

PGENERAL CHEMISTRY I: ATOMS, COMPOUNDS, AND BULK SUBSTANCES



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Plass's General Chemistry 1: Atoms,
Compounds, and Bulk substances

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CHAPTER OVERVIEW

1: What do we need to know to start?

1.1: Measurements

1.2: Measurement Uncertainty, Accuracy, and Precision

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1.1: Measurements

Learning Objectives

- Explain the process of measurement and describe the three basic parts of a quantity.
- Describe the properties and units of length, mass, volume, density, temperature, and time.
- Recognize the common unit prefixes and use them to describe the magnitude of a measurement.
- Describe and calculate the density of a substance.
- Perform basic unit calculations and conversions in the metric and other unit systems.

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 0.0000025 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.

NG, equals 4 times ten to the negative 9, or 0.000000004 g. The prefix micro has the greek letter mu as its symbol and a factor of 10 to the negative sixth power. Therefore, 1 microliter, or μ L, is equal to one times ten to the negative 6 or 0.000001 L. The prefix milli has a lowercase M as its symbol and a factor of 10 to the negative third power. Therefore, 2 millimoles, or M mol, are equal to two times ten to the negative 3 or 0.002 mol. The prefix centi has a lowercase C as its symbol and a factor of 10 to the negative second power. Therefore, 7 centimeters, or C M, are equal to seven times ten to the negative 2 meters or 0.07 M O L. The prefix deci has a lowercase D as its symbol and a factor of 10 to the negative first power. Therefore, 1 deciliter, or lowercase D uppercase L, are equal to one times ten to the negative 1 meters or 0.1 L. The prefix kilo has a lowercase K as its symbol and a factor of 10 to the third power. Therefore, 1 kilometer, or K M, is equal to one times ten to the third meters or 1000 M. The prefix mega has an uppercase M as its symbol and a factor of 10 to the sixth power. Therefore, 3 megahertz, or M H Z, are equal to three times 10 to the sixth hertz, or 3000000 H Z. The prefix giga has an uppercase G as its symbol and a factor of 10 to the ninth power. Therefore, 8 gigayears, or G Y R, are equal to eight times 10 to the ninth years, or 800000000 G Y R. The prefix tera has an uppercase T as its symbol and a factor of 10 to the twelfth power. Therefore, 5 terawatts, or T W, are equal to five times 10 to the twelfth watts, or 5000000000000 W." data-quail-id="64" data-mt-width="1076">

Table 1.1.2: Common Unit Prefixes

Prefix	Symbol	Factor	Example
femto	f	10^{-15}	1 femtosecond (fs) = 1×10^{-15} s (0.000000000000001 s)
pico	p	10^{-12}	1 picometer (pm) = 1×10^{-12} m (0.000000000001 m)
nano	n	10^{-9}	4 nanograms (ng) = 4×10^{-9} g (0.000000004 g)
micro	μ	10^{-6}	1 microliter (μ L) = 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)
giga	G	10^9	8 gigayears (Gyr) = 8×10^9 yr (8,000,000,000 Gyr)
tera	T	10^{12}	5 terawatts (TW) = 5×10^{12} W (5,000,000,000,000 W)

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 ($1 \text{ km} = 1000 \text{ m} = 10^3 \text{ m}$), whereas shorter distances can be reported in centimeters ($1 \text{ cm} = 0.01 \text{ m} = 10^{-2} \text{ m}$) or millimeters ($1 \text{ mm} = 0.001 \text{ m} = 10^{-3} \text{ m}$).

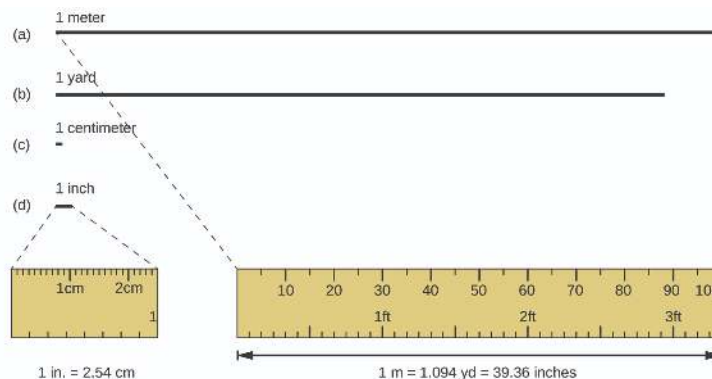


Figure 1.1.1: The relative lengths of 1 m, 1 yd, 1 cm, and 1 in. are shown (not actual size), as well as comparisons of 2.54 cm and 1 in., and of 1 m and 1.094 yd.

A ruler is shown with various lengths of black line shown above it to compare the relative lengths of 1 inch, meter, centimeter, and yard.

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). It is now defined by a certain cylinder of platinum-iridium alloy, which is kept in France (Figure 1.4.2). Any object with the same mass as this cylinder is said to have a mass of 1 kilogram. 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).



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).

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 ($^{\circ}$). The degree Celsius ($^{\circ}\text{C}$) 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 = $0.000003 \text{ s} = 3 \times 10^{-6}$ and 5 megaseconds = $5,000,000 \text{ s} = 5 \times 10^6 \text{ s}$. Alternatively, hours, days, and years can be used.

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 1.1.3). 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.

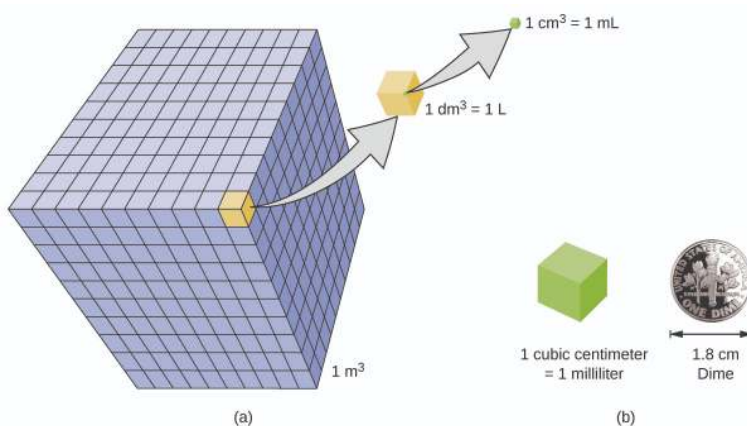


Figure 1.1.3: (a) The relative volumes are shown for cubes of 1 m^3 , 1 dm^3 (1 L), and 1 cm^3 (1 mL) (not to scale). (b) The diameter of a dime is compared relative to the edge length of a 1-cm^3 (1-mL) cube.

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 cubic centimeter) is often used by health professionals. A cubic centimeter is also called a milliliter (mL) and is 1/1000 of a liter.

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 is 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 $0.7 \text{ g}/\text{cm}^3$ (the density of gasoline) to $19 \text{ g}/\text{cm}^3$ (the density of gold). The density of air is about $1.2 \text{ g}/\text{L}$. Table 1.1.3 shows the densities of some common substances.

Table 1.1.3: 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.

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

✓ Example 1.1.1

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/cm³. 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.

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

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

(We will discuss the reason for rounding to the first decimal place in the next section.)

? Exercise 1.1.1

- To three decimal places, what is the volume of a cube (cm³) with an edge length of 0.843 cm?
- 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 cm³;

Answer b

8.91 g/cm³

✓ Example 1.1.2: 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:

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

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:

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

? Exercise 1.1.1

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

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.

Key Equations

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

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

density

ratio of mass to volume for a substance or object

kelvin (K)

SI unit of temperature; $273.15 \text{ K} = 0 \text{ }^\circ\text{C}$

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 cm³

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 cm³

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

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1.2: Measurement Uncertainty, Accuracy, and Precision

Learning Objectives

- Compare and contrast exact and uncertain numbers.
- Correctly represent uncertainty in quantities using significant figures.
- Identify the number of significant figures in value.
- Solve problems that involve various calculations and report the results with the appropriate number of significant figures.
- Apply proper rounding rules to computed quantities
- Define accuracy and precision, and use accuracy and precision to describe data sets.

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.

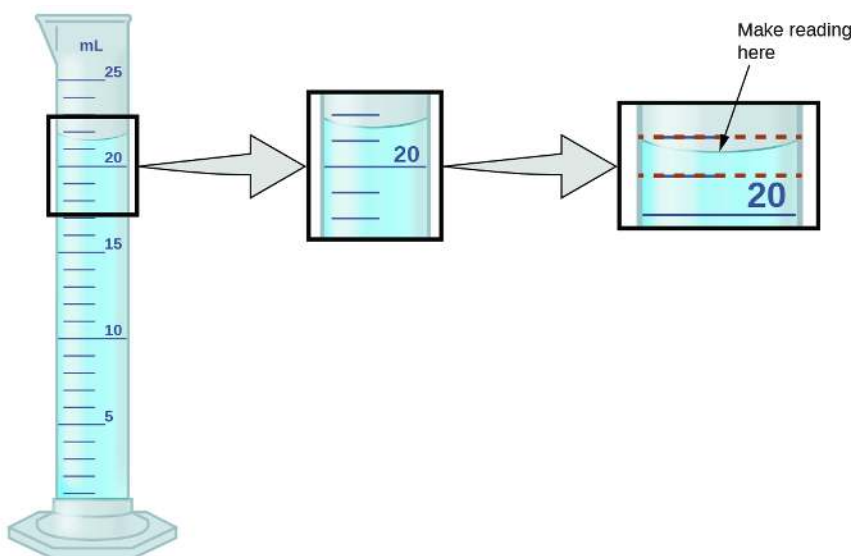


Figure 1.2.1: To measure the volume of liquid in this graduated cylinder, you must mentally subdivide the distance between the 21 and 22 mL marks into tenths of a milliliter, and then make a reading (estimate) at the bottom of the meniscus.

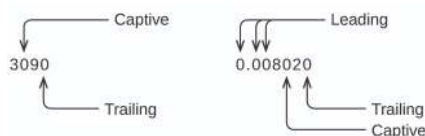
A 25 milliliter graduated cylinder filled with liquid. The markings on the cylinders is zoomed in to show the bottom of the meniscus between 21 and 22 milliliters.

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.

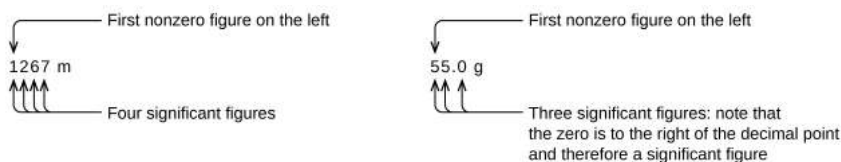
This concept holds true for all measurements, even if you do not actively make an estimate. If you place a quarter on a standard electronic balance, you may obtain a reading of 6.72 g. The digits 6 and 7 are certain, and the 2 indicates that the mass of the quarter is likely between 6.71 and 6.73 grams. 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.



The left diagram uses the example of 3090. The zero in the hundreds place is labeled "captive" and the zero in the ones place is labeled trailing. The right diagram uses the example 0.008020. The three zeros in the ones, tenths, and hundredths places are labeled "leading." The zero in the ten-thousandths place is labeled "captive" and the zero in the millionths place is labeled "trailing."

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.



The left diagram uses the example of 1267 meters. The number 1 is the first nonzero figure on the left. 1267 has 4 significant figures in total. The right diagram uses the example of 55.0 grams. The number 5 in the tens place is the first nonzero figure on the left. 55.0 has 3 significant figures. Note that the 0 is to the right of the decimal point and therefore is a significant figure.

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.

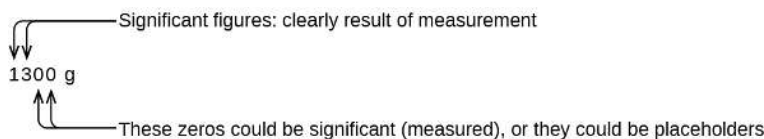


The left diagram uses the example of 70.607 milliliters. The number 7 is the first nonzero figure on the left. 70.607 has 5 significant figures in total, as all figures are measured including the 2 zeros. The right diagram uses the example of 0.00832407 M L. The number 8 is the first nonzero figure on the left. 0.00832407 has 6 significant figures.

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.



This figure uses the example of 1300 grams. The one and the 3 are significant figures as they are clearly the result of measurement. The 2 zeros could be significant if they were measured or they could be placeholders.

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)

$$\begin{array}{r}
 1.0023 \leftarrow \text{Ten thousandths place} \\
 + 4.383 \leftarrow \text{Thousandths place: least precise} \\
 \hline
 5.3853
 \end{array}$$

Round to thousandths

(a)

$$\begin{array}{r}
 486 \text{ g} \\
 - 421.23 \text{ g} \\
 \hline
 64.77 \text{ g}
 \end{array}
 \rightarrow \text{Answer is 65 g}$$

Round to ones

(b)

? Exercise 1.2.2

- Add 2.334 mL and 0.31 mL.
- 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).

- Multiply 0.6238 cm by 6.6 cm.
- Divide 421.23 g by 486 mL.

Solution

(a)

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

four significant figures $\times$ two significant figures $\rightarrow$ two significant figures answer

(b)

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

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

? Exercise 1.2.3

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

Answer a

0.747 cm²

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

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

? Exercise 1.2.4: Determination of Density Using Water Displacement

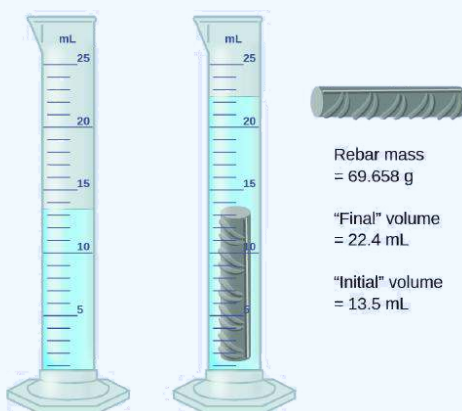
What is the density of a liquid with a mass of 31.1415 g and a volume of 30.13 cm³?

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 graduated cylinder filled with liquid is shown. One shows the level before the rebar is added and the other shows the level with the rebar submerged in the liquid. Rebar mass is 69.658 grams, final volume is 22.4 milliliters, and initial volume is 13.5 milliliters.

- Use these values to determine the density of this piece of rebar.
- 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:

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

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

The density is the mass-to-volume ratio:

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

(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 graduated cylinder filled with liquid is shown. One shows the level before the material is added and the other shows the level with the material submerged in the liquid. Mass is 51.842 grams, final volume is 19.8 milliliters, and initial volume is 17.1 milliliters.

- Use these values to determine the density of this material.
- 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).

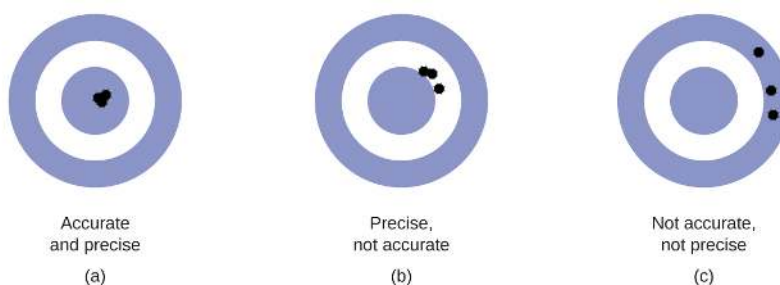


Figure 1.2.2: (a) These arrows are close to both the bull's eye and one another, so they are both accurate and precise. (b) These arrows are close to one another but not on target, so they are precise but not accurate. (c) These arrows are neither on target nor close to one another, so they are neither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

2: Atoms—They make up everything!

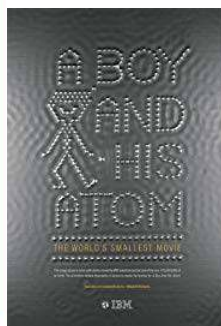
Using atoms to store renewable energy!

Sossina Haile, Professor of Materials Science and Engineering at Northwestern University, and [her students](#) (see below) are using chemistry to address one of the greatest shortcomings in renewable energy—storage and transport. They are developing technologies to create liquid fuel by splitting water into hydrogen gas or combining water and carbon dioxide using solar energy. [She invented the solid acid fuel cell](#) and her record-setting proton-conducting fuel cell made [the news](#). Haile and her students used crazy mixtures of a bunch of elements to create catalysts in highly efficient and stable devices. One component of the device contains Pr, Ba, Sr, Co, Fe, and O and another part contains Ni, Ba, Zr, Ce, Y, Yb, and O. They have to get the perfect mixture of all of these elements to give the excellent performance they have achieved. Read more in ["Bottling the Sun"](#).

Goals and expectations

1. Interconvert properties of an element using unit conversions, density, and atomic masses.
2. Describe the difference between the following on the macroscopic and microscopic scales: an element, a compound, a solution, a homogeneous mixture, a heterogeneous mixture.
3. Relate the number of protons, neutrons, and electrons to descriptors of that atom.
4. Use the concepts of isotopic mass and isotopic abundance to relate the properties of isotopes.

On an exam, you will only be provided [with a periodic table](#). All other necessary information should be in your head!



[The world's smallest movie!](#)

Transforming one descriptor of a substance to another using a conversion factor

[Starter video](#) This video by Prof. Pluss walk through doing a unit conversion, which is just one example of taking a value (a number plus units, plus the identity of the substance) and converting it to another form using a conversion factor (a ratio of two equal things).

How to do a conversion:

2 ways to think about it, math is really all the same

think about fixed ratios

$$\frac{1 \text{ dozen}}{12 \text{ cookies}} = \frac{x}{11 \text{ cookies}}$$

we know this ratio is always true

cross-multiply:

$$11 \text{ cookies} \left(\frac{1 \text{ dozen}}{12 \text{ cookies}} \right) = x$$

watch for units to cancel!

think about values
conversion factor

$$11 \text{ cookies} \left(\frac{1 \text{ dozen}}{12 \text{ cookies}} \right) =$$

value of interest conversion factor written so that units cancel

$$x = 0.92 \text{ dozen}$$

[Video of more complex problem](#) Here is a video by Prof. Plass doing a more complicated example.

Practice problems and readings for each goal

Goal #1: Interconvert properties of an element using unit conversions, density, and atomic masses.

Achieving this goal requires:

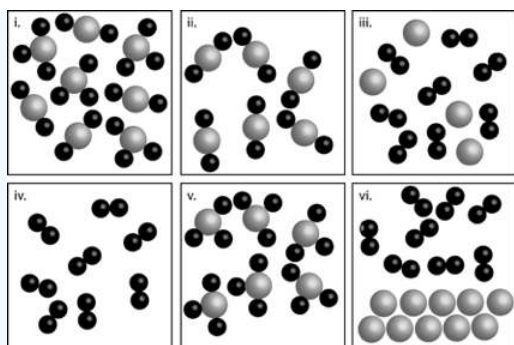
- Picturing matter as consisting of tiny particles called atoms.
- Knowing the following terms and units:
 - Atoms and elements
 - Volume (measured in L or cm^3)
 - Mass (measured in g)
 - Density = mass/volume (g/L, g/mL, etc)
 - Metric prefixes. These are the ones you will be expected to know:

Name (abbreviation)	Example conversion(s)
kilo (k)	1 kg = 1000 g AND 10^{-3} kg = 1 g
centi (c)	10^2 cm = 1 m
milli (m)	10^3 mL = 1 L
micro (μ)	10^6 μmol = 1 mol
nano (n)	10^9 nm = 1 m AND 10^{-9} nm = 1 m
pico (p)	10^{12} pm = 1 m AND 10^{-12} pm = 1 m

- Being able to perform a mathematical transformation of one descriptor of a substance to another using a conversion factor. [See above for crash course.](#)
- Interpretation of graphical data in advanced applications.

Exercise 2.1

1. Which of the following pictures represents each of the following substance types? Justify your answer in a few sentences.



An element

A pure compound

A heterogeneous mixture

A solution

Answer

Add texts here. Do not delete this text first.

An element = iv

A pure compound = v and ii

A heterogeneous mixture = vi

A solution = iii and i

THE MOLE: 6.022×10^{23}



What is a Mole?

One mole is the amount of a substance that contains 6.022×10^{23} atoms or molecules. It is specifically defined as the number of atoms contained in 12 grams of carbon-12. This is also known as 'Avogadro's Number' (N_A); it is named after the Italian scientist Amedeo Avogadro (left), a suggestion put forward by French scientist Jean Perrin to recognise Avogadro's work.



One mole is essentially
602,214,179,000,000,000,000,000
of something - in chemistry, atoms or molecules



H₂O
18.0g
Water



Fe
55.8g
Iron



O₂
32.0g
Oxygen



NaCl
58.4g
Table Salt



Au
197g
Gold



He
4.00g
Helium

ONE MOLE IS A DIFFERENT MASS FOR DIFFERENT ELEMENTS & COMPOUNDS
 This may seem confusing; however, it's similar to comparing a dozen elephants to a dozen mice. Although their masses may be very different, you still have a dozen of each!

























A mole is often referred to as 'a chemist's dozen'
 IT'S JUST AN EASIER WAY TO COUNT LARGE NUMBERS OF ATOMS & MOLECULES

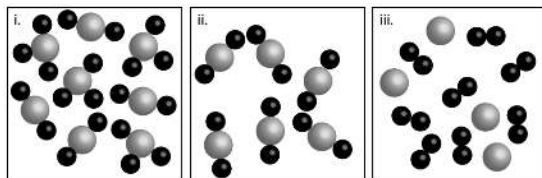
NO. OF MOLES = $\frac{\text{MASS (g)}}{\text{MASS OF 1 MOLE (g)}}$

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Goal #2: Describe the difference between the following on the macroscopic and microscopic scales: an element, a compound, a solution, a homogeneous mixture, a heterogeneous mixture.

Achieving this goal requires:

- Know the definitions of an element, a compound, a solution, a homogeneous mixture, a heterogeneous mixture.
- Relate these definitions to representations of the microscopic behavior, like these:



- Relate these definitions to macroscopic behavior.
- Recognize the microscopic representations of phase change processes (boiling, freezing, dissolution).

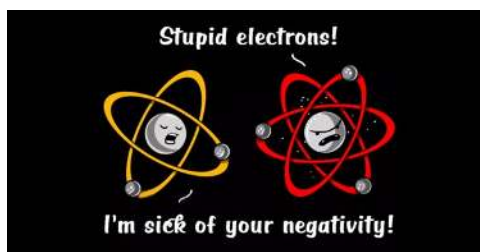


Starting practice:	HW #1, questions 1 and 2 Do if needed: OS Chapter 1 (9-19)	Further resources*: If you find any additional resources you like, please forward them to Prof. Plass!	OpenStax 1.2
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Goal #3: Relate the number of protons, neutrons, and electrons to descriptors of that atom.

Achieving this goal requires:

- Recognizing the atomic # (Z) on the periodic table and relating this to the number of protons.
- Knowing the definitions of...
 - Mass number
 - Isotope
 - Integer charge
 - Ion
 - Cation
 - Anion
 - Nucleus



Starting practice:	HW #1, question 5 Extra: Chemlibretext 1-5	Further resources*: If you find any additional resources you like, please forward them to Prof. Plass!	<ul style="list-style-type: none"> • OpenStax 2.3 • Make an atom simulation • Coulomb's law simulation
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What did the positive charge say to the negative charge after their date?



DIAGRAM OF AN ATOM



Goal #4: Use the concepts of isotopic mass and isotopic abundance to relate the properties of isotopes.

- Achieving this goal requires:
- Knowing the definitions of:
 - Isotopic mass
 - Isotopic abundance (in fractional and % forms)
 - Average atomic mass = sum of (isotopic mass)x(fractional isotopic abundance)
- Using isotopic mass and isotopic abundance to perform a mathematical transformation of one value of an isotope to another using a conversion factor.

Topic hierarchy

[2.1: Phases and Classification of Matter](#)

[2.2: Atomic Structure and Symbolism](#)

[2.3: Problems](#)

[2.3.1: Advanced problems](#)

[2.3.1.1: All about phosphorous](#)

[2.3.1.2: Strontium isotopes treat bone cancer pain](#)

[2.3.1.2.1: Strontium treats bone cancer pain- Solutions](#)

[2.3.2: Mechanical problems](#)

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2.1: Phases and Classification of Matter

Learning Objectives

- Describe the basic properties of each physical state of matter: solid, liquid, and gas.
- Define and give examples of atoms and molecules.
- Classify matter as an element, compound, homogeneous mixture, or heterogeneous mixture with regard to its physical state and composition.
- Use symbolic, particulate, or macroscopic representations to describe or classify the different types of matter.
- Distinguish between mass and weight.
- Apply the law of conservation of matter.

Matter is defined as anything that occupies space and has mass, and it is all around us. Solids and liquids are more obviously matter: We can see that they take up space, and their weight tells us that they have mass. Gases are also matter; if gases did not take up space, a balloon would stay collapsed rather than inflate when filled with gas.

Solids, liquids, and gases are the three states of matter commonly found on earth (Figure 2.1.1). A solid is rigid and possesses a definite shape. A liquid flows and takes the shape of a container, except that it forms a flat or slightly curved upper surface when acted upon by gravity. (In zero gravity, liquids assume a spherical shape.) Both liquid and solid samples have volumes that are very nearly independent of pressure. A gas takes both the shape and volume of its container.

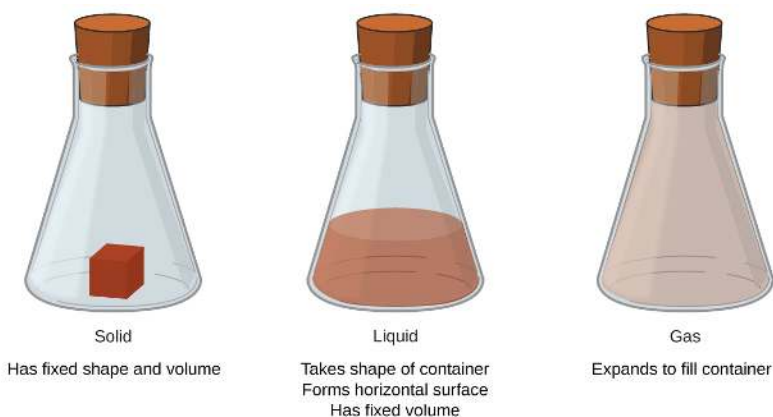


Figure 2.1.1: The three most common states or phases of matter are solid, liquid, and gas.

A beaker labeled solid contains a cube of red matter and says has fixed shape and volume. A beaker labeled liquid contains a brownish-red colored liquid. This beaker says takes shape of container, forms horizontal surfaces, has fixed volume. The beaker labeled gas is filled with a light brown gas. This beaker says expands to fill container.

A fourth state of matter, plasma, occurs naturally in the interiors of stars. A plasma is a gaseous state of matter that contains appreciable numbers of electrically charged particles (Figure 2.1.2). The presence of these charged particles imparts unique properties to plasmas that justify their classification as a state of matter distinct from gases. In addition to stars, plasmas are found in some other high-temperature environments (both natural and man-made), such as lightning strikes, certain television screens, and specialized analytical instruments used to detect trace amounts of metals.



Figure 2.1.2: A plasma torch can be used to cut metal. (credit: “Hypertherm”/Wikimedia Commons)

A cutting torch is being used to cut a piece of metal. Bright, white colored plasma can be seen near the tip of the torch, where it is contacting the metal.



Video 2.1.1: *In a tiny cell in a plasma television, the plasma emits ultraviolet light, which in turn causes the display at that location to appear a specific color. The composite of these tiny dots of color makes up the image that you see. Watch this video to learn more about plasma and the places you encounter it.*

Some samples of matter appear to have properties of solids, liquids, and/or gases at the same time. This can occur when the sample is composed of many small pieces. For example, we can pour sand as if it were a liquid because it is composed of many small grains of solid sand. Matter can also have properties of more than one state when it is a mixture, such as with clouds. Clouds appear to behave somewhat like gases, but they are actually mixtures of air (gas) and tiny particles of water (liquid or solid).

The mass of an object is a measure of the amount of matter in it. One way to measure an object’s mass is to measure the force it takes to accelerate the object. It takes much more force to accelerate a car than a bicycle because the car has much more mass. A more common way to determine the mass of an object is to use a balance to compare its mass with a standard mass.

Although weight is related to mass, it is not the same thing. Weight refers to the force that gravity exerts on an object. This force is directly proportional to the mass of the object. The weight of an object changes as the force of gravity changes, but its mass does not. An astronaut’s mass does not change just because she goes to the moon. But her weight on the moon is only one-sixth her earth-bound weight because the moon’s gravity is only one-sixth that of the earth’s. She may feel “weightless” during her trip when she experiences negligible external forces (gravitational or any other), although she is, of course, never “massless.”

The law of conservation of matter summarizes many scientific observations about matter: It states that *there is no detectable change in the total quantity of matter present when matter converts from one type to another (a chemical change) or changes among solid, liquid, or gaseous states (a physical change)*. Brewing beer and the operation of batteries provide examples of the conservation of matter (Figure 2.1.4). During the brewing of beer, the ingredients (water, yeast, grains, malt, hops, and sugar) are converted into beer (water, alcohol, carbonation, and flavoring substances) with no actual loss of substance. This is most clearly seen during the bottling process, when glucose turns into ethanol and carbon dioxide, and the total mass of the substances does not change. This can also be seen in a lead-acid car battery: The original substances (lead, lead oxide, and sulfuric acid), which are

capable of producing electricity, are changed into other substances (lead sulfate and water) that do not produce electricity, with no change in the actual amount of matter.

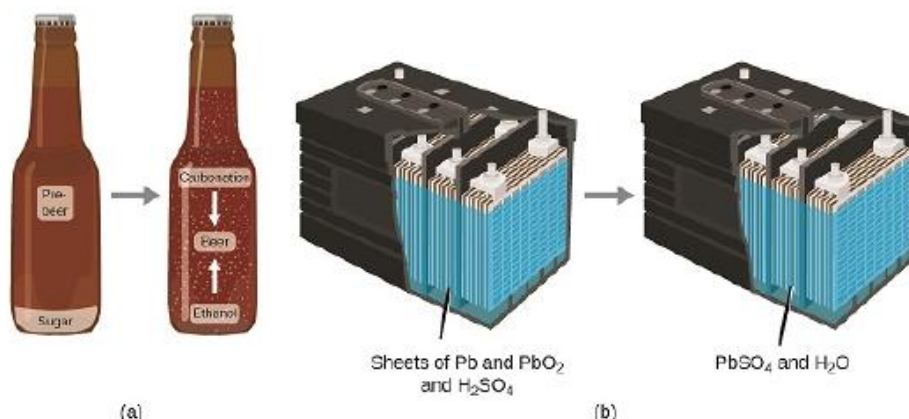


Figure 2.1.3: (a) The mass of beer precursor materials is the same as the mass of beer produced: Sugar has become alcohol and carbonation. (b) The mass of the lead, lead oxide plates, and sulfuric acid that goes into the production of electricity is exactly equal to the mass of lead sulfate and water that is formed.

Diagram A shows a beer bottle containing pre-beer and sugar. An arrow points from this bottle to a second bottle. This second bottle contains the same volume of liquid, however, the sugar has been converted into ethanol and carbonation as beer was made. Diagram B shows a car battery that contains sheets of P B and P B O subscript 2 along with H subscript 2 S O subscript 4. After the battery is used, it contains an equal mass of P B S O subscript 4 and H subscript 2 O.

Although this conservation law holds true for all conversions of matter, convincing examples are few and far between because, outside of the controlled conditions in a laboratory, we seldom collect all of the material that is produced during a particular conversion. For example, when you eat, digest, and assimilate food, all of the matter in the original food is preserved. But because some of the matter is incorporated into your body, and much is excreted as various types of waste, it is challenging to verify by measurement.

Atoms and Molecules

An atom is the smallest particle of an element that has the properties of that element and can enter into a chemical combination. Consider the element gold, for example. Imagine cutting a gold nugget in half, then cutting one of the halves in half, and repeating this process until a piece of gold remained that was so small that it could not be cut in half (regardless of how tiny your knife may be). This minimally sized piece of gold is an atom (from the Greek *atomos*, meaning “indivisible”) (Figure 1.2.4). This atom would no longer be gold if it were divided any further.

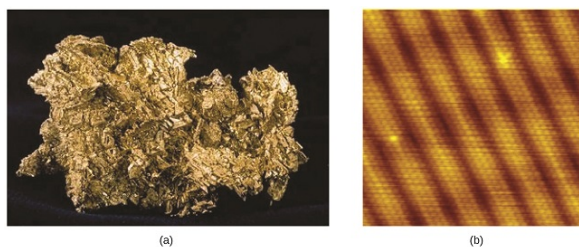


Figure 2.1.4: (a) This photograph shows a gold nugget. (b) A scanning-tunneling microscope (STM) can generate views of the surfaces of solids, such as this image of a gold crystal. Each sphere represents one gold atom. (credit a: modification of work by United States Geological Survey; credit b: modification of work by “Erwinrossen”/Wikimedia Commons)

Figure A shows a gold nugget as it would appear to the naked eye. The gold nugget is very irregular, with many sharp edges. It appears gold in color. The microscope image of a gold crystal shows many similarly sized gold stripes that are separated by dark areas. Looking closely, one can see that the gold stripes are made of many, tiny, circular atoms.

The first suggestion that matter is composed of atoms is attributed to the Greek philosophers Leucippus and Democritus, who developed their ideas in the 5th century BCE. However, it was not until the early nineteenth century that John Dalton (1766–1844), a British schoolteacher with a keen interest in science, supported this hypothesis with quantitative measurements. Since that time, repeated experiments have confirmed many aspects of this hypothesis, and it has become one of the central theories of chemistry.

Other aspects of Dalton's atomic theory are still used but with minor revisions (details of Dalton's theory are provided in the chapter on atoms and molecules).

An atom is so small that its size is difficult to imagine. One of the smallest things we can see with our unaided eye is a single thread of a spider web: These strands are about $1/10,000$ of a centimeter (0.0001 cm) in diameter. Although the cross-section of one strand is almost impossible to see without a microscope, it is huge on an atomic scale. A single carbon atom in the web has a diameter of about 0.00000015 centimeter, and it would take about 7000 carbon atoms to span the diameter of the strand. To put this in perspective, if a carbon atom were the size of a dime, the cross-section of one strand would be larger than a football field, which would require about 150 million carbon atom "dimes" to cover it. (Figure 2.1.5) shows increasingly close microscopic and atomic-level views of ordinary cotton.

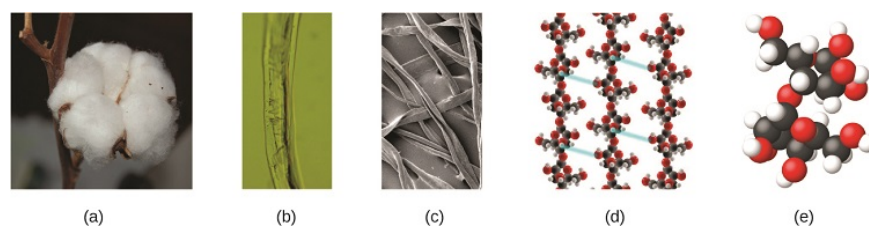


Figure 2.1.5: These images provide an increasingly closer view: (a) a cotton boll, (b) a single cotton fiber viewed under an optical microscope (magnified 40 times), (c) an image of a cotton fiber obtained with an electron microscope (much higher magnification than with the optical microscope); and (d and e) atomic-level models of the fiber (spheres of different colors represent atoms of different elements). (credit c: modification of work by "Featheredtar"/Wikimedia Commons)

Figure A shows a puffy white cotton boll growing on a brown twig. Figure B shows a magnified cotton strand. The strand appears transparent but contains dark areas within its interior. Figure C shows the surface of several crisscrossing and overlapping cotton fibers. Its surface is rough along the edges but smooth near the center of each strand. Figure D shows three strands of molecules connected into three vertical chains. Each strand contains about five molecules. Figure E shows that the cotton molecule contains about a dozen atoms. The black carbon atoms form rings that are connected by red oxygen atoms. Many of the carbon atoms are also bonded to hydrogen atoms, shown as white balls, or other oxygen atoms.

An atom is so light that its mass is also difficult to imagine. A billion lead atoms ($1,000,000,000$ atoms) weigh about 3×10^{-13} grams, a mass that is far too light to be weighed on even the world's most sensitive balances. It would require over $300,000,000,000,000$ lead atoms (300 trillion, or 3×10^{14}) to be weighed, and they would weigh only 0.0000001 gram.

