of ice initially at 1 atm and −23°C as heat is added at a constant rate: A–B: heating solid ice; B–C: melting ice; C–D: heating liquid water; D–E: vaporizing water; E–F: heating steam.

Thus *the temperature of a system does not change during a phase change*. In this example, as long as even a tiny amount of ice is present, the temperature of the system remains at 0°C during the melting process, and as long as even a small amount of liquid water is present, the temperature of the system remains at 100°C during the boiling process. The rate at which heat is added does *not* affect the temperature of the ice/water or water/steam mixture because the added heat is being used exclusively to overcome the attractive forces that hold the more condensed phase together. Many cooks think that food will cook faster if the heat is turned up higher so that the water boils more rapidly. Instead, the pot of water will boil to dryness sooner, but the temperature of the water does not depend on how vigorously it boils.

> *The temperature of a sample does not change during a phase change.*

If heat is added at a constant rate, as in Figure $7.6.4.3$, then the length of the horizontal lines, which represents the time during which the temperature does not change, is directly proportional to the magnitude of the enthalpies associated with the phase changes. In Figure $7.6.4.3$, the horizontal line at 100°C is much longer than the line at 0°C because the enthalpy of vaporization of water is several times greater than the enthalpy of fusion.

A superheated liquid is a sample of a liquid at the temperature and pressure at which it should be a gas. Superheated liquids are not stable; the liquid will eventually boil, sometimes violently. The phenomenon of superheating causes “bumping” when a liquid is heated in the laboratory. When a test tube containing water is heated over a Bunsen burner, for example, one portion of the liquid can easily become too hot. When the superheated liquid converts to a gas, it can push or “bump” the rest of the liquid out of the test tube. Placing a stirring rod or a small piece of ceramic (a “boiling chip”) in the test tube allows bubbles of vapor to form on the surface of the object so the liquid boils instead of becoming superheated. Superheating is the reason a liquid heated in a smooth cup in a microwave oven may not boil until the cup is moved, when the motion of the cup allows bubbles to form.

Cooling Curves

The cooling curve, a plot of temperature versus cooling time, in Figure 7.6.4.4 plots temperature versus time as a 75 g sample of steam, initially at 1 atm and 200°C, is cooled. Although we might expect the cooling curve to be the mirror image of the heating curve in Figure 7.6.4.3, the cooling curve is *not* an identical mirror image. As heat is removed from the steam, the temperature falls until it reaches 100°C. At this temperature, the steam begins to condense to liquid water. No further temperature change occurs until all the steam is converted to the liquid; then the temperature again decreases as the water is cooled. We might expect to reach another plateau at 0°C, where the water is converted to ice; in reality, however, this does not always occur. Instead, the temperature often drops below the freezing point for some time, as shown by the little dip in the cooling curve below 0°C. This region corresponds to an unstable form of the liquid, a supercooled liquid. If the liquid is allowed to stand, if cooling is continued, or if a small crystal of the solid phase is added (a seed crystal), the supercooled liquid will convert to a solid, sometimes quite suddenly. As the water freezes, the temperature increases slightly due to the heat evolved during the freezing process and then holds constant at the melting point as the rest of the water freezes. Subsequently, the temperature of the ice decreases again as more heat is removed from the system.

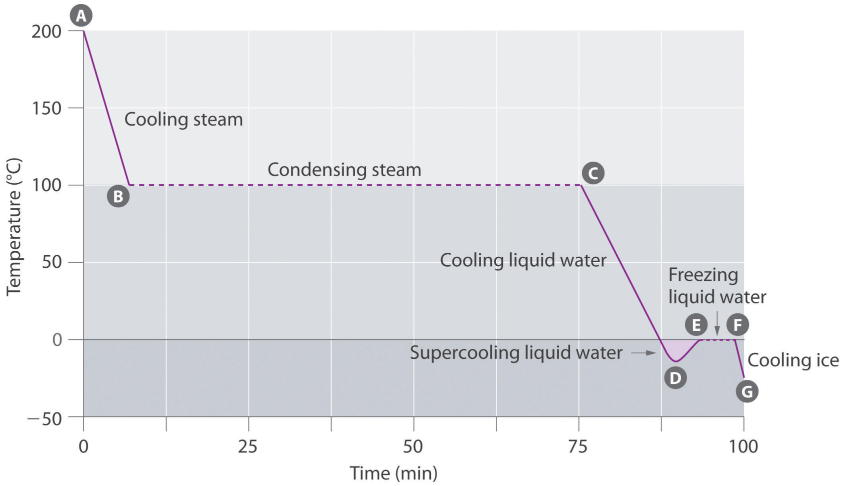

Figure 7.6.4.2: A Cooling Curve for Water. This plot of temperature shows what happens to a 75 g sample of steam initially at 1 atm and 200°C as heat is removed at a constant rate: A–B: cooling steam; B–C: condensing steam; C–D: cooling liquid water to give a supercooled liquid; D–E: warming the liquid as it begins to freeze; E–F: freezing liquid water; F–G: cooling ice.

Supercooling effects have a huge impact on Earth’s climate. For example, supercooling of water droplets in clouds can prevent the clouds from releasing precipitation over regions that are persistently arid as a result. Clouds consist of tiny droplets of water, which in principle should be dense enough to fall as rain. In fact, however, the droplets must aggregate to reach a certain size before they can fall to the ground. Usually a small particle (a *nucleus*) is required for the droplets to aggregate; the nucleus can be a dust particle, an ice crystal, or a particle of silver iodide dispersed in a cloud during *seeding* (a method of inducing rain). Unfortunately, the small droplets of water generally remain as a supercooled liquid down to about −10°C, rather than freezing into ice crystals that are more suitable nuclei for raindrop formation. One approach to producing rainfall from an existing cloud is to cool the water droplets so that they crystallize to provide nuclei around which raindrops can grow. This is best done by dispersing small granules of solid CO_2 (dry ice) into the cloud from an airplane. Solid CO_2 sublimes directly to the gas at pressures of 1 atm or lower, and the enthalpy of sublimation is substantial (25.3 kJ/mol). As the CO_2 sublimes, it absorbs heat from the cloud, often with the desired results.

7.6.4.1 Example : Cooling Hot Tea

If a 50.0 g ice cube at 0.0°C is added to 500 mL of tea at 20.0°C, what is the temperature of the tea when the ice cube has just melted? Assume that no heat is transferred to or from the surroundings. The density of water (and iced tea) is 1.00 g/mL over the range 0°C–20°C, the specific heats of liquid water and ice are 4.184 J/(g•°C) and 2.062 J/(g•°C), respectively, and the enthalpy of fusion of ice is 6.01 kJ/mol.

Given: mass, volume, initial temperature, density, specific heats, and ΔH_{fus}

Asked for: final temperature

Strategy:

Substitute the values given into the general equation relating heat gained to heat lost (Equation 5.39) to obtain the final temperature of the mixture.

Solution:

When two substances or objects at different temperatures are brought into contact, heat will flow from the warmer one to the cooler. The amount of heat that flows is given by

$$q = mC_s \Delta T \tag{7.6.4.1}$$

where q is heat, m is mass, C_s is the specific heat, and ΔT is the temperature change. Eventually, the temperatures of the two substances will become equal at a value somewhere between their initial temperatures. Calculating the temperature of iced tea after adding an ice cube is slightly more complicated. The general equation relating heat gained and heat lost is still valid, but in this case we also have to take into account the amount of heat required to melt the ice cube from ice at 0.0°C to liquid water at 0.0°C.

7.6.4.1 Exercise : Death by Freezing

Suppose you are overtaken by a blizzard while ski touring and you take refuge in a tent. You are thirsty, but you forgot to bring liquid water. You have a choice of eating a few handfuls of snow (say 400 g) at −5.0°C immediately to quench your thirst or setting up your propane stove, melting the snow, and heating the water to body temperature before drinking it. You recall that the survival guide you leafed through at the hotel said something about not eating snow, but you cannot remember why—after all, it's just frozen water. To understand the guide's recommendation, calculate the amount of heat that your body will have to supply to bring 400 g of snow at −5.0°C to your body's internal temperature of 37°C. Use the data in Example 7.6.4.1

Answer

200 kJ (4.1 kJ to bring the ice from −5.0°C to 0.0°C, 133.6 kJ to melt the ice at 0.0°C, and 61.9 kJ to bring the water from 0.0°C to 37°C), which is energy that would not have been expended had you first melted the snow.

7.E: Solids, Liquids, and Phase Changes (Exercises)

Properties of Liquids

1. What is the difference between evaporation and boiling?
2. What is the difference between a gas and vapor?
3. Define *normal boiling point* in terms of vapor pressure.
4. Is the boiling point higher or lower at higher environmental pressures? Explain your answer.
5. Referring to Fig. 10.4.3, if the pressure is 400 torr, which liquid boils at the lowest temperature?
6. Referring to Fig. 10.4.3, if the pressure is 100 torr, which liquid boils at the lowest temperature?
7. Referring to Fig. 10.4.3, estimate the boiling point of ethanol at 200 torr.
8. Referring to Fig. 10.4.3, at approximately what pressure is the boiling point of water 40°C?
9. Explain how surface tension works.
10. From what you know of intermolecular forces, which substance do you think might have a higher surface tension—ethyl alcohol or mercury? Why?
11. Under what conditions would a liquid demonstrate a capillary rise?
12. Under what conditions would a liquid demonstrate a capillary depression?

Answers

1. Evaporation occurs when a liquid becomes a gas at temperatures below that liquid's boiling point, whereas boiling is the conversion of a liquid to a gas at the liquid's boiling point.
2.
3. the temperature at which the vapor pressure of a liquid is 760 torr
4.
5. diethyl ether
6.
7. 48°C
8.
9. Surface tension is an imbalance of attractive forces between liquid molecules at the surface of a liquid.
10.
11. Adhesion must be greater than cohesion.

Solids

1. What is the difference between a crystalline solid and an amorphous solid?
2. What two properties do solids have in common? What two properties of solids can vary?
3. Explain how the bonding in an ionic solid explains some of the properties of these solids.
4. Explain how the bonding in a molecular solid explains some of the properties of these solids.
5. Explain how the bonding in a covalent network solid explains some of the properties of these solids.
6. Explain how the bonding in a metallic solid explains some of the properties of these solids.
7. Which type(s) of solid has/have high melting points?
8. Which type(s) of solid conduct(s) electricity in their solid state? In their liquid state?
9. Which type of solid(s) is/are considered relatively soft?
10. Which type of solid(s) is/are considered very hard?
11. Predict the type of solid exhibited by each substance.
    a. Hg
    b. PH_3
    c. CaF_2
12. Predict the type of solid exhibited by each substance.

   a. $(CH_2)_n$ (polyethylene, a form of plastic)
   b. PCl_3
   c. NH_4Cl
13. Predict the type of solid exhibited by each substance.
   a. SO_3
   b. Br_2
   c. Na_2SO_3
14. Predict the type of solid exhibited by each substance.
   a. BN (boron nitride, a diamond-like compound)
   b. B_2O_3
   c. $NaBF_4$
15. Predict the type of solid exhibited by each substance.
   a. H_2S
   b. Si
   c. CsF
16. Predict the type of solid exhibited by each substance.
   a. Co
   b. CO
   c. $CaCO_3$

Answers

1. At the atomic level, a crystalline solid has a regular arrangement of atoms, whereas an amorphous solid has a random arrangement of atoms.
2.
3. The oppositely charged ions are very strongly held together, so ionic crystals have high melting points. Ionic crystals are also brittle because any distortion of the crystal moves same-charged ions closer to each other, so they repel.
4.
5. The covalent network solid is essentially one molecule, making it very hard and giving it a very high melting point.
6.
7. ionic solids, covalent network solids
8.
9. molecular solids
10.
11. a. metallic
   b. molecular solid
   c. ionic crystal
12.
13. a. molecular solid
   b. molecular solid
   c. ionic crystal
14.
15. a. molecular solid
   b. molecular solid
   c. ionic crystal

7.4 Temperature

1. Perform the following conversions.

255°F to degrees Celsius

−255°F to degrees Celsius

50.0°C to degrees Fahrenheit

−50.0°C to degrees Fahrenheit

2. Perform the following conversions.

1,065°C to degrees Fahrenheit

−222°C to degrees Fahrenheit

400.0°F to degrees Celsius

200.0°F to degrees Celsius

3. Perform the following conversions.

100.0°C to kelvins

−100.0°C to kelvins

100 K to degrees Celsius

300 K to degrees Celsius

4. Perform the following conversions.

1,000.0 K to degreesCelsius

50.0 K to degrees Celsius

37.0°C to kelvins

−37.0°C to kelvins

Convert 0 K to degreesCelsius. What is the significance of the temperature in

degrees Celsius?

Convert 0 K to degreesFahrenheit. What is the significance of the temperature in degreesFahrenheit?

5. The hottest temperature ever recorded on the surface of the earth was 136°F in Libya in 1922. What is the temperature in degrees Celsius and in kelvins?

6. The coldest temperature ever recorded on the surface of the earth was −128.6°F in Vostok, Antarctica, in 1983. What is the temperature in

degrees Celsius and in kelvins?

Answers

1. 124°C
2. −159°C
3. 122°F
4. −58°F
5.
6. 1. 373 K
   2. 173 K
   3. −173°C
   4. 27°C
7.
8. −273°C. This is the lowest possible temperature in

   degrees

   Celsius.
9.
10. 57.8°C; 331 K
11.

7.5 - 7.6 Energy and Heat Capacities.

Note: you will need to consult a table of heat capacities, such as the one included here, in order to solve many of these problems.

0. A pot of water is set on a hot burner of a stove. What is the direction of heat flow?

1. Some uncooked macaroni is added to a pot of boiling water. What is the direction of heat flow?
2. How much energy in joules is required to heat 150. g of H_2O from 0.0°C to 100.0°C?
3. How much energy in joules is required to heat 125 g of Fe from 25.0°C to 150.0°C?
4. If 250 cal of heat were added to 43.8 g of Al at 22.5°C, what is the final temperature of the aluminum?
5. If 195 cal of heat were added to 33.2 g of Hg at 56.2°C, what is the final temperature of the mercury?
6. A sample of copper absorbs 607 J of energy, and its temperature rises from 37.8°C to 41.7°C. What is the mass of the copper?
7. A large, nugget of gold absorbs 410. J of heat. If its temperature rises from 22.0°C to 29.7°C, what is the mass of the gold nugget?
8. If 1.00 g of each substance in this Table were to absorb 100 cal of heat, which substance would experience the largest temperature change?
9. If 1.00 g of each substance in this Table were to absorb 100 cal of heat, which substance would experience the smallest temperature change?
10. Determine the heat capacity of a substance if 23.6 g of the substance gives off 199 cal of heat when its temperature changes from 37.9°C to 20.9°C.
11. What is the heat capacity of gold if a 250 g sample needs 133 cal of energy to increase its temperature from 23.0°C to 40.1°C?

*Note: For the next two questions, you will need a table of heat of fusion (melting) or vaporization, which you can find here.

12. What quantity of heat is required to melt 2.00 kg of iron at its melting point (1809 K)? For iron, $\Delta H_{fus} = 13.80$ kJ/mol.
13. What mass of water would need to evaporate from your skin in order to dissipate 1.70×10^5 J of heat from the surface of your body?

    $H_2O(l) \rightarrow H_2O(g) \quad \Delta H_{vap} = 40.7$ kJ/mol

Answers

1. Heat flows into the pot of water.
2. 62700 J
3. 7020 J
4. 49.1 °C
5. 231.7 °C
6. 404 g
7.
8. Lead and Gold would have the highest temperature change
9.
10.
11.
12. 494 kJ
13. 75.2 g

CHAPTER OVERVIEW

8: Gases

Of the three basic phases of matter—solids, liquids, and gases—only one of them has predictable physical properties: gases. In fact, the study of the properties of gases was the beginning of the development of modern chemistry from its alchemical roots. The interesting thing about some of these properties is that they are independent of the identity of the gas. That is, it doesn't matter if the gas is helium gas, oxygen gas, or sulfur vapors; some of their behavior is predictable and very similar. In this chapter, we will review some of the common behaviors of gases. Gases have no definite shape or volume; they tend to fill whatever container they are in. They can compress and expand, sometimes to a great extent. Gases have extremely low densities, a one-thousandth or less of the density of a liquid or solid. Combinations of gases tend to mix together spontaneously—that is, they form solutions. Air, for example, is a solution of mostly nitrogen and oxygen. Any understanding of the properties of gases must be able to explain these characteristics.

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8.1: Solids, Liquids, and Gases- A Molecular Comparison

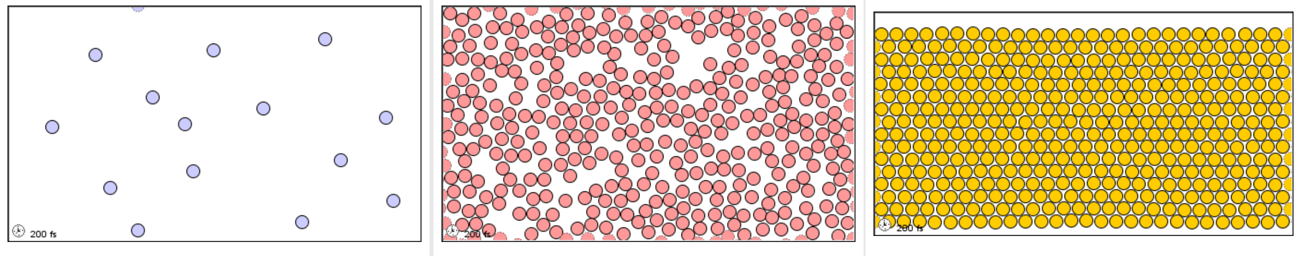
Learning Objectives

- To be familiar with the kinetic molecular description of solids, liquids, and gases.

The *physical* properties of a substance depends upon its physical state. Water vapor, liquid water and ice all have the same *chemical* properties, but their *physical* properties are considerably different. In general *covalent bonds* determine: molecular shape, bond energies, *chemical* properties, while *intermolecular forces* (non-covalent bonds) influence the *physical* properties of liquids and solids. The kinetic molecular theory of gases gives a reasonably accurate description of the behavior of gases. A similar model can be applied to liquids, but it must take into account the nonzero volumes of particles and the presence of strong intermolecular attractive forces.

Figure 8.1.1: The three common states of matter. From the left, they are solid, liquid, and gas, represented by an ice sculpture, a drop of water, and the air around clouds, respectively. Images used with permission from Wikipedia.

The *state* of a substance depends on the balance between the *kinetic energy* of the individual particles (molecules or atoms) and the *intermolecular forces*. The kinetic energy keeps the molecules apart and moving around, and is a function of the temperature of the substance. The intermolecular forces are attractive forces that try to draw the particles together (Figure 8.1.2). A discussed previously, gasses are very sensitive to temperatures and pressure. However, these also affect liquids and solids too. Heating and cooling can change the *kinetic energy* of the particles in a substance, and so, we can change the physical state of a substance by heating or cooling it. Increasing the pressure on a substance forces the molecules closer together, which *increases* the strength of intermolecular forces.



(a) in the gaseous state

(b) as a liquid

(c) *in solid form*

Figure 8.1.2: Molecular level picture of gases, liquids and solids.

Below is an overview of the general properties of the three different phases of matter.

Properties of Gases

- A collection of widely separated molecules
- The kinetic energy of the molecules is greater than any attractive forces between the molecules
- The lack of any significant attractive force between molecules allows a gas to expand to fill its container
- If attractive forces become large enough, then the gases exhibit non-ideal behavior

Properties of Liquids

- The intermolecular attractive forces are strong enough to hold molecules close together
- Liquids are more dense and less compressible than gasses
- Liquids have a definite volume, independent of the size and shape of their container

- The attractive forces are ***not*** strong enough, however, to keep neighboring molecules in a fixed position and molecules are free to move past or slide over one another

> *Thus, liquids can be poured and assume the shape of their containers.*

Properties of Solids

- The intermolecular forces between neighboring molecules are strong enough to keep them locked in position
- Solids (like liquids) are not very compressible due to the lack of space between molecules
- If the molecules in a solid adopt a highly ordered packing arrangement, the structures are said to be ***crystalline***

> *Due to the strong intermolecular forces between neighboring molecules, solids are rigid.*

Contributors and Attributions

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8.2: Pressure - The Result of Constant Molecular Collisions

Learning Objectives

- Define *pressure*.
- Learn the units of pressure and how to convert between them.

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. Even 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 atm=760 mmHg=760 torr

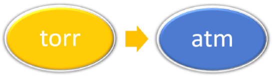
We can use these equivalents as with any equivalence—to perform conversions from one unit to another. Relating these to the formal SI unit of pressure, 1 atm = 101,325 Pa.

Example 8.2.1: Pressure Conversion

How many atmospheres are there in 595 torr?

Solution

Solutions to Example 11.3.1

Steps for Problem Solving	Unit Conversion
Identify the "given" information and what the problem is asking you to "find."	Given: 595 torr Find: ? atm
List other known quantities.	1 atm = 760 torr
Prepare a concept map.	 $\frac{1\ atm}{760\ torr}$
Cancel units and calculate.	$595\ \cancel{torr} \times \frac{1\ atm}{760\ \cancel{torr}} = 0.783\ atm$
Think about your result.	595 torr is less than 760 torr so the final answer should be less than 1 atm.

Exercise 8.2.1

How many atmospheres are there in 1,022 torr?

Answer

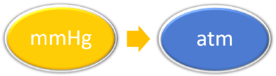
1.345 atm

Example 8.2.2: Mars

The atmosphere on Mars is largely CO_2 at a pressure of 6.01 mmHg. What is this pressure in atmospheres?

Solution

Solutions to Example 11.3.2

Steps for Problem Solving	Unit Conversion
Identify the "given" information and what the problem is asking you to "find."	Given: 6.01mmHg Find: ? atm
List other known quantities.	1 atm = 760 mmHg
Prepare a concept map.	 $\frac{1\ atm}{760\ mmHg}$
Cancel units and calculate.	$6.01\ \cancel{mmHg} \times \frac{1\ atm}{760\ \cancel{mmHg}} = 0.00791\ atm = 7.91 \times 10^{-3} atm$
Think about your result.	6.01 is a very small number relative to 760 mmHg, just like the value in atmospheres.

Exercise 8.2.2

Atmospheric pressure is low in the eye of a hurricane. In a 1979 hurricane in the Pacific Ocean, a pressure of 0.859 atm was reported inside the eye. What is this pressure in torr?

Answer

652 torr

Summary

- Pressure is a force exerted over an area.
- Pressure has several common units that can be converted.

8.3: Kinetic Molecular Theory- A Model for Gases

Learning Objectives

- State the major concepts behind the kinetic theory of gases.
- Relate the general properties of gases to the kinetic theory.

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 $8.3.1$ shows a representation of how we mentally picture the gas phase.

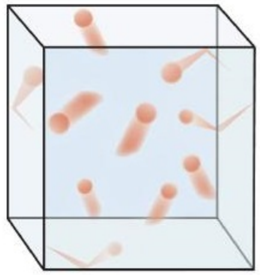


Figure $8.3.1$: The Kinetic Theory of Gases. The kinetic theory of gases describes this state of matter as composed of tiny particles in constant motion with a lot of distance between the particles.

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. Unfortunately, *real gases* are not ideal. Many gases 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.

- The physical behavior of gases is explained by the kinetic theory of gases.
- An ideal gas adheres exactly to the kinetic theory of gases.

8.4: Simple Gas Laws

Learning Objectives

- Learn what is meant by the term *gas laws*.

Researchers in the 1600s to 1800s were able to perform experiments which showed relationships between properties of gases. The results of these experiments are called the gas laws. A **gas law** is a simple mathematical formula that allows you to model, or predict, the behavior of a gas. We will start by introducing the simple gas laws, which only relate changes in one measurable property to changes in one other measurable property. Later, we will show a few ways in which we can relate 3, or even all 4 of these properties.

As you are introduced to these gas laws, focus more upon the relationship itself than the details of when that relationship was discovered, and after whom that relationship was named. The following lists some things to consider while learning these gas laws:

· If one property increases, does the other property increase or decrease?

· How do you show this relationship mathematically?

· What behaviors of real gases can help you remember this relationship?

· What connection can you make between this relationship and kinetic molecular theory?

If you are able to consider these questions, it might be easier to learn these gas laws that if you view them simply as a list of equations to memorize.

8.4.1: Boyle’s Law - Pressure and Volume

Learning Objectives

- Learn and apply Boyle’s Law.

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:

$$P \times V = \text{ constant at constant n and T} \tag{8.4.1.1}$$

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

$$P_1V_1 = \text{constant} = P_2V_2 \tag{8.4.1.2}$$

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

$$P_1V_1 = P_2V_2 \text{ at constant n and T} \tag{8.4.1.3}$$

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 8.4.1.1shows two representations of how Boyle’s Law works.

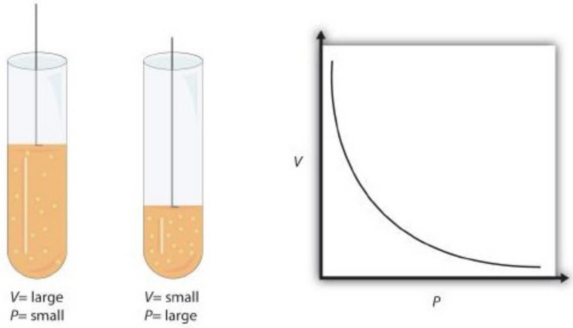


Figure 8.4.1.1: Boyle’s Law. A piston having a certain pressure and volume (left piston) will have half the volume when its pressure is twice as much (right piston). One can also plot *P* versus *V* for a given amount of gas at a certain temperature; such a plot will look like the graph on the right.

Boyle’s Law is an example of a second type of mathematical problem we see in chemistry—one based on a mathematical formula. Tactics for working with mathematical formulas are different from tactics for working with conversion factors. First, most of the questions you will have to answer using formulas are word-type questions, so the first step is to identify what quantities are known and assign them to variables. Second, in most formulas, some mathematical rearrangements (i.e., algebra) must be performed to solve for an unknown variable. The rule is that to find the value of the unknown variable, you must mathematically isolate the unknown variable *by itself and in the numerator* of one side of the equation. Finally, units must be consistent. For example, in Boyle’s Law there are two pressure variables; they must have the same unit. There are also two volume variables; they also must have the same unit. In most cases, it won’t matter *what* the unit is, but the unit must be the *same* on both sides of the equation.

Example 8.4.1.1

A sample of gas has an initial pressure of 2.44 atm and an initial volume of 4.01 L. Its pressure changes to 1.93 atm. What is the new volume if temperature and amount are kept constant?

Solution

Steps for Problem Solving	
Identify the "given" information and what the problem is asking you to "find."	Given: P_1 = 2.44 atm and V_1 = 4.01 L P_2 = 1.93 atm Find: V_2 = ? L
List other known quantities.	none
Plan the problem.	First, rearrange the equation algebraically to solve for V_2. $V_2 = \frac{P_1 \times V_1}{P_2}$ (8.4.1.4)
Cancel units and calculate.	Now substitute the known quantities into the equation and solve. $V_2 = \frac{2.44\ \cancel{\text{atm}} \times 4.01\ \text{L}}{1.93\ \cancel{atm}} = 5.07\ \text{L}$ (8.4.1.5)
Think about your result.	We know that pressure and volume are inversely related; as one decreases, the other increases. Pressure is decreasing (from 2.44 atm to 1.93 atm), so volume should be increasing to compensate, and it is (from 4.01 L to 5.07 L). So the answer makes sense based on Boyle's Law.

Exercise 8.4.1.1

If P_1 = 334 torr, V_1 = 37.8 mL, and P_2 = 102 torr, what is V_2?

Answer

124 mL

As mentioned, you can use any units for pressure and volume, but both pressures must be expressed in the same units, and both volumes must be expressed in the same units.

Example 8.4.1.2:

A sample of gas has an initial pressure of 722 torr and an initial volume of 88.8 mL. Its volume changes to 0.663 L. What is the new pressure?

Solution

Steps for Problem Solving	
Identify the "given" information and what the problem is asking you to "find."	Given: P_1 = 722 torr and V_1 = 88.8 mL V_2 = 0.663 L Find: P_2 = ? torr
List other known quantities.	1 L = 1000 mL to have the same units for volume.
Plan the problem.	1. Perform the conversion of the second volume unit from L to mL. 2. Rearrange the equation algebraically to solve for P_2. $P_2 = \frac{P_1 \times V_1}{V_2}$ (8.4.1.6)

Steps for Problem Solving	
Cancel units and calculate.	1. $$0.663\ \cancel{L} \times \frac{1000\,ml}{1\ \cancel{L}} = 663\,ml \tag{8.4.1.7}$$ 2. Substitute the known quantities into the equation and solve. $$P_2 = \frac{722\ \text{torr} \times 88.8\ \ \text{m}\cancel{\text{L}}}{663\ \ \text{m}\cancel{\text{L}}} = 96.7\ \text{torr} \tag{8.4.1.8}$$
Think about your result.	When the volume increased, the pressure decreased, which is as expected for Boyle’s Law.

? Exercise 8.4.1.2

If V_1 = 456 mL, P_1 = 308 torr, and P_2 = 1.55 atm, what is V_2?

Answer

119 mL

Summary

- The behavior of gases can be modeled with gas laws.
- Boyle’s Law relates the pressure and volume of a gas at constant temperature and amount.

Contributions & Attributions

This page was constructed from content via the following contributor(s) and edited (topically or extensively) by the LibreTexts development team to meet platform style, presentation, and quality:

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8.4.2: Charles's Law- Volume and Temperature

Learning Objectives

- Learn and apply Charles's Law.

Everybody enjoys the smell and taste of freshly-baked bread. It is light and fluffy as a result of the action of yeast on sugar. The yeast converts the sugar to carbon dioxide, which at high temperatures causes the dough to expand. The end result is an enjoyable treat, especially when covered with melted butter.

Charles's Law

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.

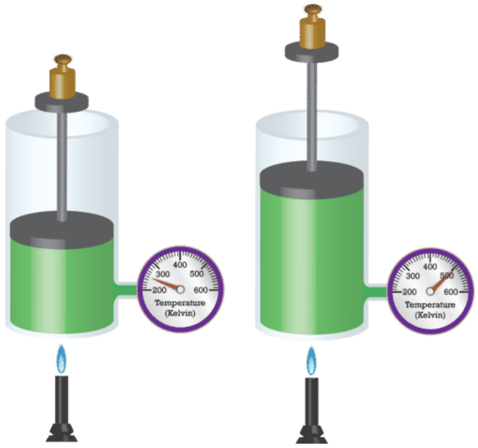

Figure 8.4.2.1: As a container of confined gas is heated, its molecules increase in kinetic energy and push the movable piston outward, resulting in an increase in volume.

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

$$\frac{V}{T}=k$$

As with Boyle's Law, k is constant only for a given gas sample. 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.

Table 8.4.2.1: Temperature-Volume Data

Temperature (K)	**Volume** (mL)	$\frac{V}{T}=k\left(\frac{\mathrm{mL}}{\mathrm{K}}\right)$
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.

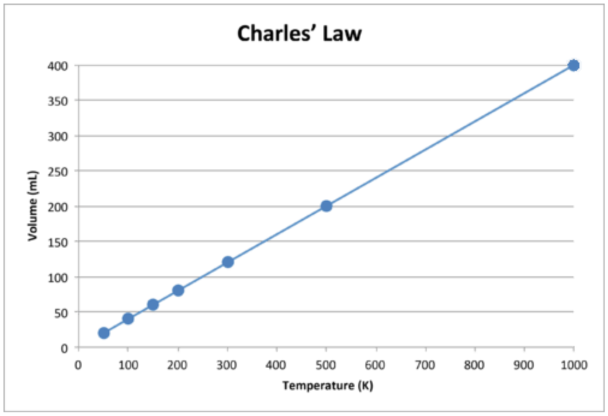

Figure 8.4.2.2:The volume of a gas increases as the Kelvin temperature increases.

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. The temperature at which this change into the liquid state occurs varies for different gases.

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:

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

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 $\text{K} = {}^\circ\text{C} + 273$.

✓ Example 8.4.2.1:

A balloon is filled to a volume of 2.20 L at a temperature of 22°C. The balloon is then heated to a temperature of 71°C. Find the new volume of the balloon.

Solution

Solutions to Example 11.5.1

Steps for Problem Solving	
Identify the "given" information and what the problem is asking you to "find."	Given: $V_1 = 2.20 \text{ L}$ and $T_1 = 22^\circ\text{C} = 295 \text{ K}$ $T_2 = 71^\circ\text{C} = 344 \text{ K}$ Find: V_2 = ? L
List other known quantities.	The temperatures have first been converted to Kelvin.
Plan the problem.	First, rearrange the equation algebraically to solve for V_2. $$V_2 = \frac{V_1 \times T_2}{T_1}$$
Cancel units and calculate.	Now substitute the known quantities into the equation and solve. $$V_2 = \frac{2.20 \text{ L} \times 344 \cancel{\text{K}}}{295 \cancel{\text{K}}} = 2.57 \text{ L}$$
Think about your result.	The volume increases as the temperature increases. The result has three significant figures.

Exercise 8.4.2.1

If V_1 = 3.77 L and T_1 = 255 K, what is V_2 if T_2 = 123 K?

Answer

1.82 L

Example 8.4.2.2:

A sample of a gas has an initial volume of 34.8 L and an initial temperature of −67°C. What must be the temperature of the gas for its volume to be 25.0 L?

Solution

Solutions to Example 11.5.2

Steps for Problem Solving	
Identify the "given" information and what the problem is asking you to "find."	Given: Given:T_1 = -67^{o}C and V_1 = 34.8 L V_2 = 25.0 L Find: T_2 = ? K
List other known quantities.	K = -67^{o}C + 273
Plan the problem.	1. Convert the initial temperature to Kelvin 2. Rearrange the equation algebraically to solve for T_2. $$T_2 = \frac{V_2 \times T_1}{V_1}$$
Cancel units and calculate.	1. −67°C + 273 = 206 K 2. Substitute the known quantities into the equation and solve. $$T_2 = \frac{25.0\ \cancel{\mathrm{L}} \times 206\ \mathrm{K}}{34.8\ \cancel{\mathrm{L}}} = 148\ \mathrm{K}$$
Think about your result.	This is also equal to −125°C. As temperature decreases, volume decreases—which it does in this example.

Exercise 8.4.2.2

If V_1 = 623 mL, T_1 = 255°C, and V_2 = 277 mL, what is T_2?

Answer

235 K, or −38°C

Summary

- Charles's Law relates the volume and temperature of a gas at constant pressure and amount.

8.4.3: Gay-Lussac's Law- Temperature and Pressure

Learning Objectives

- Explain Gay-Lussac's Law.

Propane tanks are widely used with barbeque grills. But it's not fun to find out halfway through grilling that you have run out of gas. You can buy gauges that measure the pressure inside the tank to see how much is left. The gauge measures pressure and will register a higher pressure on a hot day than it will on a cold day. So you need to take the air temperature into account when you decide whether or not to refill the tank before your next cook-out.

Gay-Lussac's Law

When the temperature of a sample of gas in a rigid container is increased, the pressure of the gas increases as well. The increase in kinetic energy results in the molecules of gas striking the walls of the container with more force, resulting in a greater pressure. The French chemist Joseph Gay-Lussac (1778-1850) discovered the relationship between the pressure of a gas and its absolute temperature. **Gay-Lussac's Law** states that the pressure of a given mass of gas varies directly with the absolute temperature of the gas, when the volume is kept constant. Gay-Lussac's Law is very similar to Charles's Law, with the only difference being the type of container. Whereas the container in a Charles's Law experiment is flexible, it is rigid in a Gay-Lussac's Law experiment.

Figure 8.4.3.1: Joseph Gay-Lussac.

The mathematical expressions for Gay-Lussac's Law are likewise similar to those of Charles's Law:

$$\frac{P}{T} \text{ and } \frac{P_1}{T_1} = \frac{P_2}{T_2}$$

A graph of pressure vs. temperature also illustrates a direct relationship. As a gas is cooled at constant volume, its pressure continually decreases until the gas condenses to a liquid.

Example 8.4.3.1

The gas in an aerosol can is under a pressure of 3.00 atm at a temperature of 25°C. It is dangerous to dispose of an aerosol can by incineration. What would the pressure in the aerosol can be at a temperature of 845°C?

Solution

Solutions to Example 11.10.1

Steps for Problem Solving	
Identify the "given" information and what the problem is asking you to "find."	Given: $P_1 = 3.00 \text{ atm}$ $T_1 = 25^\circ\text{C} = 298 \text{ K}$ $T_2 = 845^\circ\text{C} = 1118 \text{ K}$ Find: $P_2 = ? \text{ atm}$
List other known quantities.	The temperatures have first been converted to Kelvin.
Plan the problem.	First, rearrange the equation algebraically to solve for P_2. $$P_2 = \frac{P_1 \times T_2}{T_1}$$

Steps for Problem Solving	
Calculate.	Now substitute the known quantities into the equation and solve. $$P_2 = \frac{3.00 \text{ atm} \times 1118 \cancel{\text{ K}}}{298 \cancel{\text{ K}}} = 11.3 \text{ atm}$$
Think about your result.	The pressure increases dramatically due to a large increase in temperature.

Summary

- Pressure and temperature at constant volume are directly proportional.

8.4.4: Avogadro’s Law- Volume and Moles

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

You have learned about Avogadro's hypothesis: equal volumes of any gas at the same temperature and pressure contain the same number of molecules. It follows that the volume of a gas is directly proportional to the number of moles of gas present in the sample. **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:

$$V = k \times n$$

or

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

where n is the number of moles of gas and k is a constant. 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.

If the container holding the gas is rigid rather than flexible, pressure can be substituted for volume in Avogadro's Law. Adding gas to a rigid container makes the pressure increase.

✓ Example 8.4.4.1

A balloon has been filled to a volume of 1.90 L with 0.0920 mol of helium gas. If 0.0210 mol of additional helium is added to the balloon while the temperature and pressure are held constant, what is the new volume of the balloon?

Solution

Solutions to Example 11.11.1

Steps for Problem Solving	
Identify the "given" information and what the problem is asking you to "find."	Given: $V_1 = 1.90 \text{ L}$ $n_1 = 0.0920 \text{ mol}$ Find: $V_2 = ? \text{ L}$
List other known quantities.	Note that the final number of moles has to be calculated by adding the original number of moles to the moles of added helium. $n_2 = 0.0920 + 0.0210 = 0.1130 \text{ mol}$
Plan the problem.	First, rearrange the equation algebraically to solve for V_2. $$V_2 = \frac{V_1 \times n_2}{n_1}$$
Calculate.	Now substitute the known quantities into the equation and solve. $$V_2 = \frac{1.90 \text{ L} \times 0.1130 \cancel{\text{mol}}}{0.0920 \cancel{\text{mol}}} = 2.33 \text{ L}$$
Think about your result.	Since a relatively small amount of additional helium was added to the balloon, its volume increases slightly.

? Exercise 8.4.4.1

A 12.8 L volume of gas contains .000498 moles of oxygen gas. At constant temperature and pressure, what volume does .0000136 moles of the gas fill?

Answer

0.350 L

Summary

- Calculations for relationships between volume and number of moles of a gas can be performed using Avogadro's Law.

8.5: The Ideal Gas Law and Some Applications

Learning Objectives

- Learn the ideal gas law.
- Apply the ideal gas law to any set of conditions of a gas.
- Apply the ideal gas law to molar volumes, density, and stoichiometry problems.

So far, the gas laws we have considered have all required that the gas change its conditions; then we predict a resulting change in one of its properties. Are there any gas laws that relate the physical properties of a gas at any given time? Consider a further extension of the combined gas law to include *n*. By analogy to Avogadro's law, *n* is positioned in the denominator of the fraction, opposite the volume. So,

$$\frac{PV}{nT} = constant$$

Because pressure, volume, temperature, and amount are the only four independent physical properties of a gas, the constant in the above equation is truly a constant. Indeed, because we do not need to specify the identity of a gas to apply the gas laws, this constant is the same for all gases. We define this constant with the symbol *R*, so the previous equation is written as

$$\frac{PV}{nT} = R$$

which is usually rearranged as

$$PV = nRT$$

This equation is called the **ideal gas law**. It relates the four independent properties of a gas at any time. The constant \(*R*\) is called the **ideal gas law constant**. Its value depends on the units used to express pressure and volume.

Table 8.5.1: Values of the Ideal Gas Law Constant lists the numerical values of R.

Numerical Value	Units
0.08205	$\frac{L.atm}{mol.K}$
62.36	$\frac{L.torr}{mol.K} = \frac{L.mmHg}{mol.K}$
8.314	$\frac{J}{mol.K}$

The ideal gas law is used like any other gas law, with attention paid to the unit and expression of the temperature in kelvin. However, *the ideal gas law does not require a change in the conditions of a gas sample*. The ideal gas law implies that if you know any three of the physical properties of a gas, you can calculate the fourth property.

Example 8.5.1

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

The first step is to convert temperature to kelvins:

$$34 + 273 = 307\,\mathrm{K}$$

Now we can substitute the conditions into the ideal gas law:

$$(1.21 atm)(V) = (4.22\,mol)\left(0.08205 \frac{L.\,atm}{mol.\,K}\right)(307\,K)$$

The *atm* unit is in the numerator of both sides, so it cancels. On the right side of the equation, the *mol* and *K* units appear in the numerator and the denominator, so they cancel as well. The only unit remaining is *L*, which is the unit of volume that we are looking for. We isolate the volume variable by dividing both sides of the equation by 1.21:

$$V = \frac{(4.22)(0.08205)(307)}{1.21} L$$

Then solving for volume, we get V = 87.9 L

Exercise 8.5.1

A 0.0997 mol sample of O_2 has a pressure of 0.692 atm and a temperature of 333 K. What is its volume?

Answer

3.94 L

Example 8.5.2

At a given temperature, 0.00332 g of Hg in the gas phase has a pressure of 0.00120 mmHg and a volume of 435 L. What is its temperature?

Solution

We are not given the number of moles of Hg directly, but we are given a mass. We can use the molar mass of Hg to convert to the number of moles.

$$0.00332\ g\,\cancel{Hg} \times \frac{1\,mol\,Hg}{200.59\ g\ \cancel{Hg}} = 0.0000165\,mol = 1.65 \times 10^{-5} mol$$

Pressure is given in units of millimeters of mercury. We can either convert this to atmospheres or use the value of the ideal gas constant that includes the mmHg unit. We will take the second option. Substituting into the ideal gas law,

$$(0.00332\,mm\ Hg)(435\ L) = (1.65 \times 10^{-5} mol)(62.36 \frac{L.\,mmHg}{mol.\,K})T$$

The mmHg, L, and mol units cancel, leaving the K unit, the unit of temperature. Isolating T on one side, we get

$$T = \frac{(0.00332)(435)}{(1.65 \times 10^{-5})(62.36)} K$$

Then solving for K, we get T = 1,404 K.

Exercise 8.5.2

For a 0.00554 mol sample of H2, P = 23.44 torr and T = 557 K. What is its volume?

Answer

8.21 L

The ideal gas law can also be used in stoichiometry problems.

Example 8.5.3

What volume of H_2 is produced at 299 K and 1.07 atm when 55.8 g of Zn metal react with excess HCl?

$$\mathrm{Zn(s) + 2\,HCl(aq) \longrightarrow ZnCl_2(aq) + H_2(g)}$$

Solution

Here we have a stoichiometry problem where we need to find the number of moles of H2 produced. Then we can use the ideal gas law, with the given temperature and pressure, to determine the volume of gas produced. First, the number of moles of H2 is calculated:

$$55.8\ g\ \cancel{Zn} \times \frac{1\ mol\ \cancel{Zn}}{65.41\ g\ \cancel{Zn}} \times \frac{1\ mol\ H_2}{1\ mol\ \cancel{Zn}} = 0.853\ H_2$$

Now that we know the number of moles of gas, we can use the ideal gas law to determine the volume, given the other conditions:

$$(1.07 atm)V = (0.853\ mol)\left(0.08205 \frac{L.\,atm}{mol.\,K}\right)(299\ K)$$

All the units cancel except for L, for volume, which means V = 19.6 L

? Exercise 8.5.3

What pressure of HCl is generated if 3.44 g of $\mathrm{Cl_2}$ are reacted in 4.55 L at 455 K?

$$\mathrm{H_2(g) + Cl_2(g) \rightarrow 2\,HCl(g)}$$

Answer

0.796 atm

It should be obvious by now that some physical properties of gases depend strongly on the conditions. What we need is a set of standard conditions so that properties of gases can be properly compared to each other. **Standard Temperature and Pressure (STP)** is defined as exactly 100 kPa of pressure (0.986 atm) and 273 K (0°C). For simplicity, we will use 1 atm as standard pressure. Defining STP allows us to more directly compare the properties of gases that differ from one another.

One property shared among gases is a molar volume. The **molar volume** is the volume of 1 mol of a gas. At STP, the molar volume of a gas can be easily determined by using the ideal gas law:

$$(1\ atm)V = (1\ mol)\left(0.08205 \frac{L.\,atm}{mol.\,K}\right)(273\ K)$$

All the units cancel except for L, the unit of volume. So V = 22.4 L

Note that we have not specified the identity of the gas; we have specified only that the pressure is 1 atm and the temperature is 273 K. This makes for a very useful approximation: *any gas at STP has a volume of 22.4 L per mole of gas*; that is, the molar volume at STP is 22.4 L/mol (Figure 8.5.1). This molar volume makes a useful conversion factor in stoichiometry problems if the conditions are at STP. If the conditions are not at STP, a molar volume of 22.4 L/mol is not applicable. However, if the conditions are at STP, the combined gas law can be used to calculate what the volume of the gas would be if at STP; then the 22.4 L/mol molar volume can be used.

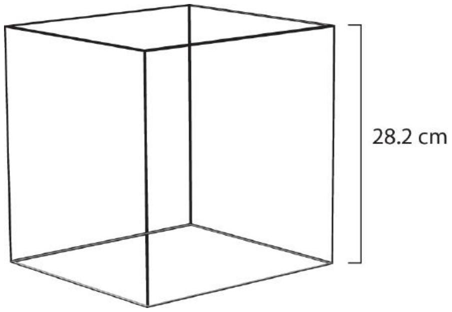

Figure 8.5.1: Molar Volume. A mole of gas at STP occupies 22.4 L, the volume of a cube that is 28.2 cm on a side.

✓ Example 8.5.4

How many moles of Ar are present in 38.7 L at STP?

Solution

We can use the molar volume, 22.4 L/mol, as a conversion factor, but we need to reverse the fraction so that the L units cancel and mol units are introduced. It is a one-step conversion:

$$38.7\ \cancel{L} \times \frac{1\,mol}{22.4\ \cancel{L}} = 1.73\,mol$$

Exercise 8.5.4

What volume does 4.87 mol of Kr have at STP?

Answer

109 L

The ideal gas law can also be used to determine the **density of gases**. Density, recall, is defined as the mass of a substance divided by its volume:

$$d = \frac{m}{V} \tag{8.5.1}$$

Assume that you have exactly 1 mol of a gas. If you know the identity of the gas, you can determine the molar mass of the substance. Using the ideal gas law, you can also determine the volume of that mole of gas, using whatever the temperature and pressure conditions are. Then you can calculate the density of the gas by using

$$\text{density} = \frac{\text{molar mass}}{\text{molar volume}}$$

Example 8.5.6

What is the density of N_2 at 25°C and 0.955 atm?

Solution

First, we must convert the temperature into kelvin:

$$25 + 273 = 298\,\text{K}$$

If we assume exactly 1 mol of N_2, then we know its mass: 28.0 g. Using the ideal gas law, we can calculate the volume:

$$(0.955\,atm)V = (1\,mol)\left(0.08205\frac{L.\,atm}{mol.\,K}\right)(298\,K)$$

All the units cancel except for L, the unit of volume. So $V = 25.6\,\text{L}$

Knowing the molar mass and the molar volume, we can determine the density of N_2 under these conditions using Equation 8.5.1:

$$d = \frac{28.0\,g}{25.6\,L} = 1.09\,g/L$$

Exercise 8.5.6

What is the density of CO_2 at a pressure of 0.0079 atm and 227 K? (These are the approximate atmospheric conditions on Mars.)

Answer

0.019 g/L

Chemistry is Everywhere: Breathing

Breathing (more properly called *respiration*) is the process by which we draw air into our lungs so that our bodies can take up oxygen from the air. Let us apply the gas laws to breathing.

Start by considering pressure. We draw air into our lungs because the diaphragm, a muscle underneath the lungs, moves down to reduce pressure in the lungs, causing external air to rush in to fill the lower-pressure volume. We expel air by the diaphragm pushing against the lungs, increasing pressure inside the lungs and forcing the high-pressure air out. What are the pressure changes involved? A quarter of an atmosphere? A tenth of an atmosphere? Actually, under normal conditions, it's only 1 or 2 torr of pressure difference that makes us breathe in and out.

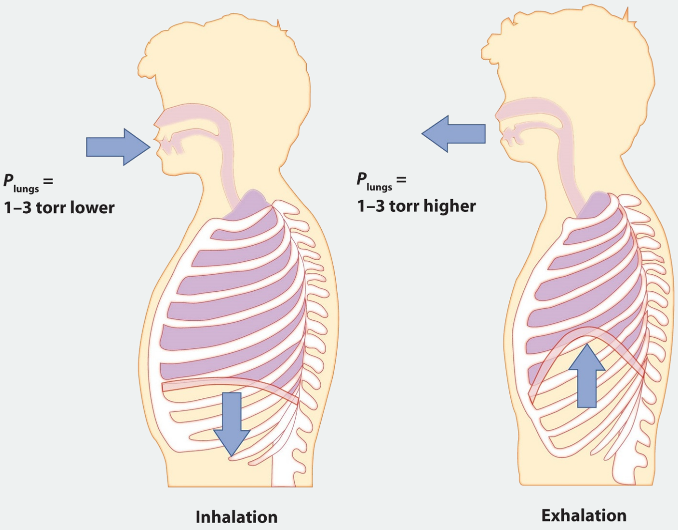

Figure 8.5.2: Breathing Mechanics. Breathing involves pressure differences between the inside of the lungs and the air outside. The pressure differences are only a few torr.

A normal breath is about 0.50 L. If room temperature is about 22°C, then the air has a temperature of about 295 K. With normal pressure being 1.0 atm, how many moles of air do we take in for every breath? The ideal gas law gives us an answer:

$$(1.0\,atm)(0.50\,L) = n\left(0.08205\frac{L.\,atm}{mol.\,K}\right)(295\,K)$$

Solving for the number of moles, we get

$$n = 0.021\,\text{mol air}$$

This ends up being about 0.6 g of air per breath—not much, but enough to keep us alive.

Summary

- The ideal gas law relates the four independent physical properties of a gas at any time.
- The ideal gas law can be used in stoichiometry problems with chemical reactions that involve gases.
- Standard temperature and pressure (STP) are a useful set of benchmark conditions to compare other properties of gases.
- At STP, gases have a volume of 22.4 L per mole.
- The ideal gas law can be used to determine the density of gases.

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8.6: Mixtures of Gases

Learning Objectives

- Explain Dalton's Law of Partial Pressures.

The atmosphere of Venus is markedly different from that of Earth. The gases in the Venusian atmosphere are 96.5% carbon dioxide and 3% nitrogen. The atmospheric pressure on Venus is roughly 92 times that of Earth, so the amount of nitrogen on Venus would contribute a pressure well over 2700 mm Hg. And there is no oxygen present, so we couldn't breathe there. Not that we would want to go to Venus, as the surface temperature is usually over 460^{o}C.

Dalton's Law of Partial Pressures

Gas pressure results from collisions between gas particles and the inside walls of their container. If more gas is added to a rigid container, the gas pressure increases. The identities of the two gases do not matter. 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 1.00 atm, then the pressure of just the nitrogen in the air is 0.78 atm. The pressure of the oxygen in the air is 0.21 atm.

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_{N_2}. **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:

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

The figure below shows two gases that are in separate, equal-sized containers at the same temperature and pressure. Each exerts a different pressure, P_1 and P_2, 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 $P_1 = 300 \text{ mm Hg}$ and $P_2 = 500 \text{ mm Hg}$, then $P_{\text{total}} = 800 \text{ mm Hg}$.

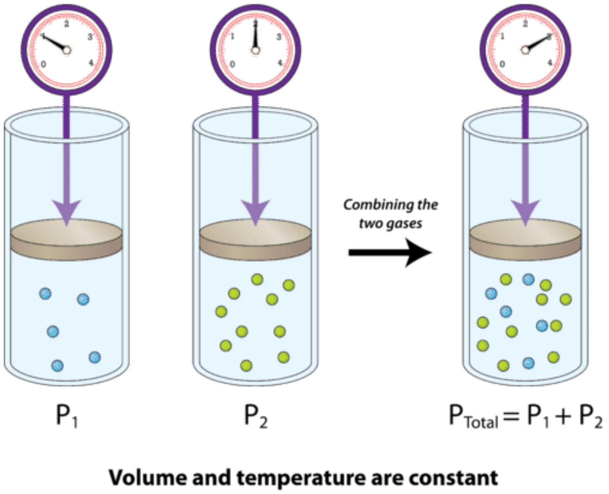

Figure 8.6.1: Dalton's Law states that the pressure of a gas mixture is equal to the partial pressures of the combining gases.

Collecting Gases Over Water

You need to do a lab experiment where hydrogen gas is generated. In order to calculate the yield of gas, you have to know the pressure inside the tube where the gas is collected. But how can you get a barometer in there? Very simple: you don't. All you need is the atmospheric pressure in the room. As the gas pushes out the water, it is pushing against the atmosphere, so the pressure inside is equal to the pressure outside.

Gas Collection by Water Displacement

Gases that are produced in laboratory experiments are often collected by a technique called **water displacement** (Figure $8.6.2$). A bottle is filled with water and placed upside-down in a pan 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 bottle. When the bottle is full of the gas, it can be sealed with a lid.

Figure $8.6.2$: 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 amount of the desired gas by subtracting the contribution of the water vapor.

$$P_{\text{Total}} = P_g + P_{H_2O}$$

where P_g is the pressure of the desired gas, which can be solved for:

$$P_g = P_{Total} - P_{H_2O}$$

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.

Table $8.6.1$: Vapor Pressure of Water (mm Hg) at Selected Temperatures $(^\circ\text{C})$

0	**5**	**10**	**15**	**20**	**25**	**30**	**35**	**40**	**45**	**50**	**55**	**60**
4.58	6.54	9.21	12.79	17.54	23.76	31.82	42.18	55.32	71.88	92.51	118.04	149.38

✓ Example 14.14.1

A certain experiment generates 2.58 L of hydrogen gas, which is collected over water. The temperature is 20°C and the atmospheric pressure is 98.60 kPa Find the volume that the dry hydrogen would occupy at STP.

Solution

Step 1: List the known quantities and plan the problem.

Known

- $V_{\text{Total}} = 2.58 \text{ L}$
- $T = 20^\circ\text{C} = 293 \text{ K}$
- $P_{\text{Total}} = 98.60 \text{ kPa} = 739.7 \text{ mm Hg}$

Unknown

- V_{H_2} at STP $= ? \text{ L}$

The atmospheric pressure is converted from kPa to mm Hg in order to match units with the table. The sum of the pressures of the hydrogen and the water vapor is equal to the atmospheric pressure. The pressure of the hydrogen is found by subtraction. Then, the volume of the gas at STP can be calculated by using the combined gas law.

Step 2: Solve.

$$\begin{aligned} P_{H_2} &= P_{\text{Total}} - P_{H_2O} \\ &= 739.7 \text{ mm Hg} - 17.54 \text{ mm Hg} \\ &= 722.2 \text{ mm Hg} \end{aligned}$$

Now the combined gas law is used, solving for V_2, the volume of hydrogen at STP.

$$\begin{aligned} V_2 &= \frac{P_1 \times V_1 \times T_2}{P_2 \times T_1} \\ &= \frac{722.2 \text{ mm Hg} \times 2.58 \text{ L} \times 273 \text{ K}}{760 \text{ mm Hg} \times 293 \text{ K}} \\ &= 2.28 \text{ L H}_2 \end{aligned}$$

Step 3: Think about your result.

If the hydrogen gas were to be collected at STP and without the presence of the water vapor, its volume would be 2.28 L. This is less than the actual collected volume because some of that is water vapor. The conversion using STP is useful for stoichiometry purposes.

Summary

- Dalton's Law of Partial Pressures states that the total pressure in a system is equal to the sum of the partial pressures of the gases present.
- The vapor pressure due to water in a sample can be corrected for, in order to get the true value for the pressure of the gas.

8.E: Gases (Exercises)

Ch 8.1 -8.5

1. Explain the differences between the microscopic and the macroscopic properties of matter. Is the boiling point of a compound a microscopic or macroscopic property? molecular mass? Why?
2. How do the microscopic properties of matter influence the macroscopic properties? Can you relate molecular mass to boiling point? Why or why not?
3. For a substance that has gas, liquid, and solid phases, arrange these phases in order of increasing density.
   a. strength of intermolecular interactions.
   b. compressibility.
   c. molecular motion.
   d. order in the arrangement of the molecules or atoms.
4. Which elements of the periodic table exist as gases at room temperature and pressure? Of these, which are diatomic molecules and which are monatomic? Which elements are liquids at room temperature and pressure? Which portion of the periodic table contains elements whose binary hydrides are most likely gases at room temperature?
5. A 1.00 mol sample of gas at 25°C and 1.0 atm has an initial volume of 22.4 L. Calculate the results of each change, assuming all the other conditions remain constant.
   a. The pressure is changed to 85.7 mmHg. How many milliliters does the gas occupy?
   b. The volume is reduced to 275 mL. What is the pressure in millimeters of mercury?
   c. The pressure is increased to 25.3 atm. What is the temperature in degrees Celsius?
   d. The sample is heated to 30°C. What is the volume in liters?
   e. The sample is compressed to 1255 mL, and the pressure is increased to 2555 torr. What is the temperature of the gas in kelvins?
6. A 1.00 mol sample of gas is at 300 K and 4.11 atm. What is the volume of the gas under these conditions? The sample is compressed to 6.0 atm at constant temperature, giving a volume of 3.99 L. Is this result consistent with Boyle's law?
7. A 8.60 L tank of nitrogen gas at a pressure of 455 mmHg is connected to an empty tank with a volume of 5.35 L. What is the final pressure in the system after the valve connecting the two tanks is opened? Assume that the temperature is constant.
8. At constant temperature, what pressure in atmospheres is needed to compress 14.2 L of gas initially at 25.2 atm to a volume of 12.4 L? What pressure is needed to compress 27.8 L of gas to 20.6 L under similar conditions?
9. One method for preparing hydrogen gas is to pass HCl gas over hot aluminum; the other product of the reaction is $AlCl_3$. If you wanted to use this reaction to fill a balloon with a volume of 28,500 L at sea level and a temperature of 78°F, what mass of aluminum would you need? What volume of HCl at STP would you need?
10. An 3.50 g sample of acetylene is burned in excess oxygen according to the following reaction:

    $$2\,C_2H_2(g) + 5\,O_2(g) \rightarrow 4\,CO_2(g) + 2\,H_2O(l)$$

    At STP, what volume of $CO_2(g)$ is produced?
11. Calculate the density of ethylene (C_2H_4) under each set of conditions.
    a. 7.8 g at 0.89 atm and 26°C
    b. 6.3 mol at 102.6 kPa and 38°C
    c. 9.8 g at 3.1 atm and −45°C
12. At 140°C, the pressure of a diatomic gas in a 3.0 L flask is 635 kPa. The mass of the gas is 88.7 g. What is the most likely identity of the gas?
13. What volume must a balloon have to hold 6.20 kg of H_2 for an ascent from sea level to an elevation of 20,320 ft, where the temperature is −37°C and the pressure is 369 mmHg?
14. What must be the volume of a balloon that can hold 313.0 g of helium gas and ascend from sea level to an elevation of 1.5 km, where the temperature is 10.0°C and the pressure is 635.4 mmHg?
15. A typical automobile tire is inflated to a pressure of 28.0 lb/in.^{2} Assume that the tire is inflated when the air temperature is 20°C; the car is then driven at high speeds, which increases the temperature of the tire to 43°C. What is the pressure in the tire? If the volume of the tire had increased by 8% at the higher temperature, what would the pressure be?

16. The average respiratory rate for adult humans is 20 breaths per minute. If each breath has a volume of 310 mL of air at 20°C and 0.997 atm, how many moles of air does a person inhale each day? If the density of air is 1.19 kg/m^3, what is the average molecular mass of air?
17. Kerosene has a self-ignition temperature of 255°C. It is a common accelerant used by arsonists, but its presence is easily detected in fire debris by a variety of methods. If a 1.0 L glass bottle containing a mixture of air and kerosene vapor at an initial pressure of 1 atm and an initial temperature of 23°C is pressurized, at what pressure would the kerosene vapor ignite?

Answers

1.
2.
3.
4.
5.
    a. 1.99×10^5 mL
    b. 6.19×10^4 mmHg
    c. 7270°C
    d. 22.8 L
    e. 51.4 K
6.
7. 281 mmHg
8.
9. 20.9 kg Al, 5.20×10^4 L HCl
10.
11.
    a. 1.0 g/L
    b. 1.1 g/L
    c. 4.6 g/L
12.
13.
14. 2174 L

? Additional Exercises

1. What is the pressure in pascals if a force of 4.88 kN is pressed against an area of 235 cm^2?
2. What is the pressure in pascals if a force of 3.44×10^4 MN is pressed against an area of 1.09 km^2?
3. What is the final temperature of a gas whose initial conditions are 667 mL, 822 torr, and 67°C and whose final volume and pressure are 1.334 L and 2.98 atm, respectively? Assume the amount remains constant.
4. What is the final pressure of a gas whose initial conditions are 1.407 L, 2.06 atm, and −67°C and whose final volume and temperature are 608 mL and 449 K, respectively? Assume the amount remains constant.
5. Propose a combined gas law that relates volume, pressure, and amount at constant temperature.
6. Propose a combined gas law that relates amount, pressure, and temperature at constant volume.
7. A sample of 6.022×10^{23} particles of gas has a volume of 22.4 L at 0°C and a pressure of 1.000 atm. Although it may seem silly to contemplate, what volume would 1 particle of gas occupy?
8. One mole of liquid N_2 has a volume of 34.65 mL at −196°C. At that temperature, 1 mol of N_2 gas has a volume of 6.318 L if the pressure is 1.000 atm. What pressure is needed to compress the N_2 gas to 34.65 mL?
9. Use two values of R to determine the ratio between an atmosphere and a torr. Does the number make sense?
10. Use two values of R to determine how many joules are in a liter·atmosphere.
11. At an altitude of 40 km above the earth's surface, the atmospheric pressure is 5.00 torr, and the surrounding temperature is −20°C. If a weather balloon is filled with 1.000 mol of He at 760 torr and 22°C, what is its
    a. initial volume before ascent?
    b. final volume when it reaches 40 km in altitude? (Assume the pressure of the gas equals the surrounding pressure.)
12. If a balloon is filled with 1.000 mol of He at 760 torr and 22°C, what is its
    a. initial volume before ascent?

    b. final volume if it descends to the bottom of the Mariana Trench, where the surrounding temperature is 1.4°C and the pressure is 1,060 atm?

13. Air, a mixture of mostly N_2 and O_2, can be approximated as having a molar mass of 28.8 g/mol. What is the density of air at 1.00 atm and 22°C? (This is approximately sea level.)
14. Air, a mixture of mostly N_2 and O_2, can be approximated as having a molar mass of 28.8 g/mol. What is the density of air at 0.26 atm and −26°C? (This is approximately the atmospheric condition at the summit of Mount Everest.)
15. On the surface of Venus, the atmospheric pressure is 91.8 atm, and the temperature is 460°C. What is the density of CO_2 under these conditions? (The Venusian atmosphere is composed largely of CO_2.)
16. On the surface of Mars, the atmospheric pressure is 4.50 torr, and the temperature is −87°C. What is the density of CO_2 under these conditions? (The Martian atmosphere, similar to its Venusian counterpart, is composed largely of CO_2.)
17. HNO_3 reacts with iron metal according to

$Fe(s) + 2HNO_3(aq) \rightarrow Fe(NO_3)_2(aq) + H_2(g)$

In a reaction vessel, 23.8 g of Fe are reacted but only 446 mL of H_2 are collected over water at 25°C and a pressure of 733 torr. What is the percent yield of the reaction?

18. $NaHCO_3$ is decomposed by heat according to

    $2NaHCO_3(s) \rightarrow Na_2CO_3(s) + H_2O(\ell) + CO_2(g)$

    If you start with 100.0 g of $NaHCO_3$ and collect 10.06 L of CO_2 over water at 20°C and 0.977 atm, what is the percent yield of the decomposition reaction?

? Answers

1. 208,000 Pa
2.
3. 1,874 K
4.
5. $$\frac{P_1V_1}{n_1} = \frac{P_2V_2}{n_2}$$
6.
7. 3.72×10^{-23} L
8.
9. 1 atm = 760 torr
10.
11.
    1. 24.2 L
    2. 3155 L
12.
13. 1.19 g/L
14.
15. 67.2 g/L
16.
17. 3.99%

CHAPTER OVERVIEW

9: Aqueous Solutions

Solutions were introduced in an earlier chapter as the mixture in which the substances involved are mixed at the molecular level. There was also a discussion about how solutions form based on the intermolecular forces that occur between solvent and solute particles. These ideas about solutions are important to understand as we move forward in this chapter to focus on a particular type of solution which is both very common and very important: aqueous solutions.

9.1: Solutions - Homogeneous Mixtures

Learning Objectives

- Learn terminology involving solutions.

Attractive forces are also important for the formation of solutions. We will discuss why attractive forces are important in one of the subsections of this chapter, but first we will define a few terms that are important for solutions.

The substance that does not change it's phase or the major component of a solution is called the **solvent.** The substance that changes phase or the minor component of a solution is called the **solute**. By major and minor we mean whichever component has the greater or lesser presence by mass or by moles. Sometimes this becomes confusing, especially with substances with very different molar masses. However, here we will confine the discussion to solutions for which the major component and the minor component are obvious.

Solutions exist for every possible phase of the solute and the solvent. Salt water, for example, is a solution of solid NaCl in liquid water, while air is a solution of a gaseous solute (O_2) in a gaseous solvent (N_2). In all cases, however, the overall phase of the solution is the same phase as the solvent. Table $9.1.1$ lists some common types of solutions, with examples of each.

Table 9.1.1: Types of Solutions

Solvent Phase	Solute Phase	Example
gas	gas	air
liquid	gas	carbonated beverages
liquid	liquid	ethanol (C_2H_5OH) in H_2O (alcoholic beverages)
liquid	solid	salt water
solid	gas	H_2 gas absorbed by Pd metal
solid	liquid	Hg(ℓ) in dental fillings
solid	solid	steel alloys

Figure 9.1.1: Making a saline water solution by dissolving table salt (NaCl) in water. The salt is the solute and the water the solvent. (CC-BY-SA 3.0; Chris 73).

Example 9.1.1: Sugar and Water

A solution is made by dissolving 1.00 g of sucrose ($C_{12}H_{22}O_{11}$) in 100.0 g of liquid water. Identify the solvent and solute in the resulting solution.

Solution

Either by mass or by moles, the obvious minor component is **sucrose**, so it is **the solute**. **Water**—the majority component—is **the solvent**. The fact that the resulting solution is the same phase as water also suggests that water is the solvent.

Exercise 9.1.1

A solution is made by dissolving 3.33 g of $HCl(g)$ in 40.0 g of liquid methyl alcohol (CH_3OH). Identify the solvent and solute in the resulting solution.

Answer

solute: HCl(g); solvent: CH3OH

Summary

- Solutions are composed of a solvent (keeps phase or major component) and a solute (changes phase or minor component).

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9.1.1: How Solutions Form

Learning Objectives

- Explain the significance of the statement "like dissolves like."
- Explain why certain substances dissolve in other substances.

A simple way to predict which compounds will dissolve in other compounds is the phrase "like dissolves like". What this means is that polar compounds dissolve polar compounds, nonpolar compounds dissolve nonpolar compounds, but polar and nonpolar do not dissolve in each other.

Even some nonpolar substances dissolve in water but only to a limited degree. Have you ever wondered why fish are able to breathe? Oxygen gas, a nonpolar molecule, does dissolve in water—it is this oxygen that the fish take in through their gills. The reason we can enjoy carbonated sodas is also due to a nonpolar compound that dissolves in water. Pepsi-cola and all the other sodas have carbon dioxide gas, CO_2, a nonpolar compound, dissolved in a sugar-water solution. In this case, to keep as much gas in solution as possible, the sodas are kept under pressure.

This general trend of "like dissolves like" is summarized in the following table:

Table 9.1.1.2: Summary of Solubilities

Solute (Polarity of Compound)	Solvent (Polarity of Compound)	Dominant Intermolecular Force	Is Solution Formed?
Polar	Polar	Dipole-Dipole Force and/or Hydrogen Bond	yes
Non-polar	Non-polar	Dispersion Force	yes
Polar	Non-polar		no
Non-polar	Polar		no
Ionic	Polar	Ion-Dipole	yes
Ionic	Non-polar		no

Note that every time charged particles (ionic compounds or polar substances) are mixed, a solution is formed. When particles with no charges (nonpolar compounds) are mixed, they will form a solution. However, if substances with charges are mixed with other substances without charges, a solution does not form. When an ionic compound is considered "insoluble", it doesn't necessarily mean the compound is completely untouched by water. All ionic compounds dissolve to some extent. An insoluble compound just doesn't dissolve in any noticeable or appreciable amount.

What is it that makes a solute soluble in some solvents but not others?

The answer is intermolecular interactions. The intermolecular interactions include London dispersion forces, dipole-dipole interactions, and hydrogen bonding (as described in Chapter 10). From experimental studies, it has been determined that if molecules of a solute experience the same intermolecular forces that the solvent does, the solute will likely dissolve in that solvent. So, NaCl—a very polar substance because it is composed of ions—dissolves in water, which is very polar, but not in oil, which is generally nonpolar. Nonpolar wax dissolves in nonpolar hexane, but not in polar water.

Figure 9.1.1.2: Water (clear liquid) and oil (yellow) do not form liquid solutions. (CC BY-SA 1.0 Generic; Victor Blacus)

✓ Example 9.1.1.2: Polar and Nonpolar Solvents

Would I_2 be more soluble in CCl_4 or H_2O? Explain your answer.

Solution

I_2 is nonpolar. Of the two solvents, CCl_4 is nonpolar and H_2O is polar, so I_2 would be expected to be more soluble in CCl_4.

? Exercise 9.1.1.2

Would C_3H_7OH be more soluble in CCl_4 or H_2O? Explain your answer.

Answer

H_2O, because both experience hydrogen bonding.

✓ Example 9.1.1.3

Water is considered a polar solvent. Which substances should dissolve in water?

a. methanol (CH_3OH)
b. sodium sulfate (Na_2SO_4)
c. octane (C_8H_{18})

Solution

Because water is polar, substances that are polar or ionic will dissolve in it.

a. Because of the OH group in methanol, we expect its molecules to be polar. Thus, we expect it to be soluble in water. As both water and methanol are liquids, the word *miscible* can be used in place of *soluble*.
b. Sodium sulfate is an ionic compound, so we expect it to be soluble in water.
c. Like other hydrocarbons, octane is nonpolar, so we expect that it would not be soluble in water.

? Exercise 9.1.1.3

Toluene ($C_6H_5CH_3$) is widely used in industry as a nonpolar solvent. Which substances should dissolve in toluene?

a. water (H_2O)
b. sodium sulfate (Na_2SO_4)
c. octane (C_8H_{18})

Answer

Octane (C_8H_{18}) will dissolve. It is also non-polar.

Summary

- “Like dissolves like” is a useful rule for deciding if a solute will be soluble in a solvent.

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9.1.2: Electrolytes and Nonelectrolytes

Learning Objectives

- Define electrolytes and non electrolytes
- Discuss the idea of water as the "universal solvent".
- Explain how water molecules attract ionic solids when they dissolve in water.

When some substances are dissolved in water, they undergo either a physical or a chemical 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 or chemical 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 (good conductor). If only a relatively small fraction of the dissolved substance undergoes the ion-producing process, the substance is a weak electrolyte (does not conduct electricity as well).

Substances may be identified as strong, weak, or nonelectrolytes by measuring the electrical conductance of an aqueous solution containing the substance. To conduct electricity, a substance must contain freely mobile, charged species. Most familiar is the conduction of electricity through metallic wires, in which case the mobile, charged entities are electrons. Solutions may also conduct electricity if they contain dissolved ions, with conductivity increasing as ion concentration increases. Applying a voltage to electrodes immersed in a solution permits assessment of the relative concentration of dissolved ions, either quantitatively, by measuring the electrical current flow, or qualitatively, by observing the brightness of a light bulb included in the circuit (Figure $9.1.2.1$).

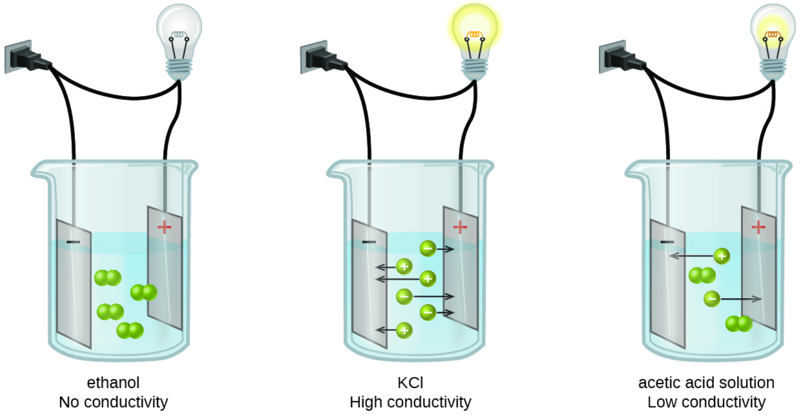

Figure $9.1.2.1$: Solutions of nonelectrolytes, such as ethanol, do not contain dissolved ions and cannot conduct electricity. Solutions of electrolytes contain ions that permit the passage of electricity. The conductivity of an electrolyte solution is related to the strength of the electrolyte.

Water and other polar molecules are attracted to ions, as shown in Figure $9.1.2.2$ The electrostatic attraction between an ion and a molecule with a dipole is called an **ion-dipole attraction**. They are similar to the dipole-dipole interactions which were discussed earlier, but often stronger due to the full charge on the ions. These interactions are strong enough to play an important role in the dissolution of ionic compounds in water.

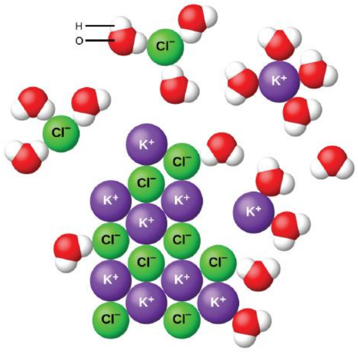

Figure 9.1.2.2: As potassium chloride (KCl) dissolves in water, the ions are hydrated. The polar water molecules are attracted by the charges on the K^+ and Cl^- ions. Water molecules in front of and behind the ions are not shown.

When ionic compounds dissolve in water, the ions in the solid separate and disperse uniformly throughout the solution because water molecules surround and solvate the ions, reducing the strong electrostatic forces between them. 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.

✓ Example 9.1.2.1: Identifying Ionic Compounds

Which compound(s) will dissolve in solution to separate into ions?

a. LiF
b. P_2F_5
c. C_2H_5OH

Solution

LiF will separate into ions when dissolved in solution, because it is an ionic compound. P_2F_5 and C_2H_5OH are both covalent and will stay as molecules in a solution.

? Exercise 9.1.2.1

Which compounds will dissolve in solution to separate into ions?

a. $C_6H_{12}O_{11}$, glucose
b. CCl_4
c. $CaCl_2$
d. $AgNO_3$

Answer

c & d

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9.1.3: Aqueous Solutions and Solubility - Compounds Dissolved in Water

Learning Objectives

- Know how to use solubility rules.

Water and other polar molecules are attracted to ions, as shown in Figure $9.1.3.2$ 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.

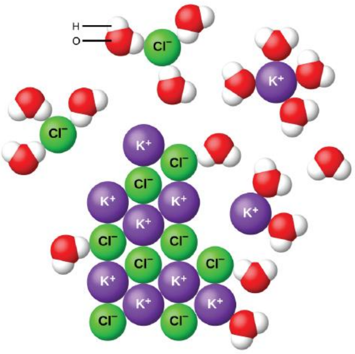


Figure $9.1.3.2$: As potassium chloride (KCl) dissolves in water, the ions are hydrated. The polar water molecules are attracted by the charges on the K^+ and Cl^- ions. Water molecules in front of and behind the ions are not shown.

When ionic compounds dissolve in water, the ions in the solid separate and disperse uniformly throughout the solution because water molecules surround and solvate the ions, reducing the strong electrostatic forces between them. 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.

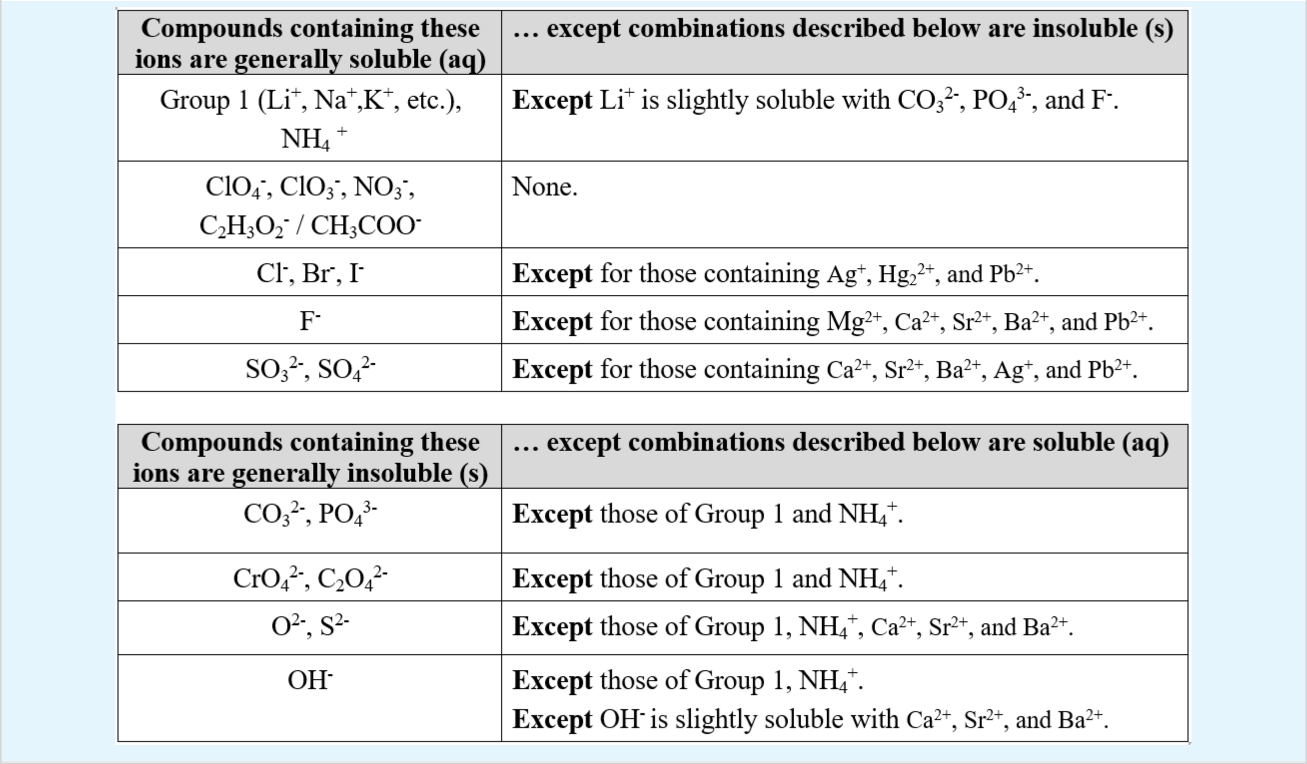
Let us consider what happens at the microscopic level when we add solid KCl to water. Ion-dipole forces attract the positive (hydrogen) end of the polar water molecules to the negative chloride ions at the surface of the solid, and they attract the negative (oxygen) ends to the positive potassium ions. The water molecules penetrate between individual K^+ and Cl^- ions and surround them, reducing the strong interionic forces that bind the ions together and letting them move off into solution as solvated ions, as Figure $9.1.3.2$ shows. The reduction of the electrostatic attraction permits the independent motion of each hydrated ion in a dilute solution, resulting in an increase in the disorder of the system, as the ions change from their fixed and ordered positions in the crystal to mobile and much more disordered states in solution. This increased disorder is responsible for the dissolution of many ionic compounds, including KCl, which dissolve with absorption of heat.

