OIT: CHE 101 - INTRODUCTION TO GENERAL CHEMISTRY



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OIT: CHE 101 - Introduction to General Chemistry

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1: MAKING MEASUREMENTS

Most everything you do and encounter during your day involves chemistry. Making coffee, cooking eggs, and toasting bread involve chemistry. The products you use—like soap and shampoo, the fabrics you wear, the electronics that keep you connected to your world, the gasoline that propels your car—all of these and more involve chemical substances and processes. Whether you are aware or not, chemistry is part of your everyday world. In this course, you will learn many of the essential principles underlying the chemistry of modern-day life.

Unit 1 Objectives

By the end of this unit, you will be able to:

- Solve dimensional analysis using metric and English units. (note: metric unit definitions will not be provided on quiz.)
- Identify the appropriate metric unit for measuring items of various dimensions.
- Calculate area, volume, density, and thickness and convert to various units.
- Perform calculations involving heat, specific heat, and temperature change.
- Calculate heat in calories, kilocalories, dietary calories and Joules.
- Record measurements and perform calculations to the correct significance with appropriate units.

1.1: Measurements

1.2: Measurement Uncertainty, Accuracy, and Precision

1.3: Conversions

1.4: Volume, Thickness, and Density

1.5: Energy Basics

1.6: Calorimetry

1.7: Unit 1 Practice Problems

Contributors

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- Christy VanRooyen, Oregon Tech

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1.1: Measurements

Learning Objectives

- Identify the appropriate metric unit for measuring items of various dimensions.
- Solve dimensional analysis using metric and English units. (note: metric unit definitions will not be provided on quiz.)

Measurements provide the macroscopic information that is the basis of most of the hypotheses, theories, and laws that describe the behavior of matter and energy in both the macroscopic and microscopic domains of chemistry. Every measurement provides three kinds of information: the size or magnitude of the measurement (a number); a standard of comparison for the measurement (a unit); and an indication of the uncertainty of the measurement. While the number and unit are explicitly represented when a quantity is written, the uncertainty is an aspect of the measurement result that is more implicitly represented and will be discussed later.

The number in the measurement can be represented in different ways, including decimal form and scientific notation. For example, the maximum takeoff weight of a Boeing 777-200ER airliner is 298,000 kilograms, which can also be written as 2.98×10^5 kg. The mass of the average mosquito is about 0.00000025 kilograms, which can be written as 2.5×10^{-6} kg.

Units, such as liters, pounds, and centimeters, are standards of comparison for measurements. When we buy a 2-liter bottle of a soft drink, we expect that the volume of the drink was measured, so it is two times larger than the volume that everyone agrees to be 1 liter. The meat used to prepare a 0.25-pound hamburger is measured so it weighs one-fourth as much as 1 pound. Without units, a number can be meaningless, confusing, or possibly life threatening. Suppose a doctor prescribes phenobarbital to control a patient's seizures and states a dosage of "100" without specifying units. Not only will this be confusing to the medical professional giving the dose, but the consequences can be dire: 100 mg given three times per day can be effective as an anticonvulsant, but a single dose of 100 g is more than 10 times the lethal amount.

We usually report the results of scientific measurements in SI units, an updated version of the metric system, using the units listed in Table 1.1.1. Other units can be derived from these base units. The standards for these units are fixed by international agreement, and they are called the International System of Units or SI Units (from the French, *Le Système International d'Unités*). SI units have been used by the United States National Institute of Standards and Technology (NIST) since 1964.

***Table** 1.1.1**:** Base Units of the SI System*

Property Measured	Name of Unit	Symbol of Unit
length	meter	m
mass	kilogram	kg
time	second	s
temperature	kelvin	K
electric current	ampere	A
amount of substance	mole	mol
luminous intensity	candela	cd

Sometimes we use units that are fractions or multiples of a base unit. Ice cream is sold in quarts (a familiar, non-SI base unit), pints (0.5 quart), or gallons (4 quarts). We also use fractions or multiples of units in the SI system, but these fractions or multiples are always powers of 10. Fractional or multiple SI units are named using a prefix and the name of the base unit. For example, a length of 1000 meters is also called a kilometer because the prefix *kilo* means "one thousand," which in scientific notation is 10^3 (1 kilometer = 1000 m = 10^3 m). The prefixes used and the powers to which 10 are raised are listed in Table 1.1.2.

Table 1.1.2***:*** *Common Unit Prefixes*

Prefix	Symbol	Factor	Example
angstrom	Å	10^{-10}	5 angstrom (Å) =5 × 10^{-10} m (0.0000000001 m)
nano	n	10^{-9}	1 nanogram (ng) = 1 × 10^{-9} g (0.000000001 g)
micro	μ	10^{-6}	1 microliter (μL) = 1 × 10^{-6} L (0.000001 L)
milli	m	10^{-3}	2 millimoles (mmol) = 2 × 10^{-3} mol (0.002 mol)
centi	c	10^{-2}	7 centimeters (cm) = 7 × 10^{-2} m (0.07 m)
deci	d	10^{-1}	1 deciliter (dL) = 1 × 10^{-1} L (0.1 L)
kilo	k	10^{3}	1 kilometer (km) = 1 × 10^{3} m (1000 m)
mega	M	10^{6}	3 megahertz (MHz) = 3 × 10^{6} Hz (3,000,000 Hz)

SI Base Units

The initial units of the metric system, which eventually evolved into the SI system, were established in France during the French Revolution. The original standards for the meter and the kilogram were adopted there in 1799 and eventually by other countries. This section introduces four of the SI base units commonly used in chemistry. Other SI units will be introduced in subsequent chapters.

Length

The standard unit of length in both the SI and original metric systems is the meter (m). A meter was originally specified as 1/10,000,000 of the distance from the North Pole to the equator. It is now defined as the distance light in a vacuum travels in 1/299,792,458 of a second. A meter is about 3 inches longer than a yard (Figure 1.1.1); one meter is about 39.37 inches or 1.094 yards. Longer distances are often reported in kilometers (1 km = 1000 m = 10^{3} m), whereas shorter distances can be reported in centimeters (1 cm = 0.01 m = 10^{-2} m) or millimeters (1 mm = 0.001 m = 10^{-3} m).

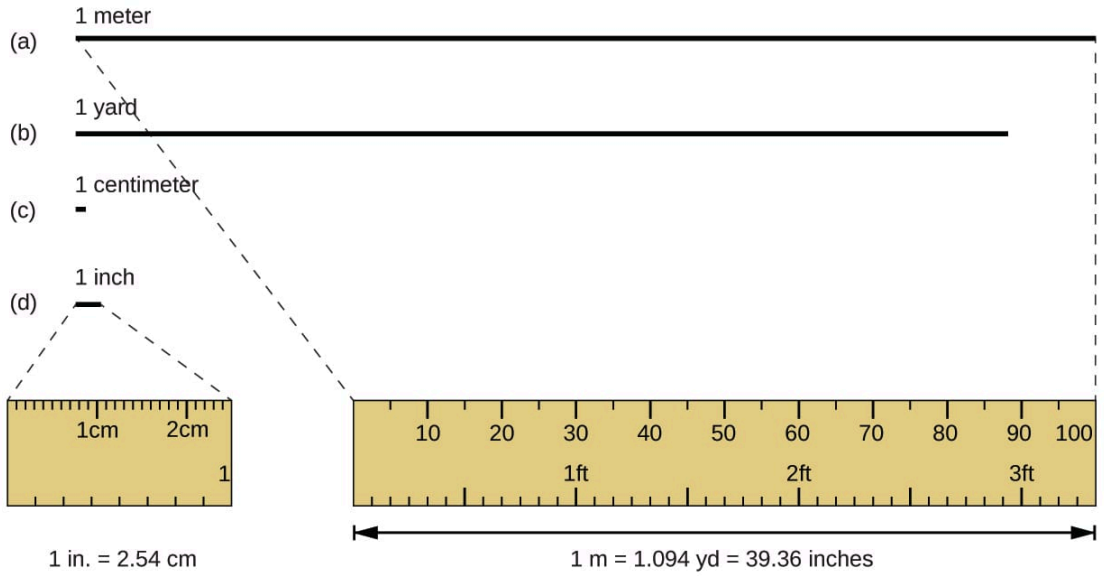


Figure 1.1.1: The relative lengths of 1 m, 1 yd, 1 cm, and 1 in. are shown (not actual size), as well as comparisons of 2.54 cm and 1 in., and of 1 m and 1.094 yd.

Mass

The standard unit of mass in the SI system is the kilogram (kg). A kilogram was originally defined as the mass of a liter of water (a cube of water with an edge length of exactly 0.1 meter). In 1889, it was redefined by a certain cylinder of platinum-iridium alloy, which was kept in France (Figure 1.1.2). Any object with the same mass as this cylinder was said to have a mass of 1 kilogram (which can lead to uncertainties unacceptable to the precision of modern instrumentation). One kilogram is about 2.2 pounds. The gram (g) is exactly equal to 1/1000 of the mass of the kilogram (10^{-3} kg). Over the past 100 years, the IPK has lost 50 millionths of a gram - a seemingly negligible amount, but something that has caused it to be lighter - or all standard replicas to be heavier - and changing the definition of a kilogram in the process. As all balances in the world are standardized to this value, it is important that this value, itself, be standard. On May 20, 2019, a new definition will be used for the kilogram, based on the unchanging Planck's constant.[1]



***Figure** 1.1.2**:** This replica prototype kilogram is housed at the National Institute of Standards and Technology (NIST) in Maryland. (credit: National Institutes of Standards and Technology).*

YouTube Video

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

View this YouTube Video online

Video** 1.1.2**: For more information on the new definition of the kilogram, check out this video!

Temperature

Temperature is an intensive property. The SI unit of temperature is the kelvin (K). The IUPAC convention is to use kelvin (all lowercase) for the word, K (uppercase) for the unit symbol, and neither the word “degree” nor the degree symbol (°). The degree Celsius (°C) is also allowed in the SI system, with both the word “degree” and the degree symbol used for Celsius measurements. Celsius degrees are the same magnitude as those of kelvin, but the two scales place their zeros in different places. Water freezes at 273.15 K (0 °C) and boils at 373.15 K (100 °C) by definition, and normal human body temperature is approximately 310 K (37 °C). The conversion between these two units and the Fahrenheit scale will be discussed later in this chapter.

Time

The SI base unit of time is the second (s). Small and large time intervals can be expressed with the appropriate prefixes; for example, 3 microseconds = 0.000003 s = 3×10^{-6} and 5 megaseconds = 5,000,000 s = 5×10^{6} s. Alternatively, hours, days, and years can be used.

Volume

Volume is the measure of the amount of space occupied by an object. The standard SI unit of volume is defined by the base unit of length (Figure 1.1.3). The standard volume is a cubic meter (m^3), a cube with an edge length of exactly one meter. To dispense a cubic meter of water, we could build a cubic box with edge lengths of exactly one meter. This box would hold a cubic meter of water or any other substance.

A more commonly used unit of volume is derived from the decimeter (0.1 m, or 10 cm). A cube with edge lengths of exactly one decimeter contains a volume of one cubic decimeter (dm^3). A liter (L) is the more common name for the cubic decimeter. One liter is about 1.06 quarts. A cubic centimeter (cm^3) is the volume of a cube with an edge length of exactly one centimeter. The abbreviation **cc** (for **c**ubic **c**entimeter) is often used by health professionals. A cubic centimeter is also called a milliliter (mL) and is 1/1000 of a liter.

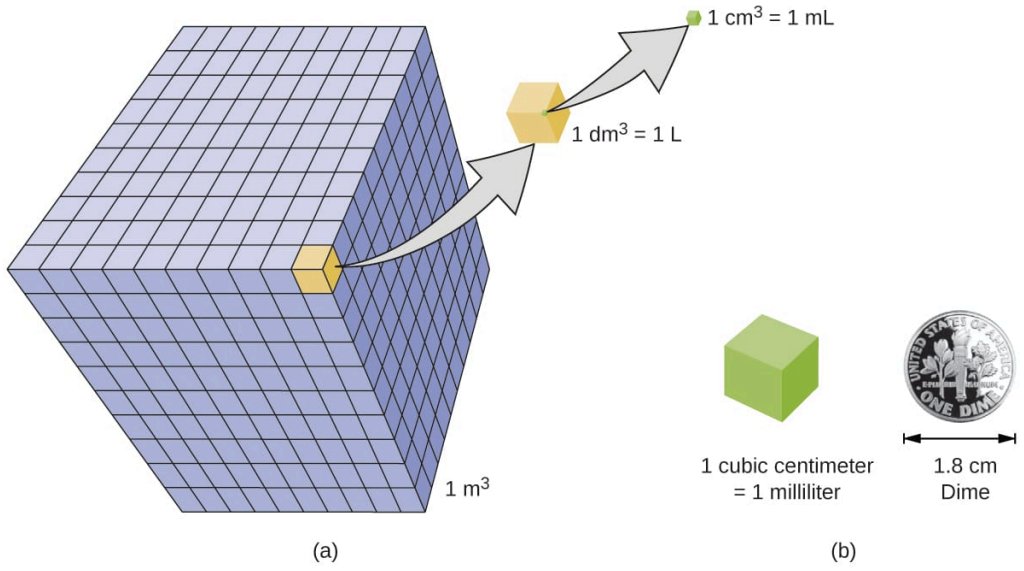


Figure 1.1.3: (a) The relative volumes are shown for cubes of 1 m^3, 1 dm^3 (1 L), and 1 cm^3 (1 mL) (not to scale). (b) The diameter of a dime is compared relative to the edge length of a 1-cm^3 (1-mL) cube.

Summary

Measurements provide quantitative information that is critical in studying and practicing chemistry. Each measurement has an amount, a unit for comparison, and an uncertainty. Measurements can be represented in either decimal or scientific notation. Scientists primarily use the SI (International System) or metric systems. We use base SI units such as meters, seconds, and kilograms, as well as derived units, such as liters (for volume) and g/cm^3 (for density). In many cases, we find it convenient to use unit prefixes that yield fractional and multiple units, such as microseconds (10^{-6} seconds) and megahertz (10^{6} hertz), respectively.

Glossary

Celsius (°C)
unit of temperature; water freezes at 0 °C and boils at 100 °C on this scale

cubic centimeter (cm^3 or cc)
volume of a cube with an edge length of exactly 1 cm

cubic meter (m^3)
SI unit of volume

kelvin (K)
SI unit of temperature; 273.15 K = 0 °C

kilogram (kg)
standard SI unit of mass; 1 kg = approximately 2.2 pounds

length
measure of one dimension of an object

liter (L)
(also, cubic decimeter) unit of volume; 1 L = 1,000 cm^3

meter (m)
standard metric and SI unit of length; 1 m = approximately 1.094 yards

milliliter (mL)
1/1,000 of a liter; equal to 1 cm^3

second (s)
SI unit of time

SI units (International System of Units)
standards fixed by international agreement in the International System of Units (*Le Système International d'Unités*)

unit
standard of comparison for measurements

volume
amount of space occupied by an object

Contributors

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- Christy VanRooyen, Oregon Tech
- Crash Course Chemistry: Crash Course is a division of Complexly and videos are free to stream for educational purposes.
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1.2: Measurement Uncertainty, Accuracy, and Precision

Learning Objectives

- Record measurements and perform calculations to the correct significance with appropriate units.
- Identify and describe common equipment used in the chemistry lab.

Counting is the only type of measurement that is free from uncertainty, provided the number of objects being counted does not change while the counting process is underway. The result of such a counting measurement is an example of an exact number. If we count eggs in a carton, we know *exactly* how many eggs the carton contains. The numbers of defined quantities are also exact. By definition, 1 foot is exactly 12 inches, 1 inch is exactly 2.54 centimeters, and 1 gram is exactly 0.001 kilogram. Quantities derived from measurements other than counting, however, are uncertain to varying extents due to practical limitations of the measurement process used.

Significant Figures in Measurement

The numbers of measured quantities, unlike defined or directly counted quantities, are not exact. To measure the volume of liquid in a graduated cylinder, you should make a reading at the bottom of the meniscus, the lowest point on the curved surface of the liquid.

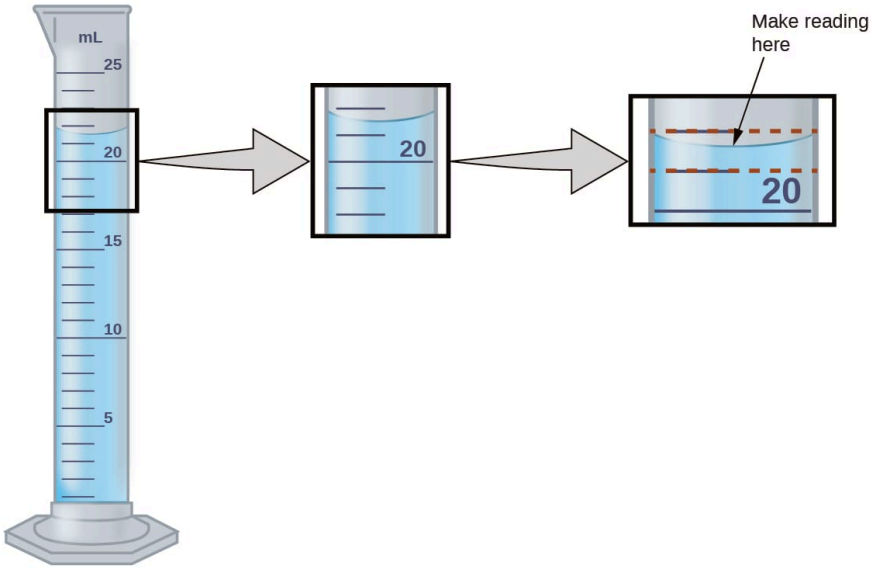


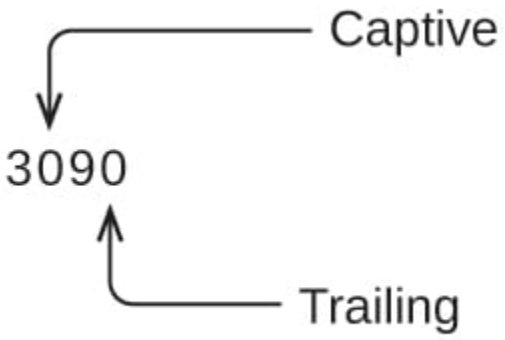
Figure 1.2.1**:** To measure the volume of liquid in this graduated cylinder, you must mentally subdivide the distance between the 21 and 22 mL marks into tenths of a milliliter, and then make a reading (estimate) at the bottom of the meniscus.

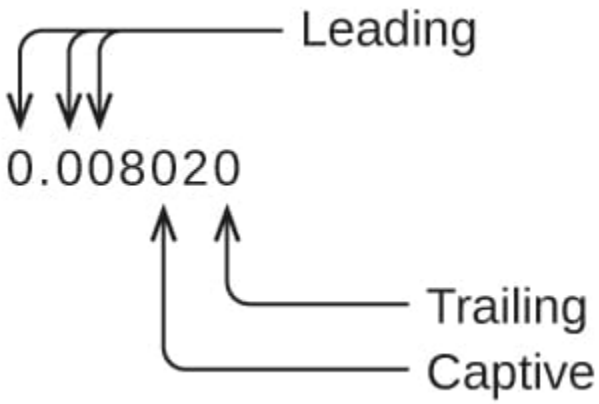
Refer to the illustration in Figure 1.2.1. The bottom of the meniscus in this case clearly lies between the 21 and 22 markings, meaning the liquid volume is *certainly* greater than 21 mL but less than 22 mL. The meniscus appears to be a bit closer to the 22-mL mark than to the 21-mL mark, and so a reasonable estimate of the liquid's volume would be 21.6 mL. In the number 21.6, then, the digits 2 and 1 are certain, but the 6 is an estimate. Some people might estimate the meniscus position to be equally distant from each of the markings and estimate the tenth-place digit as 5, while others may think it to be even closer to the 22-mL mark and estimate this digit to be 7. Note that it would be pointless to attempt to estimate a digit for the hundredths place, given that the tenths-place digit is uncertain. In general, numerical scales such as the one on this graduated cylinder will permit measurements to one-tenth of the smallest scale division. The scale in this case has 1-mL divisions, and so volumes may be measured to the nearest 0.1 mL.

This concept holds true for all measurements, even if you do not actively make an estimate. If you place a quarter on a standard

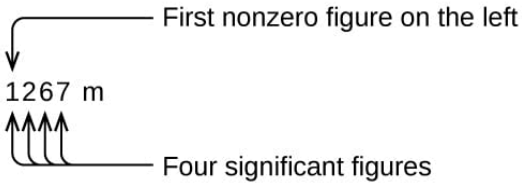
electronic balance, you may obtain a reading of 6.72 g. The digits 6 and 7 are certain, and the 2 indicates that the mass of the quarter is likely between 6.71 and 6.73 grams. The quarter weighs *about* 6.72 grams, with a nominal uncertainty in the measurement of ± 0.01 gram. If we weigh the quarter on a more sensitive balance, we may find that its mass is 6.723 g. This means its mass lies between 6.722 and 6.724 grams, an uncertainty of 0.001 gram. Every measurement has some uncertainty, which depends on the device used (and the user's ability). All of the digits in a measurement, including the uncertain last digit, are called significant figures or significant digits. Note that zero may be a measured value; for example, if you stand on a scale that shows weight to the nearest pound and it shows "120," then the 1 (hundreds), 2 (tens) and 0 (ones) are all significant (measured) values.

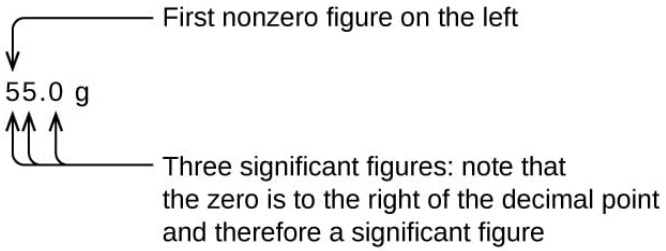
Whenever you make a measurement properly, all the digits in the result are significant. But what if you were analyzing a reported value and trying to determine what is significant and what is not? Well, for starters, all nonzero digits are significant, and it is only zeros that require some thought. We will use the terms "leading," "trailing," and "captive" for the zeros and will consider how to deal with them.



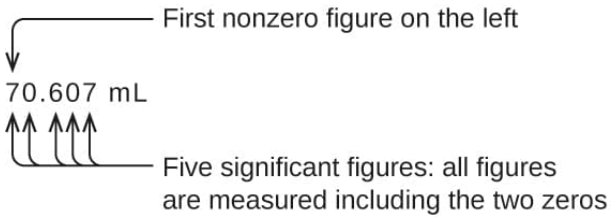


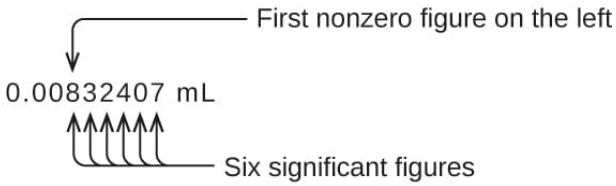
Starting with the first nonzero digit on the left, count this digit and all remaining digits to the right. This is the number of significant figures in the measurement unless the last digit is a trailing zero lying to the left of the decimal point.





Captive zeros result from measurement and are therefore always significant. Leading zeros, however, are never significant—they merely tell us where the decimal point is located.

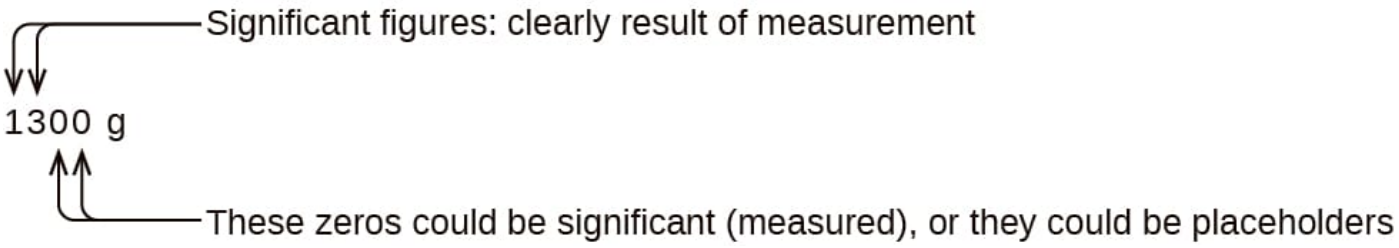




The leading zeros in this example are not significant. We could use exponential notation (as described in Appendix B) and express the number as 8.32407×10^{-3}; then the number 8.32407 contains all of the significant figures, and 10^{-3} locates the decimal point.

The number of significant figures is uncertain in a number that ends with a zero to the left of the decimal point location. The

zeros in the measurement 1,300 grams could be significant or they could simply indicate where the decimal point is located. The ambiguity can be resolved with the use of exponential notation: 1.3×10^3 (two significant figures), 1.30×10^3 (three significant figures, if the tens place was measured), or 1.300×10^3 (four significant figures, if the ones place was also measured). In cases where only the decimal-formatted number is available, it is prudent to assume that all trailing zeros are not significant.



When determining significant figures, be sure to pay attention to reported values and think about the measurement and significant figures in terms of what is reasonable or likely—that is, whether the value makes sense. For example, the official January 2014 census reported the resident population of the US as 317,297,725. Do you think the US population was correctly determined to the reported nine significant figures, that is, to the exact number of people? People are constantly being born, dying, or moving into or out of the country, and assumptions are made to account for the large number of people who are not actually counted. Because of these uncertainties, it might be more reasonable to expect that we know the population to within perhaps a million or so, in which case the population should be reported as 317 million, or 3.17×10^8 people.

Significant Figures in Calculations

A second important principle of uncertainty is that results calculated from a measurement are at least as uncertain as the measurement itself. We must take the uncertainty in our measurements into account to avoid misrepresenting the uncertainty in calculated results. One way to do this is to report the result of a calculation with the correct number of significant figures, which is determined by the following three rules for rounding numbers:

1. When we add or subtract numbers, we should round the result to the same number of decimal places as the number with the least number of decimal places (the least precise value in terms of addition and subtraction).
2. When we multiply or divide numbers, we should round the result to the same number of digits as the number with the least number of significant figures (the least precise value in terms of multiplication and division).
3. If the digit to be dropped (the one immediately to the right of the digit to be retained) is less than 5, we "round down" and leave the retained digit unchanged; if it is more than 5, we "round up" and increase the retained digit by 1; if the dropped digit *is* 5, we round up or down, whichever yields an even value for the retained digit. (The last part of this rule may strike you as a bit odd, but it's based on reliable statistics and is aimed at avoiding any bias when dropping the digit "5," since it is equally close to both possible values of the retained digit.)

The following examples illustrate the application of this rule in rounding a few different numbers to three significant figures:

- 0.028675 rounds "up" to 0.0287 (the dropped digit, 7, is greater than 5)
- 18.3384 rounds "down" to 18.3 (the dropped digit, 3, is less than 5)
- 6.8752 rounds "up" to 6.88 (the dropped digit is 5, and the retained digit is even)
- 92.85 rounds "down" to 92.8 (the dropped digit is 5, and the retained digit is even)

Let's work through these rules with a few examples.

Example 1.2.1: Rounding Numbers

Round the following to the indicated number of significant figures:

a. 31.57 (to two significant figures)
b. 8.1649 (to three significant figures)
c. 0.051065 (to four significant figures)
d. 0.90275 (to four significant figures)

Solution

a. 31.57 rounds “up” to 32 (the dropped digit is 5, and the retained digit is even)
b. 8.1649 rounds “down” to 8.16 (the dropped digit, 4, is less than 5)
c. 0.051065 rounds “down” to 0.05106 (the dropped digit is 5, and the retained digit is even)
d. 0.90275 rounds “up” to 0.9028 (the dropped digit is 5, and the retained digit is even)

Exercise 1.2.1

Round the following to the indicated number of significant figures:

a. 0.424 (to two significant figures)
b. 0.0038661 (to three significant figures)
c. 421.25 (to four significant figures)
d. 28,683.5 (to five significant figures)

Answer a

0.42

Answer b

0.00387

Answer c

421.2

Answer d

28,684

Example 1.2.2: Addition and Subtraction with Significant Figures Rule:

When we add or subtract numbers, we should round the result to the same number of decimal places as the number with the least number of decimal places (i.e., the least precise value in terms of addition and subtraction).

a. Add 1.0023 g and 4.383 g.
b. Subtract 421.23 g from 486 g.

Solution

(a)

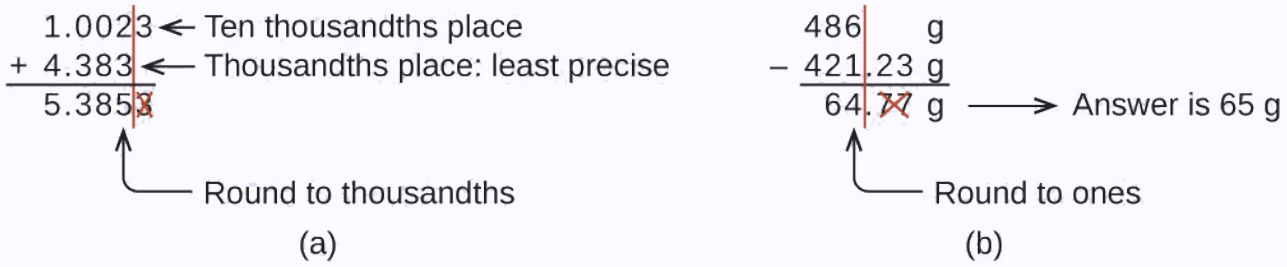
$$\begin{array}{r} 1.0023\ \text{g} \\ +\ 4.383\ \text{g} \\ \hline 5.3853\ \text{g} \end{array}$$

Answer is 5.385 g (round to the thousandths place; three decimal places)

(b)

$$\begin{array}{r} 486\ \text{g} \\ -\ 421.23\ \text{g} \\ \hline 64.77\ \text{g} \end{array}$$

Answer is 65 g (round to the ones place; no decimal places)



Exercise 1.2.2

a. Add 2.334 mL and 0.31 mL.
b. Subtract 55.8752 m from 56.533 m.

Answer a

2.64 mL

Answer b

0.658 m

Example 1.2.3: Multiplication and Division with Significant Figures

Rule: When we multiply or divide numbers, we should round the result to the same number of digits as the number with the least number of significant figures (the least precise value in terms of multiplication and division).

a. Multiply 0.6238 cm by 6.6 cm.
b. Divide 421.23 g by 486 mL.

Solution

(a)

$$0.6238\ \text{cm} \times 6.6\ \text{cm} = 4.11708\ \text{cm}^2 \rightarrow \text{result is } 4.1\ \text{cm}^2\ (\text{round to two significant figures}) \tag{1.2.1}$$

$$\text{four significant figures} \times \text{two significant figures} \rightarrow \text{two significant figures answer} \tag{1.2.2}$$

(b)

$$\frac{421.23\ \text{g}}{486\ \text{mL}} = 0.86728...\ \text{g/mL} \rightarrow \text{result is } 0.867\ \text{g/mL}\ (\text{round to three significant figures}) \tag{1.2.3}$$

$$\frac{\text{five significant figures}}{\text{three significant figures}} \rightarrow \text{three significant figures answer} \tag{1.2.4}$$

Exercise 1.2.3

a. Multiply 2.334 cm and 0.320 cm.
b. Divide 55.8752 m by 56.53 s.

Answer a

0.747 cm^2

Answer b

0.9884 m/s

In the midst of all these technicalities, it is important to keep in mind the reason why we use significant figures and rounding rules—to correctly represent the certainty of the values we report and to ensure that a calculated result is not represented as being more certain than the least certain value used in the calculation.

Example 1.2.4: Calculation with Significant Figures

One common bathtub is 13.44 dm long, 5.920 dm wide, and 2.54 dm deep. Assume that the tub is rectangular and calculate its approximate volume in liters.

Solution

$$\begin{aligned} V &= l \times w \times d \\ &= 13.44\ \text{dm} \times 5.920\ \text{dm} \times 2.54\ \text{dm} \\ &= 202.09459...\text{dm}^3\ (\text{value from calculator}) \\ &= 202\ \text{dm}^3,\ \text{or}\ 202\ \text{L}\ (\text{answer rounded to three significant figures}) \end{aligned}$$

Exercise 1.2.4: Determination of Density Using Water Displacement

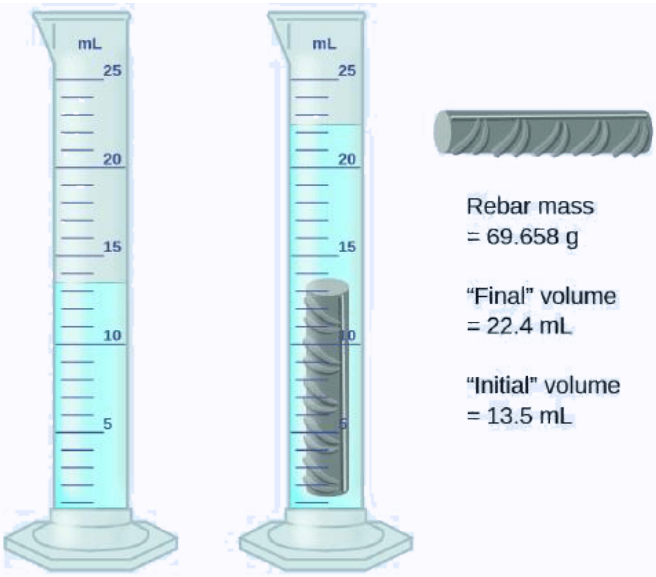
What is the density of a liquid with a mass of 31.1415 g and a volume of 30.13 cm^3?

Answer

1.034 g/mL

Example 1.2.4

A piece of rebar is weighed and then submerged in a graduated cylinder partially filled with water, with results as shown.



a. Use these values to determine the density of this piece of rebar.
b. Rebar is mostly iron. Does your result in (a) support this statement? How?

Solution

The volume of the piece of rebar is equal to the volume of the water displaced:

$$\text{volume} = 22.4\ \text{mL} - 13.5\ \text{mL} = 8.9\ \text{mL} = 8.9\ \text{cm}^3 onumber \tag{1.2.5}$$

(rounded to the nearest 0.1 mL, per the rule for addition and subtraction)

The density is the mass-to-volume ratio:

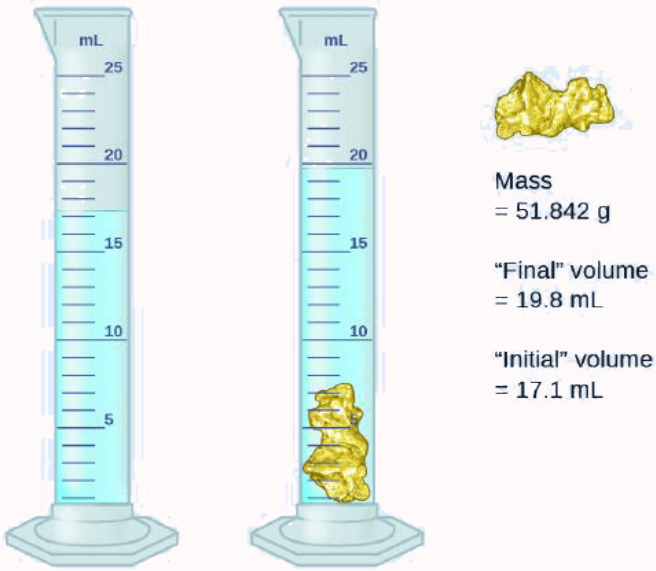
$$\text{density} = \frac{\text{mass}}{\text{volume}} = \frac{69.658\ \text{g}}{8.9\ \text{cm}^3} = 7.8\ \text{g/cm}^3 onumber \tag{1.2.6}$$

(rounded to two significant figures, per the rule for multiplication and division)

The density of iron is 7.9 g/cm^3, very close to that of rebar, which lends some support to the fact that rebar is mostly iron.

Exercise 1.2.4

An irregularly shaped piece of a shiny yellowish material is weighed and then submerged in a graduated cylinder, with results as shown.



a. Use these values to determine the density of this material.
b. Do you have any reasonable guesses as to the identity of this material? Explain your reasoning.

Answer a

$19\ g/cm^3$

Answer b

It is likely gold; it has the right appearance for gold and very close to the density given for gold.

Accuracy and Precision

Scientists typically make repeated measurements of a quantity to ensure the quality of their findings and to know both the precision and the accuracy of their results. Measurements are said to be precise if they yield very similar results when repeated in the same manner. A measurement is considered accurate if it yields a result that is very close to the true or accepted value. Precise values agree with each other; accurate values agree with a true value. These characterizations can be extended to other contexts, such as the results of an archery competition (Figure 1.2.2).

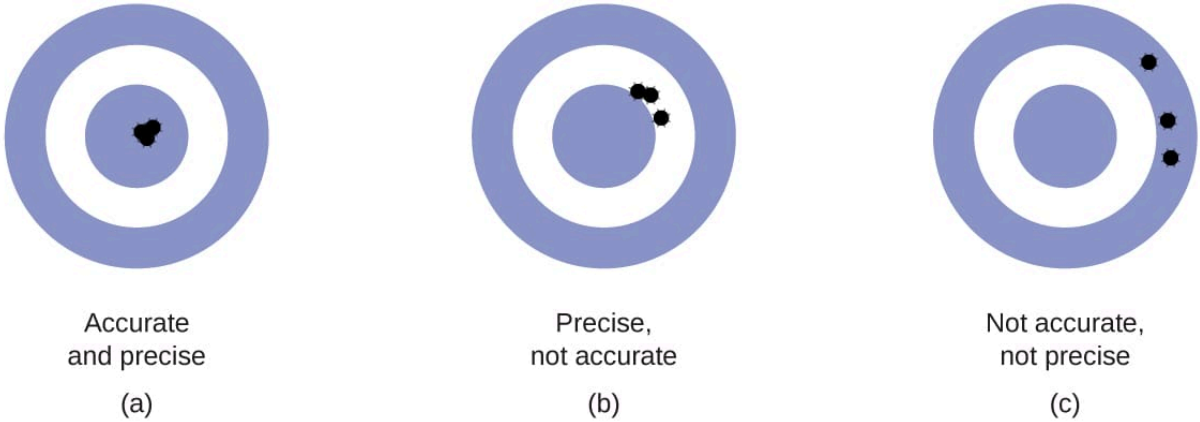


Figure 1.2.2: (a) These arrows are close to both the bull's eye and one another, so they are both accurate and precise. (b) These arrows are close to one another but not on target, so they are precise but not accurate. (c) These arrows are neither on target nor close to one another, so they are neither accurate nor precise.

Suppose a quality control chemist at a pharmaceutical company is tasked with checking the accuracy and precision of three different machines that are meant to dispense 10 ounces (296 mL) of cough syrup into storage bottles. She proceeds to use each machine to fill five bottles and then carefully determines the actual volume dispensed, obtaining the results tabulated in Table 1.2.2.

Table 1.2.2***:*** *Volume (mL) of Cough Medicine Delivered by 10-oz (296 mL) Dispensers*

Dispenser #1	Dispenser #2	Dispenser #3
283.3	298.3	296.1
284.1	294.2	295.9
283.9	296.0	296.1
284.0	297.8	296.0
284.1	293.9	296.1

Considering these results, she will report that dispenser #1 is precise (values all close to one another, within a few tenths of a milliliter) but not accurate (none of the values are close to the target value of 296 mL, each being more than 10 mL too low). Results for dispenser #2 represent improved accuracy (each volume is less than 3 mL away from 296 mL) but worse precision (volumes vary by more than 4 mL). Finally, she can report that dispenser #3 is working well, dispensing cough syrup both accurately (all volumes within 0.1 mL of the target volume) and precisely (volumes differing from each other by no more than 0.2 mL).

Summary

Quantities can be exact or measured. Measured quantities have an associated uncertainty that is represented by the number of significant figures in the measurement. The uncertainty of a calculated value depends on the uncertainties in the values used in the calculation and is reflected in how the value is rounded. Measured values can be accurate (close to the true value) and/or precise (showing little variation when measured repeatedly).

Glossary

uncertainty
: estimate of amount by which measurement differs from true value

significant figures
: (also, significant digits) all of the measured digits in a determination, including the uncertain last digit

rounding
: procedure used to ensure that calculated results properly reflect the uncertainty in the measurements used in the calculation

precision
: how closely a measurement matches the same measurement when repeated

exact number
: number derived by counting or by definition

accuracy
: how closely a measurement aligns with a correct value

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- Christy VanRooyen, Oregon Tech

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1.3: Conversions

Skills to Develop

- Solve dimensional analysis using metric and English units. (note: metric unit definitions will not be provided on quiz.)

It is often the case that a quantity of interest may not be easy (or even possible) to measure directly but instead must be calculated from other directly measured properties and appropriate mathematical relationships. For example, consider measuring the average speed of an athlete running sprints. This is typically accomplished by measuring the *time* required for the athlete to run from the starting line to the finish line, and the *distance* between these two lines, and then computing *speed* from the equation that relates these three properties:

$$\text{speed} = \frac{\text{distance}}{\text{time}} \tag{1.3.1}$$

An Olympic-quality sprinter can run 100 m in approximately 10 s, corresponding to an average speed of

$$\frac{100\ \text{m}}{10\ \text{s}} = 10\ \text{m/s} \tag{1.3.2}$$

Note that this simple arithmetic involves dividing the numbers of each measured quantity to yield the number of the computed quantity (100/10 = 10) *and likewise* dividing the units of each measured quantity to yield the unit of the computed quantity (m/s = m/s). Now, consider using this same relation to predict the time required for a person running at this speed to travel a distance of 25 m. The same relation between the three properties is used, but in this case, the two quantities provided are a speed (10 m/s) and a distance (25 m). To yield the sought property, time, the equation must be rearranged appropriately:

$$\text{time} = \frac{\text{distance}}{\text{speed}} \tag{1.3.3}$$

The time can then be computed as:

$$\frac{25\ \text{m}}{10\ \text{m/s}} = 2.5\ \text{s} \tag{1.3.4}$$

Again, arithmetic on the numbers (25/10 = 2.5) was accompanied by the same arithmetic on the units (m/m/s = s) to yield the number and unit of the result, 2.5 s. Note that, just as for numbers, when a unit is divided by an identical unit (in this case, m/m), the result is "1"—or, as commonly phrased, the units "cancel."

These calculations are examples of a versatile mathematical approach known as dimensional analysis (or the factor-label method). Dimensional analysis is based on this premise: *the units of quantities must be subjected to the same mathematical operations as their associated numbers*. This method can be applied to computations ranging from simple unit conversions to more complex, multi-step calculations involving several different quantities.

Conversion Factors and Dimensional Analysis

A ratio of two equivalent quantities expressed with different measurement units can be used as a unit conversion factor. For example, the lengths of 2.54 cm and 1 in. are equivalent (by definition), and so a unit conversion factor may be derived from the ratio,

$$\frac{2.54\ \text{cm}}{1\ \text{in.}}\ (2.54\ \text{cm} = 1\ \text{in.})\ \text{or}\ 2.54\ \frac{\text{cm}}{\text{in.}} \tag{1.3.5}$$

Several other commonly used conversion factors are given in Table 1.3.1.

Table 1.3.1***:*** *Common Conversion Factors*

Length	Volume	Mass
1 m = 1.0936 yd	1 L = 1.0567 qt	1 kg = 2.2046 lb
1 in. = 2.54 cm (exact)	1 qt = 0.94635 L	1 lb = 453.59 g
1 km = 0.62137 mi	1 ft^3 = 28.317 L	1 (avoirdupois) oz = 28.349 g
1 mi = 1609.3 m	1 tbsp = 14.787 mL	1 (troy) oz = 31.103 g

When we multiply a quantity (such as distance given in inches) by an appropriate unit conversion factor, we convert the quantity to an equivalent value with different units (such as distance in centimeters). For example, a basketball player's vertical jump of 34 inches can be converted to centimeters by:

$$34 \cancel{\text{ in.}} \times \frac{2.54 \text{ cm}}{1 \cancel{\text{ in.}}} = 86 \text{ cm} \tag{1.3.6}$$

Since this simple arithmetic involves *quantities*, the premise of dimensional analysis requires that we multiply both *numbers and units*. The numbers of these two quantities are multiplied to yield the number of the product quantity, 86, whereas the units are multiplied to yield

$$\frac{\text{in.} \times \text{cm}}{\text{in.}}. \tag{1.3.7}$$

Just as for numbers, a ratio of identical units is also numerically equal to one,

$$\frac{\text{in.}}{\text{in.}} = 1 \tag{1.3.8}$$

and the unit product thus simplifies to *cm*. (When identical units divide to yield a factor of 1, they are said to "cancel.") Using dimensional analysis, we can determine that a unit conversion factor has been set up correctly by checking to confirm that the original unit will cancel, and the result will contain the sought (converted) unit.

Example 1.3.1: Using a Unit Conversion Factor

The mass of a competition Frisbee is 125 g. Convert its mass to ounces using the unit conversion factor derived from the relationship 1 oz = 28.349 g (Table 1.3.1).

Solution

If we have the conversion factor, we can determine the mass in kilograms using an equation similar the one used for converting length from inches to centimeters.

$$x \text{ oz} = 125 \text{ g} \times \text{unit conversion factor}$$

We write the unit conversion factor in its two forms:

$$\frac{1 \text{ oz}}{28.349 \text{ g}} \text{ and } \frac{28.349 \text{ g}}{1 \text{ oz}}$$

The correct unit conversion factor is the ratio that cancels the units of grams and leaves ounces.

$$\begin{aligned} x \text{ oz} &= 125 \cancel{\text{ g}} \times \frac{1 \text{ oz}}{28.349 \cancel{\text{ g}}} \\ &= \left(\frac{125}{28.349}\right) \text{ oz} \\ &= 4.41 \text{ oz (three significant figures)} \end{aligned}$$

Exercise 1.3.1

Convert a volume of 9.345 qt to liters.

Answer

8.844 L

Beyond simple unit conversions, the factor-label method can be used to solve more complex problems involving computations. Regardless of the details, the basic approach is the same—all the *factors* involved in the calculation must be appropriately oriented to insure that their *labels* (units) will appropriately cancel and/or combine to yield the desired unit in the result. This is why it is referred to as the factor-label method. As your study of chemistry continues, you will encounter many opportunities to apply this approach.

Example 1.3.2: Computing Quantities from Measurement Results

What is the density of common antifreeze in units of g/mL? A 4.00-qt sample of the antifreeze weighs 9.26 lb.

Solution

Since $\text{density} = \dfrac{\text{mass}}{\text{volume}}$, we need to divide the mass in grams by the volume in milliliters. In general: the number of units of B = the number of units of A $\times$ unit conversion factor. The necessary conversion factors are given in Table 1.7.1: 1 lb = 453.59 g; 1 L = 1.0567 qt; 1 L = 1,000 mL. We can convert mass from pounds to grams in one step:

$$9.26 \cancel{\text{ lb}} \times \frac{453.59 \text{ g}}{1 \cancel{\text{ lb}}} = 4.20 \times 10^3 \text{ g}$$

We need to use two steps to convert volume from quarts to milliliters.

1. *Convert quarts to liters.*

$$4.00 \cancel{\text{ qt}} \times \frac{1 \text{ L}}{1.0567 \cancel{\text{ qt}}} = 3.78 \text{ L}$$

2. *Convert liters to milliliters.*

$$3.78 \cancel{\text{ L}} \times \frac{1000 \text{ mL}}{1 \cancel{\text{ L}}} = 3.78 \times 10^3 \text{ mL}$$

Then,

$$\text{density} = \frac{4.20 \times 10^3 \text{ g}}{3.78 \times 10^3 \text{ mL}} = 1.11 \text{ g/mL}$$

Alternatively, the calculation could be set up in a way that uses three unit conversion factors sequentially as follows:

$$\frac{9.26 \cancel{\text{ lb}}}{4.00 \cancel{\text{ qt}}} \times \frac{453.59 \text{ g}}{1 \cancel{\text{ lb}}} \times \frac{1.0567 \cancel{\text{ qt}}}{1 \cancel{\text{ L}}} \times \frac{1 \cancel{\text{ L}}}{1000 \text{ mL}} = 1.11 \text{ g/mL}$$

Exercise 1.3.2

What is the volume in liters of 1.000 oz, given that 1 L = 1.0567 qt and 1 qt = 32 oz (exactly)?

Answer

$2.956 \times 10^{-2}\ \text{L}$

Example 1.3.3: Computing Quantities from Measurement Results

While being driven from Philadelphia to Atlanta, a distance of about 1250 km, a 2014 Lamborghini Aventador Roadster uses 213 L gasoline.

a. What (average) fuel economy, in miles per gallon, did the Roadster get during this trip?
b. If gasoline costs $3.80 per gallon, what was the fuel cost for this trip?

Solution

(a) We first convert distance from kilometers to miles:

$$1250\ \text{km} \times \frac{0.62137\ \text{mi}}{1\ \text{km}} = 777\ \text{mi}$$

and then convert volume from liters to gallons:

$$213\ \cancel{\text{L}} \times \frac{1.0567\ \cancel{\text{qt}}}{1\ \cancel{\text{L}}} \times \frac{1\ \text{gal}}{4\ \cancel{\text{qt}}} = 56.3\ \text{gal}$$

Then,

$$\text{(average) mileage} = \frac{777\ \text{mi}}{56.3\ \text{gal}} = 13.8\ \text{miles/gallon} = 13.8\ \text{mpg}$$

Alternatively, the calculation could be set up in a way that uses all the conversion factors sequentially, as follows:

$$\frac{1250\ \cancel{\text{km}}}{213\ \cancel{\text{L}}} \times \frac{0.62137\ \text{mi}}{1\ \cancel{\text{km}}} \times \frac{1\ \cancel{\text{L}}}{1.0567\ \cancel{\text{qt}}} \times \frac{4\ \cancel{\text{qt}}}{1\ \text{gal}} = 13.8\ \text{mpg}$$

(b) Using the previously calculated volume in gallons, we find:

$$56.3\ \text{gal} \times \frac{\$3.80}{1\ \text{gal}} = \$214$$

Exercise 1.3.3

A Toyota Prius Hybrid uses 59.7 L gasoline to drive from San Francisco to Seattle, a distance of 1300 km (two significant digits).

a. What (average) fuel economy, in miles per gallon, did the Prius get during this trip?
b. If gasoline costs $3.90 per gallon, what was the fuel cost for this trip?

Answer a

51 mpg

Answer b

$62

Units Raised to a Power

When calculating area or volume, you multiply together lengths, widths, and heights. Just like in our dimensional analysis above, our units and our numbers both undergo the mathematical operation, meaning that multiplying the quantity of length by the quantity of width also multiplies the units.

$$42cm * 33cm = 1386cm^2 \tag{1.3.9}$$

This complicates the conversion of units, however, since our GIVEN conversion factors often only account for one dimension, not two or three. When building a conversion factor for units raised to a power, we simply raise the conversion factor to the power we want our final units in. The trick is to remember to raise the QUANTITY and UNITS by the power.

Example 1.3.4: Computing Quantities from Measurement Results

Convert 5.70 L to in^3.

Solution

We must first convert L to mL, which as we saw in Section 1.1, is equivalent to cm^3.

$$5.70L * \frac{1000mL}{1L} * \frac{1cm^3}{1mL} = 5700cm^3 \tag{1.3.10}$$

Now, if we examine the table of conversion factors (*Table* 1.3.1), we find that there is 16.4 cm^3 in 1 in^3.

$$5700cm^3 * \frac{1in^3}{16.4cm^3} = 347.6cm^3 \tag{1.3.11}$$

We could have just as easily have done this if we hadn't been given the direct conversion factor between cm^3 and in^3. We simply would have had to raise the conversion factor between cm and in to the third power.

$$5700cm^3 * \left(\frac{1in}{2.54cm}\right)^3 = 347.6in^3 \tag{1.3.12}$$

The trick with this way of doing the calculation is you have to remember to apply the power to EVERYTHING:

$$\left(\frac{1in}{2.54cm}\right)^3 = \frac{(1^3in^3)}{2.54^3cm^3} \tag{1.3.13}$$

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1.4: Volume, Thickness, and Density

Learning Objectives

- Calculate area, volume, density, and thickness and convert to various units.

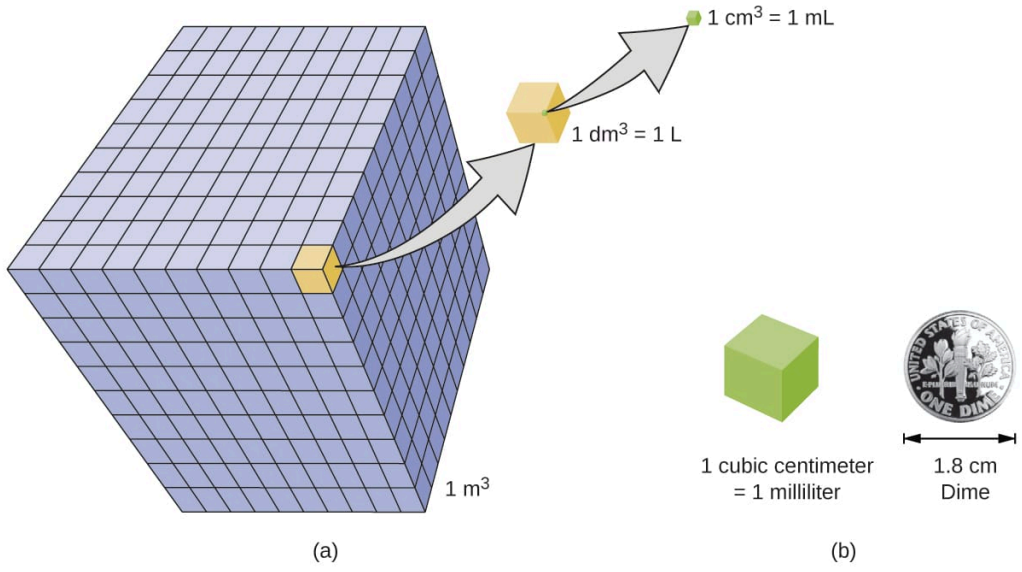
Derived SI Units

We can derive many units from the seven SI base units. For example, we can use the base unit of length to define a unit of volume, and the base units of mass and length to define a unit of density.

Volume

Volume is the measure of the amount of space occupied by an object. The standard SI unit of volume is defined by the base unit of length (Figure 1.4.3). The standard volume is a cubic meter (m^3), a cube with an edge length of exactly one meter. To dispense a cubic meter of water, we could build a cubic box with edge lengths of exactly one meter. This box would hold a cubic meter of water or any other substance.

A more commonly used unit of volume is derived from the decimeter (0.1 m, or 10 cm). A cube with edge lengths of exactly one decimeter contains a volume of one cubic decimeter (dm^3). A liter (L) is the more common name for the cubic decimeter. One liter is about 1.06 quarts. A cubic centimeter (cm^3) is the volume of a cube with an edge length of exactly one centimeter. The abbreviation **cc** (for **c**ubic **c**entimeter) is often used by health professionals. A cubic centimeter is also called a milliliter (mL) and is 1/1000 of a liter.



<

Figure 1.4.3: (a) The relative volumes are shown for cubes of 1 m^3, 1 dm^3 (1 L), and 1 cm^3 (1 mL) (not to scale). (b) The diameter of a dime is compared relative to the edge length of a 1-cm^3 (1-mL) cube.

Density

We use the mass and volume of a substance to determine its density. Thus, the units of density are defined by the base units of mass and length.

The density of a substance is the ratio of the mass of a sample of the substance to its volume. The SI unit for density is the kilogram per cubic meter (kg/m^3). For many situations, however, this as an inconvenient unit, and we often use grams per cubic centimeter (g/cm^3) for the densities of solids and liquids, and grams per liter (g/L) for gases. Although there are exceptions, most liquids and solids have densities that range from about 0.7 g/cm^3 (the density of gasoline) to 19 g/cm^3 (the density of gold). The density of air is about 1.2 g/L. Table 1.4.3 shows the densities of some common substances.

Table 1.4.3***:*** *Densities of Common Substances*

Solids	Liquids	Gases (at 25 °C and 1 atm)
ice (at 0 °C) 0.92 g/cm^3	water 1.0 g/cm^3	dry air 1.20 g/L
oak (wood) 0.60–0.90 g/cm^3	ethanol 0.79 g/cm^3	oxygen 1.31 g/L
iron 7.9 g/cm^3	acetone 0.79 g/cm^3	nitrogen 1.14 g/L
copper 9.0 g/cm^3	glycerin 1.26 g/cm^3	carbon dioxide 1.80 g/L
lead 11.3 g/cm^3	olive oil 0.92 g/cm^3	helium 0.16 g/L
silver 10.5 g/cm^3	gasoline 0.70–0.77 g/cm^3	neon 0.83 g/L
gold 19.3 g/cm^3	mercury 13.6 g/cm^3	radon 9.1 g/L

While there are many ways to determine the density of an object, perhaps the most straightforward method involves separately finding the mass and volume of the object, and then dividing the mass of the sample by its volume. In the following example, the mass is found directly by weighing, but the volume is found indirectly through length measurements.

$$\text{density} = \frac{\text{mass}}{\text{volume}} \tag{1.4.1}$$

Example 1.4.1

Calculation of Density Gold—in bricks, bars, and coins—has been a form of currency for centuries. In order to swindle people into paying for a brick of gold without actually investing in a brick of gold, people have considered filling the centers of hollow gold bricks with lead to fool buyers into thinking that the entire brick is gold. It does not work: Lead is a dense substance, but its density is not as great as that of gold, 19.3 g/cm^3. What is the density of lead if a cube of lead has an edge length of 2.00 cm and a mass of 90.7 g?

Solution

The density of a substance can be calculated by dividing its mass by its volume. The volume of a cube is calculated by cubing the edge length.

$$\text{volume of lead cube} = 2.00\ \text{cm} \times 2.00\ \text{cm} \times 2.00\ \text{cm} = 8.00\ \text{cm}^3 \tag{1.4.2}$$

$$\text{density} = \frac{\text{mass}}{\text{volume}} = \frac{90.7\ \text{g}}{8.00\ \text{cm}^3} = \frac{11.3\ \text{g}}{1.00\ \text{cm}^3} = 11.3\ \text{g/cm}^3 \tag{1.4.3}$$

Exercise 1.4.1

a. To three decimal places, what is the volume of a cube (cm^3) with an edge length of 0.843 cm?
b. If the cube in part (a) is copper and has a mass of 5.34 g, what is the density of copper to two decimal places?

Answer a

0.599 cm^3;

Answer b

8.91 g/cm^3

Example 1.4.2: Using Displacement of Water to Determine Density

This PhET simulation illustrates another way to determine density, using displacement of water. Determine the density of the red and yellow blocks.

Solution

When you open the density simulation and select Same Mass, you can choose from several 5.00-kg colored blocks that you can drop into a tank containing 100.00 L water. The yellow block floats (it is less dense than water), and the water level rises to 105.00 L. While floating, the yellow block displaces 5.00 L water, an amount equal to the weight of the block. The red block sinks (it is more dense than water, which has density = 1.00 kg/L), and the water level rises to 101.25 L.

The red block therefore displaces 1.25 L water, an amount equal to the volume of the block. The density of the red block is:

$$\text{density} = \frac{\text{mass}}{\text{volume}} = \frac{5.00\ \text{kg}}{1.25\ \text{L}} = 4.00\ \text{kg/L} \tag{1.4.4}$$

Note that since the yellow block is not completely submerged, you cannot determine its density from this information. But if you hold the yellow block on the bottom of the tank, the water level rises to 110.00 L, which means that it now displaces 10.00 L water, and its density can be found:

$$\text{density} = \frac{\text{mass}}{\text{volume}} = \frac{5.00\ \text{kg}}{10.00\ \text{L}} = 0.500\ \text{kg/L} \tag{1.4.5}$$

Exercise 1.4.1

Remove all of the blocks from the water and add the green block to the tank of water, placing it approximately in the middle of the tank. Determine the density of the green block.

Answer

2.00 kg/L

Thickness

The width of an object is also sometimes defined as thickness (T). This generally occurs when the width of the object is significantly smaller than the other dimensions. Measuring thickness requires a tool with great precision such as calipers. However, if you know the area, mass, and density of a substance, then you could calculate the thickness.

Use this formula to calculate thickness: $\text{thickness} = \frac{\text{volume}}{\text{area}}$

To find the volume, you would rearrange the density formula. $\text{volume} = \frac{\text{mass}}{\text{density}}$

Example 1.4.2: Calculating Thickness

A piece of aluminum foil has a mass of 0.018g and is 5.0cm on each side. Given the density of aluminum is 2.7g/cc, what is the thickness of aluminum in cm?

Solution

$$\text{thickness} = \frac{\text{volume}}{\text{area}}$$

First find the volume of the foil.

$$\text{volume} = \frac{\text{mass}}{\text{density}} = \frac{0.018\ \text{g}}{2.7\ \text{g/cc}} = 0.00667\ \text{cc} \tag{1.4.6}$$

Next find the area of the foil.

$$\text{area} = 5.0\ \text{cm} \times 5.0\ \text{cm} = 25\ \text{cm}^2 \tag{1.4.7}$$

Solve for Thickness

$$\text{thickness} = \frac{\text{volume}}{\text{area}} = \frac{0.00667\ \text{cc}}{25\ \text{cm}^2} = 0.00027\ \text{cm} \tag{1.4.8}$$

Summary

Scientists use derived units, such as liters (for volume) and g/cm^3 (for density). Thickness is a way to express the width of an object when that dimension is small.

Key Equations

- $\text{density} = \frac{\text{mass}}{\text{volume}}$
- $\text{thickness} = \frac{\text{volume}}{\text{area}}$

Glossary

density
ratio of mass to volume for a substance or object

liter (L)
(also, cubic decimeter) unit of volume; 1 L = 1,000 cm^3

milliliter (mL)
1/1,000 of a liter; equal to 1 cm^3

second (s)
SI unit of time

SI units (International System of Units)
standards fixed by international agreement in the International System of Units (*Le Système International d'Unités*)

thickness
another way to express the width of an object which can be caluculated by taking the volume of the object divided by the area

volume
amount of space occupied by an object

Contributors

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- Christy VanRooyen, Oregon Tech

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1.5: Energy Basics

Learning Objectives

- Perform calculations involving heat, specific heat, and temperature change
- Calculate heat in joules, calories, kilocalories, and dietary calories.

Chemical changes and their accompanying changes in energy are important parts of our everyday world (Figure 1.5.1). The macronutrients in food (proteins, fats, and carbohydrates) undergo metabolic reactions that provide the energy to keep our bodies functioning. We burn a variety of fuels (gasoline, natural gas, coal) to produce energy for transportation, heating, and the generation of electricity. Industrial chemical reactions use enormous amounts of energy to produce raw materials (such as iron and aluminum). Energy is then used to manufacture those raw materials into useful products, such as cars, skyscrapers, and bridges.



Figure 1.5.1: The energy involved in chemical changes is important to our daily lives: (a) A cheeseburger for lunch provides the energy you need to get through the rest of the day; (b) the combustion of gasoline provides the energy that moves your car (and you) between home, work, and school; and (c) coke, a processed form of coal, provides the energy needed to convert iron ore into iron, which is essential for making many of the products we use daily. (credit a: modification of work by “Pink Sherbet Photography”/Flickr; credit b: modification of work by Jeffery Turner).

Over 90% of the energy we use comes originally from the sun. Every day, the sun provides the earth with almost 10,000 times the amount of energy necessary to meet all of the world’s energy needs for that day. Our challenge is to find ways to convert and store incoming solar energy so that it can be used in reactions or chemical processes that are both convenient and nonpolluting. Plants and many bacteria capture solar energy through photosynthesis. We release the energy stored in plants when we burn wood or plant products such as ethanol. We also use this energy to fuel our bodies by eating food that comes directly from plants or from animals that got their energy by eating plants. Burning coal and petroleum also releases stored solar energy: These fuels are fossilized plant and animal matter.

This chapter will introduce the basic ideas of an important area of science concerned with the amount of heat absorbed or released during chemical and physical changes—an area called thermochemistry. The concepts introduced in this chapter are widely used in almost all scientific and technical fields. Food scientists use them to determine the energy content of foods. Biologists study the energetics of living organisms, such as the metabolic combustion of sugar into carbon dioxide and water. The oil, gas, and transportation industries, renewable energy providers, and many others endeavor to find better methods to produce energy for our commercial and personal needs. Engineers strive to improve energy efficiency, find better ways to heat and cool our homes, refrigerate our food and drinks, and meet the energy and cooling needs of computers and electronics, among other applications. Understanding thermochemical principles is essential for chemists, physicists, biologists, geologists, every type of engineer, and just about anyone who studies or does any kind of science.

Energy

Energy can be defined as the capacity to supply heat or do work. One type of work (w) is the process of causing matter to move against an opposing force. For example, we do work when we inflate a bicycle tire—we move matter (the air in the pump) against

the opposing force of the air surrounding the tire.

Like matter, energy comes in different types. One scheme classifies energy into two types: potential energy, the energy an object has because of its relative position, composition, or condition, and kinetic energy, the energy that an object possesses because of its motion. Water at the top of a waterfall or dam has potential energy because of its position; when it flows downward through generators, it has kinetic energy that can be used to do work and produce electricity in a hydroelectric plant (Figure 1.5.2). A battery has potential energy because the chemicals within it can produce electricity that can do work.



Figure 1.5.2: (a) Water that is higher in elevation, for example, at the top of Victoria Falls, has a higher potential energy than water at a lower elevation. As the water falls, some of its potential energy is converted into kinetic energy. (b) If the water flows through generators at the bottom of a dam, such as the Hoover Dam shown here, its kinetic energy is converted into electrical energy. (credit a: modification of work by Steve Jurvetson; credit b: modification of work by "curimedia"/Wikimedia commons).

Energy can be converted from one form into another, but all of the energy present before a change occurs always exists in some form after the change is completed. This observation is expressed in the law of conservation of energy: during a chemical or physical change, energy can be neither created nor destroyed, although it can be changed in form. (This is also one version of the first law of thermodynamics, as you will learn later.)

When one substance is converted into another, there is always an associated conversion of one form of energy into another. Heat is usually released or absorbed, but sometimes the conversion involves light, electrical energy, or some other form of energy. For example, chemical energy (a type of potential energy) is stored in the molecules that compose gasoline. When gasoline is combusted within the cylinders of a car's engine, the rapidly expanding gaseous products of this chemical reaction generate mechanical energy (a type of kinetic energy) when they move the cylinders' pistons.

According to the law of conservation of matter (seen in an earlier chapter), there is no detectable change in the total amount of matter during a chemical change. When chemical reactions occur, the energy changes are relatively modest and the mass changes are too small to measure, so the laws of conservation of matter and energy hold well. However, in nuclear reactions, the energy changes are much larger (by factors of a million or so), the mass changes are measurable, and matter-energy conversions are significant. This will be examined in more detail in a later chapter on nuclear chemistry. To encompass both chemical and nuclear changes, we combine these laws into one statement: The total quantity of matter and energy in the universe is fixed.

Thermal Energy, Temperature, and Heat

Thermal energy is kinetic energy associated with the random motion of atoms and molecules. Temperature is a quantitative measure of "hot" or "cold." When the atoms and molecules in an object are moving or vibrating quickly, they have a higher average kinetic energy (KE), and we say that the object is "hot." When the atoms and molecules are moving slowly, they have lower KE, and we say that the object is "cold" (Figure 1.5.3). Assuming that no chemical reaction or phase change (such as melting or vaporizing) occurs, increasing the amount of thermal energy in a sample of matter will cause its temperature to increase. And, assuming that no chemical reaction or phase change (such as condensation or freezing) occurs, decreasing the amount of thermal energy in a

sample of matter will cause its temperature to decrease.

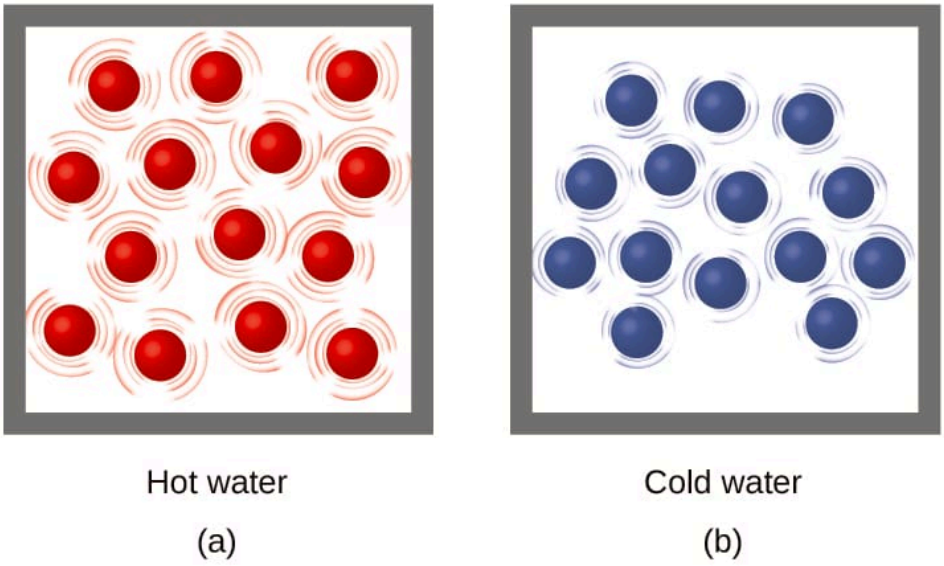


Figure 1.5.3: (a) The molecules in a sample of hot water move more rapidly than (b) those in a sample of cold water.

PhET Simulation

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

View this PhET Simulation online

Most substances expand as their temperature increases and contract as their temperature decreases. This property can be used to measure temperature changes, as shown in Figure 1.5.4. The operation of many thermometers depends on the expansion and contraction of substances in response to temperature changes.

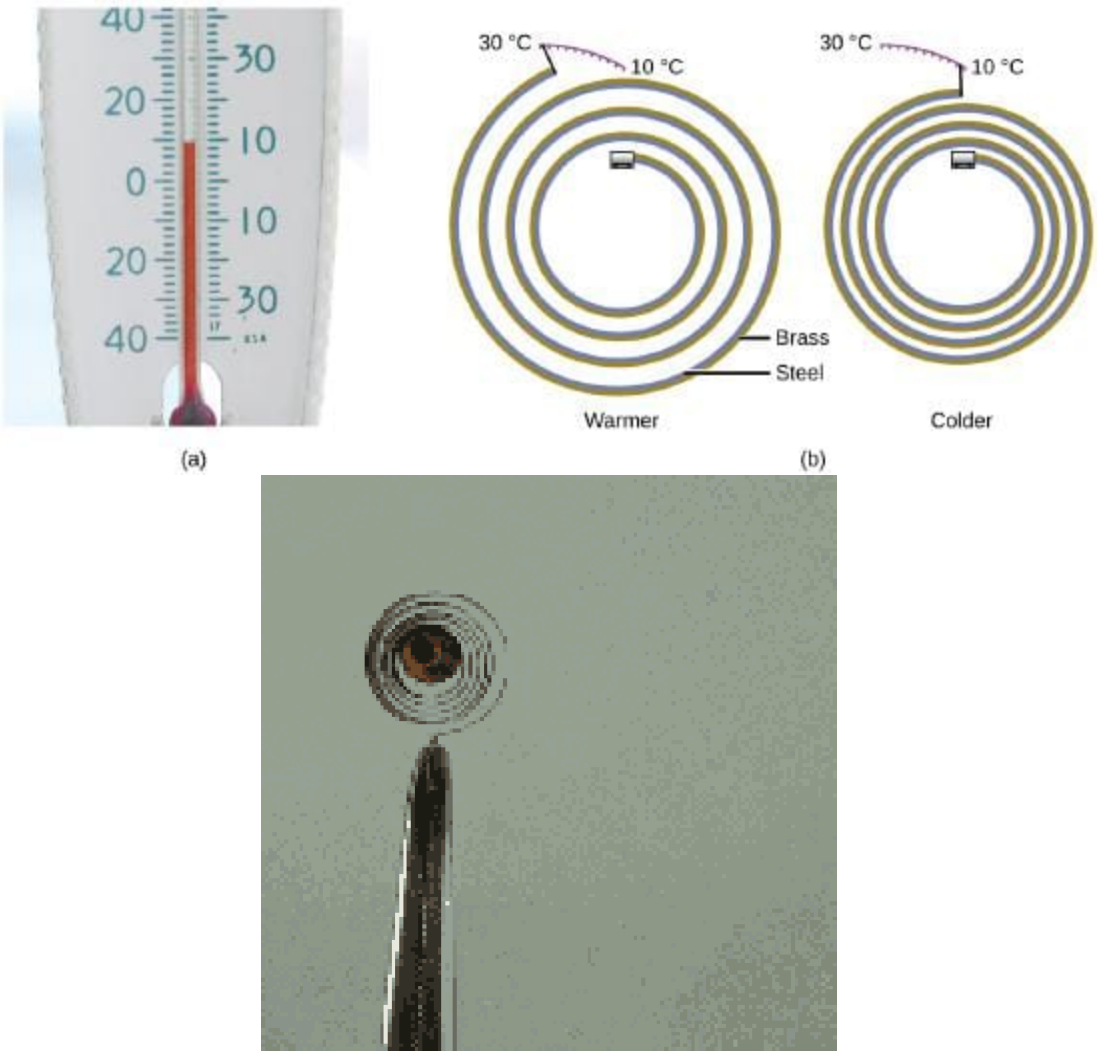


Figure 1.5.4: (a) In an alcohol or mercury thermometer, the liquid (dyed red for visibility) expands when heated and contracts when cooled, much more so than the glass tube that contains the liquid. (b) In a bimetallic thermometer, two different metals (such as brass and steel) form a two-layered strip. When heated or cooled, one of the metals (brass) expands or contracts more than the other metal (steel), causing the strip to coil or uncoil. Both types of thermometers have a calibrated scale that indicates the temperature. (credit a: modification of work by "dwstucke"/Flickr). (c) The demonstration allows one to view the effects of heating and cooling a coiled bimetallic strip.A bimetallic coil from a thermometer reacts to the heat from a lighter, by uncoiling and then coiling back up when the lighter is removed. Animation used with permission from Hustvedt (via Wikipedia)

Heat (q) is the transfer of thermal energy between two bodies at different temperatures. Heat flow (a redundant term, but one commonly used) increases the thermal energy of one body and decreases the thermal energy of the other. Suppose we initially have a high temperature (and high thermal energy) substance (H) and a low temperature (and low thermal energy) substance (L). The atoms and molecules in H have a higher average KE than those in L. If we place substance H in contact with substance L, the thermal energy will flow spontaneously from substance H to substance L. The temperature of substance H will decrease, as will the average KE of its molecules; the temperature of substance L will increase, along with the average KE of its molecules. Heat flow will continue until the two substances are at the same temperature (Figure 1.5.5).

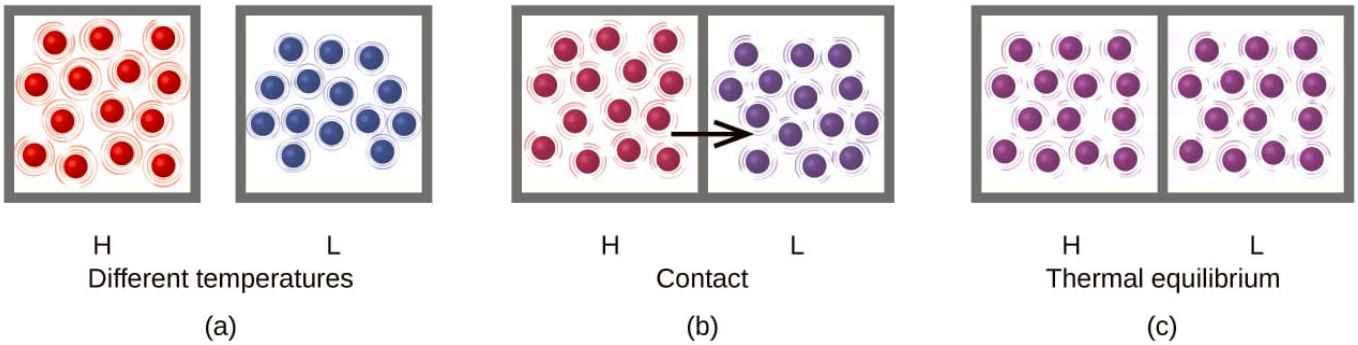


Figure 1.5.5: (a) Substances H and L are initially at different temperatures, and their atoms have different average kinetic energies. (b) When they are put into contact with each other, collisions between the molecules result in the transfer of kinetic (thermal) energy from the hotter to the cooler matter. (c) The two objects reach "thermal equilibrium" when both substances are at the same temperature, and their molecules have the same average kinetic energy.

Matter undergoing chemical reactions and physical changes can release or absorb heat. A change that releases heat is called an exothermic process. For example, the combustion reaction that occurs when using an oxyacetylene torch is an exothermic process—this process also releases energy in the form of light as evidenced by the torch's flame (Figure 1.5.6*a*). A reaction or change that absorbs heat is an endothermic process. A cold pack used to treat muscle strains provides an example of an endothermic process. When the substances in the cold pack (water and a salt like ammonium nitrate) are brought together, the resulting process absorbs heat, leading to the sensation of cold.



Figure 1.5.6: (a) An oxyacetylene torch produces heat by the combustion of acetylene in oxygen. The energy released by this exothermic reaction heats and then melts the metal being cut. The sparks are tiny bits of the molten metal flying away. (b) A cold pack uses an endothermic process to create the sensation of cold. (credit a: modification of work by "Skatebiker"/Wikimedia commons).

Measuring Energy and Heat Capacity

Historically, energy was measured in units of calories (cal). A calorie is the amount of energy required to raise one gram of water by 1 degree C (1 kelvin). However, this quantity depends on the atmospheric pressure and the starting temperature of the water. The ease of measurement of energy changes in calories has meant that the calorie is still frequently used. The Calorie (with a capital C), or large calorie, commonly used in quantifying food energy content, is a kilocalorie. The SI unit of heat, work, and energy is the joule. A joule (J) is defined as the amount of energy used when a force of 1 newton moves an object 1 meter. It is named in honor of the English physicist James Prescott Joule. One joule is equivalent to 1 kg m^2/s^2, which is also called 1 newton–meter. A kilojoule (kJ) is 1000 joules. To standardize its definition, 1 calorie has been set to equal 4.184 joules.

We now introduce two concepts useful in describing heat flow and temperature change. The heat capacity (*C*) of a body of matter is the quantity of heat (*q*) it absorbs or releases when it experiences a temperature change (ΔT) of 1 degree Celsius (or equivalently, 1 kelvin)

$$C = \frac{q}{\Delta T} \tag{1.5.1}$$

Heat capacity is determined by both the type and amount of substance that absorbs or releases heat. It is therefore an extensive property—its value is proportional to the amount of the substance.

For example, consider the heat capacities of two cast iron frying pans. The heat capacity of the large pan is five times greater than that of the small pan because, although both are made of the same material, the mass of the large pan is five times greater than the mass of the small pan. More mass means more atoms are present in the larger pan, so it takes more energy to make all of those atoms vibrate faster. The heat capacity of the small cast iron frying pan is found by observing that it takes 18,150 J of energy to raise the temperature of the pan by 50.0 °C

$$C_{\text{small pan}} = \frac{18,140 \text{ J}}{50.0 \text{ °C}} = 363 \text{ J/°C} \tag{1.5.2}$$

The larger cast iron frying pan, while made of the same substance, requires 90,700 J of energy to raise its temperature by 50.0 °C. The larger pan has a (proportionally) larger heat capacity because the larger amount of material requires a (proportionally) larger amount of energy to yield the same temperature change:

$$C_{\text{large pan}} = \frac{90,700 \text{ J}}{50.0 \text{ °C}} = 1814 \text{ J/°C} \tag{1.5.3}$$

The specific heat capacity (*c*) of a substance, commonly called its “specific heat,” is the quantity of heat required to raise the temperature of 1 gram of a substance by 1 degree Celsius (or 1 kelvin):

$$c = \frac{q}{\text{m}\Delta\text{T}} \tag{1.5.4}$$

Specific heat capacity depends only on the kind of substance absorbing or releasing heat. It is an intensive property—the type, but not the amount, of the substance is all that matters. For example, the small cast iron frying pan has a mass of 808 g. The specific heat of iron (the material used to make the pan) is therefore:

$$c_{\text{iron}} = \frac{18,140 \text{ J}}{(808 \text{ g})(50.0 \text{ °C})} = 0.449 \text{ J/g °C} \tag{1.5.5}$$

The large frying pan has a mass of 4040 g. Using the data for this pan, we can also calculate the specific heat of iron:

$$c_{\text{iron}} = \frac{90,700 \text{ J}}{(4,040 \text{ g})(50.0 \text{ °C})} = 0.449 \text{ J/g °C} \tag{1.5.6}$$

Although the large pan is more massive than the small pan, since both are made of the same material, they both yield the same value for specific heat (for the material of construction, iron). Note that specific heat is measured in units of energy per temperature per mass and is an intensive property, being derived from a ratio of two extensive properties (heat and mass). The molar heat capacity, also an intensive property, is the heat capacity per mole of a particular substance and has units of J/mol °C (Figure 1.5.7).



Figure 1.5.7: Due to its larger mass, a large frying pan has a larger heat capacity than a small frying pan. Because they are made of the same material, both frying pans have the same specific heat. (credit: Mark Blaser).

Liquid water has a relatively high specific heat (about 4.2 J/g °C); most metals have much lower specific heats (usually less than 1 J/g °C). The specific heat of a substance varies somewhat with temperature. However, this variation is usually small enough that we will treat specific heat as constant over the range of temperatures that will be considered in this chapter. Specific heats of some common substances are listed in Table 1.5.1.

***Table** 1.5.1**:** Specific Heats of Common Substances at 25 °C and 1 bar*

Substance	Symbol (state)	Specific Heat (J/g °C)
helium	$He(g)$	5.193
water	$H_2O(l)$	4.184
ethanol	$C_2H_6O(l)$	2.376
ice	$H_2O(s)$	2.093 (at −10 °C)
water vapor	$H_2O(g)$	1.864
nitrogen	$N_2(g)$	1.040

Substance	Symbol (state)	Specific Heat (J/g °C)
air		1.007
oxygen	$O_2(g)$	0.918
aluminum	Al(s)	0.897
carbon dioxide	$CO_2(g)$	0.853
argon	Ar(*g*)	0.522
iron	Fe(s)	0.449
copper	Cu(s)	0.385
lead	Pb(s)	0.130
gold	Au(s)	0.129
silicon	Si(s)	0.712

If we know the mass of a substance and its specific heat, we can determine the amount of heat, *q*, entering or leaving the substance by measuring the temperature change before and after the heat is gained or lost:

$$q = (\text{specific heat}) \times (\text{mass of substance}) \times (\text{temperature change})$$
$$q = c \times m \times \Delta T = c \times m \times (T_{\text{final}} - T_{\text{initial}})$$

In this equation, c is the specific heat of the substance, *m* is its mass, and ΔT (which is read “delta T”) is the temperature change, $T_{\text{final}} - T_{\text{initial}}$. If a substance gains thermal energy, its temperature increases, its final temperature is higher than its initial temperature, $T_{\text{final}} - T_{\text{initial}}$ has a positive value, and the value of *q* is positive. If a substance loses thermal energy, its temperature decreases, the final temperature is lower than the initial temperature, $T_{\text{final}} - T_{\text{initial}}$ has a negative value, and the value of *q* is negative.

Example 1.5.1: Measuring Heat

A flask containing 8.0×10^2 g of water is heated, and the temperature of the water increases from 21 °C to 85 °C. How much heat did the water absorb?

Solution

To answer this question, consider these factors:

- the specific heat of the substance being heated (in this case, water)
- the amount of substance being heated (in this case, 800 g)
- the magnitude of the temperature change (in this case, from 21 °C to 85 °C).

The specific heat of water is 4.184 J/g °C, so to heat 1 g of water by 1 °C requires 4.184 J. We note that since 4.184 J is required to heat 1 g of water by 1 °C, we will need 800 times as much to heat 800 g of water by 1 °C. Finally, we observe that since 4.184 J are required to heat 1 g of water by 1 °C, we will need 64 times as much to heat it by 64 °C (that is, from 21 °C to 85 °C).

This can be summarized using the equation:

$$q = c \times m \times \Delta T = c \times m \times (T_{\text{final}} - T_{\text{initial}})$$

$$= (4.184 \text{ J/}\cancel{\text{g}}^\circ\text{C}) \times (800\ \cancel{\text{g}}) \times (85 - 21)^\circ\text{C}$$
$$= (4.184 \text{ J/}\cancel{\text{g}}^\circ\cancel{\text{C}}) \times (800\ \cancel{\text{g}}) \times (64)^\circ\cancel{\text{C}}$$
$$= 210,000 \text{ J} (= 210 \text{ kJ})$$

Because the temperature increased, the water absorbed heat and q is positive.

Exercise 1.5.1

How much heat, in joules, must be added to a 5.00×10^2 g iron skillet to increase its temperature from 25 °C to 250 °C? The specific heat of iron is 0.451 J/g °C.

Answer

5.05×10^4 J

Note that the relationship between heat, specific heat, mass, and temperature change can be used to determine any of these quantities (not just heat) if the other three are known or can be deduced.

Example 1.5.2: Determining Other Quantities

A piece of unknown metal weighs 348 g. When the metal piece absorbs 6.64 kJ of heat, its temperature increases from 22.4 °C to 43.6 °C. Determine the specific heat of this metal (which might provide a clue to its identity).

Solution

Since mass, heat, and temperature change are known for this metal, we can determine its specific heat using the relationship:

$$q = c \times m \times \Delta T = c \times m \times (T_{\text{final}} - T_{\text{initial}}) \tag{1.5.7}$$

Substituting the known values:

$$6,640 \text{ J} = c \times (348 \text{ g}) \times (43.6 - 22.4)\ ^\circ\text{C} \tag{1.5.8}$$

Solving:

$$c = \frac{6,640 \text{ J}}{(348 \text{ g}) \times (21.2°\text{C})} = 0.900 \text{ J/g °C} \tag{1.5.9}$$

Comparing this value with the values in Table 1.5.1, this value matches the specific heat of aluminum, which suggests that the unknown metal may be aluminum.

Exercise 1.5.2

A piece of unknown metal weighs 217 g. When the metal piece absorbs 1.43 kJ of heat, its temperature increases from 24.5 °C to 39.1 °C. Determine the specific heat of this metal, and predict its identity.

Answer

$c = 0.45$ J/g °C; the metal is likely to be iron from checking Table 1.5.1.

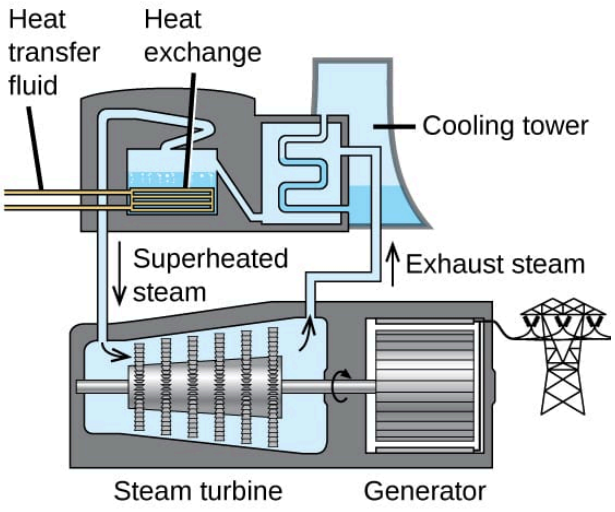
Solar Thermal Energy Power Plants

The sunlight that reaches the earth contains thousands of times more energy than we presently capture. Solar thermal systems provide one possible solution to the problem of converting energy from the sun into energy we can use. Large-scale solar thermal plants have different design specifics, but all concentrate sunlight to heat some substance; the heat "stored" in that substance is then converted into electricity.

The Solana Generating Station in Arizona's Sonora Desert produces 280 megawatts of electrical power. It uses parabolic mirrors that focus sunlight on pipes filled with a heat transfer fluid (HTF) (Figure 1.5.8). The HTF then does two things: It turns water into steam, which spins turbines, which in turn produces electricity, and it melts and heats a mixture of salts, which functions as a thermal energy storage system. After the sun goes down, the molten salt mixture can then release enough of its stored heat to produce steam to run the turbines for 6 hours. Molten salts are used because they possess a number of beneficial properties, including high heat capacities and thermal conductivities.



(a)



(b)

Figure 1.5.8: This solar thermal plant uses parabolic trough mirrors to concentrate sunlight. (credit a: modification of work by Bureau of Land Management)

The 377-megawatt Ivanpah Solar Generating System, located in the Mojave Desert in California, is the largest solar thermal power plant in the world (Figure 1.5.9). Its 170,000 mirrors focus huge amounts of sunlight on three water-filled towers, producing steam at over 538 °C that drives electricity-producing turbines. It produces enough energy to power 140,000 homes. Water is used as

the working fluid because of its large heat capacity and heat of vaporization.



Figure 1.5.9: (a) The Ivanpah solar thermal plant uses 170,000 mirrors to concentrate sunlight on water-filled towers. (b) It covers 4000 acres of public land near the Mojave Desert and the California-Nevada border. (credit a: modification of work by Craig Dietrich; credit b: modification of work by "USFWS Pacific Southwest Region"/Flickr)

Summary

Energy is the capacity to do work (applying a force to move matter). Kinetic energy (KE) is the energy of motion; potential energy is energy due to relative position, composition, or condition. When energy is converted from one form into another, energy is neither created nor destroyed (law of conservation of energy or first law of thermodynamics). Matter has thermal energy due to the KE of its molecules and temperature that corresponds to the average KE of its molecules. Heat is energy that is transferred between objects at different temperatures; it flows from a high to a low temperature. Chemical and physical processes can absorb heat (endothermic) or release heat (exothermic). The SI unit of energy, heat, and work is the joule (J). Specific heat and heat capacity are measures of the energy needed to change the temperature of a substance or object. The amount of heat absorbed or released by a substance depends directly on the type of substance, its mass, and the temperature change it undergoes.

Key Equations

- $q = c \times m \times \Delta T = c \times m \times (T_{\text{final}} - T_{\text{initial}})$

Glossary

calorie (cal)
: unit of heat or other energy; the amount of energy required to raise 1 gram of water by 1 degree Celsius; 1 cal is defined as 4.184 J

endothermic process
: chemical reaction or physical change that absorbs heat

energy
: capacity to supply heat or do work

exothermic process
: chemical reaction or physical change that releases heat

heat (*q*)
: transfer of thermal energy between two bodies

heat capacity (*C*)
: extensive property of a body of matter that represents the quantity of heat required to increase its temperature by 1 degree Celsius (or 1 kelvin)

joule (J)
: SI unit of energy; 1 joule is the kinetic energy of an object with a mass of 2 kilograms moving with a velocity of 1 meter per second, 1 J = 1 kg m^2/s and 4.184 J = 1 cal

kinetic energy
: energy of a moving body, in joules, equal to $\frac{1}{2}mv^2$ (where *m* = mass and *v* = velocity)

potential energy
: energy of a particle or system of particles derived from relative position, composition, or condition

specific heat capacity (*c*)
: intensive property of a substance that represents the quantity of heat required to raise the temperature of 1 gram of the substance by 1 degree Celsius (or 1 kelvin)

temperature
: intensive property of matter that is a quantitative measure of “hotness” and “coldness”

thermal energy
: kinetic energy associated with the random motion of atoms and molecules

thermochemistry
: study of measuring the amount of heat absorbed or released during a chemical reaction or a physical change

work (*w*)
: energy transfer due to changes in external, macroscopic variables such as pressure and volume; or causing matter to move against an opposing force

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1.6: Calorimetry

Learning Objectives

- Explain the technique of calorimetry
- Calculate and interpret heat and related properties using typical calorimetry data

One technique we can use to measure the amount of heat involved in a chemical or physical process is known as calorimetry. Calorimetry is used to measure amounts of heat transferred to or from a substance. To do so, the heat is exchanged with a calibrated object (calorimeter). The change in temperature of the measuring part of the calorimeter is converted into the amount of heat (since the previous calibration was used to establish its heat capacity). The measurement of heat transfer using this approach requires the definition of a system (the substance or substances undergoing the chemical or physical change) and its surroundings (the other components of the measurement apparatus that serve to either provide heat to the system or absorb heat from the system). Knowledge of the heat capacity of the surroundings, and careful measurements of the masses of the system and surroundings and their temperatures before and after the process allows one to calculate the heat transferred as described in this section.

A calorimeter is a device used to measure the amount of heat involved in a chemical or physical process. For example, when an exothermic reaction occurs in solution in a calorimeter, the heat produced by the reaction is absorbed by the solution, which increases its temperature. When an endothermic reaction occurs, the heat required is absorbed from the thermal energy of the solution, which decreases its temperature (Figure 1.6.1). The temperature change, along with the specific heat and mass of the solution, can then be used to calculate the amount of heat involved in either case.

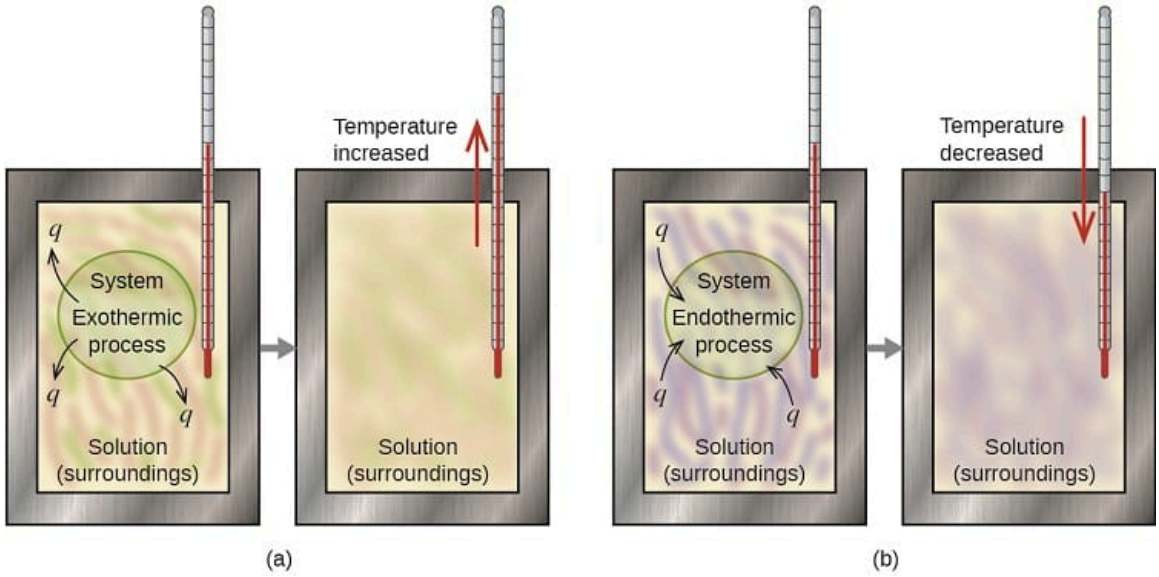


Figure 1.6.1: In a calorimetric determination, either (a) an exothermic process occurs and heat, q, is negative, indicating that thermal energy is transferred from the system to its surroundings, or (b) an endothermic process occurs and heat, q, is positive, indicating that thermal energy is transferred from the surroundings to the system.

By convention, q is given a negative (-) sign when the system releases heat to the surroundings (exothermic); q is given a positive (+) sign when the system absorbs heat from the surroundings (endothermic).

Scientists use well-insulated calorimeters that all but prevent the transfer of heat between the calorimeter and its environment. This enables the accurate determination of the heat involved in chemical processes, the energy content of foods, and so on. General chemistry students often use simple calorimeters constructed from polystyrene cups (Figure 1.6.2). These easy-to-use "coffee cup" calorimeters allow more heat exchange with their surroundings, and therefore produce less accurate energy values.

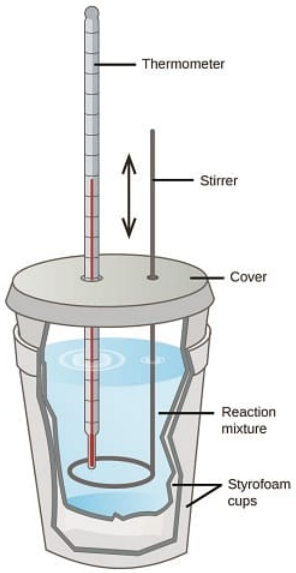


Figure 1.6.2: A simple calorimeter can be constructed from two polystyrene cups. A thermometer and stirrer extend through the cover into the reaction mixture.

Commercial solution calorimeters are also available. Relatively inexpensive calorimeters often consist of two thin-walled cups that are nested in a way that minimizes thermal contact during use, along with an insulated cover, handheld stirrer, and simple thermometer. More expensive calorimeters used for industry and research typically have a well-insulated, fully enclosed reaction vessel, motorized stirring mechanism, and a more accurate temperature sensor (Figure 1.6.3).

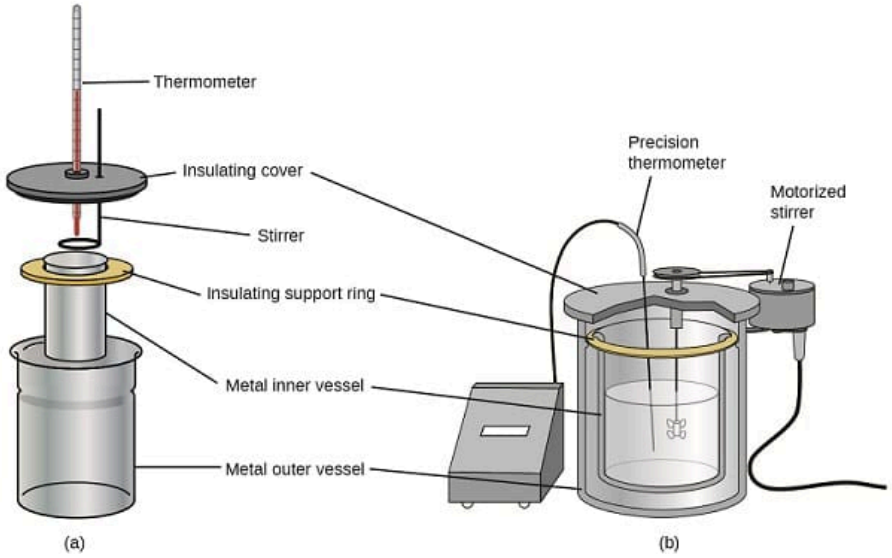


Figure 1.6.3: Commercial solution calorimeters range from (a) simple, inexpensive models for student use to (b) expensive, more accurate models for industry and research.

Before we practice calorimetry problems involving chemical reactions, consider a simple example that illustrates the core idea behind calorimetry. Suppose we initially have a high-temperature substance, such as a hot piece of metal (M), and a low-temperature substance, such as cool water (W). If we place the metal in the water, heat will flow from M to W. The temperature of M will decrease, and the temperature of W will increase, until the two substances have the same temperature—that is, when they reach thermal equilibrium (Figure 1.6.4). If this occurs in a calorimeter, ideally all of this heat transfer occurs between the two substances, with no heat gained or lost by either the calorimeter or the calorimeter's surroundings. Under these ideal circumstances, the net heat change is zero:

$$q_{\text{substance M}} + q_{\text{substance W}} = 0 \tag{1.6.1}$$

This relationship can be rearranged to show that the heat gained by substance M is equal to the heat lost by substance W:

$$q_{\text{substance M}} = -q_{\text{substance W}} \tag{1.6.2}$$

The magnitude of the heat (change) is therefore the same for both substances, and the negative sign merely shows that $q_{\text{substance M}}$ and $q_{\text{substance W}}$ are opposite in direction of heat flow (gain or loss) but does not indicate the arithmetic sign of either q value (that is determined by whether the matter in question gains or loses heat, per definition). In the specific situation described, $q_{\text{substance M}}$ is a negative value and $q_{\text{substance W}}$ is positive, since heat is transferred from M to W.

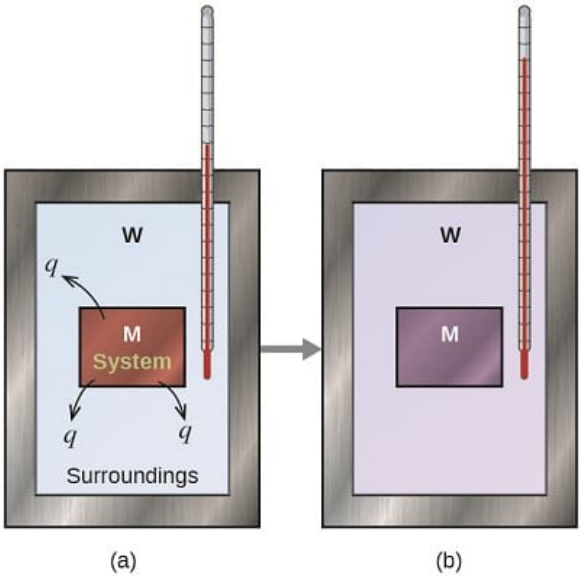


Figure 1.6.4: In a simple calorimetry process, (a) heat, q, is transferred from the hot metal, M, to the cool water, W, until (b) both are at the same temperature.

Example 1.6.1: Heat Transfer between Substances at Different Temperatures

A hot 360-g piece of rebar (a steel rod used for reinforcing concrete) is dropped into 425 mL of water at 24.0 °C. The final temperature of the water is measured as 42.7 °C. Calculate the initial temperature of the piece of rebar. Assume the specific heat of steel is approximately the same as that for iron (Table T4), and that all heat transfer occurs between the rebar and the water (there is no heat exchange with the surroundings).

Solution

The temperature of the water increases from 24.0 °C to 42.7 °C, so the water absorbs heat. That heat came from the piece of rebar, which initially was at a higher temperature. Assuming that all heat transfer was between the rebar and the water, with no heat "lost" to the surroundings, then heat given off by rebar = – heat taken in by water, or:

$$q_{\text{rebar}} = -q_{\text{water}} \tag{1.6.3}$$

Since we know how heat is related to other measurable quantities, we have:

$$(c \times m \times \Delta T)_{\text{rebar}} = -(c \times m \times \Delta T)_{\text{water}} \tag{1.6.4}$$

Letting f = final and i = initial, in expanded form, this becomes:

$$c_{\text{rebar}} \times m_{\text{rebar}} \times (T_{\text{f,rebar}} - T_{\text{i,rebar}}) = -c_{\text{water}} \times m_{\text{water}} \times (T_{\text{f,water}} - T_{\text{i,water}}) \tag{1.6.5}$$

The density of water is 1.0 g/mL, so 425 mL of water = 425 g. Noting that the final temperature of both the rebar and water is 42.7 °C, substituting known values yields:

$$(0.449\ \text{J/g °C})(360\text{g})(42.7\text{°C} - T_{\text{i,rebar}}) = -(4.184\ \text{J/g °C})(425\ \text{g})(42.7\text{°C} - 24.0\text{°C}) \tag{1.6.6}$$

$$T_{\text{i,rebar}} = \frac{(4.184\ \text{J/g °C})(425\ \text{g})(42.7\text{°C} - 24.0\text{°C})}{(0.449\ \text{J/g °C})(360\ \text{g})} + 42.7\text{°C} \tag{1.6.7}$$

Solving this gives Ti,rebar= 248 °C, so the initial temperature of the rebar was 248 °C.

Exercise 1.6.1A

A 248-g piece of copper is dropped into 390 mL of water at 22.6 °C. The final temperature of the water was measured as 39.9 °C. Calculate the initial temperature of the piece of copper. Assume that all heat transfer occurs between the copper and the water.