It is rare to find collections of individual atoms. Only a few elements, such as the gases helium, neon, and argon, consist of a collection of individual atoms that move about independently of one another. Other elements, such as the gases hydrogen, nitrogen, oxygen, and chlorine, are composed of units that consist of pairs of atoms (Figure 2.1.6). One form of the element phosphorus consists of units composed of four phosphorus atoms. The element sulfur exists in various forms, one of which consists of units composed of eight sulfur atoms. These units are called molecules. A molecule consists of two or more atoms joined by strong forces called chemical bonds. The atoms in a molecule move around as a unit, much like the cans of soda in a six-pack or a bunch of keys joined together on a single key ring. A molecule may consist of two or more identical atoms, as in the molecules found in the elements hydrogen, oxygen, and sulfur, or it may consist of two or more different atoms, as in the molecules found in water. Each water molecule is a unit that contains two hydrogen atoms and one oxygen atom. Each glucose molecule is a unit that contains 6 carbon atoms, 12 hydrogen atoms, and 6 oxygen atoms. Like atoms, molecules are incredibly small and light. If an ordinary glass of water were enlarged to the size of the earth, the water molecules inside it would be about the size of golf balls.

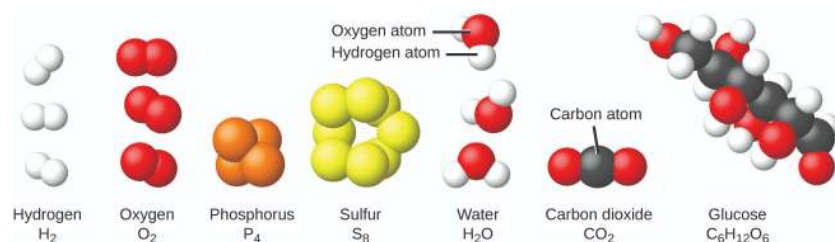


Figure 2.1.6: The elements hydrogen, oxygen, phosphorus, and sulfur form molecules consisting of two or more atoms of the same element. The compounds water, carbon dioxide, and glucose consist of combinations of atoms of different elements.

The hydrogen molecule, H_2 , is shown as two small, white balls bonded together. The oxygen molecule O_2 , is shown as two red balls bonded together. The phosphorous molecule, P_4 , is shown as four orange balls bonded tightly together. The sulfur molecule, S_8 , is shown as 8 yellow balls linked together. Water molecules, H_2O , consist of one red oxygen atom bonded to two smaller white hydrogen atoms. The hydrogen atoms are at an angle on the oxygen molecule. Carbon dioxide, CO_2 , consists of one carbon atom and two oxygen atoms. One oxygen atom is bonded to the carbon's right side and the other oxygen is bonded to the carbon's left side. Glucose, $\text{C}_6\text{H}_{12}\text{O}_6$, contains a chain of carbon atoms that have attached oxygen or hydrogen atoms.

Classifying Matter

We can classify matter into several categories. Two broad categories are mixtures and pure substances. A pure substance has a constant composition. All specimens of a pure substance have exactly the same makeup and properties. Any sample of sucrose (table sugar) consists of 42.1% carbon, 6.5% hydrogen, and 51.4% oxygen by mass. Any sample of sucrose also has the same physical properties, such as melting point, color, and sweetness, regardless of the source from which it is isolated.

We can divide pure substances into two classes: elements and compounds. Pure substances that cannot be broken down into simpler substances by chemical changes are called elements. Iron, silver, gold, aluminum, sulfur, oxygen, and copper are familiar examples of the more than 100 known elements, of which about 90 occur naturally on the earth, and two dozen or so have been created in laboratories.

Pure substances that can be broken down by chemical changes are called compounds. This breakdown may produce either elements or other compounds, or both. Mercury(II) oxide, an orange, crystalline solid, can be broken down by heat into the elements mercury and oxygen (Figure 2.1.7). When heated in the absence of air, the compound sucrose is broken down into the element carbon and the compound water. (The initial stage of this process, when the sugar is turning brown, is known as caramelization—this is what imparts the characteristic sweet and nutty flavor to caramel apples, caramelized onions, and caramel). Silver(I) chloride is a white solid that can be broken down into its elements, silver and chlorine, by absorption of light. This property is the basis for the use of this compound in photographic films and photochromic eyeglasses (those with lenses that darken when exposed to light).

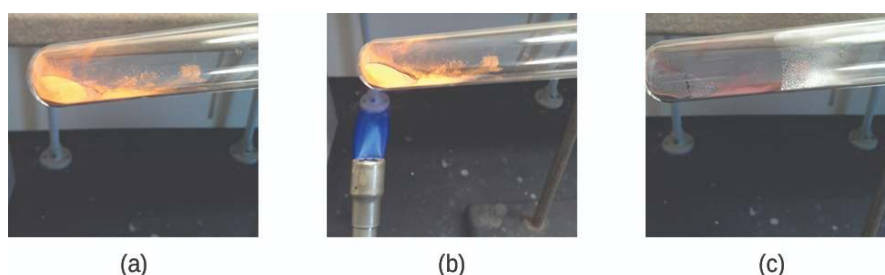


Figure 2.1.7: (a)The compound mercury(II) oxide, (b)when heated, (c) decomposes into silvery droplets of liquid mercury and invisible oxygen gas. (credit: modification of work by Paul Flowers)

This figure shows a series of three photos labeled a, b, and c. Photo a shows the bottom of a test tube that is filled with an orange-red substance. A slight amount of a silver substance is also visible. Photo b shows the substance in the test tube being heated over a flame. Photo c shows a test tube that is not longer being heated. The orange-red substance is almost completely gone, and small, silver droplets of a substance are left.

The properties of combined elements are different from those in the free, or uncombined, state. For example, white crystalline sugar (sucrose) is a compound resulting from the chemical combination of the element carbon, which is a black solid in one of its uncombined forms, and the two elements hydrogen and oxygen, which are colorless gases when uncombined. Free sodium, an element that is a soft, shiny, metallic solid, and free chlorine, an element that is a yellow-green gas, combine to form sodium chloride (table salt), a compound that is a white, crystalline solid.

A mixture is composed of two or more types of matter that can be present in varying amounts and can be separated by physical changes, such as evaporation (you will learn more about this later). A mixture with a composition that varies from point to point is called a heterogeneous mixture. Italian dressing is an example of a heterogeneous mixture (Figure 2.1.1a). Its composition can vary because we can make it from varying amounts of oil, vinegar, and herbs. It is not the same from point to point throughout the mixture—one drop may be mostly vinegar, whereas a different drop may be mostly oil or herbs because the oil and vinegar separate and the herbs settle. Other examples of heterogeneous mixtures are chocolate chip cookies (we can see the separate bits of chocolate, nuts, and cookie dough) and granite (we can see the quartz, mica, feldspar, and more).

A homogeneous mixture, also called a solution, exhibits a uniform composition and appears visually the same throughout. An example of a solution is a sports drink, consisting of water, sugar, coloring, flavoring, and electrolytes mixed together uniformly (Figure 2.1.1b). Each drop of a sports drink tastes the same because each drop contains the same amounts of water, sugar, and other components. Note that the composition of a sports drink can vary—it could be made with somewhat more or less sugar, flavoring, or other components, and still be a sports drink. Other examples of homogeneous mixtures include air, maple syrup, gasoline, and a solution of salt in water.



Figure 2.1.7: (a) Oil and vinegar salad dressing is a heterogeneous mixture because its composition is not uniform throughout. (b) A commercial sports drink is a homogeneous mixture because its composition is uniform throughout. (credit a “left”: modification of work by John Mayer; credit a “right”: modification of work by Umberto Salvagnin; credit b “left”: modification of work by Jeff Bedford)

Diagram A shows a glass containing a red liquid with a layer of yellow oil floating on the surface of the red liquid. A zoom in box is magnifying a portion of the red liquid that contains some of the yellow oil. The zoomed in image shows that oil is forming round droplets within the red liquid. Diagram B shows a photo of Gatorade G 2. A zoom in box is magnifying a portion of the Gatorade, which is uniformly red.

Although there are just over 100 elements, tens of millions of chemical compounds result from different combinations of these elements. Each compound has a specific composition and possesses definite chemical and physical properties by which we can distinguish it from all other compounds. And, of course, there are innumerable ways to combine elements and compounds to form different mixtures. A summary of how to distinguish between the various major classifications of matter is shown in (Figure 1.2.8).

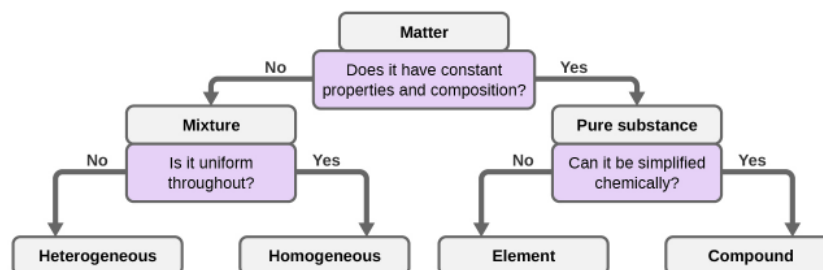


Figure 2.1.8: Depending on its properties, a given substance can be classified as a homogeneous mixture, a heterogeneous mixture, a compound, or an element.

This flow chart begins with matter at the top and the question: does the matter have constant properties and composition? If no, then it is a mixture. This leads to the next question: is it uniform throughout? If no, it is heterogeneous. If yes, it is homogenous. If the matter does have constant properties and composition, it is a pure substance. This leads to the next question: can it be simplified chemically? If no, it is an element. If yes, then it is a compound.

Eleven elements make up about 99% of the earth’s crust and atmosphere (Table 2.1.1). Oxygen constitutes nearly one-half and silicon about one-quarter of the total quantity of these elements. A majority of elements on earth are found in chemical combinations with other elements; about one-quarter of the elements are also found in the free state.

Table 2.1.1: Elemental Composition of Earth

Element	Symbol	Percent Mass	Element	Symbol	Percent Mass
oxygen	O	49.20	chlorine	Cl	0.19
silicon	Si	25.67	phosphorus	P	0.11
aluminum	Al	7.50	manganese	Mn	0.09
iron	Fe	4.71	carbon	C	0.08
calcium	Ca	3.39	sulfur	S	0.06
sodium	Na	2.63	barium	Ba	0.04
potassium	K	2.40	nitrogen	N	0.03
magnesium	Mg	1.93	fluorine	F	0.03
hydrogen	H	0.87	strontium	Sr	0.02
titanium	Ti	0.58	all others	-	0.47

Decomposition of Water / Production of Hydrogen

Water consists of the elements hydrogen and oxygen combined in a 2 to 1 ratio. Water can be broken down into hydrogen and oxygen gases by the addition of energy. One way to do this is with a battery or power supply, as shown in (Figure 2.1.9).

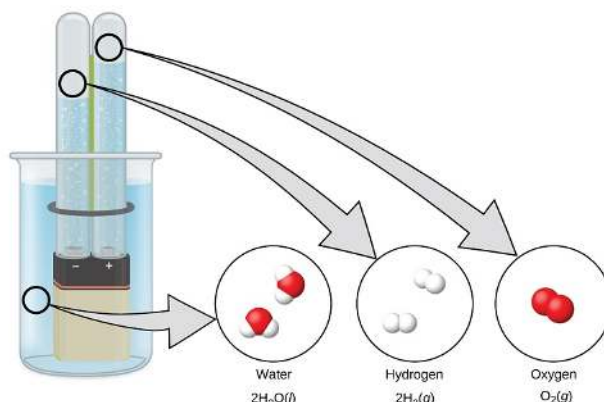


Figure 2.1.9: The decomposition of water is shown at the macroscopic, microscopic, and symbolic levels. The battery provides an electric current (microscopic) that decomposes water. At the macroscopic level, the liquid separates into the gases hydrogen (on the left) and oxygen (on the right). Symbolically, this change is presented by showing how liquid H_2O separates into H_2 and O_2 gases.

A rectangular battery is immersed in a beaker filled with liquid. Each of the battery terminals are covered by an overturned test tube. The test tubes each contain a bubbling liquid. Zoom in areas indicate that the liquid in the beaker is water, 2 H subscript 2 O liquid. The bubbles in the test tube over the negative terminal are hydrogen gas, 2 H subscript 2 gas. The bubbles in the test tube over the positive terminal are oxygen gas, O subscript 2 gas.

The breakdown of water involves a rearrangement of the atoms in water molecules into different molecules, each composed of two hydrogen atoms and two oxygen atoms, respectively. Two water molecules form one oxygen molecule and two hydrogen molecules. The representation for what occurs, $2\text{H}_2\text{O}(l) \rightarrow 2\text{H}_2(g) + \text{O}_2(g)$, will be explored in more depth in later chapters.

The two gases produced have distinctly different properties. Oxygen is not flammable but is required for combustion of a fuel, and hydrogen is highly flammable and a potent energy source. How might this knowledge be applied in our world? One application involves research into more fuel-efficient transportation. Fuel-cell vehicles (FCV) run on hydrogen instead of gasoline (Figure 2.1.10). They are more efficient than vehicles with internal combustion engines, are nonpolluting, and reduce greenhouse gas emissions, making us less dependent on fossil fuels. FCVs are not yet economically viable, however, and current hydrogen production depends on natural gas. If we can develop a process to economically decompose water, or produce hydrogen in another environmentally sound way, FCVs may be the way of the future.

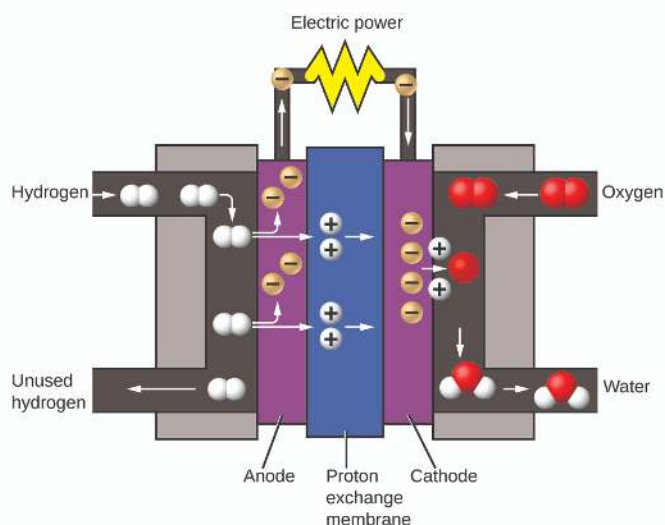


Figure 2.1.10: A fuel cell generates electrical energy from hydrogen and oxygen via an electrochemical process and produces only water as the waste product.

The fuel cell consists of a proton exchange membrane sandwiched between an anode and a cathode. Hydrogen gas enters the battery near the anode. Oxygen gas enters the battery near the cathode. The entering hydrogen gas is broken up into single white spheres that each have a positive charge. These are protons. The protons repel negatively-charged electrons within the anode. These electrons travel through a circuit, providing electricity to anything attached to the battery. The protons continue through the proton exchange membrane and through the cathode to reach the oxygen gas molecules at the opposite end of the battery. There, the oxygen atoms split up into single red spheres. Each oxygen atom takes on two of the incoming protons to form a water molecule.

Chemistry of Cell Phones

Imagine how different your life would be without cell phones (Figure 2.1.11) and other smart devices. Cell phones are made from numerous chemical substances, which are extracted, refined, purified, and assembled using an extensive and in-depth understanding of chemical principles. About 30% of the elements that are found in nature are found within a typical smart phone. The case/body/frame consists of a combination of sturdy, durable polymers comprised primarily of carbon, hydrogen, oxygen, and nitrogen [acrylonitrile butadiene styrene (ABS) and polycarbonate thermoplastics], and light, strong, structural metals, such as aluminum, magnesium, and iron. The display screen is made from a specially toughened glass (silica glass strengthened by the addition of aluminum, sodium, and potassium) and coated with a material to make it conductive (such as indium tin oxide). The circuit board uses a semiconductor material (usually silicon); commonly used metals like copper, tin, silver, and gold; and more unfamiliar elements such as yttrium, praseodymium, and gadolinium. The battery relies upon lithium ions and a variety of other materials, including iron, cobalt, copper, polyethylene oxide, and polyacrylonitrile.



Figure 2.1.11: Almost one-third of naturally occurring elements are used to make a modern cell phone. (credit: modification of work by John Taylor)

A cell phone is labeled to show what its components are made of. The case components are made of polymers such as A B S and/or metals such as aluminum, iron, and magnesium. The processor components are made of silicon, common metals such as copper, tin and gold, and uncommon elements such as yttrium and gadolinium. The screen components are made of silicon oxide, also known as glass. The glass is strengthened by the addition of aluminum, sodium, and potassium. The battery components contain lithium combined with other metals such as cobalt, iron, and copper.

Summary

Matter is anything that occupies space and has mass. The basic building block of matter is the atom, the smallest unit of an element that can enter into combinations with atoms of the same or other elements. In many substances, atoms are combined into molecules. On earth, matter commonly exists in three states: solids, of fixed shape and volume; liquids, of variable shape but fixed volume; and gases, of variable shape and volume. Under high-temperature conditions, matter also can exist as a plasma. Most matter is a mixture: It is composed of two or more types of matter that can be present in varying amounts and can be separated by physical means. Heterogeneous mixtures vary in composition from point to point; homogeneous mixtures have the same composition from point to point. Pure substances consist of only one type of matter. A pure substance can be an element, which consists of only one type of atom and cannot be broken down by a chemical change, or a compound, which consists of two or more types of atoms.

Glossary

atom

smallest particle of an element that can enter into a chemical combination

compound

pure substance that can be decomposed into two or more elements

element

substance that is composed of a single type of atom; a substance that cannot be decomposed by a chemical change

gas

state in which matter has neither definite volume nor shape

heterogeneous mixture

combination of substances with a composition that varies from point to point

homogeneous mixture

(also, solution) combination of substances with a composition that is uniform throughout

liquid

state of matter that has a definite volume but indefinite shape

law of conservation of matter

when matter converts from one type to another or changes form, there is no detectable change in the total amount of matter present

mass

fundamental property indicating amount of matter

matter

anything that occupies space and has mass

mixture

matter that can be separated into its components by physical means

molecule

bonded collection of two or more atoms of the same or different elements

plasma

gaseous state of matter containing a large number of electrically charged atoms and/or molecules

pure substance

homogeneous substance that has a constant composition

solid

state of matter that is rigid, has a definite shape, and has a fairly constant volume

weight

force that gravity exerts on an object

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2.2: Atomic Structure and Symbolism

Learning Objectives

- Write and interpret symbols that depict the atomic number, mass number, and charge of an atom or ion
- Define the atomic mass unit and average atomic mass
- Calculate average atomic mass and isotopic abundance

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).

The diagram on the left shows a picture of an atom with a nucleus. The central figure shows a photograph of an American football stadium. The figure on the right shows a photograph of a handful of blueberries.

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: $1 \text{ amu} = 1.6605 \times 10^{-24}$ 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 $e = 1.602 \times 10^{-19}$ 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: $A - Z = \text{number of neutrons}$.

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

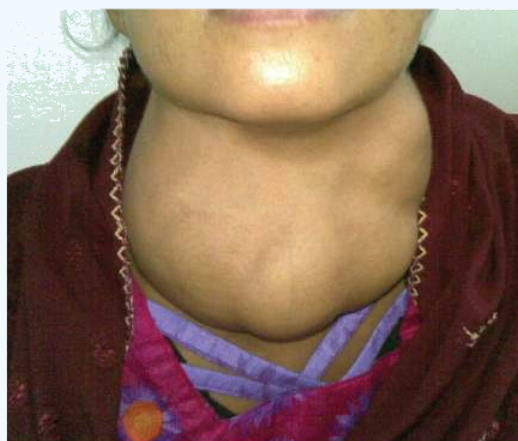
Atoms are electrically neutral if they contain the same number of positively charged protons and negatively charged electrons. When the numbers of these subatomic particles are *not* equal, the atom is electrically charged and is called an ion. The charge of an atom is defined as follows:

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

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).



(a)



(b)

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)

Figure A shows a photo of a person who has a very swollen thyroid in his or her neck. Figure B shows a photo of a canister of Morton iodized salt.

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. from Wikipedia (user: Materialschemist).

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 <i>ferrum</i>)
bromine	Br	lead	Pb (from <i>plumbum</i>)
calcium	Ca	magnesium	Mg
carbon	C	mercury	Hg (from <i>hydrargyrum</i>)
chlorine	Cl	nitrogen	N
chromium	Cr	oxygen	O
cobalt	Co	potassium	K (from <i>kalium</i>)
copper	Cu (from <i>cuprum</i>)	silicon	Si
fluorine	F	silver	Ag (from <i>argentum</i>)
gold	Au (from <i>aurum</i>)	sodium	Na (from <i>natrium</i>)
helium	He	sulfur	S
hydrogen	H	tin	Sn (from <i>stannum</i>)
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.

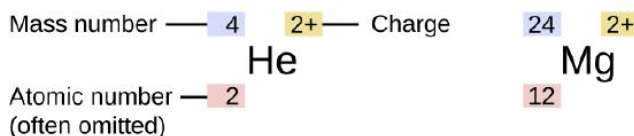


Figure 2.2.4: The symbol for an atom indicates the element via its usual two-letter symbol, the mass number as a left superscript, the atomic number as a left subscript (sometimes omitted), and the charge as a right superscript.

This diagram shows the symbol for helium, "He." The number to the upper left of the symbol is the mass number, which is 4. The number to the upper right of the symbol is the charge which is positive 2. The number to the lower left of the symbol is the atomic number, which is 2. This number is often omitted. Also shown is "Mg" which stands for magnesium. It has a mass number of 24, a charge of positive 2, and an atomic number of 12.

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 ^2H , is also called deuterium and sometimes symbolized D. Hydrogen-3, symbolized ^3H , 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	${}^1_1\text{H}$ (protium)	1	1	0	1.0078	99.989
	${}^2_1\text{H}$ (deuterium)	1	1	1	2.0141	0.0115
	${}^3_1\text{H}$ (tritium)	1	1	2	3.01605	— (trace)
helium	${}^3_2\text{He}$	2	2	1	3.01603	0.00013
	${}^4_2\text{He}$	2	2	2	4.0026	100
lithium	${}^6_3\text{Li}$	3	3	3	6.0151	7.59
	${}^7_3\text{Li}$	3	3	4	7.0160	92.41
beryllium	${}^9_4\text{Be}$	4	4	5	9.0122	100
boron	${}^{10}_5\text{B}$	5	5	5	10.0129	19.9
	${}^{11}_5\text{B}$	5	5	6	11.0093	80.1
carbon	${}^{12}_6\text{C}$	6	6	6	12.0000	98.89
	${}^{13}_6\text{C}$	6	6	7	13.0034	1.11
	${}^{14}_6\text{C}$	6	6	8	14.0032	— (trace)
nitrogen	${}^{14}_7\text{N}$	7	7	7	14.0031	99.63
	${}^{15}_7\text{N}$	7	7	8	15.0001	0.37
oxygen	${}^{16}_8\text{O}$	8	8	8	15.9949	99.757
	${}^{17}_8\text{O}$	8	8	9	16.9991	0.038
	${}^{18}_8\text{O}$	8	8	10	17.9992	0.205
fluorine	${}^{19}_9\text{F}$	9	9	10	18.9984	100
neon	${}^{20}_{10}\text{Ne}$	10	10	10	19.9924	90.48
	${}^{21}_{10}\text{Ne}$	10	10	11	20.9938	0.27
	${}^{22}_{10}\text{Ne}$	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.

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

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.

✓ Example 2.2.2: Calculation of Average Atomic Mass

A meteorite found in central Indiana contains traces of the noble gas neon picked up from the solar wind during the meteorite's trip through the solar system. Analysis of a sample of the gas showed that it consisted of 91.84% ^{20}Ne (mass 19.9924 amu), 0.47% ^{21}Ne (mass 20.9940 amu), and 7.69% ^{22}Ne (mass 21.9914 amu). What is the average mass of the neon in the solar wind?

Solution

$$\begin{aligned}\text{average mass} &= (0.9184 \times 19.9924 \text{ amu}) + (0.0047 \times 20.9940 \text{ amu}) + (0.0769 \times 21.9914 \text{ amu}) \\ &= (18.36 + 0.099 + 1.69) \text{ amu} \\ &= 20.15 \text{ amu}\end{aligned}$$

The average mass of a neon atom in the solar wind is 20.15 amu. (The average mass of a terrestrial neon atom is 20.1796 amu. This result demonstrates that we may find slight differences in the natural abundance of isotopes, depending on their origin.)

? Exercise 2.2.2

A sample of magnesium is found to contain 78.70% of ^{24}Mg atoms (mass 23.98 amu), 10.13% of ^{25}Mg atoms (mass 24.99 amu), and 11.17% of ^{26}Mg atoms (mass 25.98 amu). Calculate the average mass of a Mg atom.

Answer

24.31 amu

We can also do variations of this type of calculation, as shown in the next example.

✓ Example 2.2.3: Calculation of Percent Abundance

Naturally occurring chlorine consists of ^{35}Cl (mass 34.96885 amu) and ^{37}Cl (mass 36.96590 amu), with an average mass of 35.453 amu. What is the percent composition of Cl in terms of these two isotopes?

Solution

The average mass of chlorine is the fraction that is ^{35}Cl times the mass of ^{35}Cl plus the fraction that is ^{37}Cl times the mass of ^{37}Cl .

$$\text{average mass} = (\text{fraction of } ^{35}\text{Cl} \times \text{mass of } ^{35}\text{Cl}) + (\text{fraction of } ^{37}\text{Cl} \times \text{mass of } ^{37}\text{Cl})$$

If we let x represent the fraction that is ^{35}Cl , then the fraction that is ^{37}Cl is represented by $1.00 - x$.

(The fraction that is ^{35}Cl + the fraction that is ^{37}Cl must add up to 1, so the fraction of ^{37}Cl must equal $1.00 - \text{the fraction of } ^{35}\text{Cl}$.)

Substituting this into the average mass equation, we have:

$$\begin{aligned}35.453 \text{ amu} &= (x \times 34.96885 \text{ amu}) + [(1.00 - x) \times 36.96590 \text{ amu}] \\ 35.453 &= 34.96885x + 36.96590 - 36.96590x \\ 1.99705x &= 1.513 \\ x &= \frac{1.513}{1.99705} = 0.7576\end{aligned}$$

So solving yields: $x = 0.7576$, which means that $1.00 - 0.7576 = 0.2424$. Therefore, chlorine consists of 75.76% ^{35}Cl and 24.24% ^{37}Cl .

? Exercise 2.2.3

Naturally occurring copper consists of ^{63}Cu (mass 62.9296 amu) and ^{65}Cu (mass 64.9278 amu), with an average mass of 63.546 amu. What is the percent composition of Cu in terms of these two isotopes?

Answer

69.15% Cu-63 and 30.85% Cu-65

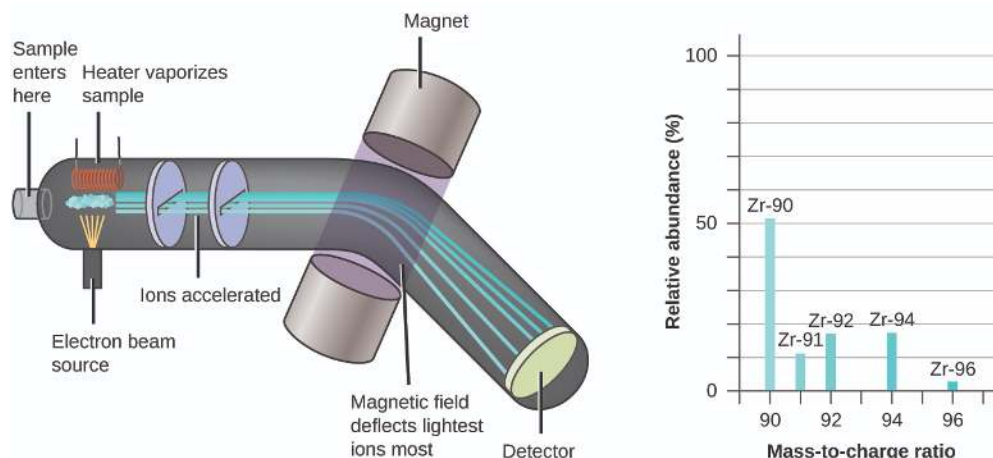


Figure 2.2.5: Analysis of zirconium in a mass spectrometer produces a mass spectrum with peaks showing the different isotopes of Zr.

The left diagram shows how a mass spectrometer works. The graph to the right of the spectrometer shows a mass spectrum of zirconium. The relative abundance, as a percentage from 0 to 100, is graphed on the y axis, and the mass to charge ratio is graphed on the x axis. The sample contains five different isomers of zirconium.

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 than 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.



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 $\frac{1}{12}$ 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 $e = 1.602 \times 10^{-19} \text{ C}$

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

- 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](https://creativecommons.org/licenses/by/4.0/) license. Download for free at <http://cnx.org/contents/85abf193-2bd...a7ac8df6@9.110>).

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SECTION OVERVIEW

2.3: Problems

Topic hierarchy

2.3.1: Advanced problems

2.3.1.1: All about phosphorous

2.3.1.2: Strontium isotopes treat bone cancer pain

2.3.1.2.1: Strontium treats bone cancer pain- Solutions

2.3.2: Mechanical problems

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2.3.1: Advanced problems

Advanced Problems require application of the knowledge you gained in the Mechanical Problems for this topic to a previously unseen situation. These problems test how deeply you understand the material and provide the challenge you need to grow intellectually. While doing these problems, push yourself. Try completing the problems without looking at the solutions until your next study session. Remember, your brain will keep working while you take a hard-earned break! When you come to an Advanced Problem that you are stuck on, use the solutions—which model how to think about the problems—to try to explain how to do the problem and identify why/how you were stuck. These are great problems to discuss with your classmates and Q&SC tutors. Explaining how to do these complicated problems out loud will really help you assess what you do and don't understand.

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2.3.1.1: All about phosphorous

THE CHEMISTRY OF MATCHES

How Matches Work

The composition of matches varies depending on type, but safety matches are the most commonly used. They contain a strong oxidizing agent in the match head, and red phosphorus in the striking surface. Striking the match causes small amounts of the oxidizer and phosphorus to combine, and the heat generated by the friction of the striking causes them to ignite.

Prior to the 1900s, white phosphorus was the active ingredient in most matches, but this could cause phossy jaw and bone disorders, and was also toxic, so was replaced.

The Match

POTASSIUM CHLORATE
Main ingredient (40-50%) in heads of safety matches.

PHOSPHORUS SESQUI SULFIDE
Compounds in the heads of "strike anywhere" matches.

ANTIMONY (III) SULFIDE
Added to some matches to make them burn more vigorously.

Additionally, the matches contain ammonium phosphates to prevent afterglow, glue to bind materials, and paraffin wax to ease of burning.

The Match Box

The striking surface of safety match boxes contains red phosphorus and an abrasive substance. When struck, a small amount of white phosphorus is produced, which ignites.



Red Phosphorus (above); White Phosphorus (below).



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- Phosphorous (P) is interesting! Here are some questions related to phosphorous in the human body, based on [the following information I found on Wikipedia](#):
 - An average adult human contains about 0.7 kg of phosphorus, about 90% in bones and teeth in the form of apatite, and the remainder in soft tissues and extracellular fluids (~1%). The phosphorus content increases from about 0.5 weight% in infancy to 0.65–1.1 weight% in adults. Average phosphorus concentration in the blood is about 0.4 g/L, about 70% of that is organic and 30% inorganic phosphates. An adult with healthy diet consumes and excretes about 1–3 grams of phosphorus per day, with consumption in the form of inorganic phosphate and phosphorus-containing biomolecules such as nucleic acids and phospholipids; and excretion almost exclusively in the form of phosphate ions.
 - How many atoms of phosphorous are in the bones and teeth of an average adult?
 - Given a typical volume of blood is 5 L, how many atoms of phosphorous are present in the blood stream in the form of inorganic phosphates?
- Phosphorous is essential for healthy body function, but too much is poisonous. "Phossy jaw" is a horrible bone necrosis in the jaw that resulted when people breathed in gaseous phosphorous. It was prevalent in matchstick factory workers in the late 1800's and early 1900's until the match making process started to use red phosphorous rather than white phosphorous (shown in the graphic above). The dangerous white phosphorous contains 4 P atoms chemically bound together. Red phosphorous contains many more P atoms in a chain and therefore is not as easily turned into breathable gas. The Occupational Safety and Health Administration (OSHA) currently sets an inhalation exposure limit for white phosphorus in the workplace during an 8-hour workday at 0.1 milligram per cubic meter of air (mg/m³). Matchstick factory workers who got phossy jaw would typically contract this illness after working ~13 hours/day, 7 days/week (the weekend was not implemented in the US until later in the 1900's!), for 5 years (say 260 weeks).
 - How many hours were workers exposed to phosphorous before getting sick?
 - If these workers breath in 35 L of air per hour and worked in a factory that followed OSHA guidelines, how many moles of phosphorous would they breath over this five year period? Note that 1 m³ = 1000 L.
 - Assuming that matchstick workers were exposed to 100x greater levels than those required by OSHA, how many more atoms of phosphorous would they breath over that 5 year period compared to workers in an OSHA-approved factory?

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2.3.1.2: Strontium isotopes treat bone cancer pain

The element strontium (Sr) is right underneath calcium (Ca) on the periodic table, which means that they tend to have similar chemical behavior and Sr can easily bind to bones in the same places Ca would. This can be useful—Sr is used in Sensodyne toothpaste to minimize tooth sensitivity and ^{89}Sr (isotopic mass = 88.907 g/mol) is used to treat pain in bone cancer patients. The radioactive ^{90}Sr (isotopic mass = 89.908 g/mol) released by the Chernobyl disaster, however, is extremely dangerous for this same reason.

1. Use the following information about the 3 naturally occurring isotopes of Sr to calculate its average atomic mass. Does your calculation match that on the periodic table? Why are we calculating the average atomic mass using only these three isotopes when we mentioned above that ^{89}Sr and ^{90}Sr exist?

Isotope	Isotopic abundance (%)	Isotopic mass (g/mol)
^{86}Sr	?	85.90926
^{87}Sr	7.00%	86.90888
^{88}Sr	82.58%	87.90561

2. I would like to know how many moles of ^{89}Sr are administered to a cancer patient who weighs 16 kg. A radiation dose of 1.5 MBq/kg of body mass using ^{89}Sr will decrease pain [in 80% of bone cancer patients without significant toxicity](#). Note that Bq are a unit of radiation and MBq is “mega” Bq. ^{89}Sr is delivered as a drug called Metastron™ that delivers 37 MBq/mL. Each mL of Metastron contains 15 mg of the drug, which is 55% ^{89}Sr by mass.

Solutions

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2.3.1.2.1: Strontium treats bone cancer pain- Solutions

The element strontium (Sr) is right underneath calcium (Ca) on the periodic table, which means that they tend to have similar chemical behavior and Sr can easily bind to bones in the same places Ca would. This can be good—Sr is used in Sensodyne toothpaste minimize tooth sensitivity and ^{89}Sr (isotopic mass = 88.907 g/mol) is used to treat pain in bone cancer patients. The ^{90}Sr isotopes released by the Chernobyl disaster, however, are extremely dangerous for this same reason.

1. Use the following information about the 3 naturally occurring isotopes of Sr to calculate its average atomic mass. Does your calculation match that on the periodic table?

Isotope	Isotopic abundance (%)	Isotopic mass (g/mol)
^{86}Sr	?	85.90926
^{87}Sr	7.00%	86.90888
^{88}Sr	82.58%	87.90561

I have the isotopic abundance for 2 of the 3 naturally occurring isotopes, so I can find the 3rd given that the percentages must add up to 100%.

Isotopic abundance of ^{86}Sr is $100.00 - 7.00 - 82.58\% = 10.44\%$. Wait, but you said that ^{89}Sr and ^{90}Sr exist, too? Why don't I have to include them? The question asked you to focus on the 3 *naturally occurring isotopes* of Sr. ^{89}Sr and ^{90}Sr are highly radioactive elements that are man-made. They occur in such small quantities they don't change the average atomic mass of Sr.

Now that I know the fractional isotopic abundances and isotopic masses for each naturally occurring isotope, I can find the average atomic mass using the following equation:

NEEDS equation

$$\text{Average} = 0.8256 \times 87.90561 \text{ g/mol}$$

$$0.0700 \times 86.90888 \text{ g/mol}$$

$$+ 0.1044 \times 85.90926 \text{ g/mol}$$

$$87.6 \text{ g/mol}$$

This is the same value as the periodic table given that the 3 significant figures from $0.0700 \times 86.90888 \text{ g/mol}$ limit the outcome to 3 sig figs.

2. I would like to know how many moles of ^{89}Sr are administered to a cancer patient who weighs 16 kg. A radiation dose of 1.5 MBq/kg of body mass using ^{89}Sr will decrease pain in 80% of bone cancer patients without significant toxicity. Note that Bq are a unit of radiation and MBq is “mega” Bq. ^{89}Sr is delivered as a drug called MetastronTM that delivers 37 MBq/mL. Each mL of Metastron contains 15 mg of the drug, which is 55% ^{89}Sr by mass.