In other cases, the electrostatic attractions between the ions in a crystal are so large, or the ion-dipole attractive forces between the ions and water molecules are so weak, that the increase in disorder cannot compensate for the energy required to separate the ions, and the crystal is insoluble. Such is the case for compounds such as calcium carbonate (limestone), calcium phosphate (the inorganic component of bone), and iron oxide (rust).

Solubility Rules

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. Every ion is a spectator ion and there is no net ionic equation at all. 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 $9.1.3.1$ and $9.1.3.2$).

Table $9.1.3.1$: Solubility Rules for Soluble Substances



Compounds containing these ions are generally soluble (aq)	… except combinations described below are insoluble (s)
Group 1 (Li^+, Na^+,K^+, etc.), $NH_4{}^+$	**Except** Li^+ is slightly soluble with $CO_3{}^{2-}$, $PO_4{}^{3-}$, and F^-.
$ClO_4{}^-$, $ClO_3{}^-$, $NO_3{}^-$, $C_2H_3O_2{}^-$ / CH_3COO^-	None.
Cl^-, Br^-, I^-	**Except** for those containing Ag^+, $Hg_2{}^{2+}$, and Pb^{2+}.
F^-	**Except** for those containing Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, and Pb^{2+}.
$SO_3{}^{2-}$, $SO_4{}^{2-}$	**Except** for those containing Ca^{2+}, Sr^{2+}, Ba^{2+}, Ag^+, and Pb^{2+}.

Compounds containing these ions are generally insoluble (s)	… except combinations described below are soluble (aq)
$CO_3{}^{2-}$, $PO_4{}^{3-}$	**Except** those of Group 1 and $NH_4{}^+$.
$CrO_4{}^{2-}$, $C_2O_4{}^{2-}$	**Except** those of Group 1 and $NH_4{}^+$.
O^{2-}, S^{2-}	**Except** those of Group 1, $NH_4{}^+$, Ca^{2+}, Sr^{2+}, and Ba^{2+}.
OH^-	**Except** those of Group 1, $NH_4{}^+$. **Except** OH^- is slightly soluble with Ca^{2+}, Sr^{2+}, and Ba^{2+}.

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

$$\mathrm{Cs^+}\,(aq) + \mathrm{Br^-}\,(aq) + \mathrm{Pb^{2+}}\,(aq) + 2\mathrm{NO_3^-}\,(aq) \rightarrow ?$$

The potential precipitates from a double-replacement reaction are cesium nitrate and lead (II) bromide. According to the solubility rules table, 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 balanced net ionic reaction is:

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

✓ Example 9.1.3.1: Solubility

Classify each compound as soluble or insoluble

a. $Zn(NO_3)_2$
b. $PbBr_2$
c. $Sr_3(PO_4)_2$

Solution

a. All nitrates are soluble in water, so $Zn(NO_3)_2$ is soluble.
b. All bromides are soluble in water, except those combined with Pb^{2+}, so $PbBr_2$ is insoluble.
c. All phosphates are insoluble, so $Sr_3(PO_4)_2$ is insoluble.

? Exercise 9.1.3.1: Solubility

Classify each compound as soluble or insoluble.

a. $Mg(OH)_2$
b. KBr
c. $Pb(NO_3)_2$

Answer a

insoluble

Answer b

soluble

Answer c

soluble

Summary

Substances that dissolve in water to yield ions are called electrolytes. Nonelectrolytes are substances that do not produce ions when dissolved in water. Solubility rules allow prediction of what products will be insoluble in water.

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9.2: Solubility Trends

Learning Objectives

- Define solubility and saturation.

We have learned that solutions can be formed in a variety of combinations using solids, liquids, and gases. We also know that solutions have the same composition throughout, and that the ratio of components can be varied up to a point to maintain the homogeneous nature of the solution. In this section, we will discuss how that restriction on components is defined, and how changing external conditions might change the range of possible compositions for a solution.

Solubility and Saturation

Table salt (NaCl) readily dissolves in water. In most cases, only a certain maximum amount of solute can be dissolved in a given amount of solvent. This maximum amount is specified as the **solubility** of the solute. It is usually expressed in terms of the amount of solute that can dissolve in 100 g of the solvent at a given temperature. Table $9.2.1$ lists the solubilities of some simple ionic compounds. These solubilities vary widely. NaCl can dissolve up to 31.6 g per 100 g of H_2O, while AgCl can dissolve only 0.00019 g per 100 g of H_2O.

Table $9.2.1$: Solubilities of Some Ionic Compounds

Solute	Solubility (g per 100 g of H_2O at 25°C)
AgCl	0.00019
$CaCO_3$	0.0006
KBr	70.7
NaCl	36.1
$NaNO_3$	94.6

When the maximum amount of solute has been dissolved in a given amount of solvent, we say that the solution is **saturated** with solute. When less than the maximum amount of solute is dissolved in a given amount of solute, the solution is **unsaturated**. These terms are also qualitative terms because each solute has its own solubility. A solution of 0.00019 g of AgCl per 100 g of H_2O may be saturated, but with so little solute dissolved, it is also rather dilute. A solution of 36.1 g of NaCl in 100 g of H_2O is also saturated, but rather concentrated. In some circumstances, it is possible to dissolve more than the maximum amount of a solute in a solution. Usually, this happens by heating the solvent, dissolving more solute than would normally dissolve at regular temperatures, and letting the solution cool down slowly and carefully. Such solutions are called **supersaturated** solutions and are not stable; given an opportunity (such as dropping a crystal of solute in the solution), the excess solute will precipitate from the solution.The figure below illustrates the above process and shows the distinction between unsaturated and saturated.

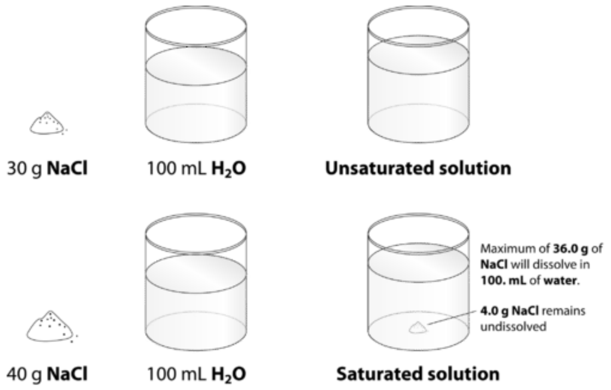

Figure $9.2.1$: When $30.0\ \mathrm{g}$ of NaCl is added to $100\ \mathrm{mL}$, it all dissolves, forming an unsaturated solution. When $40.0\ \mathrm{g}$ is added, $36.0\ \mathrm{g}$ dissolves and $4.0\ \mathrm{g}$ remains undissolved, forming a saturated solution.

How can you tell if a solution is saturated or unsaturated? If more solute is added and it does not dissolve, then the original solution was saturated. If the added solute dissolves, then the original solution was unsaturated. A solution that has been allowed to reach equilibrium, but which has extra undissolved solute at the bottom of the container, must be saturated. In the subsections that follow, we will discuss how some external properties might affect the solubility of a solution.

Summary

- Solubility is the specific amount of solute that can dissolve in a given amount of solvent.
- Saturated and unsaturated solutions are defined.

Vocabulary

- **Miscible** - Liquids that have the ability to dissolve in each other.
- **Immiscible** - Liquids that do not have the ability to dissolve in each other.

9.2.1: Solutions of Solids Dissolved in Water

Learning Objectives

- Explain how temperature influences solubility of solids.

The **solubility** of a substance is the amount of that substance that is required to form a saturated solution in a given amount of solvent at a specified temperature. Solubility is often measured as the grams of solute per 100 g of solvent. The solubility of sodium chloride in water is 36.0 g per 100 g water at $20^{o}C$. The temperature must be specified because solubility varies with temperature. For gases, the pressure must also be specified. Solubility is specific for a particular solvent. We will consider solubility of material in water as solvent.

The solubility of the majority of solid substances increases as the temperature increases. However, the effect is difficult to predict and varies widely from one solute to another. The temperature dependence of solubility can be visualized with the help of a **solubility curve**, a graph of the solubility vs. temperature (Figure $9.2.1.4$).

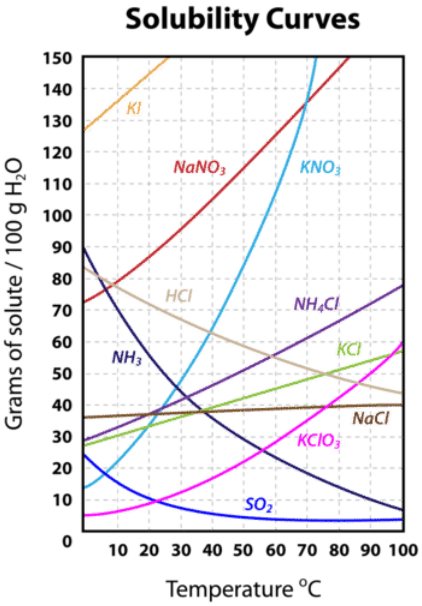

Figure $9.2.1.4$: Solubility curves for several compounds.

Notice how the temperature dependence of $NaCl$ is fairly flat, meaning that an increase in temperature has relatively little effect on the solubility of $NaCl$. The curve for KNO_3, on the other hand, is very steep and so an increase in temperature dramatically increases the solubility of KNO_3.

The trends for gas solubility in aqueous solution are often different than those for solids. You may notice on the graph that there are several substances—HCl, NH_3, and SO_2— which have solubility that decreases as temperature increases. They are all gases at standard pressure. Additionally, changes in pressure can affect solubility of gases whereas they generally have little or no effect on solubility of solids. Trends of gas solubility will be discussed in the next subsection.

Solubility curves can be used to determine if a given solution is saturated or unsaturated. Suppose that 80 g of KNO_3 is added to 100 g of water at $30^{o}C$. According to the solubility curve, approximately 48 g of KNO_3 will dissolve at $30^{o}C$. This means that the solution will be saturated since 48 g is less than 80 g. We can also determine that there will be $80 - 48 = 32$ g of undissolved KNO_3 remaining at the bottom of the container. Now suppose that this saturated solution is heated to $60^{o}C$. According to the curve, the solubility of KNO_3 at $60^{o}C$ is about 107 g. Now the solution is unsaturated since it contains only the original 80 g of dissolved solute. Now suppose the solution is cooled all the way down to $0^{o}C$. The solubility at $0^{o}C$ is about 14 g, meaning that $80 - 14 = 66$ g of the KNO_3 will re-crystallize.

Summary

- The solubility of a solid in water usually increases with an increase in temperature.

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9.2.2: Solutions of Gases in Water

Learning Objectives

- Explain how temperature and pressure affect the solubility of gases.

In an earlier section of this book, the effect of intermolecular attractive forces on solution formation was discussed. The chemical structures of the solute and solvent dictate the types of forces possible and, consequently, are important factors in determining solubility. For example, under similar conditions, the water solubility of oxygen is approximately three times greater than that of helium, but 100 times less than the solubility of chloromethane, $CHCl_3$. Considering the role of the solvent's chemical structure, note that the solubility of oxygen in the liquid hydrocarbon hexane, C_6H_{14}, is approximately 20 times greater than it is in water.

Other factors also affect the solubility of a given substance in a given solvent. Temperature is one such factor, with gas solubility typically decreasing as temperature increases (Figure 9.2.2.1). This is one of the major impacts resulting from the thermal pollution of natural bodies of water.

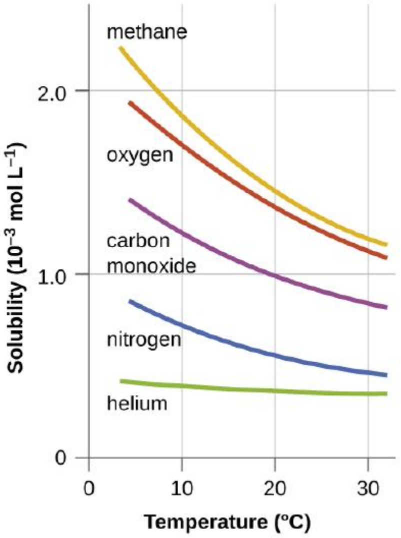

Figure 9.2.2.1: The solubilities of these gases in water decrease as the temperature increases. All solubilities were measured with a constant pressure of 101.3 kPa (1 atm) of gas above the solutions.

When the temperature of a river, lake, or stream is raised abnormally high, usually due to the discharge of hot water from some industrial process, the solubility of oxygen in the water is decreased. Decreased levels of dissolved oxygen may have serious consequences for the health of the water's ecosystems and, in severe cases, can result in large-scale fish kills (Figure 9.2.2.2).

Figure 9.2.2.2: (a) The small bubbles of air in this glass of chilled water formed when the water warmed to room temperature and the solubility of its dissolved air decreased. (b) The decreased solubility of oxygen in natural waters subjected to thermal pollution can result in large-scale fish kills. (Credit a: modification of work by Liz West; credit b: modification of work by U.S. Fish and Wildlife Service.)

The solubility of a gaseous solute is also affected by the partial pressure of solute in the gas to which the solution is exposed. Gas solubility increases as the pressure of the gas increases. Carbonated beverages provide a nice illustration of this relationship. The carbonation process involves exposing the beverage to a relatively high pressure of carbon dioxide gas and then sealing the beverage container, thus saturating the beverage with CO_2 at this pressure. When the beverage container is opened, a familiar hiss is heard as the carbon dioxide gas pressure is released, and some of the dissolved carbon dioxide is typically seen leaving solution in the form of small bubbles (Figure $9.2.2.3$). At this point, the beverage is *supersaturated* with carbon dioxide and, with time, the dissolved carbon dioxide concentration will decrease to its equilibrium value and the beverage will become "flat."

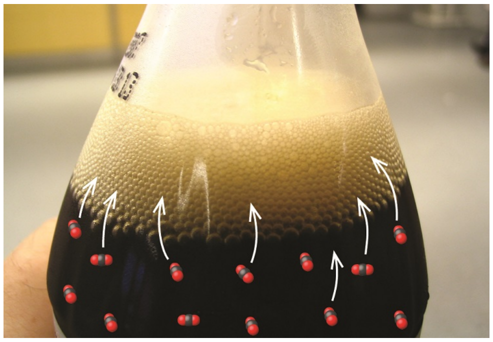

Figure $9.2.2.3$: Opening the bottle of carbonated beverage reduces the pressure of the gaseous carbon dioxide above the beverage. The solubility of CO_2 is thus lowered, and some dissolved carbon dioxide may be seen leaving the solution as small gas bubbles. (Credit: modification of work by Derrick Coetzee.)

"Fizz"

The dissolution in a liquid, also known as fizz, usually involves carbon dioxide under high pressure. When the pressure is reduced, the carbon dioxide is released from the solution as small bubbles, which causes the solution to become effervescent, or fizzy. A common example is the dissolving of carbon dioxide in water, resulting in carbonated water.

Carbon dioxide is weakly soluble in water, therefore it separates into a gas when the pressure is released. This process is generally represented by the following reaction, where a pressurized dilute solution of carbonic acid in water releases gaseous carbon dioxide at decompression:

$$H_2CO_3(aq) \rightarrow H_2O(l) + CO_2(g)$$

In simple terms, it is the result of the chemical reaction occurring in the liquid which produces a gaseous product.

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9.3: Measures of Concentration

Learning Objectives

- Understand what is meant by the term solution concentration.

To define a solution precisely, we need to state its concentration: how much solute is dissolved in a certain amount of solvent. Words such as *dilute* or *concentrated* are used to describe solutions that have a little or a lot of dissolved solute, respectively, but these are relative terms with meanings that depend on various factors.

Concentration is the measure of how much of a given substance is mixed with another substance. Solutions are said to be either dilute or concentrated. When we say that vinegar is 5% acetic acid in water, we are giving the concentration. If we said the mixture was 10% acetic acid, this would be more concentrated than the vinegar solution.

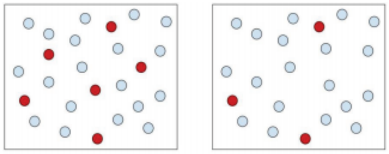

Figure $9.3.1$: The solution on the left is more concentrated than the solution on the right because there is a greater ratio of solute (red balls) to solvent (blue balls) particles. The solution particles are closer together. The solution on the right is more dilute (less concentrated). (CC-SA-BY-3.0 Tracy Poulsen).

A **concentrated** solution is one in which there is a large amount of solute in a given amount of solvent. A **dilute** solution is one in which there is a small amount of solute in a given amount of solvent. A dilute solution is a concentrated solution that has been, in essence, watered down. Think of the frozen juice containers you buy in the grocery store. To make juice, you have to mix the frozen juice concentrate from inside these containers with three or four times the container size full of water. Therefore, you are diluting the concentrated juice. In terms of solute and solvent, the concentrated solution has a lot of solute versus the dilute solution that would have a smaller amount of solute.

The terms "concentrated" and "dilute" provide qualitative methods of describing concentration. Although qualitative observations are necessary and have their place in every part of science, including chemistry, we have seen throughout our study of science that there is a definite need for quantitative measurements in science. This is particularly true in solution chemistry. In this section, we will explore some quantitative methods of expressing solution concentration.

There have been many ways that people have measured concentrations. We will be looking at a few of them in this book in the following subsections.

Contributors and Attributions

- Marisa Alviar-Agnew (Sacramento City College)
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9.3.1: Percent Solutions

There are human cultures that do not recognize numbers above three. Anything greater than that is simply referred to as "much" or "many". Although this form of calculation may seem very limited, American culture does the same thing to a certain degree. For example, there are several ways to express the amount of solute in a solution in a quantitative manner. The **concentration** of a solution is a measure of the amount of solute that has been dissolved in a given amount of solvent or solution. A **concentrated** solution is one that has a relatively large amount of dissolved solute. A **dilute** solution is one that has a relatively small amount of dissolved solute. However, those terms are vague, and it is often necessary to express concentration with numbers.

Percent Solutions

One way to describe the concentration of a solution is by the percent of a solute in the solvent. The percent can further be determined in one of two ways: (1) the ratio of the mass of the solute divided by the mass of the solution or (2) the ratio of the volume of the solute divided by the volume of the solution.

Mass Percent

When the solute in a solution is a solid, a convenient way to express the concentration is by mass percent $\left(\frac{\text{mass}}{\text{mass}}\right)$, which is the grams of solute per 100 g of solution.

$$\text{Percent by mass} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 100\%$$

Suppose that a solution was prepared by dissolving 25.0 g of sugar into 100 g of water. The percent by mass would be calculated by:

$$\text{Percent by mass} = \frac{25\text{ g sugar}}{125\text{ g solution}} \times 100\% = 20\%\text{ sugar}$$

Sometimes you may want to make up a particular mass of solution of a given percent by mass, and need to calculate what mass of the solvent to use. For example, you need to make 3000 g of a 5% solution of sodium chloride. You can rearrange and solve for the mass of solute:

$$\text{mass of solute} = \frac{\text{percent by mass}}{100\%} \times \text{mass of solution} = \frac{5\%}{100\%} \times 3000\text{ g} = 150\text{ g NaCl}$$

You would need to weigh out 150 g of NaCl and add it to 2850 g of water. Notice that it was necessary to subtract the mass of the NaCl (150 g) from the mass of solution (3000 g) to calculate the mass of the water that would need to be added.

Volume Percent

The percentage of solute in a solution can be determined by volume when the solute and solvent are both liquids. The volume of the solute divided by the volume of the solution, expressed as a percent, yields the percent by volume $\left(\frac{\text{volume}}{\text{volume}}\right)$ of the solution. If a solution is made by adding 40 mL of ethanol to enough water to make 240 mL of the resulting solution, the percent by volume is:

$$\begin{aligned} \text{Percent by volume } &= \frac{\text{volume of solute}}{\text{volume of solution}} \times 100\% \\ &= \frac{40\text{ mL ethanol}}{240\text{ mL solution}} \times 100\% \\ &= 16.7\%\text{ ethanol} \end{aligned}$$

Frequently, ingredient labels on food products and medicines have amounts listed as percentages (see figure below).

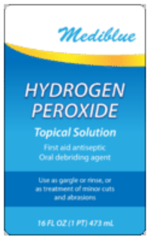


Figure 9.3.1.1: Hydrogen peroxide is commonly labeled as a 3% by volume solution for use as a disinfectant.

Summary

- The concentration of a solution is a measure of the amount of solute that has been dissolved in a given amount of solvent or solution.
- A concentrated solution has a relatively large amount of dissolved solute.
- A dilute solution has a relatively small amount of dissolved solute.
- Techniques for calculation of percent mass and percent volume solution concentrations are described.

9.3.2: Solution Concentration- Molarity

Learning Objectives

- Use molarity to determine quantities in chemical reactions.
- Use molarity as a conversion factor in calculations.

Another way of expressing concentration 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.

$$\text{molarity} = \frac{\text{number of moles of solute}}{\text{number of liters of solution}} \tag{9.3.2.1}$$

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 $\left[\text{Ag}^+\right]$ 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

$$\frac{1.5 \text{ mol NaCl}}{0.500 \text{ L solution}} = 3.0 \text{ M NaCl} \tag{9.3.2.2}$$

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.

> *Be sure to note that molarity is calculated as the total volume of the* ***entire*** *solution, not just volume of solvent! The solute contributes to total volume.*

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. For example, what is the molar concentration of a solution of 22.4 g of HCl dissolved in 1.56 L?

First, convert the mass of solute to moles using the molar mass of HCl (36.5 g/mol):

$$22.4\, g\cancel{HCl} \times \frac{1\, mol\ HCl}{36.5\, g\cancel{HCl}} = 0.614\, mol\ HCl \tag{9.3.2.3}$$

Now we can use the definition of molarity to determine a concentration:

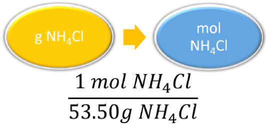
$$M\ = \frac{0.614\, mol\ HCl}{1.56 L\ solution} = 0.394\, M HCl \tag{9.3.2.4}$$

Before a molarity concentration can be calculated, the amount of the solute must be expressed in moles, and the volume of the solution must be expressed in liters, as demonstrated in the following example.

Example 9.3.2.1

A solution is prepared by dissolving 42.23 g of NH_4Cl into enough water to make 500.0 mL of solution. Calculate its molarity.

Solution

Steps for Problem Solving	
Identify the "given" information and what the problem is asking you to "find."	Given: Mass $= 42.23 \text{ g NH}_4\text{Cl}$ Volume solution $= 500.0 \text{ mL} = 0.5000 \text{ L}$ Find: Molarity = ? M
List other known quantities.	Molar mass $\text{NH}_4\text{Cl} = 53.50 \text{ g/mol}$
Plan the problem.	1. The mass of the ammonium chloride is first converted to moles.  2. Then the molarity is calculated by dividing by liters. Note the given volume has been converted to liters. $\text{M} = \frac{\text{mol NH}_4\text{Cl}}{\text{L solution}}$
Cancel units and calculate.	Now substitute the known quantities into the equation and solve. $$42.23 \text{ g } \cancel{\text{NH}_4\text{Cl}} \times \frac{1 \text{ mol } \cancel{\text{NH}_4\text{Cl}}}{53.50 \text{ g NH}_4\text{Cl}} = 0.7893 \text{ mol NH}_4\text{Cl} \tag{9.3.2.5}$$ $$\frac{0.7893 \text{ mol NH}_4\text{Cl}}{0.5000 \text{ L solution}} = 1.579 \text{ M} \tag{9.3.2.6}$$

Steps for Problem Solving	
Think about your result.	The molarity is 1.579 M, meaning that a liter of the solution would contain 1.579 mol NH_4Cl. Four significant figures are appropriate.

? Exercise 9.3.2.1

What is the molarity of a solution made when 66.2 g of $C_6H_{12}O_6$ are dissolved to make 235 mL of solution?

Answer

1.57 M $C_6H_{12}O_6$

? Exercise 9.3.2.2

What is the concentration, in $\mathrm{mol/L}$, where $137\ \mathrm{g}$ of NaCl has been dissolved in enough water to make $500\ \mathrm{mL}$ of solution?

Answer

4.69 M NaCl

Using Molarity in Calculations

Concentration can be a conversion factor between the amount of solute and the amount of solution or solvent (depending on the definition of the concentration unit). As such, concentrations can be useful in a variety of stoichiometry problems. In many cases, it is best to use the original definition of the concentration unit; it is that definition that provides the conversion factor.

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 do the calculation again as a unit conversion, rather than as a definition.

Determining Moles of Solute, Given the Concentration and Volume of a Solution

For example, suppose we ask how many moles of solute are present in 0.108 L of a 0.887 M NaCl solution. Because 0.887 M means 0.887 mol/L, we can use this second expression for the concentration as a conversion factor:

Solution

$$\frac{0.887\ mol\ NaCl}{1\ L\ solution}$$

$$0.108\ L\ \cancel{NaCl} \times \frac{0.887\, mol\ NaCl}{1 L\ \cancel{solution}} = 0.0958\, mol\ NaCl \tag{9.3.2.7}$$

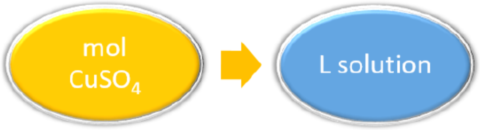
If we used the definition approach, we get the same answer, but now we are using conversion factor skills. Like any other conversion factor that relates two different types of units, the reciprocal of the concentration can be also used as a conversion factor.

Determining Volume of a Solution, Given the Concentration and Moles of Solute

Using concentration as a conversion factor, how many liters of 2.35 M $CuSO_4$ are needed to obtain 4.88 mol 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:



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

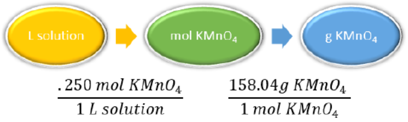
$$4.88\ mol\ \cancel{CuSO_4} \times \frac{1\ L\ solution}{2.35\ mol\ \cancel{CuSO_4}} = 2.08\ L\ of\ solution \tag{9.3.2.8}$$

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 9.3.2.2

A chemist needs to prepare $3.00\ \text{L}$ of a $0.250\ \text{M}$ solution of potassium permanganate $\left(\text{KMnO}_4\right)$. What mass of KMnO_4 does she need to make the solution?

Solution

Steps for Problem Solving	
Identify the "given" information and what the problem is asking you to "find."	Given: Molarity $= 0.250\ \text{M}$ Volume $= 3.00\ \text{L}$ Find: Mass $\text{KMnO}_4 = ?\ \text{g}$
List other known quantities.	Molar mass $\text{KMnO}_4 = 158.04\ \text{g/mol}$ 0.250 mol $KMnO_4$ to 1 L of $KMnO_4$ solution
Plan the problem.	
Cancel units and calculate.	Now substitute the known quantities into the equation and solve. $\text{mol KMnO}_4 = 0.250\ \text{M KMnO}_4 \times 3.00\ \text{L} = 0.750\ \text{mol K}$ $3.00\ L\ \cancel{solution} \times \frac{0.250\ \text{mol}\ \cancel{\text{KMnO}_4}}{1\ L\ \cancel{solution}} \times \frac{158.04\ \text{g KMnO}_4}{1\ \text{mol}\ \cancel{\text{KMnO}_4}} = 119\ \text{g KMn}$
Think about your result.	When $119\ \text{g}$ of potassium permanganate is dissolved into water to make $3.00\ \text{L}$ of solution, the molarity is $0.250\ \text{M}$.

? Exercise 9.3.2.3

Using concentration as a conversion factor, how many liters of 0.0444 M CH_2O are needed to obtain 0.0773 mol of CH_2O?

Answer

1.74 L

? Exercise 9.3.2.4

Answer the problems below using concentration as a conversion factor.

a. What mass of solute is present in 1.08 L of 0.0578 M H_2SO_4?
b. What volume of 1.50 M HCl solution contains 10.0 g of hydrogen chloride?

Answer a

6.12 g

Answer b

183 mL or 0.183L

How to Indicate Concentration

- Square brackets are often used to represent concentration, e.g., [NaOH] = 0.50 M.
- Use the capital letter M for molarity, not a lower case m (this is a different concentration unit called *molality*).

Watch as the Flinn Scientific Tech Staff demonstrates "How To Prepare Solutions."

It is important to note that there are many different ways you can set up and solve your chemistry equations. Some students prefer to answer multi-step calculations in one long step, while others prefer to work out each step individually. Neither method is necessarily better or worse than the other method—whichever makes the most sense to ***you*** is the one that you should use. In this text, we will typically use unit analysis (also called dimension analysis or factor analysis).

Contributors and Attributions

- Peggy Lawson (Oxbow Prairie Heights School). Funded by Saskatchewan Educational Technology Consortium.
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9.4: Concentration Calculations

Many examples of calculations based on the molarity concept were already introduced in the previous section. In this section, we will build on those ideas by looking at some specific calculations which involve molarity. Please make sure you are comfortable with the molarity concept before continuing in this section.

9.4.1: A Mole Map for Concentration

When we make stoichiometric calculations on solutions, we will be using molarity as the measure of concentration. Remember, the formula for molarity is:

$$\text{molarity} = \frac{\text{number of moles of solute}}{\text{number of liters of solution}} \tag{9.4.1.1}$$

You have already seen a few examples of calculations using the definition of molarity. There are numerous possible ways to use the molarity concept in a calculation. You could be using molarity as a conversion factor to find either moles of solute for liters of solution. Or you could be finding the molarity if provided the moles of solute and liters of solution. And of course, the point of a mole roadmap is to have a method for going through a series of several calculations, so you would not necessarily be given everything that is suggested in the examples above in every single problem.

Take a moment to add something to your mole roadmap which incorporates the concept of molarity along with the concepts already listed in your mole roadmap. Please refer back to the examples in the section where molarity was first introduced as you come up with your mole roadmap. Once you have completed your mole roadmap, move on through the remainder of the subsections and see if applying your mole roadmap works for solving the problems listed there. If not, revise your mole roadmap as appropriate.

9.4.2: Solution Dilution

Learning Objectives

- Explain how concentrations can be changed in the lab.
- Understand how stock solutions are used in the laboratory.

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. These terms also do not tell us whether or not the solution is saturated or unsaturated, or whether the solution is "strong" or "weak". These last two terms will have special meanings when we discuss acids and bases, so be careful not to confuse them.

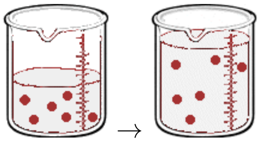
Stock Solutions

It is often necessary to have a solution with a concentration that is very precisely known. Solutions containing a precise mass of solute in a precise volume of solution are called **stock (or standard) solutions.** To prepare a standard solution, a piece of lab equipment called a volumetric flask should be used. These flasks range in size from 10 mL to 2000 mL and are carefully calibrated to a single volume. On the narrow stem is a **calibration mark**. The precise mass of solute is dissolved in a bit of the solvent, and this is added to the flask. Then, enough solvent is added to the flask until the level reaches the calibration mark.

Often, it is convenient to prepare a series of solutions of known concentrations by first preparing a single **stock solution**, as described in the previous section. **Aliquots** (carefully measured volumes) of the stock solution can then be diluted to any desired volume. In other cases, it may be inconvenient to weigh a small mass of sample accurately enough to prepare a small volume of a dilute solution. Each of these situations requires that a solution be diluted to obtain the desired concentration.

Dilutions of Stock (or Standard) Solutions

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:



Before Dilution and After Dilution

The molarity of solution 1 is

$$M_1 = \frac{\text{moles}_1}{\text{liter}_1}$$

and the molarity of solution 2 is

$$M_2 = \frac{\text{moles}_2}{\text{liter}_2}$$

rearrange the equations to find moles:

$$\text{moles}_1 = M_1 \text{liter}_1$$

and

$$\text{moles}_2 = M_2 \text{liter}_2$$

What stayed the same and what changed between the two solutions? 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,

$$moles_1 = moles_2$$

Therefore

$$\boxed{M_1 V_1 = M_2 V_2} \tag{9.4.2.1}$$

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

Preparing dilutions is a common activity in the chemistry lab and elsewhere. Once you understand the above relationship, the calculations are simple.

Suppose that you have $100.\ \text{mL}$ of a $2.0\ \text{M}$ solution of HCl. You dilute the solution by adding enough water to make the solution volume $500.\ \text{mL}$. The new molarity can easily be calculated by using the above equation and solving for M_2.

$$M_2 = \frac{M_1 \times V_1}{V_2} = \frac{2.0\ \text{M} \times 100.\ \text{mL}}{500.\ \text{mL}} = 0.40\ \text{M HCl}$$

The solution has been diluted by one-fifth since the new volume is five times as great as the original volume. Consequently, the molarity is one-fifth of its original value.

Another common dilution problem involves calculating what amount of a highly concentrated solution is required to make a desired quantity of solution of lesser concentration. The highly concentrated solution is typically referred to as the stock solution.

✓ Example 9.4.2.1: Diluting Nitric Acid

Nitric acid $\left(\text{HNO}_3\right)$ is a powerful and corrosive acid. When ordered from a chemical supply company, its molarity is $16\ \text{M}$. How much of the stock solution of nitric acid needs to be used to make $8.00\ \text{L}$ of a $0.50\ \text{M}$ solution?

Solution

Solutions to Example13.7.1

Steps for Problem Solving	
Identify the "given" information and what the problem is asking you to "find."	Given: M_1, Stock $\text{HNO}_3 = 16\ \text{M}$ $V_2 = 8.00\ \text{L}$ $M_2 = 0.50\ \text{M}$ Find: Volume stock $\text{HNO}_3\ (V_1) = ?\ \text{L}$
List other known quantities.	none
Plan the problem.	First, rearrange the equation algebraically to solve for V_1. $$V_1 = \frac{M_2 \times V_2}{M_1}$$
Calculate and cancel units.	Now substitute the known quantities into the equation and solve. $$V_1 = \frac{0.50\ \text{M} \times 8.00\ \text{L}}{16\ \text{M}} = 0.25\ \text{L} = 250\ \text{mL}$$
Think about your result.	$250\ \text{mL}$ of the stock HNO_3 needs to be diluted with water to a final volume of $8.00\ \text{L}$. The dilution is by a factor of 32 to go from 16 M to 0.5 M.

Exercise 9.4.2.1

A 0.885 M solution of KBr with an initial volume of 76.5 mL has more water added until its concentration is 0.500 M. What is the new volume of the solution?

Answer

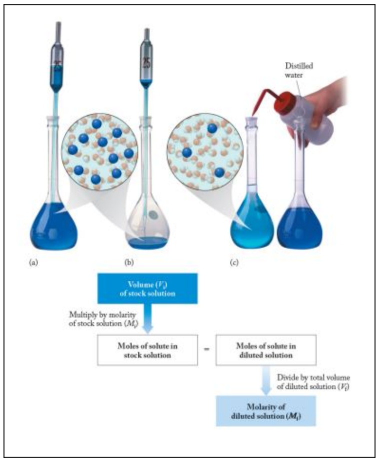
135.4 mL

Note that the calculated volume will have the same dimensions as the input volume, and dimensional analysis tells us that in this case we don't need to convert to liters, since L cancels when we divide M (mol/L) by M (mol/L).

Diluting and Mixing Solutions

Diluting and Mixing Solutions

How to Dilute a Solution by CarolinaBiological



9.5: Colligative Properties and Molality

Colligative properties are properties that differ based on the concentration of solute in a solvent, but not on the type of solute. What changes are the properties of the solvent. What causes this change is the number of solute particles in the solution. As we will see, solute particles refers to the number of particles as they exist in solution which may be different than the number of particles as they exist prior to being dissolved. For covalent compounds this will be the same, but for ionic compounds this will be different as the solvent falls apart the compound into ions.

There are several colligative properties, but we will be looking at just a few of them in this textbook. First we will look at changes in the temperatures of phase changes (both melting point and boiling point). Then we will look at changes related to flow across membranes. All three of these colligative properties are things that affect our everyday lives.

Before we begin this discussion, it is necessary to learn about a new concentration unit. It is called **Molality (*m*).**

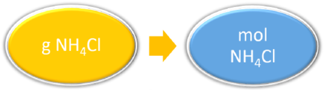
$$\text{molality} = \frac{\text{number of moles of solute}}{\text{number of kilograms of solvent}} \tag{9.5.1}$$

Molality differs from other concentration units we have discussed in that the quantity on the bottom of the fraction is just the solvent mass, not the total solution.

✓ Example 9.5.1

A solution is prepared by dissolving $42.23\ \text{g}$of NH_4Cl into $500.0\ \text{g}$of water. Calculate its molality.

Solution

Steps for Problem Solving	
Identify the "given" information and what the problem is asking you to "find."	Given: Mass Solute $= 42.23\ \text{g NH}_4\text{Cl}$ Mass Solvent $= 500.0\ \text{g} = 0.5000\ \text{kg}$ Find: Molality = ? *m*
List other known quantities.	Molar mass $\text{NH}_4\text{Cl} = 53.50\ \text{g/mol}$
Plan the problem.	1. The mass of the ammonium chloride is first converted to moles.  $\frac{1\ mol\ NH_4Cl}{53.50g\ NH_4Cl}$ 2. Then the molarity is calculated by dividing by liters. Note the given volume has been converted to liters. $\text{m} = \frac{\text{mol NH}_4\text{Cl}}{\text{kg solvent}}$
Cancel units and calculate.	Now substitute the known quantities into the equation and solve. $42.23\ \cancel{\text{g NH}_4\text{Cl}} \times \frac{1\ \text{mol NH}_4\cancel{\text{Cl}}}{53.50\ \text{g NH}_4\text{Cl}} = 0.7893\ \text{mol NH}_4\text{Cl}$ (9.5.2 $\frac{0.7893\ \text{mol NH}_4\text{Cl}}{0.5000\ \text{kg solvent}} = 1.579\ m$ (9.5.3
Think about your result.	The molality is $1.579\ m$, meaning that a liter of water would contain $1.579\ \text{mol NH}_4\text{Cl}$. Four significant figures are appropriate.

9.5.1: Freezing Point Depression and Boiling Point Elevation

Learning Objectives

- Explain what the term "colligative" means, and list the colligative properties.
- Indicate what happens to the boiling point and the freezing point of a solvent when a solute is added to it.
- Calculate boiling point elevations and freezing point depressions for a solution.

People who live in colder climates have seen trucks put salt on the roads when snow or ice is forecast. Why is this done? As a result of the information you explore in this section, you will understand why these events occur. You will also learn to calculate exactly how much of an effect a specific solute can have on the boiling point or freezing point of a solution.

The example given in the introduction is an example of a colligative property. **Colligative properties** are properties that differ based on the concentration of solute in a solvent, but not on the type of solute. What this means for the example above is that people in colder climates do not necessarily need salt to get the same effect on the roads—any solute will work. However, the higher the concentration of solute, the more these properties will change.

Boiling Point Elevation

Water boils at 100^oC at $1 \: \text{atm}$ of pressure, but a solution of saltwater does not . When table salt is added to water, the resulting solution has a higher boiling point than the water did by itself. The ions form an attraction with the solvent particles that prevents the water molecules from going into the gas phase. Therefore, the saltwater solution will not boil at 100^oC. In order for the saltwater solution to boil, the temperature must be raised about 100^oC. This is true for any solute added to a solvent; the boiling point will be higher than the boiling point of the pure solvent (without the solute). In other words, when anything is dissolved in water, the solution will boil at a higher temperature than pure water would.

The boiling point elevation due to the presence of a solute is also a colligative property. That is, the amount of change in the boiling point is related to the number of particles of solute in a solution and is not related to the chemical composition of the solute. A $0.20 \: \text{m}$solution of table salt and a $0.20 \: \text{m}$solution of hydrochloric acid would have the same effect on the boiling point.

Freezing Point Depression

The effect of adding a solute to a solvent has the opposite effect on the freezing point of a solution as it does on the boiling point. A solution will have a lower freezing point than a pure solvent. The **freezing point** is the temperature at which the liquid changes to a solid. At a given temperature, if a substance is added to a solvent (such as water), the solute-solvent interactions prevent the solvent from going into the solid phase. The solute-solvent interactions require the temperature to decrease further in order to solidify the solution. A common example is found when salt is used on icy roadways. Salt is put on roads so that the water on the roads will not freeze at the normal 0^oC but at a lower temperature, as low as -9^oC. The de-icing of planes is another common example of freezing point depression in action. A number of solutions are used, but commonly a solution such as ethylene glycol, or a less toxic monopropylene glycol, is used to de-ice an aircraft. The aircrafts are sprayed with the solution when the temperature is predicted to drop below the freezing point. The **freezing point depression** is the difference in the freezing points of the solution from the pure solvent. This is true for any solute added to a solvent; the freezing point of the solution will be lower than the freezing point of the pure solvent (without the solute). Thus, when anything is dissolved in water, the solution will freeze at a lower temperature than pure water would.

The freezing point depression due to the presence of a solute is also a colligative property. That is, the amount of change in the freezing point is related to the number of particles of solute in a solution and is not related to the chemical composition of the solute. A $0.20 \: \text{m}$solution of table salt and a $0.20 \: \text{m}$solution of hydrochloric acid would have the same effect on the freezing point.

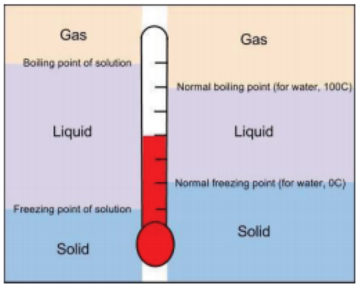


Figure 9.5.1.1: Comparison of boiling and freezing points of a pure liquid (right side) with a solution (left side).

Comparing the Freezing and Boiling Point of Solutions

Recall that covalent and ionic compounds do not dissolve in the same way. Ionic compounds break up into cations and anions when they dissolve. Covalent compounds typically do not break up. For example a sugar/water solution stays as sugar and water, with the sugar molecules staying as molecules. Remember that colligative properties are due to the number of solute particles in the solution. Adding 10 molecules of sugar to a solvent will produce 10 solute particles in the solution. When the solute is ionic, such as $NaCl$ however, adding 10 formulas of solute to the solution will produce 20 ions (solute particles) in the solution. Therefore, adding enough $NaCl$ solute to a solvent to produce a $0.20\ m$ solution will have twice the effect of adding enough sugar to a solvent to produce a $0.20\ m$ solution. Colligative properties depend on the number of solute particles in the solution.

"i" is the number of particles that the solute will dissociate into upon mixing with the solvent. For example, sodium chloride, $NaCl$, will dissociate into two ions so for $NaCl$, $i = 2$; for lithium nitrate, $LiNO_3$, $i = 2$; and for calcium chloride, $CaCl_2$, $i = 3$. For covalent compounds, i is always equal to 1.

By knowing the *molality* of a solution and the number of particles a compound will dissolve to form, it is possible to predict which solution in a group will have the lowest freezing point. To compare the boiling or freezing points of solutions, follow these general steps:

1. Label each solute as ionic or covalent.
2. If the solute is ionic, determine the number of *ions* in the formula. Be careful to look for polyatomic ions.
3. Multiply the original molality (m) of the solution by the number of particles formed when the solution dissolves. This will give you the total concentration of particles dissolved.
4. Compare these values. The higher total concentration will result in a higher boiling point and a lower freezing point.

✓ Example 9.5.1.1

Rank the following solutions in water in order of *increasing* (lowest to highest) freezing point:

- $0.1\ m\ NaCl$
- $0.1\ m\ C_6H_{12}O_6$
- $0.1\ m\ CaI_2$

Solution

To compare freezing points, we need to know the total concentration of all particles when the solute has been dissolved.

- $0.1\ m\ NaCl$: This compound is ionic (metal with nonmetal), and will dissolve into 2 parts. The total final concentration is: $(0.1\ m)(2) = 0.2\ m$
- $0.1\ m\ C_6H_{12}O_6$: This compound is covalent (nonmetal with nonmetal), and will stay as 1 part. The total final concentration is: $(0.1\ m)(1) = 0.1\ m$
- $0.1\ m\ CaI_2$: This compound is ionic (metal with nonmetal), and will dissolve into 3 parts. The total final concentration is: $(0.1\ m)(3) = 0.3\ m$

Remember, the greater the concentration of particles, the lower the freezing point will be. $0.1\ m\ CaI_2$ will have the lowest freezing point, followed by $0.1\ m\ NaCl$, and the highest of the three solutions will be $0.1\ m\ C_6H_{12}O_6$, but all three of them will have a lower freezing point than pure water.

The boiling point of a solution is higher than the boiling point of a pure solvent, and the freezing point of a solution is lower than the freezing point of a pure solvent. However, the amount to which the boiling point increases or the freezing point decreases depends on the amount of solute that is added to the solvent. A mathematical equation is used to calculate the boiling point elevation or the freezing point depression.

The boiling point elevation is the amount that the boiling point temperature *increases* compared to the original solvent. For example, the boiling point of pure water at $1.0\ \mathrm{atm}$ is $100^{\circ}\mathrm{C}$ while the boiling point of a 2% saltwater solution is about $102^{\circ}\mathrm{C}$. Therefore, the boiling point elevation would be $2^{\circ}\mathrm{C}$. The freezing point depression is the amount that the freezing temperature *decreases*.

Both the boiling point elevation and the freezing point depression are related to the molality of the solution. Looking at the formula for the boiling point elevation and freezing point depression, we see similarities between the two. The equation used to calculate the increase in the boiling point is:

$$\Delta T_b = k_b \cdot \mathrm{m} \cdot i \tag{9.5.1.1}$$

Where:

- $\Delta T_b =$ the amount the boiling point increases.
- $k_b =$ the boiling point elevation constant which depends on the solvent (for water, this number is $0.515^{\circ}\mathrm{C}/\mathrm{m}$).
- $\mathrm{m} =$ the molality of the solution.
- $i =$ the number of particles formed when that compound dissolves (for covalent compounds, this number is always 1).

The following equation is used to calculate the decrease in the freezing point:

$$\Delta T_f = k_f \cdot \mathrm{m} \cdot i \tag{9.5.1.2}$$

Where:

- $\Delta T_f =$ the amount the freezing temperature decreases.
- $k_f =$ the freezing point depression constant which depends on the solvent (for water, this number is $1.86^{\circ}\mathrm{C}/\mathrm{m}$).
- $\mathrm{m} =$ the molality of the solution.
- $i =$ the number of particles formed when that compound dissolves (for covalent compounds, this number is always 1).

Table 9.5.1: Boiling and Freezing Constants of Selected Solvents

Substance	Chemical Formula	Normal Melting Point (°C)	Normal Boiling Point (°C)	K_f (°C/*m*)	K_b (°C/*m*)
Water	H_2O	0.0	100.0	1.86	0.512
Diethyl Ether	$C_4H_{10}O$	-116.3	34.5	1.76	2.02
Ethanol	C_2H_5OH	-114.1	78.3	1.99	1.22

Substance	Chemical Formula	Normal Melting Point (°C)	Normal Boiling Point (°C)	K_f (°C/*m*)	K_b (°C/*m*)
Benzene	C_6H_6	5.50	80.1	5.10	2.53

Example 9.5.1.2: Adding Antifreeze to Protein Engines

Antifreeze is used in automobile radiators to keep the coolant from freezing. In geographical areas where winter temperatures go below the freezing point of water, using pure water as the coolant could allow the water to freeze. Since water expands when it freezes, freezing coolant could crack engine blocks, radiators, and coolant lines. The main component in antifreeze is ethylene glycol, $\text{C}_2\text{H}_4(\text{OH})_2$. What is the concentration of ethylene glycol in a solution of water, in molality, if the freezing point dropped by 2.64^{o}C? The freezing point constant, k_f, for water is $1.86^{o}\text{C}/\text{m}$.

Solution

Use the equation for freezing point depression of solution (Equation 9.5.1.2):

$$\Delta T_f = k_f \cdot \text{m} \cdot i$$

Substituting in the appropriate values we get:

$$2.64^{o}\text{C} = (1.86^{o}\text{C}/\text{m})\,(\text{m})\,(1)$$

Solve for m by dividing both sides by $1.86^{o}\text{C}/\text{m}$.

$$\text{m} = 1.42$$

Example 9.5.1.3: Adding Salt to Elevate Boiling Temperature

A solution of $10.0\ \text{g}$ of sodium chloride is added to $100.0\ \text{g}$ of water in an attempt to elevate the boiling point. What is the boiling point of the solution? k_b for water is $0.512^{o}\text{C}/\text{m}$.

Solution

Use the equation for boiling point elevation of solution (Equation 9.5.1.1):

$$\Delta T_b = k_b \cdot \text{m} \cdot i$$

We need to be able to substitute each variable into this equation.

- $k_b = 0.52^{o}\text{C}/\text{m}$
- m: We must solve for this using stoichiometry. Given: $10.0\ \text{g NaCl}$ and $100.0\ \text{g H}_2\text{O}$ Find: $\text{mol NaCl}/\text{kg H}_2\text{O}$. Ratios: molar mass of NaCl, $1000\ \text{g} = 1\ \text{kg}$

$$\frac{10.0\ \ \text{g}\ \cancel{\text{NaCl}}}{100.0\ \ \text{g}\ \cancel{\text{H}_2\text{O}}} \cdot \frac{1\ \text{mol NaCl}}{58.45\ \ \text{g}\ \cancel{\text{NaCl}}} \cdot \frac{1000\ \ \text{g}\ \cancel{\text{H}_2\text{O}}}{1\ \text{kg H}_2\text{O}} = 1.71\ \text{m}$$

- For NaCl, $i = 2$

Substitute these values into the equation $\Delta T_b = k_b \cdot \text{m} \cdot i$. We get:

$$\Delta T_b = \left(0.512 \frac{^\text{o}\text{C}}{\cancel{\text{m}}}\right)(1.71\ \cancel{\text{m}})(2) = 1.75^\text{o}\text{C}$$

Water normally boils at 100^oC, but our calculation shows that the boiling point increased by 1.75^oC. Our new boiling point is 101.75^oC.

Note: Since sea water contains roughly 28.0 g of NaCl per liter, this saltwater solution is approximately **four times** more concentrated than sea water (all for a 2° C rise of boiling temperature).

Summary

- Colligative properties are properties that are due only to the number of particles in solution, and are not related to the chemical properties of the solute.
- Boiling points of solutions are higher than the boiling points of the pure solvents.
- Freezing points of solutions are lower than the freezing points of the pure solvents.
- Ionic compounds split into ions when they dissolve, forming more particles. Covalent compounds stay as complete molecules when they dissolve.

Vocabulary

- **Colligative property** - A property that is due only to the number of particles in solution, and not the type of the solute.
- **Boiling point elevation** - The amount that the boiling point of a solution increases from the boiling point of the pure solvent.
- **Freezing point depression** - The amount that the freezing point of a solution decreases from the freezing point of the pure solvent.

9.5.2: Osmosis

Learning Objectives

- Explain the how osmosis works.

Before we introduce the final colligative property, we need to present a new concept. A **semipermeable membrane** is a thin membrane that will pass certain small molecules, but not others. A thin sheet of cellophane, for example, acts as a semipermeable membrane. Consider the system in Figure $9.5.2.1$.

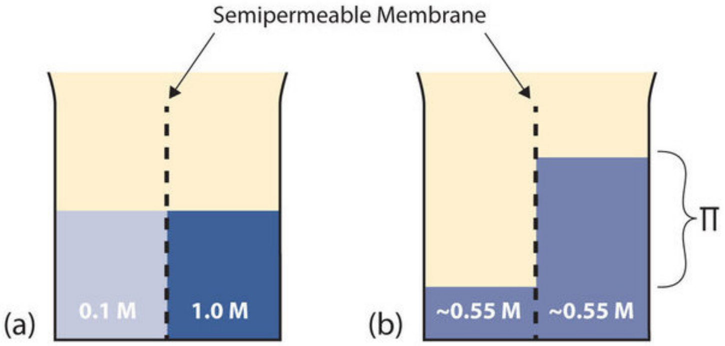


Figure $9.5.2.1$: Osmosis. (a) Two solutions of differing concentrations are placed on either side of a semipermeable membrane. (b) When osmosis occurs, solvent molecules selectively pass through the membrane from the dilute solution to the concentrated solution, diluting it until the two concentrations are the same. The pressure exerted by the different height of the solution on the right is called the osmotic pressure. (CC BY-SA-NC 3.0; anonymous)

a. A semipermeable membrane separates two solutions having the different concentrations marked. Curiously, this situation is not stable; there is a tendency for water molecules to move from the dilute side (on the left) to the concentrated side (on the right) until the concentrations are equalized, as in Figure $9.5.2.1b$.
b. This tendency is called **osmosis**. In osmosis, the solute remains in its original side of the system; only solvent molecules move through the semipermeable membrane. In the end, the two sides of the system will have different volumes. Because a column of liquid exerts a pressure, there is a pressure difference (Π) on the two sides of the system that is proportional to the height of the taller column. This pressure difference is called the **osmotic pressure**, which is a colligative property.

The osmotic pressure of a solution is easy to calculate:

$$\Pi = MRT \tag{9.5.2.1}$$

where Π is the osmotic pressure of a solution, M is the molarity of the solution, R is the ideal gas law constant, and T is the absolute temperature. This equation is reminiscent of the ideal gas law we considered in Chapter 6.

Example $9.5.2.5$: Osmotic Pressure

What is the osmotic pressure of a 0.333 M solution of $C_6H_{12}O_6$ at 25°C?

Solution

First we need to convert our temperature to kelvins:

$$T = 25 + 273 = 298 \text{ K}$$

Now we can substitute into the equation for osmotic pressure, recalling the value for R:

$$\Pi = (0.333 M)\left(0.08205 \frac{L.\,atm}{mol.\,K}\right)(298 K)$$

The units may not make sense until we realize that molarity is defined as moles per liter:

$$\Pi = \left(0.333 \frac{mol}{L}\right)\left(0.08205 \frac{L.\,atm}{mol.\,K}\right)(298 K)$$

Now we see that the moles, liters, and kelvins cancel, leaving atmospheres, which is a unit of pressure. Solving,

$$\Pi = 8.14\, atm$$

This is a substantial pressure! It is the equivalent of a column of water 84 m tall.

Exercise 9.5.2.5

What is the osmotic pressure of a 0.0522 M solution of $C_{12}H_{22}O_{11}$ at 55°C?

Answer

1.40 atm

Osmotic pressure is important in biological systems because cell walls are semipermeable membranes. In particular, when a person is receiving intravenous (IV) fluids, the osmotic pressure of the fluid needs to be approximately the same as blood serum to avoid any negative consequences. Figure $9.5.2.3$shows three red blood cells:

- A healthy red blood cell.
- A red blood cell that has been exposed to a lower concentration than normal blood serum (a *hypotonic* solution); the cell has plumped up as solvent moves into the cell to dilute the solutes inside.
- A red blood cell exposed to a higher concentration than normal blood serum (*hypertonic*); water leaves the red blood cell, so it collapses onto itself. Only when the solutions inside and outside the cell are the same (*isotonic*) will the red blood cell be able to do its job.

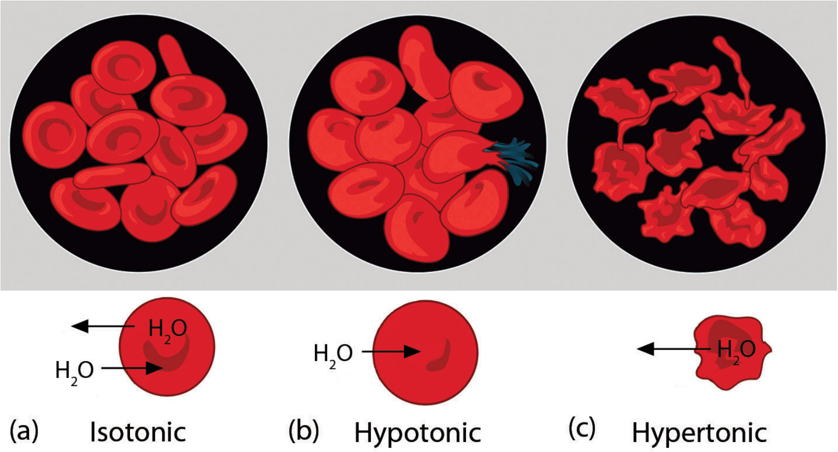


Figure $9.5.2.3$: Osmotic Pressure and Red Blood Cells. (a) This is what a normal red blood cell looks like. (b) When a red blood cell is exposed to a hypotonic solution, solvent goes through the cell membrane and dilutes the inside of the cell. (c) When a red blood cell is exposed to a hypertonic solution, solvent goes from the cell to the surrounding solution, diluting the hypertonic solution and collapsing the cell. Neither of these last two cases is desirable, so IV solutions must be isotonic with blood serum to not cause deleterious effects. (Public Domain; Mariana Ruiz Villareal)

Osmotic pressure is also the reason you should not drink seawater if you're stranded on a lifeboat in the ocean; seawater has a higher osmotic pressure than most of the fluids in your body. You *can* drink the water, but ingesting it will pull water out of your cells as osmosis works to dilute the seawater. Ironically, your cells will die of thirst, and you will also die. (It is okay to drink the water if you are stranded on a body of freshwater, at least from an osmotic pressure perspective.) Osmotic pressure is also thought to be important—in addition to capillary action—in getting water to the tops of tall trees.

Summary

- Osmotic pressure is caused by concentration differences between solutions separated by a semipermeable membrane, and is an important biological consideration.

Contributions & Attributions

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9.E: Solutions (Exercises)

The following questions are related to the material covered in this chapter. For additional discussion on each topic, also check the links included in each heading.

Solubility

1. Which of the following are likely to dissolve in water?
   a. A polar molecule with hydrogen bonding
   b. A non-polar molecule
   c. An ionic compound
2. Which of the following ionic compounds would you expect to dissolve in water?
   a. $NaCl$
   b. $BaCO_3$
   c. Al_2S_3
   d. $Al(NO_3)_3$
   e. $(NH_4)_3PO_4$
3. Classify each of the following as strong electrolyte, weak electrolyte, or non-electrolyte
   a. $NaCl$
   b. HCl
   c. $NaOH$
   d. CH_3OH
   e. $HC_2H_3O_2$
4. A solution of $SrCl_2$ is 0.664 M. What are the molarities of Sr^{2+} and Cl^- in this solution?

Answers

1. a. Dissolves in water, b. Does not dissolve in water, c. Maybe, see solubility rules
2. $NaCl$, $Al(NO_3)_3$, $(NH_4)_3PO_4$
3. $NaCl$ = strong, HCl = strong, $NaOH$ = strong, CH_3OH = non-electrolyte, $HC_2H_3O_2$ = weak electrolyte
4. 0.664 M Sr^{2+}, 1.33 M Cl^-

Dilutions and Concentrations

1. What is the difference between dilution and concentration?
2. What quantity remains constant when you dilute a solution?
3. A 1.88 M solution of NaCl has an initial volume of 34.5 mL. What is the final concentration of the solution if it is diluted to 134 mL?
4. A 0.664 M solution of NaCl has an initial volume of 2.55 L. What is the final concentration of the solution if it is diluted to 3.88 L?
5. If 1.00 mL of a 2.25 M H_2SO_4 solution needs to be diluted to 1.00 M, what will be its final volume?
6. If 12.00 L of a 6.00 M HNO_3 solution needs to be diluted to 0.750 M, what will be its final volume?
7. If 665 mL of a 0.875 M KBr solution are boiled gently to concentrate the solute to 1.45 M, what will be its final volume?
8. If 1.00 L of an LiOH solution is boiled down to 164 mL and its initial concentration is 0.00555 M, what is its final concentration?
9. How much water must be added to 75.0 mL of 0.332 M $FeCl_3(aq)$ to reduce its concentration to 0.250 M?
10. How much water must be added to 1.55 L of 1.65 M $Sc(NO_3)_3(aq)$ to reduce its concentration to 1.00 M?

Answers

1. Dilution is a decrease in a solution’s concentration, whereas concentration is an increase in a solution’s concentration.
2.
3. 0.484 M

4.
5. 2.25 mL
6.
7. 401 mL
8.
9. 24.6 mL

Concentrations as Conversion Factors

1. Using concentration as a conversion factor, how many moles of solute are in 3.44 L of 0.753 M $CaCl_2$?
2. Using concentration as a conversion factor, how many moles of solute are in 844 mL of 2.09 M $MgSO_4$?
3. Using concentration as a conversion factor, how many liters are needed to provide 0.822 mol of NaBr from a 0.665 M solution?
4. Using concentration as a conversion factor, how many liters are needed to provide 2.500 mol of $(NH_2)_2CO$ from a 1.087 M solution?
5. What is the mass of solute in 24.5 mL of 0.755 M $CoCl_2$?
6. What is the mass of solute in 3.81 L of 0.0232 M $Zn(NO_3)_2$?
7. What volume of solution is needed to provide 9.04 g of NiF_2 from a 0.332 M solution?
8. What volume of solution is needed to provide 0.229 g of CH_2O from a 0.00560 M solution?
9. What volume of 3.44 M HCl will react with 5.33 mol of $CaCO_3$? $2HCl + CaCO_3 \rightarrow CaCl_2 + H_2O + CO_2$
10. What volume of 0.779 M NaCl will react with 40.8 mol of $Pb(NO_3)_2$? $Pb(NO_3)_2 + 2NaCl \rightarrow PbCl_2 + 2NaNO_3$
11. What volume of 0.905 M H_2SO_4 will react with 26.7 mL of 0.554 M NaOH? $H_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + 2H_2O$
12. What volume of 1.000 M Na_2CO_3 will react with 342 mL of 0.733 M H_3PO_4? $3Na_2CO_3 + 2H_3PO_4 \rightarrow 2Na_3PO_4 + 3H_2O + 3CO_2$
13. It takes 23.77 mL of 0.1505 M HCl to titrate with 15.00 mL of $Ca(OH)_2$. What is the concentration of $Ca(OH)_2$? You will need to write the balanced chemical equation first.
14. It takes 97.62 mL of 0.0546 M NaOH to titrate a 25.00 mL sample of H_2SO_4. What is the concentration of H_2SO_4? You will need to write the balanced chemical equation first.
15. It takes 4.667 mL of 0.0997 M HNO_3 to dissolve some solid Cu. What mass of Cu can be dissolved? $Cu + 4HNO_3(aq) \rightarrow Cu(NO_3)_2(aq) + 2NO_2 + 2H_2O$
16. It takes 49.08 mL of 0.877 M NH_3 to dissolve some solid AgCl. What mass of AgCl can be dissolved? $AgCl(s) + 4NH_3(aq) \rightarrow Ag(NH_3)_4Cl(aq)$
17. What mass of 3.00% H_2O_2 is needed to produce 66.3 g of $O_2(g)$? $2H_2O_2(aq) \rightarrow 2H_2O(\ell) + O_2(g)$
18. A 0.75% solution of Na_2CO_3 is used to precipitate Ca^{2+} ions from solution. What mass of solution is needed to precipitate 40.7 L of solution with a concentration of 0.0225 M $Ca^{2+}(aq)$?

$Na_2CO_3(aq) + Ca^{2+}(aq) \rightarrow CaCO_3(s) + 2Na^{+}(aq)$

Answers

1. 2.59 mol
2.
3. 1.24 L
4.
5. 2.40 g
6.
7. 0.282 L
8.
9. 3.10 L
10.
11. 8.17 mL
12.
13. 0.1192 M
14.
15. 7.39 mg
16.

17. 4.70 kg

Colligative Properties of Solutions

1. What are the three colligative properties that involve phase changes?
2. Which colligative property does not involve a phase change? Give an example of its importance.
3. If 45.0 g of C_6H_6 and 60.0 g of $C_6H_5CH_3$ are mixed together, what is the mole fraction of each component?
4. If 125 g of N_2 are mixed with 175 g of O_2, what is the mole fraction of each component?
5. If 36.5 g of NaCl are mixed with 63.5 g of H_2O, what is the mole fraction of each component?
6. An alloy of stainless steel is prepared from 75.4 g of Fe, 12.6 g of Cr, and 10.8 g of C. What is the mole fraction of each component?
7. A solution is made by mixing 12.0 g of $C_{10}H_8$ in 45.0 g of C_6H_6. If the vapor pressure of pure C_6H_6 is 76.5 torr at a particular temperature, what is the vapor pressure of the solution at the same temperature?
8. A solution is made by mixing 43.9 g of $C_6H_{12}C_6$ in 100.0 g of H_2O. If the vapor pressure of pure water is 26.5 torr at a particular temperature, what is the vapor pressure of the solution at the same temperature?
9. At 300°C, the vapor pressure of Hg is 32.97 torr. If 0.775 g of Au were dissolved into 3.77 g of Hg, what would be the vapor pressure of the solution?
10. At 300°C, the vapor pressure of Hg is 32.97 torr. What mass of Au would have to be dissolved in 5.00 g of Hg to lower its vapor pressure to 25.00 torr?

*For the following problems, you will want to access table 9.5.1.

11. If 25.0 g of $C_6H_{12}O_6$ are dissolved in 0.100 kg of H_2O, what is the boiling point of this solution?
12. If 123 g of $C_{10}H_{16}O$ are dissolved in 355 g of C_6H_6, what is the boiling point of this solution?
13. If 1 mol of solid CBr_4 is mixed with 2 mol of CCl_4, what is the boiling point of this solution?
14. A solution of $C_2H_2O_4$ in CH_3COOH has a boiling point of 123.40°C. What is the molality of the solution?
15. If 0.808 mol of $C_{10}H_{16}O$ are dissolved in 0.355 kg of C_6H_6, what is the freezing point of this solution?
16. If 25.0 g of $C_6H_{12}O_6$ are dissolved in 100.0 g of H_2O, what is the freezing point of this solution?
17. $C_8H_{17}OH$ is a nonvolatile solid that dissolves in C_6H_{12}. If 7.22 g of $C_8H_{17}OH$ is dissolved in 45.3 g of C_6H_{12}, what is the freezing point of this solution?
18. A solution of $C_2H_2O_4$ in CH_3COOH has a freezing point of 10.00°C. What is the molality of the solution?
19. If 25.0 g of $C_6H_{12}O_6$ are dissolved in H_2O to make 0.100 L of solution, what is the osmotic pressure of this solution at 25°C?
20. If 2.33 g of $C_{27}H_{46}O$ are dissolved in liquid CS_2 to make 50.00 mL of solution, what is the osmotic pressure of this solution at 298 K?
21. At 298 K, what concentration of solution is needed to have an osmotic pressure of 1.00 atm?
22. The osmotic pressure of blood is about 7.65 atm at 37°C. What is the approximate concentration of dissolved solutes in blood? (There are many different solutes in blood, so the answer is indeed an approximation.)

Answers

1. boiling point elevation, freezing point depression, vapor pressure depression
2.
3. mole fraction C_6H_6: 0.469; mole fraction $C_6H_5CH_3$: 0.531
4.
5. mole fraction NaCl: 0.157; mole fraction H_2O: 0.843
6.
7. 65.8 torr
8.
9. 27.26 torr
10.
11. 100.71°C
12.
13. 92.9°C
14.
15. −6.11°C

16.
17. −18.3°C
18.
19. 33.9 atm
20.
21. 0.0409 M

? Additional Exercises

1. One brand of ethyl alcohol (Everclear) is 95% ethyl alcohol, with the remaining 5% being water. What is the solvent and what is the solute of this solution?
2. Give an example of each type of solution from your own experience.
    a. A solution composed of a gas solute in a liquid solvent.
    b. A solution composed of a solid solute in a liquid solvent.
    c. A solution composed of a liquid solute in a liquid solvent.
    d. A solution composed of a solid solute in a solid solvent. (Hint: usually such solutions are made as liquids and then solidified.)
3. Differentiate between the terms *saturated* and *concentrated*.
4. Differentiate between the terms *unsaturated* and *dilute*.
5. What mass of $FeCl_2$ is present in 445 mL of 0.0812 M $FeCl_2$ solution?
6. What mass of SO_2 is present in 26.8 L of 1.22 M SO_2 solution?
7. What volume of 0.225 M $Ca(OH)_2$ solution is needed to deliver 100.0 g of $Ca(OH)_2$?
8. What volume of 12.0 M HCl solution is needed to obtain exactly 1.000 kg of HCl?
9. The World Health Organization recommends that the maximum fluoride ion concentration in drinking water is 1.0 ppm. Assuming water has the maximum concentration, if an average person drinks 1,920 mL of water per day, how many milligrams of fluoride ion are being ingested?
10. For sanitary reasons, water in pools should be chlorinated to a maximum level of 3.0 ppm. In a typical 5,000 gal pool that contains 21,200 kg of water, what mass of chlorine must be added to obtain this concentration?
11. Given its notoriety, you might think that uranium is very rare, but it is present at about 2–4 ppm of the earth's crust, which is more abundant than silver or mercury. If the earth's crust is estimated to have a mass of 8.50×10^{20} kg, what range of mass is thought to be uranium in the crust?
12. Chromium is thought to be an ultratrace element, with about 8.9 ng present in a human body. If the average body mass is 75.0 kg, what is the concentration of chromium in the body in pptr?
13. What mass of 3.00% H_2O_2 solution is needed to produce 35.7 g of $O_2(g)$ at 295 K at 1.05 atm pressure?

    $2H_2O_2(aq) \rightarrow 2H_2O(\ell) + O_2(g)$
14. What volume of pool water is needed to generate 1.000 L of $Cl_2(g)$ at standard temperature and pressure if the pool contains 4.0 ppm HOCl and the water is slightly acidic? The chemical reaction is as follows:

    $HOCl(aq) + HCl(aq) \rightarrow H_2O(\ell) + Cl_2(g)$

    Assume the pool water has a density of 1.00 g/mL.
15. A 0.500 *m* solution of $MgCl_2$ has a freezing point of −2.60°C. What is the true van 't Hoff factor of this ionic compound? Why is it less than the ideal value?
16. The osmotic pressure of a 0.050 M LiCl solution at 25.0°C is 2.26 atm. What is the true van 't Hoff factor of this ionic compound? Why is it less than the ideal value?
17. Order these solutions in order of increasing boiling point, assuming an ideal van 't Hoff factor for each: 0.10 *m* $C_6H_{12}O_6$, 0.06 *m* NaCl, 0.4 *m* $Au(NO_3)_3$, and 0.4 *m* $Al_2(SO_4)_3$.

18. Order these solutions in order of decreasing osmotic pressure, assuming an ideal van 't Hoff factor: 0.1 M HCl, 0.1 M $CaCl_2$, 0.05 M $MgBr_2$, and 0.07 M $Ga(C_2H_3O_2)_3$

Answers

1. solvent: ethyl alcohol; solute: water
2.
3. Saturated means all the possible solute that can dissolve is dissolved, whereas concentrated implies that a lot of solute is dissolved.
4.
5. 4.58 g
6.
7. 6.00 L
8.
9. 1.92 mg
10.
11. 1.7×10^{15} to 3.4×10^{15} kg
12.
13. 2,530 g
14.
15. 2.80; it is less than 3 because not all ions behave as independent particles.
16.
17. 0.10 m $C_6H_{12}O_6$ < 0.06 m NaCl < 0.4 m $Au(NO_3)_3$ < 0.4 m $Al_2(SO_4)_3$

CHAPTER OVERVIEW

10: Chemical Reactions

We first introduced the idea of a chemical change in a previous chapter. This idea can also be referred to as a chemical reaction. We use chemical equations to keep track of these chemical changes. In the first 3 sections of this chapter we introduce ideas about chemical equations that will be important to understand in later chapters. In section 5.4 and 5.5 we introduce ideas related to categorizing and predicting reactions. Categorizing and predicting reactions will both show up in later chapters. This is your first glimpse of something that will continue to be important going forward.

10.1: Word Equations

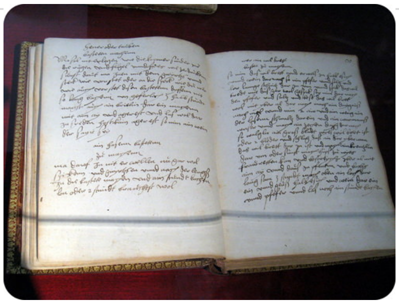


Figure 10.1.1 (Credit: User:Daderot/Wikimedia Commons; Source: http://commons.wikimedia.org/wiki/File:Innsbruck_-_Schloss_Ambras_-_cookbook_of_Philippine_Welser.jpg(opens in new window); License: Public Domain)

What's for Dinner?

Various ways of recording recipes have developed over the centuries. The cookbook shown above was written by a woman who probably collected all her own recipes. Later, printed cookbooks became available (even guys had no excuse for not being able to cook). Today we can find recipes on a number of internet sites and can quickly search for information on how to cook anything we want. Reading a recipe sometimes requires we understand a few codes and symbols (what's the difference between a tsp and a Tsp?), but the information on what we start with and what we end up with is there.

Writing Chemical Equations

Chemical reactions are occurring all around us. Plants use sunlight to drive their photosynthetic process and produce energy. Cars and other vehicles burn gasoline in order to power their engines. Batteries use electrochemical reactions to produce energy and power many everyday devices. Many chemical reactions are going on within the human body as well, particularly during the digestion of food.

In math class, you have written and solved many mathematical equations. Chemists keep track of chemical reactions by writing equations as well. In any chemical reaction, one or more substances—called **reactants**—are converted into one or more new substances—called **products**. The general form of the equation for such a process looks like this:

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

Unlike a math equation, a chemical equation does not use an equal sign. Instead, the arrow is called a yield sign and so the equation is described as "reactants yield products".

Word Equations

You can describe a chemical reaction by writing a **word equation**. When silver metal is exposed to sulfur, it reacts to form silver sulfide. Silver sulfide is commonly known as tarnish and turns the surface of silver objects dark and streaky black (see figure below). The sulfur that contributes to tarnish can come from traces of sulfur in the air, or from foods such as eggs. The word equation for the process is:

$$\text{Silver} + \text{sulfur} \rightarrow \text{Silver sulfide}$$

The silver and the sulfur are the reactants in the equation, while the silver sulfide is the product.

Figure 10.1.2**:** You can see dark spots of tarnished (silver sulfide) forming on this ring as it reacts with sulfur compounds in the air. (Credit: CK-12 Foundation; Source: CK-12 Foundation; License: CK-12 Curriculum Materials license)

Another common chemical reaction is the burning of methane gas. Methane is the major component of natural gas and is commonly burned on a gas stove or in a Bunsen burner (figure below). Burning is a chemical reaction in which some type of fuel is reacted with oxygen gas. The products of the reaction in the burning of methane, as well as other fuels, are carbon dioxide and water. The word equation for this reaction is:

$$\text{Methane} + \text{oxygen} \rightarrow \text{carbon dioxide} + \text{water}$$

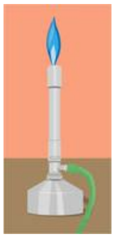


Figure 10.1.3: A Bunsen burner is commonly used to heat substances in a chemistry lab. Methane is reacted with oxygen to form carbon dioxide and water. (Credit: CK-12 Foundation; Source: CK-12 Foundation; License: CK-12 Curriculum Materials license)

Word equations can be very useful, but do have one major drawback—they cannot be used for any quantitative work. A word equation does not tell how many moles of each material are needed, or how many moles of product are formed.

Summary

- Word equations are used to describe the conversion of reactants to products.

Review

1. Write the generic form of a chemical reaction.
2. What are reactants?
3. What are products?

10.2: Chemical Equations

Figure 10.2.1 (Credit: jons2 at pdphoto.org; Source: http://commons.wikimedia.org/wiki/File:Shrimp_gumbo.jpg(opens in new window); License: Public Domain)

How do you make shrimp gumbo?

Shrimp gumbo is one of many dishes that are part of the Cajun culture in Louisiana. It's a spicy dish that needs careful control of all the ingredients so that it has a "kick", but is not overwhelming. Recipes convey not only what the preparation entails, but also describe how much of each ingredient is needed, and the details of how to cook the meal. Similarly, we need this type of information in order to carry out chemical reactions successfully and safely.

Chemical Equations

Word equations are time-consuming to write and do not prove to be convenient for many of the things that chemists need to do with equations. A **chemical equation** is a representation of a chemical reaction that displays the reactants and products with chemical formulas. The chemical equation for the reaction of methane with oxygen is shown:

$$\mathrm{CH_4 + O_2 \rightarrow CO_2 + H_2O}$$

The equation above, called a **skeleton equation**, is an equation that shows only the formulas of the reactants and products with nothing to indicate the relative amounts. The first step in writing an accurate chemical equation is to write the skeleton equation, making sure that the formulas of all substances involved are written correctly. All reactants are written to the left of the yield arrow, separated from one another by a plus sign. Likewise, products are written to the right of the yield arrow, also separated with a plus sign.

It is often important to know the physical states of the reactants and products taking part in a reaction. To do this, put the appropriate symbol in parentheses after each formula: (s) for solid, (l) for liquid, (g) for gas, and (aq) for an aqueous (water-based) solution. The previous reaction becomes:

$$\mathrm{CH_4}\,(g) + \mathrm{O_2}\,(g) \rightarrow \mathrm{CO_2}\,(g) + \mathrm{H_2O}\,(l)$$

The table below shows a listing of symbols used in chemical equations. Some, such as the double arrow which represents equilibrium, and the use of a catalyst in a reaction, will be detailed in other concepts.

Table 10.2.1: Symbols Used in Chemical Equations

Symbols	Description
$+$	Used to separate multiple reactants or products.
$\rightarrow$	Yield sign; separates reactants from products.
$\rightleftharpoons$	Replaces the yield sign for reversible reactions that reach equilibrium.
(s)	Reactant or product in the solid state.
(l)	Reactant or product in the liquid state.
(g)	Reactant or product in the gaseous state.
(aq)	Reactant or product in an aqueous solution (dissolved in water).

Symbols	Description
$\xrightarrow{\text{Pt}}$	Formula written above the arrow is used as a catalyst in the reaction.
$\xrightarrow{\Delta}$	Triangle indicates that the reaction is being heated.

Summary

- A chemical equation is representation a chemical reaction using chemical formulas reactants and products, as well as symbols.
- Symbols used in chemical equations are described and explained.

Review

1. What does a skeleton equation tell you?
2. Why would you want to know the physical state of materials in a chemical reaction?
3. In a chemical reaction what does symbol → mean?
4. If I see Δ over the arrow, what does this indicate?

10.3: Balancing Equations

Figure 10.3.1 (Credit: Joseph Allen; Source: http://commons.wikimedia.org/wiki/File:John_Dalton.jpeg(opens in new window); License: Public Domain)

Any leftovers?

When you cook a meal, quite often there are leftovers because you prepared more than people would eat at one sitting. Sometimes when you repair a piece of equipment, you end up with what are called "pocket parts"—small pieces you put in your pocket because you're not sure where they belong. Chemistry tries to avoid leftovers and pocket parts. In normal chemical processes, we cannot create or destroy matter (law of conservation of mass). If we start out with ten carbon atoms, we need to end up with ten carbon atoms. John Dalton's atomic theory said that chemical reactions basically involve the rearrangement of atoms. Chemical equations need to follow these principles in order to be correct.