Answer available at the end of this section.

Exercise 1.6.1B

A 248-g piece of copper initially at 314 °C is dropped into 390 mL of water initially at 22.6 °C. Assuming that all heat transfer occurs between the copper and the water, calculate the final temperature.

Answer available at the end of this section.

This method can also be used to determine other quantities, such as the specific heat of an unknown metal.

Example 1.6.2: Identifying a Metal by Measuring Specific Heat

A 59.7 g piece of metal that had been submerged in boiling water was quickly transferred into 60.0 mL of water initially at 22.0 °C. The final temperature is 28.5 °C. Use these data to determine the specific heat of the metal. Use this result to identify the metal.

Solution

Assuming perfect heat transfer, heat given off by metal = –heat taken in by water, or:

$$q_{\text{metal}} = -q_{\text{water}} \tag{1.6.8}$$

In expanded form, this is:

$$c_{\text{metal}} \times m_{\text{metal}} \times (T_{\text{f,metal}} - T_{\text{i,metal}}) = -c_{\text{water}} \times m_{\text{water}} \times (T_{\text{f,water}} - T_{\text{i,water}}) \tag{1.6.9}$$

Noting that since the metal was submerged in boiling water, its initial temperature was 100.0 °C; and that for water, 60.0 mL = 60.0 g; we have:

$$(c_{\text{metal}})(59.7\ \text{g})(28.5\text{°C} - 100.0\text{°C}) = -(4.18\ \text{J/g °C})(60.0\ \text{g})(28.5\text{°C} - 22.0\text{°C}) \tag{1.6.10}$$

Solving this:

$$c_{\text{metal}} = \frac{-(4.184\ \text{J/g °C})(60.0\ \text{g})(6.5\text{°C})}{(59.7\ \text{g})(-71.5\text{°C})} = 0.38\ \text{J/g °C} \tag{1.6.11}$$

Comparing this with values in Table T4, our experimental specific heat is closest to the value for copper (0.39 J/g °C), so we identify the metal as copper.

Exercise 1.6.2

A 92.9-g piece of a silver/gray metal is heated to 178.0 °C, and then quickly transferred into 75.0 mL of water initially at 24.0 °C. After 5 minutes, both the metal and the water have reached the same temperature: 29.7 °C. Determine the specific heat and the identity of the metal. (Note: You should find that the specific heat is close to that of two different metals. Explain how you can confidently determine the identity of the metal).

Answer available at the end of this section.

When we use calorimetry to determine the heat involved in a chemical reaction, the same principles we have been discussing apply. The amount of heat absorbed by the calorimeter is often small enough that we can neglect it (though not for highly accurate measurements, as discussed later), and the calorimeter minimizes energy exchange with the surroundings. Because energy is neither created nor destroyed during a chemical reaction, there is no overall energy change during the reaction. The heat produced or consumed in the reaction (the "system"), q_{reaction}, plus the heat absorbed or lost by the solution (the "surroundings"), q_{solution}, must add up to zero:

$$q_{\text{reaction}} + q_{\text{solution}} = 0 \tag{1.6.12}$$

This means that the amount of heat produced or consumed in the reaction equals the amount of heat absorbed or lost by the solution:

$$q_{\text{reaction}} = -q_{\text{solution}} \tag{1.6.13}$$

This concept lies at the heart of all calorimetry problems and calculations.

Example 1.6.3: Heat Produced by an Exothermic Reaction

When 50.0 mL of 0.10 M HCl(*aq*) and 50.0 mL of 1.00 M NaOH(*aq*), both at 22.0 °C, are added to a coffee cup calorimeter, the temperature of the mixture reaches a maximum of 28.9 °C. What is the approximate amount of heat produced by this reaction?

$$\text{HCl}(aq) + \text{NaOH}(aq) \longrightarrow \text{NaCl}(aq) + \text{H}_2\text{O}(l)$$

Solution

To visualize what is going on, imagine that you could combine the two solutions so quickly that no reaction took place while they mixed; then after mixing, the reaction took place. At the instant of mixing, you have 100.0 mL of a mixture of HCl and NaOH at 22.0 °C. The HCl and NaOH then react until the solution temperature reaches 28.9 °C.

The heat given off by the reaction is equal to that taken in by the solution. Therefore:

$$q_{\text{reaction}} = -q_{\text{solution}}$$

(It is important to remember that this relationship only holds if the calorimeter does not absorb any heat from the reaction, and there is no heat exchange between the calorimeter and its surroundings.)

Next, we know that the heat absorbed by the solution depends on its specific heat, mass, and temperature change:

$$q_{\text{solution}} = (c \times m \times \Delta T)_{\text{solution}}$$

To proceed with this calculation, we need to make a few more reasonable assumptions or approximations. Since the solution is aqueous, we can proceed as if it were water in terms of its specific heat and mass values. The density of water is approximately 1.0 g/mL, so 100.0 mL has a mass of about 1.0×10^2 g (two significant figures). The specific heat of water is approximately 4.18 J/g °C, so we use that for the specific heat of the solution. Substituting these values gives:

$$q_{\text{solution}} = (4.184\ \text{J/g °C})(1.0 \times 10^2\ \text{g})(28.9°\text{C} - 22.0°\text{C}) = 2.89 \times 10^3\ \text{J} \tag{1.6.14}$$

Finally, since we are trying to find the heat of the reaction, we have:

$$q_{\text{reaction}} = -q_{\text{solution}} = -2.89 \times 10^3\ J$$

The negative sign indicates that the reaction is exothermic. It produces 2.89 kJ of heat.

Exercise 1.6.3

When 100 mL of 0.200 M NaCl(*aq*) and 100 mL of 0.200 M $AgNO_3$(*aq*), both at 21.9 °C, are mixed in a coffee cup calorimeter, the temperature increases to 23.5 °C as solid AgCl forms. How much heat is produced by this precipitation reaction? What assumptions did you make to determine your value?

Answer available at the end of this section.

Thermochemistry of Hand Warmers

When working or playing outdoors on a cold day, you might use a hand warmer to warm your hands (Figure 1.6.5). A common reusable hand warmer contains a supersaturated solution of $NaC_2H_3O_2$ (sodium acetate) and a metal disc. Bending the disk creates nucleation sites around which the metastable $NaC_2H_3O_2$ quickly crystallizes (a later chapter on solutions will investigate saturation and supersaturation in more detail).

The process $\mathrm{NaC_2H_3O_2}(aq) \longrightarrow \mathrm{NaC_2H_3O_2}(s)$ is exothermic, and the heat produced by this process is absorbed by your hands, thereby warming them (at least for a while). If the hand warmer is reheated, the $NaC_2H_3O_2$ redissolves and can be reused.



Figure 1.6.5: Chemical hand warmers produce heat that warms your hand on a cold day. In this one, you can see the metal disc that initiates the exothermic precipitation reaction. (credit: modification of work by Science Buddies TV/YouTube)

Another common hand warmer produces heat when it is ripped open, exposing iron and water in the hand warmer to oxygen in the air. One simplified version of this exothermic reaction is

$$2\,\mathrm{Fe}(s) + \frac{3}{2}\mathrm{O_2}(g) \longrightarrow \mathrm{Fe_2O_3}(s). \tag{1.6.15}$$

Salt in the hand warmer catalyzes the reaction, so it produces heat more rapidly; cellulose, vermiculite, and activated carbon help distribute the heat evenly. Other types of hand warmers use lighter fluid (a platinum catalyst helps lighter fluid oxidize exothermically), charcoal (charcoal oxidizes in a special case), or electrical units that produce heat by passing an electrical current from a battery through resistive wires.

Example 1.6.4: Heat Flow in an Instant Ice Pack

When solid ammonium nitrate dissolves in water, the solution becomes cold. This is the basis for an “instant ice pack” (Figure 1.6.5). When 3.21 g of solid NH_4NO_3 dissolves in 50.0 g of water at 24.9 °C in a calorimeter, the temperature decreases to 20.3 °C.

Calculate the value of *q* for this reaction and explain the meaning of its arithmetic sign. State any assumptions that you made.



Figure 1.6.5: An instant cold pack consists of a bag containing solid ammonium nitrate and a second bag of water. When the bag of water is broken, the pack becomes cold because the dissolution of ammonium nitrate is an endothermic process that removes thermal energy from the water. The cold pack then removes thermal energy from your body.

Solution

We assume that the calorimeter prevents heat transfer between the solution and its external environment (including the calorimeter itself), in which case:

$$q_{\text{rxn}} = -q_{\text{soln}} \tag{1.6.16}$$

with "rxn" and "soln" used as shorthand for "reaction" and "solution," respectively.

Assuming also that the specific heat of the solution is the same as that for water, we have:

$$\begin{aligned} q_{\text{rxn}} &= -q_{\text{soln}} = -(c \times m \times \Delta T)_{\text{soln}} \\ &= -[(4.184\text{J/g °C}) \times (53.2\text{ g}) \times (20.3\text{°C} - 24.9\text{°C})] \\ &= -[(4.184\text{J/g °C}) \times (53.2\text{ g}) \times (-4.6\text{°C})] \\ &+ 1.0 \times 10^3\text{ J} = +1.0\text{ kJ} \end{aligned}$$

The positive sign for q indicates that the dissolution is an endothermic process.

Exercise 1.6.4

When a 3.00-g sample of KCl was added to 3.00×10^2 g of water in a coffee cup calorimeter, the temperature decreased by 1.05 °C. How much heat is involved in the dissolution of the KCl? What assumptions did you make?

Answer available at the end of this section.

If the amount of heat absorbed by a calorimeter is too large to neglect or if we require more accurate results, then we must take into account the heat absorbed both by the solution and by the calorimeter.

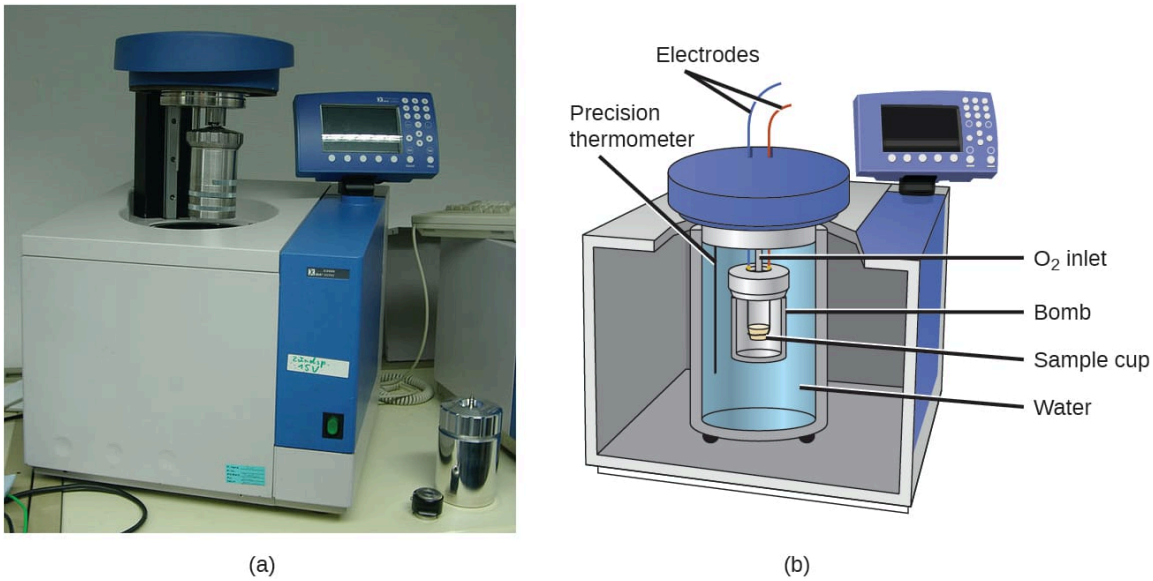


Figure 1.6.6: (a) A bomb calorimeter is used to measure heat produced by reactions involving gaseous reactants or products, such as combustion. (b) The reactants are contained in the gas-tight "bomb," which is submerged in water and surrounded by insulating materials. (credit a: modification of work by "Harbor1"/Wikimedia commons)

The calorimeters described are designed to operate at constant (atmospheric) pressure and are convenient to measure heat flow accompanying processes that occur in solution. A different type of calorimeter that operates at constant volume, colloquially known as a bomb calorimeter, is used to measure the energy produced by reactions that yield large amounts of heat and gaseous products, such as combustion reactions. (The term "bomb" comes from the observation that these reactions can be vigorous enough to resemble explosions that would damage other calorimeters.) This type of calorimeter consists of a robust steel container (the "bomb") that contains the reactants and is itself submerged in water (Figure 1.6.6). The sample is placed in the bomb, which is then filled with oxygen at high pressure. A small electrical spark is used to ignite the sample. The energy produced by the reaction is trapped in the steel bomb and the surrounding water. The temperature increase is measured and, along with the known heat capacity of the calorimeter, is used to calculate the energy produced by the reaction. Bomb calorimeters require calibration to determine the heat capacity of the calorimeter and ensure accurate results. The calibration is accomplished using a reaction with a known q, such as a measured quantity of benzoic acid ignited by a spark from a nickel fuse wire that is weighed before and after the reaction. The temperature change produced by the known reaction is used to determine the heat capacity of the calorimeter. The calibration is generally performed each time before the calorimeter is used to gather research data.

YouTube Video

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

View this YouTube Video online

Video 1.6.1: Video of view how a bomb calorimeter is prepared for action.

Example 1.6.5: Bomb Calorimetry

When 3.12 g of glucose, $C_6H_{12}O_6$, is burned in a bomb calorimeter, the temperature of the calorimeter increases from 23.8 °C to 35.6 °C. The calorimeter contains 775 g of water, and the bomb itself has a heat capacity of 893 J/°C. How much heat was produced by the combustion of the glucose sample?

Solution

The combustion produces heat that is primarily absorbed by the water and the bomb. (The amounts of heat absorbed by the reaction products and the unreacted excess oxygen are relatively small and dealing with them is beyond the scope of this text. We will neglect them in our calculations.)

The heat produced by the reaction is absorbed by the water and the bomb:

$$\begin{aligned} q_{\text{rxn}} &= -(q_{\text{water}} + q_{\text{bomb}}) \\ &= -[(4.184\ \text{J/g °C}) \times (775\ \text{g}) \times (35.6\text{°C} - 23.8\text{°C}) + 893\ \text{J/°C} \times (35.6\text{°C} - 23.8\text{°C})] \\ &= -(38,300\ \text{J} + 10,500\ \text{J}) \\ &= -48,800\ \text{J} = -48.8\ \text{kJ} \end{aligned}$$

This reaction released 48.7 kJ of heat when 3.12 g of glucose was burned.

Exercise 1.6.5

When 0.963 g of benzene, C_6H_6, is burned in a bomb calorimeter, the temperature of the calorimeter increases by 8.39 °C. The bomb has a heat capacity of 784 J/°C and is submerged in 925 mL of water. How much heat was produced by the combustion of the glucose sample?

Answer available at the end of this section.

Since the first one was constructed in 1899, 35 calorimeters have been built to measure the heat produced by a living person.[1] These whole-body calorimeters of various designs are large enough to hold an individual human being. More recently, whole-room calorimeters allow for relatively normal activities to be performed, and these calorimeters generate data that more closely reflect the real world. These calorimeters are used to measure the metabolism of individuals under different environmental conditions, different dietary regimes, and with different health conditions, such as diabetes. In humans, metabolism is typically measured in Calories per day. A nutritional calorie (Calorie) is the energy unit used to quantify the amount of energy derived from the metabolism of foods; one Calorie is equal to 1000 calories (1 kcal), the amount of energy needed to heat 1 kg of water by 1 °C.

Measuring Nutritional Calories

In your day-to-day life, you may be more familiar with energy being given in Calories, or nutritional calories, which are used to quantify the amount of energy in foods. One calorie (cal) = exactly 4.184 joules, and one Calorie (note the capitalization) = 1000 cal, or 1 kcal. (This is approximately the amount of energy needed to heat 1 kg of water by 1 °C.)

The macronutrients in food are proteins, carbohydrates, and fats or oils. Proteins provide about 4 Calories per gram, carbohydrates also provide about 4 Calories per gram, and fats and oils provide about 9 Calories/g. Nutritional labels on food packages show the caloric content of one serving of the food, as well as the breakdown into Calories from each of the three macronutrients (Figure 1.6.7).

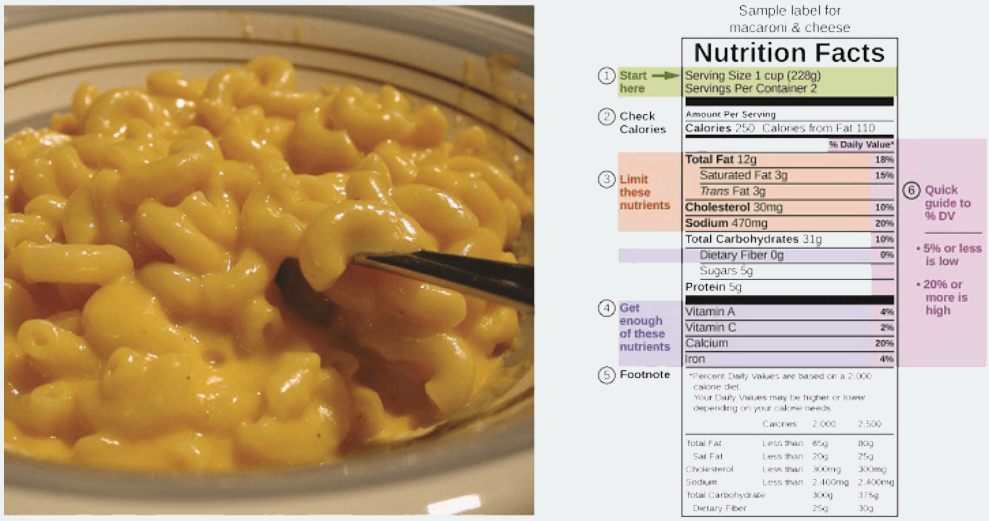


Figure 1.6.7: (a) Macaroni and cheese contain energy in the form of the macronutrients in the food. (b) The food's nutritional information is shown on the package label. In the US, the energy content is given in Calories (per serving); the rest of the world usually uses kilojoules. (credit a: modification of work by "Rex Roof"/Flickr)

For the example shown in (b), the total energy per 228-g portion is calculated by:

$$(5\text{ g protein} \times 4\text{ Calories/g}) + (31\text{ g carb} \times 4\text{ Calories/g}) + (12\text{ g fat} \times 9\text{ Calories/g}) = 252\text{ Calories} \tag{1.6.17}$$

So, you can use food labels to count your Calories. But where do the values come from? And how accurate are they? The caloric content of foods can be determined by using bomb calorimetry; that is, by burning the food and measuring the energy it contains. A sample of food is weighed, mixed in a blender, freeze-dried, ground into powder, and formed into a pellet. The pellet is burned inside a bomb calorimeter, and the measured temperature change is converted into energy per gram of food.

Today, the caloric content on food labels is derived using a method called the Atwater system that uses the average caloric content of the different chemical constituents of food, protein, carbohydrate, and fats. The average amounts are those given in the equation and are derived from the various results given by bomb calorimetry of whole foods. The carbohydrate amount is discounted a certain amount for the fiber content, which is indigestible carbohydrate. To determine the energy content of a food, the quantities of carbohydrate, protein, and fat are each multiplied by the average Calories per gram for each and the products summed to obtain the total energy.

Summary

Calorimetry is used to measure the amount of thermal energy transferred in a chemical or physical process. This requires careful measurement of the temperature change that occurs during the process and the masses of the system and surroundings. These measured quantities are then used to compute the amount of heat produced or consumed in the process using known mathematical relations. Calorimeters are designed to minimize energy exchange between the system being studied and its surroundings. They range from simple coffee cup calorimeters used by introductory chemistry students to sophisticated bomb calorimeters used to determine the energy content of food.

Footnotes

1. 1 Francis D. Reardon et al. "The Snellen human calorimeter revisited, re-engineered and upgraded: Design and performance characteristics." *Medical and Biological Engineering and Computing* 8 (2006)721–28, http://link.springer.com/article/10....517-006-0086-5.

Glossary

bomb calorimeter
: device designed to measure the energy change for processes occurring under conditions of constant volume; commonly used for reactions involving solid and gaseous reactants or products

calorimeter
: device used to measure the amount of heat absorbed or released in a chemical or physical process

calorimetry
: process of measuring the amount of heat involved in a chemical or physical process

nutritional calorie (Calorie)
: unit used for quantifying energy provided by digestion of foods, defined as 1000 cal or 1 kcal

surroundings
: all matter other than the system being studied

system
: portion of matter undergoing a chemical or physical change being studied

Contributors and Attributions

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- Christy VanRooyen, Oregon Tech

Answers

Exercise $1.6.1A$

The initial temperature of the copper was 335.6 °C.

Exercise $1.6.1B$

The final temperature (reached by both copper and water) is 38.7 °C.

Exercise $1.6.2$

$c_{metal} = 0.13\ J/g\ \ ^\circ C$

This specific heat is close to that of either gold or lead. It would be difficult to determine which metal this was based solely on the numerical values. However, the observation that the metal is silver/gray in addition to the value for the specific heat indicates that the metal is lead.

Exercise $1.6.3$

$1.34 \times 10^3\ J$; assume no heat is absorbed by the calorimeter, no heat is exchanged between the calorimeter and its surroundings, and that the specific heat and mass of the solution are the same as those for water

Exercise $1.6.4$

1.33 kJ; assume that the calorimeter prevents heat transfer between the solution and its external environment (including the calorimeter itself) and that the specific heat of the solution is the same as that for water.

Exercise $1.6.5$

39.0 kJ

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1.7: Unit 1 Practice Problems

Question 1.

Give the name and symbol of the prefixes used with SI units to indicate multiplication by the following exact quantities.

(a) 10^3

(b) 10^{-2}

(c) 0.1

(d) 10^{-3}

(e) 1,000,000

(f) 0.0000001

Answer a

kilo- (k)

Answer b

centi- (c)

Answer c

deci- (d)

Answer d

milli- (m)

Answer e

Mega- (M)

Answer f

micro- (μ)

Question 2.

1 m = _____ km?

Answer

0.001km

1 dm = _____ m?

Answer

0.1m

One 1 m = _____ µm?

Answer

10^6 µm

One nm = _____ m?

Answer

10^{-9}nm

Question 3.

Indicate the SI base units or derived units that are appropriate for the following measurements.

(a) the length of a marathon race (26.2 miles)

(b) the mass of an automobile

(c) the volume of a swimming pool

(d) the density of gold

(f) the area of a football field

Answer a

meter

Answer b

kilogram

Answer c

cubic meter

Answer d

kilogram per cubic meter

Answer c

cubic meter

Answer b

square meter

Question 4.

50.0 inches is equivalent to how many meters? (1m = 39.37in)

Answer

$$50.0 \cancel{\text{in.}} \times \frac{1 \text{ m}}{39.37 \cancel{\text{in.}}} = 1.27 \text{ m} \tag{1.7.1}$$

Question 5.

1.8 yards is equivalent to how many centimeters? (1in = 2.54cm)

Answer

$$1.8 \cancel{\text{ yrd.}} \times \frac{36 \text{ in}}{1 \cancel{\text{ yrd.}}} \times \frac{2.54 \text{ cm}}{1 \cancel{\text{ in.}}} = 160 \text{ cm} \tag{1.7.2}$$

Question 6.

A car gets 23.4 mi/gal. Express this mileage in km/L. (1 mi = 1.61km and 1 gal = 3.785L)

Answer

$$\frac{23.4 \cancel{\text{ mi.}}}{1 \cancel{\text{ gal.}}} \times \frac{1.61 \text{ km}}{1 \cancel{\text{ mi.}}} \times \frac{1 \cancel{\text{ gal}}}{3.785 \text{ L}} = 9.95 \text{ km/L}$$

Question 7.

The area of a table is 24.0ft^2. What is this area in dm^2? (1ft = 3.048dm)

Answer

$$24.0 ft^2 * \left(\frac{3.048 dm}{1 ft} \right)^2 = 223 dm^2 \tag{1.7.3}$$

Question 8.

The dimensions of a block are 3.46cm by 4.87cm by 102mm. What is the volume of the block in cm^3 and m^3?

Answer

Volume = 3.46cm x 4.87cm x 10.2cm = 173cm^3

$$173 cm^3 * \left(\frac{1m}{100cm} \right)^3 = 0.000173 m^3 \tag{1.7.4}$$

Question 9.

What is the density of a liquid with a mass of 31.1415 g and a volume of 30.13 cm^3?

Answer

Density = 31.145g / 30.13 cm^3 = 1.034 g/cm^3

Question 10.

What is the mass of a piece of aluminum that has a volume of 12.5mL and a density of 2.7g/cc.

Answer

Remember that 1mL = 1cc M = V x D = 12.5cc * 2.7g/cc = 34g

Question 11.

What is the thickness of a piece of iron foil with the dimensions of 4.8cm by 5.3cm and a mass of 0.402g? The density of iron is

$7.9 g/cm^3$.

Answer

T = V/A

V = 0.402g/7.9g/cc = 0.051cc

T = 0.051cc/(4.8cm * 5.3cm) = 0.0020cm

Question 12.

When a serving of mango sticky rice is tested in a bomb calorimeter, the temperature of 4.20L of water rises from 21.0°C to 73.5°C . How many dietary calories are in the sticky rice? The specific heat of water is 1g/cal°C .

Answer

$q=m \times c \times (T_{final} - T_{initial})$

mass of water = V * D = 4200mL * 1g/mL = 4200g

q = 4200g * 1cal/g°C * (73.5-21.0) = 220,500cals = 221 kcals or dietary calories

Contributors

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2: ATOMS AND THE PERIODIC TABLE

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General Chemistry

This chapter will describe some of the fundamental chemical principles related to the composition of matter, including those central to the concept of molecular identity.

Unit 2 Objectives

By the end of this unit, you will be able to:

- Define: proton, neutron, electron, mass number, atomic number, isotope, ion, cation, anion, and orbital.
- Differentiate between the three major subatomic particles by charge and location in an atom and determine how many of each an atom has.
- State the law of conservation of mass and describe how it relates to chemistry.
- Identify the elements by name and symbol.
- Extract relevant information from the periodic table.
- Name the various groups on the periodic table.
- Draw the shape of an s orbital, a p orbital, and a p subshell. Determine the number of electrons each orbital and subshell can hold (s, p, d, f).
- Give the electron configuration for an atom using Bohr's model, Noble Gas configuration, quantum mechanical notation, and box orbital diagrams.

2.1: Evolution of Atomic Theory

2.2: Atomic Structure and Symbolism

2.3: The Periodic Table

2.4: Memorizing Element Names and Symbols

2.5: Development of Quantum Theory

2.6: Electron Configurations

2.7: Unit 2 Practice Problems

2.8: Electromagnetic Energy - Lab 4

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2.1: Evolution of Atomic Theory

Learning Objectives

- Define: proton, neutron, electron, mass number, atomic number, isotope, and orbital.
- Differentiate between the three major subatomic particles by charge and location in an atom and determine how many of each an atom has.
- State the law of conservation of mass and describe how it relates to chemistry.

A Video Introduction to Atomic Theory through the Nineteenth Century From Crash Course Chemistry

YouTube Video

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Video $2.1.1$***:* Lavoisier's discovery of The Law of Conservation of Matter led to the Laws of Definite and Multiple Proportions and eventually Dalton's Atomic Theory.**

Atomic Theory through the Nineteenth Century

The earliest recorded discussion of the basic structure of matter comes from ancient Greek philosophers, the scientists of their day. In the fifth century BC, Leucippus and Democritus argued that all matter was composed of small, finite particles that they called *atomos*, a term derived from the Greek word for “indivisible.” They thought of atoms as moving particles that differed in shape and size, and which could join together. Later, Aristotle and others came to the conclusion that matter consisted of various combinations of the four “elements”—fire, earth, air, and water—and could be infinitely divided. Interestingly, these philosophers thought about atoms and “elements” as philosophical concepts, but apparently never considered performing experiments to test their ideas.

The Aristotelian view of the composition of matter held sway for over two thousand years, until English schoolteacher John Dalton helped to revolutionize chemistry with his hypothesis that the behavior of matter could be explained using an atomic theory. First published in 1807, many of Dalton’s hypotheses about the microscopic features of matter are still valid in modern atomic theory. Here are the postulates of Dalton’s atomic theory.

1. Matter is composed of exceedingly small particles called atoms. An atom is the smallest unit of an element that can participate in a chemical change.
2. An element consists of only one type of atom, which has a mass that is characteristic of the element and is the same for all atoms of that element (Figure $2.1.1$). A macroscopic sample of an element contains an incredibly large number of atoms, all of which have identical chemical properties.
3. Atoms of one element differ in properties from atoms of all other elements.
4. A compound consists of atoms of two or more elements combined in a small, whole-number ratio. In a given compound, the numbers of atoms of each of its elements are always present in the same ratio (Figure $2.1.2$).
5. Atoms are neither created nor destroyed during a chemical change, but are instead rearranged to yield substances that are different from those present before the change (Figure $2.1.3$).

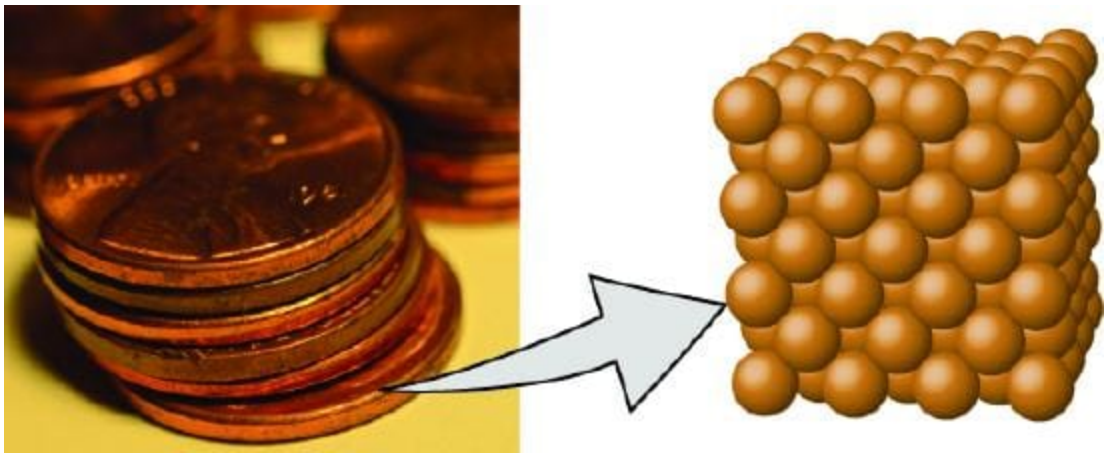


Figure 2.1.1***:*** *A pre-1982 copper penny (left) contains approximately* 3×10^{22} *copper atoms (several dozen are represented as brown spheres at the right), each of which has the same chemical properties. (credit: modification of work by "slgckgc"/Flickr)*

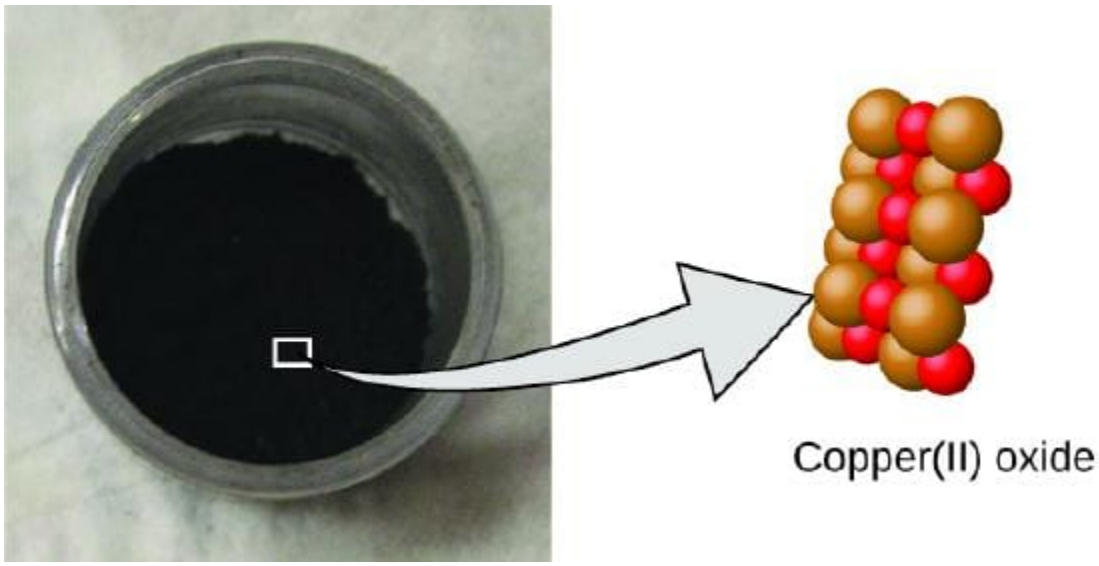


Figure 2.1.2***:*** *Copper(II) oxide, a powdery, black compound, results from the combination of two types of atoms—copper (brown spheres) and oxygen (red spheres)—in a 1:1 ratio. (credit: modification of work by "Chemicalinterest"/Wikimedia Commons)*

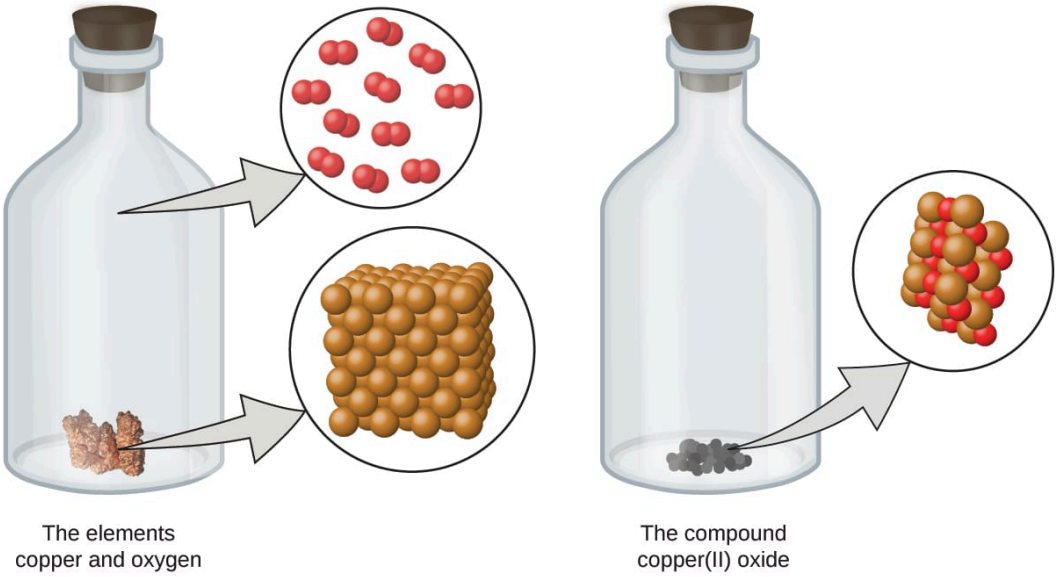


Figure 2.1.3*: When the elements copper (a shiny, red-brown solid, shown here as brown spheres) and oxygen (a clear and colorless gas, shown here as red spheres) react, their atoms rearrange to form a compound containing copper and oxygen (a powdery, black solid). (credit copper: modification of work by http://images-of-elements.com/copper.php).*

Dalton's atomic theory provides a microscopic explanation of the many macroscopic properties of matter that you've learned about. For example, if an element such as copper consists of only one kind of atom, then it cannot be broken down into simpler substances, that is, into substances composed of fewer types of atoms. And if atoms are neither created nor destroyed during a chemical change, then the total mass of matter present when matter changes from one type to another will remain constant (the law of conservation of matter (or mass)).

Want to learn more about the Law of Conservation of Mass?

YouTube Video

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Video 2.1.2***: "We are made of star stuff" - Carl Sagan.***

Example 2.1.1: Testing Dalton's Atomic Theory

In the following drawing, the green spheres represent atoms of a certain element. The purple spheres represent atoms of another element. If the spheres touch, they are part of a single unit of a compound. Does the following chemical change represented by these symbols violate any of the ideas of Dalton's atomic theory? If so, which one?

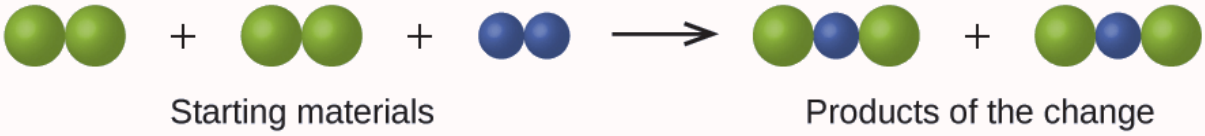


Solution

The starting materials consist of two green spheres and two purple spheres. The products consist of only one green sphere and one purple sphere. This violates Dalton's postulate that atoms are neither created nor destroyed during a chemical change, but are merely redistributed. (In this case, atoms appear to have been destroyed.)

Exercise 2.1.1

In the following drawing, the green spheres represent atoms of a certain element. The purple spheres represent atoms of another element. If the spheres touch, they are part of a single unit of a compound. Does the following chemical change represented by these symbols violate any of the ideas of Dalton's atomic theory? If so, which one



Answer

The starting materials consist of four green spheres and two purple spheres. The products consist of four green spheres and two purple spheres. This does not violate any of Dalton's postulates: Atoms are neither created nor destroyed, but are redistributed in small, whole-number ratios.

Dalton knew of the experiments of French chemist Joseph Proust, who demonstrated that *all samples of a pure compound contain the same elements in the same proportion by mass*. This statement is known as the law of definite proportions or the law of constant composition. The suggestion that the numbers of atoms of the elements in a given compound always exist in the same ratio is consistent with these observations. For example, when different samples of isooctane (a component of gasoline and one of the standards used in the octane rating system) are analyzed, they are found to have a carbon-to-hydrogen mass ratio of 5.33:1, as shown in Table 2.1.1.

Table 2.1.1*: Constant Composition of Isooctane*

Sample	Carbon	Hydrogen	Mass Ratio
A	14.82 g	2.78 g	$\frac{14.82\ \text{g carbon}}{2.78\ \text{g hydrogen}} = \frac{5.33\ \text{g carbon}}{1.00\ \text{g hydrogen}}$
B	22.33 g	4.19 g	$\frac{22.33\ \text{g carbon}}{4.19\ \text{g hydrogen}} = \frac{5.33\ \text{g carbon}}{1.00\ \text{g hydrogen}}$
C	19.40 g	3.64 g	$\frac{19.40\ \text{g carbon}}{3.63\ \text{g hydrogen}} = \frac{5.33\ \text{g carbon}}{1.00\ \text{g hydrogen}}$

It is worth noting that although all samples of a particular compound have the same mass ratio, the converse is not true in general. That is, samples that have the same mass ratio are not necessarily the same substance. For example, there are many compounds other than isooctane that also have a carbon-to-hydrogen mass ratio of 5.33:1.00.

Dalton also used data from Proust, as well as results from his own experiments, to formulate another interesting law. The law of multiple proportions states that *when two elements react to form more than one compound, a fixed mass of one element will react with masses of the other element in a ratio of small, whole numbers*. For example, copper and chlorine can form a green,

crystalline solid with a mass ratio of 0.558 g chlorine to 1 g copper, as well as a brown crystalline solid with a mass ratio of 1.116 g chlorine to 1 g copper. These ratios by themselves may not seem particularly interesting or informative; however, if we take a ratio of these ratios, we obtain a useful and possibly surprising result: a small, whole-number ratio.

$$\frac{\frac{1.116\ \text{g Cl}}{1\ \text{g Cu}}}{\frac{0.558\ \text{g Cl}}{1\ \text{g Cu}}} = \frac{2}{1} \tag{2.1.1}$$

This 2-to-1 ratio means that the brown compound has twice the amount of chlorine per amount of copper as the green compound.

This can be explained by atomic theory if the copper-to-chlorine ratio in the brown compound is 1 copper atom to 2 chlorine atoms, and the ratio in the green compound is 1 copper atom to 1 chlorine atom. The ratio of chlorine atoms (and thus the ratio of their masses) is therefore 2 to 1 (Figure 2.1.4).

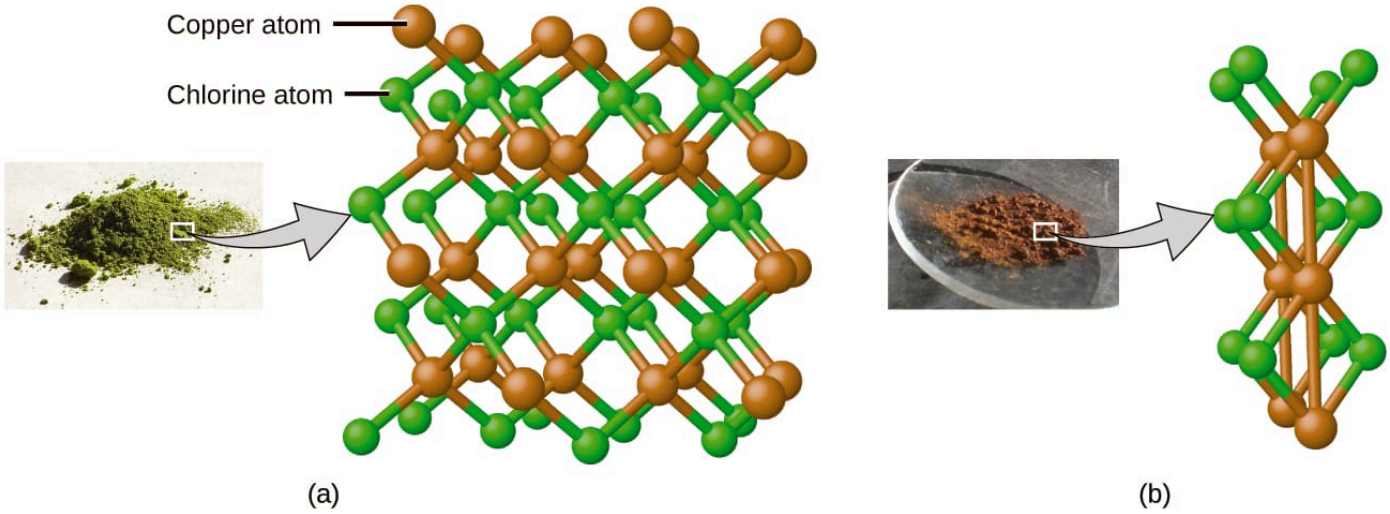


Figure 2.1.4*: Compared to the copper chlorine compound in (a), where copper is represented by brown spheres and chlorine by green spheres, the copper chlorine compound in (b) has twice as many chlorine atoms per copper atom. (credit a: modification of work by "Benjah-bmm27"/Wikimedia Commons; credit b: modification of work by "Walkerma"/Wikimedia Commons)*

Atomic Theory after the Nineteenth Century

If matter were composed of atoms, what were atoms composed of? Were they the smallest particles, or was there something smaller? In the late 1800s, a number of scientists interested in questions like these investigated the electrical discharges that could be produced in low-pressure gases, with the most significant discovery made by English physicist J. J. Thomson using a cathode ray tube. This apparatus consisted of a sealed glass tube from which almost all the air had been removed; the tube contained two metal electrodes. When high voltage was applied across the electrodes, a visible beam called a cathode ray appeared between them. This beam was deflected toward the positive charge and away from the negative charge, and was produced in the same way with identical properties when different metals were used for the electrodes. In similar experiments, the ray was simultaneously deflected by an applied magnetic field, and measurements of the extent of deflection and the magnetic field strength allowed Thomson to calculate the charge-to-mass ratio of the cathode ray particles. The results of these measurements indicated that these particles were much lighter than atoms (Figure 2.1.1).

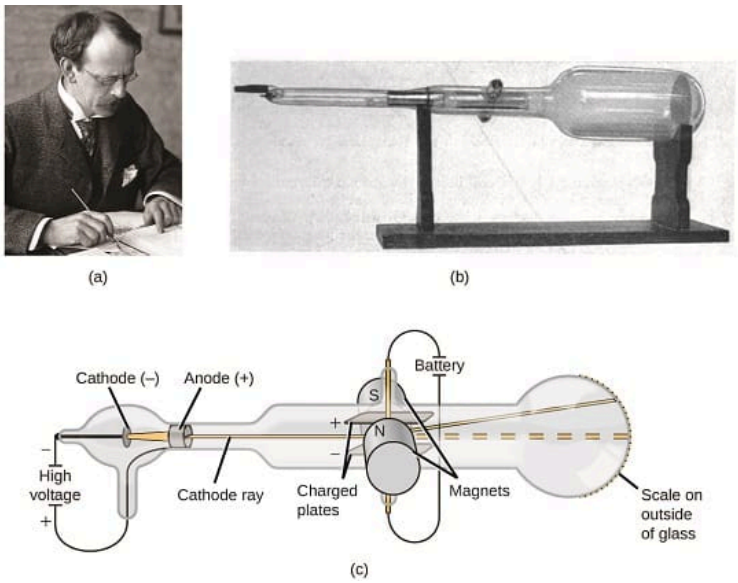
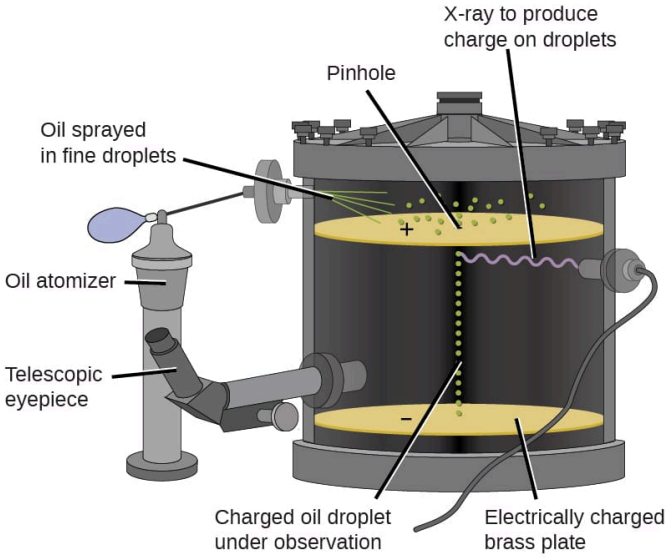


Figure 2.1.5*: (a) J. J. Thomson produced a visible beam in a cathode ray tube. (b) This is an early cathode ray tube, invented in 1897 by Ferdinand Braun. (c) In the cathode ray, the beam (shown in yellow) comes from the cathode and is accelerated past the anode toward a fluorescent scale at the end of the tube. Simultaneous deflections by applied electric and magnetic fields permitted Thomson to calculate the mass-to-charge ratio of the particles composing the cathode ray. (credit a: modification of work by Nobel Foundation; credit b: modification of work by Eugen Nesper; credit c: modification of work by "Kurzon"/Wikimedia Commons).*

Based on his observations, here is what Thomson proposed and why: The particles are attracted by positive (+) charges and repelled by negative (–) charges, so they must be negatively charged (like charges repel and unlike charges attract); they are less massive than atoms and indistinguishable, regardless of the source material, so they must be fundamental, subatomic constituents of all atoms. Although controversial at the time, Thomson's idea was gradually accepted, and his cathode ray particle is what we now call an electron, a negatively charged, subatomic particle with a mass more than one thousand-times less that of an atom. The term "electron" was coined in 1891 by Irish physicist George Stoney, from "*electr*ic i*on*."

In 1909, more information about the electron was uncovered by American physicist Robert A. Millikan via his "oil drop" experiments. Millikan created microscopic oil droplets, which could be electrically charged by friction as they formed or by using X-rays. These droplets initially fell due to gravity, but their downward progress could be slowed or even reversed by an electric field lower in the apparatus. By adjusting the electric field strength and making careful measurements and appropriate calculations, Millikan was able to determine the charge on individual drops (Figure 2.1.2).



Oil drop	Charge in coulombs (C)
A	4.8×10^{-19} C
B	3.2×10^{-19} C
C	6.4×10^{-19} C
D	1.6×10^{-19} C
E	4.8×10^{-19} C

Figure 2.1.6***:*** *Millikan's experiment measured the charge of individual oil drops. The tabulated data are examples of a few possible values.*

Looking at the charge data that Millikan gathered, you may have recognized that the charge of an oil droplet is always a multiple of a specific charge, 1.6×10^{-19} C. Millikan concluded that this value must therefore be a fundamental charge—the charge of a single electron—with his measured charges due to an excess of one electron (1 times 1.6×10^{-19} C), two electrons (2 times 1.6×10^{-19} C), three electrons (3 times 1.6×10^{-19} C), and so on, on a given oil droplet. Since the charge of an electron was now known due to Millikan's research, and the charge-to-mass ratio was already known due to Thomson's research (1.759×10^{11} C/kg), it only required a simple calculation to determine the mass of the electron as well.

$$\text{Mass of electron} = 1.602 \times 10^{-19} \cancel{\text{C}} \times \frac{1 \text{ kg}}{1.759 \times 10^{11} \cancel{\text{C}}} = 9.107 \times 10^{-31} \text{ kg} \tag{2.3.1}$$

Scientists had now established that the atom was not indivisible as Dalton had believed, and due to the work of Thomson, Millikan, and others, the charge and mass of the negative, subatomic particles—the electrons—were known. However, the positively charged part of an atom was not yet well understood. In 1904, Thomson proposed the "plum pudding" model of atoms, which described a positively charged mass with an equal amount of negative charge in the form of electrons embedded in it, since all atoms are electrically neutral. A competing model had been proposed in 1903 by Hantaro Nagaoka, who postulated a Saturn-like atom, consisting of a positively charged sphere surrounded by a halo of electrons (Figure 2.1.3).

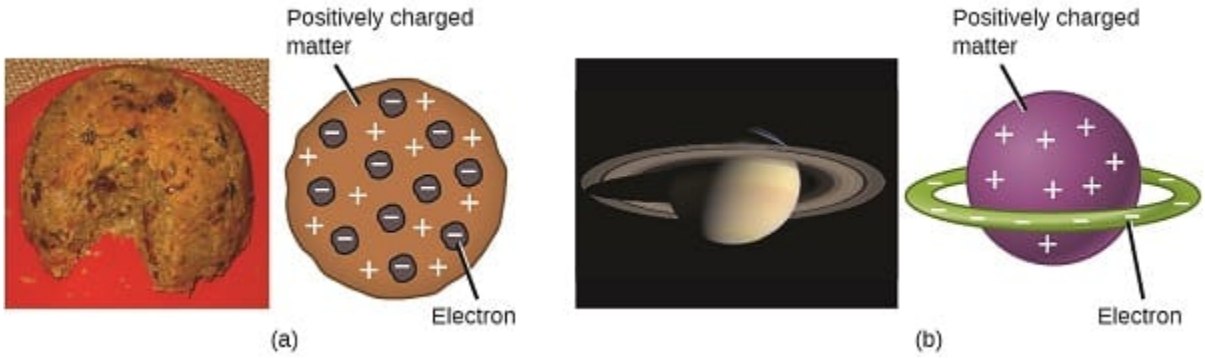


Figure 2.1.7*: (a) Thomson suggested that atoms resembled plum pudding, an English dessert consisting of moist cake with embedded raisins ("plums"). (b) Nagaoka proposed that atoms resembled the planet Saturn, with a ring of electrons surrounding a positive "planet." (credit a: modification of work by "Man vyi"/Wikimedia Commons; credit b: modification of work by "NASA"/Wikimedia Commons).*

The next major development in understanding the atom came from Ernest Rutherford, a physicist from New Zealand who largely spent his scientific career in Canada and England. He performed a series of experiments using a beam of high-speed, positively charged alpha particles (α particles) that were produced by the radioactive decay of radium; α particles consist of two protons and two neutrons (you will learn more about radioactive decay in the chapter on nuclear chemistry). Rutherford and his colleagues Hans Geiger (later famous for the Geiger counter) and Ernest Marsden aimed a beam of α particles, the source of which was embedded in a lead block to absorb most of the radiation, at a very thin piece of gold foil and examined the resultant scattering of the α particles using a luminescent screen that glowed briefly where hit by an α particle.

What did they discover? Most particles passed right through the foil without being deflected at all. However, some were diverted slightly, and a very small number were deflected almost straight back toward the source (Figure 2.1.4). Rutherford described finding these results: "It was quite the most incredible event that has ever happened to me in my life. It was almost as incredible as if you fired a 15-inch shell at a piece of tissue paper and it came back and hit you"[1] (p. 68).

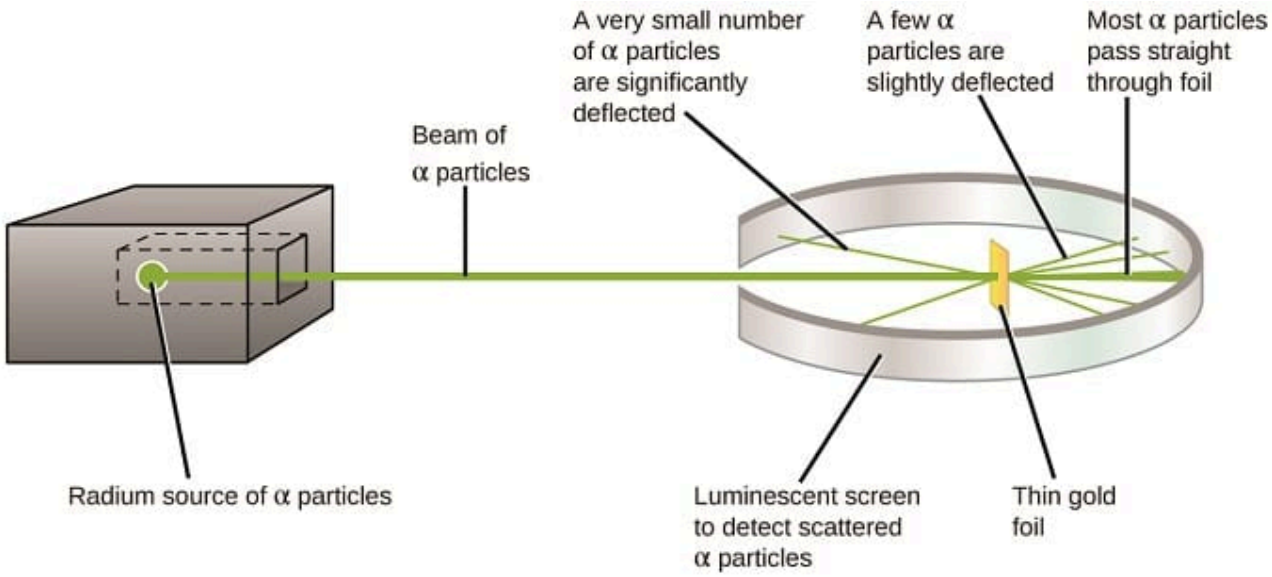


Figure 2.1.8***:*** *Geiger and Rutherford fired α particles at a piece of gold foil and detected where those particles went, as shown in this schematic diagram of their experiment. Most of the particles passed straight through the foil, but a few were deflected slightly and a very small number were significantly deflected.*

Here is what Rutherford deduced: Because most of the fast-moving α particles passed through the gold atoms undeflected, they must have traveled through essentially empty space inside the atom. Alpha particles are positively charged, so deflections arose when they encountered another positive charge (like charges repel each other). Since like charges repel one another, the few positively charged α particles that changed paths abruptly must have hit, or closely approached, another body that also had a highly concentrated, positive charge. Since the deflections occurred a small fraction of the time, this charge only occupied a small amount of the space in the gold foil. Analyzing a series of such experiments in detail, Rutherford drew two conclusions:

1. The volume occupied by an atom must consist of a large amount of empty space.
2. A small, relatively heavy, positively charged body, the nucleus, must be at the center of each atom.

This analysis led Rutherford to propose a model in which an atom consists of a very small, positively charged nucleus, in which most of the mass of the atom is concentrated, surrounded by the negatively charged electrons, so that the atom is electrically neutral (Figure 2.1.5).

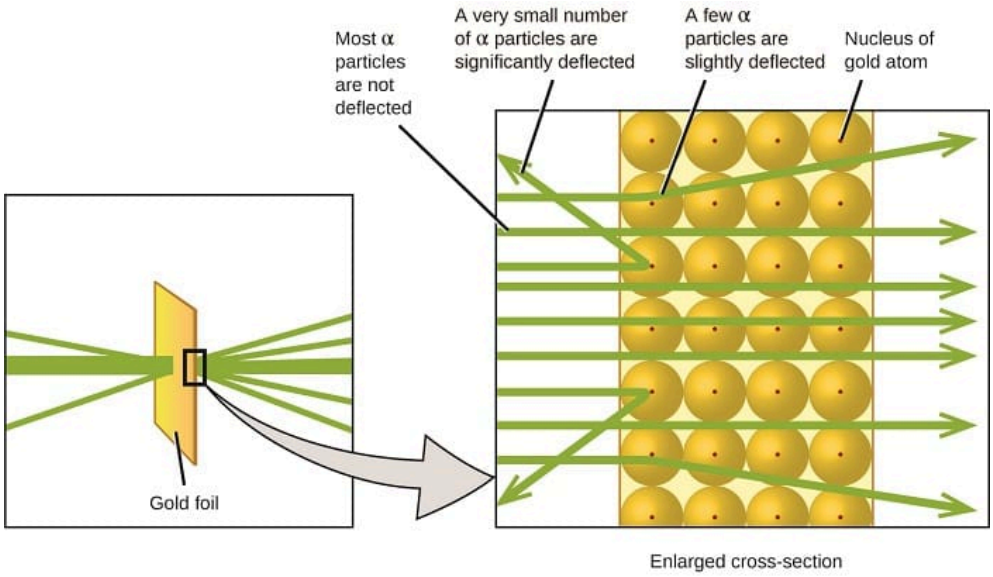


Figure 2.1.9*: The α particles are deflected only when they collide with or pass close to the much heavier, positively charged gold nucleus. Because the nucleus is very small compared to the size of an atom, very few α particles are deflected. Most pass through the relatively large region occupied by electrons, which are too light to deflect the rapidly moving particles.*

After many more experiments, Rutherford also discovered that the nuclei of other elements contain the hydrogen nucleus as a "building block," and he named this more fundamental particle the proton, the positively charged, subatomic particle found in the nucleus. With one addition, which you will learn next, this nuclear model of the atom, proposed over a century ago, is still used today.

Another important finding was the discovery of isotopes. During the early 1900s, scientists identified several substances that appeared to be new elements, isolating them from radioactive ores. For example, a "new element" produced by the radioactive decay of thorium was initially given the name mesothorium. However, a more detailed analysis showed that mesothorium was chemically identical to radium (another decay product), despite having a different atomic mass. This result, along with similar findings for other elements, led the English chemist Frederick Soddy to realize that an element could have types of atoms with different masses that were chemically indistinguishable. These different types are called isotopes—atoms of the same element that differ in mass. Soddy was awarded the Nobel Prize in Chemistry in 1921 for this discovery.

One puzzle remained: The nucleus was known to contain almost all of the mass of an atom, with the number of protons only providing half, or less, of that mass. Different proposals were made to explain what constituted the remaining mass, including the existence of neutral particles in the nucleus. As you might expect, detecting uncharged particles is very challenging, and it was not until 1932 that James Chadwick found evidence of neutrons, uncharged, subatomic particles with a mass approximately the same as that of protons. The existence of the neutron also explained isotopes: They differ in mass because they have different numbers of neutrons, but they are chemically identical because they have the same number of protons. This will be explained in more detail later in this unit.

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Video 2.1.2***: An Introduction to Subatomic Particles***

Atomic Structure

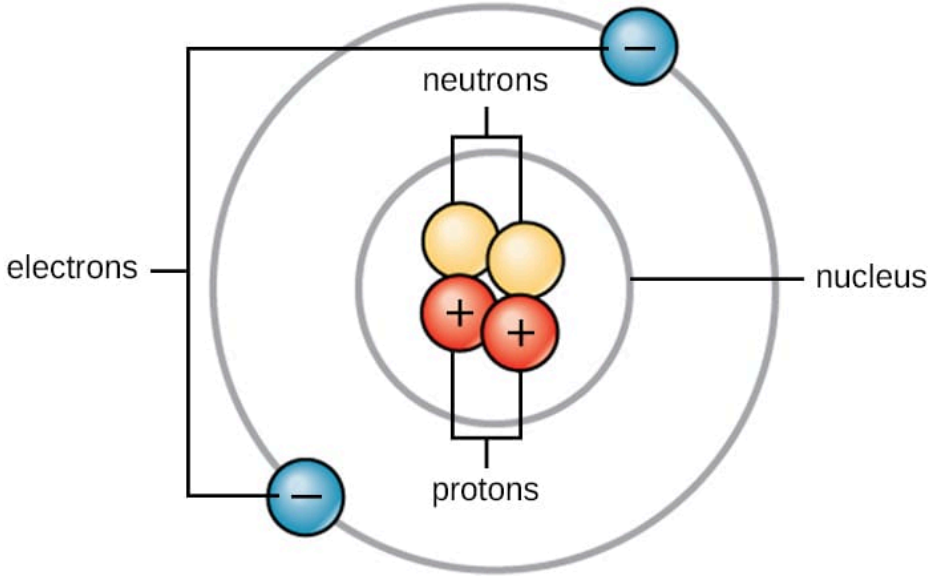


Figure** 2.1.10**: Diagram of the structure of an atom including the nucleus with protons and neutrons and the outlying electrons.

Summary

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***Video** 2.1.3**: A summary of discoveries in atomic theory.*

YouTube Video

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***Video** 2.1.4**: A different summary of discoveries in atomic theory.*

The ancient Greeks proposed that matter consists of extremely small particles called atoms. Dalton postulated that each element has a characteristic type of atom that differs in properties from atoms of all other elements, and that atoms of different elements can combine in fixed, small, whole-number ratios to form compounds. Samples of a particular compound all have the same elemental proportions by mass. When two elements form different compounds, a given mass of one element will combine

with masses of the other element in a small, whole-number ratio. During any chemical change, atoms are neither created nor destroyed.

Although no one has actually seen the inside of an atom, experiments have demonstrated much about atomic structure. Thomson's cathode ray tube showed that atoms contain small, negatively charged particles called **electrons**. Millikan discovered that there is a fundamental electric charge—the charge of an electron. Rutherford's gold foil experiment showed that atoms have a small, dense, positively charged nucleus; the positively charged particles within the nucleus are called **protons**. Chadwick discovered that the nucleus also contains neutral particles called **neutrons**. Soddy demonstrated that atoms of the same element can differ in mass; these are called **isotopes**.

Footnotes

1. Ernest Rutherford, "The Development of the Theory of Atomic Structure," ed. J. A. Ratcliffe, in *Background to Modern Science*, eds. Joseph Needham and Walter Pagel, (Cambridge, UK: Cambridge University Press, 1938), 61–74. Accessed September 22, 2014, https://ia600508.us.archive.org/3/it...e032734mbp.pdf.

Glossary

Dalton's atomic theory
: set of postulates that established the fundamental properties of atoms

law of constant composition
: (also, law of definite proportions) all samples of a pure compound contain the same elements in the same proportions by mass

law of multiple proportions
: when two elements react to form more than one compound, a fixed mass of one element will react with masses of the other element in a ratio of small whole numbers

law of definite proportions
: (also, law of constant composition) all samples of a pure compound contain the same elements in the same proportions by mass

alpha particle (α particle)
: positively charged particle consisting of two protons and two neutrons

electron
: negatively charged, subatomic particle of relatively low mass located outside the nucleus

isotopes
: atoms that contain the same number of protons but different numbers of neutrons

neutron
: uncharged, subatomic particle located in the nucleus

proton
: positively charged, subatomic particle located in the nucleus

nucleus
: massive, positively charged center of an atom made up of protons and neutrons

Contributors

- Paul Flowers (University of North Carolina - Pembroke), Klaus Theopold (University of Delaware) and Richard Langley (Stephen F. Austin State University) with contributing authors. Textbook content produced by OpenStax College is licensed under a Creative Commons Attribution License 4.0 license. Download for free at http://cnx.org/contents/85abf193-2bd...a7ac8df6@9.110).

- Adelaide Clark, Oregon Institute of Technology
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2.2: Atomic Structure and Symbolism

Learning Objectives

- Identify the elements by name and symbol.
- Define: proton, neutron, electron, mass number, atomic number, isotope, ion, cation, and anion.
- Extract relevant information from the periodic table.

The development of modern atomic theory revealed much about the inner structure of atoms. It was learned that an atom contains a very small nucleus composed of positively charged protons and uncharged neutrons, surrounded by a much larger volume of space containing negatively charged electrons. The nucleus contains the majority of an atom's mass because protons and neutrons are much heavier than electrons, whereas electrons occupy almost all of an atom's volume. The diameter of an atom is on the order of 10^{-10} m, whereas the diameter of the nucleus is roughly 10^{-15} m—about 100,000 times smaller. For a perspective about their relative sizes, consider this: If the nucleus were the size of a blueberry, the atom would be about the size of a football stadium (Figure 2.2.1).

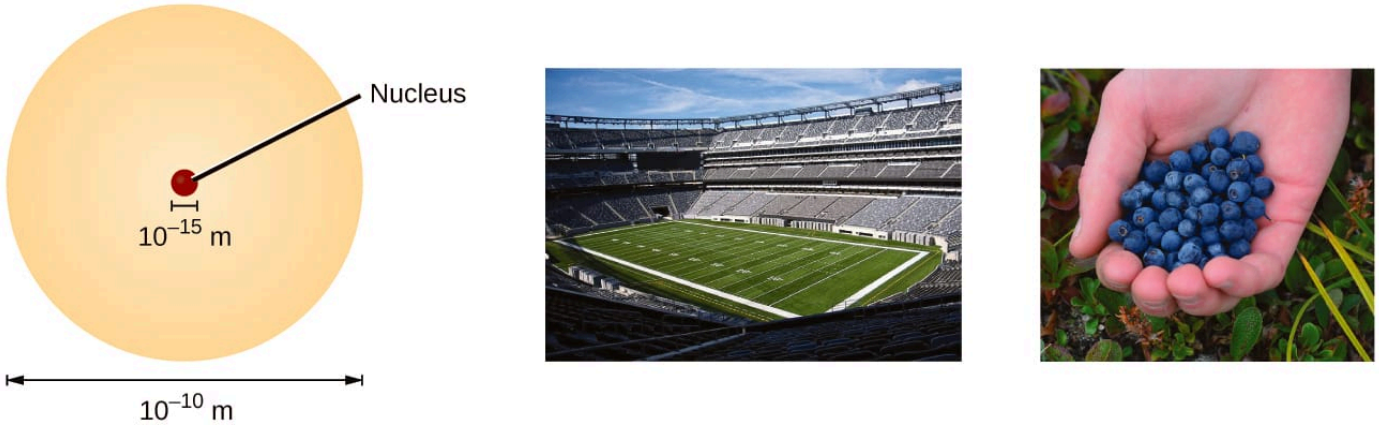


Figure 2.2.1: If an atom could be expanded to the size of a football stadium, the nucleus would be the size of a single blueberry. (credit middle: modification of work by "babyknight"/Wikimedia Commons; credit right: modification of work by Paxson Woelber).

Atoms—and the protons, neutrons, and electrons that compose them—are extremely small. For example, a carbon atom weighs less than 2×10^{-23} g, and an electron has a charge of less than 2×10^{-19} C (coulomb). When describing the properties of tiny objects such as atoms, we use appropriately small units of measure, such as the atomic mass unit (amu) and the fundamental unit of charge (e). The amu was originally defined based on hydrogen, the lightest element, then later in terms of oxygen. Since 1961, it has been defined with regard to the most abundant isotope of carbon, atoms of which are assigned masses of exactly 12 amu. (This isotope is known as "carbon-12" as will be discussed later in this module.) Thus, one amu is exactly $1/12$ of the mass of one carbon-12 atom: 1 amu = 1.6605×10^{-24} g. (The Dalton (Da) and the unified atomic mass unit (u) are alternative units that are equivalent to the amu.) The fundamental unit of charge (also called the elementary charge) equals the magnitude of the charge of an electron (e) with e = 1.602×10^{-19} C.

A proton has a mass of 1.0073 amu and a charge of 1+. A neutron is a slightly heavier particle with a mass 1.0087 amu and a charge of zero; as its name suggests, it is neutral. The electron has a charge of 1– and is a much lighter particle with a mass of about 0.00055 amu (it would take about 1800 electrons to equal the mass of one proton. The properties of these fundamental particles are summarized in Table 2.2.1. (An observant student might notice that the sum of an atom's subatomic particles does not equal the atom's actual mass: The total mass of six protons, six neutrons, and six electrons is 12.0993 amu, slightly larger than the 12.00 amu of an actual carbon-12 atom. This "missing" mass is known as the mass defect, and you will learn about it in the chapter on nuclear chemistry.)

Table 2.2.1*: Properties of Subatomic Particles*

Name	Location	Charge (C)	Unit Charge	Mass (amu)	Mass (g)
electron	outside nucleus	-1.602×10^{-19}	1–	0.00055	0.00091×10^{-24}
proton	nucleus	1.602×10^{-19}	1+	1.00727	1.67262×10^{-24}
neutron	nucleus	0	0	1.00866	1.67493×10^{-24}

The number of protons in the nucleus of an atom is its atomic number (Z). This is the defining trait of an element: Its value determines the identity of the atom. For example, any atom that contains six protons is the element carbon and has the atomic number 6, regardless of how many neutrons or electrons it may have. A neutral atom must contain the same number of positive and negative charges, so the number of protons equals the number of electrons. Therefore, the atomic number also indicates the number of electrons in an atom. The total number of protons and neutrons in an atom is called its mass number (A). The number of neutrons is therefore the difference between the mass number and the atomic number: A – Z = number of neutrons.

$$\begin{aligned} \text{atomic number (Z)} &= \text{number of protons} \\ \text{mass number (A)} &= \text{number of protons} + \text{number of neutrons} \\ \text{A} - \text{Z} &= \text{number of neutrons} \end{aligned}$$

Atoms are electrically neutral if they contain the same number of positively charged protons and negatively charged electrons. When the numbers of these subatomic particles are *not* equal, the atom is electrically charged and is called an ion. The charge of an atom is defined as follows:

$$\text{Atomic charge} = \text{number of protons} - \text{number of electrons}$$

As will be discussed in more detail later in this chapter, atoms (and molecules) typically acquire charge by gaining or losing electrons. An atom that gains one or more electrons will exhibit a negative charge and is called an anion. Positively charged atoms called cations are formed when an atom loses one or more electrons. For example, a neutral sodium atom (Z = 11) has 11 electrons. If this atom loses one electron, it will become a cation with a 1+ charge (11 – 10 = 1+). A neutral oxygen atom (Z = 8) has eight electrons, and if it gains two electrons it will become an anion with a 2– charge (8 – 10 = 2–).

Example 2.2.1: Composition of an Atom

Iodine is an essential trace element in our diet; it is needed to produce thyroid hormone. Insufficient iodine in the diet can lead to the development of a goiter, an enlargement of the thyroid gland (Figure 2.2.2).

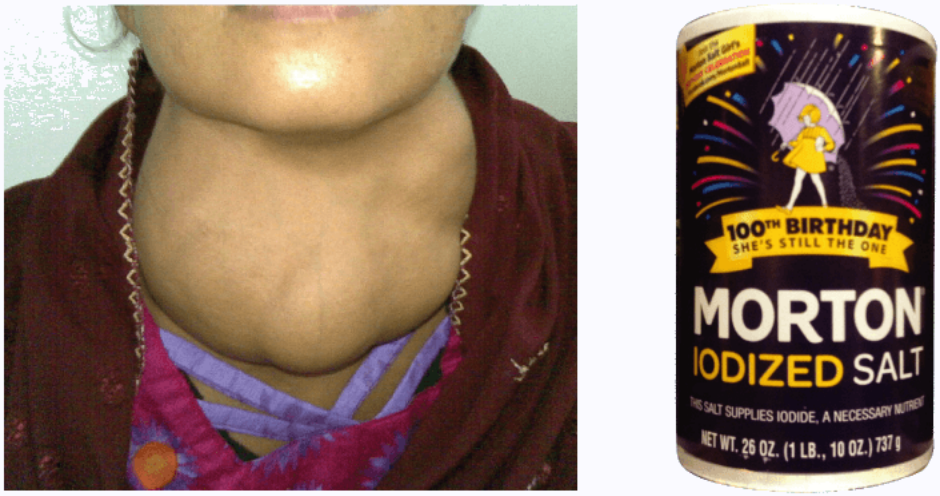


Figure 2.2.2: (a) Insufficient iodine in the diet can cause an enlargement of the thyroid gland called a goiter. (b) The addition of small amounts of iodine to salt, which prevents the formation of goiters, has helped eliminate this concern in the US where salt consumption is high. (credit a: modification of work by "Almazi"/Wikimedia Commons; credit b: modification of work by Mike Mozart)

The addition of small amounts of iodine to table salt (iodized salt) has essentially eliminated this health concern in the United States, but as much as 40% of the world's population is still at risk of iodine deficiency. The iodine atoms are added as anions, and each has a 1– charge and a mass number of 127. Determine the numbers of protons, neutrons, and electrons in one of these iodine anions.

Solution

The atomic number of iodine (53) tells us that a neutral iodine atom contains 53 protons in its nucleus and 53 electrons outside its nucleus. Because the sum of the numbers of protons and neutrons equals the mass number, 127, the number of neutrons is 74 (127 – 53 = 74). Since the iodine is added as a 1– anion, the number of electrons is 54 [53 – (1–) = 54].

Exercise 2.2.1

An ion of platinum has a mass number of 195 and contains 74 electrons. How many protons and neutrons does it contain, and what is its charge?

Answer

78 protons; 117 neutrons; charge is 4+

Chemical Symbols

A chemical symbol is an abbreviation that we use to indicate an element or an atom of an element. For example, the symbol for mercury is Hg (Figure 2.2.3). We use the same symbol to indicate one atom of mercury (microscopic domain) or to label a container of many atoms of the element mercury (macroscopic domain).

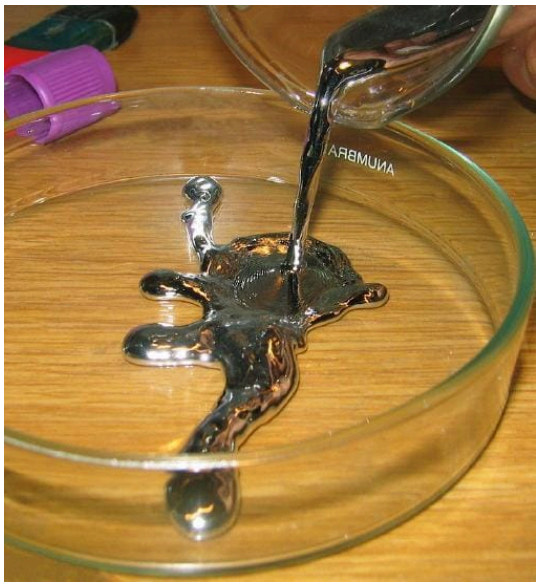


Figure 2.2.3: The symbol Hg represents the element mercury regardless of the amount; it could represent one atom of mercury or a large amount of mercury. Image used with permission from Wikipedia (user: Materialscientist).

The symbols for several common elements and their atoms are listed in Table 2.2.2. Some symbols are derived from the common name of the element; others are abbreviations of the name in another language. Symbols have one or two letters, for example, H for hydrogen and Cl for chlorine. To avoid confusion with other notations, only the first letter of a symbol is capitalized. For example, Co is the symbol for the element cobalt, but CO is the notation for the compound carbon monoxide, which contains atoms of the elements carbon (C) and oxygen (O). All known elements and their symbols are in the periodic table.

Table 2.2.2***:*** *Some Common Elements and Their Symbols*

Element	Symbol	Element	Symbol
aluminum	Al	iron	Fe (from *ferrum*)
bromine	Br	lead	Pb (from *plumbum*)
calcium	Ca	magnesium	Mg
carbon	C	mercury	Hg (from *hydrargyrum*)
chlorine	Cl	nitrogen	N
chromium	Cr	oxygen	O
cobalt	Co	potassium	K (from *kalium*)
copper	Cu (from *cuprum*)	silicon	Si
fluorine	F	silver	Ag (from *argentum*)
gold	Au (from *aurum*)	sodium	Na (from *natrium*)
helium	He	sulfur	S
hydrogen	H	tin	Sn (from *stannum*)
iodine	I	zinc	Zn

Traditionally, the discoverer (or discoverers) of a new element names the element. However, until the name is recognized by the International Union of Pure and Applied Chemistry (IUPAC), the recommended name of the new element is based on the Latin word(s) for its atomic number. For example, element 106 was called unnilhexium (Unh), element 107 was called unnilseptium (Uns), and element 108 was called unniloctium (Uno) for several years. These elements are now named after scientists or locations; for example, element 106 is now known as *seaborgium* (Sg) in honor of Glenn Seaborg, a Nobel Prize winner who was active in the discovery of several heavy elements.

Isotopes

The symbol for a specific isotope of any element is written by placing the mass number as a superscript to the left of the element symbol (Figure 2.2.4). The atomic number is sometimes written as a subscript preceding the symbol, but since this number defines the element's identity, as does its symbol, it is often omitted. For example, magnesium exists as a mixture of three isotopes, each with an atomic number of 12 and with mass numbers of 24, 25, and 26, respectively. These isotopes can be identified as ^{24}Mg, ^{25}Mg, and ^{26}Mg. These isotope symbols are read as "element, mass number" and can be symbolized consistent with this reading. For instance, ^{24}Mg is read as "magnesium 24," and can be written as "magnesium-24" or "Mg-24." ^{25}Mg is read as "magnesium 25," and can be written as "magnesium-25" or "Mg-25." All magnesium atoms have 12 protons in their nucleus. They differ only because a ^{24}Mg atom has 12 neutrons in its nucleus, a ^{25}Mg atom has 13 neutrons, and a ^{26}Mg has 14 neutrons.

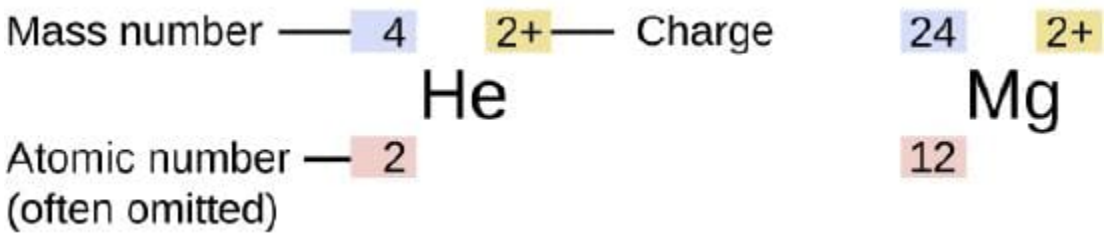


Figure 2.2.4: The symbol for an atom indicates the element via its usual two-letter symbol, the mass number as a left superscript, the atomic number as a left subscript (sometimes omitted), and the charge as a right superscript.

Information about the naturally occurring isotopes of elements with atomic numbers 1 through 10 is given in Table 2.2.2. Note that in addition to standard names and symbols, the isotopes of hydrogen are often referred to using common names and accompanying symbols. Hydrogen-2, symbolized ^{2}H, is also called deuterium and sometimes symbolized D. Hydrogen-3,

symbolized ^{3}H, is also called tritium and sometimes symbolized T.

Table 2.2.2*: Nuclear Compositions of Atoms of the Very Light Elements*

Element	Symbol	Atomic Number	Number of Protons	Number of Neutrons	Mass (amu)	% Natural Abundance
hydrogen	$^{1}_{1}H$ (protium)	1	1	0	1.0078	99.989
	$^{2}_{1}H$ (deuterium)	1	1	1	2.0141	0.0115
	$^{3}_{1}H$ (tritium)	1	1	2	3.01605	— (trace)
helium	$^{3}_{2}He$	2	2	1	3.01603	0.00013
	$^{4}_{2}He$	2	2	2	4.0026	100
lithium	$^{6}_{3}Li$	3	3	3	6.0151	7.59
	$^{7}_{3}Li$	3	3	4	7.0160	92.41
beryllium	$^{9}_{4}Be$	4	4	5	9.0122	100
boron	$^{10}_{5}B$	5	5	5	10.0129	19.9
	$^{11}_{5}B$	5	5	6	11.0093	80.1
carbon	$^{12}_{6}C$	6	6	6	12.0000	98.89
	$^{13}_{6}C$	6	6	7	13.0034	1.11
	$^{14}_{6}C$	6	6	8	14.0032	— (trace)
nitrogen	$^{14}_{7}N$	7	7	7	14.0031	99.63
	$^{15}_{7}N$	7	7	8	15.0001	0.37
oxygen	$^{16}_{8}O$	8	8	8	15.9949	99.757
	$^{17}_{8}O$	8	8	9	16.9991	0.038
	$^{18}_{8}O$	8	8	10	17.9992	0.205
fluorine	$^{19}_{9}F$	9	9	10	18.9984	100
neon	$^{20}_{10}Ne$	10	10	10	19.9924	90.48
	$^{21}_{10}Ne$	10	10	11	20.9938	0.27
	$^{22}_{10}Ne$	10	10	12	21.9914	9.25

Atomic Mass

Because each proton and each neutron contribute approximately one amu to the mass of an atom, and each electron contributes far less, the atomic mass of a single atom is approximately equal to its mass number (a whole number). However, the average masses of atoms of most elements are not whole numbers because most elements exist naturally as mixtures of two or more isotopes.

The mass of an element shown in a periodic table or listed in a table of atomic masses is a weighted, average mass of all the isotopes present in a naturally occurring sample of that element. This is equal to the sum of each individual isotope's mass multiplied by its fractional abundance.

$$\text{average mass} = \sum_{i} (\text{fractional abundance} \times \text{isotopic mass})_i \tag{2.2.1}$$

For example, the element boron is composed of two isotopes: About 19.9% of all boron atoms are ^{10}B with a mass of 10.0129 amu, and the remaining 80.1% are ^{11}B with a mass of 11.0093 amu. The average atomic mass for boron is calculated to be:

$$\begin{aligned}\text{boron average mass} &= (0.199 \times 10.0129\,\text{amu}) + (0.801 \times 11.0093\,\text{amu}) \\ &= 1.99\,\text{amu} + 8.82\,\text{amu} \\ &= 10.81\,\text{amu}\end{aligned}$$

It is important to understand that no single boron atom weighs exactly 10.8 amu; 10.8 amu is the average mass of all boron atoms, and individual boron atoms weigh either approximately 10 amu or 11 amu.

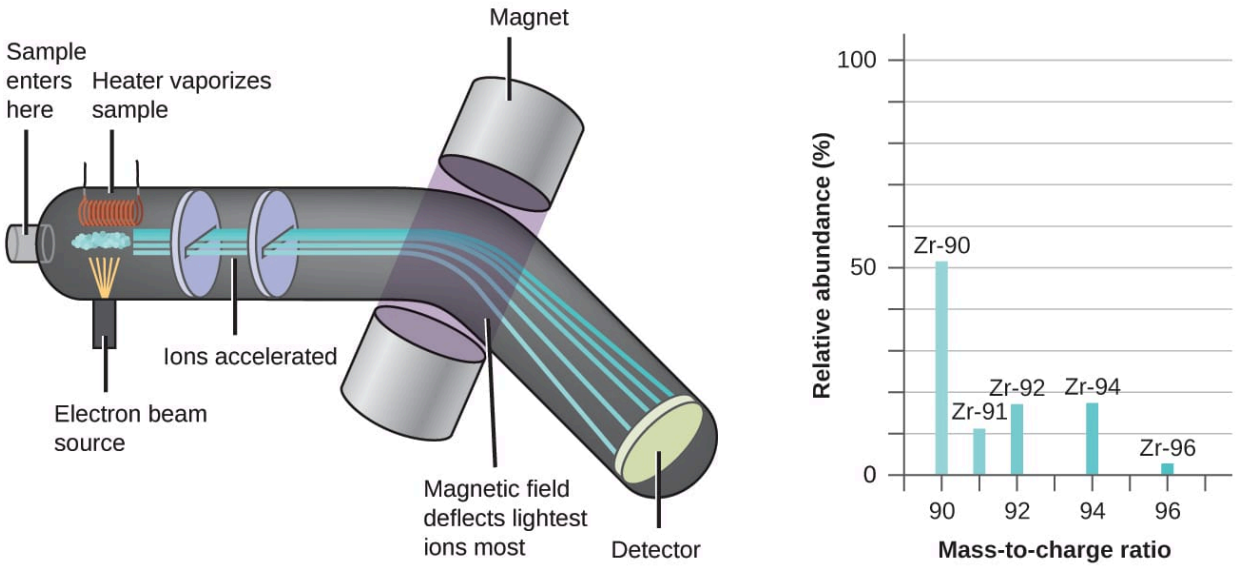


Figure 2.2.5***:*** *Analysis of zirconium in a mass spectrometer produces a mass spectrum with peaks showing the different isotopes of Zr.*

The occurrence and natural abundances of isotopes can be experimentally determined using an instrument called a mass spectrometer. Mass spectrometry (MS) is widely used in chemistry, forensics, medicine, environmental science, and many other fields to analyze and help identify the substances in a sample of material. In a typical mass spectrometer (Figure 2.2.5), the sample is vaporized and exposed to a high-energy electron beam that causes the sample's atoms (or molecules) to become electrically charged, typically by losing one or more electrons. These cations then pass through a (variable) electric or magnetic field that deflects each cation's path to an extent that depends on both its mass and charge (similar to how the path of a large steel ball bearing rolling past a magnet is deflected to a lesser extent that that of a small steel BB). The ions are detected, and a plot of the relative number of ions generated versus their mass-to-charge ratios (a *mass spectrum*) is made. The height of each vertical feature or peak in a mass spectrum is proportional to the fraction of cations with the specified mass-to-charge ratio. Since its initial use during the development of modern atomic theory, MS has evolved to become a powerful tool for chemical analysis in a wide range of applications.

YouTube Video

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Video 2.2.1*: Watch this video from the Royal Society for Chemistry for a brief description of the rudiments of mass spectrometry.*

Summary

An atom consists of a small, positively charged nucleus surrounded by electrons. The nucleus contains protons and neutrons; its diameter is about 100,000 times smaller than that of the atom. The mass of one atom is usually expressed in atomic mass units (amu), which is referred to as the atomic mass. An amu is defined as exactly $1/12$ of the mass of a carbon-12 atom and is equal to 1.6605×10^{-24} g.

Protons are relatively heavy particles with a charge of 1+ and a mass of 1.0073 amu. Neutrons are relatively heavy particles with no charge and a mass of 1.0087 amu. Electrons are light particles with a charge of 1– and a mass of 0.00055 amu. The number of protons in the nucleus is called the atomic number (Z) and is the property that defines an atom's elemental identity. The sum of the numbers of protons and neutrons in the nucleus is called the mass number and, expressed in amu, is approximately equal to the mass of the atom. An atom is neutral when it contains equal numbers of electrons and protons.

Isotopes of an element are atoms with the same atomic number but different mass numbers; isotopes of an element, therefore, differ from each other only in the number of neutrons within the nucleus. When a naturally occurring element is composed of several isotopes, the atomic mass of the element represents the average of the masses of the isotopes involved. A chemical symbol identifies the atoms in a substance using symbols, which are one-, two-, or three-letter abbreviations for the atoms.

Key Equations

- $\text{average mass} = \sum_i (\text{fractional abundance} \times \text{isotopic mass})_i$

Glossary

anion
: negatively charged atom or molecule (contains more electrons than protons)

atomic mass
: average mass of atoms of an element, expressed in amu

atomic mass unit (amu)
: (also, unified atomic mass unit, u, or Dalton, Da) unit of mass equal to $\frac{1}{12}$ of the mass of a ^{12}C atom

atomic number (Z)
: number of protons in the nucleus of an atom

cation
: positively charged atom or molecule (contains fewer electrons than protons)

chemical symbol
: one-, two-, or three-letter abbreviation used to represent an element or its atoms

Dalton (Da)
: alternative unit equivalent to the atomic mass unit

fundamental unit of charge
: (also called the elementary charge) equals the magnitude of the charge of an electron (e) with e = 1.602×10^{-19} C

ion
: electrically charged atom or molecule (contains unequal numbers of protons and electrons)

mass number (A)
: sum of the numbers of neutrons and protons in the nucleus of an atom

unified atomic mass unit (u)
: alternative unit equivalent to the atomic mass unit

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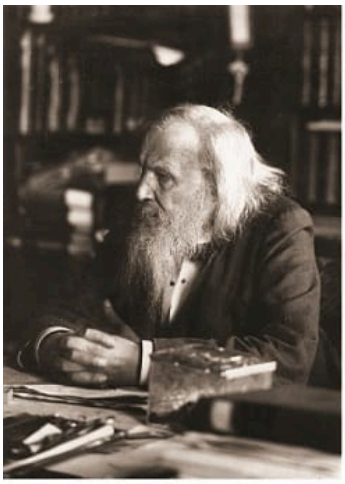
2.3: The Periodic Table

Learning Objectives

- Extract relevant information from the periodic table.
- Name the various groups on the periodic table.

As early chemists worked to purify ores and discovered more elements, they realized that various elements could be grouped together by their similar chemical behaviors. One such grouping includes lithium (Li), sodium (Na), and potassium (K): These elements all are shiny, conduct heat and electricity well, and have similar chemical properties. A second grouping includes calcium (Ca), strontium (Sr), and barium (Ba), which also are shiny, good conductors of heat and electricity, and have chemical properties in common. However, the specific properties of these two groupings are notably different from each other. For example: Li, Na, and K are much more reactive than are Ca, Sr, and Ba; Li, Na, and K form compounds with oxygen in a ratio of two of their atoms to one oxygen atom, whereas Ca, Sr, and Ba form compounds with one of their atoms to one oxygen atom. Fluorine (F), chlorine (Cl), bromine (Br), and iodine (I) also exhibit similar properties to each other, but these properties are drastically different from those of any of the elements above.

Dimitri Mendeleev in Russia (1869) and Lothar Meyer in Germany (1870) independently recognized that there was a periodic relationship among the properties of the elements known at that time. Both published tables with the elements arranged according to increasing atomic mass. But Mendeleev went one step further than Meyer: He used his table to predict the existence of elements that would have the properties similar to aluminum and silicon, but were yet unknown. The discoveries of gallium (1875) and germanium (1886) provided great support for Mendeleev's work. Although Mendeleev and Meyer had a long dispute over priority, Mendeleev's contributions to the development of the periodic table are now more widely recognized (Figure 2.3.1).



(a)

Reihen	Gruppe I. — R^1O	Gruppe II. — RO	Gruppe III. — R^2O^3	Gruppe IV. RH^4 RO^2	Gruppe V. RH^3 R^2O^5	Gruppe VI. RH^2 RO^3	Gruppe VII. RH R^2O^7	Gruppe VIII. — RO^4
1	H=1							
2	Li=7	Be=9,4	B=11	C=12	N=14	O=16	F=19	
3	Na=23	Mg=24	Al=27,3	Si=28	P=31	S=32	Cl=35,5	
4	K=39	Ca=40	—=44	Ti=48	V=51	Cr=52	Mn=55	Fe=56, Co=59, Ni=59, Cu=63.
5	(Cu=63)	Zn=65	—=68	—=72	As=75	Se=78	Br=80	
6	Rb=85	Sr=87	?Yt=88	Zr=90	Nb=94	Mo=96	—=100	Ru=104, Rh=104, Pd=106, Ag=108.
7	(Ag=108)	Cd=112	In=113	Sn=118	Sb=122	Te=125	J=127	
8	Cs=133	Ba=137	?Di=138	?Ce=140	—	—	—	— — — —
9	(—)	—	—	—	—	—	—	
10	—	—	?Er=178	?La=180	Ta=182	W=184	—	Os=195, Ir=197, Pt=198, Au=199.
11	(Au=199)	Hg=200	Tl=204	Pb=207	Bi=208	—	—	
12	—	—	—	Th=231	—	U=240	—	— — — —

(b)

Figure 2.3.1: (a) Dimitri Mendeleev is widely credited with creating (b) the first periodic table of the elements. (credit a: modification of work by Serge Lachinov; credit b: modification of work by "Den fjättrade ankan"/Wikimedia Commons)

By the twentieth century, it became apparent that the periodic relationship involved atomic numbers rather than atomic masses. The modern statement of this relationship, the periodic law, is as follows: *the properties of the elements are periodic functions of their atomic numbers*. A modern periodic table arranges the elements in increasing order of their atomic numbers and groups atoms with similar properties in the same vertical column (Figure 2.3.2). Each box represents an element and contains its atomic number, symbol, average atomic mass, and (sometimes) name. The elements are arranged in seven horizontal rows, called periods or series, and 18 vertical columns, called groups. Groups are labeled at the top of each column. In the United States, the labels traditionally were numerals with capital letters. However, IUPAC recommends that the numbers 1 through 18 be used, and these labels are more common. For the table to fit on a single page, parts of two of the rows, a total of 14 columns, are usually written below the main body of the table.

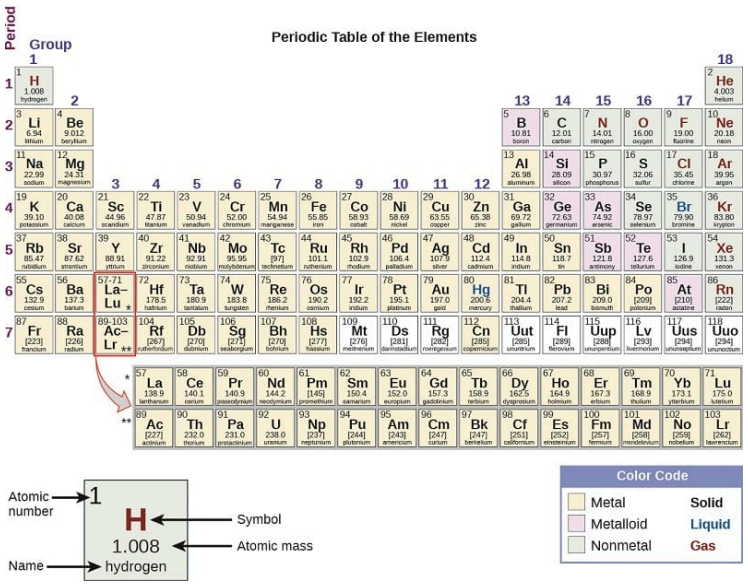


Figure 2.3.2*: Elements in the periodic table are organized according to their properties.*

Many elements differ dramatically in their chemical and physical properties, but some elements are similar in their behaviors. For example, many elements appear shiny, are malleable (able to be deformed without breaking) and ductile (can be drawn into wires), and conduct heat and electricity well. Other elements are not shiny, malleable, or ductile, and are poor conductors of heat and electricity. We can sort the elements into large classes with common properties: metals (elements that are shiny, malleable, good conductors of heat and electricity—shaded yellow); nonmetals (elements that appear dull, poor conductors of heat and electricity—shaded green); and metalloids (elements that conduct heat and electricity moderately well, and possess some properties of metals and some properties of nonmetals—shaded purple).

The elements can also be classified into the main-group elements (or representative elements) in the columns labeled 1, 2, and 13–18; the transition metals in the columns labeled 3–12; and inner transition metals in the two rows at the bottom of the table (the top-row elements are called lanthanides and the bottom-row elements are actinides; Figure 2.3.3). The elements can be subdivided further by more specific properties, such as the composition of the compounds they form. For example, the elements in group 1 (the first column) form compounds that consist of one atom of the element and one atom of hydrogen. These elements (except hydrogen) are known as alkali metals, and they all have similar chemical properties. The elements in group 2 (the second column) form compounds consisting of one atom of the element and two atoms of hydrogen: These are called alkaline earth metals, with similar properties among members of that group. Other groups with specific names are the pnictogens (group 15), chalcogens (group 16), halogens (group 17), and the noble gases (group 18, also known as inert gases). The groups can also be referred to by the first element of the group: For example, the chalcogens can be called the oxygen group or oxygen family. Hydrogen is a unique, nonmetallic element with properties similar to both group 1 and group 17 elements. For that reason, hydrogen may be shown at the top of both groups, or by itself.

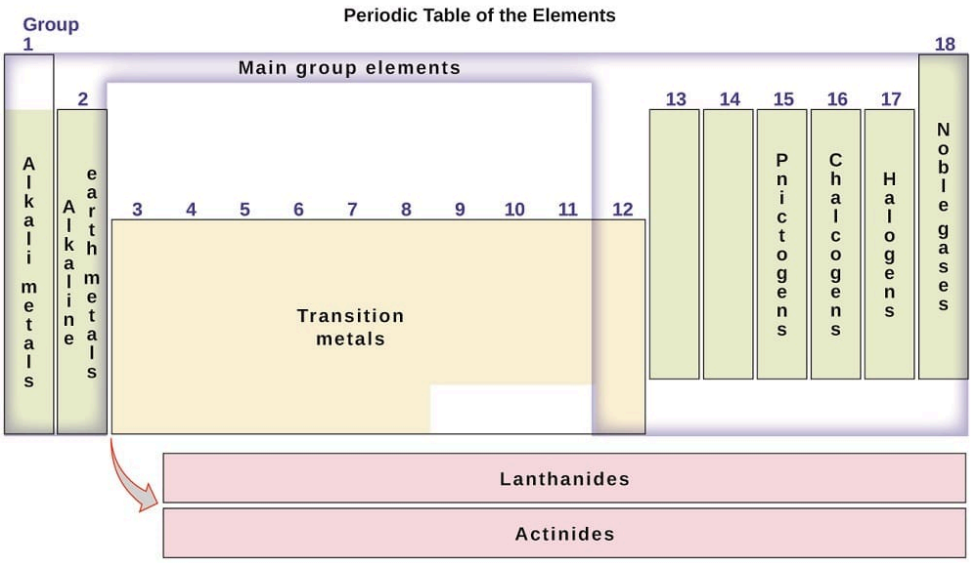


Figure 2.3.3***:*** *The periodic table organizes elements with similar properties into groups.*

Example 2.3.1: Naming Groups of Elements

Atoms of each of the following elements are essential for life. Give the group name for the following elements:

a. chlorine
b. calcium
c. sodium
d. sulfur

Solution

The family names are as follows:

a. halogen
b. alkaline earth metal
c. alkali metal
d. chalcogen

Exercise 2.3.1

Give the group name for each of the following elements:

a. krypton
b. selenium
c. barium
d. lithium

Answer a

noble gas

Answer b

chalcogen

Answer c

alkaline earth metal

Answer d

alkali metal

In studying the periodic table, you might have noticed something about the atomic masses of some of the elements. Element 43 (technetium), element 61 (promethium), and most of the elements with atomic number 84 (polonium) and higher have their atomic mass given in square brackets. This is done for elements that consist entirely of unstable, radioactive isotopes (you will learn more about radioactivity in the nuclear chemistry chapter). An average atomic weight cannot be determined for these elements because their radioisotopes may vary significantly in relative abundance, depending on the source, or may not even exist in nature. The number in square brackets is the atomic mass number (and approximate atomic mass) of the most stable isotope of that element.

Periodic Table Used for CHE 101

This is the periodic table you will be given for all quizzes and exams in CHE 101 at Oregon Tech.

Periodic Table of the Elements

Periods																		
1	1 H 1.008																	2 He 4.003
2	3 Li 6.94	4 Be 9.012											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
3	11 Na 22.99	12 Mg 24.31											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.06	17 Cl 35.45	18 Ar 39.95
4	19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.88	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.39	31 Ga 69.72	32 Ge 72.64	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.79
5	37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc (98)	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
6	55 Cs 132.9	56 Ba 137.3	* 71 Lu 175.0	72 Hf 178.5	73 Ta 180.9	74 W 183.9	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.5	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po (209)	85 At (210)	86 Rn (222)
7	87 Fr (223)	88 Ra (226)	** 103 Lr (262)	104 Rf (265)	105 Db (268)	106 Sg (271)	107 Bh (270)	108 Hs (277)	109 Mt (276)	110 Ds (281)	111 Rg (280)	112 Cn (285)	113 Nh (284)	114 Fl (289)	115 Mc (288)	116 Lv (293)	117 Ts (294)	118 Og (294)

*	57 La 138.9	58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm (145)	62 Sm 150.4	63 Eu 152.0	64 Gd 157.2	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0
**	89 Ac (227)	90 Th 232	91 Pa 231	92 U 238	93 Np (237)	94 Pu (242)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)

Summary

The discovery of the periodic recurrence of similar properties among the elements led to the formulation of the periodic table, in which the elements are arranged in order of increasing atomic number in rows known as periods and columns known as groups. Elements in the same group of the periodic table have similar chemical properties. Elements can be classified as metals, metalloids, and nonmetals, or as a main-group elements, transition metals, and inner transition metals. Groups are numbered 1–18 from left to right. The elements in group 1 are known as the alkali metals; those in group 2 are the alkaline earth metals; those in 15 are the pnictogens; those in 16 are the chalcogens; those in 17 are the halogens; and those in 18 are the noble gases.

Glossary

actinide
inner transition metal in the bottom of the bottom two rows of the periodic table

alkali metal
element in group 1

alkaline earth metal
element in group 2

chalcogen
element in group 16

group
vertical column of the periodic table

halogen
element in group 17

inert gas
(also, noble gas) element in group 18

inner transition metal
(also, lanthanide or actinide) element in the bottom two rows; if in the first row, also called lanthanide, or if in the second row, also called actinide

lanthanide
inner transition metal in the top of the bottom two rows of the periodic table

main-group element
(also, representative element) element in columns 1, 2, and 12–18

metal
element that is shiny, malleable, good conductor of heat and electricity

metalloid
element that conducts heat and electricity moderately well, and possesses some properties of metals and some properties of nonmetals

noble gas
(also, inert gas) element in group 18

nonmetal
element that appears dull, poor conductor of heat and electricity

period
(also, series) horizontal row of the periodic table

periodic law
properties of the elements are periodic function of their atomic numbers.

periodic table
table of the elements that places elements with similar chemical properties close together

pnictogen
element in group 15

representative element
(also, main-group element) element in columns 1, 2, and 12–18

transition metal
element in columns 3–11

series
(also, period) horizontal row of the period table

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- Christy VanRooyen, Oregon Tech

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2.4: Memorizing Element Names and Symbols

Skills to Develop

- Identify the elements by name and symbol.

Elements You Should Know

Memorize the names and symbols for the following elements. Flash cards can be found on Canvas.

Hydrogen	H
Helium	He
Lithium	Li
Beryllium	Be
Boron	B
Carbon	C
Nitrogen	N
Oxygen	O
Fluorine	F
Neon	Ne
Sodium	Na
Magnesium	Mg
Aluminum	Al
Silicon	Si
Phosphorus	P
Sulfur	S
Chlorine	Cl
Argon	Ar
Potassium	K
Calcium	Ca
Scandium	Sc
Titanium	Ti

Vanadium	V
Chromium	Cr
Manganese	Mn
Iron	Fe
Cobalt	Co
Nickel	Ni
Copper	Cu
Zinc	Zn
Gallium	Ga
Germanium	Ge
Arsenic	As
Selenium	Se
Bromine	Br
Krypton	Kr
Technetium	Tc
Silver	Ag
Tin	Sn
Iodine	I
Barium	Ba
Platinum	Pt
Gold	Au
Mercury	Hg
Lead	Pb
Radon	Rn
Uranium	U
Plutonium	Pu

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2.5: Development of Quantum Theory

Learning Objectives

- Give the electron configuration for an atom using Bohr's model.
- Draw the shape of an s orbital, a p orbital, and a p subshell. Determine the number of electrons each orbital and subshell can hold (s, p, d, f).