Soooo many conversions to do....

What I know:

Patient mass = 16 kg

Dose = 1.5 MBq/kg

Dose delivered by Metastron = 37 MBq/mL

Metastron contains 15 mg of drug/mL

Metastron is 55% ^{89}Sr by mass

isotopic mass of ^{89}Sr = 88.907 g/mol

Thought process

I am going to do a problem-solving bottom-up strategy, starting with recognizing that the answer I need is in terms of moles of ^{89}Sr . I see a whole bunch of information above, but the two things involving ^{89}Sr are the isotopic mass and the fact that Metastron is 55% ^{89}Sr by mass. So, if I can figure out the mass of Metastron delivered, I will know the mass of ^{89}Sr and I can convert that to moles. I see that there are 15 mg of Metastron/mL, so if I can figure out the volume delivered I can get the mass of Metastron. The dose of the medicine is 37 MBq/mL, so if I get the total radiation in MBq needed, I can get the volume. And lastly, I have the dose required (1.5 MBq/kg), so I can use this plus the mass to get the total radiation. Here is the process:

Step 1: Use the patient mass to get how much radiation we need.

$$16 \text{ kg} \times 1.5 \text{ MBq/kg} = 24 \text{ MBq}$$

Step 2: Use the total radiation needed to find out what volume of the drug we need.

$$24 \text{ MBq} (1 \text{ mL}/37 \text{ MBq}) = 0.65 \text{ mL}$$

Step 3: Use the volume of the drug to find out the mass needed.

$$0.65 \text{ mL} \times 15 \text{ mg/mL} = 975 \text{ mg}$$

Step 4: Use the mass of Metastron to get the mass of ^{89}Sr

$$0.975 \text{ g Metastron} \times 0.55 \text{ g } ^{89}\text{Sr/g Metastron} = 0.536 \text{ g } ^{89}\text{Sr}$$

Step 5: Convert the mass of ^{89}Sr to moles of ^{89}Sr

$$0.536 \text{ g } ^{89}\text{Sr} \times 1 \text{ mol}/88.907 \text{ g } ^{89}\text{Sr} = 6.0 \times 10^{-3} \text{ mol } ^{89}\text{Sr}$$

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CHAPTER OVERVIEW

3: Electronic structure of atoms- Electron jumping makes beautiful colors!

Topic hierarchy

[3.1: Electromagnetic Energy](#)

[3.2: The Bohr Model](#)

[3.3: Electronic Structure of Atoms \(Electron Configurations\)](#)

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3.1: Electromagnetic Energy

Learning Objectives

- Explain the basic behavior of waves, including traveling waves and standing waves
- Describe the wave nature of light
- Use appropriate equations to calculate related light-wave properties such as period, frequency, wavelength, and energy
- Distinguish between line and continuous emission spectra
- Describe the particle nature of light

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 3.1.1, 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, ($1 \text{ MHz} = 1 \times 10^6$ Hz) and gigahertz ($1 \text{ GHz} = 1 \times 10^9$ 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.

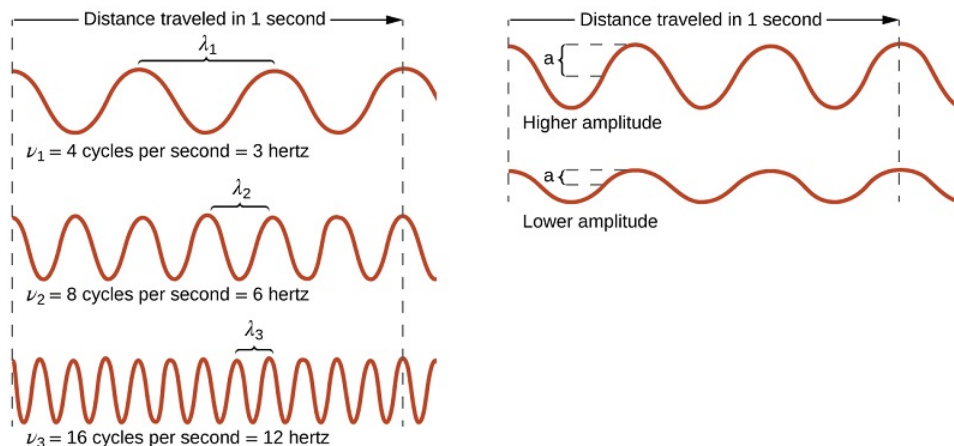


Figure 3.1.1: One-dimensional sinusoidal waves show the relationship among wavelength, frequency, and speed. The wave with the shortest wavelength has the highest frequency. Amplitude is one-half the height of the wave from peak to trough. (CC by 4.0; OpenStax)

This figure includes 5 one-dimensional sinusoidal waves in two columns. The column on the left includes three waves, and the column on the right includes two waves. In each column, dashed vertical line segments extend down the left and right sides of the column. A right pointing arrow extends from the left dashed line to the right dashed line in both columns and is labeled, “Distance traveled in 1 second.” The waves all begin on the left side at a crest. The wave at the upper left shows 3 peaks to the right of the starting point. A bracket labeled, “lambda subscript 1,” extends upward from the second and third peaks. Beneath this wave is the label, “nu subscript 1 equals 4 cycles per second equals 3 hertz.” The wave below has six peaks to the right of the starting point with a bracket similarly connecting the third and fourth peaks which is labeled, “lambda subscript 2.” Beneath this wave is the label, “nu subscript 2 equals 8 cycles per second equals 6 hertz.” The third wave in the column has twelve peaks to the right of the starting point with a bracket similarly connecting the seventh and eighth peaks which is labeled, “lambda subscript 3.” Beneath this wave is the label, “nu subscript 3 equals 12 cycles per second equals 12 hertz.” All waves in this column appear to have the same vertical distance from peak to trough. In the second column, the two waves are similarly shown, but lack the lambda labels. The top wave in this column has a greater vertical distance between the peaks and troughs and is labeled, “Higher amplitude.” The wave beneath it has a lesser distance between the peaks and troughs and is labeled, “Lower amplitude.”

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:

$$c = 2.998 \times 10^8 \text{ ms}^{-1} = \lambda\nu \quad (3.1.1)$$

Wavelength and frequency are inversely proportional: As the wavelength increases, the frequency decreases. The inverse proportionality is illustrated in Figure 3.1.2. 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).

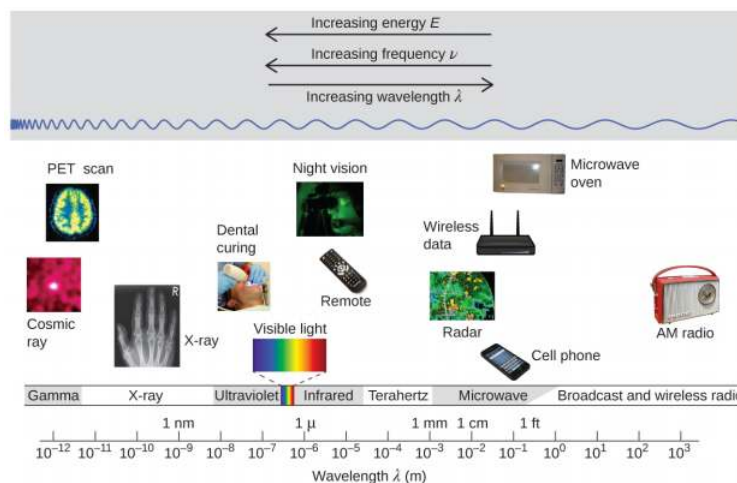


Figure 3.1.2: Portions of the electromagnetic spectrum are shown in order of decreasing frequency and increasing wavelength. Examples of some applications for various wavelengths include positron emission tomography (PET) scans, X-ray imaging, remote controls, wireless Internet, cellular telephones, 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 3.1.1: Determining the Frequency and Wavelength of Radiation

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

Solution

We can rearrange the Equation 3.1.1 to solve for the frequency:

$$\nu = \frac{c}{\lambda}$$

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

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

? Exercise 3.1.1

One of the frequencies used to transmit and receive cellular telephone signals in the United States is 850 MHz. What is the wavelength in meters of these radio waves?

Answer

$$0.353 \text{ m} = 35.3 \text{ cm}$$

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 3.1.5). In FM radio, by contrast, the amplitude is constant and the instantaneous frequency varies.

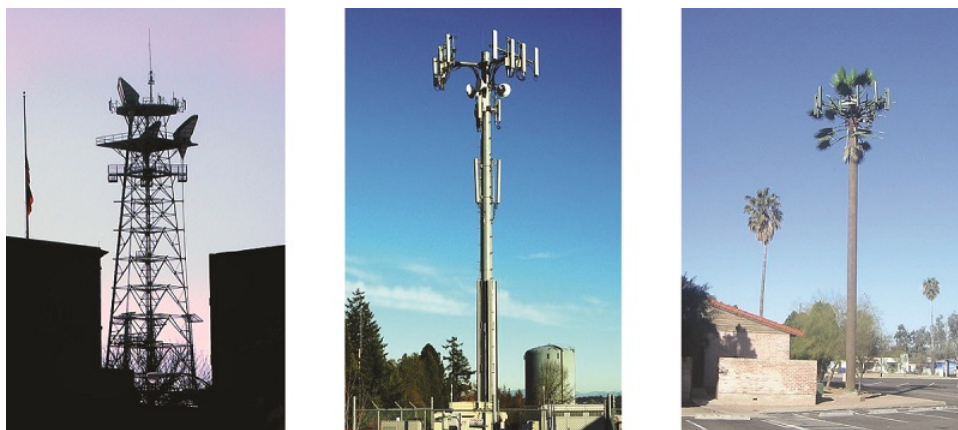


Figure 3.1.3: Radio and cell towers are typically used to transmit long-wavelength electromagnetic radiation. Increasingly, cell towers are designed to blend in with the landscape, as with the Tucson, Arizona, cell tower (right) disguised as a palm tree. (credit left: modification of work by Sir Mildred 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.

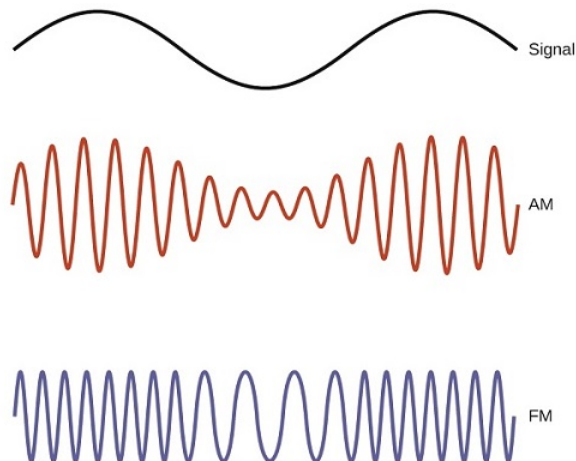


Figure 3.1.4: This schematic depicts how amplitude modulation (AM) and frequency modulation (FM) can be used to transmit a radio wave.

One particularly characteristic phenomenon of waves results when two or more waves come into contact: They interfere with each other. Figure 3.1.5 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 3.1.5 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.

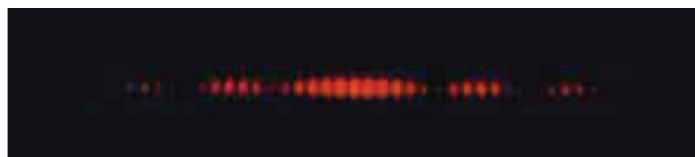


Figure 3.1.5: Interference fringe patterns are shown for light passing through two closely spaced, narrow slits. The spacing of the fringes depends on the wavelength, with the fringes being more closely spaced for the shorter-wavelength blue light. (credit: PASCO)

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 B₁₂, 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 travelling 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 3.1.6 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 3.1.6. 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.

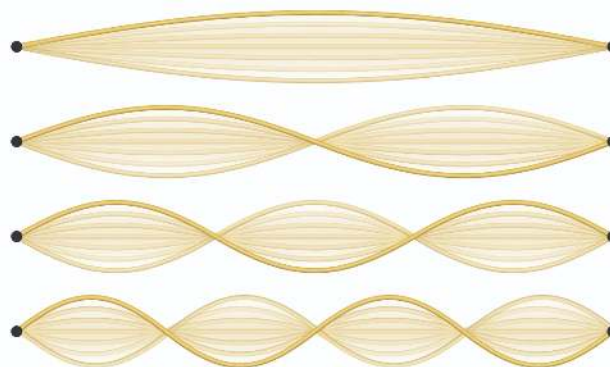


Figure 3.1.6: A vibrating string shows some one-dimensional standing waves. Since the two end points of the string are held fixed, only waves having an integer number of half-wavelengths can form. The points on the string between the end points that are not moving are called the nodes.

An example of two-dimensional standing waves is shown in Figure 3.1.7 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 3.1.7 shows two radial nodes, while the image in the lower right shows the vibrational pattern associated with three radial nodes and two angular nodes.

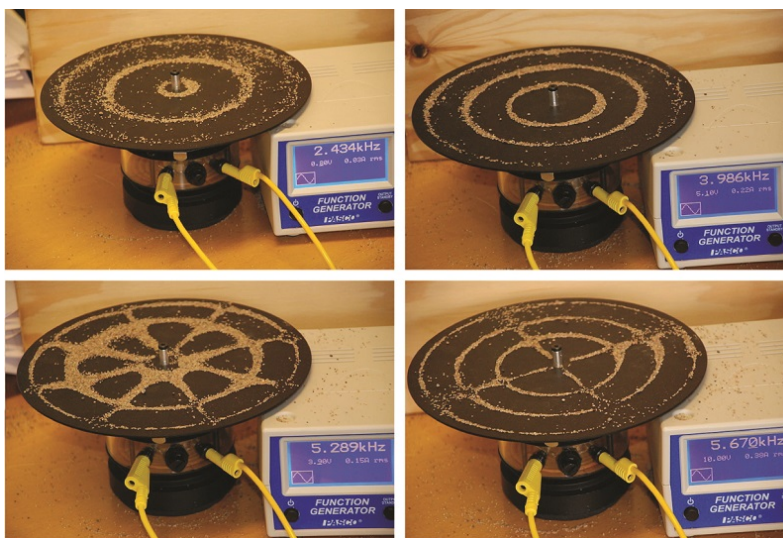


Figure 3.1.7: Two-dimensional standing waves can be visualized on a vibrating surface. The surface has been sprinkled with a powder that collects near the nodal lines. There are two types of nodes visible: radial nodes (circles) and angular nodes (radii). [For a more animated video, check this link out.](#)

Blackbody Radiation and the Ultraviolet Catastrophe

The last few decades of the nineteenth century witnessed intense research activity in commercializing newly discovered electric lighting. This required obtaining a better understanding of the distributions of light emitted from various sources being considered. Artificial lighting is usually designed to mimic natural sunlight within the limitations of the underlying technology. Such lighting consists of a range of broadly distributed frequencies that form a continuous spectrum. Figure 3.1.8 shows the wavelength

distribution for sunlight. The most intense radiation is in the visible region, with the intensity dropping off rapidly for shorter wavelength ultraviolet (UV) light, and more slowly for longer wavelength infrared (IR) light.

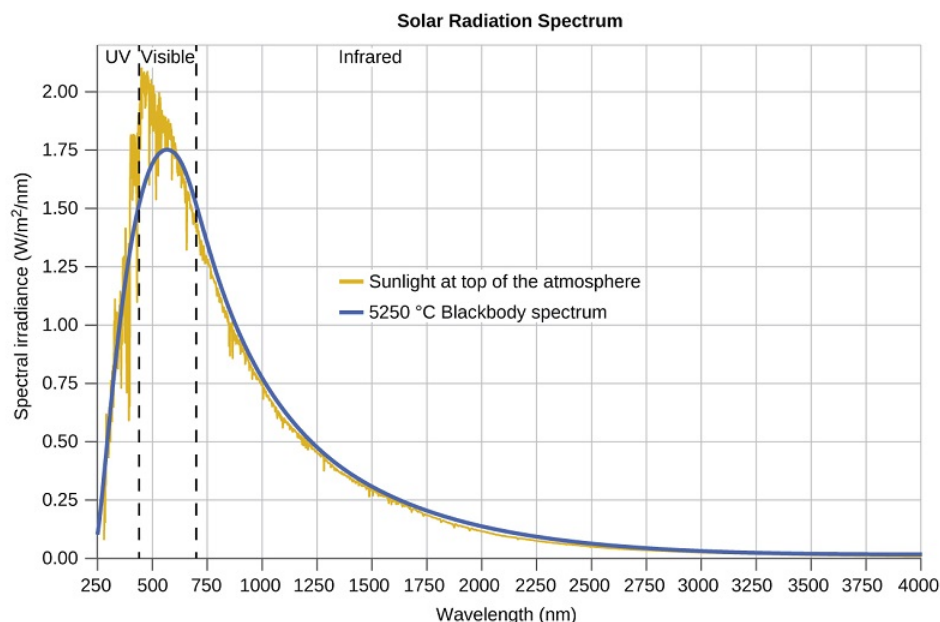


Figure 3.1.8: The spectral distribution (light intensity vs. wavelength) of sunlight reaches the Earth's atmosphere as UV light, visible light, and IR light. The unabsorbed sunlight at the top of the atmosphere has a distribution that approximately matches the theoretical distribution of a blackbody at 5250 °C, represented by the blue curve. (credit: modification of work by American Society for Testing and Materials (ASTM) Terrestrial Reference Spectra for Photovoltaic Performance Evaluation)

In Figure 3.1.8, the solar distribution is compared to a representative distribution, called a blackbody spectrum, that corresponds to a temperature of 5250 °C. The blackbody spectrum matches the solar spectrum quite well. A blackbody is a convenient, ideal emitter that approximates the behavior of many materials when heated. It is “ideal” in the same sense that an ideal gas is a convenient, simple representation of real gases that works well, provided that the pressure is not too high nor the temperature too low. A good approximation of a blackbody that can be used to observe blackbody radiation is a metal oven that can be heated to very high temperatures. The oven has a small hole allowing for the light being emitted within the oven to be observed with a spectrometer so that the wavelengths and their intensities can be measured. Figure 3.1.8 shows the resulting curves for some representative temperatures. Each distribution depends only on a single parameter: the temperature. The maxima in the blackbody curves, λ_{max} , shift to shorter wavelengths as the temperature increases, reflecting the observation that metals being heated to high temperatures begin to glow a darker red that becomes brighter as the temperature increases, eventually becoming white hot at very high temperatures as the intensities of all of the visible wavelengths become appreciable. This common observation was at the heart of the first paradox that showed the fundamental limitations of classical physics that we will examine.

Physicists derived mathematical expressions for the blackbody curves using well-accepted concepts from the theories of classical mechanics and classical electromagnetism. The theoretical expressions as functions of temperature fit the observed experimental blackbody curves well at longer wavelengths, but showed significant discrepancies at shorter wavelengths. Not only did the theoretical curves not show a peak, they absurdly showed the intensity becoming infinitely large as the wavelength became smaller, which would imply that everyday objects at room temperature should be emitting large amounts of UV light. This became known as the “ultraviolet catastrophe” because no one could find any problems with the theoretical treatment that could lead to such unrealistic short-wavelength behavior. Finally, around 1900, Max Planck derived a theoretical expression for blackbody radiation that fit the experimental observations exactly (within experimental error). Planck developed his theoretical treatment by extending the earlier work that had been based on the premise that the atoms composing the oven vibrated at increasing frequencies (or decreasing wavelengths) as the temperature increased, with these vibrations being the source of the emitted electromagnetic radiation. But where the earlier treatments had allowed the vibrating atoms to have any energy values obtained from a continuous set of energies (perfectly reasonable, according to classical physics), Planck found that by restricting the vibrational energies to discrete values for each frequency, he could derive an expression for blackbody radiation that correctly had the intensity dropping rapidly for the short wavelengths in the UV region.

$$E = nh\nu, n = 1, 2, 3, \dots$$

The quantity h is a constant now known as Planck's constant, in his honor. Although Planck was pleased he had resolved the blackbody radiation paradox, he was disturbed that to do so, he needed to assume the vibrating atoms required quantized energies, which he was unable to explain. The value of Planck's constant is very small, 6.626×10^{-34} joule seconds (J s), which helps explain why energy quantization had not been observed previously in macroscopic phenomena.

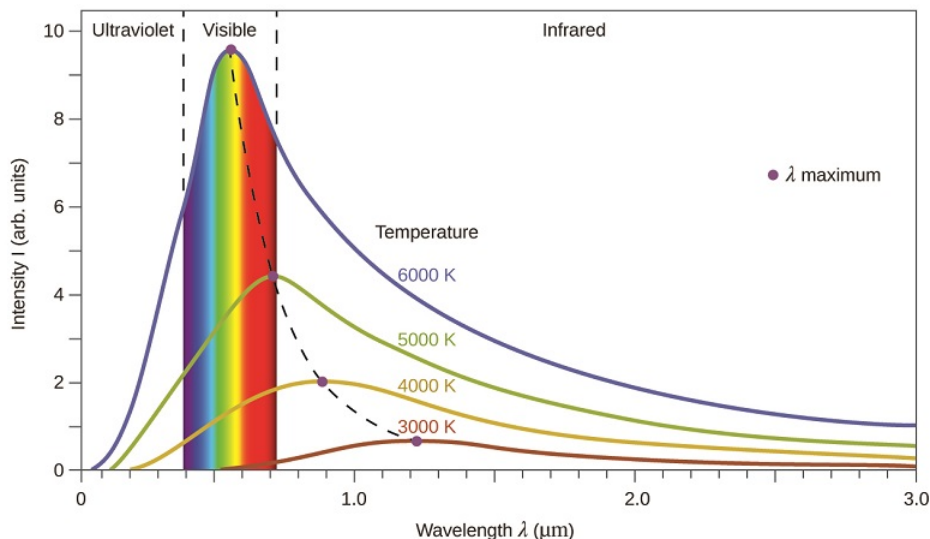


Figure 3.1.9: Blackbody spectral distribution curves are shown for some representative temperatures.

A graph is shown with a horizontal axis labeled, "Wavelength λ (micrometers)" and a vertical axis labeled, "Intensity I (a r b. units)." The horizontal axis begins at 0 and extends to 3.0 with markings provided every 0.1 micrometer. Similarly, the vertical axis begins at 0 and extends to 10 with markings every 1 unit. Two vertical dashed lines are drawn. The first appears at about 0.39 micrometers and the second at about 0.72 micrometers. To the left of the first of these lines, the label, "Ultraviolet," appears at the top of the graph. Between these lines, the label, "Visible," appears at the top of the graph. To the right of the second of these lines, the label, "Infrared," appears at the top of the graph. To the far right of the graph in open space a purple dot is placed which is labeled, " λ maximum." A "Temperature" label is located in a central region of the graph. A blue curve begins on the horizontal axis at about 0.05 micrometers. This curve increases steeply to a maximum value between the two vertical line segments of approximately 9.5 at about 0.55 micrometers. This curve decreases rapidly at first, then tapers off to reach a value of about 1.5 at the far right end of the graph. This blue curve is labeled 6000 K beneath the "Temperature" label. Curves are similarly drawn in green for 5000 K, orange for 4000 K, and red for 3000 K. As the temperature decreases, the height of the peak is lower and shifted right on the graph. The maximum value for the green curve is around 4.5 at 7.2 micrometers. This curve tapers at the right end of the graph to a value around 0.6. The maximum for the orange curve is around 2 at about 0.9 micrometers. This curve tapers at the right end of the graph to a value around 0.2. The maximum for the red curve is around 0.7 at about 1.2 micrometers. This curve tapers at the right end of the graph to a value around 0.1. The entire region under the blue curve that is between the two dashed lines, indicating the visible region, is shaded with vertical bands of color. The colors extending left to right across this region are violet, indigo, blue, green, yellow, orange, and red. A purple dot is placed at the peak of each of the four colored curves. These peaks are connected with a dashed curve.

The Photoelectric Effect

The next paradox in the classical theory to be resolved concerned the photoelectric effect (Figure 3.1.10). It had been observed that electrons could be ejected from the clean surface of a metal when light having a frequency greater than some threshold frequency was shone on it. Surprisingly, the kinetic energy of the ejected electrons did not depend on the brightness of the light, but increased with increasing frequency of the light. Since the electrons in the metal had a certain amount of binding energy keeping them there, the incident light needed to have more energy to free the electrons. According to classical wave theory, a wave's energy depends on its intensity (which depends on its amplitude), not its frequency. One part of these observations was that the number of electrons ejected within in a given time period was seen to increase as the brightness increased. In 1905, Albert Einstein was able to resolve the paradox by incorporating Planck's quantization findings into the discredited particle view of light (Einstein actually won his Nobel prize for this work, and not for his theories of relativity for which he is most famous).

Einstein argued that the quantized energies that Planck had postulated in his treatment of blackbody radiation could be applied to the light in the photoelectric effect so that the light striking the metal surface should not be viewed as a wave, but instead as a stream of particles (later called photons) whose energy depended on their frequency, according to Planck's formula, $E = h\nu$ (or, in terms of wavelength using $c = \nu\lambda$, $E = \frac{hc}{\lambda}$). Electrons were ejected when hit by photons having sufficient energy (a frequency greater than the threshold). The greater the frequency, the greater the kinetic energy imparted to the escaping electrons by the collisions. Einstein also argued that the light intensity did not depend on the amplitude of the incoming wave, but instead corresponded to the number of photons striking the surface within a given time period. This explains why the number of ejected electrons increased with increasing brightness, since the greater the number of incoming photons, the greater the likelihood that they would collide with some of the electrons.

With Einstein's findings, the nature of light took on a new air of mystery. Although many light phenomena could be explained either in terms of waves or particles, certain phenomena, such as the interference patterns obtained when light passed through a double slit, were completely contrary to a particle view of light, while other phenomena, such as the photoelectric effect, were completely contrary to a wave view of light. Somehow, at a deep fundamental level still not fully understood, light is both wavelike and particle-like. This is known as wave-particle duality.

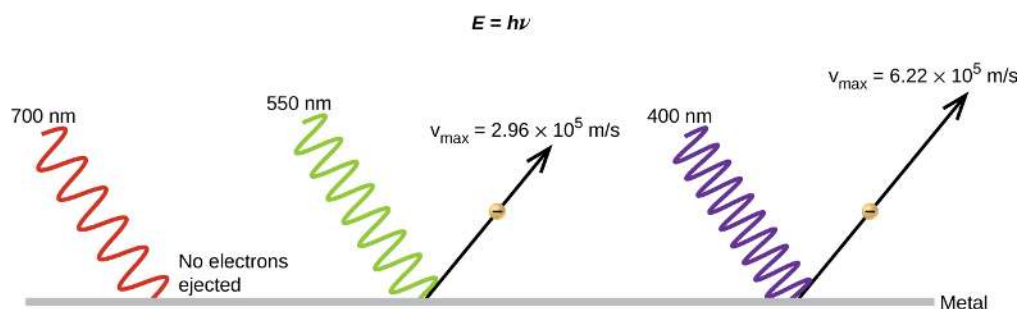


Figure 3.1.10: Photons with low frequencies do not have enough energy to cause electrons to be ejected via the photoelectric effect. For any frequency of light above the threshold frequency, the kinetic energy of an ejected electron will increase linearly with the energy of the incoming photon.

The figure includes three diagrams of waves approaching a flat, horizontal surface that is labeled, "Metal," from an angle around 45 degrees above and to the left relative to the surface. At the top of the diagram at the center is the label, "E equals h nu." At the left, a sinusoidal wave reaches the surface and stops. The portion of the diagram near the flat metal surface is labeled, "No electrons ejected," and the wave is labeled, "700 n m." To the right, a second similar, more compressed wave, which is labeled, "550 n m," reaches the flat surface. This time, an arrow extends up and to the right at an angle of approximately 45 degrees. A tiny yellow circle with a negative sign in it is at the center of the arrow shaft. Above this arrow is the equation, " v subscript max equals 2.96 times 10 superscript 5 m per s." To the far right, a third similar, even more compressed wave, which is labeled "400 n m" reaches the flat surface. This time, an arrow extends up and to the right at an angle of approximately 45 degrees. A tiny yellow circle with a negative sign in it is at the center of the arrow shaft. Above this arrow is the equation " v subscript max equals 6.22 times 10 superscript 5 m per s."

✓ Example 3.1.2: Calculating the Energy of Radiation

When we see light from a neon sign, we are observing radiation from excited neon atoms. If this radiation has a wavelength of 640 nm, what is the energy of the photon being emitted?

Solution

We use the part of Planck's equation that includes the wavelength, λ , and convert units of nanometers to meters so that the units of λ and c are the same.

$$\begin{aligned} E &= \frac{hc}{\lambda} \\ &= \frac{(6.626 \times 10^{-34} \text{ J}\cdot\text{s})(2.998 \times 10^8 \text{ m}\cdot\text{s}^{-1})}{(640 \text{ nm}) \left(\frac{1 \text{ m}}{10^9 \text{ nm}} \right)} \\ &= 3.10 \times 10^{-19} \text{ J} \end{aligned}$$

? Exercise 3.1.2

The microwaves in an oven are of a specific frequency that will heat the water molecules contained in food. (This is why most plastics and glass do not become hot in a microwave oven—they do not contain water molecules.) This frequency is about 3×10^9 Hz. What is the energy of one photon in these microwaves?

Answer

$$2 \times 10^{-24} \text{ J}$$

✓ Example 3.1.3: Photoelectric Effect

Identify which of the following statements are false and, where necessary, change the italicized word or phrase to make them true, consistent with Einstein's explanation of the photoelectric effect.

- Increasing the brightness of incoming light *increases* the kinetic energy of the ejected electrons.
- Increasing the *wavelength* of incoming light increases the kinetic energy of the ejected electrons.
- Increasing the brightness of incoming light *increases* the number of ejected electrons.
- Increasing the *frequency* of incoming light can increase the number of ejected electrons.

Solution

- False. Increasing the brightness of incoming light *has no effect* on the kinetic energy of the ejected electrons. Only energy, not the number or amplitude, of the photons influences the kinetic energy of the electrons.
- False. Increasing the *frequency* of incoming light increases the kinetic energy of the ejected electrons. Frequency is proportional to energy and inversely proportional to wavelength. Frequencies above the threshold value transfer the excess energy into the kinetic energy of the electrons.
- True. Because the number of collisions with photons increases with brighter light, the number of ejected electrons increases.
- True with regard to the threshold energy binding the electrons to the metal. Below this threshold, electrons are not emitted and above it they are. Once over the threshold value, further increasing the frequency does not increase the number of ejected electrons

? Exercise 3.1.3

Calculate the threshold energy in kJ/mol of electrons in aluminum, given that the lowest frequency photon for which the photoelectric effect is observed is 9.87×10^{14} Hz.

Answer

$$3.94 \text{ kJ/mol}$$

Line Spectra

Another 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 3.1.8, 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 3.1.9.

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 3.1.5. 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 3.1.11). Each element displays its own characteristic set of lines, as do molecules, although their spectra are generally much more complicated.



Figure 3.1.11: 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 3.1.12.

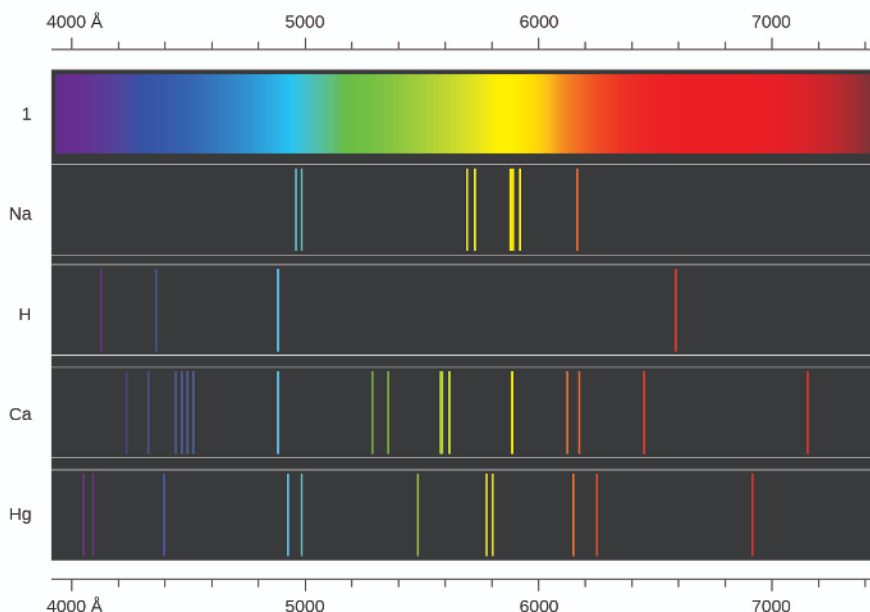


Figure 3.1.12: Line spectra of select gas. Compare the two types of emission spectra: continuous spectrum of white light (top) and the line spectra of the light from excited sodium, hydrogen, calcium, and mercury atoms.

An image is shown with 5 rows. Across the top and bottom of the image is a scale that begins at 4000 angstroms at the left and extends to 740 angstroms at the far right. The top row is a continuous band of the visible spectrum, showing the colors from violet at the far left through indigo, blue, green, yellow, orange, and red at the far right. The second row, labeled, “N a,” shows the emission spectrum for the element sodium, which includes two narrow vertical bands in the blue range, two narrow bands in the yellow-green range, two narrow bands in the yellow range, and one narrow band in the orange range. The third row, labeled, “H,” shows the emission spectrum for hydrogen. This spectrum shows single bands in the violet, indigo, blue, and orange regions. The fourth row, labeled, “C a,” shows the emission spectrum for calcium. This spectrum shows bands in the following colors and frequencies; one violet, five indigo, one blue, two green, two yellow-green, one yellow, two yellow-orange, one orange, and one red. The fifth row, labeled, “H g,” shows the emission spectrum for mercury. This spectrum shows bands in the following colors and frequencies; two violet, one indigo, two blue, one green, two yellow, two orange, and one orange-red. It is important to note that each of the color bands for the emission spectra of the elements matches to a specific wavelength of light. Extending a vertical line from the bands to the scale above or below the diagram will match the band to a specific measurement on the scale.

The origin of discrete spectra in atoms and molecules was extremely puzzling to scientists in the late nineteenth century, since according to classical electromagnetic theory, only continuous spectra should be observed. Even more puzzling, in 1885, Johann Balmer was able to derive an empirical equation that related the four visible wavelengths of light emitted by hydrogen atoms to whole integers. That equation is the following one, in which k is a constant:

$$\frac{1}{\lambda} = k \left(\frac{1}{4} - \frac{1}{n^2} \right), n = 3, 4, 5, 6$$

Other discrete lines for the hydrogen atom were found in the UV and IR regions. Johannes Rydberg generalized Balmer's work and developed an empirical formula that predicted all of hydrogen's emission lines, not just those restricted to the visible range, where, n_1 and n_2 are integers, $n_1 < n_2$, and R_∞ is the Rydberg constant ($1.097 \times 10^7 \text{ m}^{-1}$).

$$\frac{1}{\lambda} = R_\infty \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

Even in the late nineteenth century, spectroscopy was a very precise science, and so the wavelengths of hydrogen were measured to very high accuracy, which implied that the Rydberg constant could be determined very precisely as well. That such a simple formula as the Rydberg formula could account for such precise measurements seemed astounding at the time, but it was the eventual explanation for emission spectra by Neils Bohr in 1913 that ultimately convinced scientists to abandon classical physics and spurred the development of modern quantum mechanics.

Summary

Light and other forms of electromagnetic radiation move through a vacuum with a constant speed, c , of $2.998 \times 10^8 \text{ m s}^{-1}$. This radiation shows wavelike behavior, which can be characterized by a frequency, ν , and a wavelength, λ , such that $c = \lambda\nu$. 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 $E = h\nu$ (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. This line spectrum was simple enough that an empirical formula called the Rydberg formula could be derived from the spectrum. Three historically important paradoxes from the late 19th and early 20th centuries that could not be explained within the existing framework of classical mechanics and classical electromagnetism were the blackbody problem, the photoelectric effect, and the discrete spectra of atoms. The resolution of these paradoxes ultimately led to quantum theories that superseded the classical theories.