Balancing Chemical Equations

A **balanced equation** is a chemical equation in which mass is conserved and there are equal numbers of atoms of each element on both sides of the equation. We can write a chemical equation for the reaction of carbon with hydrogen gas to form methane $\left(CH_4\right)$:

$$\begin{array}{ccccc} \mathrm{C}\left(s\right) & + & \mathrm{H_2}\left(g\right) & \rightarrow & \mathrm{CH_4}\left(g\right) \\ 2 \text{ C atoms} & & 2 \text{ H atoms} & & 1 \text{ C atom, } 4 \text{ H atoms} \end{array}$$

In order to write a correct equation, you must first write the correct skeleton equation with the correct chemical formulas. Recall that hydrogen is a diatomic molecule and so is written as H_2.

When we count the number of atoms of both elements, shown under the equation, we see that the equation is not balanced. There are only 2 atoms of hydrogen on the reactant side of the equation, while there are 4 atoms of hydrogen on the product side. We can balance the above equation by adding a coefficient of 2 in front of the formula for hydrogen.

$$\mathrm{C}\left(s\right)+2\mathrm{H_2}\left(g\right)\rightarrow\mathrm{CH_4}\left(g\right)$$

A **coefficient** is a small whole number placed in front of a formula in an equation in order to balance it. The 2 in front of the H_2 means that there are a total of $2 \times 2 = 4$ atoms of hydrogen as reactants. Visually, the reaction looks like the figure below.

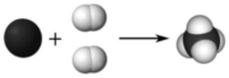


Figure 10.3.2: Reaction between carbon and hydrogen to form methane. (Credit: Ben Mills (Wikimedia: Benjah-bmm27; Source: http://commons.wikimedia.org/wiki/File:Dihydrogen-3D-vdW.png(opens in new window) and http://commons.wikimedia.org/wiki/File:Methane-3D-space-filling.png(opens in new window); License: Public Domain)

In the balanced equation, there is one atom of carbon and four atoms of hydrogen on both sides of the arrow. Below are guidelines for writing and balancing chemical equations.

1. Determine the correct chemical formulas for each reactant and product.
2. Write the skeleton equation.
3. Count the number of atoms of each element that appears as a reactant and as a product. If a polyatomic ion is unchanged on both sides of the equation, count it as a unit.
4. Balance each element one at a time by placing coefficients in front of the formulas.
    a. It is best to begin by balancing elements that only appear in one chemical formula on each side of the equation.
    b. No coefficient is written for a 1.

   c. NEVER change the subscripts in a chemical formula—you can only balance equations by using coefficients.
5. Check each atom or polyatomic ion to be sure that they are equal on both sides of the equation.
6. Make sure that all coefficients are in the lowest possible ratio. If necessary, reduce to the lowest ratio.

10.3.1 Example : Balancing Chemical Equations

Aqueous solutions of lead (II) nitrate and sodium chloride are mixed. The products of the reaction are an aqueous solution of sodium nitrate and a solid precipitate of lead (II) chloride. Write the balanced chemical equation for this reaction.

Solution

Step 1: Plan the problem.

Follow the steps for writing and balancing a chemical equation listed in the text.

Step 2: Solve.

Write the skeleton equation with the correct formulas.

$$\mathrm{Pb(NO_3)_2}\,(aq) + \mathrm{NaCl}\,(aq) \rightarrow \mathrm{NaNO_3}\,(aq) + \mathrm{PbCl_2}\,(s)$$

Count the number of each atom or polyatomic ion on both sides of the equation.

Reactants	**Products**
1 Pb atom	1 Pb atom
2 $\mathrm{NO_3^-}$ ions	1 $\mathrm{NO_3^-}$ ions
1 Na atom	1 Na atom
1 Cl atom	2 Cl atoms

The nitrate ions and the chlorine atoms are unbalanced. Start by placing a 2 in front of the NaCl. This increases the reactant counts to 2 Na atoms and 2 Cl atoms. Then place a 2 in front of the $\mathrm{NaNO_3}$. The result is:

$$\mathrm{Pb(NO_3)_2}\,(aq) + 2\mathrm{NaCl}\,(aq) \rightarrow 2\mathrm{NaNO_3}\,(aq) + \mathrm{PbCl_2}\,(s)$$

The new count for each atom and polyatomic ion becomes:

Reactants	**Products**
1 Pb atom	1 Pb atom
2 $\mathrm{NO_3^-}$ ions	2 $\mathrm{NO_3^-}$ ions
2 Na atom	2 Na atom
2 Cl atom	2 Cl atoms

Step 3: Think about your result.

The equation is now balanced since there are equal numbers of atoms of each element on both sides of the equation.

Summary

- The process of balancing chemical equations is described.

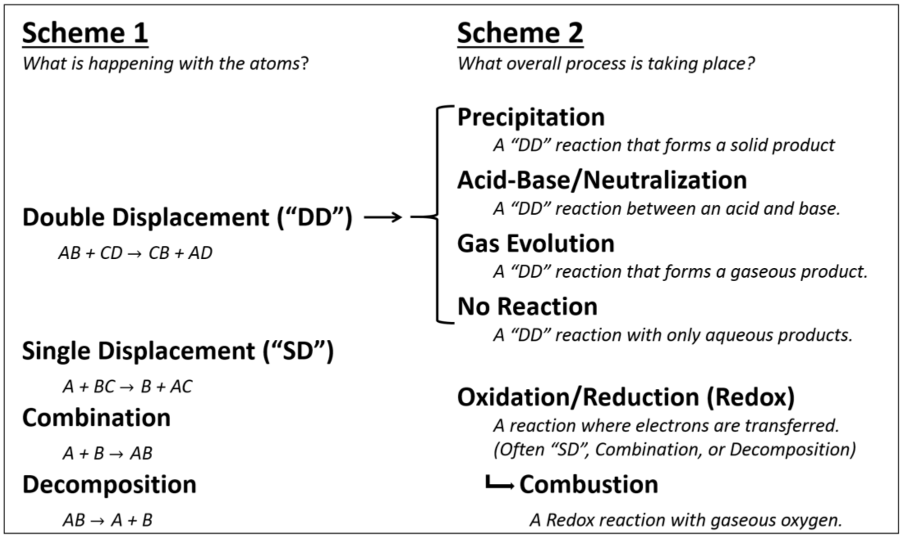
Review

1. What is the law of conservation of mass?
2. How did Dalton describe the process of a chemical reaction?
3. Why don’t we change the subscripts in order to balance an equation?

10.4: Types of Reactions

There are several ways to categorize chemical reactions, more than can possibly be covered in a single Chemistry textbook. This textbook will categorize reactions in a few places, and this is the first place where we will see it. In this section we will categorize some reactions based on recognizing patterns in the changes to reactants and products without considering the chemical identities of those reactants and products. We will also look at one type of reaction where we do consider reactants and products in the categorization of it. Before we dive in, let's look at an overview of what will be discussed in the following pages.

Here's a neater version of the reaction types shown in the video. It helps to keep the "big picture" in mind when reading the details in the upcoming sections.



10.4.1: Combination Reactions

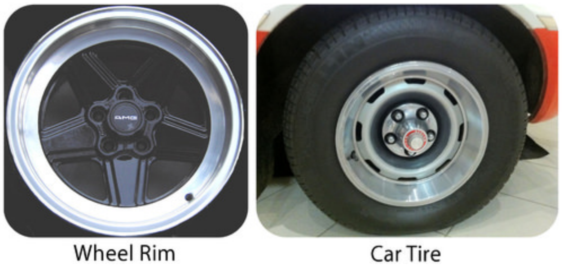


Figure 10.4.1.1 (Credit: Rim: User:Relaxatiallc/Wikimedia Commons; Wheel: Christopher Ziemnowicz; Source: Rim: http://commons.wikimedia.org/wiki/File:Ats_amgpenta.jpg(opens in new window); Wheel: http://commons.wikimedia.org/wiki/File:1975_AACA_AMC_Pacer_X_red-white_wheel.jpg(opens in new window); License: Public Domain)

How useful is a wheel rim?

A wheel rim is not very useful by itself. Driving on the rim can damage it and make for a very rough ride. When the rim is combined with a tire, the product can be put on a car and used for a safe and comfortable ride. The two separate items combine to make something that improves the car ride.

Combination Reactions

A **combination reaction** is a reaction in which two or more substances combine to form a single new substance. Combination reactions can also be called synthesis reactions. The general form of a combination reaction is:

$$\mathrm{A+B \rightarrow AB}$$

One combination reaction is two elements combining to form a compound. Solid sodium metal reacts with chlorine gas to produce solid sodium chloride.

$$\mathrm{2Na}\left(s\right)+\mathrm{Cl_2}\left(g\right)\rightarrow \mathrm{2NaCl}\left(s\right)$$

In order to write and balance the equation correctly, it is important to remember the seven elements that exist in nature as diatomic molecules: $\mathrm{H_2}$, $\mathrm{N_2}$, $\mathrm{O_2}$, $\mathrm{F_2}$, $\mathrm{Cl_2}$, $\mathrm{Br_2}$, and $\mathrm{I_2}$.

One sort of combination reaction that occurs frequently is the reaction of an element with oxygen to form an oxide. Metals and nonmetals both react readily with oxygen under most conditions. Magnesium reacts rapidly and dramatically when ignited, combining with oxygen from the air to produce a fine powder of magnesium oxide.

$$\mathrm{2Mg}\left(s\right)+\mathrm{O_2}\left(g\right)\rightarrow \mathrm{2MgO}\left(s\right)$$

Sulfur reacts with oxygen to form sulfur dioxide.

$$\mathrm{S}\,(s)+\mathrm{O}_2\,(g)\rightarrow \mathrm{SO}_2\,(g)$$

When nonmetals react with one another, the product is a molecular compound. Often, the nonmetal reactants can combine in different ratios and produce different products. Sulfur can also combine with oxygen to form sulfur trioxide.

$$2\mathrm{S}\,(s)+3\mathrm{O}_2\,(g)\rightarrow 2\mathrm{SO}_3\,(g)$$

Transition metals are capable of adopting multiple positive charges within their ionic compounds. Therefore, most transition metals are capable of forming different products in a combination reaction. Iron reacts with oxygen to form both iron (II) oxide and iron (III) oxide:

$$2\mathrm{Fe}\,(s)+\mathrm{O}_2\,(g)\rightarrow 2\mathrm{FeO}\,(s)$$

$$4\mathrm{Fe}\,(s)+3\mathrm{O}_2\,(g)\rightarrow 2\mathrm{Fe}_2\mathrm{O}_3\,(s)$$

10.4.1.1 Example : Combination Reactions

Potassium is a very reactive alkali metal that must be stored under oil in order to prevent it from reacting with air. Write the balanced chemical equation for the combination reaction of potassium with oxygen.

Solution

Step 1: Plan the problem.

Make sure formulas of all reactants and products are correct before balancing the equation. Oxygen gas is a diatomic molecule. Potassium oxide is an ionic compound and so its formula is constructed by the crisscross method. Potassium as an ion becomes K^+, while the oxide ion is O^{2-}.

Step 2: Solve.

The skeleton (unbalanced) equation:

$$\mathrm{K}\,(s) + \mathrm{O_2}\,(g) \rightarrow \mathrm{K_2O}\,(s)$$

The equation is then easily balanced with coefficients.

$$4\mathrm{K}\,(s) + \mathrm{O_2}\,(g) \rightarrow 2\mathrm{K_2O}\,(s)$$

Step 3: Think about your result.

Formulas are correct and the resulting combination reaction is balanced.

? Exercise 10.4.1.1

Can you build a balanced, combination reaction for the formation of aluminum oxide (Al_2O_3)?

Answer

$4Al + 3O_2 \rightarrow 2Al_2O_3$

Combination reactions can also take place when an element reacts with a compound to form a new compound composed of a larger number of atoms. Carbon monoxide reacts with oxygen to form carbon dioxide, according to the equation:

$$2\mathrm{CO}\,(g) + \mathrm{O_2}\,(g) \rightarrow 2\mathrm{CO_2}\,(g)$$

Two compounds may also react to form a more complex compound. A very common example is the reaction of an oxide with water. Calcium oxide reacts readily with water to produce an aqueous solution of calcium hydroxide.

$$\mathrm{CaO}\,(s) + \mathrm{H_2O}\,(l) \rightarrow \mathrm{Ca(OH)_2}\,(aq)$$

Sulfur trioxide gas reacts with water to form sulfuric acid. This is an unfortunately common reaction that occurs in the atmosphere in some places where oxides of sulfur are present as pollutants. The acid formed in the reaction falls to the ground as acid rain.

$$\mathrm{SO_3}\,(g) + \mathrm{H_2O}\,(l) \rightarrow \mathrm{H_2SO_4}\,(aq)$$

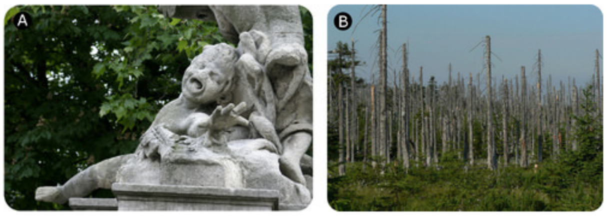


Figure 10.4.1.2: Acid rain has severe consequences on both natural and manmade objects. Acid rain degrades marble statues like the one on the left (A). The trees in the forest on the right (B) have been killed by acid rain. (Credit: (A) Nipik; (B) Nino Barbieri; Source: (A) http://commons.wikimedia.org/wiki/File:Acid_rain_woods1.JPG(opens in new window); (B) http://commons.wikimedia.org/wiki/File:Pollution_-_Damaged_by_acid_rain.jpg(opens in new window); License: (A) Public Domain; (B) CC by 2.5(opens in new window))

Summary

- Combination reactions occur when two or more substances combine to form a new substance.

Review

1. What are combination reactions?
2. Write the product of the following reaction: $Mg + H_2O \rightarrow$
3. Is $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$ a combination reaction? Explain your answer.

10.4.2: Decomposition Reactions

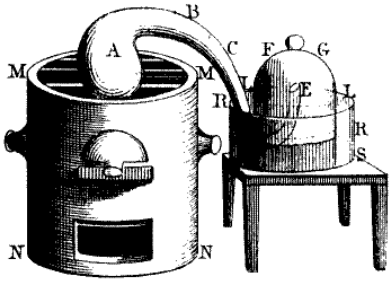


Figure 10.4.2.1 (Credit: Madame Lavoisier, modified by User: Cdang/Wikimedia Commons; Source: http://commons.wikimedia.org/wiki/File:Lavoisier_decomposition_air.png(opens in new window); License: Public Domain)

How does a decomposition reaction work?

Antoine Lavoisier is widely known as the “father of modern chemistry.” He was one of the first to study chemical reactions in detail. Lavoisier reacted mercury with oxygen to form mercuric oxide as part of his studies on the composition of the atmosphere. He was then able to show that the decomposition of mercuric oxide produced mercury and oxygen. The diagram above shows the apparatus used by Lavoisier to study the formation and decomposition of mercuric oxide.

Decomposition Reactions

A **decomposition reaction** is a reaction in which a compound breaks down into two or more simpler substances. The general form of a decomposition reaction is:

$$\mathrm{AB} \rightarrow \mathrm{A}+\mathrm{B}$$

Most decomposition reactions require an input of energy in the form of heat, light, or electricity.

Binary compounds are compounds composed of just two elements. The simplest kind of decomposition reaction is when a binary compound decomposes into its elements. Mercury (II) oxide, a red solid, decomposes when heated to produce mercury and oxygen gas.

$$2\mathrm{HgO}\,(s) \rightarrow 2\mathrm{Hg}\,(l)+\mathrm{O}_2\,(g)$$

Figure 10.4.2.2: *Mercury (II) oxide is a red solid. When it is heated, it decomposes into mercury metal and oxygen gas.* (Credit: Ben Mills (User:Benjah-bmm27/Wikimedia Commons); Source: http://commons.wikimedia.org/wiki/File:Mercury%2528II%2529-oxide.jpg(opens in new window); License: Public Domain)

A reaction is also considered to be a decomposition reaction even when one or more of the products are still compounds. A metal carbonate decomposes into a metal oxide and carbon dioxide gas. For example, calcium carbonate decomposes into calcium oxide and carbon dioxide:

$$\mathrm{CaCO}_3\,(s) \rightarrow \mathrm{CaO}\,(s)+\mathrm{CO}_2\,(g)$$

Metal hydroxides decompose on heating to yield metal oxides and water. Sodium hydroxide decomposes to produce sodium oxide and water:

$$2\mathrm{NaOH}\,(s) \rightarrow \mathrm{Na}_2\mathrm{O}\,(s)+\mathrm{H}_2\mathrm{O}\,(g)$$

Some unstable acids decompose to produce nonmetal oxides and water. Carbonic acid decomposes easily at room temperature into carbon dioxide and water:

$$H_2CO_3\,(aq) \rightarrow CO_2\,(g) + H_2O\,(l)$$

? Exercise 10.4.2.1

Can you build a balanced Chemical reaction for the decomposition of Potassium chlorate ($KClO_3$)?

Answer

$2KClO_3 \rightarrow 2KCl + 3O_2$

10.4.2.1 Example : Decomposition Reactions

When an electric current is passed through pure water, it decomposes into its elements. Write a balanced equation for the decomposition of water.

Solution

Step 1: Plan the problem.

Water is a binary compound composed of hydrogen and oxygen. The hydrogen and oxygen gases produced in the reaction are both diatomic molecules.

Step 2: Solve.

The skeleton (unbalanced) equation:

$$H_2O\,(l) \overset{\text{elec}}{\rightarrow} H_2\,(g) + O_2\,(g)$$

Note the abbreviation "elec" above the arrow to indicate the passage of an electric current to initiate the reaction. Balance the equation.

$$2H_2O\,(l) \overset{\text{elec}}{\rightarrow} 2H_2\,(g) + O_2\,(g)$$

Step 3: Think about your result.

The products are elements and the equation is balanced.

Summary

- A definition of decomposition reaction and example reactions are given.

Review

1. What is a decomposition reaction?
2. What is usually needed for a decomposition reaction to take place?
3. Are elements always the product of a decomposition reaction?

10.4.3: Combustion Reactions

Figure 10.4.3.1 (Credit: Nina Hale; Source: http://commons.wikimedia.org/wiki/File:RoastingMarshmallow.jpg(opens in new window); License: CC by 2.0(opens in new window))

How do you cook the perfect marshmallow?

Roasting marshmallows over an open fire is a favorite past-time for campers, outdoor cook-outs, and just gathering around a fire in the back yard. The trick is to get the marshmallow a nice golden brown without catching it on fire. Too often we are not successful and we see the marshmallow burning on the stick – a combustion reaction taking place right in front of us.

Combustion Reactions

A **combustion reaction** is a reaction in which a substance reacts with oxygen gas, releasing energy in the form of light and heat. Combustion reactions must involve O_2 as one reactant. The combustion of hydrogen gas produces water vapor:

$$2H_2\,(g) + O_2\,(g) \rightarrow 2H_2O\,(g)$$

Notice that this reaction also qualifies as a combination reaction.

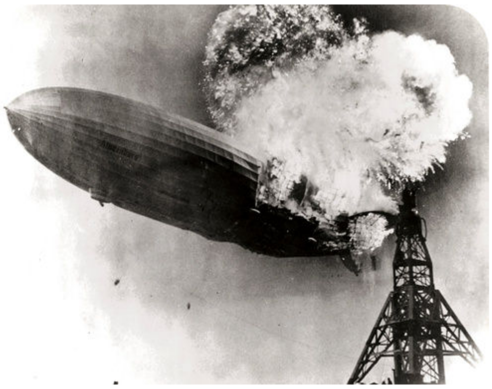


Figure 10.4.3.2: Explosion of the Hindenberg. (Credit: Courtesy of Gus Pasquerella/US Navy; Source: http://commons.wikimedia.org/wiki/File:Hindenburg_burning.jpg(opens in new window); License: Public Domain)

The *Hindenberg* was a hydrogen-filled airship that suffered an accident upon its attempted landing in New Jersey in 1937. The hydrogen immediately combusted in a huge fireball, destroying the airship and killing 36 people. The chemical reaction was a simple one: hydrogen combining with oxygen to produce water.

Many combustion reactions occur with a hydrocarbon, a compound made up solely of carbon and hydrogen. The products of the combustion of hydrocarbons are carbon dioxide and water. Many hydrocarbons are used as fuel because their combustion releases very large amounts of heat energy. Propane $\left(C_3H_8\right)$ is a gaseous hydrocarbon that is commonly used as the fuel source in gas grills.

$$C_3H_8\,(g) + 5O_2\,(g) \rightarrow 3CO_2\,(g) + 4H_2O\,(g)$$

10.4.3.1 Example : Combustion Reactions

Ethanol can be used as a fuel source in an alcohol lamp. The formula for ethanol is C_2H_5OH. Write the balanced equation for the combustion of ethanol.

Solution

Step 1: Plan the problem.

Ethanol and oxygen are the reactants. As with a hydrocarbon, the products of the combustion of an alcohol are carbon dioxide and water.

Step 2: Solve.

Write the skeleton equation:

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

Balance the equation.

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

Step 3: Think about your result.

Combustion reactions must have oxygen as a reactant. Note that the water produced is in the gas state, rather than the liquid state, because of the high temperatures that accompany a combustion reaction.

Summary

- Combustion reaction is defined and examples are given.

Review

1. What is needed for a combustion reaction to take place?
2. What is formed in any combustion reaction?
3. Mercury reacts with oxygen to form mercuric oxide. Is this a combustion reaction?
4. What are the products of any combustion reaction involving a hydrocarbon?

10.4.4: Single Displacement/Replacement Reactions

Figure 10.4.4.1 (Credit: wisteriax; Source: https://pixabay.com/photos/still-life-silver-poppies-2312788/(opens in new window); License: Pixabay License)

Why is the silver dark?

The platter and pitcher shown above provides an example of tarnish, a chemical reaction caued when silver metal reacts with hydrogen sulfide gas produced by some industrial processes or as a result of decaying animal or plant materials:

$$2\mathrm{Ag} + \mathrm{H_2S} \rightarrow \mathrm{Ag_2S} + \mathrm{H_2}$$

The tarnish can be removed using a number of polishes, but the process also removes a small amount of silver along with the tarnish.

Single-Replacement Reactions

A **single-replacement reaction** is a reaction in which one element replaces a similar element in a compound. The general form of a single-replacement (also called single-displacement) reaction is:

$$\mathrm{A} + \mathrm{BC} \rightarrow \mathrm{AC} + \mathrm{B}$$

In this general reaction, element A is a metal and replaces element B (also a metal) in the compound. When the element that is doing the replacing is a nonmetal, it must replace another nonmetal in a compound, and the general equation becomes:

$$\mathrm{Y} + \mathrm{XZ} \rightarrow \mathrm{XY} + \mathrm{Z}$$

(Where Y is a nonmetal and replaces the nonmetal Z in the compound with X.)

Metal Replacement

Magnesium is a more reactive metal than copper. When a strip of magnesium metal is placed in an aqueous solution of copper (II) nitrate, it replaces the copper. The products of the reaction are aqueous magnesium nitrate and solid copper metal.

$$\mathrm{Mg}\,(s) + \mathrm{Cu(NO_3)_2}\,(aq) \rightarrow \mathrm{Mg(NO_3)_2}\,(aq) + \mathrm{Cu}\,(s)$$

This subcategory of single-replacement reactions is called a metal replacement reaction because it is a metal that is being replaced (copper).

Hydrogen Replacement

Many metals react easily with acids and when they do so, one of the products of the reaction is hydrogen gas. Zinc reacts with hydrochloric acid to produce aqueous zinc chloride and hydrogen (figure below).

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

In a hydrogen replacement reaction, the hydrogen in the acid is replaced by an active metal.

Figure 10.4.4.2: Zinc metal reacts with hydrochloric acid to give off hydrogen gas in a single-displacement reaction. (Credit: User: Chemicalinterest/Wikimedia Commons; Source: http://commons.wikimedia.org/wiki/File:Zn_reaction_with_HCl.JPG(opens in new window); License: Public Domain)

Some metals are so reactive that they are capable of replacing the hydrogen in water. The products of such a reaction are the metal hydroxide and hydrogen gas. All group 1 metals undergo this type of reaction. Sodium reacts vigorously with water to produce aqueous sodium hydroxide and hydrogen (see figure below).

$$2\text{Na}\left(s\right)+2\text{H}_2\text{O}\left(l\right)\rightarrow 2\text{NaOH}\left(aq\right)+\text{H}_2\left(g\right)$$

Figure 10.4.4.3: Sodium metal reacts vigorously with water, giving off hydrogen gas. A large piece of sodium will often generate so much heat that the hydrogen will ignite. (Credit: User:Ajhalls/Wikimedia Commons; Source: http://commons.wikimedia.org/wiki/File:Large_Sodium_Explosion.jpg(opens in new window); License: Public Domain)

Halogen Replacement

The element chlorine reacts with an aqueous solution of sodium bromide to produce aqueous sodium chloride and elemental bromine:

$$\text{Cl}_2\left(g\right)+2\text{NaBr}\left(aq\right)\rightarrow 2\text{NaCl}\left(aq\right)+\text{Br}_2\left(l\right)$$

The reactivity of the halogen group (group 17) decreases from top to bottom within the group. Fluorine is the most reactive halogen, while iodine is the least. Since chlorine is above bromine, it is more reactive than bromine and can replace it in a halogen replacement reaction.

Summary

- The activity series describes the relative reactivities of metals and halogens.

Review

1. What is a metal replacement reaction?
2. Will a non-metal replace a metal?
3. What is the most reactive halogen?
4. What products will I get if I add potassium metal to water?

10.4.5: Double Displacement/Replacement Reactions

Figure 10.4.5.1 (Credit: F. S. Church, published in Harper's Weekly, January 17, 1874, p. 61; Source: http://commons.wikimedia.org/wiki/File:Barter-Chickens_for_Subscription.jpg(opens in new window); License: Public Domain)

Want to trade?

The practice of barter (trading one thing for another) has been in existence for a very long time. In the illustration above, items like chickens were bartered for newspapers. You have something I want, and I have something you want. So we trade and we each have something new. Some chemical reactions are like that. Compounds swap parts and you have new materials.

Double-Replacement Reactions

A **double-replacement reaction** is a reaction in which the positive and negative ions of two ionic compounds exchange places to form two new compounds. The general form of a double-replacement (also called double-displacement) reaction is:

$$\mathrm{AB} + \mathrm{CD} \rightarrow \mathrm{AD} + \mathrm{CB}$$

In this reaction, A and C are positively-charged cations, while B and D are negatively-charged anions. Double-replacement reactions generally occur between substances in aqueous solution. In order for a reaction to occur, one of the products is usually a solid precipitate, a gas, or a molecular compound such as water.

Formation of a Precipitate

A precipitate forms in a double-replacement reaction when the cations from one of the reactants combine with the anions from the other reactant to form an insoluble ionic compound. When aqueous solutions of potassium iodide and lead (II) nitrate are mixed, the following reaction occurs:

$$2\mathrm{KI}\,(aq) + \mathrm{Pb(NO_3)_2}\,(aq) \rightarrow 2\mathrm{KNO_3}\,(aq) + \mathrm{PbI_2}\,(s)$$

There are very strong attractive forces that occur between Pb^{2+} and I^- ions and the result is a brilliant yellow precipitate (see figure below). The other product of the reaction, potassium nitrate, remains soluble.

Figure 10.4.5.2: Formation of lead iodide precipitate. (Credit: Paige Powers - "Lead Iodide"; Source: https://www.flickr.com/photos/44200742@N07/5533819494(opens in new window); License: CC-BY 2.0)

Formation of a Gas

Some double-replacement reactions produce a gaseous product which then bubbles out of the solution and escapes into the air. When solutions of sodium sulfide and hydrochloric acid are mixed, the products of the reaction are aqueous sodium chloride and hydrogen sulfide gas.

$$\mathrm{Na_2S}\,(aq) + 2\mathrm{HCl}\,(aq) \rightarrow 2\mathrm{NaCl}\,(aq) + \mathrm{H_2S}\,(g)$$

Formation of a Molecular Compound

Another kind of double-replacement reaction is one that produces a molecular compound as one of its products. Many examples in this category are reactions that produce water. When aqueous hydrochloric acid is reacted with aqueous sodium hydroxide, the products are aqueous sodium chloride and water:

$$\mathrm{HCl}\,(aq) + \mathrm{NaOH}\,(aq) \rightarrow \mathrm{NaCl}\,(aq) + \mathrm{H_2O}\,(l)$$

10.4.5.1 Example : Double-Replacement Reactions

Write a complete and balanced chemical equation for the following double-replacement reactions. One product is indicated as a guide.

a. $\mathrm{NaCN}\,(aq) + \mathrm{HBr}\,(aq) \rightarrow$ (hydrogen cyanide gas is formed)
b. $\mathrm{(NH_4)_2SO_4}\,(aq) + \mathrm{Ba(NO_3)_2}\,(aq) \rightarrow$ (a precipitate of barium sulfate forms)

Solution

Step 1: Plan the problem.

In A, the production of a gas drives the reaction. In B, the production of a precipitate drives the reaction. In both cases, use the ionic charges of both reactants to construct the correct formulas of the products.

Step 2: Solve.

A. The cations of both reactants are $+1$ charged ions, while the anions are -1 charged ions. After exchanging partners, the balanced equation is:

$$\mathrm{NaCN}\,(aq) + \mathrm{HBr}\,(aq) \rightarrow \mathrm{NaBr}\,(aq) + \mathrm{HCN}\,(g)$$

B. Ammonium ion and nitrate ion are $1+$ and $1-$ respectively, while barium and sulfate are $2+$ and $2-$. This must be taken into account when exchanging partners and writing the new formulas. Then, the equation is balanced.

$$\mathrm{(NH_4)_2SO_4}\,(aq) + \mathrm{Ba(NO_3)_2}\,(aq) \rightarrow 2\mathrm{NH_4NO_3}\,(aq) + \mathrm{BaSO_4}\,(s)$$

Step 3: Think about your result.

Both are double replacement reactions. All formulas are correct and the equations are balanced.

Occasionally, a reaction will produce both a gas and a molecular compound. The reaction of a sodium carbonate solution with hydrochloric acid produces aqueous sodium chloride, carbon dioxide gas, and water.

$$\mathrm{Na_2CO_3}\,(aq) + 2\mathrm{HCl}\,(aq) \rightarrow 2\,\mathrm{NaCl}\,(aq) + \mathrm{CO_2}\,(g) + \mathrm{H_2O}\,(l)$$

Summary

- The double-replacement reaction generally takes the form of AB + CD → AD + CB where A and C are positively-charged cations, while B and D are negatively-charged anions.
- In a double replacement reactions, typically one of the products is a precipitate, a gas, or a molecular compound.

Review

1. In a double-replacement reaction, what type of compounds are usually the reactants? A double-replacement reaction occurs between sodium sulfide and hydrogen chloride. Write the rest of the chemical equation and balance it.
2. $Na_2S + HCl \rightarrow$
3. In double-replacement reaction, one of three possible types of products usually form. What are the three types?

10.5: Predicting Reactions - Single and Double Displacement Reactions

Learning Objectives

- Predict the result of single-replacement reactions or double-replacement reactions.

Up until now, we have presented balancing and categorizing chemical reactions as topics, but we have not discussed how the products of a chemical reaction can be predicted. Here we will begin our study of certain types of chemical reactions that allow us to predict what the products of the reaction will be. In later chapters of this text, we will learn more about each of these reaction types related to predicting whether or not they will occur. For now, we will use the knowledge we have of predicting the formulas of ionic compounds and balancing equations to predict the results of certain reaction types, assuming the reactions will take place.

Predicting Single Replacement Reactions

A **single-replacement reaction** is a chemical reaction in which one element is substituted for another element in a compound, generating a new element and a new compound as products. Presented below:

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

is an example of a single-replacement reaction. The hydrogen atoms in HCl are replaced by Zn atoms, and in the process a new element—hydrogen—is formed. Another example of a single-replacement reaction is

$$2\,\mathrm{NaCl(aq)} + \mathrm{F_2(g)} \rightarrow 2\,\mathrm{NaF(s)} + \mathrm{Cl_2(g)}$$

Here the negatively charged ion changes from chloride to fluoride. A typical characteristic of a single-replacement reaction is that there is one element as a reactant and another element as a product.

Not all proposed single-replacement reactions will occur between two given reactants. In a later chapter, we will learn how to predict when certain single replacement reactions will occur. For now, we will focus on correctly predicting the result of single replacement reactions which involve ionic compounds. (If you would like to cover that material now, please refer to this other textbook, which has been adapted for the content in part of this section.)

If a single replacement reaction involves an ionic compound and an element, the element will replace an element in the ionic compound which it is most similar to. That is, a metal will replace a metal and a non-metal will replace a nonmetal. Use the periodic table to determine the typical charges of the anions and cations in the product. Whichever ion exists in a compound on both sides of the reaction will typically have the same charge in each case. Make sure to balance the charge of the new compound based on the expected charges of the ions involved.

Example 10.5.1:

Identify the products of the following single-replacement reactions?

a. $\mathrm{FeCl_2} + \mathrm{Ca} \rightarrow$?
b. $\mathrm{CaBr_2} + \mathrm{F_2} \rightarrow$?

Solution

a. The products of this single-replacement reaction are $\mathrm{CaCl_2}$ and Fe.
b. The products of the reaction will be $\mathrm{CaF_2}$ and $\mathrm{Br_2}$.

Exercise 10.5.1

Identify the products of the following single-replacement reactions?

$$\mathrm{FeI_2} + \mathrm{Cl_2} \rightarrow$$

Answer

Yes; $\mathrm{FeCl_2}$ and $\mathrm{I_2}$

? Exercise 10.5.2

Identify the products of the following single-replacement reactions?

$$\mathrm{AlPO_4 + Mg \rightarrow}$$

Answer

Mg3(PO4)2 and Al (Note the charge balance in the compound)

Predicting Double Replacement Reactions

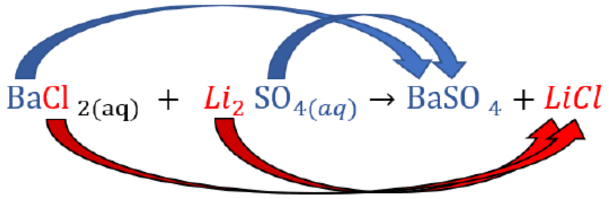
Predicting whether a double-replacement reaction occurs is somewhat more difficult than predicting a single-replacement reaction. We will explore one type of double replacement reaction in a later chapter: the precipitation reaction. For now, the goal of correctly predicting the result of a precipitation reaction involves understanding how charge balances work in the two new species which form. Similar to the single replacement reaction, not all possible double replacement reactions will occur. However, for the sake of correctly predicting the charge balance of the products, we will only consider reactions which do occur for the rest of this chapter. (If you would like to cover that material now, please refer to this other textbook, which has been adapted for the content in the remainder of this section.)

When predicting the result of a double replacement reaction, it is important to go through the following 3 steps. (Please note: when we learn how to predict whether or not the reaction occurs, we will be adding a 4th step as well.)

- Change the partners of the anions and cations on the reactant side to form new compounds (products).
- Correct the formulas of the products based on the charges of the ions.
- Balance the equation.

For example, predict what will happen when aqueous solutions of barium chloride ($BaCl_2$) and lithium sulfate (Li_2SO_4) are mixed.

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



Please note, that the only subscript which transfers across from reactant to product in this step is the 4 on the oxygen. This is because the oxygen is part of a polyatomic ion (sulfate). The subscripts of 2 on the lithium and chloride are not transferred here. These subscripts are not parts of the ion. Instead, they are telling us how many of that ion was necessary for the charge balance. If we need new subscripts, we will determine that in the next step.

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

In this particular case, there is no need to make additional changes because the ions balance as shown. Let's verify this by looking at the charges of all of the ions present: $\mathrm{Ba^{2+}}$, $\mathrm{Cl^-}$, $\mathrm{Li^+}$, and $\mathrm{SO_4^{2-}}$. (note: if you are unsure how we determined these charges, please refer to the section of this book where we first discussed ionic compounds.) Because in each case the charges of the anion and cation canceled within each compound, there was no need to change any of the coefficients from the assumed value of one.

Balance the equation:

It is only once we have correctly predicted the formulas of the products that we can consider balancing the overall equation. In this case, we will look at the initial subscripts to determine what coefficients we might need for the products. Please note, that subscripts should have been determined in the previous step. If the equation still remains unbalanced we add coefficients as shown below.

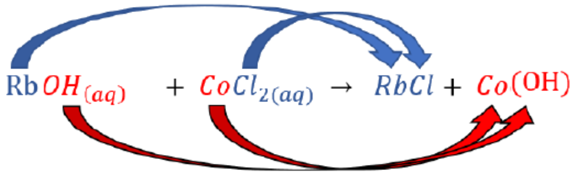
$$\mathrm{BaCl_2(aq) + Li_2SO_4(aq) \rightarrow BaSO_4 + 2\,LiCl}$$

Figure 10.5.2: An x-ray of the digestive organs of a patient who has swallowed a “barium milkshake.” A barium milkshake is a suspension of very fine $BaSO_4$ particles in water; the high atomic mass of barium makes it opaque to x-rays. (Public Domain; Glitzy queen00 via Wikipedia).

Example 10.5.1

Predict what will happen if rubidium hydroxide and cobalt(II) chloride are mixed.

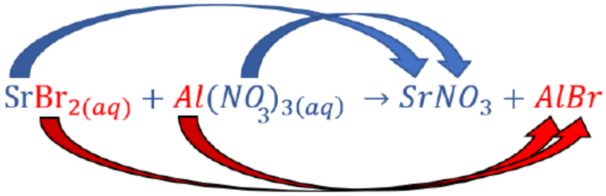
Solution

Steps	Example
Change the partners of the anions and cations on the reactant side to form new compounds (products).	
Correct the formulas of the products based on the charges of the ions.	$\mathrm{RbOH(aq) + CoCl_2(aq) \rightarrow RbCl + Co(OH)_2}$
Balance the equation.	Coefficients already balanced. $\mathrm{RbOH(aq) + CoCl_2(aq) \rightarrow RbCl(aq) + Co(OH)_2(s)}$

Example 10.5.2

Predict what will happen if aqueous solutions of strontium bromide and aluminum nitrate are mixed.

Solution

Steps	Example
Change the partners of the anions and cations on the reactant side to form new compounds (products).	
Correct the formulas of the products based on the charges of the ions.	$\mathrm{SrBr_2(aq) + Al(NO_3)_3(aq) \rightarrow Sr(NO_3)_2 + AlBr_3}$
Balance the equation.	$\mathrm{3\,SrBr_2(aq) + 2\,Al(NO_3)_3(aq) \rightarrow 3\,Sr(NO_3)_2 + 2\,AlBr_3}$

As mentioned at the start of this discussion, we will be adding a 4th step in order to determine whether these reactions will occur in a later chapter. In fact, we will revisit these same examples and decide if the reaction occurs or not. It turns out that one of them does, and one of them doesn't. For now, assume any question about double replacement reactions you see in exercises are reactions which will occur. Your job will be to use the 3 steps we discussed to determine the final balanced equation.

Summary

We have learned how to predict the results of single replacement and double replacement reactions using only concepts of charge balance within a compound and balancing equations among compounds and elements. In later chapters we will learn other considerations for predicting both of these types of reactions.

Key Takeaways

- A single-replacement reaction replaces one element for another in a compound.
- A double-replacement reaction exchanges the cations (or the anions) of two ionic compounds.

10.5.1: Precipitation Reactions

Learning Objectives

- To identify a precipitation reaction and predict solubility.

A precipitation reaction is a type of double displacement 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.

$$\mathrm{AgNO_3(aq) + K_2Cr_2O_7(aq) \rightarrow Ag_2Cr_2O_7(s) + KNO_3(aq)} \tag{10.5.1.1}$$

This unbalanced equation has the general form of an exchange reaction:

$$\mathrm{AC + BD \rightarrow \underset{\mathit{insoluble}}{AD} + BC} \tag{10.5.1.2}$$

Thus precipitation reactions are a subclass of exchange reactions that occur between ionic compounds when one of the products is insoluble. 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.

Video: Mixing potassium dichromate and silver nitrate together to initiate a precipitation reaction (Equation 10.5.1.1).

Just as important as predicting the product of a reaction is knowing when a chemical reaction will *not* occur. Simply mixing solutions of two different chemical substances does *not* guarantee that a reaction will take place. For example, if 500 mL of aqueous $NaCl$ solution is mixed with 500 mL of aqueous KBr solution, the final solution has a volume of 1.00 L and contains $\mathrm{Na^+(aq)}$, $\mathrm{Cl^-(aq)}$, $\mathrm{K^+(aq)}$, and $\mathrm{Br^-(aq)}$. As you will see in (Figure 10.5.1.1), none of these species reacts with any of the others. When these solutions are mixed, the only effect is to dilute each solution with the other.

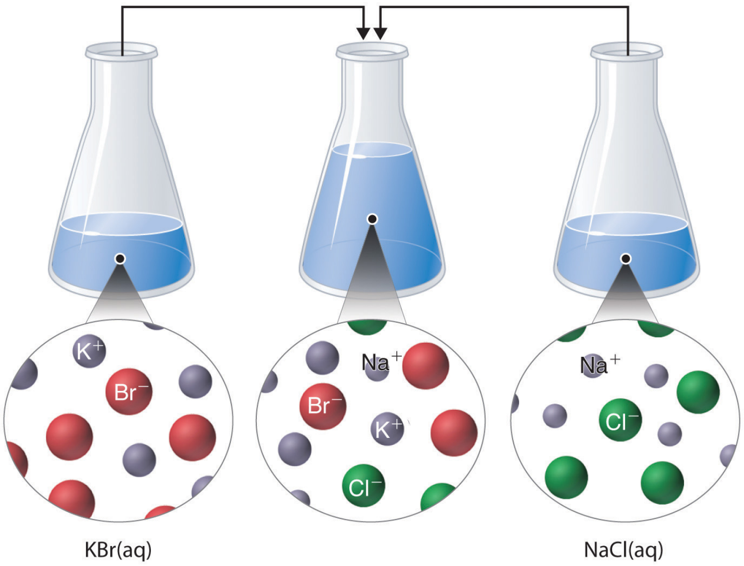


Figure 10.5.1.1: The Effect of Mixing Aqueous KBr and NaCl Solutions. Because no net reaction occurs, the only effect is to dilute each solution with the other. (Water molecules are omitted from molecular views of the solutions for clarity.)

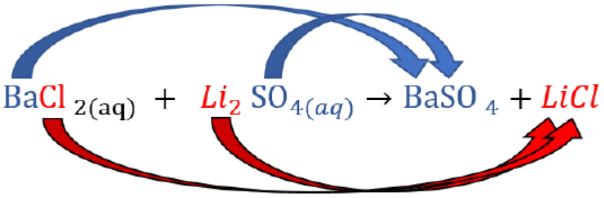
Predicting Precipitation Reactions

Previously, we had discussed the prediction of double replacement reactions without considering solubility. Now that we have learned how to use solubility rules, we will revisit double replacement reactions with this new knowledge. The steps for predicting the result of a double replacement reaction are essentially the same as before, but with an additional step included for using the solubility rules.

We will go through the same examples as previously, but adding the additional staff of using solubility rules. When a reaction does occur, we will obtain the same result but with the additional information of which of the products is solid and which is aqueous. If the reaction does not occur, we are now able to determine that using the solubility rules when we were not able to do so earlier.

Predict what will happen when aqueous solutions of barium chloride and lithium sulfate are mixed.

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



Because barium chloride and lithium sulfate are strong electrolytes, each dissociates completely in water to give a solution that contains the constituent anions and cations. Mixing the two solutions *initially* gives an aqueous solution that contains $\mathrm{Ba^{2+}}$, $\mathrm{Cl^-}$, $\mathrm{Li^+}$, and $\mathrm{SO_4^{2-}}$ ions. The only possible exchange reaction is to form LiCl and $\mathrm{BaSO_4}$.

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

No need to correct the formula as both compounds already have their charges balanced.

$$\mathrm{BaCl_2(aq) + Li_2SO_4(aq) \rightarrow BaSO_4 + LiCl}$$

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

$$\mathrm{BaCl_2(aq) + Li_2SO_4(aq) \rightarrow BaSO_4(s) + LiCl(aq)}$$

Table 7.5.1 from the previous section shows that LiCl is soluble in water, but $\mathrm{BaSO_4}$ is not soluble in water.

Balance the equation:

$$BaCl_2(aq) + Li_2SO_4(aq) \rightarrow BaSO_4(s) + 2\,LiCl(aq)$$

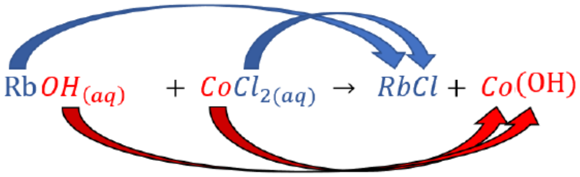
Although soluble barium salts are toxic, $BaSO_4$ is so insoluble that it can be used to diagnose stomach and intestinal problems without being absorbed into tissues. An outline of the digestive organs appears on x-rays of patients who have been given a “barium milkshake” or a “barium enema”—a suspension of very fine $BaSO_4$ particles in water.

Figure 10.5.1.2: An x-ray of the digestive organs of a patient who has swallowed a “barium milkshake.” A barium milkshake is a suspension of very fine $BaSO_4$ particles in water; the high atomic mass of barium makes it opaque to x-rays. (Public Domain; Glitzy queen00 via Wikipedia).

✓ Example 10.5.1.1

Predict what will happen if aqueous solutions of rubidium hydroxide and cobalt(II) chloride are mixed.

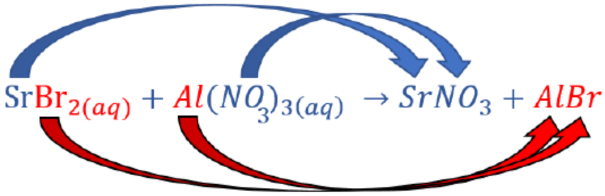
Solution

Steps	Example
Change the partners of the anions and cations on the reactant side to form new compounds (products).	
Correct the formulas of the products based on the charges of the ions.	$RbOH(aq) + CoCl_2(aq) \rightarrow RbCl + Co(OH)_2$
Refer to the solubility rules table to determine insoluble products which will therefore form a precipitate.	$RbOH(aq) + CoCl_2(aq) \rightarrow RbCl(aq) + Co(OH)_2(s)$
Balance the equation.	Coefficients already balanced. $RbOH(aq) + CoCl_2(aq) \rightarrow RbCl(aq) + Co(OH)_2(s)$

✓ Example 10.5.1.2

Predict what will happen if aqueous solutions of strontium bromide and aluminum nitrate are mixed.

Solution

Steps	Example
Change the partners of the anions and cations on the reactant side to form new compounds (products).	

Steps	Example
Correct the formulas of the products based on the charges of the ions.	$SrBr_2(aq) + Al(NO_3)_3(aq) \rightarrow Sr(NO_3)_2 + AlBr_3$
Refer to the solubility rules table to determine insoluble products which will therefore form a precipitate.	$SrBr_2(aq) + Al(NO_3)_3(aq) \rightarrow Sr(NO_3)_2(aq) + AlBr_3(aq)$ According to Table 7.5.1 from the previous section, both $AlBr_3$ (rule 4) and $Sr(NO_3)_2$ (rule 2) are soluble.
If all possible products are soluble, then no net reaction will occur.	$SrBr_2(aq) + Al(NO_3)_3(aq) \rightarrow$ **NO REACTION**

? Exercise 10.5.1.2

Using the information in Table 7.5.1 from the previous section, predict what will happen in each case involving strong electrolytes.

a. An aqueous solution of strontium hydroxide is added to an aqueous solution of iron(II) chloride.
b. Solid potassium phosphate is added to an aqueous solution of mercury(II) perchlorate.
c. Solid sodium fluoride is added to an aqueous solution of ammonium formate.
d. Aqueous solutions of calcium bromide and cesium carbonate are mixed.

Answer a

$Fe(OH)_2$ precipitate is formed.

Answer b

$Hg_3(PO_4)_2$ precipitate is formed.

Answer c

No Reaction.

Answer d

$CaCO_3$ is precipitate formed.

Summary

In a **precipitation reaction**, a subclass of exchange reactions, an insoluble material (a **precipitate**) forms when two electrolyte solutions are mixed. To predict the product of a precipitation reaction, all species initially present in the solutions are identified, as are any combinations likely to produce an insoluble salt.

Contributions & Attributions

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10.5.2: Acid–Base and Gas Evolution Reactions

Learning Objectives

- Identify when a reaction will evolve a gas.

Neutralization Reactions

Acids and bases react chemically with each other to form *salts*. A salt is a general chemical term for any ionic compound formed from an acid and a base. In reactions where the acid is a hydrogen-ion-containing compound and the base is a hydroxide-ion-containing compound, water is also a product. The general reaction is as follows:

$$\text{acid} + \text{base} \rightarrow \text{water} + \text{salt}$$

The reaction of acid and base to make water and a salt is called **neutralization**. Like any chemical equation, a neutralization chemical equation must be properly balanced. For example, the neutralization reaction between sodium hydroxide and hydrochloric acid is as follows:

$$\mathrm{NaOH(aq) + HCl(aq) \rightarrow NaCl(aq) + H_2O(\ell)} \tag{10.5.2.1}$$

with coefficients all understood to be one. The neutralization reaction between sodium hydroxide and sulfuric acid is as follows:

$$\mathrm{2\,NaOH(aq) + H_2SO_4(aq) \rightarrow Na_2SO_4(aq) + 2\,H_2O(\ell)} \tag{10.5.2.2}$$

Example 10.5.2.1: Neutralizing Nitric Acid

Nitric acid ($HNO_3(aq)$) can be neutralized by calcium hydroxide ($Ca(OH)_2(aq)$). Write a balanced chemical equation for the reaction between these two compounds and identify the salt that it produces.

Solution

Solutions to Example 7.8.1

Steps	Explanation	Equation
Write the unbalanced equation.	This is a double displacement reaction, so the cations and anions swap to create new products.	$Ca(OH)_2(aq) + HNO_3(aq) \rightarrow Ca(NO_3)_2(aq) + H_2O(\ell)$
Balance the equation.	Because there are two OH^- ions in the formula for $Ca(OH)_2$, we need two moles of HNO_3 to provide H^+ ions	$Ca(OH)_2(aq) + \underline{\mathbf{2}}HNO_3(aq) \rightarrow Ca(NO_3)_2(aq) + \underline{\mathbf{2}}H_2O(\ell)$
Additional step: identify the salt.		The salt formed is calcium nitrate.

Exercise 10.5.2.1

Hydrocyanic acid ($HCN(aq)$) can be neutralized by potassium hydroxide ($KOH(aq)$). Write a balanced chemical equation for the reaction between these two compounds and identify the salt that it produces.

Answer

\[\ce{KOH (aq) + HCN(aq) → KCN (aq) + H2O(ℓ)} \nonumber \]

Gas Evolving Reactions

A gas evolution reaction is a chemical process that produces a gas, such as oxygen or carbon dioxide. In the following examples, an acid reacts with a carbonate, producing salt, carbon dioxide, and water, respectively. For example, nitric acid reacts with sodium carbonate to form sodium nitrate, carbon dioxide, and water (Table 10.5.2.1):

$$\mathrm{2\,HNO_3(aq)^{+}Na_2CO_3(aq) \rightarrow 2\,NaNO_3(aq)^{+}CO_2(g)^{+}H_2O(l)}$$

Sulfuric acid reacts with calcium carbonate to form calcium sulfate, carbon dioxide, and water:

$$\mathrm{H_2SO_4(aq) + CaCO_3(aq) \rightarrow CaSO_4(aq) + CO_2(g)^{+}H_2O(l)}$$

Hydrochloric acid reacts with calcium carbonate to form calcium chloride, carbon dioxide, and water:

$$\mathrm{2\,HCl(aq) + CaCO_3(aq) \rightarrow CaCl_2(aq) + CO_2(g) + H_2O(l)}$$

Figure 10.5.2.1demonstrates this type of reaction:

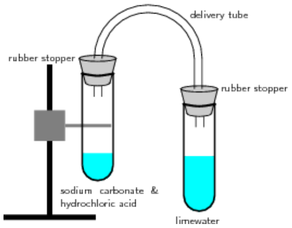

Figure 10.5.2.1: Reaction of acids with carbonates. In this reaction setup, lime water (water + calcium hydroxide) is poured into one of the test tubes and sealed with a stopper. A small amount of hydrochloric acid is carefully poured into the remaining test tube. A small amount of sodium carbonate is added to the acid, and the tube is sealed with a rubber stopper. The two tubes are connected. As a result of the acid-carbonate reaction, carbon dioxide is produced and the lime water turns milky.

In this reaction setup, lime water, a dilute calcium hydroxide ($Ca(OH)_2$) solution, is poured into one of the test tubes and sealed with a stopper. A small amount of hydrochloric acid is carefully poured into the remaining test tube. A small amount of sodium carbonate is added to the acid, and the tube is sealed with a rubber stopper. The two tubes are connected. As a result of the acid-carbonate reaction, carbon dioxide is produced and the lime water turns milky.

Table 10.5.2.1: Types of Compounds That Undergo Gas-Evolution Reactions

Reactant Type	Intermediate Product	Gas Evolved	Example
sulfide	none	H_2S	$2\,HCl(aq) + K_2S \rightarrow H_2S(g) + 2\,KCl(aq)$
carbonates and bicarbonates	H_2CO_3	CO_2	$2\,HCl(aq) + K_2CO_2 \rightarrow H_2O(l) + CO_2(g)$ -
sulfites and bisulfites	H_2SO_3	SO_2	$2\,HCl(aq) + K_2SO_2 \rightarrow H_2O(l) + SO_2(g) +$
ammonia	NH_4OH	NH_3	\(\ce{NH4Cl(aq) + KOH \rightarrow H2O (l) + NH3(g) + 2KCl (aq)}\)

The gas-evolving experiment lime water is illustrated in the following video:

Video* 10.5.2.1**:** *Carbon Dioxide (CO_2) & Limewater (Chemical Reaction). As the reaction proceeds, the limewater on the turns from clear to milky; this is due to the $CO_2(g)$ reacting with the aqueous calcium hydroxide to form calcium carbonate, which is only slightly soluble in water.*

When this experiment is repeated with nitric or sulfuric acid instead of HCl, it yields the same results: the clear limewater turns milky, indicating the production of carbon dioxide. Another method to chemically generate gas is the oxidation of metals in acidic solutions. This reaction will yield a metal salt and hydrogen gas.

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

Here, hydrochloric acid oxidizes zinc to produce an aqueous metal salt and hydrogen gas bubbles. Recall that oxidation refers to a loss of electrons, and reduction refers to the gain of electrons. In the above redox reaction, neutral zinc is oxidized to Zn^{2+}, and the acid, H^+, is reduced to $H_2(g)$. The oxidation of metals by strong acids is another common example of a gas evolution reaction.

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10.6: Writing Chemical Equations for Reactions in Solution- Complete Chemical, Complete Ionic, and Net Ionic Equations

A typical precipitation reaction occurs when an aqueous solution of barium chloride is mixed with one containing sodium sulfate. The **complete chemical equation** can be written to describe what happens, and such an equation is useful in making chemical calculations. (In some textbooks this is referred to as the molecular equation. This can be somewhat confusing, because the equation does not typically contain any molecules. For this reason, we will continue to refer to it as the complete chemical equation in this textbook.)

$$\underbrace{\mathrm{BaCl_2(aq) + Na_2SO_4(aq) \longrightarrow BaSO_4(s) + 2\,NaCl(aq)}}_{\text{Complete Chemical Equation}} \tag{10.6.1}$$

However, Equation 10.6.1 does not really represent the microscopic particles (that is, the ions) present in the solution. Below is the complete ionic equation:

$$\underbrace{\mathrm{Ba^{2+}(aq)} + \overbrace{\mathrm{2\,Cl^-(aq)}}^{\text{spectator}} + \overbrace{\mathrm{2\,Na^+(aq)}}^{\text{spectator}} + \mathrm{SO_4^{2-}(aq) \longrightarrow BaSO_4(s)} + \overbrace{\mathrm{2\,Na^+(aq)}}^{\text{spectator}} + \overbrace{\mathrm{2\,Cl^-(aq)}}^{\text{spectator}}}_{\text{Complete Ionic Equation}} \tag{10.6.2}$$

Equation 10.6.2 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 $\mathrm{BaSO_4(s)}$ will form when *any* solution containing $\mathrm{Ba^{2+}(aq)}$ is mixed with *any* solution containing $\mathrm{SO_4^{2-}(aq)}$ (provided concentrations are not extremely small). This happens independently of the $\mathrm{Cl^-(aq)}$ and $\mathrm{Na^+(aq)}$ ions in Equation 10.6.2. 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 $\mathrm{BaSO_4}$ the net ionic equation is

$$\underbrace{\mathrm{Ba^{2+}(aq) + SO_4^{2-}(aq) \longrightarrow BaSO_4(s)}}_{\text{Net Ionic Equation}} \tag{10.6.3}$$

✓ Example 10.6.1

a. When a solution of $\mathrm{AgNO_3}$ is added to a solution of $\mathrm{CaCl_2}$, insoluble AgCl precipitates. Write three equations (complete chemical equation, complete ionic equation, and net ionic equation) that describe this process.
b. Write the balanced net ionic equation to describe any reaction that occurs when the solutions of $\mathrm{Na_2SO_4}$ and $\mathrm{NH_4I}$ are mixed.

Solution

Equation Type	Example 10.6.1a	Example 10.6.1b
Complete Chemical Equation	$\mathrm{2\,AgNO_3(aq) + CaCl_2(aq) \longrightarrow}$ $\mathrm{2\,AgCl(s) + Ca(NO_3)_2(aq)}$ The proper states and formulas of all products are written and the chemical equation is balanced.	$\mathrm{Na_2SO_4(aq) + NH_4I_2(aq) \longrightarrow}$ $\mathrm{2\,NaI(aq) + (NH_4)_2SO_4(aq)}$ Both products are aqueous so there is no net ionic equation that can be written.
Complete Ionic Equation	$\mathrm{2\,Ag^+(aq) + 2\,NO_3^-(aq) + Ca^{2+}(aq) + Cl^-(aq) \longrightarrow}$ $\mathrm{2\,AgCl(s) + Ca^{2+}(aq) + 2\,NO_3^-(aq)}$ AgCl is a solid so it does not break up into ions in solution.	
Net Ionic Equation	$\mathrm{Ag^+(aq) + Cl^-(aq) \longrightarrow AgCl(s)}$ All spectator ions are removed.	NaI and $\mathrm{(NH_4)_2SO_4}$ are both soluble. No net ionic equation

The occurrence or nonoccurrence of precipitates can be used to detect the presence or absence of various species in solution. A $\mathrm{BaCl_2}$ solution, for instance, is often used as a test for the presence of $\mathrm{SO_4^{2-}(aq)}$ ions. There are several insoluble salts of Ba, but they all dissolve in dilute acid except for $BaSO_4$. Thus, if $BaCl_2$ solution is added to an unknown solution which has previously been acidified, the occurrence of a white precipitate is proof of the presence of the SO_4^{2-} ion.

Figure 10.6.1: The three common silver halide precipitates: AgI, $AgBr$ and $AgCl$ (left to right). The silver halides precipitate out of solution, but often form suspensions before settling. (CC BY-SA 3.0; Cychr).

$AgNO_3$ solutions are often used in a similar way to test for halide ions. If $AgNO_3$ solution is added to an acidified unknown solution, a white precipitate indicates the presence of Cl^- ions, a cream-colored precipitate indicates the presence of Br^- ions, and a yellow precipitate indicates the presence of I^- ions (Figure $10.6.1$). Further tests can then be made to see whether perhaps a mixture of these ions is present. When $AgNO_3$ is added to tap water, a white precipitate is almost always formed. The Cl^- ions in tap water usually come from the Cl_2 which is added to municipal water supplies to kill microorganisms.

? Exercise 10.6.1

Write balanced net ionic equations to describe any reaction that occurs when the following solutions are mixed.

a. $K_2CO_3 + SrCl_2$
b. $FeSO_4 + Ba(NO_3)_2$

Answer a

$$Sr^{2+}(aq) + CO_3^{2-}(aq) \longrightarrow SrCO_3(s)$$

Answer b

$$Ba^{2+}(aq) + SO_4^{2-}(aq) \longrightarrow Ba(SO_4)(s)$$

Precipitates are also used for quantitative analysis of solutions, that is, to determine the amount of solute or the mass of solute in a given solution. For this purpose it is often convenient to use the first of the three types of equations described above. Then the rules of stoichiometry may be applied.

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10.7: Oxidation and Reduction- Some Definitions

"Redox" is short for "oxidation and reduction", two complimentary types of chemical reactions. The term **oxidation** originally referred to substances combining with oxygen, as happens when an iron bar rusts or a campfire log burns. We often refer to these two examples as corrosion and combustion. **Reduction** originally referred to the process of converting metal ores to pure metals, a process that is accompanied by a reduction in the mass of the ore.

These two terms have broader meanings now. In all oxidation-reduction reactions, an exchange of electrons occurs—one substance loses electrons while another gains them. That is the key to understanding redox reactions. We'll define these terms below.

Figure 10.7.1: *Reaction of copper wire in a silver nitrate solution.*

A simple demonstration of a redox reaction involves placing a solid piece of copper wire in a silver nitrate solution. Within minutes, the wire begins to look fuzzy or furry as small silver crystals begin to form on the wire. Meanwhile, the originally clear silver nitrate solution begins to take on a pale bluish tint. Furthermore, if the crystals are shaken off of the wire, we see that the wire partially disintegrated.

The overall equation for our demonstration describes the events:

$$\mathrm{Cu(s)} + 2\,\mathrm{AgNO_3(aq)} \rightarrow \mathrm{Cu(NO_3)_2(aq)} + 2\,\mathrm{Ag(s)} \tag{10.7.1}$$

You may notice that this is a single replacement reaction. You may also notice that this reaction occurs in aqueous solution, and that we could write this reaction as either a complete or net ionic equation. Remember that when we have aqueous solutions of ionic compounds, the ions are really present as separate ions, not as bonded particles. So we can write an expanded equation:

$$\mathrm{Cu(s)} + 2\,\mathrm{Ag^+(aq)} + 2\,\mathrm{NO_3^-(aq)} \rightarrow \mathrm{Cu^{2+}(aq)} + 2\,\mathrm{NO_3^-(aq)} + 2\,\mathrm{Ag(s)} \tag{10.7.2}$$

Finally we remove spectator ions from the equation. Remember that spectator ions are ions that undergo no change during a reaction. Notice the nitrate ions, NO_3^-, they start as aqueous ions and end up exactly the same.

Removing the spectator ions gives us our **net ionic equation:**

$$\mathrm{Cu(s)} + 2\,\mathrm{Ag^+(aq)} \rightarrow \mathrm{Cu^{2+}(aq)} + 2\,\mathrm{Ag(s)} \tag{10.7.3}$$

We can now see a bit more clearly what changes are occurring with this reaction.

Oxidation of Copper Metal to Make Copper Ions

Copper began as a neutral atom with no charge, but changed into an ion with a charge of +2. An atom becomes a positive ion by losing electrons:

$$\mathrm{Cu(s)} \rightarrow \mathrm{Cu^{2+}(aq)} + 2\,\mathrm{e^-} \tag{10.7.4}$$

Notice that copper began as a solid, but is converted into aqueous ions—this is why the copper wire disintegrates. We say that copper was **oxidized** because it has lost electrons (i.e., electrons appear on the product side of the Equation 10.7.4).

Reduction of Silver Ions to Make Silver Metal

Silver was converted from an ion with a charge of +1, Ag+, to a neutral atom, Ag. The only way an ion can undergo this change is to gain an electron:

$$\mathrm{Ag^+(aq) + e^- \rightarrow Ag(s)} \tag{10.7.5}$$

Notice that solid silver is formed—this is what causes the fuzzy appearance to begin appearing on the wire—solid silver crystals. Silver has gained electrons, it has been reduced (i.e., electrons appear on the reactant side of Equation 10.7.5).

The electrons that silver gained had to come from somewhere—they came from copper. Conversely, a substance such as copper can only lose electrons if there is something else that will take them up, the silver ions. **One cannot occur without the other**. This exchange of electrons is what defines an **oxidation-reduction reaction**.

Definition: Oxidation

Oxidation is the **loss** of electrons.

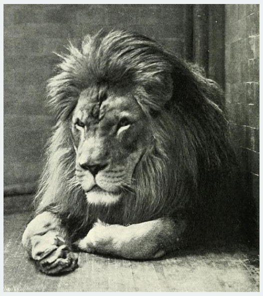
Definition: Reduction

Reduction is the **gain** of electrons.

You will be learning several new terms in this chapter and it is important that you learn them very quickly. You may find it useful to have some tricks to help you remember these terms, including the LEO/GER.

LEO the Lion Says GER

- LEO: Loss of Electrons is Oxidation.
- GER: Gain of Electrons is Reduction.



For simple single replacement reactions between metals such as the one examined here, it can be fairly straightforward to determine which of the metals is oxidized and which is reduced. The metal in its elemental form which is a reactant will always be oxidized because metals tend to lose electrons when they react. Conversely, the metal in its elemental form which is a product will always have been reduced, because it would need to gain electrons to revert from an anion back to its elemental form. Such reactions can be inspected to determine which element is oxidized and which is reduced.

However, there are many redox reactions which are much more complicated than this and need additional considerations in order to make this determination. In the next section, we will discuss the process used for such a determination.

10.8: Keeping Track of Redox Reactions

There are many important redox reactions, and not all of them can be solved by inspection. For reactions which are more complicated than the simple single replacement reactions introduced in the last section, we need to have ways of keeping track of the movement of electrons. We do this through a process of electron bookkeeping. This process starts with assigning oxidation numbers to each element. Changes in these oxidation numbers are indications of the movement of electrons, and therefore what is oxidized and what is reduced. When balancing a redox reaction, it is important to keep track of the electrons and not just the atoms. Each of these topics will be covered in one of the subsections of this section.

10.8.1: Oxidation States - Electron Bookkeeping

Redox reactions are all about electrons being transferred from one substance to another, so it is useful to have a system for keeping track of what gains and what loses electrons, and how many electrons are involved. The record-keeping system for redox reactions is called **Oxidation Numbers.** You may also remember something called **electronegativity** from earlier chemistry classes.

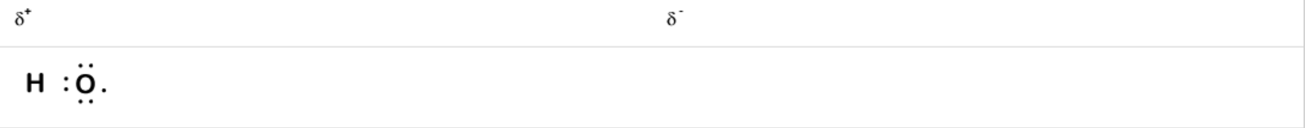
Electronegativity

The ability of a bonded atom to attract shared electrons toward itself.

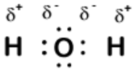
When two atoms of different elements are bonded together by a covalent bond (sharing electrons), the electrons are generally not shared equally between the two atoms due to differences in their electronegativities. Think of this as a tug-of-war for electrons. Sometimes both atoms pull with equal strength on shared electrons; other times there is clearly a stronger player that will pull the electrons closer to itself.

Consider the bond between a hydrogen atom (with one valence electron) and an oxygen atom (with its six valence electrons):

Because oxygen has a higher electronegativity than hydrogen, the shared electrons are closer to the oxygen atom than to the hydrogen atom. This is not the total transfer of electrons that would create an ion, but partial charges do form. The hydrogen end of the bond is partially positive (+1) because it has partially lost one electron, and the oxygen end of the H–O is partially negative (-1) because it has partially gained the one electron from hydrogen:



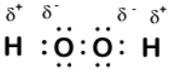
Our molecule is incomplete, however, because there is a lone electron around oxygen. Let's add one more hydrogen to complete our water molecule:



We see that each of the two hydrogens has "lost" one electron to oxygen. Oxygen has "gained" two electrons—one from each hydrogen. Again, these are not true ions, but it is useful to think of them in the same way.

Charges given to atoms in a molecule in this way are called **oxidation numbers**. We can use oxidation numbers to keep track of where electrons are in a molecule, and how they move during a reaction. In our water example, hydrogen is assigned an oxidation number of +1 because each individual hydrogen has "lost" one electron. Oxygen has an oxidation number of +2 because the single oxygen atom has "gained" a total of two electrons, one from each hydrogen.

Here is another molecule involving hydrogen and oxygen—hydrogen peroxide, H_2O_2:



In hydrogen peroxide, each hydrogen still has an oxidation number of +1 because each hydrogen "gives up" a single electron to oxygen. Oxygen, however, now has an oxidation number of -1 because each oxygen gains just one electron from its neighboring hydrogen. The electrons between the two identical oxygen atoms are shared equally, so there is no partial charge resulting from that bond.

Oxidation Number

A positive or negative number assigned to an atom in a molecule or ion that reflects a partial gain or loss of electrons.

Knowing the oxidation number of each individual element in a molecule will be a key step in our understanding of redox reactions. Fortunately it will not usually involve drawing electron dot diagrams. Instead, there are a series of rules that we can use to determine oxidation numbers. Here are the main rules:

1. The oxidation number of a pure element (by itself, and not an ion) is zero.

Element	Oxidation Number
Na	0
H_2	0
O_2	0
P_4	0

2. The oxidation number of a monatomic ion (by itself or as part of an ionic compound) is equal to its charge.
Alkali metals—elements in the first column of the periodic table—will always have an oxidation number of +1; Alkaline earth metals (column 2) are almost always +2.

Ionic Compound	Ions	Charge	Oxidation Number
NaCl	Na^+	+1	+1
	Cl^-	-1	-1
Mg_3N_2	Mg^{+2}	+2	+2
	N^{-3}	-3	-3

3. The oxidation number of hydrogen is almost always +1 when it is in a compound.

Compound	Element	Oxidation Number
HCl	H	+1
	Cl	-1
H_2S	H	+1
	S	-2

4. The oxidation number of oxygen is almost always -2 when it is in a compound.
The exceptions:
   - Peroxides, such as hydrogen peroxide. In peroxides, oxygen has an oxidation number of -1.
   - When oxygen is combined with fluorine, its oxidation number is +2.

Compound	Element	Oxidation Number
MgO magnesium oxide	Mg	+2
	O	-2
Na_2O sodium oxide	Na	+1
	O	-2
Na_2O_2 sodium peroxide	Na	+1
	O	-1

1. The oxidation number of a pure element (by itself, and not an ion) is zero.

Element	Oxidation Number
Na	0
H_2	0
O_2	0
P_4	0

5. The sum of the oxidation numbers in a compound is zero.
To determine the oxidation number of Mn in Mn_2O_7, we must work backwards:

- We know each oxygen is -2 (Rule 4).
- 7 oxygen gives a total of:

-2 × 7 atoms = -14 total
Since the sum of oxidation numbers must be zero, the total oxidation number of Mn must be +14 to cancel out oxygen's -14, but since there are 2 Mn atoms, each **individual atom** will have an oxidation number of +7:

$$\frac{+14\text{ total}}{2\text{ Mn atoms}} = +7$$

Compound	Element	Oxidation Number	Number of Atoms	Total
Mg_3N_2	Mg	+2	3	+6
	N	-3	2	-6
			SUM	0
Mn_2O_7	Mn	+7	2	+14
	O	-2	7	-14
			SUM	**0**
Cl_2O_3	Cl	+3	2	+6
	O	-2	3	-6
			SUM	**0**

6. The sum of the oxidation numbers in a polyatomic ion is equal to the charge on that ion.
Again, work backwards to determine the oxidation number of any non-oxygen or non-hydrogen atom.
To determine the oxidation number of Cr in $Cr_2O_7^{2-}$:

- Oxygen will be -2 (Rule 4), for a total of:

-2 × 7 = -14

- Since the sum of the oxidation numbers will be -2 (the charge on the entire ion), the total for all Cr must be +12 because:

+12 + (-14) = -2

- Since there are two Cr, each Cr will have an oxidation number of +6.

= +7

$$\frac{+12}{2} = +6$$

Compound	Element	Oxidation Number	Number of Atoms	Total
NO_3^-	N	+5	1	+5
	O	-2	3	-6
			SUM	-1
$Cr_2O_7^{2-}$	Cr	+6	2	+12
	O	-2	7	-14
			SUM	**-2**
SO_4^{2-}	S	+6	1	+6
	O	-2	4	-8
			SUM	**-2**

It is important to note that oxidation number always refers to ***each individual atom*** in the compound, not to the total for that element.

For example, in H_2O, the total positive "charge" for both hydrogen atoms will be +2 (which balances with the -2 from oxygen), but *each hydrogen* has an oxidation number of +1.

10.8.2: Determining Redox Reactions from Oxidation States

Learning Objectives

- Define *oxidation* and *reduction*.
- Assign oxidation numbers to atoms in simple compounds.
- Recognize a reaction as an oxidation-reduction reaction.

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 valence electrons from each zinc atom are transferred to each sulfur atom.

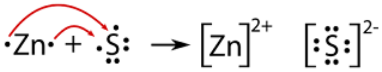


Figure 10.8.2.1: Reaction between zinc and sulfur.

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 full or partial loss of electrons or the gain of oxygen. **Reduction** is the full or partial gain of electrons or the loss of oxygen. 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.

$$\underbrace{\mathrm{Zn} \rightarrow \mathrm{Zn}^{2+} + 2\,\mathrm{e}^-}_{\text{Oxidation}} \tag{10.8.2.1}$$

$$\underbrace{\mathrm{S} + 2\,\mathrm{e}^- \rightarrow \mathrm{S}^{2-}}_{\text{Reduction}} \tag{10.8.2.2}$$

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.

Another example of an oxidation-reduction reaction involving electron transfer is the well-known combination of metallic sodium and chlorine gas to form sodium chloride:

$$2\,\mathrm{Na} + \mathrm{Cl_2} \rightarrow 2\,\mathrm{NaCl} \tag{10.8.2.3}$$

The half reactions are as follows:

$$\underbrace{2\,\mathrm{Na} \rightarrow 2\,\mathrm{Na}^+ + 2\,\mathrm{e}^-}_{\text{Oxidation}} \tag{10.8.2.4}$$

$$\underbrace{\mathrm{Cl_2} + 2\,\mathrm{e}^- \rightarrow 2\,\mathrm{Cl}^-}_{\text{Reduction}} \tag{10.8.2.5}$$

We will concern ourselves with the balancing of these equations at another time.

Oxidation Numbers

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 four rules. 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.

Assigning Oxidation Numbers

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

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

> *In H_2, both H atoms have an oxidation number of 0.*
>
> **2. Atoms in monatomic (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.**
>
> *In $MgCl_2$, magnesium has an oxidation number of +2, while chlorine has an oxidation number of −1.*
>
> **3. In compounds, fluorine is assigned a −1 oxidation number; oxygen is usually assigned a −2 oxidation number (except in peroxide compounds [where it is −1] and in binary compounds with fluorine [where it is positive]); and hydrogen is usually assigned a +1 oxidation number [except when it exists as the hydride ion (H^-), in which case rule 2 prevails].**
>
> *In H_2O, the H atoms each have an oxidation number of +1, while the O atom has an oxidation number of −2, even though hydrogen and oxygen do not exist as ions in this compound (rule 3). By contrast, by rule 3, each H atom in hydrogen peroxide (H_2O_2) has an oxidation number of +1, while each O atom has an oxidation number of −1.*
>
> **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).**
>
> *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.*

Example 10.8.2.1: Assigning Oxidation States

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.
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.
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. Now consider the 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 we have the simple algebraic equation

$$x+3(-2)=-1$$

where *x* is the oxidation number of the N atom and the −1 represents the charge on the species. Evaluating for *x*,

$$x+(-6)=-1x=+5$$

Thus the oxidation number on the N atom in the NO_3^- ion is +5.

Exercise 10.8.2.1: Assigning Oxidation States

Assign oxidation numbers to the atoms in the following:

a. H_3PO_4
b. MgO

Answer a

H: +1; O: −2; P: +5

Answer b

Mg: +2, O: −2

All redox reactions occur with a simultaneous change in the oxidation numbers of some atoms. 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 10.8.2.2: Formation of Sodium Bromide

Identify what is being oxidized and reduced in the following redox reaction.

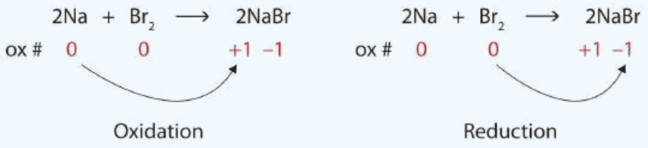
$$2\,\mathrm{Na} + \mathrm{Br_2} \rightarrow 2\,\mathrm{NaBr}$$

Solution

Both reactants are the elemental forms of their atoms, so the Na and Br atoms have oxidation numbers of 0. In the ionic product, the $\mathrm{Na^+}$ ions have an oxidation number of +1, while the $\mathrm{Br^-}$ ions have an oxidation number of −1.

$$2\underset{0}{Na} + \underset{0}{Br_2} \rightarrow 2\underset{+1-1}{NaBr}$$

Sodium is increasing its oxidation number from 0 to +1, so it is being oxidized; bromine is decreasing its oxidation number from 0 to −1, so it is being reduced:



Equation of sodium and bromine reacting, labeled with sodium's oxidation number change from 0 to +1 and bromine's oxidation number change from 0 to -1

Because oxidation numbers are changing, this is a redox reaction. The total number of electrons being lost by sodium (two, one lost from each Na atom) is gained by bromine (two, one gained for each Br atom).

Exercise 10.8.2.2: Oxidation of Carbon

Identify what is being oxidized and reduced in this redox reaction.

$$C + O_2 \rightarrow CO_2$$

Answer

C is being oxidized from 0 to +4; O is being reduced from 0 to −2

Oxidation reactions can become quite complex, as attested by the following redox reaction:

$$6H^+(aq) + 2\underset{+7}{MnO_4^-}(aq) + 5\underset{-1}{H_2O_2}(l) \rightarrow 2\underset{+2}{Mn^{2+}}(aq) + 5\underset{0}{O_2}(g) + 8H_2O(l)$$

To demonstrate that this is a redox reaction, the oxidation numbers of the species being oxidized and reduced are listed; can you determine what is being oxidized and what is being reduced? This is also an example of a net ionic reaction; spectator ions that do not change oxidation numbers are not displayed in the equation. Eventually, we will need to learn techniques for writing correct (i.e., balanced) redox reactions.

Combustion Reactions

A **combustion reaction** is a reaction in which a substance reacts with oxygen gas, releasing energy in the form of light and heat. Combustion reactions must involve $\mathrm{O_2}$ as one reactant. The combustion of hydrogen gas produces water vapor.

$$2\mathrm{H_2}\,(g) + \mathrm{O_2}\,(g) \rightarrow 2\mathrm{H_2O}\,(g) \tag{10.8.2.6}$$

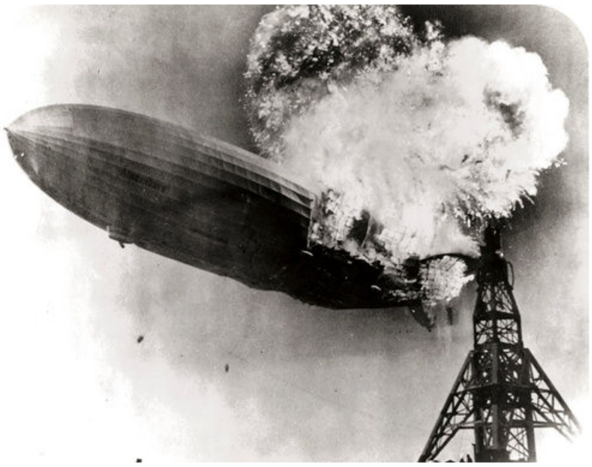


Figure 10.8.2.2: Explosion of the Hindenberg.