Bohr's Model

Following the work of Ernest Rutherford and his colleagues in the early twentieth century, the picture of atoms consisting of tiny dense nuclei surrounded by lighter and even tinier electrons continually moving about the nucleus was well established. This picture was called the planetary model, since it pictured the atom as a miniature "solar system" with the electrons orbiting the nucleus like planets orbiting the sun. The simplest atom is hydrogen, consisting of a single proton as the nucleus about which a single electron moves. This classical mechanics description of the atom is incomplete, however, since an electron moving in an elliptical orbit would be accelerating (by changing direction) and, according to classical electromagnetism, it should continuously emit electromagnetic radiation. This loss in orbital energy should result in the electron's orbit getting continually smaller until it spirals into the nucleus, implying that atoms are inherently unstable.

In 1913, Niels Bohr attempted to resolve the atomic paradox by ignoring classical electromagnetism's prediction that the orbiting electron in hydrogen would continuously emit light. Instead, he incorporated into the classical mechanics description of the atom Planck's ideas of quantization and Einstein's finding that light consists of photons whose energy is proportional to their frequency. Bohr assumed that the electron orbiting the nucleus would not normally emit any radiation (the stationary state hypothesis), but it would emit or absorb a photon if it moved to a different orbit.

Bohr's model explained the experimental data for the hydrogen atom and was widely accepted, but it also raised many questions. Why did electrons orbit at only fixed distances defined by a single quantum number n = 1, 2, 3, and so on, but never in between? Why did the model work so well describing hydrogen and one-electron ions, but could not correctly predict the emission spectrum for helium or any larger atoms? To answer these questions, scientists needed to completely revise the way they thought about matter.

One of the fundamental laws of physics is that matter is most stable with the lowest possible energy. Thus, the electron in a hydrogen atom usually moves in the $n = 1$ orbit, the orbit in which it has the lowest energy. When the electron is in this lowest energy orbit, the atom is said to be in its ground electronic state (or simply ground state). If the atom receives energy from an outside source, it is possible for the electron to move to an orbit with a higher n value and the atom is now in an excited electronic state (or simply an excited state) with a higher energy. When an electron transitions from an excited state (higher energy orbit) to a less excited state, or ground state, the difference in energy is emitted as a photon. Similarly, if a photon is absorbed by an atom, the energy of the photon moves an electron from a lower energy orbit up to a more excited one.

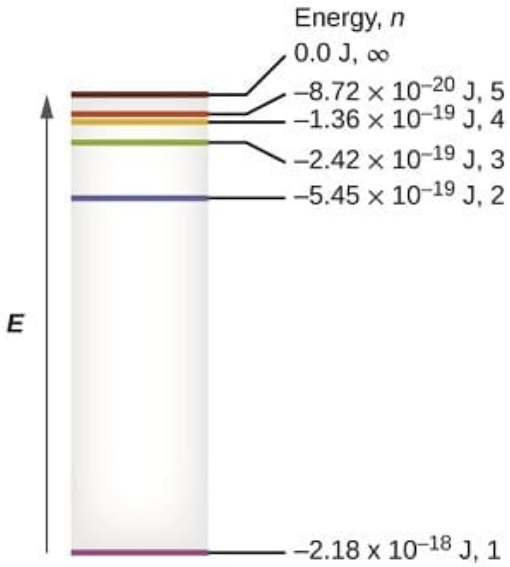


Figure 2.5.1*: Quantum numbers and energy levels in a hydrogen atom. The more negative the calculated value, the lower the energy.*

We can relate the energy of electrons in atoms to what we learned previously about energy. The law of conservation of energy says that we can neither create nor destroy energy. Thus, if a certain amount of external energy is required to excite an electron from one energy level to another, that same amount of energy will be liberated when the electron returns to its initial state (Figure 2.5.2). In effect, an atom can "store" energy by using it to promote an electron to a state with a higher energy and release it when the electron returns to a lower state. The energy can be released as one quantum of energy, as the electron returns to its ground state (say, from $n = 5$ to $n = 1$), or it can be released as two or more smaller quanta as the electron falls to an intermediate state, then to the ground state (say, from $n = 5$ to $n = 4$, emitting one quantum, then to $n = 1$, emitting a second quantum).

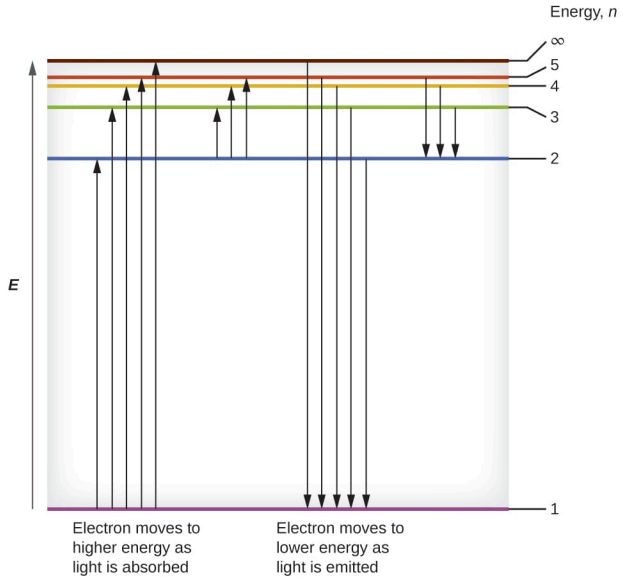


Figure 2.5.2: The horizontal lines show the relative energy of orbits in the Bohr model of the hydrogen atom, and the vertical arrows depict the energy of photons absorbed (left) or emitted (right) as electrons move between these orbits.

Since Bohr's model involved only a single electron, it could also be applied to the single electron ions He^{+}, Li^{2+}, Be^{3+}, and so forth, which differ from hydrogen only in their nuclear charges, and so one-electron atoms and ions are collectively referred to as *hydrogen-like* or *hydrogenic* atoms. The energy expression for hydrogen-like atoms is a generalization of the hydrogen atom energy, in which Z is the nuclear charge (+1 for hydrogen, +2 for He, +3 for Li, and so on) and k has a value of $2.179 \times 10^{-18}\ J$.

$$E_n = -\frac{kZ^2}{n^2} \tag{2.5.1}$$

The sizes of the circular orbits for hydrogen-like atoms are given in terms of their radii by the following expression, in which a_o is a constant called the Bohr radius, with a value of $5.292 \times 10^{-11}\ m$:

$$r = \frac{n^2}{Z} a_0 \tag{2.5.2}$$

The equation also shows us that as the electron's energy increases (as n increases), the electron is found at greater distances from the nucleus. This is implied by the inverse dependence on r in the Coulomb potential, since, as the electron moves away from the nucleus, the electrostatic attraction between it and the nucleus decreases, and it is held less tightly in the atom. Note that as n gets larger and the orbits get larger, their energies get closer to zero, and so the limits $n \longrightarrow \infty$ and $r \longrightarrow \infty$ imply that $E = 0$ corresponds to the ionization limit where the electron is completely removed from the nucleus. Thus, for hydrogen in the ground state $n = 1$, the ionization energy would be:

$$\Delta E = E_{n \longrightarrow \infty} - E_1 = 0 + k = k \tag{2.5.3}$$

With three extremely puzzling paradoxes now solved (blackbody radiation, the photoelectric effect, and the hydrogen atom), and all involving Planck's constant in a fundamental manner, it became clear to most physicists at that time that the classical theories that worked so well in the macroscopic world were fundamentally flawed and could not be extended down into the microscopic domain of atoms and molecules. Unfortunately, despite Bohr's remarkable achievement in deriving a theoretical expression for the Rydberg constant, he was unable to extend his theory to the next simplest atom, He, which only has two electrons. Bohr's model was severely flawed, since it was still based on the classical mechanics notion of precise orbits, a concept that was later found to be untenable in the microscopic domain, when a proper model of quantum mechanics was developed to supersede classical mechanics.

Behavior in the Microscopic World

We know how matter behaves in the macroscopic world—objects that are large enough to be seen by the naked eye follow the rules of classical physics. A billiard ball moving on a table will behave like a particle: It will continue in a straight line unless it collides with another ball or the table cushion, or is acted on by some other force (such as friction). The ball has a well-defined position and velocity (or a well-defined momentum, $p = mv$, defined by mass m and velocity v) at any given moment. In other words, the ball is moving in a classical trajectory. This is the typical behavior of a classical object.

When waves interact with each other, they show interference patterns that are not displayed by macroscopic particles such as the billiard ball. For example, interacting waves on the surface of water can produce interference patters similar to those shown on Figure 2.5.1. This is a case of wave behavior on the macroscopic scale, and it is clear that particles and waves are very different phenomena in the macroscopic realm.

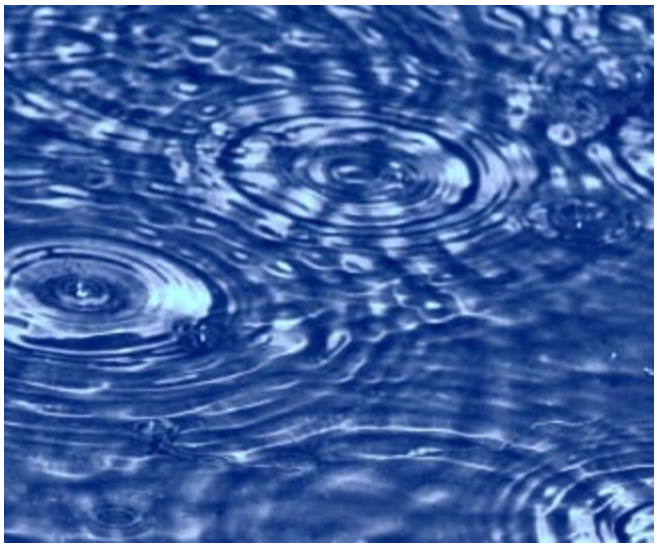


Figure 2.5.1: An interference pattern on the water surface is formed by interacting waves. The waves are caused by reflection of water from the rocks. (credit: modification of work by Sukanto Debnath)

As technological improvements allowed scientists to probe the microscopic world in greater detail, it became increasingly clear by the 1920s that very small pieces of matter follow a different set of rules from those we observe for large objects. The unquestionable separation of waves and particles was no longer the case for the microscopic world.

One of the first people to pay attention to the special behavior of the microscopic world was Louis de Broglie. He asked the question: If electromagnetic radiation can have particle-like character, can electrons and other submicroscopic particles exhibit wavelike character? In his 1925 doctoral dissertation, de Broglie extended the wave–particle duality of light that Einstein used to resolve the photoelectric-effect paradox to material particles. He predicted that a particle with mass *m* and velocity *v* (that is, with linear momentum *p*) should also exhibit the behavior of a wave with a wavelength value *λ*, given by this expression in which *h* is the familiar Planck's constant

$$\lambda = \frac{h}{mv} = \frac{h}{p} \tag{2.5.4}$$

This is called the *de Broglie wavelength*. Unlike the other values of *λ* discussed in this chapter, the de Broglie wavelength is a characteristic of particles and other bodies, not electromagnetic radiation (note that this equation involves velocity [*v*, m/s], not frequency [*ν*, Hz]. Although these two symbols are identical, they mean very different things). Where Bohr had postulated the electron as being a particle orbiting the nucleus in quantized orbits, de Broglie argued that Bohr's assumption of quantization can be explained if the electron is considered not as a particle, but rather as a circular standing wave such that only an integer number of wavelengths could fit exactly within the orbit (Figure 2.5.2).

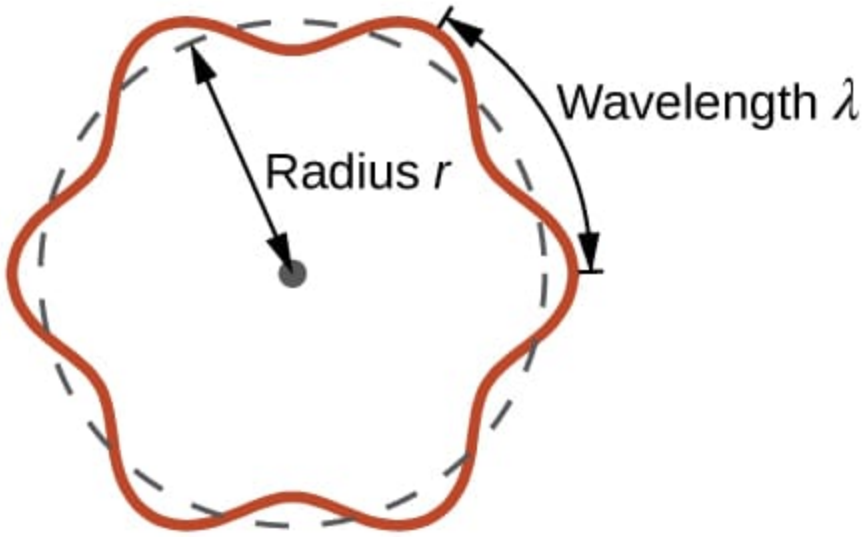


Figure 2.5.1: If an electron is viewed as a wave circling around the nucleus, an integer number of wavelengths must fit into the orbit for this standing wave behavior to be possible.

Shortly after de Broglie proposed the wave nature of matter, two scientists at Bell Laboratories, C. J. Davisson and L. H. Germer, demonstrated experimentally that electrons can exhibit wavelike behavior by showing an interference pattern for electrons travelling through a regular atomic pattern in a crystal. The regularly spaced atomic layers served as slits, as used in other interference experiments. Since the spacing between the layers serving as slits needs to be similar in size to the wavelength of the tested wave for an interference pattern to form, Davisson and Germer used a crystalline nickel target for their "slits," since the spacing of the atoms within the lattice was approximately the same as the de Broglie wavelengths of the electrons that they used. Figure 2.5.4 shows an interference pattern.

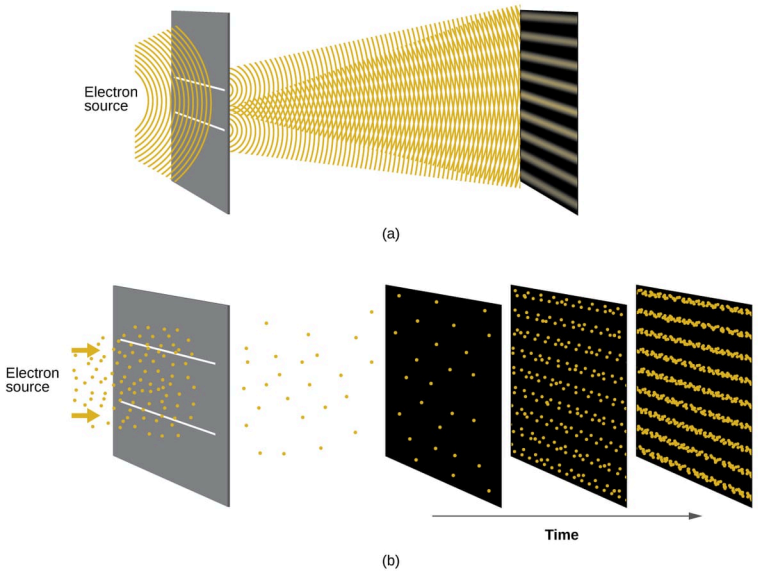


Figure 2.5.4: (a) The interference pattern for electrons passing through very closely spaced slits demonstrates that quantum particles such as electrons can exhibit wavelike behavior. (b) The experimental results illustrated here demonstrate the wave–particle duality in electrons. The electrons pass through very closely spaced slits, forming an interference pattern, with increasing numbers of electrons being recorded from the left image to the right. With only a few electrons recorded, it is clear that the electrons arrive as individual localized "particles," but in a seemingly random pattern. As more electrons arrive, a wavelike interference pattern begins to emerge. Note that the probability of the final electron location is still governed by the wave-type distribution, even for a single electron, but it can be observed more easily if many electron collisions have been recorded.

The wave–particle duality of matter can be seen by observing what happens if electron collisions are recorded over a long period of time. Initially, when only a few electrons have been recorded, they show clear particle-like behavior, having arrived in small localized packets that appear to be random. As more and more electrons arrived and were recorded, a clear interference pattern

that is the hallmark of wavelike behavior emerged. Thus, it appears that while electrons are small localized particles, their motion does not follow the equations of motion implied by classical mechanics, but instead it is governed by some type of a wave equation that governs a probability distribution even for a single electron's motion. Thus the wave–particle duality first observed with photons is actually a fundamental behavior intrinsic to all quantum particles.

YouTube Video

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

View this YouTube Video online

View the Dr. Quantum – Double Slit Experiment cartoon for an easy-to-understand description of wave–particle duality and the associated experiments.

We never think of a thrown softball having a wavelength, since this wavelength is so small it is impossible for our senses or any known instrument to detect (strictly speaking, the wavelength of a real baseball would correspond to the wavelengths of its constituent atoms and molecules, which, while much larger than this value, would still be microscopically tiny). The de Broglie wavelength is only appreciable for matter that has a very small mass and/or a very high velocity.

Werner Heisenberg considered the limits of how accurately we can measure properties of an electron or other microscopic particles. He determined that there is a fundamental limit to how accurately one can measure both a particle's position and its momentum simultaneously. The more accurately we measure the momentum of a particle, the less accurately we can determine its position at that time, and vice versa. This is summed up in what we now call the Heisenberg uncertainty principle: *It is fundamentally impossible to determine simultaneously and exactly both the momentum and the position of a particle*.

Heisenberg's principle imposes ultimate limits on what is knowable in science. The uncertainty principle can be shown to be a consequence of wave–particle duality, which lies at the heart of what distinguishes modern quantum theory from classical mechanics. Recall that the equations of motion obtained from classical mechanics are trajectories where, at any given instant in time, both the position and the momentum of a particle can be determined exactly. Heisenberg's uncertainty principle implies that such a view is untenable in the microscopic domain and that there are fundamental limitations governing the motion of quantum particles. This does not mean that microscopic particles do not move in trajectories, it is just that measurements of trajectories are limited in their precision. In the realm of quantum mechanics, measurements introduce changes into the system that is being observed.

The Quantum–Mechanical Model of an Atom

Shortly after de Broglie published his ideas that the electron in a hydrogen atom could be better thought of as being a circular standing wave instead of a particle moving in quantized circular orbits, as Bohr had argued, Erwin Schrödinger extended de Broglie's work by incorporating the de Broglie relation into a wave equation, deriving what is today known as the Schrödinger equation. Schrödinger's work, as well as that of Heisenberg and many other scientists following in their footsteps, is generally referred to as quantum mechanics.

Understanding Quantum Theory of Electrons in Atoms

The goal of this section is to understand the electron orbitals (location of electrons in atoms), their different energies, and other properties. The use of quantum theory provides the best understanding to these topics. This knowledge is a precursor to chemical bonding.

As was described previously, electrons in atoms can exist only on discrete energy levels but not between them. It is said that the energy of an electron in an atom is quantized, that is, it can be equal only to certain specific values and can jump from one energy level to another but not transition smoothly or stay between these levels.

The energy levels are labeled with an n value, where n = 1, 2, 3, ... Generally speaking, the energy of an electron in an atom is greater for greater values of n. This number, n, is referred to as the principal quantum number. The principal quantum number defines the location of the energy level. It is essentially the same concept as the n in the Bohr atom description. Another name for the principal quantum number is the shell number. The shells of an atom can be thought of concentric circles radiating out from the nucleus. The electrons that belong to a specific shell are most likely to be found within the corresponding circular area. The further we proceed from the nucleus, the higher the shell number, and so the higher the energy level (Figure 2.5.5). The positively charged protons in the nucleus stabilize the electronic orbitals by electrostatic attraction between the positive charges of the protons and the negative charges of the electrons. So the further away the electron is from the nucleus, the greater the energy it has.

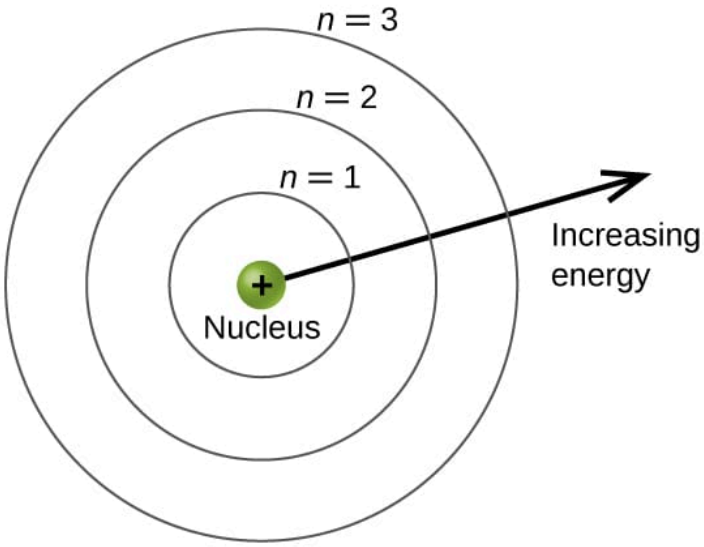


Figure 2.5.5: Different shells are numbered by principal quantum numbers.

This quantum mechanical model for where electrons reside in an atom can be used to look at electronic transitions, the events when an electron moves from one energy level to another. If the transition is to a higher energy level, energy is absorbed, and the energy change has a positive value. To obtain the amount of energy necessary for the transition to a higher energy level, a photon is absorbed by the atom. A transition to a lower energy level involves a release of energy, and the energy change is negative. This process is accompanied by emission of a photon by the atom.

The principal quantum number is one of three quantum numbers used to characterize an orbital. An atomic orbital, which is distinct from an *orbit*, is a general region in an atom within which an electron is most probable to reside. The quantum mechanical model specifies the probability of finding an electron in the three-dimensional space around the nucleus and is based on solutions of the Schrödinger equation. In addition, the principal quantum number defines the energy of an electron in a hydrogen or hydrogen-like atom or an ion (an atom or an ion with only one electron) and the general region in which discrete energy levels of electrons in a multi-electron atoms and ions are located.

Another quantum number is l, the angular momentum quantum number. It is an integer that defines the shape of the orbital, and takes on the values, l = 0, 1, 2, ..., n – 1. This means that an orbital with n = 1 can have only one value of l, l = 0, whereas n = 2 permits l = 0 and l = 1, and so on. The principal quantum number defines the general size and energy of the orbital. The l value specifies the shape of the orbital. Orbitals with the same value of l form a subshell. In addition, the greater the angular momentum quantum number, the greater is the angular momentum of an electron at this orbital.

Orbitals with l = 0 are called *s* orbitals (or the *s* subshells). The value l = 1 corresponds to the *p* orbitals. For a given n, *p* orbitals constitute a *p* subshell (e.g., 3*p* if n = 3). The orbitals with l = 2 are called the *d* orbitals, followed by the *f*-, *g*-, *and h*-orbitals for l = 3, 4, 5, and there are higher values we will not consider.

There are certain distances from the nucleus at which the probability density of finding an electron located at a particular orbital is zero. In other words, the value of the wavefunction ψ is zero at this distance for this orbital. Such a value of radius r is called a radial node. The number of radial nodes in an orbital is $n - l - 1$.

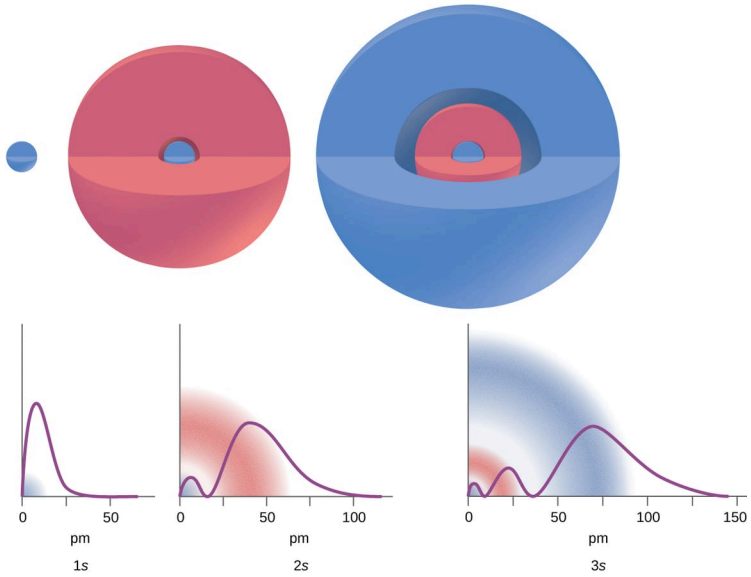


Figure 2.5.6: *The graphs show the probability (y axis) of finding an electron for the 1s, 2s, 3s orbitals as a function of distance from the nucleus.*

Consider the examples in Figure 2.5.7. The orbitals depicted are of the s type, thus $l = 0$ for all of them. It can be seen from the graphs of the probability densities that there are $1 - 0 - 1 = 0$ places where the density is zero (nodes) for 1s ($n = 1$), $2 - 0 - 1 = 1$ node for 2*s*, and $3 - 0 - 1 = 2$ nodes for the 3s orbitals.

The *s* subshell electron density distribution is spherical and the *p* subshell has a dumbbell shape. The *d* and *f* orbitals are more complex. These shapes represent the three-dimensional regions within which the electron is likely to be found.

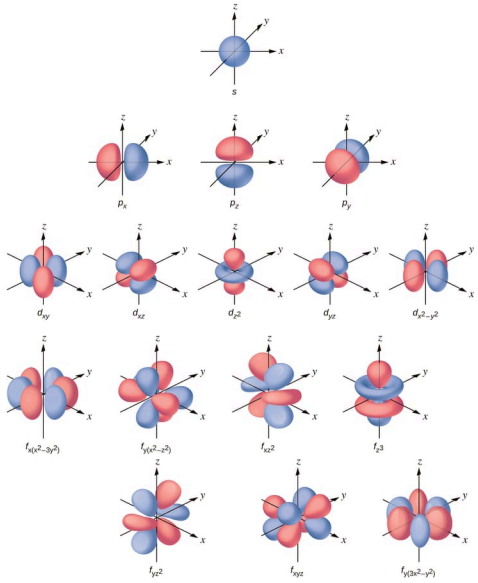


Figure 2.5.7: *Shapes of s, p, d, and f orbitals.*

If an electron has an angular momentum ($l \neq 0$), then this vector can point in different directions. In addition, the *z* component of the angular momentum can have more than one value. This means that if a magnetic field is applied in the *z* direction, orbitals with different values of the *z* component of the angular momentum will have different energies resulting from interacting with the field. The magnetic quantum number, called m_l, specifies the *z* component of the angular momentum for a particular orbital. For example, for an *s* orbital, $l = 0$, and the only value of m_l is zero. For *p* orbitals, $l = 1$, and m_l can be equal to –1, 0, or +1. Generally speaking, m_l can be equal to $-l$, $-(l - 1)$, ..., –1, 0, +1, ..., $(l - 1)$, l. The total number of possible orbitals with the same value of l (a subshell) is $2l + 1$. Thus, there is one *s*-orbital for $ml = 0$, there are three *p*-orbitals for $ml = 1$, five *d*-orbitals for $ml = 2$, seven *f*-orbitals for $ml = 3$, and so forth. The principal quantum number defines the general value of the electronic energy. The angular momentum quantum number determines the shape of the orbital. And the magnetic quantum number specifies orientation of the

orbital in space, as can be seen in Figure 2.5.7.

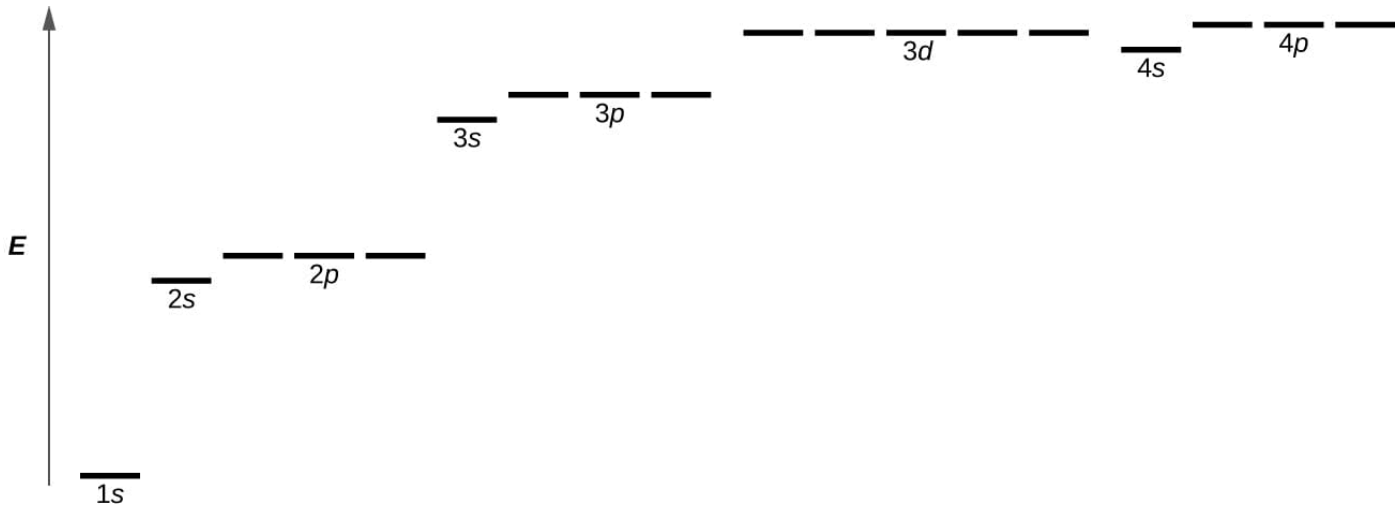


Figure 2.5.8: The chart shows the energies of electron orbitals in a multi-electron atom.

Figure 2.5.8 illustrates the energy levels for various orbitals. The number before the orbital name (such as 2s, 3*p*, and so forth) stands for the principal quantum number, *n*. The letter in the orbital name defines the subshell with a specific angular momentum quantum number l = 0 for s orbitals, 1 for *p* orbitals, 2 for *d* orbitals. Finally, there are more than one possible orbitals for $l \geq 1$, each corresponding to a specific value of m_l. In the case of a hydrogen atom or a one-electron ion (such as He^+, Li^{2+}, and so on), energies of all the orbitals with the same *n* are the same. This is called a degeneracy, and the energy levels for the same principal quantum number, *n*, are called degenerate energy levels. However, in atoms with more than one electron, this degeneracy is eliminated by the electron–electron interactions, and orbitals that belong to different subshells have different energies. Orbitals within the same subshell (for example *ns, np, nd, nf*, such as 2*p*, 3s) are still degenerate and have the same energy.

While the three quantum numbers discussed in the previous paragraphs work well for describing electron orbitals, some experiments showed that they were not sufficient to explain all observed results. It was demonstrated in the 1920s that when hydrogen-line spectra are examined at extremely high resolution, some lines are actually not single peaks but, rather, pairs of closely spaced lines. This is the so-called fine structure of the spectrum, and it implies that there are additional small differences in energies of electrons even when they are located in the same orbital. These observations led Samuel Goudsmit and George Uhlenbeck to propose that electrons have a fourth quantum number. They called this the spin quantum number, or m_s.

The other three quantum numbers, *n*, *l*, and m_l, are properties of specific atomic orbitals that also define in what part of the space an electron is most likely to be located. Orbitals are a result of solving the Schrödinger equation for electrons in atoms. The electron spin is a different kind of property. It is a completely quantum phenomenon with no analogues in the classical realm. In addition, it cannot be derived from solving the Schrödinger equation and is not related to the normal spatial coordinates (such as the Cartesian *x*, *y*, and *z*). Electron spin describes an intrinsic electron "rotation" or "spinning." Each electron acts as a tiny magnet or a tiny rotating object with an angular momentum, even though this rotation cannot be observed in terms of the spatial coordinates.

The magnitude of the overall electron spin can only have one value, and an electron can only "spin" in one of two quantized states. One is termed the α state, with the *z* component of the spin being in the positive direction of the *z* axis. This corresponds to the spin quantum number $m_s = \frac{1}{2}$. The other is called the β state, with the *z* component of the spin being negative and $m_s = -\frac{1}{2}$. Any electron, regardless of the atomic orbital it is located in, can only have one of those two values of the spin quantum number. The energies of electrons having $m_s = -\frac{1}{2}$ and $m_s = \frac{1}{2}$ are different if an external magnetic field is applied.

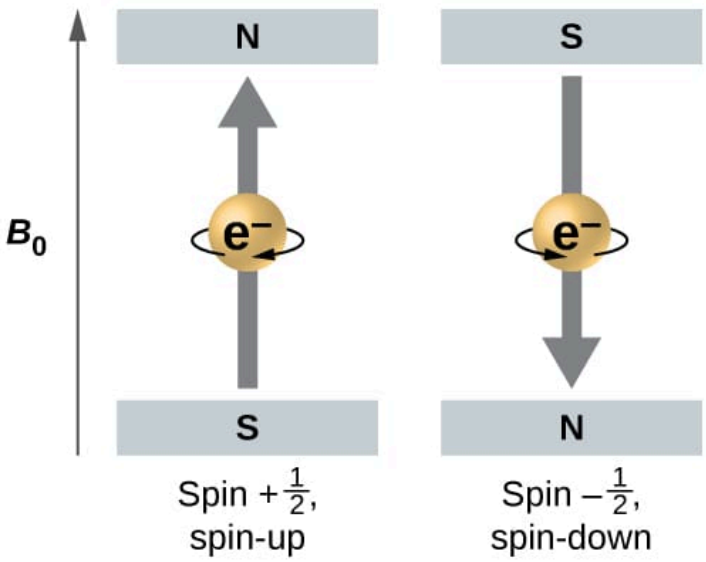


Figure 2.5.9: *Electrons with spin values* \(±\ce{1/2}\) *in an external magnetic field.*

Figure 2.5.9 illustrates this phenomenon. An electron acts like a tiny magnet. Its moment is directed up (in the positive direction of the *z* axis) for the $\frac{1}{2}$ spin quantum number and down (in the negative *z* direction) for the spin quantum number of $-\frac{1}{2}$. A magnet has a lower energy if its magnetic moment is aligned with the external magnetic field (the left electron) and a higher energy for the magnetic moment being opposite to the applied field. This is why an electron with $m_s = \frac{1}{2}$ has a slightly lower energy in an external field in the positive *z* direction, and an electron with $m_s = -\frac{1}{2}$ has a slightly higher energy in the same field. This is true even for an electron occupying the same orbital in an atom. A spectral line corresponding to a transition for electrons from the same orbital but with different spin quantum numbers has two possible values of energy; thus, the line in the spectrum will show a fine structure splitting.

The Pauli Exclusion Principle

An electron in an atom is completely described by four quantum numbers: *n*, *l*, m_l, and m_s. The first three quantum numbers define the orbital and the fourth quantum number describes the intrinsic electron property called spin. An Austrian physicist Wolfgang Pauli formulated a general principle that gives the last piece of information that we need to understand the general behavior of electrons in atoms. The Pauli exclusion principle can be formulated as follows: No two electrons in the same atom can have exactly the same set of all the four quantum numbers. What this means is that electrons can share the same orbital (the same set of the quantum numbers *n*, *l*, and m_l), but only if their spin quantum numbers m_s have different values. Since the spin quantum number can only have two values $\left(\pm\frac{1}{2}\right)$, no more than two electrons can occupy the same orbital (and if two electrons are located in the same orbital, they must have opposite spins). Therefore, any atomic orbital can be populated by only zero, one, or two electrons. The properties and meaning of the quantum numbers of electrons in atoms are briefly summarized in Table 2.5.1 .

Table 2.5.1: *Quantum Numbers, Their Properties, and Significance*

Name	Symbol	Allowed values	Physical meaning
principal quantum number	*n*	1, 2, 3, 4, ...	shell, the general region for the value of energy for an electron on the orbital
angular momentum or azimuthal quantum number	*l*	0 ≤ *l* ≤ *n* – 1	subshell, the shape of the orbital
magnetic quantum number	m_l	– *l* ≤ m_l ≤ *l*	orientation of the orbital

Name	Symbol	Allowed values	Physical meaning
spin quantum number	m_s	$\frac{1}{2}, -\frac{1}{2}$	direction of the intrinsic quantum “spinning” of the electron

Example 2.5.2: Working with Shells and Subshells

Indicate the number of subshells, the number of orbitals in each subshell, and the values of l and m_l for the orbitals in the n = 4 shell of an atom.

Solution

For n = 4, l can have values of 0, 1, 2, and 3. Thus, s, p, d, and f subshells are found in the n = 4 shell of an atom. For l = 0 (the s subshell), m_l can only be 0. Thus, there is only one 4s orbital. For l = 1 (p-type orbitals), m can have values of –1, 0, +1, so we find three 4p orbitals. For l = 2 (d-type orbitals), m_l can have values of –2, –1, 0, +1, +2, so we have five 4d orbitals. When l = 3 (f-type orbitals), m_l can have values of –3, –2, –1, 0, +1, +2, +3, and we can have seven 4f orbitals. Thus, we find a total of 16 orbitals in the n = 4 shell of an atom.

Exercise 2.5.2

Identify the subshell in which electrons with the following quantum numbers are found:

a. n = 3, l = 1;
b. n = 5, l = 3;
c. n = 2, l = 0.

Answer a

3p

Answer b

5f

Answer c

2s

Example 2.5.3: Maximum Number of Electrons

Calculate the maximum number of electrons that can occupy a shell with (a) n = 2, (b) n = 5, and (c) n as a variable. Note you are only looking at the orbitals with the specified n value, not those at lower energies.

Solution

(a) When n = 2, there are four orbitals (a single 2s orbital, and three orbitals labeled 2p). These four orbitals can contain eight electrons.

(b) When n = 5, there are five subshells of orbitals that we need to sum:

$$\begin{array}{r} 1 \text{ orbital labeled } 5s \\ 3 \text{ orbitals labeled } 5p \\ 5 \text{ orbitals labeled } 5d \\ 7 \text{ orbitals labeled } 5f \\ +9 \text{ orbitals labeled } 5g \\ \hline 25 \text{ orbitals total} \end{array}$$

Again, each orbital holds two electrons, so 50 electrons can fit in this shell.

(c) The number of orbitals in any shell *n* will equal n^2. There can be up to two electrons in each orbital, so the maximum number of electrons will be $2 \times n^2$

Exercise 2.5.3

If a shell contains a maximum of 32 electrons, what is the principal quantum number, *n*?

Answer

n = 4

Example 2.5.4: Working with Quantum Numbers

Complete the following table for atomic orbitals:

Orbital	*n*	*l*	m_l degeneracy	Radial nodes (no.)
4*f*				
	4	1		
	7		7	3
5*d*				

Solution

The table can be completed using the following rules:

- The orbital designation is *nl*, where *l* = 0, 1, 2, 3, 4, 5, ... is mapped to the letter sequence s, *p*, *d*, *f*, *g*, *h*, ...,
- The m_l degeneracy is the number of orbitals within an *l* subshell, and so is $2l + 1$ (there is one *s* orbital, three *p* orbitals, five *d* orbitals, seven *f* orbitals, and so forth).
- The number of radial nodes is equal to $n - l - 1$.

Orbital	*n*	*l*	m_l degeneracy	Radial nodes (no.)
4*f*	4	3	7	0
4*p*	4	1	3	2
7*f*	7	3	7	3
5*d*	5	2	5	2

Exercise 2.5.4

How many orbitals have *l* = 2 and *n* = 3?

Answer

The five degenerate 3*d* orbitals

Summary

Macroscopic objects act as particles. Microscopic objects (such as electrons) have properties of both a particle and a wave. Their exact trajectories cannot be determined. The quantum mechanical model of atoms describes the three-dimensional position of the electron in a *probabilistic* manner according to a mathematical function called a wavefunction, often denoted as ψ. Atomic wavefunctions are also called orbitals. The squared magnitude of the wavefunction describes the distribution of the probability of finding the electron in a particular region in space. Therefore, atomic orbitals describe the areas in an atom where electrons are most likely to be found.

An atomic orbital is characterized by three quantum numbers. The principal quantum number, n, can be any positive integer. The general region for value of energy of the orbital and the average distance of an electron from the nucleus are related to n. Orbitals having the same value of n are said to be in the same shell. The angular momentum quantum number, l, can have any integer value from 0 to $n - 1$. This quantum number describes the shape or type of the orbital. Orbitals with the same principal quantum number and the same l value belong to the same subshell. The magnetic quantum number, m_l, with $2l + 1$ values ranging from $-l$ to $+l$, describes the orientation of the orbital in space. In addition, each electron has a spin quantum number, m_s, that can be equal to $\pm\frac{1}{2}$. No two electrons in the same atom can have the same set of values for all the four quantum numbers.

Glossary

angular momentum quantum number (l)
quantum number distinguishing the different shapes of orbitals; it is also a measure of the orbital angular momentum

atomic orbital
mathematical function that describes the behavior of an electron in an atom (also called the wavefunction), it can be used to find the probability of locating an electron in a specific region around the nucleus, as well as other dynamical variables

***d* orbital**
region of space with high electron density that is either four lobed or contains a dumbbell and torus shape; describes orbitals with $l = 2$. An electron in this orbital is called a *d* electron

electron density
a measure of the probability of locating an electron in a particular region of space, it is equal to the squared absolute value of the wave function ψ

***f* orbital**
multilobed region of space with high electron density, describes orbitals with $l = 3$. An electron in this orbital is called an *f* electron

Heisenberg uncertainty principle
rule stating that it is impossible to exactly determine both certain conjugate dynamical properties such as the momentum and the position of a particle at the same time. The uncertainty principle is a consequence of quantum particles exhibiting wave–particle duality

magnetic quantum number (m_l)
quantum number signifying the orientation of an atomic orbital around the nucleus; orbitals having different values of m_l but the same subshell value of l have the same energy (are degenerate), but this degeneracy can be removed by application of an external magnetic field

***p* orbital**
dumbbell-shaped region of space with high electron density, describes orbitals with $l = 1$. An electron in this orbital is called a *p* electron

Pauli exclusion principle
: specifies that no two electrons in an atom can have the same value for all four quantum numbers

principal quantum number (*n*)
: quantum number specifying the shell an electron occupies in an atom

quantum mechanics
: field of study that includes quantization of energy, wave-particle duality, and the Heisenberg uncertainty principle to describe matter

s orbital
: spherical region of space with high electron density, describes orbitals with $l = 0$. An electron in this orbital is called an s electron

shell
: set of orbitals with the same principal quantum number, *n*

spin quantum number (m_s)
: number specifying the electron spin direction, either $+\frac{1}{2}$ or $-\frac{1}{2}$

subshell
: set of orbitals in an atom with the same values of *n* and *l*

wavefunction (ψ)
: mathematical description of an atomic orbital that describes the shape of the orbital; it can be used to calculate the probability of finding the electron at any given location in the orbital, as well as dynamical variables such as the energy and the angular momentum

Contributors

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2.6: Electron Configurations

Learning Objectives

- Give the electron configuration for an atom using Bohr's model, box orbital diagrams, and quantum mechanical notation.

Bohr's Model

Here are a few highlights that you learned in the last section about Bohr's model:

· Electrons can't be found just anywhere around the nucleus... they must move in well-defined paths or orbits, like orbits of the planets around the sun.

· An electron in one of these orbits has a characteristic amount of energy, depending on which level they were on.

· Different energy levels within an atom can only handle a certain number of electrons.

· The maximum number of electrons that can be in an energy level is given by the formula:

$$\mathbf{2n^2}\ \textbf{ where n = the energy level}$$

Example 2.6.1: Calculating the number of electrons in a shell

How many electrons can the first energy shell hold?

$$2\ (1)^2 = 2 \text{ electrons}$$

What about the second energy shell?

$$2\ (2)^2 = 8 \text{ electrons}$$

File:Bohr's model.svg

Figure 2.6.1: *A Bhor's model can be used to diagram the location of electrons in each energy shell for an atom. Notice that protons go in the nucleus of the atom and electrons are drawn on orbits surrounding the nucleus. Image from Wikimedia commons.*

Example 2.6.2

Draw the Bohr's model for sodium (Na).

Since Sodium is number 11 on the periodic table we know that it contains 11p+. We can assume that if the atom is neutrally charged it would also contain 11e-. The energy shells filled up from the lowest energy to highest until all 11e- were accounted for. Remember from above that the first energy shell can only hold 2e-, the second 8e-, and so forth using the formula $2n^2$ where n = the energy level.

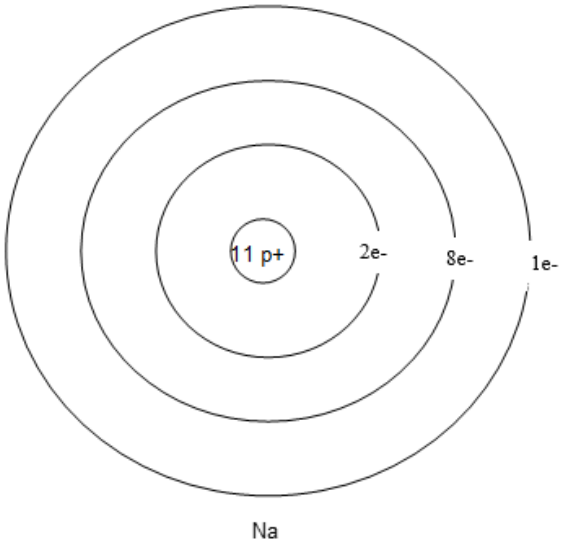


Figure 2.6.2: *A Bhor's model for sodium.*

Orbital Energies and Atomic Structure

Having introduced the basics of atomic structure and quantum mechanics, we can use our understanding of quantum numbers to determine how atomic orbitals relate to one another. This allows us to determine which orbitals are occupied by electrons in each atom. The specific arrangement of electrons in orbitals of an atom determines many of the chemical properties of that atom.

The energy of atomic orbitals increases as the principal quantum number, n, increases. In any atom with two or more electrons, the repulsion between the electrons makes energies of subshells with different values of l differ so that the energy of the orbitals increases within a shell in the order *s* < *p* < *d* < *f*. Figure 2.6.1 depicts how these two trends in increasing energy relate. The 1*s* orbital at the bottom of the diagram is the orbital with electrons of lowest energy. The energy increases as we move up to the 2*s* and then 2*p*, 3*s*, and 3*p* orbitals, showing that the increasing *n* value has more influence on energy than the increasing *l* value for small atoms. However, this pattern does not hold for larger atoms. The 3*d* orbital is higher in energy than the 4*s* orbital. Such overlaps continue to occur frequently as we move up the chart.

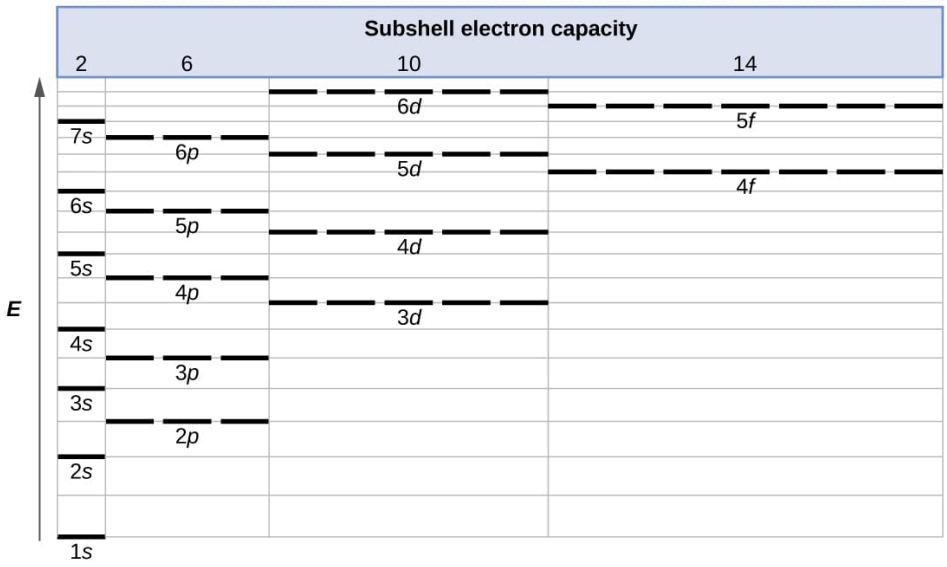


Figure 2.6.3: *Generalized energy-level diagram for atomic orbitals in an atom with two or more electrons (not to scale).*

Electrons in successive atoms on the periodic table tend to fill low-energy orbitals first. Thus, many students find it confusing that, for example, the 5*p* orbitals fill immediately after the 4*d*, and immediately before the 6s. The filling order is based on observed experimental results, and has been confirmed by theoretical calculations. As the principal quantum number, *n*, increases, the size of the orbital increases and the electrons spend more time farther from the nucleus. Thus, the attraction to the nucleus is weaker and the energy associated with the orbital is higher (less stabilized). But this is not the only effect we have to take into account. Within each shell, as the value of *l* increases, the electrons are less penetrating (meaning there is less electron density found close to the nucleus), in the order *s* > *p* > *d* > *f*. Electrons that are closer to the nucleus slightly repel electrons that are farther out, offsetting the more dominant electron–nucleus attractions slightly (recall that all electrons have –1 charges, but nuclei have +*Z* charges). This phenomenon is called shielding and will be discussed in more detail in the next section. Electrons in orbitals that experience more shielding are less stabilized and thus higher in energy. For small orbitals (1s through 3*p*), the increase in energy due to *n* is more significant than the increase due to *l*; however, for larger orbitals the two trends are comparable and cannot be simply predicted. We will discuss methods for remembering the observed order.

The arrangement of electrons in the orbitals of an atom is called the electron configuration of the atom. We describe an electron configuration with a symbol that contains three pieces of information (Figure 2.6.2):

1. The number of the principal quantum shell, *n*,
2. The letter that designates the orbital type (the subshell, *l*), and
3. A superscript number that designates the number of electrons in that particular subshell.

For example, the notation $2p^4$ (read "two–p–four") indicates four electrons in a *p* subshell (*l* = 1) with a principal quantum number (*n*) of 2. The notation $3d^8$ (read "three–d–eight") indicates eight electrons in the *d* subshell (i.e., *l* = 2) of the principal shell for which *n* = 3.

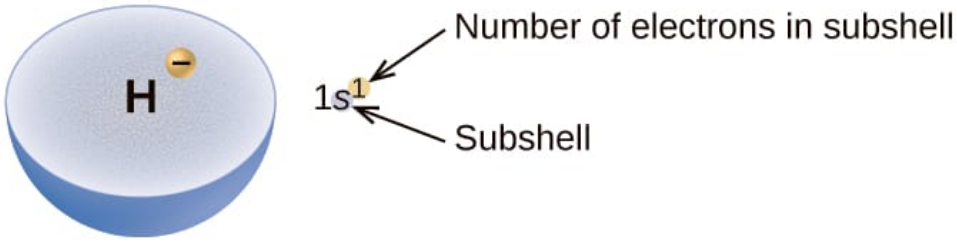


Figure 2.6.4: *The diagram of an electron configuration specifies the subshell (n and l value, with letter symbol) and superscript number of electrons.*

The Aufbau Principle

To determine the electron configuration for any particular atom, we can “build” the structures in the order of atomic numbers. Beginning with hydrogen, and continuing across the periods of the periodic table, we add one proton at a time to the nucleus and one electron to the proper subshell until we have described the electron configurations of all the elements. This procedure is called the Aufbau principle, from the German word *Aufbau* (“to build up”). Each added electron occupies the subshell of lowest energy available (in the order shown in Figure 2.6.3), subject to the limitations imposed by the allowed quantum numbers according to the Pauli exclusion principle. Electrons enter higher-energy subshells only after lower-energy subshells have been filled to capacity. Figure 2.6.3 illustrates the traditional way to remember the filling order for atomic orbitals.

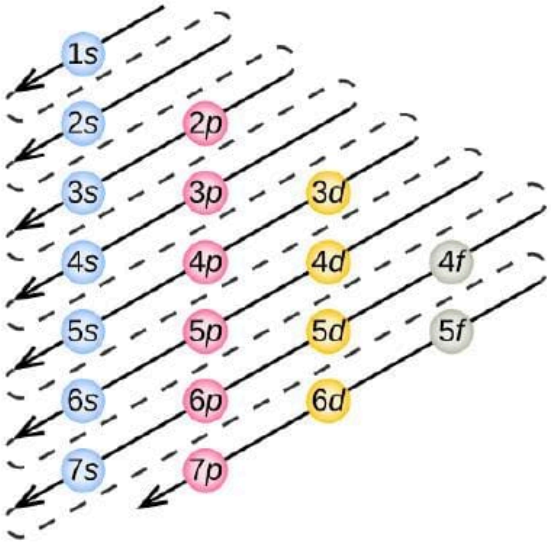


Figure $2.6.5$: *The arrow leads through each subshell in the appropriate filling order for electron configurations. This chart is straightforward to construct. Simply make a column for all the s orbitals with each n shell on a separate row. Repeat for p, d, and f. Be sure to only include orbitals allowed by the quantum numbers (no 1p or 2d, and so forth). Finally, draw diagonal lines from top to bottom as shown.*

Since the arrangement of the periodic table is based on the electron configurations, Figure $2.6.4$ provides an alternative method for determining the electron configuration. The filling order simply begins at hydrogen and includes each subshell as you proceed in increasing *Z* order. For example, after filling the 3*p* block up to Ar, we see the orbital will be 4s (K, Ca), followed by the 3*d* orbitals.

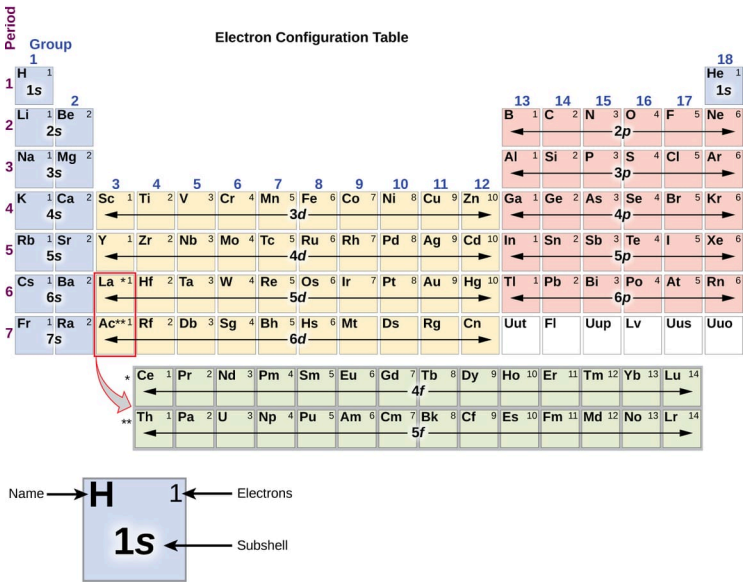
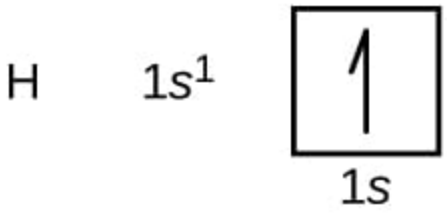
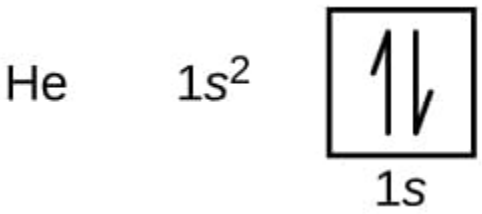


Figure $2.6.6$: *This periodic table shows the electron configuration for each subshell. By "building up" from hydrogen, this table can be used to determine the electron configuration for any atom on the periodic table.*

We will now construct the ground-state electron configuration and orbital diagram for a selection of atoms in the first and second periods of the periodic table. Orbital diagrams are pictorial representations of the electron configuration, showing the individual orbitals and the pairing arrangement of electrons. We start with a single hydrogen atom (atomic number 1), which consists of one proton and one electron. Referring to either Figure $2.6.3$ or $2.6.4$, we would expect to find the electron in the 1s orbital. By convention, the $m_s = +\frac{1}{2}$ value is usually filled first. The electron configuration and the orbital diagram are:

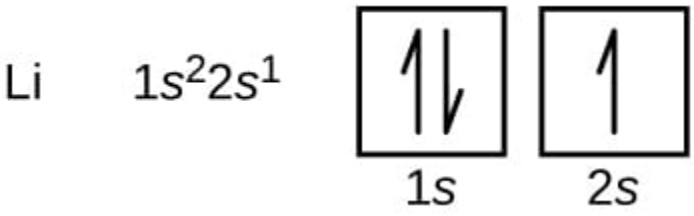


Following hydrogen is the noble gas helium, which has an atomic number of 2. The helium atom contains two protons and two electrons. The first electron has the same four quantum numbers as the hydrogen atom electron (n = 1, l = 0, m_l = 0, $m_s = +\frac{1}{2}$). The second electron also goes into the 1s orbital and fills that orbital. The second electron has the same n, l, and m_l quantum numbers, but must have the opposite spin quantum number, $m_s = -\frac{1}{2}$. This is in accord with the Pauli exclusion principle: No two electrons in the same atom can have the same set of four quantum numbers. For orbital diagrams, this means two arrows go in each box (representing two electrons in each orbital) and the arrows must point in opposite directions (representing paired spins). The electron configuration and orbital diagram of helium are:

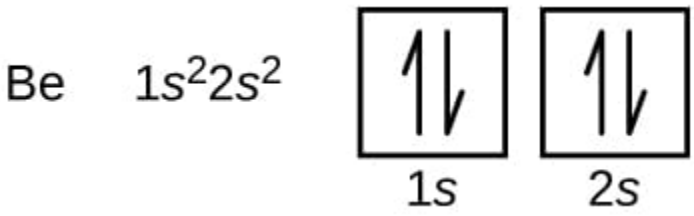


The n = 1 shell is completely filled in a helium atom.

The next atom is the alkali metal lithium with an atomic number of 3. The first two electrons in lithium fill the 1s orbital and have the same sets of four quantum numbers as the two electrons in helium. The remaining electron must occupy the orbital of next lowest energy, the 2s orbital (Figure 2.6.3 or 2.6.4). Thus, the electron configuration and orbital diagram of lithium are:

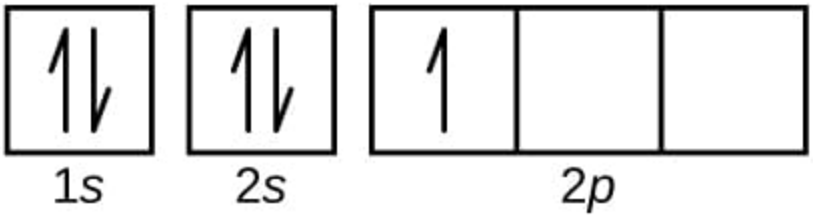


An atom of the alkaline earth metal beryllium, with an atomic number of 4, contains four protons in the nucleus and four electrons surrounding the nucleus. The fourth electron fills the remaining space in the 2s orbital.



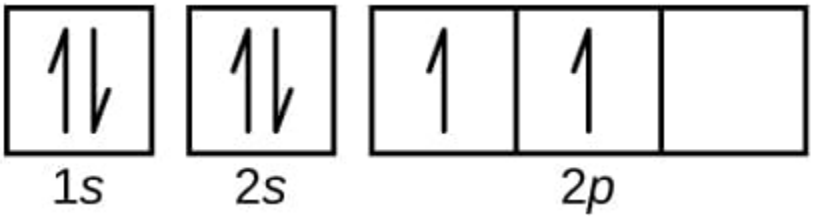
An atom of boron (atomic number 5) contains five electrons. The n = 1 shell is filled with two electrons and three electrons will occupy the n = 2 shell. Because any s subshell can contain only two electrons, the fifth electron must occupy the next energy level, which will be a 2p orbital. There are three degenerate 2p orbitals (m_l = –1, 0, +1) and the electron can occupy any one of these p orbitals. When drawing orbital diagrams, we include empty boxes to depict any empty orbitals in the same subshell that we are filling.

B $1s^2 2s^2 2p^1$



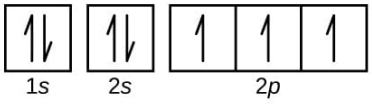
Carbon (atomic number 6) has six electrons. Four of them fill the 1s and 2s orbitals. The remaining two electrons occupy the 2*p* subshell. We now have a choice of filling one of the 2*p* orbitals and pairing the electrons or of leaving the electrons unpaired in two different, but degenerate, *p* orbitals. The orbitals are filled as described by Hund's rule: the lowest-energy configuration for an atom with electrons within a set of degenerate orbitals is that having the maximum number of unpaired electrons. Thus, the two electrons in the carbon 2*p* orbitals have identical n, l, and m_s quantum numbers and differ in their m_l quantum number (in accord with the Pauli exclusion principle). The electron configuration and orbital diagram for carbon are:

C $1s^2 2s^2 2p^2$

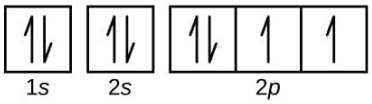


Nitrogen (atomic number 7) fills the 1s and 2s subshells and has one electron in each of the three 2*p* orbitals, in accordance with Hund's rule. These three electrons have unpaired spins. Oxygen (atomic number 8) has a pair of electrons in any one of the 2*p* orbitals (the electrons have opposite spins) and a single electron in each of the other two. Fluorine (atomic number 9) has only one 2*p* orbital containing an unpaired electron. All of the electrons in the noble gas neon (atomic number 10) are paired, and all of the orbitals in the $n = 1$ and the $n = 2$ shells are filled. The electron configurations and orbital diagrams of these four elements are:

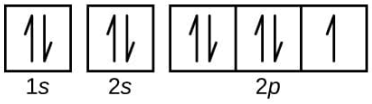
N $1s^2 2s^2 2p^3$



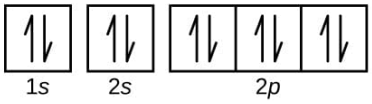
O $1s^2 2s^2 2p^4$



F $1s^2 2s^2 2p^5$



Ne $1s^2 2s^2 2p^6$



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 $1s^2 2s^2 2p^6 3s^1$ 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 2.6.5). 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, ($1s^2 2s^2 2p^6$) and our abbreviated or

condensed configuration is [Ne]$3s^1$.

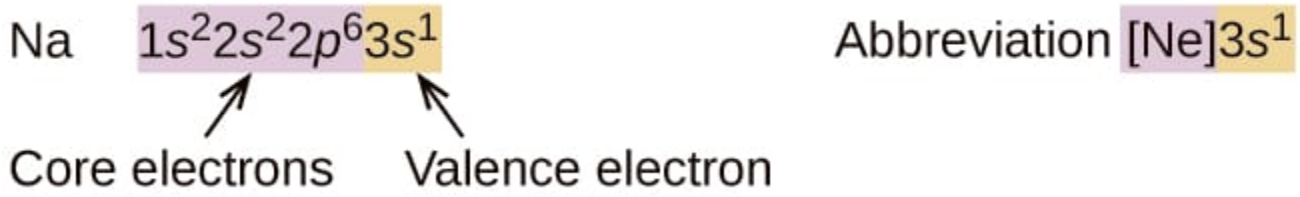


Figure 2.6.7: *A core-abbreviated electron configuration (right) replaces the core electrons with the noble gas symbol whose configuration matches the core electron configuration of the other element.*

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.

$$\begin{aligned} \text{Li} &: [\text{He}]\, 2s^1 \\ \text{Na} &: [\text{Ne}]\, 3s^1 \end{aligned} \tag{2.6.1}$$

The alkaline earth metal magnesium (atomic number 12), with its 12 electrons in a [Ne]$3s^2$ configuration, is analogous to its family member beryllium, [He]$2s^2$. Both atoms have a filled s subshell outside their filled inner shells. Aluminum (atomic number 13), with 13 electrons and the electron configuration [Ne]$3s^2 3p^1$, is analogous to its family member boron, [He]$2s^2 2p^1$.

The electron configurations of silicon (14 electrons), phosphorus (15 electrons), sulfur (16 electrons), chlorine (17 electrons), and argon (18 electrons) are analogous in the electron configurations of their outer shells to their corresponding family members carbon, nitrogen, oxygen, fluorine, and neon, respectively, except that the principal quantum number of the outer shell of the heavier elements has increased by one to n = 3. Figure 2.6.6 shows the lowest energy, or ground-state, electron configuration for these elements as well as that for atoms of each of the known elements.

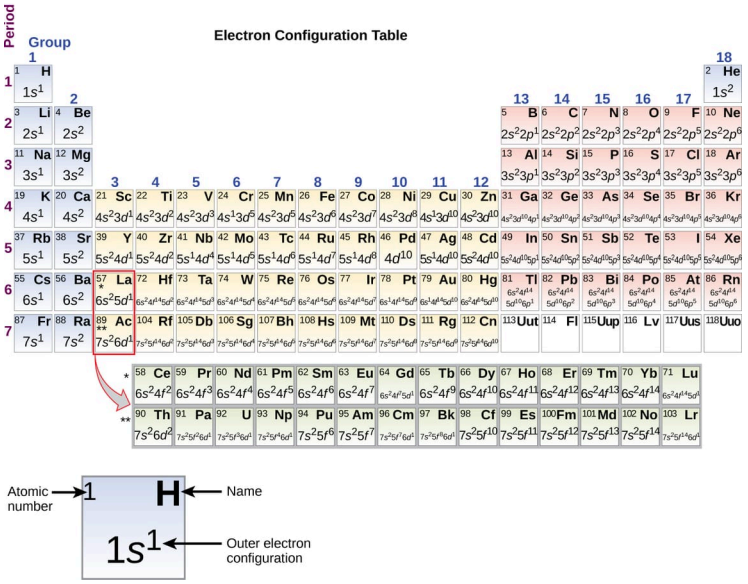


Figure 2.6.8: *This version of the periodic table shows the outer-shell electron configuration of each element. Note that down each group, the configuration is often similar.*

When we come to the next element in the periodic table, the alkali metal potassium (atomic number 19), we might expect that we would begin to add electrons to the 3*d* subshell. However, all available chemical and physical evidence indicates that potassium is like lithium and sodium, and that the next electron is not added to the 3*d* level but is, instead, added to the 4*s* level (Figure

2.6.3 or 2.6.4). As discussed previously, the 3*d* orbital with no radial nodes is higher in energy because it is less penetrating and more shielded from the nucleus than the 4s, which has three radial nodes. Thus, potassium has an electron configuration of [Ar]$4s^1$. Hence, potassium corresponds to Li and Na in its valence shell configuration. The next electron is added to complete the 4s subshell and calcium has an electron configuration of [Ar]$4s^2$. This gives calcium an outer-shell electron configuration corresponding to that of beryllium and magnesium.

Beginning with the transition metal scandium (atomic number 21), additional electrons are added successively to the 3*d* subshell. This subshell is filled to its capacity with 10 electrons (remember that for $l = 2$ [*d* orbitals], there are $2l + 1 = 5$ values of m_l, meaning that there are five *d* orbitals that have a combined capacity of 10 electrons). The 4*p* subshell fills next. Note that for three series of elements, scandium (Sc) through copper (Cu), yttrium (Y) through silver (Ag), and lutetium (Lu) through gold (Au), a total of 10 *d* electrons are successively added to the $(n - 1)$ shell next to the *n* shell to bring that $(n - 1)$ shell from 8 to 18 electrons. For two series, lanthanum (La) through lutetium (Lu) and actinium (Ac) through lawrencium (Lr), 14 *f* electrons ($l = 3$, $2l + 1 = 7$ m_l values; thus, seven orbitals with a combined capacity of 14 electrons) are successively added to the $(n - 2)$ shell to bring that shell from 18 electrons to a total of 32 electrons.

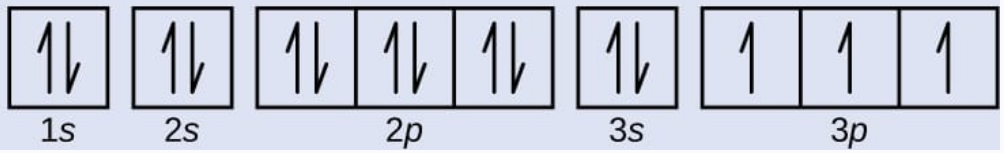
Example 2.6.3: Quantum Numbers and Electron Configurations

What is the electron configuration and orbital diagram for a phosphorus atom? What are the four quantum numbers for the last electron added?

Solution

The atomic number of phosphorus is 15. Thus, a phosphorus atom contains 15 electrons. The order of filling of the energy levels is 1s, 2s, 2*p*, 3s, 3*p*, 4s, . . . The 15 electrons of the phosphorus atom will fill up to the 3*p* orbital, which will contain three electrons:

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



The last electron added is a 3*p* electron. Therefore, $n = 3$ and, for a *p*-type orbital, $l = 1$. The m_l value could be –1, 0, or +1. The three *p* orbitals are degenerate, so any of these m_l values is correct. For unpaired electrons, convention assigns the value of $+\frac{1}{2}$ for the spin quantum number; thus, $m_s = +\frac{1}{2}$.

Exercise 2.6.1

Identify the atoms from the electron configurations given:

a. [Ar]$4s^2 3d^5$
b. [Kr]$5s^2 4d^{10} 5p^6$

Answer a

Mn

Answer b

Xe

The periodic table can be a powerful tool in predicting the electron configuration of an element. However, we do find exceptions to the order of filling of orbitals that are shown in Figure 2.6.3 or 2.6.4. For instance, the electron configurations of the transition metals chromium (Cr; atomic number 24) and copper (Cu; atomic number 29), among others, are not those we would expect. In

general, such exceptions involve subshells with very similar energy, and small effects can lead to changes in the order of filling.

In the case of Cr and Cu, we find that half-filled and completely filled subshells apparently represent conditions of preferred stability. This stability is such that an electron shifts from the 4*s* into the 3*d* orbital to gain the extra stability of a half-filled 3*d* subshell (in Cr) or a filled 3*d* subshell (in Cu). Other exceptions also occur. For example, niobium (Nb, atomic number 41) is predicted to have the electron configuration [Kr]$5s^2 4d^3$. Experimentally, we observe that its ground-state electron configuration is actually [Kr]$5s^1 4d^4$. We can rationalize this observation by saying that the electron–electron repulsions experienced by pairing the electrons in the 5*s* orbital are larger than the gap in energy between the 5*s* and 4*d* orbitals. There is no simple method to predict the exceptions for atoms where the magnitude of the repulsions between electrons is greater than the small differences in energy between subshells.

Electron Configurations and the Periodic Table

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Video 2.6.1: *A trick for writing electron configurations based on the organization of the periodic table.*

As described earlier, the periodic table arranges atoms based on increasing atomic number so that elements with the same chemical properties recur periodically. When their electron configurations are added to the table (Figure 2.6.6), we also see a periodic recurrence of similar electron configurations in the outer shells of these elements. Because they are in the outer shells of an atom, valence electrons play the most important role in chemical reactions. The outer electrons have the highest energy of the electrons in an atom and are more easily lost or shared than the core electrons. Valence electrons are also the determining factor in some physical properties of the elements.

Elements in any one group (or column) have the same number of valence electrons; the alkali metals lithium and sodium each have only one valence electron, the alkaline earth metals beryllium and magnesium each have two, and the halogens fluorine and chlorine each have seven valence electrons. The similarity in chemical properties among elements of the same group occurs because they have the same number of valence electrons. It is the loss, gain, or sharing of valence electrons that defines how elements react.

It is important to remember that the periodic table was developed on the basis of the chemical behavior of the elements, well before any idea of their atomic structure was available. Now we can understand why the periodic table has the arrangement it has—the arrangement puts elements whose atoms have the same number of valence electrons in the same group. This arrangement is emphasized in Figure 2.6.6, which shows in periodic-table form the electron configuration of the last subshell to be filled by the Aufbau principle. The colored sections of Figure 2.6.6 show the three categories of elements classified by the orbitals being filled: main group, transition, and inner transition elements. These classifications determine which orbitals are counted in the valence shell, or highest energy level orbitals of an atom.

1. **Main group elements** (sometimes called **representative elements**) are those in which the last electron added enters an *s* or a *p* orbital in the outermost shell, shown in blue and red in Figure 2.6.6. This category includes all the nonmetallic elements, as well as many metals and the intermediate semimetallic elements. The valence electrons for main group elements are those with the highest *n* level. For example, gallium (Ga, atomic number 31) has the electron configuration [Ar]$\underline{4s^2} 3d^{10} \underline{4p^1}$, which contains three valence electrons (underlined). The completely filled *d* orbitals count as core, not valence, electrons.
2. **Transition elements or transition metals**. These are metallic elements in which the last electron added enters a *d* orbital. The valence electrons (those added after the last noble gas configuration) in these elements include the *ns* and $(n - 1)$ *d* electrons. The official IUPAC definition of transition elements specifies those with partially filled *d* orbitals. Thus, the elements with completely filled orbitals (Zn, Cd, Hg, as well as Cu, Ag, and Au in Figure 2.6.6) are not technically transition elements. However, the term is frequently used to refer to the entire *d* block (colored yellow in Figure 2.6.6), and we will adopt this usage in this textbook.

3. **Inner transition elements** are metallic elements in which the last electron added occupies an *f* orbital. They are shown in green in Figure 2.6.6. The valence shells of the inner transition elements consist of the (*n* – 2)*f*, the (*n* – 1)*d*, and the *n*s subshells. There are two inner transition series:
   1. The lanthanide series: lanthanide (La) through lutetium (Lu)
   2. The actinide series: actinide (Ac) through lawrencium (Lr)

Lanthanum and actinium, because of their similarities to the other members of the series, are included and used to name the series, even though they are transition metals with no *f* electrons.

Electron Configurations of Ions

We have seen that ions are formed when atoms gain or lose electrons. A cation (positively charged ion) forms when one or more electrons are removed from a parent atom. For main group elements, the electrons that were added last are the first electrons removed. For transition metals and inner transition metals, however, electrons in the *s* orbital are easier to remove than the *d* or *f* electrons, and so the highest *n*s electrons are lost, and then the (*n* – 1)*d* or (*n* – 2)*f* electrons are removed. An anion (negatively charged ion) forms when one or more electrons are added to a parent atom. The added electrons fill in the order predicted by the Aufbau principle.

Example 2.6.2: Predicting Electron Configurations of Ions

What is the electron configuration and orbital diagram of:

a. Na^+
b. P^{3-}
c. Al^{2+}
d. Fe^{2+}
e. Sm^{3+}

Solution

First, write out the electron configuration for each parent atom. We have chosen to show the full, unabbreviated configurations to provide more practice for students who want it, but listing the core-abbreviated electron configurations is also acceptable.

Next, determine whether an electron is gained or lost. Remember electrons are negatively charged, so ions with a positive charge have *lost* an electron. For main group elements, the last orbital gains or loses the electron. For transition metals, the last *s* orbital loses an electron before the *d* orbitals.

a. Na: $1s^2 2s^2 2p^6 3s^1$. Sodium cation loses one electron, so Na^+: $1s^2 2s^2 2p^6 3s^1$ = Na^+: $1s^2 2s^2 2p^6$.
b. P: $1s^2 2s^2 2p^6 3s^2 3p^3$. Phosphorus trianion gains three electrons, so P^{3-}: $1s^2 2s^2 2p^6 3s^2 3p^6$.
c. Al: $1s^2 2s^2 2p^6 3s^2 3p^1$. Aluminum dication loses two electrons Al^{2+}: $1s^2 2s^2 2p^6 3s^2 3p^1$ = Al^{2+}: $1s^2 2s^2 2p^6 3s^1$.
d. Fe: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$. Iron(II) loses two electrons and, since it is a transition metal, they are removed from the 4s orbital Fe^{2+}: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$ = $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6$.
e. Sm: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^6$. Samarium trication loses three electrons. The first two will be lost from the 6s orbital, and the final one is removed from the 4*f* orbital. Sm^{3+}: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^6$ = $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 4f^5$.

Exercise 2.6.2

a. Which ion with a +2 charge has the electron configuration $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^5$?
b. Which ion with a +3 charge has this configuration?

Answer a

Tc^{2+}

Answer b

Ru^{3+}

Summary

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Video 2.6.2: *An overview of the role of orbitals in electron configurations and how to write electron configurations.*

The relative energy of the subshells determine the order in which atomic orbitals are filled (1*s*, 2*s*, 2*p*, 3*s*, 3*p*, 4*s*, 3*d*, 4*p*, and so on). Electron configurations and orbital diagrams can be determined by applying the Pauli exclusion principle (no two electrons can have the same set of four quantum numbers) and Hund's rule (whenever possible, electrons retain unpaired spins in degenerate orbitals).

Electrons in the outermost orbitals, called valence electrons, are responsible for most of the chemical behavior of elements. In the periodic table, elements with analogous valence electron configurations usually occur within the same group. There are some exceptions to the predicted filling order, particularly when half-filled or completely filled orbitals can be formed. The periodic table can be divided into three categories based on the orbital in which the last electron to be added is placed: main group elements (*s* and *p* orbitals), transition elements (*d* orbitals), and inner transition elements (*f* orbitals).

Glossary

Aufbau principle
: procedure in which the electron configuration of the elements is determined by "building" them in order of atomic numbers, adding one proton to the nucleus and one electron to the proper subshell at a time

core electron
: electron in an atom that occupies the orbitals of the inner shells

electron configuration
: electronic structure of an atom in its ground state given as a listing of the orbitals occupied by the electrons

Hund's rule
: every orbital in a subshell is singly occupied with one electron before any one orbital is doubly occupied, and all electrons in singly occupied orbitals have the same spin

orbital diagram
: pictorial representation of the electron configuration showing each orbital as a box and each electron as an arrow

valence electrons
: electrons in the outermost or valence shell (highest value of *n*) of a ground-state atom; determine how an element reacts

valence shell
: outermost shell of electrons in a ground-state atom; for main group elements, the orbitals with the highest *n* level

(s and *p* subshells) are in the valence shell, while for transition metals, the highest energy s and *d* subshells make up the valence shell and for inner transition elements, the highest *s*, *d,* and *f* subshells are included

Contributors

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2.7: Unit 2 Practice Problems

Question 1.

Which subatomic particle(s) determine an atom's **name**?

Answer

protons and neutrons

Which subatomic particle(s) determine an atom's **mass**?

Answer

protons and neutrons

Which subatomic particle(s) determine an atom's **charge**?

Answer

electrons and protons

Question 2.

Write the symbol for each of the following ions:

(a) the ion with a 1+ charge, atomic number 55, and mass number 133

(b) the ion with 54 electrons, 53 protons, and 74 neutrons

(c) the ion with atomic number 15, mass number 31, and a 3– charge

Answer

(a) $^{133}Cs^{+1}$ (b) $^{127}I^{-1}$ (c) $^{31}P^{-3}$

Question 3.

How many protons, neutrons, and electrons are in the following?

(a) $^{87}Sr^{+2}$

(b) ^{75}As

Answer

(a) protons = 38 neutrons = 49 electrons = 36

(b) protons = 33 neutrons = 42 electrons = 33

Question 4.

According to Bhor's model, how many electrons are in the 4th energy level?

Answer

electrons = $2(4)^2$ = 32 electrons

Question 5.

Give the electron configuration for Ge using quantum mechanical notation.

Answer

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

Question 6.

Give the electron configuration for Lu using noble gas configuration.

Answer

[Xe] $6s^2\ 4f^{14}\ 5d^1$

Question 7.

Give the electron configuration for S^{-2} using quantum mechanical notation.

Answer

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

Question 8.

Which atom has the electron configuration: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^2$?

Answer

Zr

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- Christy VanRooyen, Oregon Tech

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2.8: Electromagnetic Energy - Lab 4

Learning Objectives

- Characterize light based on its electromagnetic radiation.

The nature of light has been a subject of inquiry since antiquity. In the seventeenth century, Isaac Newton performed experiments with lenses and prisms and was able to demonstrate that white light consists of the individual colors of the rainbow combined together. Newton explained his optics findings in terms of a "corpuscular" view of light, in which light was composed of streams of extremely tiny particles travelling at high speeds according to Newton's laws of motion. Others in the seventeenth century, such as Christiaan Huygens, had shown that optical phenomena such as reflection and refraction could be equally well explained in terms of light as waves travelling at high speed through a medium called "luminiferous aether" that was thought to permeate all space. Early in the nineteenth century, Thomas Young demonstrated that light passing through narrow, closely spaced slits produced interference patterns that could not be explained in terms of Newtonian particles but could be easily explained in terms of waves. Later in the nineteenth century, after James Clerk Maxwell developed his theory of electromagnetic radiation and showed that light was the visible part of a vast spectrum of electromagnetic waves, the particle view of light became thoroughly discredited. By the end of the nineteenth century, scientists viewed the physical universe as roughly comprising two separate domains: matter composed of particles moving according to Newton's laws of motion, and electromagnetic radiation consisting of waves governed by Maxwell's equations. Today, these domains are referred to as classical mechanics and classical electrodynamics (or classical electromagnetism). Although there were a few physical phenomena that could not be explained within this framework, scientists at that time were so confident of the overall soundness of this framework that they viewed these aberrations as puzzling paradoxes that would ultimately be resolved somehow within this framework. As we shall see, these paradoxes led to a contemporary framework that intimately connects particles and waves at a fundamental level called wave-particle duality, which has superseded the classical view.

Visible light and other forms of electromagnetic radiation play important roles in chemistry, since they can be used to infer the energies of electrons within atoms and molecules. Much of modern technology is based on electromagnetic radiation. For example, radio waves from a mobile phone, X-rays used by dentists, the energy used to cook food in your microwave, the radiant heat from red-hot objects, and the light from your television screen are forms of electromagnetic radiation that all exhibit wavelike behavior.

Waves

A wave is an oscillation or periodic movement that can transport energy from one point in space to another. Common examples of waves are all around us. Shaking the end of a rope transfers energy from your hand to the other end of the rope, dropping a pebble into a pond causes waves to ripple outward along the water's surface, and the expansion of air that accompanies a lightning strike generates sound waves (thunder) that can travel outward for several miles. In each of these cases, kinetic energy is transferred through matter (the rope, water, or air) while the matter remains essentially in place. An insightful example of a wave occurs in sports stadiums when fans in a narrow region of seats rise simultaneously and stand with their arms raised up for a few seconds before sitting down again while the fans in neighboring sections likewise stand up and sit down in sequence. While this wave can quickly encircle a large stadium in a few seconds, none of the fans actually travel with the wave-they all stay in or above their seats.

Waves need not be restricted to travel through matter. As Maxwell showed, electromagnetic waves consist of an electric field oscillating in step with a perpendicular magnetic field, both of which are perpendicular to the direction of travel. These waves can travel through a vacuum at a constant speed of 2.998×10^8 m/s, the speed of light (denoted by c).

All waves, including forms of electromagnetic radiation, are characterized by, a wavelength (denoted by λ, the lowercase Greek letter lambda), a frequency (denoted by ν, the lowercase Greek letter nu), and an amplitude. As can be seen in Figure $2.8.1$, the wavelength is the distance between two consecutive peaks or troughs in a wave (measured in meters in the SI system). Electromagnetic waves have wavelengths that fall within an enormous range-wavelengths of kilometers (10^3 m) to picometers (10^{-12} m) have been observed. The frequency is the number of wave cycles that pass a specified point in space in a specified amount of time (in the SI system, this is measured in seconds). A cycle corresponds to one complete wavelength. The unit for

frequency, expressed as cycles per second [s^{-1}], is the hertz (Hz). Common multiples of this unit are megahertz, (1 MHz = 1 × 10^6 Hz) and gigahertz (1 GHz = 1 × 10^9 Hz). The amplitude corresponds to the magnitude of the wave's displacement and so, in Figure, this corresponds to one-half the height between the peaks and troughs. The amplitude is related to the intensity of the wave, which for light is the brightness, and for sound is the loudness.

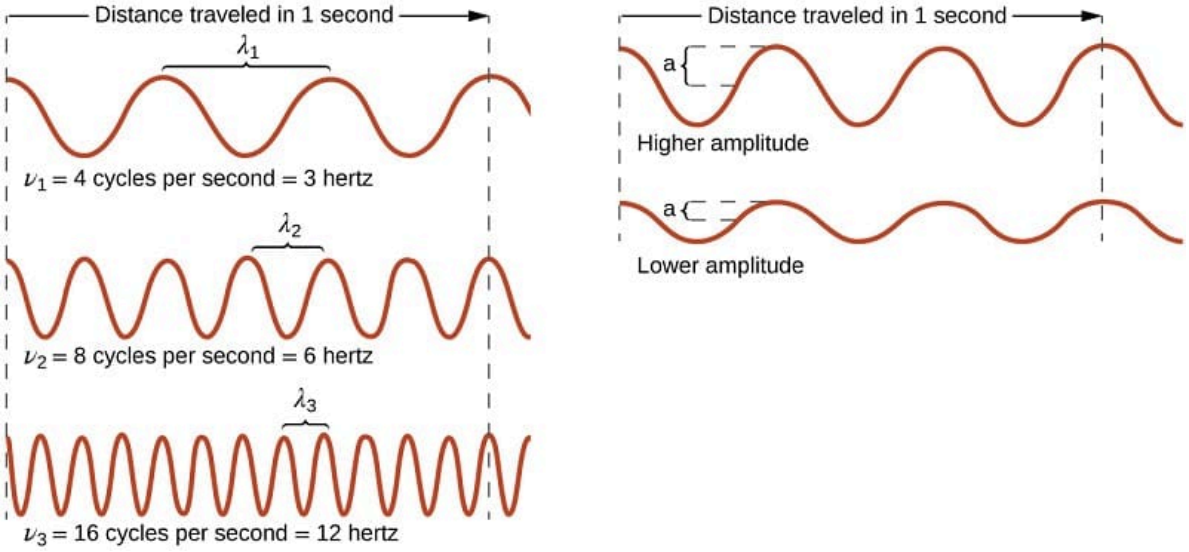


Figure 2.8.1: One-dimensional sinusoidal waves show the relationship among wavelength, frequency, and speed. The wave with the shortest wavelength has the highest frequency. Amplitude is one-half the height of the wave from peak to trough.

The product of a wave's wavelength (λ) and its frequency (ν), $\lambda\nu$, is the speed of the wave. Thus, for electromagnetic radiation in a vacuum:

$$c = 2.998 \times 10^8\,\mathrm{ms}^{-1} = \lambda\nu \tag{2.8.1}$$

Wavelength and frequency are inversely proportional: As the wavelength increases, the frequency decreases. The inverse proportionality is illustrated in Figure 2.8.2. This figure also shows the electromagnetic spectrum, the range of all types of electromagnetic radiation. Each of the various colors of visible light has specific frequencies and wavelengths associated with them, and you can see that visible light makes up only a small portion of the electromagnetic spectrum. Because the technologies developed to work in various parts of the electromagnetic spectrum are different, for reasons of convenience and historical legacies, different units are typically used for different parts of the spectrum. For example, radio waves are usually specified as frequencies (typically in units of MHz), while the visible region is usually specified in wavelengths (typically in units of nm or angstroms).

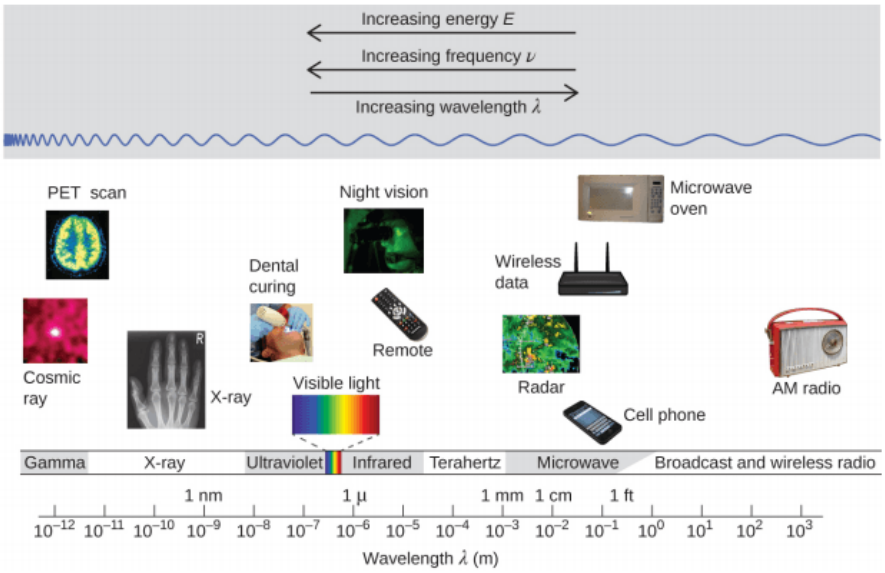


Figure 2.8.2: Portions of the electromagnetic spectrum are shown in order of decreasing frequency and increasing wavelength. Examples of some applications for various wavelengths include positron emission tomography (PET) scans, X-ray imaging, remote controls, wireless Internet, cellular telephones, and radios. (credit “Cosmic ray": modification of work by NASA; credit “PET scan": modification of work by the National Institute of Health; credit “X-ray": modification of work by Dr. Jochen Lengerke; credit “Dental curing": modification of work by the Department of the Navy; credit “Night vision": modification of work by the Department of the Army; credit “Remote": modification of work by Emilian Robert Vicol; credit “Cell phone": modification of work by Brett Jordan; credit “Microwave oven": modification of work by Billy Mabray; credit “Ultrasound": modification of work by Jane Whitney; credit “AM radio": modification of work by Dave Clausen)

Example 2.8.1: Determining the Frequency and Wavelength of Radiation

A sodium streetlight gives off yellow light that has a wavelength of 589 nm (1 nm = 1×10^{-9} m). What is the frequency of this light?

Solution

We can rearrange the Equation 2.8.1 to solve for the frequency:

$$u = \frac{c}{\lambda} \tag{2.8.2}$$

Since *c* is expressed in meters per second, we must also convert 589 nm to meters.

$$u = \left(\frac{2.998 \times 10^{8} \cancel{\text{m}}\,\text{s}^{-1}}{589 \cancel{\text{nm}}}\right)\left(\frac{1 \times 10^{9} \cancel{\text{nm}}}{1 \cancel{\text{m}}}\right) = 5.09 \times 10^{14}\,\text{s}^{-1} \tag{2.8.3}$$

Wireless Communication

Many valuable technologies operate in the radio (3 kHz-300 GHz) frequency region of the electromagnetic spectrum. At the low frequency (low energy, long wavelength) end of this region are AM (amplitude modulation) radio signals (540-2830 kHz) that can travel long distances. FM (frequency modulation) radio signals are used at higher frequencies (87.5-108.0 MHz). In AM radio, the information is transmitted by varying the amplitude of the wave (Figure 2.8.5). In FM radio, by contrast, the amplitude is constant and the instantaneous frequency varies.



Figure 2.8.3: Radio and cell towers are typically used to transmit long-wavelength electromagnetic radiation. Increasingly, cell towers are designed to blend in with the landscape, as with the Tucson, Arizona, cell tower (right) disguised as a palm tree. (credit left: modification of work by Sir Mildred Pierce; credit middle: modification of work by M.O. Stevens)

Other technologies also operate in the radio-wave portion of the electromagnetic spectrum. For example, 4G cellular telephone signals are approximately 880 MHz, while Global Positioning System (GPS) signals operate at 1.228 and 1.575 GHz, local area wireless technology (Wi-Fi) networks operate at 2.4 to 5 GHz, and highway toll sensors operate at 5.8 GHz. The frequencies associated with these applications are convenient because such waves tend not to be absorbed much by common building materials.

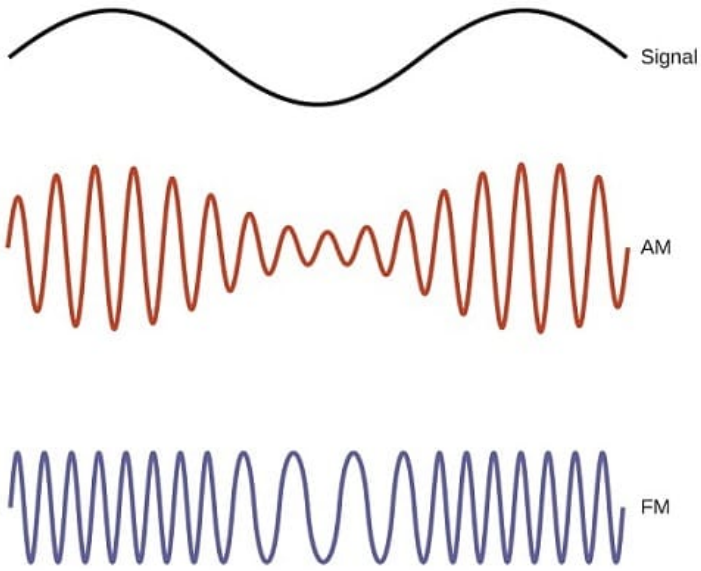


Figure 2.8.4: This schematic depicts how amplitude modulation (AM) and frequency modulation (FM) can be used to transmit a radio wave.

One particularly characteristic phenomenon of waves results when two or more waves come into contact: They interfere with each other. Figure 2.8.5 shows the interference patterns that arise when light passes through narrow slits closely spaced about a wavelength apart. The fringe patterns produced depend on the wavelength, with the fringes being more closely spaced for shorter wavelength light passing through a given set of slits. When the light passes through the two slits, each slit effectively acts as a new source, resulting in two closely spaced waves coming into contact at the detector (the camera in this case). The dark regions in Figure 2.8.5 correspond to regions where the peaks for the wave from one slit happen to coincide with the troughs for the wave from the other slit (destructive interference), while the brightest regions correspond to the regions where the peaks for the two waves (or their two troughs) happen to coincide (constructive interference). Likewise, when two stones are tossed close together into a pond, interference patterns are visible in the interactions between the waves produced by the stones. Such interference

patterns cannot be explained by particles moving according to the laws of classical mechanics.



Figure 2.8.5: Interference fringe patterns are shown for light passing through two closely spaced, narrow slits. The spacing of the fringes depends on the wavelength, with the fringes being more closely spaced for the shorter-wavelength blue light. (credit: PASCO)

Dorothy Hodgkin

Because the wavelengths of X-rays (10-10,000 picometers [pm]) are comparable to the size of atoms, X-rays can be used to determine the structure of molecules. When a beam of X-rays is passed through molecules packed together in a crystal, the X-rays collide with the electrons and scatter. Constructive and destructive interference of these scattered X-rays creates a specific diffraction pattern. Calculating backward from this pattern, the positions of each of the atoms in the molecule can be determined very precisely. One of the pioneers who helped create this technology was Dorothy Crowfoot Hodgkin.

She was born in Cairo, Egypt, in 1910, where her British parents were studying archeology. Even as a young girl, she was fascinated with minerals and crystals. When she was a student at Oxford University, she began researching how X-ray crystallography could be used to determine the structure of biomolecules. She invented new techniques that allowed her and her students to determine the structures of vitamin B_{12}, penicillin, and many other important molecules. Diabetes, a disease that affects 382 million people worldwide, involves the hormone insulin. Hodgkin began studying the structure of insulin in 1934, but it required several decades of advances in the field before she finally reported the structure in 1969. Understanding the structure has led to better understanding of the disease and treatment options.

Not all waves are traveling waves. Standing waves (also known as stationary waves) remain constrained within some region of space. As we shall see, standing waves play an important role in our understanding of the electronic structure of atoms and molecules. The simplest example of a standing wave is a one-dimensional wave associated with a vibrating string that is held fixed at its two end points. Figure 2.8.6 shows the four lowest-energy standing waves (the fundamental wave and the lowest three harmonics) for a vibrating string at a particular amplitude. Although the string's motion lies mostly within a plane, the wave itself is considered to be one dimensional, since it lies along the length of the string. The motion of string segments in a direction perpendicular to the string length generates the waves and so the amplitude of the waves is visible as the maximum displacement of the curves seen in Figure 2.8.6. The key observation from the figure is that only those waves having an integer number, n, of half-wavelengths between the end points can form. A system with fixed end points such as this restricts the number and type of the possible waveforms. This is an example of quantization, in which only discrete values from a more general set of continuous values of some property are observed. Another important observation is that the harmonic waves (those waves displaying more than one-half wavelength) all have one or more points between the two end points that are not in motion. These special points are nodes. The energies of the standing waves with a given amplitude in a vibrating string increase with the number of half-wavelengths n. Since the number of nodes is $n - 1$, the energy can also be said to depend on the number of nodes, generally increasing as the number of nodes increases.

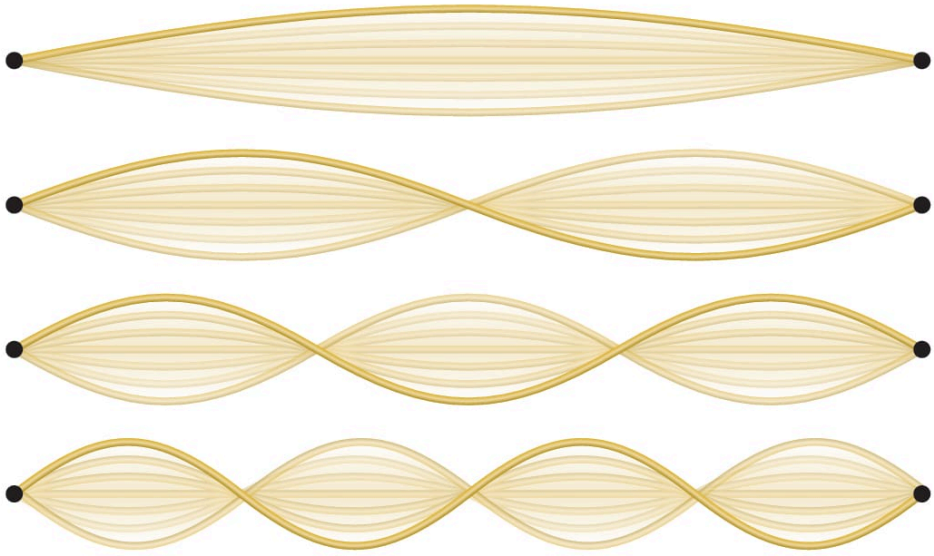


Figure 2.8.6*:* A vibrating string shows some one-dimensional standing waves. Since the two end points of the string are held fixed, only waves having an integer number of half-wavelengths can form. The points on the string between the end points that are not moving are called the nodes.

An example of two-dimensional standing waves is shown in Figure 2.8.7 which shows the vibrational patterns on a flat surface. Although the vibrational amplitudes cannot be seen like they could in the vibrating string, the nodes have been made visible by sprinkling the drum surface with a powder that collects on the areas of the surface that have minimal displacement. For one-dimensional standing waves, the nodes were points on the line, but for two-dimensional standing waves, the nodes are lines on the surface (for three-dimensional standing waves, the nodes are two-dimensional surfaces within the three-dimensional volume). Because of the circular symmetry of the drum surface, its boundary conditions (the drum surface being tightly constrained to the circumference of the drum) result in two types of nodes: radial nodes that sweep out all angles at constant radii and, thus, are seen as circles about the center, and angular nodes that sweep out all radii at constant angles and, thus, are seen as lines passing through the center. The upper left image in Figure 2.8.7 shows two radial nodes, while the image in the lower right shows the vibrational pattern associated with three radial nodes and two angular nodes.

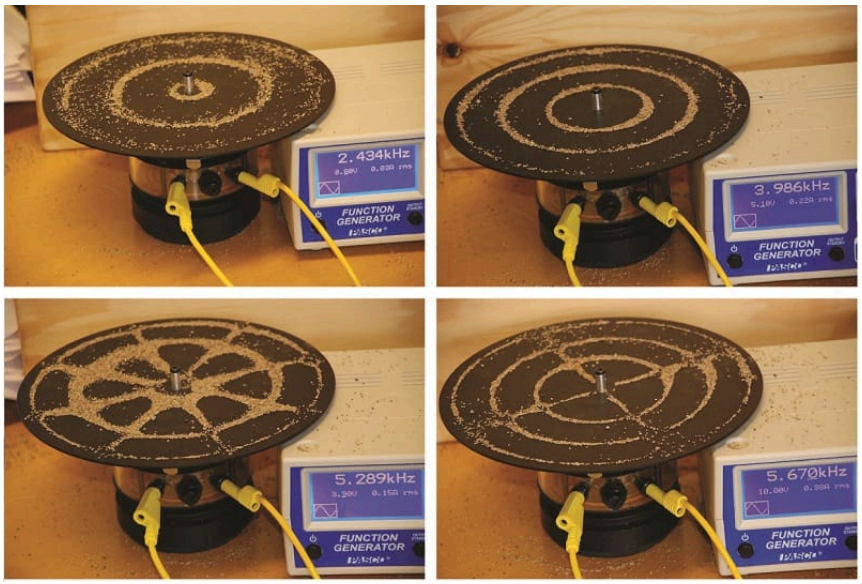


Figure 2.8.7*: Two-dimensional standing waves can be visualized on a vibrating surface. The surface has been sprinkled with a powder that collects near the nodal lines. There are two types of nodes visible: radial nodes (circles) and angular nodes (radii). For a more animated video, check this link out.*

Line Spectra

One paradox within the classical electromagnetic theory that scientists in the late nineteenth century struggled with concerned the light emitted from atoms and molecules. When solids, liquids, or condensed gases are heated sufficiently, they radiate some of the excess energy as light. Photons produced in this manner have a range of energies, and thereby produce a continuous spectrum in which an unbroken series of wavelengths is present. Most of the light generated from stars (including our sun) is produced in this fashion. You can see all the visible wavelengths of light present in sunlight by using a prism to separate them. As can be seen in Figure 6.2.8, sunlight also contains UV light (shorter wavelengths) and IR light (longer wavelengths) that can be detected using instruments but that are invisible to the human eye. Incandescent (glowing) solids such as tungsten filaments in incandescent lights also give off light that contains all wavelengths of visible light. These continuous spectra can often be approximated by blackbody radiation curves at some appropriate temperature, such as those shown in Figure 2.8.9.

In contrast to continuous spectra, light can also occur as discrete or line spectra having very narrow line widths interspersed throughout the spectral regions such as those shown in Figure 2.8.5. Exciting a gas at low partial pressure using an electrical current, or heating it, will produce line spectra. Fluorescent light bulbs and neon signs operate in this way (Figure 2.8.11). Each element displays its own characteristic set of lines, as do molecules, although their spectra are generally much more complicated.



Figure 2.8.11**:** Neon signs operate by exciting a gas at low partial pressure using an electrical current. This sign shows the elaborate artistic effects that can be achieved. (credit: Dave Shaver)

Each emission line consists of a single wavelength of light, which implies that the light emitted by a gas consists of a set of discrete energies. For example, when an electric discharge passes through a tube containing hydrogen gas at low pressure, the H_2 molecules are broken apart into separate H atoms, and we see a blue-pink color. Passing the light through a prism produces a line spectrum, indicating that this light is composed of photons of four visible wavelengths, as shown in Figure 2.8.12.