Key Equations

- $c = \lambda\nu$
- $E = h\nu = \frac{hc}{\lambda}$, where $h = 6.626 \times 10^{-34} \text{ J s}$
- $\frac{1}{\lambda} = R_{\infty} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$

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)

blackbody

idealized perfect absorber of all incident electromagnetic radiation; such bodies emit electromagnetic radiation in characteristic continuous spectra called blackbody radiation

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)

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3.2: The Bohr Model

Learning Objectives

- Describe the Bohr model of the hydrogen atom
- Use the Rydberg equation to calculate energies of light emitted or absorbed by hydrogen atoms

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. The electrostatic force attracting the electron to the proton depends only on the distance between the two particles.

$$F_{\text{gravity}} = G \frac{m_1 m_2}{r^2}$$

with

- G is a gravitational constant
- m_1 and m_2 are the masses of particle 1 and 2, respectively
- r is the distance between the two particles

The electrostatic force has the same form as the gravitational force between two mass particles except that the electrostatic force depends on the magnitudes of the charges on the particles (+1 for the proton and -1 for the electron) instead of the magnitudes of the particle masses that govern the gravitational force.

$$F_{\text{electrostatic}} = k \frac{m_1 m_2}{r^2}$$

with

- k is a constant
- m_1 and m_2 are the masses of particle 1 and 2, respectively
- r is the distance between the two particles

Since forces can be derived from potentials, it is convenient to work with potentials instead, since they are forms of energy. The electrostatic potential is also called the *Coulomb potential*. Because the electrostatic potential has the same form as the gravitational potential, according to classical mechanics, the equations of motion should be similar, with the electron moving around the nucleus in circular or elliptical orbits (hence the label “planetary” model of the atom). Potentials of the form $V(r)$ that depend only on the radial distance r are known as central potentials. Central potentials have spherical symmetry, and so rather than specifying the position of the electron in the usual Cartesian coordinates (x, y, z), it is more convenient to use polar spherical coordinates centered at the nucleus, consisting of a linear coordinate r and two angular coordinates, usually specified by the Greek letters theta (θ) and phi (Φ). These coordinates are similar to the ones used in GPS devices and most smart phones that track positions on our (nearly) spherical earth, with the two angular coordinates specified by the latitude and longitude, and the linear coordinate specified by sea-level elevation. Because of the spherical symmetry of central potentials, the energy and angular momentum of the classical hydrogen atom are constants, and the orbits are constrained to lie in a plane like the planets orbiting the sun. 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. The energy absorbed or emitted would reflect differences in the orbital energies according to this equation:

$$|\Delta E| = |E_f - E_i| = hu = \frac{hc}{\lambda} \quad (3.2.1)$$

In this equation, h is Planck's constant and E_i and E_f are the initial and final orbital energies, respectively. The absolute value of the energy difference is used, since frequencies and wavelengths are always positive. Instead of allowing for continuous values for the angular momentum, energy, and orbit radius, Bohr assumed that only discrete values for these could occur (actually, quantizing any one of these would imply that the other two are also quantized). Bohr's expression for the quantized energies is:

$$E_n = -\frac{k}{n^2} \quad (3.2.2)$$

with $n = 1, 2, 3, \dots$

In this expression, k is a constant comprising fundamental constants such as the electron mass and charge and Planck's constant. Inserting the expression for the orbit energies into the equation for ΔE gives

$$\Delta E = k \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) = \frac{hc}{\lambda} \quad (3.2.3)$$

or

$$\frac{1}{\lambda} = \frac{k}{hc} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \quad (3.2.4)$$

The lowest few energy levels are shown in Figure 3.2.1. 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.

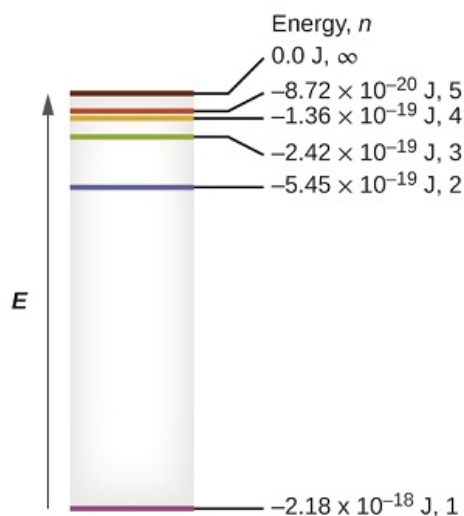


Figure 3.2.1: Quantum numbers and energy levels in a hydrogen atom. The more negative the calculated value, the lower the energy.

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 3.2.2). 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).

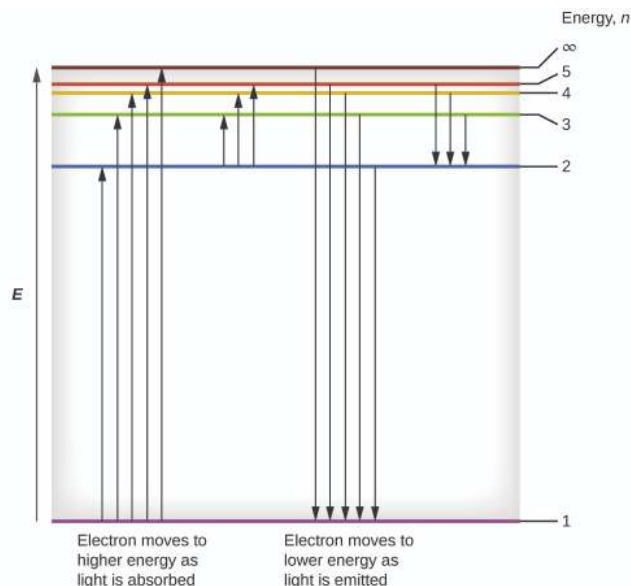


Figure 3.2.2: The horizontal lines show the relative energy of orbits in the Bohr model of the hydrogen atom, and the vertical arrows depict the energy of photons absorbed (left) or emitted (right) as electrons move between these orbits.

The figure includes a diagram representing the relative energy levels of the quantum numbers of the hydrogen atom. An upward pointing arrow at the left of the diagram is labeled, “E.” A grey shaded vertically oriented rectangle is placed just right of the arrow. The rectangle height matches the arrow length. Colored, horizontal line segments are placed inside the rectangle and labels are placed to the right of the box, arranged in a column with the heading, “Energy, n.” At the very base of the rectangle, a purple horizontal line segment is drawn. A black line extends to the right to the label, “1.” At a level approximately three-quarters of the distance to the top of the rectangle, a blue horizontal line segment is drawn. A black line extends to the right to the label, “2.” At a level approximately seven-eighths the distance from the base of the rectangle, a green horizontal line segment is drawn. A black line extends to the right to the label, “3.” Just a short distance above this segment, an orange horizontal line segment is drawn. A black line segment extends to the right to the label, “4.” Just above this segment, a red horizontal line segment is drawn. A black line extends to the right to the label, “5.” Just a short distance above this segment, a brown horizontal line segment is drawn. A black line extends to the right to the label, “infinity.” Arrows are drawn to depict energies of photons absorbed, as shown by upward pointing arrows on the left, or released as shown by downward pointing arrows on the right side of the diagram between the colored line segments. The label, “Electron moves to higher energy as light is absorbed,” is placed beneath the upward pointing arrows. Similarly, the label, “Electron moves to lower energy as light is emitted,” appears beneath the downward pointing arrows. Moving left to right across the diagram, arrows extend from one colored line segment to the next in the following order: purple to blue, purple to green, purple to orange, purple to red, purple to brown, blue to green, blue to orange, and blue to red. The arrows originating from the same colored segment are grouped together by close placement of the arrows. Similarly, the downward arrows follow in this sequence; brown to purple, red to purple, orange to purple, green to purple, blue to purple, red to blue, orange to blue, and green to blue. Arrows are again grouped by close placement according to the color at which the arrows end.

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 $2.179 \times 10^{-18} \text{ J}$.

$$E_n = -\frac{kZ^2}{n^2} \quad (3.2.5)$$

The sizes of the circular orbits for hydrogen-like atoms are given in terms of their radii by the following expression, in which a_0 is a constant called the Bohr radius, with a value of $5.292 \times 10^{-11} \text{ m}$:

$$r = \frac{n^2}{Z} a_0 \quad (3.2.6)$$

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 $n \rightarrow \infty$ and $r \rightarrow \infty$ 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:

$$\Delta E = E_{n \rightarrow \infty} - E_1 = 0 + k = k \quad (3.2.7)$$

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.

✓ Example 3.2.1: Calculating the Energy of an Electron in a Bohr Orbit

Early researchers were very excited when they were able to predict the energy of an electron at a particular distance from the nucleus in a hydrogen atom. If a spark promotes the electron in a hydrogen atom into an orbit with $n = 3$, what is the calculated energy, in joules, of the electron?

Solution

The energy of the electron is given by Equation 3.2.5:

$$E = \frac{-kZ^2}{n^2}$$

The atomic number, Z , of hydrogen is 1; $k = 2.179 \times 10^{-18} \text{ J}$; and the electron is characterized by an n value of 3. Thus,

$$E = \frac{-(2.179 \times 10^{-18} \text{ J}) \times (1)^2}{(3)^2} = -2.421 \times 10^{-19} \text{ J}$$

? Exercise 3.2.1

The electron in Example 3.2.1 in the $n = 3$ state is promoted even further to an orbit with $n = 6$. What is its new energy?

Answer

TBD

✓ Example 3.2.2: Calculating Electron Transitions in a One-electron System

What is the energy (in joules) and the wavelength (in meters) of the line in the spectrum of hydrogen that represents the movement of an electron from Bohr orbit with $n = 4$ to the orbit with $n = 6$? In what part of the electromagnetic spectrum do we find this radiation?

Solution

In this case, the electron starts out with $n = 4$, so $n_1 = 4$. It comes to rest in the $n = 6$ orbit, so $n_2 = 6$. The difference in energy between the two states is given by this expression:

$$\Delta E = E_1 - E_2 = 2.179 \times 10^{-18} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

$$\Delta E = 2.179 \times 10^{-18} \left(\frac{1}{4^2} - \frac{1}{6^2} \right) J$$

$$\Delta E = 2.179 \times 10^{-18} \left(\frac{1}{16} - \frac{1}{36} \right) J$$

$$\Delta E = 7.566 \times 10^{-20} J$$

This energy difference is *positive*, indicating a photon enters the system (is absorbed) to excite the electron from the $n = 4$ orbit up to the $n = 6$ orbit. The wavelength of a photon with this energy is found by the expression $E = hc\lambda$. Rearrangement gives:

$$\lambda = \frac{hc}{E}$$

From the figure of electromagnetic radiation, we can see that this wavelength is found in the infrared portion of the electromagnetic spectrum.

? Exercise 3.2.2

What is the energy in joules and the wavelength in meters of the photon produced when an electron falls from the $n = 5$ to the $n = 3$ level in a He^+ ion ($Z = 2$ for He^+)?

Answer

$6.198 \times 10^{-19} J$ and $3.205 \times 10^{-7} m$

Bohr's model of the hydrogen atom provides insight into the behavior of matter at the microscopic level, but it does not account for electron-electron interactions in atoms with more than one electron. It does introduce several important features of all models used to describe the distribution of electrons in an atom. These features include the following:

- The energies of electrons (energy levels) in an atom are quantized, described by quantum numbers: integer numbers having only specific allowed value and used to characterize the arrangement of electrons in an atom.
- An electron's energy increases with increasing distance from the nucleus.
- The discrete energies (lines) in the spectra of the elements result from quantized electronic energies.

Of these features, the most important is the postulate of quantized energy levels for an electron in an atom. As a consequence, the model laid the foundation for the quantum mechanical model of the atom. Bohr won a Nobel Prize in Physics for his contributions to our understanding of the structure of atoms and how that is related to line spectra emissions.

Summary

Bohr incorporated Planck's and Einstein's quantization ideas into a model of the hydrogen atom that resolved the paradox of atom stability and discrete spectra. The Bohr model of the hydrogen atom explains the connection between the quantization of photons and the quantized emission from atoms. Bohr described the hydrogen atom in terms of an electron moving in a circular orbit about a nucleus. He postulated that the electron was restricted to certain orbits characterized by discrete energies. Transitions between these allowed orbits result in the absorption or emission of photons. When an electron moves from a higher-energy orbit to a more stable one, energy is emitted in the form of a photon. To move an electron from a stable orbit to a more excited one, a photon of energy must be absorbed. Using the Bohr model, we can calculate the energy of an electron and the radius of its orbit in any one-electron system.

Glossary

Bohr's model of the hydrogen atom

structural model in which an electron moves around the nucleus only in circular orbits, each with a specific allowed radius; the orbiting electron does not normally emit electromagnetic radiation, but does so when changing from one orbit to another.

excited state

state having an energy greater than the ground-state energy

ground state

state in which the electrons in an atom, ion, or molecule have the lowest energy possible

quantum number

integer number having only specific allowed values and used to characterize the arrangement of electrons in an atom

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3.3: Electronic Structure of Atoms (Electron Configurations)

Learning Objectives

- Derive the predicted ground-state electron configurations of atoms
- Identify and explain exceptions to predicted electron configurations for atoms and ions
- Relate electron configurations to element classifications in the periodic table

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.

Orbital Energies and Atomic Structure

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 3.3.1 depicts how these two trends in increasing energy relate. The 1s orbital at the bottom of the diagram is the orbital with electrons of lowest energy. The energy increases as we move up to the 2s and then 2p, 3s, and 3p 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 3d orbital is higher in energy than the 4s orbital. Such overlaps continue to occur frequently as we move up the chart.

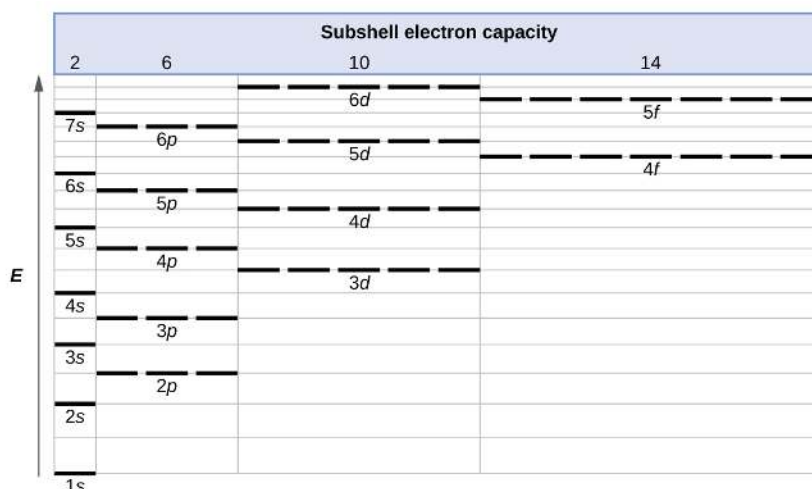


Figure 3.3.1: Generalized energy-level diagram for atomic orbitals in an atom with two or more electrons (not to scale).

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 5p orbitals fill immediately after the 4d, 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 3p), 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 3.3.2):

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 $n = 3$.

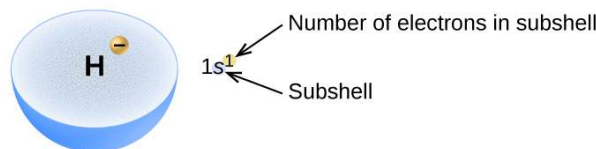


Figure 3.3.2: The diagram of an electron configuration specifies the subshell (n and l value, with letter symbol) and superscript number of electrons.

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 3.3.3), 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 3.3.3 illustrates the traditional way to remember the filling order for atomic orbitals.

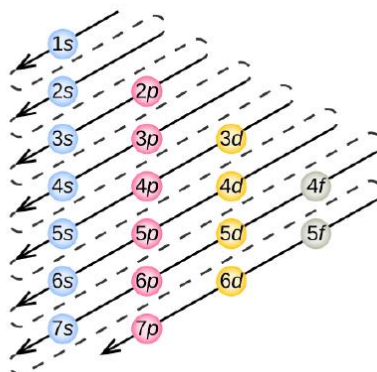


Figure 3.3.3: The arrow leads through each subshell in the appropriate filling order for electron configurations. This chart is straightforward to construct. Simply make a column for all the s orbitals with each n shell on a separate row. Repeat for p , d , and f . Be sure to only include orbitals allowed 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 3.3.4 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 $3p$ block up to Ar, we see the orbital will be $4s$ (K, Ca), followed by the $3d$ orbitals.

Electron Configuration Table

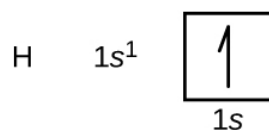
The table displays elements from Period 1 to 7. The subshells being filled are indicated by arrows: 1s, 2s, 2p, 3s, 3d, 4s, 4p, 5s, 5d, 6s, 6p, 7s, 7p, 5f, 6d, 7f. The f-block is shown below the main table, with arrows indicating the filling order for 4f and 5f.

Callout for Hydrogen (H):

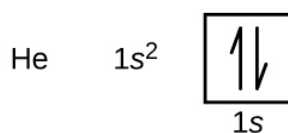
- Name → **H**
- Atomic Number → **1**
- Electrons → **1**
- Subshell → **1s**

Figure 3.3.4: 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 3.3.3 or 3.3.4, 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:

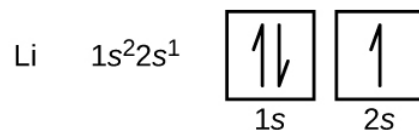


Following hydrogen is the noble gas helium, which has an atomic number of 2. The helium atom contains two protons and two electrons. The first electron has the same four quantum numbers as the hydrogen atom electron ($n = 1$, $l = 0$, $m_l = 0$, $m_s = +\frac{1}{2}$). The second electron also goes into 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:

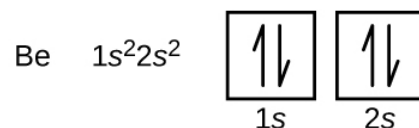


The $n = 1$ shell is completely filled in a helium atom.

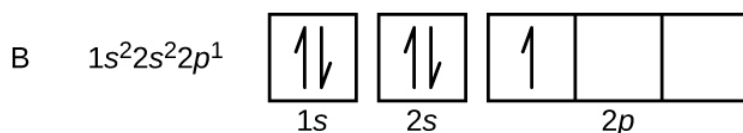
The next atom is the alkali metal lithium with an atomic number of 3. The first two electrons in lithium fill the 1s orbital and have the same sets of four quantum numbers as the two electrons in helium. The remaining electron must occupy the orbital of next lowest energy, the 2s orbital (Figure 3.3.3 or 3.3.4). Thus, the electron configuration and orbital diagram of lithium are:



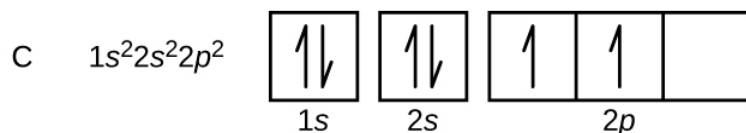
An atom of the alkaline earth metal beryllium, with an atomic number of 4, contains four protons in the nucleus and four electrons surrounding the nucleus. The fourth electron fills the remaining space in the 2s orbital.



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.



Carbon (atomic number 6) has six electrons. Four of them fill the 1s and 2s orbitals. The remaining two electrons occupy the 2p subshell. We now have a choice of filling one of the 2p 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 2p 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:



Nitrogen (atomic number 7) fills the 1s and 2s subshells and has one electron in each of the three 2p 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 2p orbitals (the electrons have opposite spins) and a single electron in each of the other two. Fluorine (atomic number 9) has only one 2p 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:

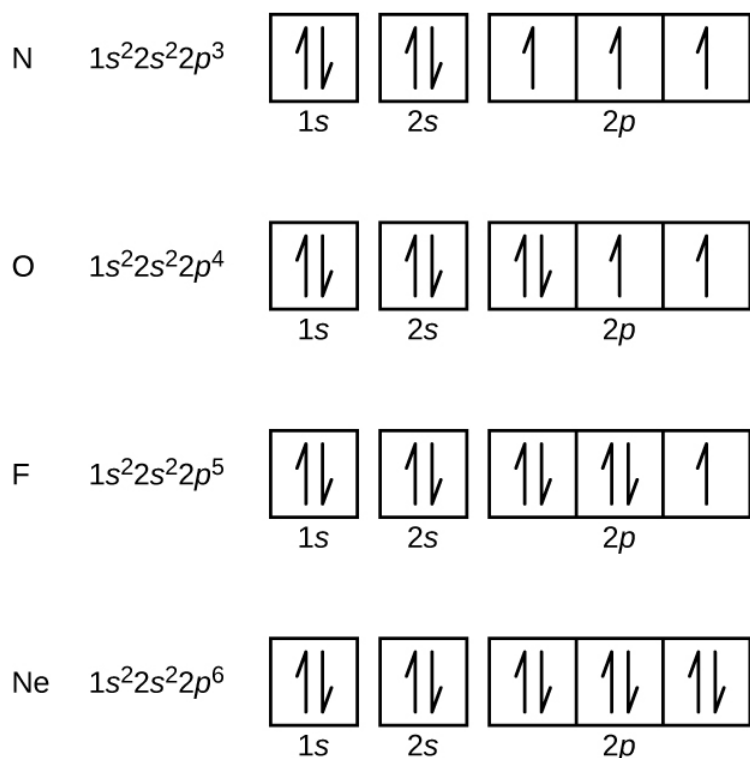


Figure 3.3.5: Since the core electron shells correspond to noble gas electron configurations, we can abbreviate electron configurations by writing the noble gas that matches the core electron configuration, along with the valence electrons in a condensed format. For our sodium example, the symbol [Ne] represents core electrons, ($1s^2 2s^2 2p^6$) and our abbreviated or condensed configuration is [Ne] $3s^1$.

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 \PageIndex{5}\PageIndex{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] $3s^1$.

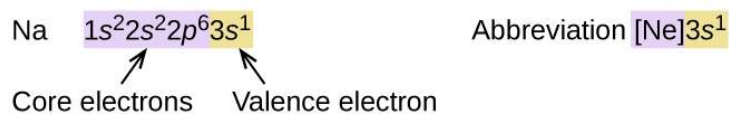
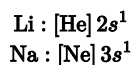


Figure 3.3.5: A core-abbreviated electron configuration (right) replaces the core electrons with the noble gas symbol whose configuration matches the core electron configuration of the other element.

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.



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 3.3.6 shows the lowest energy, or ground-state, electron configuration for these elements as well as that for atoms of each of the known elements.

Electron Configuration Table

Period	Group																18	
1	1																	2
	1s ¹																	1s ²
2	3	4											5	6	7	8	9	10
	2s ¹	2s ²											2s ² 2p ¹	2s ² 2p ²	2s ² 2p ³	2s ² 2p ⁴	2s ² 2p ⁵	2s ² 2p ⁶
3	11	12											13	14	15	16	17	18
	3s ¹	3s ²											3s ² 3p ¹	3s ² 3p ²	3s ² 3p ³	3s ² 3p ⁴	3s ² 3p ⁵	3s ² 3p ⁶
4	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36
	4s ¹	4s ²	4s ² 3d ¹	4s ² 3d ²	4s ² 3d ³	4s ¹ 3d ⁵	4s ² 3d ⁵	4s ² 3d ⁶	4s ² 3d ⁷	4s ² 3d ⁸	4s ¹ 3d ¹⁰	4s ² 3d ¹⁰	4s ² 3d ¹⁰ 4p ¹	4s ² 3d ¹⁰ 4p ²	4s ² 3d ¹⁰ 4p ³	4s ² 3d ¹⁰ 4p ⁴	4s ² 3d ¹⁰ 4p ⁵	4s ² 3d ¹⁰ 4p ⁶
5	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54
	5s ¹	5s ²	5s ² 4d ¹	5s ² 4d ²	5s ¹ 4d ⁵	5s ² 4d ⁵	5s ² 4d ⁶	5s ² 4d ⁷	5s ¹ 4d ⁸	4d ¹⁰	5s ¹ 4d ¹⁰	5s ² 4d ¹⁰	5s ² 4d ¹⁰ 5p ¹	5s ² 4d ¹⁰ 5p ²	5s ² 4d ¹⁰ 5p ³	5s ² 4d ¹⁰ 5p ⁴	5s ² 4d ¹⁰ 5p ⁵	5s ² 4d ¹⁰ 5p ⁶
6	55	56	57	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86
	6s ¹	6s ²	6s ² 5d ¹	6s ² 4f ¹⁴ 5d ¹	6s ² 4f ¹⁴ 5d ²	6s ² 4f ¹⁴ 5d ³	6s ² 4f ¹⁴ 5d ⁵	6s ² 4f ¹⁴ 5d ⁵	6s ² 4f ¹⁴ 5d ⁶	6s ² 4f ¹⁴ 5d ⁷	6s ¹ 4f ¹⁴ 5d ⁹	6s ² 4f ¹⁴ 5d ¹⁰	6s ² 4f ¹⁴ 5d ¹⁰ 6p ¹	6s ² 4f ¹⁴ 5d ¹⁰ 6p ²	6s ² 4f ¹⁴ 5d ¹⁰ 6p ³	6s ² 4f ¹⁴ 5d ¹⁰ 6p ⁴	6s ² 4f ¹⁴ 5d ¹⁰ 6p ⁵	6s ² 4f ¹⁴ 5d ¹⁰ 6p ⁶
7	87	88	89	104	105	106	107	108	109	110	111	112	113	114	115	116	117	118
	7s ¹	7s ²	7s ² 6d ¹	7s ² 5f ¹⁴ 6d ¹	7s ² 5f ¹⁴ 6d ²	7s ² 5f ¹⁴ 6d ³	7s ² 5f ¹⁴ 6d ⁵	7s ² 5f ¹⁴ 6d ⁵	7s ² 5f ¹⁴ 6d ⁶	7s ² 5f ¹⁴ 6d ⁷	7s ² 5f ¹⁴ 6d ¹⁰	7s ² 5f ¹⁴ 6d ¹⁰						
<div><div>* 58 Ce 59 Pr 60 Nd 61 Pm 62 Sm 63 Eu 64 Gd 65 Tb 66 Dy 67 Ho 68 Er 69 Tm 70 Yb 71 Lu</div><div>6s²4f² 6s²4f³ 6s²4f⁴ 6s²4f⁵ 6s²4f⁶ 6s²4f⁷ 6s²4f⁹ 6s²4f¹⁰ 6s²4f¹¹ 6s²4f¹² 6s²4f¹³ 6s²4f¹⁴ 6s²4f¹⁴</div><div>** 90 Th 91 Pa 92 U 93 Np 94 Pu 95 Am 96 Cm 97 Bk 98 Cf 99 Es 100 Fm 101 Md 102 No 103 Lr</div><div>7s²6d² 7s²5f²6d¹ 7s²5f³6d¹ 7s²5f⁴6d¹ 7s²5f⁶ 7s²5f⁷ 7s²5f⁷6d¹ 7s²5f⁸6d¹ 7s²5f¹⁰ 7s²5f¹¹ 7s²5f¹² 7s²5f¹³ 7s²5f¹⁴ 7s²5f¹⁴6d¹</div></div>																		

Atomic number → 1

H

← Name

1s¹

← Outer electron configuration

Figure 3.3.6: 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 3d 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 3d level but is, instead, added to the 4s level (Figure 3.3.3 or 3.3.4). As discussed previously, the 3d 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]4s¹. 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]4s². This gives calcium an outer-shell electron configuration corresponding to that of beryllium and magnesium.

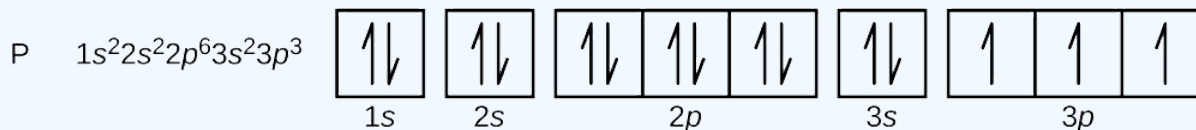
Beginning with the transition metal scandium (atomic number 21), additional electrons are added successively to the 3d subshell. This subshell is filled to its capacity with 10 electrons (remember that for $l = 2$ [d orbitals], there are $2l + 1 = 5$ values of m_l , meaning that there are five d orbitals that have a combined capacity of 10 electrons). The 4p 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 3.3.1: 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, 2p, 3s, 3p, 4s, . . . The 15 electrons of the phosphorus atom will fill up to the 3p orbital, which will contain three electrons:



The last electron added is a 3p 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 3.3.1

Identify the atoms from the electron configurations given:

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

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 3.3.3 or 3.3.4. 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 4s into the 3d orbital to gain the extra stability of a half-filled 3d subshell (in Cr) or a filled 3d subshell (in Cu). Other exceptions also occur. For example, niobium (Nb, atomic number 41) is predicted to have the electron configuration $[\text{Kr}]5s^2 4d^3$. Experimentally, we observe that its ground-state electron configuration is actually $[\text{Kr}]5s^1 4d^4$. We can rationalize this observation by saying that the electron–electron repulsions experienced by pairing the electrons in the 5s orbital are larger than the gap in energy between the 5s and 4d 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

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 3.3.6), 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 3.3.6, 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 3.3.6 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 3.3.6. 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 $[\text{Ar}]4s^23d^{10}\underline{4p^1}$, 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 3.3.6) are not technically transition elements. However, the term is frequently used to refer to the entire d block (colored yellow in Figure 3.3.6), 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 3.3.6. The valence shells of the inner transition elements consist of the $(n - 2)f$, the $(n - 1)d$, and the ns 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 ns 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 3.3.2: 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^+ : $1s^2 2s^2 2p^6 3s^1 = \text{Na}^+$: $1s^2 2s^2 2p^6$.

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+} : $1s^2 2s^2 2p^6 3s^2 3p^1 = \text{Al}^{2+}$: $1s^2 2s^2 2p^6 3s^1$.

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 4f 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 3.3.2

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

Answer a

Tc^{2+}

Answer b

Ru^{3+}

Summary

The relative energy of the subshells determine the order in which atomic orbitals are filled (1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 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

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CHAPTER OVERVIEW

4: Compounds- We can do experiments on compounds to figure out what they are made of

Topic hierarchy

5.1: Chemical Formulas

5.2: Formula Mass and the Mole Concept

5.3: Determining Empirical and Molecular Formulas

5.4: Molarity

5.5: Quantitative Chemical Analysis

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5.1: Chemical Formulas

Learning Objectives

- Symbolize the composition of molecules using molecular formulas and empirical formulas
- Represent the bonding arrangement of atoms within molecules using structural formulas

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 5.1.1). 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.

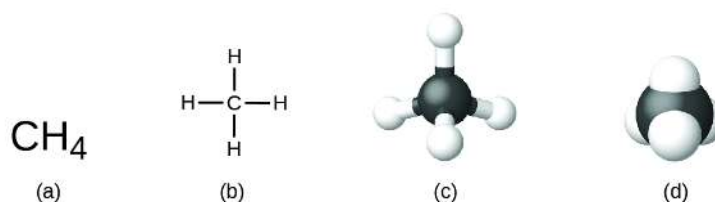


Figure 5.1.1: A methane molecule can be represented as (a) a molecular formula, (b) a structural formula, (c) a ball-and-stick model, and (d) a space-filling model. Carbon and hydrogen atoms are represented by black and white spheres, respectively.

Figure A shows C H subscript 4. Figure B shows a carbon atom that is bonded to four hydrogen atoms at right angles: one above, one to the left, one to the right, and one below. Figure C shows a 3-D, ball-and-stick model of the carbon atom bonded to four hydrogen atoms. Figure D shows a space-filling model of a carbon atom with hydrogen atoms partially embedded into the surface of the carbon atom.

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 5.1.2).

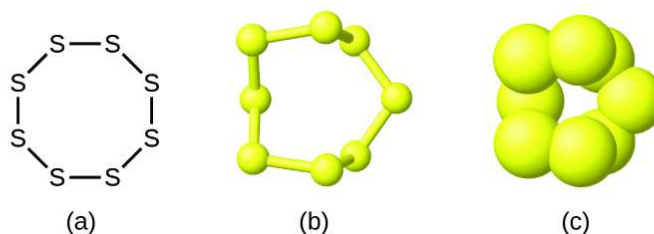


Figure 5.1.2: A molecule of sulfur is composed of eight sulfur atoms and is therefore written as S_8 . It can be represented as (a) a structural formula, (b) a ball-and-stick model, and (c) a space-filling model. Sulfur atoms are represented by yellow spheres.

Figure A shows eight sulfur atoms, symbolized with the letter S, that are bonded to each other to form an octagon. Figure B shows a 3-D, ball-and-stick model of the arrangement of the sulfur atoms. The shape is clearly not octagonal as it is represented in the structural formula. Figure C is a space-filling model that shows each sulfur atom is partially embedded into the sulfur atom it bonds with.

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 5.1.3).

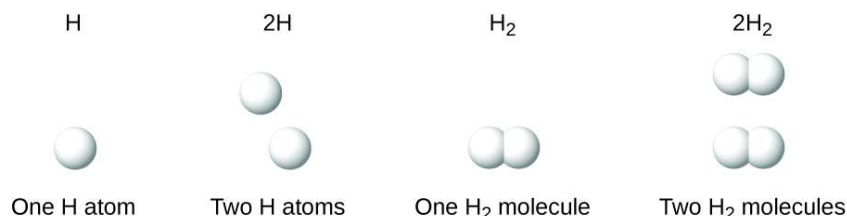


Figure 5.1.3: The symbols H , 2H , H_2 , and 2H_2 represent very different entities.

This figure shows four diagrams. The diagram for H shows a single, white sphere and is labeled one H atom. The diagram for 2H shows two white spheres that are not bonded together. It is labeled 2 H atoms. The diagram for H_2 shows two white spheres bonded together. It is labeled one H subscript 2 molecule. The diagram for 2H_2 shows two sets of bonded, white spheres. It is labeled 2 H subscript 2 molecules.

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 5.1.4).

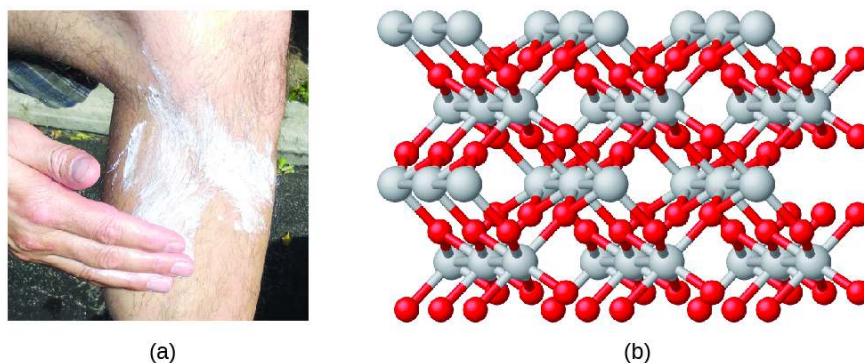


Figure 5.1.4: (a) The white compound titanium dioxide provides effective protection from the sun. (b) A crystal of titanium dioxide, TiO_2 , contains titanium and oxygen in a ratio of 1 to 2. The titanium atoms are gray and the oxygen atoms are red. (credit a: modification of work by "osseous"/Flickr).

Figure A shows a photo of a person applying suntan lotion to his or her lower leg. Figure B shows a 3-D ball-and-stick model of the molecule titanium dioxide, which involves a complicated interlocking of many titanium and oxygen atoms. The titanium atoms in the molecule are shown as silver spheres and the oxygen atoms are shown as red spheres. There are twice as many oxygen atoms as titanium atoms in the molecule.

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 5.1.5).

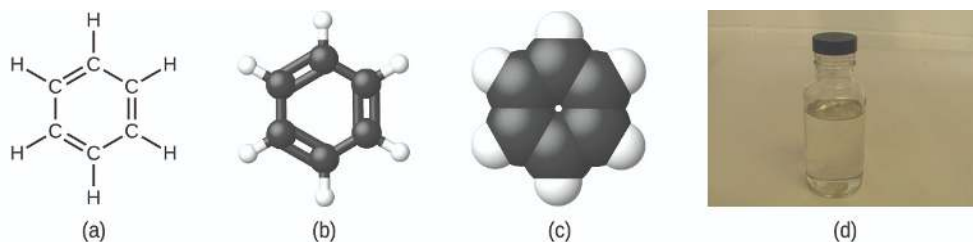


Figure 5.1.5: Benzene, C_6H_6 , is produced during oil refining and has many industrial uses. A benzene molecule can be represented as (a) a structural formula, (b) a ball-and-stick model, and (c) a space-filling model. (d) Benzene is a clear liquid. (credit d: modification of work by Sahar Atwa).

Figure A shows that benzene is composed of six carbons shaped like a hexagon. Every other bond between the carbon atoms is a double bond. Each carbon also has a single bonded hydrogen atom. Figure B shows a 3-D, ball-and-stick drawing of benzene. The six carbon atoms are black spheres while the six hydrogen atoms are smaller, white spheres. Figure C is a space-filling model of benzene which shows that most of the interior space is occupied by the carbon atoms. The hydrogen atoms are embedded in the outside surface of the carbon atoms. Figure d shows a small vial filled with benzene which appears to be clear.

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 5.1.6) 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.