The *Hindenberg* was a hydrogen-filled airship that suffered an accident upon its attempted landing in New Jersey in 1937. The hydrogen immediately combusted in a huge fireball, destroying the airship and killing 36 people. The chemical reaction was a simple one: hydrogen combining with oxygen to produce water (Equation 10.8.2.6).

Many combustion reactions occur with a hydrocarbon, a compound made up solely of carbon and hydrogen. The products of the combustion of hydrocarbons are carbon dioxide and water. Many hydrocarbons are used as fuel because their combustion releases very large amounts of heat energy. Propane $\left(C_3H_8\right)$ is a gaseous hydrocarbon that is commonly used as the fuel source in gas grills.

$$C_3H_8\,(g) + 5O_2\,(g) \rightarrow 3CO_2\,(g) + 4H_2O\,(g)$$

✓ Example 10.8.2.3: Combustion of Ethanol

Ethanol can be used as a fuel source in an alcohol lamp. The formula for ethanol is C_2H_5OH. Write the balanced equation for the combustion of ethanol.

Solution

Solutions to Example 7.9.3

Steps	Example Solution
Write the unbalanced reaction.	$C_2H_5OH\,(l) + O_2\,(g) \rightarrow CO_2\,(g) + H_2O\,(g)$ Ethanol and atmospheric oxygen are the reactants. As with a hydrocarbon, the products of the combustion of an alcohol are carbon dioxide and water.
Balance the equation.	$C_2H_5OH\,(l) + 3O_2\,(g) \rightarrow 2CO_2\,(g) + 3H_2O\,(g)$
Think about your result.	Combustion reactions must have oxygen as a reactant. Note that the water produced is in the gas state, rather than the liquid state, because of the high temperatures that accompany a combustion reaction.

? Exercise 10.8.2.3: Combustion of Hexane

Write the balanced equation for the combustion of hexane, C_6H_{14}

Answer

$$2\,C_6H_{14}(\ell) + 19\,O_2(g) \rightarrow 12\,CO_2(g) + 14\,H_2O(\ell)$$

Contributors & Affiliations

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10.8.3: Balancing Redox Equations

Balancing Redox Equations Using Half-Reactions

Another way to balance redox reactions is by the half-reaction method. This technique involves breaking an equation into its two separate components—the oxidation reaction and the reduction reaction. Since neither oxidation nor reduction can actually occur without the other, we refer to the separate equations as **half-reactions**.

The general technique involves the following:

- The overall equation is broken down into **two** half-reactions. If there are any spectator ions, they are removed from the equations.
- Each half-reaction is balanced separately, first for atoms and then for charge. Electrons are added to one side of the equation or the other in order to balance charge. For example, if the reactant side of the equation has a total charge of +3, the product side must also equal +3.
- Next, the two equations are compared to make sure electrons lost equal electrons gained. One of the half reactions will be an oxidation reaction, the other will be a reduction reaction.
- Finally, the two half-reactions are added together, and any spectator ions that were removed are placed back into the equation.

Consider the following reaction:

$$Mg(s) + Cl_2(g) \rightarrow MgCl_2(s)$$

In this reaction, Mg is oxidized and Cl is reduced. You may find it useful to use oxidation numbers to help you determine this. Mg changes from 0 to +2; Cl changes from 0 to -1.

When we write the half-reactions, we break apart compounds that contain either of the key elements (elements undergoing oxidation or reduction). Oxidation numbers are written as if they were ion charges. Notice that the chlorine from $MgCl_2$ is written as two separate ions, not combined, as is Cl_2. Balance the two reactions for atoms.

$Mg \rightarrow Mg^{+2}$	$Cl_2 \rightarrow 2\ Cl^-$

Next balance the equations for charge by adding electrons. Remember, one half-reaction will be an oxidation reaction (electrons on the product side) and the other will be reduction (electrons will be on the reactant side).

$Mg \rightarrow Mg^{+2} + 2\ e^-$	$Cl_2 + 2\ e^- \rightarrow 2\ Cl^-$
oxidation	**reduction**

In this example, balancing for charge results in both sides, of both equations, having net charges of 0. That won't always be the case. Be sure you see in this example how charges are balanced.

We then compare the two equations for numbers of electrons. We see that both equations have 2 electrons so we do not need to make any adjustments for that. Finally, add the two equations together:

$$Mg + Cl_2 \rightarrow Mg^{+2} + 2Cl^-$$

and reform any compounds broken apart in the earlier steps:

$$Mg + Cl_2 \rightarrow MgCl_2$$

We see that the original equation was already balanced, not just for atoms, but for electrons as well.

✓ Example 2

$$Cu(s) + AgNO3(aq) \rightarrow Cu(NO_3)_2(aq) + Ag(s)$$

Solution

Identify the elements undergoing oxidation (Cu) and reduction (Ag). The nitrate group (NO_3) is a spectator ion which we will not include in our half-reactions.

$Cu \rightarrow Cu^{+2} + 2 e^-$	$Ag^+ + 1 e^- \rightarrow Ag$
oxidation	**reduction**

After balancing for atoms and for charge, we see that the two equations do not have the same number of electrons—there are 2 in the copper reaction, but only one in the silver reaction. Multiply everything in the silver reaction by 2, then we will add the equations together:

Step 1	**Step 2**	**Step 3**
Write the balanced half-reactions	**Balance electrons**	**Add half-reactions**
$Cu \rightarrow Cu^{+2} + 2 e^-$		$Cu \rightarrow Cu^{+2} + \cancel{2 e^-}$
$Ag + 1 e^- \rightarrow Ag^-$	× 2	$2 Ag^+ + \cancel{2e^-} \rightarrow 2 Ag$
Add equations together		$Cu + 2 Ag^+ \rightarrow Cu^{+2} + 2 Ag$
Reform compound/return spectator ions		$\mathbf{Cu + 2 AgNO_3 \rightarrow Cu(NO_3)_2 + 2 Ag}$

Here is a reaction occurring in an acid solution, which accounts for the presence of the H^+ions. This example adds a little more complexity to our problem.

$MnO_4^- + Fe^{2+} + H^+ \rightarrow Mn^{2+} + Fe^{3+} + H_2O$

In this example, spectator ions have already been removed. Even though hydrogen and oxygen do not undergo changes in oxidation number, they are not spectators, and we need to work with them in our half-reactions.

We determine that Mn undergoes reduction (+7 to +2) while Fe undergoes oxidation (+2 to +3). The iron half-reaction is straight forward, but the manganese reaction is more complex—we must include hydrogen and oxygen in its half-reaction:

$Fe^{2+} \rightarrow Fe^{+3} + 1e^-$	$MnO_4^- + 8 H^+ + 5 e^- \rightarrow Mn^{2+} + 4 H_2O$
oxidation	**reduction**

To balance the manganese half-reaction, first balance for Mn and O atoms. Next balance the H atoms, and finally add enough electrons to balance the charge on both sides of the equation. Be sure you see what has been done, so that you can do it on your own.

Step 1	**Step 2**	**Step 3**
Write the balanced half-reactions		**Add half-reactions**
$Fe^{2+} \rightarrow Fe^{+3} + 1e^-$	× 5	$5Fe^{2+} \rightarrow 5Fe^{+3} + \cancel{5e^-}$
$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$		$MnO_4^- + 8 H^+ + \cancel{5e^-} \rightarrow Mn^{2+} + 4 H_2O$
Add equations together	$\mathbf{MnO_4^- + 5 Fe^{2+} + 8 H^+ \rightarrow Mn^{2+} + 5 Fe^{3+} + 4H_2O}$	

Example 3

$$HNO_3 + Cu + H^+ \rightarrow NO_2 + Cu^{2+} + H_2O$$

Solution

1. Determine what is oxidized, what is reduced, and write the two **balanced** half-reactions (Step 1).
2. Balance for electrons lost = electrons gained (Step 2).
3. Add equations together.

Step 1	**Step 2**	**Step 3**
Write the balanced half-reactions		**Add half-reactions**
$Cu \rightarrow Cu^{+2} + 2e^-$		$Cu \rightarrow Cu^{+2} + \cancel{2e^-}$
$HNO_3 + H^+ + 1\ e^- \rightarrow NO_2 + H_2O$	× 2	$2HNO_3 + 2H^+ + \cancel{2e^-} \rightarrow 2NO_2 + 2H_2O$
Add equations together		$\mathbf{2HNO_3 + Cu + 2H^+ \rightarrow 2NO_2 + Cu^{2+} + 2H_2O}$

When balancing redox reactions, either the oxidation number method or the half-reaction method may be used. Often you'll find that one method works best for some equations, while the other method is more suited for other reactions. Or you may find one method just easier to use. The practice exercises and assignments tell you which method to use for a reaction, but as you get get more experience you'll be able to make your own decision as to which method to use.

10.9: Applications of Redox Reactions

The next pages will continue to explore aspects and applications of redox reactions.

10.9.1: The Activity Series- Predicting Spontaneous Redox Reactions

Learning Objectives

- Use the activity series to predict if a reaction will occur.

We see below two metals that can be exposed to water. The picture on the left is of sodium, which has a violent reaction when it comes in contact with water. The picture on the right is of silver, a metal so unreactive with water that it can be made into drinking vessels. Both metals have a single s electron in their outer shell, so you would predict a similar reactivity from each. However, we have a tool that allows us to make better predictions about how certain elements will react with others.

Figure 10.9.1.1: On the left, sodium reacts with water. On the right, silver in the form of cups does not react with water.

The 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. Since metals replace other metals, while nonmetals replace other nonmetals, they each have a separate activity series. The table $10.9.1.1$ below is an activity series of most common metals, and the table $10.9.1.2$ is an activity series of the halogens.

Table 10.9.1.1: Activity Series of Metal Elements

Elements, from most to least reactive	Reaction Occurring
Li K Ba Sr Ca Na	React with cold water, replacing hydrogen.
Mg Al Zn Cr Fe Cd	React with steam, but not cold water, replacing hydrogen.
Co Ni Sn Pb	Do not react with water. React with acids, replacing hydrogen.
H_2	
Cu Hg Ag Pt Au	Unreactive with water or acids.

Table 10.9.1.2: Activity Series of Nonmetal elements

Elements, from most to least reactive
F_2
Cl_2
Br_2
I_2

For a single-replacement reaction, a given element is capable of replacing an element that is below it in the activity series. This can be used to predict if a reaction will occur. 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.

$$\mathrm{Ni}\,(s)+\mathrm{Pb(NO_3)_2}\,(aq)\rightarrow \mathrm{Ni(NO_3)_2}\,(aq)+\mathrm{Pb}\,(s)$$

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

In the descriptions that accompany the activity series of metals, a given metal is also capable of undergoing the reactions described below that section. For example, lithium will react with cold water, replacing hydrogen. It will also react with steam and with acids, since that requires a lower degree of reactivity.

✓ Examples 10.9.1.1

Use the activity series to predict if the following reactions will occur. If not, write NR. If the reaction does occur, write the products of the reaction and balance the equation.

a. $\mathrm{Al}\,(s)+\mathrm{Zn(NO_3)_2}\,(aq)\rightarrow$
b. $\mathrm{Ag}\,(s)+\mathrm{HCl}\,(aq)\rightarrow$

Solution

Solutions to Example 7.11.1

Steps	**Example 10.9.1.1A** $\mathrm{Al}(s)+\mathrm{Zn(NO_3)_2}(aq)\rightarrow$	**Example 10.9.1.1B** $\mathrm{Ag}(s)+\mathrm{HCl}(aq)\rightarrow$
Plan the problem.	Compare the placements of aluminum and zinc on the activity series (Table 10.9.1.1)	Compare the placements of silver and hydrogen (Table 10.9.1.1)
Solve.	Since aluminum is above zinc, it is capable of replacing it and a reaction will occur. The products of the reaction will be aqueous aluminum nitrate and solid zinc. Take care to write the correct formulas for the products before balancing the equation. Aluminum adopts a $+3$ charge in an ionic compound, so the formula for aluminum nitrate is $\mathrm{Al(NO_3)_3}$. The balanced equation is: $2\mathrm{Al}(s)+3\mathrm{Zn(NO_3)_2}(aq)\rightarrow 2\mathrm{Al(NO_3)_3}(aq)+3\mathrm{Zn}(s)$	Since silver is below hydrogen, it is not capable of replacing hydrogen in a reaction with an acid. $\mathrm{Ag}(s)+\mathrm{HCl}(aq)\rightarrow \mathrm{NR}$

? Exercise 10.9.1.1

Use the activity series to predict the products, if any, of each equation.

a. $\mathrm{FeCl_2}+\mathrm{Zn}\rightarrow$
b. $\mathrm{HNO_3}+\mathrm{Au}\rightarrow$

Answer a

The products are $ZnCl_2$ + Fe.

Answer b

No reaction.

Summary

- Metals and halogens are ranked according to their ability to displace other metals or halogens below them in the activity series.

10.9.2: Batteries- Using Chemistry to Generate Electricity

Learning Objectives

- Identify the substance being oxidized and the substance being reduced in an oxidation-reduction reaction.
- Identify the anode and the cathode given a diagram of an electrolysis apparatus that includes the compound being electrolyzed.
- Describe how batteries can produce electrical energy.

Electricity is an important form of energy that you use every day. It runs your calculators, cell phones, dishwashers, and watches. This form of energy involves moving electrons through a wire and using the energy of these electrons. Electrochemical cells used for power generation are called batteries. Although batteries come in many different shapes and sizes, there are a few basic types. You won't be required to remember details of the batteries, but some general information and features of each type are presented here. Many important chemical reactions involve the exchange of one or more electrons, and we can use this movement of electrons as electricity; batteries are one way of producing this type of energy. The reactions that drive electricity are called oxidation-reduction (or "redox") reactions.

Oxidation and Reduction

Reactions in which electrons are transferred are called oxidation-reduction (or "redox") reactions. There are two parts to these changes: one atom must lose electrons and another atom must gain them. These two parts are described by the terms "oxidation" and "reduction".

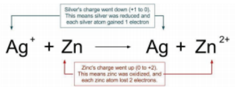
Originally, a substance was said to be oxidized when it reacted with oxygen. Today, the word "oxidized" is still used for those situations, but now we have a much broader second meaning for these words. Today, the broader sense of the word **oxidation** is defined as losing electrons. When a substance loses electrons, its charge will increase. This may feel a bit backwards, but remember that electrons are negative. If an atom loses electrons, it is losing negative particles—so its charge will increase.

The other half of this process, the gaining of electrons, also needs a name. When an atom or an ion gains electrons, the charge on the particle goes down. For example, if a sulfur atom whose charge is zero (0) gains two electrons, its charge becomes (-2); if an $\mathrm{Fe^{3+}}$ ion gains an electron, its charge changes from $+3$ to $+2$. In both cases, the charge on the particle is reduced by the gain of electrons. Remember that electrons have a negative charge, so gaining electrons will result in the charge decreasing. The word **reduction** is defined to mean gaining electrons and the reduction of charge.

In chemical systems, these two processes (oxidation and reduction) must occur simultaneously and the number of electrons lost in the oxidation must be the same as the number of electrons gained in the reduction. In oxidation-reduction reactions, electrons are transferred from one substance to another. Here is an example of an oxidation-reduction reaction:

$$\mathrm{2Ag^+}\,(aq)+\mathrm{Cu}\,(s)\rightarrow\mathrm{2Ag}\,(s)+\mathrm{Cu^{2+}}\,(aq)$$

In this reaction, the silver ions are gaining electrons to become silver atoms. Therefore, the silver ions are being reduced and the charge of silver is decreasing. The copper atoms are losing electrons to become copper $+2$ ions, are therefore being oxidized, and the charge of copper is increasing. Whenever a chemical reaction involves electrons being transferred from one substance to another, the reaction is an **oxidation-reduction reaction** (or a redox reaction).



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Half-equations are very helpful in discussing and analyzing processes, but half-reactions cannot occur as they appear. The half-reactions for the reaction above would be:

$$\mathrm{2Ag^+}\,(aq)+\mathrm{2e^-}\rightarrow\mathrm{2Ag}\,(s)$$

$$\mathrm{Cu}\,(s)\rightarrow\mathrm{Cu^{2+}}\,(aq)+\mathrm{2e^-}$$

Both oxidation and reduction must occur at the same time, so the electrons are donated and absorbed nearly simultaneously. The two half-reactions may be added together to represent a complete reaction. In order to add the half-reactions, the number of electrons donated and the number of electrons accepted must be equal.

Example 9.3.1

For each reaction, identify what is oxidized and what is reduced.

a) $\mathrm{Zn+HCl\rightarrow H_2+ZnCl_2}$

b) $\mathrm{Fe+O_2\rightarrow Fe_2O_3}$

c) $\mathrm{NaBr+I_2\rightarrow NaI+Br_2}$

Solution

In order to determine what is being oxidized and reduced, we must look at charges of atoms and see if they increase or decrease. (Remember, elements have no charge. In a compound, we can use our periodic table and what we learned in Chapter 4 to assign charges.) If the charge increases, the atom was oxidized. If the charge decreases, the atom was reduced.

a) This reaction written with charges is:

$$\mathrm{Zn^0+H^+Cl^-\rightarrow H_2^0+Zn^{2+}Cl_2^-}$$

Zn is oxidized because it went from 0 to $+2$. H is reduced because it went from $+1$ to 0. Cl was neither oxidized nor reduced.

b) This reaction written with charges is:

$$\mathrm{Fe^0+O_2^0\rightarrow Fe_2^{3+}O_3^{2-}}$$

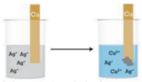
Fe is oxidized because it went from 0 to $+3$. O is reduced because it went from 0 to -2.

c) This reaction written with charges is:

$$\mathrm{Na^+Br^-+I_2^0\rightarrow Na^+I^-+Br_2^0}$$

Br is oxidized because it went from -2 to 0. I is reduced because it went from 0 to -1. Na was neither oxidized nor reduced as it stayed $+1$ the whole time.

Batteries



Redox reaction in one beaker does not produce electricity. (Source: Richard Parsons. CC-BY-SA)

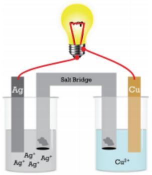
Batteries are devices that use chemical reactions to produce electrical energy. These reactions occur because the products contain less potential energy in their bonds than the reactants. The energy produced from excess potential energy not only allows the reaction to occur, but also often gives off energy to the surroundings. Some of these reactions can be physically arranged so that the energy given off is in the form of an electric current. These are the type of reactions that occur inside batteries. When a reaction is arranged to produce an electric current as it runs, the arrangement is called an **electrochemical cell** or a **Galvanic Cell.**

If a strip of copper is placed in a solution of silver nitrate, the following reaction takes place:

$$\mathrm{2Ag^+}\,(aq)+\mathrm{Cu}\,(s)\rightarrow\mathrm{2Ag}\,(s)+\mathrm{Cu^{2+}}\,(aq)$$

In this reaction, copper atoms are donating electrons to silver ions, so the silver ions are reduced to silver atoms and copper atoms are oxidized to copper (II) ions.

As the reaction occurs, an observer would see the solution slowly turn blue (Cu^{2+} ions are blue in solution) and a mass of solid silver atoms would build up on the copper strip.



In a battery, the oxidation and reduction half-reactions occur in separate containers, allowing the electrons to flow through a wire producing electricity.

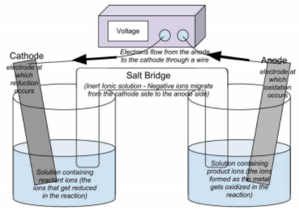
The reaction we just described is not set up in such a way as to produce electricity. It is true that electrons are being transferred, but to produce electricity, we need electrons flowing through a wire so that we can use the energy of these electrons. This reaction, $2\mathrm{Ag}^{+}(aq)+\mathrm{Cu}(s)\rightarrow 2\mathrm{Ag}(s)+\mathrm{Cu}^{2+}(aq)$, is one that could be arranged to produce electricity. To do this, the two half-reactions (oxidation and reduction) must occur in separate compartments, and the separate compartments must remain in contact through an ionic solution and an external wire.

In this electrochemical cell, the copper metal must be separated from the silver ions to avoid a direct reaction. Each electrode in its solution could be represented by a half-reaction.

$$\mathrm{Cu}\rightarrow \mathrm{Cu}^{2+}+2\mathrm{e}^{-}$$

$$2\mathrm{Ag}^{+}+2\mathrm{e}^{-}\rightarrow 2\mathrm{Ag}$$

The wire connects the two halves of the reaction, allowing electrons to flow from one metal strip to the other. In this particular example, electrons will flow from the copper electrode (which is losing electrons) into the silver electrode (which is where the silver ions gain the electrons). The cell produces electricity through the wire and will continue to do so as long as there are sufficient reactants (Ag^{+} and Cu) to continue the reaction.



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Electrochemical cells will always have two electrodes—the pieces of metal where electrons are gained or lost. (In this example, the strip of Ag metal and Cu metal are the electrodes.) The electrode where reduction occurs and electrons are gained is called the **cathode**. The electrode where oxidation occurs and electrons are lost is called the **anode**. Electrons will always move from the anode to the cathode. The electrons that pass through the external circuit can do useful work such as lighting lights, running cell phones, and so forth.

If the light bulb is removed from the circuit with the electrochemical cell and replaced with a voltmeter, the voltmeter will measure the voltage (electrical potential energy per unit charge) of the combination of half-cells. The size of the voltage produced by a cell depends on the temperature, the metals used for electrodes, and the concentrations of the ions in the solutions. If you increase the concentration of the reactant ion (not the product ion), the reaction rate will increase and so will the voltage.

It may seem complicated to construct an electrochemical cell due to all of their complexities. Electrochemical cells are actually easy to make and sometimes even occur accidentally. If you take two coins of different denomination, push them part way through the peel of a whole lemon, and then connect the two coins with a wire, a small electric current will flow.

1. Primary Batteries (Dry Cell Batteries)

- Non-rechargeable.
- Electrolytes are present as a paste rather than as a liquid.
- General purpose battery used for flashlights, transistor radios, toys, etc.
- The basic dry cell battery consists of: zinc case as the anode (oxidation); a graphite rod as the cathode (reduction) surrounded by a moist paste of either MnO_2, NH_4Cl, and $ZnCl_2$ (or, in alkaline dry cells, a KOH electrolytic paste).
- General reactions for the battery: manganese (IV) oxide-zinc cell (different batteries have different reactions—you don't need to remember any of these reactions).

cathode	$2MnO_{2(s)} + 2\ NH_4^{+}{}_{(aq)} + 2e^{-} \rightarrow Mn_2O_{3\ (s)} + H_2O_{(l)} + 2NH_{3\ (aq)}$
anode	$Zn_{(s)} \rightarrow Zn^{2+}{}_{(aq)} + 2e^{-}$

-
  - Maximum voltage of 1.5V. By connecting several cells in a series, 90V can be achieved.
  - Advantages of alkaline batteries: consistent voltage, increased capacity, longer shelf life, and reliable operation at temperatures as low as -40°C.
  - Disadvantage: higher cost.

2. Secondary Batteries (Storage Batteries)

- Rechargeable
- An example: the lead-acid battery used in cars. The anode is a grid of lead-antimony or lead-calcium alloy packed with spongy lead; the cathode is lead (IV) oxide. The electrolyte is aqueous sulfuric acid. This battery consists of numerous small cells connected in parallels (anode to anode; cathode to cathode).
- General reaction:

cathode	$PbO_{2(s)} + 4H^{+}{}_{(aq)} + SO_4^{2-}{}_{(aq)} + 2e^{-} \rightarrow PbSO_{4\ (s)} + 2H_2O_{(l)} + 2NH_{3\ (aq)}$
anode	$Pb_{(s)} + SO_4^{2-}{}_{(aq)} \rightarrow PbSO_{4\ (s)} + 2e^{-}$

-
  - Secondary batteries are recharged by passing a current through the battery in the opposite direction. In a car battery, this occurs when the engine is running.
  - Other examples include the nickel-iron alkaline battery, nickel-zinc battery, nickel-cadmium alkaline battery, silver-zinc battery, and silver-cadmium battery.

3. Fuel Cells

- Fuel cells are electrochemical cells that convert the energy of a redox combustion reaction directly into electrical energy. Fuel cells require a continuous supply of reactants and a constant removal of products.
- The cathode reactant is usually air or pure oxygen; the anode fuel is a gas such as hydrogen, methane, or propane. Carbon electrodes typically contain a catalyst. The electrolyte is typically KOH.
- General reaction:

cathode	$O_{2(g)} + 2H_2O_{(l)} + 4e^{-} \rightarrow 4OH^{-}{}_{(aq)}$
anode	$2H_{2\ (g)} + 4OH^{-}{}_{(aq)} \rightarrow 4H_2O_{(l)} + 4e^{-}$
net	$2H_{2\ (g)} + O_{2(g)} \rightarrow 2H_2O_{(l)}$

-
  - Advantages: no toxic waste products (water is the only product); very efficient energy conversion (70-80% efficient).
  - Disadvantage: too expensive for large-scale use.

Summary

- A reaction in which there is a transfer of electrons is said to be an oxidation-reduction reaction, or a redox reaction.
- A substance that loses electrons is said to be oxidized, and the substance that gains electrons is said to be reduced.
- Redox reactions can be used in electrochemical cells to produce electricity.
- Electrochemical cells are composed of an anode and cathode in two separate solutions. These solutions are connected by a salt bridge and a conductive wire.
- An electric current consists of a flow of charged particles.
- The electrode where oxidation occurs is called the anode, and the electrode where reduction occurs is called the cathode.

Vocabulary

- **Electrochemical cell** - An arrangement of electrodes and ionic solutions in which a redox reaction is used to make electricity (a battery).
- **Electrolysis** - A chemical reaction brought about by an electric current.
- **Electroplating** - A process in which electrolysis is used as a means of coating an object with a layer of metal.

10.9.3: Corrosion - Undesirable Redox Reactions

Corrosion of metals is a serious economic problem. Corrosion occurs as a result of spontaneous electrochemical reaction as metal undergoes oxidation. For example, the rusting of iron begins with the oxidation of solid iron:

$$\mathrm{Fe(s)} \rightarrow \mathrm{Fe^{2+}(aq)} + 2\,\mathrm{e^-}$$

The corresponding reduction reaction involves water:

$$\mathrm{H_2O(l)} + \tfrac{1}{2}\mathrm{O_2(g)} + 2\,\mathrm{e^-} \rightarrow 2\,\mathrm{OH^-(aq)}$$

The flaky brown solid that we call rust forms when Fe^{2+} undergoes additional oxidation to form Fe^{3+}, then reacts with hydroxide ions to form iron (III) oxide, Fe_2O_3, and iron (III) hydroxide, $Fe(OH)_3$.

The rate of corrosion can be affected by several factors. Some examples:

- Metals corrode faster when in contact with another metal. The Statue of Liberty, for example, has a skin made of copper, but is supported by iron ribs. Since iron is oxidized more readily than copper, it acts as the anode. Earlier repairs to strengthen the statue used iron bolts, which exacerbated the problem. More recent repairs have replaced the iron ribs with stainless steel alloys. Stainless steel resists corrosion.
- Salt water speeds up the corrosion process, because the ions in salt water form a salt bridge between the anodic and cathodic sites. Salt may be great for icy roads, but it is tough on cars.

There are a number of ways to slow down corrosion, if not prevent it:

- Prevent oxygen and water from contacting the metal. This can be accomplished by paint, grease, plastic, or other methods of covering the metal.
- Cathodic protection: pieces of zinc or magnesium metal may be bolted to the surface of iron. Because they are more readily oxidized than Fe, Zn and Mg become oxidized over time, thus sparing and protecting the iron. Propeller shafts of speedboats are often protected this way. Anode rods in water heaters also work this way (they are often called **sacrificial anodes**). Galvanized nails—nails coated with the more reactive zinc—provide yet another example.
- Metal alloys: an alloy is a mixture of metals, or a mixture of a nonmetal with a metal. An alloy such as stainless steel (chromium is added to steel—a mixture of iron and other elements such as carbon—to make stainless steel) is highly resistant to corrosion, but can be prohibitively expensive.

- **16.8: Corrosion- Undesirable Redox Reactions** by Henry Agnew, Marisa Alviar-Agnew is licensed CK-12. Original source: https://www.ck12.org/c/chemistry/.

10.E: Chemical Reactions (Exercises)

The following questions are related to the material covered in this chapter.

10.1-10.3: The Chemical Equation

1. From the statement “nitrogen and hydrogen react to produce ammonia,” identify the reactants and the products.
2. From the statement “sodium metal reacts with water to produce sodium hydroxide and hydrogen,” identify the reactants and the products.
3. From the statement “magnesium hydroxide reacts with nitric acid to produce magnesium nitrate and water,” identify the reactants and the products.
4. From the statement “propane reacts with oxygen to produce carbon dioxide and water,” identify the reactants and the products.
5. Write and balance the chemical equation described by Exercise 1.
6. Write and balance the chemical equation described by Exercise 2.
7. Write and balance the chemical equation described by Exercise 3.
8. Write and balance the chemical equation described by Exercise 4. The formula for propane is C_3H_8.
9. Balance: ___$NaClO_3$ → ___$NaCl$ + ___O_2
10. Balance: ___N_2 + ___H_2 → ___N_2H_4
11. Balance: ___Al + ___O_2 → ___Al_2O_3
12. Balance: ___C_2H_4 + ___O_2 → ___CO_2 + ___H_2O
13. How would you write the balanced chemical equation in Exercise 10 if all substances were gases?
14. How would you write the balanced chemical equation in Exercise 12 if all the substances except water were gases and water itself were a liquid?

Answers

1. reactants: nitrogen and hydrogen; product: ammonia
2.
3. reactants: magnesium hydroxide and nitric acid; products: magnesium nitrate and water
4.
5. $N_2 + 3H_2 \rightarrow 2NH_3$
6.
7. $Mg(OH)_2 + 2HNO_3 \rightarrow Mg(NO_3)_2 + 2H_2O$
8.
9. $2NaClO_3 \rightarrow 2NaCl + 3O_2$
10.
11. $4Al + 3O_2 \rightarrow 2Al_2O_3$
12.
13. $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$

10.4: Composition, Decomposition, and Combustion Reactions

1. Which is a composition reaction and which is not?
   a. $NaCl + AgNO_3 \rightarrow AgCl + NaNO_3$
   b. $CaO + CO_2 \rightarrow CaCO_3$
2. Which is a composition reaction and which is not?
   a. $H_2 + Cl_2 \rightarrow 2HCl$
   b. $2HBr + Cl_2 \rightarrow 2HCl + Br_2$
3. Which is a composition reaction and which is not?
   a. $2SO_2 + O_2 \rightarrow 2SO_3$

b. $6C + 3H_2 → C_6H_6$

4. Which is a composition reaction and which is not?
   a. $4Na + 2C + 3O_2 → 2Na_2CO_3$
   b. $Na_2CO_3 → Na_2O + CO_2$
5. Which is a decomposition reaction and which is not?
   a. $HCl + NaOH → NaCl + H_2O$
   b. $CaCO_3 → CaO + CO_2$
6. Which is a decomposition reaction and which is not?
   a. $3O_2 → 2O_3$
   b. $2KClO_3 → 2KCl + 3O_2$
7. Which is a decomposition reaction and which is not?
   a. $Na_2O + CO_2 → Na_2CO_3$
   b. $H_2SO_3 → H_2O + SO_2$
8. Which is a decomposition reaction and which is not?
   a. $2C_7H_5N_3O_6 → 3N_2 + 5H_2O + 7CO + 7C$
   b. $C_6H_{12}O_6 + 6O_2 → 6CO_2 + 6H_2O$
9. Which is a combustion reaction and which is not?
   a. $C_6H_{12}O_6 + 6O_2 → 6CO_2 + 6H_2O$
   b. $2Fe_2S_3 + 9O_2 → 2Fe_2O_3 + 6SO_2$
10. Which is a combustion reaction and which is not?
    a. $CH_4 + 2F_2 → CF_4 + 2H_2$
    b. $2H_2 + O_2 → 2H_2O$
11. Which is a combustion reaction and which is not?
    a. $P_4 + 5O_2 → 2P_2O_5$
    b. $2Al_2S_3 + 9O_2 → 2Al_2O_3 + 6SO_2$
12. Which is a combustion reaction and which is not?
    a. $C_2H_4 + O_2 → C_2H_4O_2$
    b. $C_2H_4 + Cl_2 → C_2H_4Cl_2$
13. Is it possible for a composition reaction to also be a combustion reaction? Give an example to support your case.
14. Is it possible for a decomposition reaction to also be a combustion reaction? Give an example to support your case.
15. Complete and balance each combustion equation.
    a. $C_4H_9OH + O_2 → ?$
    b. $CH_3NO_2 + O_2 → ?$
16. Complete and balance each combustion equation.
    a. $B_2H_6 + O_2 → ?$ (The oxide of boron formed is B_2O_3.)
    b. $Al_2S_3 + O_2 → ?$ (The oxide of sulfur formed is SO_2.)
    c. $Al_2S_3 + O_2 → ?$ (The oxide of sulfur formed is SO_3.)

Answers

1. a. not composition
   b. composition
2.
3. a. composition
   b. composition
4.
5. a. not decomposition
   b. decomposition
6.

7. a. not decomposition
   b. decomposition
8.
9. a. combustion
   b. combustion
10.
11. a. combustion
    b. combustion
12.
13. Yes; $2H_2 + O_2 \rightarrow 2H_2O$ (answers will vary)
14.
15. a. $C_4H_9OH + 6O_2 \rightarrow 4CO_2 + 5H_2O$
    b. $4CH_3NO_2 + 3O_2 \rightarrow 4CO_2 + 6H_2O + 2N_2$

10.5 - 10.6: Types of Chemical Reactions - Single and Double Displacement Reactions

1. What are the general characteristics that help you recognize single-replacement reactions?
2. What are the general characteristics that help you recognize double-replacement reactions?
3. Assuming that each single-replacement reaction occurs, predict the products and write each balanced chemical equation.
   a. $Zn + Fe(NO_3)_2 \rightarrow ?$
   b. $F_2 + FeI_3 \rightarrow ?$
4. Assuming that each single-replacement reaction occurs, predict the products and write each balanced chemical equation.
   a. $Li + MgSO_4 \rightarrow ?$
   b. $NaBr + Cl_2 \rightarrow ?$
5. Assuming that each single-replacement reaction occurs, predict the products and write each balanced chemical equation.
   a. $Sn + H_2SO_4 \rightarrow ?$
   b. $Al + NiBr_2 \rightarrow ?$
6. Assuming that each single-replacement reaction occurs, predict the products and write each balanced chemical equation.
   a. $Mg + HCl \rightarrow ?$
   b. $HI + Br_2 \rightarrow ?$
7. Use the periodic table or the activity series to predict if each single-replacement reaction will occur and, if so, write a balanced chemical equation.
   a. $FeCl_2 + Br_2 \rightarrow ?$
   b. $Fe(NO_3)_3 + Al \rightarrow ?$
8. Use the periodic table or the activity series to predict if each single-replacement reaction will occur and, if so, write a balanced chemical equation.
   a. $Zn + Fe_3(PO_4)_2 \rightarrow ?$
   b. $Ag + HNO_3 \rightarrow ?$
9. Use the periodic table or the activity series to predict if each single-replacement reaction will occur and, if so, write a balanced chemical equation.
   a. $NaI + Cl_2 \rightarrow ?$
   b. $AgCl + Au \rightarrow ?$
10. Use the periodic table or the activity series to predict if each single-replacement reaction will occur and, if so, write a balanced chemical equation.
    a. $Pt + H_3PO_4 \rightarrow ?$
    b. $Li + H_2O \rightarrow ?$ (Hint: treat H_2O as if it were composed of H^+ and OH^- ions.)
11. Assuming that each double-replacement reaction occurs, predict the products and write each balanced chemical equation.
    a. $Zn(NO_3)_2 + NaOH \rightarrow ?$
    b. $HCl + Na_2S \rightarrow ?$

12. Assuming that each double-replacement reaction occurs, predict the products and write each balanced chemical equation.
    a. $Ca(C_2H_3O_2)_2 + HNO_3 \rightarrow ?$
    b. $Na_2CO_3 + Sr(NO_2)_2 \rightarrow ?$
13. Assuming that each double-replacement reaction occurs, predict the products and write each balanced chemical equation.
    a. $Pb(NO_3)_2 + KBr \rightarrow ?$
    b. $K_2O + MgCO_3 \rightarrow ?$
14. Assuming that each double-replacement reaction occurs, predict the products and write each balanced chemical equation.
    a. $Sn(OH)_2 + FeBr_3 \rightarrow ?$
    b. $CsNO_3 + KCl \rightarrow ?$
15. Use the solubility rules to predict if each double-replacement reaction will occur and, if so, write a balanced chemical equation.
    a. $Pb(NO_3)_2 + KBr \rightarrow ?$
    b. $K_2O + Na_2CO_3 \rightarrow ?$
16. Use the solubility rules to predict if each double-replacement reaction will occur and, if so, write a balanced chemical equation.
    a. $Na_2CO_3 + Sr(NO_2)_2 \rightarrow ?$
    b. $(NH_4)_2SO_4 + Ba(NO_3)_2 \rightarrow ?$
17. Use the solubility rules to predict if each double-replacement reaction will occur and, if so, write a balanced chemical equation.
    a. $K_3PO_4 + SrCl_2 \rightarrow ?$
    b. $NaOH + MgCl_2 \rightarrow ?$
18. Use the solubility rules to predict if each double-replacement reaction will occur and, if so, write a balanced chemical equation.
    a. $KC_2H_3O_2 + Li_2CO_3 \rightarrow ?$
    b. $KOH + AgNO_3 \rightarrow ?$

Answers

1. One element replaces another element in a compound.
2.
3. a. $Zn + Fe(NO_3)_2 \rightarrow Zn(NO_3)_2 + Fe$
   b. $3F_2 + 2FeI_3 \rightarrow 3I_2 + 2FeF_3$
4.
5. a. $Sn + H_2SO_4 \rightarrow SnSO_4 + H_2$
   b. $2Al + 3NiBr_2 \rightarrow 2AlBr_3 + 3Ni$
6.
7. a. No reaction occurs.
   b. $Fe(NO_3)_3 + Al \rightarrow Al(NO_3)_3 + Fe$
8.
9. a. $2NaI + Cl_2 \rightarrow 2NaCl + I_2$
   b. No reaction occurs.
10.
11. a. $Zn(NO_3)_2 + 2NaOH \rightarrow Zn(OH)_2 + 2NaNO_3$
    b. $2HCl + Na_2S \rightarrow 2NaCl + H_2S$
12.
13. a. $Pb(NO_3)_2 + 2KBr \rightarrow PbBr_2 + 2KNO_3$
    b. $K_2O + MgCO_3 \rightarrow K_2CO_3 + MgO$
14.
15. a. $Pb(NO_3)_2 + 2KBr \rightarrow PbBr_2(s) + 2KNO_3$
    b. No reaction occurs.
16.
17. a. $2K_3PO_4 + 3SrCl_2 \rightarrow Sr_3(PO_4)_2(s) + 6KCl$

b. $2NaOH + MgCl_2 \rightarrow 2NaCl + Mg(OH)_2(s)$

10.7 - 10.9: RedOx Reactions

1. Is the reaction $2K(s) + Br_2(\ell) \rightarrow 2KBr(s)$

an oxidation-reduction reaction? Explain your answer.

2. Is the reaction $NaCl(aq) + AgNO_3(aq) \rightarrow NaNO_3(aq) + AgCl(s)$

   an oxidation-reduction reaction? Explain your answer.

3. In the reaction $2Ca(s) + O_2(g) \rightarrow 2CaO$

   indicate what has lost electrons and what has gained electrons.

4. In the reaction $16Fe(s) + 3S_8(s) \rightarrow 8Fe_2S_3(s)$

   indicate what has lost electrons and what has gained electrons.

5. In the reaction $4\ Li(s) + O_2(g) \rightarrow 2\ Li_2O(s)$

   indicate what has been oxidized and what has been reduced.

6. In the reaction $2Ni(s) + 3I_2(s) \rightarrow 2NiI_3(s)$

   indicate what has been oxidized and what has been reduced.

7. What are two different definitions of oxidation?
8. What are two different definitions of reduction?
9. Assign oxidation numbers to each atom in each substance.
   a. P_4
   b. SO_2
   c. SO_2^{2-}
   d. $Ca(NO_3)_2$
10. Assign oxidation numbers to each atom in each substance.
    a. PF_5
    b. $(NH_4)_2S$
    c. Hg
    d. Li_2O_2 (lithium peroxide)
11. Assign oxidation numbers to each atom in each substance.
    1. CO
    2. CO_2
    3. $NiCl_2$
    4. $NiCl_3$
12. Assign oxidation numbers to each atom in each substance.
    a. NaH (sodium hydride)
    b. NO_2
    c. NO_2^-
    d. $AgNO_3$
13. Assign oxidation numbers to each atom in each substance.
    a. CH_2O
    b. NH_3
    c. Rb_2SO_4
    d. $Zn(C_2H_3O_2)_2$
14. Assign oxidation numbers to each atom in each substance.
    a. C_6H_6
    b. $B(OH)_3$

   c. Li_2S
   d. Au
15. Identify what is being oxidized and reduced in this redox equation by assigning oxidation numbers to the atoms. (In NOCl, assign oxygen's oxidation number first, then chlorine, then solve for nitrogen.)

$2NO + Cl_2 \rightarrow 2NOCl$

16. Identify what is being oxidized and reduced in this redox equation by assigning oxidation numbers to the atoms.

$Fe + SO_3 \rightarrow FeSO_3$

17. Identify what is being oxidized and reduced in this redox equation by assigning oxidation numbers to the atoms. $2KrF_2 + 2H_2O \rightarrow 2Kr + 4HF + O_2$
18. Identify what is being oxidized and reduced in this redox equation by assigning oxidation numbers to the atoms. $SO_3 + SCl_2 \rightarrow SOCl_2 + SO_2$
19. Identify what is being oxidized and reduced in this redox equation by assigning oxidation numbers to the atoms. $2K + MgCl_2 \rightarrow 2KCl + Mg$
20. Identify what is being oxidized and reduced in this redox equation by assigning oxidation numbers to the atoms.

$C_7H_{16} + 11O_2 \rightarrow 7CO_2 + 8H_2O$

Answers

1. Yes; both K and Br are changing oxidation numbers.
2.
3. Ca has lost electrons, and O has gained electrons.
4.
5. Li has been oxidized, and O has been reduced.
6.
7. loss of electrons; increase in oxidation number
8.
9. a. P: 0
   b. S: +4; O: −2
   c. S: +2; O: −2
   d. Ca: 2+; N: +5; O: −2
10.
11. a. C: +2; O: −2
   b. C: +4; O: −2
   c. Ni: +2; Cl: −1
   d. Ni: +3; Cl: −1
12.
13. a. C: 0; H: +1; O: −2
   b. N: −3; H: +1
   c. Rb: +1; S: +6; O: −2
   d. Zn: +2; C: 0; H: +1; O: −2
14.
15. N is being oxidized, and Cl is being reduced.
16.
17. O is being oxidized, and Kr is being reduced.
18.
19. K is being oxidized, and Mg is being reduced.

Additional Exercises

1. What is the difference between a combination reaction and a redox reaction? Are all combination reactions also redox reactions? Are all redox reactions also combination reactions?

2. Are combustion reactions always redox reactions as well? Explain.
3. A friend argues that the equation

$$Fe^{2+} + Na \rightarrow Fe + Na^{+}$$

   is balanced because each side has one iron atom and one sodium atom. Explain why your friend is incorrect.

4. Historically, the first true battery was the Leclanché cell, named after its discoverer, Georges Leclanché. It was based on the following reaction:

$$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$$

   Identify what is being oxidized, what is being reduced, and the respective reducing and oxidizing agents.

Answers

1. A combination reaction makes a new substance from more than one reactant; a redox reaction rearranges electrons. Not all combination reactions are redox reactions, and not all redox reactions are combination reactions.

3. Your friend is incorrect because the number of electrons transferring is not balanced.

CHAPTER OVERVIEW

11: Stoichiometry- Quantities in Chemical Reactions

Stoichiometry is a big word that simply means "the study of quantities in chemical reactions". Using the basic tools we have developed in previous chapters, we will be able to solve problems relating to these quantities.

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11.1: General Stoichiometry

The only new information we need to be able to carry out stoichiometric calculations is to understand that the coefficients in the chemical equation may be used as conversion factors. Consider the equation for the formation of water from hydrogen and oxygen.

$$2\,\mathrm{H_2} + \mathrm{O_2} \rightarrow 2\,\mathrm{H_2O}$$

We can read this reaction as “two moles of hydrogen react with one mole of oxygen to produce two moles of water.” Any of the following ratios may be deduced from this equation.

$$\frac{2\text{ mol H}_2}{1\text{ mol O}_2} \text{ or } \frac{1\text{ mol O}_2}{2\text{ mol H}_2} \tag{11.1.1}$$

$$\frac{2\text{ mol H}_2\text{O}}{1\text{ mol O}_2} \text{ or } \frac{1\text{ mol O}_2}{2\text{ mol H}_2\text{O}} \tag{11.1.2}$$

$$\frac{2\text{ mol H}_2}{2\text{ mol H}_2\text{O}} \text{ or } \frac{2\text{ mol H}_2\text{O}}{2\text{ mol H}_2} \tag{11.1.3}$$

We can use these ratios to determine what amount of a substance, in moles, will react with or produce a given number of moles of a different substance.

✓ Example 11.1.1

How many moles of oxygen react with hydrogen to produce 27.6 mol of $\mathrm{H_2O}$?

Solution

Steps for Problem Solving	**How many moles of oxygen react with hydrogen to produce 27.6 mol of $\mathrm{H_2O}$?**
Find a balanced equation that describes the reaction.	Unbalanced: $H_2 + O_2 \rightarrow H_2O$ Balanced: $\underline{2}H_2 + O_2 \rightarrow \underline{2}H_2O$
Identify the "given" information and what the problem is asking you to "find."	Given: moles H_2O Find: moles oxygen
List other known quantities.	1 mol O_2 = 2 mol H_2O
Prepare a concept map and use the proper conversion factor.	 $\frac{1\ mol\ O_2}{2\ mol\ H_2O}$
Cancel units and calculate.	$27.6\text{ mol }\cancel{\mathrm{H_2O}} \times \frac{1\text{ mol O}_2}{2\text{ mol }\cancel{\mathrm{H_2O}}} = 13.8\text{ mol O}_2$ To produce 27.6 mol of H_2O, 13.8 mol of O_2 react.
Think about your result.	Since each mole of oxygen produces twice as many moles of water, it makes sense that the produced amount is greater than the reactant amount

As we know, however, chemical quantities are not usually stated in moles of a compound, but in grams of a solid, liters of a solution, etc. For this, we will need to use the tools learned in previous sections to help us to first convert into moles. Any easy way to think about this is as follows.

Stoichiometric calculations are generally as easy as 1-2-3.

1. **Convert into moles (if not already in moles).**
2. **Change substances (mole ratio from balanced chemical equation).**

3. **Convert out of moles (if needed).**

Many people appreciate a graphical representation like the one below. To use it, just look at your given information to figure out where to start and where you want to end up, then apply the steps to carry it out. The following three pages will explain how to apply the different pathways.

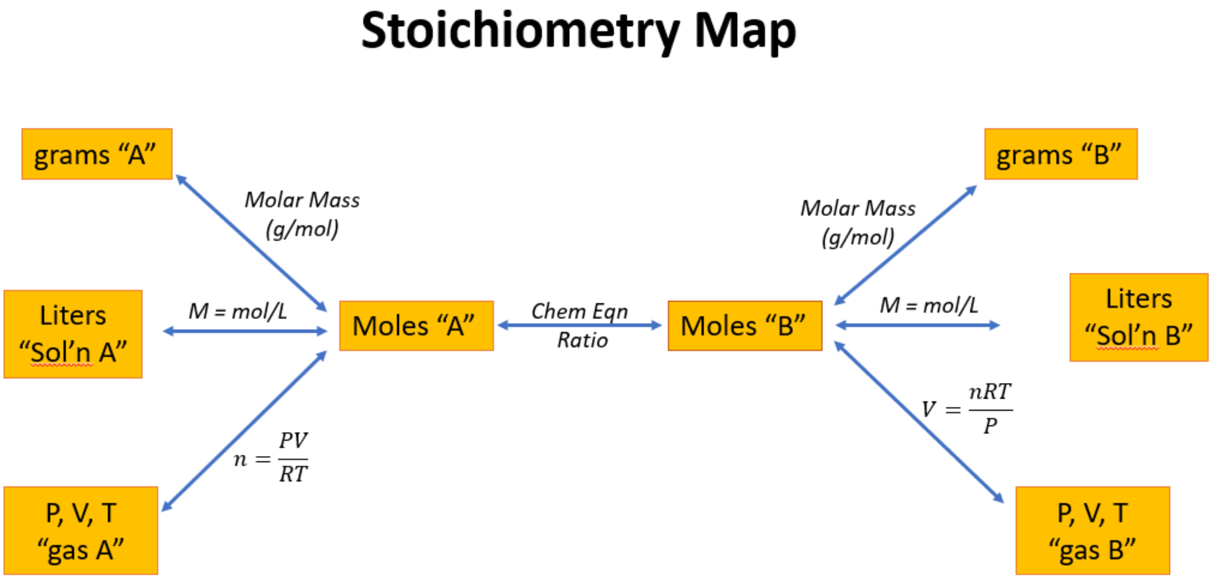


Figure 11.1.1: Stoichiometry Map

11.1.1: Mass Stoichiometry

Learning Objectives

- Convert from mass of one substance to mass of another substance in a chemical reaction.

Mass to Mass Stoichiometry Conversions

The first pathway we will look at is starting with grams of one chemical in an equation and ending with grams of another. See the highlighted portion below.

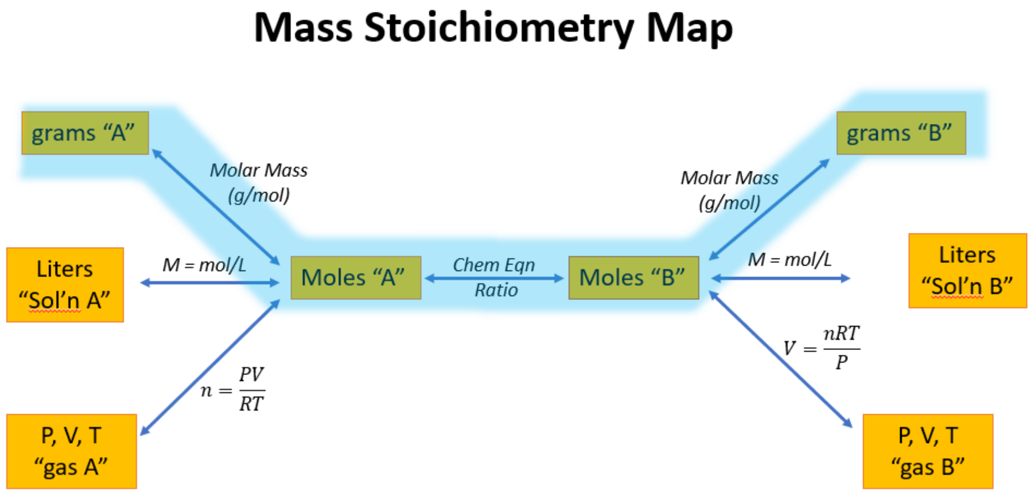


Figure 11.1.1.1: Mass stoichiometry pathway

Here's an example of how it will work.

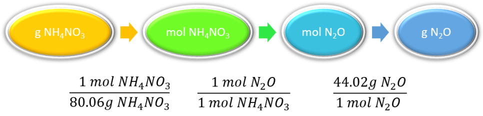
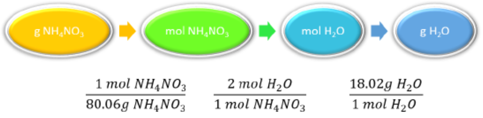
Example 11.1.1.2: Decomposition of Ammonium Nitrate

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, $45.7\ \text{g}$ of ammonium nitrate is decomposed. Find the mass of each of the products formed.

Solutions to Example 8.5.2

Steps for Problem Solving	Example 11.1.1.2
Identify the "given" information and what the problem is asking you to "find."	Given: 45.7 g NH_4NO_3 Find: Mass N_2O =? g Mass H_2O =? g
List other known quantities.	1 mol NH_4NO_3 = 80.06 g/mol 1 mol N_2O = 44.02 g/mol 1 mol H_2O = 18.02 g/mol 1 mol NH_4NO_3 to 1 mol N_2O to 2 mol H_2O
Prepare two concept maps and use the proper conversion factor.	 Flowchart of conversion factors: 1 mole NH4NO3 to 80.06 grams NH4NO3, 1 mole N2O to 1 mole NH4NO3, 44.02 grams N2O to 1 mole N2O  Flowchart of conversion factors: 1 mole NH4NO3 to 80.06 grams NH4NO3, 2 moles H2O to 1 mole NH4NO3, 18.02 grams H2O to 1 mole H2O

Steps for Problem Solving	Example 11.1.1.2
Cancel units and calculate.	$45.7\text{ g }NH_4NO_3 \times \frac{1\text{ mol }NH_4NO_3}{80.06\text{ g }NH_4NO_3} \times \frac{1\text{ mol }N_2O}{1\text{ mol }NH_4NO_3} \times \frac{44.02\text{ g }N_2O}{1\text{ mol }N_2O} = 25.1$ $45.7\text{ g }NH_4NO_3 \times \frac{1\text{ mol }NH_4NO_3}{80.06\text{ g }NH_4NO_3} \times \frac{2\text{ }H_2O}{1\text{ mol }NH_4NO_3} \times \frac{18.02\text{ g }H_2O}{1\text{ mol }H_2O} = 20.6$
Think about your result.	The total mass of the two products is equal to the mass of ammonium nitrate which decomposed, demonstrating the law of conservation of mass. Each answer has three significant figures.

? Exercise 11.1.1.2: Carbon Tetrachloride

Methane can react with elemental chlorine to make carbon tetrachloride (CCl_4). The balanced chemical equation is as follows:

$$CH_4(g) + 4\,Cl_2(g) \rightarrow CCl_2(l) + 4\,HCl(l)$$

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

Answer

908.7g HCl

Summary

- A balanced chemical reaction can be used to determine mass relationships between substances.

11.1.2: Solution Stoichiometry

- Convert from volume of a solution of one substance to volume of a solution of another substance in a chemical reaction.

Solution Stoichiometry Conversions

The second pathway we will look at is starting with volume (mL or L) of one chemical in an equation and ending with volume (mL or L) of another. See the highlighted portion below.

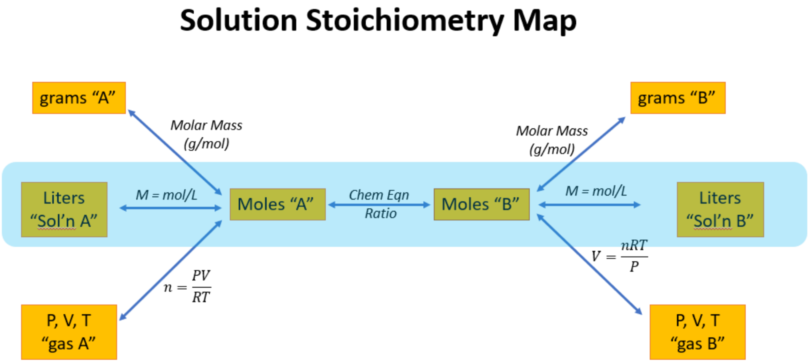


Figure 11.1.2.1: Solution stoichiometry pathway

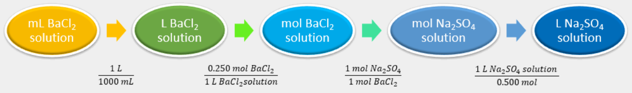
Here's an example of how it will work.

Example 11.1.2.1

What volume (in L) of 0.500 M sodium sulfate will react with 275 mL of 0.250 M barium chloride to completely precipitate all Ba^{2+} in the solution?

Solution

Solutions to Example 13.8.1

Steps for Problem Solving	Example 11.1.2.1
Identify the "given" information and what the problem is asking you to "find."	Given: 275 mL $BaCl_2$ 0.250 M $BaCl_2$ or $\frac{0.250\ mol BaCl_2}{1\ L\ BaCl_2\ solution}$ 0.500 M Na_2SO_4 or $\frac{0.500\ mol Na_2SO_4}{1\ L\ Na_2SO_4\ solution}$ Find: Volume Na_2SO_4 solution.
Set up and balance the chemical equation.	$Na_2SO_4(aq) + BaCl_2(aq) \longrightarrow BaSO_4(s) + \underline{2}NaCl(aq)$ An insoluble product is formed after the reaction.
List other known quantities.	1 mol of Na_2SO_4 to 1 mol $BaCl_2$ 1000 mL = 1 L
Prepare a concept map and use the proper conversion factor.	
Cancel units and calculate.	$275\ \cancel{mL\ BaCl_2\ solution} \times \frac{1\ \cancel{L}}{1000\ \cancel{mL}} \times \frac{0.250\ \cancel{mol\ BaCl_2}}{1\ \cancel{L\ BaCl_2\ solution}} \times \frac{1\ \cancel{mol\ Na_2}}{1\ \cancel{mol\ BaC}}$ = 0.1375 L sodium sulfate
Think about your result.	The lesser amount (almost half) of sodium sulfate is to be expected as it is more concentrated than barium chloride. Also, the units are correct.

Exercise 11.1.2.1

What volume of 0.250 M lithium hydroxide will completely react with 0.500 L of 0.250 M of sulfuric acid solution?

Answer

0.250 L LiOH solution

11.1.3: Stoichiometry and the Ideal Gas Law

Learning Objectives

- Convert from gas information of one substance to gas information of another substance in a chemical reaction.

Gas Stoichiometry Conversions

The third pathway we will look at is starting with gas information of one chemical in an equation and ending with gas information of another. See the highlighted portion below.

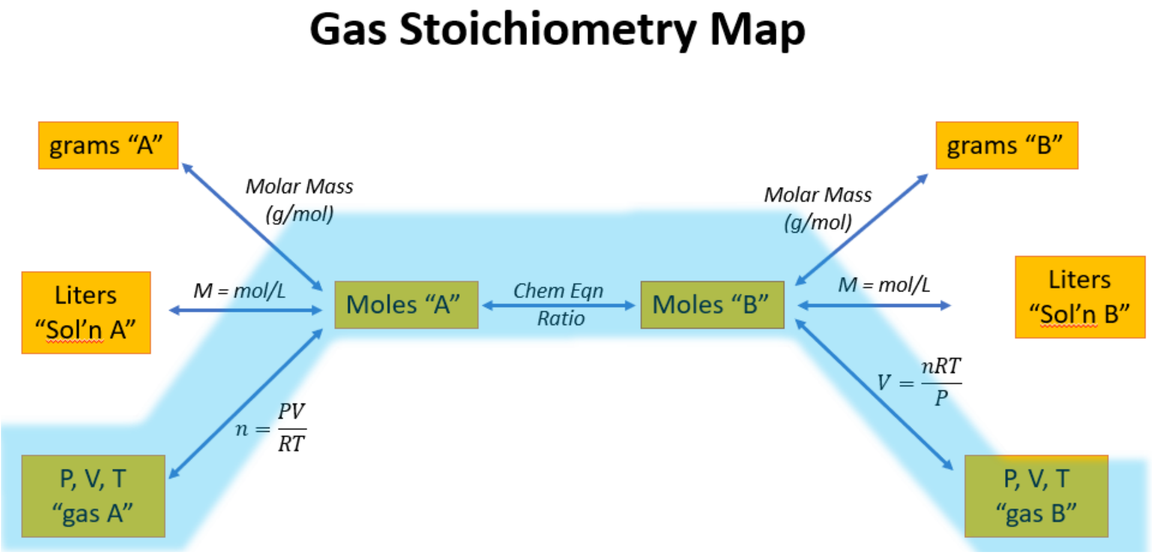


Figure 11.1.3.1: Gas stoichiometry pathway

Here's an example of how it will work.

Example 11.1.3.2B: Sulfuric Acid

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:

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

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?

Given: reaction, temperature, pressure, and mass of one product

Asked for: volume of gaseous reactant

Strategy:

A 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.

B 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.

Solution:

$$\text{mass of } H_2SO_4 \rightarrow \text{moles } H_2SO_4 \rightarrow \text{moles } O_2 \rightarrow \text{liters } O_2$$

A We begin by calculating the number of moles of H_2SO_4 in 1.00 ton:

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

We next calculate the number of moles of O_2 required:

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

B After converting all quantities to the appropriate units, we can use the ideal gas law to calculate the volume of O_2:

$$\begin{aligned} V &= \frac{nRT}{P} \\ &= \frac{1.389 \times 10^4 \text{ mol} \times 0.08206 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \times (273 + 22) \text{ K}}{745 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}}} \\ &= 3.43 \times 10^5 \ L \end{aligned}$$

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.

If you would like some additional practice applying your mole map to ideal gas stoichiometry, there are additional examples here and here. Please note that all of these examples have a similar form and that not all ideal gas stoichiometry problems will follow this particular form. However, it is probably useful to master this form prior to some of the additional considerations which follow.

? Exercise 11.1.3.2

Charles used a balloon containing approximately 31,150 L of H_2 for his initial flight in 1783. The hydrogen gas was produced by the reaction of metallic iron with dilute hydrochloric acid according to the following balanced chemical equation:

$$\mathrm{Fe(s)} + 2\,\mathrm{HCl(aq)} \rightarrow \mathrm{H_2(g)} + \mathrm{FeCl_2(aq)}$$

How much iron (in kilograms) was needed to produce this volume of H_2 if the temperature were 30°C and the atmospheric pressure was 745 mmHg?

Answer

68.6 kg of Fe (approximately 150 lb)

Additional applications of relating the mole concept to the ideal gas law can be found here, including a discussion of STP (the conditions necessary to use the original mole map.)

11.1.4: Gas Stoichiometry at STP

Learning Objectives

- State the value of standard temperature for Gas Law experiments.
- State the value of standard pressure for Gas Law experiments.
- Apply an STP conversion factor to convert between a molar quantity of a gas and its corresponding volume.
- Apply multiple conversion factors to solve problems that involve complex molar relationships.

As stated in Section 6.3, the original Gas Law experiments were limited to the investigation of two of the four measurable properties of gases. The measurements that were associated with two variables were held constant, so that any experimental change in the third quantity could only influence the value of the fourth. The subsequent sections presented and applied the Gas Laws, which relate the quantities that are altered in a particular trial. However, in order for any collected data to be meaningful, the experiment that was performed must be reproducible. Therefore, in order to complete every experimental trial under the same conditions, scientists were required to standardize the values of the two variables that were held constant.

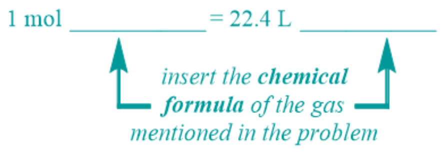
Standard Temperature and Pressure (STP)

Recall that Avogadro's Law directly relates an amount of gas to its volume under isothermal and isobarometric conditions. As described previously, the temperature and pressure of a gas impact the behaviors of its constituent particles, which, in turn, influence the volume of the gas. The application of pressure causes gaseous particles to move closer to one another, which decreases the overall volume of the gas. Additionally, by decreasing the temperature of a gas, its constituent particles move more slowly and, therefore, collide less often with the surfaces of the container in which they are held, which causes the container to shrink. Since the pressure and temperature at which a gas are held directly influence the volumetric results of an Avogadro's Law experiment, scientists who completed trials using different "constant" conditions generated inconsistent data and, therefore, were unable to corroborate the experimental findings of their peers. In order to eliminate these variations, scientists chose to perform all Avogadro's Law experiments at a temperature of 273 Kelvin and under 1 atmosphere of pressure.

Under these conditions, which became known as **standard temperature and pressure (STP),** scientists discovered that 1 mole of a gas, regardless of its identity, occupied a volume of 22.4 liters. Recall that the value of the constant, k_4, that is associated with the Avogadro's Law equation *typically* varies based on the identity of the gas that is being investigated. Therefore, since the amount of space that is occupied by a gas is *independent* of the identity of that gas at STP, the volumetric value that is given above is a chemically-significant quantity and, therefore, is defined as a molar standard.

Equality Pattern

Every molar standard has a corresponding equality pattern, which contains one number and *two* units on both sides of an equal sign. The left side of the STP equality pattern that is shown below contains a numerical value of "1," which is associated with the unit "mol." The right side of this equality pattern, which utilizes the volumetric value, "22.4," as its numerical quantity, has a primary unit of "L." The secondary unit positions, which are indicated as "blanks" in the equality pattern that is shown below, should be occupied by units that are relevant to the identity of the specific chemical that is referenced in a given problem. In particular, the chemical formula of the *gas* that is being considered should be inserted into both of these positions. A chemical name should *not* be used in this, or any, equality, and the relative order of the two units on either side of an STP equality should not be interchanged.



Indicator Phrase

Recall that all molar standards have a corresponding indicator word or phrase that identifies which relationship and, therefore, which equality pattern, must be applied to solve the problem at-hand. Because the volumetric value that is associated with this equality is only valid at an experimental temperature of 273 Kelvin and under 1 atmosphere of pressure, the phrase "at STP" must be present to indicate that an STP equality should be used to solve the given problem.

Calculations

For example, calculate how many moles of molecular chlorine gas are present in 75.0 liters of molecular chlorine at STP.

The phrase "at STP" indicates that the chemical formula for the gas that is referenced in the problem, molecular chlorine, Cl_2, should be incorporated into both of the secondary unit positions in the STP equality pattern that was developed above. The resultant equality, 1 mol Cl_2 = 22.4 L Cl_2, must then be applied as a conversion factor to eliminate the given unit, "liters of molecular chlorine." Applying the correct number of significant figures to the calculated quantity results in the final answer that is shown below.

$$75.0\ \text{L}\ \cancel{\text{Cl}_2} \times \frac{1\ \text{mol Cl}_2}{22.4\ \text{L}\ \cancel{\text{Cl}_2}} = 3.348214\ldots\text{mol Cl}_2 \approx 3.35\ \text{mol Cl}_2$$

Example 11.1.4.1

Consider the following balanced chemical equation.

$$\text{CaCN}_2\ (s) + 3\ \text{H}_2\text{O}\ (l) \rightarrow \text{CaCO}_3\ (s) + 2\ \text{NH}_3\ (g)$$

Calculate how many milliliters of nitrogen trihydride gas are generated if 0.17 moles of calcium cyanamide, CaCN_2, are consumed in this reaction at STP.

Solution

Indicator Information & Equality Patterns

Because both of the chemicals that are referenced in the problem, nitrogen trihydride, NH_3, and calcium cyanamide, CaCN_2, are also present in the given reaction equation, a stoichiometric equality should be developed and applied to solve this problem. The chemical formulas for nitrogen trihydride, NH_3, and calcium cyanamide, CaCN_2, are incorporated into the secondary unit positions on the left and rightsides, respectively, of this equality. Since the coefficient that is associated with nitrogen trihydride, NH_3, is a "2" in the given chemical equation, a 2 is inserted into the numerical position on the left side of this equality. Finally, because the coefficient that corresponds to calcium cyanamide, CaCN_2, is an unwritten "1" in the balanced chemical equation, a 1 is inserted into the numerical position on the right side of this equality, as shown below.

$$2\ \text{mol NH}_3 = 1\ \text{mol CaCN}_2$$

Additionally, the phrase "at STP" indicates that an STP equality should also be developed and applied to solve this problem. The chemical formula for the gas that is referenced in the problem, nitrogen trihydride, NH_3, should be incorporated into both of the secondary unit positions in this equality, as shown below.

$$1\ \text{mol NH}_3 = 22.4\ \text{L NH}_3$$

Dimensional Analysis

In order to completely eliminate the given unit, "moles of calcium cyanamide," a conversion factor based on the stoichiometric equality must be applied first. However, the unit that results upon the cancelation of "moles of calcium cyanamide" is "mol NH_3," which is not the desired final unit. Therefore, a second conversion factor, based on the STP equality, must be applied.

The unit that results upon the cancelation of the intermediate unit "mol NH_3" is "L NH_3," which still is not the desired final unit. In order to convert the intermediate unit "L NH_3" to the desired final unit, "milliliters of nitrogen trihydride," a prefix modifier equality that relates these two units must be developed and applied. As discussed in Section 1.8, a unit that contains a prefix modifier, such as "milliliters," can be related back to its base unit, "liters," by replacing the prefix modifier, "milli" (m), with its meaning, "10^{-3}," as shown below.

$$\text{mL} = 10^{-3}\ \text{L}$$

While not absolutely necessary, a prefix modifier equality can be simplified by rewriting the numerical quantity as a decimal, which can then be eliminated by dividing both sides of the equality by 0.001, resulting in the relationship that is shown below.

$$\text{mL} = 0.001\ \text{L}$$
$$1{,}000\ \text{mL} = \text{L}$$

Before applying one of these relationships to cancel the the intermediate unit "L NH_3," the chemical formula for nitrogen trihydride, NH_3, must be added as a secondary unit on each side of the equal sign. After incorporating this chemical formula, any of these equalities can be applied to completely cancel the intermediate unit "L NH_3," as shown below.

$$0.17\ \text{mol}\ \cancel{\text{CaCN}_2} \times \frac{2\ \cancel{\text{mol NH}_3}}{1\ \cancel{\text{mol CaCN}_2}} \times \frac{22.4\ \cancel{\text{L NH}_3}}{1\ \cancel{\text{mol NH}_3}} \times \frac{1{,}000\ \text{mL NH}_3}{\cancel{\text{L NH}_3}} = 7{,}616\ \text{mL NH}_3$$

$$\approx 7{,}600\ \text{mL NH}_3$$

The solution is calculated by multiplying the given number by the value in each numerator, and then dividing by the quantity in each denominator. When using a calculator, each conversion factor should be entered in parentheses, *or* the "=" key should be used after *each* division. Applying the correct number of significant figures to the calculated quantity results in the final answer that is shown above.

Exercise 11.1.4.1

Consider the following chemical equation.

$$\_\_\_ \, \mathrm{S}\,(s) + \_\_\_ \, \mathrm{O_2}\,(g) + \_\_\_ \, \mathrm{H_2O}\,(l) \rightarrow \_\_\_ \, \mathrm{H_2SO_4}\,(aq)$$

a. Balance this equation by writing coefficients in the "blanks," as necessary.
b. Classify this reaction as a combination, a decomposition, a single replacement, a double replacement, or a combustion reaction.
c. Identify the state of matter in which sulfur participates in this reaction.
d. Calculate the molecular weight of sulfuric acid, H_2SO_4. Represent the resultant solution as a molar equality and as a "hidden" conversion factor.
e. Calculate how many liters of molecular oxygen gas must be consumed if 76.2 grams of sulfuric acid, H_2SO_4, are generated in this reaction at STP.

Answer a

In order to balance a chemical equation, the quantities of each type of element and polyatomic ion that are present in the reactants and the products of the reaction must be determined. The product of this reaction contains hydrogen, H, and the sulfate ion, SO_4^{-2}, which is a polyatomic anion. However, because the sulfate ion is not present on the reactant side of the arrow, this ion cannot be balanced as a single entity and, therefore, must be divided into its constituent elements, sulfur, S, and oxygen, O. The quantities in which these elements are present in the given reaction equation are summarized in the table that is shown below. Note that oxygen, O, is present in two of the reactants that are shown in this equation. Therefore, in order to determine the number of oxygens that are present on the reactant side of this equation, the subscripts on both oxygens must be *added*.

Element or Ion	Reactants	Products	Balanced
S	1	1	✓
O	3	4	✗
H	2	2	✓

Since both sides of the equation contain equal amounts of sulfur, S, and hydrogen, H, those elements are balanced. Oyxgen, O, is not balanced, because this element is present in different quantities on the reactant and product sides of the reaction arrow. Therefore, one or more coefficients must be written in the "blanks" above, in order to balance this reaction.

In order to balance oxygen, O, a coefficient should be written in one of the "blanks" on the *left* side of the equation, as fewer oxygens are present on this side of the reaction arrow. However, as stated above, oxygen, O, is present in two of the reactants, molecular oxygen, O_2, and water, H_2O, in this equation. Because water, H_2O, also contains hydrogen, H, which is already balanced, a coefficient should not be placed in the "blank" that is associated with this molecule. Instead, a coefficient should be written in the "blank" that corresponds to molecular oxygen, O_2. The value of this coefficient, 1.5, is determined by *first subtracting 1* from the larger quantity of this element, 4, in order to account for the oxygen, O, that is present in water, H_2O, and then dividing the resultant quantity, 3, by the count of this element, 2, that is associated with molecular oxygen, O_2, on the left side of the equation. Inserting this coefficient results in the chemical equation that is shown below.

$$\_\_\_\ \mathrm{S}\,(s) + 1.5\ \mathrm{O_2}\,(g) + \_\_\_\ \mathrm{H_2O}\,(l) \rightarrow \_\_\_\ \mathrm{H_2SO_4}\,(aq)$$

As oxygen, O, is the only element that is present in this chemical formula, incorporating this coefficient does not alter the amounts of sulfur, S, or hydrogen, H, that are present on the reactant side of the equation. The updated quantity of this element is reflected in the table that is shown below. Because oxygen is present in *both* of the reactants, the quantities of oxygen in both of these molecules must be *added* to determine the amount of oxygen that is present on the reactant side of this equation. Inserting this coefficient balances oxygen, O, as intended. Therefore, all of the components of this equation are now balanced.

Element or Ion	Reactants	Products	Balanced
S	1	1	✓
O	$\cancel{3}$ 4	4	✓
H	2	2	✓

However, a fractional coefficient, 1.5, is written in the equation that is shown above. As a result, *all* of the coefficients in this equation, *including the unwritten "1"s that are understood to occupy the first, third, and fourth blanks,* must be *multiplied by 2*, in order to cancel this half-fraction. The doubled coefficient values are reflected in the chemical equation that is shown below.

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

By multiplying all of the coefficients in this equation by 2, the quantities in which sulfur, S, oxygen, O, and hydrogen, H, are present in the equation have changed, as shown in the table below, but their *relative ratios* have not. Therefore, all of the components of this equation are still balanced.

Element or Ion	Reactants	Products	Balanced
S	$\cancel{1}$ 2	$\cancel{1}$ 2	✓
O	$\cancel{3}$ $\cancel{4}$ 8	$\cancel{4}$ 8	✓
H	$\cancel{2}$ 4	$\cancel{2}$ 4	✓

Finally, these coefficients cannot be divided, as they do not all share a common divisor that would result in the calculation of four whole number coefficients. Therefore, the final equation that is presented above is chemically-correct, as written.

Answer b

This reaction is classified as a **combination** because only a *single molecule*, sulfuric acid, $\mathrm{H_2SO_4}$, is present on the *right* side of the reaction arrow.

Answer c

Sulfur, S, participates in this reaction as a **solid**, as indicated by the "(s)" that is associated with its formula in the given chemical equation.

Answer d

In order to calculate the molecular weight of a compound, the mass contribution of each element that is found within that compound must first be determined. Because sulfuric acid, H_2SO_4, contains three elements, the mass contributions of hydrogen, H, sulfur, S, and oxygen, O, must be calculated. In a mass contribution calculation,

- the chemical formula of the element that is being considered is written as the secondary unit for all numerical quantities;
- the subscript for the element that is being considered is inserted into the "component within" portion of the mass contribution pattern;
- the atomic mass average of the element that is being considered is recorded to the hundredths place in the numerator of the atomic weight conversion factor; and
- each resultant calculated value is reported to the hundredths place.

The mass contribution calculations for sulfuric acid, H_2SO_4, are shown below.

$$2\ \cancel{\text{mol H}} \times \frac{1.01\ \text{g H}}{1\ \cancel{\text{mol H}}} = 2.02\ \text{g H}$$

$$1\ \cancel{\text{mol S}} \times \frac{32.07\ \text{g S}}{1\ \cancel{\text{mol S}}} = 32.07\ \text{g S}$$

$$4\ \cancel{\text{mol O}} \times \frac{16.00\ \text{g O}}{1\ \cancel{\text{mol O}}} = 64.00\ \text{g O}$$

The numerical value of the molecular weight of sulfuric acid, H_2SO_4, 98.09, is determined by adding the mass contributions that are shown above and should be reported to the hundredths place.

In order to develop a molecular weight equality, the calculated molecular weight of the compound is equated to 1 mol of the compound, and the chemical formula of the *entire compound* is utilized as the secondary unit on both sides of the resultant equality, as shown below.

$$1\ \text{mol}\ H_2SO_4 = 98.09\ \text{g}\ H_2SO_4$$

Finally, this equality can be rewritten as a "hidden" conversion factor by dividing the quantity on the right side of the equal sign by the information on the left side, removing the "1," and condensing the primary unit to "g/mol." The chemical formula of the *entire compound* is still utilized as the secondary unit in this representation of molecular weight, as shown below.

$$98.09\ \text{g/mol}\ H_2SO_4$$

Answer e

Indicator Information & Equality Patterns

The mass unit "grams" indicates that a mass-based equality should be developed and applied to solve this problem. As multiple chemicals are referenced in this problem, the chemical formula for the substance that is written in closest physical proximity to the indicator word "grams," "sulfuric acid," H_2SO_4, is incorporated into the mass-based equality. Since sulfuric acid, H_2SO_4, is a compound, a molecular weight equality for this chemical, which was developed in Part (d) and is replicated below, should be applied to solve this problem.

$$1\ \text{mol}\ H_2SO_4 = 98.09\ \text{g}\ H_2SO_4$$

Additionally, because both of the chemicals that are referenced in the problem, molecular oxygen, O_2, and sulfuric acid, H_2SO_4, are also present in the given reaction equation, a stoichiometric equality should also be developed and applied to solve this problem. The chemical formulas for molecular oxygen, O_2, and sulfuric acid, H_2SO_4, are incorporated into the secondary unit positions on the left and right sides, respectively, of this equality. Since the coefficient that is associated with molecular oxygen, O_2, is a "3" in the chemical equation that was balanced in Part (a), a 3 is inserted into the numerical position on the left side of this equality. Finally, because the coefficient that corresponds to sulfuric acid, H_2SO_4, is a "2" in the balanced chemical equation, a 2 is inserted into the numerical position on the right side of this equality, as shown below.

$$3\ \text{mol}\ O_2 = 2\ \text{mol}\ H_2SO_4$$

Finally, the phrase "at STP" indicates that an STP equality should also be developed and applied to solve this problem. The chemical formula for the gas that is referenced in the problem, molecular oxygen, O_2, should be incorporated into both of the secondary unit positions in this equality, as shown below.

$$1 \text{ mol } O_2 = 22.4 \text{ L } O_2$$

Dimensional Analysis

In order to completely eliminate the given unit, "grams of sulfuric acid," a conversion factor based on the molecular weight equality must be applied first. However, the unit that results upon the cancelation of "grams of sulfuric acid" is "mol H_2SO_4," which is not the desired final unit. Therefore, a second conversion factor, based on the stoichiometric equality, must be applied. The unit that results upon the cancelation of the intermediate unit "mol H_2SO_4" is "mol O_2," which still is not the desired final unit. Therefore, the STP equality must be applied as a third conversion factor, as shown below.

$$76.2 \ \cancel{\text{g } H_2SO_4} \times \frac{1 \ \cancel{\text{mol } H_2SO_4}}{98.09 \ \cancel{\text{g } H_2SO_4}} \times \frac{3 \ \cancel{\text{mol } O_2}}{2 \ \cancel{\text{mol } H_2SO_4}} \times \frac{22.4 \text{ L } O_2}{1 \ \cancel{\text{mol } O_2}} = 26.101743\ldots \text{L } O_2 \approx 26.1 \text{ L } O_2$$

The solution is calculated by multiplying the given number by the value in each numerator, and then dividing by the quantity in each denominator. When using a calculator, each conversion factor should be entered in parentheses, *or* the "=" key should be used after *each* division. Applying the correct number of significant figures to the calculated quantity results in the final answer that is shown above.