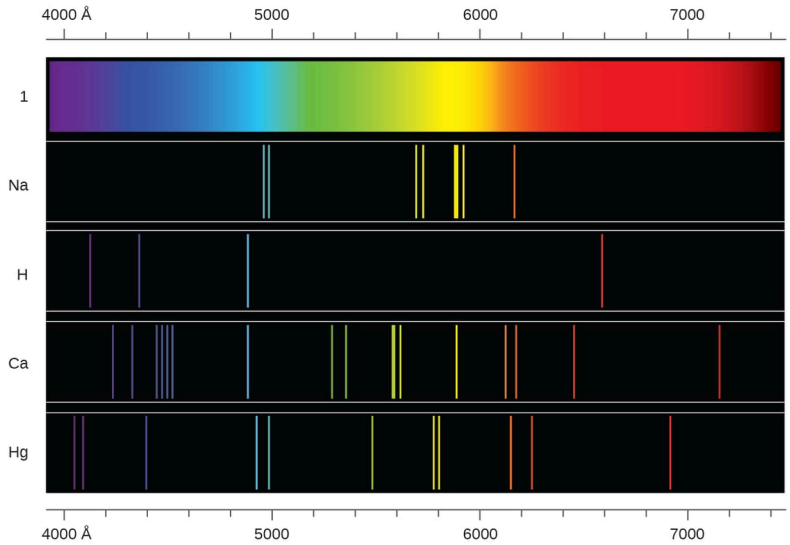


Figure 2.8.12**:** Line spectra of select gas. Compare the two types of emission spectra: continuous spectrum of white light (top) and the line spectra of the light from excited sodium, hydrogen, calcium, and mercury atoms.

Summary

Light and other forms of electromagnetic radiation move through a vacuum with a constant speed, *c*, of 2.998 × 10^8 m s^{-1}. This radiation shows wavelike behavior, which can be characterized by a frequency, *ν*, and a wavelength, *λ*, such that *c* = *λν*. Light is an example of a travelling wave. Other important wave phenomena include standing waves, periodic oscillations, and vibrations. Standing waves exhibit quantization, since their wavelengths are limited to discrete integer multiples of some characteristic lengths. Electromagnetic radiation that passes through two closely spaced narrow slits having dimensions roughly similar to the wavelength will show an interference pattern that is a result of constructive and destructive interference of the waves. Electromagnetic radiation also demonstrates properties of particles called photons. The energy of a photon is related to the frequency (or alternatively, the wavelength) of the radiation as *E* = *hν* (or $E = \frac{hc}{\lambda}$), where *h* is Planck's constant. That light demonstrates both wavelike and particle-like behavior is known as wave-particle duality. All forms of electromagnetic radiation share these properties, although various forms including X-rays, visible light, microwaves, and radio waves interact differently with matter and have very different practical applications. Electromagnetic radiation can be generated by exciting matter to higher energies, such as by heating it. The emitted light can be either continuous (incandescent sources like the sun) or discrete (from specific types of excited atoms). Continuous spectra often have distributions that can be approximated as blackbody radiation at some appropriate temperature. The line spectrum of hydrogen can be obtained by passing the light from an electrified tube of hydrogen gas through a prism.

Glossary

amplitude
: extent of the displacement caused by a wave (for sinusoidal waves, it is one-half the difference from the peak height to the trough depth, and the intensity is proportional to the square of the amplitude)

continuous spectrum
: electromagnetic radiation given off in an unbroken series of wavelengths (e.g., white light from the sun)

electromagnetic radiation
: energy transmitted by waves that have an electric-field component and a magnetic-field component

electromagnetic spectrum
: range of energies that electromagnetic radiation can comprise, including radio, microwaves, infrared, visible, ultraviolet, X-rays, and gamma rays; since electromagnetic radiation energy is proportional to the frequency and inversely proportional to the wavelength, the spectrum can also be specified by ranges of frequencies or wavelengths

frequency (ν)
: number of wave cycles (peaks or troughs) that pass a specified point in space per unit time

hertz (Hz)
: the unit of frequency, which is the number of cycles per second, s^{-1}

intensity
: property of wave-propagated energy related to the amplitude of the wave, such as brightness of light or loudness of sound

interference pattern
: pattern typically consisting of alternating bright and dark fringes; it results from constructive and destructive interference of waves

line spectrum
: electromagnetic radiation emitted at discrete wavelengths by a specific atom (or atoms) in an excited state

node
: any point of a standing wave with zero amplitude

photon
: smallest possible packet of electromagnetic radiation, a particle of light

quantization
: occurring only in specific discrete values, not continuous

standing wave
: (also, stationary wave) localized wave phenomenon characterized by discrete wavelengths determined by the boundary conditions used to generate the waves; standing waves are inherently quantized

wave
: oscillation that can transport energy from one point to another in space

wavelength (λ)
: distance between two consecutive peaks or troughs in a wave

wave-particle duality
: term used to describe the fact that elementary particles including matter exhibit properties of both particles (including localized position, momentum) and waves (including nonlocalization, wavelength, frequency)

Contributors

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3: CHEMICAL BONDING

A general chemistry Libretexts Textbook remixed and remastered from OpenStax's textbook:
General Chemistry

A chemical bond is an attraction between atoms that allows the formation of chemical substances that contain two or more atoms. The bond is caused by the electrostatic force of attraction between opposite charges, either between electrons and nuclei, or as the result of a dipole attraction. All bonds can be explained by quantum theory, but, in practice, simplification rules allow chemists to predict the strength, directionality, and polarity of bonds. The octet rule and VSEPR theory are two examples. More sophisticated theories are valence bond theory which includes orbital hybridization and resonance, and the linear combination of atomic orbitals molecular orbital method. Electrostatics are used to describe bond polarities and the effects they have on chemical substances.

Unit 3 Objectives

By the end of this unit, you will be able to:

- Define oxidation and reduction
- Determine the valence (charge) of an element.
- Determine which element is being oxidized and which is being reduced in a redox reaction.
- Define ion, anion, electronegativity, and cation.
- Give the electron configuration for an atom using Bohr's model, box orbital diagrams, and quantum mechanical notation.
- Define electronegativity.
- Determine the type of bond which exists between two atoms based on the provided electronegativity values.
- Determine formulas for simple ionic compounds.
- Derive names for common types of inorganic compounds using a systematic approach.
- Write Lewis symbols for neutral atoms and ions
- Draw Lewis structures depicting the bonding in simple molecules
- Differentiate between single, double, and triple bonds in terms of bonding pairs, orbital overlap, and strength.

3.1: Redox Reactions

3.2: Ionic Bonding

3.3: Covalent Bonding

3.4: Chemical Formulas

3.5: Chemical Nomenclature

3.6: Lewis Symbols and Structures

3.7: Molecular Structure and Polarity

3.8: Unit 3 Practice Problems

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3.1: Redox Reactions

Learning Objectives

- Define oxidation and reduction
- Determine the valence (charge) of an element.
- Determine which element is being oxidized and which is being reduced in a redox reaction.

Oxidation-Reduction Reactions

Earth's atmosphere contains about 20% molecular oxygen, O_2, a chemically reactive gas that plays an essential role in the metabolism of aerobic organisms and in many environmental processes that shape the world. The term oxidation was originally used to describe chemical reactions involving O_2, but its meaning has evolved to refer to a broad and important reaction class known as *oxidation-reduction (redox) reactions*. A few examples of such reactions will be used to develop a clear picture of this classification.

Some redox reactions involve the transfer of electrons between reactant species to yield ionic products, such as the reaction between sodium and chlorine to yield sodium chloride:

$$2\,\mathrm{Na}(s)+\mathrm{Cl_2}(g) \rightarrow 2\,\mathrm{NaCl}(s) \tag{3.1.1}$$

It is helpful to view the process with regard to each individual reactant, that is, to represent the fate of each reactant in the form of an equation called a half-reaction:

$$2\,\mathrm{Na}(s) \rightarrow 2\,\mathrm{Na^+}(s) + 2\,\mathrm{e^-} \tag{3.1.2}$$

$$\mathrm{Cl_2}(g) + 2\,\mathrm{e^-} \rightarrow 2\,\mathrm{Cl^-}(s) \tag{3.1.3}$$

These equations show that Na atoms *lose electrons* while Cl atoms (in the Cl_2 molecule) *gain electrons*, the "s" subscripts for the resulting ions signifying they are present in the form of a solid ionic compound. For redox reactions of this sort, the loss and gain of electrons define the complementary processes that occur:

$$\textbf{oxidation} = \text{loss of electrons} \tag{3.1.4}$$

$$\textbf{reduction} = \text{gain of electrons} \tag{3.1.5}$$

Remembering Oxidation and Reduction

It is common to remember the difference between oxidation and reduction using one of two pneumonic devices:

1. "LeO goes GeR"
   In Greek Mythology, Leo was a lion (like the zodiac sign). And what do lion's do? Well, they roar but that doesn't really fit, so we go with "Ger".
   Loses **e**lectrons = **O**xidation
   Gains **e**lectrons = **R**eduction



Figure 3.1.4***:*** *Lion image by Tambako, reused under the Creative Commons Attribution 2.0 Generic license.*

2. "Oil Rig"
   Oxidation **i**s **l**oss
   Reduction **i**s **g**ain



Figure 3.1.5***:*** *Image by Peter Grima, reused under the Creative Commons Attribution 2.0 Generic license.*

In this reaction, then, sodium is *oxidized* and chlorine undergoes reduction. Viewed from a more active perspective, sodium functions as a reducing agent (reductant), since it provides electrons to (or reduces) chlorine. Likewise, chlorine functions as an oxidizing agent (oxidant), as it effectively removes electrons from (oxidizes) sodium.

$$\textbf{reducing agent} = \text{species that is oxidized} \tag{3.1.6}$$
$$\textbf{oxidizing agent} = \text{species that is reduced} \tag{3.1.7}$$

Some redox processes, however, do not involve the transfer of electrons. Consider, for example, a reaction similar to the one yielding NaCl:

$$\mathrm{H_2}(g) + \mathrm{Cl_2}(g) \rightarrow 2\,\mathrm{HCl}(g) \tag{3.1.8}$$

The product of this reaction is a covalent compound, so transfer of electrons in the explicit sense is not involved. To clarify the similarity of this reaction to the previous one and permit an unambiguous definition of redox reactions, a property called *oxidation*

number has been defined. The oxidation number (or oxidation state) of an element in a compound is the charge its atoms would possess *if the compound was ionic*.

Oxidation-reduction (redox) reactions are those in which one or more elements involved undergo a change in oxidation number. While the vast majority of redox reactions involve changes in oxidation number for two or more elements, a few interesting exceptions to this rule do exist as shown below\). Definitions for the complementary processes of this reaction class are correspondingly revised as shown here:

$$\textbf{oxidation} = \text{increase in oxidation number} \tag{3.1.9}$$
$$\textbf{reduction} = \text{decrease in oxidation number} \tag{3.1.10}$$

Returning to the reactions used to introduce this topic, they may now both be identified as redox processes. In the reaction between sodium and chlorine to yield sodium chloride, sodium is oxidized (its oxidation number increases from 0 in Na to +1 in NaCl) and chlorine is reduced (its oxidation number decreases from 0 in Cl_2 to –1 in NaCl). In the reaction between molecular hydrogen and chlorine, hydrogen is oxidized (its oxidation number increases from 0 in H_2 to +1 in HCl) and chlorine is reduced (its oxidation number decreases from 0 in Cl_2 to –1 in HCl).

Several subclasses of redox reactions are recognized, including combustion reactions in which the reductant (also called a *fuel*) and oxidant (often, but not necessarily, molecular oxygen) react vigorously and produce significant amounts of heat, and often light, in the form of a flame. Solid rocket-fuel reactions such as the one depicted below are combustion processes. A typical propellant reaction in which solid aluminum is oxidized by ammonium perchlorate is represented by this equation:

$$10\,\mathrm{Al}(s) + 6\,\mathrm{NH_4ClO_4}(s) \rightarrow 4\,\mathrm{Al_2O_3}(s) + 2\,\mathrm{AlCl_3}(s) + 12\,\mathrm{H_2O}(g) + 3\,\mathrm{N_2}(g) \tag{3.1.11}$$

Watch a brief video showing the test firing of a small-scale, prototype, hybrid rocket engine planned for use in the new Space Launch System being developed by NASA. The first engines firing at 3 s (green flame) use a liquid fuel/oxidant mixture, and the second, more powerful engines firing at 4 s (yellow flame) use a solid mixture.

YouTube Video

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

View this YouTube Video online

Single-displacement (replacement) reactions are redox reactions in which an ion in solution is displaced (or replaced) via the oxidation of a metallic element. One common example of this type of reaction is the acid oxidation of certain metals:

$$\mathrm{Zn}(s) + 2\,\mathrm{HCl}(aq) \rightarrow \mathrm{ZnCl_2}(aq) + \mathrm{H_2}(g) \tag{3.1.12}$$

Metallic elements may also be oxidized by solutions of other metal salts; for example:

$$\mathrm{Cu}(s) + 2\,\mathrm{AgNO_3}(aq) \rightarrow \mathrm{Cu(NO_3)_2}(aq) + 2\,\mathrm{Ag}(s) \tag{3.1.13}$$

This reaction may be observed by placing copper wire in a solution containing a dissolved silver salt. Silver ions in solution are reduced to elemental silver at the surface of the copper wire, and the resulting Cu^{2+} ions dissolve in the solution to yield a characteristic blue color (Figure 3.1.6).

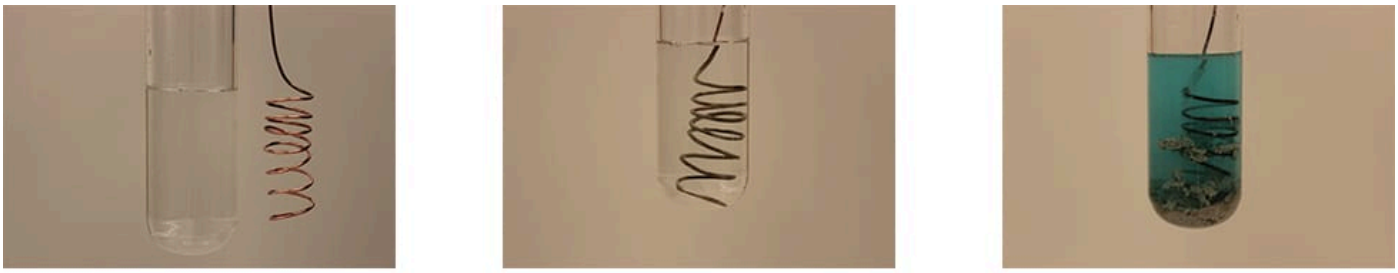


Figure 3.1.6***:*** *(a) A copper wire is shown next to a solution containing silver(I) ions. (b) Displacement of dissolved silver ions by copper ions results in (c) accumulation of gray-colored silver metal on the wire and development of a blue color in the solution, due to dissolved copper ions. (credit: modification of work by Mark Ott)*

Example 3.1.3: Describing Redox Reactions

Identify which equations represent redox reactions, providing a name for the reaction if appropriate. For those reactions identified as redox, name the oxidant and reductant.

a. $\mathrm{ZnCO_3}(s) \rightarrow \mathrm{ZnO}(s) + \mathrm{CO_2}(g)$
b. $2\,\mathrm{Ga}(l) + 3\,\mathrm{Br_2}(l) \rightarrow 2\,\mathrm{GaBr_3}(s)$
c. $2\,\mathrm{H_2O_2}(aq) \rightarrow 2\,\mathrm{H_2O}(l) + \mathrm{O_2}(g)$
d. $\mathrm{BaCl_2}(aq) + \mathrm{K_2SO_4}(aq) \rightarrow \mathrm{BaSO_4}(s) + 2\,\mathrm{KCl}(aq)$
e. $\mathrm{C_2H_4}(g) + 3\,\mathrm{O_2}(g) \rightarrow 2\,\mathrm{CO_2}(g) + 2\,\mathrm{H_2O}(l)$

Solution

Redox reactions are identified per definition if one or more elements undergo a change in oxidation number.

a. This is not a redox reaction, since oxidation numbers remain unchanged for all elements.
b. This is a redox reaction. Gallium is oxidized, its oxidation number increasing from 0 in Ga(l) to +3 in $GaBr_3$(s). The reducing agent is Ga(l). Bromine is reduced, its oxidation number decreasing from 0 in Br_2(l) to –1 in $GaBr_3$(s). The oxidizing agent is Br_2(l).
c. This is a redox reaction. It is a particularly interesting process, as it involves the same element, oxygen, undergoing both oxidation and reduction (a so-called *disproportionation reaction)*. Oxygen is oxidized, its oxidation number increasing from –1 in H_2O_2(aq) to 0 in O_2(g). Oxygen is also reduced, its oxidation number decreasing from –1 in H_2O_2(aq) to –2 in H_2O(l). For disproportionation reactions, the same substance functions as an oxidant and a reductant.
d. This is not a redox reaction, since oxidation numbers remain unchanged for all elements.
e. This is a redox reaction (combustion). Carbon is oxidized, its oxidation number increasing from –2 in C_2H_4(g) to +4 in CO_2(g). The reducing agent (fuel) is C_2H_4(g). Oxygen is reduced, its oxidation number decreasing from 0 in O_2(g) to –2 in H_2O(l). The oxidizing agent is O_2(g).

Exercise 3.1.3

This equation describes the production of tin(II) chloride:

$$\mathrm{Sn}(s) + 2\,\mathrm{HCl}(g) \rightarrow \mathrm{SnCl_2}(s) + \mathrm{H_2}(g) \tag{3.1.14}$$

Is this a redox reaction? If so, provide a more specific name for the reaction if appropriate, and identify the oxidant and reductant.

Answer

Yes, a single-replacement reaction. Sn(s)is the reductant, HCl(*g*) is the oxidant.

Summary

YouTube Video

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

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Video 3.1.1***:*** *A summary of redox reactions.*
One of your professors was a script editor for this video. Hint: It was Dr. Clark

Redox reactions involve a change in oxidation number for one or more reactant elements. Writing balanced equations for some redox reactions that occur in aqueous solutions is simplified by using a systematic approach called the half-reaction method.

Glossary

combustion reaction
vigorous redox reaction producing significant amounts of energy in the form of heat and, sometimes, light

oxidation
process in which an element's oxidation number is increased by loss of electrons

oxidation-reduction reaction
(also, redox reaction) reaction involving a change in oxidation number for one or more reactant elements

oxidation number
(also, oxidation state) the charge each atom of an element would have in a compound if the compound were ionic

oxidizing agent
(also, oxidant) substance that brings about the oxidation of another substance, and in the process becomes reduced

reduction
process in which an element's oxidation number is decreased by gain of electrons

reducing agent
(also, reductant) substance that brings about the reduction of another substance, and in the process becomes oxidized

single-displacement reaction
(also, replacement) redox reaction involving the oxidation of an elemental substance by an ionic species

Contributors

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3.2: Ionic Bonding

Learning Objectives

- Define ion, anion, electronegativity, and cation.
- Give the electron configuration for an atom using Bohr's model, box orbital diagrams, and quantum mechanical notation.

As you have learned, ions are atoms or molecules bearing an electrical charge. A cation (a positive ion) forms when a neutral atom loses one or more electrons from its valence shell, and an anion (a negative ion) forms when a neutral atom gains one or more electrons in its valence shell.

Compounds composed of ions are called ionic compounds (or salts), and their constituent ions are held together by ionic bonds: electrostatic forces of attraction between oppositely charged cations and anions. The properties of ionic compounds shed some light on the nature of ionic bonds. Ionic solids exhibit a crystalline structure and tend to be rigid and brittle; they also tend to have high melting and boiling points, which suggests that ionic bonds are very strong. Ionic solids are also poor conductors of electricity for the same reason—the strength of ionic bonds prevents ions from moving freely in the solid state. Most ionic solids, however, dissolve readily in water. Once dissolved or melted, ionic compounds are excellent conductors of electricity and heat because the ions can move about freely.

Neutral atoms and their associated ions have very different physical and chemical properties. Sodium *atoms* form sodium metal, a soft, silvery-white metal that burns vigorously in air and reacts explosively with water. Chlorine *atoms* form chlorine gas, Cl_2, a yellow-green gas that is extremely corrosive to most metals and very poisonous to animals and plants. The vigorous reaction between the elements sodium and chlorine forms the white, crystalline compound sodium chloride, common table salt, which contains sodium *cations* and chloride *anions* (Figure Figure 3.2.1). The compound composed of these ions exhibits properties entirely different from the properties of the elements sodium and chlorine. Chlorine is poisonous, but sodium chloride is essential to life; sodium atoms react vigorously with water, but sodium chloride simply dissolves in water.



Figure 3.2.1: (a) Sodium is a soft metal that must be stored in mineral oil to prevent reaction with air or water. (b) Chlorine is a pale yellow-green gas. (c) When combined, they form white crystals of sodium chloride (table salt). (credit a: modification of work by "Jurii"/Wikimedia Commons)

The Formation of Ionic Compounds

Binary ionic compounds are composed of just two elements: a metal (which forms the cations) and a nonmetal (which forms the anions). For example, NaCl is a binary ionic compound. We can think about the formation of such compounds in terms of the periodic properties of the elements. Many metallic elements have relatively low ionization potentials and lose electrons easily. These elements lie to the left in a period or near the bottom of a group on the periodic table. Nonmetal atoms have relatively high electron affinities and thus readily gain electrons lost by metal atoms, thereby filling their valence shells. Nonmetallic elements are found in the upper-right corner of the periodic table.

As all substances must be electrically neutral, the total number of positive charges on the cations of an ionic compound must equal the total number of negative charges on its anions. The formula of an ionic compound represents the simplest ratio of the numbers of ions necessary to give identical numbers of positive and negative charges. For example, the formula for aluminum oxide, Al_2O_3, indicates that this ionic compound contains two aluminum cations, Al^{3+}, for every three oxide anions, O^{2-} [thus, (2 × +3) + (3 × –2) = 0].

It is important to note, however, that the formula for an ionic compound does *not* represent the physical arrangement of its ions. It is incorrect to refer to a sodium chloride (NaCl) "molecule" because there is not a single ionic bond, per se, between any specific pair of sodium and chloride ions. The attractive forces between ions are isotropic—the same in all directions—meaning that any particular ion is equally attracted to all of the nearby ions of opposite charge. This results in the ions arranging themselves into a tightly bound, three-dimensional lattice structure. Sodium chloride, for example, consists of a regular arrangement of equal numbers of Na^+ cations and Cl^- anions (Figure Figure 3.2.2).

Two diagrams are shown and labeled "a" and "b." Diagram a shows a cube made up of twenty-seven alternating purple and green spheres. The purple spheres are smaller than the green spheres. Diagram b shows the same spheres, but this time, they are spread out and connected in three dimensions by white rods. The purple spheres are labeled "N superscript postive sign" while the green are labeled "C l superscript negative sign."

Figure 3.2.2: The atoms in sodium chloride (common table salt) are arranged to (a) maximize opposite charges interacting. The smaller spheres represent sodium ions, the larger ones represent chloride ions. In the expanded view (b), the geometry can be seen more clearly. Note that each ion is "bonded" to all of the surrounding ions—six in this case.

The strong electrostatic attraction between Na^+ and Cl^- ions holds them tightly together in solid NaCl. It requires 769 kJ of energy to dissociate one mole of solid NaCl into separate gaseous Na^+ and Cl^- ions:

$$\mathrm{NaCl}(s) \longrightarrow \mathrm{Na}^+(g) + \mathrm{Cl}^-(g) \quad \Delta H = 769\ \mathrm{kJ} \tag{3.2.1}$$

Electronic Structures of Cations

When forming a cation, an atom of a main group element tends to lose all of its valence electrons, thus assuming the electronic structure of the noble gas that precedes it in the periodic table. For groups 1 (the alkali metals) and 2 (the alkaline earth metals), the group numbers are equal to the numbers of valence shell electrons and, consequently, to the charges of the cations formed from atoms of these elements when all valence shell electrons are removed. For example, calcium is a group 2 element whose neutral atoms have 20 electrons and a ground state electron configuration of $1s^22s^22p^63s^23p^64s^2$. When a Ca atom loses both of its valence electrons, the result is a cation with 18 electrons, a 2+ charge, and an electron configuration of $1s^22s^22p^63s^23p^6$. The Ca^{2+} ion is therefore isoelectronic with the noble gas Ar.

For groups 12–17, the group numbers exceed the number of valence electrons by 10 (accounting for the possibility of full *d* subshells in atoms of elements in the fourth and greater periods). Thus, the charge of a cation formed by the loss of all valence electrons is equal to the group number minus 10. For example, aluminum (in group 13) forms 3+ ions (Al^{3+}).

Exceptions to the expected behavior involve elements toward the bottom of the groups. In addition to the expected ions Tl^{3+}, Sn^{4+}, Pb^{4+}, and Bi^{5+}, a partial loss of these atoms' valence shell electrons can also lead to the formation of Tl^+, Sn^{2+}, Pb^{2+}, and Bi^{3+} ions. The formation of these 1+, 2+, and 3+ cations is ascribed to the inert pair effect, which reflects the relatively low energy of the valence *s*-electron pair for atoms of the heavy elements of groups 13, 14, and 15. Mercury (group 12) also exhibits an unexpected behavior: it forms a diatomic ion, $\mathrm{Hg_2}^{2+}$ (an ion formed from two mercury atoms, with an Hg-Hg bond), in addition to the expected monatomic ion Hg^{2+} (formed from only one mercury atom).

Transition and inner transition metal elements behave differently than main group elements. Most transition metal cations have 2+ or 3+ charges that result from the loss of their outermost *s* electron(s) first, sometimes followed by the loss of one or two *d* electrons from the next-to-outermost shell. For example, iron ($1s^22s^22p^63s^23p^63d^64s^2$) forms the ion Fe^{2+} ($1s^22s^22p^63s^23p^63d^6$) by the loss of the 4*s* electrons and the ion Fe^{3+} ($1s^22s^22p^63s^23p^63d^5$) by the loss of the 4*s* electrons and one of the 3*d* electrons. Although the *d* orbitals of the transition elements are—according to the Aufbau principle—the last to fill when building up electron configurations, the outermost *s* electrons are the first to be lost when these atoms ionize. When the inner transition metals form ions, they usually have a 3+ charge, resulting from the loss of their outermost *s* electrons and a *d* or *f* electron.

Example 3.2.1: Determining the Electronic Structures of Cations

There are at least 14 elements categorized as “essential trace elements” for the human body. They are called “essential” because they are required for healthy bodily functions, “trace” because they are required only in small amounts, and “elements” in spite of the fact that they are really ions. Two of these essential trace elements, chromium and zinc, are required as Cr^{3+} and Zn^{2+}. Write the electron configurations of these cations.

Solution

First, write the electron configuration for the neutral atoms:

- Zn: $[Ar]3d^{10}4s^2$
- Cr: $[Ar]3d^5 4s^1$

Next, remove electrons from the highest energy orbital. For the transition metals, electrons are removed from the *s* orbital first and then from the *d* orbital. For the *p*-block elements, electrons are removed from the *p* orbitals and then from the *s* orbital. Zinc is a member of group 12, so it should have a charge of 2+, and thus loses only the two electrons in its *s* orbital. Chromium is a transition element and should lose its *s* electrons and then its *d* electrons when forming a cation. Thus, we find the following electron configurations of the ions:

- Zn^{2+}: $[Ar]3d^{10}$
- Cr^{3+}: $[Ar]3d^3$

Exercise 3.2.1

Potassium and magnesium are required in our diet. Write the electron configurations of the ions expected from these elements.

Answer

K^+: [Ar], Mg^{2+}: [Ne]

Electronic Structures of Anions

Most monatomic anions form when a neutral nonmetal atom gains enough electrons to completely fill its outer *s* and *p* orbitals, thereby reaching the electron configuration of the next noble gas. Thus, it is simple to determine the charge on such a negative ion: The charge is equal to the number of electrons that must be gained to fill the *s* and *p* orbitals of the parent atom. Oxygen, for example, has the electron configuration $1s^2 2s^2 2p^4$, whereas the oxygen anion has the electron configuration of the noble gas neon (Ne), $1s^2 2s^2 2p^6$. The two additional electrons required to fill the valence orbitals give the oxide ion the charge of 2– (O^{2-}).

Example 3.2.2: Determining the Electronic Structure of Anions

Selenium and iodine are two essential trace elements that form anions. Write the electron configurations of the anions.

Solution

Se^{2-}: $[Ar]3d^{10}4s^2 4p^6$

I^-: $[Kr]4d^{10}5s^2 5p^6$

Exercise 3.2.2

Write the electron configurations of a phosphorus atom and its negative ion. Give the charge on the anion.

Answer

P: $[Ne]3s^2 3p^3$

P^{3-}: $[Ne]3s^2 3p^6$

Summary

Atoms gain or lose electrons to form ions with particularly stable electron configurations. The charges of cations formed by the representative metals may be determined readily because, with few exceptions, the electronic structures of these ions have either a noble gas configuration or a completely filled electron shell. The charges of anions formed by the nonmetals may also be readily determined because these ions form when nonmetal atoms gain enough electrons to fill their valence shells.

Glossary

inert pair effect
tendency of heavy atoms to form ions in which their valence s electrons are not lost

ionic bond
strong electrostatic force of attraction between cations and anions in an ionic compound

Contributors

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3.3: Covalent Bonding

Learning Objectives

- Define electronegativity.
- Determine the type of bond which exists between two atoms based on the provided electronegativity values.

In ionic compounds, electrons are transferred between atoms of different elements to form ions. But this is not the only way that compounds can be formed. Atoms can also make chemical bonds by sharing electrons between each other. Such bonds are called covalent bonds. Covalent bonds are formed between two atoms when both have similar tendencies to attract electrons to themselves (i.e., when both atoms have identical or fairly similar ionization energies and electron affinities). For example, two hydrogen atoms bond covalently to form an H_2 molecule; each hydrogen atom in the H_2 molecule has two electrons stabilizing it, giving each atom the same number of valence electrons as the noble gas He.

Compounds that contain covalent bonds exhibit different physical properties than ionic compounds. Because the attraction between molecules, which are electrically neutral, is weaker than that between electrically charged ions, covalent compounds generally have much lower melting and boiling points than ionic compounds. In fact, many covalent compounds are liquids or gases at room temperature, and, in their solid states, they are typically much softer than ionic solids. Furthermore, whereas ionic compounds are good conductors of electricity when dissolved in water, most covalent compounds, being electrically neutral, are poor conductors of electricity in any state.

Formation of Covalent Bonds

Nonmetal atoms frequently form covalent bonds with other nonmetal atoms. For example, the hydrogen molecule, H_2, contains a covalent bond between its two hydrogen atoms. Figure 3.3.1 illustrates why this bond is formed. Starting on the far right, we have two separate hydrogen atoms with a particular potential energy, indicated by the red line. Along the *x*-axis is the distance between the two atoms. As the two atoms approach each other (moving left along the *x*-axis), their valence orbitals (1s) begin to overlap. The single electrons on each hydrogen atom then interact with both atomic nuclei, occupying the space around both atoms. The strong attraction of each shared electron to both nuclei stabilizes the system, and the potential energy decreases as the bond distance decreases. If the atoms continue to approach each other, the positive charges in the two nuclei begin to repel each other, and the potential energy increases. The bond length is determined by the distance at which the lowest potential energy is achieved.

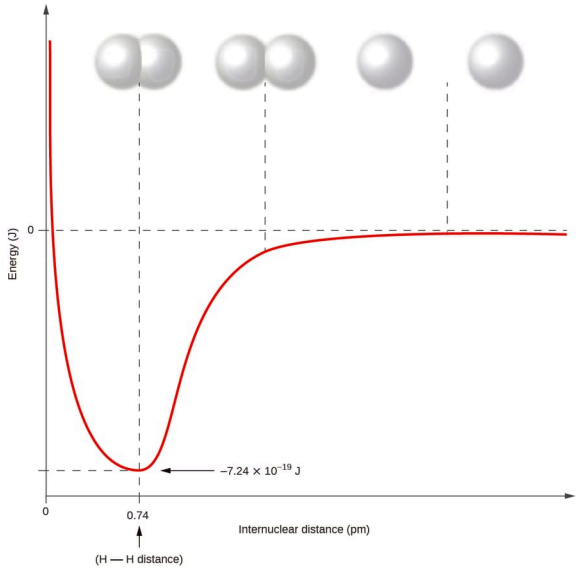


Figure 3.3.1: *The potential energy of two separate hydrogen atoms (right) decreases as they approach each other, and the single electrons on each atom are shared to form a covalent bond. The bond length is the internuclear distance at which the lowest potential energy is achieved.*

It is essential to remember that energy must be added to break chemical bonds (an endothermic process), whereas forming chemical bonds releases energy (an exothermic process). In the case of H_2, the covalent bond is very strong; a large amount of energy, 436 kJ, must be added to break the bonds in one mole of hydrogen molecules and cause the atoms to separate:

$$\mathrm{H_2}(g) \longrightarrow 2\,\mathrm{H}(g) \quad \Delta H = 436\ \mathrm{kJ} \tag{3.3.1}$$

Conversely, the same amount of energy is released when one mole of H_2 molecules forms from two moles of H atoms:

$$2\,\mathrm{H}(g) \longrightarrow \mathrm{H_2}(g) \quad \Delta H = -436\ \mathrm{kJ} \tag{3.3.2}$$

Nonpolar (pure) covalent vs. Polar Covalent Bonds

If the atoms that form a covalent bond are identical, as in H_2, Cl_2, and other diatomic molecules, then the electrons in the bond must be shared equally. We refer to this as a nonpolar covalent bond. Electrons shared in nonpolar covalent bonds have an equal probability of being near each nucleus. In the case of Cl_2, each atom starts off with seven valence electrons, and each Cl shares one electron with the other, forming one covalent bond:

$$\mathrm{Cl} + \mathrm{Cl} \longrightarrow \mathrm{Cl_2} \tag{3.3.3}$$

The total number of electrons around each individual atom consists of six nonbonding electrons and two shared (i.e., bonding) electrons for eight total electrons, matching the number of valence electrons in the noble gas argon. Since the bonding atoms are identical, Cl_2 also features a pure covalent bond.

When the atoms linked by a covalent bond are different, the bonding electrons are shared, but no longer equally. Instead, the bonding electrons are more attracted to one atom than the other, giving rise to a shift of electron density toward that atom. This unequal distribution of electrons is known as a polar covalent bond, characterized by a partial positive charge on one atom and a partial negative charge on the other. The atom that attracts the electrons more strongly acquires the partial negative charge and vice versa. For example, the electrons in the H–Cl bond of a hydrogen chloride molecule spend more time near the chlorine atom than near the hydrogen atom. Thus, in an HCl molecule, the chlorine atom carries a partial negative charge and the hydrogen atom has a partial positive charge. Figure 3.3.2 shows the distribution of electrons in the H–Cl bond. Note that the shaded area around Cl is much larger than it is around H. Compare this to Figure 3.3.1, which shows the even distribution of electrons in the H_2 nonpolar bond.

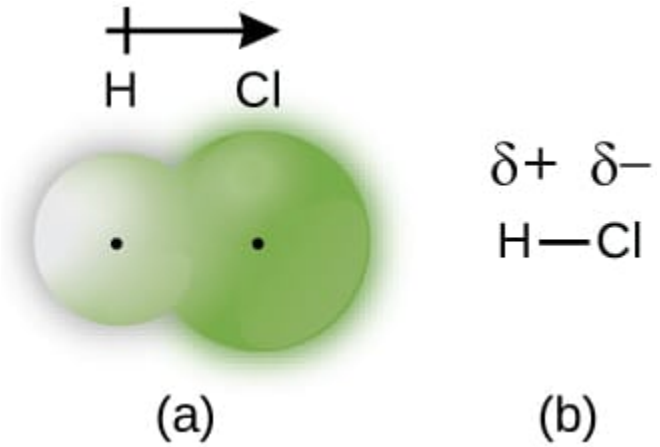


Figure 3.3.2: (a) The distribution of electron density in the HCl molecule is uneven. The electron density is greater around the chlorine nucleus. The small, black dots indicate the location of the hydrogen and chlorine nuclei in the molecule. (b) Symbols δ+ and δ– indicate the polarity of the H–Cl bond.

We sometimes designate the positive and negative atoms in a polar covalent bond using a lowercase Greek letter “delta,” δ, with a plus sign or minus sign to indicate whether the atom has a partial positive charge (δ+) or a partial negative charge (δ–). This symbolism is shown for the H–Cl molecule in Figure 3.3.2*b*.

Electronegativity

Whether a bond is nonpolar or polar covalent is determined by a property of the bonding atoms called electronegativity. Electronegativity is a measure of the tendency of an atom to attract electrons (or electron density) towards itself. It determines how the shared electrons are distributed between the two atoms in a bond. The more strongly an atom attracts the electrons in its bonds, the larger its electronegativity. Electrons in a polar covalent bond are shifted toward the more electronegative atom; thus, the more electronegative atom is the one with the partial negative charge. The greater the difference in electronegativity, the more polarized the electron distribution and the larger the partial charges of the atoms.

Figure 3.3.3 shows the electronegativity values of the elements as proposed by one of the most famous chemists of the twentieth century: Linus Pauling. In general, electronegativity increases from left to right across a period in the periodic table and decreases down a group. Thus, the nonmetals, which lie in the upper right, tend to have the highest electronegativities, with fluorine the most electronegative element of all (EN = 4.0). Metals tend to be less electronegative elements, and the group 1 metals have the lowest electronegativities. Note that noble gases are excluded from this figure because these atoms usually do not share electrons with others atoms since they have a full valence shell. (While noble gas compounds such as XeO_2 do exist, they can only be formed under extreme conditions, and thus they do not fit neatly into the general model of electronegativity.)

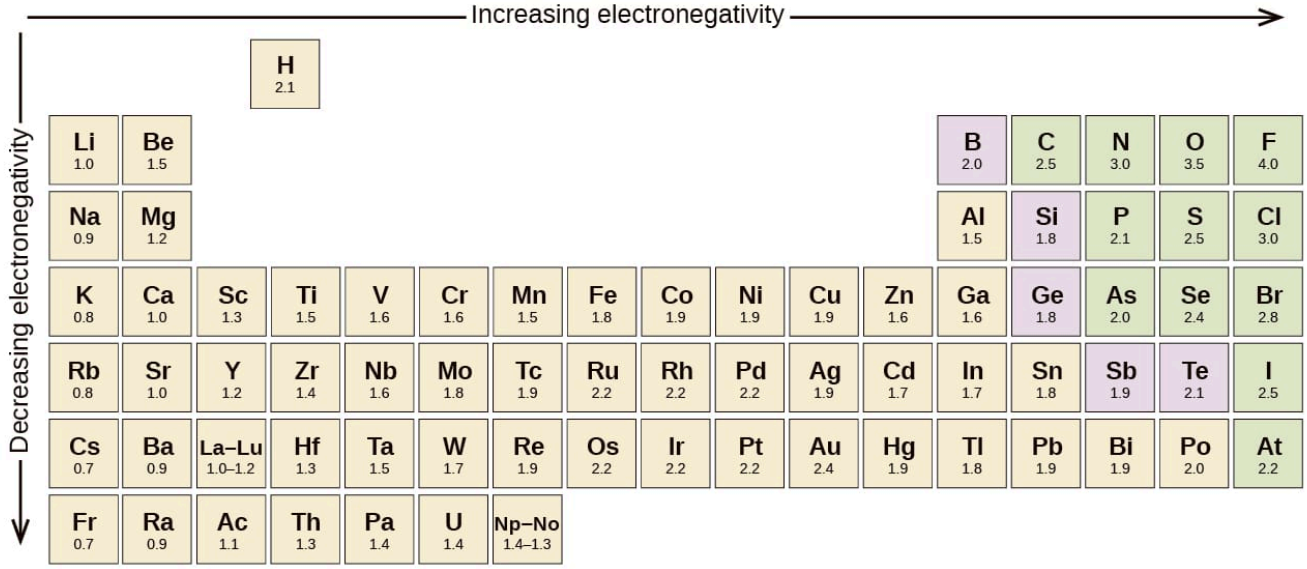
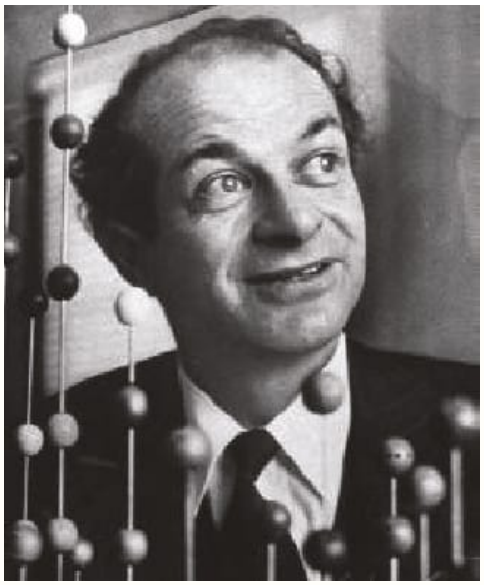


Figure 3.3.3: The electronegativity values derived by Pauling follow predictable periodic trends with the higher electronegativities toward the upper right of the periodic table.

Linus Pauling

Linus Pauling is the only person to have received two unshared (individual) Nobel Prizes: one for chemistry in 1954 for his work on the nature of chemical bonds and one for peace in 1962 for his opposition to weapons of mass destruction. He developed many of the theories and concepts that are foundational to our current understanding of chemistry, including electronegativity and resonance structures.



Linus Pauling (1901–1994) made many important contributions to the field of chemistry. He was also a prominent activist, publicizing issues related to health and nuclear weapons.

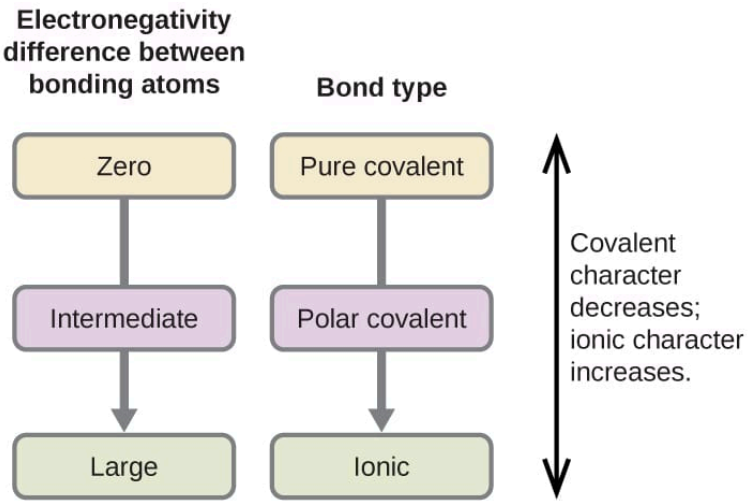
Pauling also contributed to many other fields besides chemistry. His research on sickle cell anemia revealed the cause of the disease—the presence of a genetically inherited abnormal protein in the blood—and paved the way for the field of molecular genetics. His work was also pivotal in curbing the testing of nuclear weapons; he proved that radioactive fallout from nuclear testing posed a public health risk.

Electronegativity versus Electron Affinity

We must be careful not to confuse electronegativity and electron affinity. The electron affinity of an element is a measurable physical quantity, namely, the energy released or absorbed when an isolated gas-phase atom acquires an electron, measured in kJ/mol. Electronegativity, on the other hand, describes how tightly an atom attracts electrons in a bond. It is a dimensionless quantity that is calculated, not measured. Pauling derived the first electronegativity values by comparing the amounts of energy required to break different types of bonds. He chose an arbitrary relative scale ranging from 0 to 4.

Electronegativity and Bond Type

The absolute value of the difference in electronegativity (ΔEN) of two bonded atoms provides a rough measure of the polarity to be expected in the bond and, thus, the bond type. When the difference is very small or zero, the bond is covalent and nonpolar. When it is large, the bond is polar covalent or ionic. The absolute values of the electronegativity differences between the atoms in the bonds H–H, H–Cl, and Na–Cl are 0 (nonpolar), 0.9 (polar covalent), and 2.1 (ionic), respectively. The degree to which electrons are shared between atoms varies from completely equal (pure covalent bonding) to not at all (ionic bonding). Figure 3.3.4 shows the relationship between electronegativity difference and bond type.



Bond Type	Electronegativity Difference
pure covalent	< 0.4
polar covalent	between 0.4 and 1.8
ionic	> 1.8

Figure 3.3.4: As the electronegativity difference increases between two atoms, the bond becomes more ionic.

A rough approximation of the electronegativity differences associated with covalent, polar covalent, and ionic bonds is shown in Figure 3.3.4. This table is just a general guide, however, with many exceptions. For example, the H and F atoms in HF have an electronegativity difference of 1.9, and the N and H atoms in NH_3 a difference of 0.9, yet both of these compounds form bonds that are considered polar covalent. Likewise, the Na and Cl atoms in NaCl have an electronegativity difference of 2.1, and the Mn and I atoms in MnI_2 have a difference of 1.0, yet both of these substances form ionic compounds.

The best guide to the covalent or ionic character of a bond is to consider the types of atoms involved and their relative positions in the periodic table. Bonds between two nonmetals are generally covalent; bonding between a metal and a nonmetal is often ionic.

Some compounds contain both covalent and ionic bonds. The atoms in polyatomic ions, such as OH^-, NO_3^-, and NH_4^+, are held together by polar covalent bonds. However, these polyatomic ions form ionic compounds by combining with ions of opposite charge. For example, potassium nitrate, KNO_3, contains the K^+ cation and the polyatomic NO_3^- anion. Thus, bonding in potassium nitrate is ionic, resulting from the electrostatic attraction between the ions K^+ and NO_3^-, as well as covalent between the nitrogen and oxygen atoms in NO_3^-.

Example 3.3.1: Electronegativity and Bond Polarity

Bond polarities play an important role in determining the structure of proteins. Using the electronegativity values in Table A2, arrange the following covalent bonds—all commonly found in amino acids—in order of increasing polarity. Then designate the positive and negative atoms using the symbols δ+ and δ–:

C–H, C–N, C–O, N–H, O–H, S–H

Solution

The polarity of these bonds increases as the absolute value of the electronegativity difference increases. The atom with the δ– designation is the more electronegative of the two. Table 3.3.1 shows these bonds in order of increasing polarity.

Table* 3.3.1*: Bond Polarity and Electronegativity Difference

Bond	ΔEN	Polarity
C–H	0.4	$\overset{\delta-}{\mathrm{C}}-\overset{\delta+}{\mathrm{H}}$
S–H	0.4	$\overset{\delta-}{\mathrm{S}}-\overset{\delta+}{\mathrm{H}}$
C–N	0.5	$\overset{\delta+}{\mathrm{C}}-\overset{\delta-}{\mathrm{N}}$

Bond	ΔEN	Polarity
N–H	0.9	$\overset{\delta-}{\mathrm{N}}-\overset{\delta+}{\mathrm{H}}$
C–O	1.0	$\overset{\delta+}{\mathrm{C}}-\overset{\delta-}{\mathrm{O}}$
O–H	1.4	$\overset{\delta-}{\mathrm{O}}-\overset{\delta+}{\mathrm{H}}$

Exercise 3.3.1

Silicones are polymeric compounds containing, among others, the following types of covalent bonds: Si–O, Si–C, C–H, and C–C. Using the electronegativity values in Figure 3.3.3, arrange the bonds in order of increasing polarity and designate the positive and negative atoms using the symbols δ+ and δ–.

Answer

Bond	Electronegativity Difference	Polarity
C–C	0.0	nonpolar
C–H	0.4	$\overset{\delta-}{\mathrm{C}}-\overset{\delta+}{\mathrm{H}}$
Si–C	0.7	$\overset{\delta+}{\mathrm{Si}}-\overset{\delta-}{\mathrm{C}}$
Si–O	1.7	$\overset{\delta+}{\mathrm{Si}}-\overset{\delta-}{\mathrm{O}}$

Summary

Covalent bonds form when electrons are shared between atoms and are attracted by the nuclei of both atoms. In pure covalent bonds, the electrons are shared equally. In polar covalent bonds, the electrons are shared unequally, as one atom exerts a stronger force of attraction on the electrons than the other. The ability of an atom to attract a pair of electrons in a chemical bond is called its electronegativity. The difference in electronegativity between two atoms determines how polar a bond will be. In a diatomic molecule with two identical atoms, there is no difference in electronegativity, so the bond is nonpolar or pure covalent. When the electronegativity difference is very large, as is the case between metals and nonmetals, the bonding is characterized as ionic.

Glossary

bond length
: distance between the nuclei of two bonded atoms at which the lowest potential energy is achieved

covalent bond
: bond formed when electrons are shared between atoms

electronegativity
: tendency of an atom to attract electrons in a bond to itself

polar covalent bond
: covalent bond between atoms of different electronegativities; a covalent bond with a positive end and a negative end

pure covalent bond
: (also, nonpolar covalent bond) covalent bond between atoms of identical electronegativities

Contributors

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3.4: Chemical Formulas

Learning Objectives

- Write the correct formula for an ionic molecule.

A molecular formula is a representation of a molecule that uses chemical symbols to indicate the types of atoms followed by subscripts to show the number of atoms of each type in the molecule. (A subscript is used only when more than one atom of a given type is present.) Molecular formulas are also used as abbreviations for the names of compounds.

The structural formula for a compound gives the same information as its molecular formula (the types and numbers of atoms in the molecule) but also shows how the atoms are connected in the molecule. The structural formula for methane contains symbols for one C atom and four H atoms, indicating the number of atoms in the molecule (Figure 3.4.1). The lines represent bonds that hold the atoms together. (A chemical bond is an attraction between atoms or ions that holds them together in a molecule or a crystal.) We will discuss chemical bonds and see how to predict the arrangement of atoms in a molecule later. For now, simply know that the lines are an indication of how the atoms are connected in a molecule. A ball-and-stick model shows the geometric arrangement of the atoms with atomic sizes not to scale, and a space-filling model shows the relative sizes of the atoms.

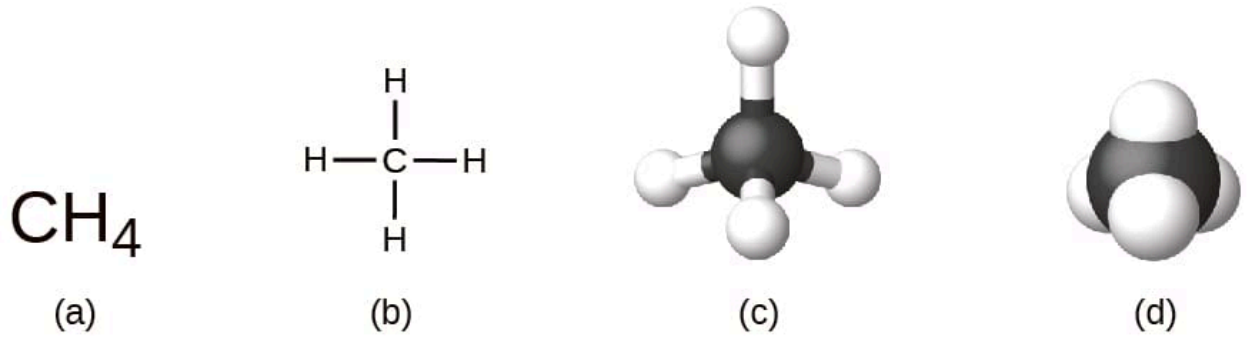


Figure 3.4.1: A methane molecule can be represented as (a) a molecular formula, (b) a structural formula, (c) a ball-and-stick model, and (d) a space-filling model. Carbon and hydrogen atoms are represented by black and white spheres, respectively.

Although many elements consist of discrete, individual atoms, some exist as molecules made up of two or more atoms of the element chemically bonded together. For example, most samples of the elements hydrogen, oxygen, and nitrogen are composed of molecules that contain two atoms each (called diatomic molecules) and thus have the molecular formulas H_2, O_2, and N_2, respectively. Other elements commonly found as diatomic molecules are fluorine (F_2), chlorine (Cl_2), bromine (Br_2), and iodine (I_2). The most common form of the element sulfur is composed of molecules that consist of eight atoms of sulfur; its molecular formula is S_8 (Figure 3.4.2).

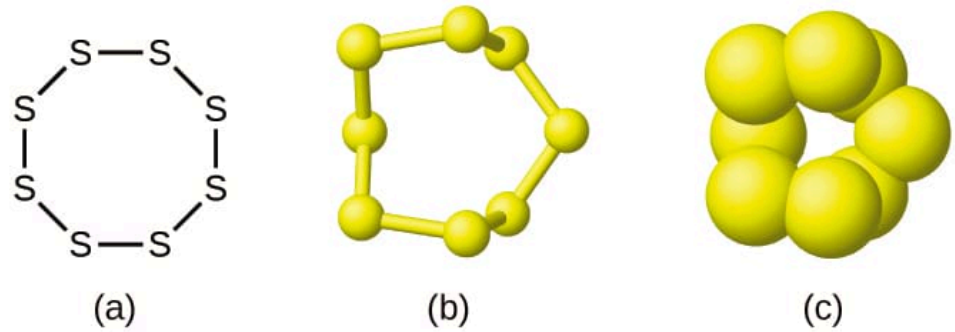


Figure 3.4.2: A molecule of sulfur is composed of eight sulfur atoms and is therefore written as S_8. It can be represented as (a) a structural formula, (b) a ball-and-stick model, and (c) a space-filling model. Sulfur atoms are represented by yellow spheres.

It is important to note that a subscript following a symbol and a number in front of a symbol do not represent the same thing;

for example, H_2 and 2H represent distinctly different species. H_2 is a molecular formula; it represents a diatomic molecule of hydrogen, consisting of two atoms of the element that are chemically bonded together. The expression 2H, on the other hand, indicates two separate hydrogen atoms that are not combined as a unit. The expression $2H_2$ represents two molecules of diatomic hydrogen (Figure 3.4.3).

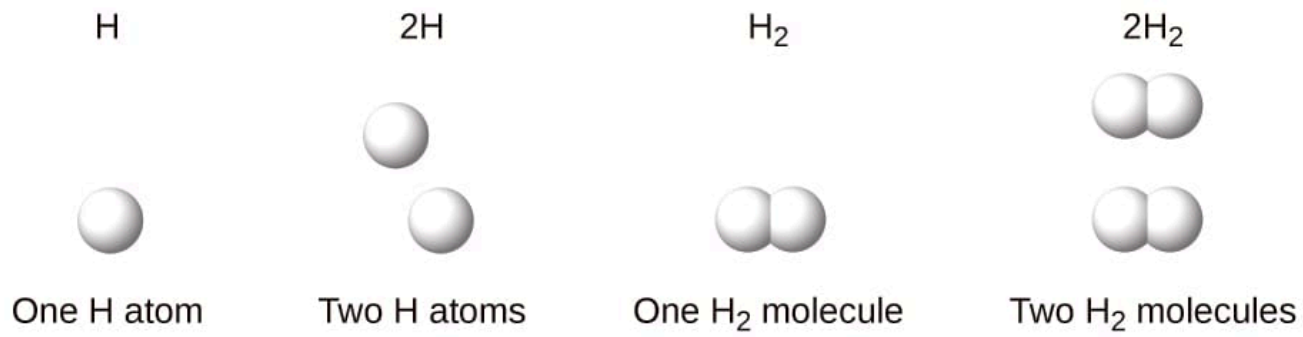


Figure 3.4.3: The symbols H, 2H, H_2, and $2H_2$ represent very different entities.

Compounds are formed when two or more elements chemically combine, resulting in the formation of bonds. For example, hydrogen and oxygen can react to form water, and sodium and chlorine can react to form table salt. We sometimes describe the composition of these compounds with an empirical formula, which indicates the types of atoms present and *the simplest whole-number ratio of the number of atoms (or ions) in the compound*. For example, titanium dioxide (used as pigment in white paint and in the thick, white, blocking type of sunscreen) has an empirical formula of TiO_2. This identifies the elements titanium (Ti) and oxygen (O) as the constituents of titanium dioxide, and indicates the presence of twice as many atoms of the element oxygen as atoms of the element titanium (Figure 3.4.4).

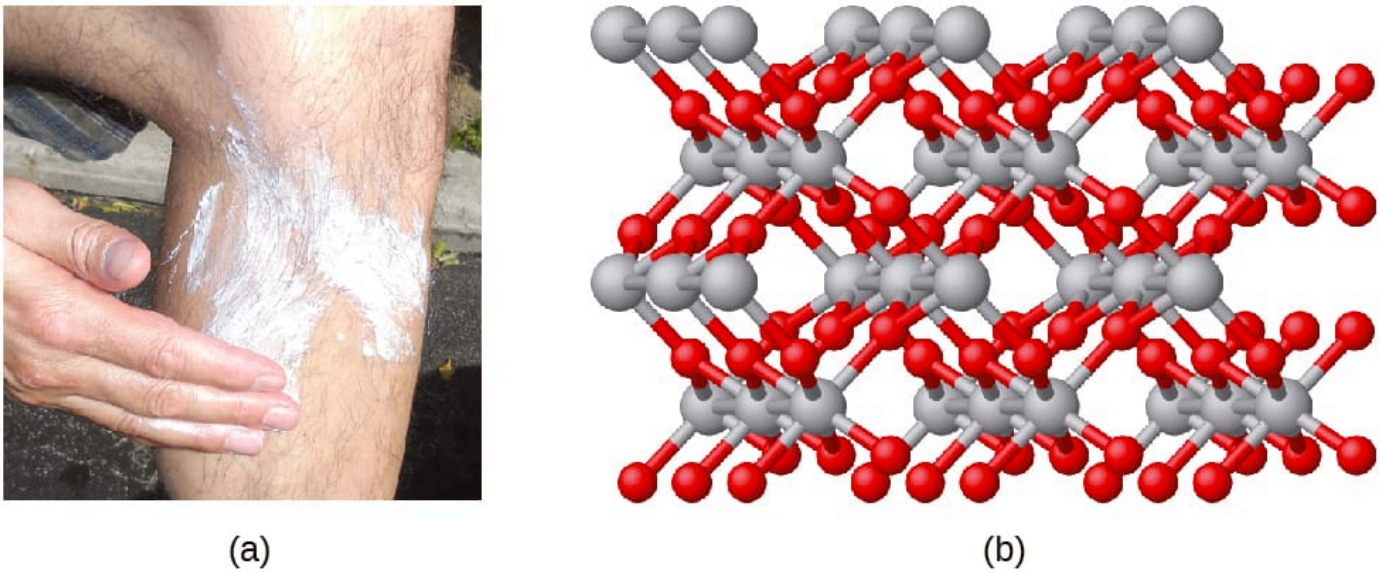


Figure 3.4.4: (a) The white compound titanium dioxide provides effective protection from the sun. (b) A crystal of titanium dioxide, TiO_2, contains titanium and oxygen in a ratio of 1 to 2. The titanium atoms are gray and the oxygen atoms are red. (credit a: modification of work by "osseous"/Flickr).

As discussed previously, we can describe a compound with a molecular formula, in which the subscripts indicate the *actual numbers of atoms* of each element in a molecule of the compound. In many cases, the molecular formula of a substance is derived from experimental determination of both its empirical formula and its molecular mass (the sum of atomic masses for all atoms composing the molecule). For example, it can be determined experimentally that benzene contains two elements, carbon (C) and hydrogen (H), and that for every carbon atom in benzene, there is one hydrogen atom. Thus, the empirical formula is CH. An experimental determination of the molecular mass reveals that a molecule of benzene contains six carbon atoms and six hydrogen atoms, so the molecular formula for benzene is C_6H_6 (Figure 3.4.5).

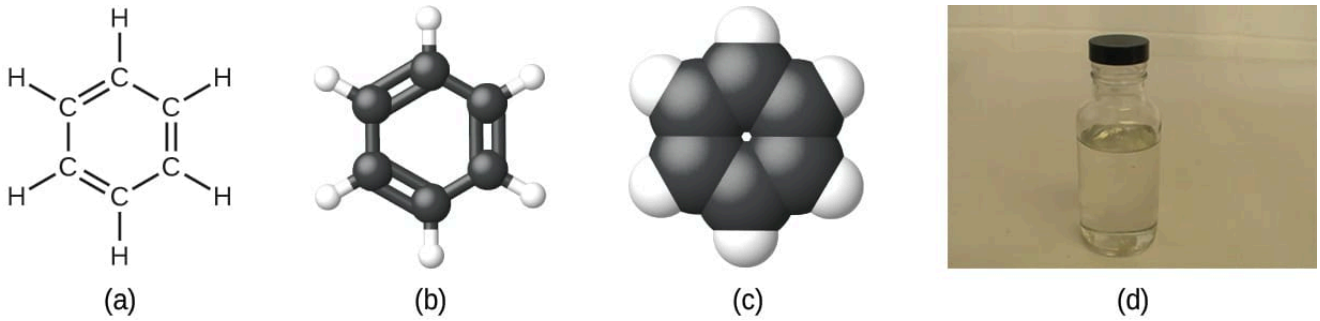


Figure 3.4.5: Benzene, C_6H_6, is produced during oil refining and has many industrial uses. A benzene molecule can be represented as (a) a structural formula, (b) a ball-and-stick model, and (c) a space-filling model. (d) Benzene is a clear liquid. (credit d: modification of work by Sahar Atwa).

If we know a compound's formula, we can easily determine the empirical formula. (This is somewhat of an academic exercise; the reverse chronology is generally followed in actual practice.) For example, the molecular formula for acetic acid, the component that gives vinegar its sharp taste, is $C_2H_4O_2$. This formula indicates that a molecule of acetic acid (Figure 3.4.6) contains two carbon atoms, four hydrogen atoms, and two oxygen atoms. The ratio of atoms is 2:4:2. Dividing by the lowest common denominator (2) gives the simplest, whole-number ratio of atoms, 1:2:1, so the empirical formula is CH_2O. Note that a molecular formula is always a whole-number multiple of an empirical formula.

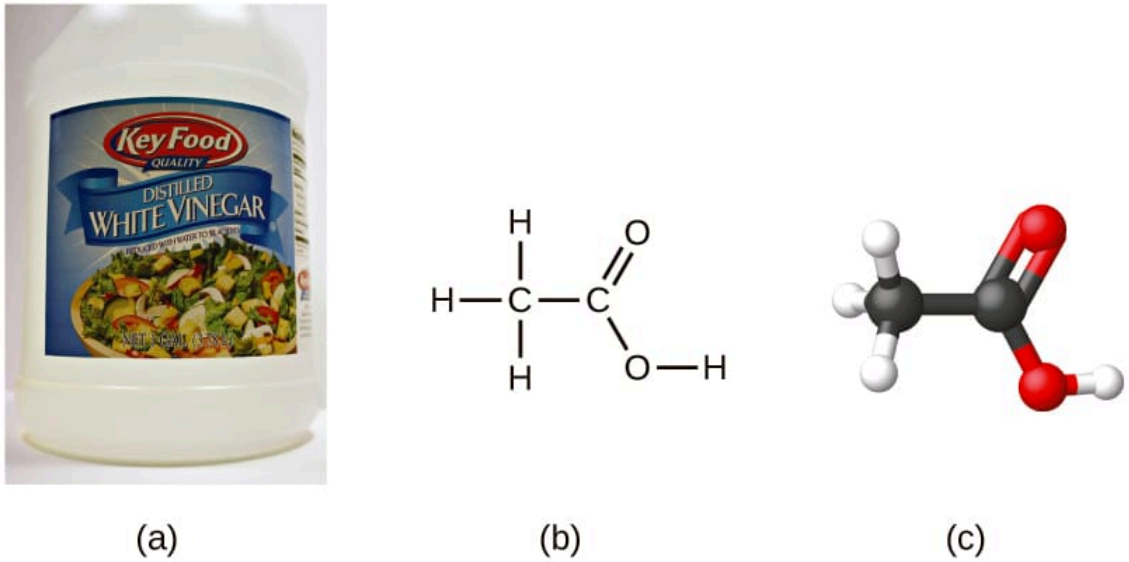


Figure 3.4.6: (a) Vinegar contains acetic acid, $C_2H_4O_2$, which has an empirical formula of CH_2O. It can be represented as (b) a structural formula and (c) as a ball-and-stick model. (credit a: modification of work by "HomeSpot HQ"/Flickr)

Example 3.4.1: Empirical and Molecular Formulas

Molecules of glucose (blood sugar) contain 6 carbon atoms, 12 hydrogen atoms, and 6 oxygen atoms. What are the molecular and empirical formulas of glucose?

Solution

The molecular formula is $C_6H_{12}O_6$ because one molecule actually contains 6 C, 12 H, and 6 O atoms. The simplest whole-number ratio of C to H to O atoms in glucose is 1:2:1, so the empirical formula is CH_2O.

Exercise 3.4.1

A molecule of metaldehyde (a pesticide used for snails and slugs) contains 8 carbon atoms, 16 hydrogen atoms, and 4 oxygen

atoms. What are the molecular and empirical formulas of metaldehyde?

Answer

Molecular formula, $C_8H_{16}O_4$; empirical formula, C_2H_4O

It is important to be aware that it may be possible for the same atoms to be arranged in different ways: Compounds with the same molecular formula may have different atom-to-atom bonding and therefore different structures. For example, could there be another compound with the same formula as acetic acid, $C_2H_4O_2$? And if so, what would be the structure of its molecules?

If you predict that another compound with the formula $C_2H_4O_2$ could exist, then you demonstrated good chemical insight and are correct. Two C atoms, four H atoms, and two O atoms can also be arranged to form methyl formate, which is used in manufacturing, as an insecticide, and for quick-drying finishes. Methyl formate molecules have one of the oxygen atoms between the two carbon atoms, differing from the arrangement in acetic acid molecules. Acetic acid and methyl formate are examples of isomers—compounds with the same chemical formula but different molecular structures (Figure 3.4.7). Note that this small difference in the arrangement of the atoms has a major effect on their respective chemical properties. You would certainly not want to use a solution of methyl formate as a substitute for a solution of acetic acid (vinegar) when you make salad dressing.

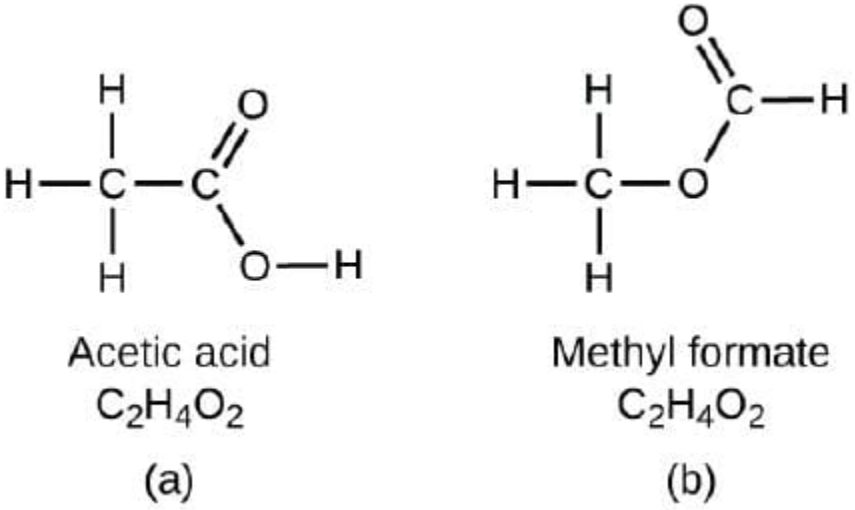


Figure 3.4.7: Molecules of (a) acetic acid and methyl formate (b) are structural isomers; they have the same formula ($C_2H_4O_2$) but different structures (and therefore different chemical properties).

Many types of isomers exist (Figure 3.4.8). Acetic acid and methyl formate are structural isomers, compounds in which the molecules differ in how the atoms are connected to each other. There are also various types of spatial isomers, in which the relative orientations of the atoms in space can be different. For example, the compound carvone (found in caraway seeds, spearmint, and mandarin orange peels) consists of two isomers that are mirror images of each other. S-(+)-carvone smells like caraway, and *R*-(−)-carvone smells like spearmint.

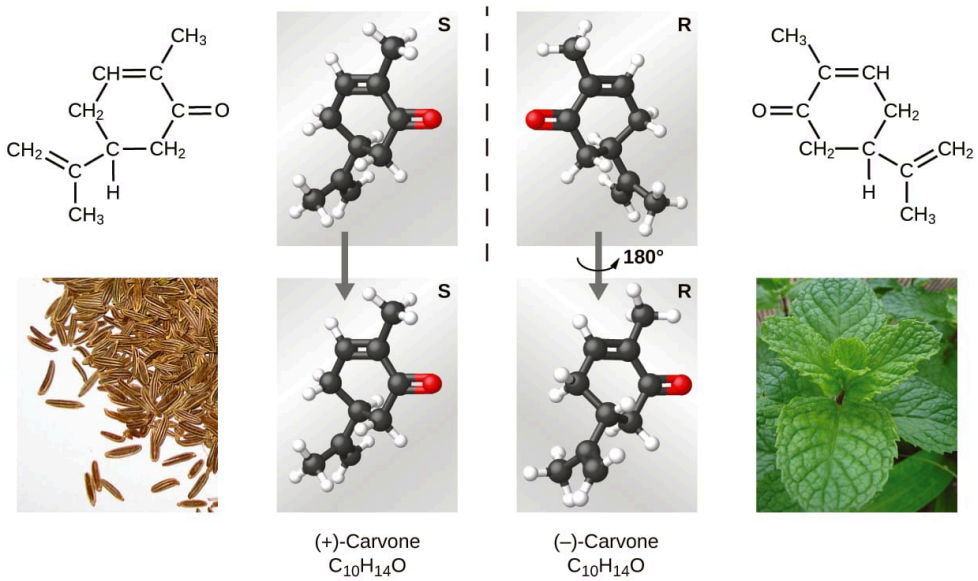


Figure 3.4.8: Molecules of carvone are spatial isomers; they only differ in the relative orientations of the atoms in space. (credit bottom left: modification of work by "Miansari66"/Wikimedia Commons; credit bottom right: modification of work by Forest & Kim Starr)

Summary

A molecular formula uses chemical symbols and subscripts to indicate the exact numbers of different atoms in a molecule or compound. An empirical formula gives the simplest, whole-number ratio of atoms in a compound. A structural formula indicates the bonding arrangement of the atoms in the molecule. Ball-and-stick and space-filling models show the geometric arrangement of atoms in a molecule. Isomers are compounds with the same molecular formula but different arrangements of atoms.

Glossary

empirical formula
: formula showing the composition of a compound given as the simplest whole-number ratio of atoms

isomers
: compounds with the same chemical formula but different structures

molecular formula
: formula indicating the composition of a molecule of a compound and giving the actual number of atoms of each element in a molecule of the compound.

spatial isomers
: compounds in which the relative orientations of the atoms in space differ

structural isomer
: one of two substances that have the same molecular formula but different physical and chemical properties because their atoms are bonded differently

structural formula
: shows the atoms in a molecule and how they are connected

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3.5: Chemical Nomenclature

Learning Objectives

- Derive names for common types of inorganic compounds using a systematic approach

Nomenclature, a collection of rules for naming things, is important in science and in many other situations. This module describes an approach that is used to name simple ionic and molecular compounds, such as NaCl, $CaCO_3$, and N_2O_4. The simplest of these are binary compounds, those containing only two elements, but we will also consider how to name ionic compounds containing polyatomic ions, and one specific, very important class of compounds known as acids (subsequent chapters in this text will focus on these compounds in great detail). We will limit our attention here to inorganic compounds, compounds that are composed principally of elements other than carbon, and will follow the nomenclature guidelines proposed by IUPAC. The rules for organic compounds, in which carbon is the principle element, will be treated in a later chapter on organic chemistry.

Ionic Compounds

To name an inorganic compound, we need to consider the answers to several questions. First, is the compound ionic or molecular? If the compound is ionic, does the metal form ions of only one type (fixed charge) or more than one type (variable charge)? Are the ions monatomic or polyatomic? If the compound is molecular, does it contain hydrogen? If so, does it also contain oxygen? From the answers we derive, we place the compound in an appropriate category and then name it accordingly. We will begin with the nomenclature rules for ionic compounds.

Compounds Containing Only Monatomic Ions

The name of a binary compound containing monatomic ions consists of the name of the cation (the name of the metal) followed by the name of the anion (the name of the nonmetallic element with its ending replaced by the suffix *–ide*). Some examples are given in Table 3.5.2.

Table 3.5.1***:*** *Names of Some Ionic Compounds*

NaCl, sodium chloride	Na_2O, sodium oxide
KBr, potassium bromide	CdS, cadmium sulfide
CaI_2, calcium iodide	Mg_3N_2, magnesium nitride
CsF, cesium fluoride	Ca_3P_2, calcium phosphide
LiCl, lithium chloride	Al_4C_3, aluminum carbide

Compounds Containing Polyatomic Ions

Compounds containing polyatomic ions are named similarly to those containing only monatomic ions, except there is no need to change to an *–ide* ending, since the suffix is already present in the name of the anion. Examples are shown in Table 3.5.2.

Table 3.5.2***:*** *Names of Some Polyatomic Ionic Compounds*

$KC_2H_3O_2$, potassium acetate	$(NH_4)Cl$, ammonium chloride
$NaHCO_3$, sodium bicarbonate	$CaSO_4$, calcium sulfate
$Al_2(CO_3)_3$, aluminum carbonate	$Mg_3(PO_4)_2$, magnesium phosphate

Ionic Compounds in Your Cabinets

Every day you encounter and use a large number of ionic compounds. Some of these compounds, where they are found, and what they are used for are listed in Table 3.5.3. Look at the label or ingredients list on the various products that you use during the next few days, and see if you run into any of those in this table, or find other ionic compounds that you could now name or write as a formula.

***Table** 3.5.3**:** Everyday Ionic Compounds*

Ionic Compound	Name	Use
NaCl	sodium chloride	ordinary table salt
KI	potassium iodide	added to “iodized” salt for thyroid health
NaF	sodium fluoride	ingredient in toothpaste
$NaHCO_3$	sodium bicarbonate	baking soda; used in cooking (and in antacids)
Na_2CO_3	sodium carbonate	washing soda; used in cleaning agents
NaOCl	sodium hypochlorite	active ingredient in household bleach
$CaCO_3$	calcium carbonate	ingredient in antacids
$Mg(OH)_2$	magnesium hydroxide	ingredient in antacids
$Al(OH)_3$	aluminum hydroxide	ingredient in antacids
NaOH	sodium hydroxide	lye; used as drain cleaner
K_3PO_4	potassium phosphate	food additive (many purposes)
$MgSO_4$	magnesium sulfate	added to purified water
Na_2HPO_4	sodium hydrogen phosphate	anti-caking agent; used in powdered products
Na_2SO_3	sodium sulfite	preservative

Compounds Containing a Metal Ion with a Variable Charge

Most of the transition metals can form two or more cations with different charges. Compounds of these metals with nonmetals are named with the same method as compounds in the first category, except the charge of the metal ion is specified by a Roman numeral in parentheses after the name of the metal. The charge of the metal ion is determined from the formula of the compound and the charge of the anion. For example, consider binary ionic compounds of iron and chlorine. Iron typically exhibits a charge of either 2+ or 3+, and the two corresponding compound formulas are $FeCl_2$ and $FeCl_3$. The simplest name, “iron chloride,” will, in this case, be ambiguous, as it does not distinguish between these two compounds. In cases like this, the charge of the metal ion is included as a Roman numeral in parentheses immediately following the metal name. These two compounds are then unambiguously named iron(II) chloride and iron(III) chloride, respectively. Other examples are provided in Table 3.5.4.

***Table** 3.5.4**:** Names of Some Transition Metal Ionic Compounds*

Transition Metal Ionic Compound	Name
$FeCl_3$	iron(III) chloride
Hg_2O	mercury(I) oxide
HgO	mercury(II) oxide
$Cu_3(PO_4)_2$	copper(II) phosphate

Out-of-date nomenclature used the suffixes *–ic* and *–ous* to designate metals with higher and lower charges, respectively: Iron(III) chloride, $FeCl_3$, was previously called ferric chloride, and iron(II) chloride, $FeCl_2$, was known as ferrous chloride. Though this naming convention has been largely abandoned by the scientific community, it remains in use by some segments of industry. For example, you may see the words *stannous fluoride* on a tube of toothpaste. This represents the formula SnF_2, which is more properly named tin(II) fluoride. The other fluoride of tin is SnF_4, which was previously called stannic fluoride but is now named tin(IV) fluoride.

Example 3.5.1: Naming Ionic Compounds

Name the following ionic compounds, which contain a metal that can have more than one ionic charge:

a. Fe_2S_3
b. CuSe
c. GaN
d. $CrCl_3$
e. $Ti_2(SO_4)_3$

Solution

The anions in these compounds have a fixed negative charge (S^{2-}, Se^{2-} , N^{3-}, Cl^-, and $SO_4{}^{2-}$), and the compounds must be neutral. Because the total number of positive charges in each compound must equal the total number of negative charges, the positive ions must be Fe^{3+}, Cu^{2+}, Ga^{3+}, Cr^{3+}, and Ti^{3+}. These charges are used in the names of the metal ions:

a. iron(III) sulfide
b. copper(II) selenide
c. gallium(III) nitride
d. chromium(III) chloride
e. titanium(III) sulfate

Exercise 3.5.1

Write the formulas of the following ionic compounds:

a. chromium(III) phosphide
b. mercury(II) sulfide
c. manganese(II) phosphate
d. copper(I) oxide
e. chromium(VI) fluoride

Answer a

CrP

Answer b

HgS

Answer c

$Mn_3(PO_4)_2$

Answer d

Cu_2O

Answer e

CrF_6

Erin Brokovich and Chromium Contamination

In the early 1990s, legal file clerk Erin Brockovich (Figure 3.5.2) discovered a high rate of serious illnesses in the small town of Hinckley, California. Her investigation eventually linked the illnesses to groundwater contaminated by Cr(VI) used by Pacific Gas & Electric (PG&E) to fight corrosion in a nearby natural gas pipeline. As dramatized in the film *Erin Brokovich* (for which Julia Roberts won an Oscar), Erin and lawyer Edward Masry sued PG&E for contaminating the water near Hinckley in 1993. The settlement they won in 1996—$333 million—was the largest amount ever awarded for a direct-action lawsuit in the US at that time.

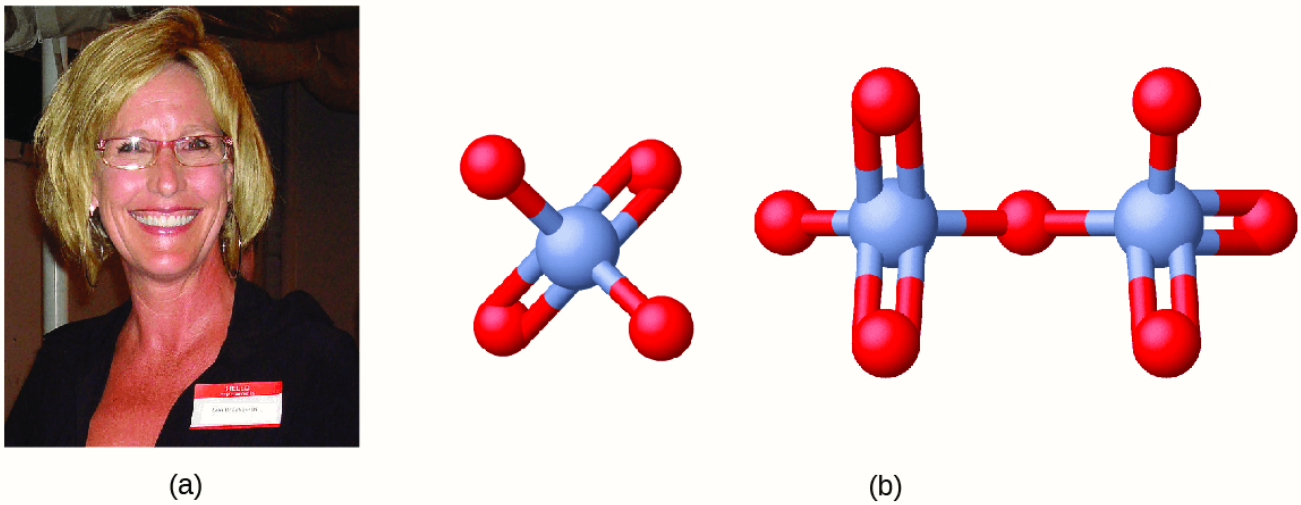


Figure 3.5.2: (a) Erin Brockovich found that Cr(VI), used by PG&E, had contaminated the Hinckley, California, water supply. (b) The Cr(VI) ion is often present in water as the polyatomic ions chromate, CrO_4^{2-} (left), and dichromate, $Cr_2O_7^{2-}$ (right).

Chromium compounds are widely used in industry, such as for chrome plating, in dye-making, as preservatives, and to prevent corrosion in cooling tower water, as occurred near Hinckley. In the environment, chromium exists primarily in either the Cr(III) or Cr(VI) forms. Cr(III), an ingredient of many vitamin and nutritional supplements, forms compounds that are not very soluble in water, and it has low toxicity. Cr(VI), on the other hand, is much more toxic and forms compounds that are reasonably soluble in water. Exposure to small amounts of Cr(VI) can lead to damage of the respiratory, gastrointestinal, and immune systems, as well as the kidneys, liver, blood, and skin.

Despite cleanup efforts, Cr(VI) groundwater contamination remains a problem in Hinckley and other locations across the globe. A 2010 study by the Environmental Working Group found that of 35 US cities tested, 31 had higher levels of Cr(VI) in their tap water than the public health goal of 0.02 parts per billion set by the California Environmental Protection Agency.

Summary

Chemists use nomenclature rules to clearly name compounds. Ionic and molecular compounds are named using somewhat-different methods. Binary ionic compounds typically consist of a metal and a nonmetal. The name of the metal is written first, followed by the name of the nonmetal with its ending changed to *–ide*. For example, K_2O is called potassium oxide. If the metal can form ions with different charges, a Roman numeral in parentheses follows the name of the metal to specify its charge. Thus, $FeCl_2$ is iron(II) chloride and $FeCl_3$ is iron(III) chloride. Some compounds contain polyatomic ions.

Glossary

binary compound
compound containing two different elements.

nomenclature

system of rules for naming objects of interest

Contributors

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3.6: Lewis Symbols and Structures

Skills to Develop

- Write Lewis symbols for neutral atoms and ions
- Draw Lewis structures depicting the bonding in simple molecules
- Differentiate between single, double, and triple bonds in terms of bonding pairs, orbital overlap, and strength.

Thus far, we have discussed the various types of bonds that form between atoms and/or ions. In all cases, these bonds involve the sharing or transfer of valence shell electrons between atoms. In this section, we will explore the typical method for depicting valence shell electrons and chemical bonds, namely Lewis symbols and Lewis structures.

Lewis Symbols

We use Lewis symbols to describe valence electron configurations of atoms and monatomic ions. A Lewis symbol consists of an elemental symbol surrounded by one dot for each of its valence electrons:



Figure 3.6.1 shows the Lewis symbols for the elements of the third period of the periodic table. Electron dots are typically arranged in four pairs located on the four "sides" of the atomic symbol.

Atoms	Electronic Configuration	Lewis Symbol
sodium	$[Ne]3s^1$	Na·
magnesium	$[Ne]3s^2$	·Mg·
aluminum	$[Ne]3s^23p^1$	·Al·
silicon	$[Ne]3s^23p^2$	·Si·
phosphorus	$[Ne]3s^23p^3$	·P·
sulfur	$[Ne]3s^23p^4$	:S·
chlorine	$[Ne]3s^23p^5$	:Cl·
argon	$[Ne]3s^23p^6$	:Ar:

Figure 3.6.1: Lewis symbols illustrating the number of valence electrons for each element in the third period of the periodic table.

Lewis symbols can be used to illustrate the formation of cations from atoms, as shown here for sodium and calcium:



Likewise, they can be used to show the formation of anions from atoms, as shown here for chlorine and sulfur:



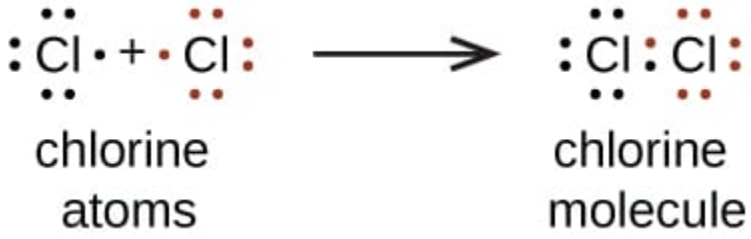
Figure 3.6.2 demonstrates the use of Lewis symbols to show the transfer of electrons during the formation of ionic compounds.

Metal		Nonmetal		Ionic Compound
Na ·	+	:Cl·	⟶	$Na^+[:Cl:]^-$
sodium atom		chlorine atom		sodium chloride (sodium ion and chloride ion)
·Mg·	+	:O·	⟶	$Mg^{2+}[:O:]^{2-}$
magnesium atom		oxygen atom		magnesium oxide (magnesium ion and oxide ion)
·Ca·	+	2 :F·	⟶	$Ca^{2+}[:F:]^-_2$
calcium atom		fluorine atoms		calcium fluoride (calcium ion and two fluoride ions)

Figure 3.6.2: Cations are formed when atoms lose electrons, represented by fewer Lewis dots, whereas anions are formed by atoms gaining electrons. The total number of electrons does not change.

Lewis Structures

We also use Lewis symbols to indicate the formation of covalent bonds, which are shown in Lewis structures, drawings that describe the bonding in molecules and polyatomic ions. For example, when two chlorine atoms form a chlorine molecule, they share one pair of electrons:



The Lewis structure indicates that each Cl atom has three pairs of electrons that are not used in bonding (called lone pairs) and one shared pair of electrons (written between the atoms). A dash (or line) is usually used to indicate a shared pair of electrons:

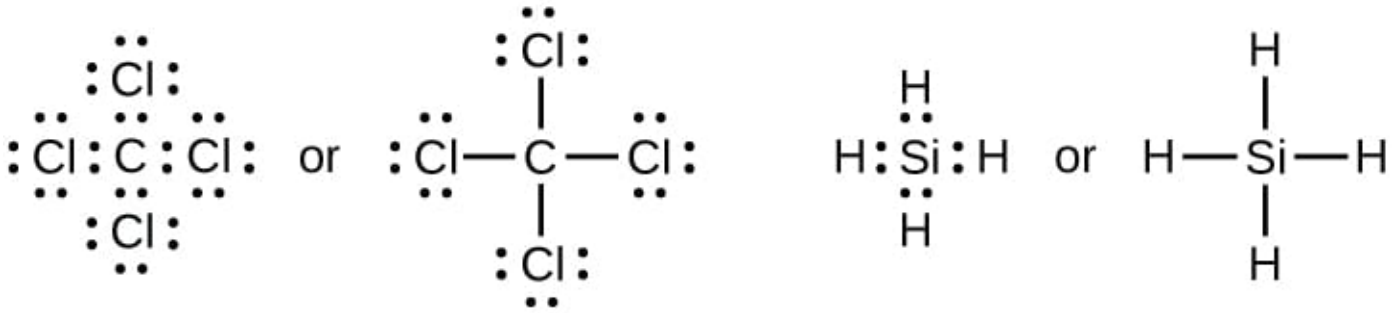


In the Lewis model, a single shared pair of electrons is a single bond. Each Cl atom interacts with eight valence electrons total: the six in the lone pairs and the two in the single bond.

The Octet Rule

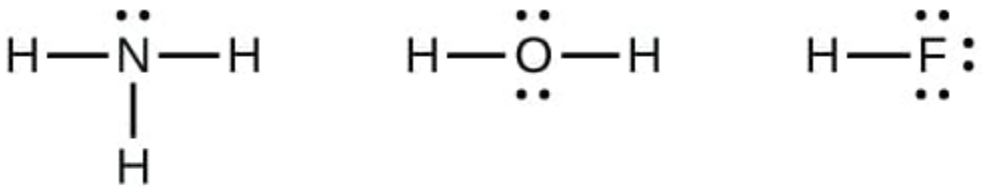
The other halogen molecules (F_2, Br_2, I_2, and At_2) form bonds like those in the chlorine molecule: one single bond between atoms and three lone pairs of electrons per atom. This allows each halogen atom to have a noble gas electron configuration. The tendency of main group atoms to form enough bonds to obtain eight valence electrons is known as the octet rule.

The number of bonds that an atom can form can often be predicted from the number of electrons needed to reach an octet (eight valence electrons); this is especially true of the nonmetals of the second period of the periodic table (C, N, O, and F). For example, each atom of a group 14 element has four electrons in its outermost shell and therefore requires four more electrons to reach an octet. These four electrons can be gained by forming four covalent bonds, as illustrated here for carbon in CCl_4 (carbon tetrachloride) and silicon in SiH_4 (silane). Because hydrogen only needs two electrons to fill its valence shell, it is an exception to the octet rule and only needs to form one bond. The transition elements and inner transition elements also do not follow the octet rule since they have d and f electrons involved in their valence shells.



carbon tetrachloride silane

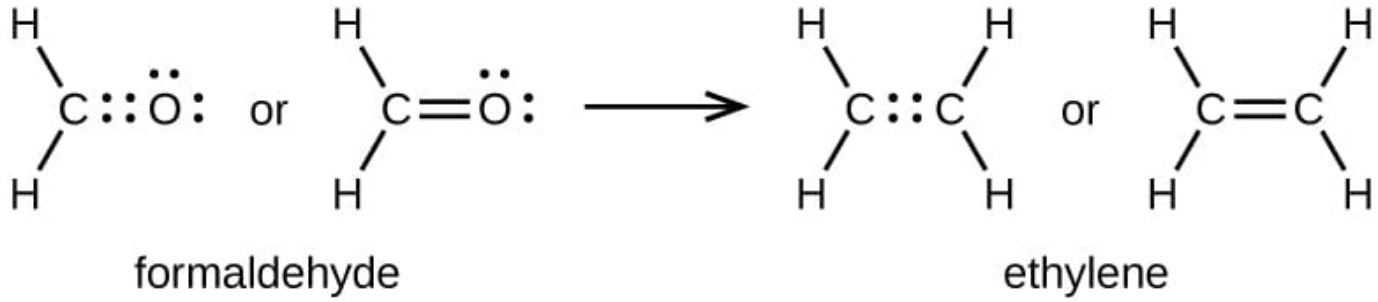
Group 15 elements such as nitrogen have five valence electrons in the atomic Lewis symbol: one lone pair and three unpaired electrons. To obtain an octet, these atoms form three covalent bonds, as in NH_3 (ammonia). Oxygen and other atoms in group 16 obtain an octet by forming two covalent bonds:



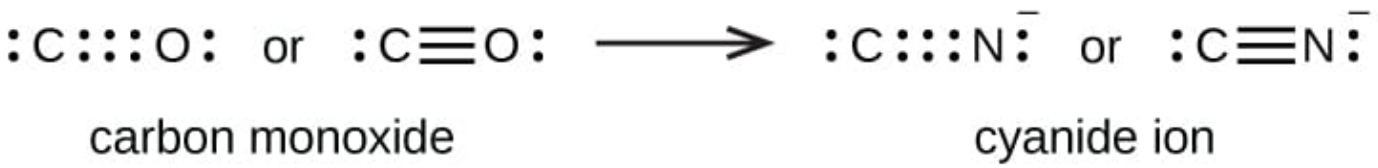
ammonia Water hydrogen fluoride

Double and Triple Bonds

As previously mentioned, when a pair of atoms shares one pair of electrons, we call this a single bond. However, a pair of atoms may need to share more than one pair of electrons in order to achieve the requisite octet. A double bond forms when two pairs of electrons are shared between a pair of atoms, as between the carbon and oxygen atoms in CH_2O (formaldehyde) and between the two carbon atoms in C_2H_4 (ethylene):

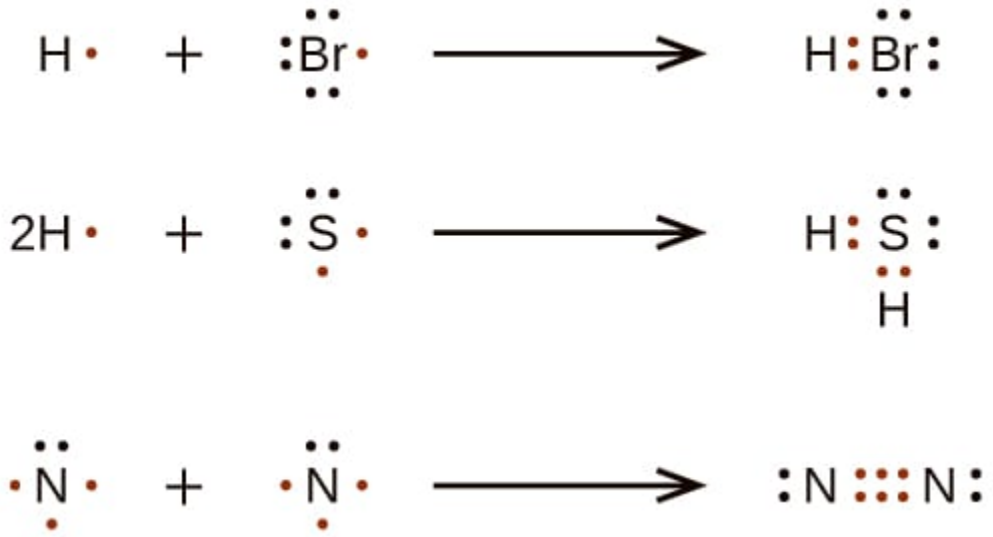


A triple bond forms when three electron pairs are shared by a pair of atoms, as in carbon monoxide (CO) and the cyanide ion (CN^-):



Writing Lewis Structures with the Octet Rule

For very simple molecules and molecular ions, we can write the Lewis structures by merely pairing up the unpaired electrons on the constituent atoms. See these examples:



For more complicated molecules and molecular ions, it is helpful to follow the step-by-step procedure outlined here:

1. Determine the total number of valence (outer shell) electrons among all the atoms. For cations, subtract one electron for each positive charge. For anions, add one electron for each negative charge.
2. Draw a skeleton structure of the molecule or ion, arranging the atoms around a central atom. (Generally, the least electronegative element should be placed in the center.) Connect each atom to the central atom with a single bond (one electron pair).
3. Distribute the remaining electrons as lone pairs on the terminal atoms (except hydrogen), completing an octet around each atom.
4. Place all remaining electrons on the central atom.
5. Rearrange the electrons of the outer atoms to make multiple bonds with the central atom in order to obtain octets wherever possible.

Let us determine the Lewis structures of SiH_4, CHO_2^-, NO^+, and OF_2 as examples in following this procedure:

1. Determine the total number of valence (outer shell) electrons in the molecule or ion.
   - For a molecule, we add the number of valence electrons on each atom in the molecule:

$$\begin{aligned} &SiH_4 && (3.6.1)\\ &\text{Si: 4 valence electrons/atom} \times \text{1 atom} = 4 && (3.6.2)\\ &+\text{H: 1 valence electron/atom} \times \text{4 atoms} = 4 && (3.6.3)\\ &= \text{8 valence electrons} && (3.6.4) \end{aligned}$$

   - For a *negative ion*, such as CHO_2^-, we add the number of valence electrons on the atoms to the number of negative charges on the ion (one electron is gained for each single negative charge):

$$\begin{aligned} CHO_2^- \ &\text{C: 4 valence electrons/atom} \times \text{1 atom} = 4 \quad \text{H: 1 valence electron/atom} \times \text{1 atom} = 1\\ &\text{O: 6 valence electrons/atom} \times \text{2 atoms} = 12 \quad + \quad \text{1 additional electron} = 1\\ &= \text{18 valence electrons} \end{aligned}$$

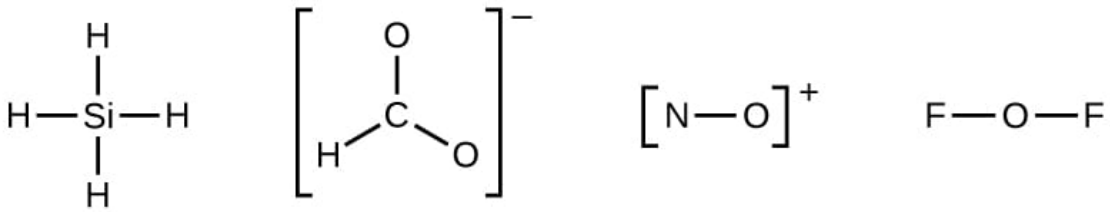
   - For a *positive ion*, such as NO^+, we add the number of valence electrons on the atoms in the ion and then subtract the number of positive charges on the ion (one electron is lost for each single positive charge) from the total number of valence electrons:

$$\begin{aligned} NO^+ \ &\text{N: 5 valence electrons/atom} \times \text{1 atom} = 5 \quad \text{O: 6 valence electron/atom} \times \text{1 atom} = 6\\ &+ -1 \text{ electron (positive charge)} = -1 \qquad = \text{10 valence electrons} \end{aligned}$$

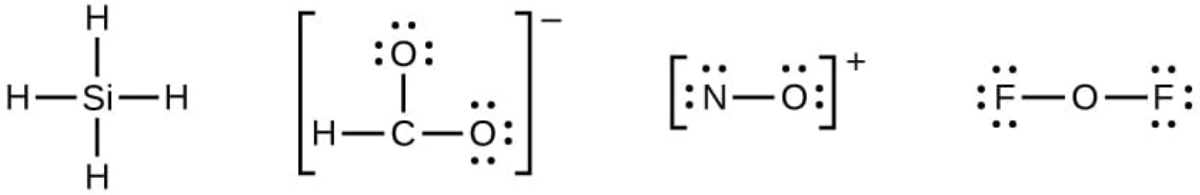
   - Since OF_2 is a neutral molecule, we simply add the number of valence electrons:

$$\begin{aligned} OF_2 \quad &\text{O: 6 valence electrons/atom} \times \text{1 atom} = 6 \quad + \text{F: 7 valence electrons/atom} \times \text{2 atoms} = 14\\ &= \text{20 valence electrons} \end{aligned}$$

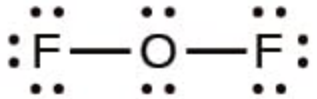
2. Draw a skeleton structure of the molecule or ion, arranging the atoms around a central atom and connecting each atom to the central atom with a single (one electron pair) bond. (Note that we denote ions with brackets around the structure, indicating the charge outside the brackets:)



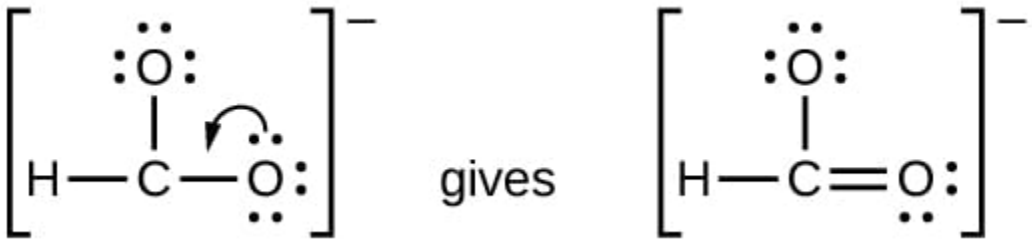
3. When several arrangements of atoms are possible, as for CHO_2^-, we must use experimental evidence to choose the correct one. In general, the less electronegative elements are more likely to be central atoms. In CHO_2^-, the less electronegative carbon atom occupies the central position with the oxygen and hydrogen atoms surrounding it. Other examples include P in $POCl_3$, S in SO_2, and Cl in ClO_4^-. An exception is that hydrogen is almost never a central atom. As the most electronegative element, fluorine also cannot be a central atom.
4. Distribute the remaining electrons as lone pairs on the terminal atoms (except hydrogen) to complete their valence shells with an octet of electrons.
   - There are no remaining electrons on SiH_4, so it is unchanged:



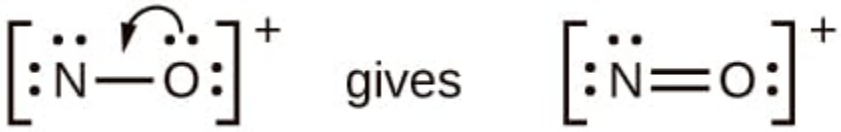
5. Place all remaining electrons on the central atom.
   - For SiH_4, CHO_2^-, and NO^+, there are no remaining electrons; we already placed all of the electrons determined in Step 1.
   - For OF_2, we had 16 electrons remaining in Step 3, and we placed 12, leaving 4 to be placed on the central atom:



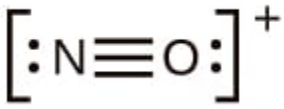
6. Rearrange the electrons of the outer atoms to make multiple bonds with the central atom in order to obtain octets wherever possible.
   - SiH_4: Si already has an octet, so nothing needs to be done.
   - CHO_2^-: We have distributed the valence electrons as lone pairs on the oxygen atoms, but the carbon atom lacks an octet:



   - NO^+: For this ion, we added eight outer electrons, but neither atom has an octet. We cannot add any more electrons since we have already used the total that we found in Step 1, so we must move electrons to form a multiple bond:



   - This still does not produce an octet, so we must move another pair, forming a triple bond:



   - In OF_2, each atom has an octet as drawn, so nothing changes.

Example 3.6.1**:** Writing Lewis Structures

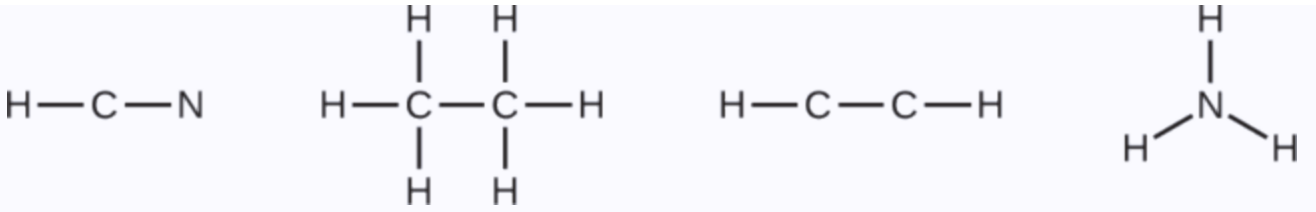
NASA's Cassini-Huygens mission detected a large cloud of toxic hydrogen cyanide (HCN) on Titan, one of Saturn's moons. Titan also contains ethane (H_3CCH_3), acetylene (HCCH), and ammonia (NH_3). What are the Lewis structures of these molecules?

Solution

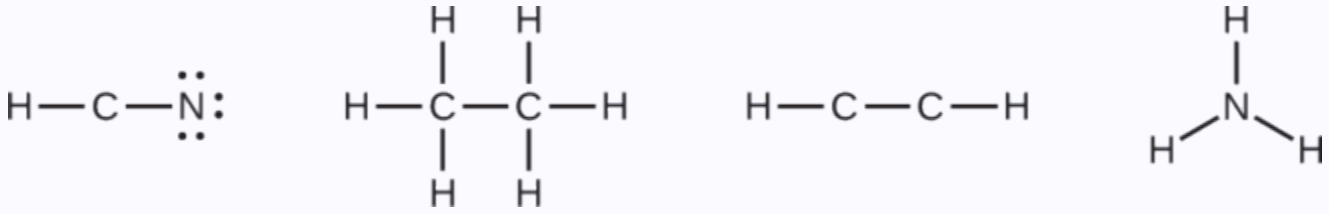
Calculate the number of valence electrons.