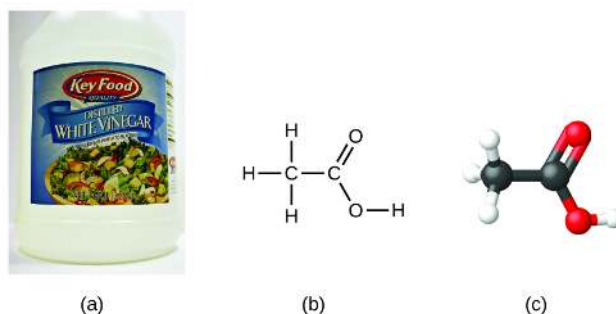


Figure 5.1.6: (a) Vinegar contains acetic acid, $C_2H_4O_2$, which has an empirical formula of CH_2O . It can be represented as (b) a structural formula and (c) as a ball-and-stick model. (credit a: modification of work by "HomeSpot HQ"/Flickr)

Figure A shows a jug of distilled, white vinegar. Figure B shows a structural formula for acetic acid which contains two carbon atoms connected by a single bond. The left carbon atom forms single bonds with three hydrogen atoms. The right carbon atom forms a double bond with an oxygen atom. The right carbon atom also forms a single bond with an oxygen atom. This oxygen forms a single bond with a hydrogen atom. Figure C shows a 3-D ball-and-stick model of acetic acid.

✓ Example 5.1.1: 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 5.1.1

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 5.1.7). 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.

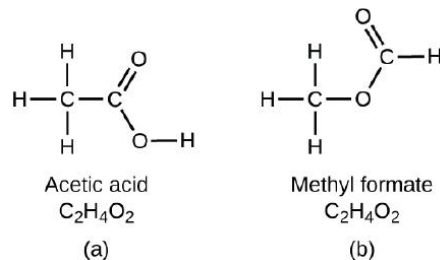


Figure 5.1.7: Molecules of (a) acetic acid and methyl formate (b) are structural isomers; they have the same formula ($C_2H_4O_2$) but different structures (and therefore different chemical properties).

Figure A shows a structural diagram of acetic acid, C subscript 2 H subscript 4 O subscript 2. Acetic acid contains two carbon atoms connected by a single bond. The left carbon atom forms single bonds with three hydrogen atoms. The carbon on the right forms a double bond with an oxygen atom. The right carbon atom also forms a single bond to an oxygen atom which forms a single bond with a hydrogen atom. Figure B shows a structural diagram of methyl formate, C subscript 2 H subscript 4 O subscript 2. This molecule contains a carbon atom which forms single bonds with three hydrogen atoms, and a single bond with an oxygen atom. The oxygen atom forms a single bond with another carbon atom which forms a double bond with another oxygen atom and a single bond with a hydrogen atom.

Many types of isomers exist (Figure 5.1.8). 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.

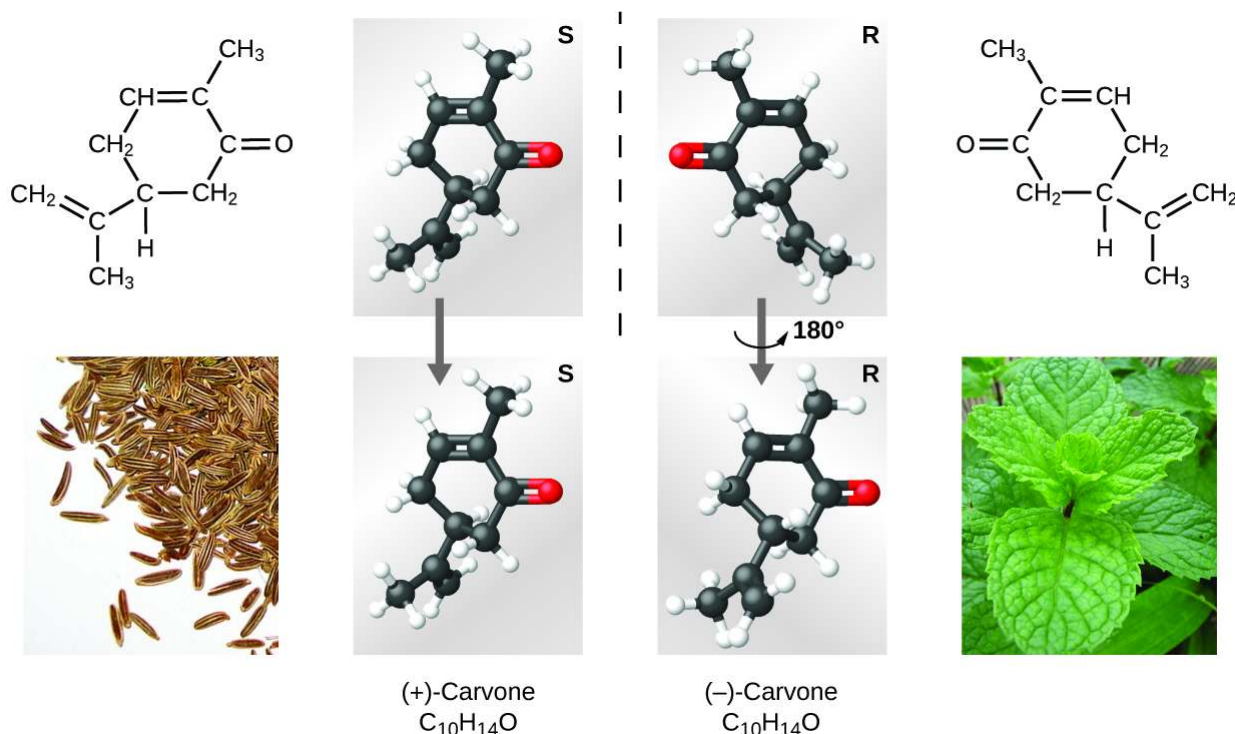


Figure 5.1.8: Molecules of carvone are spatial isomers; they only differ in the relative orientations of the atoms in space. (credit bottom left: modification of work by "Miansari66"/Wikimedia Commons; credit bottom right: modification of work by Forest & Kim Starr)

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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5.2: Formula Mass and the Mole Concept

Learning Objectives

- Calculate formula masses for covalent and ionic compounds
- Define the amount unit mole and the related quantity Avogadro'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 5.2.1 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

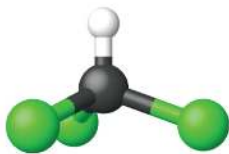


Figure 5.2.1: The average mass of a chloroform molecule, CHCl_3 , is 119.37 amu, which is the sum of the average atomic masses of each of its constituent atoms. The model shows the molecular structure of chloroform.

A table and diagram are shown. The table is made up of six columns and five rows. The header row reads: "Element," "Quantity," a blank space, "Average atomic mass (a m u)," a blank space, and "Subtotal (a m u)." The first column contains the symbols "C," "H," "Cl" and a blank, merged cell that runs the width of the first five columns. The second column contains the numbers "1," "1," and "3" as well as the merged cell. The third column contains the multiplication symbol in each cell except for the last, merged cell. The fourth column contains the numbers "12.01," "1.008," and "35.45" as well as the merged cell. The fifth column contains the symbol "=" in each cell except for the last, merged cell. The sixth column contains the values "12.01," "1.008," "106.35," and "119.37." There is a thick black line below the number 106.35. The merged cell under the first five columns reads "Molecular mass." To the left of the table is a diagram of a molecule. Three green spheres are attached to a slightly smaller black sphere, which is also attached to a smaller white sphere. The green spheres lie beneath and to the sides of the black sphere while the white sphere is located straight up from the black sphere.

Likewise, the molecular mass of an aspirin molecule, $\text{C}_9\text{H}_8\text{O}_4$, 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 5.2.2).

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



Figure 5.2.2: The average mass of an aspirin molecule is 180.15 amu. The model shows the molecular structure of aspirin, $C_9H_8O_4$. A table and diagram are shown. The table is made up of six columns and five rows. The header row reads: “Element,” “Quantity,” a blank space, “Average atomic mass (a m u),” a blank space, and “Subtotal (a m u).” The first column contains the symbols “C,” “H,” “O,” and a merged cell. The merged cell runs the length of the first five columns. The second column contains the numbers “9,” “8,” and “4” as well as the merged, cell. The third column contains the multiplication symbol in each cell except for the last, merged cell. The fourth column contains the numbers “12.01,” “1.008,” and “16.00” as well as the merged cell. The fifth column contains the symbol “=” in each cell except for the last, merged cell. The sixth column contains the values: “108.09,” “8.064,” “64.00,” and “180.15.” There is a thick black line below the number 64.00. The merged cell under the first five columns reads “Molecular mass.” To the left of the table is a diagram of a molecule. Six black spheres are located in a six-sided ring and connected by alternating double and single black bonds. Attached to each of the four black spheres is one smaller white sphere. Attached to the farthest right black sphere is a red sphere, connected to two more black spheres, all in a row. Attached to the last black sphere of that row are two more white spheres. Attached to the first black sphere of that row is another red sphere. A black sphere, attached to two red spheres and a white sphere is attached to the black sphere on the top right of the six-sided ring.

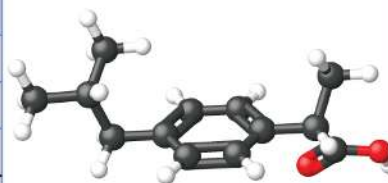
✓ Example 5.2.1: Computing Molecular Mass for a Covalent Compound

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	=	18.144
O	2	×	16.00	=	32.00
Molecular mass					206.27



? Exercise 5.2.1

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 5.2.3).

Element	Quantity		Average atomic mass (amu)	Subtotal	
Na	1	×	22.99	=	22.99
Cl	1	×	35.45	=	35.45
Formula mass					58.44



Figure 5.2.3: Table salt, NaCl, contains an array of sodium and chloride ions combined in a 1:1 ratio. Its formula mass is 58.44 amu. A table and diagram are shown. The table is made up of six columns and four rows. The header row reads: “Element,” “Quantity,” a blank space, “Average atomic mass (a m u),” a blank space and “Subtotal (a m u).” The first column contains the symbols “N a”, “C l,” and a merged cell. The merged cell runs the length of the first five columns. The second column contains the numbers “1” and “1” as well as the merged cell. The third column contains the multiplication symbol in each cell except for the last, merged cell. The fourth column contains the numbers “22.99” and “35.45” as well as the merged cell. The fifth column contains the symbol “=” in each cell except for the last, merged cell. The sixth column contains the values “22.99,” “35.45,” and “58.44.” There is a thick black line below the number “35.45.” The merged cell under the first five columns reads “Formula mass.” To the left of the table is a diagram of a chemical structure. The diagram shows green and purple spheres placed in an alternating pattern, making up the corners of eight stacked cubes to form one larger cube. The green spheres are slightly smaller than the purple spheres.

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.

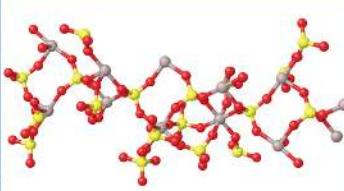
✓ Example 5.2.2: Computing Formula Mass for an Ionic Compound

Aluminum sulfate, $\text{Al}_2(\text{SO}_4)_3$, 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, $\text{Al}_2\text{S}_3\text{O}_{12}$. 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 5.2.2

Calcium phosphate, $\text{Ca}_3(\text{PO}_4)_2$, 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 5.2.4).

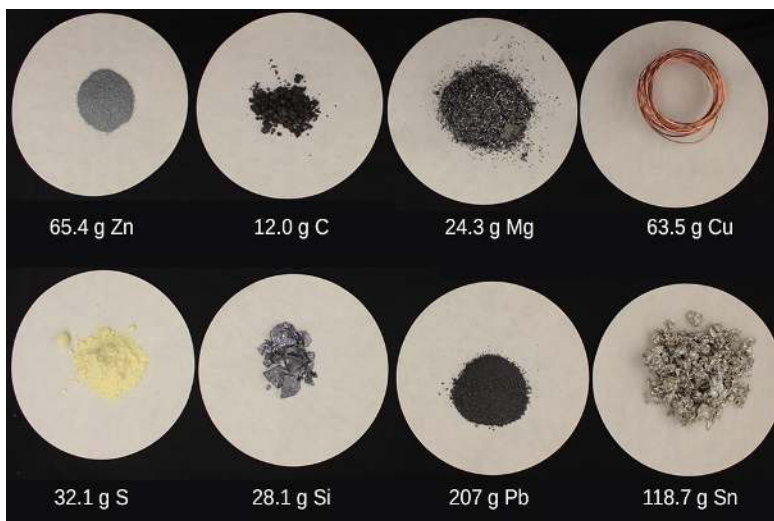


Figure 5.2.4: Each sample contains 6.022×10^{23} atoms —1.00 mol of atoms. From left to right (top row): 65.4 g zinc, 12.0 g carbon, 24.3 g magnesium, and 63.5 g copper. From left to right (bottom row): 32.1 g sulfur, 28.1 g silicon, 207 g lead, and 118.7 g tin. (credit: modification of work by Mark Ott).

This figure contains eight different substances displayed on white circles. The amount of each substance is visibly different.

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 5.2.5).

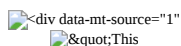


Figure 5.2.5: Each sample contains 6.022×10^{23} molecules or formula units—1.00 mol of the compound or element. Clock-wise from the upper left: 130.2 g of $C_8H_{17}OH$ (1-octanol, formula mass 130.2 amu), 454.4 g of HgI_2 (mercury(II) iodide, formula mass 454.4 amu), 32.0 g of CH_3OH (methanol, formula mass 32.0 amu) and 256.5 g of S_8 (sulfur, formula mass 256.5 amu). (credit: Sahar Atwa).

Table 5.2.1: 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}
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.



Video 5.2.1: 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.

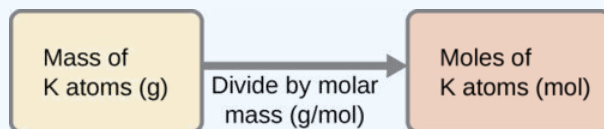
✓ Example 5.2.3: Deriving Moles from Grams for an Element

According to nutritional guidelines from the U.S. 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:”

$$4.7 \cancel{\text{g K}} \left(\frac{\text{mol K}}{39.10 \cancel{\text{g}}} \right) = 0.12 \text{ mol K}$$

The calculated magnitude (0.12 mol K) is consistent with our ballpark expectation, since it is a bit greater than 0.1 mol.

? Exercise 5.2.3: 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

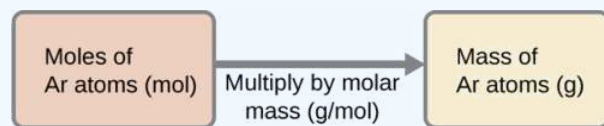
0.360 mol

✓ Example 5.2.4: 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 ($\sim 10^{-3}$) 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):

$$9.2 \times 10^{-4} \cancel{\text{mol Ar}} \left(\frac{39.95 \text{ g}}{\cancel{\text{mol Ar}}} \right) = 0.037 \text{ g Ar}$$

The result is in agreement with our expectations, around 0.04 g Ar.

? Exercise 5.2.4

What is the mass of 2.561 mol of gold?

Answer

504.4 g

✓ Example 5.2.6: Deriving Number of Atoms from Mass for an Element

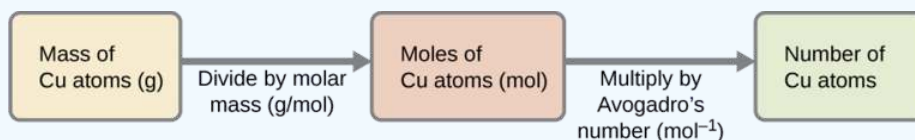
Copper is commonly used to fabricate electrical wire (Figure 5.2.6). How many copper atoms are in 5.00 g of copper wire?



Figure 5.2.6: 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:

$$5.00 \text{ g Cu} \left(\frac{\cancel{\text{mol Cu}}}{63.55 \text{ g}} \right) \left(\frac{6.022 \times 10^{23} \text{ atoms}}{\cancel{\text{mol}}} \right) = 4.74 \times 10^{22} \text{ atoms of copper}$$

The factor-label method yields the desired cancellation of units, and the computed result is on the order of 10^{22} as expected.

? Exercise 5.2.6

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

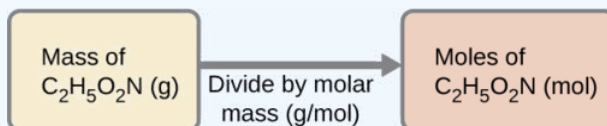
$$4.586 \times 10^{22} \text{ Au atoms}$$

✓ Example 5.2.7: 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 $\text{C}_2\text{H}_5\text{O}_2\text{N}$. How many moles of glycine molecules are contained in 28.35 g of glycine?

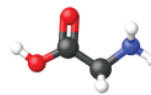
Solution

We can derive the number of moles of a compound from its mass following the same procedure we used for an element in Example 5.2.6:



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, $\text{C}_2\text{H}_5\text{O}_2\text{N}$, 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



A table is shown that is made up of six columns and six rows. The header row reads: “Element,” “Quantity (mol element / mol compound),” a blank space, “Molar mass (g / mol element),” a blank space, and “Subtotal (a m u).” The first column contains the symbols “C,” “H,” “O,” “N,” and a merged cell. The merged cell runs the width of the first five columns. The second column contains the numbers “2,” “5,” “2,” and “1” as well as the merged cell. The third column contains the multiplication symbol in each cell except for the last, merged cell. The fourth column contains the numbers “12.01,” “1.008,” “16.00,” and “14.007” as well as the merged cell. The fifth column contains the symbol “=” in each cell except for the last, merged cell. The sixth column contains the values “24.02,” “5.040,” “32.00,” “14.007,” and “75.07.” There is a thick black line under the number 14.007. The merged cell under the first five columns reads “Molar mass (g / mol compound).” There is a ball-and-stick drawing to the right of this table. It shows a black sphere that forms a double bond with a slightly smaller red sphere, a single bond with another red sphere, and a single bond with another black sphere. The red sphere that forms a single bond with the black sphere also forms a single bond with a smaller, white sphere. The second black sphere forms a single bond with a smaller, white sphere and a smaller blue sphere. The blue sphere forms a single bond with two smaller, white spheres each.

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:

$$28.35 \text{ g glycine} \left(\frac{\text{mol glycine}}{75.07 \text{ g}} \right) = 0.378 \text{ mol glycine}$$

This result is consistent with our rough estimate.

? Exercise 5.2.7

How many moles of sucrose, $C_{12}H_{22}O_{11}$, are in a 25-g sample of sucrose?

Answer

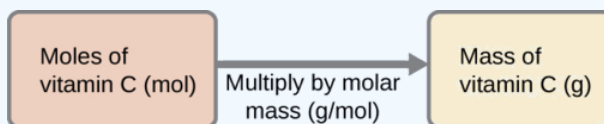
0.073 mol

✓ Example 5.2.8: 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 ($\sim 10^{-4}$ 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:

$$1.42 \times 10^{-4} \text{ mol vitamin C} \left(\frac{176.124 \text{ g}}{\text{mol vitamin C}} \right) = 0.0250 \text{ g vitamin C}$$

This is consistent with the anticipated result.

? Exercise 5.2.8

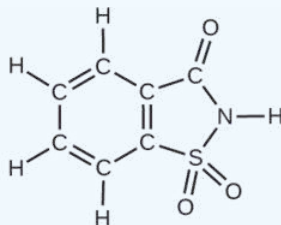
What is the mass of 0.443 mol of hydrazine, N_2H_4 ?

Answer

14.2 g

✓ Example 5.2.9: Deriving the Number of Molecules from the Compound Mass

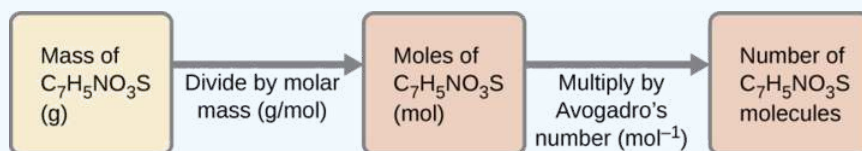
A packet of an artificial sweetener contains 40.0 mg of saccharin ($C_7H_5NO_3S$), which has the structural formula:



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 5.2.8, and then multiplying by Avogadro's number:



Using the provided mass and molar mass for saccharin yields:

$$0.0400 \text{ g } C_7H_5NO_3S \left(\frac{1 \text{ mol } C_7H_5NO_3S}{183.18 \text{ g } C_7H_5NO_3S} \right) \left(\frac{6.022 \times 10^{23} \text{ } C_7H_5NO_3S \text{ molecules}}{1 \text{ mol } C_7H_5NO_3S} \right) = 1.31 \times 10^{20} \text{ } C_7H_5NO_3S \text{ molecules}$$

The compound's formula shows that each molecule contains seven carbon atoms, and so the number of C atoms in the provided sample is:

$$1.31 \times 10^{20} \text{ } C_7H_5NO_3S \text{ molecules} \left(\frac{7 \text{ C atoms}}{1 \text{ } C_7H_5NO_3S \text{ molecule}} \right) = 9.20 \times 10^{21} \text{ C atoms}$$

? Exercise 5.2.9

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 approximately 18 amu and 1 mole of H_2O molecules weighs approximately 18 g).

Footnotes

1. Omiatsek, 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 $6.022 \times 10^{23} \text{ mol}^{-1}$

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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5.3: Determining Empirical and Molecular Formulas

Learning Objectives

- Compute the percent composition of a compound
- Determine the empirical formula of a compound
- Determine the molecular formula of a compound

In the previous section, we discussed the relationship between the bulk mass of a substance and the number of atoms or molecules it contains (moles). Given the chemical formula of the substance, we were able to determine the amount of the substance (moles) from its mass, and vice versa. But what if the chemical formula of a substance is unknown? In this section, we will explore how to apply these very same principles in order to derive the chemical formulas of unknown substances from experimental mass measurements.

Percent Composition

The elemental makeup of a compound defines its chemical identity, and chemical formulas are the most succinct way of representing this elemental makeup. When a compound's formula is unknown, measuring the mass of each of its constituent elements is often the first step in the process of determining the formula experimentally. The results of these measurements permit the calculation of the compound's percent composition, defined as the percentage by mass of each element in the compound. For example, consider a gaseous compound composed solely of carbon and hydrogen. The percent composition of this compound could be represented as follows:

$$\%H = \frac{\text{mass H}}{\text{mass compound}} \times 100\%$$

$$\%C = \frac{\text{mass C}}{\text{mass compound}} \times 100\%$$

If analysis of a 10.0-g sample of this gas showed it to contain 2.5 g H and 7.5 g C, the percent composition would be calculated to be 25% H and 75% C:

$$\%H = \frac{2.5 \text{ g H}}{10.0 \text{ g compound}} \times 100\% = 25\%$$

$$\%C = \frac{7.5 \text{ g C}}{10.0 \text{ g compound}} \times 100\% = 75\%$$

✓ Example 5.3.1: Calculation of Percent Composition

Analysis of a 12.04-g sample of a liquid compound composed of carbon, hydrogen, and nitrogen showed it to contain 7.34 g C, 1.85 g H, and 2.85 g N. What is the percent composition of this compound?

Solution

To calculate percent composition, we divide the experimentally derived mass of each element by the overall mass of the compound, and then convert to a percentage:

$$\%C = \frac{7.34 \text{ g C}}{12.04 \text{ g compound}} \times 100\% = 61.0\%$$

$$\%H = \frac{1.85 \text{ g H}}{12.04 \text{ g compound}} \times 100\% = 15.4\%$$

$$\%N = \frac{2.85 \text{ g N}}{12.04 \text{ g compound}} \times 100\% = 23.7\%$$

The analysis results indicate that the compound is 61.0% C, 15.4% H, and 23.7% N by mass.

? Exercise 5.3.1

A 24.81-g sample of a gaseous compound containing only carbon, oxygen, and chlorine is determined to contain 3.01 g C, 4.00 g O, and 17.81 g Cl. What is this compound's percent composition?

Answer

12.1% C, 16.1% O, 71.8% Cl

Determining Percent Composition from Formula Mass

Percent composition is also useful for evaluating the relative abundance of a given element in different compounds of known formulas. As one example, consider the common nitrogen-containing fertilizers ammonia (NH_3), ammonium nitrate (NH_4NO_3), and urea ($\text{CH}_4\text{N}_2\text{O}$). The element nitrogen is the active ingredient for agricultural purposes, so the mass percentage of nitrogen in the compound is a practical and economic concern for consumers choosing among these fertilizers. For these sorts of applications, the percent composition of a compound is easily derived from its formula mass and the atomic masses of its constituent elements. A molecule of NH_3 contains one N atom weighing 14.01 amu and three H atoms weighing a total of (3×1.008 amu) = 3.024 amu. The formula mass of ammonia is therefore (14.01 amu + 3.024 amu) = 17.03 amu, and its percent composition is:

$$\%N = \frac{14.01 \text{ amu N}}{17.03 \text{ amu NH}_3} \times 100\% = 82.27\%$$

$$\%H = \frac{3.024 \text{ amu H}}{17.03 \text{ amu NH}_3} \times 100\% = 17.76\%$$

This same approach may be taken considering a pair of molecules, a dozen molecules, or a mole of molecules, etc. The latter amount is most convenient and would simply involve the use of molar masses instead of atomic and formula masses, as demonstrated Example 5.3.2. As long as we know the chemical formula of the substance in question, we can easily derive percent composition from the formula mass or molar mass.

✓ Example 5.3.2: Determining Percent Composition from a Molecular Formula

Aspirin is a compound with the molecular formula $\text{C}_9\text{H}_8\text{O}_4$. What is its percent composition?

Solution

To calculate the percent composition, we need to know the masses of C, H, and O in a known mass of $\text{C}_9\text{H}_8\text{O}_4$. It is convenient to consider 1 mol of $\text{C}_9\text{H}_8\text{O}_4$ and use its molar mass (180.159 g/mol, determined from the chemical formula) to calculate the percentages of each of its elements:

$$\begin{aligned} \%C &= \frac{9 \text{ mol C} \times \text{molar mass C}}{\text{molar mass C}_9\text{H}_8\text{O}_4} \times 100 \\ &= \frac{9 \times 12.01 \text{ g/mol}}{180.159 \text{ g/mol}} \times 100 = \frac{108.09 \text{ g/mol}}{180.159 \text{ g/mol}} \times 100 \end{aligned}$$

$$\%C = 60.00\% \text{ C}$$

$$\begin{aligned} \%H &= \frac{8 \text{ mol H} \times \text{molar mass H}}{\text{molar mass C}_9\text{H}_8\text{O}_4} \times 100 \\ &= \frac{8 \times 1.008 \text{ g/mol}}{180.159 \text{ g/mol}} \times 100 = \frac{8.064 \text{ g/mol}}{180.159 \text{ g/mol}} \times 100 \end{aligned}$$

$$\%H = 4.476\% \text{ H}$$

$$\begin{aligned} \%O &= \frac{4 \text{ mol O} \times \text{molar mass O}}{\text{molar mass C}_9\text{H}_8\text{O}_4} \times 100 \\ &= \frac{4 \times 16.00 \text{ g/mol}}{180.159 \text{ g/mol}} \times 100 = \frac{64.00 \text{ g/mol}}{180.159 \text{ g/mol}} \times 100 \end{aligned}$$

$$\%O = 35.52\%$$

Note that these percentages sum to equal 100.00% when appropriately rounded.

? Exercise 5.3.2

To three significant digits, what is the mass percentage of iron in the compound Fe_2O_3 ?

Answer

69.9% Fe

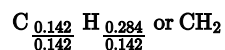
Determination of Empirical Formulas

As previously mentioned, the most common approach to determining a compound's chemical formula is to first measure the masses of its constituent elements. However, we must keep in mind that chemical formulas represent the relative *numbers*, not masses, of atoms in the substance. Therefore, any experimentally derived data involving mass must be used to derive the corresponding numbers of atoms in the compound. To accomplish this, we can use molar masses to convert the mass of each element to a number of moles. We then consider the moles of each element relative to each other, converting these numbers into a whole-number ratio that can be used to derive the empirical formula of the substance. Consider a sample of compound determined to contain 1.71 g C and 0.287 g H. The corresponding numbers of atoms (in moles) are:

$$1.71 \text{ g C} \times \frac{1 \text{ mol C}}{12.01 \text{ g C}} = 0.142 \text{ mol C}$$

$$0.287 \text{ g H} \times \frac{1 \text{ mol H}}{1.008 \text{ g H}} = 0.284 \text{ mol H}$$

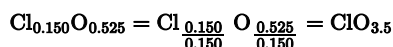
Thus, we can accurately represent this compound with the formula $\text{C}_{0.142}\text{H}_{0.284}$. Of course, per accepted convention, formulas contain whole-number subscripts, which can be achieved by dividing each subscript by the smaller subscript:



(Recall that subscripts of "1" are not written, but rather assumed if no other number is present.)

The empirical formula for this compound is thus CH_2 . This may or not be the compound's *molecular formula* as well; however, we would need additional information to make that determination (as discussed later in this section).

Consider as another example a sample of compound determined to contain 5.31 g Cl and 8.40 g O. Following the same approach yields a tentative empirical formula of:



In this case, dividing by the smallest subscript still leaves us with a decimal subscript in the empirical formula. To convert this into a whole number, we must multiply each of the subscripts by two, retaining the same atom ratio and yielding Cl_2O_7 as the final empirical formula.

Procedure

In summary, empirical formulas are derived from experimentally measured element masses by:

1. Deriving the number of moles of each element from its mass
2. Dividing each element's molar amount by the smallest molar amount to yield subscripts for a tentative empirical formula
3. Multiplying all coefficients by an integer, if necessary, to ensure that the smallest whole-number ratio of subscripts is obtained

Figure 5.3.1 outlines this procedure in flow chart fashion for a substance containing elements A and X.

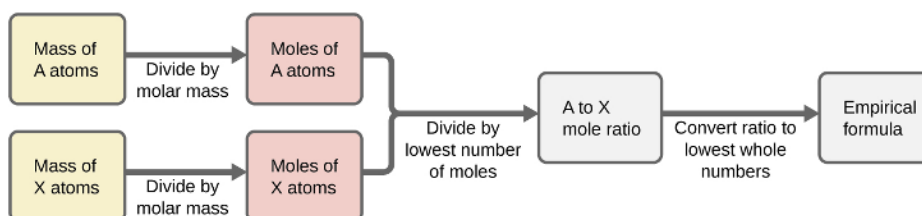


Figure 5.3.1: The empirical formula of a compound can be derived from the masses of all elements in the sample.

A flow chart is shown that is composed of six boxes, two of which are connected together by a right facing arrow and located above two more that are also connected by a right-facing arrow. These two rows of boxes are connected vertically by a line that leads to a right-facing arrow and the last two boxes, connected by a final right facing arrow. The first two upper boxes have the phrases, “Mass of A atoms” and “Moles of A atoms” respectively, while the arrow that connects them has the phrase, “Divide by molar mass,” written below it. The second two bottom boxes have the phrases, “Mass of X atoms” and “Moles of X atoms” respectively, while the arrow that connects them has the phrase, “Divide by molar mass” written below it. The arrow that connects the upper and lower boxes to the last two boxes has the phrase “Divide by lowest number of moles” written below it. The last two boxes have the phrases, “A to X mole ratio” and “Empirical formula” respectively, while the arrow that connects them has the phrase, “Convert ratio to lowest whole numbers” written below it.

✓ Example 5.3.3: Determining an Empirical Formula from Masses of Elements

A sample of the black mineral hematite (Figure 5.3.2), an oxide of iron found in many iron ores, contains 34.97 g of iron and 15.03 g of oxygen. What is the empirical formula of hematite?



Figure 5.3.2: Hematite is an iron oxide that is used in jewelry. (credit: Mauro Cateb)

Solution

For this problem, we are given the mass in grams of each element. Begin by finding the moles of each:

$$34.97 \text{ g Fe} \left(\frac{\text{mol Fe}}{55.85 \text{ g}} \right) = 0.6261 \text{ mol Fe}$$

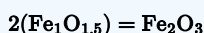
$$15.03 \text{ g O} \left(\frac{\text{mol O}}{16.00 \text{ g}} \right) = 0.9394 \text{ mol O}$$

Next, derive the iron-to-oxygen molar ratio by dividing by the lesser number of moles:

$$\frac{0.6261}{0.6261} = 1.000 \text{ mol Fe}$$

$$\frac{0.9394}{0.6261} = 1.500 \text{ mol O}$$

The ratio is 1.000 mol of iron to 1.500 mol of oxygen ($\text{Fe}_1\text{O}_{1.5}$). Finally, multiply the ratio by two to get the smallest possible whole number subscripts while still maintaining the correct iron-to-oxygen ratio:



The empirical formula is Fe_2O_3 .

? Exercise 5.3.3

What is the empirical formula of a compound if a sample contains 0.130 g of nitrogen and 0.370 g of oxygen?

Answer



Video 5.3.1: Additional worked examples illustrating the derivation of empirical formulas are presented in the brief video clip.

Deriving Empirical Formulas from Percent Composition

Finally, with regard to deriving empirical formulas, consider instances in which a compound's percent composition is available rather than the absolute masses of the compound's constituent elements. In such cases, the percent composition can be used to calculate the masses of elements present in any convenient mass of compound; these masses can then be used to derive the empirical formula in the usual fashion.

✓ Example 5.3.4: Determining an Empirical Formula from Percent Composition

The bacterial fermentation of grain to produce ethanol forms a gas with a percent composition of 27.29% C and 72.71% O (Figure 5.3.3). What is the empirical formula for this gas?



Figure 5.3.3: An oxide of carbon is removed from these fermentation tanks through the large copper pipes at the top. (credit: "Dual Freq"/Wikimedia Commons)

A picture is shown of four copper-colored industrial containers with a large pipe connecting to the top of each one.

Solution

Since the scale for percentages is 100, it is most convenient to calculate the mass of elements present in a sample weighing 100 g. The calculation is "most convenient" because, per the definition for percent composition, the mass of a given element in grams is numerically equivalent to the element's mass percentage. This numerical equivalence results from the definition of the

“percentage” unit, whose name is derived from the Latin phrase *per centum* meaning “by the hundred.” Considering this definition, the mass percentages provided may be more conveniently expressed as fractions:

$$27.29\% \text{ C} = \frac{27.29 \text{ g C}}{100 \text{ g compound}}$$

$$72.71\% \text{ O} = \frac{72.71 \text{ g O}}{100 \text{ g compound}}$$

The molar amounts of carbon and hydrogen in a 100-g sample are calculated by dividing each element’s mass by its molar mass:

$$27.29 \text{ g C} \left(\frac{\text{mol C}}{12.01 \text{ g}} \right) = 2.272 \text{ mol C}$$

$$72.71 \text{ g O} \left(\frac{\text{mol O}}{16.00 \text{ g}} \right) = 4.544 \text{ mol O}$$

Coefficients for the tentative empirical formula are derived by dividing each molar amount by the lesser of the two:

$$\frac{2.272 \text{ mol C}}{2.272} = 1$$

$$\frac{4.544 \text{ mol O}}{2.272} = 2$$

Since the resulting ratio is one carbon to two oxygen atoms, the empirical formula is CO_2 .

? Exercise 5.3.4

What is the empirical formula of a compound containing 40.0% C, 6.71% H, and 53.28% O?

Answer



Derivation of Molecular Formulas

Recall that empirical formulas are symbols representing the *relative* numbers of a compound’s elements. Determining the *absolute* numbers of atoms that compose a single molecule of a covalent compound requires knowledge of both its empirical formula and its molecular mass or molar mass. These quantities may be determined experimentally by various measurement techniques. Molecular mass, for example, is often derived from the mass spectrum of the compound (see discussion of this technique in the previous chapter on atoms and molecules). Molar mass can be measured by a number of experimental methods, many of which will be introduced in later chapters of this text.

Molecular formulas are derived by comparing the compound’s molecular or molar mass to its empirical formula mass. As the name suggests, an empirical formula mass is the sum of the average atomic masses of all the atoms represented in an empirical formula. If we know the molecular (or molar) mass of the substance, we can divide this by the empirical formula mass in order to identify the number of empirical formula units per molecule, which we designate as n :

$$\frac{\text{molecular or molar mass} \left(\text{amu or } \frac{\text{g}}{\text{mol}} \right)}{\text{empirical formula mass} \left(\text{amu or } \frac{\text{g}}{\text{mol}} \right)} = n \text{ formula units/molecule}$$

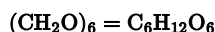
The molecular formula is then obtained by multiplying each subscript in the empirical formula by n , as shown by the generic empirical formula A_xB_y :

Double subscripts: use braces to clarify

For example, consider a covalent compound whose empirical formula is determined to be CH_2O . The empirical formula mass for this compound is approximately 30 amu (the sum of 12 amu for one C atom, 2 amu for two H atoms, and 16 amu for one O atom). If the compound's molecular mass is determined to be 180 amu, this indicates that molecules of this compound contain six times the number of atoms represented in the empirical formula:

$$\frac{180 \text{ amu/molecule}}{30 \frac{\text{amu}}{\text{formula unit}}} = 6 \text{ formula units/molecule}$$

Molecules of this compound are then represented by molecular formulas whose subscripts are six times greater than those in the empirical formula:



Note that this same approach may be used when the molar mass (g/mol) instead of the molecular mass (amu) is used. In this case, we are merely considering one mole of empirical formula units and molecules, as opposed to single units and molecules.