11.1.5: Acid–Base Titration

Learning Objectives

- Understand the basics of acid-base titrations.
- Understand the use of indicators.
- Perform a titration calculation correctly.

The reaction of an acid with a base to make a salt and water is a common reaction in the laboratory, partly because so many compounds can act as acids or bases. Another reason that acid-base reactions are so prevalent is because they are often used to determine quantitative amounts of one or the other. Performing chemical reactions quantitatively to determine the exact amount of a reagent is called a **titration**. A titration can be performed with almost any chemical reaction for which the balanced chemical equation is known. Here, we will consider titrations that involve acid-base reactions.

During an acid-base titration, an acid with a known concentration (a **standard solution**) is slowly added to a base with an unknown concentration (or vice versa). A few drops of indicator solution are added to the base. The indicator will signal, by color change, when the base has been neutralized (when $[H^+] = [OH^-]$). At that point—called the **equivalence point,** or **end point**—the titration is stopped. By knowing the volumes of acid and base used, and the concentration of the standard solution, calculations allow us to determine the concentration of the other solution.

> It is important to accurately measure volumes when doing titrations. The instrument you would use is called a burette (or buret).

Figure 11.1.5.1: Equipment for Titrations. A burette is a type of liquid dispensing system that can accurately indicate the volume of liquid dispensed.

For example, suppose 25.66 mL (or 0.02566 L) of 0.1078 M HCl was used to titrate an unknown sample of NaOH. What mass of NaOH was in the sample? We can calculate the number of moles of HCl reacted:

$$\text{\# mol HCl} = (0.02566\ \text{L})(0.1078\ \text{M}) = 0.002766\ \text{mol HCl}$$

We also have the balanced chemical reaction between HCl and NaOH:

$$\mathrm{HCl + NaOH \rightarrow NaCl + H_2O}$$

So we can construct a conversion factor to convert to number of moles of NaOH reacted:

$$0.002766\ mol\ \cancel{HCl} \times \frac{1\, mol\ NaOH}{1\ mol\ \cancel{HCl}} = 0.002766\, mol\ NaOH$$

Then we convert this amount to mass, using the molar mass of NaOH (40.00 g/mol):

$$0.002766\ mol\ \cancel{HCl} \times \frac{40.00\, g\, NaOH}{1\ mol\ \cancel{HCl}} = 0.1106\, g\, NaOH$$

This type of calculation is performed as part of a titration.

Example 11.1.5.1: Equivalence Point

What mass of $Ca(OH)_2$ is present in a sample if it is titrated to its equivalence point with 44.02 mL of 0.0885 M HNO_3? The balanced chemical equation is as follows:

$$\mathrm{2\,HNO_3 + Ca(OH)_2 \rightarrow Ca(NO_3)_2 + 2\,H_2O}$$

Solution

In liters, the volume is 0.04402 L. We calculate the number of moles of titrant:

moles HNO_3 = (0.04402 L)(0.0885 M) = 0.00390 mol HNO_3

Using the balanced chemical equation, we can determine the number of moles of $Ca(OH)_2$ present in the analyte:

$$0.00390\ mol\ \cancel{HNO_3} \times \frac{1\ mol\ Ca(OH)_2}{2\ mol\ \cancel{HNO_3}} = 0.00195\ mol\ Ca(OH)_2$$

Then we convert this to a mass using the molar mass of $Ca(OH)_2$:

$$0.00195\ mol\ \cancel{Ca(OH)_2} \times \frac{74.1\ g\ Ca(OH)_2}{mol\ \cancel{Ca(OH)_2}} = 0.144\ g\ Ca(OH)_2$$

? Exercise 11.1.5.1

What mass of $H_2C_2O_4$ is present in a sample if it is titrated to its equivalence point with 18.09 mL of 0.2235 M NaOH? The balanced chemical reaction is as follows:

$$\mathrm{H_2C_2O_4 + 2\,NaOH \rightarrow Na_2C_2O_4 + 2\,H_2O}$$

Answer

0.182 g

? Exercise 11.1.5.2

If 25.00 mL of HCl solution with a concentration of 0.1234 M is neutralized by 23.45 mL of NaOH, what is the concentration of the base?

Answer

0.1316 M NaOH

? Exercise 11.1.5.3

A 20.0 mL solution of strontium hydroxide, $Sr(OH)_2$, is placed in a flask and a drop of indicator is added. The solution turns color after 25.0 mL of a standard 0.0500 M HCl solution is added. What was the original concentration of the $Sr(OH)_2$ solution?

Answer

$3.12 \times 10^{-2}\ M$ $Sr(OH)_2$

Indicator Selection for Titrations

The indicator used depends on the type of titration performed. The indicator of choice should change color when enough of one substance (acid or base) has been added to exactly use up the other substance. Only when a strong acid and a strong base are produced will the resulting solution be neutral. The three main types of acid-base titrations, and suggested indicators, are:

The three main types of acid-base titrations, suggested indicators, and explanations

Titration between . . .	Indicator	Explanation
strong acid and strong base	any	
strong acid and weak base	methyl orange	changes color in the acidic range (3.2 - 4.4)
weak acid and strong base	phenolphthalein	changes color in the basic range (8.2 - 10.6)

Summary

A titration is the quantitative reaction of an acid and a base. Indicators are used to show that all the analyte has reacted with the titrant.

Contributions & Attributions

- Peggy Lawson (Oxbow Prairie Heights School). Funded by Saskatchewan Educational Technology Consortium.

11.2: Limiting Reactant

Learning Objectives

- Identify the limiting reactant (limiting reagent) in a given chemical reaction.
- Calculate how much product will be produced from the limiting reactant.
- Calculate how much reactant(s) remains when the reaction is complete.

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 reactant. The reactant that remains after a reaction has gone to completion is in excess.

Consider a nonchemical example. Assume you have invited some friends for dinner and want to bake brownies for dessert. You find two boxes of brownie mix in your pantry and see that each package requires two eggs. The balanced equation for brownie preparation is:

$$1 \text{ box mix} + 2 \text{ eggs} \rightarrow 1 \text{ batch brownies} \tag{11.2.1}$$

If you have a dozen eggs, which ingredient will determine the number of batches of brownies that you can prepare? Because each box of brownie mix requires two eggs and you have two boxes, you need four eggs. Twelve eggs is eight more eggs than you need. Although the ratio of eggs to boxes in is 2:1, the ratio in your possession is 6:1. Hence the eggs are the ingredient (reactant) present in excess, and the brownie mix is the limiting reactant. Even if you had a refrigerator full of eggs, you could make only two batches of brownies.

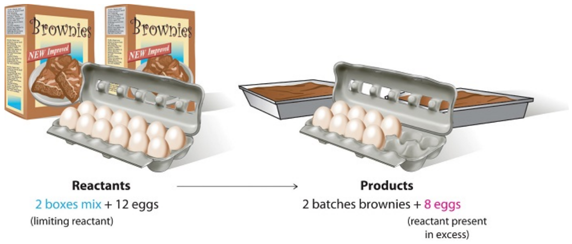


Figure 11.2.1: The Concept of a Limiting Reactant in the Preparation of Brownies. For a chemist, the **balanced** chemical equation is the recipe that must be followed. 2 boxes of brownie mix and 12 eggs results in 2 batches of brownies and 8 eggs; in this case the 8 eggs are reactant present in excess

PhET Simulation: Reactants, Products and Leftovers

View this interactive simulation illustrating the concepts of limiting and excess reactants.

Consider this concept now with regard to a chemical process, the reaction of hydrogen with chlorine to yield hydrogen chloride:

$$H_2 + Cl_2(g) \rightarrow 2\,HCl(g)$$

The balanced equation shows that hydrogen and chlorine react in a 1:1 stoichiometric ratio. If these reactants are provided in any other amounts, one of the reactants will nearly always be entirely consumed, thus limiting the amount of product that may be generated. This substance is the limiting reactant, and the other substance is the excess reactant. Identifying the limiting and excess reactants for a given situation requires computing the molar amounts of each reactant provided and comparing them to the stoichiometric amounts represented in the balanced chemical equation. For example, imagine combining 3 moles of H_2 and 2 moles of Cl_2. This represents a 3:2 (or 1.5:1) ratio of hydrogen to chlorine present for reaction, which is greater than the stoichiometric ratio of 1:1. Hydrogen, therefore, is present in excess, and chlorine is the limiting reactant. Reaction of all the provided chlorine (2 mol) will consume 2 mol of the 3 mol of hydrogen provided, leaving 1 mol of hydrogen non-reacted.

An alternative 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. For the example, in the previous paragraph, complete reaction of the hydrogen would yield:

$$\text{mol HCl produced} = 3 \text{ mol H}_2 \times \frac{2 \text{ mol HCl}}{1 \text{ mol H}_2} = 6 \text{ mol HCl}$$

Complete reaction of the provided chlorine would produce:

$$\text{mol HCl produced} = 2 \text{ mol Cl}_2 \times \frac{2 \text{ mol HCl}}{1 \text{ mol Cl}_2} = 4 \text{ mol HCl}$$

The chlorine will be completely consumed once 4 moles of HCl have been produced. Since enough hydrogen was provided to yield 6 moles of HCl, there will be non-reacted hydrogen remaining once this reaction is complete. Chlorine, therefore, is the limiting reactant and hydrogen is the excess reactant (Figure $11.2.2$).

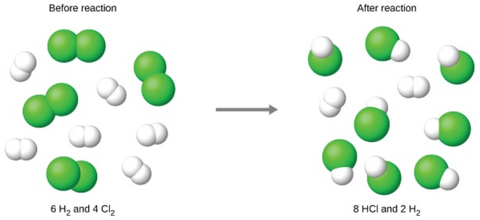


Figure 11.2.2: When H_2 and Cl_2 are combined in nonstoichiometric amounts, one of these reactants will limit the amount of HCl that can be produced. This illustration shows a reaction in which hydrogen is present in excess and chlorine is the limiting reactant. The figure shows a space-filling molecular models reacting. There is a reaction arrow pointing to the right in the middle. To the left of the reaction arrow there are three molecules each consisting of two green spheres bonded together. There are also five molecules each consisting of two smaller, white spheres bonded together. Above these molecules is the label, "Before reaction," and below these molecules is the label, "6 H subscript 2 and 4 C l subscript 2." To the right of the reaction arrow, there are eight molecules each consisting of one green sphere bonded to a smaller white sphere. There are also two molecules each consisting of two white spheres bonded together. Above these molecules is the label, "After reaction," and below these molecules is the label, "8 H C l and 2 H subscript 2."

A similar situation exists for many chemical reactions: you usually run out of one reactant before all of the other reactant has reacted. The reactant you run out of is called the limiting reactant; the other reactant or reactants are considered to be *in excess*. A crucial skill in evaluating the conditions of a chemical process is to determine which reactant is the limiting reactant and which is in excess.

How to Identify the Limiting Reactant (Limiting Reagent)

There are two ways to determine the limiting reactant. One method is to find and compare the mole ratio of the reactants used in the reaction (Approach 1). Another way is to calculate the grams of products produced from the given quantities of reactants; the reactant that produces the **smallest** amount of product is the limiting reactant (Approach 2). This section will focus more on the second method.

Approach 1 (The "Reactant Mole Ratio Method"): Find the limiting reactant by looking at the number of moles of each reactant.

1. Determine the balanced chemical equation for the chemical reaction.
2. Convert all given information into moles (most likely, through the use of molar mass as a conversion factor).
3. Calculate the mole ratio from the given information. Compare the calculated ratio to the actual ratio.
4. Use the amount of limiting reactant to calculate the amount of product produced.
5. If necessary, calculate how much is left in excess of the non-limiting (excess) reactant.

Approach 2 (The "The Product Method"): 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.

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. What we need to do is determine an amount of one product (either moles or mass) assuming all of each reactant reacts. Whichever reactant gives the least amount of that particular product is the limiting reactant. 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 that knowing the final mass of product can be useful.

✓ Example 11.2.1: Identifying the Limiting Reactant

As an example, consider the balanced equation

$$4\,C_2H_3Br_3 + 11\,O_2 \rightarrow 8\,CO_2 + 6\,H_2O + 6\,Br_2$$

What is the limiting reactant if 76.4 grams of $C_2H_3Br_3$ reacted with 49.1 grams of O_2?

Solution

Using Approach 1:

Step 1: *Balance the chemical equation.*

The equation is already balanced with the relationship

$$4 \text{ mol } C_2H_3Br_3 \text{ to } 11 \text{ mol } O_2 \text{ to } 6 \text{ mol } H_2O \text{ to } 6 \text{ mol Br}$$

Step 2: Convert all given information into moles.

$$76.4 \text{ g } \cancel{C_2H_3Br_3} \times \frac{1 \text{ mol } C_2H_3Br_3}{266.72 \text{ g } \cancel{C_2H_3B_3}} = 0.286 \text{ mol } C_2H_3Br_3$$

$$49.1 \text{ g } \cancel{O_2} \times \frac{1 \text{ mol } O_2}{32.00 \text{ g } \cancel{O_2}} = 1.53 \text{ mol } O_2$$

Step 3: Calculate the mole ratio from the given information. Compare the calculated ratio to the actual ratio.

Assuming that all of the oxygen is used up,

$$1.53\ \cancel{\text{mol}O_2} \times \frac{4\ \text{mol}C_2H_3Br_3}{11\ \cancel{\text{mol}O_2}} = 0.556 \text{ mol } C_2H_3Br_3 \text{ are required.}$$

Because 0.556 moles of $C_2H_3Br_3$ required > 0.286 moles of $C_2H_3Br_3$ available, $\underline{C_2H_3Br_3}$ is the limiting reactant.

Using Approach 2:

Step 1: *Balance the chemical equation.*

The equation is already balanced with the relationship

4 mol $C_2H_3Br_3$ to 11 mol O_2 to 6 mol H_2O to 6 mol Br

Step 2 and Step 3: Convert mass to moles and stoichiometry.

$$76.4\ \text{g}\ \cancel{C_2H_3Br_3} \times \frac{1\ \text{mol}\ \cancel{C_2H_3Br_3}}{266.72\ \text{g}\ \cancel{C_2H_3Br_3}} \times \frac{8\ \text{mol}\ \cancel{CO_2}}{4\ \text{mol}\ \cancel{C_2H_3Br_3}} \times \frac{44.01\ \text{g}\ CO_2}{1\ \text{mol}\ \cancel{CO_2}} = 25.2\ \text{g}\ CO_2$$

$$49.1\ \text{g}\ \cancel{O_2} \times \frac{1\ \text{mol}\ \cancel{O_2}}{32.00\ \text{g}\ \cancel{O_2}} \times \frac{8\ \text{mol}\ \cancel{CO_2}}{11\ \text{mol}\ \cancel{O_2}} \times \frac{44.01\ \text{g}\ CO_2}{1\ \text{mol}\ \cancel{CO_2}} = 49.1\ \text{g}\ CO_2$$

Step 4: The reactant that produces a smaller amount of product is the limiting reactant.

Therefore, by either method, $C_2H_3Br_3$ is the limiting reactant.

✓ Example 11.2.2: Identifying the Limiting Reactant and the Mass of Excess Reactant

For example, in the reaction of magnesium metal and oxygen, calculate the mass of magnesium oxide that can be produced if 2.40 g Mg reacts with 10.0 g O_2. Also determine the amount of excess reactant. MgO is the only product in the reaction.

Solution

Following Approach 1:

Step 1: Balance the chemical equation.

$$\underline{2}\ \text{Mg (s)} + O_2\ \text{(g)} \rightarrow \underline{2}\ \text{MgO (s)}$$

The balanced equation provides the relationship of 2 mol Mg to 1 mol O_2 to 2 mol MgO

Step 2 and Step 3: Convert mass to moles and stoichiometry.

$$2.40\ \text{g}\ \cancel{\text{Mg}} \times \frac{1\ \text{mol}\ \cancel{\text{Mg}}}{24.31\ \text{g}\ \cancel{\text{Mg}}} \times \frac{2\ \text{mol}\ \cancel{\text{MgO}}}{2\ \text{mol}\ \cancel{\text{Mg}}} \times \frac{40.31\ \text{g MgO}}{1\ \text{mol}\ \cancel{\text{MgO}}} = 3.98\ \text{g MgO}$$

$$10.0\ \text{g}\ \cancel{O_2} \times \frac{1\ \text{mol}\ \cancel{O_2}}{32.00\ \text{g}\ \cancel{O_2}} \times \frac{2\ \text{mol}\ \cancel{\text{MgO}}}{1\ \text{mol}\ \cancel{O_2}} \times \frac{40.31\ \text{g MgO}}{1\ \text{mol}\ \cancel{\text{MgO}}} = 25.2\ \text{g MgO}$$

Step 4: The reactant that produces a smaller amount of product is the limiting reactant.

Mg produces less MgO than does O_2 (3.98 g MgO vs. 25.2 g MgO), therefore Mg is the limiting reactant in this reaction.

Step 5: The reactant that produces a larger amount of product is the excess reactant.

O_2 produces more amount of MgO than Mg (25.2g MgO vs. 3.98 MgO), therefore O_2 is the excess reactant in this reaction.

Step 6: Find the amount of remaining excess reactant by subtracting the mass of the excess reactant consumed from the total mass of excess reactant given.

Mass of excess reactant calculated using the limiting reactant:

$$2.40\ \text{g}\ \cancel{\text{Mg}} \times \frac{1\ \text{mol}\ \cancel{\text{Mg}}}{24.31\ \text{g}\ \cancel{\text{Mg}}} \times \frac{1\ \text{mol}\ \cancel{O_2}}{2\ \text{mol}\ \cancel{\text{Mg}}} \times \frac{32.00\ \text{g}\ O_2}{1\ \text{mol}\ \cancel{O_2}} = 1.58\ \text{g}\ O_2$$

OR

Mass of excess reactant calculated using the mass of the product:

$$3.98\ \text{g}\ \cancel{\text{MgO}} \times \frac{1\ \text{mol}\ \cancel{\text{MgO}}}{40.31\ \text{g}\ \cancel{\text{MgO}}} \times \frac{1\ \text{mol}\ \cancel{O_2}}{2\ \text{mol}\ \cancel{\text{MgO}}} \times \frac{32.0\ \text{g}\ O_2}{1\ \text{mol}\ \cancel{O_2}} = 1.58\ \text{g}\ O_2$$

Mass of total excess reactant given – mass of excess reactant consumed in the reaction:

10.0g O_2 - (available) 1.58g O_2 (used) = 8.42g O_2 (excess)

Therefore, O_2 is in excess.

✓ Example 11.2.3: Limiting Reactant

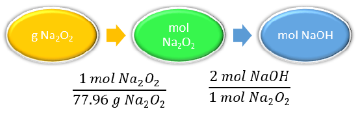
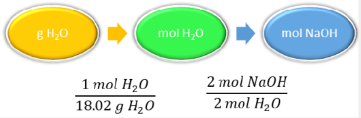
What is the limiting reactant if 78.0 grams of Na_2O_2 were reacted with 29.4 grams of H_2O? The unbalanced chemical equation is

$$\mathrm{Na_2O_2(s) + H_2O(l) \rightarrow NaOH(aq) + H_2O_2(l)}$$

Solution

Solutions to Example 8.4.3

Steps for Problem Solving- The Product Method	Example 11.2.1
Identify the "given" information and what the problem is asking you to "find."	Given: 78.0 grams of Na_2O_2 29.4 g H_2O Find: limiting reactant
List other known quantities.	1 mol Na_2O_2= 77.96 g/mol 1 mol H_2O = 18.02 g/mol Since the amount of product in grams is not required, only the molar mass of the reactants is needed.

Steps for Problem Solving- The Product Method	Example 11.2.1
Balance the equation.	Na_2O_2 (s) + 2H_2O (l) → 2NaOH (aq) + H_2O_2 (l) The balanced equation provides the relationship of 1 mol Na_2O_2 to 2 mol H_2O 2mol NaOH to 1 mol H_2O_2
Prepare a concept map and use the proper conversion factor.	  Because the question only asks for the limiting reactant, we can perform two **mass-mole** calculations and determine which amount is less.
Cancel units and calculate.	$78.0\text{ g Na}_2\text{O}_2 \times \frac{1\text{ mol Na}_2\text{O}_2}{77.96\text{ g Na}_2\text{O}_2} \times \frac{2\text{ mol NaOH}}{1\text{ mol Na}_2\text{O}_2} \times \frac{40\text{ g NaOH}}{1\text{ mol NaOH}} = 2.00\text{ mol NaOH}$ $29.4\text{ g H}_2\text{O} \times \frac{1\text{ mol H}_2\text{O}}{18.02\text{ g H}_2\text{O}} \times \frac{2\text{ mol NaOH}}{2\text{ mol Na}_2\text{O}_2} \times \frac{40\text{ g NaOH}}{1\text{ mol NaOH}} = 1.63\text{ mol NaOH}$ Therefore, H_2O is the *limiting reactant*.

Think about your result.

✓ Example 11.2.4: Limiting Reactant and Mass of Excess Reactant

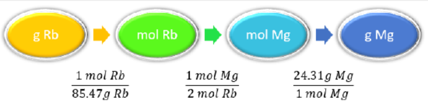
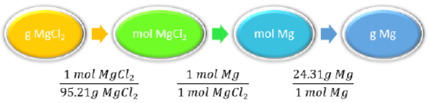
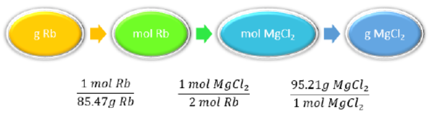
A 5.00 g quantity of Rb is combined with 3.44 g of $\mathrm{MgCl_2}$ according to this chemical reaction:

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

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

Solution

Solutions to Example 8.4.10

Steps for Problem Solving- The Product Method	Example 11.2.2
Steps for Problem Solving	A 5.00 g quantity of Rb is combined with 3.44 g of MgCl2 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 remaining reactant is left over?
Identify the "given" information and what the problem is asking you to "find."	Given: 5.00g Rb, 2.44g MgCl2 Find: mass of Mg formed, mass of remaining reactant
List other known quantities.	• molar mass: Rb = 85.47 g/mol • molar mass: $MgCl_2$ = 95.21 g/mol • molar mass: Mg = 24.31 g/mol
Prepare concept maps and use the proper conversion factor.	Find mass Mg formed based on mass of Rb  Find mass of Mg formed based on mass of $MgCl_2$  Conversion factors: 1 mole MgCl2 to 95.21 grams MgCl2, 1 mole Mg to 1 mole MgCl2, 24.31 grams Mg to 1 mole Mg Use limiting reactant to determine amount of excess reactant consumed  Conversion factors: 1 mole Rb to 85.47 grams Rb, 1 mole MgCl2 to 2 moles Rb, 95.21 grams MgCl2 to 1 mole MgCl2

Steps for Problem Solving- The Product Method	Example $11.2.2$
Cancel units and calculate.	Because the question asks what mass of magnesium is formed, we can perform two mass-mass calculations and determine which amount is less. $5.00\, g\, \cancel{Rb} \times \frac{1\, mol\, \cancel{Rb}}{85.47\, g\, \cancel{Rb}} \times \frac{1\, mol\, \cancel{Mg}}{2\, mol\, \cancel{Rb}} \times \frac{24.31\, g\, Mg}{1\, mol\, \cancel{Mg}} = 0.711\, g\, Mg$ $3.44\, g\, \cancel{MgCl_2} \times \frac{1\, mol\, \cancel{MgCl_2}}{95.21\, g\, \cancel{MgCl_2}} \times \frac{1\, mol\, \cancel{Mg}}{1\, mol\, \cancel{MgCl_2}} \times \frac{24.31\, g\, Mg}{1\, mol\, \cancel{Mg}} = 0.878\, g\, Mg$ The 0.711 g of Mg is the lesser quantity, so the associated reactant—5.00 g of Rb—is the limiting reactant. To determine how much of the other reactant is left, we have to do one more mass-mass calculation to determine what mass of $MgCl_2$ reacted with the 5.00 g of Rb, and then subtract the amount reacted from the original amount. $5.00\, g\, \cancel{Rb} \times \frac{1\, mol\, \cancel{Rb}}{85.47\, g\, \cancel{Rb}} \times \frac{1\, mol\, \cancel{MgCl_2}}{2\, mol\, \cancel{Rb}} \times \frac{95.21\, g\, MgCl_2}{1\, mol\, \cancel{MgCl_2}} = 2.78\, g\, MgCl_2\ \ reacted$ Because we started with 3.44 g of $MgCl_2$, we have 3.44 g $MgCl_2$ − 2.78 g $MgCl_2$ reacted = 0.66 g $MgCl_2$ left
Think about your result.	It usually is not possible to determine the limiting reactant using just the initial masses, as the reagents have different molar masses and coefficients.

? Exercise 11.2.1

Given the initial amounts listed, what is the limiting reactant, and what is the mass of the leftover reactant?

$$\underbrace{22.7\, g}_{MgO(s)} + \underbrace{17.9\, g}_{H_2S} \rightarrow MgS(s) + H_2O(l)$$

Answer

H_2S is the limiting reagent; 1.5 g of MgO are left over.

11.3: Theoretical Yield, and Percent Yield

Learning Objectives

- Calculate percentage or actual yields from known amounts of reactants.

The world of pharmaceutical production is an expensive one. Many drugs have several steps in their synthesis and use costly chemicals. A great deal of research takes place to develop better ways to make drugs faster and more efficiently. Studying how much of a compound is produced in any given reaction is an important part of cost control.

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 **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. However, percent yields greater than 100% are possible if the measured product of the reaction contains impurities that cause its mass to be greater than it actually would be if the product was pure. When a chemist synthesizes a desired chemical, he or she is always careful to purify the products of the reaction. Example $11.3.1$ illustrates the steps for determining percent yield.

✓ Example $11.3.1$: Decomposition of Potassium Chlorate

Potassium chlorate decomposes upon slight heating in the presence of a catalyst, according to the reaction below:

$$2\text{KClO}_3\,(s) \rightarrow 2\text{KCl}\,(s) + 3\text{O}_2\,(g)$$

In a certain experiment, 40.0 g KClO_3 is heated until it completely decomposes. The experiment is performed and the oxygen gas is collected and its mass is found to be 14.9 g

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

Solution

a. Calculation of theoretical yield

First, we will calculate the theoretical yield based on the stoichiometry.

Step 1: Identify the "given" information and what the problem is asking you to "find".

Given: Mass of $\text{KClO}_3 = 40.0 \text{ g}$

Mass of O_2 collected = 14.9g

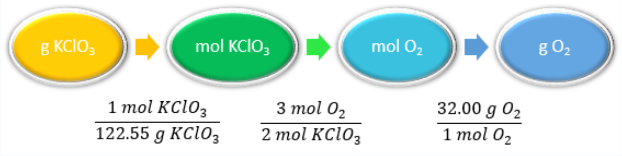
Find: Theoretical yield, g O_2

Step 2: List other known quantities and plan the problem.

1 mol $KClO_3$ = 122.55 g/mol

1 mol O_2 - 32.00 g/mol

Step 3: Apply stoichiometry to convert from the mass of a reactant to the mass of a product:



Step 4: Solve.

$$40.0 \text{ g } \cancel{KClO_3} \times \frac{1 \text{ mol } \cancel{KClO_3}}{122.55 \text{ g } \cancel{KClO_3}} \times \frac{3 \text{ mol } \cancel{O_2}}{2 \text{ mol } \cancel{KClO_3}} \times \frac{32.00 \text{ g } O_2}{1 \text{ mol } \cancel{O_2}} = 15.7 \text{ g } O_2$$

The theoretical yield of O_2 is 15.7 g, $15.\underline{6}7$ g unrounded.

Step 5: Think about your result.

The mass of oxygen gas must be less than the 40.0 g of potassium chlorate that was decomposed.

b. Calculation of percent yield

Now we will use the actual yield and the theoretical yield to calculate the percent yield.

Step 1: Identify the "given" information and what the problem is asking you to "find".

Given: Theoretical yield =$15.\underline{6}7$ g, use the un-rounded number for the calculation.

Actual yield = 14.9g

Find: Percent yield, % Yield

Step 2: List other known quantities and plan the problem.

No other quantities needed.

Step 3: Use the percent yield equation below.

$$\text{Percent Yield} = \frac{\text{Actual Yield}}{\text{Theoretical Yield}} \times 100\%$$

Step 4: Solve.

$$\text{Percent Yield} = \frac{14.9 \text{ g}}{15.\underline{6}7 \text{ g}} \times 100\% = 94.9\%$$

Step 5: Think about your result.

Since the actual yield is slightly less than the theoretical yield, the percent yield is just under 100%.

✓ Example 11.3.2: Oxidation of Zinc

Upon reaction of 1.274 g of copper sulfate with excess zinc metal, 0.392 g copper metal was obtained according to the equation:

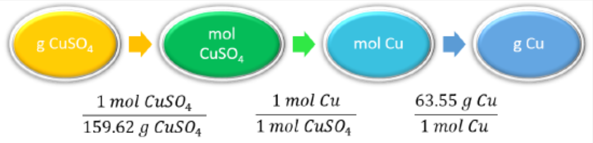
$$CuSO_4(aq) + Zn(s) \rightarrow Cu(s) + ZnSO_4(aq)$$

What is the percent yield?

Solution

Solutions to Example 8.6.2

Steps for Problem Solving-The Product Method	Example 11.3.1
Identify the "given" information and what the problem is asking you to "find."	Given: 1.274 g CuSO4 Actual yield = 0.392 g Cu Find: Percent yield
List other known quantities.	1 mol CuSO4= 159.62 g/mol 1 mol Cu = 63.55 g/mol Since the amount of product in grams is not required, only the molar mass of the reactants is needed.
Balance the equation.	The chemical equation is already balanced. The balanced equation provides the relationship of 1 mol CuSO4 to 1 mol Zn to 1 mol Cu to 1 mol ZnSO4.

Steps for Problem Solving-The Product Method	Example 11.3.1
Prepare a concept map and use the proper conversion factor.	 The provided information identifies copper sulfate as the limiting reactant, and so the theoretical yield (g Cu) is found by performing **mass-mass** calculation based on the initial amount of $CuSO_4$.
Cancel units and calculate.	$1.274\ \ \mathrm{g}\ \cancel{\mathrm{Cu_SO_4}} \times \frac{1\ \ \mathrm{mol}\ \cancel{\mathrm{CuSO_4}}}{159.62\ \ \mathrm{g}\ \cancel{\mathrm{CuSO_4}}} \times \frac{1\ \ \mathrm{mol}\ \cancel{\mathrm{Cu}}}{1\ \ \mathrm{mol}\ \cancel{\mathrm{CuSO_4}}} \times \frac{63.55\ \mathrm{g\ Cu}}{1\ \ \mathrm{mol}\ \cancel{\mathrm{Cu}}} = 0.507$ Using this theoretical yield and the provided value for actual yield, the percent yield is calculated to be: $\begin{aligned} \text{percent yield} &= \left(\frac{\text{actual yield}}{\text{theoretical yield}}\right) \times 100 \\ &= \left(\frac{0.392\, g\, \mathrm{Cu}}{0.5072\, g\, \mathrm{Cu}}\right) \times 100 \\ &= 77.3\% \end{aligned}$
Think about your result.	Since the actual yield is slightly less than the theoretical yield, the percent yield is just under 100%.

? Exercise 11.3.1

What is the percent yield of a reaction that produces 12.5 g of the Freon CF_2Cl_2 from 32.9 g of CCl_4 and excess HF?

$$\mathrm{CCl_4 + 2\,HF \rightarrow CF_2Cl_2 + 2\,HCl}$$

Answer

48.3%

Summary

Theoretical yield is calculated based on the stoichiometry of the chemical equation. The actual yield is experimentally determined. The percent yield is determined by calculating the ratio of actual yield to theoretical yield.

11.4: Enthalpy Change is a Measure of the Heat Evolved or Absorbed

When physical or chemical changes occur, they are generally accompanied by a transfer of energy. The **law of conservation of energy** states that in any physical or chemical process, energy is neither created nor destroyed. In other words, the entire energy in the universe is conserved. In order to better understand the energy changes taking place during a reaction, we need to define two parts of the universe, called the system and the surroundings. The **system** is the specific portion of matter in a given space that is being studied during an experiment or an observation. The **surroundings** are everything in the universe that is not part of the system. In practical terms for a laboratory chemist, the system is the particular chemicals being reacted, while the surroundings is the immediate vicinity within the room. During most processes, energy is exchanged between the system and the surroundings. If the system loses a certain amount of energy, that same amount of energy is gained by the surroundings. If the system gains a certain amount of energy, that energy is supplied by the surroundings.

A chemical reaction or physical change is **endothermic** if heat is absorbed by the system from the surroundings. In the course of an endothermic process, the system gains heat from the surroundings and so the temperature of the surroundings decreases. The quantity of heat for a process is represented by the letter q. The sign of q for an endothermic process is positive because the system is gaining heat. A chemical reaction or physical change is **exothermic** if heat is released by the system into the surroundings. Because the surroundings are gaining heat from the system, the temperature of the surroundings increases. The sign of q for an exothermic process is negative because the system is losing heat.

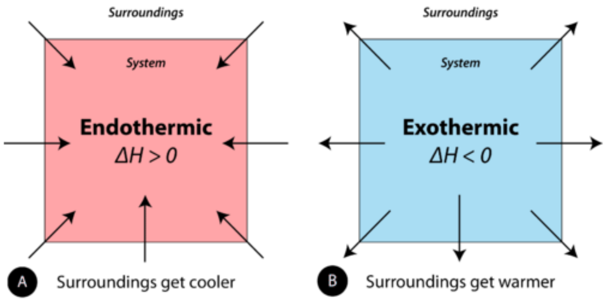


Figure 11.4.1: (A) Endothermic reaction. (B) Exothermic reaction.

Enthalpy

Heat changes in chemical reactions are often measured in the laboratory under conditions in which the reacting system is open to the atmosphere. In that case, the system is at a constant pressure. **Enthalpy** $(\boldsymbol{H})$ is the heat content of a system at constant pressure. Chemists routinely measure changes in enthalpy of chemical systems as reactants are converted into products. The heat that is absorbed or released by a reaction at constant pressure is the same as the enthalpy change, and is given the symbol ΔH. Unless otherwise specified, all reactions in this material are assumed to take place at constant pressure.

The change in enthalpy of a reaction is a measure of the differences in enthalpy of the reactants and products. The enthalpy of a system is determined by the energies needed to break chemical bonds and the energies needed to form chemical bonds. Energy needs to be put into the system in order to break chemical bonds, as they do not come apart spontaneously in most cases. Bond formation to produce products will involve release of energy. The change in enthalpy shows the trade-offs made in these two processes. Does it take more energy to break bonds than that needed to form bonds? If so, the reaction is endothermic and the enthalpy change is positive. If more energy is produced in bond formation than that needed for bond breaking, the reaction is exothermic and the enthalpy is negative.

Several factors influence the enthalpy of a system. Enthalpy is an extensive property, determined in part by the amount of material we work with. The state of reactants and products (solid, liquid, or gas) influences the enthalpy value for a system. The direction of the reaction affects the enthalpy value. A reaction that takes place in the opposite direction has the same numerical enthalpy value, but the opposite sign.

Thermochemical Equation

When methane gas is combusted, heat is released, making the reaction exothermic. Specifically, the combustion of 1 mol of methane releases 890.4 kilojoules of heat energy. This information can be shown as part of the balanced equation:

$$\mathrm{CH_4}\,(g) + 2\mathrm{O_2}\,(g) \rightarrow \mathrm{CO_2}\,(g) + 2\mathrm{H_2O}\,(l) + 890.4\text{ kJ}$$

The equation tells us that 1 mol of methane combines with 2 mol of oxygen to produce 1 mol of carbon dioxide and 2 mol of water. In the process, 890.4 kJ is released and so it is written as a product of the reaction. A **thermochemical equation** is a chemical equation that includes the enthalpy change of the reaction. The process in the above thermochemical equation can be shown visually in Figure $11.4.2$.

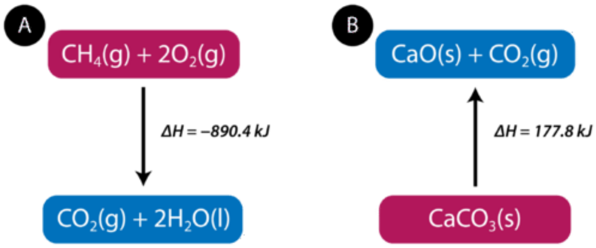


Figure $11.4.2$: (A) As reactants are converted to products in an exothermic reaction, enthalpy is released into the surroundings. The enthalpy change of the reaction is negative. (B) As reactants are converted to products in an endothermic reaction, enthalpy is absorbed from the surroundings. The enthalpy change of the reaction is positive.

In the combustion of methane example, the enthalpy change is negative because heat is being released by the system. Therefore, the overall enthalpy of the system decreases. The **heat of reaction** is the enthalpy change for a chemical reaction. In the case above, the heat of reaction is -890.4 kJ. The thermochemical reaction can also be written in this way:

$$\mathrm{CH_4}\left(g\right) + 2\mathrm{O_2}\left(g\right) \rightarrow \mathrm{CO_2}\left(g\right) + 2\mathrm{H_2O}\left(l\right) \qquad \Delta H = -890.4 \text{ kJ}$$

Heats of reaction are typically measured in kilojoules. It is important to include the physical states of the reactants and products in a thermochemical equation as the value of the ΔH depends on those states.

Endothermic reactions absorb energy from the surroundings as the reaction occurs. When 1 mol of calcium carbonate decomposes into 1 mol of calcium oxide and 1 mol of carbon dioxide, 177.8 kJ of heat is absorbed. The process is shown visually in Figure $11.4.2B$. The thermochemical reaction is shown below.

$$\mathrm{CaCO_3}\left(s\right) + 177.8 \text{ kJ} \rightarrow \mathrm{CaO}\left(s\right) + \mathrm{CO_2}\left(g\right)$$

Because the heat is absorbed by the system, the 177.8 kJ is written as a reactant. The heat of reaction is positive for an endothermic reaction.

$$\mathrm{CaCO_3}\left(s\right) \rightarrow \mathrm{CaO}\left(s\right) + \mathrm{CO_2}\left(g\right) \qquad \Delta H = 177.8 \text{ kJ}$$

The way in which a reaction is written influences the value of the enthalpy change for the reaction. Many reactions are reversible, meaning that the product(s) of the reaction are capable of combining and reforming the reactant(s). If a reaction is written in the reverse direction, the sign of the ΔH changes. For example, we can write an equation for the reaction of calcium oxide with carbon dioxide to form calcium carbonate.

$$\mathrm{CaO}\left(s\right) + \mathrm{CO_2}\left(g\right) \rightarrow \mathrm{CaCO_3}\left(s\right) + 177.8 \text{ kJ}$$

The reaction is exothermic and thus the sign of the enthalpy change is negative.

$$\mathrm{CaO}\left(s\right) + \mathrm{CO_2}\left(g\right) \rightarrow \mathrm{CaCO_3}\left(s\right) \qquad \Delta H = -177.8 \text{ kJ}$$

Stoichiometric Calculations and Enthalpy Changes

Chemistry problems that involve enthalpy changes can be solved by techniques similar to stoichiometry problems. Refer again to the combustion reaction of methane. Since the reaction of 1 mol of methane released 890.4 kJ, the reaction of 2 mol of methane would release $2 \times 890.4 \text{ kJ} = 1781 \text{ kJ}$. The reaction of 0.5 mol of methane would release $\frac{890,4 \text{ kJ}}{2} = 445.2 \text{ kJ}$. As with other stoichiometry problems, the moles of a reactant or product can be linked to mass or volume.

✓ Example $11.4.1$

Sulfur dioxide gas reacts with oxygen to form sulfur trioxide in an exothermic reaction, according to the following thermochemical equation.

$$2\mathrm{SO_2}\left(g\right) + \mathrm{O_2}\left(g\right) \rightarrow 2\mathrm{SO_3}\left(g\right) + 198 \text{ kJ}$$

Calculate the enthalpy change that occurs when $58.0\ \text{g}$ of sulfur dioxide is reacted with excess oxygen.

Solution

Step 1: List the known quantities and plan the problem.

- Mass $\text{SO}_2 = 58.0\ \text{g}$
- Molar mass $\text{SO}_2 = 64.07\ \text{g/mol}$
- $\Delta H = -198\ \text{kJ}$ for the reaction of $2\ \text{mol SO}_2$

Unknown

- $\Delta H = ?\ \text{kJ}$

The calculation requires two steps. The mass of SO_2 is converted to moles. Then the moles of SO_2 is multiplied by the conversion factor of $\left(\frac{-198\ \text{kJ}}{2\ \text{mol SO}_2}\right)$.

Step 2: Solve.

$$\Delta H = 58.0\ \text{g SO}_2 \times \frac{1\ \text{mol SO}_2}{64.07\ \text{g SO}_2} \times \frac{-198\ \text{kJ}}{2\ \text{mol SO}_2} = 89.6\ \text{kJ}$$

Step 3: Think about your result.

The mass of sulfur dioxide is slightly less than $1\ \text{mol}$. Since $198\ \text{kJ}$ is released for every $2\ \text{mol}$ of SO_2 that reacts, the heat released when about $1\ \text{mol}$ reacts is one half of 198. The $89.6\ \text{kJ}$ is slightly less than half of 198. The sign of ΔH is negative because the reaction is exothermic.

11.E: Stoichiometry Applications (Exercises)

The following questions are related to the material covered in this chapter. For additional discussion on each topic, also check the links included in each heading.

11.1: Stoichiometry

1. Think back to the pound cake recipe. What possible conversion factors can you construct relating the components of the recipe?
2. Think back to the pancake recipe. What possible conversion factors can you construct relating the components of the recipe?
3. What are all the conversion factors that can be constructed from the balanced chemical reaction:

$$2\,H_2(g) + O_2(g) \rightarrow 2\,H_2O(\ell)? \tag{11.E.1}$$

4. What are all the conversion factors that can be constructed from the balanced chemical reaction N_2(g) + $3H_2$(g) → $2NH_3$(g)?
5. Given the chemical equation : Na(s) + H_2O(ℓ) → NaOH(aq) + H_2(g)
   a. Balance the equation.
   b. How many molecules of H_2 are produced when 332 atoms of Na react?
6. Given the chemical equation: S(s) + O_2(g) → SO_3(g)
   a. Balance the equation.
   b. How many molecules of O_2 are needed when 38 atoms of S react?
7. For the balanced chemical equation:

$6H^+$(aq) + $2MnO_4^-$(aq) + $5H_2O_2$(ℓ) → $2Mn^{2+}$(aq) + $5O_2$(g) + $8H_2O$(ℓ)

how many molecules of H_2O are produced when 75 molecules of H_2O_2 react?

8. how many molecules of CO_2 are produced when 56 molecules of C_6H_6 react?
9. how many molecules of $Fe_2(SO_4)_3$ are produced if 321 atoms of S are reacted?
10. how many molecules of CuS are formed if 9,044 atoms of H react?
11. suppose we need to make 145,000 molecules of $Fe_2(SO_4)_3$. How many molecules of SO_3 do we need?

12. One way to make sulfur hexafluoride is to react thioformaldehyde, CH_2S, with elemental fluorine:

CH_2S + $6F_2$ → CF_4 + 2HF + SF_6

If 45,750 molecules of SF_6 are needed, how many molecules of F_2 are required?

13. Construct the three independent conversion factors possible for these two reactions:
    a. $2H_2$ + O_2 → $2H_2O$
    b. H_2 + O_2 → H_2O_2

Why are the ratios between H_2 and O_2 different?

The conversion factors are different because the stoichiometries of the balanced chemical reactions are different.

14. Construct the three independent conversion factors possible for these two reactions:
    a. 2Na + Cl_2 → 2NaCl
    b. 4Na + $2Cl_2$ → 4NaCl

What similarities, if any, exist in the conversion factors from these two reactions?

Answers

1.

$$\frac{1\,pound\,butter}{1\,pound\,flour} \tag{11.E.2}$$

or

$$\frac{1\,pound\,sugar}{1\,pound\,eggs} \tag{11.E.3}$$

are two conversion factors that can be constructed from the pound cake recipe. Other conversion factors are also possible.

2.

3. 2 molecules H21 molecule O2" role="presentation" style="position:relative;" tabindex="0">

$$\frac{2\,molecules\,H_2}{1\,molecule\,O_2} \tag{11.E.4}$$

,

$$\frac{1\,molecule\,O_2}{2\,molecules\,H_2O} \tag{11.E.5}$$

,

$$\frac{2\,molecules\,H_2}{2\,molecules\,H_2O} \tag{11.E.6}$$

and their reciprocals are the conversion factors that can be constructed. 2 molecules H21 molecule O2" role="presentation" style="position:relative;" tabindex="0">

4.
5. a. $2Na(s) + 2H_2O(\ell) \rightarrow 2NaOH(aq) + H_2(g)$
   b. 166 molecules
6.
7. 120 molecules
8.
9. 107 molecules
10.
11. 435,000 molecules
12.
13. a.

$$\frac{2\,molecules\,H_2}{1\,molecule\,O_2},\frac{1\,molecule\,O_2}{2\,molecules\,H_2O},\frac{2\,molecules\,H_2}{2\,molecules\,H_2O} \tag{11.E.7}$$

   b.

$$\frac{1\,molecules\,H_2}{1\,molecule\,O_2},\frac{1\,molecule\,O_2}{2\,molecules\,H_2O_2},\frac{1\,molecule\,H_2}{1\,molecule\,H_2O_2} \tag{11.E.8}$$

11.1.1: Mole-Mass and Mass-Mass Calculations

1. What mass of CO_2 is produced by the combustion of 1.00 mol of CH_4?$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(\ell)$
2. What mass of H_2O is produced by the combustion of 1.00 mol of CH_4? $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(\ell)$
3. What mass of HgO is required to produce 0.692 mol of O_2? $2HgO(s) \rightarrow 2Hg(\ell) + O_2(g)$
4. What mass of $NaHCO_3$ is needed to produce 2.659 mol of CO_2? $2NaHCO_3(s) \rightarrow Na_2CO_3(s) + H_2O(\ell) + CO_2(g)$
5. How many moles of Al can be produced from 10.87 g of Ag? $Al(NO_3)_3(s) + 3Ag \rightarrow Al + 3AgNO_3$
6. How many moles of HCl can be produced from 0.226 g of $SOCl_2$? $SOCl_2(\ell) + H_2O(\ell) \rightarrow SO_2(g) + 2HCl(g)$
7. How many moles of O_2 are needed to prepare 1.00 g of $Ca(NO_3)_2$? $Ca(s) + N_2(g) + 3O_2(g) \rightarrow Ca(NO_3)_2(s)$
8. How many moles of C_2H_5OH are needed to generate 106.7 g of H_2O? $C_2H_5OH(\ell) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(\ell)$
9. What mass of O_2 can be generated by the decomposition of 100.0 g of $NaClO_3$? $2NaClO_3 \rightarrow 2NaCl(s) + 3O_2(g)$
10. What mass of Li_2O is needed to react with 1,060 g of CO_2? $Li_2O(aq) + CO_2(g) \rightarrow Li_2CO_3(aq)$
11. What mass of Fe_2O_3 must be reacted to generate 324 g of Al_2O_3? $Fe_2O_3(s) + 2Al(s) \rightarrow 2Fe(s) + Al_2O_3(s)$
12. What mass of Fe is generated when 100.0 g of Al are reacted? $Fe_2O_3(s) + 2Al(s) \rightarrow 2Fe(s) + Al_2O_3(s)$
13. What mass of MnO_2 is produced when 445 g of H_2O are reacted? $H_2O(\ell) + 2MnO_4^-(aq) + Br^-(aq) \rightarrow BrO_3^-(aq) + 2MnO_2(s) + 2OH^-(aq)$
14. What mass of $PbSO_4$ is produced when 29.6 g of H_2SO_4 are reacted? $Pb(s) + PbO_2(s) + 2H_2SO_4(aq) \rightarrow 2PbSO_4(s) + 2H_2O(\ell)$
15. If 83.9 g of ZnO are formed, what mass of Mn_2O_3 is formed with it? $Zn(s) + 2MnO_2(s) \rightarrow ZnO(s) + Mn_2O_3(s)$
16. If 14.7 g of NO_2 are reacted, what mass of H_2O is reacted with it? $3NO_2(g) + H_2O(\ell) \rightarrow 2HNO_3(aq) + NO(g)$
17. If 88.4 g of CH_2S are reacted, what mass of HF is produced? $CH_2S + 6F_2 \rightarrow CF_4 + 2HF + SF_6$
18. If 100.0 g of Cl_2 are needed, what mass of NaOCl must be reacted?

$NaOCl + HCl \rightarrow NaOH + Cl_2$

Answers

1. 44.0 g
2.
3. 3.00×10^2 g
4.
5. 0.0336 mol
6.
7. 0.0183 mol
8.
9. 45.1 g
10.
11. 507 g
12.
13. 4.30×10^3 g
14.
15. 163 g
16.
17. 76.7 g

11.1.3: Solution Stoichiometry

1. What volume of 3.44 M HCl will react with 5.33 mol of $CaCO_3$? $2HCl + CaCO_3 \rightarrow CaCl_2 + H_2O + CO_2$
2. What volume of 0.779 M NaCl will react with 40.8 mol of $Pb(NO_3)_2$? $Pb(NO_3)_2 + 2NaCl \rightarrow PbCl_2 + 2NaNO_3$
3. What volume of 0.905 M H_2SO_4 will react with 26.7 mL of 0.554 M NaOH? $H_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + 2H_2O$
4. What volume of 1.000 M Na_2CO_3 will react with 342 mL of 0.733 M H_3PO_4? $3Na_2CO_3 + 2H_3PO_4 \rightarrow 2Na_3PO_4 + 3H_2O + 3CO_2$
5. It takes 23.77 mL of 0.1505 M HCl to titrate with 15.00 mL of $Ca(OH)_2$. What is the concentration of $Ca(OH)_2$? You will need to write the balanced chemical equation first.
6. It takes 97.62 mL of 0.0546 M NaOH to titrate a 25.00 mL sample of H_2SO_4. What is the concentration of H_2SO_4? You will need to write the balanced chemical equation first.
7. It takes 4.667 mL of 0.0997 M HNO_3 to dissolve some solid Cu. What mass of Cu can be dissolved? $Cu + 4HNO_3(aq) \rightarrow Cu(NO_3)_2(aq) + 2NO_2 + 2H_2O$
8. It takes 49.08 mL of 0.877 M NH_3 to dissolve some solid AgCl. What mass of AgCl can be dissolved? $AgCl(s) + 4NH_3(aq) \rightarrow Ag(NH_3)_4Cl(aq)$
9. What mass of 3.00% H_2O_2 is needed to produce 66.3 g of $O_2(g)$? $2H_2O_2(aq) \rightarrow 2H_2O(\ell) + O_2(g)$

Answers

1. 3.10 L
2.
3. 8.17 mL
4.
5. 0.1192 M
6.
7. 7.39 mg

8.
9. 4.70 kg

11.1.4: Gas Stoichiometry

1. How many liters, at STP, of CO_2 are produced from 100.0 g of C_8H_{18}, the approximate formula of gasoline? $2C_8H_{18}(\ell) + 25O_2(g) \rightarrow 16CO_2(g) + 18H_2O(\ell)$
2. How many liters, at STP, of O_2 are required to burn 3.77 g of butane from a disposable lighter?

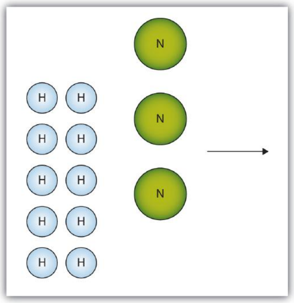
$2C_4H_{10}(g) + 13O_2(g) \rightarrow 8CO_2(g) + 10H_2O(\ell)$

Answers

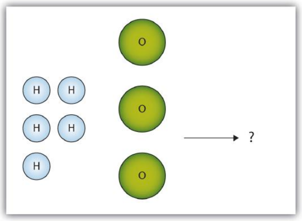
1. 157 L
2.

11.2: Limiting Reagents

1. The box below shows a group of nitrogen and hydrogen molecules that will react to produce ammonia, NH_3. What is the limiting reagent?



2. The box below shows a group of hydrogen and oxygen molecules that will react to produce water, H_2O. What is the limiting reagent?



3. Given the statement “20.0 g of methane is burned in excess oxygen,” is it obvious which reactant is the limiting reagent?
4. Given the statement “the metal is heated in the presence of excess hydrogen,” is it obvious which substance is the limiting reagent despite not specifying any quantity of reactant?
5. What is the limiting reagent? How much of the other reactant is in excess?
6. What is the limiting reagent? How much of the other reactant is in excess?
7. Given the initial amounts listed, what is the limiting reagent, and how much of the other reactant is in excess?

$$\underset{35.6\ g}{P_4O_6(s)} + \underset{4.77\ g}{6H_2O(l)} \rightarrow 4H_3PO_4 \tag{11.E.9}$$

8. Given the initial amounts listed, what is the limiting reagent, and how much of the other reactant is in excess?

$$\underset{377\ g}{3NO_2(g)} + \underset{244\ g}{H_2O(l)} \rightarrow 2HNO_3(aq) + NO(g) \tag{11.E.10}$$

9. To form the precipitate $PbCl_2$, 2.88 g of NaCl and 7.21 g of $Pb(NO_3)_2$ are mixed in solution. How much precipitate is formed? How much of which reactant is in excess?

10. In a neutralization reaction, 18.06 g of KOH are reacted with 13.43 g of HNO_3. What mass of H_2O is produced, and what mass of which reactant is in excess?

Answers

1. Nitrogen is the limiting reagent.
2.
3. Yes; methane is the limiting reagent.
4.
5. C is the limiting reagent; 4.33 g of H_2 are left over.
6.
7. H_2O is the limiting reagent; 25.9 g of P_4O_6 are left over.
8.
9. 6.06 g of $PbCl_2$ are formed; 0.33 g of NaCl is left over.

11.3: Yields

1. What is the difference between the theoretical yield and the actual yield?
2. What is the difference between the actual yield and the percent yield?
3. A worker isolates 2.675 g of SiF_4 after reacting 2.339 g of SiO_2 with HF. What are the theoretical yield and the actual yield? $SiO_2(s) + 4HF(g) \rightarrow SiF_4(g) + 2H_2O(\ell)$
4. A worker synthesizes aspirin, $C_9H_8O_4$, according to this chemical equation. If 12.66 g of $C_7H_6O_3$ are reacted and 12.03 g of aspirin are isolated, what are the theoretical yield and the actual yield? $C_7H_6O_3 + C_4H_6O_3 \rightarrow C_9H_8O_4 + HC_2H_3O_2$
5. A chemist decomposes 1.006 g of $NaHCO_3$ and obtains 0.0334 g of Na_2CO_3. What are the theoretical yield and the actual yield? $2NaHCO_3(s) \rightarrow Na_2CO_3(s) + H_2O(\ell) + CO_2(g)$
6. A chemist combusts a 3.009 g sample of C_5H_{12} and obtains 3.774 g of H_2O. What are the theoretical yield and the actual yield? $C_5H_{12}(\ell) + 8O_2(g) \rightarrow 5CO_2 + 6H_2O(\ell)$
7. What is the percent yield in Exercise 3?
8. What is the percent yield in Exercise 4?
9. What is the percent yield in Exercise 5?
10. What is the percent yield in Exercise 6?

Answers

1. Theoretical yield is what you expect stoichiometrically from a chemical reaction; actual yield is what you actually get from a chemical reaction.
2.
3. theoretical yield = 4.052 g; actual yield = 2.675 g
4.
5. theoretical yield = 0.635 g; actual yield = 0.0334 g
6.
7. 66.02%
8.
9. 5.26%

1.
11.4 Energy and Chemical Processes

Sulfur dioxide (SO_2) is a pollutant gas that is one cause of acid rain. It is oxidized in the atmosphere to sulfur trioxide (SO_3), which then combines with water to make sulfuric acid (H_2SO_4).

   1. Write the balanced reaction for the oxidation of SO_2 to make SO_3. (The other reactant is diatomic oxygen.)

2. When 1 mol of SO_2 reacts to make SO_3, 23.6 kcal of energy are given off. If 100 lb (1 lb = 454 g) of SO_2 were converted to SO_3, what would be the total energy change?

Ammonia (NH_3) is made by the direct combination of H_2 and N_2 gases according to this reaction:

$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g) + 22.0$ kcal

1. Is this reaction endothermic or exothermic?
2. What is the overall energy change if 1,500 g of N_2 are reacted to make ammonia?

A 5.69 g sample of iron metal was heated in boiling water to 99.8°C. Then it was dropped into a beaker containing 100.0 g of H_2O at 22.6°C. Assuming that the water gained all the heat lost by the iron, what is the final temperature of the H_2O and Fe?

A 5.69 g sample of copper metal was heated in boiling water to 99.8°C. Then it was dropped into a beaker containing 100.0 g of H_2O at 22.6°C. Assuming that the water gained all the heat lost by the copper, what is the final temperature of the H_2O and Cu?

When 1 g of steam condenses, 540 cal of energy is released. How many grams of ice can be melted with 540 cal?

When 1 g of water freezes, 79.9 cal of energy is released. How many grams of water can be boiled with 79.9 cal?

The change in energy is +65.3 kJ for each mole of calcium hydroxide [$Ca(OH)_2$] according to the following reaction:

$Ca(OH)_2(s) \rightarrow CaO(s) + H_2O(g)$

How many grams of $Ca(OH)_2$ could be reacted if 575 kJ of energy were available?

The thermite reaction gives off so much energy that the elemental iron formed as a product is typically produced in the liquid state:

$2Al(s) + Fe_2O_3(s) \rightarrow Al_2O_3(s) + 2Fe(\ell) + 204$ kcal

How much heat will be given off if 250 g of Fe are to be produced?

A normal adult male requires 2,500 kcal per day to maintain his metabolism.

1. Nutritionists recommend that no more than 30% of the calories in a person’s diet come from fat. At 9 kcal/g, what is the maximum mass of fat an adult male should consume daily?
2. At 4 kcal/g each, how many grams of protein and carbohydrates should an adult male consume daily?

A normal adult male requires 2,500 kcal per day to maintain his metabolism.

1. At 9 kcal/g, what mass of fat would provide that many kilocalories if the diet was composed of nothing but fats?
2. At 4 kcal/g each, what mass of protein and/or carbohydrates is needed to provide that many kilocalories?

The volume of the world’s oceans is approximately 1.34×10^{24} cm^3.

1. How much energy would be needed to increase the temperature of the world’s oceans by 1°C? Assume that the heat capacity of the oceans is the same as pure water.
2. If Earth receives 6.0×10^{22} J of energy per day from the sun, how many days would it take to warm the oceans by 1°C, assuming all the energy went into warming the water?

Does a substance that has a small specific heat require a small or large amount of energy to change temperature? Explain.

Some biology textbooks represent the conversion of adenosine triphosphate (ATP) to adenosine diphosphate (ADP) and phosphate ions as follows:

ATP → ADP + phosphate + energy

What is wrong with this reaction?

Assuming that energy changes are additive, how much energy is required to change 15.0 g of ice at −15°C to 15.0 g of steam at 115°C? (Hint: you will have five processes to consider.)

Answers

1. $2SO_2 + O_2 \rightarrow 2SO_3$
2. 16,700 kcal

2.

exothermic 1177 kcal

about 23.1°C

4. about 23.0°C

5. 6.76 g

6. 0.148 g

652 g

8. 457 kcal

   1. 83.3 g
   2. 438 g

10.

a. 278 g

b. 625 g

11.

1.34×10^{24} cal 93 days

12. A substance with **smaller specific heat** requires **less energy** per unit of mass to raise its temperature,

13. A reactant is missing: H_2O is missing.

14. Total energy = 11,019 cal

11: Additional Exercises

1. How many molecules of O_2 will react with 6.022×10^{23} molecules of H_2 to make water? The reaction is $2H_2(g) + O_2(g) \rightarrow 2H_2O(\ell)$.
2. How many molecules of H_2 will react with 6.022×10^{23} molecules of N_2 to make ammonia? The reaction is $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$.
3. How many moles are present in 6.411 kg of CO_2? How many molecules is this?
4. How many moles are present in 2.998 mg of SCl_4? How many molecules is this?
5. What is the mass in milligrams of 7.22×10^{20} molecules of CO_2?
6. What is the mass in kilograms of 3.408×10^{25} molecules of SiS_2?
7. What is the mass in grams of 1 molecule of H_2O?
8. What is the mass in grams of 1 atom of Al?
9. What is the volume of 3.44 mol of Ga if the density of Ga is 6.08 g/mL?
10. What is the volume of 0.662 mol of He if the density of He is 0.1785 g/L?
11. assume that 13.4 g of C_4H_{10} reacts completely to products. The density of CO_2 is 1.96 g/L. What volume in liters of CO_2 is produced?
12. if 223 g of $GaCl_3$ reacts completely to products and the density of Ga is 6.08 g/mL, what volume in milliliters of Ga is produced?
13. What do you notice about the sum of the masses of the products? What concept is being illustrated here?
14. What do you notice about the sum of the masses of the products? What concept is being illustrated here?
15. What mass of CO_2 is produced from the combustion of 1 gal of gasoline? The chemical formula of gasoline can be approximated as C_8H_{18}. Assume that there are 2,801 g of gasoline per gallon.
16. What mass of H_2O is produced from the combustion of 1 gal of gasoline? The chemical formula of gasoline can be approximated as C_8H_{18}. Assume that there are 2,801 g of gasoline per gallon.
17. A chemical reaction has a theoretical yield of 19.98 g and a percent yield of 88.40%. What is the actual yield?
18. A chemical reaction has an actual yield of 19.98 g and a percent yield of 88.40%. What is the theoretical yield?
19. Given the initial amounts listed, what is the limiting reagent, and how much of the other reactants are in excess?

$$\underset{35.0\ g}{P_4} + \underset{12.7\ g}{3NaOH} + \underset{9.33\ g}{3H_2O} \rightarrow 2Na_2HPO_4 + PH_3 \tag{11.E.11}$$

20. Given the initial amounts listed, what is the limiting reagent, and how much of the other reactants are in excess?

$$\underset{46.3\ g}{2NaCrO_2} + \underset{88.2\ g}{3NaBrO_4} + \underset{32.5\ g}{2NaOH} \rightarrow 3NaBrO_3 + 2Na_2CrO_4 + H_2O \tag{11.E.12}$$

21. Verify that it does not matter which product you use to predict the limiting reagent by using both products in this combustion reaction to determine the limiting reagent and the amount of the reactant in excess. Initial amounts of each reactant are given.

$$\underset{26.3\ g}{C_3H_8} + \underset{21.8\ g}{5O_2} \rightarrow 3CO_2(g) + 4H_2O(l) \tag{11.E.13}$$

22. Just in case you suspect Exercise 21 is rigged, do it for another chemical reaction and verify that it does not matter which product you use to predict the limiting reagent by using both products in this combustion reaction to determine the limiting reagent and the amount of the reactant in excess. Initial amounts of each reactant are given.

$$\underset{35.0\ g}{2P_4} + \underset{12.7\ g}{6NaOH} + \underset{9.33\ g}{6H_2O} \rightarrow 3Na_2HPO_4 + 5PH_3 \tag{11.E.14}$$

1. 1.2044 × 10^{24} molecules
2.
3. 145.7 mol; 8.77 × 10^{25} molecules
4.
5. 52.8 mg
6.
7. 2.99 × 10^{-23} g
8.
9. 39.4 mL
10.
11. 20.7 L
12.
13. 67.91 g of $CuCl_2$; 32.09 g of Cu. The two masses add to 100.0 g, the initial amount of starting material, demonstrating the law of conservation of matter.
14.
15. 8,632 g
16.
17. 17.66 g
18.
19. The limiting reagent is NaOH; 21.9 g of P_4 and 3.61 g of H_2O are left over.
20.
21. Both products predict that O_2 is the limiting reagent; 20.3 g of C_3H_8 are left over.

CHAPTER OVERVIEW

12: Acids and Bases

Acids and bases are common substances found in many every day items, from fruit juices and soft drinks to soap. In this chapter, we will examine the properties of acids and bases, and learn about the chemical nature of these important compounds. We will cover pH, and how to calculate the pH of a solution.

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SECTION OVERVIEW

12.1: Properties of Acids and Bases

In ancient times, acids and bases were mostly defined by their properties. We will be looking at modern definitions more in a forthcoming section, however these properties are still useful to talk about. Many of the ways in which we interact with acids and bases on an every day basis as well as determine acid or base properties in the laboratory setting are related to these properties which will be explored in this section.

12.1.1: Acids- Properties and Examples

Learning Objectives

- Examine properties of acids.

Many people enjoy drinking coffee. A cup first thing in the morning helps start the day. But keeping the coffee maker clean can be a problem. Lime deposits build up after a while and slow down the brewing process. The best cure for this is to put vinegar (dilute acetic acid) in the pot and run it through the brewing cycle. The vinegar dissolves the deposits and cleans the maker, which will speed up the brewing process back to its original rate. Just be sure to run water through the brewing process after the vinegar, or you will get some really horrible coffee.

Acids

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. Acids are a distinct class of compounds because of the properties of their aqueous solutions as outlined below:

1. Aqueous solutions of acids are electrolytes, meaning that they conduct electrical current. Some acids are strong electrolytes because they ionize completely in water, yielding a great many ions. Other acids are weak electrolytes that exist primarily in a non-ionized form when dissolved in water.
2. Acids have a sour taste. Lemons, vinegar, and sour candies all contain acids.
3. Acids change the color of certain acid-base indicates. Two common indicators are litmus and phenolphthalein. Blue litmus turns red in the presence of an acid, while phenolphthalein turns colorless.
4. Acids react with active metals to yield hydrogen gas. Recall that an activity series is a list of metals in descending order of reactivity. Metals that are above hydrogen in the activity series will replace the hydrogen from an acid in a single-replacement reaction, as shown below:

$$\mathrm{Zn}\left(s\right)+\mathrm{H_2SO_4}\left(aq\right)\rightarrow\mathrm{ZnSO_4}\left(aq\right)+\mathrm{H_2}\left(g\right) \tag{12.1.1.1}$$

5. Acids react with bases to produce a salt compound and water. When equal moles of an acid and a base are combined, the acid is neutralized by the base. The products of this reaction are an ionic compound, which is labeled as a salt, and water.

It should not be hard for you to name several common acids (but you might find that listing bases is a little more difficult). Below is a partial list of some common acids, along with some chemical formulas:

Table 12.1.1.1: Common Acids and Their Uses

Chemist Name	Common Name	Uses
hydrochloric acid, HCl	muriatic acid (used in pools) and stomach acid is HCl	Used in cleaning (refining) metals, in maintenance of swimming pools, and for household cleaning.
sulfuric acid, H_2SO_4		Used in car batteries, and in the manufacture of fertilizers.
nitric acid, HNO_3		Used in the manufacture of fertilizers, explosives and in extraction of gold.
acetic acid, $HC_2H_3O_2$	vinegar	Main ingredient in vinegar.
carbonic acid, H_2CO_3	responsible for the "fizz" in carbonated drinks	As an ingredient in carbonated drinks.
citric acid, $C_6H_8O_7$		Used in food and dietary supplements. Also added as an acidulant in creams, gels, liquids, and lotions.
acetylsalicylic acid, $C_6H_4(OCOCH_3)CO_2H$	aspirin	The active ingredient in aspirin.

What exactly makes an acid an acid, and what makes a base act as a base? Take a look at the formulas given in the above table and take a guess.

Hydrochloric Acid

Hydrochloric acid is a corrosive, strong mineral acid with many industrial uses. A colorless, highly pungent solution of hydrogen chloride (HCl) in water. Hydrochloric acid is usually prepared by treating HCl with water.

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

Hydrochloric acid can therefore be used to prepare chloride salts. Hydrochloric acid is a strong acid, since it is completely dissociated in water. Hydrochloric acid is the preferred acid in titration for determining the amount of bases.

Sulfuric Acid

Sulfuric acid is a highly corrosive strong mineral acid with the molecular formula $\mathrm{H_2SO_4}$. Sulfuric acid is a diprotic acid and has a wide range of applications including use in domestic acidic drain cleaners,[as an electrolyte in lead-acid batteries, and in various cleaning agents. It is also a central substance in the chemical industry.

Figure 12.1.1.1: Drops of concentrated sulfuric acid rapidly decompose a piece of cotton towel by dehydration. (CC BY-SA 3.0; Toxic Walker).

Because the hydration of sulfuric acid is thermodynamically favorable (and is highly exothermic) and the affinity of it for water is sufficiently strong, sulfuric acid is an excellent dehydrating agent. Concentrated sulfuric acid has a very powerful dehydrating property, removing water ($\mathrm{H_2O}$) from other compounds including sugar and other carbohydrates and producing carbon, heat, steam. Sulfuric acid behaves as a typical acid in its reaction with most metals by generating hydrogen gas (Equation 12.1.1.2).

$$\mathrm{M} + \mathrm{H_2SO_4} \rightarrow \mathrm{M(SO_4)} + \mathrm{H_2} \tag{12.1.1.2}$$

Nitric Acid

Nitric acid ($\mathrm{HNO_3}$) is a highly corrosive mineral acid and is also commonly used as a strong oxidizing agent. Nitric acid is normally considered to be a strong acid at ambient temperatures. Nitric acid can be made by reacting nitrogen dioxide ($\mathrm{NO_2(g)}$) with water.

$$3\,\mathrm{NO_2(g)} + \mathrm{H_2O(l)} \rightarrow 2\,\mathrm{HNO_3(ag)} + \mathrm{NO(g)}$$

Nitric acid reacts with most metals, but the details depend on the concentration of the acid and the nature of the metal. Dilute nitric acid behaves as a typical acid in its reaction with most metals (e.g., nitric acid with magnesium, manganese or zinc will liberate $\mathrm{H_2}$ gas):

$$\mathrm{Mg} + 2\,\mathrm{HNO_3} \rightarrow \mathrm{Mg(NO_3)_2} + \mathrm{H_2}$$

$$\mathrm{Mn} + 2\,\mathrm{HNO_3} \rightarrow \mathrm{Mn(NO_3)_2} + \mathrm{H_2}$$

$$\mathrm{Zn} + 2\,\mathrm{HNO_3} \rightarrow \mathrm{Zn(NO_3)_2} + \mathrm{H_2}$$

Nitric acid is a corrosive acid and a powerful oxidizing agent. The major hazard it poses is chemical burn, as it carries out acid hydrolysis with proteins (amide) and fats (ester) which consequently decomposes living tissue (Figure 12.1.1.2). Concentrated nitric acid stains human skin yellow due to its reaction with the keratin

Figure 12.1.1.2: Second degree burn caused by nitric acid. (CC BY-SA 3.0; Alcamán).

Carbonic Acid

Carbonic acid is a chemical compound with the chemical formula H_2CO_3 and is also a name sometimes given to solutions of carbon dioxide in water (carbonated water), because such solutions contain small amounts of $H_2CO_3(aq)$. Carbonic acid, which is a weak acid, forms two kinds of salts: the carbonates and the bicarbonates. In geology, carbonic acid causes limestone to dissolve, producing calcium bicarbonate—which leads to many limestone features such as stalactites and stalagmites. Carbonic acid is a polyprotic acid, specifically it is diprotic, meaning that it has two protons which may dissociate from the parent molecule.

When carbon dioxide dissolves in water, it exists in chemical equilibrium (discussed in Chapter 15), producing carbonic acid:

$$CO_2 + H_2O \rightleftharpoons H_2CO_3$$

The reaction can be pushed to favor the reactants to generate $CO_2(g)$ from solution, which is key to the bubbles observed in carbonated beverages (Figure $12.1.1.3$).

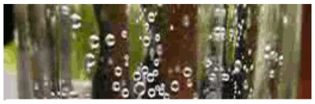


Figure 12.1.1.3: A glass of sparkling water. (CC BY-SA 3.0; Nevit Dilmen).

Formic Acid

Formic acid (HCO_2H) is the simplest carboxylic acid and is an important intermediate in chemical synthesis and occurs naturally, most notably in some ants. The word "formic" comes from the Latin word for ant, formica, referring to its early isolation by the distillation of ant bodies. Formic acid occurs widely in nature as its conjugate base formate.

Citric Acid

Citric acid $(C_6H_8O_7)$ is a weak organic tricarboxylic acid that occurs naturally in citrus fruits. The citrate ion is an intermediate in the TCA cycle (Krebs cycle), a central metabolic pathway for animals, plants and bacteria. Because it is one of the stronger edible acids, the dominant use of citric acid is used as a flavoring and preservative in food and beverages, especially soft drinks.

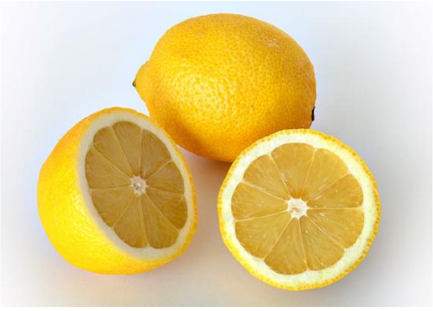


Figure 12.1.1.4: Lemons, oranges, limes, and other citrus fruits possess high concentrations of citric acid (CC BY-SA 2.5; André Karwath).

Acetylsalicylic Acid

Acetylsalicylic acid (also known as aspirin) is a medication used to treat pain, fever, and inflammation. Aspirin, in the form of leaves from the willow tree, has been used for its health effects for at least 2,400 years.

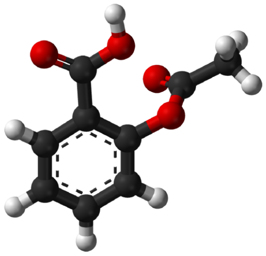


Figure 12.1.1.5: Ball-and-stick model of the aspirin molecule. (Public Domain; Ben Mills).

Aspirin is a white, crystalline, weakly acidic substance.

Summary

A brief summary of key aspects of several acids commonly encountered by students was given. Acids are a distinct class of compounds because of the properties of their aqueous solutions.

Contributions & Attributions

-
- Peggy Lawson (Oxbow Prairie Heights School). Funded by Saskatchewan Educational Technology Consortium.

12.1.2: Bases- Properties and Examples

Learning Objectives

- Examine properties of bases.

~~Perhaps you have eaten too much pizza and felt very uncomfortable hours later. This feeling is due to excess stomach acid being~~ produced. The discomfort can be dealt with by taking an antacid. The base in the antacid will react with the HCl in the stomach and neutralize it, taking care of that unpleasant feeling.

Bases

Bases have properties that mostly contrast with those of acids.

1. Aqueous solutions of bases are also electrolytes. Bases can be either strong or weak, just as acids can.
2. Bases often have a bitter taste and are found in foods less frequently than acids. Many bases, like soaps, are slippery to the touch.
3. Bases also change the color of indicators. Litmus turns blue in the presence of a base, while phenolphthalein turns pink.
4. Bases do not react with metals in the way that acids do.
5. Bases react with acids to produce a salt and water.

Figure 12.1.2.1: Phenolphthalein indicator in presence of base.

Warning!

Tasting chemicals and touching them are NOT good lab practices and should be avoided—in other words—don't do this at home.

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. Various common bases and corresponding uses are given in Table $12.1.2.2$

Table 12.1.2.1: Common Bases and Corresponding Uses

Some Common Bases	Uses
sodium hydroxide, NaOH (lye or caustic soda)	Used in the manufacture of soaps and detergents, and as the main ingredient in oven and drain cleaners.
potassium hydroxide, KOH (lye or caustic potash)	Used in the production of liquid soaps and soft soaps. Used in alkaline batteries.
magnesium hydroxide, $Mg(OH)_2$ (milk of magnesia)	Used as an ingredient in laxatives, antacids, and deodorants. Also used in the neutralization of acidic wastewater.
calcium hydroxide, $Ca(OH)_2$ (slaked lime)	Used in the manufacture of cement and lime water. Also, added to neutralize acidic soil.
aluminum hydroxide	Used in water purification and as an ingredient in antacids.
ammonia, NH_3	Used as a building block for the synthesis of many pharmaceutical products and in many commercial cleaning products. Used in the manufacture of fertilizers.

Sodium Hydroxide

Sodium hydroxide, also known as lye and caustic soda, is an inorganic compound with formula NaOH. It is a white solid ionic compound consisting of sodium cations $\mathrm{Na^+}$ and hydroxide anions $\mathrm{OH^-}$.

Dissolution of solid sodium hydroxide in water is a highly exothermic reaction:

$$\mathrm{NaOH(s) \rightarrow Na^+(aq) + OH^-(aq)}$$

The resulting solution is usually colorless and odorless and feels slippery when it comes in contact with skin.

Figure 12.1.2.1: Sample of sodium hydroxide as pellets in a watch glass. (Public Domain; Walkerma.)

Potassium Hydroxide

Potassium hydroxide is an inorganic compound with the formula KOH, and is commonly called caustic potash. Along with sodium hydroxide (NaOH), this colorless solid is a prototypical strong base. It has many industrial and niche applications, most of which exploit its corrosive nature and its reactivity toward acids. Its dissolution in water is strongly exothermic.

$$\mathrm{KOH(s) \rightarrow K^+(aq) + OH^-(aq)}$$

Concentrated aqueous solutions are sometimes called *potassium lyes*.

Magnesium Hydroxide

Magnesium hydroxide is the inorganic compound with the chemical formula $\mathrm{Mg(OH)_2}$. Magnesium hydroxide is a common component of antacids, such as milk of magnesia, as well as laxatives.

Figure 12.1.2.1: Bottle of Antacid tablets. (CC BY 2.,5; Midnightcomm).

It is a white solid with low solubility in water. Combining a solution of many magnesium salts with basic water induces precipitation of solid $\mathrm{Mg(OH)_2}$. However, a weak concentration of dissociated ions can be found in solution:

$$\mathrm{Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2\,OH^-(aq)}$$

Calcium Hydroxide

Calcium hydroxide (traditionally called slaked lime) is an inorganic compound with the chemical formula $\mathrm{Ca(OH)_2}$. It is a colorless crystal or white powder. It has many names including hydrated lime, caustic lime, builders' lime, slaked lime, cal, or pickling lime. Calcium hydroxide is used in many applications, including food preparation. Limewater is the common name for a saturated solution of calcium hydroxide.

Calcium hydroxide is relatively insoluble in water, but is large enough that its solutions are basic according to the following reaction:

$$\mathrm{Ca(OH)_2(s) \rightleftharpoons Ca^{2+}(aq) + 2\,OH^-(aq)}$$

Ammonia

Ammonia is a compound of nitrogen and hydrogen with the formula NH_3 and is a colorless gas with a characteristic pungent smell. It is the active product of “smelling salts,” and can quickly revive the faint of heart and light of head. Although common in nature and in wide use, ammonia is both caustic and hazardous in its concentrated form.

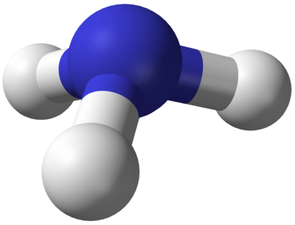


Figure 12.1.2.1: Ball-and-stick model of the ammonia molecule. (Public Domain; Ben Mills).

In aqueous solution, ammonia acts as a base, acquiring hydrogen ions from H_2O to yield ammonium and hydroxide ions:

$$\mathrm{NH_3(g) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)}$$

Ammonia is also a building block for the synthesis of many pharmaceutical products and is used in many commercial cleaning products.

Summary

- A brief summary of properties of bases was given.
- The properties of bases mostly contrast those of acids.
- Bases have many, varied uses.

12.2: Chemistry of Acids and Bases

In this section we will be exploring some of the chemistry of acids and bases. We will start with a couple of different definitions and look at the chemistry which results from these definitions.