- HCN: (1 × 1) + (4 × 1) + (5 × 1) = 10
- H_3CCH_3: (1 × 3) + (2 × 4) + (1 × 3) = 14
- HCCH: (1 × 1) + (2 × 4) + (1 × 1) = 10
- NH_3: (5 × 1) + (3 × 1) = 8

Draw a skeleton and connect the atoms with single bonds. Remember that H is never a central atom:

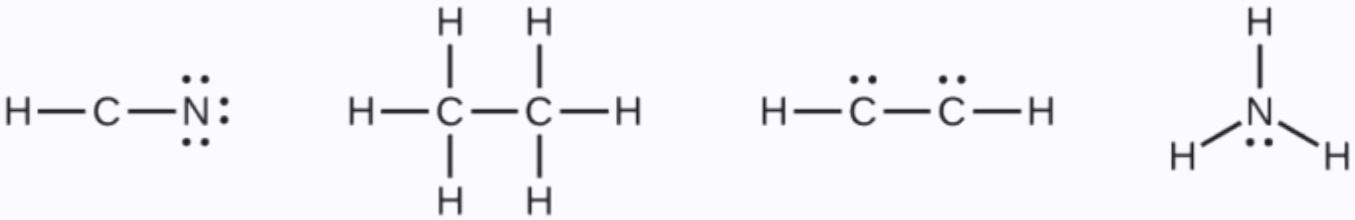


Where needed, distribute electrons to the terminal atoms:



- HCN: six electrons placed on N
- H_3CCH_3: no electrons remain
- HCCH: no terminal atoms capable of accepting electrons
- NH_3: no terminal atoms capable of accepting electrons

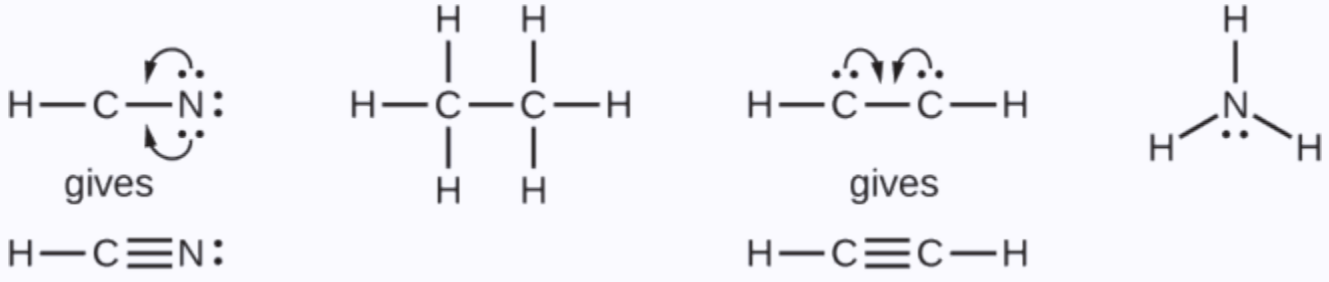
Where needed, place remaining electrons on the central atom:



- HCN: no electrons remain
- H_3CCH_3: no electrons remain
- HCCH: four electrons placed on carbon
- NH_3: two electrons placed on nitrogen

Where needed, rearrange electrons to form multiple bonds in order to obtain an octet on each atom:

- HCN: form two more C–N bonds
- H_3CCH_3: all atoms have the correct number of electrons
- HCCH: form a triple bond between the two carbon atoms
- NH_3: all atoms have the correct number of electrons



Exercise 3.6.1

Both carbon monoxide, CO, and carbon dioxide, CO_2, are products of the combustion of fossil fuels. Both of these gases also cause problems: CO is toxic and CO_2 has been implicated in global climate change. What are the Lewis structures of these two molecules?

Answer



Fullerene Chemistry

Carbon soot has been known to man since prehistoric times, but it was not until fairly recently that the molecular structure of the main component of soot was discovered. In 1996, the Nobel Prize in Chemistry was awarded to Richard Smalley, Robert Curl, and Harold Kroto for their work in discovering a new form of carbon, the C_{60} buckminsterfullerene molecule. An entire class of compounds, including spheres and tubes of various shapes, were discovered based on C_{60}. This type of molecule, called a fullerene, consists of a complex network of single- and double-bonded carbon atoms arranged in such a way that each carbon atom obtains a full octet of electrons. Because of their size and shape, fullerenes can encapsulate other molecules, so they have shown potential in various applications from hydrogen storage to targeted drug delivery systems. They also possess unique electronic and optical properties that have been put to good use in solar powered devices and chemical sensors.

Exceptions to the Octet Rule

Many covalent molecules have central atoms that do not have eight electrons in their Lewis structures. These molecules fall into three categories:

- Odd-electron molecules have an odd number of valence electrons, and therefore have an unpaired electron.
- Electron-deficient molecules have a central atom that has fewer electrons than needed for a noble gas configuration.
- Hypervalent molecules have a central atom that has more electrons than needed for a noble gas configuration.

In CHE 101 we will avoid these exceptions to the octet rule.

Summary

Valence electronic structures can be visualized by drawing Lewis symbols (for atoms and monatomic ions) and Lewis structures (for molecules and polyatomic ions). Lone pairs, unpaired electrons, and single, double, or triple bonds are used to indicate where the valence electrons are located around each atom in a Lewis structure. Most structures—especially those containing second row elements—obey the octet rule, in which every atom (except H) is surrounded by eight electrons. Exceptions to the octet rule occur for odd-electron molecules (free radicals), electron-deficient molecules, and hypervalent molecules.

Glossary

double bond
: covalent bond in which two pairs of electrons are shared between two atoms

free radical
: molecule that contains an odd number of electrons

hypervalent molecule
molecule containing at least one main group element that has more than eight electrons in its valence shell

Lewis structure
diagram showing lone pairs and bonding pairs of electrons in a molecule or an ion

Lewis symbol
symbol for an element or monatomic ion that uses a dot to represent each valence electron in the element or ion

lone pair
two (a pair of) valence electrons that are not used to form a covalent bond

octet rule
guideline that states main group atoms will form structures in which eight valence electrons interact with each nucleus, counting bonding electrons as interacting with both atoms connected by the bond

single bond
bond in which a single pair of electrons is shared between two atoms

triple bond
bond in which three pairs of electrons are shared between two atoms

Contributors

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3.7: Molecular Structure and Polarity

Learning Objectives

- Define ionic and molecular (covalent) compounds
- Predict the type of compound formed from elements based on their location within the periodic table
- Determine formulas for simple ionic compounds

In ordinary chemical reactions, the nucleus of each atom (and thus the identity of the element) remains unchanged. Electrons, however, can be added to atoms by transfer from other atoms, lost by transfer to other atoms, or shared with other atoms. The transfer and sharing of electrons among atoms govern the chemistry of the elements. During the formation of some compounds, atoms gain or lose electrons, and form electrically charged particles called ions (Figure 3.7.1).

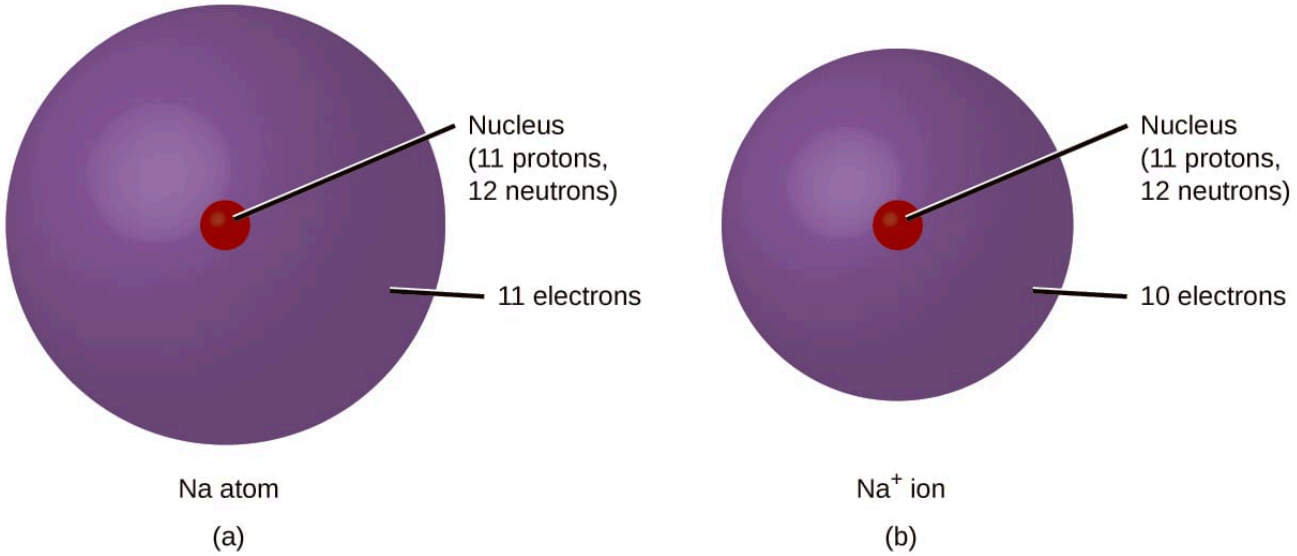


Figure 3.7.1: (a) A sodium atom (Na) has equal numbers of protons and electrons (11) and is uncharged. (b) A sodium cation (Na^+) has lost an electron, so it has one more proton (11) than electrons (10), giving it an overall positive charge, signified by a superscripted plus sign.

You can use the periodic table to predict whether an atom will form an anion or a cation, and you can often predict the charge of the resulting ion. Atoms of many main-group metals lose enough electrons to leave them with the same number of electrons as an atom of the preceding noble gas. To illustrate, an atom of an alkali metal (group 1) loses one electron and forms a cation with a 1+ charge; an alkaline earth metal (group 2) loses two electrons and forms a cation with a 2+ charge, and so on. For example, a neutral calcium atom, with 20 protons and 20 electrons, readily loses two electrons. This results in a cation with 20 protons, 18 electrons, and a 2+ charge. It has the same number of electrons as atoms of the preceding noble gas, argon, and is symbolized Ca^{2+}. The name of a metal ion is the same as the name of the metal atom from which it forms, so Ca^{2+} is called a calcium ion.

When atoms of nonmetal elements form ions, they generally gain enough electrons to give them the same number of electrons as an atom of the next noble gas in the periodic table. Atoms of group 17 gain one electron and form anions with a 1– charge; atoms of group 16 gain two electrons and form ions with a 2– charge, and so on. For example, the neutral bromine atom, with 35 protons and 35 electrons, can gain one electron to provide it with 36 electrons. This results in an anion with 35 protons, 36 electrons, and a 1– charge. It has the same number of electrons as atoms of the next noble gas, krypton, and is symbolized Br^-. (A discussion of the theory supporting the favored status of noble gas electron numbers reflected in these predictive rules for ion formation is provided in a later chapter of this text.)

Note the usefulness of the periodic table in predicting likely ion formation and charge (Figure 3.7.2). Moving from the far left to the right on the periodic table, main-group elements tend to form cations with a charge equal to the group number. That is, group 1 elements form 1+ ions; group 2 elements form 2+ ions, and so on. Moving from the far right to the left on the periodic table, elements often form anions with a negative charge equal to the number of groups moved left from the noble gases. For example,

group 17 elements (one group left of the noble gases) form 1– ions; group 16 elements (two groups left) form 2– ions, and so on. This trend can be used as a guide in many cases, but its predictive value decreases when moving toward the center of the periodic table. In fact, transition metals and some other metals often exhibit variable charges that are not predictable by their location in the table. For example, copper can form ions with a 1+ or 2+ charge, and iron can form ions with a 2+ or 3+ charge.

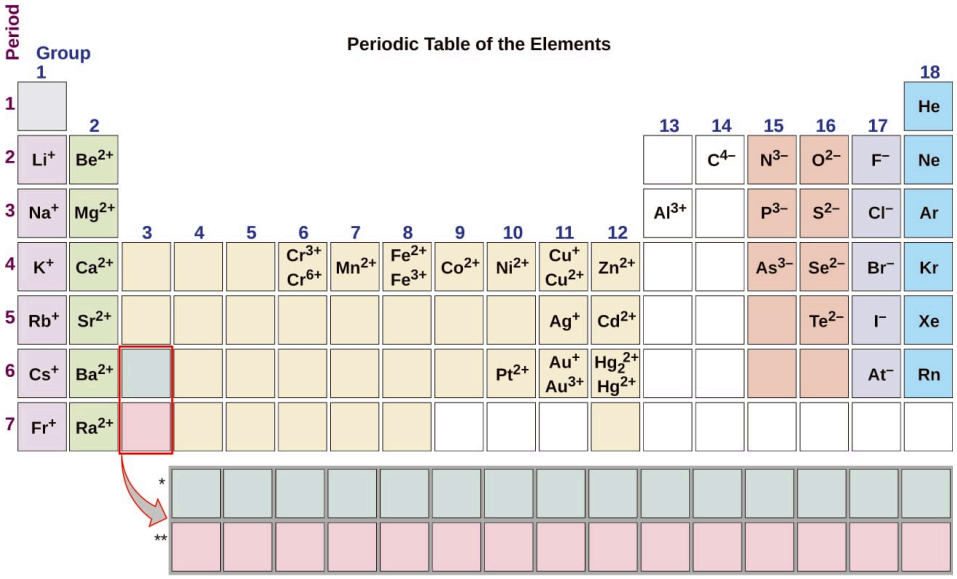


Figure 3.7.2: Some elements exhibit a regular pattern of ionic charge when they form ions.

Example 3.7.1: Composition of Ions

An ion found in some compounds used as antiperspirants contains 13 protons and 10 electrons. What is its symbol?

Solution

Because the number of protons remains unchanged when an atom forms an ion, the atomic number of the element must be 13. Knowing this lets us use the periodic table to identify the element as Al (aluminum). The Al atom has lost three electrons and thus has three more positive charges (13) than it has electrons (10). This is the aluminum cation, Al^{3+}.

Exercise 3.7.1

Give the symbol and name for the ion with 34 protons and 36 electrons.

Answer

Se^{2-}, the selenide ion

Example 3.7.2: Formation of Ions

Magnesium and nitrogen react to form an ionic compound. Predict which forms an anion, which forms a cation, and the charges of each ion. Write the symbol for each ion and name them.

Solution

Magnesium's position in the periodic table (group 2) tells us that it is a metal. Metals form positive ions (cations). A magnesium atom must lose two electrons to have the same number electrons as an atom of the previous noble gas, neon. Thus, a magnesium atom will form a cation with two fewer electrons than protons and a charge of 2+. The symbol for the ion is Mg^{2+},

and it is called a magnesium ion.

Nitrogen's position in the periodic table (group 15) reveals that it is a nonmetal. Nonmetals form negative ions (anions). A nitrogen atom must gain three electrons to have the same number of electrons as an atom of the following noble gas, neon. Thus, a nitrogen atom will form an anion with three more electrons than protons and a charge of 3–. The symbol for the ion is N^{3-}, and it is called a nitride ion.

Exercise 3.7.2

Aluminum and carbon react to form an ionic compound. Predict which forms an anion, which forms a cation, and the charges of each ion. Write the symbol for each ion and name them.

Answer

Al will form a cation with a charge of 3+: Al^{3+}, an aluminum ion. Carbon will form an anion with a charge of 4–: C^{4-}, a carbide ion.

The ions that we have discussed so far are called monatomic ions, that is, they are ions formed from only one atom. We also find many polyatomic ions. These ions, which act as discrete units, are electrically charged molecules (a group of bonded atoms with an overall charge). Some of the more important polyatomic ions are listed in Table 3.7.1. Oxyanions are polyatomic ions that contain one or more oxygen atoms. Because you will use them repeatedly, they will soon become familiar.

Table 3.7.1***:*** *Common Polyatomic Ions*

ammonium	NH_4^+		
hydronium	H_3O^+		
oxide	O^{2-}		
peroxide	O_2^{2-}		
hydroxide	OH^-		
acetate	CH_3COO^-	acetic acid	CH_3COOH
cyanide	CN^-	hydrocyanic acid	HCN
azide	N_3^-	hydrazoic acid	HN_3
carbonate	CO_3^{2-}	carbonic acid	H_2CO_3
bicarbonate	HCO_3^-		
nitrate	NO_3^-	nitric acid	HNO_3
nitrite	NO_2^-	nitrous acid	HNO_2
sulfate	SO_4^{2-}	sulfuric acid	H_2SO_4
hydrogen sulfate	HSO_4^-		
sulfite	SO_3^{2-}	sulfurous acid	H_2SO_3
hydrogen sulfite	HSO_3^-		
phosphate	PO_4^{3-}	phosphoric acid	H_3PO_4
hydrogen phosphate	HPO_4^{2-}		
dihydrogen phosphate	$H_2PO_4^-$		
perchlorate	ClO_4^-	perchloric acid	$HClO_4$
chlorate	ClO_3^-	chloric acid	$HClO_3$

chlorite	ClO_2^-	chlorous acid	$HClO_2$
hypochlorite	ClO^-	hypochlorous acid	$HClO$
chromate	CrO_4^{2-}	chromic acid	H_2CrO_4
dichromate	$Cr_2O_7^{2-}$	dichromic acid	$H_2Cr_2O_7$
permanganate	MnO_4^-	permanganic acid	$HMnO_4$

Note that there is a system for naming some polyatomic ions; *-ate* and *-ite* are suffixes designating polyatomic ions containing more or fewer oxygen atoms. *Per-* (short for "hyper") and *hypo-* (meaning "under") are prefixes meaning more oxygen atoms than *-ate* and fewer oxygen atoms than *-ite*, respectively. For example, perchlorate is ClO_4^-, chlorate is ClO_3^-, chlorite is ClO_2^- and hypochlorite is ClO^-. Unfortunately, the number of oxygen atoms corresponding to a given suffix or prefix is not consistent; for example, nitrate is NO_3^- while sulfate is SO_4^{2-}. This will be covered in more detail in the next module on nomenclature.

The nature of the attractive forces that hold atoms or ions together within a compound is the basis for classifying chemical bonding. When electrons are transferred and ions form, ionic bonds result. Ionic bonds are electrostatic forces of attraction, that is, the attractive forces experienced between objects of opposite electrical charge (in this case, cations and anions). When electrons are "shared" and molecules form, covalent bonds result. Covalent bonds are the attractive forces between the positively charged nuclei of the bonded atoms and one or more pairs of electrons that are located between the atoms. Compounds are classified as ionic or molecular (covalent) on the basis of the bonds present in them.

CHE 101 Polyatomic Ion List to Memorize

As the name implies, a polyatomic ion is a charged molecule. Many polyatomic ions exist, but in CHE 101 we expect that you will learn the name, formula, and charge of these specific ions.

1+	ammonium ion	NH_4^{+1}
1-	hydrogen carbonate (bicarbonate) ion	HCO_3^{-1}
	hydrogen sulfate (bisulfate) ion	HSO_4^{-1}
	nitrite ion	NO_2^{-1}
	nitrate ion	NO_3^{-1}
	cyanide ion	CN^{-1}
	hydroxide ion	OH^{-1}
	dihydrogen phosphate ion	$H_2PO_4^{-1}$
2-	carbonate ion	CO_3^{-2}
	sulfate ion	SO_4^{-2}
	monohydrogen phosphate ion	HPO_4^{-2}
3-	phosphate ion	PO_4^{-3}

Ionic Compounds

When an element composed of atoms that readily lose electrons (a metal) reacts with an element composed of atoms that readily gain electrons (a nonmetal), a transfer of electrons usually occurs, producing ions. The compound formed by this transfer is stabilized by the electrostatic attractions (ionic bonds) between the ions of opposite charge present in the compound. For example, when each sodium atom in a sample of sodium metal (group 1) gives up one electron to form a sodium cation, Na^+, and each chlorine atom in a sample of chlorine gas (group 17) accepts one electron to form a chloride anion, Cl^-, the resulting compound, NaCl, is composed of sodium ions and chloride ions in the ratio of one Na^+ ion for each Cl^- ion. Similarly, each calcium atom (group 2) can give up two electrons and transfer one to each of two chlorine atoms to form $CaCl_2$, which is composed of Ca^{2+} and Cl^- ions in the ratio of one Ca^{2+} ion to two Cl^- ions.

A compound that contains ions and is held together by ionic bonds is called an ionic compound. The periodic table can help us recognize many of the compounds that are ionic: When a metal is combined with one or more nonmetals, the compound is usually ionic. This guideline works well for predicting ionic compound formation for most of the compounds typically encountered in an introductory chemistry course. However, it is not always true (for example, aluminum chloride, $AlCl_3$, is not ionic).

You can often recognize ionic compounds because of their properties. Ionic compounds are solids that typically melt at high temperatures and boil at even higher temperatures. For example, sodium chloride melts at 801 °C and boils at 1413 °C. (As a comparison, the molecular compound water melts at 0 °C and boils at 100 °C.) In solid form, an ionic compound is not electrically conductive because its ions are unable to flow ("electricity" is the flow of charged particles). When molten, however, it can conduct electricity because its ions are able to move freely through the liquid (Figure 3.7.3).

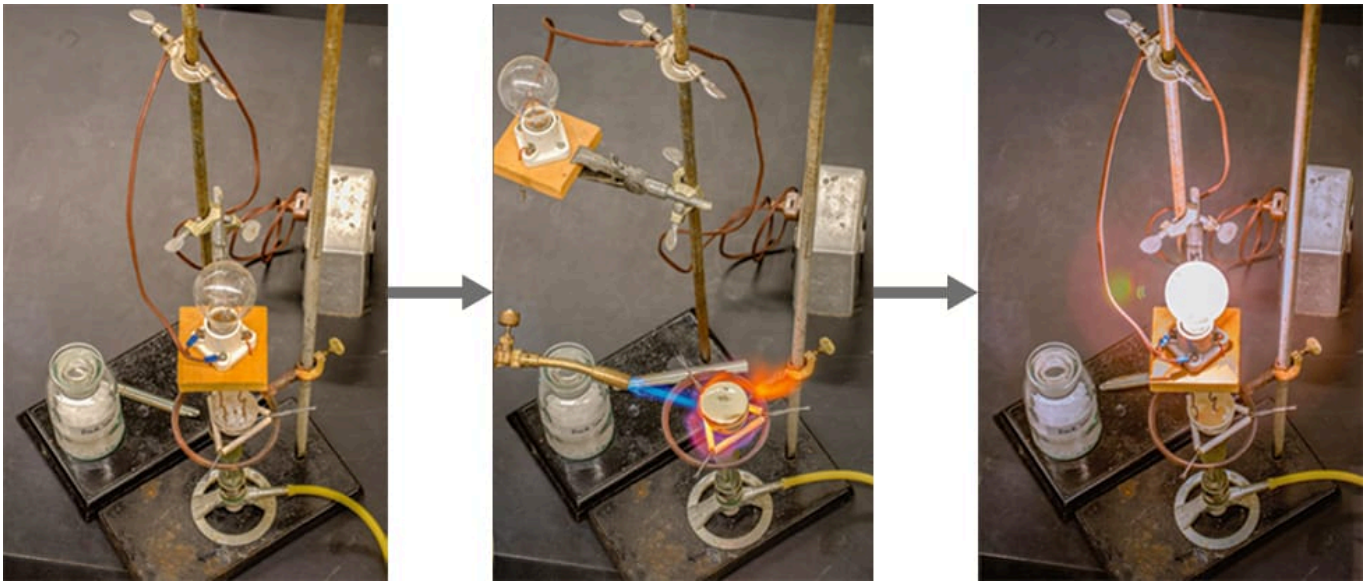


Figure 3.7.3: Sodium chloride melts at 801 °C and conducts electricity when molten. (credit: modification of work by Mark Blaser and Matt Evans)

In every ionic compound, the total number of positive charges of the cations equals the total number of negative charges of the anions. Thus, ionic compounds are electrically neutral overall, even though they contain positive and negative ions. We can use this observation to help us write the formula of an ionic compound. The formula of an ionic compound must have a ratio of ions such that the numbers of positive and negative charges are equal.

Example 3.7.3: Predicting the Formula of an Ionic Compound

The gemstone sapphire (Figure 3.7.4) is mostly a compound of aluminum and oxygen that contains aluminum cations, Al^{3+}, and oxygen anions, O^{2-}. What is the formula of this compound?



Figure 3.7.4: Although pure aluminum oxide is colorless, trace amounts of iron and titanium give blue sapphire its characteristic color. (credit: modification of work by Stanislav Doronenko)

Solution Because the ionic compound must be electrically neutral, it must have the same number of positive and negative charges. Two aluminum ions, each with a charge of 3+, would give us six positive charges, and three oxide ions, each with a charge of 2–, would give us six negative charges. The formula would be Al_2O_3.

Exercise 3.7.3

Predict the formula of the ionic compound formed between the sodium cation, Na^+, and the sulfide anion, S^{2-}.

Answer

Na_2S

Many ionic compounds contain polyatomic ions (Table 3.7.1) as the cation, the anion, or both. As with simple ionic compounds, these compounds must also be electrically neutral, so their formulas can be predicted by treating the polyatomic ions as discrete units. We use parentheses in a formula to indicate a group of atoms that behave as a unit. For example, the formula for calcium phosphate, one of the minerals in our bones, is $Ca_3(PO_4)_2$. This formula indicates that there are three calcium ions (Ca^{2+}) for every two phosphate $(PO_4{}^{3-})$ groups. The $PO_4{}^{3-}$ groups are discrete units, each consisting of one phosphorus atom and four oxygen atoms, and having an overall charge of 3–. The compound is electrically neutral, and its formula shows a total count of three Ca, two P, and eight O atoms.

Example 3.7.4: Predicting the Formula of a Compound with a Polyatomic Anion

Baking powder contains calcium dihydrogen phosphate, an ionic compound composed of the ions Ca^{2+} and $H_2PO_4{}^-$. What is the formula of this compound?

Solution

The positive and negative charges must balance, and this ionic compound must be electrically neutral. Thus, we must have two negative charges to balance the 2+ charge of the calcium ion. This requires a ratio of one Ca^{2+} ion to two $H_2PO_4{}^-$ ions. We designate this by enclosing the formula for the dihydrogen phosphate ion in parentheses and adding a subscript 2. The formula is $Ca(H_2PO_4)_2$.

Exercise $3.7.4$

Predict the formula of the ionic compound formed between the lithium ion and the peroxide ion, O_2^{2-} (Hint: Use the periodic table to predict the sign and the charge on the lithium ion.)

Answer

Li_2O_2

Because an ionic compound is not made up of single, discrete molecules, it may not be properly symbolized using a *molecular* formula. Instead, ionic compounds must be symbolized by a formula indicating the *relative numbers* of its constituent ions. For compounds containing only monatomic ions (such as NaCl) and for many compounds containing polyatomic ions (such as $CaSO_4$), these formulas are just the empirical formulas introduced earlier in this chapter. However, the formulas for some ionic compounds containing polyatomic ions are not empirical formulas. For example, the ionic compound sodium oxalate is comprised of Na^+ and $C_2O_4^{2-}$ ions combined in a 2:1 ratio, and its formula is written as $Na_2C_2O_4$. The subscripts in this formula are not the smallest-possible whole numbers, as each can be divided by 2 to yield the empirical formula, $NaCO_2$. This is not the accepted formula for sodium oxalate, however, as it does not accurately represent the compound's polyatomic anion, $C_2O_4^{2-}$.

Summary

Metals (particularly those in groups 1 and 2) tend to lose the number of electrons that would leave them with the same number of electrons as in the preceding noble gas in the periodic table. By this means, a positively charged ion is formed. Similarly, nonmetals (especially those in groups 16 and 17, and, to a lesser extent, those in Group 15) can gain the number of electrons needed to provide atoms with the same number of electrons as in the next noble gas in the periodic table. Thus, nonmetals tend to form negative ions. Positively charged ions are called cations, and negatively charged ions are called anions. Ions can be either monatomic (containing only one atom) or polyatomic (containing more than one atom).

Compounds that contain ions are called ionic compounds. Ionic compounds generally form from metals and nonmetals. Compounds that do not contain ions, but instead consist of atoms bonded tightly together in molecules (uncharged groups of atoms that behave as a single unit), are called covalent compounds. Covalent compounds usually form from two or more nonmetals.

Glossary

covalent bond
attractive force between the nuclei of a molecule's atoms and pairs of electrons between the atoms

covalent compound
(also, molecular compound) composed of molecules formed by atoms of two or more different elements

ionic bond
electrostatic forces of attraction between the oppositely charged ions of an ionic compound

ionic compound
compound composed of cations and anions combined in ratios, yielding an electrically neutral substance

molecular compound
(also, covalent compound) composed of molecules formed by atoms of two or more different elements

monatomic ion
ion composed of a single atom

polyatomic ion
ion composed of more than one atom

oxyanion
polyatomic anion composed of a central atom bonded to oxygen atoms

Contributors

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3.8: Unit 3 Practice Problems

Question 1

The loss of electrons from an atom is called _____.

Answer

oxidation

The gain of electrons by an atom is called _____.

Answer

Reduction

An atom with a charge (either positive or negative) is called _____.

Answer

ion

A positively charged atom is called _____.

Answer

cation

A negatively charged atom is called _____.

Answer

anion

Question 2

Name the following ionic compounds.

MgS

NaCl

Ca_3N_2

KOH

$AlPO_4$

Answer

magnesium sulfide

sodium chloride

calcium nitride

potassium hydroxide

aluminum phosphate

Question 3

Given the following electronegativity values, determine the type of bond (polar covalent, nonpolar covalent, or ionic) which will occur between the atoms below.

Electronegativity values (will be provided on HW and tests)				
H = 2.1	Li = 1.0	Na = 0.9	K = 0.8	Be = 1.5
Mg = 1.2	Ca = 1.0	B = 2.0	Al = 1.5	C = 2.5
N = 3.0	P = 2.1	O = 3.5	S = 2.5	F = 4.0
Cl = 3.0	Br = 2.8	Cu = 1.9	Ag = 1.9	

Li - F

C - O

C - H

Answer

Li - F: ionic bond

C - O: polar covalent bond

C - H: nonpoloar covalent

Question 4

Given the name, write the formula for the following compounds.

calcium bromide

magnesium nitrate

iron (III) oxide

silver (I) sulfide

ammonium hydrogen phosphate

Answer

$CaBr_2$

$Mg(NO_3)_2$

Fe_2O_3

Ag_2S

$(NH_4)_2HPO_4$

Question 5

Write Lewis structures for the following:

(a) H_2

(b) HBr

(c) PCl_3

(d) SF_2

(e) C_2H_4

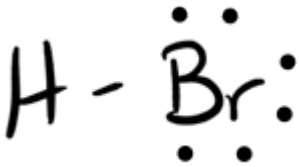
(f) NO-

(g) CN^-

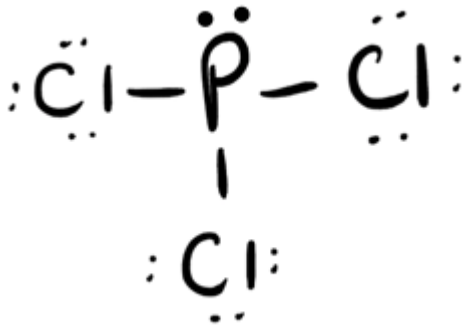
Answer a



Answer b



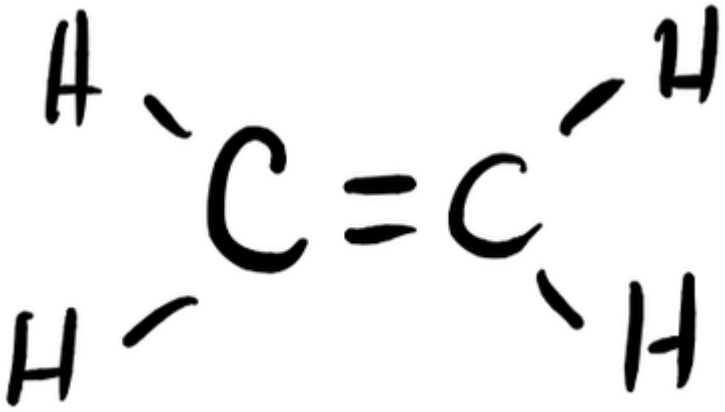
Answer c



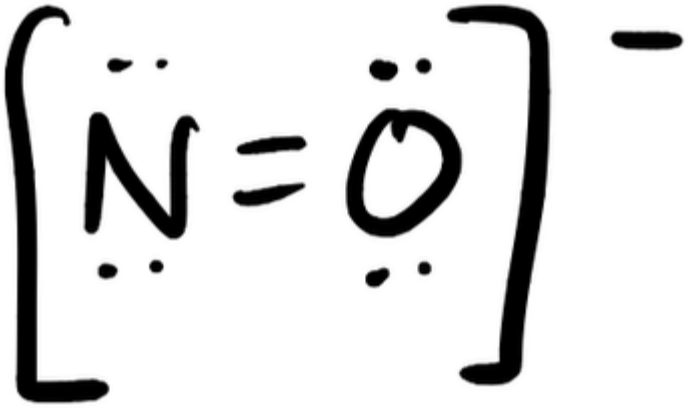
Answer d



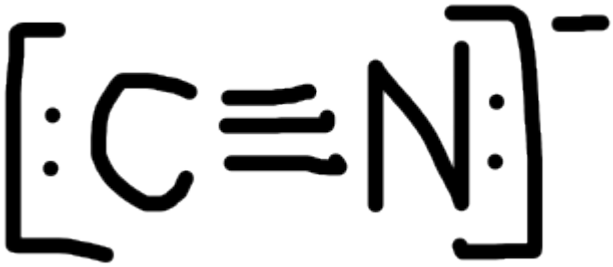
Answer e



Answer f



Answer g



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4: STOICHIOMETRY OF CHEMICAL REACTIONS

A general chemistry Libretexts Textbook remixed and remastered from OpenStax's textbook:
General Chemistry

This chapter will describe how to symbolize chemical reactions using chemical equations, how to classify some common chemical reactions by identifying patterns of reactivity, and how to determine the quantitative relations between the amounts of substances involved in chemical reactions—that is, the reaction *stoichiometry*.

Unit 4 Objectives

By the end of this unit, you will be able to:

- Identify the parts of a chemical equation including reactants, products, spectator ions, coefficients, and catalysts.
- Balance chemical equations.
- Determine the molecular weight of any molecule given the molecular formula.
- Define mole and Avagadro's number.
- Explain the relation between mass, moles, and numbers of atoms or molecules, and perform calculations deriving these quantities from one another.
- Categorize reactions by type: synthesis, decomposition, single replacement, double replacement, and combustion.
- Given a redox reaction equation, identify the element being oxidized, the one being reduced, and any spectator ions.
- Write balanced equations for single replacement, double replacement, and combustion reactions.
- Use stoichiometry to calculate the amount (in moles or grams) of a particular substance produced or used in a chemical reaction.
- Use stoichiometry to determine molecular formulas.
- Calculate the yield for a reaction under specified conditions.
- Identify the limiting reactant in a chemical equation.
- Describe three ways to speed up a reaction.
- Differentiate between reversible exothermic, irreversible exothermic, and endothermic reactions and draw appropriate graphs to represent each which include axis labels, activation energy, and the effect a catalyst would have on the graph.

4.1: Writing and Balancing Chemical Equations

4.2: Formula Mass and the Mole Concept

4.3: Types of Reactions

4.4: Reaction Stoichiometry

4.5: Reaction Yields

4.6: Exothermic and Endothermic Reactions

4.7: Unit 4 Practice Problems

Contributors

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- Christy VanRooyen, Oregon Tech

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4.1: Writing and Balancing Chemical Equations

Skills to Develop

- Identify the parts of a chemical equation including reactants, products, spectator ions, coefficients, and catalysts.
- Balance chemical equations.

The preceding chapter introduced the use of element symbols to represent individual atoms. When atoms gain or lose electrons to yield ions, or combine with other atoms to form molecules, their symbols are modified or combined to generate chemical formulas that appropriately represent these species. Extending this symbolism to represent both the identities and the relative quantities of substances undergoing a chemical (or physical) change involves writing and balancing a chemical equation. Consider as an example the reaction between one methane molecule (CH_4) and two diatomic oxygen molecules (O_2) to produce one carbon dioxide molecule (CO_2) and two water molecules (H_2O). The chemical equation representing this process is provided in the upper half of Figure 4.1.1, with space-filling molecular models shown in the lower half of the figure.

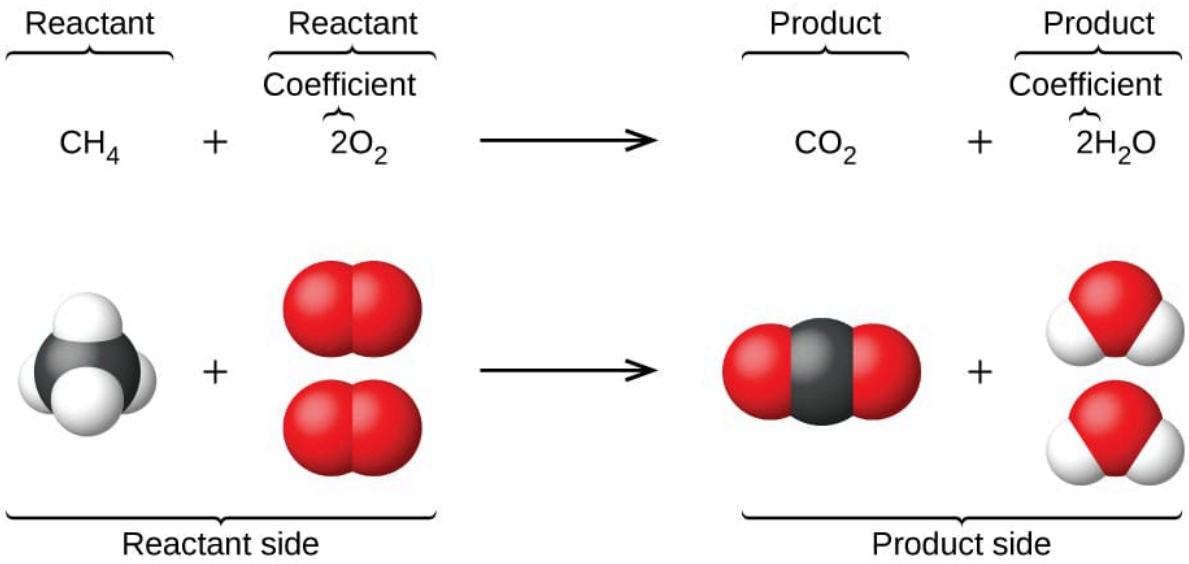


Figure 4.1.1: The reaction between methane and oxygen to yield carbon dioxide and water (shown at bottom) may be represented by a chemical equation using formulas (top).

This example illustrates the fundamental aspects of any chemical equation:

1. The substances undergoing reaction are called reactants, and their formulas are placed on the left side of the equation.
2. The substances generated by the reaction are called products, and their formulas are placed on the right sight of the equation.
3. Plus signs (+) separate individual reactant and product formulas, and an arrow (⟢) separates the reactant and product (left and right) sides of the equation.
4. The relative numbers of reactant and product species are represented by coefficients (numbers placed immediately to the left of each formula). A coefficient of 1 is typically omitted.

It is common practice to use the smallest possible whole-number coefficients in a chemical equation, as is done in this example. Realize, however, that these coefficients represent the *relative* numbers of reactants and products, and, therefore, they may be correctly interpreted as ratios. Methane and oxygen react to yield carbon dioxide and water in a 1:2:1:2 ratio. This ratio is satisfied if the numbers of these molecules are, respectively, 1-2-1-2, or 2-4-2-4, or 3-6-3-6, and so on (Figure 4.1.2). Likewise, these coefficients may be interpreted with regard to any amount (number) unit, and so this equation may be correctly read in many ways, including:

- *One* methane molecule and *two* oxygen molecules react to yield *one* carbon dioxide molecule and *two* water molecules.

- *One dozen* methane molecules and *two dozen* oxygen molecules react to yield *one dozen* carbon dioxide molecules and *two dozen* water molecules.
- *One mole* of methane molecules and *2 moles* of oxygen molecules react to yield *1 mole* of carbon dioxide molecules and *2 moles* of water molecules.

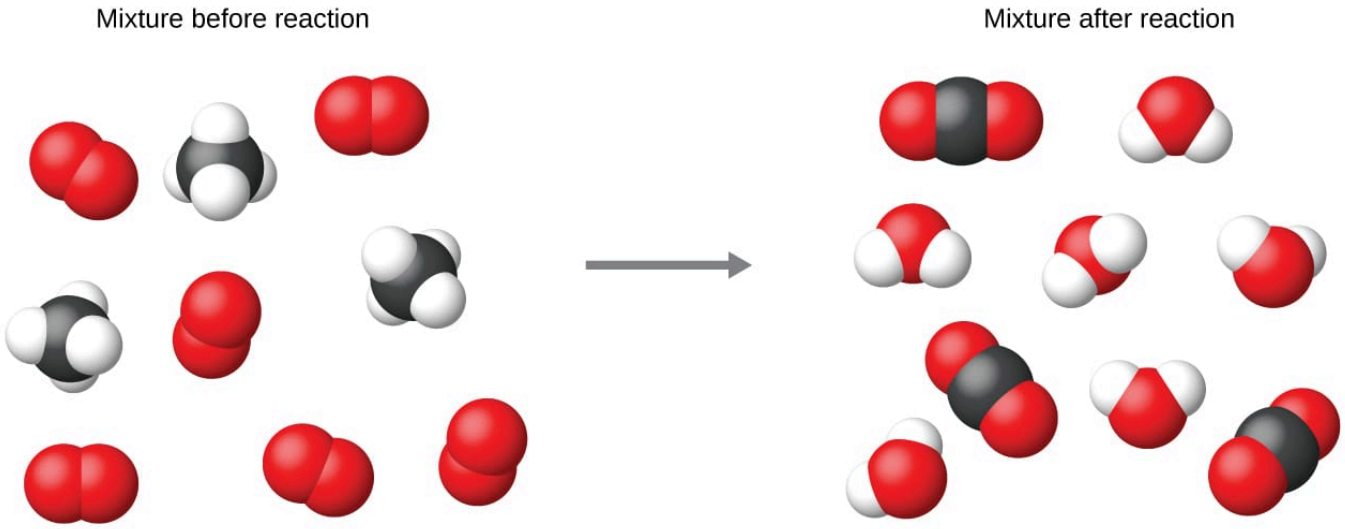


Figure 4.1.2: Regardless of the absolute number of molecules involved, the ratios between numbers of molecules of each species that react (the reactants) and molecules of each species that form (the products) are the same and are given in the chemical equation.

Balancing Equations

When a chemical equation is balanced it means that equal numbers of atoms for each element involved in the reaction are represented on the reactant and product sides. This is a requirement the equation must satisfy to be consistent with the law of conservation of matter. It may be confirmed by simply summing the numbers of atoms on either side of the arrow and comparing these sums to ensure they are equal. Note that the number of atoms for a given element is calculated by multiplying the coefficient of any formula containing that element by the element's subscript in the formula. If an element appears in more than one formula on a given side of the equation, the number of atoms represented in each must be computed and then added together. For example, both product species in the example reaction, $\mathrm{CO_2}$ and $\mathrm{H_2O}$, contain the element oxygen, and so the number of oxygen atoms on the product side of the equation is

$$\left(1\ \cancel{\mathrm{CO_2\ molecule}} \times \frac{2\ \mathrm{O\ atoms}}{\cancel{\mathrm{CO_2\ molecule}}}\right) + \left(\cancel{2\,\mathrm{H_2O\ molecule}} \times \frac{1\ \mathrm{O\ atom}}{\cancel{\mathrm{H_2O\ molecule}}}\right) = 4\ \mathrm{O\ atoms} \tag{4.1.1}$$

The equation for the reaction between methane and oxygen to yield carbon dioxide and water is confirmed to be balanced per this approach, as shown here:

$$\mathrm{CH_4} + 2\,\mathrm{O_2} \rightarrow \mathrm{CO_2} + 2\,\mathrm{H_2O} \tag{4.1.2}$$

Element	Reactants	Products	Balanced?
C	1 × 1 = 1	1 × 1 = 1	1 = 1, yes
H	4 × 1 = 4	2 × 2 = 4	4 = 4, yes
O	2 × 2 = 4	(1 × 2) + (2 × 1) = 4	4 = 4, yes

A balanced chemical equation often may be derived from a qualitative description of some chemical reaction by a fairly simple approach known as balancing by inspection. Consider as an example the decomposition of water to yield molecular hydrogen and oxygen. This process is represented qualitatively by an *unbalanced* chemical equation:

$$\mathrm{H_2O} \rightarrow \mathrm{H_2} + \mathrm{O_2} \qquad \text{(unbalanced)}$$

Comparing the number of H and O atoms on either side of this equation confirms its imbalance:

Element	Reactants	Products	Balanced?
H	1 × 2 = 2	1 × 2 = 2	2 = 2, yes
O	1 × 1 = 1	1 × 2 = 2	1 ≠ 2, no

The numbers of H atoms on the reactant and product sides of the equation are equal, but the numbers of O atoms are not. To achieve balance, the *coefficients* of the equation may be changed as needed. Keep in mind, of course, that the *formula subscripts* define, in part, the identity of the substance, and so these cannot be changed without altering the qualitative meaning of the equation. For example, changing the reactant formula from H_2O to H_2O_2 would yield balance in the number of atoms, but doing so also changes the reactant's identity (it's now hydrogen peroxide and not water). The O atom balance may be achieved by changing the coefficient for H_2O to 2.

$$2\,H_2O \rightarrow H_2 + O_2 \qquad \text{(unbalanced)}$$

Element	Reactants	Products	Balanced?
H	**2** × 2 = 4	1 × 2 = 2	4 ≠ 2, no
O	2 × 1 = 2	1 × 2 = 2	2 = 2, yes

The H atom balance was upset by this change, but it is easily reestablished by changing the coefficient for the H_2 product to 2.

$$2\,H_2O \rightarrow 2\,H_2 + O_2 \qquad \text{(balanced)}$$

Element	Reactants	Products	Balanced?
H	2 × 2 = 4	**2** × 2 = 2	4 = 4, yes
O	2 × 1 = 2	1 × 2 = 2	2 = 2, yes

These coefficients yield equal numbers of both H and O atoms on the reactant and product sides, and the balanced equation is, therefore:

$$2\,H_2O \rightarrow 2\,H_2 + O_2 \qquad (4.1.3)$$

Example 4.1.1: Balancing Chemical Equations

Write a balanced equation for the reaction of molecular nitrogen (N_2) and oxygen (O_2) to form dinitrogen pentoxide.

Solution

First, write the unbalanced equation.

$$N_2 + O_2 \rightarrow N_2O_5 \qquad \text{(unbalanced)}$$

Next, count the number of each type of atom present in the unbalanced equation.

Element	Reactants	Products	Balanced?
N	1 × 2 = 2	1 × 2 = 2	2 = 2, yes
O	1 × 2 = 2	1 × 5 = 5	2 ≠ 5, no

Though nitrogen is balanced, changes in coefficients are needed to balance the number of oxygen atoms. To balance the number of oxygen atoms, a reasonable first attempt would be to change the coefficients for the O_2 and N_2O_5 to integers that

will yield 10 O atoms (the least common multiple for the O atom subscripts in these two formulas).

$$N_2 + 5\,O_2 \rightarrow 2\,N_2O_5 \quad \text{(unbalanced)}$$

Element	Reactants	Products	Balanced?
N	1 × 2 = 2	**2** × 2 = 4	2 ≠ 4, no
O	**5** × 2 = 10	**2** × 5 = 10	10 = 10, yes

The N atom balance has been upset by this change; it is restored by changing the coefficient for the reactant N_2 to 2.

$$2\,N_2 + 5\,O_2 \rightarrow 2\,N_2O_5 \quad (4.1.4)$$

Element	Reactants	Products	Balanced?
N	**2** × 2 = 4	2 × 2 = 4	4 = 4, yes
O	5 × 2 = 10	2 × 5 = 10	10 = 10, yes

The numbers of N and O atoms on either side of the equation are now equal, and so the equation is balanced.

Exercise 4.1.1

Write a balanced equation for the decomposition of ammonium nitrate to form molecular nitrogen, molecular oxygen, and water. (Hint: Balance oxygen last, since it is present in more than one molecule on the right side of the equation.)

Answer

$$2\,NH_4NO_3 \rightarrow 2\,N_2 + O_2 + 4\,H_2O$$

It is sometimes convenient to use fractions instead of integers as intermediate coefficients in the process of balancing a chemical equation. When balance is achieved, all the equation's coefficients may then be multiplied by a whole number to convert the fractional coefficients to integers without upsetting the atom balance. For example, consider the reaction of ethane (C_2H_6) with oxygen to yield H_2O and CO_2, represented by the unbalanced equation:

$$C_2H_6 + O_2 \rightarrow H_2O + CO_2 \quad \text{(unbalanced)}$$

Following the usual inspection approach, one might first balance C and H atoms by changing the coefficients for the two product species, as shown:

$$C_2H_6 + O_2 \rightarrow 3\,H_2O + 2\,CO_2 \quad \text{(unbalanced)}$$

This results in seven O atoms on the product side of the equation, an odd number—no integer coefficient can be used with the O_2 reactant to yield an odd number, so a fractional coefficient, $\frac{7}{2}$, is used instead to yield a provisional balanced equation:

$$C_2H_6 + \tfrac{7}{2}\,O_2 \rightarrow 3\,H_2O + 2\,CO_2$$

A conventional balanced equation with integer-only coefficients is derived by multiplying each coefficient by 2:

$$2\,C_2H_6 + 7\,O_2 \rightarrow 6\,H_2O + 4\,CO_2 \quad (4.1.5)$$

Finally with regard to balanced equations, recall that convention dictates use of the *smallest whole-number coefficients*. Although the equation for the reaction between molecular nitrogen and molecular hydrogen to produce ammonia is, indeed, balanced,

$$3\,N_2 + 9\,H_2 \rightarrow 6\,NH_3 \quad (4.1.6)$$

the coefficients are not the smallest possible integers representing the relative numbers of reactant and product molecules. Dividing each coefficient by the greatest common factor, 3, gives the preferred equation:

$$\mathrm{N_2 + 3\,H_2 \rightarrow 2\,NH_3} \tag{4.1.7}$$

Phet Simulation

Use this interactive tutorial for additional practice balancing equations.

Additional Information in Chemical Equations

The physical states of reactants and products in chemical equations very often are indicated with a parenthetical abbreviation following the formulas. Common abbreviations include *s* for solids, *l* for liquids, *g* for gases, and *aq* for substances dissolved in water (*aqueous solutions*, as introduced in the preceding chapter). These notations are illustrated in the example equation here:

$$\mathrm{2\,Na\,(s) + 2\,H_2O\,(l) \rightarrow 2\,NaOH\,(aq) + H_2\,(g)} \tag{4.1.8}$$

This equation represents the reaction that takes place when sodium metal is placed in water. The solid sodium reacts with liquid water to produce molecular hydrogen gas and the ionic compound sodium hydroxide (a solid in pure form, but readily dissolved in water).

Special conditions necessary for a reaction are sometimes designated by writing a word or symbol above or below the equation's arrow. For example, a reaction carried out by heating may be indicated by the uppercase Greek letter delta (Δ) over the arrow.

$$\mathrm{CaCO_3}(s) \xrightarrow{\Delta} \mathrm{CaO}(s) + \mathrm{CO_2}(g) \tag{4.1.9}$$

Other examples of these special conditions will be encountered in more depth in later chapters.

Equations for Ionic Reactions

Given the abundance of water on earth, it stands to reason that a great many chemical reactions take place in aqueous media. When ions are involved in these reactions, the chemical equations may be written with various levels of detail appropriate to their intended use. To illustrate this, consider a reaction between ionic compounds taking place in an aqueous solution. When aqueous solutions of $\mathrm{CaCl_2}$ and $\mathrm{AgNO_3}$ are mixed, a reaction takes place producing aqueous $\mathrm{Ca(NO_3)_2}$ and solid AgCl:

$$\mathrm{CaCl_2}(aq) + 2\,\mathrm{AgNO_3}(aq) \rightarrow \mathrm{Ca(NO_3)_2}(aq) + 2\,\mathrm{AgCl}(s) \tag{4.1.10}$$

This balanced equation, derived in the usual fashion, is called a molecular equation because it doesn't explicitly represent the ionic species that are present in solution. When ionic compounds dissolve in water, they may *dissociate* into their constituent ions, which are subsequently dispersed homogenously throughout the resulting solution (a thorough discussion of this important process is provided in the chapter on solutions). Ionic compounds dissolved in water are, therefore, more realistically represented as dissociated ions, in this case:

$$\mathrm{CaCl_2}(aq) \rightarrow [redacted](aq) + 2\,\mathrm{Cl^-}(aq) \tag{4.1.11}$$

$$\mathrm{2\,AgNO_3}(aq) \rightarrow \mathrm{2\,Ag^+}(aq) + \mathrm{2\,NO_3^-}(aq) \tag{4.1.12}$$

$$\mathrm{Ca(NO_3)_2}(aq) \rightarrow \mathrm{Ca^{2+}}(aq) + \mathrm{2\,NO_3^-}(aq) \tag{4.1.13}$$

Unlike these three ionic compounds, AgCl does not dissolve in water to a significant extent, as signified by its physical state notation, *(s)*.

Explicitly representing all dissolved ions results in a complete ionic equation. In this particular case, the formulas for the dissolved ionic compounds are replaced by formulas for their dissociated ions:

$$[redacted](aq) + \mathrm{2\,Cl^-}(aq) + \mathrm{2\,Ag^+}(aq) + \mathrm{2\,NO_3^-}(aq) \rightarrow [redacted](aq) + \mathrm{2\,NO_3^-}(aq) + \mathrm{2\,AgCl}(s) \tag{4.1.14}$$

Examining this equation shows that two chemical species are present in identical form on both sides of the arrow, $\mathrm{Ca^{2+}\,(aq)}$ and $\mathrm{NO_3^-}(aq)$. These spectator ions—ions whose presence is required to maintain charge neutrality—are neither chemically nor physically changed by the process, and so they may be eliminated from the equation to yield a more succinct representation

called a net ionic equation:

$$[redacted](aq) + 2\,Cl^-(aq) + 2\,Ag^+(aq) + 2\,NO_3^-(aq) \rightarrow [redacted](aq) + 2\,NO_3^-(aq) + 2\,AgCl(s) \quad (4.1.15)$$

$$2\,Cl^-(aq) + 2\,Ag^+(aq) \rightarrow 2\,AgCl(s) \quad (4.1.16)$$

Following the convention of using the smallest possible integers as coefficients, this equation is then written:

$$Cl^-(aq) + Ag^+(aq) \rightarrow AgCl(s) \quad (4.1.17)$$

This net ionic equation indicates that solid silver chloride may be produced from dissolved chloride and silver(I) ions, regardless of the source of these ions. These molecular and complete ionic equations provide additional information, namely, the ionic compounds used as sources of Cl^- and Ag^+.

Example 4.1.2: Molecular and Ionic Equations

When carbon dioxide is dissolved in an aqueous solution of sodium hydroxide, the mixture reacts to yield aqueous sodium carbonate and liquid water. Write balanced molecular, complete ionic, and net ionic equations for this process.

Solution

Begin by identifying formulas for the reactants and products and arranging them properly in chemical equation form:

$$CO_2\,(aq) + NaOH\,(aq) \rightarrow Na_2CO_3\,(aq) + H_2O\,(l) \quad \text{(unbalanced)}$$

Balance is achieved easily in this case by changing the coefficient for NaOH to 2, resulting in the molecular equation for this reaction:

$$CO_2(aq) + 2\,NaOH(aq) \rightarrow Na_2CO_3\,(aq) + H_2O(l)$$

The two dissolved ionic compounds, NaOH and Na_2CO_3, can be represented as dissociated ions to yield the complete ionic equation:

$$CO_2\,(aq) + 2\,Na^+\,(aq) + 2\,OH^-\,(aq) \rightarrow 2\,Na^+\,(aq) + {CO_3}^{2-}\,(aq) + H_2O\,(l)$$

Finally, identify the spectator ion(s), in this case $Na^+(aq)$, and remove it from each side of the equation to generate the net ionic equation:

$$CO_2(aq) + 2\,Na^+(aq) + 2\,OH^-(aq) \rightarrow 2\,Na^+(aq) + {CO_3}^{2-}(aq) + H_2O(l)$$
$$CO_2(aq) + 2\,OH^-(aq) \rightarrow {CO_3}^{2-}(aq) + H_2O(l)$$

Exercise 4.1.2

Diatomic chlorine and sodium hydroxide (lye) are commodity chemicals produced in large quantities, along with diatomic hydrogen, via the electrolysis of brine, according to the following unbalanced equation:

$$NaCl\,(aq) + H_2O\,(l) \xrightarrow{\text{electricity}} NaOH\,(aq) + H_2\,(g) + Cl_2\,(g)$$

Write balanced molecular, complete ionic, and net ionic equations for this process.

Answer

Balanced molecular equation:

Extra close brace or missing open brace

Balanced ionic equation:

Extra close brace or missing open brace

Balanced net ionic equation:

Extra close brace or missing open brace

Key Concepts and Summary

Chemical equations are symbolic representations of chemical and physical changes. Formulas for the substances undergoing the change (reactants) and substances generated by the change (products) are separated by an arrow and preceded by integer coefficients indicating their relative numbers. Balanced equations are those whose coefficients result in equal numbers of atoms for each element in the reactants and products. Chemical reactions in aqueous solution that involve ionic reactants or products may be represented more realistically by complete ionic equations and, more succinctly, by net ionic equations.

Glossary

balanced equation
chemical equation with equal numbers of atoms for each element in the reactant and product

chemical equation
symbolic representation of a chemical reaction

coefficient
number placed in front of symbols or formulas in a chemical equation to indicate their relative amount

complete ionic equation
chemical equation in which all dissolved ionic reactants and products, including spectator ions, are explicitly represented by formulas for their dissociated ions

molecular equation
chemical equation in which all reactants and products are represented as neutral substances

net ionic equation
chemical equation in which only those dissolved ionic reactants and products that undergo a chemical or physical change are represented (excludes spectator ions)

product
substance formed by a chemical or physical change; shown on the right side of the arrow in a chemical equation

reactant
substance undergoing a chemical or physical change; shown on the left side of the arrow in a chemical equation

spectator ion
ion that does not undergo a chemical or physical change during a reaction, but its presence is required to maintain charge neutrality

Contributors

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4.2: Formula Mass and the Mole Concept

Skills to Develop

- Determine the molecular weight of any molecule given the molecular formula.
- Define mole and Avagadro's number.
- Explain the relation between mass, moles, and numbers of atoms or molecules, and perform calculations deriving these quantities from one another

We can argue that modern chemical science began when scientists started exploring the quantitative as well as the qualitative aspects of chemistry. For example, Dalton's atomic theory was an attempt to explain the results of measurements that allowed him to calculate the relative masses of elements combined in various compounds. Understanding the relationship between the masses of atoms and the chemical formulas of compounds allows us to quantitatively describe the composition of substances.

Formula Mass

In an earlier chapter, we described the development of the atomic mass unit, the concept of average atomic masses, and the use of chemical formulas to represent the elemental makeup of substances. These ideas can be extended to calculate the formula mass of a substance by summing the average atomic masses of all the atoms represented in the substance's formula.

Formula Mass for Covalent Substances

For covalent substances, the formula represents the numbers and types of atoms composing a single molecule of the substance; therefore, the formula mass may be correctly referred to as a molecular mass. Consider chloroform ($CHCl_3$), a covalent compound once used as a surgical anesthetic and now primarily used in the production of tetrafluoroethylene, the building block for the "anti-stick" polymer, Teflon. The molecular formula of chloroform indicates that a single molecule contains one carbon atom, one hydrogen atom, and three chlorine atoms. The average molecular mass of a chloroform molecule is therefore equal to the sum of the average atomic masses of these atoms. Figure 4.2.1 outlines the calculations used to derive the molecular mass of chloroform, which is 119.37 amu.

Element	Quantity		Average atomic mass (amu)		Subtotal (amu)
C	1	×	12.01	=	12.01
H	1	×	1.008	=	1.008
Cl	3	×	35.45	=	106.35
				Molecular mass	119.37

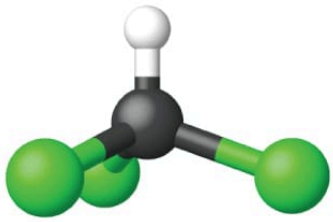
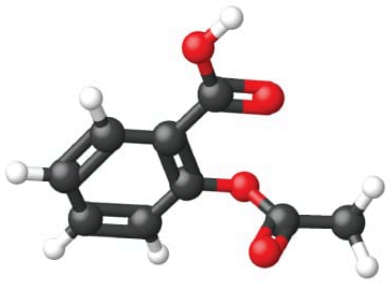


Figure 4.2.1: The average mass of a chloroform molecule, $CHCl_3$, is 119.37 amu, which is the sum of the average atomic masses of each of its constituent atoms. The model shows the molecular structure of chloroform.

Likewise, the molecular mass of an aspirin molecule, $C_9H_8O_4$, is the sum of the atomic masses of nine carbon atoms, eight hydrogen atoms, and four oxygen atoms, which amounts to 180.15 amu (Figure 4.2.2).

Element	Quantity		Average atomic mass (amu)		Subtotal (amu)
C	9	×	12.01	=	108.09
H	8	×	1.008	=	8.064
O	4	×	16.00	=	64.00
				Molecular mass	180.15



Element	Quantity		Average atomic mass (amu)		Subtotal (amu)
C	9	×	12.01	=	108.09
H	8	×	1.008	=	8.064
O	4	×	16.00	=	64.00
				Molecular mass	180.15

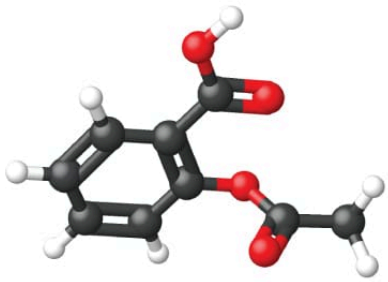


Figure *4.2.2: The average mass of an aspirin molecule is 180.15 amu. The model shows the molecular structure of aspirin, $C_9H_8O_4$.*

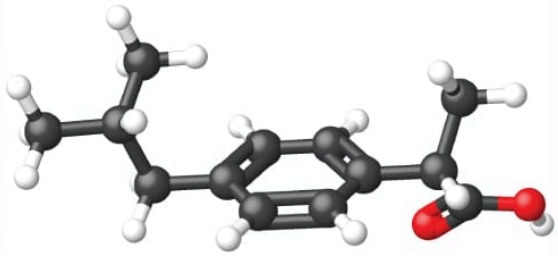
Example 4.2.1: Computing Molecular Mass for a Covalent Compound

Ibuprofen, $C_{13}H_{18}O_2$, is a covalent compound and the active ingredient in several popular nonprescription pain medications, such as Advil and Motrin. What is the molecular mass (amu) for this compound?

Solution

Molecules of this compound are comprised of 13 carbon atoms, 18 hydrogen atoms, and 2 oxygen atoms. Following the approach described above, the average molecular mass for this compound is therefore:

Element	Quantity		Average atomic mass (amu)		Subtotal (amu)
C	13	×	12.01	=	156.13
H	18	×	1.008	=	18.114
O	2	×	16.00	=	32.00
				Molecular mass	206.27



Exercise 4.2.1

Acetaminophen, $C_8H_9NO_2$, is a covalent compound and the active ingredient in several popular nonprescription pain medications, such as Tylenol. What is the molecular mass (amu) for this compound?

Answer

151.16 amu

Formula Mass for Ionic Compounds

Ionic compounds are composed of discrete cations and anions combined in ratios to yield electrically neutral bulk matter. The formula mass for an ionic compound is calculated in the same way as the formula mass for covalent compounds: by summing the average atomic masses of all the atoms in the compound's formula. Keep in mind, however, that the formula for an ionic compound does not represent the composition of a discrete molecule, so it may not correctly be referred to as the "molecular mass."

As an example, consider sodium chloride, NaCl, the chemical name for common table salt. Sodium chloride is an ionic compound composed of sodium cations, Na^+, and chloride anions, Cl^-, combined in a 1:1 ratio. The formula mass for this compound is computed as 58.44 amu (Figure 4.2.3).

Element	Quantity		Average atomic mass (amu)		Subtotal
Na	1	×	22.99	=	22.99
Cl	1	×	35.45	=	35.45
				Formula mass	58.44

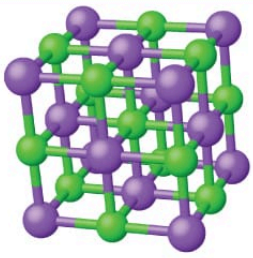


Figure 4.2.3: Table salt, NaCl, contains an array of sodium and chloride ions combined in a 1:1 ratio. Its formula mass is 58.44 amu.

Note that the average masses of neutral sodium and chlorine atoms were used in this computation, rather than the masses for sodium cations and chlorine anions. This approach is perfectly acceptable when computing the formula mass of an ionic compound. Even though a sodium cation has a slightly smaller mass than a sodium atom (since it is missing an electron), this difference will be offset by the fact that a chloride anion is slightly more massive than a chloride atom (due to the extra electron). Moreover, the mass of an electron is negligibly small with respect to the mass of a typical atom. Even when calculating the mass of an isolated ion, the missing or additional electrons can generally be ignored, since their contribution to the overall mass is negligible, reflected only in the nonsignificant digits that will be lost when the computed mass is properly rounded. The few exceptions to this guideline are very light ions derived from elements with precisely known atomic masses.

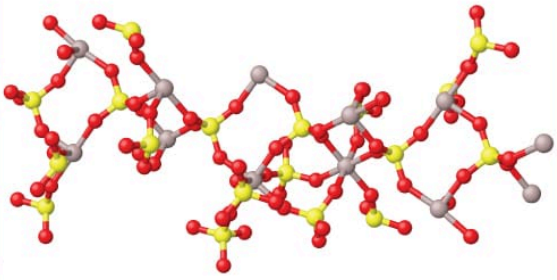
Example 4.2.2: Computing Formula Mass for an Ionic Compound

Aluminum sulfate, $Al_2(SO_4)_3$, is an ionic compound that is used in the manufacture of paper and in various water purification processes. What is the formula mass (amu) of this compound?

Solution

The formula for this compound indicates it contains Al^{3+} and SO_4^{2-} ions combined in a 2:3 ratio. For purposes of computing a formula mass, it is helpful to rewrite the formula in the simpler format, $Al_2S_3O_{12}$. Following the approach outlined above, the formula mass for this compound is calculated as follows:

Element	Quantity		Average atomic mass (amu)		Subtotal (amu)
Al	2	×	26.98	=	53.96
S	3	×	32.06	=	96.18
O	12	×	16.00	=	192.00
				Molecular mass	342.14



Exercise 4.2.2

Calcium phosphate, $Ca_3(PO_4)_2$, is an ionic compound and a common anti-caking agent added to food products. What is the formula mass (amu) of calcium phosphate?

Answer

310.18 amu

The Mole

The identity of a substance is defined not only by the types of atoms or ions it contains, but by the quantity of each type of atom or ion. For example, water, H_2O, and hydrogen peroxide, H_2O_2, are alike in that their respective molecules are composed of hydrogen and oxygen atoms. However, because a hydrogen peroxide molecule contains two oxygen atoms, as opposed to the water molecule, which has only one, the two substances exhibit very different properties. Today, we possess sophisticated instruments that allow the direct measurement of these defining microscopic traits; however, the same traits were originally derived from the measurement of macroscopic properties (the masses and volumes of bulk quantities of matter) using relatively simple tools (balances and volumetric glassware). This experimental approach required the introduction of a new unit for amount of substances, the *mole*, which remains indispensable in modern chemical science.

The mole is an amount unit similar to familiar units like pair, dozen, gross, etc. It provides a specific measure of *the number* of atoms or molecules in a bulk sample of matter. A mole is defined as the amount of substance containing the same number of discrete entities (such as atoms, molecules, and ions) as the number of atoms in a sample of pure ^{12}C weighing exactly 12 g. One Latin connotation for the word “mole” is “large mass” or “bulk,” which is consistent with its use as the name for this unit. The mole provides a link between an easily measured macroscopic property, bulk mass, and an extremely important fundamental property, number of atoms, molecules, and so forth.

The number of entities composing a mole has been experimentally determined to be $6.02214179 \times 10^{23}$, a fundamental constant named Avogadro’s number (N_A) or the Avogadro constant in honor of Italian scientist Amedeo Avogadro. This constant is properly reported with an explicit unit of “per mole,” a conveniently rounded version being $6.022 \times 10^{23}/\text{mol}$.

Consistent with its definition as an amount unit, 1 mole of any element contains the same number of atoms as 1 mole of any other element. The masses of 1 mole of different elements, however, are different, since the masses of the individual atoms are drastically different. The molar mass of an element (or compound) is the mass in grams of 1 mole of that substance, a property expressed in units of grams per mole (g/mol) (Figure 4.2.4).

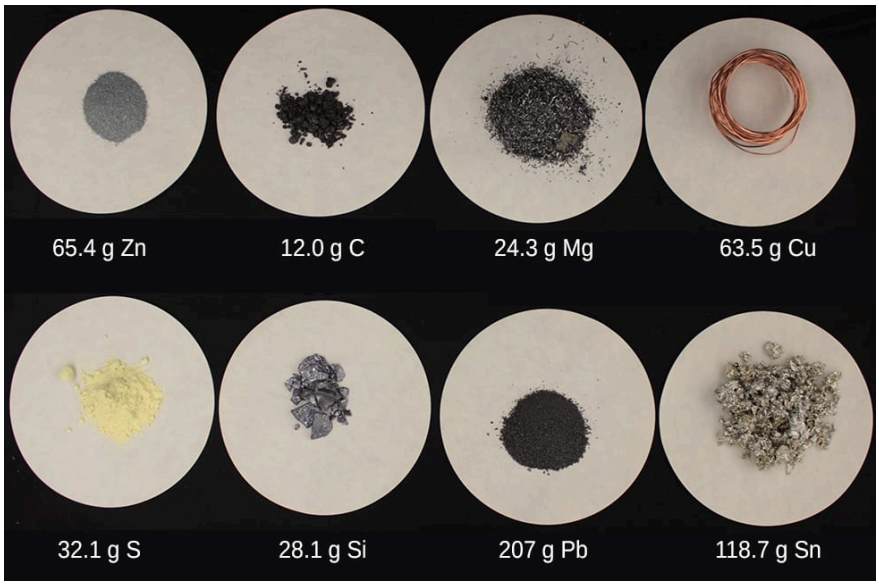


Figure 4.2.4: Each sample contains 6.022×10^{23} atoms —1.00 mol of atoms. From left to right (top row): 65.4 g zinc, 12.0 g carbon, 24.3 g magnesium, and 63.5 g copper. From left to right (bottom row): 32.1 g sulfur, 28.1 g silicon, 207 g lead, and 118.7 g tin. (credit: modification of work by Mark Ott).

Because the definitions of both the mole and the atomic mass unit are based on the same reference substance, ^{12}C, the molar mass of any substance is numerically equivalent to its atomic or formula weight in amu. Per the amu definition, a single ^{12}C atom weighs 12 amu (its atomic mass is 12 amu). According to the definition of the mole, 12 g of ^{12}C contains 1 mole of ^{12}C atoms (its molar mass is 12 g/mol). This relationship holds for all elements, since their atomic masses are measured relative to that of the amu-reference substance, ^{12}C. Extending this principle, the molar mass of a compound in grams is likewise numerically equivalent to its formula mass in amu (Figure 4.2.5).



Figure 4.2.5: Each sample contains 6.022×10^{23} molecules or formula units—1.00 mol of the compound or element. Clock-wise from the upper left: 130.2 g of $C_8H_{17}OH$ (1-octanol, formula mass 130.2 amu), 454.4 g of HgI_2 (mercury(II) iodide, formula mass 454.4 amu), 32.0 g of CH_3OH (methanol, formula mass 32.0 amu) and 256.5 g of S_8 (sulfur, formula mass 256.5 amu). (credit: Sahar Atwa).

Table* 4.2.1*: Mass of one mole of elements

Element	Average Atomic Mass (amu)	Molar Mass (g/mol)	Atoms/Mole
C	12.01	12.01	6.022×10^{23}

Element	Average Atomic Mass (amu)	Molar Mass (g/mol)	Atoms/Mole
H	1.008	1.008	6.022×10^{23}
O	16.00	16.00	6.022×10^{23}
Na	22.99	22.99	6.022×10^{23}
Cl	33.45	35.45	6.022×10^{23}

While atomic mass and molar mass are numerically equivalent, keep in mind that they are vastly different in terms of scale, as represented by the vast difference in the magnitudes of their respective units (amu versus g). To appreciate the enormity of the mole, consider a small drop of water after a rainfall. Although this represents just a tiny fraction of 1 mole of water (~18 g), it contains more water molecules than can be clearly imagined. If the molecules were distributed equally among the roughly seven billion people on earth, each person would receive more than 100 billion molecules.

YouTube Video

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

View this YouTube Video online

Video 4.2.1*: The mole is used in chemistry to represent* 6.022×10^{23} *of something, but it can be difficult to conceptualize such a large number. Watch this video and then complete the "Think" questions that follow. Explore more about the mole by reviewing the information under "Dig Deeper."*

The relationships between formula mass, the mole, and Avogadro's number can be applied to compute various quantities that describe the composition of substances and compounds. For example, if we know the mass and chemical composition of a substance, we can determine the number of moles and calculate number of atoms or molecules in the sample. Likewise, if we know the number of moles of a substance, we can derive the number of atoms or molecules and calculate the substance's mass.

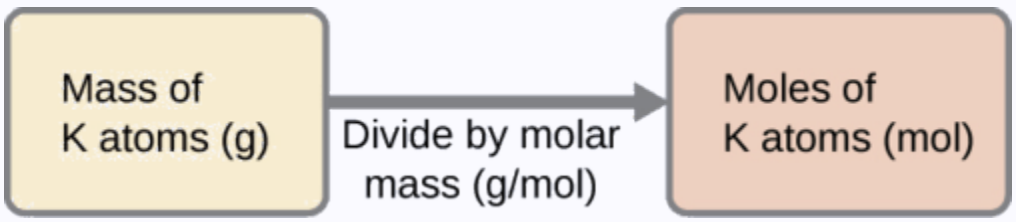
Example 4.2.3: Deriving Moles from Grams for an Element

According to nutritional guidelines from the US Department of Agriculture, the estimated average requirement for dietary potassium is 4.7 g. What is the estimated average requirement of potassium in moles?

Solution

The mass of K is provided, and the corresponding amount of K in moles is requested. Referring to the periodic table, the atomic mass of K is 39.10 amu, and so its molar mass is 39.10 g/mol. The given mass of K (4.7 g) is a bit more than one-tenth the molar mass (39.10 g), so a reasonable "ballpark" estimate of the number of moles would be slightly greater than 0.1 mol.

The molar amount of a substance may be calculated by dividing its mass (g) by its molar mass (g/mol):



The factor-label method supports this mathematical approach since the unit "g" cancels and the answer has units of "mol:"

$$4.7\ \cancel{g}\text{K}\left(\frac{\text{mol K}}{39.10\ \cancel{g}}\right) = 0.12\ \text{mol K} onumber \tag{4.2.1}$$

The calculated magnitude (0.12 mol K) is consistent with our ballpark expectation, since it is a bit greater than 0.1 mol.

Exercise 4.2.3: Beryllium

Beryllium is a light metal used to fabricate transparent X-ray windows for medical imaging instruments. How many moles of Be are in a thin-foil window weighing 3.24 g?

Answer

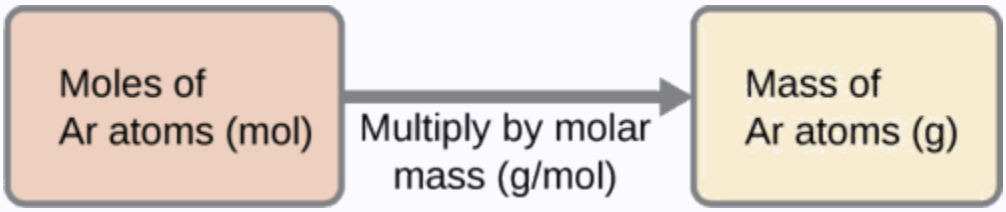
0.360 mol

Example 4.2.4: Deriving Grams from Moles for an Element

A liter of air contains 9.2×10^{-4} mol argon. What is the mass of Ar in a liter of air?

Solution

The molar amount of Ar is provided and must be used to derive the corresponding mass in grams. Since the amount of Ar is less than 1 mole, the mass will be less than the mass of 1 mole of Ar, approximately 40 g. The molar amount in question is approximately one-one thousandth (~10^{-3}) of a mole, and so the corresponding mass should be roughly one-one thousandth of the molar mass (~0.04 g):



In this case, logic dictates (and the factor-label method supports) multiplying the provided amount (mol) by the molar mass (g/mol):

$$9.2 \times 10^{-4}\ \cancel{\text{mol}}\ \text{Ar}\left(\frac{39.95\ \text{g}}{\cancel{\text{mol}}\ \text{Ar}}\right) = 0.037\ \text{g Ar} onumber \tag{4.2.2}$$

The result is in agreement with our expectations, around 0.04 g Ar.

Exercise 4.2.4

What is the mass of 2.561 mol of gold?

Answer

504.4 g

Example 4.2.6: Deriving Number of Atoms from Mass for an Element

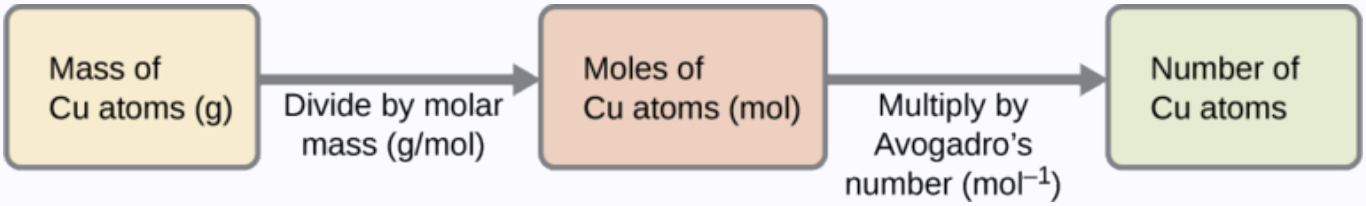
Copper is commonly used to fabricate electrical wire (Figure 4.2.6). How many copper atoms are in 5.00 g of copper wire?



Figure 4.2.6: Copper wire is composed of many, many atoms of Cu. (credit: Emilian Robert Vicol)

Solution

The number of Cu atoms in the wire may be conveniently derived from its mass by a two-step computation: first calculating the molar amount of Cu, and then using Avogadro's number (N_A) to convert this molar amount to number of Cu atoms:



Considering that the provided sample mass (5.00 g) is a little less than one-tenth the mass of 1 mole of Cu (~64 g), a reasonable estimate for the number of atoms in the sample would be on the order of one-tenth N_A, or approximately 10^{22} Cu atoms. Carrying out the two-step computation yields:

$$5.00 \cancel{g}\ \text{Cu} \left(\frac{\cancel{\text{mol}}\ \text{Cu}}{63.55 \cancel{g}}\right) \left(\frac{6.022 \times 10^{23}\ \text{atoms}}{\cancel{\text{mol}}}\right) = 4.74 \times 10^{22}\ \text{atoms of copper} \tag{4.2.3}$$

The factor-label method yields the desired cancellation of units, and the computed result is on the order of 10^{22} as expected.

Exercise 4.2.6

A prospector panning for gold in a river collects 15.00 g of pure gold. How many Au atoms are in this quantity of gold?

Answer

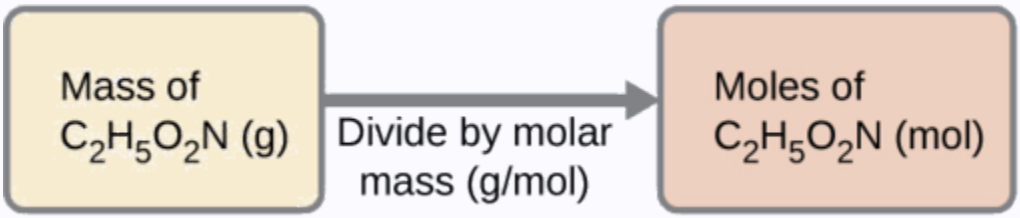
$4.586 \times 10^{22}\ \ Au$ atoms

Example 4.2.7: Deriving Moles from Grams for a Compound

Our bodies synthesize protein from amino acids. One of these amino acids is glycine, which has the molecular formula $C_2H_5O_2N$. How many moles of glycine molecules are contained in 28.35 g of glycine?

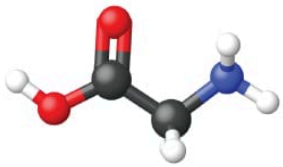
Solution

We can derive the number of moles of a compound from its mass following the same procedure we used for an element in Example 4.2.6:



The molar mass of glycine is required for this calculation, and it is computed in the same fashion as its molecular mass. One mole of glycine, $C_2H_5O_2N$, contains 2 moles of carbon, 5 moles of hydrogen, 2 moles of oxygen, and 1 mole of nitrogen:

Element	Quantity (mol element/ mol compound)		Molar mass (g/mol element)		Subtotal (g/mol compound)
C	2	×	12.01	=	24.02
H	5	×	1.008	=	5.040
O	2	×	16.00	=	32.00
N	1	×	14.007	=	14.007
Molecular mass (g/mol compound)					75.07



The provided mass of glycine (~28 g) is a bit more than one-third the molar mass (~75 g/mol), so we would expect the computed result to be a bit greater than one-third of a mole (~0.33 mol). Dividing the compound's mass by its molar mass yields:

$$28.35 \cancel{\text{ g}} \text{ glycine} \left(\frac{\text{mol glycine}}{75.07 \cancel{\text{ g}}} \right) = 0.378 \text{ mol glycine} onumber \tag{4.2.4}$$

This result is consistent with our rough estimate.

Exercise 4.2.7

How many moles of sucrose, $C_{12}H_{22}O_{11}$, are in a 25-g sample of sucrose?

Answer

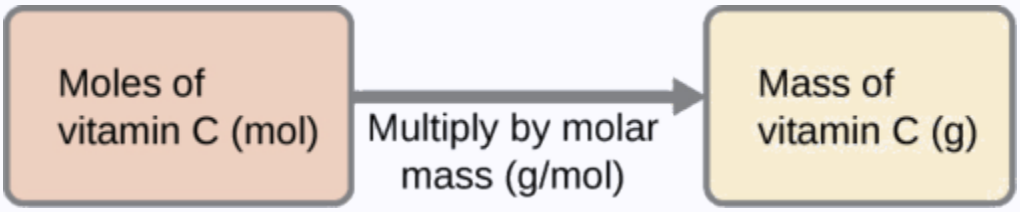
0.073 mol

Example 4.2.8: Deriving Grams from Moles for a Compound

Vitamin C is a covalent compound with the molecular formula $C_6H_8O_6$. The recommended daily dietary allowance of vitamin C for children aged 4–8 years is 1.42×10^{-4} mol. What is the mass of this allowance in grams?

Solution

As for elements, the mass of a compound can be derived from its molar amount as shown:



The molar mass for this compound is computed to be 176.124 g/mol. The given number of moles is a very small fraction of a mole (~10^{-4} or one-ten thousandth); therefore, we would expect the corresponding mass to be about one-ten thousandth of the molar mass (~0.02 g). Performing the calculation, we get:

$$1.42 \times 10^{-4} \cancel{\text{mol}}\ \text{vitamin C} \left(\frac{176.124\ \text{g}}{\cancel{\text{mol}}\ \text{vitamin C}} \right) = 0.0250\ \text{g vitamin C} onumber \tag{4.2.5}$$

This is consistent with the anticipated result.

Exercise 4.2.8

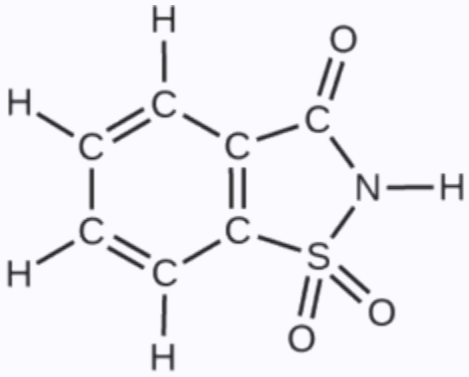
What is the mass of 0.443 mol of hydrazine, N_2H_4?

Answer

14.2 g

Example 4.2.9: Deriving the Number of Molecules from the Compound Mass

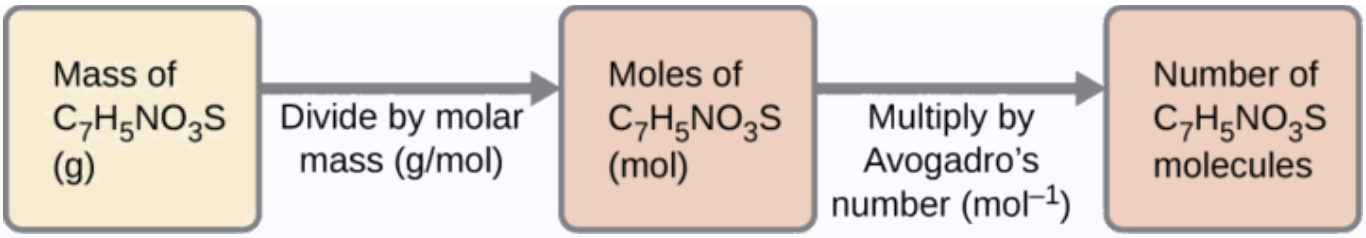
A packet of an artificial sweetener contains 40.0 mg of saccharin ($C_7H_5NO_3S$), which has the structural formula:



Given that saccharin has a molar mass of 183.18 g/mol, how many saccharin molecules are in a 40.0-mg (0.0400-g) sample of saccharin? How many carbon atoms are in the same sample?

Solution

The number of molecules in a given mass of compound is computed by first deriving the number of moles, as demonstrated in Example 4.2.8, and then multiplying by Avogadro's number:



Using the provided mass and molar mass for saccharin yields:

$$0.0400 \cancel{g}\ C_7H_5NO_3S \left(\frac{\cancel{mol}\ C_7H_5NO_3S}{183.18 \cancel{g}\ C_7H_5NO_3S}\right)\left(\frac{6.022 \times 10^{23}\ C_7H_5NO_3S\ \text{molecules}}{1\ \cancel{mol}\ C_7H_5NO_3S}\right) = 1.31 \times 10^{20}\ C_7H_5NO_3S\ \text{molecules} \quad (4.2.6)$$

The compound's formula shows that each molecule contains seven carbon atoms, and so the number of C atoms in the provided sample is:

$$1.31 \times 10^{20}\ C_7H_5NO_3S\ \text{molecules}\left(\frac{7\ \text{C atoms}}{1\ C_7H_5NO_3S\ \text{molecule}}\right) = 9.20 \times 10^{21}\ \text{C atoms} onumber \quad (4.2.7)$$

Exercise 4.2.9

How many C_4H_{10} molecules are contained in 9.213 g of this compound? How many hydrogen atoms?

Answer

- 9.545×10^{22} molecules C_4H_{10}
- 9.545×10^{23} atoms H

Summary

The formula mass of a substance is the sum of the average atomic masses of each atom represented in the chemical formula and is expressed in atomic mass units. The formula mass of a covalent compound is also called the molecular mass. A convenient amount unit for expressing very large numbers of atoms or molecules is the mole. Experimental measurements have determined the number of entities composing 1 mole of substance to be 6.022 × 10^{23}, a quantity called Avogadro's number. The mass in grams of 1 mole of substance is its molar mass. Due to the use of the same reference substance in defining the atomic mass unit and the mole, the formula mass (amu) and molar mass (g/mol) for any substance are numerically equivalent (for example, one H_2O molecule weighs approximately18 amu and 1 mole of H_2O molecules weighs approximately 18 g).

Footnotes

1. 1 Omiatek, Donna M., Amanda J. Bressler, Ann-Sofie Cans, Anne M. Andrews, Michael L. Heien, and Andrew G. Ewing. "The Real Catecholamine Content of Secretory Vesicles in the CNS Revealed by Electrochemical Cytometry." *Scientific Report* 3 (2013): 1447, accessed January 14, 2015, doi:10.1038/srep01447.

Glossary

Avogadro's number (N_A)
: experimentally determined value of the number of entities comprising 1 mole of substance, equal to 6.022 × 10^{23} mol^{-1}

formula mass
: sum of the average masses for all atoms represented in a chemical formula; for covalent compounds, this is also the molecular mass

mole
: amount of substance containing the same number of atoms, molecules, ions, or other entities as the number of atoms in exactly 12 grams of ^{12}C

molar mass
: mass in grams of 1 mole of a substance

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4.3: Types of Reactions

Learning Objectives

- Categorize reactions by type: synthesis, decomposition, single replacement, double replacement, and combustion.
- Given a redox reaction equation, identify the element being oxidized, the one being reduced, and any spectator ions.
- Write balanced equations for single replacement, double replacement, and combustion reactions.

Humans interact with one another in various and complex ways, and we classify these interactions according to common patterns of behavior. When two humans exchange information, we say they are communicating. When they exchange blows with their fists or feet, we say they are fighting. Faced with a wide range of varied interactions between chemical substances, scientists have likewise found it convenient (or even necessary) to classify chemical interactions by identifying common patterns of reactivity.

Decomposition Reactions

A ***decomposition reaction*** is a type of chemical reaction in which one reactant yields two or more products. The general form for a decomposition reaction is:

$$AB \rightarrow A + B$$

Consider the decomposition of calcium carbonate:

$$CaCO_{3(s)} \rightarrow CaO_{(s)} + CO_{2(g)}$$

calcium carbonate — calcium oxide — carbon dioxide

Synthesis Reactions

A **synthesis reaction** is a type of chemical reaction in which two or more simple substances combine to form a more complex product. The reactants may be elements or compounds, while the product is always a compound. The general equation for a synthesis reaction is:

$$A + B \rightarrow AB$$

For example, the synthesis of hydrochloric acid from hydrogen and chlorine:

$$2Cl + H_2 \rightarrow 2HCl$$

Oxidation-Reduction Reactions

Earth's atmosphere contains about 20% molecular oxygen, O_2, a chemically reactive gas that plays an essential role in the metabolism of aerobic organisms and in many environmental processes that shape the world. The term oxidation was originally used to describe chemical reactions involving O_2, but its meaning has evolved to refer to a broad and important reaction class known as *oxidation-reduction (redox) reactions*. A few examples of such reactions will be used to develop a clear picture of this classification.

Some redox reactions involve the transfer of electrons between reactant species to yield ionic products, such as the reaction between sodium and chlorine to yield sodium chloride:

$$2\,\mathrm{Na}(s)+\mathrm{Cl_2}(g) \rightarrow 2\,\mathrm{NaCl}(s) \tag{4.3.1}$$

It is helpful to view the process with regard to each individual reactant, that is, to represent the fate of each reactant in the form of an equation called a half-reaction:

$$2\,\mathrm{Na}(s) \rightarrow 2\,\mathrm{Na}^{+}(s) + 2\,\mathrm{e}^{-}$$
$$\mathrm{Cl}_2(g) + 2\,\mathrm{e}^{-} \rightarrow 2\,\mathrm{Cl}^{-}(s)$$

These equations show that Na atoms *lose electrons* while Cl atoms (in the Cl_2 molecule) *gain electrons*, the "s" subscripts for the resulting ions signifying they are present in the form of a solid ionic compound. For redox reactions of this sort, the loss and gain of electrons define the complementary processes that occur:

$$\textbf{oxidation} = \text{loss of electrons} \tag{4.3.2}$$
$$\textbf{reduction} = \text{gain of electrons} \tag{4.3.3}$$

In this reaction, then, sodium is *oxidized* and chlorine undergoes reduction. Viewed from a more active perspective, sodium functions as a reducing agent (reductant), since it provides electrons to (or reduces) chlorine. Likewise, chlorine functions as an oxidizing agent (oxidant), as it effectively removes electrons from (oxidizes) sodium.

$$\textbf{reducing agent} = \text{species that is oxidized} \tag{4.3.4}$$
$$\textbf{oxidizing agent} = \text{species that is reduced} \tag{4.3.5}$$

Some redox processes, however, do not involve the transfer of electrons. Consider, for example, a reaction similar to the one yielding NaCl:

$$\mathrm{H}_2(g) + \mathrm{Cl}_2(g) \rightarrow 2\,\mathrm{HCl}(g) \tag{4.3.6}$$

The product of this reaction is a covalent compound, so transfer of electrons in the explicit sense is not involved. To clarify the similarity of this reaction to the previous one and permit an unambiguous definition of redox reactions, a property called *oxidation number* has been defined. The oxidation number (or oxidation state) of an element in a compound is the charge its atoms would possess *if the compound was ionic*. The following guidelines are used to assign oxidation numbers to each element in a molecule or ion.

1. The oxidation number of an atom in an elemental substance is zero.
2. The oxidation number of a monatomic ion is equal to the ion's charge.
3. Oxidation numbers for common nonmetals are usually assigned as follows:
   - Hydrogen: +1 when combined with nonmetals, –1 when combined with metals
   - Oxygen: –2 in most compounds, sometimes –1 (so-called peroxides, $\mathrm{O_2}^{2-}$), very rarely $-\frac{1}{2}$ (so-called superoxides, $\mathrm{O_2}^{-}$), positive values when combined with F (values vary)
   - Halogens: –1 for F always, –1 for other halogens except when combined with oxygen or other halogens (positive oxidation numbers in these cases, varying values)
4. The sum of oxidation numbers for all atoms in a molecule or polyatomic ion equals the charge on the molecule or ion.

Note: The proper convention for reporting charge is to write the number first, followed by the sign (e.g., 2+), while oxidation number is written with the reversed sequence, sign followed by number (e.g., +2). This convention aims to emphasize the distinction between these two related properties.

Example 4.3.3: Assigning Oxidation Numbers

Follow the guidelines in this section of the text to assign oxidation numbers to all the elements in the following species:

a. H_2S
b. $\mathrm{SO_3}^{2-}$
c. Na_2SO_4

Solution

(a) According to guideline 1, the oxidation number for H is +1.

Using this oxidation number and the compound's formula, guideline 4 may then be used to calculate the oxidation number for sulfur:

$$\text{charge on } H_2S = 0 = (2 \times +1) + (1 \times x)$$

$$x = 0 - (2 \times +1) = -2$$

(b) Guideline 3 suggests the oxidation number for oxygen is –2.

Using this oxidation number and the ion's formula, guideline 4 may then be used to calculate the oxidation number for sulfur:

$$\text{charge on } {SO_3}^{2-} = -2 = (3 \times -2) + (1 \times x)$$
$$x = -2 - (3 \times -2) = +4$$

(c) For ionic compounds, it's convenient to assign oxidation numbers for the cation and anion separately.

According to guideline 2, the oxidation number for sodium is +1.

Assuming the usual oxidation number for oxygen (–2 per guideline 3), the oxidation number for sulfur is calculated as directed by guideline 4:

$$\text{charge on } {SO_4}^{2-} = -2 = (4 \times -2) + (1 \times x)$$

$$x = -2 - (4 \times -2) = +6$$

Exercise 4.3.3

Assign oxidation states to the elements whose atoms are underlined in each of the following compounds or ions:

a. $K\underline{N}O_3$
b. $\underline{Al}H_3$
c. $\underline{N}H_4^+$
d. [redacted]

Answer a

N, +5

Answer b

Al, +3

Answer c

N, –3

Answer d

P, +5

Using the oxidation number concept, an all-inclusive definition of redox reaction has been established. Oxidation-reduction (redox) reactions are those in which one or more elements involved undergo a change in oxidation number. While the vast majority of redox reactions involve changes in oxidation number for two or more elements, a few interesting exceptions to this rule do exist as shown below\). Definitions for the complementary processes of this reaction class are correspondingly revised as shown here:

$$\textbf{oxidation} = \text{increase in oxidation number} \tag{4.3.7}$$
$$\textbf{reduction} = \text{decrease in oxidation number} \tag{4.3.8}$$

Returning to the reactions used to introduce this topic, they may now both be identified as redox processes. In the reaction between sodium and chlorine to yield sodium chloride, sodium is oxidized (its oxidation number increases from 0 in Na to +1 in NaCl) and chlorine is reduced (its oxidation number decreases from 0 in Cl_2 to –1 in NaCl). In the reaction between molecular hydrogen and chlorine, hydrogen is oxidized (its oxidation number increases from 0 in H_2 to +1 in HCl) and chlorine is reduced (its oxidation number decreases from 0 in Cl_2 to –1 in HCl).Single-replacement reactions are redox reactions in which an ion in solution is displaced (or replaced) via the oxidation of a metallic element. One common example of this type of reaction is the acid oxidation of certain metals:

$$\mathrm{Zn}(s) + 2\,\mathrm{HCl}(aq) \rightarrow \mathrm{ZnCl_2}(aq) + \mathrm{H_2}(g) \tag{4.3.9}$$

Metallic elements may also be oxidized by solutions of other metal salts; for example:

$$\mathrm{Cu}(s) + 2\,\mathrm{AgNO_3}(aq) \rightarrow \mathrm{Cu(NO_3)_2}(aq) + 2\,\mathrm{Ag}(s) \tag{4.3.10}$$

This reaction may be observed by placing copper wire in a solution containing a dissolved silver salt. Silver ions in solution are reduced to elemental silver at the surface of the copper wire, and the resulting Cu^{2+} ions dissolve in the solution to yield a characteristic blue color (Figure 4.3.4).

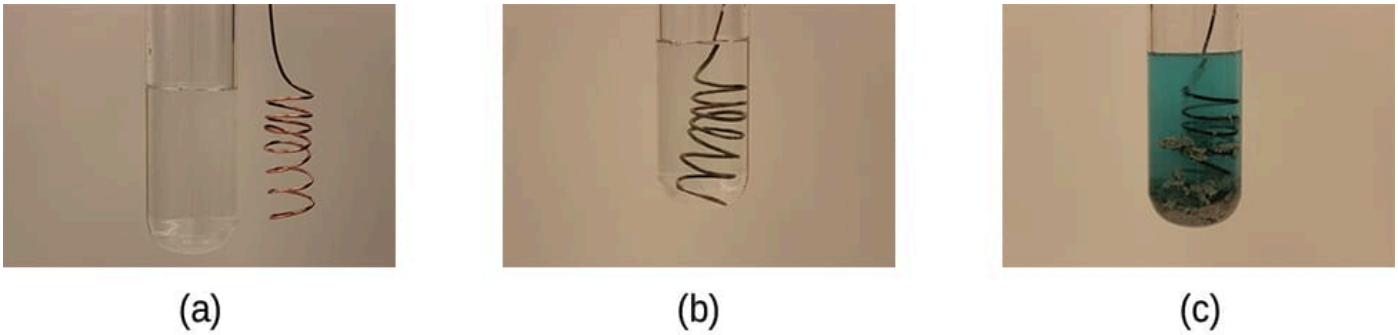


Figure 4.3.4: (a) A copper wire is shown next to a solution containing silver(I) ions. (b) Displacement of dissolved silver ions by copper ions results in (c) accumulation of gray-colored silver metal on the wire and development of a blue color in the solution, due to dissolved copper ions. (credit: modification of work by Mark Ott)

Example 4.3.4: Describing Redox Reactions

Identify which equations represent redox reactions, providing a name for the reaction if appropriate. For those reactions identified as redox, name the oxidant and reductant.

a. $\mathrm{ZnCO_3}(s) \rightarrow \mathrm{ZnO}(s) + \mathrm{CO_2}(g)$
b. $2\,\mathrm{Ga}(l) + 3\,\mathrm{Br_2}(l) \rightarrow 2\,\mathrm{GaBr_3}(s)$
c. $2\,\mathrm{H_2O_2}(aq) \rightarrow 2\,\mathrm{H_2O}(l) + \mathrm{O_2}(g)$
d. $\mathrm{BaCl_2}(aq) + \mathrm{K_2SO_4}(aq) \rightarrow \mathrm{BaSO_4}(s) + 2\,\mathrm{KCl}(aq)$
e. $\mathrm{C_2H_4}(g) + 3\,\mathrm{O_2}(g) \rightarrow 2\,\mathrm{CO_2}(g) + 2\,\mathrm{H_2O}(l)$

Solution

Redox reactions are identified per definition if one or more elements undergo a change in oxidation number.

a. This is not a redox reaction, since oxidation numbers remain unchanged for all elements.
b. This is a redox reaction. Gallium is oxidized, its oxidation number increasing from 0 in Ga(*l*) to +3 in $GaBr_3$(s). The reducing agent is Ga(*l*). Bromine is reduced, its oxidation number decreasing from 0 in Br_2(*l*) to –1 in $GaBr_3$(s). The oxidizing agent is Br_2(*l*).
c. This is a redox reaction. It is a particularly interesting process, as it involves the same element, oxygen, undergoing both oxidation and reduction (a so-called *disproportionation reaction)*. Oxygen is oxidized, its oxidation number increasing from –1 in H_2O_2(*aq*) to 0 in O_2(*g*). Oxygen is also reduced, its oxidation number decreasing from –1 in H_2O_2(*aq*) to –2 in H_2O(*l*). For disproportionation reactions, the same substance functions as an oxidant and a reductant.

d. This is not a redox reaction, since oxidation numbers remain unchanged for all elements.
e. This is a redox reaction (combustion). Carbon is oxidized, its oxidation number increasing from −2 in $C_2H_4(g)$ to +4 in $CO_2(g)$. The reducing agent (fuel) is $C_2H_4(g)$. Oxygen is reduced, its oxidation number decreasing from 0 in $O_2(g)$ to −2 in $H_2O(l)$. The oxidizing agent is $O_2(g)$.

Exercise 4.3.4

This equation describes the production of tin(II) chloride:

$$\mathrm{Sn}(s) + 2\,\mathrm{HCl}(g) \rightarrow \mathrm{SnCl_2}(s) + \mathrm{H_2}(g) onumber \tag{4.3.11}$$

Is this a redox reaction? If so, provide a more specific name for the reaction if appropriate, and identify the oxidant and reductant.

Answer

Yes, a single-replacement reaction. Sn(s) is the reductant, HCl(g) is the oxidant.

Combustion Reactions

Several subclasses of redox reactions are recognized, including combustion reactions in which the reductant (also called a *fuel*) and oxidant (often, but not necessarily, molecular oxygen) react vigorously and produce significant amounts of heat, and often light, in the form of a flame. This is the basic structure of a combustion reaction in which oxygen from air is the oxidizing agent:

$$\mathrm{fuel} + \mathrm{O_2} \rightarrow \mathrm{CO_2} + \mathrm{H_2O} \tag{4.3.12}$$

Note that the equation must be balanced based on the type of fuel being burnt.

Solid rocket-fuel reactions such as the one depicted below are combustion processes. A typical propellant reaction in which solid aluminum is oxidized by ammonium perchlorate is represented by this equation:

$$10\,\mathrm{Al}(s) + 6\,\mathrm{NH_4ClO_4}(s) \rightarrow 4\,\mathrm{Al_2O_3}(s) + 2\,\mathrm{AlCl_3}(s) + 12\,\mathrm{H_2O}(g) + 3\,\mathrm{N_2}(g) \tag{4.3.13}$$

Watch a brief video showing the test firing of a small-scale, prototype, hybrid rocket engine planned for use in the new Space Launch System being developed by NASA. The first engines firing at 3 s (green flame) use a liquid fuel/oxidant mixture, and the second, more powerful engines firing at 4 s (yellow flame) use a solid mixture.

YouTube Video

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

View this YouTube Video online

Precipitation Reactions and Solubility Rules

A precipitation reaction is one in which dissolved substances react to form one (or more) solid products. Many reactions of this type involve the exchange of ions between ionic compounds in aqueous solution and are sometimes referred to as *double displacement*, *double replacement*, or *metathesis* reactions. These reactions are common in nature and are responsible for the

formation of coral reefs in ocean waters and kidney stones in animals. They are used widely in industry for production of a number of commodity and specialty chemicals. Precipitation reactions also play a central role in many chemical analysis techniques, including spot tests used to identify metal ions and *gravimetric methods* for determining the composition of matter (see the last module of this chapter).