✓ Example 5.3.5: Determination of the Molecular Formula for Nicotine

Nicotine, an alkaloid in the nightshade family of plants that is mainly responsible for the addictive nature of cigarettes, contains 74.02% C, 8.710% H, and 17.27% N. If 40.57 g of nicotine contains 0.2500 mol nicotine, what is the molecular formula?

Solution

Determining the molecular formula from the provided data will require comparison of the compound's empirical formula mass to its molar mass. As the first step, use the percent composition to derive the compound's empirical formula. Assuming a convenient, a 100-g sample of nicotine yields the following molar amounts of its elements:

$$(74.02 \text{ g C}) \left(\frac{1 \text{ mol C}}{12.01 \text{ g C}} \right) = 6.163 \text{ mol C} \quad (5.3.1)$$

$$(8.710 \text{ g H}) \left(\frac{1 \text{ mol H}}{1.01 \text{ g H}} \right) = 8.624 \text{ mol H} \quad (5.3.2)$$

$$(17.27 \text{ g N}) \left(\frac{1 \text{ mol N}}{14.01 \text{ g N}} \right) = 1.233 \text{ mol N} \quad (5.3.3)$$

Next, we calculate the molar ratios of these elements relative to the least abundant element, N.

$$6.163 \text{ mol C} / 1.233 \text{ mol N} = 5$$

$$8.624 \text{ mol H} / 1.233 \text{ mol N} = 7$$

$$1.233 \text{ mol N} / 1.233 \text{ mol N} = 1$$

$$1.233/1.233 = 1.000 \text{ mol N}$$

$$6.163/1.233 = 4.998 \text{ mol C}$$

$$8.624/1.233 = 6.994 \text{ mol H}$$

The C-to-N and H-to-N molar ratios are adequately close to whole numbers, and so the empirical formula is $\text{C}_5\text{H}_7\text{N}$. The empirical formula mass for this compound is therefore 81.13 amu/formula unit, or 81.13 g/mol formula unit.

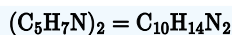
We calculate the molar mass for nicotine from the given mass and molar amount of compound:

$$\frac{40.57 \text{ g nicotine}}{0.2500 \text{ mol nicotine}} = \frac{162.3 \text{ g}}{\text{mol}}$$

Comparing the molar mass and empirical formula mass indicates that each nicotine molecule contains two formula units:

$$\frac{162.3 \text{ g/mol}}{81.13 \frac{\text{g}}{\text{formula unit}}} = 2 \text{ formula units/molecule}$$

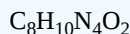
Thus, we can derive the molecular formula for nicotine from the empirical formula by multiplying each subscript by two:



? Exercise 5.3.5

What is the molecular formula of a compound with a percent composition of 49.47% C, 5.201% H, 28.84% N, and 16.48% O, and a molecular mass of 194.2 amu?

Answer



Summary

The chemical identity of a substance is defined by the types and relative numbers of atoms composing its fundamental entities (molecules in the case of covalent compounds, ions in the case of ionic compounds). A compound's percent composition provides the mass percentage of each element in the compound, and it is often experimentally determined and used to derive the compound's empirical formula. The empirical formula mass of a covalent compound may be compared to the compound's molecular or molar mass to derive a molecular formula.

Key Equations

- $\%X = \frac{\text{mass X}}{\text{mass compound}} \times 100\%$
- $\frac{\text{molecular or molar mass (amu or } \frac{\text{g}}{\text{mol}})}{\text{empirical formula mass (amu or } \frac{\text{g}}{\text{mol}})} = n \text{ formula units/molecule}$
- $(\text{A}_x\text{B}_y)_n = \text{A}_{nx}\text{B}_{ny}$

Glossary

percent composition

percentage by mass of the various elements in a compound

empirical formula mass

sum of average atomic masses for all atoms represented in an empirical formula

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5.4: Molarity

Learning Objectives

- Describe the fundamental properties of solutions
- Calculate solution concentrations using molarity
- Perform dilution calculations using the dilution equation

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 5.4.1). In this section, we will describe one of the most common ways in which the relative compositions of mixtures may be quantified.



Figure 5.4.1: 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. 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:

$$M = \frac{\text{mol solute}}{\text{L solution}} \quad (5.4.1)$$

✓ Example 5.4.1: 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:

$$\begin{aligned} M &= \frac{\text{mol solute}}{\text{L solution}} \\ &= \frac{0.133 \text{ mol}}{355 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}}} \\ &= 0.375 \text{ M} \end{aligned}$$

? Exercise 5.4.1

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 5.4.2: 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 5.4.1?

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:

$$M = \frac{\text{mol solute}}{\text{L solution}} \tag{5.4.2}$$

Multiple \label

? Exercise 5.4.2

What volume (mL) of the sweetened tea described in Example 5.4.1 contains the same amount of sugar (mol) as 10 mL of the soft drink in this example?

Answer

80 mL

✓ Example 5.4.3: Calculating Molar Concentrations from the Mass of Solute

Distilled white vinegar (Figure 5.4.2) is a solution of acetic acid, $\text{CH}_3\text{CO}_2\text{H}$, 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 5.4.3: Distilled white vinegar is a solution of acetic acid in water.

A label on a container is shown. The label has a picture of a salad with the words “Distilled White Vinegar,” and, “Reduced with water to 5% acidity,” written above it.

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:

$$M = \frac{\text{mol solute}}{\text{L solution}} = \frac{25.2 \text{ g CH}_3\text{CO}_2\text{H} \times \frac{1 \text{ mol CH}_3\text{CO}_2\text{H}}{60.052 \text{ g CH}_3\text{CO}_2\text{H}}}{0.500 \text{ L solution}} = 0.839 \text{ M} \quad (5.4.3)$$

$$M = \frac{0.839 \text{ mol solute}}{1.00 \text{ L solution}}$$

Nov 29, 2019, 5:24 PM

$$M = \frac{\text{mol solute}}{\text{L solution}} = 0.839 \text{ M} \quad (5.4.4)$$

? Exercise 5.4.3

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 5.4.4: 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 5.4.3:

$$M = \frac{\text{mol solute}}{\text{L solution}} \quad (5.4.5)$$

$$\text{mol solute} = M \times \text{L solution} \quad (5.4.6)$$

$$\text{mol solute} = 5.30 \frac{\text{mol NaCl}}{\text{L}} \times 0.250 \text{ L} = 1.325 \text{ mol NaCl} \quad (5.4.7)$$

Finally, this molar amount is used to derive the mass of NaCl:

$$1.325 \text{ mol NaCl} \times \frac{58.44 \text{ g NaCl}}{\text{mol NaCl}} = 77.4 \text{ g NaCl} \quad (5.4.8)$$

? Exercise 5.4.4

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 5.4.3, it is important to refrain from rounding any intermediate calculation results, which can lead to rounding errors in the final result. In Example 5.4.4, 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 5.4.5). This eliminates intermediate steps so that only the final result is rounded.

✓ Example 5.4.5: Determining the Volume of Solution

In Example 5.4.3, 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:

$$\text{g solute} \times \frac{\text{mol solute}}{\text{g solute}} = \text{mol solute} \quad (5.4.9)$$

Then, use the molarity of the solution to calculate the volume of solution containing this molar amount of solute:

$$\text{mol solute} \times \frac{\text{L solution}}{\text{mol solute}} = \text{L solution} \quad (5.4.10)$$

Combining these two steps into one yields:

$$\text{g solute} \times \frac{\text{mol solute}}{\text{g solute}} \times \frac{\text{L solution}}{\text{mol solute}} = \text{L solution} \quad (5.4.11)$$

$$75.6 \text{ g CH}_3\text{CO}_2\text{H} \left(\frac{\text{mol CH}_3\text{CO}_2\text{H}}{60.05 \text{ g}} \right) \left(\frac{\text{L solution}}{0.839 \text{ mol CH}_3\text{CO}_2\text{H}} \right) = 1.50 \text{ L solution} \quad (5.4.12)$$

? Exercise 5.4.5:

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 5.4.2).

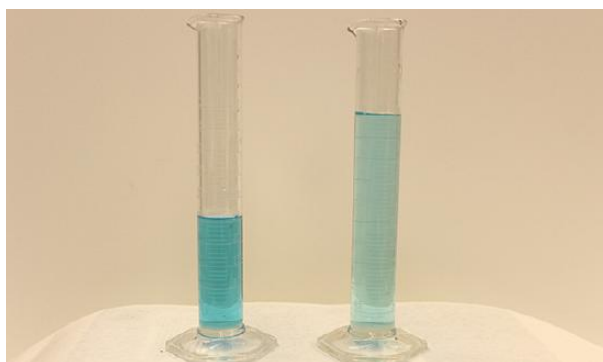


Figure 5.4.2: Both solutions contain the same mass of copper nitrate. The solution on the right is more dilute because the copper nitrate is dissolved in more solvent. (credit: Mark Ott).

This figure shows two graduated cylinders side-by-side. The first has about half as much blue liquid as the second. The blue liquid is darker in the first cylinder than in the second.

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 5.4.3).



Figure 5.4.3: A solution of $KMnO_4$ is prepared by mixing water with 4.74 g of $KMnO_4$ in a flask. (credit: modification of work by Mark Ott)

This figure shows two photos. In the first, there is an empty glass container, 4.75 g of $KMnO_4$ powder on a white circle, and a bottle of distilled water. In the second photo the powder and about half the water have been added to the glass container. The liquid in the glass container is almost black in color.

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:

$$n = ML$$

Expressions like these may be written for a solution before and after it is diluted:

$$n_1 = M_1L_1$$

$$n_2 = M_2L_2$$

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:

$$M_1L_1 = M_2L_2$$

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:

$$C_1V_1 = C_2V_2$$

where C and V are concentration and volume, respectively.

✓ Example 5.4.6: Determining the Concentration of a Diluted Solution

If 0.850 L of a 5.00- M solution of copper nitrate, $\text{Cu}(\text{NO}_3)_2$, 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 :

$$C_1V_1 = C_2V_2$$

$$C_2 = \frac{C_1V_1}{V_2}$$

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:

$$C_2 = \frac{0.850 \text{ L} \times 5.00 \frac{\text{mol}}{\text{L}}}{1.80 \text{ L}} = 2.36 \text{ M}$$

This result compares well to our ballpark estimate (it's a bit less than one-half the stock concentration, 5 M).

? Exercise 5.4.6

What is the concentration of the solution that results from diluting 25.0 mL of a 2.04- M solution of CH_3OH to 500.0 mL?

Answer

0.102 M CH_3OH

✓ Example 5.4.7: 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 :

$$C_1V_1 = C_2V_2$$

$$V_2 = \frac{C_1V_1}{C_2}$$

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:

$$V_2 = \frac{(0.45 \text{ M})(0.011 \text{ L})}{(0.12 \text{ M})}$$

$$V_2 = 0.041 \text{ L}$$

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 5.4.7

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 5.4.8: 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 :

$$C_1 V_1 = C_2 V_2$$

$$V_1 = \frac{C_2 V_2}{C_1}$$

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:

$$V_1 = \frac{(0.100 \text{ M})(5.00 \text{ L})}{1.59 \text{ M}}$$

$$V_1 = 0.314 \text{ L}$$

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 5.4.8

What volume of a 0.575-M solution of glucose, $\text{C}_6\text{H}_{12}\text{O}_6$, can be prepared from 50.00 mL of a 3.00-M glucose solution?

Answer

0.261

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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5.5: Quantitative Chemical Analysis

Learning Objectives

- Describe the fundamental aspects of titrations and gravimetric analysis.
- Perform stoichiometric calculations using typical titration and gravimetric 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, $\text{CH}_3\text{CO}_2\text{H}$, the compound primarily responsible for the odor and taste of vinegar. Acetic acid reacts with potassium carbonate according to the following equation:



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 5.5.1) 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.

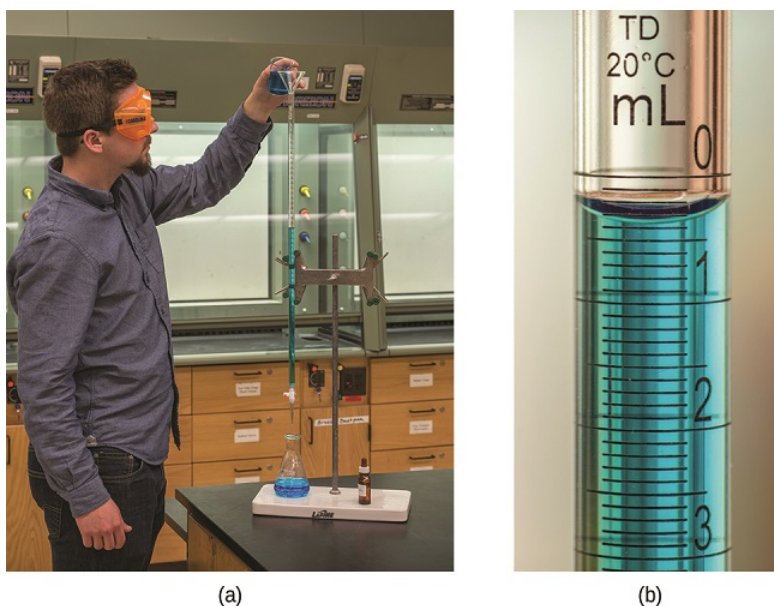
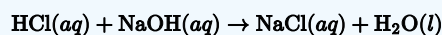


Figure 5.5.1: (a) A student fills a buret in preparation for a titration analysis. (b) A typical buret permits volume measurements to the nearest 0.1 mL. (credit a: modification of work by Mark Blaser and Matt Evans; credit b: modification of work by Mark Blaser and Matt Evans)

Two pictures are shown. In a, a person is shown pouring a liquid from a small beaker into a buret. The person is wearing goggles and gloves as she transfers the solution into the buret. In b, a close up view of the markings on the side of the buret is shown. The markings for 10, 15, and 20 are clearly shown with horizontal rings printed on the buret. Between each of these whole number markings, half markings are also clearly shown with horizontal line segment markings.

✓ Example 5.5.1: 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:

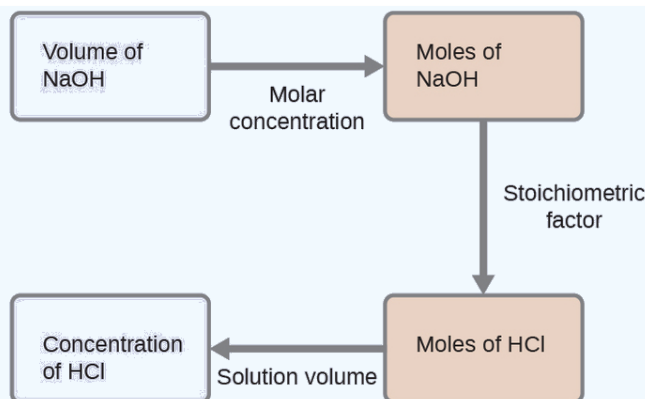


What is the molarity of the HCl?

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:



This figure shows four rectangles. The first is shaded lavender and is labeled, “Volume of N a O H.” This rectangle is followed by an arrow pointing right which is labeled, “Molar concentration,” to a second rectangle. This second rectangle is shaded pink and is labeled, “Moles of N a O H.” This rectangle is followed by an arrow pointing right which is labeled, “Stoichiometric factor,” to a third rectangle which is shaded pink and is labeled, “Moles of H C l.” This rectangle is followed by an arrow labeled, “Solution volume,” which points right to a fourth rectangle. This fourth rectangle is shaded lavender and is labeled, “Concentration of H C l.”

The molar amount of HCl is calculated to be:

$$35.23 \text{ mL NaOH} \times \frac{1 \text{ L}}{1000 \text{ mL}} \times \frac{0.250 \text{ mol NaOH}}{1 \text{ L}} \times \frac{1 \text{ mol HCl}}{1 \text{ mol NaOH}} = 8.81 \times 10^{-3} \text{ mol HCl}$$

Using the provided volume of HCl solution and the definition of molarity, the HCl concentration is:

$$M = \frac{\text{mol HCl}}{\text{L solution}}$$

$$M = \frac{8.81 \times 10^{-3} \text{ mol HCl}}{50.00 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}}}$$

$$M = 0.176 \text{ M}$$

Note: For these types of titration calculations, it is convenient to recognize that solution molarity is also equal to the number of *millimoles* of solute per *milliliter* of solution:

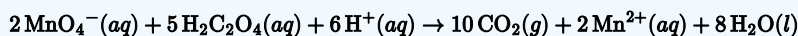
$$M = \frac{\text{mol solute}}{\text{L solution}} \times \frac{\frac{10^3 \text{ mmol}}{\text{mol}}}{\frac{10^3 \text{ mL}}{\text{L}}} = \frac{\text{mmol solute}}{\text{mL solution}}$$

Using this version of the molarity unit will shorten the calculation by eliminating two conversion factors:

$$\frac{35.23 \text{ mL NaOH} \times \frac{0.250 \text{ mmol NaOH}}{\text{mL NaOH}} \times \frac{1 \text{ mmol HCl}}{1 \text{ mmol NaOH}}}{50.00 \text{ mL solution}} = 0.176 \text{ M HCl}$$

? Exercise 5.5.1

A 20.00-mL sample of aqueous oxalic acid, $\text{H}_2\text{C}_2\text{O}_4$, was titrated with a 0.09113-M solution of potassium permanganate, KMnO_4 .



A volume of 23.24 mL was required to reach the end point. What is the oxalic acid molarity?

Answer

0.2648 M

Gravimetric Analysis

A gravimetric analysis is one in which a sample is subjected to some treatment that causes a change in the physical state of the analyte that permits its separation from the other components of the sample. Mass measurements of the sample, the isolated analyte, or some other component of the analysis system, used along with the known stoichiometry of the compounds involved, permit calculation of the analyte concentration. Gravimetric methods were the first techniques used for quantitative chemical analysis, and they remain important tools in the modern chemistry laboratory.

The required change of state in a gravimetric analysis may be achieved by various physical and chemical processes. For example, the moisture (water) content of a sample is routinely determined by measuring the mass of a sample before and after it is subjected to a controlled heating process that evaporates the water. Also common are gravimetric techniques in which the analyte is subjected to a precipitation reaction of the sort described earlier in this chapter. The precipitate is typically isolated from the reaction mixture by filtration, carefully dried, and then weighed (Figure 5.5.2). The mass of the precipitate may then be used, along with relevant stoichiometric relationships, to calculate analyte concentration.

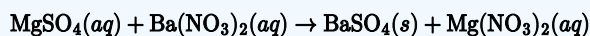


Figure 5.5.2: Precipitate may be removed from a reaction mixture by filtration.

"A photo is shown of a flask and funnel used for filtration. The flask contains a slightly opaque liquid filtrate with a slight yellow tint. A funnel, which contains a bright yellow and orange material, sits atop the flask. The flask is held in place by a clamp and is connected to a vacuum line. The connection between the funnel and flask is sealed with a rubber bung or gasket."

✓ Example 5.5.2: Gravimetric Analysis

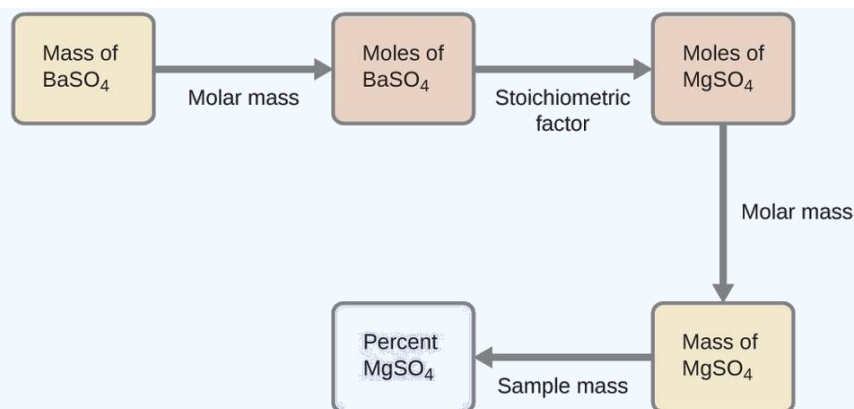
A 0.4550-g solid mixture containing MgSO_4 is dissolved in water and treated with an excess of $\text{Ba}(\text{NO}_3)_2$, resulting in the precipitation of 0.6168 g of BaSO_4 .



What is the concentration (percent) of MgSO_4 in the mixture?

Solution

The plan for this calculation is similar to others used in stoichiometric calculations, the central step being the connection between the moles of BaSO_4 and MgSO_4 through their stoichiometric factor. Once the mass of MgSO_4 is computed, it may be used along with the mass of the sample mixture to calculate the requested percentage concentration.



"This figure shows five rectangles. The first is shaded yellow and is labeled "Mass of B a S O subscript 4." This rectangle is followed by an arrow pointing right to a second rectangle. The arrow is labeled, "Molar mass." The second rectangle is shaded pink and is labeled, "Moles of B a S O subscript 4." This rectangle is followed by an arrow pointing right to a third rectangle. The arrow is labeled, "Stoichiometric factor." This third rectangle is shaded pink and is labeled, "Moles of M g S O subscript 4." This rectangle is followed by an arrow labeled, "Molar mass," which points downward to a fourth rectangle. This fourth rectangle is shaded yellow and is labeled, "Mass of M g S O subscript 4." This rectangle is followed by an arrow labeled, "Sample mass," which points left to a fifth rectangle. This fifth rectangle is shaded lavender and is labeled, "Percent M g S O subscript 4."

The mass of MgSO_4 that would yield the provided precipitate mass is

$$0.6168 \text{ g BaSO}_4 \times \frac{1 \text{ mol BaSO}_4}{233.43 \text{ g BaSO}_4} \times \frac{1 \text{ mol MgSO}_4}{1 \text{ mol BaSO}_4} \times \frac{120.37 \text{ g MgSO}_4}{1 \text{ mol MgSO}_4} = 0.3181 \text{ g MgSO}_4$$

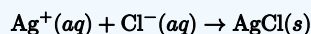
The concentration of MgSO_4 in the sample mixture is then calculated to be

$$\text{percent MgSO}_4 = \frac{\text{mass MgSO}_4}{\text{mass sample}} \times 100\%$$

$$\frac{0.3181 \text{ g}}{0.4550 \text{ g}} \times 100\% = 69.91\%$$

? Exercise 5.5.2

What is the percent of chloride ion in a sample if 1.1324 g of the sample produces 1.0881 g of AgCl when treated with excess Ag^+ ?



Answer

23.76%

Combustion Analysis

The elemental composition of hydrocarbons and related compounds may be determined via a gravimetric method known as combustion analysis. In a combustion analysis, a weighed sample of the compound is heated to a high temperature under a stream of oxygen gas, resulting in its complete combustion to yield gaseous products of known identities. The complete combustion of hydrocarbons, for example, will yield carbon dioxide and water as the only products. The gaseous combustion products are swept through separate, preweighed collection devices containing compounds that selectively absorb each product (Figure 5.5.3). The mass increase of each device corresponds to the mass of the absorbed product and may be used in an appropriate stoichiometric calculation to derive the mass of the relevant element.

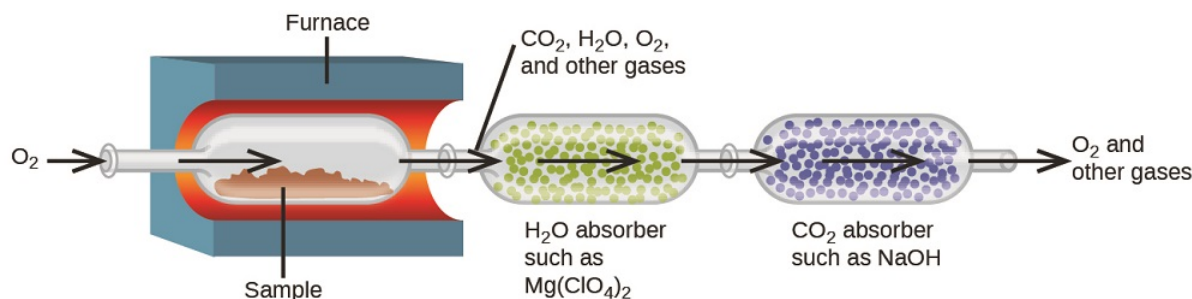


Figure 5.5.3: This schematic diagram illustrates the basic components of a combustion analysis device for determining the carbon and hydrogen content of a sample.

This diagram shows an arrow pointing from O_2 into a tube that leads into a vessel containing a red material, labeled "Sample." This vessel is inside a blue container with a red inner lining which is labeled "Furnace." An arrow points from the tube to the right into the vessel above the red sample material. An arrow leads out of this vessel through a tube into a second vessel outside the furnace. An arrow points from this tube to a label above the diagram that reads " $C O_2$, H_2O , O_2 , and other gases." Many small green spheres are visible in the second vessel which is labeled below, " H_2O absorber such as $Mg(ClO_4)_2$." An arrow points to the right through the vessel, and another arrow points right heading out of the vessel through a tube into a third vessel. The third vessel contains many small blue spheres. It is labeled " CO_2 absorber such as $NaOH$." An arrow points right through this vessel, and a final arrow points out of a tube at the right end of the vessel. Outside the end of this tube at the end of the arrow is the label, " O_2 and other gases."

✓ Example 5.5.3: Combustion Analysis

Polyethylene is a hydrocarbon polymer used to produce food-storage bags and many other flexible plastic items. A combustion analysis of a 0.00126-g sample of polyethylene yields 0.00394 g of CO_2 and 0.00161 g of H_2O . What is the empirical formula of polyethylene?

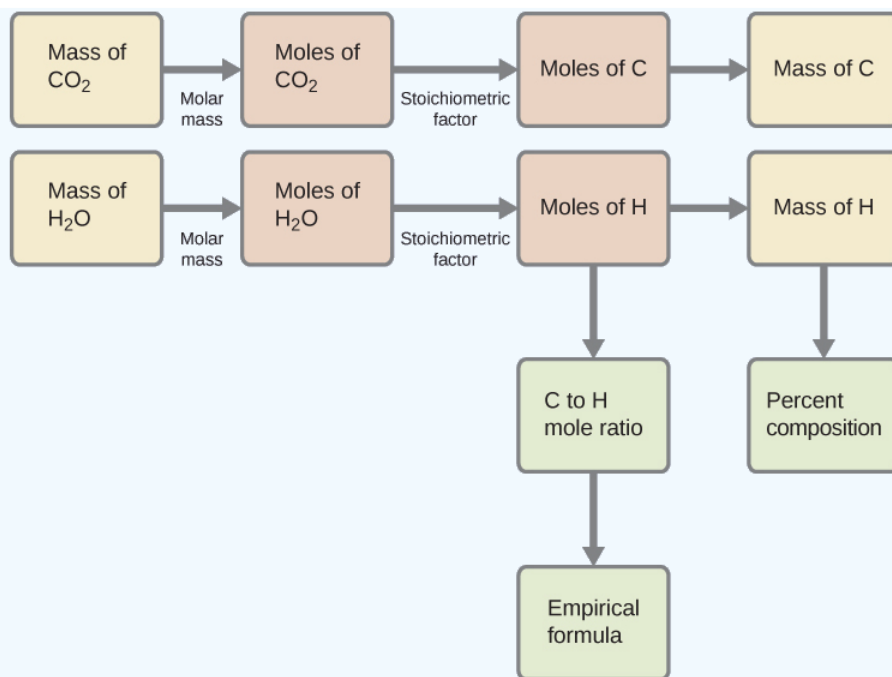
Solution

The primary assumption in this exercise is that all the carbon in the sample combusted is converted to carbon dioxide, and all the hydrogen in the sample is converted to water:

Double subscripts: use braces to clarify

Note that a balanced equation is not necessary for the task at hand. To derive the empirical formula of the compound, only the subscripts x and y are needed.

First, calculate the molar amounts of carbon and hydrogen in the sample, using the provided masses of the carbon dioxide and water, respectively. With these molar amounts, the empirical formula for the compound may be written as described in the previous chapter of this text. An outline of this approach is given in the following flow chart:



This figure shows two flowcharts. The first row is a single flow chart. In this row, a rectangle at the left is shaded yellow and is labeled, “Mass of C O subscript 2.” This rectangle is followed by an arrow pointing right to a second rectangle. The arrow is labeled, “Molar mass.” The second rectangle is shaded pink and is labeled, “Moles of C O subscript 2.” This rectangle is followed by an arrow pointing right to a third rectangle. The arrow is labeled, “Stoichiometric factor.” The third rectangle is shaded pink and is labeled, “Moles of C.” This rectangle is followed by an arrow labeled “Molar mass” which points right to a fourth rectangle. The fourth rectangle is shaded yellow and is labeled “Mass of C.” Below, is a second flowchart. It begins with a yellow shaded rectangle on the left which is labeled, “Mass of H subscript 2 O.” This rectangle is followed by an arrow labeled, “Molar mass,” which points right to a second rectangle. The second rectangle is shaded pink and is labeled, “Moles of H subscript 2 O.” This rectangle is followed by an arrow pointing right to a third rectangle. The arrow is labeled, “Stoichiometric factor.” The third rectangle is shaded pink and is labeled “Moles of H.” This rectangle is followed to the right by an arrow labeled, “Molar mass,” which points to a fourth rectangle. The fourth rectangle is shaded yellow and is labeled “Mass of H.” An arrow labeled, “Sample mass” points down beneath this rectangle to a green shaded rectangle. This rectangle is labeled, “Percent composition.” An arrow extends beneath the pink rectangle labeled, “Moles of H,” to a green shaded rectangle labeled, “C to H mole ratio.” Beneath this rectangle, an arrow extends to a second green shaded rectangle which is labeled, “Empirical formula.”

$$\text{mol C} = 0.00394 \text{ g CO}_2 \times \frac{1 \text{ mol CO}_2}{44.01 \text{ g/mol}} \times \frac{1 \text{ mol C}}{1 \text{ mol CO}_2} = 8.95 \times 10^{-5} \text{ mol C}$$

$$\text{mol H} = 0.00161 \text{ g H}_2\text{O} \times \frac{1 \text{ mol H}_2\text{O}}{18.02 \text{ g/mol}} \times \frac{2 \text{ mol H}}{1 \text{ mol H}_2\text{O}} = 1.79 \times 10^{-4} \text{ mol H}$$

The empirical formula for the compound is then derived by identifying the smallest whole-number multiples for these molar amounts. The H-to-C molar ratio is

$$\frac{\text{mol H}}{\text{mol C}} = \frac{1.79 \times 10^{-4} \text{ mol H}}{8.95 \times 10^{-5} \text{ mol C}} = \frac{2 \text{ mol H}}{1 \text{ mol C}}$$

and the empirical formula for polyethylene is CH₂.

? Exercise 5.5.3

A 0.00215-g sample of polystyrene, a polymer composed of carbon and hydrogen, produced 0.00726 g of CO₂ and 0.00148 g of H₂O in a combustion analysis. What is the empirical formula for polystyrene?

Answer

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

gravimetric analysis

quantitative chemical analysis method involving the separation of an analyte from a sample by a physical or chemical process and subsequent mass measurements of the analyte, reaction product, and/or sample

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

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CHAPTER OVERVIEW

4: Periodicity- The periodic table is an amazing tool to understand the behaviors of elements and compounds

Topic hierarchy

[4.1: Periodic Variations in Element Properties](#)

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4.1: Periodic Variations in Element Properties

Learning Objectives

- Describe and explain the observed trends in atomic size, ionization energy, and electron affinity of the elements

The elements in groups (vertical columns) of the periodic table exhibit similar chemical behavior. This similarity occurs because the members of a group have the same number and distribution of electrons in their valence shells. However, there are also other patterns in chemical properties on the periodic table. For example, as we move down a group, the metallic character of the atoms increases. Oxygen, at the top of Group 16 (6A), is a colorless gas; in the middle of the group, selenium is a semiconducting solid; and, toward the bottom, polonium is a silver-grey solid that conducts electricity.

As we go across a period from left to right, we add a proton to the nucleus and an electron to the valence shell with each successive element. As we go down the elements in a group, the number of electrons in the valence shell remains constant, but the principal quantum number increases by one each time. An understanding of the electronic structure of the elements allows us to examine some of the properties that govern their chemical behavior. These properties vary periodically as the electronic structure of the elements changes. They are (1) size (radius) of atoms and ions, (2) ionization energies, and (3) electron affinities.

Variation in Covalent Radius

The quantum mechanical picture makes it difficult to establish a definite size of an atom. However, there are several practical ways to define the radius of atoms and, thus, to determine their relative sizes that give roughly similar values. We will use the covalent radius (Figure 4.1.1), which is defined as one-half the distance between the nuclei of two identical atoms when they are joined by a covalent bond (this measurement is possible because atoms within molecules still retain much of their atomic identity).

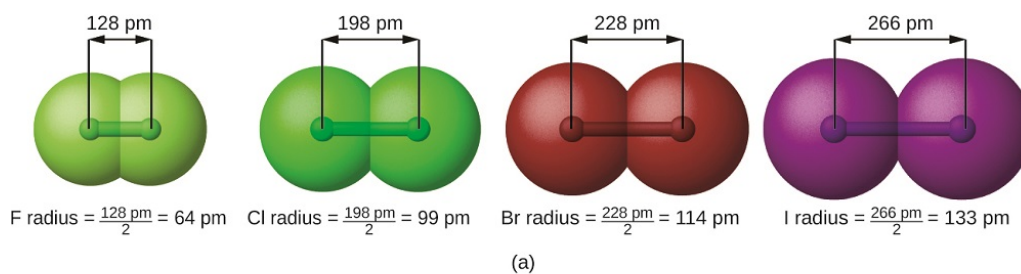
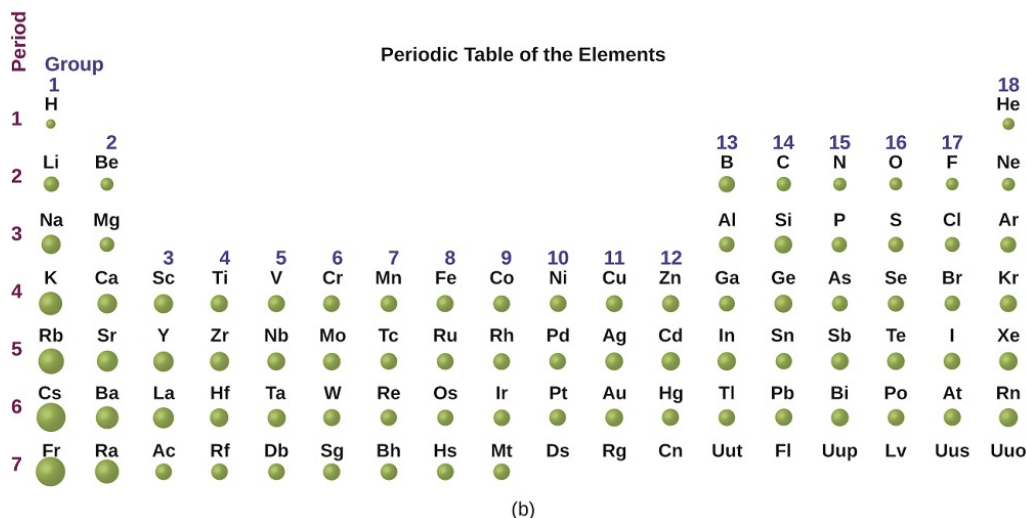


Figure 4.1.1: (a) The radius of an atom is defined as one-half the distance between the nuclei in a molecule consisting of two identical atoms joined by a covalent bond. The atomic radius for the halogens increases down the group as n increases. (b) Covalent radii of the elements are shown to scale. The general trend is that radii increase down a group and decrease across a period.

This figure has two parts: a and b. In figure a, 4 diatomic molecules are shown to illustrate the method of determining the atomic radius of an atom. The first model, in light green, is used to find the F atom radius. Two spheres are pushed very tightly together. The distance between the centers of the two atoms is indicated above the diagram with a double headed arrow labeled, “128 p m.” The endpoints of this arrow connect to line segments that extend to the atomic radii below. Beneath the molecule is the label, “F radius equals 128 p m divided by 2 equals 64 p m.” The next three models are similarly used to show the atomic radii of additional atoms. The second diatomic molecule is in a darker shade of green. The distance between the radii is 198 p m. Beneath the molecule is the label, “C l radius equals 198 p m divided by 2 equals 99 p m.” The third diatomic molecule is in red. The distance between the radii is 228 p m. Beneath the molecule is the label, “B r radius equals 228 p m divided by 2 equals 114 p m.” The fourth diatomic molecule is in purple. The distance between the radii is 266 p m. Beneath the molecule is the label, “I radius equals 266 p m divided by 2 equals 133 p m.” In figure b, a periodic table layout is used to compare relative sizes of atoms using green spheres. No spheres are provided for the noble or inert gas, group 18 elements. General trends noted are increasing circle size moving from top to bottom in a group, with a general tendency toward increasing atomic radii toward the lower left corner of the periodic table.