12.2.1: Molecular Definitions of Acids and Bases

Learning Objectives

- Identify an Arrhenius acid and an Arrhenius base.
- Identify a Brønsted-Lowry acid and a Brønsted-Lowry base.
- Identify conjugate acid-base pairs in an acid-base reaction.

There are three major classifications of substances known as acids or bases. The theory developed by Svante Arrhenius in 1883, the Arrhenius definition, states that an acid produces H^+ in solution and a base produces OH^-. Later, two more sophisticated and general theories were proposed. These theories are the Brønsted-Lowry and Lewis definitions of acids and bases. This section will cover the Arrhenius and Brønsted-Lowry theories; the Lewis theory is discussed elsewhere.

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.

$$\mathrm{HCl(aq) \rightarrow H^+(aq) + Cl^-(aq)}$$

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:

$$\mathrm{HCl(aq) + H_2O(l) \rightarrow H_3O^+(aq) + Cl^-(aq)}$$

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:

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

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 in solution and Arrhenius bases are substances which produce hydroxide ions in solution.*

Limitations to the Arrhenius Theory

The Arrhenius theory has many more limitations than the other two theories. The theory does not explain the weak base ammonia (NH_3), which in the presence of water, releases hydroxide ions into solution, but does not contain OH- itself. The Arrhenius definition of acid and base is also limited to aqueous (i.e., water) solutions.

The Brønsted-Lowry Theory of Acids and Bases

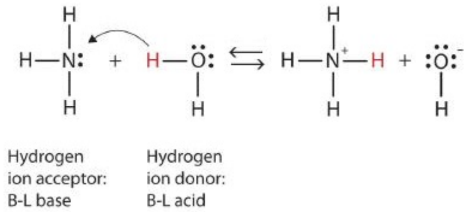
In 1923, Danish chemist Johannes Brønsted and English chemist Thomas Lowry independently proposed new definitions for acids and bases, ones that focus on proton transfer. A **Brønsted-Lowry acid** is any species that can donate a proton (H^+) to another molecule. A **Brønsted-Lowry base** is any species that can accept a proton from another molecule. In short, **a Brønsted-Lowry acid** is a **proton donor (PD)**, while **a Brønsted-Lowry base** is a **proton acceptor (PA)**.

> *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:

$$\mathrm{NH_3(aq) + H_2O(\ell) \rightleftharpoons NH_4^+(aq) + OH^-(aq)} \tag{12.2.1.1}$$

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:

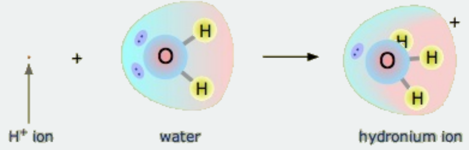


Because the water molecule donates a hydrogen ion to the ammonia, it is the Brønsted-Lowry acid, while the ammonia molecule—which accepts the hydrogen ion—is the Brønsted-Lowry base. Thus, ammonia acts as a base in both the Arrhenius sense and the Brønsted-Lowry sense.

Is an Arrhenius acid like hydrochloric acid still an acid in the Brønsted-Lowry sense? Yes, but it requires us to understand what really happens when HCl is dissolved in water. Recall that the hydrogen *atom* is a single proton surrounded by a single electron. To make the hydrogen *ion*, we remove the electron, leaving a bare proton. Do we *really* have bare protons floating around in aqueous solution? No, we do not. What really happens is that the H^+ ion attaches itself to H_2O to make H_3O^+, which is called the *hydronium ion*. For most purposes, H^+ and H_3O^+ represent the same species, but writing H_3O^+ instead of H^+ shows that we understand that there are no bare protons floating around in solution. Rather, these protons are actually attached to solvent molecules.

The Hydronium Ion

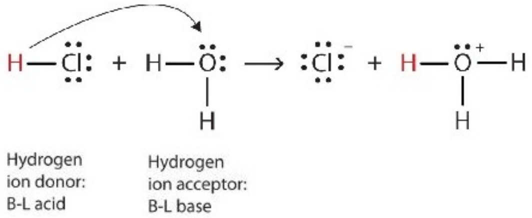
A proton in aqueous solution may be surrounded by more than one water molecule, leading to formulas like $H_5O_2^+$ or $H_9O_4^+$ rather than H_3O^+. It is simpler, however, to use H_3O^+ to represent the hydronium ion.



With this in mind, how do we define HCl as an acid in the Brønsted-Lowry sense? Consider what happens when HCl is dissolved in H_2O:

$$HCl(g) + H_2O(\ell) \rightarrow H_3O^+(aq) + Cl^-(aq) \tag{12.2.1.2}$$

We can depict this process using Lewis electron dot diagrams:



Now we see that a hydrogen ion is transferred from the HCl molecule to the H_2O molecule to make chloride ions and hydronium ions. As the hydrogen ion donor, HCl acts as a Brønsted-Lowry acid; as a hydrogen ion acceptor, H_2O is a Brønsted-Lowry base. So HCl is an acid not just in the Arrhenius sense, but also in the Brønsted-Lowry sense. Moreover, by the Brønsted-Lowry definitions, H_2O is a base in the formation of aqueous HCl. So the Brønsted-Lowry definitions of an acid and a base classify the dissolving of HCl in water as a reaction between an acid and a base—although the Arrhenius definition would not have labeled H_2O a base in this circumstance.

- A Brønsted-Lowry acid is a proton (hydrogen ion) donor.
- A Brønsted-Lowry base is a proton (hydrogen ion) acceptor.

- All Arrhenius acids and bases are Brønsted-Lowry acids and bases as well. However, not all Brønsted-Lowry acids and bases are Arrhenius acids and bases.

✓ Example 12.2.1.1

Aniline ($C_6H_5NH_2$) is slightly soluble in water. It has a nitrogen atom that can accept a hydrogen ion from a water molecule, just like the nitrogen atom in ammonia does. Write the chemical equation for this reaction and identify the Brønsted-Lowry acid and base.

Solution

$C_6H_5NH_2$ and H_2O are the reactants. When $C_6H_5NH_2$ accepts a proton from H_2O, it gains an extra H and a positive charge and leaves an OH^- ion behind. The reaction is as follows:

$$\mathrm{C_6H_5NH_2(aq) + H_2O(\ell) \rightleftharpoons C_6H_5NH_3^+(aq) + OH^-(aq)}$$

Because $C_6H_5NH_2$ accepts a proton, it is the Brønsted-Lowry base. The H_2O molecule, because it donates a proton, is the Brønsted-Lowry acid.

? Exercise 12.2.1.1

Identify the Brønsted-Lowry acid and the Brønsted-Lowry base in this chemical equation.

$$\mathrm{H_2PO_4^- + H_2O \rightleftharpoons HPO_4^{2\,-} + H_3O^+}$$

Answer

Brønsted-Lowry acid: $H_2PO_4^-$; Brønsted-Lowry base: H_2O

? Exercise 12.2.1.2

Which of the following compounds is a Bronsted-Lowry base?

a. HCl
b. HPO_4^{2-}
c. H_3PO_4
d. NH_4^+
e. $CH_3NH_3^+$

Answer

A Brønsted-Lowry Base is a proton acceptor, which means it will take in an H^+. This eliminates HCl, $\mathrm{H_3PO_4}$, $\mathrm{NH_4^+}$ and $\mathrm{CH_3NH_3^+}$ because they are Bronsted-Lowry acids. They all give away protons. In the case of $\mathrm{HPO_4^{2\,-}}$, consider the following equation:

$$\mathrm{HPO_4^{2\,-}(aq) + H_2O(l) \rightarrow PO_4^{3\,-}(aq) + H_3O^+(aq)}$$

Here, it is clear that HPO_4^{2-} is the acid since it donates a proton to water to make H_3O^+ and PO_4^{3-}. Now consider the following equation:

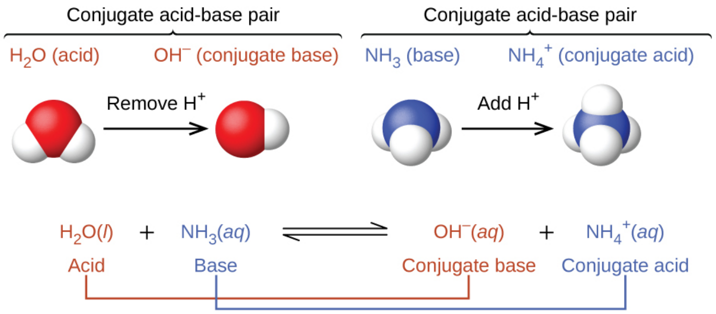
$$\mathrm{HPO_4^{2\,-}(aq) + H_2O(l) \rightarrow H_2PO_4^- + OH^-(aq)}$$

In this case, HPO_4^{2-} is the base since it accepts a proton from water to form $H_2PO_4^-$ and OH^-. Thus, HPO_4^{2-} is an acid and base together, making it amphoteric.

Since HPO_4^{2-} is the only compound from the options that can act as a base, the answer is **(b) HPO_4^{2-}.**

Conjugate Acid-Base Pair

In reality, all acid-base reactions involve the transfer of protons between acids and bases. For example, consider the acid-base reaction that takes place when ammonia is dissolved in water. A water molecule (functioning as an acid) transfers a proton to an ammonia molecule (functioning as a base), yielding the conjugate base of water, OH^-, and the conjugate acid of ammonia, NH_4^+:



This figure has three parts in two rows. In the first row, two diagrams of acid-base pairs are shown. On the left, a space filling model of H subscript 2 O is shown with a red O atom at the center and two smaller white H atoms attached in a bent shape. Above this model is the label "H subscript 2 O (acid)" in purple. An arrow points right, which is labeled "Remove H superscript plus." To the right is another space filling model with a single red O atom to which a single smaller white H atom is attached. The label in purple above this model reads, "O H superscript negative (conjugate base)." Above both of these red and white models is an upward pointing bracket that is labeled "Conjugate acid-base pair." To the right is a space filling model with a central blue N atom to which three smaller white H atoms are attached in a triangular pyramid arrangement. A label in green above reads "N H subscript 3 (base)." An arrow labeled "Add H superscript plus" points right. To the right of the arrow is another space filling model with a blue central N atom and four smaller white H atoms in a tetrahedral arrangement. The green label above reads "N H subscript 3 superscript plus (conjugate acid)." Above both of these blue and white models is an upward pointing bracket that is labeled "Conjugate acid-base pair." The second row of the figure shows the chemical reaction, H subscript 2 O (l) is shown in purple, and is labeled below in purple as "acid," plus N H subscript 3 (a q) in green, labeled below in green as "base," followed by a double sided arrow arrow and O H superscript negative (a q) in purple, labeled in purple as "conjugate base," plus N H subscript 4 superscript plus (a q)" in green, which is labeled in green as "conjugate acid." The acid on the left side of the equation is connected to the conjugate base on the right with a purple line. Similarly, the base on the left is connected to the conjugate acid on the right side.

In the reaction of ammonia with water to give ammonium ions and hydroxide ions, ammonia acts as a base by accepting a proton from a water molecule, which in this case means that water is acting as an acid. In the reverse reaction, an ammonium ion acts as an acid by donating a proton to a hydroxide ion, and the hydroxide ion acts as a base. The conjugate acid–base pairs for this reaction are NH_4^+/NH_3 and H_2O/OH^-.

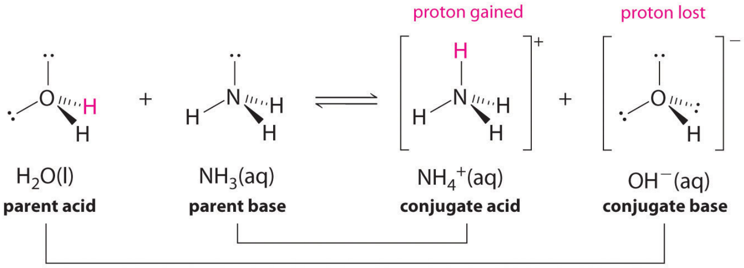
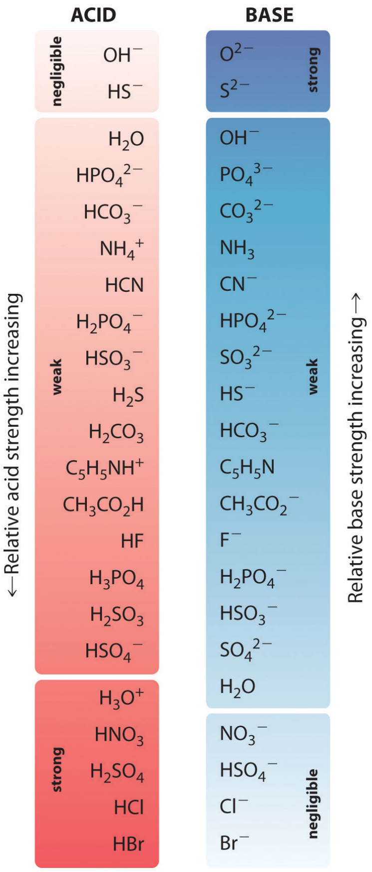


Figure 12.2.1.1. The pairing of parent acids and bases with conjugate acids and bases.



	ACID	BASE	
negligible	OH^-	O^{2-}	strong
	HS^-	S^{2-}	
weak	H_2O	OH^-	weak
	HPO_4^{2-}	PO_4^{3-}	
	HCO_3^-	CO_3^{2-}	
	NH_4^+	NH_3	
	HCN	CN^-	
	$H_2PO_4^-$	HPO_4^{2-}	
	HSO_3^-	SO_3^{2-}	
	H_2S	HS^-	
	H_2CO_3	HCO_3^-	
	$C_5H_5NH^+$	C_5H_5N	
	CH_3CO_2H	$CH_3CO_2^-$	
	HF	F^-	
	H_3PO_4	$H_2PO_4^-$	
	H_2SO_3	HSO_3^-	
	HSO_4^-	SO_4^{2-}	
strong	H_3O^+	H_2O	
	HNO_3	NO_3^-	negligible
	H_2SO_4	HSO_4^-	
	HCl	Cl^-	
	HBr	Br^-	

Figure 12.2.1.1: The Relative Strengths of Some Common Conjugate Acid-Base Pairs. The strongest acids are at the bottom left, and the strongest bases are at the top right. The conjugate base of a strong acid is a very weak base, and, conversely, the conjugate acid of a strong base is a very weak acid.

Example 12.2.1.2

Identify the conjugate acid-base pairs in this equilibrium.

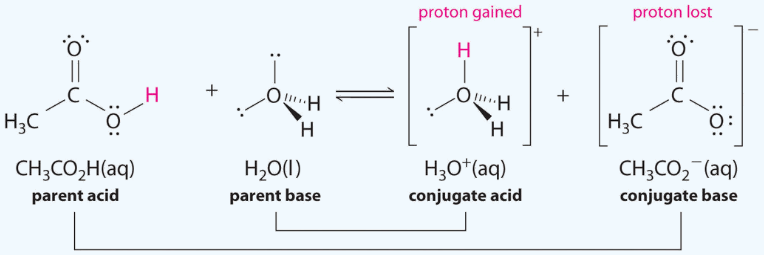
$$\mathrm{CH_3CO_2H + H_2O \rightleftharpoons H_3O^+ + CH_3CO_2^-}$$

Solution

Similarly, in the reaction of acetic acid with water, acetic acid **donates** a proton to water, which acts as the base. In the reverse reaction, H_3O^+ is the acid that donates a proton to the acetate ion, which acts as the base.

Once again, we have two conjugate acid-base pairs:

- the parent acid and its conjugate base ($CH_3CO_2H/CH_3CO_2^-$) and
- the parent base and its conjugate acid (H_3O^+/H_2O).



✓ Example 12.2.1.3

Identify the conjugate acid-base pairs in this equilibrium.

$$(CH_3)_3N + H_2O \rightleftharpoons (CH_3)_3NH^+ + OH^-$$

Solution

One pair is H_2O and OH^-, where H_2O has one more H^+ and is the conjugate acid, while OH^- has one less H^+ and is the conjugate base.

The other pair consists of $(CH_3)_3N$ and $(CH_3)_3NH^+$, where $(CH_3)_3NH^+$ is the conjugate acid (it has an additional proton) and $(CH_3)_3N$ is the conjugate base.

? Exercise 12.2.1.3

Identify the conjugate acid-base pairs in this equilibrium.

$$NH_2^- + H_2O \rightleftharpoons NH_3 + OH^-$$

Answer

H_2O (acid) and OH^- (base); NH_2^- (base) and NH_3 (acid)

12.2.2: Reactions of Acids and Bases

Learning Objectives

- Write acid-base neutralization reactions.
- Write reactions of acids with metals.
- Write reactions of bases with metals.

Neutralization Reactions

The reaction that happens when an acid, such as HCl, is mixed with a base, such as NaOH:

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

When an acid and a base are combined, water and a salt are the products. Salts are ionic compounds containing a positive ion other than $\mathrm{H^+}$ and a negative ion other than the hydroxide ion, $\mathrm{OH^-}$. Double displacement reactions of this type are called **neutralization reactions**. We can write an expanded version of this equation, with aqueous substances written in their longer form:

$$\mathrm{H^+(aq)} + \mathrm{Cl^-(aq)} + \mathrm{Na^+(aq)} + \mathrm{OH^-(aq)} \rightarrow \mathrm{Na^+(aq)} + \mathrm{Cl^-(aq)} + \mathrm{H_2O(l)}$$

After removing the spectator ions, we get the net ionic equation:

$$\mathrm{H^+(aq)} + \mathrm{OH^-(aq)} \rightarrow \mathrm{H_2O(l)}$$

When a strong acid and a strong base are combined in the proper amounts—when $[\mathrm{H^+}]$ equals $[\mathrm{OH^-}]$\)—a neutral solution results in which pH = 7. The acid and base have neutralized each other, and the acidic and basic properties are no longer present.

Salt solutions do not always have a pH of 7, however. Through a process known as **hydrolysis**, the ions produced when an acid and base combine may react with the water molecules to produce a solution that is slightly acidic or basic. As a general concept, if a strong acid is mixed with a weak base, the resulting solution will be slightly acidic. If a strong base is mixed with a weak acid, the solution will be slightly basic.

Video: Equimolar (~0.01 M) and equivolume solutions of HCl and NaOH are combined to make salt water. https://youtu.be/TS-I9KrUjB0

Example 12.2.2.1: Propionic Acid + Calcium Hydroxide

Calcium propionate is used to inhibit the growth of molds in foods, tobacco, and some medicines. Write a balanced chemical equation for the reaction of aqueous propionic acid ($CH_3CH_2CO_2H$) with aqueous calcium hydroxide [$Ca(OH)_2$].

Solution

Solutions to Example 14.5.1

Steps	Reaction

Steps	Reaction
Write the unbalanced equation. This is a double displacement reaction, so the cations and anions swap to create the water and the salt.	$CH_3CH_2CO_2H(aq) + Ca(OH)_2(aq) \rightarrow (CH_3CH_2CO_2)_2Ca(aq) + H_2O(l)$
Balance the equation. Because there are two OH^- ions in the formula for $Ca(OH)_2$, we need two moles of propionic acid, $CH_3CH_2CO_2H$, to provide H^+ ions.	$\underline{2}CH_3CH_2CO_2H(aq) + Ca(OH)_2(aq) \rightarrow (CH_3CH_2CO_2)_2Ca(aq) + \underline{2}H_2O(l)$

? Exercise 12.2.2.1

Write a balanced chemical equation for the reaction of solid barium hydroxide with dilute acetic acid.

Answer

$$\mathrm{Ba(OH)_2(s) + 2\,CH_3CO_2H(aq) \rightarrow Ba(CH_3CO_2)_2(aq) + 2\,H_2O(l)}$$

Acids and Bases React with Metals

Acids react with most metals to form a salt and hydrogen gas. As discussed previously, metals that are more active than acids can undergo a **single displacement reaction**. For example, zinc metal reacts with hydrochloric acid, producing zinc chloride and hydrogen gas.

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

Bases also react with certain metals, like zinc or aluminum, to produce hydrogen gas. For example, sodium hydroxide reacts with zinc and water to form sodium zincate and hydrogen gas.

$$\mathrm{Zn(s) + 2\,NaOH(aq) + 2\,H_2O(l) \rightarrow Na_2Zn(OH)_4(aq) + H_2(g).}$$

12.2.3: Strong and Weak Acids and Bases

Learning Objectives

- Define a strong and a weak acid and base.
- Recognize an acid or a base as strong or weak.
- Determine if a salt produces an acidic or a basic solution.

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^+(aq) and Cl^-(aq) ions; all the HCl molecules become ions:

$$HCl \overset{100\%}{\rightarrow} H^+(aq) + Cl^-(aq)$$

Any acid that dissociates 100% into ions is called a **strong acid**. If it does not dissociate 100%, it is a **weak acid**. $HC_2H_3O_2$ is an example of a weak acid:

$$HC_2H_3O_2 \xrightarrow{\sim 5\%} H^+(aq) + C_2H_3O_2^-(aq)$$

Because this reaction does not go 100% to completion, it is more appropriate to write it as **a reversible reaction**:

$$HC_2H_3O_2 \rightleftharpoons H^+(aq) + C_2H_3O_2^-(aq)$$

As it turns out, there are very few strong acids, which are given in Table 12.2.3.1. If an acid is not listed here, it is a weak acid. It may be 1% ionized or 99% ionized, but it is still classified as a weak acid.

> *Any acid that dissociates 100% into ions is called a strong acid. If it does not dissociate 100%, it is a weak acid.*

Table 12.2.3.1: Strong Acids and Bases

Acids	Bases
HCl	LiOH
HBr	NaOH
HI	KOH
HNO_3	RbOH
H_2SO_4	CsOH
$HClO_3$	$Mg(OH)_2$
$HClO_4$	$Ca(OH)_2$
	$Sr(OH)_2$
	$Ba(OH)_2$

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 12.2.3.1); any base not listed is a weak base. All strong bases are OH^- 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.

Example 12.2.3.1: Identifying Strong and Weak Acids and Bases

Identify each acid or base as strong or weak.

a. HCl
b. $Mg(OH)_2$
c. C_5H_5N

Solution

a. Because HCl is listed in Table 12.2.3.1, it is a strong acid.
b. Because $Mg(OH)_2$ is listed in Table 12.2.3.1, it is a strong base.
c. The nitrogen in C_5H_5N would act as a proton acceptor and therefore can be considered a base, but because it does not contain an OH compound, it cannot be considered a strong base; it is a weak base.

Exercise 12.2.3.1

Identify each acid or base as strong or weak.

a. RbOH
b. HNO_2

Answer a

strong base

Answer b

weak acid

Example 12.2.3.2: Characterizing Base Ionization

Write the balanced chemical equation for the dissociation of $Ca(OH)_2$ and indicate whether it proceeds 100% to products or not.

Solution

This is an ionic compound of Ca^{2+} ions and OH^- ions. When an ionic compound dissolves, it separates into its constituent ions:

$$\mathrm{Ca(OH)_2 \rightarrow Ca^{2+}(aq) + 2\,OH^-(aq)}$$

Because $Ca(OH)_2$ is listed in Table 12.2.3.1, this reaction proceeds 100% to products.

? Exercise 12.2.3.2

Write the balanced chemical equation for the dissociation of hydrazoic acid (HN_3) and indicate whether it proceeds 100% to products or not.

Answer a

The reaction is as follows:

$$HN_3 \rightarrow H^+(aq) + N_3^-(aq)$$

It does not proceed 100% to products because hydrazoic acid is not a strong acid.

Key Takeaways

- Strong acids and bases are 100% ionized in aqueous solution.
- Weak acids and bases are less than 100% ionized in aqueous solution.
- Salts of weak acids or bases can affect the acidity or basicity of their aqueous solutions.

Contributions & Attributions

12.3: Acid-Base Equilibria

We will explore the general concept of chemical equilibrium in a later chapter in this textbook, but will explore it here only as it relates to acid-base chemistry. As it turns out, acid-base equilibrium is present in every sample of water that you will ever encounter in your life!

12.3.1: Water - Acid and Base in One

Learning Objectives

- Describe the autoionization of water.
- Calculate the concentrations of H_3O^+ and OH^- in aqueous solutions, knowing the other concentration.

We have already seen that H_2O 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:

$$\underbrace{H_2O}_{\text{acid}} + \underbrace{H_2O}_{\text{base}} \rightleftharpoons H_3O^+ + OH^- \tag{12.3.1.1}$$

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 of water**.

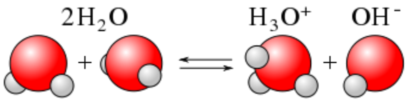


Figure 12.3.1.1: Autoionization of water, resulting in hydroxide and hydronium ions.

At this level, the concentration of both $H_3O^+(aq)$ and $OH^-(aq)$ in a sample of pure H_2O is about $1.0 \times 10^{-7}\ M$ (at room temperature). If we use square brackets—[ ]—around a dissolved species to imply the molar concentration of that species, we have

$$[H_3O^+]=[OH^-] = 1.0 \times 10^{-7} \tag{12.3.1.2}$$

for *any* sample of pure water because H2O can act as both an acid and a base. The product of these two concentrations is 1.0×10^{-14}:

$$[H_3O^+] \times [OH^-] = (1.0 \times 10^{-7})(1.0 \times 10^{-7}) = 1.0 \times 10^{-14}$$

- For acids, the concentration of $H_3O^+(aq)$ (i.e., $[H_3O^+]$) is greater than $1.0 \times 10^{-7}\ M$.
- For bases the concentration of $OH^-(aq)$ (i.e., $[OH^-]$) is greater than $1.0 \times 10^{-7}\ M$.

However, the *product* of the two concentrations—$[H_3O^+][OH^-]$—is *always* equal to 1.0×10^{-14}, no matter whether the aqueous solution is an acid, a base, or neutral:

$$[H_3O^+][OH^-] = 1.0 \times 10^{-14}$$

This value of the product of concentrations is so important for aqueous solutions that it is called the **autoionization constant of water** and is denoted K_w:

$$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14} \tag{12.3.1.3}$$

This means that if you know $[H_3O^+]$ for a solution, you can calculate what $[OH^-]$) has to be for the product to equal 1.0×10^{-14}; or if you know $[OH^-]$), you can calculate $[H_3O^+]$. 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.

Warning: Temperature Matters

The degree of autoionization of water (Equation 12.3.1.1)—and hence the value of K_w—changes with temperature, so Equations 12.3.1.2- 12.3.1.3are accurate only at room temperature.

Example 12.3.1.1: Hydroxide Concentration

What is $[\mathrm{OH^-}]$) of an aqueous solution if $[\mathrm{H_3O^+}]$ is $1.0 \times 10^{-4}\,M$?

Solution

Solutions to Example 14.7.1

Steps for Problem Solving	
Identify the "given" information and what the problem is asking you to "find."	Given: $[\mathrm{H_3O^+}] = 1.0 \times 10^{-4}\ M$ Find: $[\mathrm{OH^-}]$ = ? M
List other known quantities.	none
Plan the problem.	Using the expression for K_w, (Equation 12.3.1.3), rearrange the equation algebraically to solve for $[\mathrm{OH^-}]$. $$[\mathrm{OH^-}] = \frac{1.0 \times 10^{-14}}{[H_3O^+]}$$
Calculate.	Now substitute the known quantities into the equation and solve. $$[\mathrm{OH^-}] = \frac{1.0 \times 10^{-14}}{1.0 \times 10^{-4}} = 1.0 \times 10^{-10}\,M$$ It is assumed that the concentration unit is molarity, so $[\mathrm{OH^-}]$ is 1.0 × 10^{-10} M.
Think about your result.	The concentration of the acid is high (> 1 x 10^{-7} M), so $[\mathrm{OH^-}]$ should be low.

Exercise 12.3.1.1

What is $[\mathrm{OH^-}]$ in a 0.00032 M solution of H_2SO_4?

Hint

Assume **both** protons ionize from the molecule...although this is not the case.

Answer

$3.1 \times 10^{-11}\ M$

When you have a solution of a particular acid or base, you need to look at the formula of the acid or base to determine the number of H_3O^+ or OH^- ions in the formula unit because $[\mathrm{H_3O^+}]$ or $[\mathrm{OH^-}]$) may not be the same as the concentration of the acid or base itself.

Example 12.3.1.2: Hydronium Concentration

What is $[\mathrm{H_3O^+}]$ in a 0.0044 M solution of $\mathrm{Ca(OH)_2}$?

Solution

Solutions to Example 14.7.2

Steps for Problem Solving	
Identify the "given" information and what the problem is asking you to "find."	Given: $[\mathrm{Ca(OH)_2}] = 0.0044\ M$ Find: $[\mathrm{H_3O^+}]$ = ? M

Steps for Problem Solving	
List other known quantities.	We begin by determining $[\mathrm{OH}^-]$. The concentration of the solute is 0.0044 M, but because $\mathrm{Ca(OH)_2}$ is a strong base, there are two OH^- ions in solution for every formula unit dissolved, so the actual $[\mathrm{OH}^-]$ is two times this: $[\mathrm{OH}^-]{=}2\ \times 0\ \cdot 0044\ \mathrm{M}{=}0\ \cdot 0088\ \mathrm{M}\cdot$
Plan the problem.	Use the expression for K_w (Equation 12.3.1.3) and rearrange the equation algebraically to solve for $[\mathrm{H_3O^+}]$. $[H_3O^+] = \frac{1.0 \times 10^{-14}}{[OH^-]}$
Calculate.	Now substitute the known quantities into the equation and solve. $[H_3O^+] = \frac{1.0 \times 10^{-14}}{(0.0088)} = 1.1 \times 10^{-12} M$ $[\mathrm{H_3O^+}]$ has decreased significantly in this basic solution.
Think about your result.	The concentration of the base is high (> 1 x 10^{-7} M) so $[\mathrm{H_3O^+}]$ should be low.

? Exercise 12.3.1.2

What is $[\mathrm{H_3O^+}]$ of an aqueous solution if $[\mathrm{OH^-}]$ is $1.0 \times 10^{-9}\ M$?

Answer

1.0×10^{-5} M

In any aqueous solution, the product of $[\mathrm{H_3O^+}]$ and $[\mathrm{OH^-}]$ equals 1.0×10^{-14} (at room temperature).

Contributions & Attributions

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12.3.2: The pH and pOH Scales - Ways to Express Acidity and Basicity

Learning Objectives

- Define pH and pOH.
- Determine the pH of acidic and basic solutions.
- Determine the hydronium ion concentration and pOH from pH.

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 logarithmic function of $[H_3O^+]$:

$$pH = -\log[H_3O^+] \tag{12.3.2.1}$$

pH is usually (but not always) between 0 and 14. Knowing the dependence of pH on $[H_3O^+]$, we can summarize as follows:

- If pH < 7, then the solution is acidic.
- If pH = 7, then the solution is neutral.
- If pH > 7, then the solution is basic.

This is known as the pH scale. 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 12.3.2.1 illustrates this relationship, along with some examples of various solutions. Because hydrogen ion concentrations are generally less than one (for example $1.3 \times 10^{-3}\ M$), 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.

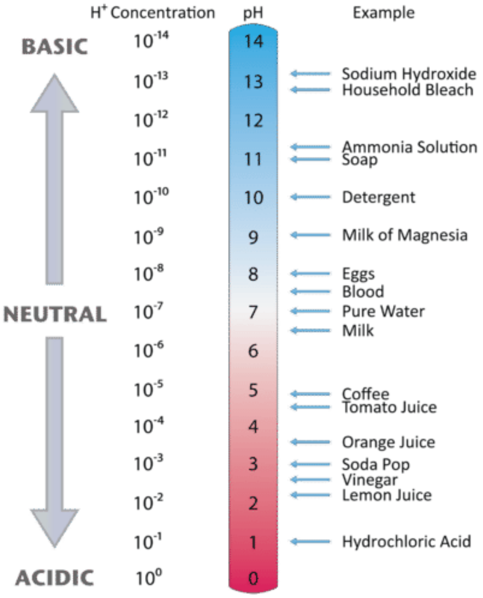


Figure 12.3.2.1: The pH values for several common materials.

Example 12.3.2.1

Label each solution as acidic, basic, or neutral based only on the stated pH.

a. milk of magnesia, pH = 10.5
b. pure water, pH = 7
c. wine, pH = 3.0

Answer

a. With a pH greater than 7, milk of magnesia is basic. (Milk of magnesia is largely $Mg(OH)_2$.)
b. Pure water, with a pH of 7, is neutral.

c. With a pH of less than 7, wine is acidic.

Exercise 12.3.2.1

Identify each substance as acidic, basic, or neutral based only on the stated pH.

a. human blood with pH = 7.4
b. household ammonia with pH = 11.0
c. cherries with pH = 3.6

Answer a

basic

Answer b

basic

Answer c

acidic

Calculating pH from Hydronium Concentration

The pH of solutions can be determined by using logarithms as illustrated in the next example for stomach acid. Stomach acid is a solution of HCl with a hydronium ion concentration of $1.2 \times 10^{-3}\ M$, what is the pH of the solution?

$$\begin{aligned} \mathrm{pH} &= -\log[\mathrm{H_3O^+}] \\ &= -\log(1.2 \times 10^{-3}) \\ &= -(-2.92) = 2.92 \end{aligned}$$

Logarithms

To get the **log value** on your calculator, enter the number (in this case, the hydronium ion concentration) first, then press the LOG key.

If the number is 1.0 x 10^{-5} (for $[H_3O^+]$ = 1.0 x 10^{-5} M) you should get an answer of "-5".

If you get a different answer, or an error, try pressing the LOG key before you enter the number.

Example 12.3.2.2: Converting Ph to Hydronium Concentration

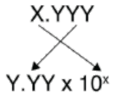
Find the pH, given the $[H_3O^+]$ of the following:

a. 1 $\times 10^{-3}$ M
b. 2.5 $\times 10^{-11}$ M
c. 4.7 $\times 10^{-9}$ M

Solution

Solutions to Example 14.9.2

Steps for Problem Solving	
Identify the "given" information and what the problem is asking you to "find."	Given: a. $[H_3O^+]$ =1 × 10^{-3} M b. $[H_3O^+]$ =2.5 ×10^{-11} M c. $[H_3O^+]$ = 4.7 ×10^{-9} M Find: ? pH
Plan the problem.	Need to use the expression for pH (Equation 12.3.2.1). pH = - log $[H_3O^+]$

Steps for Problem Solving	
Calculate.	Now substitute the known quantity into the equation and solve. a. pH = - log [<u>1</u> × 10^{-3}] = 3.<u>0</u> (1 decimal places since 1 has 1 significant figure) b. pH = - log [<u>2.5</u> ×10^{-11}] = 10.<u>60</u> (2 decimal places since 2.5 has 2 significant figures) c. pH = - log [<u>4.7</u> ×10^{-9}] = 8.<u>30</u> (2 decimal places since 4.7 has 2 significant figures) The other issue that concerns us here is significant figures. Because the number(s) before the decimal point in a logarithm relate to the power on 10, the number of digits *after* the decimal point is what determines the number of significant figures in the final answer: 

Exercise 12.3.2.2

Find the pH, given [H_3O^+] of the following:

a. 5.8 ×10^{-4} M
b. 1.0×10^{-7}

Answer a

3.22

Answer b

7.00

Calculating Hydronium Concentration from pH

Sometimes you need to work "backwards"—you know the pH of a solution and need to find $[H_3O^+]$, or even the concentration of the acid solution. How do you do that? To convert pH into $[H_3O^+]$ we solve Equation 12.3.2.1 for $[H_3O^+]$. This involves taking the antilog (or inverse log) of the negative value of pH .

$$[\mathrm{H_3O^+}] = \mathrm{antilog}(-pH)$$

or

$$[\mathrm{H_3O^+}] = 10^{-pH} \tag{12.3.2.2}$$

As mentioned above, different calculators work slightly differently—make sure you can do the following calculations using ***your*** calculator.

Calculator Skills

We have a solution with a pH = 8.3. What is [H_3O^+] ?

With some calculators you will do things in the following order:

1. Enter 8.3 as a negative number (use the key with both the +/- signs, not the subtraction key).
2. Use your calculator's 2nd or Shift or INV (inverse) key to type in the symbol found above the LOG key. The shifted function should be 10^x.
3. You should get the answer **5.0 × 10^{-9}**.

Other calculators require you to enter keys in the order they appear in the equation.

1. Use the Shift or second function to key in the 10^x function.

2. Use the +/- key to type in a negative number, then type in 8.3.
3. You should get the answer **5.0×10^{-9}**.

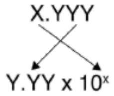
If neither of these methods work, try rearranging the order in which you type in the keys. Don't give up—you must master your calculator!

✓ Example 12.3.2.3: Calculating Hydronium Concentration from pH

Find the hydronium ion concentration in a solution with a pH of 12.6. Is this solution an acid or a base? How do you know?

Solution

Solutions to Example 14.9.3

Steps for Problem Solving	
Identify the "given" information and what the problem is asking you to "find."	Given: pH = 12.6 Find: $[H_3O^+]$ = ? M
Plan the problem.	Need to use the expression for $[H_3O^+]$ (Equation 12.3.2.2). $[H_3O^+]$ = antilog (-pH) or $[H_3O^+] = 10^{-pH}$
Calculate.	Now substitute the known quantity into the equation and solve. $[H_3O^+]$ = antilog (12.$\underline{60}$) = $\underline{2.5}$ x 10^{-13} M (2 significant figures since 4.7 has 12.60 2 decimal places) or $[H_3O^+] = 10^{-12.\underline{60}}$ = $\underline{2.5}$ x 10^{-13} M (2 significant figures since 4.7 has 12.60 2 decimal places) The other issue that concerns us here is significant figures. Because the number(s) before the decimal point in a logarithm relate to the power on 10, the number of digits *after* the decimal point is what determines the number of significant figures in the final answer: 

? Exercise 12.3.2.3

If moist soil has a pH of 7.84, what is $[H_3O^+]$ of the soil solution?

Answer

1.5 x 10^{-8} M

The pOH scale

As with the hydrogen-ion concentration, the concentration of the hydroxide ion can be expressed logarithmically by the pOH. The **pOH** of a solution is the negative logarithm of the hydroxide-ion concentration.

$$\mathrm{pOH} = -\log\left[\mathrm{OH}^-\right]$$

The relation between the hydronium and hydroxide ion concentrations expressed as p-functions is easily derived from the K_w expression:

$$K_\mathrm{w} = [\mathrm{H_3O^+}][\mathrm{OH^-}] \tag{12.3.2.3}$$

$$-\log K_\mathrm{w} = -\log([\mathrm{H_3O^+}][\mathrm{OH^-}]) = -\log[\mathrm{H_3O^+}] + -\log[\mathrm{OH^-}] \tag{12.3.2.4}$$

$$\mathrm{p}K_\mathrm{w} = \mathrm{pH} + \mathrm{pOH} \tag{12.3.2.5}$$

At 25 °C, the value of K_w is 1.0×10^{-14}, and so:

$$14.00 = \mathrm{pH} + \mathrm{pOH} \tag{12.3.2.6}$$

The hydronium ion molarity in pure water (or any neutral solution) is $1.0 \times 10^{-7}\ M$ at 25 °C. The pH and pOH of a neutral solution at this temperature are therefore:

$$\mathrm{pH} = -\log[\mathrm{H_3O^+}] = -\log(1.0 \times 10^{-7}) = 7.00 \tag{12.3.2.7}$$

$$\mathrm{pOH} = -\log[\mathrm{OH^-}] = -\log(1.0 \times 10^{-7}) = 7.00 \tag{12.3.2.8}$$

And so, at this temperature, acidic solutions are those with hydronium ion molarities greater than $1.0 \times 10^{-7}\ M$ and hydroxide ion molarities less than $1.0 \times 10^{-7}\ M$ (corresponding to pH values less than 7.00 and pOH values greater than 7.00). Basic solutions are those with hydronium ion molarities less than $1.0 \times 10^{-7}\ M$ and hydroxide ion molarities greater than $1.0 \times 10^{-7}\ M$ (corresponding to pH values greater than 7.00 and pOH values less than 7.00).

✓ Example 12.3.2.4:

Find the pOH of a solution with a pH of 4.42.

Solution

Solutions to Example 14.9.4

Steps for Problem Solving	
Identify the "given" information and what the problem is asking you to "find."	Given: pH =4.42 Find: ? pOH
Plan the problem.	Need to use the expression pOH = 14 - pH
Calculate.	Now substitute the known quantity into the equation and solve. pOH=14−4.42=9.58
Think about your result.	The pH is that of an acidic solution, and the resulting pOH is the difference after subtracting from 14. The answer has two significant figures because the given pH has two decimal places.

? Exercise 12.3.2.4

The pH of a solution is 8.22. What is the pOH?

Answer

5.78

The diagram below shows all of the interrelationships between [H3O+][H3O+], [OH−][OH−], pH, and pOH.

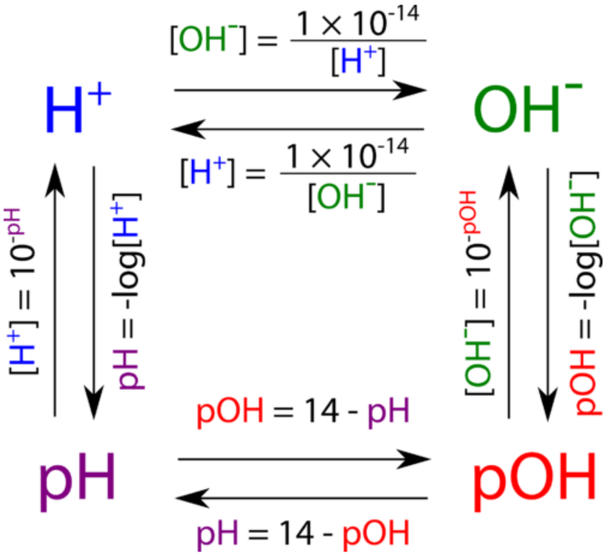


Figure 12.3.2.1: Relationships between hydrogen ion concentration, hydroxide ion concentration, pH and pOH.

Contributions & Attributions

- Peggy Lawson (Oxbow Prairie Heights School). Funded by Saskatchewan Educational Technology Consortium.
-
- Template:OpenStax

12.4: Buffers are Solutions that Resist pH Change

Learning Objective

- Define *buffer* and describe how it reacts with an acid or a base.

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.

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 derived from that weak acid, or a weak base plus a salt 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 ($NaC_2H_3O_2$, a salt derived from that acid). Another example of a buffer is a solution containing ammonia (NH_3, a weak base) and ammonium chloride (NH_4Cl, a salt derived from that base).

Let us use an acetic acid–sodium acetate buffer to demonstrate how buffers work. If a strong base—a source of $OH^-(aq)$ ions—is added to the buffer solution, those hydroxide ions will react with the acetic acid in an acid-base reaction:

$$HC_2H_3O_2(aq) + OH^-(aq) \rightarrow H_2O(\ell) + C_2H_3O_2^-(aq) \tag{12.4.1}$$

Rather than changing the pH dramatically by making the solution basic, the added hydroxide ions react to make water, and the pH does not change much.

> Many people are aware of the concept of buffers from *buffered aspirin*, which is aspirin that also has magnesium carbonate, calcium carbonate, magnesium oxide, or some other salt. The salt acts like a base, while aspirin is itself a weak acid.

If a strong acid—a source of H^+ ions—is added to the buffer solution, the H^+ ions will react with the anion from the salt. Because $HC_2H_3O_2$ is a weak acid, it is not ionized much. This means that if lots of hydrogen ions and acetate ions (from sodium acetate) are present in the same solution, they will come together to make acetic acid:

$$H^+(aq) + C_2H_3O_2^-(aq) \rightarrow HC_2H_3O_2(aq) \tag{12.4.2}$$

Rather than changing the pH dramatically and making the solution acidic, the added hydrogen ions react to make molecules of a weak acid. Figure 12.4.1 illustrates both actions of a buffer.

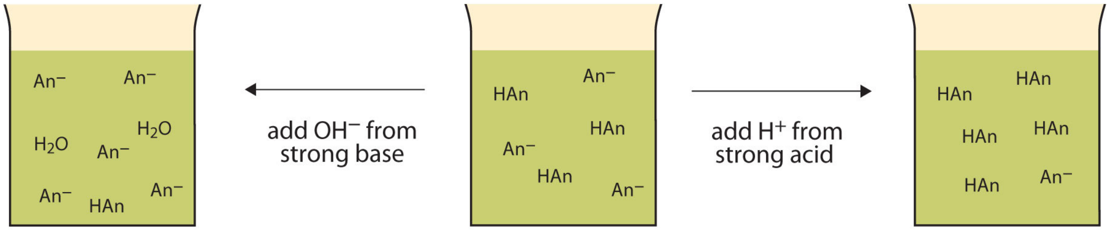


Figure 12.4.1: The Action of Buffers. Buffers can react with both strong acids (top) and strong bases (bottom) to minimize large changes in pH.

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:

$$NH_3(aq) + H^+(aq) \rightarrow NH_4^+(aq) \tag{12.4.3}$$

while the **ammonium ion** ($NH_4^+(aq)$) can react with any hydroxide ions introduced by strong bases:

$$NH_4^+(aq) + OH^-(aq) \rightarrow NH_3(aq) + H_2O(\ell) \tag{12.4.4}$$

✓ Example 12.4.1: Making Buffer Solutions

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.

? Exercise 12.4.1

Which solute combinations can make a buffer solution? Assume that all are aqueous solutions.

a. $NaHCO_3$ and NaCl
b. H_3PO_4 and NaH_2PO_4
c. NH_3 and $(NH_4)_3PO_4$
d. NaOH and NaCl

Answer a

Yes.

Answer b

No. Need a weak acid or base and a salt of its conjugate base or acid.

Answer c

Yes.

Answer d

No. Need a weak base or acid.

Buffers work well only for limited amounts of added strong acid or base. Once either solute is all reacted, the solution is no longer a buffer, and rapid changes in pH may occur. We say that a buffer has a certain **capacity**. Buffers that have more solute dissolved in them to start with have larger capacities, as might be expected.

Human blood has a buffering system to minimize extreme changes in pH. One buffer in blood is based on the presence of HCO_3^- and H_2CO_3 [H_2CO_3 is another way to write $CO_2(aq)$]. With this buffer present, even if some stomach acid were to find its way directly into the bloodstream, the change in the pH of blood would be minimal. Inside many of the body's cells, there is a buffering system based on phosphate ions.

Career Focus: Blood Bank Technology Specialist

At this point in this text, you should have the idea that the chemistry of blood is fairly complex. Because of this, people who work with blood must be specially trained to work with it properly.

> A blood bank technology specialist is trained to perform routine and special tests on blood samples from blood banks or transfusion centers. This specialist measures the pH of blood, types it (according to the blood's ABO+/− type, Rh factors, and other typing schemes), tests it for the presence or absence of various diseases, and uses the blood to determine if a patient has any of several medical problems, such as anemia. A blood bank technology specialist may also interview and prepare donors to give blood and may actually collect the blood donation.
>
> Blood bank technology specialists are well trained. Typically, they require a college degree with at least a year of special training in blood biology and chemistry. In the United States, training must conform to standards established by the American Association of Blood Banks.

Key Takeaway

- A buffer is a solution that resists sudden changes in pH.

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12.E: Acids and Bases

The following questions are related to the material covered in this chapter. For additional discussion on each topic, also check the links included in each heading.

12.2.1: Arrhenius Acids and Bases

1. Define *Arrhenius acid*.
2. Define *Arrhenius base*.
3. What are some general properties of Arrhenius acids?
4. What are some general properties of Arrhenius bases?
5. Identify each substance as an Arrhenius acid, an Arrhenius base, or neither.
    a. NaOH
    b. C_2H_5OH
    c. H_3PO_4
6. Identify each substance as an Arrhenius acid, an Arrhenius base, or neither.
    a. $C_6H_{12}O_6$
    b. HNO_2
    c. $Ba(OH)_2$
7. Write the balanced chemical equation for the neutralization reaction between KOH and $H_2C_2O_4$. What is the salt?
8. Write the balanced chemical equation for the neutralization reaction between $Sr(OH)_2$ and H_3PO_4. What is the salt?
9. Write the balanced chemical equation for the neutralization reaction between HCl and $Fe(OH)_3$. What is the salt?
10. Write the balanced chemical equation for the neutralization reaction between H_2SO_4 and $Cr(OH)_3$. What is the salt?
11. $CaCl_2$ would be the product of the reaction of what acid and what base?
12. $Zn(NO_3)_2$ would be product of the reaction of what acid and what base?
13. $BaSO_4$ would be product of the reaction of what acid and what base?
14. Na_3PO_4 would be product of the reaction of what acid and what base?

Answers

1. a compound that increases the H^+ concentration in water
2.
3. sour taste, react with metals, and turn litmus red
4.
5. a. Arrhenius base
    b. neither
    c. Arrhenius acid
6.
7. $2KOH + H_2C_2O_4 \rightarrow 2H_2O + K_2C_2O_4$; $K_2C_2O_4$
8.
9. $3HCl + Fe(OH)_3 \rightarrow 3H_2O + FeCl_3$; $FeCl_3$
10.
11. HCl and $Ca(OH)_2$
12.
13. H_2SO_4 and $Ba(OH)_2$

12.2.1: Brønsted-Lowry Acids and Bases

Exercise $12.E.1$

1. Define *Brønsted-Lowry acid*. How does it differ from an Arrhenius acid?
2. Define *Brønsted-Lowry base*. How does it differ from an Arrhenius base?
3. Write the dissociation of hydrogen bromide in water as a Brønsted-Lowry acid-base reaction and identify the proton donor and proton acceptor.
4. Write the dissociation of nitric acid in water as a Brønsted-Lowry acid-base reaction and identify the proton donor and proton acceptor.
5. Pyridine (C_5H_5N) acts as a Brønsted-Lowry base in water. Write the hydrolysis reaction for pyridine and identify the Brønsted-Lowry acid and Brønsted-Lowry base.
6. The methoxide ion ($CH_3O^−$) acts as a Brønsted-Lowry base in water. Write the hydrolysis reaction for the methoxide ion and identify the Brønsted-Lowry acid and Brønsted-Lowry base.
7. Identify the Brønsted-Lowry acid and Brønsted-Lowry base in this chemical equation.

   $H_3PO_4 + OH^− \rightarrow H_2PO_4^− + H_2O$

8. Identify the Brønsted-Lowry acid and Brønsted-Lowry base in this chemical equation.

   $H_2C_2O_4 + 2F^− \rightarrow 2HF + C_2O_4^{2−}$

9. Predict the products of this reaction, assuming it undergoes a Brønsted-Lowry acid-base reaction.

   $HC_2H_3O_2 + C_5H_5N \rightarrow ?$

10. Predict the products of this reaction, assuming it undergoes a Brønsted-Lowry acid-base reaction.

    $(C_2H_5)_3N + H_2O \rightarrow ?$

11. What is the conjugate acid of H_2O? of NH_3?
12. What is the conjugate acid of $H_2PO_4^−$? of $NO_3^−$?
13. What is the conjugate base of $HSO_4^−$? of H_2O?
14. What is the conjugate base of H_3O^+? of H_2SO_4?
15. Identify the conjugate acid-base pairs in this reaction.

    $HSO_4^− + PO_4^{3−} \rightarrow SO_4^{2−} + HPO_4^{2−}$

16. Identify the conjugate acid-base pairs in this reaction.

    $HClO_3 + (C_2H_5)_3N \rightarrow ClO_3^− + (C_2H_5)_3NH^+$

17. Identify the conjugate acid-base pairs in this reaction.

    $NH_3 + C_6H_5O^− \rightarrow C_6H_5OH + NH_2^−$

18. Identify the conjugate acid-base pairs in this reaction.

    $C_5H_5NH^+ + C_2O_4^{2−} \rightarrow C_5H_5N + HC_2O_4^−$

nswers

1. A Brønsted-Lowry acid is a proton donor. It does not necessarily increase the H^+ concentration in water.
2.

3. $HBr + H_2O \rightarrow H_3O^+ + Br^−$; PD: HBr; PA: H_2O

4.

5. $C_5H_5N + H_2O \rightarrow C_5H_5NH^+ + OH^−$; PD: H_2O; PA: C_5H_5N

6.

7. BL acid: H_3PO_4; BL base: $OH^−$

8.

9. $C_2H_3O_2^−$ and $C_5H_5NH^+$

10.

11. H_3O^+; NH_4^+

12.

13. SO_4^{2-}; OH^-

14.

15. HSO_4^- and SO_4^{2-}; PO_4^{3-} and HPO_4^{2-}

16.

17. NH_3 and NH_2^-; $C_6H_5O^-$ and C_6H_5OH

12.2.3: Strong and Weak Acids and Bases and their Salts

? Exercise $12.E.1$

1. Differentiate between a strong acid and a weak acid.
2. Differentiate between a strong base and a weak base.
3. Identify each as a strong acid or a weak acid. Assume aqueous solutions.
    a. HF
    b. HCl
    c. HC_2O_4
4. Identify each as a strong base or a weak base. Assume aqueous solutions.
    a. NaOH
    b. $Al(OH)_3$
    c. $C_4H_9NH_2$
5. Write a chemical equation for the ionization of each acid and indicate whether it proceeds 100% to products or not.
    a. HNO_3
    b. HNO_2
    c. HI_3
6. Write a chemical equation for the ionization of each base and indicate whether it proceeds 100% to products or not.
    a. NH_3
    b. $(CH_3)_3N$
    c. $Mg(OH)_2$
7. Write the balanced chemical equation for the reaction of each acid and base pair.
    a. $HCl + C_5H_5N$
    b. $H_2C_2O_4 + NH_3$
    c. $HNO_2 + C_7H_9N$
8. Write the balanced chemical equation for the reaction of each acid and base pair.
    a. $H_3C_5H_5O_7 + Mg(OH)_2$
    b. $HC_3H_3O_3 + (CH_3)_3N$
    c. $HBr + Fe(OH)_3$
9. Write the hydrolysis reaction that occurs, if any, when each salt dissolves in water.
    a. K_2SO_3
    b. KI
    c. NH_4ClO_3
10. Write the hydrolysis reaction that occurs, if any, when each salt dissolves in water.
    a. $NaNO_3$
    b. CaC_2O_4
    c. C_5H_5NHCl

11. When NH_4NO_2 dissolves in H_2O, both ions hydrolyze. Write chemical equations for both reactions. Can you tell if the solution will be acidic or basic overall?
12. When pyridinium acetate ($C_5H_5NHC_2H_3O_2$) dissolves in H_2O, both ions hydrolyze. Write chemical equations for both reactions. Can you tell if the solution will be acidic or basic overall?
13. A lab technician mixes a solution of 0.015 M $Mg(OH)_2$. Is the resulting $OH^−$ concentration greater than, equal to, or less than 0.015 M? Explain your answer.
14. A lab technician mixes a solution of 0.55 M HNO_3. Is the resulting H^+ concentration greater than, equal to, or less than 0.55 M? Explain your answer.

Answers

1. A strong acid is 100% ionized in aqueous solution, whereas a weak acid is not 100% ionized.
2.
3. a. weak acid
   b. strong acid
   c. weak acid
4.
5. a. $HNO_3(aq) \rightarrow H^+(aq) + NO_3^−(aq)$; proceeds 100%
   b. $HNO_2(aq) \rightarrow H^+(aq) + NO_2^−(aq)$; does not proceed 100%
   c. $HI_3(aq) \rightarrow H^+(aq) + I_3^−(aq)$; does not proceed 100%
6.
7. a. $HCl + C_5H_5N \rightarrow Cl^− + C_5H_5NH^+$
   b. $H_2C_2O_4 + 2NH_3 \rightarrow C_2O_4^{2−} + 2NH_4^+$
   c. $HNO_2 + C_7H_9N \rightarrow NO_2^− + C_7H_9NH^+$
8.
9. a. $SO_3^{2−} + H_2O \rightarrow HSO_3^− + OH^−$
   b. no reaction
   c. $NH_4^+ + H_2O \rightarrow NH_3 + H_3O^+$
10.
11. $NH_4^+ + H_2O \rightarrow NH_3 + H_3O^+$; $NO_2^− + H_2O \rightarrow HNO_2 + OH^−$; it is not possible to determine whether the solution will be acidic or basic.
12.
13. greater than 0.015 M because there are two $OH^−$ ions per formula unit of $Mg(OH)_2$

12.3.1: Autoionization of Water

? Exercise $12.E.4$

1. Does $[H^+]$ remain constant in all aqueous solutions? Why or why not?
2. Does $[OH^−]$ remain constant in all aqueous solutions? Why or why not?
3. What is the relationship between $[H^+]$ and K_w? Write a mathematical expression that relates them.
4. What is the relationship between $[OH^−]$ and K_w? Write a mathematical expression that relates them.
5. Write the chemical equation for the autoionization of water and label the conjugate acid-base pairs.
6. Write the reverse of the reaction for the autoionization of water. It is still an acid-base reaction? If so, label the acid and base.
7. For a given aqueous solution, if $[H^+] = 1.0 \times 10^{−3}$ M, what is $[OH^−]$?
8. For a given aqueous solution, if $[H^+] = 1.0 \times 10^{−9}$ M, what is $[OH^−]$?
9. For a given aqueous solution, if $[H^+] = 7.92 \times 10^{−5}$ M, what is $[OH^−]$?
10. For a given aqueous solution, if $[H^+] = 2.07 \times 10^{−11}$ M, what is $[H^+]$?
11. For a given aqueous solution, if $[OH^−] = 1.0 \times 10^{−5}$ M, what is $[H^+]$?
12. For a given aqueous solution, if $[OH^−] = 1.0 \times 10^{−12}$ M, what is $[H^+]$?
13. For a given aqueous solution, if $[OH^−] = 3.77 \times 10^{−4}$ M, what is $[H^+]$?
14. For a given aqueous solution, if $[OH^−] = 7.11 \times 10^{−10}$ M, what is $[H^+]$?

15. What are $[H^+]$ and $[OH^-]$ in a 0.344 M solution of HNO_3?
16. What are $[H^+]$ and $[OH^-]$ in a 2.86 M solution of HBr?
17. What are $[H^+]$ and $[OH^-]$ in a 0.00338 M solution of KOH?
18. What are $[H^+]$ and $[OH^-]$ in a 6.02×10^{-4} M solution of $Ca(OH)_2$?
19. If HNO_2 is dissociated only to an extent of 0.445%, what are $[H^+]$ and $[OH^-]$ in a 0.307 M solution of HNO_2?
20. If $(C_2H_5)_2NH$ is dissociated only to an extent of 0.077%, what are $[H^+]$ and $[OH^-]$ in a 0.0955 M solution of $(C_2H_5)_2NH$?

Answers

1. $[H^+]$ varies with the amount of acid or base in a solution.
2.
3. $$[H^+] = \frac{K_W}{[OH^-]} \tag{12.E.1}$$
4.
5. $H_2O + H_2O \rightarrow H_3O^+ + OH^-$; H_2O/H_3O^+ and H_2O/OH^-
6.
7. 1.0×10^{-11} M
8.
9. 1.26×10^{-10} M
10.
11. 1.0×10^{-9} M
12.
13. 2.65×10^{-11} M
14.
15. $[H^+] = 0.344$ M; $[OH^-] = 2.91 \times 10^{-14}$ M
16.
17. $[OH^-] = 0.00338$ M; $[H^+] = 2.96 \times 10^{-12}$ M
18.
19. $[H^+] = 0.00137$ M; $[OH^-] = 7.32 \times 10^{-12}$ M

12.3.2: The pH Scale

? Exercise 12.E.1

1. Define *pH*. How is it related to pOH?
2. Define *pOH*. How is it related to pH?
3. What is the pH range for an acidic solution?
4. What is the pH range for a basic solution?
5. What is $[H^+]$ for a neutral solution?
6. What is $[OH^-]$ for a neutral solution? Compare your answer to Exercise 6. Does this make sense?

7. Which substances in Table 12.7.1 are acidic?
8. Which substances in Table 12.7.1 are basic?
9. What is the pH of a solution when $[H^+]$ is 3.44×10^{-4} M?
10. What is the pH of a solution when $[H^+]$ is 9.04×10^{-13} M?

11. What is the pH of a solution when [OH^-] is 6.22 × 10^{-7} M?
12. What is the pH of a solution when [OH^-] is 0.0222 M?
13. What is the pOH of a solution when [H^+] is 3.44 × 10^{-4} M?
14. What is the pOH of a solution when [H^+] is 9.04 × 10^{-13} M?
15. What is the pOH of a solution when [OH^-] is 6.22 × 10^{-7} M?
16. What is the pOH of a solution when [OH^-] is 0.0222 M?
17. If a solution has a pH of 0.77, what is its pOH, [H^+], and [OH^-]?
18. If a solution has a pOH of 13.09, what is its pH, [H^+], and [OH^-]?

Answers

1. pH is the negative logarithm of [H^+] and is equal to 14 − pOH.
2.
3. pH < 7
4.
5. 1.0 × 10^{-7} M
6.
7. Every entry above pure water is acidic.
8.
9. 3.46
10.
11. 7.79
12.
13. 10.54
14.
15. 6.21
16.
17. pOH = 13.23; [H^+] = 1.70 × 10^{-1} M; [OH^-] = 5.89 × 10^{-14} M

12.4: Buffers

Exercise 12.E.1

1. Define *buffer*. What two related chemical components are required to make a buffer?
2. Can a buffer be made by combining a strong acid with a strong base? Why or why not?
3. Which combinations of compounds can make a buffer? Assume aqueous solutions.
   a. HCl and NaCl
   b. HNO_2 and $NaNO_2$
   c. NH_4NO_3 and HNO_3
   d. NH_4NO_3 and NH_3
4. Which combinations of compounds can make a buffer? Assume aqueous solutions.
   a. H_3PO_4 and Na_3PO_4
   b. $NaHCO_3$ and Na_2CO_3
   c. $NaNO_3$ and $Ca(NO_3)_2$
   d. HN_3 and NH_3
5. For each combination in Exercise 3 that is a buffer, write the chemical equations for the reactions of the buffer components when a strong acid and a strong base is added.

6. For each combination in Exercise 4 that is a buffer, write the chemical equations for the reactions of the buffer components when a strong acid and a strong base is added.
7. The complete phosphate buffer system is based on four substances: H_3PO_4, $H_2PO_4^-$, HPO_4^{2-}, and PO_4^{3-}. What different buffer solutions can be made from these substances?
8. Explain why NaBr cannot be a component in either an acidic or a basic buffer.
9. Two solutions are made containing the same concentrations of solutes. One solution is composed of H_3PO_4 and Na_3PO_4, while the other is composed of HCN and NaCN. Which solution should have the larger capacity as a buffer?
10. Two solutions are made containing the same concentrations of solutes. One solution is composed of NH_3 and NH_4NO_3, while the other is composed of H_2SO_4 and Na_2SO_4. Which solution should have the larger capacity as a buffer?

Answers

1. A buffer is the combination of a weak acid or base and a salt of that weak acid or base.
2.
3. a. no
   b. yes
   c. no
   d. yes
4.
5. 3b: strong acid: $NO_2^- + H^+ \rightarrow HNO_2$; strong base: $HNO_2 + OH^- \rightarrow NO_2^- + H_2O$; 3d: strong base: $NH_4^+ + OH^- \rightarrow NH_3 + H_2O$; strong acid: $NH_3 + H^+ \rightarrow NH_4^+$
6.
7. Buffers can be made from three combinations: (1) H_3PO_4 and $H_2PO_4^-$, (2) $H_2PO_4^-$ and HPO_4^{2-}, and (3) HPO_4^{2-} and PO_4^{3-}. (Technically, a buffer can be made from any two components.)
8.
9. The phosphate buffer should have the larger capacity.

CHAPTER OVERVIEW

13: Chemical Equilibrium

So far in this text, when presented a chemical reaction, it has been implicitly assumed that the reaction goes to completion. Indeed, previous stoichiometric calculations were based on this; when asked how much of a product is produced when so much of a reactant reacts, it was assumed that *all* of a reactant reacts. However, this is usually not the case; many reactions do not go to completion, and many chemists have to deal with that. In this chapter, we will study this phenomenon and see ways in which we can affect the extent of chemical reactions.

13.1: Collision Theory and Reaction Rates

Learning Objectives

- Describe collision theory and its connection to reaction rates.
- Define activation energy and how it relates to energy diagrams.
- Use collision theory to describe how concentration, temperature, and catalysts affect reaction rates.

Collision Theory

Postulates of Collision theory

1. The rate of a reaction is proportional to the rate of reactant collisions:

$$\text{reaction rate} \propto \frac{\#\,\text{collisions}}{\text{time}}$$

2. The reacting species must collide in an orientation that allows contact between the atoms that will become bonded together in the product.
3. The collision must occur with adequate energy to permit mutual penetration of the reacting species' valence shells so that the electrons can rearrange and form new bonds (and new chemical species).

The behavior of the reactant atoms, molecules, or ions is responsible for the rates of a given chemical reaction. **Collision theory** *is a set of principles based around the idea that reactant particles form products when they collide with one another, but only when those collisions have enough kinetic energy and the correct orientation to cause a reaction.* Particles that lack the necessary kinetic energy may collide, but the particles will simply bounce off one another unchanged. The figure below illustrates the difference. In the first collision, the particles bounce off one another, and no rearrangement of atoms has occurred. The second collision occurs with greater kinetic energy, and so the bond between the two red atoms breaks. One red atom bonds with the other molecule as one product, while the single red atom is the other product. The first collision is called an ineffective collision, while the second collision is called an effective collision.

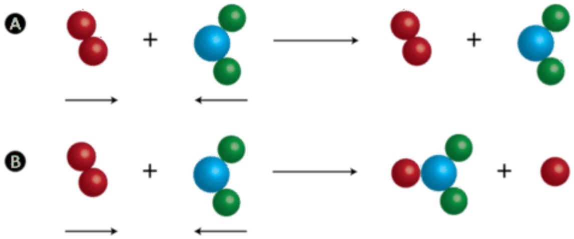

Figure 13.1.1: (A) An ineffective collision is one that does not result in product formation. (B) An effective collision is one in which chemical bonds are broken, and a product is formed.

Supplying reactant particles with energy causes the bonds between the atoms to vibrate with a greater frequency. This increase in vibrational energy makes a chemical bond more likely to break and a chemical reaction more likely to occur when those particles collide with other particles. Additionally, more energetic particles have more forceful collisions, which also increases the likelihood that a rearrangement of atoms will take place. The **activation energy** *for a reaction is the minimum energy that colliding particles must have in order to undergo a reaction*. Some reactions occur readily at room temperature because most of the reacting particles already have the requisite activation energy at that temperature. Other reactions only occur when heated because the particles do not have enough energy to react unless more is provided by an external source of heat.

Potential Energy Diagrams

Then energy changes that occur during a chemical reaction can be shown in a diagram called a potential energy diagram, sometimes called a reaction progress curve. A **potential energy diagram** *shows the change in the potential energy of a system as reactants are converted into products*. The figure below shows basic potential energy diagrams for an endothermic (left) and an exothermic (right) reaction. Recall that the enthalpy change (ΔH) is positive for an endothermic reaction and negative for an exothermic reaction. This can be seen in the potential energy diagrams. The total potential energy of the system increases for the endothermic reaction as the system absorbs energy from the surroundings. The total potential energy of the system decreases for the exothermic reaction as the system releases energy to the surroundings.

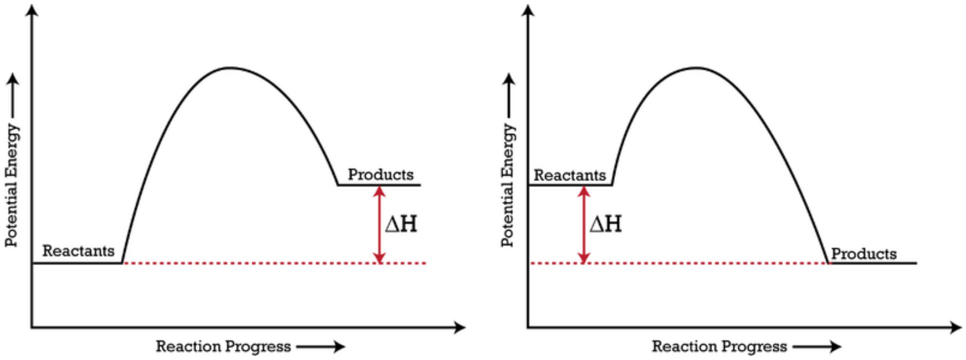

Figure 13.1.2: A potential energy diagram shows the total potential energy of a reacting system as the reaction proceeds. (Left) In an endothermic reaction, the energy of the products is greater than the energy of the reactants, and ΔH is positive. (Right) In an exothermic reaction, the energy of the products is lower than the energy of the reactants, and ΔH is negative.

The activation energy for a reaction is illustrated in the potential energy diagram by the height of the hill between the reactants and the products. For this reason, the activation energy of a reaction is sometimes referred to as the activation energy barrier. Reacting particles must have enough energy so that when they collide, they can overcome this barrier (see figure below).

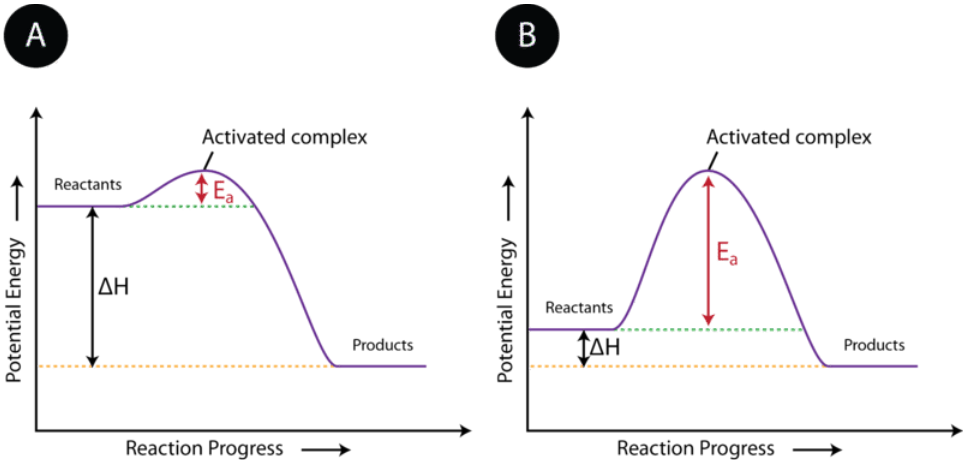

Figure 13.1.3: The activation energy (E_a) of a reaction is the barrier that must be overcome in order for the reactants to become products. (A) The activation energy is low, meaning that the reaction is likely to be fast. (B) The activation energy is high, meaning that the reaction is likely to be slow.

As discussed earlier, reactant particles sometimes collide with one another and yet remain unchanged by the collision. Other times, the collision leads to the formation of products. The state of the particles that is in between the reactants and products is called the activated complex. An **activated complex** *is an unstable arrangement of atoms that exists momentarily at the peak of the activation energy barrier*. Because of its high energy, the activated complex exists only for an extremely short period of time (about 10^{-13} s). The activated complex is equally likely to either reform the original reactants or go on to form the products. The figure below shows the formation of a possible activated complex between colliding hydrogen and oxygen molecules. Because of their unstable nature and brief existence, very little is known about the exact structures of most activated complexes.

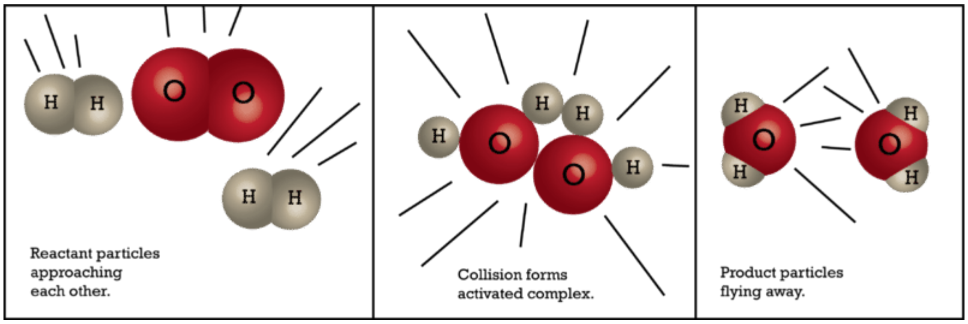

Figure 13.1.4: An activated complex is a short-lived state in which the colliding particles are at the peak of the potential energy curve.

13.1.1: Effects of Temperature, Concentration, and Catalysts on Reaction Rates

Learning Outcomes

- Describe how changing the temperature and concentration of a reaction affects the rate of a reaction.
- Define a catalyst and how a catalyst affects the rate of a reaction.

By their nature, some reactions occur very quickly, while others are very slow. However, certain changes in the reaction conditions can have an effect on the rate of a given chemical reaction. Collision theory can be utilized to explain these rate effects.

Effect of Temperature on Rate of Reaction

The rate of reaction was discussed in terms of three factors: collision frequency, the collision energy, and the geometric orientation. Remember that the collision frequency is the number of collisions per second. The collision frequency is dependent, among other factors, on the temperature of the reaction.

When the temperature is increased, the average velocity of the particles is increased. The average kinetic energy of these particles is also increased. The result is that the particles will collide more frequently, because the particles move around faster and will encounter more reactant particles. However, this is only a minor part of the reason why the rate is increased. Just because the particles are colliding more frequently does not mean that the reaction will definitely occur.

The major effect of increasing the temperature is that more of the particles that collide will have the amount of energy needed to have an effective collision. In other words, more particles will have the necessary activation energy.

At room temperature, the hydrogen and oxygen in the atmosphere do not have sufficient energy to attain the activation energy needed to produce water:

$$\mathrm{O_2}\,(g) + \mathrm{H_2}\,(g) \rightarrow \text{No reaction}$$

At any one moment in the atmosphere, there are many collisions occurring between these two reactants. But what we find is that water is not formed from the oxygen and hydrogen molecules colliding in the atmosphere, because the activation energy barrier is just too high, and all the collisions are resulting in rebound. When we increase the temperature of the reactants or give them energy in some other way, the molecules have the necessary activation energy and are able to react to produce water:

$$\mathrm{O_2}\,(g) + \mathrm{H_2}\,(g) \rightarrow \mathrm{H_2O}\,(l)$$

There are times when the rate of a reaction needs to be slowed down. Lowering the temperature could also be used to decrease the number of collisions that would occur and lowering the temperature would also reduce the kinetic energy available for activation energy. If the particles have insufficient activation energy, the collisions will result in rebound rather than reaction. Using this idea, when the rate of a reaction needs to be lower, keeping the particles from having sufficient activation energy will definitely keep the reaction at a lower rate.

Society uses the effects of temperature on reaction rate every day. Food storage is a prime example of how the temperature effect on reaction rate is utilized by society. Consumers store food in freezers and refrigerators to slow down the processes that cause it to spoil. The decrease in temperature decreases the rate at which food will break down or be broken down by bacteria. In the early years of the 20^{th} century, explorers were fascinated with being the first to reach the South Pole. In order to attempt such a difficult task at a time without most of the technology that we take for granted today, they devised a variety of ways of surviving. One method was to store their food in the snow to be used later during their advances to the pole. On some explorations, they buried so much food that they didn't need to use all of it, and some was left behind. Many years later, when this food was located and thawed, it was found to still be edible.

When milk, for example, is stored in the refrigerator, the molecules in the milk have less energy. This means that while molecules will still collide with other molecules, few of them will react (which means in this case "spoil") because the molecules do not have sufficient energy to overcome the activation energy barrier. The molecules do have energy and are colliding, however, and so, over time, even in the refrigerator, the milk will spoil. Eventually the higher energy molecules will gain the energy needed to react and when enough of these reactions occur, the milk becomes "soured".

However, if that same carton of milk was at room temperature, the milk would react (in other words, "spoil") much more quickly. Most of the molecules would have sufficient energy to overcome the energy barrier at room temperature, and many more collisions would occur. This allows for the milk to spoil in a fairly short amount of time. This is also the reason why most fruits and vegetables ripen in the summer when the temperature is much warmer. You may have experienced this first hand if you have ever bitten into an unripe banana—it was probably sour tasting and might even have felt like biting into a piece of wood! When a banana ripens, numerous reactions occur that produce all the compounds that we expect to taste in a banana. But this can only happen if the temperature is high enough to allow these reactions to make those products.

Effect of Concentration on Rate of Reaction

If you had an enclosed space, like a classroom, and there was one red ball and one green ball flying around the room in random motion, undergoing perfectly elastic collisions with the walls and with each other, in a given amount of time, the balls would collide with each other a certain number of times determined by probability. If you now put two red balls and one green ball in the room under the same conditions, the probability of a collision between a red ball and the green ball would exactly double. The green ball would have twice the chance of encountering a red ball in the same amount of time.

In terms of chemical reactions, a similar situation exists. Particles of two gaseous reactants or two reactants in solution have a certain probability of undergoing collisions with each other in a reaction vessel. If you double the concentration of either reactant, the probability of a collision doubles. The rate of reaction is proportional to the number of collisions per unit time. If one concentration is doubled, the number of collisions will also double. Assuming that the percent of collisions that are successful does not change, then having twice as many collisions will result in twice as many successful collisions. The rate of reaction is proportional to the number of collisions over time; increasing the concentration of either reactant increases the number of collisions, and therefore increases the number of successful collisions and the reaction rate.

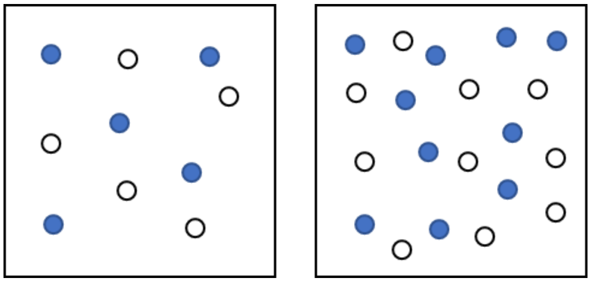

Figure 13.1.1.1: The left reaction container has a lower concentration than the right. In the right container, you can see that there are more opportunities for the reactants to collide because the concentration is higher.

For example, the chemical test used to identify a gas as oxygen, or not, relies on the fact that increasing the concentration of a reactant increases reaction rate. The reaction we call combustion refers to a reaction in which a flammable substance reacts with oxygen. If we light a wooden splint (a thin splinter of wood) on fire and then blow the fire out, the splint will continue to glow in air for a period of time. If we insert that glowing splint into any gas that does not contain oxygen, the splint will immediately cease to glow—that is, the reaction stops. Oxygen is the only gas that will support combustion, Air is approximately 20% oxygen gas. If we take that glowing splint and insert it into pure oxygen gas, the reaction will increase its rate by a factor of five, since pure oxygen has 5 times the concentration of oxygen that is in the air. When the reaction occurring on the glowing splint increases its rate by a factor of five, the glowing splint will suddenly burst back into full flame. This test, of thrusting a glowing splint into a gas, is used to identify the gas as oxygen. Only a greater concentration of oxygen than that found in air will cause the glowing splint to burst into flame.

Catalysts

The rates of some chemical reactions can be increased dramatically by introducing certain other substances into the reaction mixture. Hydrogen peroxide is used as a disinfectant for scrapes and cuts, and it can be found in many medicine cabinets as a 3% aqueous solution. Hydrogen peroxide naturally decomposes to produce water and oxygen gas, but the reaction is very slow. A bottle of hydrogen peroxide will last for several years before it needs to be replaced. However, the addition of just a small amount of manganese (IV) oxide to hydrogen peroxide will cause it to decompose completely in just a matter of minutes. A **catalyst** *is a substance that increases the rate of a chemical reaction without being used up in the reaction*. It accomplishes this task by providing an alternate reaction pathway that has a lower activation energy barrier. After the reaction occurs, a catalyst returns to its original state, so catalysts can be used over and over again. Because it is neither a reactant nor a product, a catalyst is shown in a chemical equation by being written above the yield arrow.

$$2\mathrm{H_2O_2}\,(aq) \overset{\mathrm{MnO_2}}{\rightarrow} 2\mathrm{H_2O}\,(l) + \mathrm{O_2}\,(g) \tag{13.1.1.1}$$

A catalyst works by changing the mechanism of the reaction, which can be thought of as the specific set of smaller steps by which the reactants become products. The important point is that the use of a catalyst lowers the overall activation energy of the reaction (see figure below). With a lower activation energy barrier, a greater percentage of reactant molecules are able to have effective collisions, and the reaction rate increases.