The extent to which a substance may be dissolved in water, or any solvent, is quantitatively expressed as its solubility, defined as the maximum concentration of a substance that can be achieved under specified conditions. Substances with relatively large solubilities are said to be soluble. A substance will precipitate when solution conditions are such that its concentration exceeds its solubility. Substances with relatively low solubilities are said to be insoluble, and these are the substances that readily precipitate from solution. More information on these important concepts is provided in the text chapter on solutions. For purposes of predicting the identities of solids formed by precipitation reactions, one may simply refer to patterns of solubility that have been observed for many ionic compounds (Table 4.3.1).

Table 4.3.1***:*** *Solubilities of Common Ionic Compounds in Water*

Soluble compounds contain	**Exceptions** to these solubility rules include
• group 1 metal cations (Li^+, Na^+, K^+, Rb^+, and Cs^+) and ammonium ion (NH_4^+) • the halide ions (Cl^-, Br^-, and I^-) • the acetate ($C_2H_3O_2^-$), bicarbonate (HCO_3^-), nitrate (NO_3^-), and chlorate (ClO_3^-) ions • the sulfate (SO_4^-) ion	• halides of Ag^+, Hg_2^{2+}, and Pb^{2+} • sulfates of Ag^+, Ba^{2+}, Ca^{2+}, Hg_2^{2+}, Pb^{2+}, and Sr^{2+}
Insoluble compounds contain	**Exceptions** to these insolubility rules include
• carbonate (CO_3^{2-}), chromate (CrO_4^{2-}), phosphate (PO_4^{3-}), and sulfide (S^{2-}) ions • hydroxide ion (OH^-)	• compounds of these anions with group 1 metal cations and ammonium ion • hydroxides of group 1 metal cations and Ba^{2+}

A vivid example of precipitation is observed when solutions of potassium iodide and lead nitrate are mixed, resulting in the formation of solid lead iodide:

$$2\,\mathrm{KI}(aq) + \mathrm{Pb(NO_3)_2}(aq) \rightarrow \mathrm{PbI_2}(s) + 2\,\mathrm{KNO_3}(aq) \tag{4.3.14}$$

This observation is consistent with the solubility guidelines: The only insoluble compound among all those involved is lead iodide, one of the exceptions to the general solubility of iodide salts.

The net ionic equation representing this reaction is:

$$\blacksquare(aq) + 2\,\mathrm{I^-}(aq) \rightarrow \mathrm{PbI_2}(s) \tag{4.3.15}$$

Lead iodide is a bright yellow solid that was formerly used as an artist's pigment known as iodine yellow (Figure 4.3.1). The properties of pure PbI_2 crystals make them useful for fabrication of X-ray and gamma ray detectors.



Figure 4.3.1: A precipitate of PbI_2 forms when solutions containing Pb^{2+} and I^- are mixed. (credit: Der Kreole/Wikimedia Commons)

The solubility guidelines in Table 4.3.1 may be used to predict whether a precipitation reaction will occur when solutions of soluble ionic compounds are mixed together. One merely needs to identify all the ions present in the solution and then consider if possible cation/anion pairing could result in an insoluble compound. For example, mixing solutions of silver nitrate and sodium fluoride will yield a solution containing Ag^+, NO_3^-, Na^+, and F^- ions. Aside from the two ionic compounds originally present in the solutions, $AgNO_3$ and NaF, two additional ionic compounds may be derived from this collection of ions: $NaNO_3$ and AgF. The solubility guidelines indicate all nitrate salts are soluble but that AgF is one of the exceptions to the general solubility of fluoride salts. A precipitation reaction, therefore, is predicted to occur, as described by the following equations:

$$\mathrm{NaF}(aq)+\mathrm{AgNO_3}(aq) \rightarrow \mathrm{AgF}(s)+\mathrm{NaNO_3}(aq) \quad (\text{molecular}) \tag{4.3.16}$$

$$\mathrm{Ag^+}(aq) + \mathrm{F^-}(aq) \rightarrow \mathrm{AgF}(s) \quad (\text{net ionic}) \tag{4.3.17}$$

Example 4.3.1: Predicting Precipitation Reactions

Predict the result of mixing reasonably concentrated solutions of the following ionic compounds. If precipitation is expected, write a balanced net ionic equation for the reaction.

a. potassium sulfate and barium nitrate
b. lithium chloride and silver acetate
c. lead nitrate and ammonium carbonate

Solution

(a) The two possible products for this combination are KNO_3 and $BaSO_4$. The solubility guidelines indicate $BaSO_4$ is insoluble, and so a precipitation reaction is expected. The net ionic equation for this reaction, derived in the manner detailed in the previous module, is

$$[redacted](aq) + \mathrm{SO_4}^{2-}(aq) \rightarrow \mathrm{BaSO_4}(s) onumber \tag{4.3.18}$$

(b) The two possible products for this combination are $LiC_2H_3O_2$ and AgCl. The solubility guidelines indicate AgCl is insoluble, and so a precipitation reaction is expected. The net ionic equation for this reaction, derived in the manner detailed in the previous module, is

$$\mathrm{Ag^+}(aq) + \mathrm{Cl^-}(aq) \rightarrow \mathrm{AgCl}(s) onumber \tag{4.3.19}$$

(c) The two possible products for this combination are $PbCO_3$ and NH_4NO_3. The solubility guidelines indicate $PbCO_3$ is insoluble, and so a precipitation reaction is expected. The net ionic equation for this reaction, derived in the manner detailed

in the previous module, is

$$\blacksquare(aq) + \mathrm{CO_3}^{2-}(aq) \rightarrow \mathrm{PbCO_3}(s) onumber \tag{4.3.20}$$

Steps for Writing Displacement Reactions

1. Figure out what the reactants and products will be.
   - The cations will switch places in the products for double replacement reactions.
   - The element will replace the cation in the reacting compound and result in a new product for single replacement reactions.
2. Make sure that all of the compound formulas are correctly written based on the oxidation state of the elements involved.
3. Balance the equation.

Summary

Chemical reactions are classified according to similar patterns of behavior. Redox reactions involve a change in oxidation number for one or more reactant elements. Precipitation reactions involve the formation of one or more insoluble products. A synthesis reaction is a type of chemical reaction in which two or more simple substances combine to form a more complex product. A decomposition reaction is a type of chemical reaction in which one reactant yields two or more products.

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4.4: Reaction Stoichiometry

Learning Objectives

- Use stoichiometry to calculate the amount (in moles or grams) of a particular substance produced or used in a chemical reaction.
- Use stoichiometry to determine molecular formulas.

A balanced chemical equation provides a great deal of information in a very succinct format. Chemical formulas provide the identities of the reactants and products involved in the chemical change, allowing classification of the reaction. Coefficients provide the relative numbers of these chemical species, allowing a quantitative assessment of the relationships between the amounts of substances consumed and produced by the reaction. These quantitative relationships are known as the reaction's stoichiometry, a term derived from the Greek words *stoicheion* (meaning "element") and *metron* (meaning "measure"). In this module, the use of balanced chemical equations for various stoichiometric applications is explored.

The general approach to using stoichiometric relationships is similar in concept to the way people go about many common activities. Cooking, for example, offers an appropriate comparison. Suppose a recipe for making eight pancakes calls for 1 cup pancake mix, $\frac{3}{4}$ cup milk, and one egg. The "equation" representing the preparation of pancakes per this recipe is

$$1 \text{ cup mix} + \frac{3}{4} \text{ cup milk} + 1 \text{ egg} \rightarrow 8 \text{ pancakes} \tag{4.4.1}$$

If two dozen pancakes are needed for a big family breakfast, the ingredient amounts must be increased proportionally according to the amounts given in the recipe. For example, the number of eggs required to make 24 pancakes is

$$24 \ \cancel{\text{pancakes}} \times \frac{1 \text{ egg}}{8 \ \cancel{\text{pancakes}}} = 3 \text{ eggs} \tag{4.4.2}$$

Balanced chemical equations are used in much the same fashion to determine the amount of one reactant required to react with a given amount of another reactant, or to yield a given amount of product, and so forth. **The coefficients in the balanced equation are used to derive stoichiometric factors (mole bridges)** that permit computation of the desired quantity. To illustrate this idea, consider the production of ammonia by reaction of hydrogen and nitrogen:

$$\mathrm{N_2}(g) + 3\,\mathrm{H_2}(g) \rightarrow 2\,\mathrm{NH_3}(g) \tag{4.4.3}$$

This equation shows that ammonia molecules are produced from hydrogen molecules in a 2:3 ratio, and stoichiometric factors may be derived using any amount (number) unit:

$$\frac{2NH3\ molecules}{3H2\ molecules} \text{ or } \frac{2\ doz\ NH3\ molecules}{3\ doz\ H2\ molecules} \text{ or } \frac{2\ mol\ NH3\ molecules}{3\ mol\ H2\ molecules} \tag{4.4.4}$$

These stoichiometric factors can be used to compute the number of ammonia molecules produced from a given number of hydrogen molecules, or the number of hydrogen molecules required to produce a given number of ammonia molecules. Similar factors may be derived for any pair of substances in any chemical equation.

Example 4.4.1: Moles of Reactant Required in a Reaction

How many moles of $\mathrm{I_2}$ are required to react with 0.429 mol of Al according to the following equation (see Figure 4.4.2)?

$$2\,\mathrm{Al} + 3\,\mathrm{I_2} \rightarrow 2\,\mathrm{AlI_3} \tag{4.4.5}$$

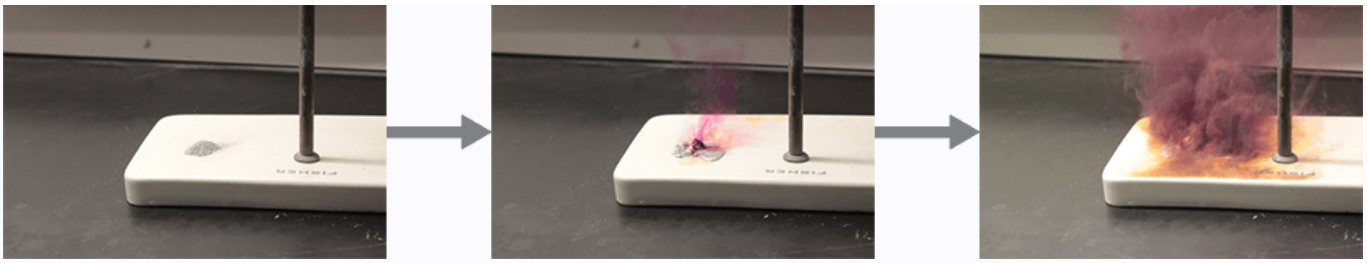
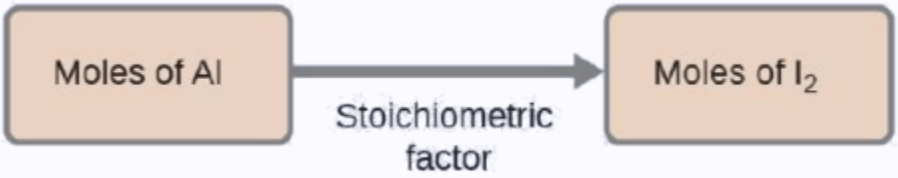


Figure 4.4.1: Aluminum and iodine react to produce aluminum iodide. The heat of the reaction vaporizes some of the solid iodine as a purple vapor. (credit: modification of work by Mark Ott)

Solution

Referring to the balanced chemical equation, the stoichiometric factor (mole bridge) relating the two substances of interest is $\frac{3\ mol\ I2}{2\ mol\ Al}$. The molar amount of iodine is derived by multiplying the provided molar amount of aluminum by this factor:



$$\begin{aligned}\text{mol I}_2 &= 0.429\ \cancel{\text{mol Al}} \times \frac{3\ \text{mol I}_2}{2\ \cancel{\text{mol Al}}} \\ &= 0.644\ \text{mol I}_2\end{aligned}$$

Exercise 4.4.1

How many moles of $Ca(OH)_2$ are required to react with 1.36 mol of H_3PO_4 to produce $Ca_3(PO_4)_2$ according to the equation $3\,\text{Ca(OH)}_2 + 2\,\text{H}_3\text{PO}_4 \rightarrow \text{Ca}_3(\text{PO}_4)_2 + 6\,\text{H}_2\text{O}$?

Answer

2.04 mol

Example 4.4.2: Number of Product Molecules Generated by a Reaction

How many carbon dioxide molecules are produced when 0.75 mol of propane is combusted according to this equation?

$$\text{C}_3\text{H}_8 + 5\,\text{O}_2 \rightarrow 3\,\text{CO}_2 + 4\,\text{H}_2\text{O} \tag{4.4.6}$$

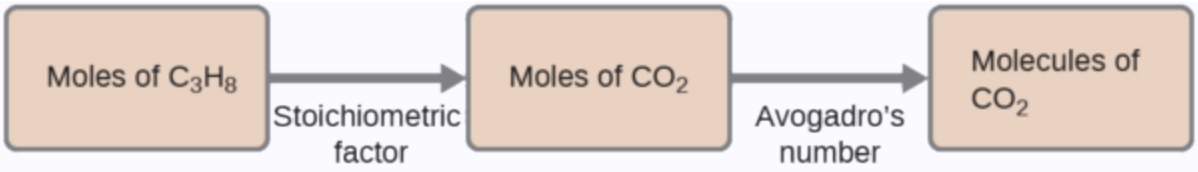
Solution

The approach here is the same as for Example 4.4.1, though the absolute number of molecules is requested, not the number of moles of molecules. This will simply require use of the moles-to-numbers conversion factor, Avogadro's number.

The balanced equation shows that carbon dioxide is produced from propane in a 3:1 ratio:

$$\frac{3\ mol\ CO2}{1\ mol\ C3H8} \tag{4.4.7}$$

Using this stoichiometric factor, the provided molar amount of propane, and Avogadro's number,



$$0.75 \ \cancel{\text{mol } C_3H_8} \times \frac{3 \ \cancel{\text{mol } CO_2}}{1 \ \cancel{\text{mol } C_3H_8}} \times \frac{6.022 \times 10^{23} \ \text{CO}_2 \text{ molecules}}{\cancel{\text{mol } CO_2}} = 1.4 \times 10^{24} \ \text{CO}_2 \text{ molecules} \tag{4.4.8}$$

Exercise 4.4.1

How many NH_3 molecules are produced by the reaction of 4.0 mol of $Ca(OH)_2$ according to the following equation:

$$(\text{NH}_4)_2\text{SO}_4 + \text{Ca(OH)}_2 \ \rightarrow 2\,\text{NH}_3 + \text{CaSO}_4 + 2\,\text{H}_2\text{O} onumber \tag{4.4.9}$$

Answer

4.8×10^{24} NH_3 molecules

These examples illustrate the ease with which the amounts of substances involved in a chemical reaction of known stoichiometry may be related. Directly measuring numbers of atoms and molecules is, however, not an easy task, and the practical application of stoichiometry requires that we use the more readily measured property of mass.

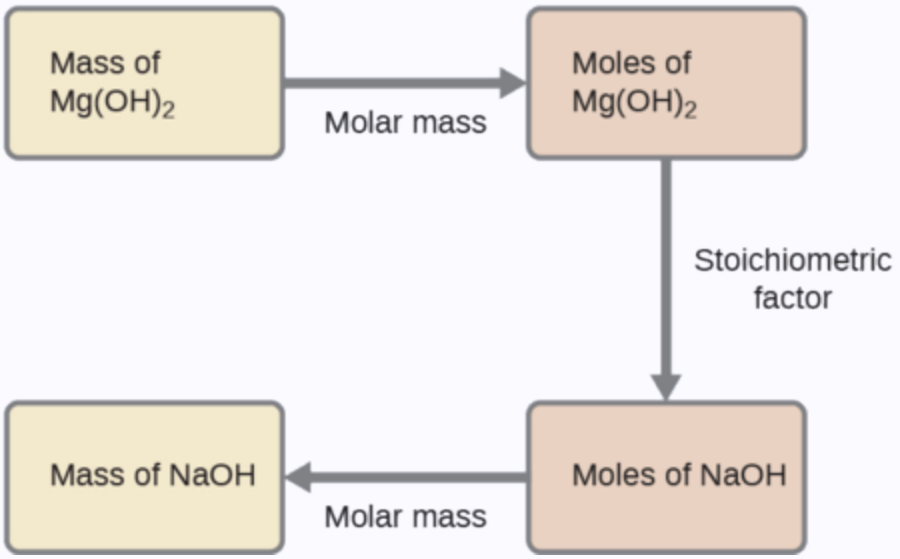
Example 4.4.3: Relating Masses of Reactants and Products

What mass of sodium hydroxide, NaOH, would be required to produce 16 g of the antacid milk of magnesia [magnesium hydroxide, $Mg(OH)_2$] by the following reaction?

$$\text{MgCl}_2(aq) + 2\,\text{NaOH}(aq) \rightarrow \text{Mg(OH)}_2(s) + 2\,\text{NaCl}(aq)$$

Solution

The approach used previously in Examples 4.4.1 and 4.4.2 is likewise used here; that is, we must derive an appropriate stoichiometric factor from the balanced chemical equation and use it to relate the amounts of the two substances of interest. In this case, however, masses (not molar amounts) are provided and requested, so additional steps of the sort learned in the previous chapter are required. The calculations required are outlined in this flowchart:



$$16\ \cancel{\text{g Mg(OH)}_2} \times \frac{1\ \cancel{\text{mol Mg(OH)}_2}}{58.3\ \cancel{\text{g Mg(OH)}_2}} \times \frac{2\ \cancel{\text{mol NaOH}}}{1\ \cancel{\text{mol Mg(OH)}_2}} \times \frac{40.0\ \text{g NaOH}}{\cancel{\text{mol NaOH}}} = 22\ \text{g NaOH} \tag{4.4.10}$$

Exercise 4.4.3

What mass of gallium oxide, Ga_2O_3, can be prepared from 29.0 g of gallium metal? The equation for the reaction is $4\,\text{Ga} + 3\,\text{O}_2 \rightarrow 2\,\text{Ga}_2\text{O}_3$.

Answer

39.0 g

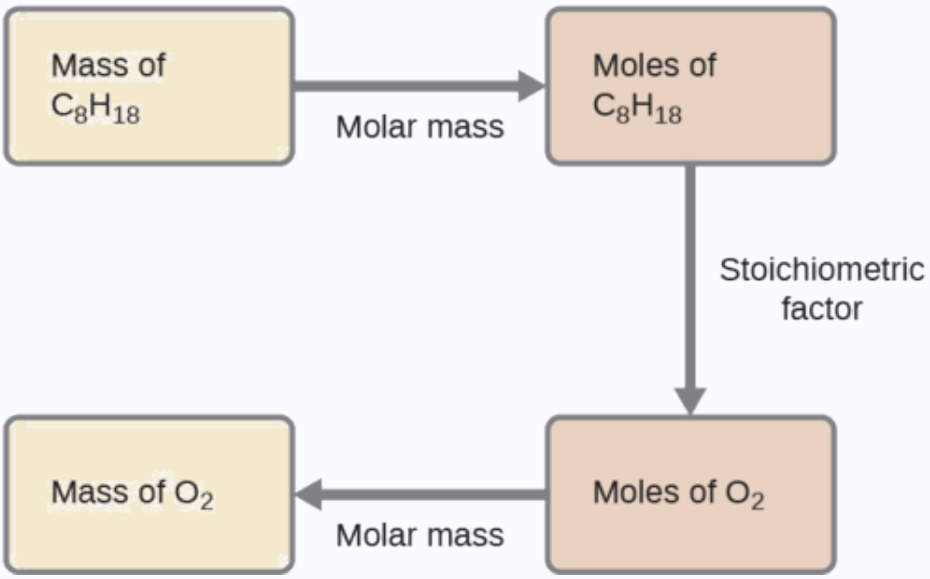
Example 4.4.4: Relating Masses of Reactants

What mass of oxygen gas, O_2, from the air is consumed in the combustion of 702 g of octane, C_8H_{18}, one of the principal components of gasoline?

$$2\,\text{C}_8\text{H}_{18} + 25\,\text{O}_2 \rightarrow 16\,\text{CO}_2 + 18\,\text{H}_2\text{O} onumber \tag{4.4.11}$$

Solution

The approach required here is the same as for the Example 4.4.3, differing only in that the provided and requested masses are both for reactant species.



$$702\ \cancel{\text{g C}_8\text{H}_{18}} \times \frac{1\ \cancel{\text{mol C}_8\text{H}_{18}}}{114.23\ \cancel{\text{g C}_8\text{H}_{18}}} \times \frac{25\ \cancel{\text{mol O}_2}}{2\ \cancel{\text{mol C}_8\text{H}_{18}}} \times \frac{32.00\ \text{g O}_2}{\cancel{\text{mol O}_2}} = 2.46 \times 10^3\ \text{g O}_2$$

Exercise 4.4.4

What mass of CO is required to react with 25.13 g of Fe_2O_3 according to the equation $\text{Fe}_2\text{O}_3 + 3\,\text{CO} \rightarrow 2\,\text{Fe} + 3\,\text{CO}_2$?

Answer

13.22 g

These examples illustrate just a few instances of reaction stoichiometry calculations. Numerous variations on the beginning and ending computational steps are possible depending upon what particular quantities are provided and sought (volumes, solution concentrations, and so forth). Regardless of the details, all these calculations share a common essential component: the use of stoichiometric factors derived from balanced chemical equations. Figure 4.4.2 provides a general outline of the various computational steps associated with many reaction stoichiometry calculations.

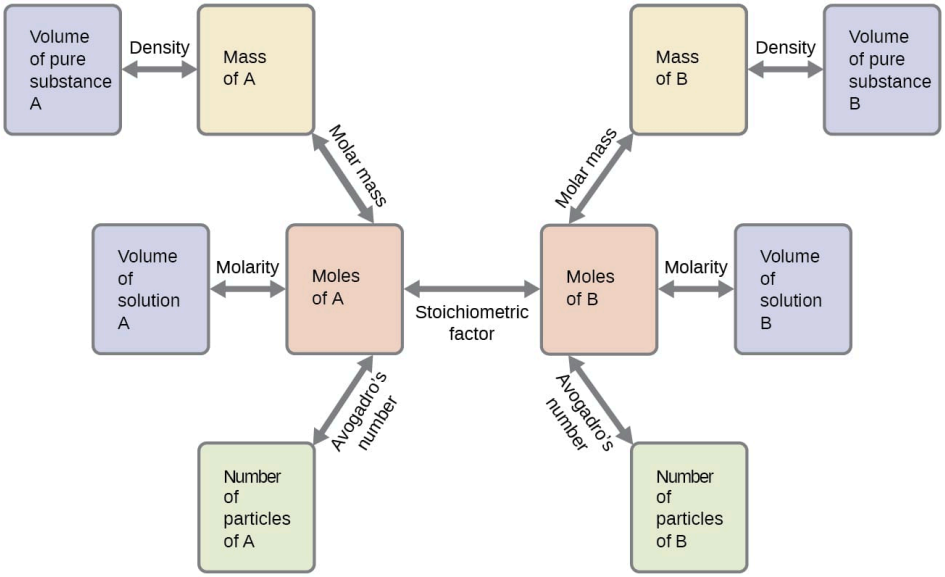


Figure 4.4.2: The flowchart depicts the various computational steps involved in most reaction stoichiometry calculations.

Using Stoichiometry to Determine Molecular Formulas

Since a chemical formula is the mole ratios of elements when they combine, if we are given the mass of the elements that reacted with each other, we should be able to figure the moles from this, and then the ratios.

Example 4.4.4: Determining A Molecular Formula from Mole Ratios

If 1.5875 g of copper react with 0.8875 g of chlorine to form copper chloride, write the chemical formula for the copper chloride.

Step 1: Determine the number of moles of an element which reacted. In this case, Cu.

$$1.5875 \ \cancel{\text{g Cu}} \times \frac{1 \ \cancel{\text{mol Cu}}}{63.5 \ \cancel{\text{g Cu}}} = 0.025 \ \text{mol Cu} \tag{4.4.12}$$

Step 2: Determine the number of moles of the other element which reacted. In this case, Cl.

$$0.8875 \ \cancel{\text{g Cl}} \times \frac{1 \ \cancel{\text{mol Cl}}}{35.5 \ \cancel{\text{g Cl}}} = 0.025 \ \text{mol Cl} \tag{4.4.13}$$

Step 3: Make a ratio of moles one element in a compound to moles of the other element in the compound (as a general rule, the larger number will go on top of the ratio.) Since we are trying to find the formula of copper chloride, we would use moles copper to and moles chlorine.

0.025 moles Cu / 0.025 moles Cl = 1 mole Cu / 1 mole Cl or Cu Cl

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4.5: Reaction Yields

Learning Objectives

- Calculate the yield for a reaction under specified conditions.
- Identify the limiting reactant in a chemical equation.

The relative amounts of reactants and products represented in a balanced chemical equation are often referred to as *stoichiometric amounts*. All the exercises of the preceding module involved stoichiometric amounts of reactants. For example, when calculating the amount of product generated from a given amount of reactant, it was assumed that any other reactants required were available in stoichiometric amounts (or greater). In this module, more realistic situations are considered, in which reactants are not present in stoichiometric amounts.

Limiting Reactant

Consider another food analogy, making grilled cheese sandwiches (Figure 4.5.1):

$$1 \text{ slice of cheese} + 2 \text{ slices of bread} \rightarrow 1 \text{ sandwich} \tag{4.5.1}$$

Stoichiometric amounts of sandwich ingredients for this recipe are bread and cheese slices in a 2:1 ratio. Provided with 28 slices of bread and 11 slices of cheese, one may prepare 11 sandwiches per the provided recipe, using all the provided cheese and having six slices of bread left over. In this scenario, the number of sandwiches prepared has been *limited* by the number of cheese slices, and the bread slices have been provided in *excess*.

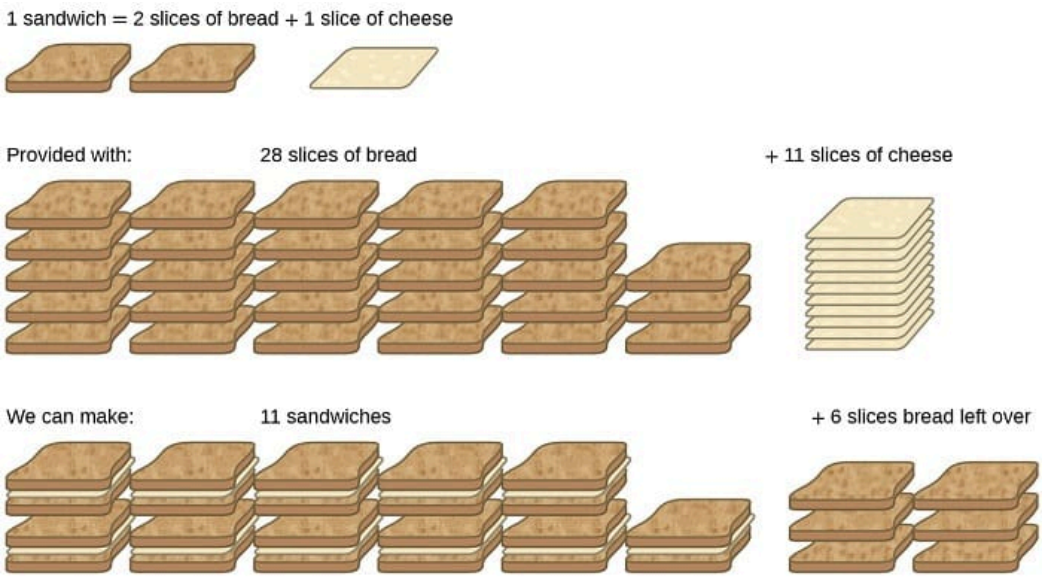


Figure 4.5.1: Sandwich making can illustrate the concepts of limiting and excess reactants.

Consider this concept now with regard to a chemical process, the reaction of hydrogen with chlorine to yield hydrogen chloride:

$$\mathrm{Cl_2}(g) \rightarrow 2\,\mathrm{HCl}(g) \tag{4.5.2}$$

The balanced equation shows the 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 nonreacted.

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

$$\text{mol HCl produced} = 3\ \text{mol H}_2 \times \frac{2\ \text{mol HCl}}{1\ \text{mol H}_2} = 6\ \text{mol HCl} \tag{4.5.3}$$

Complete reaction of the provided chlorine would produce

$$\text{mol HCl produced} = 2\ \text{mol Cl}_2 \times \frac{2\ \text{mol HCl}}{1\ \text{mol Cl}_2} = 4\ \text{mol HCl} \tag{4.5.4}$$

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 4.5.2).

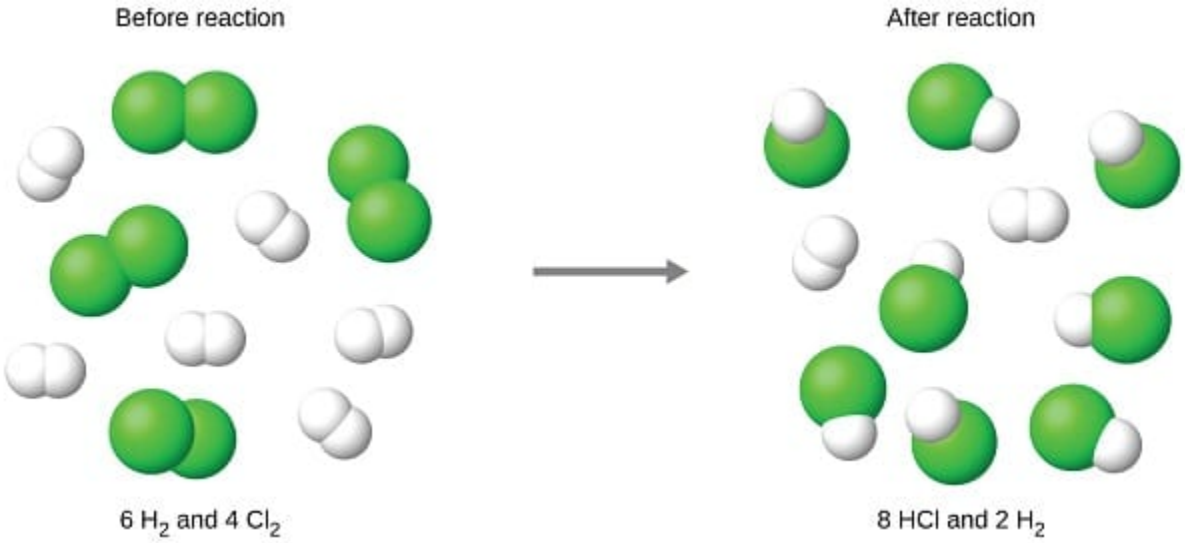


Figure 4.5.2: When H_2 and Cl_2 are combined in nonstoichiometric amounts, one of these reactants will limit the amount of HCl that can be produced. This illustration shows a reaction in which hydrogen is present in excess and chlorine is the limiting reactant.

Example 4.5.1: Identifying the Limiting Reactant

Silicon nitride is a very hard, high-temperature-resistant ceramic used as a component of turbine blades in jet engines. It is prepared according to the following equation:

$$3\,\text{Si}(s) + 2\,\text{N}_2(g) \rightarrow \text{Si}_3\text{N}_4(s) \tag{4.5.5}$$

Which is the limiting reactant when 2.00 g of Si and 1.50 g of N_2 react?

Solution

Compute the provided molar amounts of reactants, and then compare these amounts to the balanced equation to identify the limiting reactant.

$$\text{mol Si} = 2.00\ \cancel{\text{g Si}} \times \frac{1\ \text{mol Si}}{28.09\ \cancel{\text{g Si}}} = 0.0712\ \text{mol Si} \tag{4.5.6}$$

$$\text{mol N}_2 = 1.50 \cancel{\text{ g N}_2} \times \frac{1 \text{ mol N}_2}{28.02 \cancel{\text{ g N}_2}} = 0.0535 \text{ mol N}_2 \tag{4.5.7}$$

The provided Si:N_2 molar ratio is:

$$\frac{0.0712 \text{ mol Si}}{0.0535 \text{ mol N}_2} = \frac{1.33 \text{ mol Si}}{1 \text{ mol N}_2} \tag{4.5.8}$$

The stoichiometric Si:N_2 ratio is:

$$\frac{3 \text{ mol Si}}{2 \text{ mol N}_2} = \frac{1.5 \text{ mol Si}}{1 \text{ mol N}_2} \tag{4.5.9}$$

Comparing these ratios shows that Si is provided in a less-than-stoichiometric amount, and so is the limiting reactant.

Exercise 4.5.1

Which is the limiting reactant when 5.00 g of H_2 and 10.0 g of O_2 react and form water?

Answer

O_2

Glossary

actual yield
: amount of product formed in a reaction

excess reactant
: reactant present in an amount greater than required by the reaction stoichiometry

limiting reactant
: reactant present in an amount lower than required by the reaction stoichiometry, thus limiting the amount of product generated

theoretical yield

: amount of product that may be produced from a given amount of reactant(s) according to the reaction stoichiometry

Contributors

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4.6: Exothermic and Endothermic Reactions

Learning Objectives

- Describe three ways to speed up a reaction.
- Differentiate between reversible exothermic, irreversible exothermic, and endothermic reactions and draw appropriate graphs to represent each which include axis labels, activation energy, and the effect a catalyst would have on the graph.

Energy

Energy can be defined as the capacity to supply heat or do work. One type of work (*w*) is the process of causing matter to move against an opposing force. For example, we do work when we inflate a bicycle tire—we move matter (the air in the pump) against the opposing force of the air surrounding the tire.

Like matter, energy comes in different types. One scheme classifies energy into two types: potential energy, the energy an object has because of its relative position, composition, or condition, and kinetic energy, the energy that an object possesses because of its motion. Water at the top of a waterfall or dam has potential energy because of its position; when it flows downward through generators, it has kinetic energy that can be used to do work and produce electricity in a hydroelectric plant (Figure 4.6.2). A battery has potential energy because the chemicals within it can produce electricity that can do work.

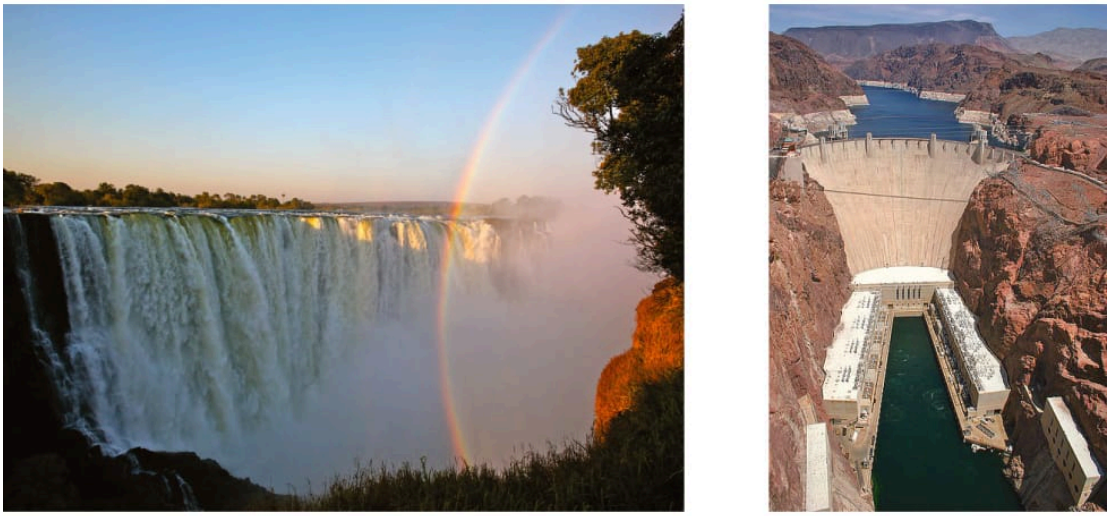


Figure 4.6.2: (a) Water that is higher in elevation, for example, at the top of Victoria Falls, has a higher potential energy than water at a lower elevation. As the water falls, some of its potential energy is converted into kinetic energy. (b) If the water flows through generators at the bottom of a dam, such as the Hoover Dam shown here, its kinetic energy is converted into electrical energy. (credit a: modification of work by Steve Jurvetson; credit b: modification of work by “curimedia”/Wikimedia commons).

Energy can be converted from one form into another, but all of the energy present before a change occurs always exists in some form after the change is completed. This observation is expressed in the law of conservation of energy: during a chemical or physical change, energy can be neither created nor destroyed, although it can be changed in form. (This is also one version of the first law of thermodynamics, as you will learn later.)

When one substance is converted into another, there is always an associated conversion of one form of energy into another. Heat is usually released or absorbed, but sometimes the conversion involves light, electrical energy, or some other form of energy. For example, chemical energy (a type of potential energy) is stored in the molecules that compose gasoline. When gasoline is combusted within the cylinders of a car’s engine, the rapidly expanding gaseous products of this chemical reaction generate mechanical energy (a type of kinetic energy) when they move the cylinders’ pistons.

According to the law of conservation of matter (seen in an earlier chapter), there is no detectable change in the total amount of matter during a chemical change. When chemical reactions occur, the energy changes are relatively modest and the mass changes are too small to measure, so the laws of conservation of matter and energy hold well. However, in nuclear reactions, the energy changes are much larger (by factors of a million or so), the mass changes are measurable, and matter-energy conversions are significant. This will be examined in more detail in a later chapter on nuclear chemistry. To encompass both chemical and nuclear changes, we combine these laws into one statement: The total quantity of matter and energy in the universe is fixed.

Thermal Energy, Temperature, and Heat

Thermal energy is kinetic energy associated with the random motion of atoms and molecules. Temperature is a quantitative measure of "hot" or "cold." When the atoms and molecules in an object are moving or vibrating quickly, they have a higher average kinetic energy (KE), and we say that the object is "hot." When the atoms and molecules are moving slowly, they have lower KE, and we say that the object is "cold" (Figure 4.6.3). Assuming that no chemical reaction or phase change (such as melting or vaporizing) occurs, increasing the amount of thermal energy in a sample of matter will cause its temperature to increase. And, assuming that no chemical reaction or phase change (such as condensation or freezing) occurs, decreasing the amount of thermal energy in a sample of matter will cause its temperature to decrease.

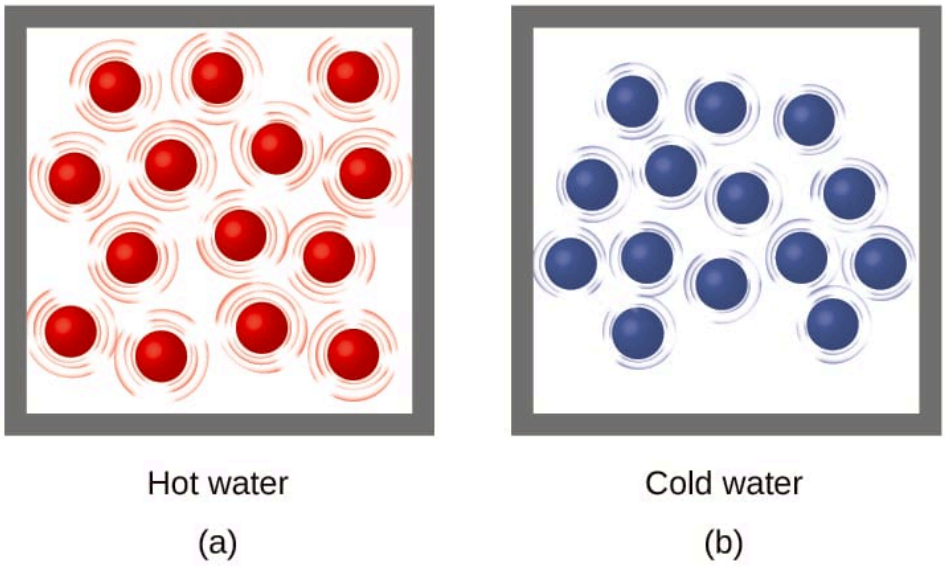


Figure 4.6.3: (a) The molecules in a sample of hot water move more rapidly than (b) those in a sample of cold water.

PhET Simulation

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

View this PhET Simulation online

Most substances expand as their temperature increases and contract as their temperature decreases. This property can be used to measure temperature changes, as shown in Figure 4.6.4. The operation of many thermometers depends on the expansion and contraction of substances in response to temperature changes.

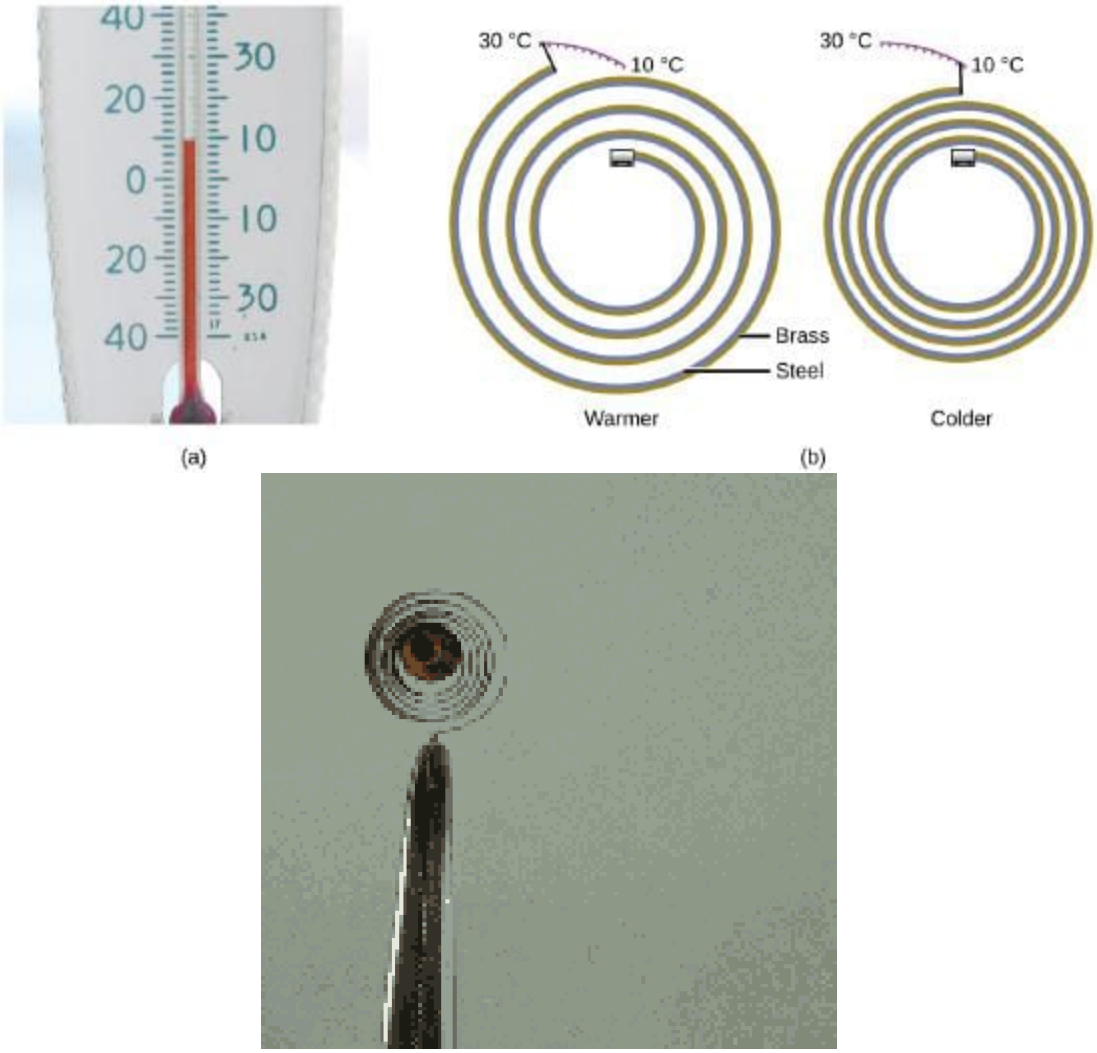


Figure 4.6.4: (a) In an alcohol or mercury thermometer, the liquid (dyed red for visibility) expands when heated and contracts when cooled, much more so than the glass tube that contains the liquid. (b) In a bimetallic thermometer, two different metals (such as brass and steel) form a two-layered strip. When heated or cooled, one of the metals (brass) expands or contracts more than the other metal (steel), causing the strip to coil or uncoil. Both types of thermometers have a calibrated scale that indicates the temperature. (credit a: modification of work by "dwstucke"/Flickr). (c) The demonstration allows one to view the effects of heating and cooling a coiled bimetallic strip.A bimetallic coil from a thermometer reacts to the heat from a lighter, by uncoiling and then coiling back up when the lighter is removed. Animation used with permission from Hustvedt (via Wikipedia)

Heat (q) is the transfer of thermal energy between two bodies at different temperatures. Heat flow (a redundant term, but one commonly used) increases the thermal energy of one body and decreases the thermal energy of the other. Suppose we initially have a high temperature (and high thermal energy) substance (H) and a low temperature (and low thermal energy) substance (L). The atoms and molecules in H have a higher average KE than those in L. If we place substance H in contact with substance L, the thermal energy will flow spontaneously from substance H to substance L. The temperature of substance H will decrease, as will the average KE of its molecules; the temperature of substance L will increase, along with the average KE of its molecules. Heat flow will continue until the two substances are at the same temperature (Figure 4.6.5).

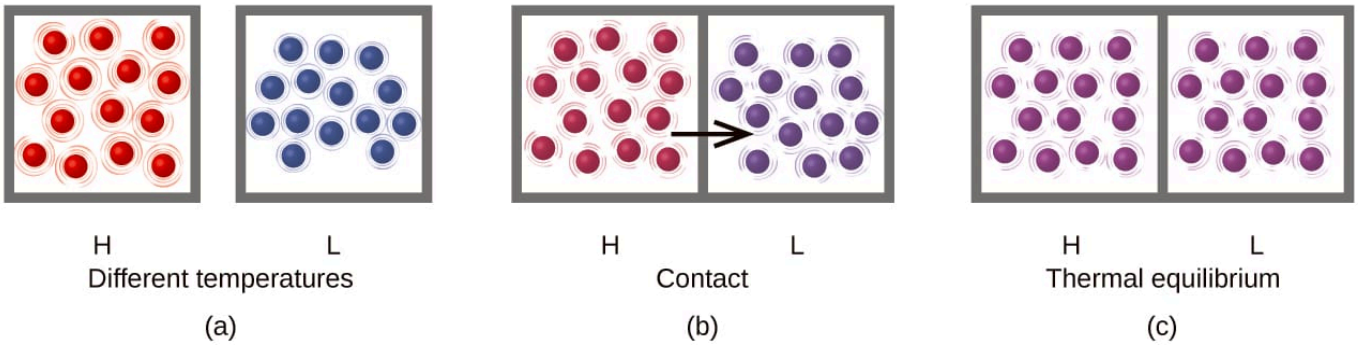


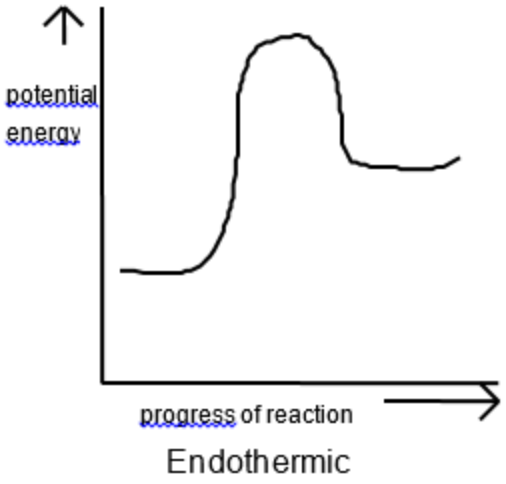
Figure 4.6.5: (a) Substances H and L are initially at different temperatures, and their atoms have different average kinetic energies. (b) When they are put into contact with each other, collisions between the molecules result in the transfer of kinetic (thermal) energy from the hotter to the cooler matter. (c) The two objects reach "thermal equilibrium" when both substances are at the same temperature, and their molecules have the same average kinetic energy.

Matter undergoing chemical reactions and physical changes can release or absorb heat. A change that releases heat is called an **exothermic process**. For example, the combustion reaction that occurs when using an oxyacetylene torch is an exothermic process—this process also releases energy in the form of light as evidenced by the torch's flame (Figure 4.6.6*a*). A reaction or change that absorbs heat is an **endothermic process**. A cold pack used to treat muscle strains provides an example of an endothermic process. When the substances in the cold pack (water and a salt like ammonium nitrate) are brought together, the resulting process absorbs heat, leading to the sensation of cold.

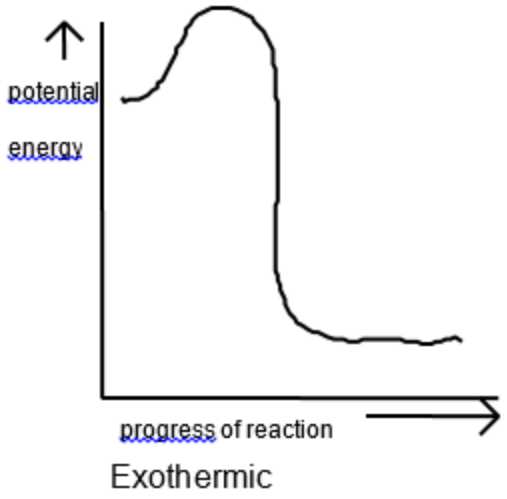


Figure 4.6.6: (a) An oxyacetylene torch produces heat by the combustion of acetylene in oxygen. The energy released by this exothermic reaction heats and then melts the metal being cut. The sparks are tiny bits of the molten metal flying away. (b) A cold pack uses an endothermic process to create the sensation of cold. (credit a: modification of work by "Skatebiker"/Wikimedia commons).

Each chemical bond is stored energy. For a reaction to occur, the bonds of the reactants must be broken. This process always requires energy. At the same time, the bonds between the products must form, this process always releases energy. If the energy required to break the bonds of the reactants is less than that given off by the formation of bonds in the products, the excess energy will be released from the reaction. If the energy required to break the bonds of the reactants is greater than that given off by the formation of bonds in the products, the reaction will need an external supply of energy and the reaction will be endothermic.



Endothermic

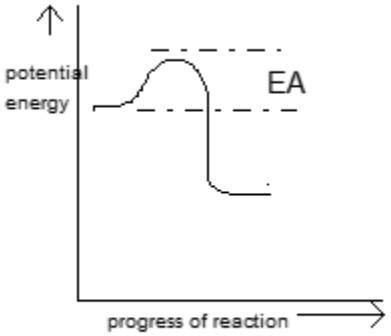


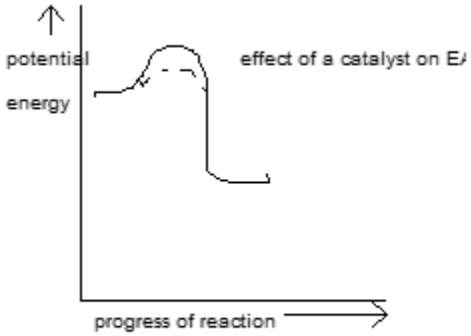
Exothermic

Activation energy: Also called energy of activation. It is the amount of energy required to get the reaction started. Some reactions require very little energy, in others a great deal of energy is required.

Catalyst: Is a substance that when added to the reaction reduces the amount of energy required to start the reaction, but itself does not become part of the product and thus can be re-used in the reaction. If a catalyst is involved in a reaction, it is written above the arrow, as it does not become a part of the product.

$$\text{Sucrose} + H_2O \xrightarrow{HCl} \text{Glucose} + \text{fructose}$$

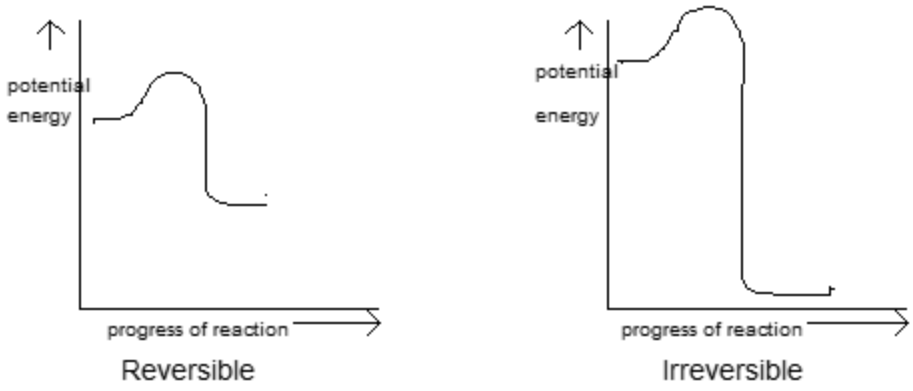




EA = energy of activation

Reversible reaction: The energy hill may be approached from either side.

Irreversible reaction: The change in energy is so great, that the energy hill cannot be approached from the opposite side.



Glossary

endothermic process
chemical reaction or physical change that absorbs heat

exothermic process
chemical reaction or physical change that releases heat

heat (*q*)
transfer of thermal energy between two bodies

kinetic energy
energy of a moving body, in joules, equal to $\frac{1}{2}mv^2$ (where *m* = mass and *v* = velocity)

potential energy
energy of a particle or system of particles derived from relative position, composition, or condition

thermal energy
kinetic energy associated with the random motion of atoms and molecules

thermochemistry
study of measuring the amount of heat absorbed or released during a chemical reaction or a physical change

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4.7: Unit 4 Practice Problems

Problem 1.

Balance the following equations:

1. $PCl_5(s)+H_2O(l) \rightarrow POCl_3(l)+HCl(aq)$
2. $Cu(s)+HNO_3(aq) \rightarrow Cu(NO_3)_2(aq)+H_2O(l)+NO(g)$
3. $H_2(g)+I_2(s) \rightarrow HI(s)$
4. $Fe(s)+O_2(g) \rightarrow Fe_2O_3(s)$
5. $Na(s)+H_2O(l) \rightarrow NaOH(aq)+H_2(g)$
6. $(NH_4)_2Cr_2O_7(s) \rightarrow Cr_2O_3(s)+N_2(g)+H_2O(g)$

Answer 1

$$PCl_5(s)+H_2O(l) \rightarrow POCl_3(l)+2HCl$$

Answer 2

$$3Cu(s)+8HNO_3(aq) \rightarrow 3Cu(NO_3)_2(aq)+4H_2O(l)+2NO(g)$$

Answer 3

$$H_2(g)+I_2(s) \rightarrow 2HI(s)$$

Answer 4

$$4Fe(s)+3O_2(g) \rightarrow 2Fe_2O_3(s)$$

Answer 5

$$2Na(s)+2H_2O(l) \rightarrow 2NaOH(aq)+H_2(g)$$

Answer 6

$$(NH_4)_2Cr_2O_7(s) \rightarrow Cr_2O_3(s)+N_2(g)+4H_2O(g)$$

Question 2.

Write the balanced chemical equation for the combustion of gaseous butane, C_4H_{10}.

Answer

$$2C_4H_{10}(g)+13O_2(g) \rightarrow 8CO_2(g)+10H_2O(g)$$

Question 3.

What is the mass of 0.54mole of CO_2?

Answer

$$0.54 \cancel{\text{ mole}} \times \frac{44 \text{ g}}{1 \cancel{\text{ mole}}} = 24 \text{ g} \tag{4.7.1}$$

Question 4.

230 grams of O is how many moles of O?

Answer

$$230 \cancel{g} \times \frac{1 \text{ mole}}{16 \cancel{g}} = 14 \text{ moleO} \tag{4.7.2}$$

Question 5.

What is the mass of 1.00 mole of magnesium nitrate?

Answer

The formula for magnesium nitrate is $Mg(NO_3)_2$ mass = (1 x 24.31) + (2 x 14.01) + (6 x 16.00) = 148 g $Mg(NO_3)_2$

Question 6.

How many atoms are on 1.76 moles of phosphorus?

Answer

$$1.76 \cancel{\text{mole}} \times \frac{6.02\text{e}23 \text{ atoms}}{1 \cancel{\text{mole}}} = 1.06\text{e}24 \text{ atoms} \tag{4.7.3}$$

1.06×10^{24} atoms

Question 7.

What is the mass of 3.57×10^{24} molecules of CaS?

Answer

3.57×10^{24} molecules | 1 mole / 6.02×10^{23} molecules | 72.14 g CaS / 1 mole CaS = 428 g CaS

Question 8.

Automotive air bags inflate when a sample of sodium azide, NaN_3, is very rapidly decomposed.

$2NaN_3(s) \rightarrow 2Na(s) + 3N_2(g)$

If this reaction begins with only 1.46 moles of NaN_3, how many moles of nitrogen gas, N2, will be produced?

Answer

$$1.47 \text{ moles } NaN_3 \left| \frac{3 \text{ moles } N_2}{2 \text{ moles } NaN_3} \right. = 2.20 \text{ moles } N_2$$

Question 9.

What mass of silver oxide, Ag_2O, is required to produce 25.0 g of silver sulfadiazine, $AgC_{10}H_9N_4SO_2$, from the reaction of silver oxide and sulfadiazine?

$2C_{10}H_{10}N_4SO_2 + Ag_2O \rightarrow 2AgC_{10}H_9N_4SO_2 + H_2O$

Answer

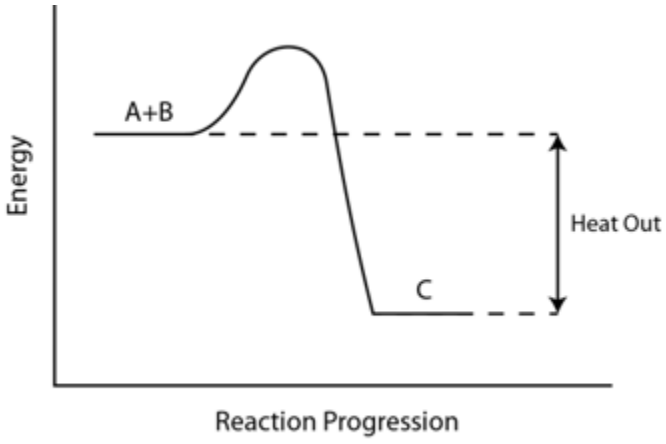
$$25.0 \text{ g} \left| \frac{1 \text{ mole}}{357.172 \text{ g}} \right| \frac{1 \text{ mole } Ag_2O}{2 \text{ mole } AgC_{10}H_9N_4SO_2} \left| \frac{231.8 \text{ g } Ag_2O}{1 \text{ mole } Ag_2O} \right.$$

= 8.11 g Ag_2O

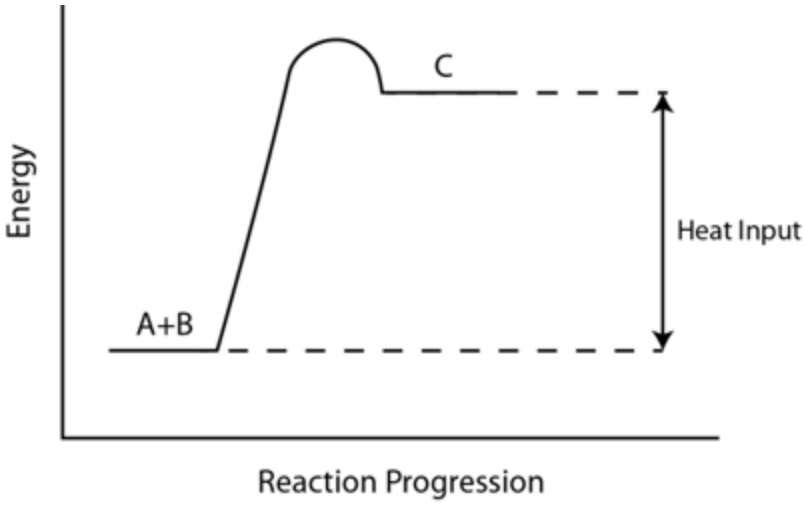
Question 10.

Identify the energy graphs A and B as being for an endothermic or exothermic reaction.

A.



B.



Answer

A. exothermic B. endothermic

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5: ACTIVITY SERIES

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General Chemistry

This chapter introduces the concept of activity, or an element's ability to oxidize, and provides the framework for writing activity series.

Unit 5 Objectives

By the end of this unit, you will be able to:

- Define activity and determine which element in a reaction is more active given the balanced chemical equation
- Write an activity series for 3 or more elements based on a multiple replacement reactions.

5.1: Activity Series
5.2: Unit 5 Practice Problems

Contributors

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5.1: Activity Series

Learning Objectives

- Define activity and determine which element in a reaction is more active given the balanced chemical equation
- Write an activity series for 3 or more elements based on a multiple replacement reactions.

Activity Series

Groups, IA, IIA, and IIIA tend to lose electrons. Transition elements tend to lose electrons too, but are more difficult to predict. Some elements lose their electrons more easily than others.

Activity is the ability of an element to lose electrons (oxidize)**.** Notice that this is the opposite of electronegativity which is a value associated with how easily an element gains electrons.

Activity series list elements according to how easily they lose electrons.

Figure 5.1.1, provides an example of an activity series.

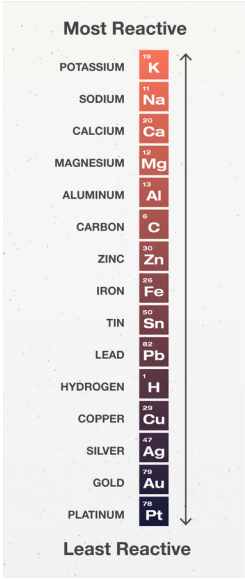


Figure 5.1.1: An activity series for common metals.

example: Zn and Cu both tend to lose 2 electrons, but the zinc wants to lose them more, so much so that it can force the two electrons on Cu^{2+} and make it become Cu again.

$$Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$$

We say that Zn is more active than the copper. Positive ions (cations) can't just be floating around by themselves in solution, they have to have a negative ion (anion) to balance them. In the equation below, nitrate is there to balance the charges.

$$Zn + Cu(NO_3)_2 \rightarrow Zn(NO_3)_2 + Cu$$

Nitrate ion in both the reactants and the products has a -1 charge. When an ion keeps the same charge in a reaction and is just there to balance out the opposite charges, we call it a **Spectator Ion**.

Suppose a piece of copper was placed in a solution of $SnCl_2$, and nothing happens. In this case the tin is more active than the copper, as the copper is not able to force its electrons onto the tin.

$$Cu + SnCl_2 \rightarrow NR$$

If a piece of zinc is placed in the $SnCl_2$ a reaction occurs.

$$Zn + SnCl_2 \rightarrow ZnCl_2 + Sn$$

Using all three of the reactions above, we can make an activity series for Cu, Zn, and Tin. In the first reaction we determined that zinc is more active than copper and the third reaction shows us that zinc is also more active than tin. Therefore zinc is the most active metal. The second equation shows us that tin is more active then copper. Basined on this information, an activity series for these three metals would be:

Zn Sn Cu

most active least active

Metals and Acid

Acids lose H+ ions when in solution. If you place a metal that is more active than the H+ in an acid the metal will force the electrons onto the hydrogen ion. The Hydrogen ions then link up and form hydrogen gas, H_2. When conducting such an experiment the H_2 appears as bubbles.

$$Mg + 2HCl \rightarrow MgCl_2 + H_2$$

Is the Mg higher or lower in activity than hydrogen?

Mg is higher in activity than H+

Writing Equations to Make an activity Series

Notice that all of the above equations are displacement reactions. Regardless of what the description of the reaction, the equation will always be a single or double displacement reaction which we learned about in Unit 4. Let's review the steps to writing displacement reactions.

1. Figure out what the reactants and products will be.
   - The cations will switch places in the products for double replacement reactions.
   - The element will replace the cation in the reacting compound and result in a new product for single replacement reactions.
2. Make sure that all of the compound formulas are correctly written based on the oxidation state of the elements involved.
3. Balance the equation.

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5.2: Unit 5 Practice Problems

Question 1.

Given that the following reactions occur, rank the elements Li, K, Ca, and Ba in an activity series from highest activity to lowest.

$2K + BaCl_2 \rightarrow 2KCl + Ba$

$Li + KCl \rightarrow LiCl + K$

$Ba + CaCl_2 \rightarrow 2BaCl + Ca$

Answer

Li, K, Ba, Ca

Question 2.

Write the balanced chemical equations for the following reactions and then rank the metals in an activity series from highest to lowest.

- magnesium metal reacts with zinc (II) nitrate to form magnesium nitrate and zinc metal.
- zinc metal reacts with iron (III) nitrate to form zinc (II) nitrate and iron metal.
- iron metal reacts with cobalt (II) nitrate to form iron (III) nitrate and cobalt metal.

Answer

$Mg + Zn(NO_3)_2 \rightarrow Mg(NO_3)_2 + Zn$

$3Zn + 2Fe(NO_3)_3 \rightarrow 3Zn(NO_3)_2 + 2Fe$

$2Fe + 3Co(NO_3)_2 \rightarrow 2Fe(NO_3)_3 + 3Co$

Mg, Zn, Fe, Co

Question 3.

Write the balanced chemical equations for the following reactions and indicate which metals are more active than hydrogen.

- magnesium reacts with HCl to form magnesium chloride and H_2 gas.
- gallium reacts with HCl to form gallium chloride and H_2 gas.
- Sr reacts with nitric acid (HNO_3) to form strontium nitrate and H_2 gas.
- Hg does not react with nitric acid.

Answer

$Mg + 2HCl \rightarrow MgCl_2 + H_2$

$2Ga + 6HCl \rightarrow 2GaCl_3 + 3H_2$

$Sr + 2HNO_3 \rightarrow Sr(NO_3)_2 + H_2$

$Hg + HNO_3 \rightarrow$ No reaction

Mg, Ga, and Sr are more active than hydrogen and Hg is less active.

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6: CONCENTRATIONS

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General Chemistry

This chapter will describe some of the fundamental chemical principles related to the solubility and provide the quantitative methods for calculating concentrations.

Unit 6 Objectives

By the end of this unit, you will be able to:

- Define solution and differentiate between the solute and the solvent in a solution.
- Predict the solubility of two substances based on their polarity.
- Explain“like dissolves like”.
- Define electrolyte and list examples of common electrolytes.
- Describe the effects of temperature and pressure on solubility
- Explain the degrees of solubility possible for liquid-liquid solutions
- Define emulsifying agent.
- Draw a picture of the molecular structure of an emulsifying agent and label the polar and nonpolar ends.
- Give 3 examples of common emulsifying agents.
- Calculate solution concentrations in g/L, g/dL, %, mg/dL, mg%, and molarity (M)
- Perform dosage calculations.
- Appropriately use the solution dilution formula.
- Accurately use the % by volume formula for calculations.
- Perform computations relating a solution’s concentration and its components’ volumes and/or masses.
- Calculate concentration in ppm and ppb. Use the resulting concentrations to evaluate the level of toxins in a sample.
- Accurately perform a titration to calculate the unknown concentration of a solution in a neutralization reaction.
- Perform stoichiometric calculations using typical titration data.

6.1: The Dissolution Process

6.2: Electrolytes

6.3: Solubility

6.4: Colloids and Emulsifying Agents

6.5: Weight by Volume and Molarity

6.6: Other Units for Solution Concentrations

6.7: Titrations - Lab 8

6.8: Unit 6 Practice Problems

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6.1: The Dissolution Process

Learning Objectives

- Define solution and differentiate between the solute and the solvent in a solution.
- Predict the solubility of two substances based on their polarity.
- Explain“like dissolves like”.

Solutions are defined as homogeneous mixtures of two or more substances. Often, one component of a solution is present at a significantly greater concentration, in which case it is called the **solvent**. The other components of the solution present in relatively lesser concentrations are called **solutes**. Sugar is a covalent solid composed of sucrose molecules, $\mathrm{C_{12}H_{22}O_{11}}$. When this compound dissolves in water, its molecules become uniformly distributed among the molecules of water:

$$\mathrm{C_{12}H_{22}O_{11}\,(s) \longrightarrow C_{12}H_{22}O_{11}\,(aq)} \tag{6.1.1}$$

The subscript “aq” in the equation signifies that the sucrose molecules are solutes and are therefore *individually dispersed* throughout the *aqueous solution* (water is the solvent). Although sucrose molecules are heavier than water molecules, they remain dispersed throughout the solution; gravity does not cause them to “settle out” over time.

Potassium dichromate, $\mathrm{K_2Cr_2O_7}$, is an ionic compound composed of colorless potassium ions, $\mathrm{K^+}$, and orange dichromate ions, $\mathrm{Cr_2O_7{}^{2-}}$. When a small amount of solid potassium dichromate is added to water, the compound dissolves and dissociates to yield potassium ions and dichromate ions uniformly distributed throughout the mixture (Figure 6.1.1), as indicated in this equation:

$$\mathrm{K_2Cr_2O_7\,(s) \longrightarrow 2\,K^+\,(aq) + Cr_2O_7{}^{2-}\,(aq)} \tag{6.1.2}$$

As with the mixture of sugar and water, this mixture is also an aqueous solution. Its solutes, potassium and dichromate ions, remain individually dispersed among the solvent (water) molecules.



Figure 6.1.1: When potassium dichromate ($\mathrm{K_2Cr_2O_7}$) is mixed with water, it forms a homogeneous orange solution. (credit: modification of work by Mark Ott).

Water is used so often as a solvent that the word solution has come to imply an aqueous solution to many people. However, almost any gas, liquid, or solid can act as a solvent. Many alloys are solid solutions of one metal dissolved in another; for example, US five-cent coins contain nickel dissolved in copper. Air is a gaseous solution, a homogeneous mixture of nitrogen, oxygen, and several other gases. Oxygen (a gas), alcohol (a liquid), and sugar (a solid) all dissolve in water (a liquid) to form liquid solutions. Table 6.1.1 gives examples of several different solutions and the phases of the solutes and solvents.

Table 6.1.1***:*** *Different Types of Solutions*

Solution	Solute	Solvent
air	$O_2(g)$	$N_2(g)$
soft drinks	$CO_2(g)$	$H_2O(l)$
hydrogen in palladium	$H_2(g)$	Pd(s)

Solution	Solute	Solvent
rubbing alcohol	$H_2O(l)$	$C_3H_8O(l)$ (2-propanol)
saltwater	NaCl(s)	$H_2O(l)$
brass	Zn(s)	Cu(s)

Solutions exhibit these defining traits:

- They are homogeneous; that is, after a solution is mixed, it has the same composition at all points throughout (its composition is uniform).
- The physical state of a solution—solid, liquid, or gas—is typically the same as that of the solvent, as demonstrated by the examples in Table 6.1.1.
- The components of a solution are dispersed on a molecular scale; that is, they consist of a mixture of separated molecules, atoms, and/or ions.
- The dissolved solute in a solution will not settle out or separate from the solvent.
- The composition of a solution, or the concentrations of its components, can be varied continuously, within limits.

The Formation of Solutions

The formation of a solution is an example of a spontaneous process, a process that occurs under specified conditions without the requirement of energy from some external source. Sometimes we stir a mixture to speed up the dissolution process, but this is not necessary; a homogeneous solution would form if we waited long enough. The topic of spontaneity is critically important to the study of chemical thermodynamics and is treated more thoroughly in a later chapter of this text. For purposes of this chapter's discussion, it will suffice to consider two criteria that *favor*, but do not guarantee, the spontaneous formation of a solution:

1. a decrease in the internal energy of the system (an exothermic change, as discussed in the previous chapter on thermochemistry)
2. an increase in the disorder in the system (which indicates an increase in the *entropy* of the system, as you will learn about in the later chapter on thermodynamics)

In the process of dissolution, an internal energy change often, but not always, occurs as heat is absorbed or evolved. An increase in disorder always results when a solution forms.

When the strengths of the intermolecular forces of attraction between solute and solvent species in a solution are no different than those present in the separated components, the solution is formed with no accompanying energy change. Such a solution is called an ideal solution. A mixture of ideal gases (or gases such as helium and argon, which closely approach ideal behavior) is an example of an ideal solution, since the entities comprising these gases experience no significant intermolecular attractions.

When containers of helium and argon are connected, the gases spontaneously mix due to diffusion and form a solution (Figure 6.1.2). The formation of this solution clearly involves an increase in disorder, since the helium and argon atoms occupy a volume twice as large as that which each occupied before mixing.

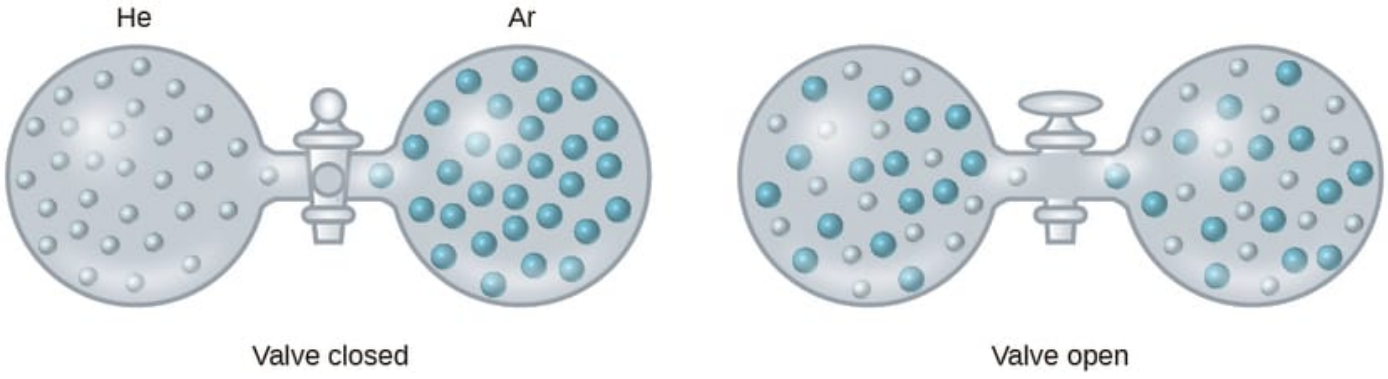


Figure 6.1.2: Samples of helium and argon spontaneously mix to give a solution in which the disorder of the atoms of the two

gases is increased.

Ideal solutions may also form when structurally similar liquids are mixed. For example, mixtures of the alcohols methanol (CH_3OH) and ethanol (C_2H_5OH) form ideal solutions, as do mixtures of the hydrocarbons pentane, C_5H_{12}, and hexane, C_6H_{14}. Placing methanol and ethanol, or pentane and hexane, in the bulbs shown in Figure $6.1.2$ will result in the same diffusion and subsequent mixing of these liquids as is observed for the He and Ar gases (although at a much slower rate), yielding solutions with no significant change in energy. Unlike a mixture of gases, however, the components of these liquid-liquid solutions do, indeed, experience intermolecular attractive forces. But since the molecules of the two substances being mixed are structurally very similar, the intermolecular attractive forces between like and unlike molecules are essentially the same, and the dissolution process, therefore, does not entail any appreciable increase or decrease in energy. These examples illustrate how diffusion alone can provide the driving force required to cause the spontaneous formation of a solution. In some cases, however, the relative magnitudes of intermolecular forces of attraction between solute and solvent species may prevent dissolution.

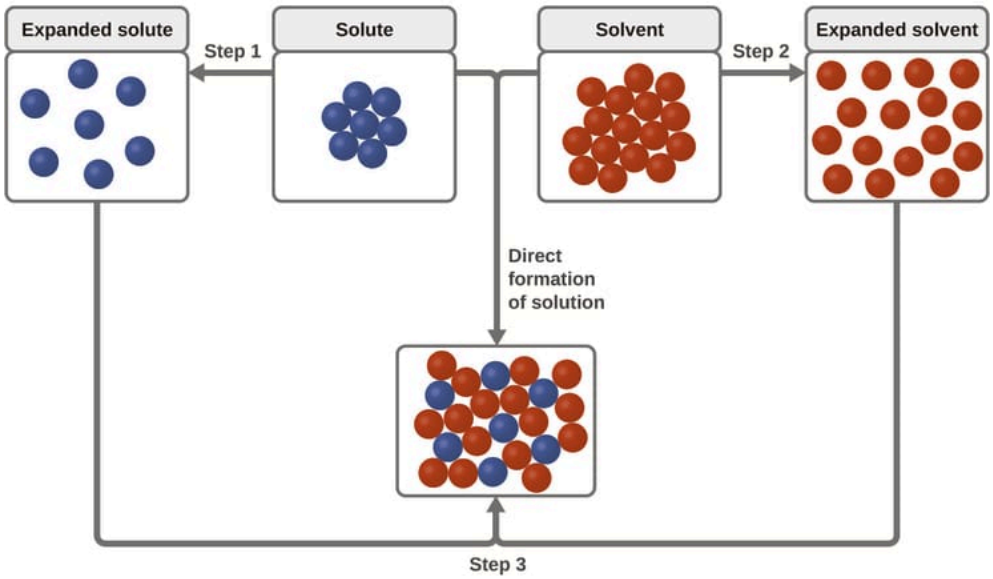


Figure $6.1.3$: This schematic representation of dissolution shows a stepwise process involving the endothermic separation of solute and solvent species (Steps 1 and 2) and exothermic solvation (Step 3).

Three types of intermolecular attractive forces are relevant to the dissolution process: solute-solute, solvent-solvent, and solute-solvent. As illustrated in Figure $6.1.3$, the formation of a solution may be viewed as a stepwise process in which energy is consumed to overcome solute-solute and solvent-solvent attractions (endothermic processes) and released when solute-solvent attractions are established (an exothermic process referred to as solvation). The relative magnitudes of the energy changes associated with these stepwise processes determine whether the dissolution process overall will release or absorb energy. In some cases, solutions do not form because the energy required to separate solute and solvent species is so much greater than the energy released by solvation.



Figure 6.1.4: A mixture of nonpolar cooking oil and polar water does not yield a solution. (credit: Gautam Dogra).

For example, cooking oils and water will not mix to any appreciable extent to yield solutions (Figure 6.1.4). Water is a polar substance and will not mix with the nonpolar hydrocarbon molecules of cooking oils are not capable of hydrogen bonding, instead being held together by dispersion forces. Forming an oil-water solution would require overcoming the very strong hydrogen bonding in water, as well as the significantly strong dispersion forces between the relatively large oil molecules. And, since the polar water molecules and nonpolar oil molecules would not experience very strong intermolecular attraction, very little energy would be released by solvation.

On the other hand, a mixture of ethanol and water will mix in any proportions to yield a solution because they are both polar substances.



Figure 6.1.5: An instant cold pack gets cold when certain salts, such as ammonium nitrate, dissolve in water—an endothermic process.

"Like Dissolves Like". In other words, ionic and polar covalent solutes dissolve in ionic and polar covalent solvents, and nonpolar covalent solutes dissolve in nonpolar covalent solvents.

As noted at the beginning of this module, spontaneous solution formation is favored, but not guaranteed, by exothermic dissolution processes. While many soluble compounds do, indeed, dissolve with the release of heat, some dissolve endothermically. Ammonium nitrate (NH_4NO_3) is one such example and is used to make instant cold packs for treating injuries like the one pictured in Figure 6.1.5. A thin-walled plastic bag of water is sealed inside a larger bag with solid NH_4NO_3. When

the smaller bag is broken, a solution of NH_4NO_3 forms, absorbing heat from the surroundings (the injured area to which the pack is applied) and providing a cold compress that decreases swelling. Endothermic dissolutions such as this one require a greater energy input to separate the solute species than is recovered when the solutes are solvated, but they are spontaneous nonetheless due to the increase in disorder that accompanies formation of the solution.

YouTube Video

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

View this YouTube Video online

Video 6.1.1*: Watch this brief video illustrating endothermic and exothermic dissolution processes.*

Summary

A solution forms when two or more substances combine physically to yield a mixture that is homogeneous at the molecular level. The solvent is the most concentrated component and determines the physical state of the solution. The solutes are the other components typically present at concentrations less than that of the solvent. Solutions may form endothermically or exothermically, depending upon the relative magnitudes of solute and solvent intermolecular attractive forces. Ideal solutions form with no appreciable change in energy.

Footnotes

1. If bubbles of gas are observed within the liquid, the mixture is not homogeneous and, thus, not a solution.

Glossary

alloy
: solid mixture of a metallic element and one or more additional elements

ideal solution
: solution that forms with no accompanying energy change

solvation
: exothermic process in which intermolecular attractive forces between the solute and solvent in a solution are established

spontaneous process
: physical or chemical change that occurs without the addition of energy from an external source

Contributors

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6.2: Electrolytes

Learning Objectives

- Define electrolyte and list examples of common electrolytes.

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. If only a relatively small fraction of the dissolved substance undergoes the ion-producing process, it is called a weak electrolyte.

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 6.2.1).

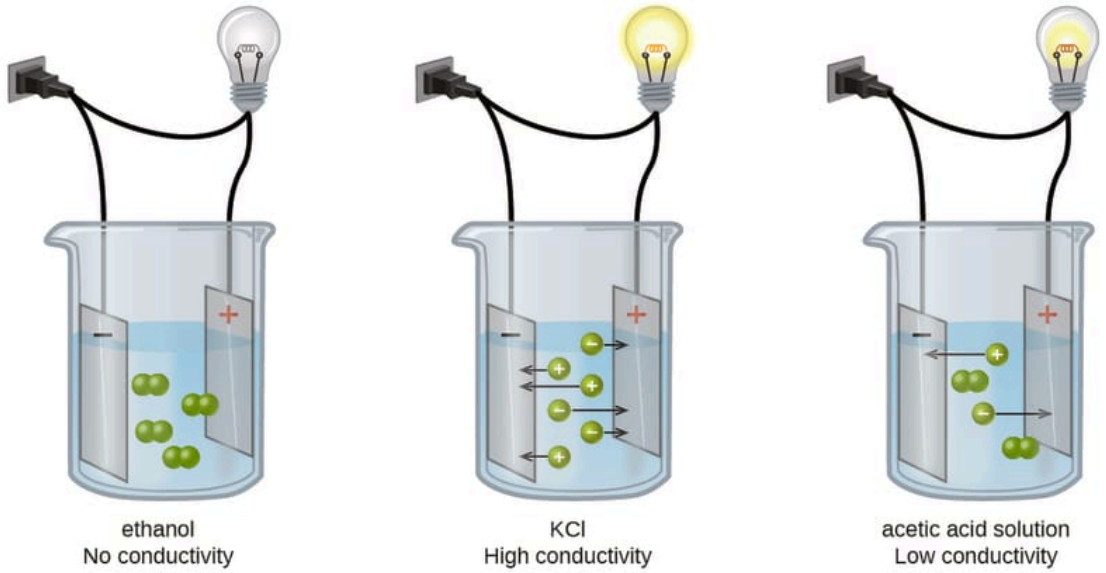


Figure 6.2.1: Solutions of nonelectrolytes such as ethanol do not contain dissolved ions and cannot conduct electricity. Solutions of electrolytes contain ions that permit the passage of electricity. The conductivity of an electrolyte solution is related to the strength of the electrolyte.

Ionic Electrolytes

Water and other polar molecules are attracted to ions, as shown in Figure 6.2.2. The electrostatic attraction between an ion and a molecule with a dipole is called an ion-dipole attraction. These attractions play an important role in the dissolution of ionic compounds in water.

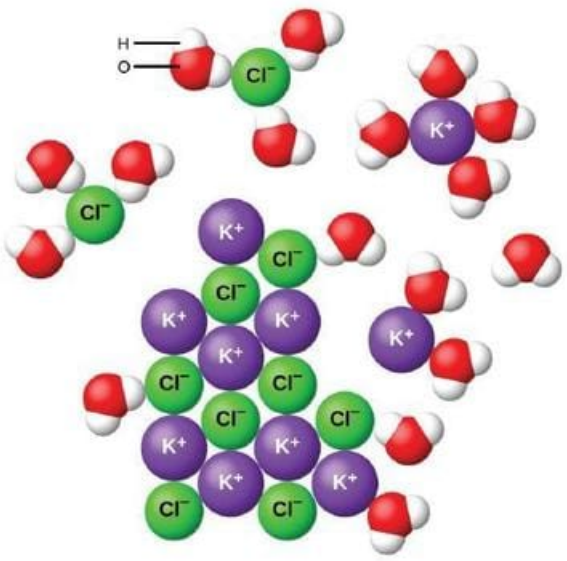


Figure 6.2.2: As potassium chloride (KCl) dissolves in water, the ions are hydrated. The polar water molecules are attracted by the charges on the K^+ and Cl^- ions. Water molecules in front of and behind the ions are not shown.

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 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).

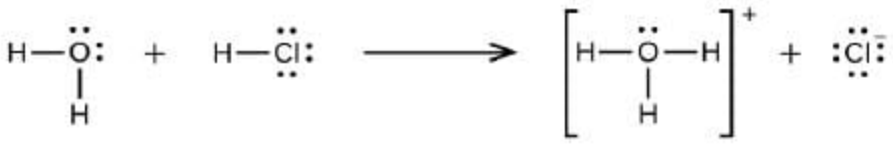
Covalent Electrolytes

Pure water is an extremely poor conductor of electricity because it is only very slightly ionized—only about two out of every 1 billion molecules ionize at 25 °C. Water ionizes when one molecule of water gives up a proton to another molecule of water, yielding hydronium and hydroxide ions.

$$\mathrm{H_2O\ (l)^+\ H_2O\,(l)\ \rightleftharpoons H_3O^+\,(aq) + OH^-\,(aq)} \tag{6.2.1}$$

In some cases, we find that solutions prepared from covalent compounds conduct electricity because the solute molecules react chemically with the solvent to produce ions. For example, pure hydrogen chloride is a gas consisting of covalent HCl molecules. This gas contains no ions. However, when we dissolve hydrogen chloride in water, we find that the solution is a very good conductor. The water molecules play an essential part in forming ions: Solutions of hydrogen chloride in many other solvents, such as benzene, do not conduct electricity and do not contain ions.

Hydrogen chloride is an *acid*, and so its molecules react with water, transferring H^+ ions to form hydronium ions (H_3O^+) and chloride ions (Cl^-):



This reaction is essentially 100% complete for HCl (i.e., it is a *strong acid* and, consequently, a strong electrolyte). Likewise, weak acids and bases that only react partially generate relatively low concentrations of ions when dissolved in water and are classified as weak electrolytes. The reader may wish to review the discussion of strong and weak acids provided in the earlier chapter of this text on reaction classes and stoichiometry.

Summary

Substances that dissolve in water to yield ions are called electrolytes. Electrolytes may be covalent compounds that chemically react with water to produce ions (for example, acids and bases), or they may be ionic compounds that dissociate to yield their constituent cations and anions, when dissolved. Dissolution of an ionic compound is facilitated by ion-dipole attractions between the ions of the compound and the polar water molecules. Soluble ionic substances and strong acids ionize completely and are strong electrolytes, while weak acids and bases ionize to only a small extent and are weak electrolytes. Nonelectrolytes are substances that do not produce ions when dissolved in water.

Glossary

dissociation
: physical process accompanying the dissolution of an ionic compound in which the compound's constituent ions are solvated and dispersed throughout the solution

electrolyte
: substance that produces ions when dissolved in water

ion-dipole attraction
: electrostatic attraction between an ion and a polar molecule

nonelectrolyte
: substance that does not produce ions when dissolved in water

strong electrolyte
: substance that dissociates or ionizes completely when dissolved in water

weak electrolyte
: substance that ionizes only partially when dissolved in water

Contributors

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6.3: Solubility

Learning Objectives

- Describe the effects of temperature and pressure on solubility
- Explain the degrees of solubility possible for liquid-liquid solutions

Imagine adding a small amount of salt to a glass of water, stirring until all the salt has dissolved, and then adding a bit more. You can repeat this process until the salt concentration of the solution reaches its natural limit, a limit determined primarily by the relative strengths of the solute-solute, solute-solvent, and solvent-solvent attractive forces discussed in the previous two modules of this chapter. You can be certain that you have reached this limit because, no matter how long you stir the solution, undissolved salt remains. The concentration of salt in the solution at this point is known as its solubility.

The solubility of a solute in a particular solvent is the maximum concentration that may be achieved under given conditions when the dissolution process is *at equilibrium*. Referring to the example of salt in water:

$$\mathrm{NaCl}(s) \rightleftharpoons \mathrm{Na}^{+}(aq) + \mathrm{Cl}^{-}(aq) \tag{6.3.1}$$

When a solute's concentration is equal to its solubility, the solution is said to be saturated with that solute. If the solute's concentration is less than its solubility, the solution is said to be unsaturated. A solution that contains a relatively low concentration of solute is called dilute, and one with a relatively high concentration is called concentrated.

If we add more salt to a saturated solution of salt, we see it fall to the bottom and no more seems to dissolve. In fact, the added salt does dissolve, as represented by the forward direction of the dissolution equation. Accompanying this process, dissolved salt will precipitate, as depicted by the reverse direction of the equation. The system is said to be at equilibrium when these two reciprocal processes are occurring at equal rates, and so the amount of undissolved and dissolved salt remains constant. Support for the simultaneous occurrence of the dissolution and precipitation processes is provided by noting that the number and sizes of the undissolved salt crystals will change over time, though their combined mass will remain the same.

YouTube Video

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

View this YouTube Video online

Video $6.3.1$***:*** *Watch this impressive video showing the precipitation of sodium acetate from a supersaturated solution.*

Solutions may be prepared in which a solute concentration *exceeds* its solubility. Such solutions are said to be supersaturated, and they are interesting examples of *nonequilibrium* states. For example, the carbonated beverage in an open container that has not yet "gone flat" is supersaturated with carbon dioxide gas; given time, the CO_2 concentration will decrease until it reaches its equilibrium value.

Solutions of Gases in Liquids

In an earlier module of this chapter, 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 6.3.1). This is one of the major impacts resulting from the thermal pollution of natural bodies of water.

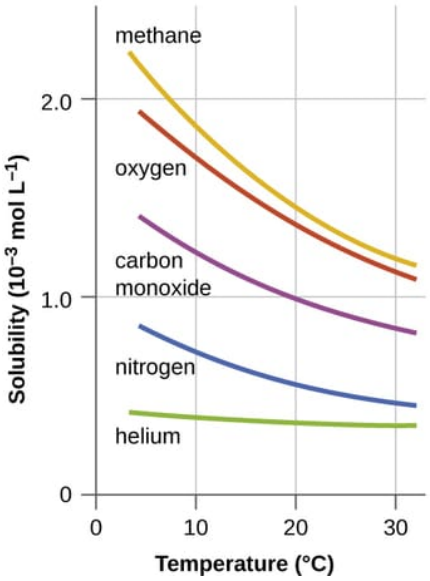


Figure 6.3.1: The solubilities of these gases in water decrease as the temperature increases. All solubilities were measured with a constant pressure of 101.3 kPa (1 atm) of gas above the solutions.

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 6.3.2).



Figure 6.3.2: (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 6.3.3). 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."

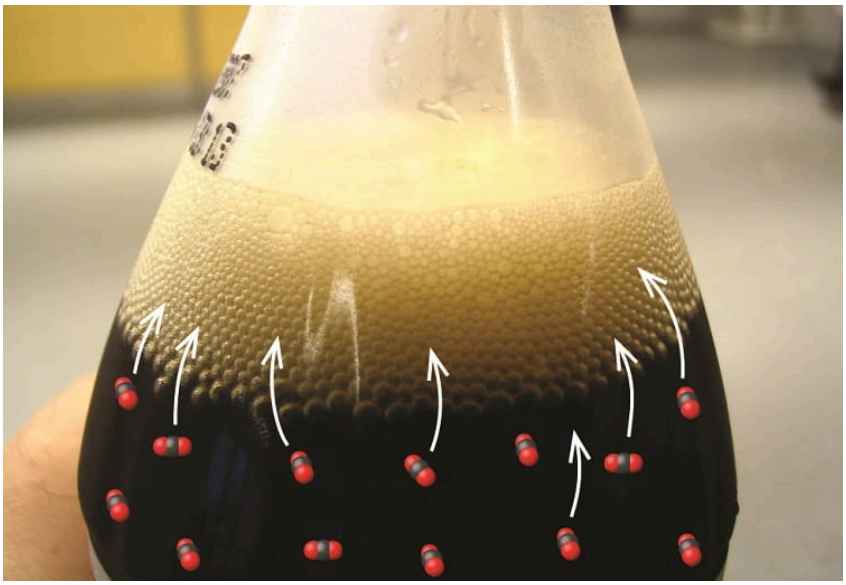


Figure 6.3.3: Opening the bottle of carbonated beverage reduces the pressure of the gaseous carbon dioxide above the beverage. The solubility of CO_2 is thus lowered, and some dissolved carbon dioxide may be seen leaving the solution as small gas bubbles. (credit: modification of work by Derrick Coetzee)

For many gaseous solutes, the relation between solubility, C_g, and partial pressure, P_g, is a proportional one:

$$C_g = kP_g \tag{6.3.2}$$

where *k* is a proportionality constant that depends on the identities of the gaseous solute and solvent, and on the solution temperature. This is a mathematical statement of Henry's law: *The quantity of an ideal gas that dissolves in a definite volume of liquid is directly proportional to the pressure of the gas.*

Case Study: Decompression Sickness ("The Bends")

Decompression sickness (DCS), or "the bends," is an effect of the increased pressure of the air inhaled by scuba divers when swimming underwater at considerable depths. In addition to the pressure exerted by the atmosphere, divers are subjected to additional pressure due to the water above them, experiencing an increase of approximately 1 atm for each 10 m of depth. Therefore, the air inhaled by a diver while submerged contains gases at the corresponding higher ambient pressure, and the concentrations of the gases dissolved in the diver's blood are proportionally higher per Henry's law.

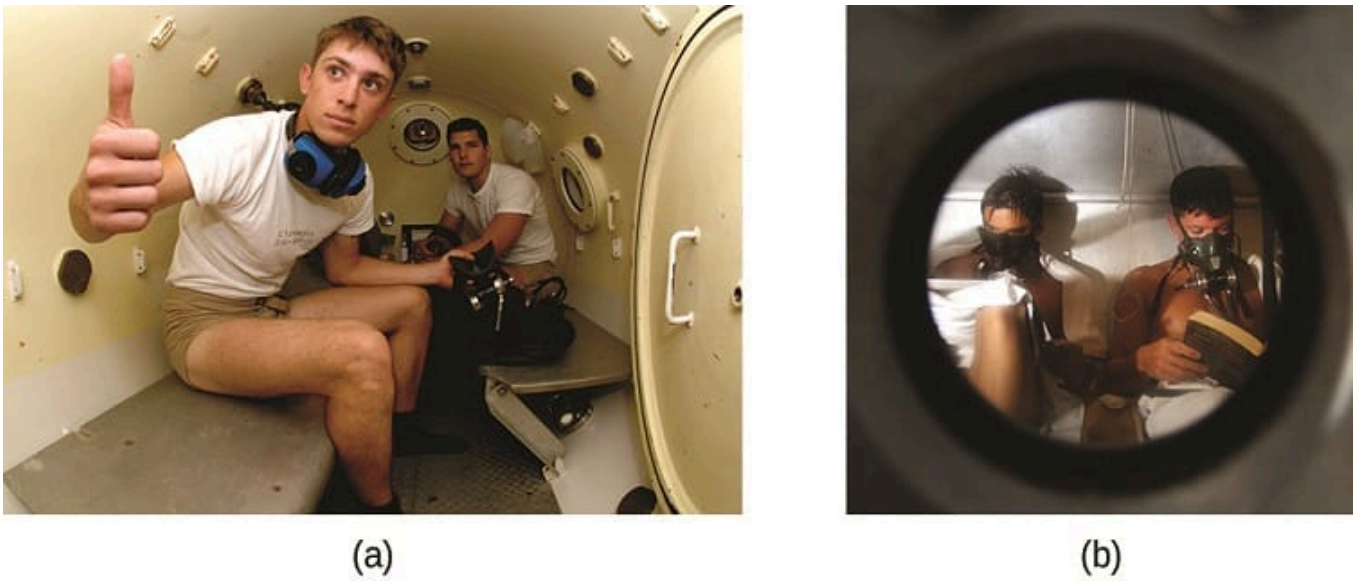
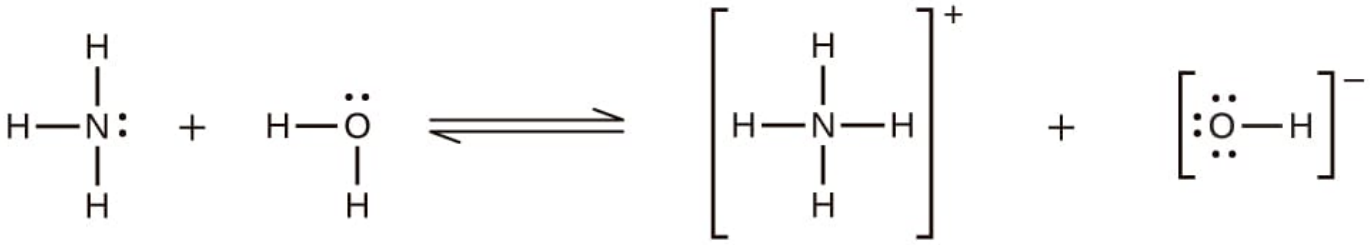


Figure 6.3.4: (a) US Navy divers undergo training in a recompression chamber. (b) Divers receive hyperbaric oxygen therapy.

As the diver ascends to the surface of the water, the ambient pressure decreases and the dissolved gases becomes less soluble. If the ascent is too rapid, the gases escaping from the diver's blood may form bubbles that can cause a variety of symptoms ranging from rashes and joint pain to paralysis and death. To avoid DCS, divers must ascend from depths at relatively slow speeds (10 or 20 m/min) or otherwise make several decompression stops, pausing for several minutes at given depths during the ascent. When these preventive measures are unsuccessful, divers with DCS are often provided hyperbaric oxygen therapy in pressurized vessels called decompression (or recompression) chambers (Figure 6.3.4).

Deviations from Henry's law are observed when a chemical reaction takes place between the gaseous solute and the solvent. Thus, for example, the solubility of ammonia in water does not increase as rapidly with increasing pressure as predicted by the law because ammonia, being a base, reacts to some extent with water to form ammonium ions and hydroxide ions.



Gases can form supersaturated solutions. If a solution of a gas in a liquid is prepared either at low temperature or under pressure (or both), then as the solution warms or as the gas pressure is reduced, the solution may become supersaturated. In 1986, more than 1700 people in Cameroon were killed when a cloud of gas, almost certainly carbon dioxide, bubbled from Lake Nyos (Figure 6.3.5), a deep lake in a volcanic crater. The water at the bottom of Lake Nyos is saturated with carbon dioxide by volcanic activity beneath the lake. It is believed that the lake underwent a turnover due to gradual heating from below the lake, and the warmer, less-dense water saturated with carbon dioxide reached the surface. Consequently, tremendous quantities of dissolved CO_2 were released, and the colorless gas, which is denser than air, flowed down the valley below the lake and suffocated humans and animals living in the valley.



Figure 6.3.5: (a) It is believed that the 1986 disaster that killed more than 1700 people near Lake Nyos in Cameroon resulted when a large volume of carbon dioxide gas was released from the lake. (b) A CO_2 vent has since been installed to help outgas the lake in a slow, controlled fashion and prevent a similar catastrophe from happening in the future. (credit a: modification of work by Jack Lockwood; credit b: modification of work by Bill Evans)

Solutions of Liquids in Liquids

We know that some liquids mix with each other in all proportions; in other words, they have infinite mutual solubility and are said to be miscible. Ethanol, sulfuric acid, and ethylene glycol (popular for use as antifreeze, pictured in Figure 6.3.6) are examples of liquids that are completely miscible with water. Two-cycle motor oil is miscible with gasoline.



Figure 6.3.6: Water and antifreeze are miscible; mixtures of the two are homogeneous in all proportions. (credit: “dno1967”/Wikimedia commons)

Liquids that mix with water in all proportions are usually polar substances or substances that form hydrogen bonds. For such liquids, the dipole-dipole attractions (or hydrogen bonding) of the solute molecules with the solvent molecules are at least as strong as those between molecules in the pure solute or in the pure solvent. Hence, the two kinds of molecules mix easily. Likewise, nonpolar liquids are miscible with each other because there is no appreciable difference in the strengths of solute-solute, solvent-solvent, and solute-solvent intermolecular attractions. The solubility of polar molecules in polar solvents and of nonpolar molecules in nonpolar solvents is, again, an illustration of the chemical axiom “like dissolves like.”

Two liquids that do not mix to an appreciable extent are called immiscible. Layers are formed when we pour immiscible liquids

into the same container. Gasoline, oil (Figure 6.3.7), benzene, carbon tetrachloride, some paints, and many other nonpolar liquids are immiscible with water. The attraction between the molecules of such nonpolar liquids and polar water molecules is ineffectively weak. The only strong attractions in such a mixture are between the water molecules, so they effectively squeeze out the molecules of the nonpolar liquid. The distinction between immiscibility and miscibility is really one of degrees, so that miscible liquids are of infinite mutual solubility, while liquids said to be immiscible are of very low (though not zero) mutual solubility.



Figure 6.3.7: Water and oil are immiscible. Mixtures of these two substances will form two separate layers with the less dense oil floating on top of the water. (credit: "Yortw"/Flickr)

Two liquids, such as bromine and water, that are of *moderate* mutual solubility are said to be partially miscible. Two partially miscible liquids usually form two layers when mixed. In the case of the bromine and water mixture, the upper layer is water, saturated with bromine, and the lower layer is bromine saturated with water. Since bromine is nonpolar, and, thus, not very soluble in water, the water layer is only slightly discolored by the bright orange bromine dissolved in it. Since the solubility of water in bromine is very low, there is no noticeable effect on the dark color of the bromine layer (Figure 6.3.8).



Figure 6.3.8: Bromine (the deep orange liquid on the left) and water (the clear liquid in the middle) are partially miscible. The top layer in the mixture on the right is a saturated solution of bromine in water; the bottom layer is a saturated solution of water in bromine. (credit: Paul Flowers)

Solutions of Solids in Liquids

The dependence of solubility on temperature for a number of inorganic solids in water is shown by the solubility curves in Figure 6.3.9. Reviewing these data indicate a general trend of increasing solubility with temperature, although there are exceptions, as illustrated by the ionic compound cerium sulfate.

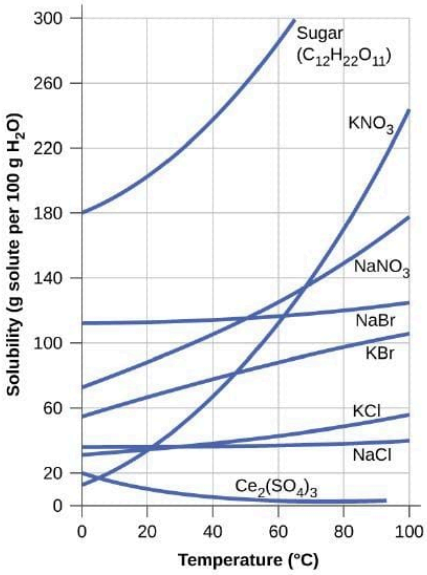


Figure 6.3.9: This graph shows how the solubility of several solids changes with temperature.

The temperature dependence of solubility can be exploited to prepare supersaturated solutions of certain compounds. A solution may be saturated with the compound at an elevated temperature (where the solute is more soluble) and subsequently cooled to a lower temperature without precipitating the solute. The resultant solution contains solute at a concentration greater than its equilibrium solubility at the lower temperature (i.e., it is supersaturated) and is relatively stable. Precipitation of the excess solute can be initiated by adding a seed crystal (see the video in the Link to Learning earlier in this module) or by mechanically agitating the solution. Some hand warmers, such as the one pictured in Figure 6.3.10, take advantage of this behavior.