We know that as we scan down a group, the principal quantum number, n , increases by one for each element. Thus, the electrons are being added to a region of space that is increasingly distant from the nucleus. Consequently, the size of the atom (and its covalent radius) must increase as we increase the distance of the outermost electrons from the nucleus. This trend is illustrated for the covalent radii of the halogens in Table 4.1.1 and Figure 4.1.1. The trends for the entire periodic table can be seen in Figure 4.1.2.

Table 4.1.1: Covalent Radii of the Halogen Group Elements

Atom	Covalent radius (pm)	Nuclear charge
F	64	+9
Cl	99	+17
Br	114	+35
I	133	+53
At	148	+85

As shown in Figure 4.1.2, as we move across a period from left to right, we generally find that each element has a smaller covalent radius than the element preceding it. This might seem counterintuitive because it implies that atoms with more electrons have a smaller atomic radius. This can be explained with the concept of effective nuclear charge, Z_{eff} . This is the pull exerted on a specific electron by the nucleus, taking into account any electron–electron repulsions. For hydrogen, there is only one electron and so the nuclear charge (Z) and the effective nuclear charge (Z_{eff}) are equal. For all other atoms, the inner electrons partially *shield* the outer electrons from the pull of the nucleus, and thus:

$$Z_{\text{eff}} = Z - \text{shielding}$$

Shielding is determined by the probability of another electron being between the electron of interest and the nucleus, as well as by the electron–electron repulsions the electron of interest encounters. Core electrons are adept at shielding, while electrons in the same valence shell do not block the nuclear attraction experienced by each other as efficiently. Thus, each time we move from one element to the next across a period, Z increases by one, but the shielding increases only slightly. Thus, Z_{eff} increases as we move from left to right across a period. The stronger pull (higher effective nuclear charge) experienced by electrons on the right side of the periodic table draws them closer to the nucleus, making the covalent radii smaller.

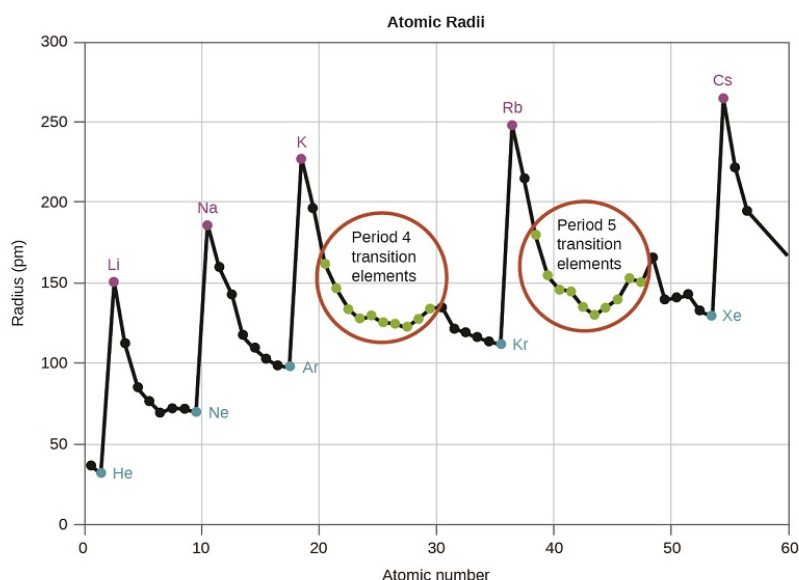


Figure 4.1.2: Within each period, the trend in atomic radius decreases as Z increases; for example, from K to Kr. Within each group (e.g., the alkali metals shown in purple), the trend is that atomic radius increases as Z increases.

This graph is labeled Atomic Number on the horizontal axis and Radius (p m) on the vertical axis. A black jagged line connects the radii values for elements with atomic numbers 1 through 60 on the graph. Peaks are evident at the locations of the alkali metals: L i, N a, K, R b, and C s. Similarly, minima exist at the locations of noble or inert gases: H e, N e, A r, K r, X e, and R n. The locations of period 4 and period 5 transition elements are provided with green dots.

Thus, as we would expect, the outermost or valence electrons are easiest to remove because they have the highest energies, are shielded more, and are farthest from the nucleus. As a general rule, when the representative elements form cations, they do so by the loss of the ns or np electrons that were added last in the Aufbau process. The transition elements, on the other hand, lose the ns electrons before they begin to lose the $(n - 1)d$ electrons, even though the ns electrons are added first, according to the Aufbau principle.

✓ Example 4.1.1: Sorting Atomic Radii

Predict the order of increasing covalent radius for Ge, Fl, Br, Kr.

Solution

Radius increases as we move down a group, so $\text{Ge} < \text{Fl}$ (Note: Fl is the symbol for flerovium, element 114, NOT fluorine). Radius decreases as we move across a period, so $\text{Kr} < \text{Br} < \text{Ge}$. Putting the trends together, we obtain $\text{Kr} < \text{Br} < \text{Ge} < \text{Fl}$.

? Exercise 4.1.1

Give an example of an atom whose size is smaller than fluorine.

Answer

Ne or He

Variation in Ionic Radii

Ionic radius is the measure used to describe the size of an ion. A cation always has fewer electrons and the same number of protons as the parent atom; it is smaller than the atom from which it is derived (Figure 4.1.3). For example, the covalent radius of an aluminum atom ($1s^2 2s^2 2p^6 3s^2 3p^1$) is 118 pm, whereas the ionic radius of an Al^{3+} ($1s^2 2s^2 2p^6$) is 68 pm. As electrons are removed from the outer valence shell, the remaining core electrons occupying smaller shells experience a greater effective nuclear charge Z_{eff} (as discussed) and are drawn even closer to the nucleus.



Figure 4.1.3: The radius for a cation is smaller than the parent atom (Al), due to the lost electrons; the radius for an anion is larger than the parent (S), due to the gained electrons.

The figure includes spheres in green to represent the relative sizes of Al and S atoms. Beneath each of these spheres is a red sphere. The red sphere represents the ionic states of aluminum and sulfur respectively. While radius for the aluminum cation is smaller than aluminum, the sulfur anion has a greater radius than sulfur.

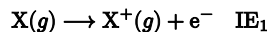
Cations with larger charges are smaller than cations with smaller charges (e.g., V^{2+} has an ionic radius of 79 pm, while that of V^{3+} is 64 pm). Proceeding down the groups of the periodic table, we find that cations of successive elements with the same charge generally have larger radii, corresponding to an increase in the principal quantum number, n .

An anion (negative ion) is formed by the addition of one or more electrons to the valence shell of an atom. This results in a greater repulsion among the electrons and a decrease in Z_{eff} per electron. Both effects (the increased number of electrons and the decreased Z_{eff}) cause the radius of an anion to be larger than that of the parent atom (Figure 4.1.3). For example, a sulfur atom ($[\text{Ne}]3s^2 3p^4$) has a covalent radius of 104 pm, whereas the ionic radius of the sulfide anion ($[\text{Ne}]3s^2 3p^6$) is 170 pm. For consecutive elements proceeding down any group, anions have larger principal quantum numbers and, thus, larger radii.

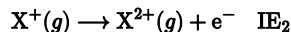
Atoms and ions that have the same electron configuration are said to be isoelectronic. Examples of isoelectronic species are N^{3-} , O^{2-} , F^- , Ne , Na^+ , Mg^{2+} , and Al^{3+} ($1s^2 2s^2 2p^6$). Another isoelectronic series is P^{3-} , S^{2-} , Cl^- , Ar , K^+ , Ca^{2+} , and Sc^{3+} ($[\text{Ne}]3s^2 3p^6$). For atoms or ions that are isoelectronic, the number of protons determines the size. The greater the nuclear charge, the smaller the radius in a series of isoelectronic ions and atoms.

Variation in Ionization Energies

The amount of energy required to remove the most loosely bound electron from a gaseous atom in its ground state is called its first ionization energy (IE_1). The first ionization energy for an element, X, is the energy required to form a cation with +1 charge:



The energy required to remove the second most loosely bound electron is called the second ionization energy (IE_2).



The energy required to remove the third electron is the third ionization energy, and so on. Energy is always required to remove electrons from atoms or ions, so ionization processes are endothermic and IE values are always positive. For larger atoms, the most loosely bound electron is located farther from the nucleus and so is easier to remove. Thus, as size (atomic radius) increases, the

ionization energy should decrease. Relating this logic to what we have just learned about radii, we would expect first ionization energies to decrease down a group and to increase across a period.

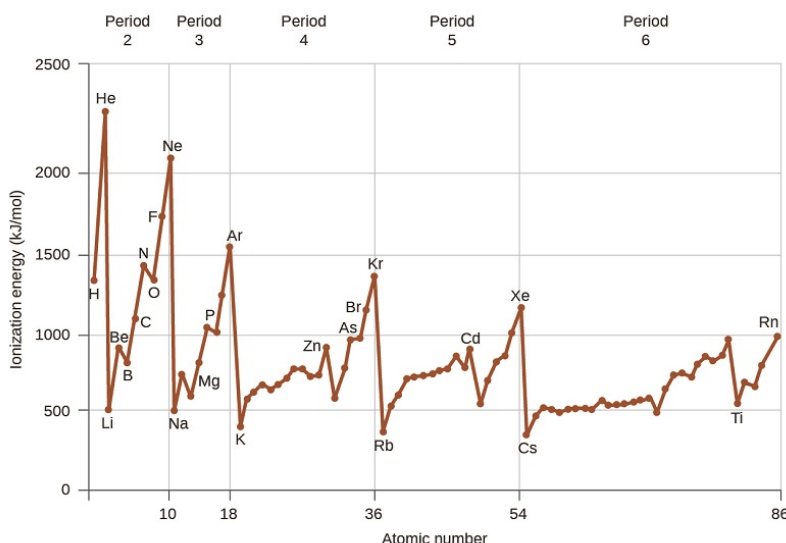


Figure 4.1.4: The first ionization energy of the elements in the first five periods are plotted against their atomic number.

This figure includes Atomic Number on the horizontal axis and, Ionization Energy (kJ divided by mol) on the vertical axis. A red jagged line connects the ionization energies for elements with atomic numbers 1 through 86 on the graph. Peaks are evident at the locations of the noble or inert gases: He, Ne, Ar, Kr, Xe, and Rn. Similarly, minima exist at the locations of the alkali metals: Li, Na, K, Rb, and Cs.

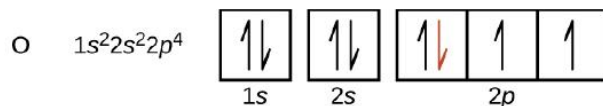
Figure 4.1.4 graphs the relationship between the first ionization energy and the atomic number of several elements. Within a period, the values of first ionization energy for the elements (IE_1) generally increases with increasing Z . Down a group, the IE_1 value generally decreases with increasing Z . There are some systematic deviations from this trend, however. Note that the ionization energy of boron (atomic number 5) is less than that of beryllium (atomic number 4) even though the nuclear charge of boron is greater by one proton. This can be explained because the energy of the subshells increases as l increases, due to penetration and shielding (as discussed previously in this chapter). Within any one shell, the s electrons are lower in energy than the p electrons. This means that an s electron is harder to remove from an atom than a p electron in the same shell. The electron removed during the ionization of beryllium ($[\text{He}]2s^2$) is an s electron, whereas the electron removed during the ionization of boron ($[\text{He}]2s^22p^1$) is a p electron; this results in a lower first ionization energy for boron, even though its nuclear charge is greater by one proton. Thus, we see a small deviation from the predicted trend occurring each time a new subshell begins.

Period		First Ionization Energies of Some Elements (kJ/mol)																	
Group																			
1	2	13	14	15	16	17	18												
1	H 1310						He 2370												
2	Li 520	Be 900						B 800	C 1090	N 1400	O 1310	F 1680	Ne 2080						
3	Na 490	Mg 730						Al 580	Si 780	P 1060	S 1000	Cl 1250	Ar 1520						
4	K 420	Ca 590	Sc 630	Ti 660	V 650	Cr 660	Mn 710	Fe 760	Co 760	Ni 730	Cu 740	Zn 910	Ga 580	Ge 780	As 960	Se 950	Br 1140	Kr 1350	
5	Rb 400	Sr 550	Y 620	Zr 660	Nb 670	Mo 680	Tc 700	Ru 710	Rh 720	Pd 800	Ag 730	Cd 870	In 560	Sn 700	Sb 830	Te 870	I 1010	Xe 1170	
6	Cs 380	Ba 500	La 540	Hf 700	Ta 760	W 770	Re 760	Os 840	Ir 890	Pt 870	Au 890	Hg 1000	Tl 590	Pb 710	Bi 800	Po 810	At ...	Rn 1030	
7	Fr ...	Ra 510																	

Figure 4.1.5: This version of the periodic table shows the first ionization energy of (IE_1), in kJ/mol, of selected elements.

The trends for first ionization energies across periods and down groups are shown in this version of the periodic table.

Another deviation occurs as orbitals become more than one-half filled. The first ionization energy for oxygen is slightly less than that for nitrogen, despite the trend in increasing IE_1 values across a period. Looking at the orbital diagram of oxygen, we can see that removing one electron will eliminate the electron–electron repulsion caused by pairing the electrons in the $2p$ orbital and will result in a half-filled orbital (which is energetically favorable). Analogous changes occur in succeeding periods (note the dip for sulfur after phosphorus in Figure 4.1.4).



The electronic configuration for oxygen is $1s^2 2s^2 2p^4$. An orbital diagram shows 2 squares each filled with a pair of opposite pointing arrows to represent the $1s$ and $2s$ orbitals. Each of the three connected square which represents the $2p$ orbitals are filled with one arrow respectively with the addition of 1 red arrow in the first of the three squares.

Removing an electron from a cation is more difficult than removing an electron from a neutral atom because of the greater electrostatic attraction to the cation. Likewise, removing an electron from a cation with a higher positive charge is more difficult than removing an electron from an ion with a lower charge. Thus, successive ionization energies for one element always increase. As seen in Table 4.1.2, there is a large increase in the ionization energies (color change) for each element. This jump corresponds to removal of the core electrons, which are harder to remove than the valence electrons. For example, Sc and Ga both have three valence electrons, so the rapid increase in ionization energy occurs after the third ionization.

Table 4.1.2: Successive Ionization Energies for Selected Elements (kJ/mol)

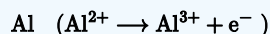
Element	IE_1	IE_2	IE_3	IE_4	IE_5	IE_6	IE_7
K	418.8	3051.8	4419.6	5876.9	7975.5	9590.6	11343
Ca	589.8	1145.4	4912.4	6490.6	8153.0	10495.7	12272.9
Sc	633.1	1235.0	2388.7	7090.6	8842.9	10679.0	13315.0
Ga	578.8	1979.4	2964.6	6180	8298.7	10873.9	13594.8
Ge	762.2	1537.5	3302.1	4410.6	9021.4	Not available	Not available
As	944.5	1793.6	2735.5	4836.8	6042.9	12311.5	Not available

✓ Example 4.1.2: Ranking Ionization Energies

Predict the order of increasing energy for the following processes: IE_1 for Al, IE_1 for Tl, IE_2 for Na, IE_3 for Al.

Solution

Removing the $6p^1$ electron from Tl is easier than removing the $3p^1$ electron from Al because the higher n orbital is farther from the nucleus, so $IE_1(\text{Tl}) < IE_1(\text{Al})$. Ionizing the third electron from



requires more energy because the cation Al^{2+} exerts a stronger pull on the electron than the neutral Al atom, so $IE_1(\text{Al}) < IE_3(\text{Al})$. The second ionization energy for sodium removes a core electron, which is a much higher energy process than removing valence electrons. Putting this all together, we obtain:

$$IE_1(\text{Tl}) < IE_1(\text{Al}) < IE_3(\text{Al}) < IE_2(\text{Na}).$$

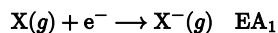
? Exercise 4.1.2

Which has the lowest value for IE_1 : O, Po, Pb, or Ba?

Answer

Variation in Electron Affinities

The electron affinity [EA] is the energy change for the process of adding an electron to a gaseous atom to form an anion (negative ion).



This process can be either endothermic or exothermic, depending on the element. The EA of some of the elements is given in Figure 4.1.6. You can see that many of these elements have negative values of EA, which means that energy is released when the gaseous atom accepts an electron. However, for some elements, energy is required for the atom to become negatively charged and the value of their EA is positive. Just as with ionization energy, subsequent EA values are associated with forming ions with more charge. The second EA is the energy associated with adding an electron to an anion to form a -2 ion, and so on.

Electron Affinity Values for Selected Elements (kJ/mol)

Period	Group 1	Group 2																Group 18
1	H -72																	He +20*
2	Li -60	Be +240*											B -23	C -123	N 0	O -141	F -322	Ne -30
3	Na -53	Mg +230*											Al -44	Si -120	P -74	S -20	Cl -348	Ar +35*
4	K -48	Ca +150*	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga -40*	Ge -115	As -7	Se -195	Br -324	Kr +40*
5	Rb -46	Sr +160*	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In -40*	Sn -121	Sb -101	Te -190	I -295	Xe +40*
6	Cs -45	Ba +50*	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl -50	Pb -101	Bi -101	Po -170	At -270*	Rn +40*
7	Fr	Ra																

* Calculated value

Figure 4.1.6: This version of the periodic table displays the electron affinity values (in kJ/mol) for selected elements.:

The trend for electron affinity values across periods and down groups is shown in this version of the periodic table. Values are not shown for groups 3 to 12 as well as period 7.

As we might predict, it becomes easier to add an electron across a series of atoms as the effective nuclear charge of the atoms increases. We find, as we go from left to right across a period, EAs tend to become more negative. The exceptions found among the elements of group 2 (2A), group 15 (5A), and group 18 (8A) can be understood based on the electronic structure of these groups. The noble gases, group 18 (8A), have a completely filled shell and the incoming electron must be added to a higher n level, which is more difficult to do. Group 2 (2A) has a filled ns subshell, and so the next electron added goes into the higher energy np , so, again, the observed EA value is not as the trend would predict. Finally, group 15 (5A) has a half-filled np subshell and the next electron must be paired with an existing np electron. In all of these cases, the initial relative stability of the electron configuration disrupts the trend in EA.

We also might expect the atom at the top of each group to have the largest EA; their first ionization potentials suggest that these atoms have the largest effective nuclear charges. However, as we move down a group, we see that the second element in the group most often has the greatest EA. The reduction of the EA of the first member can be attributed to the small size of the $n = 2$ shell and the resulting large electron–electron repulsions. For example, chlorine, with an EA value of -348 kJ/mol, has the highest value of any element in the periodic table. The EA of fluorine is -322 kJ/mol. When we add an electron to a fluorine atom to form a fluoride anion (F^{-}), we add an electron to the $n = 2$ shell. The electron is attracted to the nucleus, but there is also significant repulsion from the other electrons already present in this small valence shell. The chlorine atom has the same electron configuration in the valence shell, but because the entering electron is going into the $n = 3$ shell, it occupies a considerably larger region of space and the

electron–electron repulsions are reduced. The entering electron does not experience as much repulsion and the chlorine atom accepts an additional electron more readily.

The properties discussed in this section (size of atoms and ions, effective nuclear charge, ionization energies, and electron affinities) are central to understanding chemical reactivity. For example, because fluorine has an energetically favorable EA and a large energy barrier to ionization (IE), it is much easier to form fluorine anions than cations. Metallic properties including conductivity and malleability (the ability to be formed into sheets) depend on having electrons that can be removed easily. Thus, metallic character increases as we move down a group and decreases across a period in the same trend observed for atomic size because it is easier to remove an electron that is farther away from the nucleus.

Summary

Electron configurations allow us to understand many periodic trends. Covalent radius increases as we move down a group because the n level (orbital size) increases. Covalent radius mostly decreases as we move left to right across a period because the effective nuclear charge experienced by the electrons increases, and the electrons are pulled in tighter to the nucleus. Anionic radii are larger than the parent atom, while cationic radii are smaller, because the number of valence electrons has changed while the nuclear charge has remained constant. Ionization energy (the energy associated with forming a cation) decreases down a group and mostly increases across a period because it is easier to remove an electron from a larger, higher energy orbital. Electron affinity (the energy associated with forming an anion) is more favorable (exothermic) when electrons are placed into lower energy orbitals, closer to the nucleus. Therefore, electron affinity becomes increasingly negative as we move left to right across the periodic table and decreases as we move down a group. For both IE and electron affinity data, there are exceptions to the trends when dealing with completely filled or half-filled subshells.

Glossary

covalent radius

one-half the distance between the nuclei of two identical atoms when they are joined by a covalent bond

effective nuclear charge

charge that leads to the Coulomb force exerted by the nucleus on an electron, calculated as the nuclear charge minus shielding

electron affinity

energy required to add an electron to a gaseous atom to form an anion

ionization energy

energy required to remove an electron from a gaseous atom or ion. The associated number (e.g., second ionization energy) corresponds to the charge of the ion produced (X^{2+})

isoelectronic

group of ions or atoms that have identical electron configurations

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7.1: Writing and Balancing Chemical Equations

Learning Objectives

- Derive chemical equations from narrative descriptions of chemical reactions.
- Write and balance chemical equations in molecular, total ionic, and net ionic formats.

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 7.1.1, with space-filling molecular models shown in the lower half of the figure.

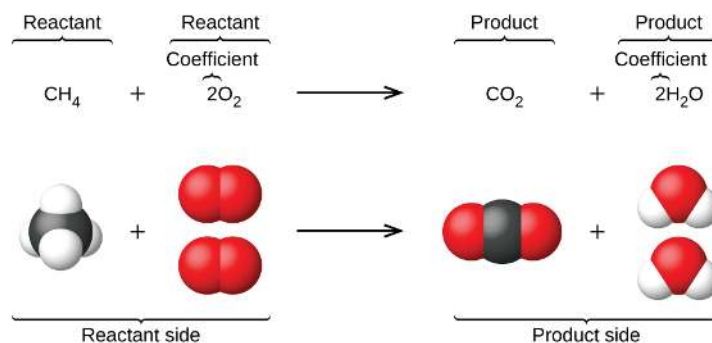


Figure 7.1.1: The reaction between methane and oxygen to yield carbon dioxide and water (shown at bottom) may be represented by a chemical equation using formulas (top).

This figure shows a balanced chemical equation followed below by a representation of the equation using space-filling models. The equation reads C H subscript 4 plus 2 O subscript 2 arrow C O subscript 2 plus 2 H subscript 2 O. Under the C H subscript 4, the molecule is shown with a central black sphere, representing a C atom, to which 4 smaller white spheres, representing H atoms, are distributed evenly around. All four H atoms are bonded to the central black C atom. This is followed by a plus sign. Under the 2 O subscript 2, two molecules are shown. The molecules are each composed of two red spheres bonded together. The red spheres represent O atoms. To the right of an arrow and under the C O subscript 2, appears a single molecule with a black central sphere with two red spheres bonded to the left and right. Following a plus sign and under the 2 H subscript 2 O, are two molecules, each with a central red sphere and two smaller white spheres attached to the lower right and lower left sides of the central red sphere. Note that in space filling models of molecules, spheres appear slightly compressed in regions where there is a bond between two atoms.

This example illustrates the fundamental aspects of any chemical equation:

- The substances undergoing reaction are called reactants, and their formulas are placed on the left side of the equation.
- The substances generated by the reaction are called products, and their formulas are placed on the right side of the equation.
- Plus signs (+) separate individual reactant and product formulas, and an arrow ($\rightarrow$) separates the reactant and product (left and right) sides of the equation.
- 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 7.1.2). 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.

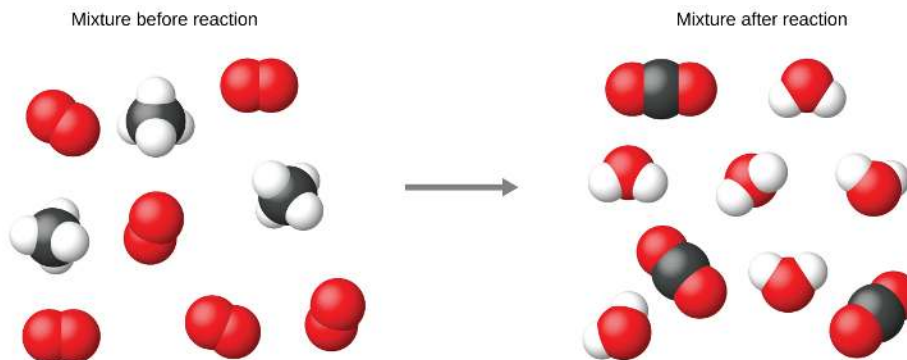


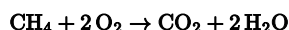
Figure 7.1.2: Regardless of the absolute number of molecules involved, the ratios between numbers of molecules of each species that react (the reactants) and molecules of each species that form (the products) are the same and are given in the chemical equation.

Balancing Equations

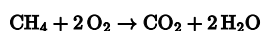
When a chemical equation is balanced it means that equal numbers of atoms for each element involved in the reaction are represented on the reactant and product sides. This is a requirement the equation must satisfy to be consistent with the law of conservation of matter. It may be confirmed by simply 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, CO_2 and H_2O , contain the element oxygen, and so the number of oxygen atoms on the product side of the equation is

$$\left(1 \text{ CO}_2 \text{ molecule} \times \frac{2 \text{ O atoms}}{\text{CO}_2 \text{ molecule}} \right) + \left(2 \text{ H}_2\text{O molecule} \times \frac{1 \text{ O atom}}{\text{H}_2\text{O molecule}} \right) = 4 \text{ O atoms}$$

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:



Equation for the reaction



Element	Reactants	Products	Balanced?
C	$1 \times 1 = 1$	$1 \times 1 = 1$	$1 = 1$, yes
H	$4 \times 1 = 4$	$2 \times 2 = 4$	$4 = 4$, yes
O	$2 \times 2 = 4$	$(1 \times 2) + (2 \times 1) = 4$	$4 = 4$, 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:



Comparing the number of H and O atoms on either side of this equation confirms its imbalance:

Comparisons between H and O atoms

Element	Reactants	Products	Balanced?
H	$1 \times 2 = 2$	$1 \times 2 = 2$	$2 = 2$, yes
O	$1 \times 1 = 1$	$1 \times 2 = 2$	$1 \neq 2$, 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.



O atom balance may be achieved by changing the coefficient for H_2O to 2

Element	Reactants	Products	Balanced?
H	$2 \times 2 = 4$	$1 \times 2 = 2$	$4 \neq 2$, no
O	$2 \times 1 = 2$	$1 \times 2 = 2$	$2 = 2$, yes

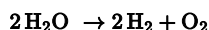
The H atom balance was upset by this change, but it is easily reestablished by changing the coefficient for the H_2 product to 2.



H atom balance upset but easily reestablished by changing the coefficient for the H_2 product to 2.

Element	Reactants	Products	Balanced?
H	$2 \times 2 = 4$	$2 \times 2 = 4$	$4 = 4$, yes
O	$2 \times 1 = 2$	$1 \times 2 = 2$	$2 = 2$, yes

These coefficients yield equal numbers of both H and O atoms on the reactant and product sides, and the balanced equation is, therefore:



✓ Example 7.1.1: 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.



Next, count the number of each type of atom present in the unbalanced equation.

Unbalanced Equation

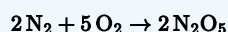
Element	Reactants	Products	Balanced?
N	$1 \times 2 = 2$	$1 \times 2 = 2$	$2 = 2$, yes
O	$1 \times 2 = 2$	$1 \times 5 = 5$	$2 \neq 5$, no

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).



Element	Reactants	Products	Balanced?
N	$1 \times 2 = 2$	$2 \times 2 = 4$	$2 \neq 4$, no
O	$5 \times 2 = 10$	$2 \times 5 = 10$	$10 = 10$, 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.



N atom balance upset but restored by changing the coefficient for the reactant N_2 to 2.

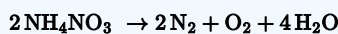
Element	Reactants	Products	Balanced?
N	$2 \times 2 = 4$	$2 \times 2 = 4$	$4 = 4$, yes
O	$5 \times 2 = 10$	$2 \times 5 = 10$	$10 = 10$, yes

The numbers of N and O atoms on either side of the equation are now equal, and so the equation is balanced.

? Exercise 7.1.1

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



Balancing Reactions Which Contain Polyatomics: [Balancing Reactions Which Contain Polyatomics](https://youtu.be/236464)(opens in new window) [youtu.be]

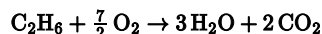
It is sometimes convenient to use fractions instead of integers as intermediate coefficients in the process of balancing a chemical equation. When balance is achieved, all the equation's coefficients may then be multiplied by a whole number to convert the fractional coefficients to integers without upsetting 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:



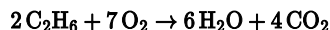
Following the usual inspection approach, one might first balance C and H atoms by changing the coefficients for the two product species, as shown:



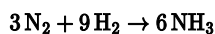
This results in seven O atoms on the product side of the equation, an odd number—no integer coefficient can be used with the O_2 reactant to yield an odd number, so a fractional coefficient, $\frac{7}{2}$, is used instead to yield a provisional balanced equation:



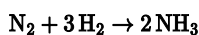
A conventional balanced equation with integer-only coefficients is derived by multiplying each coefficient by 2:



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,



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:

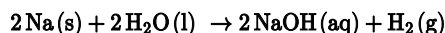


Phet Simulation

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:



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).

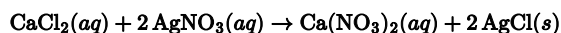
Special conditions necessary for a reaction are sometimes designated by writing a word or symbol above or below the equation's arrow. For example, a reaction carried out by heating may be indicated by the uppercase Greek letter delta (Δ) over the arrow.



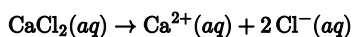
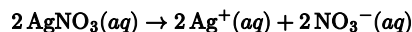
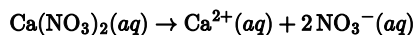
Other examples of these special conditions will be encountered in more depth in later chapters.

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 CaCl_2 and AgNO_3 are mixed, a reaction takes place producing aqueous $\text{Ca}(\text{NO}_3)_2$ and solid AgCl :

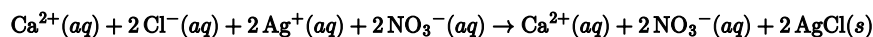


This balanced equation, derived in the usual fashion, is called a molecular equation because it doesn't explicitly represent the ionic species that are present in solution. When ionic compounds dissolve in water, they may *dissociate* into their constituent ions, which are subsequently dispersed homogeneously 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:

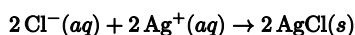


Unlike these three ionic compounds, AgCl does not dissolve in water to a significant extent, as signified by its physical state notation, (s).

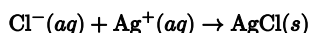
Explicitly representing all dissolved ions results in a complete ionic equation. In this particular case, the formulas for the dissolved ionic compounds are replaced by formulas for their dissociated ions:



Examining this equation shows that two chemical species are present in identical form on both sides of the arrow, $\text{Ca}^{2+}(aq)$ and $\text{NO}_3^{-}(aq)$. 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:



Following the convention of using the smallest possible integers as coefficients, this equation is then written:



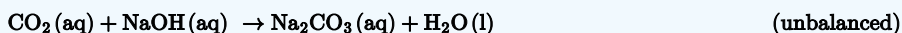
This net ionic equation indicates that solid silver chloride may be produced from dissolved chloride and silver(I) ions, regardless of the source of these ions. These molecular and complete ionic equations provide additional information, namely, the ionic compounds used as sources of Cl^{-} and Ag^{+} .

✓ Example 7.1.2: Molecular and Ionic Equations

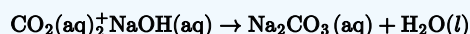
When carbon dioxide is dissolved in an aqueous solution of sodium hydroxide, the mixture reacts to yield aqueous sodium carbonate and liquid water. Write balanced molecular, complete ionic, and net ionic equations for this process.

Solution

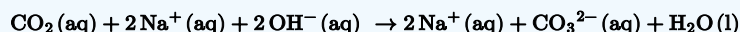
Begin by identifying formulas for the reactants and products and arranging them properly in chemical equation form:



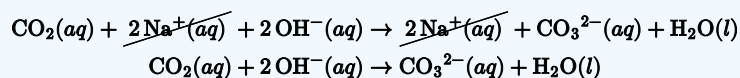
Balance is achieved easily in this case by changing the coefficient for NaOH to 2, resulting in the molecular equation for this reaction:



The two dissolved ionic compounds, NaOH and Na_2CO_3 , can be represented as dissociated ions to yield the complete ionic equation:

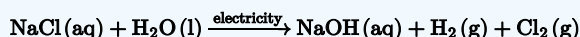


Finally, identify the spectator ion(s), in this case $\text{Na}^{+}(aq)$, and remove it from each side of the equation to generate the net ionic equation:



? Exercise 7.1.2

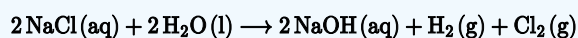
Diatomic chlorine and sodium hydroxide (lye) are commodity chemicals produced in large quantities, along with diatomic hydrogen, via the electrolysis of brine, according to the following unbalanced equation:



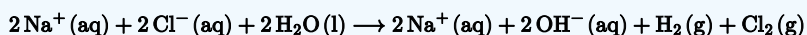
Write balanced molecular, complete ionic, and net ionic equations for this process.

Answer

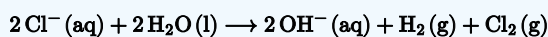
Balanced molecular equation:



Balanced ionic equation:



Balanced net ionic equation:



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

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7.2: Reaction Stoichiometry

Learning Objectives

- Explain the concept of stoichiometry as it pertains to chemical reactions
- Use balanced chemical equations to derive stoichiometric factors relating amounts of reactants and products
- Perform stoichiometric calculations involving mass, moles, and solution molarity

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



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

$$24 \text{ ~~pancakes~~} \times \frac{1 \text{ egg}}{8 \text{ ~~pancakes~~}} = 3 \text{ eggs} \quad (7.2.2)$$

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 that permit computation of the desired quantity. To illustrate this idea, consider the production of ammonia by reaction of hydrogen and nitrogen:



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:

$$\frac{2 \text{NH}_3 \text{ molecules}}{3 \text{H}_2 \text{ molecules}} \text{ or } \frac{2 \text{ doz NH}_3 \text{ molecules}}{3 \text{ doz H}_2 \text{ molecules}} \text{ or } \frac{2 \text{ mol NH}_3 \text{ molecules}}{3 \text{ mol H}_2 \text{ molecules}} \quad (7.2.4)$$

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 7.2.1: Moles of Reactant Required in a Reaction

How many moles of I_2 are required to react with 0.429 mol of Al according to the following equation (see Figure 7.2.2)?



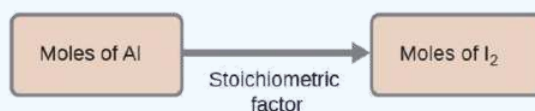


Figure 7.2.1: Aluminum and iodine react to produce aluminum iodide. The heat of the reaction vaporizes some of the solid iodine as a purple vapor. (credit: modification of work by Mark Ott)

Three pictures showing the progression of the reaction between iodine and aluminum. The first diagram shows only a pile of silver powder while the second diagram shows small amount of vapor forming. The final picture shows a large release of purple vapor.

Solution

Referring to the balanced chemical equation, the stoichiometric factor relating the two substances of interest is $\frac{3 \text{ mol } I_2}{2 \text{ mol } Al}$. 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 7.2.1

How many moles of $\text{Ca}(\text{OH})_2$ are required to react with 1.36 mol of H_3PO_4 to produce $\text{Ca}_3(\text{PO}_4)_2$ according to the equation $3 \text{Ca}(\text{OH})_2 + 2 \text{H}_3\text{PO}_4 \rightarrow \text{Ca}_3(\text{PO}_4)_2 + 6 \text{H}_2\text{O}$?

Answer

2.04 mol

✓ Example 7.2.2: 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?