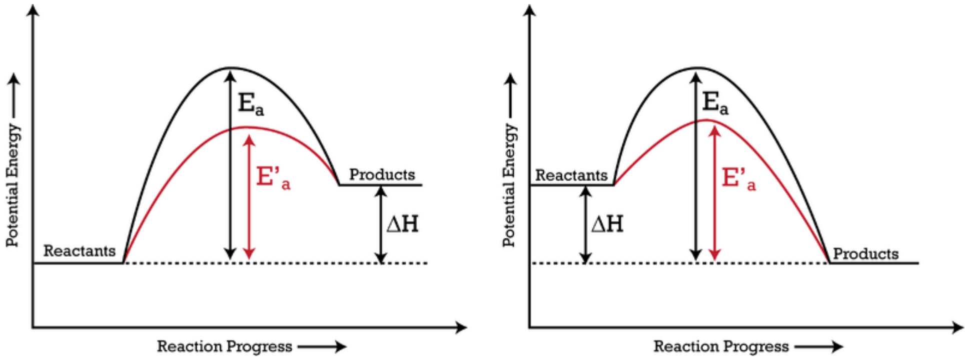

Figure 13.1.1.2: The addition of a catalyst to a reaction lowers the activation energy, increasing the rate of the reaction. The activation energy of the uncatalyzed reaction is shown by E_a, while the catalyzed reaction is shown by E_a'. The heat of reaction (ΔH) is unchanged by the presence of the catalyst.

Catalysts are extremely important parts of many chemical reactions. Enzymes in your body act as nature's catalysts, allowing important biochemical reactions to occur at reasonable rates. Chemical companies constantly search for new and better catalysts to make reactions go faster and thus make the company more profitable.

Contributors and Attributions

-
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13.2: Dynamic Equilibrium

Learning Objectives

- Describe and identify reversible reactions.
- Define chemical equilibrium and identify when a reaction has reached equilibrium.

In the previous sections, we discussed the principles of chemical kinetics, which deal with the *rate of change*, or how quickly a given chemical reaction occurs. We now turn our attention to the *extent* to which a reaction occurs and how reaction conditions affect the final concentrations of reactants and products. For most of the reactions that we have discussed so far, you may have assumed that once reactants are converted to products, they are likely to remain that way. In fact, however, virtually all chemical reactions are *reversible* to some extent. That is, an opposing reaction occurs in which the products react, to a greater or lesser degree, to re-form the reactants. These reactions will not convert all reactants to products, but will instead reach a **chemical equilibrium** where some of both reactants and products remain, but the amounts of each are no longer changing. Consider this demonstration of how the process works.

Reversible Reactions

A **reversible reaction** is one where the forward and reverse reaction happens at the same time. Consider the following reaction occurring in a closed container (so that no material can go in or out):

$$\mathrm{H_2 + I_2 \rightarrow 2HI}$$

This is simply the reaction between elemental hydrogen and elemental iodine to make hydrogen iodide. The way the equation is written, we are led to believe that the reaction goes to completion, that all the $\mathrm{H_2}$ and the $\mathrm{I_2}$ react to make HI.

However, this is not the case. The reverse chemical reaction is also taking place:

$$\mathrm{2HI \rightarrow H_2 + I_2}$$

It acts to undo what the first reaction does. Because two opposing processes are occurring at once, it is conventional to represent an equilibrium using a double arrow, like this:

$$H_2 + I_2 \rightleftharpoons 2HI$$

The *double arrow* implies that the reaction is going in both directions. Note that the reaction must still be balanced. So how do we know when these reactions stop, and can we predict the amount of products and reactants when the reaction is over?

Dynamic Equilibrium

Figure 13.2.1: Dinitrogen tetroxide is a powerful oxidizer that reacts spontaneously upon contact with various forms of hydrazine, which makes the pair a popular propellant combination for rockets. Nitrogen dioxide at −196 °C, 0 °C, 23 °C, 35 °C, and 50 °C. (NO_2) converts to the colorless dinitrogen tetroxide (N_2O_4) at low temperatures, and reverts to NO_2 at higher temperatures. (CC BY-SA 3.0; Eframgoldberg).

Chemical equilibrium is a dynamic process that consists of a forward reaction, in which reactants are converted to products, and a reverse reaction, in which products are converted to reactants. At equilibrium, the forward and reverse reactions proceed at equal rates. Consider, for example, a simple system that contains only one reactant and one product, the reversible dissociation of dinitrogen tetroxide (N_2O_4) to nitrogen dioxide (NO_2). You may recall that NO_2 is responsible for the brown color we associate with smog. When a sealed tube containing solid N_2O_4 (mp = −9.3°C; bp = 21.2°C) is heated from −78.4°C to 25°C, the red-brown color of NO_2 appears (Figure 13.2.1). The reaction can be followed visually because the product (NO_2) is colored, whereas the reactant (N_2O_4) is colorless:

$$\underset{colorless}{N_2O_4(g)} \rightleftharpoons \underset{red-brown}{2\,NO_2(g)} \tag{13.2.1}$$

The double arrow indicates that both the forward reaction

$$N_2O_4(g) \longrightarrow 2\,NO_2(g) \tag{13.2.2}$$

and reverse reaction

$$2\,NO_2(g) \longrightarrow N_2O_4(g) \tag{13.2.3}$$

occurring simultaneously (i.e, the reaction is reversible). However, this does not necessarily mean the system is at equilibrium.

Figure 13.2.2 shows how the composition of this system would vary as a function of time at a constant temperature. If the initial concentration of NO_2 were zero, then it increases as the concentration of N_2O_4 decreases. Eventually the composition of the system stops changing with time, and chemical equilibrium is achieved. Conversely, if we start with a sample that contains no N_2O_4 but an initial NO_2 concentration twice the initial concentration of N_2O_4 (Figure 13.2.2a), in accordance with the stoichiometry of the reaction, we reach exactly the same equilibrium composition (Figure 13.2.2b). Thus equilibrium can be approached from either direction in a chemical reaction.

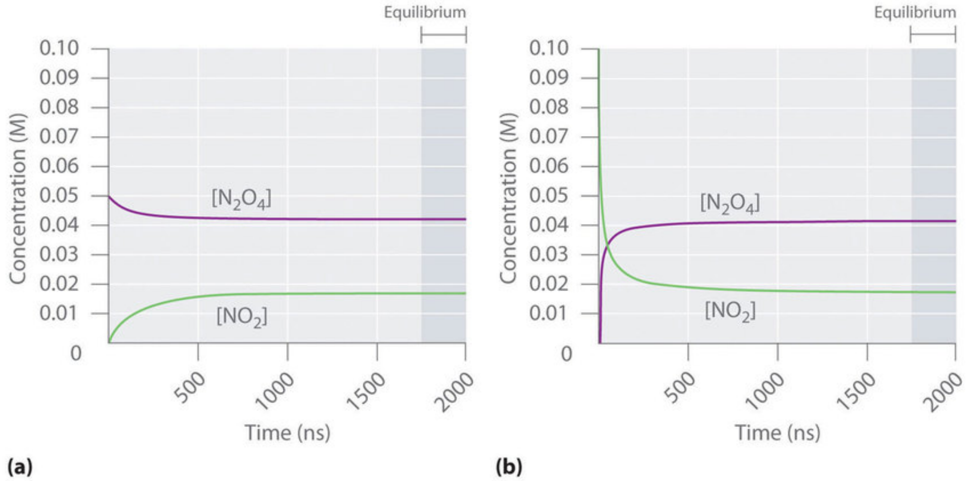


Figure 13.2.2: The Composition of N_2O_4/NO_2 Mixtures as a Function of Time at Room Temperature. (a) Initially, this idealized system contains 0.0500 M gaseous N_2O_4 and no gaseous NO_2. The concentration of N_2O_4 decreases with time as the concentration of NO_2 increases. (b) Initially, this system contains 0.1000 M NO_2 and no N_2O_4. The concentration of NO_2 decreases with time as the concentration of N_2O_4 increases. In both cases, the final concentrations of the substances are the same: [N_2O_4] = 0.0422 M and [NO_2] = 0.0156 M at equilibrium. (CC BY-SA-NC; Anonymous by request)

Figure 13.2.3 shows the forward and reverse reaction rates for a sample that initially contains pure NO_2. Because the initial concentration of N_2O_4 is zero, the forward reaction rate (dissociation of N_2O_4) is initially zero as well. In contrast, the reverse reaction rate (dimerization of NO_2) is initially very high ($2.0 \times 10^6 \, M/s$), but it decreases rapidly as the concentration of NO_2 decreases. As the concentration of N_2O_4 increases, the rate of dissociation of N_2O_4 increases—but more slowly than the dimerization of NO_2—because the reaction is only first order in N_2O_4 (rate = $k_f[N_2O_4]$, where k_f is the rate constant for the forward reaction in Equations 13.2.1 and 13.2.2). Eventually, the forward and reverse reaction rates become identical, $k_f = k_r$, and the system has reached chemical equilibrium. If the forward and reverse reactions occur at different rates, then the system is not at equilibrium.

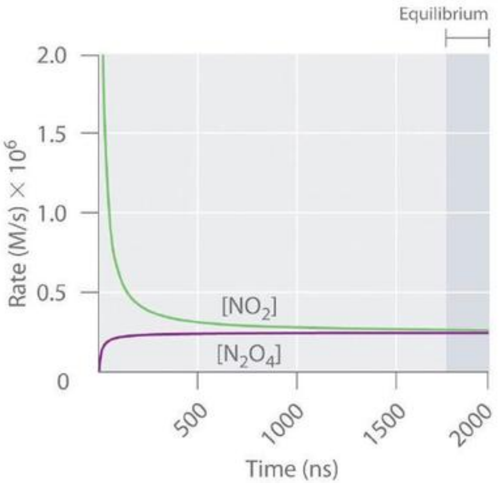


Figure 13.2.3: The Forward and Reverse Reaction Rates as a Function of Time for the $N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$ System Shown in Part (b) in Figure 13.2.2. (CC BY-SA-NC; Anonymous by request)

The rate of dimerization of NO_2 (reverse reaction) decreases rapidly with time, as expected for a second-order reaction. Because the initial concentration of N_2O_4 is zero, the rate of the dissociation reaction (forward reaction) at $t = 0$ is also zero. As the dimerization reaction proceeds, the N_2O_4 concentration increases, and its rate of dissociation also increases. Eventually the rates of the two reactions are equal: chemical equilibrium has been reached, and the concentrations of N_2O_4 and NO_2 no longer change.

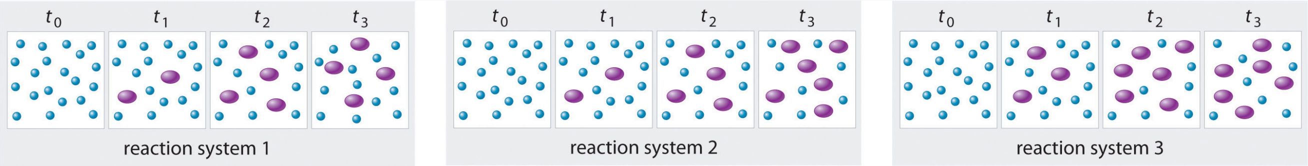
> *At equilibrium, the forward reaction rate is equal to the reverse reaction rate.*

Example 13.2.1

The three reaction systems (1, 2, and 3) depicted in the accompanying illustration can all be described by the equation:

$$2A \rightleftharpoons B$$

where the blue circles are A and the purple ovals are B. Each set of panels shows the changing composition of one of the three reaction mixtures as a function of time. Which system took the longest to reach chemical equilibrium?



Given: three reaction systems

Asked for: relative time to reach chemical equilibrium

Strategy:

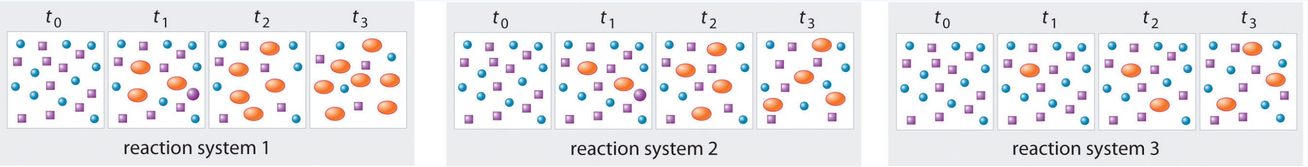
Compare the concentrations of A and B at different times. The system whose composition takes the longest to stabilize took the longest to reach chemical equilibrium.

Solution:

In systems 1 and 3, the concentration of A decreases from t_0 through t_2 but is the same at both t_2 and t_3. Thus systems 1 and 3 are at equilibrium by t_3. In system 2, the concentrations of A and B are still changing between t_2 and t_3, so system 2 may not yet have reached equilibrium by t_3. Thus system 2 took the longest to reach chemical equilibrium.

Exercise 13.2.1

In the following illustration, A is represented by blue circles, B by purple squares, and C by orange ovals; the equation for the reaction is A + B ⇌ C. The sets of panels represent the compositions of three reaction mixtures as a function of time. Which, if any, of the systems shown has reached equilibrium?



Answer

system 2

A Video Introduction to Dynamic Equilibrium: https://youtu.be/4AJbFuzW2cs

Summary

At equilibrium, the forward and reverse reactions of a system proceed at equal rates. Chemical equilibrium is a dynamic process consisting of forward and reverse reactions that proceed at equal rates. At equilibrium, the composition of the system no longer changes with time. The composition of an equilibrium mixture is independent of the direction from which equilibrium is approached.

13.3: The Equilibrium Constant Expression

Learning Objectives

- Describe equilibrium constants.
- To write an equilibrium constant expression for any reaction.
- Compare the extent to which a reaction proceeds towards the products using equilibrium constants.

Is a system where the forward and reverse reaction happen at the same time, how do we predict the concentrations, or amounts, or products and reactants when the reaction reaches equilibrium? The rate of the forward and reverse reactions are equal when equilibrium is reached, and the ratio of products to reactants is constant. In equilibrium, we call this ratio the equilibrium constant.

Developing an Equilibrium Constant Expression

In 1864, the Norwegian chemists Cato Guldberg (1836–1902) and Peter Waage (1833–1900) carefully measured the compositions of many reaction systems at equilibrium. They discovered that for any reversible reaction of the general form

$$aA + bB \rightleftharpoons cC + dD \tag{13.3.1}$$

where A and B are reactants, C and D are products, and a, b, c, and d are the stoichiometric coefficients in the balanced chemical equation for the reaction, the ratio of the product of the equilibrium concentrations of the products (raised to their coefficients in the balanced chemical equation) to the product of the equilibrium concentrations of the reactants (raised to their coefficients in the balanced chemical equation) is always a constant under a given set of conditions. This relationship is known as the law of mass action and can be stated as follows:

$$K = \frac{[C]^c[D]^d}{[A]^a[B]^b} \tag{13.3.2}$$

where K is the equilibrium constant for the reaction. Equation 13.3.1 is called the equilibrium equation, and the right side of Equation 13.3.2 is called the equilibrium constant expression. The relationship shown in Equation 13.3.2 is true for any pair of opposing reactions regardless of the mechanism of the reaction or the number of steps in the mechanism.

Writing Equilibrium Constant Expressions

There are some rules about writing equilibrium constant expressions that need to be learned:

1. The products are on top and the reactants are on the bottom.
2. Brackets are used around each species in the reaction to indicate concentration (molarity)
3. Concentrations of products are multiplied on the top of the expression. Concentrations of reactants are multiplied together on the bottom.
4. Coefficients in the equation become exponents in the equilibrium constant expression. When the coefficient is one, it is not written as an exponent.
5. Solids, liquids, and solvents are assigned a value of 1, so their concentrations do not affect the value of K.

The equilibrium constant can vary over a wide range of values. The values of K shown in Table $13.3.1$, for example, vary by 60 orders of magnitude. Because products are in the numerator of the equilibrium constant expression and reactants are in the denominator, values of K greater than 10^3 indicate a strong tendency for reactants to form products. In this case, chemists say that equilibrium lies to the right as written, favoring the formation of products. An example is the reaction between H_2 and Cl_2 to produce HCl, which has an equilibrium constant of 1.6×10^{33} at 300 K. Because H_2 is a good reductant and Cl_2 is a good oxidant, the reaction proceeds essentially to completion. In contrast, values of K less than 10^{-3} indicate that the ratio of products to reactants at equilibrium is very small. That is, reactants do not tend to form products readily, and the equilibrium lies to the left as written, favoring the formation of reactants.

Table 13.3.1: Equilibrium Constants for Selected Reactions*

Reaction	Temperature (K)	Equilibrium Constant (K)
*Equilibrium constants vary with temperature. The K values shown are for systems at the indicated temperatures.		

Reaction	Temperature (K)	Equilibrium Constant (K)
$S(s) + O_2(g) \rightleftharpoons SO_2(g)$	300	4.4×10^{53}
$2\,H_2(g) + O_2(g) \rightleftharpoons 2\,H_2O(g)$	500	2.4×10^{47}
$H_2(g) + Cl_2(g) \rightleftharpoons 2\,HCl(g)$	300	1.6×10^{33}
$H_2(g) + Br_2(g) \rightleftharpoons 2\,HBr(g)$	300	4.1×10^{18}
$2\,NO(g) + O_2(g) \rightleftharpoons 2\,NO_2(g)$	300	4.2×10^{13}
$3\,H_2(g) + N_2(g) \rightleftharpoons 2\,NH_3(g)$	300	2.7×10^{8}
$H_2(g) + D_2(g) \rightleftharpoons 2\,HD(g)$	100	1.92
$H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g)$	300	2.9×10^{-1}
$I_2(g) \rightleftharpoons 2\,I(g)$	800	$4.6\times^{10-7}$
$Br_2(g) \rightleftharpoons 2\,Br(g)$	1000	4.0×10^{-7}
$Cl_2(g) \rightleftharpoons 2\,Cl(g)$	1000	1.8×10^{-9}
$F_2(g) \rightleftharpoons 2\,F(g)$	500	7.4×10^{-13}

*Equilibrium constants vary with temperature. The K values shown are for systems at the indicated temperatures.

Many reactions have equilibrium constants between 1000 and 0.001 ($10^3 \geq K \geq 10^{-3}$), neither very large nor very small. At equilibrium, these systems tend to contain significant amounts of both products and reactants, indicating that there is not a strong tendency to form either products from reactants or reactants from products. An example of this type of system is the reaction of gaseous hydrogen and deuterium, a component of high-stability fiber-optic light sources used in ocean studies, to form HD:

$$H_{2(g)} + D_{2(g)} \rightleftharpoons 2HD_{(g)} \tag{13.3.3}$$

The equilibrium constant expression for this reaction is

$$K = \frac{[HD]^2}{[H_2][D_2]} \tag{13.3.4}$$

with K varying between 1.9 and 4 over a wide temperature range (100–1000 K). Thus an equilibrium mixture of H_2, D_2, and HD contains significant concentrations of both product and reactants.

Figure $13.3.1$ summarizes the relationship between the magnitude of K and the relative concentrations of reactants and products at equilibrium for a general reaction, written as

$$\text{reactants} \rightleftharpoons \text{products}. \tag{13.3.5}$$

When K is a **large** number, the concentration of products at equilibrium predominate. This corresponds to an essentially irreversible reaction. Conversely, when K is a very **small** number, the reaction produces almost no products as written. Systems for which K is neither large nor small, the equilibrium will have significant concentrations of both reactants and products.

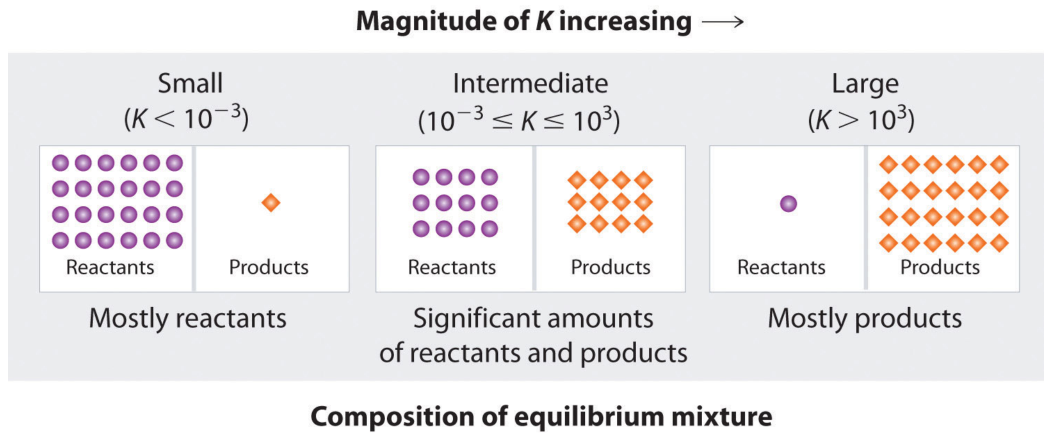


Figure 13.3.1: The Relationship between the Composition of the Mixture at Equilibrium and the Magnitude of the Equilibrium Constant. The larger the K, the farther the reaction proceeds to the right before equilibrium is reached, and the greater the ratio of products to reactants at equilibrium.

> A large value of the equilibrium constant K means that products predominate at equilibrium; a small value means that reactants predominate at equilibrium.

Example 13.3.1

Write the equilibrium constant expression for each reaction.

- $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$
- $CO_{(g)} + \frac{1}{2}O_{2(g)} \rightleftharpoons CO_{2(g)}$
- $2CO_{2(g)} \rightleftharpoons 2CO_{(g)} + O_{2(g)}$

Given: balanced chemical equations

Asked for: equilibrium constant expressions

Strategy:

Refer to Equation ???. Place the arithmetic product of the concentrations of the products (raised to their stoichiometric coefficients) in the numerator and the product of the concentrations of the reactants (raised to their stoichiometric coefficients) in the denominator.

Solution:

The only product is ammonia, which has a coefficient of 2. For the reactants, N_2 has a coefficient of 1 and H2 has a coefficient of 3. The equilibrium constant expression is as follows:

$$\frac{[NH_3]^2}{[N_2][H_2]^3} \tag{13.3.6}$$

The only product is carbon dioxide, which has a coefficient of 1. The reactants are CO, with a coefficient of 1, and O_2, with a coefficient of $\frac{1}{2}$. Thus the equilibrium constant expression is as follows:

$$\frac{[CO_2]}{[CO][O_2]^{1/2}} \tag{13.3.7}$$

This reaction is the reverse of the reaction in part b, with all coefficients multiplied by 2 to remove the fractional coefficient for O_2. The equilibrium constant expression is therefore the inverse of the expression in part b, with all exponents multiplied by 2:

$$\frac{[CO]^2[O_2]}{[CO_2]^2} \tag{13.3.8}$$

Exercise 13.3.1

Write the equilibrium constant expression for each reaction.

a. $N_2O_{(g)} \rightleftharpoons N_{2(g)} + \frac{1}{2}O_{2(g)}$
b. $2C_8H_{18(g)} + 25O_{2(g)} \rightleftharpoons 16CO_{2(g)} + 18H_2O_{(g)}$
c. $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$

Answer:

a. $K = \dfrac{[N_2][O_2]^{1/2}}{[N_2O]}$
b. $K = \dfrac{[CO_2]^{16}[H_2O]^{18}}{[C_8H_{18}]^2[O_2]^{25}}$
c. $K = \dfrac{[HI]^2}{[H_2][I_2]}$

Example 13.3.2

Predict which systems at equilibrium will (a) contain essentially only products, (b) contain essentially only reactants, and (c) contain appreciable amounts of both products and reactants.

a. $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)} \qquad K_{(700K)} = 54$
b. $2CO_{2(g)} \rightleftharpoons 2CO_{(g)} + O_{2(g)} \qquad K_{(1200K)} = 3.1 \times 10^{-18}$
c. $PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)} \qquad K_{(613K)} = 97$
d. $2O_{3(g)} \rightleftharpoons 3O_{2(g)} \qquad K_{(298K)} = 5.9 \times 10^{55}$

Given: systems and values of K

Asked for: composition of systems at equilibrium

Strategy:

Use the value of the equilibrium constant to determine whether the equilibrium mixture will contain essentially only products, essentially only reactants, or significant amounts of both.

Solution:

a. Only system 4 has $K \gg 10^3$, so at equilibrium it will consist of essentially only products.
b. System 2 has $K \ll 10^{-3}$, so the reactants have little tendency to form products under the conditions specified; thus, at equilibrium the system will contain essentially only reactants.
c. Both systems 1 and 3 have equilibrium constants in the range $10^3 \geq K \geq 10^{-3}$, indicating that the equilibrium mixtures will contain appreciable amounts of both products and reactants.

Exercise 13.3.2

Hydrogen and nitrogen react to form ammonia according to the following balanced chemical equation:

$$3H_{2(g)} + N_{2(g)} \rightleftharpoons 2NH_{3(g)} \tag{13.3.9}$$

Values of the equilibrium constant at various temperatures were reported as

- $K_{25^\circ C} = 3.3 \times 10^8$,
- $K_{177^\circ C} = 2.6 \times 10^3$, and
- $K_{327^\circ C} = 4.1$.

At which temperature would you expect to find the highest proportion of H_2 and N_2 in the equilibrium mixture?

Assuming that the reaction rates are fast enough so that equilibrium is reached quickly, at what temperature would you design a commercial reactor to operate to maximize the yield of ammonia?

Answer:

a. 327°C, where K is smallest
b. 25°C

The equilibrium constant expression is an equation that we can use to solve for K or for the concentration of a reactant or product.

Example 13.3.3

Determine the value of K for the reaction

$$\mathrm{SO_2}\,(g) + \mathrm{NO_2}\,(g) \rightleftharpoons \mathrm{SO_3}\,(g) + \mathrm{NO}\,(g)$$

when the equilibrium concentrations are: $[\mathrm{SO_2}] = 1.20\ \mathrm{M}$, $[\mathrm{NO_2}] = 0.60\ \mathrm{M}$, $[\mathrm{NO}] = 1.6\ \mathrm{M}$, and $\left[\mathrm{SO_3}\right] = 2.2\ \mathrm{M}$.

Solution

Step 1: Write the equilibrium constant expression:

$$K = \frac{\left[\mathrm{SO_3}\right][\mathrm{NO}]}{[\mathrm{SO_2}][\mathrm{NO_2}]}$$

Step 2: Substitute in given values and solve:

$$K = \frac{(2.2)(1.6)}{(1.20)(0.60)} = 4.9$$

Determining the Equilibrium Expression: https://youtu.be/ZK9cMIWFerY

Summary

- The law of mass action describes a system at equilibrium in terms of the concentrations of the products and the reactants.
- For a system involving one or more gases, either the molar concentrations of the gases or their partial pressures can be used.
- Definition of equilibrium constant in terms of forward and reverse rate constants:

$$K = \frac{k_f}{k_r}$$

- Equilibrium constant expression (law of mass action):

$$K = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

The ratio of the rate constants for the forward and reverse reactions at equilibrium is the equilibrium constant (K), a unitless quantity. The composition of the equilibrium mixture is therefore determined by the magnitudes of the forward and reverse rate constants at equilibrium. Under a given set of conditions, a reaction will always have the same K. For a system at equilibrium, the law of mass action relates K to the ratio of the equilibrium concentrations of the products to the concentrations of the reactants raised to their respective powers to match the coefficients in the equilibrium equation. The ratio is called the equilibrium constant expression. When a reaction is written in the reverse direction, K and the equilibrium constant expression are inverted.

13.4: Le Chatelier's Principle

Learning Outcomes

- Define Le Chatelier's principle.
- Predict how the change in amounts of substances, temperature, or pressure will affect amounts of reactants and products present at equilibrium.

Le Chatelier's Principle

Chemical equilibrium was studied by the French chemist Henri Le Chatelier (1850 - 1936) and his description of how a system responds to a stress to equilibrium has become known as **Le Chatelier's principle**: When a chemical system that is at equilibrium is disturbed by a stress, the system will respond in order to relieve the stress. Stresses to a chemical system involve changes in the concentrations of reactants or products, changes in the temperature of the system, or changes in the pressure of the system. We will discuss each of these stresses separately. The change to the equilibrium position in every case is either a favoring of the forward reaction or a favoring of the reverse reaction. When the forward reaction is favored, the concentrations of products increase, while the concentrations of reactants decrease. When the reverse reaction is favored, the concentrations of the products decrease, while the concentrations of reactants increase.

Original Equilibrium	**Favored Reaction**	**Result**
$\text{A} \rightleftharpoons \text{B}$	Forward: $\text{A} \rightarrow \text{B}$	$[\text{A}]$ decreases; $[\text{B}]$ increases
$\text{A} \rightleftharpoons \text{B}$	Reverse: $\text{A} \leftarrow \text{B}$	$[\text{A}]$ increases; $[\text{B}]$ decreases

Figure 9.6.1: *Henri Le Chatelier*.

Effect of Concentration

A change in concentration of one of the substances in an equilibrium system typically involves either the addition or the removal of one of the reactants or products. Consider the Haber-Bosch process for the industrial production of ammonia from nitrogen and hydrogen gases.

$$\text{N}_2 \left(g \right) + 3 \text{H}_2 \left(g \right) \rightleftharpoons 2 \text{NH}_3 \left(g \right)$$

If the concentration of one substance in a system is increased, the system will respond by favoring the reaction that removes that substance. When more N_2 is added, the forward reaction will be favored because the forward reaction uses up N_2 and converts it to NH_3. The forward reaction speeds up temporarily as a result of the addition of a reactant. The position of equilibrium shifts as more NH_3 is produced. The concentration of NH_3 increases, while the concentrations of N_2 and H_2 decrease. After some time passes, equilibrium is reestablished with new concentrations of all three substance. As can be seen in the figure below, if more N_2 is added, a new equilibrium is achieved by the system. The new concentration of NH_3 is higher because of the favoring of the forward reaction. The new concentration of the H_2 is lower .The concentration of N_2 is higher than in the original equilibrium, but went down slightly following the addition of the N_2 that disturbed the original equilibrium. By responding in this way, the value of the equilibrium constant for the reaction, K_eq, does not change as a result of the stress to the system.

In other words, the amount of each substance is different but the ratio of the amount of each remains the same.

If more NH_3 were added, the reverse reaction would be favored. This "favoring" of a reaction means temporarily speeding up the reaction in that direction until equilibrium is reestablished. Recall that once equilibrium is reestablished, the rates of the forward and reverse reactions are again equal. The addition of NH_3 would result in increased formation of the reactants, N_2 and H_2.

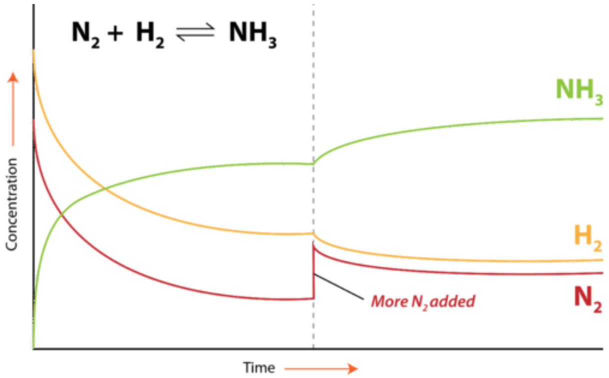


Figure 9.6.2: *The Haber-Bosch process is an equilibrium between reactants* N_2 *and* H_2 *and product* NH_3.

An equilibrium can also be disrupted by the removal of one of the substances. If the concentration of a substance is decreased, the system will respond by favoring the reaction that replaces that substance. In the industrial Haber-Bosch process, NH_3 is removed from the equilibrium system as the reaction proceeds. As a result, the forward reaction is favored so that more NH_3 is produced. The concentrations of N_2 and H_2 decrease. Continued removal of NH_3 will eventually force the reaction to go to completion until all of the reactants are used up. If either N_2 or H_2 were removed from the equilibrium system, the reverse reaction would be favored and the concentration of NH_3 would decrease.

The effect of changes in concentration on an equilibrium system according to Le Chatelier's principle is summarized in the table below.

Table 9.6.1

Stress	Response
addition of reactant	forward reaction favored
addition of product	reverse reaction favored
removal of reactant	reverse reaction favored
removal of product	forward reaction favored

✓ Example 13.4.1

Given this reaction at equilibrium:

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

How will it affect the reaction if the equilibrium is stressed by each change?

1. H_2 is added.
2. NH_3 is added.
3. NH_3 is removed.

Solution

1. If H_2 is added, there is now more reactant, so the reaction will shift to the right (toward products) to reduce the added H_2.
2. If NH_3 is added, there is now more product, so the reaction will shift to the left (toward reactants) to reduce the added NH_3.
3. If NH_3 is removed, there is now less product, so the reaction will shift to the right (toward products) to replace the product removed.

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Given this reaction at equilibrium:

$$CO(g) + Br_2(g) \rightleftharpoons COBr_2(g)$$

How will it affect the reaction if the equilibrium is stressed by each change?

1. Br_2 is removed.
2. $COBr_2$ is added.

Answer

1. shift to the left (toward reactants)
2. shift to the left (toward reactants)

Effect of Temperature

Increasing or decreasing the temperature of a system at equilibrium is also a stress to the system. The equation for the Haber-Bosch process is written again below, as a thermochemical equation (i.e. it contains information about the energy gained or lost when the reaction occurs).

$$\mathrm{N_2}\,(g) + 3\mathrm{H_2}\,(g) \rightleftharpoons 2\mathrm{NH_3}\,(g) + 91\ \mathrm{kJ}$$

The forward reaction is the exothermic direction: the formation of $\mathrm{NH_3}$ releases heat which is why that is shown as a product. The reverse reaction is the endothermic direction: as $\mathrm{NH_3}$ decomposes to $\mathrm{N_2}$ and $\mathrm{H_2}$, heat is absorbed. An increase in the temperature for this is like adding a product because heat is being released by the reaction. If we add a product then the reaction proceeds towards the formation of more reactants. Reducing the temperature for this system would be similar to removing a product which would favor the formation of more products. The amount of $\mathrm{NH_3}$ will increase and the amount of $\mathrm{N_2}$ and $\mathrm{H_2}$ will decrease.

For changes in concentration, the system responds in such a way that the value of the equilibrium constant, K_{eq} is unchanged. However, a change in temperature shifts the equilibrium and the K_{eq} value either increases or decreases. As discussed in the previous section, values of K_{eq} are dependent on the temperature. When the temperature of the system for the Haber-Bosch process is increased, the resultant shift in equilibrium towards the reactants means that the K_{eq} value decreases. When the temperature is decreased, the shift in equilibrium towards the products means that the K_{eq} value increases.

Le Chatelier's principle as related to temperature changes can be illustrated easily be the reaction in which dinitrogen tetroxide is in equilibrium with nitrogen dioxide.

$$\mathrm{N_2O_4}\,(g) + \mathrm{heat} \rightleftharpoons 2\mathrm{NO_2}\,(g)$$

Dinitrogen tetroxide $\left(\mathrm{N_2O_4}\right)$ is colorless, while nitrogen dioxide $\left(\mathrm{NO_2}\right)$ is dark brown in color. When $\mathrm{N_2O_4}$ breaks down into $\mathrm{NO_2}$, heat is absorbed (endothermic) according to the forward reaction above. Therefore, an increase in temperature (adding heat) of the system will favor the forward reaction. Conversely, a decrease in temperature (removing heat) will favor the reverse reaction.

✓ Example 13.4.2

Predict the effect of increasing the temperature on this equilibrium.

$$PCl_3 + Cl_2 \rightleftharpoons PCl_5 + 60kJ$$

Solution

Because energy is listed as a product, it is being produced, so the reaction is exothermic. If the temperature is increasing, a product is being added to the equilibrium, so the equilibrium shifts to minimize the addition of extra product: it shifts to the left (back toward reactants).

cise

Predict the effect of decreasing the temperature on this equilibrium.

$$N_2O_4 + 57kJ \rightleftharpoons 2NO_2$$

Answer

Equilibrium shifts to the left (toward reactants).

Effect of Pressure

Changing the pressure of an equilibrium system in which gases are involved is also a stress to the system. A change in the pressure on a liquid or a solid has a negligible effect. We will return again the equilibrium for the Haber-Bosch process. Imagine the gases are contained in a closed system in which the volume of the system is controlled by an adjustable piston as shown in the figure below.

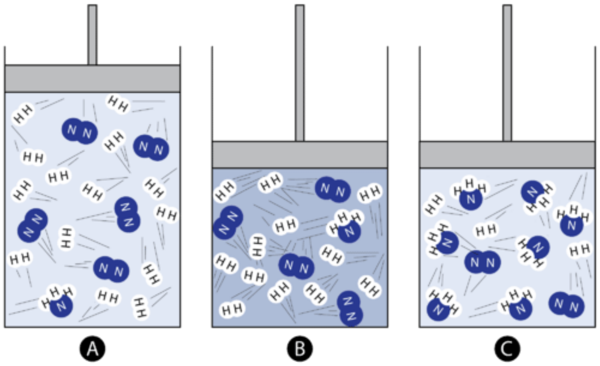

Figure 9.6.3: *Effect of pressure on equilibrium. (A) is at equilibrium, (B) increase of pressure through decreased volume, and (C) equilibrium is reestablished.*

On the far left, the reaction system contains primarily N_2 and H_2, with only one molecule of NH_3 present. As the piston is pushed inwards, the pressure of the system increases according to Boyle's law. This is a stress to the equilibrium. In the middle image, the same number of molecules is now confined in a smaller space and so the pressure has increased. According to Le Chatelier's principle, the system responds in order to relieve the stress. In the image on the right, the forward reaction has been favored and more NH_3 is produced. The overall result is a decrease in the number of gas molecules in the entire system. This in turn decreases the pressure and provides a relief to the original stress of a pressure increase. An increase in pressure on an equilibrium system favors the reaction which products fewer total moles of gas. In this case, it is the forward reaction that is favored.

A decrease in pressure on the above system could be achieved by pulling the piston outward, increasing the container volume. The equilibrium would respond by favoring the reverse reaction in which NH_3 decomposes to N_2 and H_2. This is because the overall number of gas molecules would increase and so would the pressure. A decrease in pressure on an equilibrium system favors the reaction which produces more total moles of gas. This is summarized in the table below.

Table 9.6.2

Stress	Response
pressure increase	reaction produces fewer gas molecules
pressure decrease	reaction produces more gas molecules

Like changes in concentration, the K_{eq} value for a given reaction is unchanged by a change in pressure. The amounts of each substance will change but the ratio will not. It is important to remember when analyzing the effect of a pressure change on equilibrium that only gases are affected. If a certain reaction involves liquids or solids, they should be ignored. For example, calcium carbonate decomposes according to the equilibrium reaction:

$$\mathrm{CaCO_3}\,(s) \rightleftharpoons \mathrm{CaO}\,(s) + \mathrm{O_2}\,(g)$$

Oxygen is the only gas in the system. An increase in the pressure of the system slows the rate of decomposition of $\mathrm{CaCO_3}$ because the reverse reaction is favored. When a system contains equal moles of gas on both sides of the equation, pressure has no effect on the equilibrium position, as in the formation of HCl from H_2 and Cl_2.

$$\mathrm{H_2}\,(g) + \mathrm{Cl_2}\,(g) \rightleftharpoons 2\mathrm{HCl}\,(g)$$

Example 13.4.3

What is the effect on this equilibrium if pressure is increased?

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

Solution

According to Le Chatelier's principle, if pressure is increased, then the equilibrium shifts to the side with the fewer number of moles of gas. This particular reaction shows a total of 4 mol of gas as reactants and 2 mol of gas as products, so the reaction shifts to the right (toward the products side).

cise

What is the effect on this equilibrium if pressure is decreased?

$$3O_2(g) \rightleftharpoons 2O_3(g)$$

Answer

Reaction shifts to the left (toward reactants).

Application of Le Chatelier's Principle

Oxygen transport by the blood

In aerobic respiration, oxygen is transported to the cells where it is combined with glucose and metabolized to carbon dioxide, which then moves back to the lungs from which it is expelled.

hemoglobin + O_2 $\rightleftharpoons$ oxyhemoglobin

The partial pressure of O_2 in the air is 0.2 atm, sufficient to allow these molecules to be taken up by hemoglobin (the red pigment of blood) in which it becomes loosely bound in a complex known as oxyhemoglobin. At the ends of the capillaries which deliver the blood to the tissues, the O_2 concentration is reduced by about 50% owing to its consumption by the cells. This shifts the equilibrium to the left, releasing the oxygen so it can diffuse into the cells.

Key Takeaways

- In a reaction at equilibrium, the introduction of more products will shift the mass balance towards more reactants, and the introduction of more reactants will lead to the formation of more products, but the *ratio* of *Products/Reactants* (*equilibrium constant*), *K* is unchanged.
- If temperature is changed, the numeric value *K* will change. If a reaction is *exothermic* (releases heat), an increase in the **temperature** will force the equilibrium to the left, causing the system to absorb heat and thus partially offsetting the rise in temperature. The opposite effect occurs for *endothermic* reactions, which are shifted to the right by rising temperature.
- The effect of **pressure** on an equilibrium is significant only for reactions which involve different numbers of moles of gases on the two sides of the equation. An increase in the total pressure will shift to the side with fewer moles of gas. A decrease in pressure will shift to the side with more moles of gas.

Contributors and Attributions

-
- Allison Soult, Ph.D. (Department of Chemistry, University of Kentucky)

13.5: Some Special Types of Equilibria

Learning Objective

- Identify several special chemical equilibria and construct their K_a expressions.

In one sense, all chemical equilibria are treated the same. However, there are several classes of reactions that are noteworthy because of either the identities of the reactants and products, or the form of the K_{eq} expression.

Weak Acids and Bases

In Chapter 12 - Acids and Bases, we noted how some acids and bases are strong and some are weak. If an acid or base is strong, it is ionized 100% in H_2O. HCl(aq) is an example of a strong acid:

$$HCl(aq) \xrightarrow{100\%} H^+(aq) + Cl^-(aq)$$

However, if an acid or base is weak, it may dissolve in H_2O, but does not ionize completely. This means that there is an equilibrium between the unionized acid or base and the ionized form. $HC_2H_3O_2$ is an example of a weak acid:

$$HC_2H_3O_2(aq) \rightleftharpoons H^+(aq) + C_2H_3O_2^-(aq)$$

$HC_2H_3O_2$ is soluble in H_2O (in fact, it is the acid in vinegar), so the reactant concentration will appear in the equilibrium constant expression. But not all the molecules separate into ions. This is the case for all weak acids and bases.

An **acid dissociation constant**, K_a, is the equilibrium constant for the dissociation of a weak acid into ions. Note the *a* subscript on the K; it implies that the substance is acting as an acid. The larger K_a is, the stronger the acid is. Table 13.5.1 - Acid Dissociation Constants for Some Weak Acids, lists several acid dissociation constants. Keep in mind that they are just equilibrium constants.

Table, two columns and 7 rows. The first column on the right has different acids in the rows underneath. The second column on the right side has the acid dissociation content for the corresponding acid in the rows underneath.

Acid	K_a
$HC_2H_3O_2$	1.8×10^{-5}
$HClO_2$	1.1×10^{-2}
$H_2PO_4^-$	6.2×10^{-8}
HCN	6.2×10^{-10}
HF	6.3×10^{-4}
HNO_2	5.6×10^{-4}
H_3PO_4	7.5×10^{-3}

Table 13.5.1 Acid Dissociation Constants for Some Weak Acids

Note also that the acid dissociation constant refers to *one* H^+ ion coming off of the initial reactant. Thus the acid dissociation constant for H_3PO_4 refers to this equilibrium:

$$H_3PO_4(aq) \rightleftharpoons H^+(aq) + H_2PO_4^-(aq) \qquad K_a = 7.5 \times 10^{-3}$$

The $H_2PO_4^-$ ion, called the dihydrogen phosphate ion, is also a weak acid with its own acid dissociation constant:

$$H_2PO_4^-(aq) \rightleftharpoons H^+(aq) + HPO_4^{2-}(aq) \qquad K_a = 6.2 \times 10^{-8}$$

Thus, for so-called *polyprotic* acids, each H^+ ion comes off in sequence; each H^+ ion that ionizes does so with its own characteristic K_a.

✓ Example 13.5.1

Write the equilibrium equation and the K_a expression for HSO_4^- acting as a weak acid.

Solution

HSO_4^- acts as a weak acid by separating into an H^+ ion and an SO_4^{2-} ion:

$$HSO_4^-(aq) \rightleftharpoons H^+(aq) + SO_4^{2-}(aq)$$

The K_a is written just like any other equilibrium constant, in terms of the concentrations of products divided by concentrations of reactants:

$$K_a = \frac{[H^+][SO_4^2-]}{[HSO_4^-]}$$

? Exercise 13.5.1

Write the equilibrium equation and the K_a expression for HPO_4^{2-} acting as a weak acid.

Answer

$$HPO_4^{2-}(aq) \rightleftharpoons H^+(aq) + PO_4^{3-}(aq) \qquad K_a = \frac{[H^+][PO_4^{3-}]}{[HPO_4^{2-}]}$$

Autoionization of water

In Chapter 12, "Acids and Bases," we introduced the autoionization of water—the idea that water can act as a proton donor and proton acceptor simultaneously. Because water is not a strong acid (Table 12.5.1 - Strong Acids and Bases), it must be a weak acid, which means that its behavior as an acid must be described as an equilibrium. That equilibrium is as follows:

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

The equilibrium constant includes $[H_3O^+]$ and $[OH^-]$ but not $[H_2O(\ell)]$ because it is a pure liquid. Hence the expression *does not have any terms in its denominator*:

$K = [H_3O^+][OH^-] \equiv K_w = 1.0 \times 10^{-14}$

This is the same K_w that was introduced in Chapter 12 and the same 1.0×10^{-14} that appears in the relationship between the K_a and the K_b of a conjugate acid-base pair. In fact, we can rewrite this relationship as follows:

$K_a \times K_b = K_w$

Insoluble Compounds

In Chapter 4, section 4.3: "Types of Chemical Reactions - Single and Double Displacement Reactions," the concept of soluble and insoluble compounds was introduced. Solubility rules were presented that allow a person to predict whether certain simple ionic compounds will or will not dissolve.

Describing a substance as soluble or insoluble is a bit misleading because virtually all substances are soluble; they are just soluble to different extents. In particular, for ionic compounds, what we typically describe as an *insoluble* compound can actually be ever so slightly soluble; an equilibrium is quickly established between the solid compound and the ions that do form in solution. Thus, the hypothetical compound MX does in fact dissolve but only very slightly. That means we can write an equilibrium for it:

$$MX(s) \rightleftharpoons M^+(aq) + X^-(aq)$$

The equilibrium constant for a compound normally considered insoluble is called a **solubility product constant** and is labeled K_{sp} (with the subscript *sp*, meaning "solubility product"). Because the reactant is a solid, its concentration does not appear in the K_{sp}

expression, so like K_W, expressions for K_{sp} do not have denominators. For example, the chemical equation and the expression for the K_{sp} for AgCl, normally considered insoluble, are as follows:

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq) \qquad K_{sp} = [Ag^+][Cl^-]$$

Table 13.5.2- Solubility Product Constants for Slightly Soluble Ionic Compounds, lists some values of the K_{sp} for slightly soluble ionic compounds.

Table, two columns and 8 rows. The first column on the right has different compounds in the rows underneath. The second column on the right side has the acid dissociation content for the corresponding compounds in the rows underneath.

Compound	K_{sp}
$BaSO_4$	1.1×10^{-10}
$Ca(OH)_2$	5.0×10^{-6}
$Ca_3(PO_4)_2$	2.1×10^{-33}
$Mg(OH)_2$	5.6×10^{-12}
HgI_2	2.9×10^{-29}
AgCl	1.8×10^{-10}
AgI	8.5×10^{-17}
Ag_2SO_4	1.5×10^{-5}

Table 13.5.2 Solubility Product Constants for Slightly Soluble Ionic Compounds.

✓ Example 13.5.4

Write the K_{sp} expression for $Ca_3(PO_4)_2$.

Solution

Recall that when an ionic compound dissolves, it separates into its individual ions. For $Ca_3(PO_4)_2$, the ionization reaction is as follows:

$$Ca_3(PO_4)_2(s) \rightleftharpoons 3Ca^{2+}(aq) + 2PO_4^{3-}(aq)$$

Hence the K_{sp} expression is

$K_{sp} = [Ca^{2+}]^3[PO_4{}^{3-}]^2$

? Exercise 13.5.4

Write the K_{sp} expression Ag_2SO_4.

Answer

$K_{sp} = [Ag^+]^2[SO_4{}^{2-}]$

✓ Food and Drink Application: Solids in Your Wine Bottle

People who drink wine from bottles (as opposed to boxes) will occasionally notice some insoluble materials in the wine, either crusting the bottle, stuck to the cork, or suspended in the liquid wine itself. The accompanying figure shows a cork encrusted with colored crystals. What are these crystals?

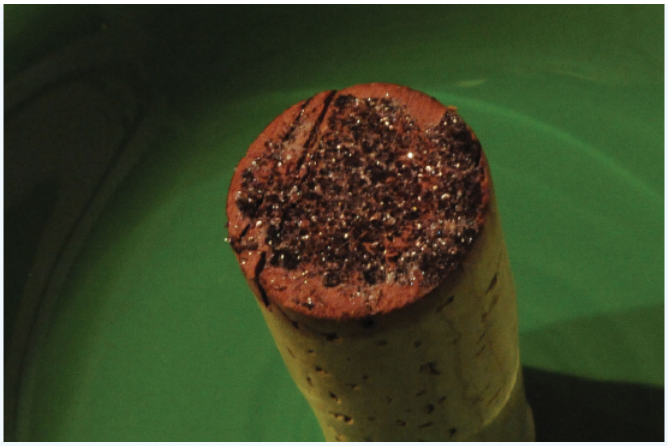

Figure 13.5.1 Wine Cork. The red crystals on the top of the wine cork are from insoluble compounds that are not soluble in the wine. Source: Photo courtesy of Paul A. Hernandez, flickr(opens in new window).

One of the acids in wine is tartaric acid ($H_2C_4H_4O_6$). Like the other acids in wine (citric and malic acids, among others), tartaric acid imparts a slight tartness to the wine. Tartaric acid is rather soluble in H_2O, dissolving over 130 g of the acid in only 100 g of H_2O. However, the potassium salt of singly ionized tartaric acid, potassium hydrogen tartrate ($KHC_4H_4O_6$; also known as potassium bitartrate and better known in the kitchen as cream of tartar), has a solubility of only 6 g per 100 g of H_2O. Thus, over time, wine stored at cool temperatures will slowly precipitate potassium hydrogen tartrate. The crystals precipitate in the wine or grow on the insides of the wine bottle and, if the bottle is stored on its side, on the bottom of the cork. The color of the crystals comes from pigments in the wine; pure potassium hydrogen tartrate is clear in its crystalline form, but in powder form it is white.

The crystals are harmless to ingest; indeed, cream of tartar is used as an ingredient in cooking. However, most wine drinkers do not like to chew their wine, so if tartrate crystals are present in a wine, the wine is usually filtered or decanted to remove the crystals. Tartrate crystals are almost exclusively in red wines; white and rose wines do not have as much tartaric acid in them.

Key Takeaway

- Equilibrium constants exist for certain groups of equilibria, such as weak acids, weak bases, the autoionization of water, and slightly soluble salts.

13.E: Exercises

Additional Exercises

1. What is the relationship between the K_{sp} expressions for a chemical reaction and its reverse chemical reaction?
2. What is the relationship between the K_w value for H_2O and its reverse chemical reaction?
3. For the equilibrium

$$PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g) + 60kJ$$

   list four stresses that serve to increase the amount of PCl_5.
4. For the equilibrium

$$N_2O_4 + 57kJ \rightleftharpoons 2NO_2$$

   list four stresses that serve to increase the amount of NO_2.
5. Does a very large K_{eq} favor the reactants or the products? Explain your answer.
6. Is the K_{eq} for reactions that favor reactants large or small? Explain your answer.
7. Write the Equilibrium Constant Expression for the following

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

8.
   a. Write the equation for NaCl dissolving in water.
   b. Write the equilibrium constant expression for NaCl dissolving in water. (Remember to leave out things that are not mixed or whose concentration remains constants- In this case, solids or liquids in the chemical equation.)
   c. Solve for the solubility equilibrium constant of NaCl if the concentrations of a saturated solution are [Na$^+$] = 6.14 M and [Cl$^-$] = 6.14 M

Answers

1. They are reciprocals of each other.
2.
3. increase the pressure; decrease the temperature; add PCl_3; add Cl_2; remove PCl_5
4.
5. favor products because the numerator of the ratio for the K_{eq} is larger than the denominator
6.
7. Keq = $[NH_3]^2$ / $[N_2][H_2]^3$
8.
   a. NaCl (s) $\rightleftharpoons$ Na$^+$ (aq) + Cl$^-$ (aq)
   b. Ksp = [Na$^+$] [Cl$^-$]
   c. Ksp = 37.7

CHAPTER OVERVIEW

14: Radioactivity and Nuclear Chemistry

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In today's society, the term *radioactivity* conjures up a variety of images:

- Nuclear power plants producing hydrocarbon-free energy, but with potentially deadly by-products that are difficult to store safely.
- Bombs with the capacity to use nuclear reactions that produce devastating explosions with horrible side effects on the earth as we know it, and on the surviving populations that inhabit it.
- Medical technology that utilizes nuclear chemistry to peer inside living things to detect disease, and the power to irradiate tissues to potentially cure these diseases.
- Fusion reactors that hold the promise of limitless energy with few toxic side products.

Radioactivity has a colorful history and clearly presents a variety of social and scientific dilemmas. In this chapter we will introduce the basic concepts of radioactivity, nuclear equations, and the processes involved in nuclear fission and nuclear fusion.

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14.1: The Discovery of Radioactivity

Learning Objectives

- List the most common emissions from naturally radioactive nuclei.
- Compare the energy released per gram of matter in nuclear reactions to that in chemical reactions.
- Express the relationship between nuclear stability and the nuclei's binding energy per nucleon ratio.

No one could have known in the 1800's that the discovery of the fascinating science and art form of photography would eventually lead to the splitting of the atom. The basis of photography is the fact that visible light causes certain chemical reactions. If the chemicals are spread thinly on a surface but protected from light by a covering, no reaction occurs. When the covering is removed, however, light acting on the chemicals causes them to darken. With millions of cameras in use today, we do not think of it as a strange phenomenon—but at the time of its discovery, photography was a strange and wonderful thing.

Even stranger was the discovery by Wilhelm Roentgen—that radiation other than visible light could expose photographic film. He found that film wrapped in dark paper would react when x-rays went through the paper and struck the film.

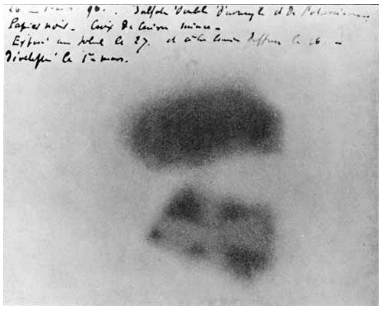

Figure 14.1.1: Image of Becquerel's photographic plate, which has been fogged by exposure to radiation from a uranium salt. The shadow of a metal Maltese Cross placed between the plate and the uranium salt is clearly visible (Public Domain).

When Henri Becquerel heard about Roentgen's discovery, he wondered if his fluorescent minerals would give the same x-rays. Becquerel placed some of his rock crystals on top of a well-covered photographic plate and sat them in the sunlight. The sunlight made the crystals glow with a bright fluorescent light, but when Becquerel developed the film he was very disappointed. He found that only one of his minerals, a uranium salt, had fogged the photographic plate. He decided to try again, and this time, to leave them out in the sun for a longer period of time. Fortunately, the weather didn't cooperate, and Becquerel had to leave the crystals and film stored in a drawer for several cloudy days. Before continuing his experiments, Becquerel decided to check one of the photographic plates to make sure the chemicals were still good. To his amazement, he found that the plate had been exposed in spots where it had been near the uranium containing rocks, and some of these rocks had not been exposed to sunlight at all. In later experiments, Becquerel confirmed that the radiation from the uranium had no connection with light or fluorescence, but the amount of radiation was directly proportional to the concentration of uranium in the rock. Becquerel had discovered **radioactivity**.

The Curies and Radium

One of Becquerel's assistants, a young Polish scientist named Maria Sklowdowska (to become Marie Curie after she married Pierre Curie), became interested in the phenomenon of radioactivity. With her husband, she decided to find out if chemicals other than uranium were radioactive. The Austrian government was happy to send the Curies a ton of pitchblende from the mining region of Joachimstahl, because it was waste material that had to be disposed of anyway. The Curies wanted the pitchblende because it was the residue of uranium mining. From the ton of pitchblende, the Curies separated 0.10 g of a previously unknown element, radium, in the form of the compound radium chloride. This radium was many times more radioactive than uranium.

By 1902, the world was aware of a new phenomenon called radioactivity and of new elements which exhibited natural radioactivity. For this work, Becquerel and the Curies shared the 1903 Nobel Prize and for subsequent work; Marie Cure received a second Nobel Prize in 1911. She is the only person ever to receive two Nobel Prizes in science.

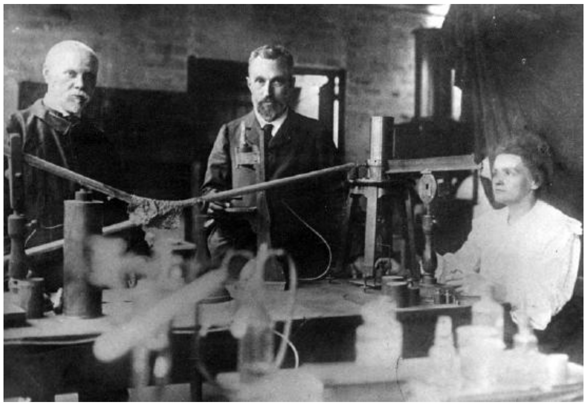

Figure 14.1.2: Marie Curie (right) and Pierre Curie (middle) with Henri Becquerel (left) shared the 1903 Nobel Prize.

Further experiments provided information about the characteristics of the penetrating emissions from radioactive substances. It was soon discovered that there were three common types of radioactive emissions. Some of the radiation could pass easily through aluminum foil while some of the radiation was stopped by the foil. Some of the radiation could even pass through foil up to a centimeter thick. The three basic types of radiation were named alpha, beta, and gamma radiation. The actual composition of the three types of radiation was still not known.

Eventually, scientists were able to demonstrate experimentally that the alpha particle, α, was a helium nucleus (a particle containing two protons and two neutrons), a beta particle, β, was a high speed electron, and gamma rays, γ, were a very high energy form of light (even higher energy than x-rays).

Unstable Nuclei May Disintegrate

A nucleus (with one exception, hydrogen-1) consists of some number of protons and neutrons pulled together in an extremely tiny volume. Since protons are positively charged and like charges repel, it is clear that protons cannot remain together in the nucleus unless there is a powerful force holding them there. The force which holds the nucleus together is generated by **nuclear binding energy**.

A nucleus with a large amount of binding energy per nucleon (proton or neutron) will be held together tightly and is referred to as stable. These nuclei do not break apart. When there is too little binding energy per nucleon, the nucleus will be less stable and may disintegrate (come apart). Such disintegration is referred to as **natural radioactivity**. It is also possible for scientists to smash nuclear particles together and cause nuclear reactions between normally stable nuclei. This disintegration is referred to as **artificial radioactivity**. None of the elements above #92 on the periodic table occur on earth naturally—they are all products of artificial (manmade) radioactivity.

When nuclei come apart, they come apart violently accompanied by a tremendous release of energy in the form of heat, light, and radiation. This energy comes from some of the nuclear binding energy. In nuclear changes, the energy involved comes from the nuclear binding energy. However, in chemical reactions, the energy comes from electrons moving energy levels. A typical nuclear change (such as fission) may involve millions of times more energy per atom changing compared to a chemical change (such as burning)!

Summary

- Henri Becquerel, Marie Curie, and Pierre Curie shared the discovery of radioactivity.

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14.2: Types of Radioactivity- Alpha, Beta, and Gamma Decay

Learning Objectives

- Compare qualitatively the ionizing and penetration power of alpha particles (α), beta particles (β), and gamma rays (γ).
- Express the changes in the atomic number and mass number of a radioactive nuclei when an alpha, beta, or gamma particle is emitted.
- Write nuclear equations for alpha and beta decay reactions.

Many nuclei are radioactive; that is, they decompose by emitting particles and in doing so, become a different nucleus. In our studies up to this point, atoms of one element were unable to change into different elements. That is because in all other types of changes discussed, only the electrons were changing. In these changes, the nucleus, which contains the protons that dictate which element an atom is, is changing. All nuclei with 84 or more protons are radioactive, and elements with less than 84 protons have both stable and unstable isotopes. All of these elements can go through nuclear changes and turn into different elements.

In natural radioactive decay, three common emissions occur. When these emissions were originally observed, scientists were unable to identify them as some already known particles and so named them:

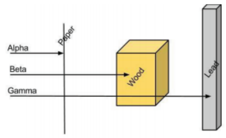
- alpha particles (α)
- beta particles (β)
- gamma rays (γ)

These particles were named using the first three letters of the Greek alphabet. Some later time, alpha particles were identified as helium-4 nuclei, beta particles were identified as electrons, and gamma rays as a form of electromagnetic radiation like x-rays, except much higher in energy and even more dangerous to living systems.

The Ionizing and Penetration Power of Radiation

With all the radiation from natural and man-made sources, we should quite reasonably be concerned about how all the radiation might affect our health. The damage to living systems is done by radioactive emissions when the particles or rays strike tissue, cells, or molecules and alter them. These interactions can alter molecular structure and function; cells no longer carry out their proper function and molecules, such as DNA, no longer carry the appropriate information. Large amounts of radiation are very dangerous, even deadly. In most cases, radiation will damage a single (or very small number) of cells by breaking the cell wall or otherwise preventing a cell from reproducing.

The ability of radiation to damage molecules is analyzed in terms of what is called **ionizing power**. When a radiation particle interacts with atoms, the interaction can cause the atom to lose electrons and thus become ionized. The greater the likelihood that damage will occur by an interaction is the ionizing power of the radiation.



Alpha particles can be blocked with paper. Beta particles penetrate through paper, but are blocked by wood. Gamma particles are capable of penetrating paper and wood but can be blocked by a few inches of lead.
CC Tracy Poulsen

Much of the threat from radiation is involved with the ease or difficulty of protecting oneself from the particles. How thick of a wall do you need to hide behind to be safe? The ability of each type of radiation to pass through matter is expressed in terms of **penetration power.** The more material the radiation can pass through, the greater the penetration power and the more dangerous it is. In general, the greater mass present, the greater the ionizing power, and the lower the penetration power.

Comparing only the three common types of ionizing radiation, alpha particles have the greatest mass. Alpha particles have approximately four times the mass of a proton or neutron and approximately 8,000 times the mass of a beta particle. Because of the large mass of the alpha particle, it has the highest ionizing power and the greatest ability to damage tissue. That same large size of alpha particles, however, makes them less able to penetrate matter. They collide with molecules very quickly when striking matter, add two electrons, and become a harmless helium atom. Alpha particles have the least penetration power and can be stopped by a thick sheet of paper or even a layer of clothes. They are also stopped by the outer layer of dead skin on people. This may seem to remove the threat from alpha particles, but it is only from external sources. In a nuclear explosion or some sort of nuclear accident, where radioactive emitters are spread around in the environment, the emitters can be inhaled or taken in with food or water and once the alpha emitter is inside you, you have no protection at all.

Beta particles are much smaller than alpha particles and therefore, have much less ionizing power (less ability to damage tissue), but their small size gives them much greater penetration power. Most resources say that beta particles can be stopped by a one-quarter inch thick sheet of aluminum. Once again, however, the greatest danger occurs when the beta emitting source gets inside of you.

Gamma rays are not particles, but a high energy form of electromagnetic radiation (like x-rays, except more powerful). Gamma rays are energy that has no mass or charge. Gamma rays have tremendous penetration power and require several inches of dense material (like lead) to shield them. Gamma rays may pass all the way through a human body without striking anything. They are considered to have the least ionizing power and the greatest penetration power.

Table 14.2.1 Comparison of Penetrating Power,Ionizing Power and Shielding of Alpha and Beta Particles, and Gamma Rays.

Particle	Symbol	Mass	Penetrating Power	Ionizing Power	Shielding
Alpha	α	$4 \mathrm{amu}$	Very Low	Very High	Paper Skin
Beta	β	$1/2000 \mathrm{amu}$	Intermediate	Intermediate	Aluminum
Gamma	γ	0 (energy only)	Very High	Very Low	2 inches lead

The safest amount of radiation to the human body is zero. It is impossible to completely avoid ionizing radiation, so the next best goal is to be exposed to as little as possible. The two best ways to minimize exposure are to limit time of exposure, and to increase distance from the source.

Alpha Decay

The nuclear disintegration process that emits alpha particles is called alpha decay. An example of a nucleus that undergoes alpha decay is uranium-238. The alpha decay of U-238 is

$$^{238}_{92}\mathrm{U} \rightarrow {}^{4}_{2}\mathrm{He} + {}^{234}_{90}\mathrm{Th} \tag{14.2.1}$$

In this nuclear change, the uranium atom $\left({}^{238}_{92}\mathrm{U}\right)$ transmuted into an atom of thorium $\left({}^{234}_{90}\mathrm{Th}\right)$ and, in the process, gave off an alpha particle. Look at the symbol for the alpha particle: ${}^{4}_{2}\mathrm{He}$. Where does an alpha particle get this symbol? The bottom number in a nuclear symbol is the number of protons. That means that the alpha particle has two protons in it that were lost by the uranium atom. The two protons also have a charge of $+2$. The top number, 4, is the mass number or the total of the protons and neutrons in the particle. Because it has two protons, and a total of four protons and neutrons, alpha particles must also have two neutrons. Alpha particles always have this same composition: two protons and two neutrons.

Another alpha particle producer is thorium-230.

$$^{230}_{90}\mathrm{Th} \rightarrow {}^{4}_{2}\mathrm{He} + {}^{226}_{88}\mathrm{Ra} \tag{14.2.2}$$

These types of equations are called nuclear equations and are similar to the chemical equivalent discussed through the previous chapters.

Beta Decay

Another common decay process is beta particle emission, or beta decay. A beta particle is simply a high energy electron that is emitted from the nucleus. It may occur to you that we have a logically difficult situation here. Nuclei do not contain electrons and yet during beta decay, an electron is emitted from a nucleus. At the same time that the electron is being ejected from the nucleus, a neutron is becoming a proton. It is tempting to picture this as a neutron breaking into two pieces with the pieces being a proton and an electron. That would be convenient for simplicity, but unfortunately that is not what happens (more on this subject will be explained at the end of this section). For convenience, we will treat beta decay as a neutron splitting into a proton and an electron. The proton stays in the nucleus, increasing the atomic number of the atom by one. The electron is ejected from the nucleus and is the particle of radiation called beta.

To insert an electron into a nuclear equation and have the numbers add up properly, an atomic number and a mass number had to be assigned to an electron. The mass number assigned to an electron is zero (0), which is reasonable since the mass number is the number of protons plus neutrons, and an electron contains no protons and no neutrons. The atomic number assigned to an electron is negative one (-1), because that allows a nuclear equation containing an electron to balance atomic numbers. Therefore, the nuclear symbol representing an electron (beta particle) is

$$^{0}_{-1}\text{e or } ^{0}_{-1}\beta$$

Thorium-234 is a nucleus that undergoes beta decay. Here is the nuclear equation for this beta decay:

$$^{234}_{90}\text{Th} \rightarrow ^{0}_{-1}\text{e} + ^{234}_{91}\text{Pa} \tag{14.2.3}$$

Gamma Radiation

Frequently, gamma ray production accompanies nuclear reactions of all types. In the alpha decay of U-238, two gamma rays of different energies are emitted in addition to the alpha particle.

$$^{238}_{92}\text{U} \rightarrow ^{4}_{2}\text{He} + ^{234}_{90}\text{Th} + 2^{0}_{0}\gamma$$

Virtually all of the nuclear reactions in this chapter also emit gamma rays, but for simplicity the gamma rays are generally not shown. Nuclear reactions produce a great deal more energy than chemical reactions. Chemical reactions release the difference between the chemical bond energy of the reactants and products, and the energies released have an order of magnitude of $1 \times 10^{3}\ \text{kJ/mol}$. Nuclear reactions release some of the binding energy and may convert tiny amounts of matter into energy. The energy released in a nuclear reaction has an order of magnitude of $1 \times 10^{18}\ \text{kJ/mol}$. That means that nuclear changes involve almost **one million times more energy** per atom than chemical changes!

Note

Virtually all of the nuclear reactions in this chapter also emit gamma rays, but for simplicity the gamma rays are generally not shown.

The essential features of each reaction are shown in Figure 17.3.2

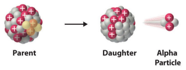
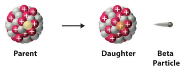
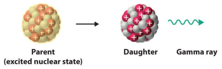
Decay Type	Radiation Emitted	Generic Equation	Model
Alpha decay	$^{4}_{2}\alpha$	$^{A}_{Z}\text{X} \longrightarrow ^{A-4}_{Z-2}\text{X}' + ^{4}_{2}\alpha$	
Beta decay	$^{0}_{-1}\beta$	$^{A}_{Z}\text{X} \longrightarrow ^{A}_{Z+1}\text{X}' + ^{0}_{-1}\beta$	
Gamma emission	$^{0}_{0}\gamma$	$^{A}_{Z}\text{X}^{*} \xrightarrow{\text{Relaxation}} ^{A}_{Z}\text{X}' + ^{0}_{0}\gamma$	

***Figure 17.3.2**: Three most common modes of nuclear decay.*

"Nuclear Accounting"

When writing nuclear equations, there are some general rules that will help you:

- The sum of the mass numbers (top numbers) on the reactant side equal the sum of the mass numbers on the product side.
- The atomic numbers (bottom numbers) on the two sides of the reaction will also be equal.

In the alpha decay of ^{238}U (Equation 14.2.1), both atomic and mass numbers are conserved:

- mass number: $238 = 4 + 234$
- atomic number: $92 = 2 + 90$

Confirm that this equation is correctly balanced by adding up the reactants' and products' atomic and mass numbers. Also, note that because this was an alpha reaction, one of the products is the alpha particle, $^{4}_{2}\text{He}$.

Note that both the mass numbers and the atomic numbers add up properly for the beta decay of thorium-234 (Equation 14.2.3):

- mass number: $234 = 0 + 234$
- atomic number: $90 = -1 + 91$

The mass numbers of the original nucleus and the new nucleus are the same because a neutron has been lost, but a proton has been gained, and so the sum of protons plus neutrons remains the same. The atomic number in the process has been increased by one since the new nucleus has one more proton than the original nucleus. In this beta decay, a thorium-234 nucleus has one more proton than the original nucleus. In this beta decay, a thorium-234 nucleus has become a protactinium-234 nucleus. Protactinium-234 is also a beta emitter and produces uranium-234.

$$^{234}_{91}\text{Pa} \rightarrow ^{0}_{-1}\text{e} + ^{234}_{92}\text{U} \tag{14.2.4}$$

Once again, the atomic number increases by one and the mass number remains the same; this confirms that the equation is correctly balanced.

What About Balancing Charge?

Both alpha and beta particles are charged, but nuclear reactions in Equations 14.2.1, 14.2.3, and most of the other nuclear reactions above, are not balanced with respect to charge, as discussed when balancing redox reactions. When studying nuclear reactions in general, there is typically little information or concern about the chemical state of the radioactive isotopes, because the electrons from the electron cloud are not directly involved in the nuclear reaction (in contrast to chemical reactions).

So it is acceptable to **ignore** charge in balancing nuclear reactions, and concentrate on balancing mass and atomic numbers only.

Example 14.2.1

Complete the following nuclear reaction by filling in the missing particle.

$$^{210}_{86}\text{Rn} \rightarrow ^{4}_{2}\text{He} + ?$$

Solution

This reaction is an alpha decay. We can solve this problem one of two ways:

Solution 1: When an atom gives off an alpha particle, its atomic number drops by 2 and its mass number drops by 4, leaving: $^{206}_{84}\text{Po}$. We know the symbol is Po, for polonium, because this is the element with 84 protons on the periodic table.

Solution 2: Remember that the mass numbers on each side must total up to the same amount. The same is true of the atomic numbers.

- Mass numbers: $210 = 4 + ?$
- Atomic numbers: $86 = 2 + ?$

We are left with ${}^{206}_{84}\text{Po}$.

Example 14.2.2

Write each of the following nuclear reactions.

a) Carbon-14, used in carbon dating, decays by beta emission.

b) Uranium-238 decays by alpha emission.

Solution

a) Beta particles have the symbol ${}^{0}_{-1}\text{e}$. Emitting a beta particle causes the atomic number to increase by 1 and the mass number to not change. We get atomic numbers and symbols for elements using our periodic table. We are left with the following reaction:

$${}^{14}_{6}\text{C} \rightarrow {}^{0}_{-1}\text{e} + {}^{14}_{7}\text{N}$$

b) Alpha particles have the symbol ${}^{4}_{2}\text{He}$. Emitting an alpha particle causes the atomic number to decrease by 2 and the mass number to decrease by 4. We are left with:

$${}^{238}_{92}\text{U} \rightarrow {}^{4}_{2}\text{He} + {}^{234}_{90}\text{Th}$$

Decay Series

The decay of a radioactive nucleus is a move toward becoming stable. Often, a radioactive nucleus cannot reach a stable state through a single decay. In such cases, a series of decays will occur until a stable nucleus is formed. The decay of U-238 is an example of this. The U-238 decay series starts with U-238 and goes through fourteen separate decays to finally reach a stable nucleus, Pb-206 (Figure 17.3.3). There are similar decay series for U-235 and Th-232. The U-235 series ends with Pb-207 and the Th-232 series ends with Pb-208.

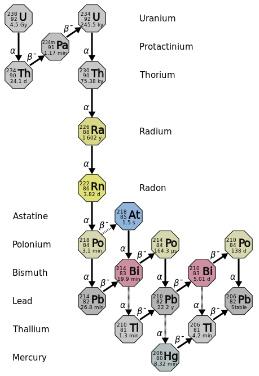


Figure 17.3.3: Uranium-238 decay chain. (CC-BY-3.0 Tosaka)

Several of the radioactive nuclei that are found in nature are present there because they are produced in one of the radioactive decay series. For example, there may have been radon on the earth at the time of its formation, but that original radon would have all decayed by this time. The radon that is present now is present because it was formed in a decay series (mostly by U-238).

Summary

A nuclear reaction is one that changes the structure of the nucleus of an atom. The atomic numbers and mass numbers in a nuclear equation must be balanced. Protons and neutrons are made up of quarks. The two most common modes of natural radioactivity are alpha decay and beta decay. Most nuclear reactions emit energy in the form of gamma rays.

Vocabulary

- **Alpha decay** - A common mode of radioactive decay in which a nucleus emits an alpha particle (a helium-4 nucleus).
- **Beta decay** - A common mode of radioactive decay in which a nucleus emits beta particles. The daughter nucleus will have a higher atomic number than the original nucleus.
- **Quark** - Particles that form one of the two basic constituents of matter. Various species of quarks combine in specific ways to form protons and neutrons, in each case taking exactly three quarks to make the composite particle.

14.3: Radioactivity and Half-Life

Learning Objectives

- Define *half-life*.
- Determine the amount of radioactive substance remaining after a given number of half-lives.
- Describe common radiometric carbon-14 dating technique.

Whether or not a given isotope is radioactive is a characteristic of that particular isotope. Some isotopes are stable indefinitely, while others are radioactive and decay through a characteristic form of emission. As time passes, less and less of the radioactive isotope will be present, and the level of radioactivity decreases. An interesting and useful aspect of radioactive decay is **half life** (**$t_{1/2}$**), which is the amount of time it takes for one-half of a radioactive isotope to decay. The half-life of a specific radioactive isotope is constant; it is unaffected by conditions and is independent of the initial amount of that isotope.

Each radioactive nuclide has a characteristic, constant half-life ($t_{1/2}$), the time required for half of the atoms in a sample to decay. An isotope's half-life allows us to determine how long a sample of a useful isotope will be available, and how long a sample of an undesirable or dangerous isotope must be stored before it decays to a low-enough radiation level that is no longer a problem.

For example, cobalt-60 source, since half of the $^{60}_{27}\text{Co}$ nuclei decay every 5.27 years, both the amount of material and the intensity of the radiation emitted is cut in half every 5.27 years. (Note that for a given substance, the intensity of radiation that it produces is directly proportional to the rate of decay of the substance and the amount of the substance.) Thus, a cobalt-60 source that is used for cancer treatment must be replaced regularly to continue to be effective.

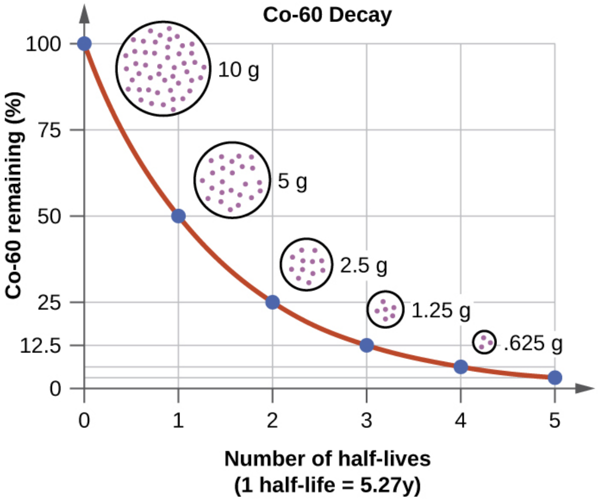


Figure 14.3.1: For cobalt-60, which has a half-life of 5.27 years, 50% remains after 5.27 years (one half-life), 25% remains after 10.54 years (two half-lives), 12.5% remains after 15.81 years (three half-lives), and so on. (CC BY 4.0; OpenStax)

We can determine the amount of a radioactive isotope remaining after a given number half-lives by using the following expression:

$$\text{amount remaining} = \text{initial amount} \times \left(\frac{1}{2}\right)^{n} \tag{14.3.1}$$

where n is the number of half-lives. This expression works even if the number of half-lives is not a whole number.

Example : Fluorine-20

The half-life of fluorine-20 is 11.0 s. If a sample initially contains 5.00 g of fluorine-20, how much remains after 44.0 s?

Solution

If we compare the time that has passed to the isotope's half-life, we note that 44.0 s is exactly 4 half-lives, so using the previous expression, $n = 4$. Substituting and solving results in the following:

$$\begin{aligned}\text{amount remaining} &= 5.00\,g \times \left(\frac{1}{2}\right)^4 \\ &= 5.00\,g \times \left(\frac{1}{16}\right) \\ &= 0.313\,g\end{aligned}$$

Less than one-third of a gram of fluorine-20 remains.

Exercise : Titanium-44

The half-life of titanium-44 is 60.0 y. A sample of titanium contains 0.600 g of titanium-44. How much remains after 240.0 y?

Answer

0.0375 g

Half-lives of isotopes range from fractions of a microsecond to billions of years. Table 14.3.1- Half-Lives of Various Isotopes, lists the half-lives of some isotopes.