Figure 6.3.10: This hand warmer produces heat when the sodium acetate in a supersaturated solution precipitates. Precipitation of the solute is initiated by a mechanical shockwave generated when the flexible metal disk within the solution is “clicked.” (credit: modification of work by “Velela”/Wikimedia Commons)

YouTube Video

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

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Video $6.3.2$***:*** *This video shows the crystallization process occurring in a hand warmer.*

Summary

The extent to which one substance will dissolve in another is determined by several factors, including the types and relative strengths of intermolecular attractive forces that may exist between the substances' atoms, ions, or molecules. This tendency to dissolve is quantified as substance's solubility, its maximum concentration in a solution at equilibrium under specified conditions. A saturated solution contains solute at a concentration equal to its solubility. A supersaturated solution is one in which a solute's concentration exceeds its solubility—a nonequilibrium (unstable) condition that will result in solute precipitation when the solution is appropriately perturbed. Miscible liquids are soluble in all proportions, and immiscible liquids exhibit very low mutual solubility. Solubilities for gaseous solutes decrease with increasing temperature, while those for most, but not all, solid solutes increase with temperature. The concentration of a gaseous solute in a solution is proportional to the partial pressure of the gas to which the solution is exposed, a relation known as Henry's law.

Key Equations

- $C_{\mathrm{g}} = kP_{\mathrm{g}}$

Glossary

Henry's law
: law stating the proportional relationship between the concentration of dissolved gas in a solution and the partial pressure of the gas in contact with the solution

immiscible
: of negligible mutual solubility; typically refers to liquid substances

miscible
: mutually soluble in all proportions; typically refers to liquid substances

partially miscible
: of moderate mutual solubility; typically refers to liquid substances

saturated
: of concentration equal to solubility; containing the maximum concentration of solute possible for a given temperature and pressure

solubility
: extent to which a solute may be dissolved in water, or any solvent

supersaturated
: of concentration that exceeds solubility; a nonequilibrium state

unsaturated
: of concentration less than solubility

Contributors

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6.4: Colloids and Emulsifying Agents

Learning Objectives

- Define emulsifying agent.
- Draw a picture of the molecular structure of an emulsifying agent and label the polar and nonpolar ends.
- Give 3 examples of common emulsifying agents.

As a child, you may have made suspensions such as mixtures of mud and water, flour and water, or a suspension of solid pigments in water, known as tempera paint. These suspensions are heterogeneous mixtures composed of relatively large particles that are visible (or that can be seen with a magnifying glass). They are cloudy, and the suspended particles settle out after mixing. On the other hand, when we make a solution, we prepare a homogeneous mixture in which no settling occurs and in which the dissolved species are molecules or ions. Solutions exhibit completely different behavior from suspensions. A solution may be colored, but it is transparent, the molecules or ions are invisible, and they do not settle out on standing. A group of mixtures called colloids (or colloidal dispersions) exhibit properties intermediate between those of suspensions and solutions (Figure 6.4.1). The particles in a colloid are larger than most simple molecules; however, colloidal particles are small enough that they do not settle out upon standing.

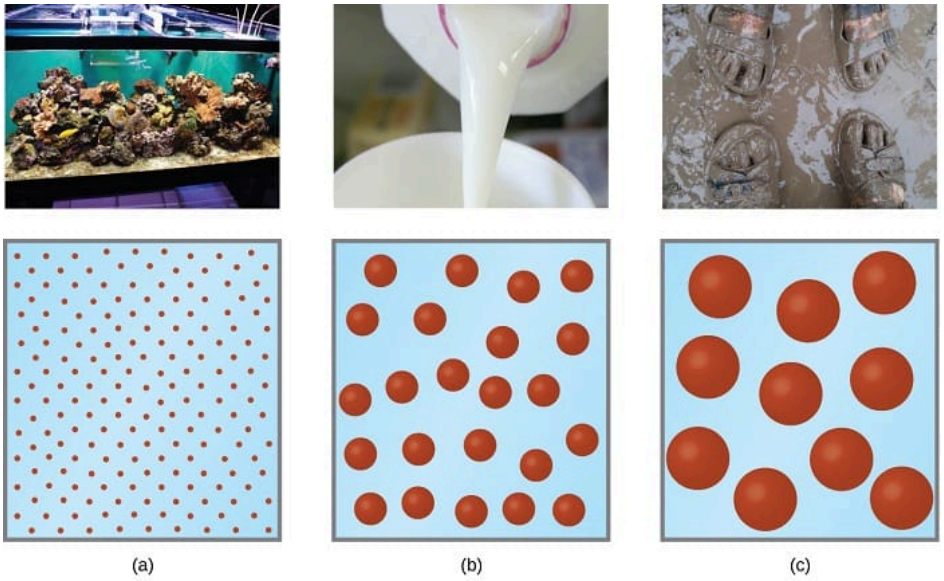


Figure 6.4.1: (a) A solution is a homogeneous mixture that appears clear, such as the saltwater in this aquarium. (b) In a colloid, such as milk, the particles are much larger but remain dispersed and do not settle. (c) A suspension, such as mud, is a heterogeneous mixture of suspended particles that appears cloudy and in which the particles can settle. (credit a photo: modification of work by Adam Wimsatt; credit b photo: modification of work by Melissa Wiese; credit c photo: modification of work by Peter Burgess)

The particles in a colloid are large enough to scatter light, a phenomenon called the Tyndall effect. This can make colloidal mixtures appear cloudy or opaque, such as the searchlight beams shown in Figure 6.4.2. Clouds are colloidal mixtures. They are composed of water droplets that are much larger than molecules, but that are small enough that they do not settle out.



Figure 6.4.2: The paths of searchlight beams are made visible when light is scattered by colloidal-size particles in the air (fog, smoke, etc.). (credit: "Bahman"/Wikimedia Commons)

The term "colloid"—from the Greek words *kolla*, meaning "glue," and *eidos*, meaning "like"—was first used in 1861 by Thomas Graham to classify mixtures such as starch in water and gelatin. Many colloidal particles are aggregates of hundreds or thousands of molecules, but others (such as proteins and polymer molecules) consist of a single extremely large molecule. The protein and synthetic polymer molecules that form colloids may have molecular masses ranging from a few thousand to many million atomic mass units.

Analogous to the identification of solution components as "solute" and "solvent," the components of a colloid are likewise classified according to their relative amounts. The particulate component typically present in a relatively minor amount is called the dispersed phase and the substance or solution throughout which the particulate is dispersed is called the dispersion medium. Colloids may involve virtually any combination of physical states (gas in liquid, liquid in solid, solid in gas, etc.), as illustrated by the examples of colloidal systems given in Table 6.4.1.

Table* 6.4.2*: Examples of Colloidal Systems

Dispersed Phase	Dispersion Medium	Common Examples	Name
solid	gas	smoke, dust	—
solid	liquid	starch in water, some inks, paints, milk of magnesia	sol
solid	solid	some colored gems, some alloys	—
liquid	gas	clouds, fogs, mists, sprays	aerosol
liquid	liquid	milk, mayonnaise, butter	emulsion
liquid	solid	jellies, gels, pearl, opal (H_2O in SiO_2)	gel
gas	liquid	foams, whipped cream, beaten egg whites	foam
gas	solid	pumice, floating soaps	—

Preparation of Colloidal Systems

We can prepare a colloidal system by producing particles of colloidal dimensions and distributing these particles throughout a

dispersion medium. Particles of colloidal size are formed by two methods:

1. Dispersion methods: that is, by breaking down larger particles. For example, paint pigments are produced by dispersing large particles by grinding in special mills.
2. Condensation methods: that is, growth from smaller units, such as molecules or ions. For example, clouds form when water molecules condense and form very small droplets.

A few solid substances, when brought into contact with water, disperse spontaneously and form colloidal systems. Gelatin, glue, starch, and dehydrated milk powder behave in this manner. The particles are already of colloidal size; the water simply disperses them. Powdered milk particles of colloidal size are produced by dehydrating milk spray. Some atomizers produce colloidal dispersions of a liquid in air.

We can prepare an emulsion by shaking together or blending two immiscible liquids. This breaks one liquid into droplets of colloidal size, which then disperse throughout the other liquid. Oil spills in the ocean may be difficult to clean up, partly because wave action can cause the oil and water to form an emulsion. In many emulsions, however, the dispersed phase tends to coalesce, form large drops, and separate. Therefore, emulsions are usually stabilized by an **emulsifying agent**, a substance that inhibits the coalescence of the dispersed liquid. For example, a little soap will stabilize an emulsion of kerosene in water. Milk is an emulsion of butterfat in water, with the protein casein as the emulsifying agent. Mayonnaise is an emulsion of oil in vinegar, with egg yolk components as the emulsifying agents.

Condensation methods form colloidal particles by aggregation of molecules or ions. If the particles grow beyond the colloidal size range, drops or precipitates form, and no colloidal system results. Clouds form when water molecules aggregate and form colloid-sized particles. If these water particles coalesce to form adequately large water drops of liquid water or crystals of solid water, they settle from the sky as rain, sleet, or snow. Many condensation methods involve chemical reactions. We can prepare a red colloidal suspension of iron(III) hydroxide by mixing a concentrated solution of iron(III) chloride with hot water:

$$\mathrm{Fe^{3+}}_{(aq)} + 3\mathrm{Cl^-}_{(aq)} + 6\mathrm{H_2O}_{(l)} \longrightarrow \mathrm{Fe(OH)}_{3(s)} + \mathrm{H_3O^+}_{(aq)} + 3\mathrm{Cl^-}_{(aq)} \tag{6.4.1}$$

A colloidal gold sol results from the reduction of a very dilute solution of gold(III) chloride by a reducing agent such as formaldehyde, tin(II) chloride, or iron(II) sulfate:

$$\mathrm{Au^{3+}} + 3\,\mathrm{e^-} \rightarrow \mathrm{Au} \tag{6.4.2}$$

Some gold sols prepared in 1857 are still intact (the particles have not coalesced and settled), illustrating the long-term stability of many colloids.

Soaps and Detergents

Pioneers made soap by boiling fats with a strongly basic solution made by leaching potassium carbonate, $\mathrm{K_2CO_3}$, from wood ashes with hot water. Animal fats contain polyesters of fatty acids (long-chain carboxylic acids). When animal fats are treated with a base like potassium carbonate or sodium hydroxide, glycerol and salts of fatty acids such as palmitic, oleic, and stearic acid are formed. The salts of fatty acids are called soaps. The sodium salt of stearic acid, sodium stearate, has the formula $\mathrm{C_{17}H_{35}CO_2Na}$ and contains an uncharged nonpolar hydrocarbon chain, the $\mathrm{C_{17}H_{35}-}$ unit, and an ionic carboxylate group, the $-\mathrm{CO_2^-}$ unit (Figure 6.4.3).

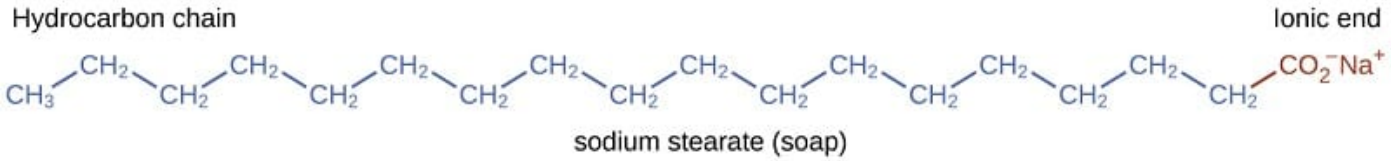
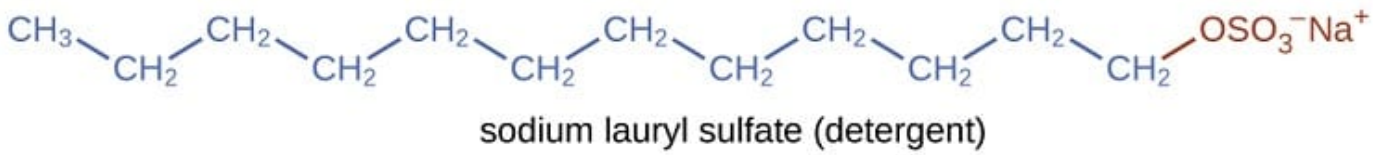


Figure 6.4.3: Soaps contain a nonpolar hydrocarbon end (blue) and an ionic end (red). The ionic end is a carboxylate group. The length of the hydrocarbon end can vary from soap to soap.

*Deterg*ents (soap substitutes) also contain nonpolar hydrocarbon chains, such as $\mathrm{C_{12}H_{25}}$—, and an ionic group, such as a sulfate $—\mathrm{OSO_3^-}$, or a sulfonate $—\mathrm{SO_3^-}$ (Figure 6.4.4). Soaps form insoluble calcium and magnesium compounds in hard water; detergents form water-soluble products—a definite advantage for detergents.



sodium lauryl sulfate (detergent)

Figure 6.4.4: Detergents contain a nonpolar hydrocarbon end (blue) and an ionic end (red). The ionic end can be either a sulfate or a sulfonate. The length of the hydrocarbon end can vary from detergent to detergent.

The cleaning action of soaps and detergents can be explained in terms of the structures of the molecules involved. The hydrocarbon (nonpolar) end of a soap or detergent molecule dissolves in, or is attracted to, nonpolar substances such as oil, grease, or dirt particles. The ionic end is attracted by water (polar), illustrated in Figure 6.4.5. As a result, the soap or detergent molecules become oriented at the interface between the dirt particles and the water so they act as a kind of bridge between two different kinds of matter, nonpolar and polar. Molecules such as this are termed amphiphilic since they have both a hydrophobic ("water-fearing") part and a hydrophilic ("water-loving") part. As a consequence, dirt particles become suspended as colloidal particles and are readily washed away.

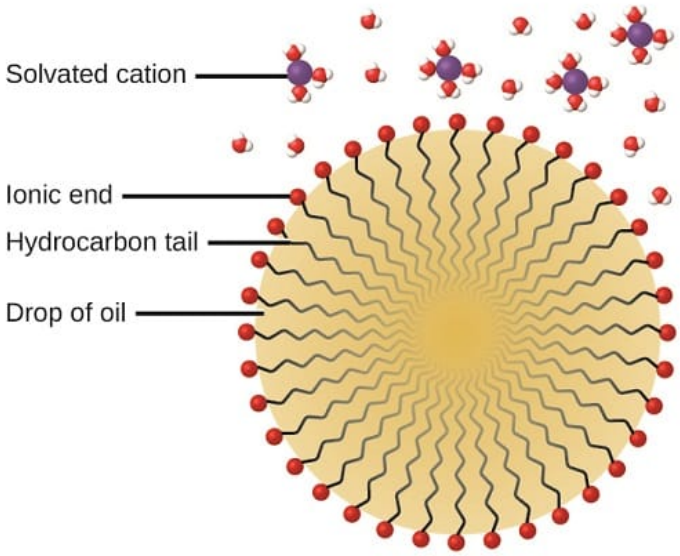


Figure 6.4.5: This diagrammatic cross section of an emulsified drop of oil in water shows how soap or detergent acts as an emulsifier.

Deepwater Horizon Oil Spill

The blowout of the Deepwater Horizon oil drilling rig on April 20, 2010, in the Gulf of Mexico near Mississippi began the largest marine oil spill in the history of the petroleum. In the 87 days following the blowout, an estimated 4.9 million barrels (210 million gallons) of oil flowed from the ruptured well 5000 feet below the water's surface. The well was finally declared sealed on September 19, 2010.

Crude oil is immiscible with and less dense than water, so the spilled oil rose to the surface of the water. Floating booms, skimmer ships, and controlled burns were used to remove oil from the water's surface in an attempt to protect beaches and wetlands along the Gulf coast. In addition to removal of the oil, attempts were also made to lessen its environmental impact by rendering it "soluble" (in the loose sense of the term) and thus allowing it to be diluted to hopefully less harmful levels by the vast volume of ocean water. This approach used 1.84 million gallons of the oil dispersant Corexit 9527, most of which was injected underwater at the site of the leak, with small amounts being sprayed on top of the spill. Corexit 9527 contains 2-butoxyethanol ($C_6H_{14}O_2$), an amphiphilic molecule whose polar and nonpolar ends are useful for emulsifying oil into small droplets, increasing the surface area of the oil and making it more available to marine bacteria for digestion (Figure 6.4.6). While this approach avoids many of the immediate hazards that bulk oil poses to marine and coastal ecosystems, it

introduces the possibility of long-term effects resulting from the introduction of the complex and potential toxic components of petroleum into the ocean's food chain. A number of organizations are involved in monitoring the extended impact of this oil spill, including the National Oceanic and Atmospheric Administration.



Figure 6.4.6: (a) This NASA satellite image shows the oil slick from the Deepwater Horizon spill. (b) A US Air Force plane sprays Corexit, a dispersant. (c) The molecular structure of 2-butoxyethanol is shown. (credit a: modification of work by "NASA, FT2, demis.nl"/Wikimedia Commons; credit b: modification of work by "NASA/MODIS Rapid Response Team"/Wikimedia Commons)

Electrical Properties of Colloidal Particles

Dispersed colloidal particles are often electrically charged. A colloidal particle of iron(III) hydroxide, for example, does not contain enough hydroxide ions to compensate exactly for the positive charges on the iron(III) ions. Thus, each individual colloidal particle bears a positive charge, and the colloidal dispersion consists of charged colloidal particles and some free hydroxide ions, which keep the dispersion electrically neutral. Most metal hydroxide colloids have positive charges, whereas most metals and metal sulfides form negatively charged dispersions. All colloidal particles in any one system have charges of the same sign. This helps keep them dispersed because particles containing like charges repel each other.

We can take advantage of the charge on colloidal particles to remove them from a variety of mixtures. If we place a colloidal dispersion in a container with charged electrodes, positively charged particles, such as iron(III) hydroxide particles, would move to the negative electrode. There, the colloidal particles lose their charge and coagulate as a precipitate.

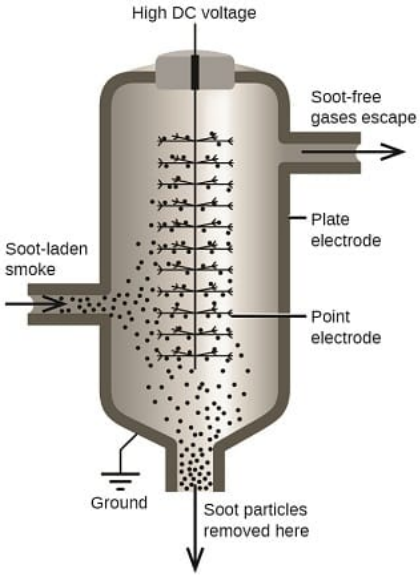


Figure 6.4.7: In a Cottrell precipitator, positively and negatively charged particles are attracted to highly charged electrodes, where they are neutralized and deposited as dust.

The carbon and dust particles in smoke are often colloidally dispersed and electrically charged. The charged particles are attracted to highly charged electrodes, where they are neutralized and deposited as dust (Figure 6.4.7. This is one of the important

methods used to clean up the smoke from a variety of industrial processes. The process is also important in the recovery of valuable products from the smoke and flue dust of smelters, furnaces, and kilns. There are also ionic air filters designed for home use to improve indoor air quality.

Gels

When we make gelatin, such as Jell-O, we are making a type of colloid (Figure 6.4.8). Gelatin sets on cooling because the hot aqueous mixture of gelatin coagulates as it cools and the whole mass, including the liquid, sets to an extremely viscous body known as a gel, a colloid in which the dispersing medium is a solid and the dispersed phase is a liquid. It appears that the fibers of the dispersing medium form a complex three-dimensional network, the interstices being filled with the liquid medium or a dilute solution of the dispersing medium. Because the formation of a gel is accompanied by the taking up of water or some other solvent, the gel is said to be hydrated or solvated.

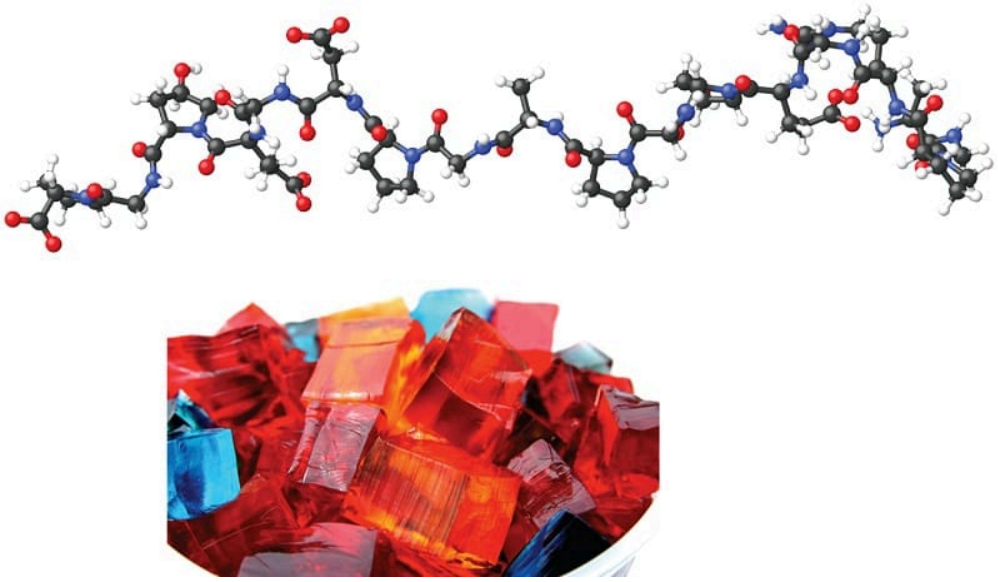


Figure 6.4.8: Gelatin desserts are colloids in which an aqueous solution of sweeteners and flavors is dispersed throughout a medium of solid proteins. (credit photo: modification of work by Steven Depolo).

Pectin, a carbohydrate from fruit juices, is a gel-forming substance important in jelly making. Silica gel, a colloidal dispersion of hydrated silicon dioxide, is formed when dilute hydrochloric acid is added to a dilute solution of sodium silicate. Canned Heat is a gel made by mixing alcohol and a saturated aqueous solution of calcium acetate.

Summary

Colloids are mixtures in which one or more substances are dispersed as relatively large solid particles or liquid droplets throughout a solid, liquid, or gaseous medium. The particles of a colloid remain dispersed and do not settle due to gravity, and they are often electrically charged. Colloids are widespread in nature and are involved in many technological applications.

Glossary

amphiphilic
: molecules possessing both hydrophobic (nonpolar) and a hydrophilic (polar) parts

colloid
: (also, colloidal dispersion) mixture in which relatively large solid or liquid particles are dispersed uniformly throughout a gas, liquid, or solid

dispersion medium
: solid, liquid, or gas in which colloidal particles are dispersed

dispersed phase
substance present as relatively large solid or liquid particles in a colloid

emulsifying agent
amphiphilic substance used to stabilize the particles of some emulsions

emulsion
colloid formed from immiscible liquids

gel
colloidal dispersion of a liquid in a solid

Tyndall effect
scattering of visible light by a colloidal dispersion

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6.5: Weight by Volume and Molarity

Learning Objectives

- Calculate solution concentrations in g/L, g/dL, %, mg/dL, mg%, and molarity (M)
- Perform dosage calculations.
- Appropriately use the solution dilution formula.

In preceding sections, we focused on the composition of substances: samples of matter that contain only one type of element or compound. However, mixtures—samples of matter containing two or more substances physically combined—are more commonly encountered in nature than are pure substances. Similar to a pure substance, the relative composition of a mixture plays an important role in determining its properties. The relative amount of oxygen in a planet's atmosphere determines its ability to sustain aerobic life. The relative amounts of iron, carbon, nickel, and other elements in steel (a mixture known as an "alloy") determine its physical strength and resistance to corrosion. The relative amount of the active ingredient in a medicine determines its effectiveness in achieving the desired pharmacological effect. The relative amount of sugar in a beverage determines its sweetness (Figure 6.5.1).



Figure 6.5.1: Sugar is one of many components in the complex mixture known as coffee. The amount of sugar in a given amount of coffee is an important determinant of the beverage's sweetness. (credit: Jane Whitney)

Solutions

We have previously defined solutions as homogeneous mixtures, meaning that the composition of the mixture (and therefore its properties) is uniform throughout its entire volume. Solutions occur frequently in nature and have also been implemented in many forms of manmade technology. We will explore a more thorough treatment of solution properties in the chapter on solutions and colloids, but here we will introduce some of the basic properties of solutions.

The relative amount of a given solution component is known as its concentration. Often, though not always, a solution contains one component with a concentration that is significantly greater than that of all other components. This component is called the solvent and may be viewed as the medium in which the other components are dispersed, or dissolved. Solutions in which water is the solvent are, of course, very common on our planet. A solution in which water is the solvent is called an aqueous solution.

A solute is a component of a solution that is typically present at a much lower concentration than the solvent. Solute concentrations are often described with qualitative terms such as dilute (of relatively low concentration) and concentrated (of relatively high concentration).

Concentrations may be quantitatively assessed using a wide variety of measurement units, each convenient for particular applications.

Weight by Volume

This value is derived from the weight of the solute divided by the total volume of the solute and the solvent, and it can be measured in several ways.

grams per liter

$$g/L = \frac{\text{g solute}}{\text{L solution}} \tag{6.5.1}$$

grams per deciliter or **%**

$$g/dL = \frac{\text{g solute}}{\text{dL solution}} \tag{6.5.2}$$

milligrams per deciliter or **mg%**

$$g/dL = \frac{\text{mg solute}}{\text{dL solution}} \tag{6.5.3}$$

Molarity

Molarity (*M*) is a useful concentration unit for many applications in chemistry. Molarity is defined as the number of moles of solute in exactly 1 liter (1 L) of the solution:

$$M = \frac{\text{mol solute}}{\text{L solution}} \tag{6.5.4}$$

Example 6.5.1: Calculating Molar Concentrations

A 355-mL soft drink sample contains 0.133 mol of sucrose (table sugar). What is the molar concentration of sucrose in the beverage?

Solution

Since the molar amount of solute and the volume of solution are both given, the molarity can be calculated using the definition of molarity. Per this definition, the solution volume must be converted from mL to L:

$$\begin{aligned} M &= \frac{mol\ solute}{L\ solution} \\ &= \frac{0.133\ mol}{355\ mL \times \dfrac{1\ L}{1000\ mL}} \\ &= 0.375\ M \end{aligned}$$

Exercise 6.5.1

A teaspoon of table sugar contains about 0.01 mol sucrose. What is the molarity of sucrose if a teaspoon of sugar has been dissolved in a cup of tea with a volume of 200 mL?

Answer

0.05 M

Example 6.5.2: Deriving Moles and Volumes from Molar Concentrations

How much sugar (mol) is contained in a modest sip (~10 mL) of the soft drink from Example 6.5.1?

Solution

In this case, we can rearrange the definition of molarity to isolate the quantity sought, moles of sugar. We then substitute the value for molarity that we derived in Example 3.4.2, 0.375 *M*:

$$M = \frac{\text{mol solute}}{\text{L solution}} onumber \tag{6.5.5}$$

Multiple \label

Exercise 6.5.2

What volume (mL) of the sweetened tea described in Example 6.5.1 contains the same amount of sugar (mol) as 10 mL of the soft drink in this example?

Answer

80 mL

Example 6.5.3: Calculating Molar Concentrations from the Mass of Solute

Distilled white vinegar (Figure 6.5.2) is a solution of acetic acid, CH_3CO_2H, in water. A 0.500-L vinegar solution contains 25.2 g of acetic acid. What is the concentration of the acetic acid solution in units of molarity?



Figure 6.5.3: Distilled white vinegar is a solution of acetic acid in water.

Solution

As in previous examples, the definition of molarity is the primary equation used to calculate the quantity sought. In this case, the mass of solute is provided instead of its molar amount, so we must use the solute's molar mass to obtain the amount of solute in moles:

$$M = \frac{\text{mol solute}}{\text{L solution}} = \frac{25.2\ \text{g}\ \text{CH}_3\text{CO}_2\text{H} \times \frac{1\ \text{mol}\ \text{CH}_3\text{CO}_2\text{H}}{60.052\ \text{g}\ \text{CH}_3\text{CO}_2\text{H}}}{0.500\ \text{L solution}} = 0.839\ M \tag{6.5.6}$$

$$M = \frac{\text{mol solute}}{\text{L solution}} = 0.839\ M \tag{6.5.7}$$

$$M = \frac{0.839\ \text{mol solute}}{1.00\ \text{L solution}} \tag{6.5.8}$$

Exercise 6.5.3

Calculate the molarity of 6.52 g of $CoCl_2$ (128.9 g/mol) dissolved in an aqueous solution with a total volume of 75.0 mL.

Answer

0.674 M

Example 6.5.4: Determining the Mass of Solute in a Given Volume of Solution

How many grams of NaCl are contained in 0.250 L of a 5.30-*M* solution?

Solution

The volume and molarity of the solution are specified, so the amount (mol) of solute is easily computed as demonstrated in Example 6.5.3:

$$M = \frac{\text{mol solute}}{\text{L solution}} \tag{6.5.9}$$

$$\text{mol solute} = M \times \text{L solution} \tag{6.5.10}$$

$$\text{mol solute} = 5.30\ \frac{\text{mol NaCl}}{\text{L}} \times 0.250\ \text{L} = 1.325\ \text{mol NaCl} \tag{6.5.11}$$

Finally, this molar amount is used to derive the mass of NaCl:

$$1.325\ \text{mol NaCl} \times \frac{58.44\ \text{g NaCl}}{\text{mol NaCl}} = 77.4\ \text{g NaCl} \tag{6.5.12}$$

Exercise 6.5.4

How many grams of $CaCl_2$ (110.98 g/mol) are contained in 250.0 mL of a 0.200-M solution of calcium chloride?

Answer

5.55 g $CaCl_2$

When performing calculations stepwise, as in Example 6.5.3, it is important to refrain from rounding any intermediate calculation results, which can lead to rounding errors in the final result. In Example 6.5.4, the molar amount of NaCl computed in the first step, 1.325 mol, would be properly rounded to 1.32 mol if it were to be reported; however, although the last digit (5) is not significant, it must be retained as a guard digit in the intermediate calculation. If we had not retained this guard digit, the final calculation for the mass of NaCl would have been 77.1 g, a difference of 0.3 g.

In addition to retaining a guard digit for intermediate calculations, we can also avoid rounding errors by performing computations in a single step (Example 6.5.5). This eliminates intermediate steps so that only the final result is rounded.

Example 6.5.5: Determining the Volume of Solution

In Example 6.5.3, we found the typical concentration of vinegar to be 0.839 *M*. What volume of vinegar contains 75.6 g of acetic acid?

Solution

First, use the molar mass to calculate moles of acetic acid from the given mass:

$$\text{g solute} \times \frac{\text{mol solute}}{\text{g solute}} = \text{mol solute} \tag{6.5.13}$$

Then, use the molarity of the solution to calculate the volume of solution containing this molar amount of solute:

$$\text{mol solute} \times \frac{\text{L solution}}{\text{mol solute}} = \text{L solution} \tag{6.5.14}$$

Combining these two steps into one yields:

$$\text{g solute} \times \frac{\text{mol solute}}{\text{g solute}} \times \frac{\text{L solution}}{\text{mol solute}} = \text{L solution} \tag{6.5.15}$$

$$75.6\ \text{g}\ \text{CH}_3\text{CO}_2\text{H}\left(\frac{\text{mol}\ \text{CH}_3\text{CO}_2\text{H}}{60.05\ \text{g}}\right)\left(\frac{\text{L solution}}{0.839\ \text{mol}\ \text{CH}_3\text{CO}_2\text{H}}\right) = 1.50\ \text{L solution} \tag{6.5.16}$$

Exercise 6.5.5:

What volume of a 1.50-M KBr solution contains 66.0 g KBr?

Answer

0.370 L

Dilution of Solutions

Dilution is the process whereby the concentration of a solution is lessened by the addition of solvent. For example, we might say that a glass of iced tea becomes increasingly diluted as the ice melts. The water from the melting ice increases the volume of the solvent (water) and the overall volume of the solution (iced tea), thereby reducing the relative concentrations of the solutes that give the beverage its taste (Figure 6.5.2).

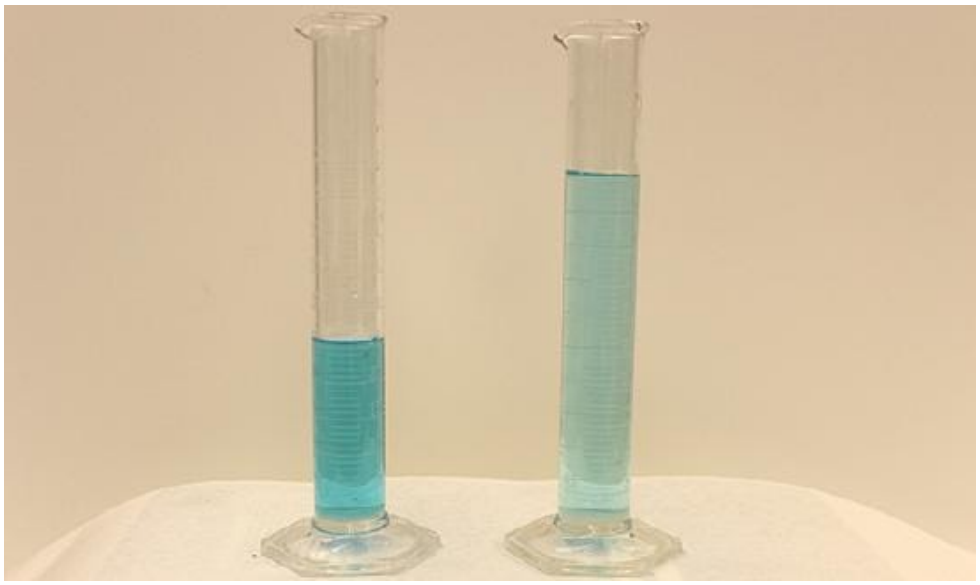


Figure 6.5.2: Both solutions contain the same mass of copper nitrate. The solution on the right is more dilute because the copper nitrate is dissolved in more solvent. (credit: Mark Ott).

Dilution is also a common means of preparing solutions of a desired concentration. By adding solvent to a measured portion of a more concentrated *stock solution*, we can achieve a particular concentration. For example, commercial pesticides are typically sold as solutions in which the active ingredients are far more concentrated than is appropriate for their application. Before they can be used on crops, the pesticides must be diluted. This is also a very common practice for the preparation of a number of common laboratory reagents (Figure 6.5.3).



Figure 6.5.3: A solution of $KMnO_4$ is prepared by mixing water with 4.74 g of KMnO4 in a flask. (credit: modification of work by Mark Ott)

A simple mathematical relationship can be used to relate the volumes and concentrations of a solution before and after the dilution process. According to the definition of molarity, the molar amount of solute in a solution is equal to the product of the solution's molarity and its volume in liters:

$$n = ML \tag{6.5.17}$$

Expressions like these may be written for a solution before and after it is diluted:

$$n_1 = M_1 L_1 \tag{6.5.18}$$

$$n_2 = M_2 L_2 \tag{6.5.19}$$

where the subscripts “1” and “2” refer to the solution before and after the dilution, respectively. Since the dilution process *does not change the amount of solute in the solution,*$n_1 = n_2$. Thus, these two equations may be set equal to one another:

$$M_1 L_1 = M_2 L_2 \tag{6.5.20}$$

This relation is commonly referred to as the dilution equation. Although we derived this equation using molarity as the unit of concentration and liters as the unit of volume, other units of concentration and volume may be used, so long as the units properly cancel per the factor-label method. Reflecting this versatility, the dilution equation is often written in the more general form:

$$C_1 V_1 = C_2 V_2 \tag{6.5.21}$$

where C and V are concentration and volume, respectively.

Example 6.5.6: Determining the Concentration of a Diluted Solution

If 0.850 L of a 5.00-*M* solution of copper nitrate, $Cu(NO_3)_2$, is diluted to a volume of 1.80 L by the addition of water, what is the molarity of the diluted solution?

Solution

We are given the volume and concentration of a stock solution, V_1 and C_1, and the volume of the resultant diluted solution, V_2. We need to find the concentration of the diluted solution, C_2. We thus rearrange the dilution equation in order to isolate C_2:

$$C_1 V_1 = C_2 V_2 \tag{6.5.22}$$

$$C_2 = \frac{C_1 V_1}{V_2} \tag{6.5.23}$$

Since the stock solution is being diluted by more than two-fold (volume is increased from 0.85 L to 1.80 L), we would expect the diluted solution’s concentration to be less than one-half 5 *M*. We will compare this ballpark estimate to the calculated result to check for any gross errors in computation (for example, such as an improper substitution of the given quantities). Substituting the given values for the terms on the right side of this equation yields:

$$C_2 = \frac{0.850\ \text{L} \times 5.00\ \dfrac{\text{mol}}{\text{L}}}{1.80\ \text{L}} = 2.36\ M \tag{6.5.24}$$

This result compares well to our ballpark estimate (it’s a bit less than one-half the stock concentration, 5 *M*).

Exercise 6.5.6

What is the concentration of the solution that results from diluting 25.0 mL of a 2.04-M solution of CH3OH to 500.0 mL?

Answer

0.102 M CH_3OH

Example 6.5.7: Volume of a Diluted Solution

What volume of 0.12 *M* HBr can be prepared from 11 mL (0.011 L) of 0.45 *M* HBr?

Solution

We are given the volume and concentration of a stock solution, V_1 and C_1, and the concentration of the resultant diluted solution, C_2. We need to find the volume of the diluted solution, V_2. We thus rearrange the dilution equation in order to isolate V_2:

$$C_1V_1 = C_2V_2 \tag{6.5.25}$$

$$V_2 = \frac{C_1V_1}{C_2} \tag{6.5.26}$$

Since the diluted concentration (0.12 *M*) is slightly more than one-fourth the original concentration (0.45 *M*), we would expect the volume of the diluted solution to be roughly four times the original volume, or around 44 mL. Substituting the given values and solving for the unknown volume yields:

$$V_2 = \frac{(0.45\ M)(0.011\ \text{L})}{(0.12\ M)} \tag{6.5.27}$$

$$V_2 = 0.041\ \text{L} \tag{6.5.28}$$

The volume of the 0.12-*M* solution is 0.041 L (41 mL). The result is reasonable and compares well with our rough estimate.

Exercise 6.5.7

A laboratory experiment calls for 0.125 M HNO_3. What volume of 0.125 M HNO_3 can be prepared from 0.250 L of 1.88 M HNO_3?

Answer

3.76 L

Example 6.5.8: Volume of a Concentrated Solution Needed for Dilution

What volume of 1.59 *M* KOH is required to prepare 5.00 L of 0.100 *M* KOH?

Solution

We are given the concentration of a stock solution, C_1, and the volume and concentration of the resultant diluted solution, V_2 and C_2. We need to find the volume of the stock solution, V_1. We thus rearrange the dilution equation in order to isolate V_1:

$$C_1V_1 = C_2V_2 \tag{6.5.29}$$

$$V_1 = \frac{C_2V_2}{C_1} \tag{6.5.30}$$

Since the concentration of the diluted solution 0.100 *M* is roughly one-sixteenth that of the stock solution (1.59 *M*), we would expect the volume of the stock solution to be about one-sixteenth that of the diluted solution, or around 0.3 liters. Substituting the given values and solving for the unknown volume yields:

$$V_1 = \frac{(0.100\ M)(5.00\ \text{L})}{1.59\ M} \tag{6.5.31}$$

$$V_1 = 0.314\ \text{L} \tag{6.5.32}$$

Thus, we would need 0.314 L of the 1.59-*M* solution to prepare the desired solution. This result is consistent with our rough estimate.

Exercise 6.5.8

What volume of a 0.575-M solution of glucose, $C_6H_{12}O_6$, can be prepared from 50.00 mL of a 3.00-M glucose solution?

Answer

0.261 L

Summary

Solutions are homogeneous mixtures. Many solutions contain one component, called the solvent, in which other components, called solutes, are dissolved. An aqueous solution is one for which the solvent is water. The concentration of a solution is a measure of the relative amount of solute in a given amount of solution. Concentrations may be measured using various units, with one very useful unit being molarity, defined as the number of moles of solute per liter of solution. The solute concentration of a solution may be decreased by adding solvent, a process referred to as dilution. The dilution equation is a simple relation between concentrations and volumes of a solution before and after dilution.

Key Equations

- $M = \frac{\text{mol solute}}{\text{L solution}}$
- $C_1V_1 = C_2V_2$

Glossary

aqueous solution
: solution for which water is the solvent

concentrated
: qualitative term for a solution containing solute at a relatively high concentration

concentration
: quantitative measure of the relative amounts of solute and solvent present in a solution

dilute
: qualitative term for a solution containing solute at a relatively low concentration

dilution
: process of adding solvent to a solution in order to lower the concentration of solutes

dissolved
: describes the process by which solute components are dispersed in a solvent

molarity (*M*)
: unit of concentration, defined as the number of moles of solute dissolved in 1 liter of solution

solute
: solution component present in a concentration less than that of the solvent

solvent
: solution component present in a concentration that is higher relative to other components

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6.6: Other Units for Solution Concentrations

Learning Objectives

- Accurately use the % by volume formula for calculations.
- Perform computations relating a solution's concentration and its components' volumes and/or masses.
- Calculate concentration in ppm and ppb. Use the resulting concentrations to evaluate the level of toxins in a sample.

In the previous section, we introduced molarity, a very useful measurement unit for evaluating the concentration of solutions. However, molarity is only one measure of concentration. In this section, we will introduce some other units of concentration that are commonly used in various applications, either for convenience or by convention.

Mass Percentage

Earlier in this chapter, we introduced percent composition as a measure of the relative amount of a given element in a compound. Percentages are also commonly used to express the composition of mixtures, including solutions. The mass percentage of a solution component is defined as the ratio of the component's mass to the solution's mass, expressed as a percentage:

$$\text{mass percentage} = \frac{\text{mass of component}}{\text{mass of solution}} \times 100\% \tag{6.6.1}$$

We are generally most interested in the mass percentages of solutes, but it is also possible to compute the mass percentage of solvent.

Mass percentage is also referred to by similar names such as *percent mass, percent weight, weight/weight percent*, and other variations on this theme. The most common symbol for mass percentage is simply the percent sign, %, although more detailed symbols are often used including %mass, %weight, and (w/w)%. Use of these more detailed symbols can prevent confusion of mass percentages with other types of percentages, such as volume percentages (to be discussed later in this section).

Mass percentages are popular concentration units for consumer products. The label of a typical liquid bleach bottle (Figure 6.6.1) cites the concentration of its active ingredient, sodium hypochlorite (NaOCl), as being 7.4%. A 100.0-g sample of bleach would therefore contain 7.4 g of NaOCl.



Figure 6.6.1: Liquid bleach is an aqueous solution of sodium hypochlorite (NaOCl). This brand has a concentration of 7.4% NaOCl by mass.

Example 6.6.1: Calculation of Percent by Mass

A 5.0-g sample of spinal fluid contains 3.75 mg (0.00375 g) of glucose. What is the percent by mass of glucose in spinal fluid?

Solution

The spinal fluid sample contains roughly 4 mg of glucose in 5000 mg of fluid, so the mass fraction of glucose should be a bit less than one part in 1000, or about 0.1%. Substituting the given masses into the equation defining mass percentage yields:

$$\%\,\text{glucose} = \frac{3.75\ \text{mg glucose} \times \frac{1\ \text{g}}{1000\ \text{mg}}}{5.0\ \text{g spinal fluid}} = 0.075\% \tag{6.6.2}$$

The computed mass percentage agrees with our rough estimate (it's a bit less than 0.1%).

Note that while any mass unit may be used to compute a mass percentage (mg, g, kg, oz, and so on), the same unit must be used for both the solute and the solution so that the mass units cancel, yielding a dimensionless ratio. In this case, we converted the units of solute in the numerator from mg to g to match the units in the denominator. We could just as easily have converted the denominator from g to mg instead. As long as identical mass units are used for both solute and solution, the computed mass percentage will be correct.

Exercise 6.6.1

A bottle of a tile cleanser contains 135 g of HCl and 775 g of water. What is the percent by mass of HCl in this cleanser?

Answer

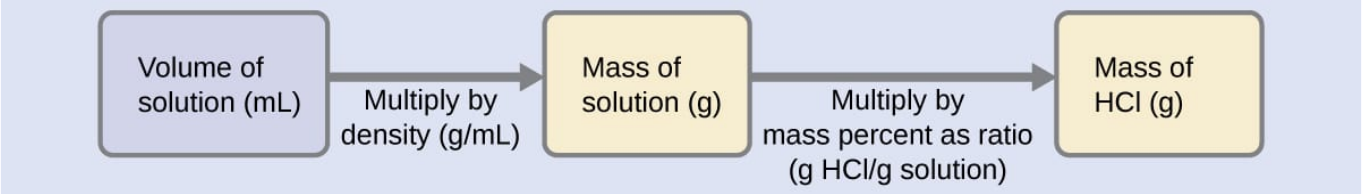
14.8%

Example 6.6.2: Calculations using Mass Percentage

"Concentrated" hydrochloric acid is an aqueous solution of 37.2% HCl that is commonly used as a laboratory reagent. The density of this solution is 1.19 g/mL. What mass of HCl is contained in 0.500 L of this solution?

Solution

The HCl concentration is near 40%, so a 100-g portion of this solution would contain about 40 g of HCl. Since the solution density isn't greatly different from that of water (1 g/mL), a reasonable estimate of the HCl mass in 500 g (0.5 L) of the solution is about five times greater than that in a 100 g portion, or $5 \times 40 = 200$ g. To derive the mass of solute in a solution from its mass percentage, we need to know the corresponding mass of the solution. Using the solution density given, we can convert the solution's volume to mass, and then use the given mass percentage to calculate the solute mass. This mathematical approach is outlined in this flowchart:



For proper unit cancellation, the 0.500-L volume is converted into 500 mL, and the mass percentage is expressed as a ratio, 37.2 g HCl/g solution:

$$500\ \text{mL solution}\left(\frac{1.19\ \text{g solution}}{\text{mL solution}}\right)\left(\frac{37.2\ \text{g HCl}}{100\ \text{g solution}}\right) = 221\ \text{g HCl} \tag{6.6.3}$$

This mass of HCl is consistent with our rough estimate of approximately 200 g.

Exercise 6.6.2

What volume of concentrated HCl solution contains 125 g of HCl?

Answer

282 mL

Volume Percentage

Liquid volumes over a wide range of magnitudes are conveniently measured using common and relatively inexpensive laboratory equipment. The concentration of a solution formed by dissolving a liquid solute in a liquid solvent is therefore often expressed as a volume percentage, %vol or (v/v)%:

Example 6.6.3: Calculations using Volume Percentage

Rubbing alcohol (isopropanol) is usually sold as a 70%vol aqueous solution. If the density of isopropyl alcohol is 0.785 g/mL, how many grams of isopropyl alcohol are present in a 355 mL bottle of rubbing alcohol?

Solution

Per the definition of volume percentage, the isopropanol volume is 70% of the total solution volume. Multiplying the isopropanol volume by its density yields the requested mass:

Exercise 6.6.3

Wine is approximately 12% ethanol (CH_3CH_2OH) by volume. Ethanol has a molar mass of 46.06 g/mol and a density 0.789 g/mL. How many moles of ethanol are present in a 750-mL bottle of wine?

Answer

1.5 mol ethanol

Mass-Volume Percentage

“Mixed” percentage units, derived from the mass of solute and the volume of solution, are popular for certain biochemical and medical applications. A mass-volume percent is a ratio of a solute’s mass to the solution’s volume expressed as a percentage. The specific units used for solute mass and solution volume may vary, depending on the solution. For example, physiological saline solution, used to prepare intravenous fluids, has a concentration of 0.9% mass/volume (m/v), indicating that the composition is 0.9 g of solute per 100 mL of solution. The concentration of glucose in blood (commonly referred to as “blood sugar”) is also typically expressed in terms of a mass-volume ratio. Though not expressed explicitly as a percentage, its concentration is usually given in milligrams of glucose per deciliter (100 mL) of blood (Figure 6.6.2).



(a) (b)

Figure 6.6.2: “Mixed” mass-volume units are commonly encountered in medical settings. (a) The NaCl concentration of physiological saline is 0.9% (m/v). (b) This device measures glucose levels in a sample of blood. The normal range for glucose concentration in blood (fasting) is around 70–100 mg/dL. (credit a: modification of work by “The National Guard”/Flickr; credit b: modification of work by Biswarup Ganguly).

Parts per Million and Parts per Billion

Very low solute concentrations are often expressed using appropriately small units such as parts per million (ppm) or parts per billion (ppb). Like percentage (“part per hundred”) units, ppm and ppb may be defined in terms of masses, volumes, or mixed mass-volume units. There are also ppm and ppb units defined with respect to numbers of atoms and molecules.

The mass-based definitions of ppm and ppb are given here:

$$\text{ppm} = \frac{\text{mass solute}}{\text{mass solution}} \times 10^6 \text{ ppm} \tag{6.6.4}$$

$$\text{ppb} = \frac{\text{mass solute}}{\text{mass solution}} \times 10^9 \text{ ppb} \tag{6.6.5}$$

Both ppm and ppb are convenient units for reporting the concentrations of pollutants and other trace contaminants in water. Concentrations of these contaminants are typically very low in treated and natural waters, and their levels cannot exceed relatively low concentration thresholds without causing adverse effects on health and wildlife. For example, the EPA has identified the maximum safe level of fluoride ion in tap water to be 4 ppm. Inline water filters are designed to reduce the concentration of fluoride and several other trace-level contaminants in tap water (Figure 6.6.3).



(a) (b)

Figure 6.6.3: (a) In some areas, trace-level concentrations of contaminants can render unfiltered tap water unsafe for drinking and cooking. (b) Inline water filters reduce the concentration of solutes in tap water. (credit a: modification of work by Jenn Durfey; credit b: modification of work by "vastateparkstaff"/Wikimedia commons).

Example 6.6.4: Parts per Million and Parts per Billion Concentrations

According to the EPA, when the concentration of lead in tap water reaches 15 ppb, certain remedial actions must be taken. What is this concentration in ppm? At this concentration, what mass of lead (μg) would be contained in a typical glass of water (300 mL)?

Solution

The definitions of the ppm and ppb units may be used to convert the given concentration from ppb to ppm. Comparing these two unit definitions shows that ppm is 1000 times greater than ppb (1 ppm = 10^3 ppb). Thus:

$$15 \cancel{\text{ ppb}} \times \frac{1 \text{ ppm}}{10^3 \cancel{\text{ ppb}}} = 0.015 \text{ ppm} \tag{6.6.6}$$

The definition of the ppb unit may be used to calculate the requested mass if the mass of the solution is provided. However, only the volume of solution (300 mL) is given, so we must use the density to derive the corresponding mass. We can assume the density of tap water to be roughly the same as that of pure water (~1.00 g/mL), since the concentrations of any dissolved substances should not be very large. Rearranging the equation defining the ppb unit and substituting the given quantities yields:

$$\text{ppb} = \frac{\text{mass solute}}{\text{mass solution}} \times 10^9 \text{ ppb} \tag{6.6.7}$$

$$\text{mass solute} = \frac{\text{ppb} \times \text{mass solution}}{10^9 \text{ ppb}} \tag{6.6.8}$$

$$\text{mass solute} = \frac{15 \text{ ppb} \times 300 \text{ mL} \times \dfrac{1.00 \text{ g}}{\text{mL}}}{10^9 \text{ ppb}} = 4.5 \times 10^{-6} \text{ g} \tag{6.6.9}$$

Finally, convert this mass to the requested unit of micrograms:

$$4.5 \times 10^{-6} \text{ g} \times \frac{1 \ \mu\text{g}}{10^{-6} \text{ g}} = 4.5 \ \mu\text{g} \tag{6.6.10}$$

Exercise 6.6.4

A 50.0-g sample of industrial wastewater was determined to contain 0.48 mg of mercury. Express the mercury concentration of the wastewater in ppm and ppb units.

Answer

9.6 ppm, 9600 ppb

Summary

In addition to molarity, a number of other solution concentration units are used in various applications. Percentage concentrations based on the solution components' masses, volumes, or both are useful for expressing relatively high concentrations, whereas lower concentrations are conveniently expressed using ppm or ppb units. These units are popular in environmental, medical, and other fields where mole-based units such as molarity are not as commonly used.

Glossary

mass percentage
ratio of solute-to-solution mass expressed as a percentage

mass-volume percent
ratio of solute mass to solution volume, expressed as a percentage

parts per billion (ppb)
ratio of solute-to-solution mass multiplied by 10^9

parts per million (ppm)
ratio of solute-to-solution mass multiplied by 10^6

volume percentage
ratio of solute-to-solution volume expressed as a percentage

Contributors

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6.7: Titrations - Lab 8

Skills to Develop

- Accurately perform a titration to calculate the unknown concentration of a solution in a neutralization reaction.
- Perform stoichiometric calculations using typical titration data.

In the 18th century, the strength (actually the concentration) of vinegar samples was determined by noting the amount of potassium carbonate, K_2CO_3, which had to be added, a little at a time, before bubbling ceased. The greater the weight of potassium carbonate added to reach the point where the bubbling ended, the more concentrated the vinegar.

We now know that the effervescence that occurred during this process was due to reaction with acetic acid, CH_3CO_2H, the compound primarily responsible for the odor and taste of vinegar. Acetic acid reacts with potassium carbonate according to the following equation:

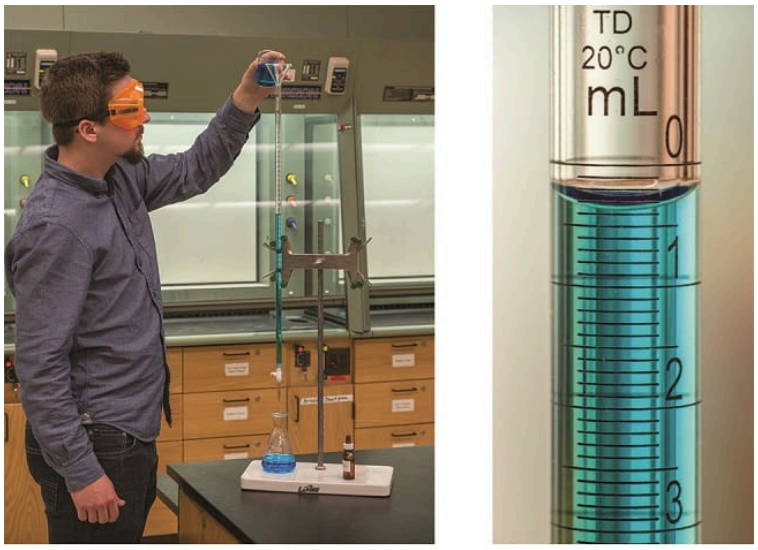
$$2\,\mathrm{CH_3CO_2H}(aq)+\mathrm{K_2CO_3}(s) \rightarrow 2\mathrm{KCH_3CO_3}(aq) + \mathrm{CO_2}(g) + \mathrm{H_2O}(l) \tag{6.7.1}$$

The bubbling was due to the production of CO_2.

The test of vinegar with potassium carbonate is one type of quantitative analysis—the determination of the amount or concentration of a substance in a sample. In the analysis of vinegar, the concentration of the solute (acetic acid) was determined from the amount of reactant that combined with the solute present in a known volume of the solution. In other types of chemical analyses, the amount of a substance present in a sample is determined by measuring the amount of product that results.

Titration

The described approach to measuring vinegar strength was an early version of the analytical technique known as titration analysis. A typical titration analysis involves the use of a buret (Figure $6.7.1$) to make incremental additions of a solution containing a known concentration of some substance (the titrant) to a sample solution containing the substance whose concentration is to be measured (the analyte). The titrant and analyte undergo a chemical reaction of known stoichiometry, and so measuring the volume of titrant solution required for complete reaction with the analyte (the equivalence point of the titration) allows calculation of the analyte concentration. The equivalence point of a titration may be detected visually if a distinct change in the appearance of the sample solution accompanies the completion of the reaction. The halt of bubble formation in the classic vinegar analysis is one such example, though, more commonly, special dyes called indicators are added to the sample solutions to impart a change in color at or very near the equivalence point of the titration. Equivalence points may also be detected by measuring some solution property that changes in a predictable way during the course of the titration. Regardless of the approach taken to detect a titration's equivalence point, the volume of titrant actually measured is called the end point. Properly designed titration methods typically ensure that the difference between the equivalence and end points is negligible. Though any type of chemical reaction may serve as the basis for a titration analysis, the three described in this chapter (precipitation, acid-base, and redox) are most common. Additional details regarding titration analysis are provided in the chapter on acid-base equilibria.



(a) (b)

Figure 6.7.1: (a) A student fills a buret in preparation for a titration analysis. (b) A typical buret permits volume measurements to the nearest 0.1 mL. (credit a: modification of work by Mark Blaser and Matt Evans; credit b: modification of work by Mark Blaser and Matt Evans)

Example 6.7.1: Titration Analysis

The end point in a titration of a 50.00-mL sample of aqueous HCl was reached by addition of 35.23 mL of 0.250 M NaOH titrant. The titration reaction is:

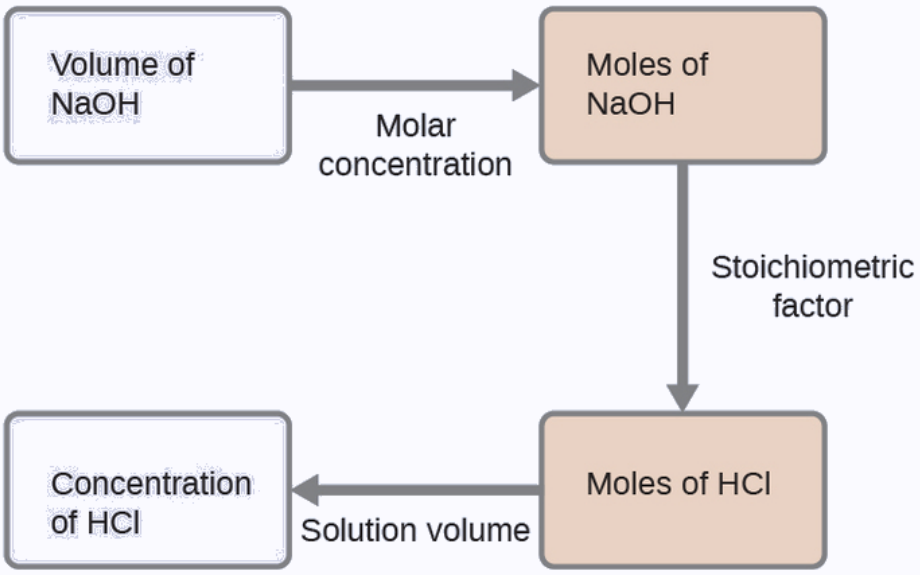
$$\mathrm{HCl}(aq) + \mathrm{NaOH}(aq) \rightarrow \mathrm{NaCl}(aq) + \mathrm{H_2O}(l) \tag{6.7.2}$$

What is the molarity of the HCl?

Solution

As for all reaction stoichiometry calculations, the key issue is the relation between the molar amounts of the chemical species of interest as depicted in the balanced chemical equation. The approach outlined in previous modules of this chapter is followed, with additional considerations required, since the amounts of reactants provided and requested are expressed as solution concentrations.

For this exercise, the calculation will follow the following outlined steps:



The molar amount of HCl is calculated to be:

$$35.23\ \cancel{\text{mL NaOH}} \times \frac{1\ \cancel{L}}{1000\ \cancel{\text{mL}}} \times \frac{0.250\ \cancel{\text{mol NaOH}}}{1\ \cancel{L}} \times \frac{1\ \text{mol HCl}}{1\ \cancel{\text{mol NaOH}}} = 8.81 \times 10^{-3}\ \text{mol HCl} \tag{6.7.3}$$

Using the provided volume of HCl solution and the definition of molarity, the HCl concentration is:

$$M = \frac{\text{mol HCl}}{\text{L solution}}$$
$$M = \frac{8.81 \times 10^{-3}\ \text{mol HCl}}{50.00\ \text{mL} \times \frac{1\ \text{L}}{1000\ \text{mL}}}$$
$$M = 0.176\ M$$

Note: For these types of titration calculations, it is convenient to recognize that solution molarity is also equal to the number of *milli*moles of solute per *milli*liter of solution:

$$M = \frac{\text{mol solute}}{\text{L solution}} \times \frac{\frac{10^3\ \text{mmol}}{\text{mol}}}{\frac{10^3\ \text{mL}}{\text{L}}} = \frac{\text{mmol solute}}{\text{mL solution}} \tag{6.7.4}$$

Using this version of the molarity unit will shorten the calculation by eliminating two conversion factors:

$$\frac{35.23\ \text{mL NaOH} \times \frac{0.250\ \text{mmol NaOH}}{\text{mL NaOH}} \times \frac{1\ \text{mmol HCl}}{1\ \text{mmol NaOH}}}{50.00\ \text{mL solution}} = 0.176\ M\ \text{HCl} \tag{6.7.5}$$

Exercise 6.7.1

A 20.00-mL sample of aqueous oxalic acid, $H_2C_2O_4$, was titrated with a 0.09113-*M* solution of potassium permanganate, $KMnO_4$.

$$2\,MnO_4^-(aq) + 5\,H_2C_2O_4(aq) + 6\,H^+(aq) \rightarrow 10\,CO_2(g) + 2\,Mn^{2+}(aq) + 8\,H_2O(l) \tag{6.7.6}$$

A volume of 23.24 mL was required to reach the end point. What is the oxalic acid molarity?

Answer

0.2648 *M*

Summary

The stoichiometry of chemical reactions may serve as the basis for quantitative chemical analysis methods. Titrations involve measuring the volume of a titrant solution required to completely react with a sample solution. This volume is then used to calculate the concentration of analyte in the sample using the stoichiometry of the titration reaction. Gravimetric analysis involves separating the analyte from the sample by a physical or chemical process, determining its mass, and then calculating its concentration in the sample based on the stoichiometry of the relevant process. Combustion analysis is a gravimetric method used to determine the elemental composition of a compound by collecting and weighing the gaseous products of its combustion.

Glossary

analyte
chemical species of interest

buret
device used for the precise delivery of variable liquid volumes, such as in a titration analysis

combustion analysis
gravimetric technique used to determine the elemental composition of a compound via the collection and weighing of its gaseous combustion products

end point
measured volume of titrant solution that yields the change in sample solution appearance or other property expected for stoichiometric equivalence (see *equivalence point*)

equivalence point
volume of titrant solution required to react completely with the analyte in a titration analysis; provides a stoichiometric amount of titrant for the sample's analyte according to the titration reaction

indicator

substance added to the sample in a titration analysis to permit visual detection of the end point

quantitative analysis
the determination of the amount or concentration of a substance in a sample

titrant
solution containing a known concentration of substance that will react with the analyte in a titration analysis

titration analysis
quantitative chemical analysis method that involves measuring the volume of a reactant solution required to completely react with the analyte in a sample

Contributors

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6.8: Unit 6 Practice Problems

Question 1.

In a solution, the substance being dissolved is called the _____.

Answer

solute

In a solution, the substance that does the dissolving is called the _____.

Answer

solvent

Question 2.

If 3.0g of Na_2SO_4 is dissolved in 450mL of water. What is the concentration of the resulting solution in g/L, g/dL, % w/v, mg/dL, mg%, *M* and m*M*.

Answer

$450mL \left| \frac{1L}{1000mL} \right. = 0.45L$

$\frac{3g}{0.45L} = 6.7g/L \times \left| \frac{1L}{10dL} \right. = 0.67\frac{g}{dL} = 0.67\%$

$0.67\frac{g}{dL} \left| \frac{1000mg}{1g} \right. = \frac{670mg}{dL} = 670\ mg\%$

$3g\ Na_2SO_4 \left| \frac{1\ mole}{142.04g} \right. = \frac{0.02112\ moles}{0.45L} = 0.047M \left| \frac{1000mM}{1M} \right. = 47mM$

Question 3.

What is the % by volume concentration of a solution of acid which contains 56mL HCl dissolved in 0.70L of distilled water?

Answer

$$\frac{56\text{mL HCl}}{756\text{mL solution}} \times 100 = 7.4\%$$

Question 4.

A patient needs to be injected with 5.0mg of a drug. The drug is in a solution with a concentration of 2.0mg/mL. How many mL of this medication should be given to the patient?

Answer

$$5.0\text{mg} \left| \frac{1\text{mL}}{2.0\text{mg}} \right. = 2.5\text{mL}$$

Question 5.

If you have 41 mL of 0.36M KCl and you add 150mL of distilled water to the solution, what is the concentration in mM of the diluted KCl solution?

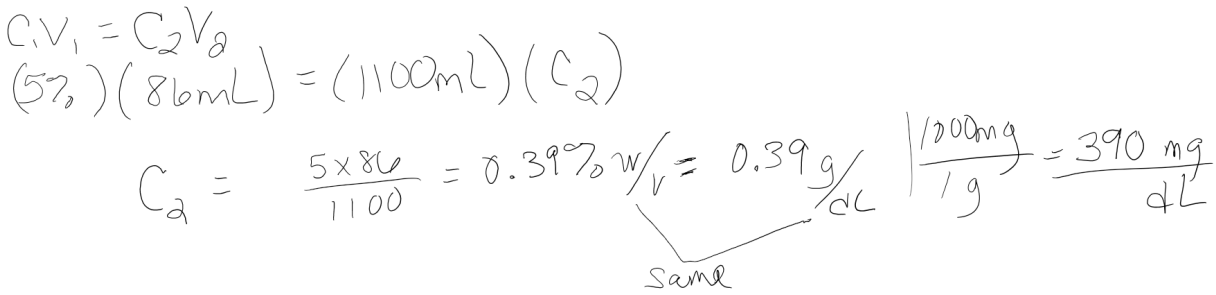
Answer

$$C_1V_1 = C_2V_2$$
$$(41\text{mL})(0.36\text{M}) = (191\text{mL})\,C_2$$
$$C_2 = 0.077\text{M} \left| \frac{1000\text{mM}}{1\text{M}} \right. = 77\text{mM}$$

Question 6.

If 86 mL of 5.0% w/v NaCl solution is diluted to 1.1L what is the concentration of the resulting solution in %w/v and mg/dL?

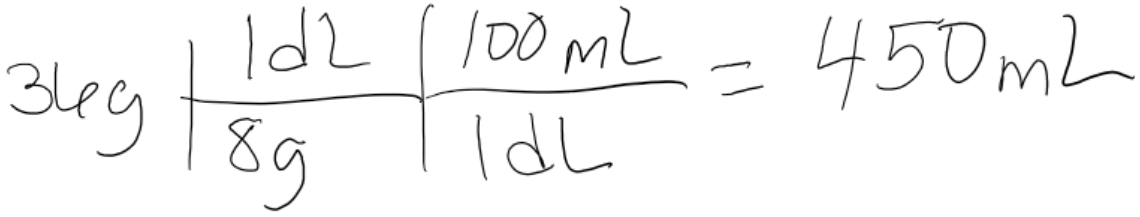
Answer



Question 7.

How many mL of a 8.0g/dL NaOH solution would be needed to provide a total of 36g of NaOH.

Answer



Question 8.

Predict whether N_2 will be more soluble in water (a polar substance) or gasoline (a nonpolar substance).

Answer

N_2 will be more soluble in gasoline because N_2 is also nonpolar (like dissolves like)

If ascorbic acid is soluble in water, would you expect it to be soluble in fat (a nonpolar substance)?

Answer

Since ascorbic acid is soluble in water, it is reasonable to assume that it is polar (or ionic) making it insoluble in fat.

Question 9.

What is the concentration in ppm if 0.0130 grams $MgCl_2$ is dissolved in 1.20L of water?

Answer

$$ppm = \frac{g\ solute}{g\ solution} \times 10^6$$

$$1.2\,L\,H_2O \left| \frac{1000\,mL}{1\,L} \right| \frac{1\,g\,H_2O}{1\,mL\,H_2O} = 1200\,g\,H_2O$$

$$\frac{0.0130\,g}{1200\,g} \times 10^6 = 10.8\,ppm$$

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7: ACID-BASE EQUILIBRIA

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General Chemistry

This chapter will illustrate the chemistry of acid-base reactions and equilibria, and provide you with tools for quantifying the concentrations of acids and bases in solutions.

Unit 7 Objectives

By the end of this unit, you will be able to:

- Classify substances as acidic or basic based on their pH or chemical formula.
- List the twelve common acids and bases, providing their name, formula, and whether they are weak or strong.
- Write equations for acid and base ionization reactions
- Use the ion-product constant for water to calculate hydronium and hydroxide ion concentrations
- Explain the characterization of aqueous solutions as acidic, basic, or neutral
- Calculate pH.
- Assess the relative strengths of acids and bases according to their ionization constants.
- Write balanced chemical equations for neutralization reactions and determine if the resulting solution will be acidic, basic, or neutral.
- Determine if an acid is monoprotic, diprotic, or triprotic given the chemical formula.
- Describe the composition and function of acid–base buffers.

7.1: Acids and Bases

7.2: pH and pOH

7.3: Relative Strengths of Acids and Bases

7.4: Acid-Base Neutralization

7.5: Polyprotic Acids

7.6: Buffers

7.7: Unit 7 Practice Problems

Contributors

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- Christy VanRooyen, Oregon Tech

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7.1: Acids and Bases

Learning Objectives

- Classify substances as acidic or basic based on their pH or chemical formula.
- List the twelve common acids and bases, providing their name, formula, and whether they are weak or strong.
- Write equations for acid and base ionization reactions
- Use the ion-product constant for water to calculate hydronium and hydroxide ion concentrations

Acids and bases have been known for a long time. When Robert Boyle characterized them in 1680, he noted that acids dissolve many substances, change the color of certain natural dyes (for example, they change litmus from blue to red), and lose these characteristic properties after coming into contact with alkalis (bases). In the eighteenth century, it was recognized that acids have a sour taste, react with limestone to liberate a gaseous substance (now known to be CO_2), and interact with alkalis to form neutral substances. In 1815, Humphry Davy contributed greatly to the development of the modern acid-base concept by demonstrating that hydrogen is the essential constituent of acids. Around that same time, Joseph Louis Gay-Lussac concluded that acids are substances that can neutralize bases and that these two classes of substances can be defined only in terms of each other. The significance of hydrogen was reemphasized in 1884 when Svante Arrhenius defined an acid as a compound that dissolves in water to yield hydrogen cations (now recognized to be hydronium ions) and a base as a compound that dissolves in water to yield hydroxide anions.

An acid is a compound that dissolves in water to yield hydronium ions (H_3O^+) and a base as a compound that dissolves in water to yield hydroxide ions ($\mathrm{OH^-}$). This definition is not wrong; it is simply limited.

Acids may be compounds such as HCl or H_2SO_4, organic acids like acetic acid ($\mathrm{CH_3COOH}$) or ascorbic acid (vitamin C), or H_2O. Anions (such as $\mathrm{HSO_4^-}$, $\mathrm{H_2PO_4^-}$, $\mathrm{HS^-}$, and $\mathrm{HCO_3^-}$) and cations (such as $\mathrm{H_3O^+}$, $\mathrm{NH_4^+}$, and $\mathrm{[Al(H_2O)_6]^{3+}}$) may also act as acids. Bases fall into the same three categories. Bases may be neutral molecules (such as $\mathrm{H_2O}$, $\mathrm{NH_3}$, and $\mathrm{CH_3NH_2}$), anions (such as $\mathrm{OH^-}$, $\mathrm{HS^-}$, $\mathrm{HCO_3^-}$, $\mathrm{CO_3^{2-}}$, $\mathrm{F^-}$, and $\mathrm{PO_4^{3-}}$), or cations (such as $\mathrm{[Al(H_2O)_5OH]^{2+}}$). The most familiar bases are ionic compounds such as NaOH and $\mathrm{Ca(OH)_2}$, which contain the hydroxide ion, $\mathrm{OH^-}$. The hydroxide ion in these compounds accepts a proton from acids to form water:

$$\mathrm{H^+ + OH^- \rightarrow H_2O} \tag{7.1.1}$$

List of Acids and Bases for CHE 101

Acids

1.	**Hydrofluoric acid**	HF	weak
2.	**Carbonic acid**	H_2CO_3	weak
3.	**Phosphoric acid**	H_3PO_4	weak
4.	**Sulfuric acid**	H_2SO_4	strong
5.	**Nitric acid**	HNO_3	strong
6.	**Hydrochloric**	HCl	strong

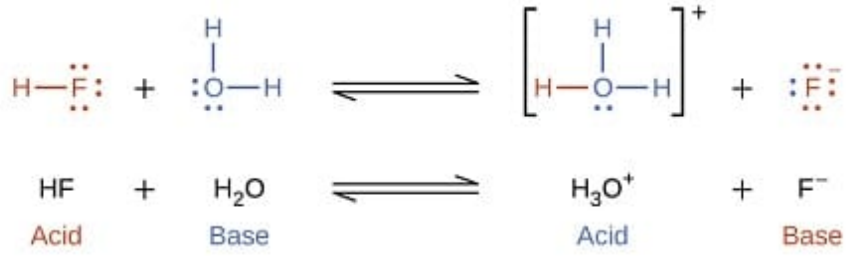
Bases

1.	**Potassium hydroxide**	KOH	strong

2.	**Calcium hydroxide**	$Ca(OH)_2$	strong
3.	**Sodium hydroxide**	NaOH	strong
4.	**Magnesium hydroxide**	$Mg(OH)_2$	strong
5.	**Aluminum hydroxide**	$Al(OH)_3$	strong
6.	**Ammonium hydroxide**	NH_4OH	weak

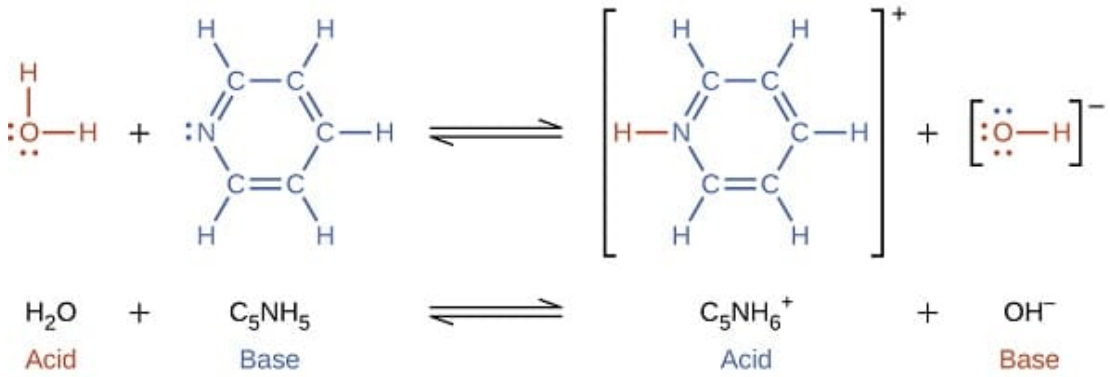
Equilibrium Constant of Water

The reaction between an acid and water is called acid ionization. For example, when hydrogen fluoride dissolves in water and ionizes, protons are transferred from hydrogen fluoride molecules to water molecules, yielding hydronium ions and fluoride ions:



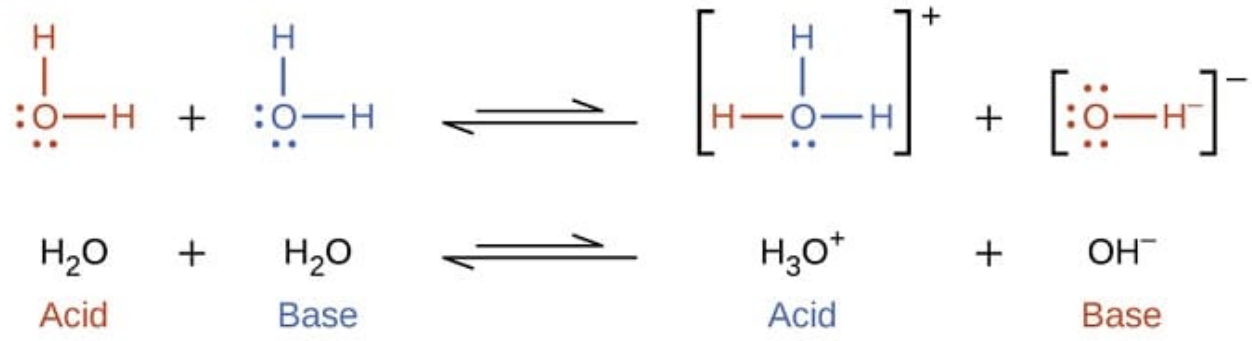
$$K = \frac{[H_3O^+][F^-]}{[HF]}$$

When we add a base to water, a base ionization reaction occurs in which protons are transferred from water molecules to base molecules. For example, adding pyridine to water yields hydroxide ions and pyridinium ions:



$$K = \frac{[C_5NH_6^+][OH^-]}{[C_5NH_5]}$$

Notice that both these ionization reactions are represented as equilibrium processes. The relative extent to which these acid and base ionization reactions proceed is an important topic treated in a later section of this chapter. In the preceding paragraphs we saw that water can function as either an acid or a base, depending on the nature of the solute dissolved in it. In fact, in pure water or in any aqueous solution, water acts both as an acid and a base. A very small fraction of water molecules donate protons to other water molecules to form hydronium ions and hydroxide ions:



This type of reaction, in which a substance ionizes when one molecule of the substance reacts with another molecule of the same substance, is referred to as **autoionization**. Pure water undergoes autoionization to a very slight extent. Only about two out of every 10^9 molecules in a sample of pure water are ionized at 25 °C. The equilibrium constant for the ionization of water is called the ion-product constant for water (K_w):

$$\mathrm{H_2O_{(l)} + H_2O_{(l)} \rightleftharpoons H_3O^+{}_{(aq)} + OH^-{}_{(aq)} \quad K_w = [H_3O^+][OH^-]} \tag{7.1.2}$$

The slight ionization of pure water is reflected in the small value of the equilibrium constant; at 25 °C, Kw has a value of 1.0×10^{-14}. The process is endothermic, and so the extent of ionization and the resulting concentrations of hydronium ion and hydroxide ion increase with temperature. For example, at 100 °C, the value for K_w is approximately 5.1×10^{-13}, roughly 50-times larger than the value at 25 °C.

Example 7.1.1: Ion Concentrations in Pure Water

What are the hydronium ion concentration and the hydroxide ion concentration in pure water at 25 °C?

Solution

The autoionization of water yields the same number of hydronium and hydroxide ions. Therefore, in pure water, $[H_3O^+] = [OH^-]$. At 25 °C:

$$K_w = [H_3O^+][OH^-] = [H_3O^+]^2 = [OH^-]^2 = 1.0 \times 10^{-14} \tag{7.1.3}$$

So:

$$[H_3O^+] = [OH^-] = \sqrt{1.0 \times 10^{-14}} = 1.0 \times 10^{-7}\ M \tag{7.1.4}$$

The hydronium ion concentration and the hydroxide ion concentration are the same, and we find that both equal $1.0 \times 10^{-7}\ M$.

Exercise 7.1.1

The ion product of water at 80 °C is 2.4×10^{-13}. What are the concentrations of hydronium and hydroxide ions in pure water at 80 °C?

Answer:

$$[H_3O^+] = [OH^-] = 4.9 \times 10^{-7}\ M$$

It is important to realize that the autoionization equilibrium for water is established in all aqueous solutions. Adding an acid or base to water will not change the position of the equilibrium. Example 14.12 demonstrates the quantitative aspects of this relation between hydronium and hydroxide ion concentrations.

Example 7.1.2: The Inverse Proportionality of $[H_3O^+]$ and $[OH^-]$

The Inverse Proportionality of [H_3O^+] and [OH^-] A solution of carbon dioxide in water has a hydronium ion concentration of $2.0 \times 10^{-6}\ M$. What is the concentration of hydroxide ion at 25 °C?

Solution

We know the value of the ion-product constant for water at 25 °C:

$$2\,H_2O_{(l)} \rightleftharpoons H_3O^+{}_{(aq)} + OH^-{}_{(aq)} \tag{7.1.5}$$

$$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14} \tag{7.1.6}$$

Thus, we can calculate the missing equilibrium concentration.

Rearrangement of the K_w expression yields that $[OH^-]$ is directly proportional to the inverse of [H_3O^+]:

$$[OH^-] = \frac{K_w}{[H_3O^+]} = \frac{1.0 \times 10^{-14}}{2.0 \times 10^{-6}} = 5.0 \times 10^{-9} \tag{7.1.7}$$

The hydroxide ion concentration in water is reduced to $5.0 \times 10^{-9}\ M$ as the hydrogen ion concentration increases to $2.0 \times 10^{-6}\ M$. This is expected from Le Châtelier's principle; the autoionization reaction shifts to the left to reduce the stress of the increased hydronium ion concentration and the $[OH^-]$ is reduced relative to that in pure water.

A check of these concentrations confirms that our arithmetic is correct:

$$\begin{aligned} K_w &= [H_3O^+][OH^-] \\ &= (2.0 \times 10^{-6})(5.0 \times 10^{-9}) \\ &= 1.0 \times 10^{-14} \end{aligned}$$

Exercise 7.1.2

What is the hydronium ion concentration in an aqueous solution with a hydroxide ion concentration of 0.001 M at 25 °C?

Answer

$$[H_3O^+] = 1 \times 10^{-11} M \tag{7.1.8}$$

Summary

A compound that can donate a proton (a hydrogen ion) to another compound is called a Brønsted-Lowry acid. The compound that accepts the proton is called a Brønsted-Lowry base. The species remaining after a Brønsted-Lowry acid has lost a proton is the conjugate base of the acid. The species formed when a Brønsted-Lowry base gains a proton is the conjugate acid of the base. Thus, an acid-base reaction occurs when a proton is transferred from an acid to a base, with formation of the conjugate base of the reactant acid and formation of the conjugate acid of the reactant base. Amphiprotic species can act as both proton donors and proton acceptors. Water is the most important amphiprotic species. It can form both the hydronium ion, H_3O^+, and the hydroxide ion, OH^- when it undergoes autoionization:

$$2\,H_2O_{(l)} \rightleftharpoons H_3O^+(aq) + OH^-(aq) \tag{7.1.9}$$

The ion product of water, K_w is the equilibrium constant for the autoionization reaction:

$$K_{\text{w}} = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14} \text{ at } 25°\text{C} \tag{7.1.10}$$

Key Equations

- $$K_{\text{w}} = [\text{H}_3\text{O}^+][\text{OH}^-\ ] = 1.0 \times 10^{-14} \text{ (at 25 °C)} \tag{7.1.11}$$

Glossary

acid ionization
: reaction involving the transfer of a proton from an acid to water, yielding hydronium ions and the conjugate base of the acid

amphiprotic
: species that may either gain or lose a proton in a reaction

amphoteric
: species that can act as either an acid or a base

autoionization
: reaction between identical species yielding ionic products; for water, this reaction involves transfer of protons to yield hydronium and hydroxide ions

base ionization
: reaction involving the transfer of a proton from water to a base, yielding hydroxide ions and the conjugate acid of the base

Brønsted-Lowry acid
: proton donor

Brønsted-Lowry base
: proton acceptor

conjugate acid
: substance formed when a base gains a proton

conjugate base
: substance formed when an acid loses a proton

ion-product constant for water (K_{w})
: equilibrium constant for the autoionization of water

Contributors

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7.2: pH and pOH

Learning Objectives

- Explain the characterization of aqueous solutions as acidic, basic, or neutral
- Use the ion-product constant for water to calculate hydronium and hydroxide ion concentrations
- Calculate pH.

As discussed earlier, hydronium and hydroxide ions are present both in pure water and in all aqueous solutions, and their concentrations are inversely proportional as determined by the ion product of water (K_w). The concentrations of these ions in a solution are often critical determinants of the solution's properties and the chemical behaviors of its other solutes, and specific vocabulary has been developed to describe these concentrations in relative terms. A solution is neutral if it contains equal concentrations of hydronium and hydroxide ions; acidic if it contains a greater concentration of hydronium ions than hydroxide ions; and basic if it contains a lesser concentration of hydronium ions than hydroxide ions.

A common means of expressing quantities, the values of which may span many orders of magnitude, is to use a logarithmic scale. One such scale that is very popular for chemical concentrations and equilibrium constants is based on the p-function, defined as shown where "X" is the quantity of interest and "log" is the base-10 logarithm:

$$\mathrm{pX} = -\log \mathrm{X} \tag{7.2.1}$$

The pH of a solution is therefore defined as shown here, where $[H_3O^+]$ is the molar concentration of hydronium ion in the solution:

$$\mathrm{pH} = -\log[\mathrm{H_3O^+}] \tag{7.2.2}$$

Rearranging this equation to isolate the hydronium ion molarity yields the equivalent expression:

$$[\mathrm{H_3O^+}] = 10^{-\mathrm{pH}} \tag{7.2.3}$$

Likewise, the hydroxide ion molarity may be expressed as a p-function, or pOH:

$$\mathrm{pOH} = -\log[\mathrm{OH^-}] \tag{7.2.4}$$

or

$$[\mathrm{OH^-}] = 10^{-\mathrm{pOH}} \tag{7.2.5}$$

Finally, the relation between these two ion concentration expressed as p-functions is easily derived from the K_w expression:

$$K_\mathrm{w} = [\mathrm{H_3O^+}][\mathrm{OH^-}] \tag{7.2.6}$$

$$-\log K_\mathrm{w} = -\log([\mathrm{H_3O^+}][\mathrm{OH^-}]) = -\log[\mathrm{H_3O^+}] + -\log[\mathrm{OH^-}] \tag{7.2.7}$$

$$\mathrm{p}K_\mathrm{w} = \mathrm{pH} + \mathrm{pOH} \tag{7.2.8}$$

At 25 °C, the value of K_w is 1.0×10^{-14}, and so:

$$14.00 = \mathrm{pH} + \mathrm{pOH} \tag{7.2.9}$$

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:

$$\mathrm{pH} = -\log[\mathrm{H_3O^+}] = -\log(1.0 \times 10^{-7}) = 7.00 \tag{7.2.10}$$

$$\mathrm{pOH} = -\log[\mathrm{OH^-}] = -\log(1.0 \times 10^{-7}) = 7.00 \tag{7.2.11}$$

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).

When $pH = 7$ Solutions are not Neutral

Since the autoionization constant K_w is temperature dependent, these correlations between pH values and the acidic/neutral/basic adjectives will be different at temperatures other than 25 °C. For example, the hydronium molarity of pure water at 80 °C is 4.9 × 10^{-7} *M*, which corresponds to pH and pOH values of:

$$\begin{aligned} pH &= -\log[\mathrm{H_3O^+}] \\ &= -\log(4.9 \times 10^{-7}) \\ &= 6.31 \end{aligned}$$

$$\begin{aligned} pOH &= -\log[\mathrm{OH^-}] \\ &= -\log(4.9 \times 10^{-7}) \\ &= 6.31 \end{aligned}$$

At this temperature, then, neutral solutions exhibit pH = pOH = 6.31, acidic solutions exhibit pH less than 6.31 and pOH greater than 6.31, whereas basic solutions exhibit pH greater than 6.31 and pOH less than 6.31. This distinction can be important when studying certain processes that occur at nonstandard temperatures, such as enzyme reactions in warm-blooded organisms. Unless otherwise noted, references to pH values are presumed to be those at standard temperature (25 °C) (Table 7.2.1).

Table 7.2.1***:*** *Summary of Relations for Acidic, Basic and Neutral Solutions*

Classification	Relative Ion Concentrations	pH at 25 °C
acidic	$[H_3O^+] > [OH^-]$	pH < 7
neutral	$[H_3O^+] = [OH^-]$	pH = 7
basic	$[H_3O^+] < [OH^-]$	pH > 7

Figure 7.2.1 shows the relationships between $[H_3O^+]$, $[OH^-]$, pH, and pOH, and gives values for these properties at standard temperatures for some common substances.

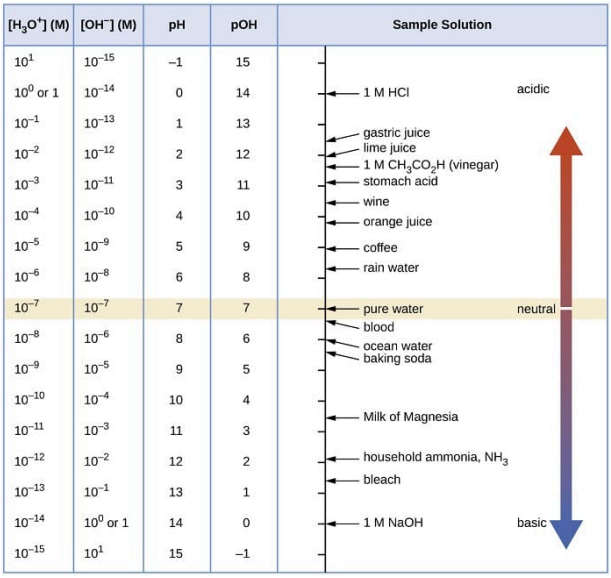


Figure 7.2.1: The pH and pOH scales represent concentrations of $[H_3O^+]$ and OH^-, respectively. The pH and pOH values of some common substances at standard temperature (25 °C) are shown in this chart.

Example 7.2.1: Calculation of pH from $[\mathrm{H_3O^+}]$

What is the pH of stomach acid, a solution of HCl with a hydronium ion concentration of $1.2 \times 10^{-3}\ M$?

Solution

$$\begin{aligned} pH &= -\log[H_3O^+] \\ &= -\log(1.2 \times 10^{-3}) \\ &= -(-2.92) \\ &= 2.92 \end{aligned}$$

Exercise 7.2.1

Water exposed to air contains carbonic acid, H_2CO_3, due to the reaction between carbon dioxide and water:

$$\mathrm{CO_2\,(aq) + H_2O\,(l)} \rightleftharpoons \mathrm{H_2CO_3\,(aq)} onumber \tag{7.2.12}$$

Air-saturated water has a hydronium ion concentration caused by the dissolved $\mathrm{CO_2}$ of $2.0 \times 10^{-6}\ M$, about 20-times larger than that of pure water. Calculate the pH of the solution at 25 °C.

Answer

5.70

Example 7.2.2: Calculation of Hydronium Ion Concentration from pH

Calculate the hydronium ion concentration of blood, the pH of which is 7.3 (slightly alkaline).

Solution

$$\mathrm{pH} = -\log[\mathrm{H_3O^+}] = 7.3 onumber \tag{7.2.13}$$

$$\log[\mathrm{H_3O^+}] = -7.3 onumber \tag{7.2.14}$$

$$[H_3O^+] = 10^{-7.3} onumber \tag{7.2.15}$$

or

$$[H_3O^+] = \text{antilog of} - 7.3 onumber \tag{7.2.16}$$

$$[H_3O^+] = 5 \times 10^{-8}\ Monumber \tag{7.2.17}$$

(On a calculator take the antilog, or the "inverse" log, of –7.3, or calculate $10^{-7.3}$.)

Exercise 7.2.2

Calculate the hydronium ion concentration of a solution with a pH of –1.07.

Answer

12 M

Environmental Science

Normal rainwater has a pH between 5 and 6 due to the presence of dissolved CO_2 which forms carbonic acid:

$$H_2O\,(l) + CO_2\,(g) \longrightarrow H_2CO_3\,(aq) \tag{7.2.18}$$

$$H_2CO_3\,(aq) \rightleftharpoons H^+\,(aq) + HCO_3{}^-\,(aq) \tag{7.2.19}$$

Acid rain is rainwater that has a pH of less than 5, due to a variety of nonmetal oxides, including CO_2, SO_2, SO_3, NO, and NO_2 being dissolved in the water and reacting with it to form not only carbonic acid, but sulfuric acid and nitric acid. The formation and subsequent ionization of sulfuric acid are shown here:

$$H_2O\,(l) + SO_3\,(g) \longrightarrow H_2SO_4\,(aq) \tag{7.2.20}$$

$$H_2SO_4\,(aq) \longrightarrow H^+\,(aq) + HSO_4{}^-\,(aq) \tag{7.2.21}$$

Carbon dioxide is naturally present in the atmosphere because we and most other organisms produce it as a waste product of metabolism. Carbon dioxide is also formed when fires release carbon stored in vegetation or when we burn wood or fossil fuels. Sulfur trioxide in the atmosphere is naturally produced by volcanic activity, but it also stems from burning fossil fuels, which have traces of sulfur, and from the process of "roasting" ores of metal sulfides in metal-refining processes. Oxides of nitrogen are formed in internal combustion engines where the high temperatures make it possible for the nitrogen and oxygen in air to chemically combine.

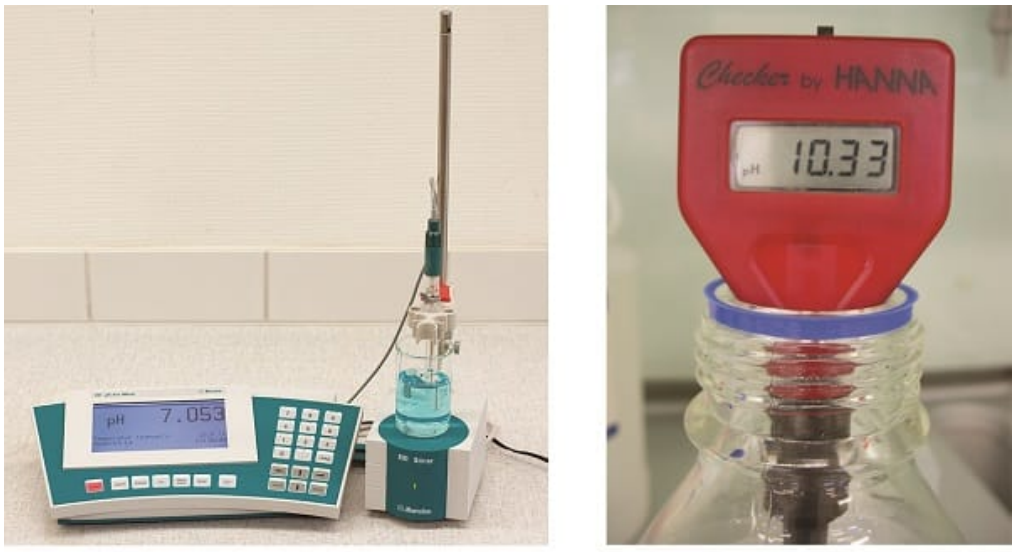
Acid rain is a particular problem in industrial areas where the products of combustion and smelting are released into the air without being stripped of sulfur and nitrogen oxides. In North America and Europe until the 1980s, it was responsible for the destruction of forests and freshwater lakes, when the acidity of the rain actually killed trees, damaged soil, and made lakes uninhabitable for all but the most acid-tolerant species. Acid rain also corrodes statuary and building facades that are made of marble and limestone (Figure 7.2.2). Regulations limiting the amount of sulfur and nitrogen oxides that can be released into the atmosphere by industry and automobiles have reduced the severity of acid damage to both natural and manmade environments in North America and Europe. It is now a growing problem in industrial areas of China and India.



(a) (b)

Figure 7.2.2: (a) Acid rain makes trees more susceptible to drought and insect infestation, and depletes nutrients in the soil. (b) It also is corrodes statues that are carved from marble or limestone. (credit a: modification of work by Chris M Morris; credit b: modification of work by "Eden, Janine and Jim"/Flickr)

The acidity of a solution is typically assessed experimentally by measurement of its pH. The pOH of a solution is not usually measured, as it is easily calculated from an experimentally determined pH value. The pH of a solution can be directly measured using a pH meter (Figure 7.2.3).



(a) (b)

Figure 7.2.3: (a) A research-grade pH meter used in a laboratory can have a resolution of 0.001 pH units, an accuracy of ± 0.002 pH units, and may cost in excess of $1000. (b) A portable pH meter has lower resolution (0.01 pH units), lower accuracy (± 0.2 pH units), and a far lower price tag. (credit b: modification of work by Jacopo Werther)

The pH of a solution may also be visually estimated using colored indicators (Figure 7.2.3).



Figure 7.2.4: (a) A universal indicator assumes a different color in solutions of different pH values. Thus, it can be added to a solution to determine the pH of the solution. The eight vials each contain a universal indicator and 0.1-M solutions of progressively weaker acids: HCl (pH = l), CH_3CO_2H (pH = 3), and NH_4Cl (pH = 5), deionized water, a neutral substance (pH = 7); and 0.1-M solutions of the progressively stronger bases: KCl (pH = 7), aniline, $C_6H_5NH_2$ (pH = 9), NH_3 (pH = 11), and NaOH (pH = 13). (b) pH paper contains a mixture of indicators that give different colors in solutions of differing pH values. (credit: modification of work by Sahar Atwa).

Summary

The concentration of hydronium ion in a solution of an acid in water is greater than $1.0 \times 10^{-7}\ M$ at 25 °C. The concentration of hydroxide ion in a solution of a base in water is greater than $1.0 \times 10^{-7}\ M$ at 25 °C. The concentration of H_3O^+ in a solution can be expressed as the pH of the solution; $\mathrm{pH} = -\log \mathrm{H_3O^+}$. The concentration of OH^- can be expressed as the pOH of the solution: $\mathrm{pOH} = -\log[\mathrm{OH^-}]$. In pure water, pH = 7.00 and pOH = 7.00

Key Equations

- $\mathrm{pH} = -\log[\mathrm{H_3O^+}]$
- $\mathrm{pOH} = -\log[\mathrm{OH^-}]$
- $[H_3O^+] = 10^{-\mathrm{pH}}$
- $[OH^-] = 10^{-\mathrm{pOH}}$
- pH + pOH = pK_w = 14.00 at 25 °C

Glossary

acidic
: describes a solution in which $[H_3O^+] > [OH^-]$

basic
: describes a solution in which $[H_3O^+] < [OH^-]$

neutral
: describes a solution in which $[H_3O^+] = [OH^-]$

pH
: logarithmic measure of the concentration of hydronium ions in a solution

pOH
: logarithmic measure of the concentration of hydroxide ions in a solution

Contributors

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7.3: Relative Strengths of Acids and Bases

Learning Objectives

- Assess the relative strengths of acids and bases according to their ionization constants

We can rank the strengths of acids by the extent to which they ionize in aqueous solution. The reaction of an acid with water is given by the general expression:

$$\mathrm{HA}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{A^-}(aq) \tag{7.3.1}$$

Water is the base that reacts with the acid HA, $\mathrm{A^-}$ is the conjugate base of the acid HA, and the hydronium ion is the conjugate acid of water. A strong acid yields 100% (or very nearly so) of $\mathrm{H_3O^+}$ and $\mathrm{A^-}$ when the acid ionizes in water; Figure $7.3.1$ lists several strong acids. A weak acid gives small amounts of $\mathrm{H_3O^+}$ and $\mathrm{A^-}$.

Figure $7.3.1$*: Some of the common strong acids and bases are listed here.*

Six Strong Acids		Six Strong Bases	
$\mathrm{HClO_4}$	perchloric acid	LiOH	lithium hydroxide
HCl	hydrochloric acid	NaOH	sodium hydroxide
HBr	hydrobromic acid	KOH	potassium hydroxide
HI	hydroiodic acid	$\mathrm{Ca(OH)_2}$	calcium hydroxide
$\mathrm{HNO_3}$	nitric acid	$\mathrm{Sr(OH)_2}$	strontium hydroxide
$\mathrm{H_2SO_4}$	sulfuric acid	$\mathrm{Ba(OH)_2}$	barium hydroxide

The relative strengths of acids may be determined by measuring their equilibrium constants in aqueous solutions. In solutions of the same concentration, stronger acids ionize to a greater extent, and so yield higher concentrations of hydronium ions than do weaker acids.

We can rank the strengths of bases by their tendency to form hydroxide ions in aqueous solution. The reaction of a base with water is given by:

$$\mathrm{B}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{HB^+}(aq) + \mathrm{OH^-}(aq) \tag{7.3.2}$$

Water is the acid that reacts with the base, $\mathrm{HB^+}$ is the conjugate acid of the base B, and the hydroxide ion is the conjugate base of water. A strong base yields 100% (or very nearly so) of $\mathrm{OH^-}$ and $\mathrm{HB^+}$ when it reacts with water; Figure $7.3.1$ lists several strong bases. A weak base yields a small proportion of hydroxide ions. Soluble ionic hydroxides such as NaOH are considered strong bases because they dissociate completely when dissolved in water.

The Ionization of Weak Acids and Weak Bases

Many acids and bases are weak; that is, they do not ionize fully in aqueous solution. A solution of a weak acid in water is a mixture of the nonionized acid, hydronium ion, and the conjugate base of the acid, with the nonionized acid present in the greatest concentration. Thus, a weak acid increases the hydronium ion concentration in an aqueous solution (but not as much as the same amount of a strong acid).

Acetic acid $(\mathrm{CH_3CO_2H})$ is a weak acid. When we add acetic acid to water, it ionizes to a small extent according to the equation:

$$\mathrm{CH_3CO_2H}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{CH_3CO_2{}^-}(aq) \tag{7.3.3}$$

giving an equilibrium mixture with most of the acid present in the nonionized (molecular) form. This equilibrium, like other equilibria, is dynamic; acetic acid molecules donate hydrogen ions to water molecules and form hydronium ions and acetate ions at the same rate that hydronium ions donate hydrogen ions to acetate ions to reform acetic acid molecules and water molecules.

We can tell by measuring the pH of an aqueous solution of known concentration that only a fraction of the weak acid is ionized at any moment (Figure 7.3.4). The remaining weak acid is present in the nonionized form.



Figure 7.3.4: pH paper indicates that a 0.1-M solution of HCl (beaker on left) has a pH of 1. The acid is fully ionized and $[\mathrm{H_3O^+}]$ = *0.1 M. A 0.1-M solution of CH_3CO_2H (beaker on right) has a pH of 3 (* $[\mathrm{H_3O^+}]$ = *0.001 M) because the weak acid CH_3CO_2H is only partially ionized. In this solution,* $[\mathrm{H_3O^+}] < [\mathrm{CH_3CO_2H}]$. *(credit: modification of work by Sahar Atwa)*

At equilibrium, a solution of a weak base in water is a mixture of the nonionized base, the conjugate acid of the weak base, and hydroxide ion with the nonionized base present in the greatest concentration. Thus, a weak base increases the hydroxide ion concentration in an aqueous solution (but not as much as the same amount of a strong base).

For example, a solution of the weak base trimethylamine, $(CH_3)_3N$, in water reacts according to the equation:

$$(\mathrm{CH_3})_3\mathrm{N}(aq) + \mathrm{H_2O}(l) \rightleftharpoons (\mathrm{CH_3})_3\mathrm{NH^+}(aq) + \mathrm{OH^-}(aq) \tag{7.3.4}$$

This gives an equilibrium mixture with most of the base present as the nonionized amine. This equilibrium is analogous to that described for weak acids.

We can confirm by measuring the pH of an aqueous solution of a weak base of known concentration that only a fraction of the base reacts with water (Figure 14.4.5). The remaining weak base is present as the unreacted form.



Figure 7.3.5: pH paper indicates that a 0.1-M solution of NH_3 (left) is weakly basic. The solution has a pOH of 3 ($[OH^-]$ = 0.001 M) because the weak base NH_3 only partially reacts with water. A 0.1-M solution of NaOH (right) has a pOH of 1 because NaOH is a strong base (credit: modification of work by Sahar Atwa).

Example 7.3.6: Formic Acid in Ant stings

Formic acid, HCO_2H, is the irritant that causes the body's reaction to ant stings.



The pain of an ant's sting is caused by formic acid. (credit: John Tann)

Summary

The strengths of acids and bases in aqueous solutions can be determined by their acid or base ionization constants. Strong acids are completely ionized in aqueous solution because their conjugate bases are weaker bases than water. Weak acids are only partially ionized because their conjugate bases are strong enough to compete successfully with water for possession of protons. Strong bases react with water to quantitatively form hydroxide ions. Weak bases give only small amounts of hydroxide ion.