Table 14.3.1 Half-Lives of Various Isotopes

Isotope	Half-Life
^{3}H	12.3 y
^{14}C	5730 y
^{40}K	1.26×10^9 y
^{51}Cr	27.70 d
^{90}Sr	29.1 y
^{131}I	8.04 d
^{222}Rn	3.823 d
^{235}U	7.04×10^8 y
^{238}U	4.47×10^9 y
^{241}Am	432.7 y
^{248}Bk	23.7 h
^{260}Sg	4 ms

Chemistry Is Everywhere: Radioactive Elements in the Body

You may not think of yourself as radioactive, but you are. A small portion of certain elements in the human body are radioactive and constantly undergo decay. Most of the radioactivity in the human body comes from potassium-40 and carbon-14. Potassium and carbon are two elements that we absolutely cannot live without, so unless we can remove all the radioactive isotopes of these elements, there is no way to escape at least some radioactivity. There is debate about which radioactive element is more problematic. There is more potassium-40 in the body than carbon-14, and it has a much longer half-life. Potassium-40 also decays with about 10 times more energy than carbon-14, making each decay potentially more problematic. However, carbon is the element that makes up the backbone of most living molecules, making carbon-14 more likely to be present around important molecules, such as proteins and DNA molecules. Most experts agree that while it is foolhardy to expect absolutely no exposure to radioactivity, we can and should minimize exposure to excess radioactivity.

Key Takeaways

- Natural radioactive processes are characterized by a half-life, the time it takes for half of the material to decay radioactively.
- The amount of material left over after a certain number of half-lives can be easily calculated.

14.4: Applications of Nuclear Chemistry

Nuclear chemistry affects our lives in numerous ways: diagnoses and treatments in medicine, power sources that avoid global warming, international diplomacy based on nuclear proliferation, and even the energy our planet gets from the sun. We will not have time to explore any of these applications in great detail, however the little bit we have covered related to nuclear chemistry is sufficient for a survey of many of these topics.

14.4.1: Detecting Radioactivity

Learning Objectives

- Understand how the Geiger counter can be used to quantify the rate of ionization radiation.

When alpha, beta or gamma particles collide with a target, some of the energy in the particle is transferred to the target, typically resulting in the promotion of an electron to an “excited state”. In many “targets”, especially gasses, this results in *ionization*. Alpha, beta and gamma radiation are broadly referred to as **ionizing radiation**. A **Geiger counter** (or Geiger-Müller counter) takes advantage of this in order to detect these particles. In a Geiger tube, the electron produced by ionization of a captive gas travels to the anode and the change in voltage is detected by the attached circuitry. Most counters of this type are designed to emit an audible “click” in response to the change in voltage, and to also show it on a digital or analog meter. A simple schematic of a Geiger counter is shown in Figure 14.4.1.1.

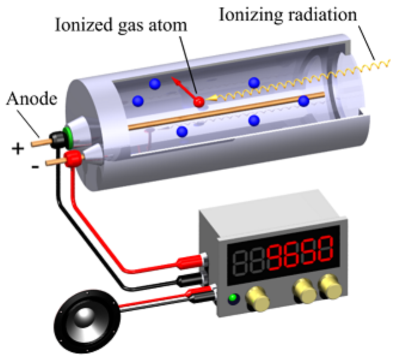


Figure 14.4.1.1: Schematic of a Geiger-Müller counter using an "end window" tube for low penetration radiation. A loudspeaker is also used for indication. (CC-BY-SA-3.0 Svjo-2 vai Wikipedia(opens in new window)).

Although scientists were not aware at the time of the Geiger counter's invention, all of us are subjected to a certain amount of radiation every day. This radiation is called **background radiation** and comes from a variety of natural and artificial radiation sources. Approximately 82% of background radiation comes from natural sources. These natural sources include:

1. Sources in the earth—including naturally occurring radioactive elements—which are incorporated in building materials, and also in the human body.
2. Sources from space in the form of cosmic rays.
3. Sources in the atmosphere, such as radioactive radon gas released from the earth; and radioactive atoms like carbon-14, produced in the atmosphere by bombardment from high-energy cosmic rays.

14.4.2: Radiocarbon Dating- Using Radioactivity to Measure the Age of Fossils and Other Artifacts

Learning Objectives

- Identify the age of materials that can be approximately determined using Radiocarbon dating.

Radiometric Dating

Several radioisotopes have half-lives and other properties that make them useful for purposes of “dating” the origin of objects such as archaeological artifacts, formerly living organisms, or geological formations. The radioactivity of carbon-14 provides a method for dating objects that were a part of a living organism. This method of radiometric dating, which is also called **radiocarbon dating** or **carbon-14 dating**, is accurate for dating carbon-containing substances that are up to about 30,000 years old, and can provide reasonably accurate dates up to a maximum of about 50,000 years old.

Naturally occurring carbon consists of three isotopes:

, which constitutes about 99% of the carbon on earth; , about 1% of the total; and trace amounts of

. Carbon-14 forms in the upper atmosphere by the reaction of nitrogen atoms with neutrons from cosmic rays in space:

All isotopes of carbon react with oxygen to produce CO_2 molecules. The ratio of

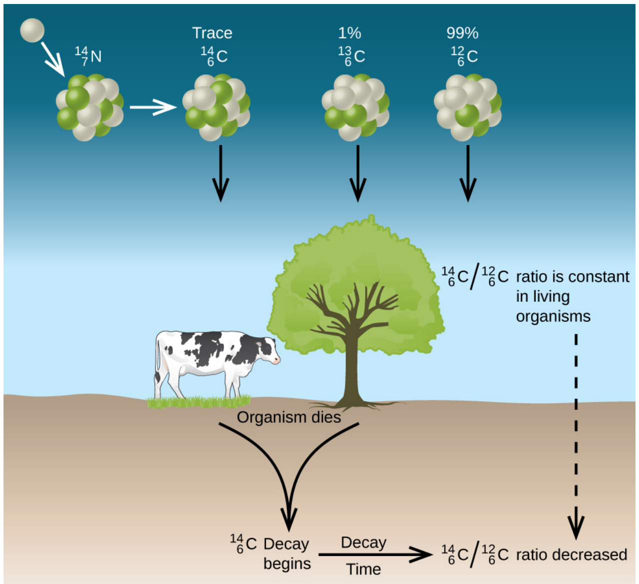
to depends on the ratio of to in the atmosphere. The natural abundance of in the atmosphere is approximately 1 part per trillion; until recently, this has generally been constant over time, as seen is gas samples found trapped in ice. The incorporation of and into plants is a regular part of the photosynthesis process, which means that the ratio found in a living plant is the same as the ratio in the atmosphere. But when the plant dies, it no longer traps carbon through photosynthesis. Because

is a stable isotope and does not undergo radioactive decay, its concentration in the plant does not change. However, carbon-14 decays by β emission with a half-life of 5730 years:

Thus, the

ratio gradually decreases after the plant dies. The decrease in the ratio with time provides a measure of the time that has elapsed since the death of the plant (or other organism that ate the plant). Figure

visually depicts this process.



Figure

: Along with stable carbon-12, radioactive carbon-14 is taken in by plants and animals, and remains at a constant level within them while they are alive. After death, the C-14 decays and the C-14:C-12 ratio in the remains decreases. Comparing this ratio to the C-14:C-12 ratio in living organisms allows us to determine how long ago the organism lived (and died). (CC BY 4.0; OpenStax)

For example, with the half-life of

being 5730 years, if the ratio in a wooden object found in an archaeological dig is half what it is in a living tree, this indicates that the wooden object is 5730 years old. Highly accurate determinations of ratios can be obtained from very small samples (as little as a milligram) by the use of a mass spectrometer.

When we speak of the element Carbon, we most often refer to the most naturally abundant stable isotope ^{12}C. Although ^{12}C is definitely essential to life, its unstable sister isotope ^{14}C has become of extreme importance to the science world. Radiocarbon dating is the process of determining the age of a sample by examining the amount of ^{14}C remaining against its known half-life, 5,730 years. The reason this process works is because when organisms are alive, they are constantly replenishing their ^{14}C supply through respiration, providing them with a constant amount of the isotope. However, when an organism ceases to exist, it no longer takes in carbon from its environment and the unstable ^{14}C isotope begins to decay. From this science, we are able to approximate the date at which the organism lived on Earth. Radiocarbon dating is used in many fields to learn information about the past conditions of organisms and the environments present on Earth.

Contributors and Attributions

- Template:ContribBarron
- Boundless (www.boundless.com)
- Wikipedia

14.4.3: The Discovery of Fission and the Atomic Bomb

Learning Objectives

- Define and give examples of fission and fusion.
- Classify nuclear reactions as fission or fusion.
- List some medical uses of nuclear energy.

Nuclei that are larger than iron-56 may undergo nuclear reactions in which they break up into two or more smaller nuclei. These reactions are called **fission** reactions. Conversely, nuclei that are smaller than iron-56 become larger nuclei in order to be more stable. These nuclei undergo a nuclear reaction in which smaller nuclei join together to form a larger nucleus. Such nuclear reactions are called **fusion** reactions.

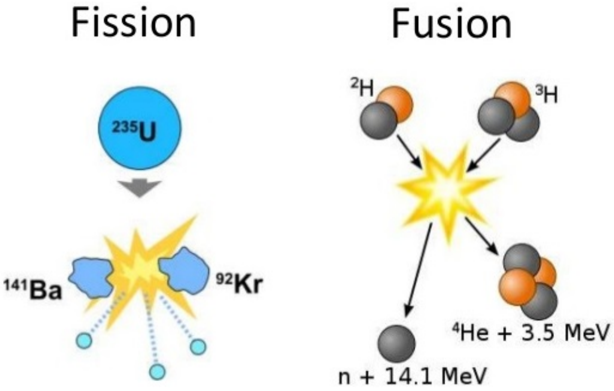


Figure 14.4.3.1: (left) Nuclear fission occurs when one large nucleus is split into two or more smaller nuclei. (right) Nuclear fusion happens when two small nuclei combine to make a larger nucleus.

Fission and Chain Reactions

In both fission and fusion, large amounts of energy are given off in the form of heat, light, and gamma radiation. Nuclear fission was discovered in the late 1930s when U-235 nuclides were bombarded with neutrons and were observed to split into two smaller-mass nuclei.

$$^{1}_{0}\mathrm{n} + ^{235}_{92}\mathrm{U} \rightarrow ^{141}_{56}\mathrm{Ba} + ^{92}_{36}\mathrm{Kr} + 3^{1}_{0}\mathrm{n}$$

The products shown are only one of many sets of products from the disintegration of a U-235 nucleus. Over 35 different elements have been observed in the fission products of U-235.

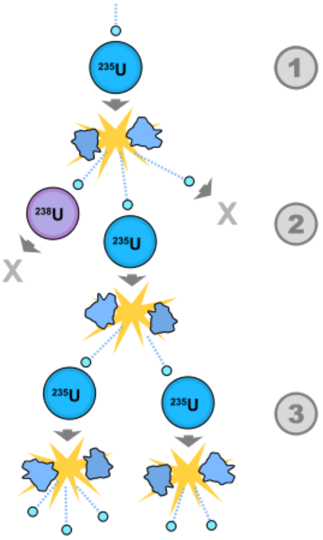


Figure 14.4.3.2: A possible nuclear fission chain reaction. 1. A uranium-235 atom absorbs a neutron, and fissions into two new atoms (fission fragments), releasing three new neutrons and a large amount of binding energy. 2. One of those neutrons is absorbed by an atom of uranium-238, and does not continue the reaction. Another neutron leaves the system without being absorbed. However, one neutron does collide with an atom of uranium-235, which then fissions and releases two neutrons and more binding energy. 3. Both of those neutrons collide with uranium-235 atoms, each of which fissions and releases a few neutrons, which can then continue the reaction. (Public Domain.)

When a neutron strikes a U-235 nucleus and the nucleus captures a neutron, it undergoes fission, producing two lighter nuclei and three free neutrons. The production of the free neutrons makes it possible to have a self-sustaining fission process—a nuclear **chain reaction**. If at least one of the neutrons goes on to cause another U-235 disintegration, the fission will be self-sustaining.

Nuclear Weapons

It is unfortunate that when the topics of radioactivity and nuclear energy come up, most thoughts probably go to weapons of war. The second thought might be about the possibility of nuclear energy contributing to the solution of the energy crisis. Nuclear energy, however, has many applications beyond bombs and the generation of electricity. Radioactivity has huge applications in scientific research, several fields of medicine both in terms of imaging and in terms of treatment, industrial processes, some very useful appliances, and even in agriculture.

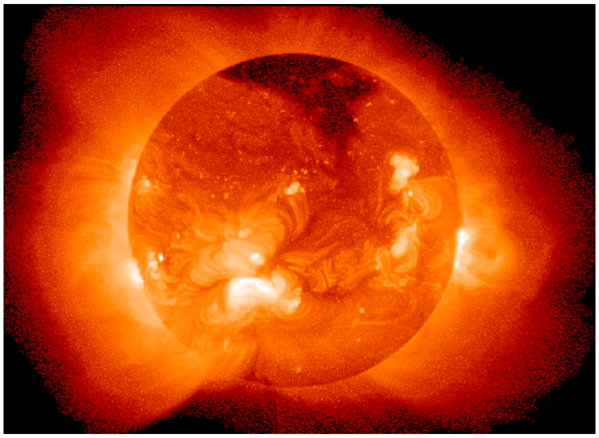


Figure 14.4.3.3: The energy that comes from the sun and other stars is produced by fusion. (Public Domain; NASA.)

Summary and Vocabulary

Naturally radioactive elements exist in the earth and are either alpha or beta emitters. Artificial transmutation of elements can be accomplished by bombarding the nuclei of some elements with alpha or subatomic particles. Nuclear radiation also has many medical uses.

- **Chain reaction** - A multi-stage nuclear reaction that sustains itself in a series of fissions, in which the release of neutrons from the splitting of one atom leads to the splitting of others.
- **Critical mass** - The smallest mass of a fissionable material that will sustain a nuclear chain reaction at a constant level.
- **Fission** - A nuclear reaction in which a heavy nucleus splits into two or more smaller fragments, releasing large amounts of energy.
- **Fusion** - A nuclear reaction in which nuclei combine to form more massive nuclei with the simultaneous release of energy.
- **Control rods** - Rods made of chemical elements capable of absorbing many neutrons, that are used to control the rate of a fission chain reaction in a nuclear reactor.

14.4.4: Nuclear Power- Using Fission to Generate Electricity

Fission Reactors

Fission reactions can be used in the production of electricity if we control the rate at which the fission occurs. The great majority of all electrical generating systems (whether coal burning power plants, hydroelectric plants, or nuclear power plants) is that they follow a reasonably simple design. The electricity is produced by spinning a coil of wire inside a magnetic field. When a fluid (air, steam, water) is forced through the pipe, it spins the fan blades, which in turn spin the axle. To generate electricity, the axle of a turbine is attached to the loop of wire in a generator. When a fluid is forced through the turbine, the fan blades turn, the turbine axle turns, and the loop of wire inside the generator turns—thus generating electricity.

The essential difference in various kinds of electrical generating systems is the method used to spin the turbine. For a wind generator, the turbine is a windmill. In a geothermal generator, steam from a geyser is forced through the turbine. In hydroelectric generating plants, water falling over a dam passes through the turbine and spins it. In fossil fuel (coal, oil, natural gas) generating plants, the fossil fuel is burned and the heat is used to boil water into steam, and then the steam passes through the turbine to make it spin. In a fission reactor generating plant, a fission reaction is used to boil the water into steam, and the steam passes through the turbine to make it spin. Once the steam is generated by the fission reaction, a nuclear power plant is essentially the same as a fossil fuel plant.

Naturally occurring uranium is composed almost totally of two uranium isotopes. It contains more than 99% uranium-238 and less than 1% uranium-235. It is the uranium-235, however, that is **fissionable** (will undergo fission). In order for uranium to be used as fuel in a fission reactor, the percentage of uranium-235 must be increased, usually to about 3%. (Uranium in which the U-235 content is more than 1% is called **enriched uranium**.)

Once the supply of U-235 is acquired, it is placed in a series of long cylindrical tubes called fuel rods. These fuel cylinders are bundled together with **control rods** made of neutron-absorbing material. The amount of U-235 in all the fuel rods taken together is adequate to carry on a chain reaction, but is less than the critical mass. (In the United States, all public nuclear power plants contain less than a critical mass of U-235 and therefore, could never produce a nuclear explosion.) The amount of heat generated by the chain reaction is controlled by the rate at which the nuclear reaction occurs. The rate of the nuclear reaction is dependent on how many neutrons are emitted by one U-235 nuclear disintegration *and* strike a new U-235 nucleus to cause another disintegration. The purpose of the control rods is to absorb some of the neutrons and thus stop them from causing further disintegration. The control rods can be raised or lowered into the fuel rod bundle. When the control rods are lowered all the way into the fuel rod bundle, they absorb so many neutrons that the chain reaction essentially stops. When more heat is desired, the control rods are raised so that they catch fewer neutrons, the chain reaction speeds up, and more heat is generated. The control rods are operated in a fail-safe system, so that power is necessary to hold them up; during a power failure, gravity will pull the control rods down into the shut off position.

U-235 nuclei can capture neutrons and disintegrate more efficiently if the neutrons are moving slower than the speed at which they are released. Fission reactors use a moderator surrounding the fuel rods to slow down the neutrons. Water is not only a good coolant, but also a good moderator. A common type of fission reactor has the fuel core submerged in a huge pool of water.

You can follow the operation of an electricity-generating fission reactor in the figure below. The reactor core is submerged in a pool of water. The heat from the fission reaction heats the water and the water is pumped into a heat exchanger container where the heated water boils the water in the heat exchanger. The steam from there is forced through a turbine which spins a generator and produces electricity. After the water passes through the turbine, it is condensed back to liquid water and pumped back to the heat exchanger.

In the United States, heavy opposition to the use of nuclear energy was mounted in the late 1960's and early 1970's. Every environmentalist organization in the US opposed the use of nuclear energy; the constant pressure from environmentalist groups caused an increase of public fear and, therefore, opposition to nuclear energy. This is not true today; at least one environmental leader has published a paper in favor of nuclear-powered electricity generation.

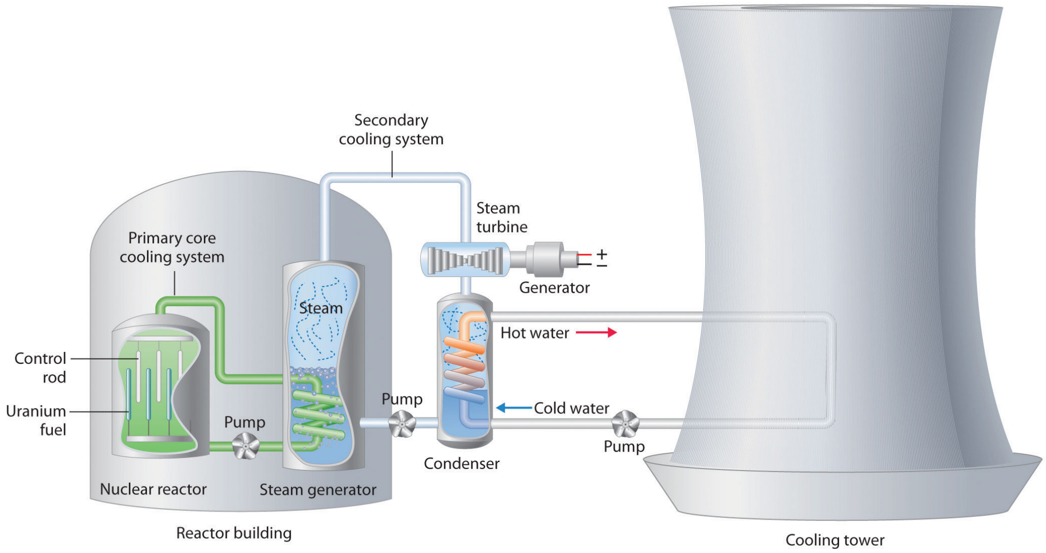


Figure 14.4.4.1: A Light-Water Nuclear Fission Reactor for the Production of Electric Power. The fuel rods are made of a corrosion-resistant alloy that encases the partially enriched uranium fuel; controlled fission of ^{235}U in the fuel produces heat. Water surrounds the fuel rods and moderates the kinetic energy of the neutrons, slowing them to increase the probability that they will induce fission. Control rods that contain elements such as boron, cadmium, or hafnium—which are very effective at absorbing neutrons—are used to control the rate of the fission reaction. A heat exchanger is used to boil water in a secondary cooling system, creating steam to drive the turbine and produce electricity. The large hyperbolic cooling tower, which is the most visible portion of the facility, condenses the steam in the secondary cooling circuit; it is often located at some distance from the actual reactor.

In 1979, a reactor core meltdown at Pennsylvania's Three Mile Island nuclear power plant reminded the entire country of the dangers of nuclear radiation. The concrete containment structure (six feet thick walls of reinforced concrete), however, did what it was designed to do—prevent radiation from escaping into the environment. Although the reactor was shut down for years, there were no injuries or deaths among nuclear workers or nearby residents. Three Mile Island was the only serious accident in the entire history of 103 civilian power plants operating for 40 years in the United States. There has never been a single injury or death due to radiation in any public nuclear power plant in the U.S. The accident at Three Mile Island did, however, frighten the public so that there has not been a nuclear power plant built in the U.S. since the accident.

The 103 nuclear power plants operating in the U.S. deliver approximately 19.4% of American electricity with zero greenhouse gas emission. There are 600 coal-burning electric plants in the US delivering 48.5% of American electricity and producing 2 billion tons of CO_2 annually, accounting for 40% of U.S. CO_2 emissions and 10% of global emissions. These coal burning plants also produce 64% of the sulfur dioxide emissions, 26% of the nitrous oxide emissions, and 33% of mercury emissions.

Fusion

Nuclear reactions, in which two or more lighter-mass nuclei join together to form a single nucleus, are called **fusion** reactions or nuclear fusions. Of particular interest are fusion reactions in which hydrogen nuclei combine to form helium. Hydrogen nuclei are positively charged and repel each other. The closer the particles come, the greater the force of repulsion. In order for fusion reactions to occur, the hydrogen nuclei must have extremely high kinetic energies, so that the velocities can overcome the forces of repulsion. These kinetic energies only occur at extreme temperatures such as those that occur in the cores of the sun and other stars. Nuclear fusion is the power source for the stars, where the necessary temperature to ignite the fusion reaction is provided by massive gravitational pressure. In stars more massive than our sun, fusion reactions involving carbon and nitrogen are possible. These reactions produce more energy than hydrogen fusion reactions.

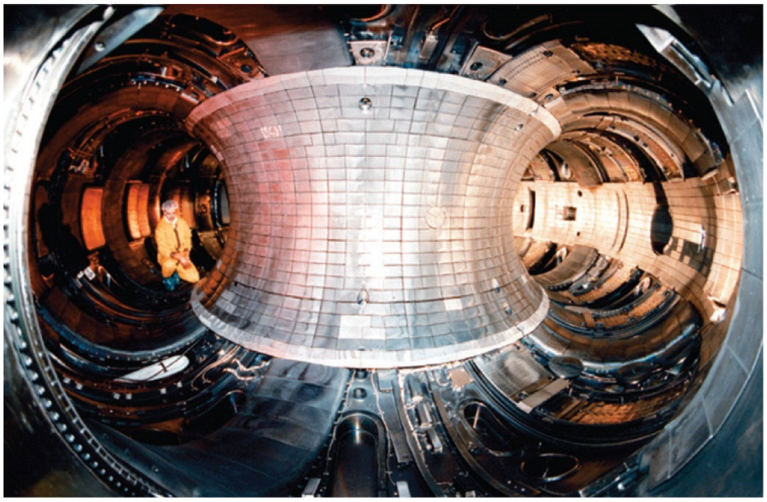


Figure 14.4.4.2: A Possible Design for a Nuclear Fusion Reactor. The extraordinarily high temperatures needed to initiate a nuclear fusion reaction would immediately destroy a container made of any known material. One way to avoid contact with the container walls is to use a high-energy plasma as the fuel. Because plasma is essentially a gas composed of ionized particles, it can be confined using a strong magnetic field shaped like a torus (a hollow donut).

Intensive research is now being conducted to develop fusion reactors for electricity generation. The two major problems slowing the development are: finding a practical means for generating the intense temperature needed, and developing a container that will not melt under the conditions of a fusion reaction. Electricity-producing fusion reactors are still a distant dream.

Summary

- Nuclear fission refers to the splitting of atomic nuclei.
- Nuclear fusion refers to the joining together of two or more smaller nuclei to form a single nucleus.
- The fission of U-235 or Pu-239 is used in nuclear reactors.

14.4.5: Nuclear Fusion- The Power of the Sun

In addition to fission, a second possible method for obtaining energy from nuclear reactions lies in the fusing together of two light nuclei to form a heavier nucleus. As we see when discussing Figure 1 from Mass-Energy Relationships, such a process results in nucleons which are more firmly bonded to each other, and hence lower in potential energy. This is particularly true if ${}^4_2\text{He}$ is formed, because this nucleus is very stable. Such a reaction occurs between the nuclei of the two heavy isotopes of hydrogen, deuterium and tritium:

$${}^2_1\text{D} + {}^3_1\text{T} \rightarrow {}^4_2\text{He} + {}^1_0n \tag{14.4.5.1}$$

For this reaction, Δm = – 0.018 88 g mol^{-1} so that ΔH_m = – 1700 GJ mol^{-1}. Although very large quantities of energy are released by a reaction like Equation 14.4.5.1, such a reaction is very difficult to achieve in practice. This is because of the very high activation energy, about 30 GJ mol^{-1}, which must be overcome to bring the nuclei close enough to fuse together. This barrier is created by coulombic repulsion between the positively charged nuclei. The only place where scientists have succeeded in producing fusion reactions on a large scale is in a **hydrogen bomb**. Here, the necessary activation energy is achieved by exploding a fission bomb to heat the reactants to a temperature of about 10^8 K. Attempts to carry out fusion in a more controlled way have met only limited success. At the very high temperatures required, all molecules dissociate and most atoms ionize. A new state of matter called a **plasma** is formed. It is neither solid, liquid, nor gas. Plasma behaves much like the universal solvent of the alchemists by converting any solid material that it contacts into vapor.

Two techniques for producing a controlled fusion reaction are currently being explored. The first is to restrict the plasma by means of a strong magnetic field, rather than the walls of a container. This has met some success, but has not yet been able to contain a plasma long enough for usable energy to be obtained. The second technique involves the sudden compression and heating of pellets of deuterium and tritium by means of a sharply focused laser beam. Again, only limited success has been obtained.

Though these attempts at a controlled fusion reaction have so far been only partially successful, they are nevertheless worth pursuing. Because of the much readier availability of lighter isotopes necessary for fusion, as opposed to the much rarer heavier isotopes required for fission, controlled nuclear fusion would offer the human race an essentially limitless supply of energy. There would still be some environmental difficulties with the production of isotopes such as tritium, but these would be nowhere near the seriousness of the problem caused by the production of the witches brew of radioactive isotopes in a fission reactor. It must be confessed, though, that at the present rate of progress, the prospect of limitless clean energy from fusion seems unlikely in the next decade or two.

14.4.6: The Effects of Radiation on Life

Learning Objectives

- Describe the biological impact of ionizing radiation.
- Define units for measuring radiation exposure.
- Explain the operation of common tools for detecting radioactivity.
- List common sources of radiation exposure in the US.

The increased use of radioisotopes has led to increased concerns over the effects of these materials on biological systems (such as humans). All radioactive nuclides emit high-energy particles or electromagnetic waves. When this radiation encounters living cells, it can cause heating, break chemical bonds, or ionize molecules. The most serious biological damage results when these radioactive emissions fragment or ionize molecules. For example, alpha and beta particles emitted from nuclear decay reactions possess much higher energies than ordinary chemical bond energies. When these particles strike and penetrate matter, they produce ions and molecular fragments that are extremely reactive. The damage this does to biomolecules in living organisms can cause serious malfunctions in normal cell processes, taxing the organism's repair mechanisms and possibly causing illness or even death (Figure 14.4.6.1).

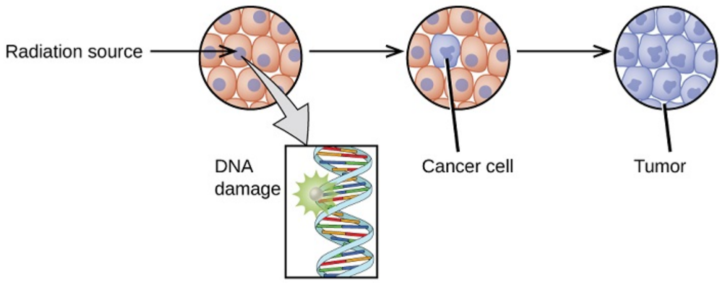


Figure 14.4.6.1: Radiation can harm biological systems by damaging the DNA of cells. If this damage is not properly repaired, the cells may divide in an uncontrolled manner and cause cancer.

A diagram is shown which has a white sphere followed by a right-facing arrow and a large sphere composed of many smaller white and green spheres. The single sphere has impacted the larger sphere. A right-facing arrow leads from the larger sphere to a pair of smaller spheres which are collections of the same white and green spheres. A starburst pattern lies between these two spheres and has three right-facing arrows leading from it to two white spheres and a circle full of ten smaller, peach-colored circles with purple dots in their centers. An arrow leads downward from this circle to a box that contains a helical shape with a starburst near its top left side and is labeled "D N A damage." A right-facing arrow leads from this circle to a second circle, with nine smaller, peach-colored circles with purple dots in their centers and one fully purple small circle labeled "Cancer cell." A right-facing arrow leads to a final circle, this time full of the purple cells, that is labeled "Tumor."

Ionizing vs. Nonionizing Radiation

There is a large difference in the magnitude of the biological effects of nonionizing radiation (for example, light and microwaves) and ionizing radiation, emissions energetic enough to knock electrons out of molecules (for example, α and β particles, γ rays, X-rays, and high-energy ultraviolet radiation) (Figure 14.4.6.2).

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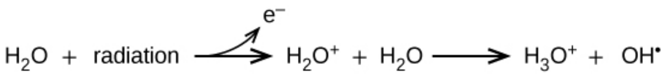
Figure 14.4.6.2: Lower frequency, lower-energy electromagnetic radiation is nonionizing, and higher frequency, higher-energy electromagnetic radiation is ionizing.

Energy absorbed from nonionizing radiation speeds up the movement of atoms and molecules, which is equivalent to heating the sample. Although biological systems are sensitive to heat (as we might know from touching a hot stove or spending a day at the beach in the sun), a large amount of nonionizing radiation is necessary before dangerous levels are reached. Ionizing radiation, however, may cause much more severe damage by breaking bonds or removing electrons in biological molecules, disrupting their structure and function. The damage can also be done indirectly, by first ionizing H_2O (the most abundant molecule in living organisms), which forms a H_2O^+ ion that reacts with water, forming a hydronium ion and a hydroxyl radical:



$$H_2O + \text{radiation} \xrightarrow{e^-} H_2O^+ + H_2O \longrightarrow H_3O^+ + OH^\bullet$$

Figure 14.4.6.3.

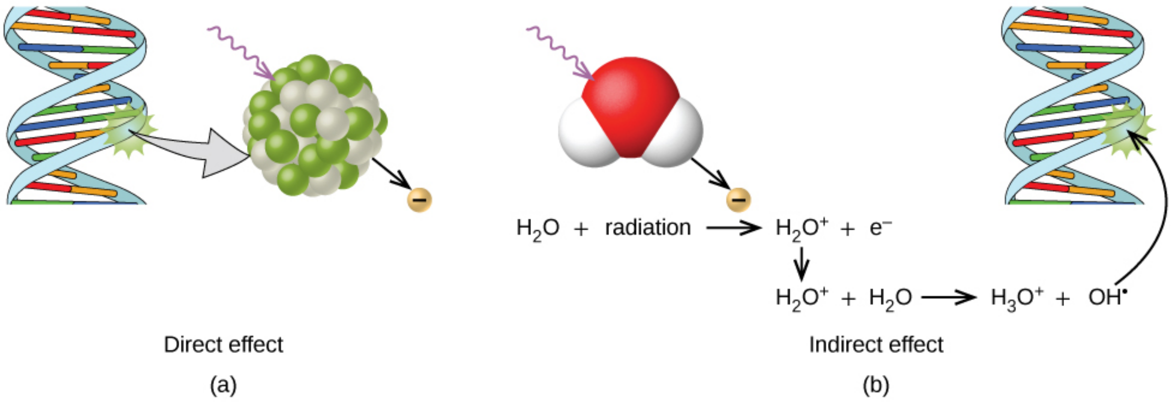


Figure 14.4.6.3: Ionizing radiation can (a) directly damage a biomolecule by ionizing it or breaking its bonds, or (b) create an H_2O^+ ion, which reacts with H_2O to form a hydroxyl radical, which in turn reacts with the biomolecule, causing damage indirectly.

Biological Effects of Exposure to Radiation

Radiation can harm either the whole body (somatic damage) or eggs and sperm (genetic damage). Its effects are more pronounced in cells that reproduce rapidly, such as the stomach lining, hair follicles, bone marrow, and embryos. This is why patients undergoing radiation therapy often feel nauseous or sick to their stomach, lose hair, have bone aches, and so on, and why particular care must be taken when undergoing radiation therapy during pregnancy.

Different types of radiation have differing abilities to pass through material (Figure 14.4.6.4). A very thin barrier, such as a sheet or two of paper, or the top layer of skin cells, usually stops alpha particles. Because of this, alpha particle sources are usually not dangerous if outside the body, but are quite hazardous if ingested or inhaled (see the Chemistry in Everyday Life feature on Radon Exposure). Beta particles will pass through a hand, or a thin layer of material like paper or wood, but are stopped by a thin layer of metal. Gamma radiation is very penetrating and can pass through a thick layer of most materials. Some high-energy gamma radiation is able to pass through a few feet of concrete. Certain dense, high atomic number elements (such as lead) can effectively attenuate gamma radiation with thinner material and are used for shielding. The ability of various kinds of emissions to cause ionization varies greatly, and some particles have almost no tendency to produce ionization. Alpha particles have about twice the ionizing power of fast-moving neutrons, about 10 times that of β particles, and about 20 times that of γ rays and X-rays.

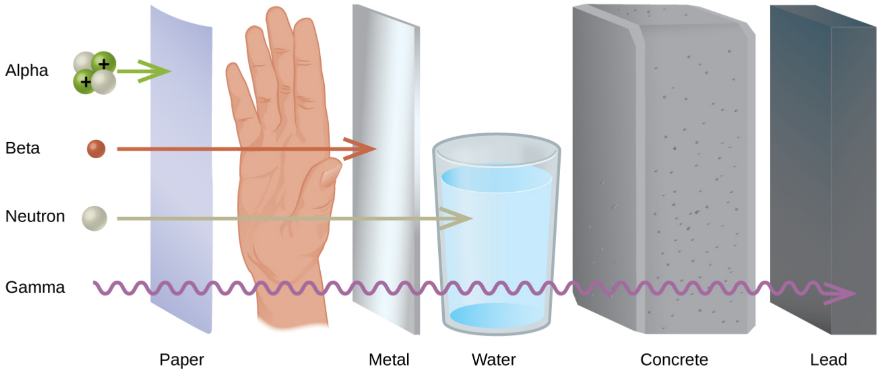


Figure 14.4.6.4: The ability of different types of radiation to pass through material is shown. From least to most penetrating, they are alpha < beta < neutron < gamma.

A diagram shows four particles in a vertical column on the left, followed by an upright sheet of paper, a person’s hand, an upright sheet of metal, a glass of water, a thick block of concrete and an upright, thick piece of lead. The top particle listed is made up of two white spheres and two green spheres that are labeled with positive signs and is labeled “Alpha.” A right-facing arrow leads from this to the paper. The second particle is a red sphere labeled “Beta” and is followed by a right-facing arrow that passes through the paper and stops at the hand. The third particle is a white sphere labeled “Neutron” and is followed by a right-facing arrow that passes through the paper, hand and metal but is stopped at the glass of water. The fourth particle is shown by a squiggly arrow and it passes through all of the substances but stops at the lead. Terms at the bottom read, from left to right, “Paper,” “Metal,” “Water,” “Concrete” and “Lead.”

For many people, one of the largest sources of exposure to radiation is from radon gas (Rn-222). Radon-222 is an α emitter with a half–life of 3.82 days. It is one of the products of the radioactive decay series of U-238, which is found in trace amounts in soil and rocks. The radon gas that is produced slowly escapes from the ground and gradually seeps into homes and other structures above.

Since it is about eight times more dense than air, radon gas accumulates in basements and lower floors, and slowly diffuses throughout buildings (Figure 14.4.6.5).

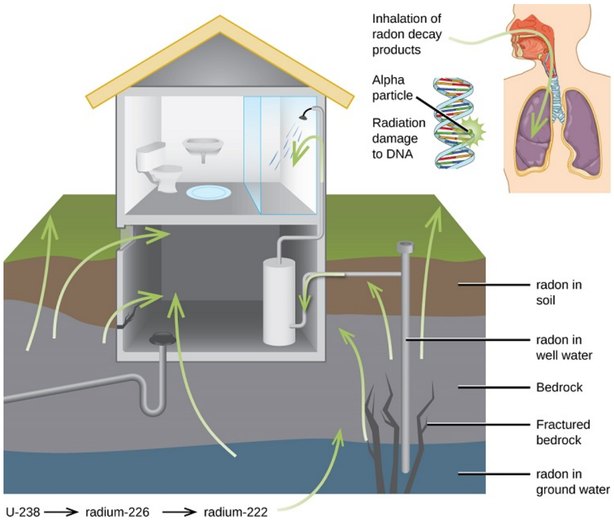


Figure 14.4.6.5: Radon-222 seeps into houses and other buildings from rocks that contain uranium-238, a radon emitter. The radon enters through cracks in concrete foundations and basement floors, stone or porous cinderblock foundations, and openings for water and gas pipes.

A cut-away image of the side of a house and four layers of the ground it rests on is shown, as well as a second cut-away image of a person's head and chest cavity. The house is shown with a restroom on the second floor and a basement with a water heater as the first floor. Green arrows lead from the lowest ground layer, labeled "radon in ground water," from the third ground layer, labeled "Bedrock" and "Fractured bedrock," from the second layer, labeled "radon in well water," and from the top layer, labeled "radon in soil to the inside of the basement area. In the smaller image of the torso, a green arrow is shown to enter the person's nasal passage and travel to the lungs. This is labeled "Inhalation of radon decay products." A small coiled, helical structure next to the torso is labeled "alpha particle" on one section where it has a starburst pattern and "Radiation damage to D N A" on another segment.

Radon is found in buildings across the country, with amounts dependent on location. The average concentration of radon inside houses in the US (1.25 pCi/L) is about three times the level found in outside air, and about one in six houses have radon levels high enough that remediation efforts to reduce the radon concentration are recommended. Exposure to radon increases one's risk of getting cancer (especially lung cancer), and high radon levels can be as bad for health as smoking a carton of cigarettes a day. Radon is the number one cause of lung cancer in nonsmokers and the second leading cause of lung cancer overall. Radon exposure is believed to cause over 20,000 deaths in the US per year.

Measuring Radiation Exposure

Several different devices are used to detect and measure radiation, including Geiger counters, scintillation counters (scintillators), and radiation dosimeters (Figure 14.4.6.6). Probably the best-known radiation instrument, the Geiger counter (also called the Geiger-Müller counter) detects and measures radiation. Radiation causes the ionization of the gas in a Geiger-Müller tube. The rate of ionization is proportional to the amount of radiation. A scintillation counter contains a scintillator—a material that emits light (luminesces) when excited by ionizing radiation—and a sensor that converts the light into an electric signal. Radiation dosimeters also measure ionizing radiation and are often used to determine personal radiation exposure. Commonly used types are electronic, film badge, thermoluminescent, and quartz fiber dosimeters.

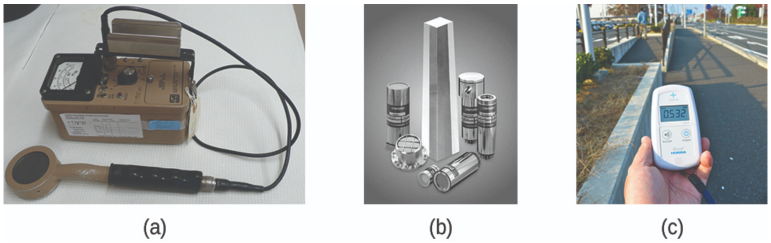


Figure 14.4.6.6: Devices such as (a) Geiger counters, (b) scintillators, and (c) dosimeters can be used to measure radiation. (Credit c: modification of work by “osaMu”/Wikimedia commons.)

Three photographs are shown and labeled “a,” “b” and “c.” Photo a shows a Geiger counter sitting on a table. It is made up of a metal box with a read-out screen and a wire leading away from the box connected to a sensor wand. Photograph b shows a collection of tall and short vertical tubes arranged in a grouping while photograph c shows a person’s hand holding a small machine with a digital readout while standing on the edge of a roadway.

A variety of units are used to measure various aspects of radiation (Table $14.4.6.1$). The SI unit for rate of radioactive decay is the becquerel (Bq), with 1 Bq = 1 disintegration per second. The curie (Ci) and millicurie (mCi) are much larger units and are frequently used in medicine (1 curie = 1 Ci = 3.7×10^{10} disintegrations per second). The SI unit for measuring radiation dose is the gray (Gy), with 1 Gy = 1 J of energy absorbed per kilogram of tissue. In medical applications, the radiation absorbed dose (rad) is more often used (1 rad = 0.01 Gy; 1 rad results in the absorption of 0.01 J/kg of tissue). The SI unit measuring tissue damage caused by radiation is the sievert (Sv). This takes into account both the energy and the biological effects of the type of radiation involved in the radiation dose.

Table 14.4.6.1: Units Used for Measuring Radiation

Measurement Purpose	Unit	Quantity Measured	Description
activity of source	becquerel (Bq)	radioactive decays or emissions	amount of sample that undergoes 1 decay/second
	curie (Ci)		amount of sample that undergoes 3.7×10^{10} decays/second
absorbed dose	gray (Gy)	energy absorbed per kg of tissue	1 Gy = 1 J/kg tissue
	radiation absorbed dose (rad)		1 rad = 0.01 J/kg tissue
biologically effective dose	sievert (Sv)	tissue damage	Sv = RBE × Gy
	roentgen equivalent for man (rem)		Rem = RBE × rad

The roentgen equivalent for man (rem) is the unit for radiation damage that is used most frequently in medicine (1 rem = 1 Sv). Note that the tissue damage units (rem or Sv) includes the energy of the radiation dose (rad or Gy), along with a biological factor referred to as the RBE (for relative biological effectiveness), that is an approximate measure of the relative damage done by the radiation. These are related by:

$$\text{number of rems} = \text{RBE} \times \text{number of rads} \tag{14.4.6.1}$$

with RBE approximately 10 for α radiation, 2(+) for protons and neutrons, and 1 for β and γ radiation.

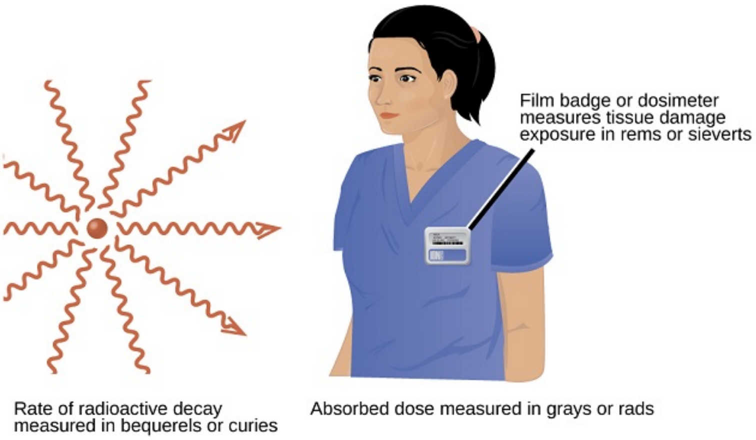


Figure $14.4.6.7$: Different units are used to measure the rate of emission from a radioactive source, the energy that is absorbed from the source, and the amount of damage the absorbed radiation does. (CC by 4.0; OpenStax)

Two images are shown. The first, labeled “Rate of radioactive decay measured in becquerels or curies,” shows a red sphere with ten red squiggly arrows facing away from it in a 360 degree circle. The second image shows the head and torso of a woman wearing medical scrubs with a badge on her chest. The caption to the badge reads “Film badge or dosimeter measures tissue damage exposure in rems or sieverts” while a phrase under this image states “Absorbed dose measured in grays or rads.”

Effects of Long-term Radiation Exposure on the Human Body

The effects of radiation depend on the type, energy, and location of the radiation source, and the length of exposure. As shown in Figure $14.4.6.8$, the average person is exposed to background radiation, including cosmic rays from the sun and radon from uranium in the ground (see the Chemistry in Everyday Life feature on Radon Exposure); radiation from medical exposure, including CAT scans, radioisotope tests, X-rays, and so on; and small amounts of radiation from other human activities, such as airplane flights (which are bombarded by increased numbers of cosmic rays in the upper atmosphere), radioactivity from consumer products, and a variety of radionuclides that enter our bodies when we breathe (for example, carbon-14) or through the food chain (for example, potassium-40, strontium-90, and iodine-131).

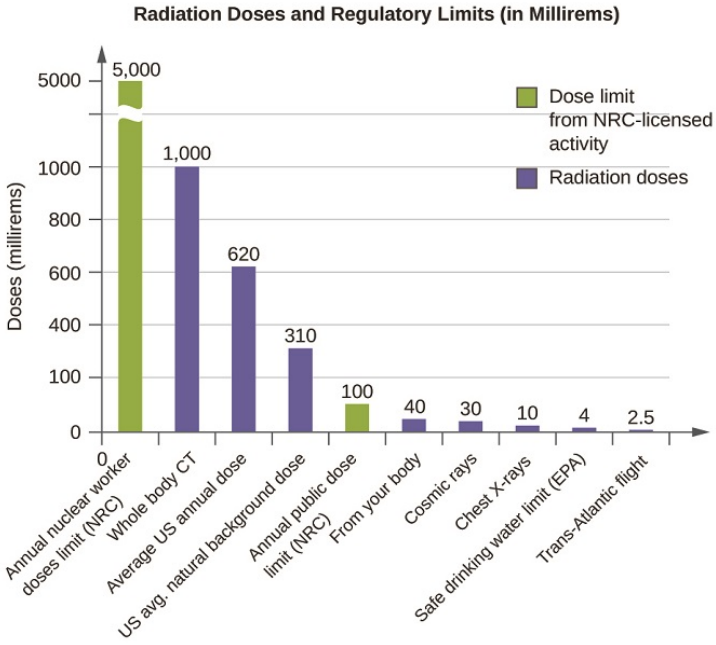


Figure 14.4.6.8: The total annual radiation exposure for a person in the US is about 620 mrem. The various sources and their relative amounts are shown in this bar graph. (source: U.S. Nuclear Regulatory Commission).

A bar graph titled "Radiation Doses and Regulatory Limits, open parenthesis, in Millirems, close parenthesis" is shown. The y-axis is labeled "Doses in Millirems" and has values from 0 to 5000 with a break between 1000 and 5000 to indicate a different scale to the top of the graph. The y-axis is labeled corresponding to each bar. The first bar, measured to 5000 on the y-axis, is drawn in red and is labeled "Annual Nuclear Worker Doses Limit, open parenthesis, N R C, close parenthesis." The second bar, measured to 1000 on the y-axis, is drawn in blue and is labeled "Whole Body C T" while the third bar, measured to 620 on the y-axis, is drawn in blue and is labeled "Average U period S period Annual Dose." The fourth bar, measured to 310 on the y-axis, is drawn in blue and is labeled "U period S period Natural Background Dose" while the fifth bar, measured to 100 on the y-axis and drawn in red reads "Annual Public Dose Limit, open parenthesis, N R C, close parenthesis." The sixth bar, measured to 40 on the y-axis, is drawn in blue and is labeled "From Your Body" while the seventh bar, measured to 30 on the y-axis and drawn in blue reads "Cosmic rays." The eighth bar, measured to 4 on the y-axis, is drawn in blue and is labeled "Safe Drinking Water Limit, open parenthesis, E P A, close parenthesis" while the ninth bar, measured to 2.5 on the y-axis and drawn in red reads "Trans Atlantic Flight." A legend on the graph shows that red means "Dose Limit From N R C dash licensed activity" while blue means "Radiation Doses."

A short-term, sudden dose of a large amount of radiation can cause a wide range of health effects, from changes in blood chemistry to death. Short-term exposure to tens of rems of radiation will likely cause very noticeable symptoms or illness; a dose of about 500 rems is estimated to have a 50% probability of causing the death of the victim within 30 days of exposure. Exposure to radioactive emissions has a cumulative effect on the body during a person's lifetime, which is another reason why it is important to avoid any unnecessary exposure to radiation. Health effects of short-term exposure to radiation are shown in Table 14.4.6.2

Table 14.4.6.2: Health Effects of Radiation

Exposure (rem)	Health Effect	Time to Onset (Without Treatment)
5–10	changes in blood chemistry	—
50	nausea	hours
55	fatigue	—
70	vomiting	—
75	hair loss	2–3 weeks
90	diarrhea	—
100	hemorrhage	—
400	possible death	within 2 months
1000	destruction of intestinal lining	—

Exposure (rem)	Health Effect	Time to Onset (Without Treatment)
	internal bleeding	—
	death	1–2 weeks
2000	damage to central nervous system	—
	loss of consciousness	minutes
	death	hours to days

It is impossible to avoid some exposure to ionizing radiation. We are constantly exposed to background radiation from a variety of natural sources, including cosmic radiation, rocks, medical procedures, consumer products, and even our own atoms. We can minimize our exposure by blocking or shielding the radiation, moving farther from the source, and limiting the time of exposure.

Summary

We are constantly exposed to radiation from a variety of naturally occurring and human-produced sources. This radiation can affect living organisms. Ionizing radiation is the most harmful because it can ionize molecules or break chemical bonds, which damages the molecule and causes malfunctions in cell processes. It can also create reactive hydroxyl radicals that damage biological molecules and disrupt physiological processes. Radiation can cause somatic or genetic damage, and is most harmful to rapidly reproducing cells. Types of radiation differ in their ability to penetrate material and damage tissue, with alpha particles the least penetrating, but potentially most damaging, and gamma rays the most penetrating.

Various devices, including Geiger counters, scintillators, and dosimeters, are used to detect and measure radiation, and monitor radiation exposure. We use several units to measure radiation: becquerels or curies for rates of radioactive decay; gray or rads for energy absorbed; and rems or sieverts for biological effects of radiation. Exposure to radiation can cause a wide range of health effects, from minor to severe, including death. We can minimize the effects of radiation by shielding with dense materials such as lead, moving away from the source of radiation, and limiting time of exposure.

Footnotes

1. 1 Source: US Environmental Protection Agency

Glossary

becquerel (Bq)

SI unit for rate of radioactive decay; 1 Bq = 1 disintegration/s.

curie (Ci)

Larger unit for rate of radioactive decay frequently used in medicine; 1 Ci = 3.7×10^{10} disintegrations/s.

Geiger counter

Instrument that detects and measures radiation via the ionization produced in a Geiger-Müller tube.

gray (Gy)

SI unit for measuring radiation dose; 1 Gy = 1 J absorbed/kg tissue.

ionizing radiation

Radiation that can cause a molecule to lose an electron and form an ion.

millicurie (mCi)

Larger unit for rate of radioactive decay frequently used in medicine; 1 Ci = 3.7×10^{10} disintegrations/s.

nonionizing radiation

Radiation that speeds up the movement of atoms and molecules; it is equivalent to heating a sample, but is not energetic enough to cause the ionization of molecules.

radiation absorbed dose (rad)

SI unit for measuring radiation dose, frequently used in medical applications; 1 rad = 0.01 Gy.

radiation dosimeter

Device that measures ionizing radiation and is used to determine personal radiation exposure.

relative biological effectiveness (RBE)

Measure of the relative damage done by radiation.

roentgen equivalent man (rem)

Unit for radiation damage, frequently used in medicine; 1 rem = 1 Sv.

scintillation counter

Instrument that uses a scintillator—a material that emits light when excited by ionizing radiation—to detect and measure radiation.

sievert (Sv)

SI unit measuring tissue damage caused by radiation; takes energy and biological effects of radiation into account.

14.4.7: Radioactivity in Medicine

Learning Objectives

- Outline manifestations of nuclear medicine.

The field of nuclear medicine has expanded greatly in the last twenty years, particularly in the area of imaging. This section will focus on nuclear medicine involving the types of nuclear radiation introduced in this chapter. The x-ray imaging systems will not be covered.

Radioiodine $(\mathrm{I}-131)$ Therapy involves imaging and treatment of the thyroid gland. The thyroid gland is a gland in the neck that produces two hormones that regulate metabolism. In some individuals, this gland becomes overactive and produces too much of these hormones. The treatment for this problem uses radioactive iodine $(\mathrm{I}-131)$, which is produced for this purpose in research fission reactors, or by neutron bombardment of other nuclei.

The thyroid gland uses iodine in the process of its normal function. Any iodine in food that enters the bloodstream is usually removed by, and concentrated in, the thyroid gland. When a patient suffering from an overactive thyroid swallows a small pill containing radioactive iodine, the I-131 is absorbed into the bloodstream just like non-radioactive iodine, and follows the same process to be concentrated in the thyroid. The concentrated emissions of nuclear radiation in the thyroid destroy some of the gland's cells and control the problem of the overactive thyroid.

Smaller doses of I-131 (too small to kill cells) are also used for purposes of imaging the thyroid. Once the iodine is concentrated in the thyroid, the patient lays down on a sheet of film and the radiation from the I-131 makes a picture of the thyroid on the film. The half-life of iodine-131 is approximately 8 days so after a few weeks, virtually all of the radioactive iodine is out of the patient's system. During that time, the patient is advised that they will set off radiation detectors in airports and will need to get special permission to fly on commercial flights.

Positron Emission Tomography or PET scan is a type of nuclear medicine imaging. Depending on the area of the body being imaged, a radioactive isotope is either injected into a vein, swallowed by mouth, or inhaled as a gas. When the radioisotope is collected in the appropriate area of the body, the gamma ray emissions are detected by a PET scanner (often called a gamma camera) which works together with a computer to generate special pictures, providing details on both the structure and function of various organs. PET scans are used to:

- Detect cancer.
- Determine the amount of cancer spread.
- Assess the effectiveness of treatment plans.
- Determine blood flow to the heart muscle.
- Determine the effects of a heart attack.
- Evaluate brain abnormalities, such as tumors and memory disorders.
- Map brain and heart function.

External Beam Therapy (EBT) is a method of delivering a high energy beam of radiation to the precise location of a patient's tumor. These beams can destroy cancer cells and, with careful planning, will not kill surrounding cells. The concept is to have several beams of radiation, each of which is sub-lethal, enter the body from different directions. The only place in the body where the beam would be lethal is at the point where all the beams intersect. Before the EBT process, the patient is three-dimensionally mapped using CT scans and x-rays. The patient receives small tattoos to allow the therapist to line up the beams exactly. Alignment lasers are used to precisely locate the target. The radiation beam is usually generated with a linear accelerator. EBT is used to treat the following diseases, as well as others:

- Breast cancer
- Colorectal cancer
- Head and neck cancer
- Lung cancer
- Prostate cancer

14.E: Nuclear Chemistry (Exercises)

14.2: Radioactivity

1. Define *radioactivity*.
2. Give an example of a radioactive element. How do you know if it is radioactive?
3. How many protons and neutrons are in each isotope?
   a. ${}^{11}_{5}\mathrm{B}$
   b. ${}^{27}_{13}\mathrm{Al}$
   c. ${}^{56}\mathrm{Fe}$
   d. ${}^{224}\mathrm{Rn}$
4. How many protons and neutrons are in each isotope?
   a. ${}^{2}_{1}\mathrm{H}$
   b. ${}^{112}_{48}\mathrm{Cd}$
   c. ${}^{252}\mathrm{Es}$
   d. ${}^{40}\mathrm{K}$
5. Describe an alpha particle. What nucleus is it equivalent to?
6. Describe a beta particle. What subatomic particle is it equivalent to?
7. What are gamma rays?
8. Why is it inappropriate to refer to gamma rays as “gamma particles”?
9. Plutonium has an atomic number of 94. Write the nuclear equation for the alpha particle emission of plutonium-244. What is the daughter isotope?
10. Francium has an atomic number of 87. Write the nuclear equation for the alpha particle emission of francium-212. What is the daughter isotope?
11. Tin has an atomic number of 50. Write the nuclear equation for the beta particle emission of tin-121. What is the daughter isotope?
12. Technetium has an atomic number of 43. Write the nuclear equation for the beta particle emission of technetium-99. What is the daughter isotope?
13. Energies of gamma rays are typically expressed in units of megaelectron volts (MeV), where 1 MeV = 1.602×10^{-13} J. Using the data provided in the text, calculate the energy in megaelectron volts of the gamma ray emitted when radon-222 decays.
14. The gamma ray emitted when oxygen-19 gives off a beta particle is 0.197 MeV. What is its energy in joules? (See Exercise 13 for the definition of a megaelectron volt.)
15. Which penetrates matter more deeply—alpha particles or beta particles? Suggest ways to protect yourself against both particles.
16. Which penetrates matter more deeply—alpha particles or gamma rays? Suggest ways to protect yourself against both emissions.
17. Define *nuclear fission*.
18. What general characteristic is typically necessary for a nucleus to undergo spontaneous fission?

Answers

1. Radioactivity is the spontaneous emission of particles and electromagnetic radiation from nuclei of unstable atoms.
2.
3. a. 5 protons; 6 neutrons
   b. 13 protons; 14 neutrons
   c. 26 protons; 30 neutrons
   d. 86 protons; 138 neutrons
4.
5. An alpha particle is a collection of two protons and two neutrons and is equivalent to a helium nucleus.
6.
7. Gamma rays are high-energy electromagnetic radiation given off in radioactive decay.
8.
9. ${}^{244}_{94}\mathrm{Pu} \rightarrow {}^{240}_{92}\mathrm{U} + {}^{4}_{2}\mathrm{He}$

daughter isotope: ${}^{240}\mathrm{U}$

10.
11. $^{121}_{50}\text{Sn} \rightarrow \, ^{121}_{51}\text{Sb} + \, ^{0}_{-1}\text{e}$

daughter isotope: ^{121}Sb

12.
13. 0.51 MeV
14.
15. Beta particles penetrate more. A thick wall of inert matter is sufficient to block both particles.
16.
17. Nuclear fission is the breaking down of large nuclei into smaller nuclei, usually with the release of excess neutrons.
18.

14.3: Half-Life

1. Do all isotopes have a half-life? Explain your answer.
2. Which is more radioactive—an isotope with a long half-life or an isotope with a short half-life?
3. How long does it take for 1.00 g of palladium-103 to decay to 0.125 g if its half-life is 17.0 d?
4. How long does it take for 2.00 g of niobium-94 to decay to 0.0625 g if its half-life is 20,000 y?
5. It took 75 y for 10.0 g of a radioactive isotope to decay to 1.25 g. What is the half-life of this isotope?
6. It took 49.2 s for 3.000 g of a radioactive isotope to decay to 0.1875 g. What is the half-life of this isotope?
7. The half-live of americium-241 is 432 y. If 0.0002 g of americium-241 is present in a smoke detector at the date of manufacture, what mass of americium-241 is present after 100.0 y? After 1,000.0 y?
8. If the half-life of tritium (hydrogen-3) is 12.3 y, how much of a 0.00444 g sample of tritium is present after 5.0 y? After 250.0 y?
9. Explain why the amount left after 1,000.0 y in Exercise 7 is not one-tenth of the amount present after 100.0 y, despite the fact that the amount of time elapsed is 10 times as long.
10. Explain why the amount left after 250.0 y in Exercise 8 is not one-fiftieth of the amount present after 5.0 y, despite the fact that the amount of time elapsed is 50 times as long.
11. An artifact containing carbon-14 contains 8.4×10^{-9} g of carbon-14 in it. If the age of the artifact is 10,670 y, how much carbon-14 did it have originally? The half-life of carbon-14 is 5,730 y.
12. Carbon-11 is a radioactive isotope used in positron emission tomography (PET) scans for medical diagnosis. Positron emission is another, though rare, type of radioactivity. The half-life of carbon-11 is 20.3 min. If 4.23×10^{-6} g of carbon-11 is left in the body after 4.00 h, what mass of carbon-11 was present initially?

Answers

1. Only radioactive isotopes have a half-life.
2.
3. 51.0 d
4.
5. 25 y
6.
7. 0.000170 g; 0.0000402 g
8.
9. Radioactive decay is an exponential process, not a linear process.
10.
11. 3.1×10^{-8} g
12.

14.4: Applications of Nuclear Chemistry

1. Define *tracer* and give an example of how tracers work.
2. Name two isotopes that have been used as tracers.
3. Explain how radioactive dating works.
4. Name two isotopes that have been used in radioactive dating.

5. The current disintegration rate for carbon-14 is 14.0 Bq. A sample of burnt wood discovered in an archeological excavation is found to have a carbon-14 disintegration rate of 3.5 Bq. If the half-life of carbon-14 is 5,730 y, approximately how old is the wood sample?
6. A small asteroid crashes to Earth. After chemical analysis, it is found to contain 1 g of technetium-99 to every 3 g of ruthenium-99, its daughter isotope. If the half-life of technetium-99 is 210,000 y, approximately how old is the asteroid?
7. What is a positive aspect of the irradiation of food?
8. What is a negative aspect of the irradiation of food?
9. Describe how iodine-131 is used to both diagnose and treat thyroid problems.
10. List at least five organs that can be imaged using radioactive isotopes.
11. Which radioactive emissions can be used therapeutically?
12. Which isotope is used in therapeutics primarily for its gamma ray emissions?

Answers

1. A tracer is a radioactive isotope that can be detected far from its original source to trace the path of certain chemicals. Hydrogen-3 can be used to trace the path of water underground.
2.
3. If the initial amount of a radioactive isotope is known, then by measuring the amount of the isotope remaining, a person can calculate how old that object is since it took up the isotope.
4.
5. 11,500 y
6.
7. increased shelf life (answers will vary)
8.
9. The thyroid gland absorbs most of the iodine, allowing it to be imaged for diagnostic purposes or preferentially irradiated for treatment purposes.
10.
11. gamma rays

_xx_ delete-test

Learning Objectives

- Describe how electrons are grouped within atoms.
- Write electron configurations for atoms.
- Connect the electron configuration of atoms to the energy levels of the electrons in the atom.

Previously we discussed the concept of electron shells and subshells. It is the arrangement of electrons into shells and subshells that most concerns us here, so we will focus on that.

General Rules of Electron Configuration

There are a set of general rules that are used to figure out the electron configuration of an atomic species: **Aufbau Principle**, **Hund's Rule** and the **Pauli-Exclusion Principle**. Before continuing, it's important to understand that each orbital can be occupied by *two* electrons.

- Rule 1 (Aufbau Principle): Electrons occupy the lowest-energy orbitals possible, starting with 1s and continuing in the order dictated by quantum mechanics
- Rule 2 (Hund's Rule): Electrons occupy degenerate orbitals (i.e. same n and ℓ quantum numbers), they must first occupy the empty orbitals before double occupying them. Furthermore, the most stable configuration results when the spins are parallel (i.e. all same m_s quantum numbers).
- Rule 3 (Pauli-Exclusion Principle): Each electron can be described with a unique set of four quantum numbers. Therefore, if two electrons occupy the same orbital, they have different spin - spin up or spin down.

Electron Configurations

Electron configurations are are shorthand descriptions of the arrangements of electrons in atoms. An example electron configuration with its general structure is shown in Figure 1. In electron configurations, we use numbers to indicate which shell an electron is in.

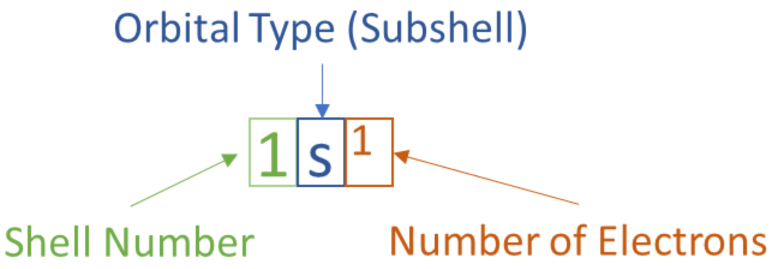


Figure 1: General structure of electron configurations.

As shown in Table 1, the first shell, closest to the nucleus and with the lowest-energy electrons, is shell 1. This first shell has only one subshell, which is labeled 1*s* and can hold a maximum of 2 electrons. We combine the shell and subshell labels when referring to the organization of electrons about a nucleus and use a superscript to indicate how many electrons are in a subshell. Thus, because a hydrogen atom has its single electron in the *s* subshell of the first shell, we use $\mathbf{1s^1}$ to describe the electronic structure of hydrogen.

Table 1: Shells and Subshells

Shell	Number of Subshells	Names of Subshells
1	1	*1s*
2	2	*2s* and *2p*
3	3	*3s*, *3p* and *3d*

Shell	Number of Subshells	Names of Subshells
4	4	*4s*, *4p*, *4d* and *4f*

Helium atoms have 2 electrons. Both electrons fit into the 1*s* subshell because *s* subshells can hold up to 2 electrons; therefore, the electron configuration for helium atoms is **$1s^2$** (spoken as “one-ess-two”). Different subshells hold a different maximum number of electrons. Any s subshell can hold up to 2 electrons; p, 6; d, 10; and f, 14 (Table 2). Hence, the 1*s* subshell cannot hold 3 electrons (because an *s* subshell can hold a maximum of 2 electrons), so the electron configuration for a lithium atom cannot be $1s^3$ (Figure 2). Two of the lithium electrons can fit into the 1*s* subshell, but the third electron must go into the second shell. The second shell has two subshells, *s* and *p*, which fill with electrons in that order. The 2*s* subshell holds a maximum of 2 electrons, and the 2*p* subshell holds a maximum of 6 electrons. Because lithium’s final electron goes into the 2*s* subshell, we write the electron configuration of a lithium atom as **$1s^22s^1$.** The shell diagram for a lithium atom (Figure 1). The shell closest to the nucleus (first shell) has 2 dots representing the 2 electrons in **1*s***, while the outermost shell (**2*s***) has 1 electron.

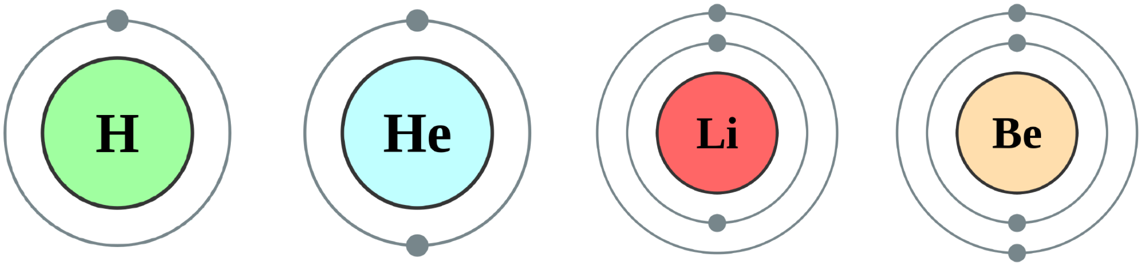


Figure 2: Shell diagrams of hydrogen (H), helium (He), lithium (Li), and Berryellium (Be) atoms. (CC BY-SA 2.0 UK; Greg Robson modified by Pumbaa via Wikipedia)

Table 2: Number of Electrons in subshells

Subshell	Maximum Number of Electrons
s	2
p	6
d	10
f	14

The next largest atom, beryllium, has 4 electrons, so its electron configuration is $1s^22s^2$. Now that the 2*s* subshell is filled, electrons in larger atoms start filling the 2*p* subshell. With neon, the 2*p* subshell is completely filled. Because the second shell has only two subshells, atoms with more electrons now must begin the third shell. The third shell has three subshells, labeled *s*, *p*, and *d*. The *d* subshell can hold a maximum of 10 electrons. The first two subshells of the third shell are filled in order—for example, the electron configuration of aluminum, with 13 electrons, is $1s^22s^22p^63s^23p^1$. However, a curious thing happens after the 3*p* subshell is filled: the 4*s* subshell begins to fill before the 3*d* subshell does. In fact, the exact ordering of subshells becomes more complicated at this point (after argon, with its 18 electrons), so we will not consider the electron configurations of larger atoms. A fourth subshell, the *f* subshell, is needed to complete the electron configurations for all elements. An *f* subshell can hold up to 14 electrons.

Table 3: Atomic Electron Configurations

Z	Element	Outer most Shell	Configuration	Noble Gas Configuration
1	H	1	$1s^1$	$1s^1$
2	He	1	$1s^2$	$1s^2$
3	Li	2	$1s^2 2s^1$	[He] $2s^1$
4	Be	2	$1s^2 2s^2$	[He] $2s^2$
5	B	2	$1s^2 2s^2 2p^1$	[He] $2s^2 2p^1$
6	C	2	$1s^2 2s^2 2p^2$	[He] $2s^2 2p^2$

Z	Element	Outer most Shell	Configuration	Noble Gas Configuration
7	N	2	$1s^2 2s^2 2p^3$	[He] $2s^2 2p^3$
8	O	2	$1s^2 2s^2 2p^4$	[He] $2s^2 2p^4$
9	F	2	$1s^2 2s^2 2p^5$	[He] $2s^2 2p^5$
10	Ne	2	$1s^2 2s^2 2p^6$	[He] $2s^2 2p^6$
11	Na	3	$1s^2 2s^2 2p^6 3s^1$	[Ne] $3s^1$
12	Mg	3	$1s^2 2s^2 2p^6 3s^2$	[Ne] $3s^2$
13	Al	3	$1s^2 2s^2 2p^6 3s^2 3p^1$	[Ne] $3s^2 3p^1$
14	Si	3	$1s^2 2s^2 2p^6 3s^2 3p^2$	[Ne]$3s^2 3p^2$
15	P	3	$1s^2 2s^2 2p^6 3s^2 3p^3$	[Ne] $3s^2 3p^3$
16	S	3	$1s^2 2s^2 2p^6 3s^2 3p^4$	[Ne] $3s^2 3p^4$
17	Cl	3	$1s^2 2s^2 2p^6 3s^2 3p^5$	[Ne] $3s^2 3p^5$
18	Ar	3	$1s^2 2s^2 2p^6 3s^2 3p^6$	[Ne] $3s^2 3p^6$
19	K	4	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$	[Ar] $4s^1$
20	Ca	4	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$	[Ar] $4s^2$

Electron filling always starts with **1*s***, the subshell closest to the nucleus. Next is **2*s*, 2*p*, 3*s*, 3*p*, 4*s*, 3*d***, **4*p***, **5s, 4d, 5p, 6s,** etc., shown in the electron shell filling order diagram in Figure 3. Follow each arrow in order **from top to bottom**. The subshells you reach along each arrow give the ordering of filling of subshells in larger atoms.

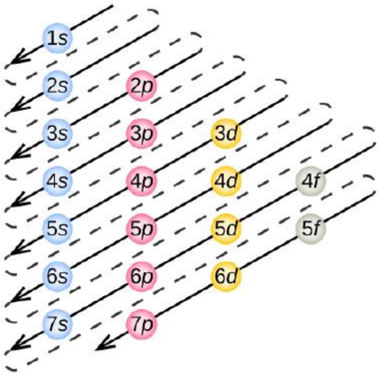


Figure 3: The order of electron filling in an atom.

Noble Gas Configuration

The electron configuration of sodium is $1s^2 2s^2 2p^6 3s^1$ (Table 3). The first ten electrons of the sodium atom are the inner-shell electrons and the configuration of just those ten electrons is exactly the same as the configuration of the element neon $(Z = 10)$. This provides the basis for a shorthand notation for electron configurations called the **noble gas configuration**, which atom consists of the elemental symbol of the last noble gas prior to that atom, followed by the configuration of the remaining electrons. So for sodium, we make the substitution of $[\mathrm{Ne}]$ for the $1s^2 2s^2 2p^6$ part of the configuration. Sodium's noble gas configuration becomes $[\mathrm{Ne}]\,3s^1$. Table 1 shows the noble gas configurations of the third period elements.

Electron Configurations and Orbital Diagrams

We construct the periodic table by following the aufbau principle (from German, meaning “building up”). First we determine the number of electrons in the atom; then we add electrons one at a time to the lowest-energy orbital available *without violating the Pauli principle*. We use the orbital energy diagram of Figure 1, recognizing that each orbital can hold two electrons, one with spin up ↑, corresponding to $m_s = +½$, which is arbitrarily written first, and one with spin down ↓, corresponding to $m_s = −½$. A filled orbital is indicated by ↑↓, in which the electron spins are said to be *paired*. Here is a schematic orbital diagram for a hydrogen atom in its ground state:

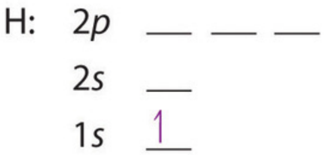
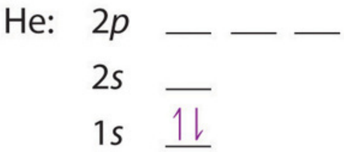


Figure 1: One electron in.

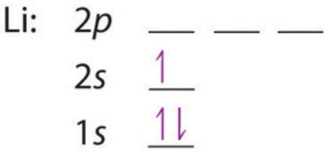
From the orbital diagram, we can write the electron configuration in an abbreviated form in which the occupied orbitals are identified by their principal quantum number *n* and their value of *l* (*s*, *p*, *d*, or *f*), with the number of electrons in the subshell indicated by a superscript. For hydrogen, therefore, the single electron is placed in the 1*s* orbital, which is the orbital lowest in energy (Figure 1), and the electron configuration is written as $1s^1$ and read as "one-s-one."

A neutral helium atom, with an atomic number of 2 ($Z = 2$), has two electrons. We place one electron in the orbital that is lowest in energy, the 1*s* orbital. From the Pauli exclusion principle, we know that an orbital can contain two electrons with opposite spin, so we place the second electron in the same orbital as the first but pointing down, so that the electrons are paired. The orbital diagram for the helium atom is therefore



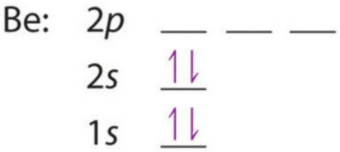
written as $1s^2$, where the superscript 2 implies the pairing of spins. Otherwise, our configuration would violate the Pauli principle.

The next element is lithium, with $Z = 3$ and three electrons in the neutral atom. We know that the 1*s* orbital can hold two of the electrons with their spins paired; the third electron must enter a higher energy orbital. Figure 6.29 tells us that the next lowest energy orbital is 2*s*, so the orbital diagram for lithium is

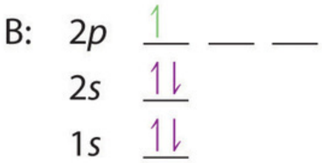


This electron configuration is written as $1s^22s^1$.

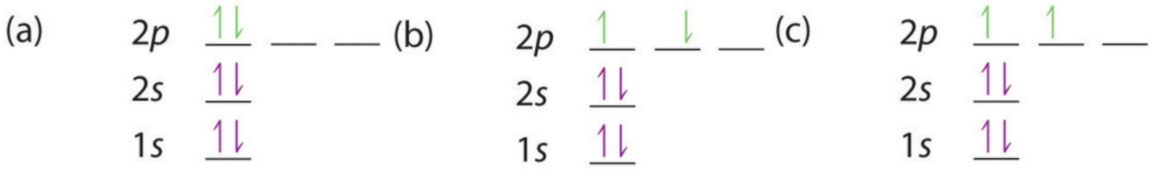
The next element is beryllium, with $Z = 4$ and four electrons. We fill both the 1*s* and 2*s* orbitals to achieve a $1s^22s^2$ electron configuration:



When we reach boron, with $Z = 5$ and five electrons, we must place the fifth electron in one of the 2*p* orbitals. Because all three 2*p* orbitals are degenerate, it doesn't matter which one we select. The electron configuration of boron is $1s^22s^22p^1$:

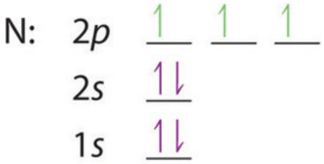


At carbon, with $Z = 6$ and six electrons, we are faced with a choice. Should the sixth electron be placed in the same 2*p* orbital that already has an electron, or should it go in one of the empty 2*p* orbitals? If it goes in an empty 2*p* orbital, will the sixth electron have its spin aligned with or be opposite to the spin of the fifth? In short, which of the following three orbital diagrams is correct for carbon, remembering that the 2*p* orbitals are degenerate?



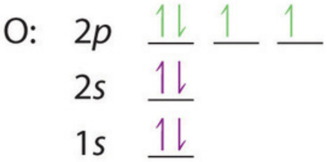
Because of electron-electron interactions, it is more favorable energetically for an electron to be in an unoccupied orbital than in one that is already occupied; hence we can eliminate choice a. Similarly, experiments have shown that choice b is slightly higher in energy (less stable) than choice c because electrons in degenerate orbitals prefer to line up with their spins parallel; thus, we can eliminate choice b. Choice c illustrates **Hund's rule** (named after the German physicist Friedrich H. Hund, 1896–1997), which today says that the lowest-energy electron configuration for an atom is the one that has the maximum number of electrons with parallel spins in degenerate orbitals. By Hund's rule, the electron configuration of carbon, which is $1s^22s^22p^2$, is understood to correspond to the orbital diagram shown in c. Experimentally, it is found that the ground state of a neutral carbon atom does indeed contain two unpaired electrons.

When we get to nitrogen (Z = 7, with seven electrons), Hund's rule tells us that the lowest-energy arrangement is

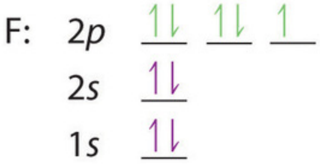


with three unpaired electrons. The electron configuration of nitrogen is thus $1s^22s^22p^3$.

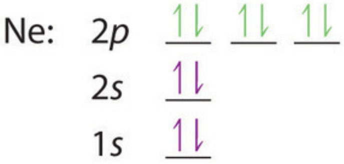
At oxygen, with Z = 8 and eight electrons, we have no choice. One electron must be paired with another in one of the 2p orbitals, which gives us two unpaired electrons and a $1s^22s^22p^4$ electron configuration. Because all the 2p orbitals are degenerate, it doesn't matter which one has the pair of electrons.



Similarly, fluorine has the electron configuration $1s^22s^22p^5$:



When we reach neon, with Z = 10, we have filled the 2p subshell, giving a $1s^22s^22p^6$ electron configuration:



Notice that for neon, as for helium, all the orbitals through the 2p level are completely filled. This fact is very important in dictating both the chemical reactivity and the bonding of helium and neon, as you will see.

Example : Electronic Configuration of Phosphorus Atoms

Using Figure 2 as your guide, write the electron configuration of a neutral phosphorus atom. The atomic number of P is 15.

Solution

A neutral phosphorus atom has 15 electrons. Two electrons can go into the 1*s* subshell, 2 can go into the 2*s* subshell, and 6 can go into the 2*p* subshell. That leaves 5 electrons. Of those 5 electrons, 2 can go into the 3*s* subshell, and the remaining 3 electrons can go into the 3*p* subshell. Thus, the electron configuration of neutral phosphorus atoms is $1s^2 2s^2 2p^6 3s^2 3p^3$.

Exercise : Electronic Configuration of Chlorine Atoms

Using Figure 2 as your guide, write the electron configuration of a neutral chlorine atom. The atomic number of Cl is 17.

Answer

A neutral chlorine atom has 17 electrons. Two electrons can go into the 1*s* subshell, 2 can go into the 2*s* subshell, and 6 can go into the 2*p* subshell. That leaves 7 electrons. Of those 7 electrons, 2 can go into the 3*s* subshell, and the remaining 5 electrons can go into the 3*p* subshell. Thus, the electron configuration of neutral chlorine atoms is $1s^2 2s^2 2p^6 3s^2 3p^5$.

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