Glossary

percent ionization
: ratio of the concentration of the ionized acid to the initial acid concentration, times 100

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7.4: Acid-Base Neutralization

Learning Objectives

- Write balanced chemical equations for neutralization reactions and determine if the resulting solution will be acidic, basic, or neutral.

As we have seen in the section on chemical reactions, when an acid and base are mixed, they undergo a neutralization reaction. The word “neutralization” seems to imply that a stoichiometrically equivalent solution of an acid and a base would be neutral. This is sometimes true, but the salts that are formed in these reactions may have acidic or basic properties of their own, as we shall now see.

Acid-Base Neutralization

A solution is neutral when it contains equal concentrations of hydronium and hydroxide ions. When we mix solutions of an acid and a base, an acid-base neutralization reaction occurs. However, even if we mix stoichiometrically equivalent quantities, we may find that the resulting solution is not neutral. It could contain either an excess of hydronium ions or an excess of hydroxide ions because the nature of the salt formed determines whether the solution is acidic, neutral, or basic. The following four situations illustrate how solutions with various pH values can arise following a neutralization reaction using stoichiometrically equivalent quantities:

1. A strong acid and a strong base, such as HCl(*aq*) and NaOH(*aq*) will react to form a neutral solution since the conjugate partners produced are of negligible strength:

$$\mathrm{HCl}(aq) + \mathrm{NaOH}(aq) \rightleftharpoons \mathrm{NaCl}(aq) + \mathrm{H_2O}(l) \tag{7.4.1}$$

2. A strong acid and a weak base yield a weakly acidic solution, not because of the strong acid involved, but because of the conjugate acid of the weak base.
3. A weak acid and a strong base yield a weakly basic solution. A solution of a weak acid reacts with a solution of a strong base to form the conjugate base of the weak acid and the conjugate acid of the strong base. The conjugate acid of the strong base is a weaker acid than water and has no effect on the acidity of the resulting solution. However, the conjugate base of the weak acid is a weak base and ionizes slightly in water. This increases the amount of hydroxide ion in the solution produced in the reaction and renders it slightly basic.
4. A weak acid plus a weak base can yield either an acidic, basic, or neutral solution. This is the most complex of the four types of reactions. When the conjugate acid and the conjugate base are of unequal strengths, the solution can be either acidic or basic, depending on the relative strengths of the two conjugates. Occasionally the weak acid and the weak base will have the *same* strength, so their respective conjugate base and acid will have the same strength, and the solution will be neutral. To predict whether a particular combination will be acidic, basic or neutral, tabulated *K* values of the conjugates must be compared.

Neutralization Reactions

This is the general format for a neutralization reaction:

Acid + Base → Salt + Water

It is important to note that neutralization reactions are just a specific type of double displacement redox reaction . Remember the rules for writing displacement reactions.

1. Figure out what the reactants and products will be.
   - The cations will switch places in the products for double replacement reactions.
   - The element will replace the cation in the reacting compound and result in a new product for single replacement reactions.
2. Make sure that all of the compound formulas are correctly written based on the oxidation state of the elements involved.

3. Balance the equation.

Example 7.4.6: Predicting the outcome of a neutralization reaction

Write the balanced chemical equation for the neutralization of HCl with $Mg(OH)_2$. Hint: neutralization reactions are a specialized type of double replacement reaction.

$2HCl + Mg(OH)_2 \rightarrow MgCl_2 + 2H_2O$

Since HCl is a strong acid and $Mg(OH)_2$ is a strong base, the resulting solution would be neutral.

Stomach Antacids

Our stomachs contain a solution of roughly 0.03 *M* HCl, which helps us digest the food we eat. The burning sensation associated with heartburn is a result of the acid of the stomach leaking through the muscular valve at the top of the stomach into the lower reaches of the esophagus. The lining of the esophagus is not protected from the corrosive effects of stomach acid the way the lining of the stomach is, and the results can be very painful. When we have heartburn, it feels better if we reduce the excess acid in the esophagus by taking an antacid. As you may have guessed, antacids are bases. One of the most common antacids is calcium carbonate, $CaCO_3$. The reaction,

$$CaCO_3(s) + 2HCl(aq) \rightleftharpoons CaCl_2(aq) + H_2O(l) + CO_2(g) \tag{7.4.2}$$

not only neutralizes stomach acid, it also produces $CO_2(g)$, which may result in a satisfying belch.

Milk of Magnesia is a suspension of the sparingly soluble base magnesium hydroxide, $Mg(OH)_2$. It works according to the reaction:

$$Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2OH^-(aq) \tag{7.4.3}$$

The hydroxide ions generated in this equilibrium then go on to react with the hydronium ions from the stomach acid, so that :

$$H_3O^+ + OH^- \rightleftharpoons 2H_2O(l) \tag{7.4.4}$$

This reaction does not produce carbon dioxide, but magnesium-containing antacids can have a laxative effect. Several antacids have aluminum hydroxide, $Al(OH)_3$, as an active ingredient. The aluminum hydroxide tends to cause constipation, and some antacids use aluminum hydroxide in concert with magnesium hydroxide to balance the side effects of the two substances.

Culinary Aspects of Chemistry

Cooking is essentially synthetic chemistry that happens to be safe to eat. There are a number of examples of acid-base chemistry in the culinary world. One example is the use of baking soda, or sodium bicarbonate in baking. $NaHCO_3$ is a base. When it reacts with an acid such as lemon juice, buttermilk, or sour cream in a batter, bubbles of carbon dioxide gas are formed from decomposition of the resulting carbonic acid, and the batter “rises.” Baking powder is a combination of sodium bicarbonate, and one or more acid salts that react when the two chemicals come in contact with water in the batter.

Many people like to put lemon juice or vinegar, both of which are acids, on cooked fish (Figure 7.4.1). It turns out that fish have volatile amines (bases) in their systems, which are neutralized by the acids to yield involatile ammonium salts. This reduces the odor of the fish, and also adds a “sour” taste that we seem to enjoy.



$CH_3COOH + NH_2CH_2CH_2CH_2CH_2NH_2 \longrightarrow CH_3COO^- + NH_3^+CH_2CH_2CH_2CH_2NH_2$

Acetic acid + Putrescine → Acetate ion + Putrescinium ion

Figure 7.4.1: A neutralization reaction takes place between citric acid in lemons or acetic acid in vinegar, and the bases in the flesh of fish.

Pickling is a method used to preserve vegetables using a naturally produced acidic environment. The vegetable, such as a cucumber, is placed in a sealed jar submerged in a brine solution. The brine solution favors the growth of beneficial bacteria and suppresses the growth of harmful bacteria. The beneficial bacteria feed on starches in the cucumber and produce lactic acid as a waste product in a process called fermentation. The lactic acid eventually increases the acidity of the brine to a level that kills any harmful bacteria, which require a basic environment. Without the harmful bacteria consuming the cucumbers they are able to last much longer than if they were unprotected. A byproduct of the pickling process changes the flavor of the vegetables with the acid making them taste sour.

Summary

The characteristic properties of aqueous solutions of Brønsted-Lowry acids are due to the presence of hydronium ions; those of aqueous solutions of Brønsted-Lowry bases are due to the presence of hydroxide ions. The neutralization that occurs when aqueous solutions of acids and bases are combined results from the reaction of the hydronium and hydroxide ions to form water. Some salts formed in neutralization reactions may make the product solutions slightly acidic or slightly basic.

Contributors

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7.5: Polyprotic Acids

Learning Objectives

- Determine if an acid is monoprotic, diprotic, or triprotic given the chemical formula.

Monoprotic

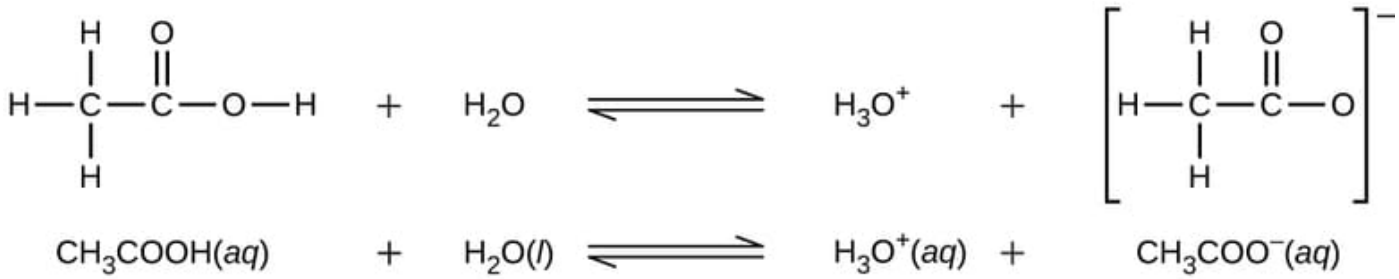
We can classify acids by the number of protons per molecule that they can give up in a reaction. Acids such as HCl, $\mathrm{HNO_3}$, and HCN that contain one ionizable hydrogen atom in each molecule are called monoprotic acids. Their reactions with water are:

$$\mathrm{HCl}(aq) + \mathrm{H_2O}(l) \longrightarrow \mathrm{H_3O^+}(aq) + \mathrm{Cl^-}(aq) \tag{7.5.1}$$

$$\mathrm{HNO_3}(aq) + \mathrm{H_2O}(l) \longrightarrow \mathrm{H_3O^+}(aq) + \mathrm{NO_3^-}(aq) \tag{7.5.2}$$

$$\mathrm{HCN}(aq) + \mathrm{H_2O}(l) \longrightarrow \mathrm{H_3O^+}(aq) + \mathrm{CN^-}(aq) \tag{7.5.3}$$

Even though it contains four hydrogen atoms, acetic acid, $\mathrm{CH_3CO_2H}$, is also monoprotic because only the hydrogen atom from the carboxyl group ($-\mathrm{COOH}$) reacts with bases:



Similarly, monoprotic bases are bases that will accept a single proton.

Diprotic Acids

Diprotic acids contain two ionizable hydrogen atoms per molecule; ionization of such acids occurs in two steps. The first ionization always takes place to a greater extent than the second ionization. For example, sulfuric acid, a strong acid, ionizes as follows:

- **The first ionization is**

$$\mathrm{H_2SO_4}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{HSO_4^-}(aq) \tag{7.5.4}$$

- **The second ionization is**

$$\mathrm{HSO_4^-}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{SO_4^{2-}}(aq) \tag{7.5.5}$$

This stepwise ionization process occurs for all polyprotic acids. When we make a solution of a weak diprotic acid, we get a solution that contains a mixture of acids. Carbonic acid, $\mathrm{H_2CO_3}$, is an example of a weak diprotic acid. The first ionization of carbonic acid yields hydronium ions and bicarbonate ions in small amounts.

- **First Ionization**

$$\mathrm{H_2CO_3}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{HCO_3^-}(aq) \tag{7.5.6}$$

The bicarbonate ion can also act as an acid. It ionizes and forms hydronium ions and carbonate ions in even smaller quantities.

- **Second Ionization**

$$\mathrm{HCO_3}^-(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O}^+(aq) + \mathrm{CO_3}^{2-}(aq) \tag{7.5.7}$$

Triprotic Acids

A triprotic acid is an acid that has three dissociable protons that undergo stepwise ionization: Phosphoric acid is a typical example:

- **The first ionization is**

$$\mathrm{H_3PO_4}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O}^+(aq) + \mathrm{H_2PO_4}^-(aq) \tag{7.5.8}$$

- **The second ionization is**

$$\mathrm{H_2PO_4}^-(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O}^+(aq) + \mathrm{HPO_4}^{2-}(aq) \tag{7.5.9}$$

- **The third ionization is**

$$\mathrm{HPO_4}^{2-}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O}^+(aq) + \mathrm{PO_4}^{3-}(aq) \tag{7.5.10}$$

As with the diprotic acids, the differences in the ionization constants of these reactions tell us that in each successive step the degree of ionization is significantly weaker. This is a general characteristic of polyprotic acids and successive ionization constants often differ by a factor of about 10^5 to 10^6. This set of three dissociation reactions may appear to make calculations of equilibrium concentrations in a solution of H_3PO_4 complicated. However, because the successive ionization constants differ by a factor of 10^5 to 10^6, the calculations can be broken down into a series of parts similar to those for diprotic acids.

Polyprotic bases can accept more than one hydrogen ion in solution. The carbonate ion is an example of a diprotic base, since it can accept up to two protons. Solutions of alkali metal carbonates are quite alkaline, due to the reactions:

$$\mathrm{H_2O}(l) + \mathrm{CO_3}^{2-}(aq) \rightleftharpoons \mathrm{HCO_3}^-(aq) + \mathrm{OH}^-(aq) \tag{7.5.11}$$

and

$$\mathrm{H_2O}(l) + \mathrm{HCO_3}^-(aq) \rightleftharpoons \mathrm{H_2CO_3}(aq) + \mathrm{OH}^-(aq) \tag{7.5.12}$$

Summary

An acid that contains more than one ionizable proton is a polyprotic acid. The protons of these acids ionize in steps. The differences in the acid ionization constants for the successive ionizations of the protons in a polyprotic acid usually vary by roughly five orders of magnitude.

Glossary

diprotic acid
: acid containing two ionizable hydrogen atoms per molecule. A diprotic acid ionizes in two steps

diprotic base
: base capable of accepting two protons. The protons are accepted in two steps

monoprotic acid
: acid containing one ionizable hydrogen atom per molecule

stepwise ionization
: process in which an acid is ionized by losing protons sequentially

triprotic acid
: acid that contains three ionizable hydrogen atoms per molecule; ionization of triprotic acids occurs in three steps

Contributors

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7.6: Buffers

Learning Objectives

- Describe the composition and function of acid–base buffers

A mixture of a weak acid and its conjugate base (or a mixture of a weak base and its conjugate acid) is called a buffer solution, or a buffer. Buffer solutions resist a change in pH when small amounts of a strong acid or a strong base are added (Figure 7.6.1). A solution of acetic acid (CH_3COOH and sodium acetate CH_3COONa) is an example of a buffer that consists of a weak acid and its salt. An example of a buffer that consists of a weak base and its salt is a solution of ammonia ($NH_3\,(aq)$) and ammonium chloride ($NH_4Cl\,(aq)$).

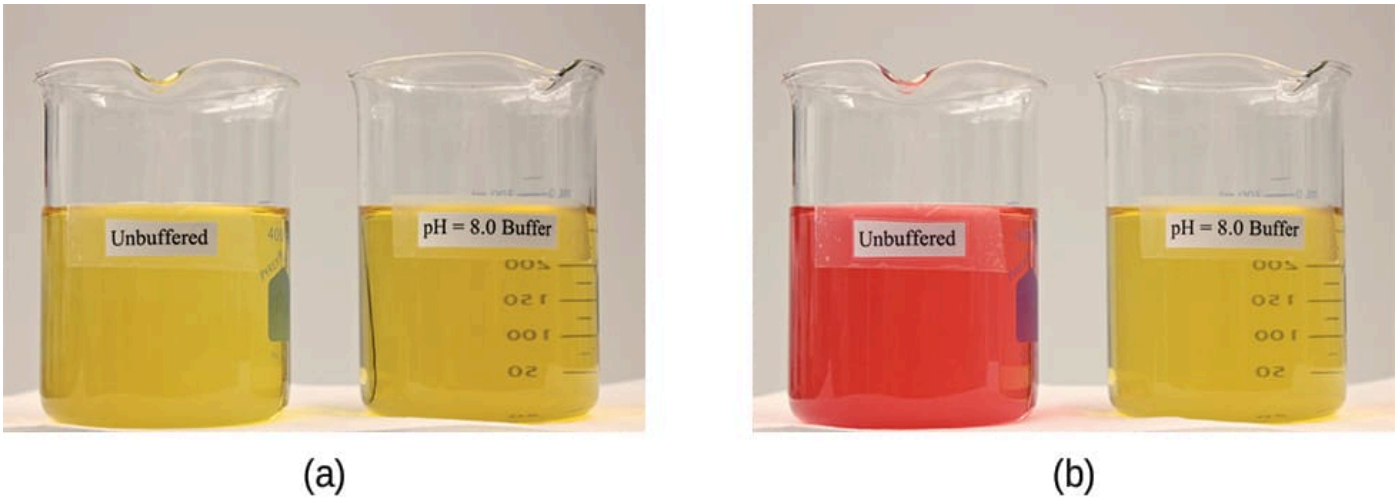


Figure 7.6.1: (a) The unbuffered solution on the left and the buffered solution on the right have the same pH (pH 8); they are basic, showing the yellow color of the indicator methyl orange at this pH. (b) After the addition of 1 mL of a 0.01-M HCl solution, the buffered solution has not detectably changed its pH but the unbuffered solution has become acidic, as indicated by the change in color of the methyl orange, which turns red at a pH of about 4. (credit: modification of work by Mark Ott)

How Buffers Work

A mixture of acetic acid and sodium acetate is a buffer because it contains both the weak acid and its salt. Hence, it acts to keep the hydronium ion concentration (and the pH) almost constant by the addition of either a small amount of a strong acid or a strong base. If we add a base such as sodium hydroxide, the hydroxide ions react with the few hydronium ions present. Then more of the acetic acid reacts with water, restoring the hydronium ion concentration almost to its original value:

$$CH_3CO_2H(aq) + H_2O(l) \longrightarrow H_3O^+(aq) + CH_3CO_2{}^-(aq) \tag{7.6.1}$$

The pH changes very little. If we add an acid such as hydrochloric acid, most of the hydronium ions from the hydrochloric acid combine with acetate ions, forming acetic acid molecules:

$$H_3O^+(aq) + CH_3CO_2{}^-(aq) \longrightarrow CH_3CO_2H(aq) + H_2O(l) \tag{7.6.2}$$

Thus, there is very little increase in the concentration of the hydronium ion, and the pH remains practically unchanged (Figure 7.6.2).

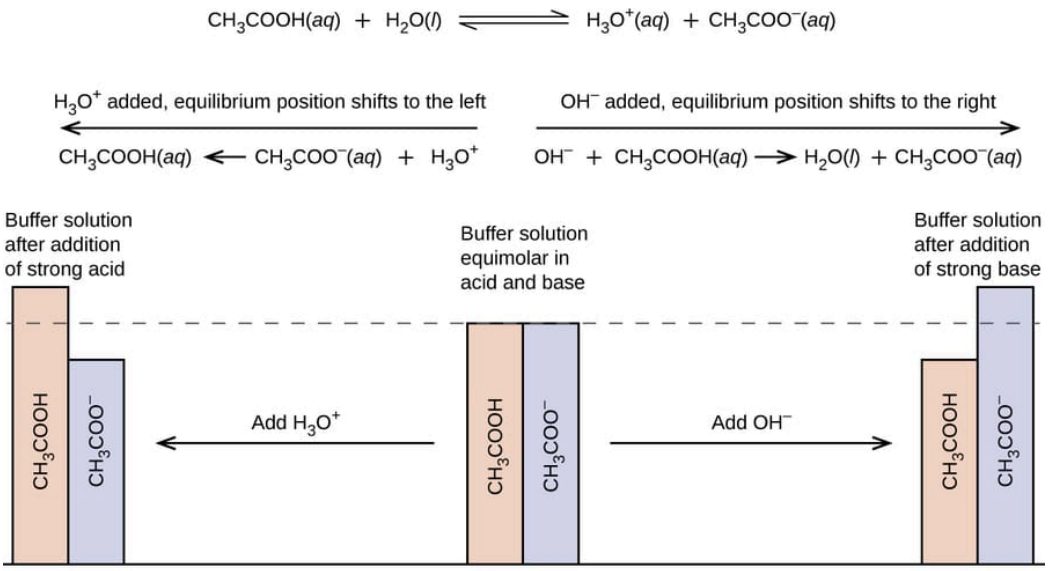


Figure 7.6.2: This diagram shows the buffer action of these reactions.

A mixture of ammonia and ammonium chloride is a buffer because it also contains the salt of the weak base. If we add a base (hydroxide ions), ammonium ions in the buffer react with the hydroxide ions to form ammonia and water and reduce the hydroxide ion concentration almost to its original value:

$$\mathrm{NH_4}^+(aq)+\mathrm{OH}^-(aq) \longrightarrow \mathrm{NH_3}(aq) + \mathrm{H_2O}(l) \tag{7.6.3}$$

If we add an acid (hydronium ions), ammonia molecules in the buffer mixture react with the hydronium ions to form ammonium ions and reduce the hydronium ion concentration almost to its original value:

$$\mathrm{H_3O}^+(aq) + \mathrm{NH_3}(aq) \longrightarrow \mathrm{NH_4}^+(aq) + \mathrm{H_2O}(l) \tag{7.6.4}$$

Buffer Capacity

Buffer solutions do not have an unlimited capacity to keep the pH relatively constant (Figure 7.6.3). If we add so much base to a buffer that the weak acid is exhausted, no more buffering action toward the base is possible. On the other hand, if we add an excess of acid, the weak base would be exhausted, and no more buffering action toward any additional acid would be possible. In fact, we do not even need to exhaust all of the acid or base in a buffer to overwhelm it; its buffering action will diminish rapidly as a given component nears depletion.



Figure 7.6.3: The indicator color (methyl orange) shows that a small amount of acid added to a buffered solution of pH 8 (beaker on the left) has little affect on the buffered system (middle beaker). However, a large amount of acid exhausts the buffering capacity of the solution and the pH changes dramatically (beaker on the right). (credit: modification of work by Mark Ott)

The buffer capacity is the amount of acid or base that can be added to a given volume of a buffer solution before the pH changes significantly, usually by one unit. Buffer capacity depends on the amounts of the weak acid and its conjugate base that are in a

buffer mixture. For example, 1 L of a solution that is 1.0 *M* in acetic acid and 1.0 *M* in sodium acetate has a greater buffer capacity than 1 L of a solution that is 0.10 *M* in acetic acid and 0.10 *M* in sodium acetate even though both solutions have the same pH. The first solution has more buffer capacity because it contains more acetic acid and acetate ion.

Selection of Suitable Buffer Mixtures

There are two useful rules of thumb for selecting buffer mixtures:

1. A good buffer mixture should have about equal concentrations of both of its components. A buffer solution has generally lost its usefulness when one component of the buffer pair is less than about 10% of the other. Figure 7.6.4 shows an acetic acid-acetate ion buffer as base is added. The initial pH is 4.74. A change of 1 pH unit occurs when the acetic acid concentration is reduced to 11% of the acetate ion concentration.

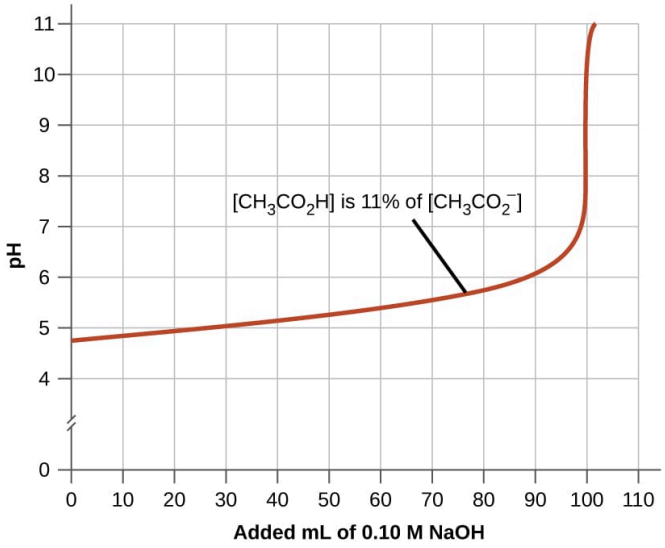


Figure 7.6.4: The graph, an illustration of buffering action, shows change of pH as an increasing amount of a 0.10-M NaOH solution is added to 100 mL of a buffer solution in which, initially, [CH3CO2H] = 0.10 M and $[\mathrm{CH_3CO_2}^-] = 0.10\ M$.

2. Weak acids and their salts are better as buffers for pHs less than 7; weak bases and their salts are better as buffers for pHs greater than 7.

Blood is an important example of a buffered solution, with the principal acid and ion responsible for the buffering action being carbonic acid, H_2CO_3, and the bicarbonate ion, $\mathrm{HCO_3}^-$. When an excess of hydrogen ion enters the blood stream, it is removed primarily by the reaction:

$$\mathrm{H_3O^+}(aq) + \mathrm{HCO_3}^-(aq) \longrightarrow \mathrm{H_2CO_3}(aq) + \mathrm{H_2O}(l) \tag{7.6.5}$$

When an excess of the hydroxide ion is present, it is removed by the reaction:

$$\mathrm{OH^-}(aq) + \mathrm{H_2CO_3}(aq) \longrightarrow \mathrm{HCO_3}^-(aq) + \mathrm{H_2O}(l) \tag{7.6.6}$$

The pH of human blood thus remains very near 7.35, that is, slightly basic. Variations are usually less than 0.1 of a pH unit. A change of 0.4 of a pH unit is likely to be fatal.

Lawrence Joseph Henderson and Karl Albert Hasselbalch

Lawrence Joseph Henderson (1878–1942) was an American physician, biochemist and physiologist, to name only a few of his many pursuits. He obtained a medical degree from Harvard and then spent 2 years studying in Strasbourg, then a part of Germany, before returning to take a lecturer position at Harvard. He eventually became a professor at Harvard and worked

there his entire life. He discovered that the acid-base balance in human blood is regulated by a buffer system formed by the dissolved carbon dioxide in blood. He wrote an equation in 1908 to describe the carbonic acid-carbonate buffer system in blood. Henderson was broadly knowledgeable; in addition to his important research on the physiology of blood, he also wrote on the adaptations of organisms and their fit with their environments, on sociology and on university education. He also founded the Fatigue Laboratory, at the Harvard Business School, which examined human physiology with specific focus on work in industry, exercise, and nutrition.

In 1916, Karl Albert Hasselbalch (1874–1962), a Danish physician and chemist, shared authorship in a paper with Christian Bohr in 1904 that described the Bohr effect, which showed that the ability of hemoglobin in the blood to bind with oxygen was inversely related to the acidity of the blood and the concentration of carbon dioxide. The pH scale was introduced in 1909 by another Dane, Sørensen, and in 1912, Hasselbalch published measurements of the pH of blood. In 1916, Hasselbalch expressed Henderson's equation in logarithmic terms, consistent with the logarithmic scale of pH, and thus the Henderson-Hasselbalch equation was born.

Medicine: The Buffer System in Blood

The normal pH of human blood is about 7.4. The carbonate buffer system in the blood uses the following equilibrium reaction:

$$\mathrm{CO_2}(g) + 2\,\mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_2CO_3}(aq) \rightleftharpoons \mathrm{HCO_3}^-(aq) + \mathrm{H_3O}^+(aq) \tag{7.6.7}$$

The concentration of carbonic acid, H_2CO_3 is approximately 0.0012 *M*, and the concentration of the hydrogen carbonate ion, $\mathrm{HCO_3}^-$, is around 0.024 *M*. Using the Henderson-Hasselbalch equation and the pK_a of carbonic acid at body temperature, we can calculate the pH of blood:

$$\mathrm{pH} = \mathrm{p}K_\mathrm{a} + \log\frac{[\mathrm{base}]}{[\mathrm{acid}]} = 6.1 + \log\frac{0.024}{0.0012} = 7.4 \tag{7.6.8}$$

The fact that the H_2CO_3 concentration is significantly lower than that of the $\mathrm{HCO_3}^-$ ion may seem unusual, but this imbalance is due to the fact that most of the by-products of our metabolism that enter our bloodstream are acidic. Therefore, there must be a larger proportion of base than acid, so that the capacity of the buffer will not be exceeded.

Lactic acid is produced in our muscles when we exercise. As the lactic acid enters the bloodstream, it is neutralized by the $\mathrm{HCO_3}^-$ ion, producing H_2CO_3. An enzyme then accelerates the breakdown of the excess carbonic acid to carbon dioxide and water, which can be eliminated by breathing. In fact, in addition to the regulating effects of the carbonate buffering system on the pH of blood, the body uses breathing to regulate blood pH. If the pH of the blood decreases too far, an increase in breathing removes CO_2 from the blood through the lungs driving the equilibrium reaction such that [H_3O^+] is lowered. If the blood is too alkaline, a lower breath rate increases CO_2 concentration in the blood, driving the equilibrium reaction the other way, increasing [H^+] and restoring an appropriate pH.

Summary

A solution containing a mixture of an acid and its conjugate base, or of a base and its conjugate acid, is called a buffer solution. Unlike in the case of an acid, base, or salt solution, the hydronium ion concentration of a buffer solution does not change greatly when a small amount of acid or base is added to the buffer solution. The base (or acid) in the buffer reacts with the added acid (or base).

Glossary

buffer capacity
: amount of an acid or base that can be added to a volume of a buffer solution before its pH changes significantly (usually by one pH unit)

buffer
: mixture of a weak acid or a weak base and the salt of its conjugate; the pH of a buffer resists change when small amounts of acid or base are added

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7.7: Unit 7 Practice Problems

Question 1.

Given the molarity, find the normality of the acid or base.

0.24 M NaOH

1.2 M H_3PO_4

0.73 M H_2SO_4

Answer

0.24M x 1 = 0.24N

1.2M x 3 = 3.6N

0.73M x 2 = 1.5N

Given the normality, find the molarity of the acid or base.

1.5N HCl

0.84N $Mg(OH)_2$

0.9N NH_4OH

Answer

1.5N / 1 = 1.5M

0.84N / 2 = 0.42M

0.9N / 1 = 0.9M

Question 2.

Given the H+ concentration, find the OH- concentration, and the pH.

[H+] = 0.0046 M

[H+] = 3.57 x 10^{-8} M

Answer

Remember the following formulas $[H+] \times [OH-] = 10^{-14}M$ $pH = -\log [H+]$

[H+] = 0.0046 M OH- = $10^{-14}/0.0046 = 2.2x10^{-12}$ M pH = -log(0.0046) = 2.3

[H+] = 3.57 x 10^{-8} M OH- = $10^{-14}/3.57x10^{-8} = 2.8 \times 10^{-7}$ M pH = $-\log(3.57x10^{-8}) = 7.4$

Question 3.

Given the pH, find the H+ concentration and the OH- concentration.

pH = 12.97

pH = 1.3

Answer

Remember the following formulas $[H+] = 10^{-pH}$ $[H+] \times [OH-] = 10^{-14}M$

pH 12.9 $[H+] = 10^{-12.9} = 1.26 \times 10^{-13} M$ $[OH-] = 10^{-14}/1.26x10^{-13} = 0.0794\ M$

pH 1.3 $[H+] = 10^{-1.3} = 0.050\ M$ $[OH-] = 10^{-14}/0.050 = 2.0 \times 10^{-13} M$

Question 4.

Given the [OH-] concentration find the pH and state whether the concentration is acidic basic or neutral.

$[OH-] = 4.6 \times 10^{-2}$ M

$[OH-] = 1.0 \times 10^{-7}$ M

$[OH-] = 5.2 \times 10^{-9}$ M

Answer

Remember the following formulas $[H+] \times [OH-] = 10^{-14}M$ $pH = -\log [H+]$

$[OH-] = 4.6 \times 10^{-2}$ M $[H+] = 10^{-14}/4.6x10^{-2} = 2.2 \times 10^{-13}$ M $pH = -\log(2.2 \times 10^{-13}) = 12.6$ pH above 7 is basic

$[OH-] = 1.0 \times 10^{-7}$ M $[H+] = 10^{-14}/1.0x10^{-7} = 1.0 \times 10^{-7}$ M $pH = -\log(1.0 \times 10^{-7}) = 7.0$ pH of 7 is neutral

$[OH-] = 5.2 \times 10^{-9}$ M $[H+] = 10^{-14}/5.2x10^{-9} = 1.9 \times 10^{-6}$ M $pH = -\log(1.9 \times 10^{-6}) = 5.7$ pH below 7 is acidic

Question 5.

Write the balanced chemical equation for the neutralization of phosphoric acid and magnesium hydroxide. Then state whether the resulting solution will be slightly acidic, slightly basic, or neutral.

Answer

$2H_3PO_4 + 3Mg(OH)_2 \rightarrow Mg_3(PO4)_2 + 6H_2O$

weak acid + strong base = slightly basic

Question 6.

20.5mL of 0.25M sulfuric acid is used to titrate 34.0mL of sodium hydroxide. What is the normality and molarity of sodium hydroxide?

Answer

$N_aV_a = N_bV_b$

Since the formula for sulfuric acid is H_2SO_4 $N_a = 0.25M \times 2 = 0.50N$

$(0.50N)(20.5mL) = (N_b)(34.0mL)$

$N_b = 0.30N$

Since the formula for sodium hydroxide is NaOH $M_b = 0.30N / 1 = 0.30M$

Question 7.

Most toilet cleaners contain acid to help remove mineral deposits from the bowl. If 38mL of toilet cleaner takes 26mL of 0.24N NaOH to titrate it, what is the normality of the toilet cleaner?

Answer

$N_aV_a = N_bV_b$

$(N_a)(38mL) = (0.24N)(26mL)$

$N_a = 0.16N$

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8: GASES

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General Chemistry

In this chapter, we examine the relationships between gas temperature, pressure, amount, and volume. We will study a simple theoretical model and use it to analyze the experimental behavior of gases. The results of these analyses will show us the limitations of the theory and how to improve on it.

Unit 8 Objectives

By the end of this unit, you will be able to:

- Define pressure and atmospheric pressure.
- List atmospheric pressure at sea level in atm, mmHg, Torr, Psi, kPa, bar, and millibar and perform atmospheric pressure unit conversions.
- Identify the mathematical relationships between the various properties of gases.
- Describe the major gas laws including Boyle's Law, Amanoton's Law, Charles' Law, the Combined Gas Law, and the Ideal Gas Law, and properly use the formulas associated with these laws.

8.1: Gas Pressure

8.2: Relating Pressure, Volume, Amount, and Temperature- The Ideal Gas Law

8.3: The Kinetic-Molecular Theory

8.4: Unit 8 Practice Problems

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8.1: Gas Pressure

LEARNING OBJECTIVES

- Define pressure and atmospheric pressure.
- List atmospheric pressure at sea level in atm, mmHg, Torr, Psi, kPa, bar, and millibar and perform atmospheric pressure unit conversions.

The earth's atmosphere exerts a pressure, as does any other gas. Although we do not normally notice atmospheric pressure, we are sensitive to pressure changes—for example, when your ears "pop" during take-off and landing while flying, or when you dive underwater. Gas pressure is caused by the force exerted by gas molecules colliding with the surfaces of objects (Figure 8.1.1). Although the force of each collision is very small, any surface of appreciable area experiences a large number of collisions in a short time, which can result in a high pressure. In fact, normal air pressure is strong enough to crush a metal container when not balanced by equal pressure from inside the container.

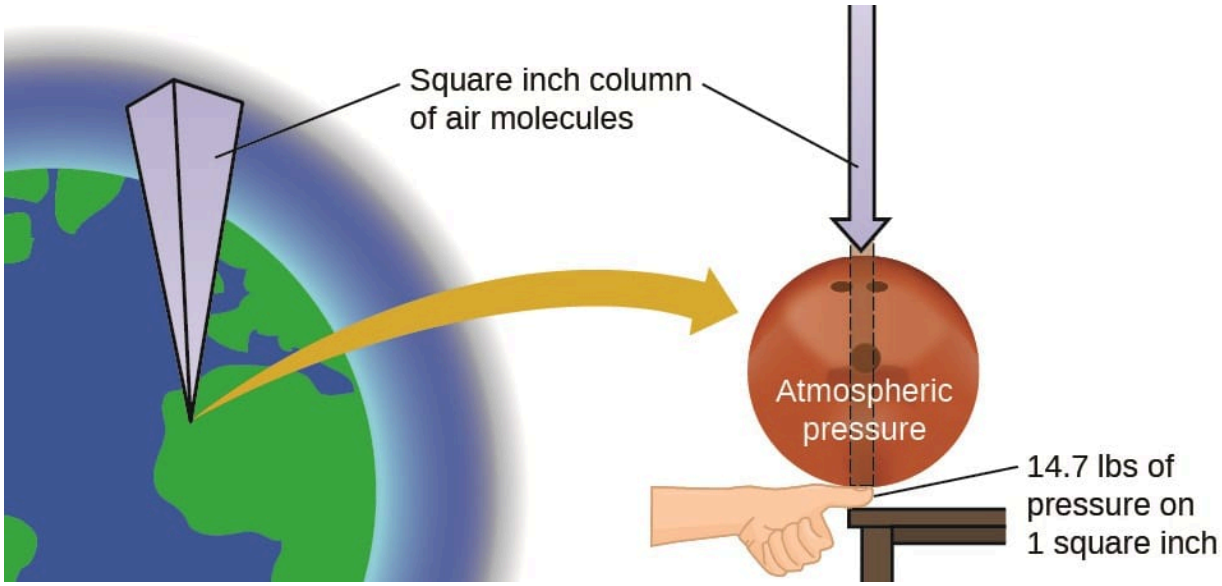


Figure 8.1.1: The atmosphere above us exerts a large pressure on objects at the surface of the earth, roughly equal to the weight of a bowling ball pressing on an area the size of a human thumbnail.

Atmospheric pressure is caused by the weight of the column of air molecules in the atmosphere above an object, such as the tanker car. At sea level, this pressure is roughly the same as that exerted by a full-grown African elephant standing on a doormat, or a typical bowling ball resting on your thumbnail. These may seem like huge amounts, and they are, but life on earth has evolved under such atmospheric pressure. If you actually perch a bowling ball on your thumbnail, the pressure experienced is twice the usual pressure, and the sensation is unpleasant.



A dramatic illustration of atmospheric pressure is provided in this brief video, which shows a railway tanker car imploding when its internal pressure is decreased.

Pressure is defined as the force exerted on a given area:

$$P = \frac{F}{A} \tag{8.1.1}$$

Since pressure is directly proportional to force and inversely proportional to area (Equation 8.1.1), pressure can be increased either by either **increasing** the amount of force or by **decreasing** the area over which it is applied. Correspondingly, pressure can be decreased by either **decreasing** the force or **increasing** the area.

Let's apply the definition of pressure (Equation 8.1.1) to determine which would be more likely to fall through thin ice in Figure 8.1.2.—the elephant or the figure skater?



Figure 8.1.2: Although (a) an elephant's weight is large, creating a very large force on the ground, (b) figure skater exerts a much higher pressure on the ice due to the small surface area of her skates. (credi modification of work by Guido da Rozze; credit b: modification of work by Ryosuke Yagi).

A large African elephant can weigh 7 tons, supported on four feet, each with a diameter of about 1.5 ft (footprint area of 250 in^2), so the pressure exerted by each foot is about 14 lb/in^2:

$$\text{pressure per elephant foot} = 14,000\frac{\text{lb}}{\text{elephant}} \times \frac{1 \text{ elephant}}{4 \text{ feet}} \times \frac{1 \text{ foot}}{250 \text{ in}^2} = 14 \text{ lb/in}^2 \tag{8.1.2}$$

The figure skater weighs about 120 lbs, supported on two skate blades, each with an area of about 2 in^2, so the pressure exerted by each blade is about 30 lb/in^2:

$$\text{pressure per skate blade} = 120\frac{\text{lb}}{\text{skater}} \times \frac{1 \text{ skater}}{2 \text{ blades}} \times \frac{1 \text{ blade}}{2 \text{ in}^2} = 30 \text{ lb/in}^2 \tag{8.1.3}$$

Even though the elephant is more than one hundred-times heavier than the skater, it exerts less than one-half of the pressure and would therefore be less likely to fall though thin ice. On the other hand, if the skater removes her skates and stands with bare feet (or regular footwear) on the ice, the larger area over which her weight is applied greatly reduces the pressure exerted:

$$\text{pressure per human foot} = 120\frac{\text{lb}}{\text{skater}} \times \frac{1 \text{ skater}}{2 \text{ feet}} \times \frac{1 \text{ foot}}{30 \text{ in}^2} = 2 \text{ lb/in}^2 \tag{8.1.4}$$

The SI unit of pressure is the pascal (Pa), with 1 Pa = 1 N/m^2, where N is the newton, a unit of force defined as 1 kg m/s^2. One pascal is a small pressure; in many cases, it is more convenient to use units of kilopascal (1 kPa = 1000 Pa) or bar (1 bar = 100,000 Pa). In the United States, pressure is often measured in pounds of force on an area of one square inch—pounds per square inch (psi)—for example, in car tires. Pressure can also be measured using the unit atmosphere (atm), which originally represented the average sea level air pressure at the approximate latitude of Paris (45°). Table 8.1.1 provides some information on these and a few other common units for pressure measurements

Table 8.1.1: Pressure Units

Unit Name and Abbreviation	Definition or Relation to Other Unit	Comment
pascal (Pa)	1 Pa = 1 N/m^2	recommended IUPAC unit

Unit Name and Abbreviation	Definition or Relation to Other Unit	Comment
kilopascal (kPa)	1 kPa = 1000 Pa	
pounds per square inch (psi)	air pressure at sea level is ~14.7 psi	
atmosphere (atm)	1 atm = 101,325 Pa	air pressure at sea level is ~1 atm
bar (bar, or b)	1 bar = 100,000 Pa (exactly)	commonly used in meteorology
millibar (mbar, or mb)	1000 mbar = 1 bar	
inches of mercury (in. Hg)	1 in. Hg = 3386 Pa	used by aviation industry, also some weather reports
torr	$1 \text{ torr} = \frac{1}{760} \text{ atm}$	named after Evangelista Torricelli, inventor of the barometer
millimeters of mercury (mm Hg)	1 mm Hg ~1 torr	

EXAMPLE 8.1.1: CONVERSION OF PRESSURE UNITS

The United States National Weather Service reports pressure in both inches of Hg and millibars. Convert a pressure of 29.2 in. Hg into:

a. torr
b. atm
c. kPa
d. mbar

Solution

This is a unit conversion problem. The relationships between the various pressure units are given in Table 9.2.1.

a. $29.2 \cancel{\text{ in Hg}} \times \frac{25.4 \cancel{\text{ mm}}}{1 \cancel{\text{ in}}} \times \frac{1 \text{ torr}}{1 \cancel{\text{ mm Hg}}} = 742 \text{ torr}$

b. $742 \cancel{\text{ torr}} \times \frac{1 \text{ atm}}{760 \cancel{\text{ torr}}} = 0.976 \text{ atm}$

c. $742 \cancel{\text{ torr}} \times \frac{101.325 \text{ kPa}}{760 \cancel{\text{ torr}}} = 98.9 \text{ kPa}$

d. $98.9 \cancel{\text{ kPa}} \times \frac{1000 \cancel{\text{ Pa}}}{1 \cancel{\text{ kPa}}} \times \frac{1 \cancel{\text{ bar}}}{100,000 \cancel{\text{ Pa}}} \times \frac{1000 \text{ mbar}}{1 \cancel{\text{ bar}}} = 989 \text{ mbar}$

EXERCISE 8.1.1

A typical barometric pressure in Kansas City is 740 torr. What is this pressure in atmospheres, in millimeters of mercury, in kilopascals, and in bar?

Answer

0.974 atm; 740 mm Hg; 98.7 kPa; 0.987 bar

We can measure atmospheric pressure, the force exerted by the atmosphere on the earth's surface, with a barometer (Figure 8.1.3). A barometer is a glass tube that is closed at one end, filled with a nonvolatile liquid such as mercury, and then inverted and immersed in a container of that liquid. The atmosphere exerts pressure on the liquid outside the tube, the column of liquid exerts pressure inside the tube, and the pressure at the liquid surface is the same inside and outside the tube. The height of the liquid in the tube is therefore proportional to the pressure exerted by the atmosphere.

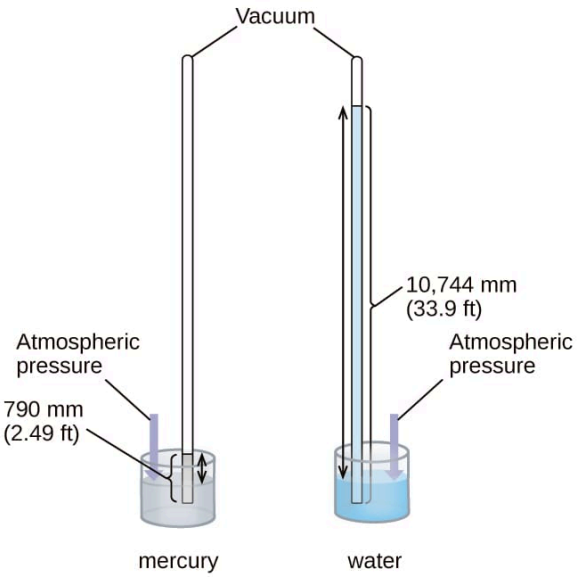


Figure 8.1.3: In a barometer, the height, h, of the column of liquid is used as a measurement of the a pressure. Using very dense liquid mercury (left) permits the construction of reasonably sized barome whereas using water (right) would require a barometer more than 30 feet tall.

If the liquid is water, normal atmospheric pressure will support a column of water over 10 meters high, which is rather inconvenient for making (and reading) a barometer. Because mercury (Hg) is about 13.6-times denser than water, a mercury barometer only needs to be $\frac{1}{13.6}$ as tall as a water barometer—a more suitable size. Standard atmospheric pressure of 1 atm at sea level (101,325 Pa) corresponds to a column of mercury that is about 760 mm (29.92 in.) high. The torr was originally intended to be a unit equal to one millimeter of mercury, but it no longer corresponds exactly.

APPLICATION: MEASURING BLOOD PRESSURE

Blood pressure is measured using a device called a sphygmomanometer (Greek *sphygmos* = "pulse"). It consists of an inflatable cuff to restrict blood flow, a manometer to measure the pressure, and a method of determining when blood flow begins and when it becomes impeded (Figure 8.1.5). Since its invention in 1881, it has been an essential medical device. There are many types of sphygmomanometers: manual ones that require a stethoscope and are used by medical professionals; mercury ones, used when the most accuracy is required; less

accurate mechanical ones; and digital ones that can be used with little training but that have limitations. When using a sphygmomanometer, the cuff is placed around the upper arm and inflated until blood flow is completely blocked, then slowly released. As the heart beats, blood forced through the arteries causes a rise in pressure. This rise in pressure at which blood flow begins is the *systolic pressure*—the peak pressure in the cardiac cycle. When the cuff's pressure equals the arterial systolic pressure, blood flows past the cuff, creating audible sounds that can be heard using a stethoscope. This is followed by a decrease in pressure as the heart's ventricles prepare for another beat. As cuff pressure continues to decrease, eventually sound is no longer heard; this is the *diastolic pressure*—the lowest pressure (resting phase) in the cardiac cycle. Blood pressure units from a sphygmomanometer are in terms of millimeters of mercury (mm Hg).

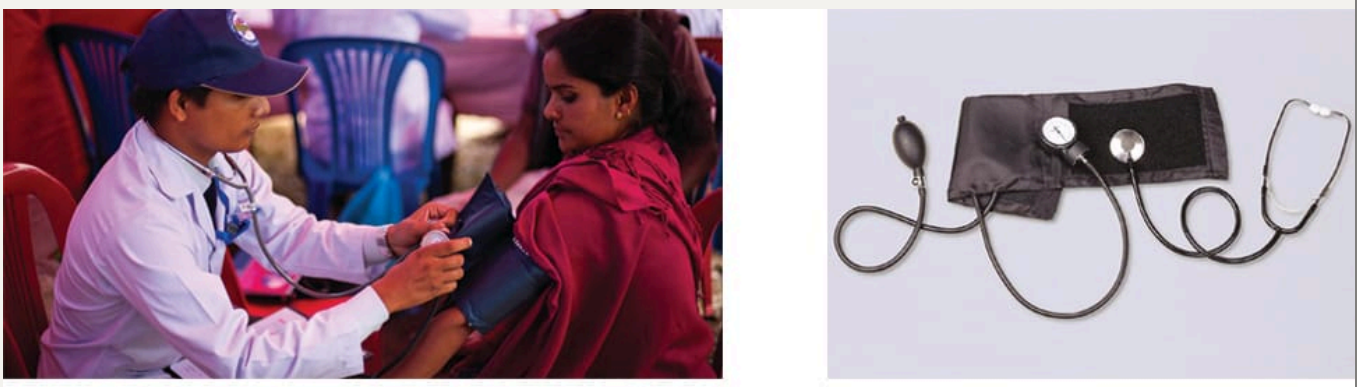


Figure 8.1.5**:** (a) A medical technician prepares to measure a patient's blood pressure with a sphygmomanometer. (b) A typical sphygmomanometer uses a valved rubber bulb to inflate the cuff an diaphragm gauge to measure pressure. (credit a: modification of work by Master Sgt. Jeffrey Allen)

Meteorology, Climatology, and Atmospheric Science

Throughout the ages, people have observed clouds, winds, and precipitation, trying to discern patterns and make predictions: when it is best to plant and harvest; whether it is safe to set out on a sea voyage; and much more. We now face complex weather and atmosphere-related challenges that will have a major impact on our civilization and the ecosystem. Several different scientific disciplines use chemical principles to help us better understand weather, the atmosphere, and climate. These are meteorology, climatology, and atmospheric science. Meteorology is the study of the atmosphere, atmospheric phenomena, and atmospheric effects on earth's weather. Meteorologists seek to understand and predict the weather in the short term, which can save lives and benefit the economy. Weather forecasts (Figure 8.1.5) are the result of thousands of measurements of air pressure, temperature, and the like, which are compiled, modeled, and analyzed in weather centers worldwide.

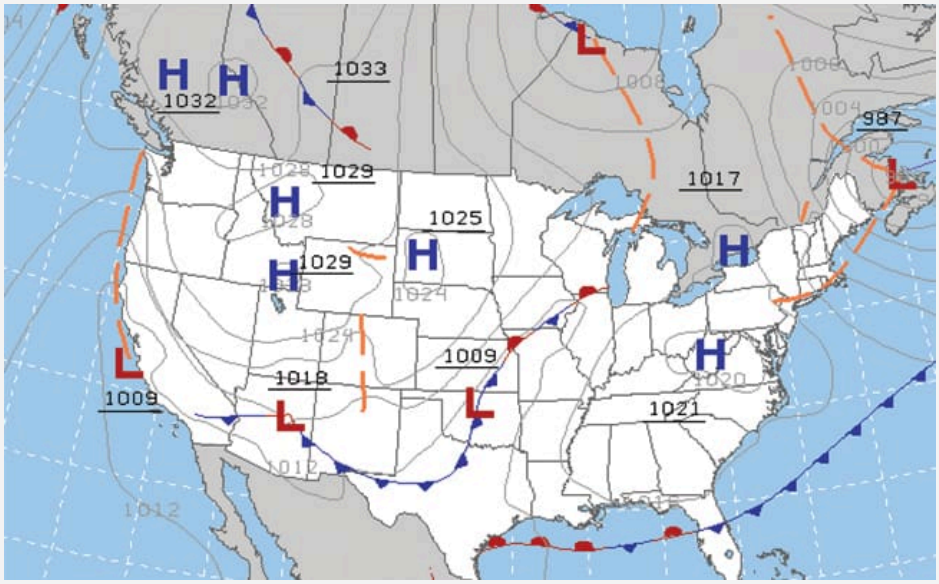


Figure 8.1.6: Meteorologists use weather maps to describe and predict weather. Regions of high (H) and (L) pressure have large effects on weather conditions. The gray lines represent locations of constant pres known as isobars. (credit: modification of work by National Oceanic and Atmospheric Administratio

In terms of weather, low-pressure systems occur when the earth's surface atmospheric pressure is lower than the surrounding environment: Moist air rises and condenses, producing clouds. Movement of moisture and air within various weather fronts instigates most weather events.

The atmosphere is the gaseous layer that surrounds a planet. Earth's atmosphere, which is roughly 100–125 km thick, consists of roughly 78.1% nitrogen and 21.0% oxygen, and can be subdivided further into the regions shown in Figure 8.1.7: the exosphere (furthest from earth, > 700 km above sea level), the thermosphere (80–700 km), the mesosphere (50–80 km), the stratosphere (second lowest level of our atmosphere, 12–50 km above sea level), and the troposphere (up to 12 km above sea level, roughly 80% of the earth's atmosphere by mass and the layer where most weather events originate). As you go higher in the troposphere, air density and temperature both decrease.

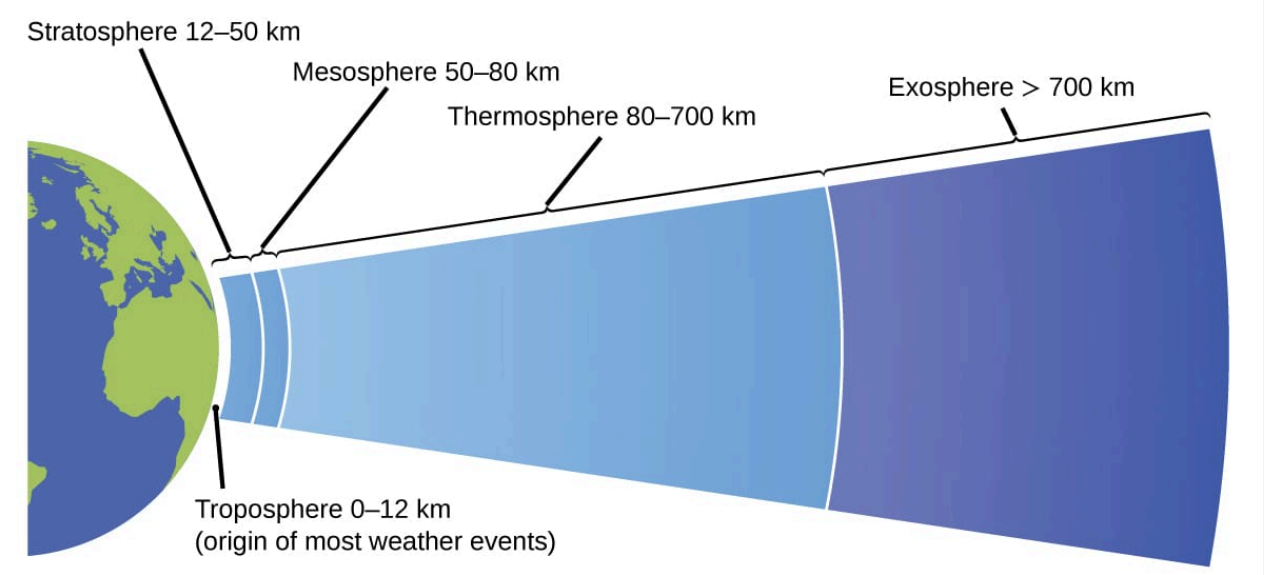


Figure 8.1.7: Earth's atmosphere has five layers: the troposphere, the stratosphere, the mesosphere, tl thermosphere, and the exosphere.

Climatology is the study of the climate, averaged weather conditions over long time periods, using atmospheric data. However, climatologists study patterns and effects that occur over decades, centuries, and millennia, rather than shorter time frames of hours, days, and weeks like meteorologists. Atmospheric science is an even broader field, combining meteorology, climatology, and other scientific disciplines that study the atmosphere.

Summary

Gases exert pressure, which is force per unit area. The pressure of a gas may be expressed in the SI unit of pascal or kilopascal, as well as in many other units including torr, atmosphere, and bar. Atmospheric pressure is measured using a barometer; other gas pressures can be measured using one of several types of manometers.

Glossary

atmosphere (atm)

unit of pressure; 1 atm = 101,325 Pa

bar

(bar or b) unit of pressure; 1 bar = 100,000 Pa

barometer

device used to measure atmospheric pressure

hydrostatic pressure

pressure exerted by a fluid due to gravity

manometer

device used to measure the pressure of a gas trapped in a container

pascal (Pa)

SI unit of pressure; 1 Pa = 1 N/m^2

pounds per square inch (psi)

unit of pressure common in the US

pressure

force exerted per unit area

torr

unit of pressure; $1 \text{ torr} = \frac{1}{760} \text{ atm}$

Contributors

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8.2: Relating Pressure, Volume, Amount, and Temperature- The Ideal Gas Law

Learning Objectives

- Identify the mathematical relationships between the various properties of gases
- Describe the major gas laws including Boyle's Law, Amanoton's Law, Charles' Law, the Combined Gas Law, and the Ideal Gas Law.
- Use the gas laws to compute the values of various gas properties under specified conditions.
- Define standard temperature and pressure and use these values to determine unknown volumes and quantities of gases.

During the seventeenth and especially eighteenth centuries, driven both by a desire to understand nature and a quest to make balloons in which they could fly (Figure 8.2.1), a number of scientists established the relationships between the macroscopic physical properties of gases, that is, pressure, volume, temperature, and amount of gas. Although their measurements were not precise by today's standards, they were able to determine the mathematical relationships between pairs of these variables (e.g., pressure and temperature, pressure and volume) that hold for an *ideal* gas—a hypothetical construct that real gases approximate under certain conditions. Eventually, these individual laws were combined into a single equation—the *ideal gas law*—that relates gas quantities for gases and is quite accurate for low pressures and moderate temperatures. We will consider the key developments in individual relationships (for pedagogical reasons not quite in historical order), then put them together in the ideal gas law.

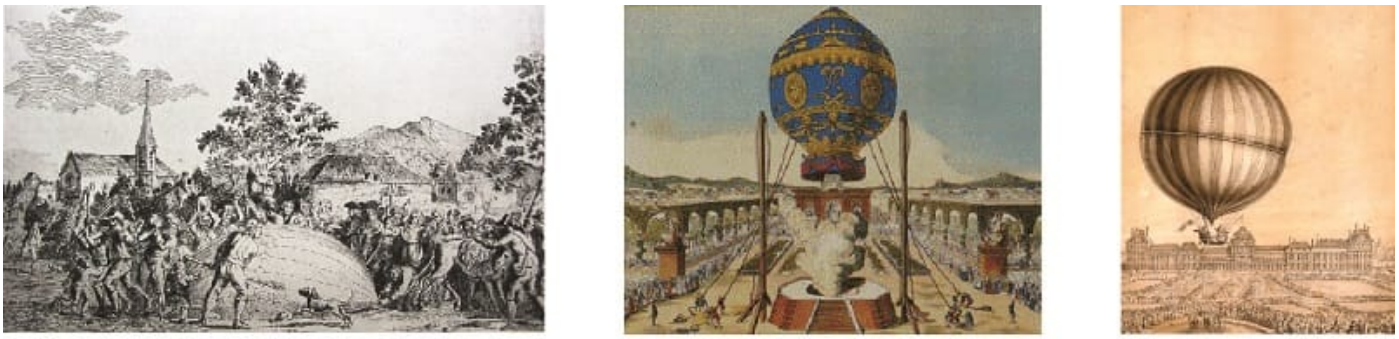


Figure 8.2.1: In 1783, the first (a) hydrogen-filled balloon flight, (b) manned hot air balloon flight, and (c) manned hydrogen-filled balloon flight occurred. When the hydrogen-filled balloon depicted in (a) landed, the frightened villagers of Gonesse reportedly destroyed it with pitchforks and knives. The launch of the latter was reportedly viewed by 400,000 people in Paris.

Pressure and Temperature: Amontons's Law

Imagine filling a rigid container attached to a pressure gauge with gas and then sealing the container so that no gas may escape. If the container is cooled, the gas inside likewise gets colder and its pressure is observed to decrease. Since the container is rigid and tightly sealed, both the volume and number of moles of gas remain constant. If we heat the sphere, the gas inside gets hotter (Figure 8.2.2) and the pressure increases.

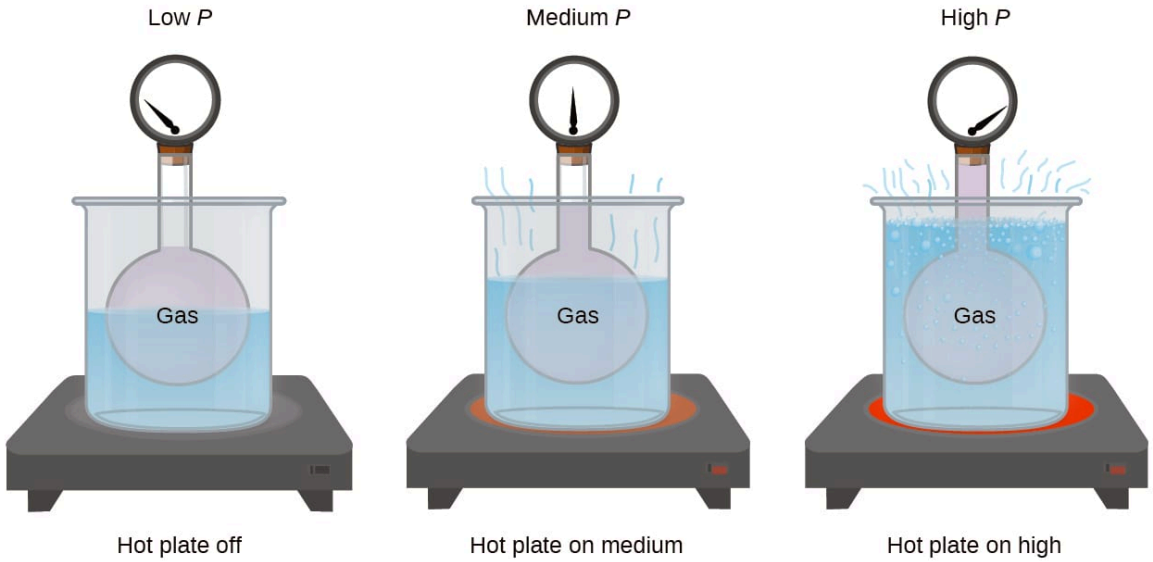


Figure 8.2.2**:** The effect of temperature on gas pressure: When the hot plate is off, the pressure of the gas in the sphere is relatively low. As the gas is heated, the pressure of the gas in the sphere increases.

This relationship between temperature and pressure is observed for any sample of gas confined to a constant volume. An example of experimental pressure-temperature data is shown for a sample of air under these conditions in Figure 8.2.3. We find that temperature and pressure are linearly related, and if the temperature is on the kelvin scale, then *P* and *T* are directly proportional (again, when *volume and moles of gas are held constant*); if the temperature on the kelvin scale increases by a certain factor, the gas pressure increases by the same factor.

Temperature (°C)	Temperature (K)	Pressure (kPa)
–150	173	36.0
–100	223	46.4
–50	273	56.7
0	323	67.1
50	373	77.5
100	423	88.0

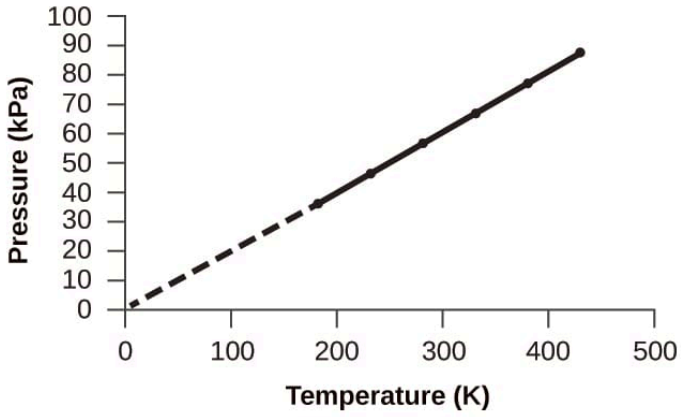


Figure 8.2.3: For a constant volume and amount of air, the pressure and temperature are directly proportional, provided the temperature is in kelvin. (Measurements cannot be made at lower temperatures because of the condensation of the gas.) When this line is extrapolated to lower pressures, it reaches a pressure of 0 at –273 °C, which is 0 on the kelvin scale and the lowest possible temperature, called absolute zero.

Guillaume Amontons was the first to empirically establish the relationship between the pressure and the temperature of a gas (~1700), and Joseph Louis Gay-Lussac determined the relationship more precisely (~1800). Because of this, the *P*-*T* relationship for gases is known as either Amontons's law or Gay-Lussac's law. Under either name, it states that *the pressure of a given amount of gas is directly proportional to its temperature on the kelvin scale when the volume is held constant*. Mathematically, this can be written:

$$P \propto T \text{ or } P = \text{constant} \times T \text{ or } P = k \times T \tag{8.2.1}$$

where $\propto$ means "is proportional to," and *k* is a proportionality constant that depends on the identity, amount, and volume of the gas.

For a confined, constant volume of gas, the ratio $\frac{P}{T}$ is therefore constant (i.e., $\frac{P}{T} = k$). If the gas is initially in "Condition 1" (with

$P = P_1$ and $T = T_1$), and then changes to "Condition 2" (with $P = P_2$ and $T = T_2$), we have that $\frac{P_1}{T_1} = k$ and $\frac{P_2}{T_2} = k$, which reduces to $\frac{P_1}{T_1} = \frac{P_2}{T_2}$. This equation is useful for pressure-temperature calculations for a confined gas at constant volume. Note that temperatures must be on the kelvin scale for any gas law calculations (0 on the kelvin scale and the lowest possible temperature is called absolute zero). (Also note that there are at least three ways we can describe how the pressure of a gas changes as its temperature changes: We can use a table of values, a graph, or a mathematical equation.)

Example 8.2.1: Predicting Change in Pressure with Temperature

A can of hair spray is used until it is empty except for the propellant, isobutane gas.

a. On the can is the warning "Store only at temperatures below 120 °F (48.8 °C). Do not incinerate." Why?
b. The gas in the can is initially at 24 °C and 360 kPa, and the can has a volume of 350 mL. If the can is left in a car that reaches 50 °C on a hot day, what is the new pressure in the can?

Solution

a. The can contains an amount of isobutane gas at a constant volume, so if the temperature is increased by heating, the pressure will increase proportionately. High temperature could lead to high pressure, causing the can to burst. (Also, isobutane is combustible, so incineration could cause the can to explode.)
b. We are looking for a pressure change due to a temperature change at constant volume, so we will use Amontons's/Gay-Lussac's law. Taking P_1 and T_1 as the initial values, T_2 as the temperature where the pressure is unknown and P_2 as the unknown pressure, and converting °C to K, we have:

$$\frac{P_1}{T_1} = \frac{P_2}{T_2} \text{ which means that } \frac{360\ k\,\text{Pa}}{297\ \text{K}} = \frac{P_2}{323\ \text{K}}$$

Rearranging and solving gives:

$$P_2 = \frac{360\ \text{kPa} \times 323\ \cancel{\text{K}}}{297\ \cancel{\text{K}}} = 390\ \text{kPa}$$

Exercise 8.2.1

A sample of nitrogen, N_2, occupies 45.0 mL at 27 °C and 600 torr. What pressure will it have if cooled to –73 °C while the volume remains constant?

Answer

400 torr

Volume and Temperature: Charles's Law

If we fill a balloon with air and seal it, the balloon contains a specific amount of air at atmospheric pressure, let's say 1 atm. If we put the balloon in a refrigerator, the gas inside gets cold and the balloon shrinks (although both the amount of gas and its pressure remain constant). If we make the balloon very cold, it will shrink a great deal, and it expands again when it warms up.

YouTube Video

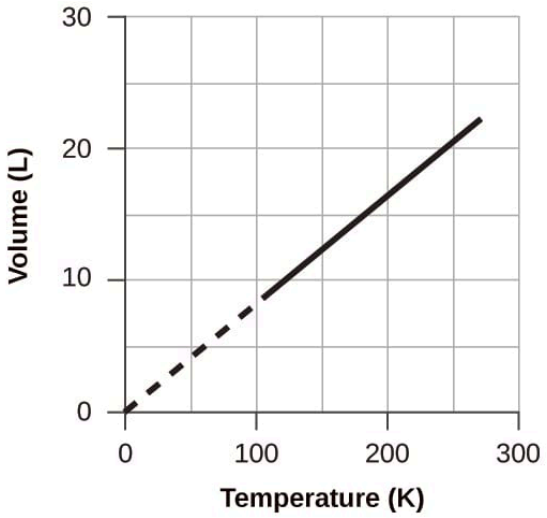
This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

View this YouTube Video online

Video 8.2.1**:** This video shows how cooling and heating a gas causes its volume to decrease or increase, respectively.

These examples of the effect of temperature on the volume of a given amount of a confined gas at constant pressure are true in general: The volume increases as the temperature increases, and decreases as the temperature decreases. Volume-temperature data for a 1-mole sample of methane gas at 1 atm are listed and graphed in Figure 8.2.2.

Temperature (°C)	Temperature (K)	Volume (L)
–3	270	22
–23	250	21
–53	220	18
–162	111	9



Figuire 8.2.4**:** The volume and temperature are linearly related for 1 mole of methane gas at a constant pressure of 1 atm. If the temperature is in kelvin, volume and temperature are directly proportional. The line stops at 111 K because methane liquefies at this temperature; when extrapolated, it intersects the graph's origin, representing a temperature of absolute zero.

The relationship between the volume and temperature of a given amount of gas at constant pressure is known as Charles's law in recognition of the French scientist and balloon flight pioneer Jacques Alexandre César Charles. Charles's law states that *the volume of a given amount of gas is directly proportional to its temperature on the kelvin scale when the pressure is held constant*.

Mathematically, this can be written as:

$$V \alpha T \text{ or } V = \text{constant} \cdot T \text{ or } V = k \cdot T \tag{8.2.2}$$

with *k* being a proportionality constant that depends on the amount and pressure of the gas.

For a confined, constant pressure gas sample, $\frac{V}{T}$ is constant (i.e., the ratio = *k*), and as seen with the *P*-*T* relationship, this leads to another form of Charles's law: $\frac{V_1}{T_1} = \frac{V_2}{T_2}$.

Example 8.2.2: Predicting Change in Volume with Temperature

A sample of carbon dioxide, CO_2, occupies 0.300 L at 10 °C and 750 torr. What volume will the gas have at 30 °C and 750 torr?

Solution

Because we are looking for the volume change caused by a temperature change at constant pressure, this is a job for Charles's law. Taking V_1 and T_1 as the initial values, T_2 as the temperature at which the volume is unknown and V_2 as the unknown volume, and converting °C into K we have:

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \text{ which means that } \frac{0.300\ \text{L}}{283\ \text{K}} = \frac{V_2}{303\ \text{K}}$$

Rearranging and solving gives: $V_2 = \dfrac{0.300\ \text{L} \times 303\ \cancel{\text{K}}}{283\ \cancel{\text{K}}} = 0.321\ \text{L}$

This answer supports our expectation from Charles's law, namely, that raising the gas temperature (from 283 K to 303 K) at a constant pressure will yield an increase in its volume (from 0.300 L to 0.321 L).

Exercise 8.2.2

A sample of oxygen, O_2, occupies 32.2 mL at 30 °C and 452 torr. What volume will it occupy at –70 °C and the same pressure?

Answer

21.6 mL

Example 8.2.3: Measuring Temperature with a Volume

Change Temperature is sometimes measured with a gas thermometer by observing the change in the volume of the gas as the temperature changes at constant pressure. The hydrogen in a particular hydrogen gas thermometer has a volume of 150.0 cm^3 when immersed in a mixture of ice and water (0.00 °C). When immersed in boiling liquid ammonia, the volume of the hydrogen, at the same pressure, is 131.7 cm^3. Find the temperature of boiling ammonia on the kelvin and Celsius scales.

Solution

A volume change caused by a temperature change at constant pressure means we should use Charles's law. Taking V_1 and T_1 as the initial values, T_2 as the temperature at which the volume is unknown and V_2 as the unknown volume, and converting °C into K we have:

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \text{ which means that } \frac{150.0\ \text{cm}^3}{273.15\ \text{K}} = \frac{131.7\ \text{cm}^3}{T_2} \tag{8.2.3}$$

Rearrangement gives $T_2 = \dfrac{131.7\ \cancel{\text{cm}^3} \times 273.15\ \text{K}}{150.0\ \text{cm}^3} = 239.8\ \text{K}$

Subtracting 273.15 from 239.8 K, we find that the temperature of the boiling ammonia on the Celsius scale is –33.4 °C.

Exercise 8.2.3

What is the volume of a sample of ethane at 467 K and 1.1 atm if it occupies 405 mL at 298 K and 1.1 atm?

Answer

635 mL

Volume and Pressure: Boyle's Law

If we partially fill an airtight syringe with air, the syringe contains a specific amount of air at constant temperature, say 25 °C. If we slowly push in the plunger while keeping temperature constant, the gas in the syringe is compressed into a smaller volume and its pressure increases; if we pull out the plunger, the volume increases and the pressure decreases. This example of the effect of volume on the pressure of a given amount of a confined gas is true in general. Decreasing the volume of a contained gas will increase its pressure, and increasing its volume will decrease its pressure. In fact, if the volume increases by a certain factor, the pressure decreases by the same factor, and vice versa. Volume-pressure data for an air sample at room temperature are graphed in Figure 8.2.5.

This figure contains a diagram and two graphs. The diagram shows a syringe labeled with a scale in m l or c c with multiples of 5 labeled beginning at 5 and ending at 30. The markings halfway between these measurements are also provided. Attached at the top of the syringe is a pressure gauge with a scale marked by fives from 40 on the left to 5 on the right. The gauge needle rests between 10 and 15, slightly closer to 15. The syringe plunger position indicates a volume measurement about halfway between 10 and 15 m l or c c. The first graph is labeled "V (m L)" on the horizontal axis and "P (p s i)" on the vertical axis. Points are labeled at 5, 10, 15, 20, and 25 m L with corresponding values of 39.0, 19.5, 13.0, 9.8, and 6.5 p s i. The points are connected with a smooth curve that is declining at a decreasing rate of change. The second graph is labeled "V (m L)" on the horizontal axis and "1 divided by P (p s i)" on the vertical axis. The horizontal axis is labeled at multiples of 5, beginning at zero and extending up to 35 m L. The vertical axis is labeled by multiples of 0.02, beginning at 0 and extending up to 0.18. Six points indicated by black dots on this graph are connected with a black line segment showing a positive linear trend.

Figure 8.2.5: When a gas occupies a smaller volume, it exerts a higher pressure; when it occupies a larger volume, it exerts a lower pressure (assuming the amount of gas and the temperature do not change). Since P and V are inversely proportional, a graph of $\frac{1}{P}$ *vs. V is linear.*

Unlike the *P*-*T* and *V*-*T* relationships, pressure and volume are not directly proportional to each other. Instead, *P* and *V* exhibit inverse proportionality: Increasing the pressure results in a decrease of the volume of the gas. Mathematically this can be written:

$$P \alpha 1/V \text{ or } P = k \cdot 1/V \text{ or } P \cdot V = k \text{ or } P_1V_1 = P_2V_2 \tag{8.2.4}$$

with *k* being a constant. Graphically, this relationship is shown by the straight line that results when plotting the inverse of the pressure $\left(\frac{1}{P}\right)$ versus the volume (*V*), or the inverse of volume $\left(\frac{1}{V}\right)$ versus the pressure (*P*). Graphs with curved lines are difficult to read accurately at low or high values of the variables, and they are more difficult to use in fitting theoretical equations and parameters to experimental data. For those reasons, scientists often try to find a way to "linearize" their data. If we plot *P* versus *V*, we obtain a hyperbola (Figure 8.2.6).

This diagram shows two graphs. In a, a graph is shown with volume on the horizontal axis and pressure on the vertical axis. A curved line is shown on the graph showing a decreasing trend with a decreasing rate of change. In b, a graph is shown with volume on the horizontal axis and one divided by pressure on the vertical axis. A line segment, beginning at the origin of the graph, shows a positive, linear trend.

Figure 8.2.6: The relationship between pressure and volume is inversely proportional. (a) The graph of P vs. V is a hyperbola, whereas (b) the graph of $\left(\frac{1}{P}\right)$ *vs. V is linear.*

The relationship between the volume and pressure of a given amount of gas at constant temperature was first published by the English natural philosopher Robert Boyle over 300 years ago. It is summarized in the statement now known as Boyle's law: *The volume of a given amount of gas held at constant temperature is inversely proportional to the pressure under which it is measured.*

Example 8.2.4: Volume of a Gas Sample

The sample of gas has a volume of 15.0 mL at a pressure of 13.0 psi. Determine the pressure of the gas at a volume of 7.5 mL, using:

a. the *P*-*V* graph in Figure 8.2.6*a*
b. the $\frac{1}{P}$ vs. *V* graph in Figure 8.2.6*b*
c. the Boyle's law equation

Comment on the likely accuracy of each method.

Solution

a. Estimating from the *P*-*V* graph gives a value for *P* somewhere around 27 psi.
b. Estimating from the $\frac{1}{P}$ versus *V* graph give a value of about 26 psi.
c. From Boyle's law, we know that the product of pressure and volume (*PV*) for a given sample of gas at a constant temperature is always equal to the same value. Therefore we have $P_1V_1 = k$ and $P_2V_2 = k$ which means that $P_1V_1 = P_2V_2$.

Using P_1 and V_1 as the known values 13.0 psi and 15.0 mL, P_2 as the pressure at which the volume is unknown, and V_2 as the unknown volume, we have:

$$P_1V_1 = P_2V_2 \text{ or } 13.0 \text{ psi} \times 15.0 \text{ mL} = P_2 \times 7.5\ m\,\text{L} \tag{8.2.5}$$

Solving:

$$P_2 = \frac{13.0 \text{ psi} \times 15.0 \cancel{\text{mL}}}{7.5 \cancel{\text{mL}}} = 26 \text{ psi} \tag{8.2.6}$$

It was more difficult to estimate well from the *P*-*V* graph, so (a) is likely more inaccurate than (b) or (c). The calculation will be as accurate as the equation and measurements allow.

Exercise $8.2.4$

The sample of gas has a volume of 30.0 mL at a pressure of 6.5 psi. Determine the volume of the gas at a pressure of 11.0 psi, using:

a. the *P*-*V* graph in Figure $8.2.6a$
b. the $\frac{1}{P}$ vs. *V* graph in Figure $8.2.6b$
c. the Boyle's law equation

Comment on the likely accuracy of each method.

Answer a

about 17–18 mL

Answer b

~18 mL

Answer c

17.7 mL; it was more difficult to estimate well from the *P*-*V* graph, so (a) is likely more inaccurate than (b); the calculation will be as accurate as the equation and measurements allow

Breathing and Boyle's Law

What do you do about 20 times per minute for your whole life, without break, and often without even being aware of it? The answer, of course, is respiration, or breathing. How does it work? It turns out that the gas laws apply here. Your lungs take in gas that your body needs (oxygen) and get rid of waste gas (carbon dioxide). Lungs are made of spongy, stretchy tissue that expands and contracts while you breathe. When you inhale, your diaphragm and intercostal muscles (the muscles between your ribs) contract, expanding your chest cavity and making your lung volume larger. The increase in volume leads to a decrease in pressure (Boyle's law). This causes air to flow into the lungs (from high pressure to low pressure). When you exhale, the process reverses: Your diaphragm and rib muscles relax, your chest cavity contracts, and your lung volume decreases, causing the

pressure to increase (Boyle's law again), and air flows out of the lungs (from high pressure to low pressure). You then breathe in and out again, and again, repeating this Boyle's law cycle for the rest of your life (Figure 8.2.7).

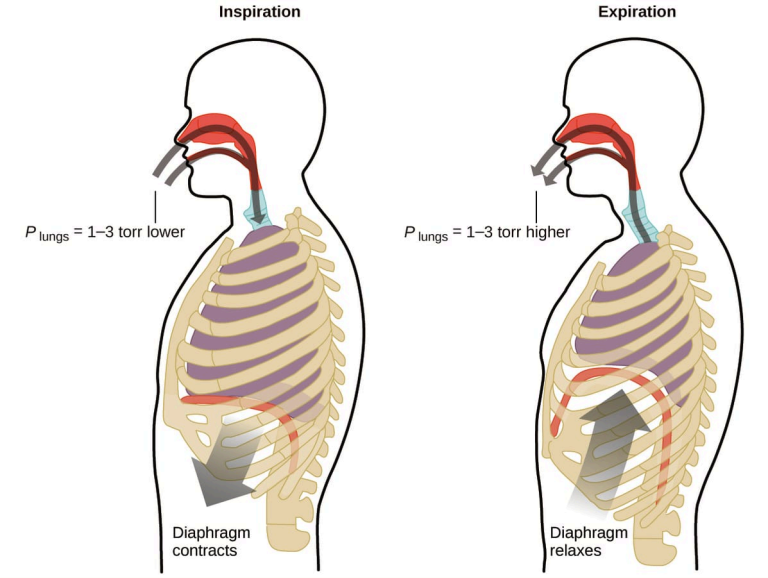


Figure 8.2.7: Breathing occurs because expanding and contracting lung volume creates small pressure differences between your lungs and your surroundings, causing air to be drawn into and forced out of your lungs.

Moles of Gas and Volume: Avogadro's Law

The Italian scientist Amedeo Avogadro advanced a hypothesis in 1811 to account for the behavior of gases, stating that equal volumes of all gases, measured under the same conditions of temperature and pressure, contain the same number of molecules. Over time, this relationship was supported by many experimental observations as expressed by Avogadro's law: *For a confined gas, the volume (V) and number of moles (n) are directly proportional if the pressure and temperature both remain constant*.

In equation form, this is written as:

$$V \propto n \text{ or } V = k \times n \text{ or } \frac{V_1}{n_1} = \frac{V_2}{n_2} \tag{8.2.7}$$

Mathematical relationships can also be determined for the other variable pairs, such as *P* versus *n*, and *n* versus *T*.

> Visit this interactive PhET simulation to investigate the relationships between pressure, volume, temperature, and amount of gas. Use the simulation to examine the effect of changing one parameter on another while holding the other parameters constant (as described in the preceding sections on the various gas laws).

The Ideal Gas Law

To this point, four separate laws have been discussed that relate pressure, volume, temperature, and the number of moles of the gas:

- Boyle's law: *PV* = constant at constant *T* and *n*
- Amontons's law: $\frac{P}{T}$ = constant at constant *V* and *n*
- Charles's law: $\frac{V}{T}$ = constant at constant *P* and *n*
- Avogadro's law: $\frac{V}{n}$ = constant at constant *P* and *T*

Combining these four laws yields the ideal gas law, a relation between the pressure, volume, temperature, and number of moles of a gas:

$$PV = nRT \tag{8.2.8}$$

where *P* is the pressure of a gas, *V* is its volume, *n* is the number of moles of the gas, *T* is its temperature on the kelvin scale, and *R* is a constant called the ideal gas constant or the universal gas constant. The units used to express pressure, volume, and temperature will determine the proper form of the gas constant as required by dimensional analysis, the most commonly encountered values being 0.08206 L atm mol^{-1} K^{-1} and 8.3145 kPa L mol^{-1} K^{-1}.

> *The ideal gas law is easy to remember and apply in solving problems, as long as you use the* ***proper values*** and units for the gas constant, R.

Gases whose properties of *P*, *V*, and *T* are accurately described by the ideal gas law (or the other gas laws) are said to exhibit *ideal behavior* or to approximate the traits of an ideal gas. An ideal gas is a hypothetical construct that may be used along with *kinetic molecular theory* to effectively explain the gas laws as will be described in a later module of this chapter. Although all the calculations presented in this module assume ideal behavior, this assumption is only reasonable for gases under conditions of relatively low pressure and high temperature. In the final module of this chapter, a modified gas law will be introduced that accounts for the *non-ideal* behavior observed for many gases at relatively high pressures and low temperatures.

The ideal gas equation contains five terms, the gas constant *R* and the variable properties *P*, *V*, *n*, and *T*. Specifying any four of these terms will permit use of the ideal gas law to calculate the fifth term as demonstrated in the following example exercises.

Example 8.2.5: Using the Ideal Gas Law

Methane, CH_4, is being considered for use as an alternative automotive fuel to replace gasoline. One gallon of gasoline could be replaced by 655 g of CH_4. What is the volume of this much methane at 25 °C and 745 torr?

Solution

We must rearrange *PV* = *nRT* to solve for *V*: $V = \dfrac{nRT}{P}$

If we choose to use *R* = 0.08206 L atm mol^{-1} K^{-1}, then the amount must be in moles, temperature must be in kelvin, and pressure must be in atm.

Converting into the "right" units:

$$n = 655 \text{ g } \cancel{CH_4} \times \frac{1 \text{ mol}}{16.043 \text{ g } \cancel{CH_4}} = 40.8 \text{ mol} \tag{8.2.9}$$

$$T = 25°\text{C} + 273 = 298 \text{ K} \tag{8.2.10}$$

$$P = 745 \cancel{\text{ torr}} \times \frac{1\text{atm}}{760 \cancel{\text{ torr}}} = 0.980 \text{ atm} \tag{8.2.11}$$

$$V = \frac{nRT}{P} = \frac{(40.8 \cancel{\text{ mol}})(0.08206 \text{ L } \cancel{\text{atm}}\cancel{\text{mol}^{-1}}\cancel{\text{K}^{-1}})(298 \text{ K})}{0.980 \cancel{\text{ atm}}} = 1.02 \times 10^3 \text{ L} \tag{8.2.12}$$

It would require 1020 L (269 gal) of gaseous methane at about 1 atm of pressure to replace 1 gal of gasoline. It requires a large container to hold enough methane at 1 atm to replace several gallons of gasoline.

Exercise 8.2.5

Calculate the pressure in bar of 2520 moles of hydrogen gas stored at 27 °C in the 180-L storage tank of a modern hydrogen-powered car.

Answer

350 bar

If the number of moles of an ideal gas are kept constant under two different sets of conditions, a useful mathematical relationship called the combined gas law is obtained: $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$ using units of atm, L, and K. Both sets of conditions are equal to the product of $n \times R$ (where n = the number of moles of the gas and R is the ideal gas law constant).

Example 8.2.6: Using the Combined Gas Law

When filled with air, a typical scuba tank with a volume of 13.2 L has a pressure of 153 atm (Figure 8.2.8). If the water temperature is 27 °C, how many liters of air will such a tank provide to a diver's lungs at a depth of approximately 70 feet in the ocean where the pressure is 3.13 atm?



Figure 8.2.8: Scuba divers use compressed air to breathe while underwater. (credit: modification of work by Mark Goodchild)

Letting *1* represent the air in the scuba tank and *2* represent the air in the lungs, and noting that body temperature (the temperature the air will be in the lungs) is 37 °C, we have:

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \longrightarrow \frac{(153\ \text{atm})(13.2\ \text{L})}{(300\ \text{K})} = \frac{(3.13\ \text{atm})(V_2)}{(310\ \text{K})} \tag{8.2.13}$$

Solving for V_2:

$$V_2 = \frac{(153\ \cancel{\text{atm}})(13.2\ \text{L})(310\ \cancel{\text{K}})}{(300\ \cancel{\text{K}})(3.13\ \cancel{\text{atm}})} = 667\ \text{L} \tag{8.2.14}$$

(Note: Be advised that this particular example is one in which the assumption of ideal gas behavior is not very reasonable, since it involves gases at relatively high pressures and low temperatures. Despite this limitation, the calculated volume can be viewed as a good "ballpark" estimate.)

Exercise 8.2.6

A sample of ammonia is found to occupy 0.250 L under laboratory conditions of 27 °C and 0.850 atm. Find the volume of this sample at 0 °C and 1.00 atm.

Answer

0.193 L

The Interdependence between Ocean Depth and Pressure in Scuba Diving

Whether scuba diving at the Great Barrier Reef in Australia (shown in Figure 8.2.9) or in the Caribbean, divers must understand how pressure affects a number of issues related to their comfort and safety.



Figure 8.2.9: Scuba divers, whether at the Great Barrier Reef or in the Caribbean, must be aware of buoyancy, pressure equalization, and the amount of time they spend underwater, to avoid the risks associated with pressurized gases in the body. (credit: Kyle Taylor).

Pressure increases with ocean depth, and the pressure changes most rapidly as divers reach the surface. The pressure a diver experiences is the sum of all pressures above the diver (from the water and the air). Most pressure measurements are given in units of atmospheres, expressed as “atmospheres absolute” or ATA in the diving community: Every 33 feet of salt water represents 1 ATA of pressure in addition to 1 ATA of pressure from the atmosphere at sea level. As a diver descends, the increase in pressure causes the body’s air pockets in the ears and lungs to compress; on the ascent, the decrease in pressure causes these air pockets to expand, potentially rupturing eardrums or bursting the lungs. Divers must therefore undergo equalization by adding air to body airspaces on the descent by breathing normally and adding air to the mask by breathing out of the nose or adding air to the ears and sinuses by equalization techniques; the corollary is also true on ascent, divers must release air from the body to maintain equalization. Buoyancy, or the ability to control whether a diver sinks or floats, is controlled by the buoyancy compensator (BCD). If a diver is ascending, the air in his BCD expands because of lower pressure according to Boyle’s law (decreasing the pressure of gases increases the volume). The expanding air increases the buoyancy of the diver, and she or he begins to ascend. The diver must vent air from the BCD or risk an uncontrolled ascent that could rupture the lungs. In descending, the increased pressure causes the air in the BCD to compress and the diver sinks much more quickly; the diver must add air to the BCD or risk an uncontrolled descent, facing much higher pressures near the ocean floor. The pressure also impacts how long a diver can stay underwater before ascending. The deeper a diver dives, the more compressed the air that is breathed because of increased pressure: If a diver dives 33 feet, the pressure is 2 ATA and the air would be compressed to one-half of its original volume. The diver uses up available air twice as fast as at the surface.

Standard Conditions of Temperature and Pressure

We have seen that the volume of a given quantity of gas and the number of molecules (moles) in a given volume of gas vary with changes in pressure and temperature. Chemists sometimes make comparisons against a standard temperature and pressure (STP) for reporting properties of gases: 273.15 K (0.00 °C) and 1 atm (101.325 kPa). At STP, an ideal gas has a volume of about 22.4 L—this is referred to as the standard molar volume (Figure 8.2.10).

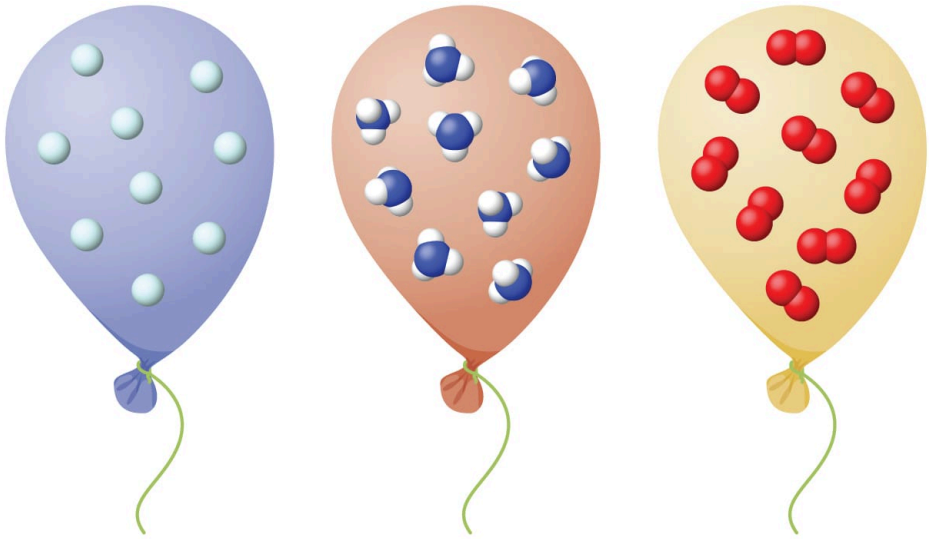


Figure 8.2.10: Since the number of moles in a given volume of gas varies with pressure and temperature changes, chemists use standard temperature and pressure (273.15 K and 1 atm or 101.325 kPa) to report properties of gases.

Contributors

Summary

The behavior of gases can be described by several laws based on experimental observations of their properties. The pressure of a given amount of gas is directly proportional to its absolute temperature, provided that the volume does not change (Amontons's law). The volume of a given gas sample is directly proportional to its absolute temperature at constant pressure (Charles's law). The volume of a given amount of gas is inversely proportional to its pressure when temperature is held constant (Boyle's law). Under the same conditions of temperature and pressure, equal volumes of all gases contain the same number of molecules (Avogadro's law).

The equations describing these laws are special cases of the ideal gas law, $PV = nRT$, where P is the pressure of the gas, V is its volume, n is the number of moles of the gas, T is its kelvin temperature, and R is the ideal (universal) gas constant.

Key Equations

- $PV = nRT$

Glossary

absolute zero
: temperature at which the volume of a gas would be zero according to Charles's law.

Amontons's law
: (also, Gay-Lussac's law) pressure of a given number of moles of gas is directly proportional to its kelvin temperature when the volume is held constant

Avogadro's law
: volume of a gas at constant temperature and pressure is proportional to the number of gas molecules

Boyle's law
: volume of a given number of moles of gas held at constant temperature is inversely proportional to the pressure under which it is measured

Charles's law
: volume of a given number of moles of gas is directly proportional to its kelvin temperature when the pressure is held constant

ideal gas
: hypothetical gas whose physical properties are perfectly described by the gas laws

ideal gas constant (*R*)
: constant derived from the ideal gas equation $R = 0.08226$ L atm mol^{-1} K^{-1} or 8.314 L kPa mol^{-1} K^{-1}

ideal gas law
: relation between the pressure, volume, amount, and temperature of a gas under conditions derived by combination of the simple gas laws

standard conditions of temperature and pressure (STP)
: 273.15 K (0 °C) and 1 atm (101.325 kPa)

standard molar volume
: volume of 1 mole of gas at STP, approximately 22.4 L for gases behaving ideally

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8.3: The Kinetic-Molecular Theory

LEARNING OBJECTIVES

- State the postulates of the kinetic-molecular theory, and use the postulates to explain the gas laws

The gas laws that we have seen to this point, as well as the ideal gas equation, are empirical, that is, they have been derived from experimental observations. The mathematical forms of these laws closely describe the macroscopic behavior of most gases at pressures less than about 1 or 2 atm. Although the gas laws describe relationships that have been verified by many experiments, they do not tell us why gases follow these relationships.

The kinetic molecular theory (KMT) is a simple microscopic model that effectively explains the gas laws described in previous modules of this chapter. This theory is based on the following five postulates described here. (Note: The term "molecule" will be used to refer to the individual chemical species that compose the gas, although some gases are composed of atomic species, for example, the noble gases.)

1. Gases are composed of molecules that are in continuous motion, travelling in straight lines and changing direction only when they collide with other molecules or with the walls of a container.
2. The molecules composing the gas are negligibly small compared to the distances between them.
3. The pressure exerted by a gas in a container results from collisions between the gas molecules and the container walls.
4. Gas molecules exert no attractive or repulsive forces on each other or the container walls; therefore, their collisions are *elastic* (do not involve a loss of energy).
5. The average kinetic energy of the gas molecules is proportional to the kelvin temperature of the gas.

The test of the KMT and its postulates is its ability to explain and describe the behavior of a gas. The various gas laws can be derived from the assumptions of the KMT, which have led chemists to believe that the assumptions of the theory accurately represent the properties of gas molecules. We will first look at the individual gas laws (Boyle's, Charles's, Amontons's, Avogadro's, and Dalton's laws) conceptually to see how the KMT explains them. Then, we will more carefully consider the relationships between molecular masses, speeds, and kinetic energies with temperature, and explain Graham's law.

The Kinetic-Molecular Theory Explains the Behavior of Gases

Recalling that gas pressure is exerted by rapidly moving gas molecules and depends directly on the number of molecules hitting a unit area of the wall per unit of time, we see that the KMT conceptually explains the behavior of a gas as follows:

- *Amontons's law.* If the temperature is increased, the average speed and kinetic energy of the gas molecules increase. If the volume is held constant, the increased speed of the gas molecules results in more frequent and more forceful collisions with the walls of the container, therefore increasing the pressure (Figure $8.3.1a$).
- *Charles's law.* If the temperature of a gas is increased, a constant pressure may be maintained only if the volume occupied by the gas increases. This will result in greater average distances traveled by the molecules to reach the container walls, as well as increased wall surface area. These conditions will decrease both the frequency of molecule-wall collisions and the number of collisions per unit area, the combined effects of which balance the effect of increased collision forces due to the greater kinetic energy at the higher temperature.
- *Boyle's law.* If the gas volume is decreased, the container wall area decreases and the molecule-wall collision frequency increases, both of which increase the pressure exerted by the gas (Figure $8.3.1b$).
- *Avogadro's law.* At constant pressure and temperature, the frequency and force of molecule-wall collisions are constant. Under such conditions, increasing the number of gaseous molecules will require a proportional increase in the container volume in order to yield a

decrease in the number of collisions per unit area to compensate for the increased frequency of collisions (Figure 8.3.1*c*).

- *Dalton's Law.* Because of the large distances between them, the molecules of one gas in a mixture bombard the container walls with the same frequency whether other gases are present or not, and the total pressure of a gas mixture equals the sum of the (partial) pressures of the individual gases.

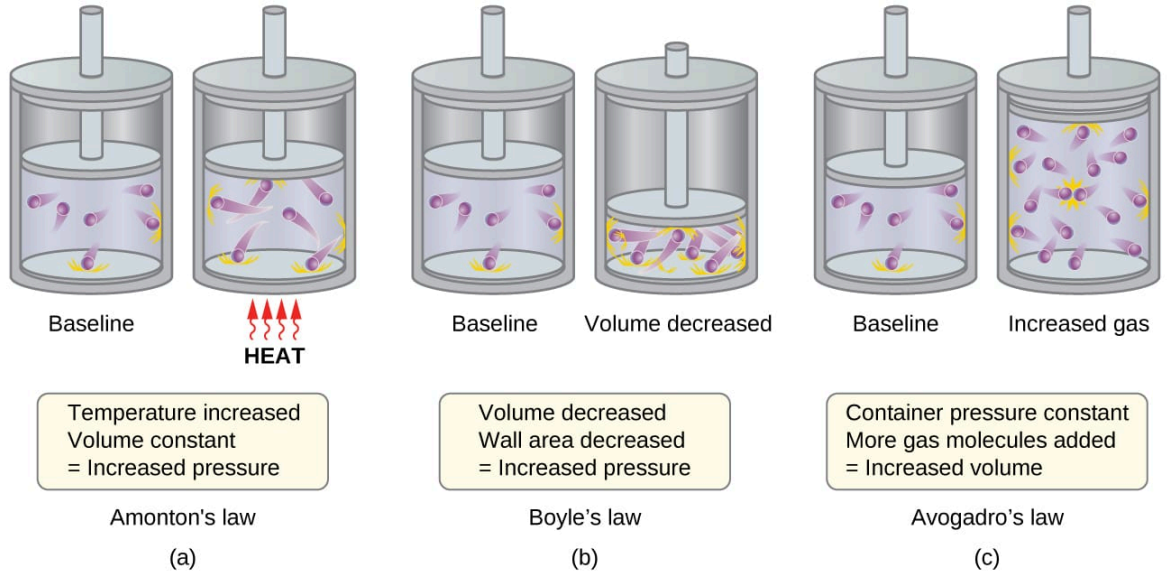


Figure 8.3.1: (a) When gas temperature increases, gas pressure increases due to increased force and frequency of molecular collisions. (b) When volume decreases, gas pressure increases due to increase frequency of molecular collisions. (c) When the amount of gas increases at a constant pressure, volur increases to yield a constant number of collisions per unit wall area per unit time.

Summary

The kinetic molecular theory is a simple but very effective model that effectively explains ideal gas behavior. The theory assumes that gases consist of widely separated molecules of negligible volume that are in constant motion, colliding elastically with one another and the walls of their container with average velocities determined by their absolute temperatures. The individual molecules of a gas exhibit a range of velocities, the distribution of these velocities being dependent on the temperature of the gas and the mass of its molecules.

Glossary

kinetic molecular theory

theory based on simple principles and assumptions that effectively explains ideal gas behavior

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8.4: Unit 8 Practice Problems

Question 1.

If the pressure inside a tank is 100. psi, what is this pressure in kPa, mPa, atm, mmHg?

Answer

$$100 \cancel{\text{ psi.}} \times \frac{101 \text{ kPa}}{14.7 \cancel{\text{ psi.}}} = 687 \text{ kPa} \tag{8.4.1}$$

$$100 \cancel{\text{ psi.}} \times \frac{0.101 \text{ MPa}}{14.7 \cancel{\text{ psi.}}} = 0.687 \text{ MPa} \tag{8.4.2}$$

$$100 \cancel{\text{ psi.}} \times \frac{1 \text{ atm}}{14.7 \cancel{\text{ psi.}}} = 6.8 \text{ atm} \tag{8.4.3}$$

$$100 \cancel{\text{ psi.}} \times \frac{760 \text{ mmHg}}{14.7 \cancel{\text{ psi.}}} = 5170 \text{ mmHg} \tag{8.4.4}$$

Question 2.

A gas occupies a volume of 17.4L at 11.2 psi, what will it's volume be if the pressure is increased to 13.6psi and the temperature is held constant?

Answer

$P_1V_1 = P_2V_2$ (11.2psi)(17.4L) = (13.6psi)(V_2) V_2 = 14.3L

Question 3.

A gas has a volume of 186mL at 32°C, what will it's volume be if the temperature of the gas is increased to 104°C and the pressure is held constant?

Answer

$V_1/T_1 = V_2/T_2$ Remember that when using gas laws, temperature should always be in K. (186mL) / (305K) = (V_2) / (377K) V_2 = 230mL

Question 4.

A container of neon at a pressure of 550mmHg and a temp of 120°C is heated (at a constant volume) until the temperature is 360°C. What is the new pressure of the heated neon?

Answer

$P_1/T_1 = P_2/T_2$ Remember that when using gas laws, temperature should always be in K. (550mmHg) / (393K) = (P_2) / (633K) P_2 = 890 mmHg

Question 5.

A cylinder containing 12.0L of compressed air at 23.0atm and -20.0°C is opened and the air escapes into a room which has a pressure of 0.960atm and warms to 28.0°C, what is the final volume of the air from the cylinder?

Answer

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \qquad \frac{(23.0\,atm)(12.0L)}{(253K)} = \frac{(0.960\,atm)(V_2)}{(301K)}$$

$$V_2 = \frac{(23.0\,atm)(12.0L)(301K)}{(0.960\,atm)(253K)} = 342L$$

Question 6.

If a gas has a volume of 19.8L at standard temperature and pressure (STP), how many moles of gas are there?

Answer

$$19.8L \left| \frac{1\,mole\,at\,STP}{22.4L} \right. = 0.884\,moles$$

Question 7.

If 1.0 grams of a gas occupies a volume of 330mL at STP, what is the molecular weight of the gas?

Answer

$$330\text{mL}\left|\frac{1\text{ L}}{1000\text{mL}}\right|\frac{1\text{ mole at STP}}{22.4\text{L}} = 0.015\text{moles}$$

$$\text{molecular weight} = \text{g/mole} = \frac{1.0\text{g}}{0.015\text{moles}} = 68\text{ g/mole}$$

Question 9.

A gas occupies 6.4L at 102kPa and 294K, what will the temperature of the gas be at 8.7L and 97kPa?

Answer

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

$$\frac{(102\text{kPa})(6.4\text{L})}{(294\text{K})} = \frac{(97\text{kPa})(8.7\text{L})}{T_2}$$

$$T_2 = \frac{(97\text{kPa})(8.7\text{L})(294\text{K})}{(102\text{kPa})(6.4\text{L})}$$

$$T_2 = 380\text{K}$$

Question 10.

If I have 2.6 moles of a gas at a pressure of 4.3 atm and a volume of 8.4 liters, what is the temperature? (R=0.0821 L*atm/mol*K)

Answer

$$PV = nRT$$

$$(4.3\text{atm})(8.4\text{L}) = (2.6\text{moles})\left(0.0821 \frac{\text{L atm}}{\text{mol K}}\right) T$$

$$T = \frac{(4.3)(8.4)}{(2.6)(0.0821)} = 170\text{K}$$

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