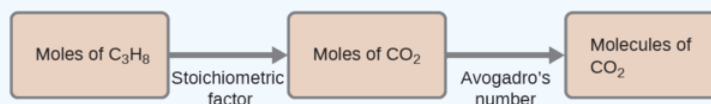
Solution

The approach here is the same as for Example 7.2.1, 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:

$$\frac{3 \text{ mol } \text{CO}_2}{1 \text{ mol } \text{C}_3\text{H}_8} \quad (7.2.7)$$

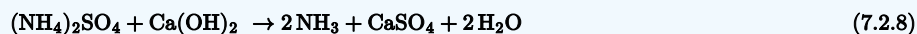
Using this stoichiometric factor, the provided molar amount of propane, and Avogadro's number,



$$\begin{aligned} 0.75 \cancel{\text{mol } \text{C}_3\text{H}_8} &\times \frac{3 \text{ mol } \text{CO}_2}{1 \cancel{\text{mol } \text{C}_3\text{H}_8}} \times \frac{6.022 \times 10^{23} \text{ CO}_2 \text{ molecules}}{1 \cancel{\text{mol } \text{CO}_2}} \\ &= 1.4 \times 10^{24} \text{ CO}_2 \text{ molecules} \end{aligned} \quad (7.2.7)$$

? Exercise 7.2.1

How many NH_3 molecules are produced by the reaction of 4.0 mol of $\text{Ca}(\text{OH})_2$ according to the following equation:



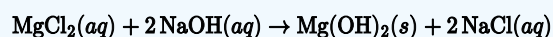
Answer

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.

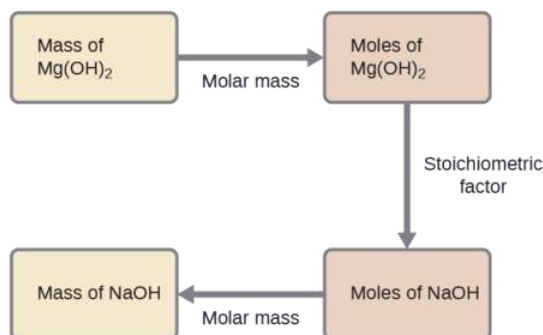
✓ Example 7.2.3: Relating Masses of Reactants and Products

What mass of sodium hydroxide, NaOH , would be required to produce 16 g of the antacid milk of magnesia [magnesium hydroxide, $\text{Mg}(\text{OH})_2$] by the following reaction?



Solution

The approach used previously in Examples 7.2.1 and 7.2.2 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:



$$16 \text{ g Mg}(\text{OH})_2 \times \frac{1 \text{ mol Mg}(\text{OH})_2}{58.3 \text{ g Mg}(\text{OH})_2} \times \frac{2 \text{ mol NaOH}}{1 \text{ mol Mg}(\text{OH})_2} \times \frac{40.0 \text{ g NaOH}}{1 \text{ mol NaOH}} = 22 \text{ g NaOH}$$

? Exercise 7.2.3

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

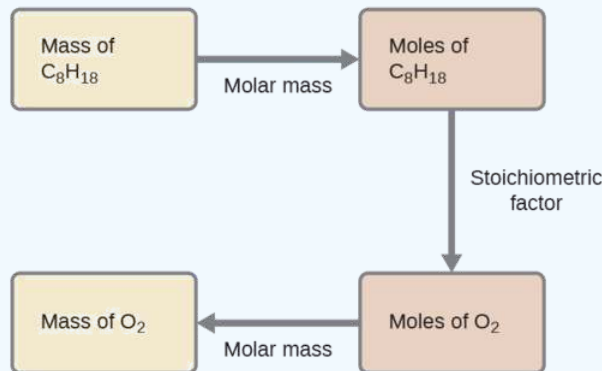
✓ Example 7.2.4: Relating Masses of Reactants

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?



Solution

The approach required here is the same as for the Example 7.2.3, differing only in that the provided and requested masses are both for reactant species.



$$702 \text{ g C}_8\text{H}_{18} \times \frac{1 \text{ mol C}_8\text{H}_{18}}{114.23 \text{ g C}_8\text{H}_{18}} \times \frac{25 \text{ mol O}_2}{2 \text{ mol C}_8\text{H}_{18}} \times \frac{32.00 \text{ g O}_2}{\text{mol O}_2} = 2.46 \times 10^3 \text{ g O}_2$$

? Exercise 7.2.4

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 7.2.2 provides a general outline of the various computational steps associated with many reaction stoichiometry calculations.

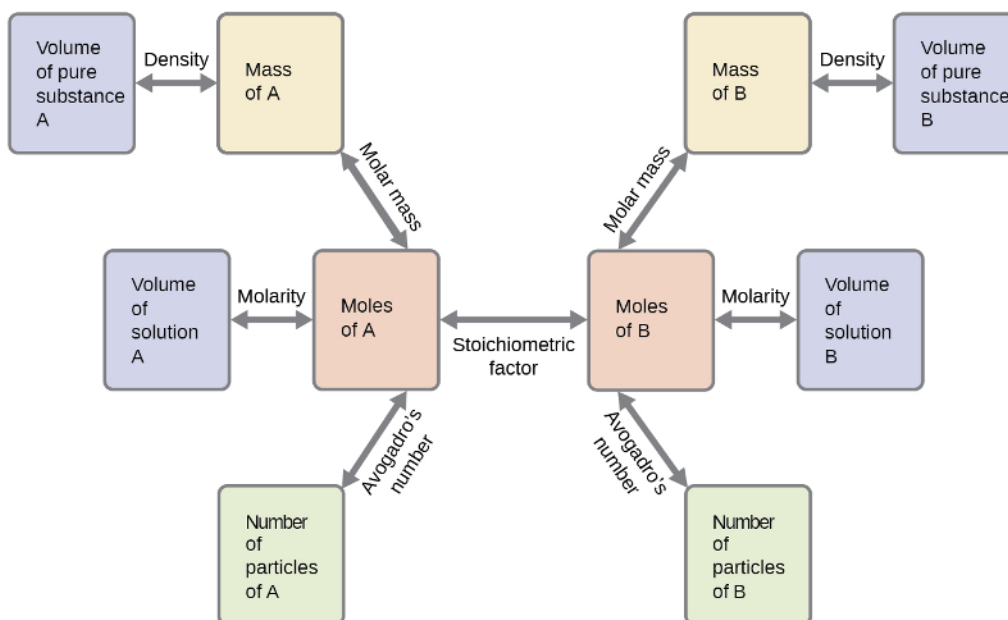
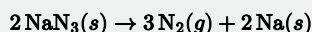


Figure 7.2.2: The flowchart depicts the various computational steps involved in most reaction stoichiometry calculations.

Schematic flowchart showing how density is used for converting volume of pure substance to mass, molar mass for mass and moles, molarity for moles and volume of solution, Avogadro's number for moles and number of particles, and stoichiometric factor for relating moles of one substance to another.

Airbags

Airbags (Figure 7.2.3) are a safety feature provided in most automobiles since the 1990s. The effective operation of an airbag requires that it be rapidly inflated with an appropriate amount (volume) of gas when the vehicle is involved in a collision. This requirement is satisfied in many automotive airbag systems through use of explosive chemical reactions, one common choice being the decomposition of sodium azide, NaN_3 . When sensors in the vehicle detect a collision, an electrical current is passed through a carefully measured amount of NaN_3 to initiate its decomposition:



This reaction is very rapid, generating gaseous nitrogen that can deploy and fully inflate a typical airbag in a fraction of a second ($\sim 0.03\text{--}0.1$ s). Among many engineering considerations, the amount of sodium azide used must be appropriate for generating enough nitrogen gas to fully inflate the air bag and ensure its proper function. For example, a small mass (~ 100 g) of NaN_3 will generate approximately 50 L of N_2 .



Figure 7.2.3: Airbags deploy upon impact to minimize serious injuries to passengers. (credit: Jon Seidman)

Summary

A balanced chemical equation may be used to describe a reaction's stoichiometry (the relationships between amounts of reactants and products). Coefficients from the equation are used to derive stoichiometric factors that subsequently may be used for computations relating reactant and product masses, molar amounts, and other quantitative properties.

Glossary

stoichiometric factor

ratio of coefficients in a balanced chemical equation, used in computations relating amounts of reactants and products

stoichiometry

relationships between the amounts of reactants and products of a chemical reaction

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7.3: Reaction Yields

Learning Objectives

- Explain the concepts of theoretical yield and limiting reactants/reagents.
- Derive the theoretical yield for a reaction under specified conditions.
- Calculate the percent yield for a reaction.

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 7.3.1):



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*.

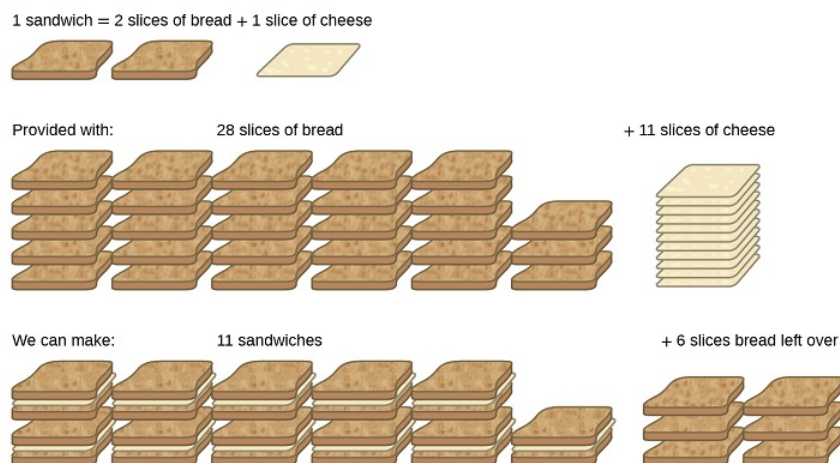
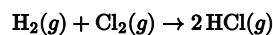


Figure 7.3.1: Sandwich making can illustrate the concepts of limiting and excess reactants.

This figure has three rows showing the ingredients needed to make a sandwich. The first row reads, “1 sandwich = 2 slices of bread + 1 slice of cheese.” Two slices of bread and one slice of cheese are shown. The second row reads, “Provided with: 28 slices of bread + 11 slices of cheese.” There are 28 slices of bread and 11 slices of cheese shown. The third row reads, “We can make: 11 sandwiches + 6 slices of bread left over.” 11 sandwiches are shown with six extra slices of bread.

Consider this concept now with regard to a chemical process, the reaction of hydrogen with chlorine to yield hydrogen chloride:



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 6 moles of H_2 and 4 moles of Cl_2 . 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, the complete reaction of the hydrogen would yield

$$\text{mol HCl produced} = 6 \text{ mol H}_2 \times \frac{2 \text{ mol HCl}}{1 \text{ mol H}_2} = 12 \text{ mol HCl}$$

The complete reaction of the provided chlorine would produce

$$\text{mol HCl produced} = 4 \text{ mol Cl}_2 \times \frac{2 \text{ mol HCl}}{1 \text{ mol Cl}_2} = 8 \text{ mol HCl}$$

The chlorine will be completely consumed once 8 moles of HCl have been produced. Since enough hydrogen was provided to yield 12 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 7.3.2). To determine the amount of excess reactant that remains, the amount of hydrogen consumed in the reaction can be subtracted from the starting quantity of hydrogen.

The amount of hydrogen consumed is

$$\text{mol H}_2 \text{ produced} = 8 \text{ mol HCl} \times \frac{1 \text{ mol H}_2}{2 \text{ mol HCl}} = 4 \text{ mol H}_2$$

Subtract the hydrogen consumed from the starting quantity

$$\text{mole of excess H}_2 = 6 \text{ mol H}_2 \text{ starting} - 4 \text{ mol H}_2 \text{ consumed} = 2 \text{ mol H}_2 \text{ excess}$$

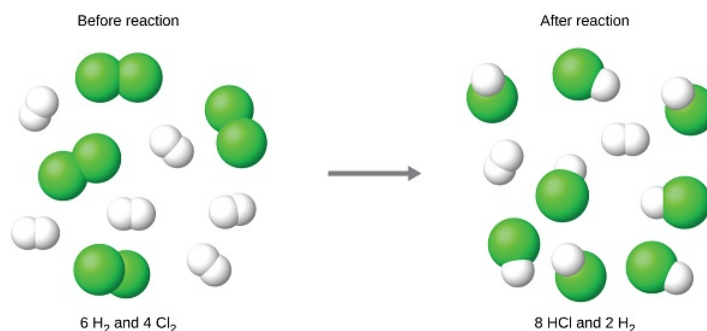
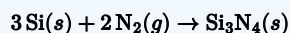


Figure 7.3.2: When H_2 and Cl_2 are combined in nonstoichiometric amounts, one of these reactants will limit the amount of HCl that can be produced. This illustration shows a reaction in which hydrogen is present in excess and chlorine is the limiting reactant.

The figure shows a space-filling molecular models reacting. There is a reaction arrow pointing to the right in the middle. To the left of the reaction arrow there are three molecules each consisting of two green spheres bonded together. There are also five molecules each consisting of two smaller, white spheres bonded together. Above these molecules is the label, "Before reaction," and below these molecules is the label, "6 H subscript 2 and 4 Cl subscript 2." To the right of the reaction arrow, there are eight molecules each consisting of one green sphere bonded to a smaller white sphere. There are also two molecules each consisting of two white spheres bonded together. Above these molecules is the label, "After reaction," and below these molecules is the label, "8 H C l and 2 H subscript 2."

✓ Example 7.3.1: 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:



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.

$$\text{mol Si} = 2.00 \text{ g Si} \times \frac{1 \text{ mol Si}}{28.09 \text{ g Si}} = 0.0712 \text{ mol Si}$$

$$\text{mol N}_2 = 1.50 \text{ g N}_2 \times \frac{1 \text{ mol N}_2}{28.02 \text{ g N}_2} = 0.0535 \text{ mol N}_2$$

The provided Si:N₂ molar ratio is:

$$\frac{0.0712 \text{ mol Si}}{0.0535 \text{ mol N}_2} = \frac{1.33 \text{ mol Si}}{1 \text{ mol N}_2}$$

The stoichiometric Si:N₂ ratio is:

$$\frac{3 \text{ mol Si}}{2 \text{ mol N}_2} = \frac{1.5 \text{ mol Si}}{1 \text{ mol N}_2}$$

Comparing these ratios shows that Si is provided in a less-than-stoichiometric amount, and so is the limiting reactant.

Alternatively, compute the amount of product expected for complete reaction of each of the provided reactants. The 0.0712 moles of silicon would yield

$$\text{mol Si}_3\text{N}_4 \text{ produced} = 0.0712 \text{ mol Si} \times \frac{1 \text{ mol Si}_3\text{N}_4}{3 \text{ mol Si}} = 0.0237 \text{ mol Si}_3\text{N}_4$$

while the 0.0535 moles of nitrogen would produce

$$\text{mol Si}_3\text{N}_4 \text{ produced} = 0.0535 \text{ mol N}_2 \times \frac{1 \text{ mol Si}_3\text{N}_4}{2 \text{ mol N}_2} = 0.0268 \text{ mol Si}_3\text{N}_4$$

Since silicon yields the lesser amount of product, it is the limiting reactant.

? Exercise 7.3.1

Which is the limiting reactant when 5.00 g of H₂ and 10.0 g of O₂ react and form water?

Answer

O₂

Percent Yield

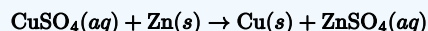
The amount of product that *may be* produced by a reaction under specified conditions, as calculated per the stoichiometry of an appropriate balanced chemical equation, is called the theoretical yield of the reaction. In practice, the amount of product obtained is called the actual yield, and it is often less than the theoretical yield for a number of reasons. Some reactions are inherently inefficient, being accompanied by *side reactions* that generate other products. Others are, by nature, incomplete (consider the partial reactions of weak acids and bases discussed earlier in this text). Some products are difficult to collect without some loss, and so less than perfect recovery will reduce the actual yield. The extent to which a reaction's theoretical yield is achieved is commonly expressed as its percent yield:

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

Actual and theoretical yields may be expressed as masses or molar amounts (or any other appropriate property; e.g., volume, if the product is a gas). As long as both yields are expressed using the same units, these units will cancel when percent yield is calculated.

✓ Example 7.3.2: Calculation of Percent Yield

Upon reaction of 1.274 g of copper sulfate with excess zinc metal, 0.392 g copper metal was obtained according to the equation:



What is the percent yield?

Solution

The provided information identifies copper sulfate as the limiting reactant, and so the theoretical yield is found by the approach illustrated in the previous module, as shown here:

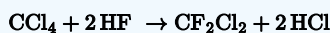
Double subscripts: use braces to clarify

Using this theoretical yield and the provided value for actual yield, the percent yield is calculated to be

$$\begin{aligned}\text{percent yield} &= \left(\frac{\text{actual yield}}{\text{theoretical yield}} \right) \times 100 \\ \text{percent yield} &= \left(\frac{0.392 \text{ g Cu}}{0.5072 \text{ g Cu}} \right) \times 100 \\ &= 77.3\%\end{aligned}$$

? Exercise 7.3.2

What is the percent yield of a reaction that produces 12.5 g of the gas Freon CF_2Cl_2 from 32.9 g of CCl_4 and excess HF?



Answer

48.3%

📌 Green Chemistry and Atom Economy

The purposeful design of chemical products and processes that minimize the use of environmentally hazardous substances and the generation of waste is known as *green chemistry*. Green chemistry is a philosophical approach that is being applied to many areas of science and technology, and its practice is summarized by guidelines known as the “Twelve Principles of Green Chemistry”. One of the 12 principles is aimed specifically at maximizing the efficiency of processes for synthesizing chemical products. The *atom economy* of a process is a measure of this efficiency, defined as the percentage by mass of the final product of a synthesis relative to the masses of *all* the reactants used:

$$\text{atom economy} = \frac{\text{mass of product}}{\text{mass of reactants}} \times 100\%$$

Though the definition of atom economy at first glance appears very similar to that for percent yield, be aware that this property represents a difference in the *theoretical* efficiencies of *different* chemical processes. The percent yield of a given chemical process, on the other hand, evaluates the efficiency of a process by comparing the yield of product actually obtained to the maximum yield predicted by stoichiometry.

The synthesis of the common nonprescription pain medication, ibuprofen, nicely illustrates the success of a green chemistry approach (Figure 7.3.3). First marketed in the early 1960s, ibuprofen was produced using a six-step synthesis that required 514 g of reactants to generate each mole (206 g) of ibuprofen, an atom economy of 40%. In the 1990s, an alternative process was developed by the BHC Company (now BASF Corporation) that requires only three steps and has an atom economy of ~80%, nearly twice that of the original process. The BHC process generates significantly less chemical waste; uses less-hazardous and recyclable materials; and provides significant cost-savings to the manufacturer (and, subsequently, the consumer). In

recognition of the positive environmental impact of the BHC process, the company received the Environmental Protection Agency's Greener Synthetic Pathways Award in 1997.

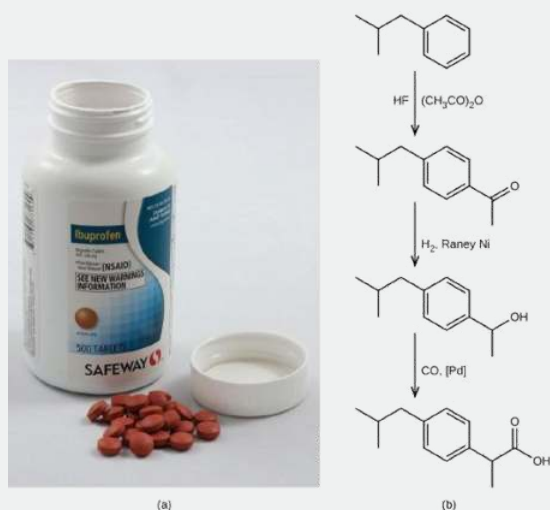


Figure 7.3.3: (a) Ibuprofen is a popular nonprescription pain medication commonly sold as 200 mg tablets. (b) The BHC process for synthesizing ibuprofen requires only three steps and exhibits an impressive atom economy. (credit a: modification of work by Derrick Coetzee)

Summary

When reactions are carried out using less-than-stoichiometric quantities of reactants, the amount of product generated will be determined by the limiting reactant. The amount of product generated by a chemical reaction is its actual yield. This yield is often less than the amount of product predicted by the stoichiometry of the balanced chemical equation representing the reaction (its theoretical yield). The extent to which a reaction generates the theoretical amount of product is expressed as its percent yield.

Key Equations

- percent yield = $\left(\frac{\text{actual yield}}{\text{theoretical yield}} \right) \times 100$

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

percent yield

measure of the efficiency of a reaction, expressed as a percentage of the theoretical yield

theoretical yield

amount of product that may be produced from a given amount of reactant(s) according to the reaction stoichiometry

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CHAPTER OVERVIEW

8: Molecular connectivity. Drawing meaningful pictures of how atoms are connected

Topic hierarchy

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8.2: Strengths of Ionic and Covalent Bonds

8.3: Chemical Formulas

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8.5.1: Hydrocarbons

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8: Molecular connectivity. Drawing meaningful pictures of how atoms are connected is shared under a [not declared](#) license and was authored, remixed, and/or curated by LibreTexts.

8.1: Formal Charges and Resonance

Learning Objectives

- Compute formal charges for atoms in any Lewis structure
- Use formal charges to identify the most reasonable Lewis structure for a given molecule
- Explain the concept of resonance and draw Lewis structures representing resonance forms for a given molecule

Previously, we discussed how to write Lewis structures for molecules and polyatomic ions. In some cases, however, there is seemingly more than one valid structure for a molecule. We can use the concept of formal charges to help us predict the most appropriate Lewis structure when more than one is reasonable.

Calculating Formal Charge

The formal charge of an atom in a molecule is the *hypothetical* charge the atom would have if we could redistribute the electrons in the bonds evenly between the atoms. Another way of saying this is that formal charge results when we take the number of valence electrons of a neutral atom, subtract the nonbonding electrons, and then subtract the number of bonds connected to that atom in the Lewis structure.

Thus, we calculate formal charge as follows:

Misplaced '#'

We can double-check formal charge calculations by determining the sum of the formal charges for the whole structure. The sum of the formal charges of all atoms in a molecule must be zero; the sum of the formal charges in an ion should equal the charge of the ion.

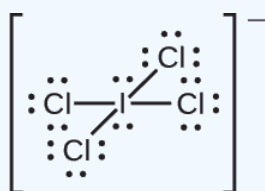
We must remember that the formal charge calculated for an atom is not the *actual* charge of the atom in the molecule. Formal charge is only a useful bookkeeping procedure; it does not indicate the presence of actual charges.

✓ Example 8.1.1: Calculating Formal Charge from Lewis Structures

Assign formal charges to each atom in the interhalogen ion ICl_4^- .

Solution

We divide the bonding electron pairs equally for all $\text{I}-\text{Cl}$ bonds:



We assign lone pairs of electrons to their atoms. Each Cl atom now has seven electrons assigned to it, and the I atom has eight.

Subtract this number from the number of valence electrons for the neutral atom:

- I: $7 - 8 = -1$
- Cl: $7 - 7 = 0$

The sum of the formal charges of all the atoms equals -1 , which is identical to the charge of the ion (-1).

? Exercise 8.1.1

Calculate the formal charge for each atom in the carbon monoxide molecule:



Answer

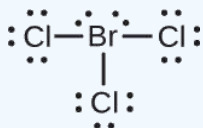
C -1, O +1

✓ Example 8.1.2: Calculating Formal Charge from Lewis Structures

Assign formal charges to each atom in the interhalogen molecule BrCl_3 .

Solution

Assign one of the electrons in each Br–Cl bond to the Br atom and one to the Cl atom in that bond:



Assign the lone pairs to their atom. Now each Cl atom has seven electrons and the Br atom has seven electrons.

Subtract this number from the number of valence electrons for the neutral atom. This gives the formal charge:

- Br: $7 - 7 = 0$
- Cl: $7 - 7 = 0$

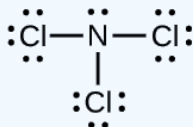
All atoms in BrCl_3 have a formal charge of zero, and the sum of the formal charges totals zero, as it must in a neutral molecule.

? Exercise 8.1.2

Determine the formal charge for each atom in NCl_3 .

Answer

N: 0; all three Cl atoms: 0



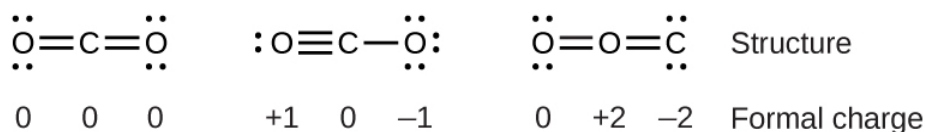
Using Formal Charge to Predict Molecular Structure

The arrangement of atoms in a molecule or ion is called its molecular structure. In many cases, following the steps for writing Lewis structures may lead to more than one possible molecular structure—different multiple bond and lone-pair electron placements or different arrangements of atoms, for instance. A few guidelines involving formal charge can be helpful in deciding which of the possible structures is most likely for a particular molecule or ion.

📌 Predicting Molecular Structure Guidelines

1. A molecular structure in which all formal charges are zero is preferable to one in which some formal charges are not zero.
2. If the Lewis structure must have nonzero formal charges, the arrangement with the smallest nonzero formal charges is preferable.
3. Lewis structures are preferable when adjacent formal charges are zero or of the opposite sign.
4. When we must choose among several Lewis structures with similar distributions of formal charges, the structure with the negative formal charges on the more electronegative atoms is preferable.

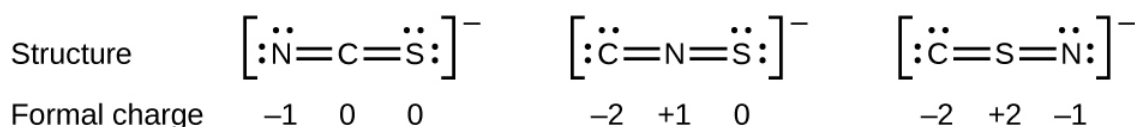
To see how these guidelines apply, let us consider some possible structures for carbon dioxide, CO_2 . We know from our previous discussion that the less electronegative atom typically occupies the central position, but formal charges allow us to understand *why* this occurs. We can draw three possibilities for the structure: carbon in the center and double bonds, carbon in the center with a single and triple bond, and oxygen in the center with double bonds:



Three Lewis structures are shown. The left and right structures show a carbon atom double bonded to two oxygen atoms, each of which has two lone pairs of electrons. The center structure shows a carbon atom that is triple bonded to an oxygen atom with one lone pair of electrons and single bonded to an oxygen atom with three lone pairs of electrons. The third structure shows an oxygen atom double bonded to another oxygen atom with two lone pairs of electrons. The first oxygen atom is also double bonded to a carbon atom with two lone pairs of electrons.

Comparing the three formal charges, we can definitively identify the structure on the left as preferable because it has only formal charges of zero (Guideline 1).

As another example, the thiocyanate ion, an ion formed from a carbon atom, a nitrogen atom, and a sulfur atom, could have three different molecular structures: CNS^- , NCS^- , or CSN^- . The formal charges present in each of these molecular structures can help us pick the most likely arrangement of atoms. Possible Lewis structures and the formal charges for each of the three possible structures for the thiocyanate ion are shown here:

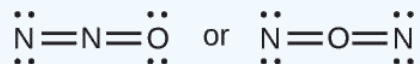


Two rows of structures and numbers are shown. The top row is labeled, "Structure" and depicts three Lewis structures and the bottom row is labeled, "Formal charge." The left structure shows a carbon atom double bonded to a nitrogen atom with two lone electron pairs on one side and double bonded to a sulfur atom with two lone electron pairs on the other. The structure is surrounded by brackets and has a superscripted negative sign. Below this structure are the numbers negative one, zero, and zero. The middle structure shows a carbon atom with two lone pairs of electrons double bonded to a nitrogen atom that is double bonded to a sulfur atom with two lone electron pairs. The structure is surrounded by brackets and has a superscripted negative sign. Below this structure are the numbers negative two, positive one, and zero. The right structure shows a carbon atom with two lone electron pairs double bonded to a sulfur atom that is double bonded to a nitrogen atom with two lone electron pairs. The structure is surrounded by brackets and has a superscripted negative sign. Below this structure are the numbers negative two, positive two, and one.

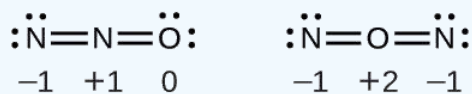
Note that the sum of the formal charges in each case is equal to the charge of the ion (-1). However, the first arrangement of atoms is preferred because it has the lowest number of atoms with nonzero formal charges (Guideline 2). Also, it places the least electronegative atom in the center, and the negative charge on the more electronegative element (Guideline 4).

✓ Example 8.1.3: Using Formal Charge to Determine Molecular Structure

Nitrous oxide, N_2O , commonly known as laughing gas, is used as an anesthetic in minor surgeries, such as the routine extraction of wisdom teeth. Which is the likely structure for nitrous oxide?



Solution Determining formal charge yields the following:



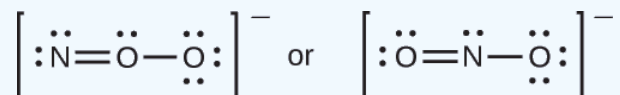
The structure with a terminal oxygen atom best satisfies the criteria for the most stable distribution of formal charge:



The number of atoms with formal charges are minimized (Guideline 2), and there is no formal charge larger than one (Guideline 2). This is again consistent with the preference for having the less electronegative atom in the central position.

? Exercise 8.1.3

Which is the most likely molecular structure for the nitrite (NO_2^-) ion?



Answer



Resonance

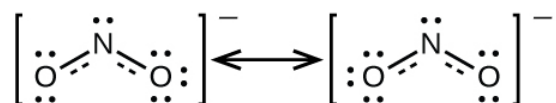
You may have noticed that the nitrite anion in Example 8.1.3 can have two possible structures with the atoms in the same positions. The electrons involved in the N–O double bond, however, are in different positions:



Two Lewis structures are shown. The left structure shows an oxygen atom with three lone pairs of electrons single bonded to a nitrogen atom with one lone pair of electrons that is double bonded to an oxygen with two lone pairs of electrons. Brackets surround this structure, and there is a superscripted negative sign. The right structure shows an oxygen atom with two lone pairs of electrons double bonded to a nitrogen atom with one lone pair of electrons that is single bonded to an oxygen atom with three lone pairs of electrons. Brackets surround this structure, and there is a superscripted negative sign.

If nitrite ions do indeed contain a single and a double bond, we would expect for the two bond lengths to be different. A double bond between two atoms is shorter (and stronger) than a single bond between the same two atoms. Experiments show, however, that both N–O bonds in NO_2^- have the same strength and length, and are identical in all other properties.

It is not possible to write a single Lewis structure for NO_2^- in which nitrogen has an octet and both bonds are equivalent. Instead, we use the concept of resonance: if two or more Lewis structures with the same arrangement of atoms can be written for a molecule or ion, the actual distribution of electrons is an *average* of that shown by the various Lewis structures. The actual distribution of electrons in each of the nitrogen-oxygen bonds in NO_2^- is the average of a double bond and a single bond. We call the individual Lewis structures resonance forms. The actual electronic structure of the molecule (the average of the resonance forms) is called a resonance hybrid of the individual resonance forms. A double-headed arrow between Lewis structures indicates that they are resonance forms. Thus, the electronic structure of the NO_2^- ion is shown as:

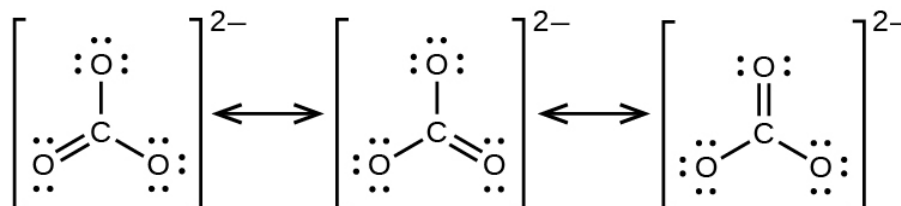


Two Lewis structures are shown with a double headed arrow drawn between them. The left structure shows an oxygen atom with two lone pairs of electrons double bonded to a nitrogen atom with one lone pair of electrons that is single bonded to an oxygen atom with three lone pairs of electrons. Brackets surround this structure, and there is a superscripted negative sign. The right structure shows an oxygen atom with three lone pairs of electrons single bonded to a nitrogen atom with one lone pair of electrons that is double bonded to an oxygen atom with two lone pairs of electrons. Brackets surround this structure, and there is a superscripted negative sign.

We should remember that a molecule described as a resonance hybrid *never* possesses an electronic structure described by either resonance form. It does not fluctuate between resonance forms; rather, the actual electronic structure is *always* the average of that

shown by all resonance forms. George Wheland, one of the pioneers of resonance theory, used a historical analogy to describe the relationship between resonance forms and resonance hybrids. A medieval traveler, having never before seen a rhinoceros, described it as a hybrid of a dragon and a unicorn because it had many properties in common with both. Just as a rhinoceros is neither a dragon sometimes nor a unicorn at other times, a resonance hybrid is neither of its resonance forms at any given time. Like a rhinoceros, it is a real entity that experimental evidence has shown to exist. It has some characteristics in common with its resonance forms, but the resonance forms themselves are convenient, imaginary images (like the unicorn and the dragon).

The carbonate anion, CO_3^{2-} , provides a second example of resonance:



Three Lewis structures are shown with double headed arrows in between. Each structure is surrounded by brackets, and each has a superscripted two negative sign. The left structure depicts a carbon atom bonded to three oxygen atoms. It is single bonded to two of these oxygen atoms, each of which has three lone pairs of electrons, and double bonded to the third, which has two lone pairs of electrons. The double bond is located between the lower left oxygen atom and the carbon atom. The central and right structures are the same as the first, but the position of the double bonded oxygen has moved to the lower right oxygen in the central structure and to the top oxygen in the right structure.

One oxygen atom must have a double bond to carbon to complete the octet on the central atom. All oxygen atoms, however, are equivalent, and the double bond could form from any one of the three atoms. This gives rise to three resonance forms of the carbonate ion. Because we can write three identical resonance structures, we know that the actual arrangement of electrons in the carbonate ion is the average of the three structures. Again, experiments show that all three C–O bonds are exactly the same.

Summary

In a Lewis structure, formal charges can be assigned to each atom by treating each bond as if one-half of the electrons are assigned to each atom. These hypothetical formal charges are a guide to determining the most appropriate Lewis structure. A structure in which the formal charges are as close to zero as possible is preferred. Resonance occurs in cases where two or more Lewis structures with identical arrangements of atoms but different distributions of electrons can be written. The actual distribution of electrons (the resonance hybrid) is an average of the distribution indicated by the individual Lewis structures (the resonance forms).

Key Equations

- Misplaced '#'

Glossary

formal charge

charge that would result on an atom by taking the number of valence electrons on the neutral atom and subtracting the nonbonding electrons and the number of bonds (one-half of the bonding electrons)

molecular structure

arrangement of atoms in a molecule or ion

resonance

situation in which one Lewis structure is insufficient to describe the bonding in a molecule and the average of multiple structures is observed

resonance forms

two or more Lewis structures that have the same arrangement of atoms but different arrangements of electrons

resonance hybrid

average of the resonance forms shown by the individual Lewis structures

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8.2: Strengths of Ionic and Covalent Bonds

Learning Objectives

- Describe the energetics of covalent and ionic bond formation and breakage
- Use the Born-Haber cycle to compute lattice energies for ionic compounds
- Use average covalent bond energies to estimate enthalpies of reaction

A bond's strength describes how strongly each atom is joined to another atom, and therefore how much energy is required to break the bond between the two atoms. In this section, you will learn about the bond strength of covalent bonds, and then compare that to the strength of ionic bonds, which is related to the lattice energy of a compound.

Bond Strength: Covalent Bonds

Stable molecules exist because covalent bonds hold the atoms together. We measure the strength of a covalent bond by the energy required to break it, that is, the energy necessary to separate the bonded atoms. Separating any pair of bonded atoms requires energy; *the stronger a bond, the greater the energy required to break it*. The energy required to break a specific covalent bond in one mole of gaseous molecules is called the bond energy or the bond dissociation energy. The bond energy for a diatomic molecule, D_{X-Y} , is defined as the standard enthalpy change for the endothermic reaction:

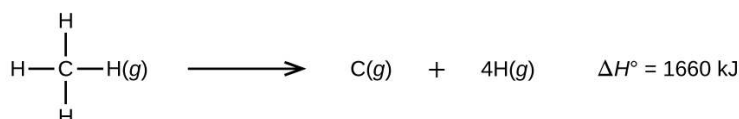


For example, the bond energy of the pure covalent H–H bond, Δ_{H-H} , is 436 kJ per mole of H–H bonds broken:



*Breaking a bond **always** require energy to be added to the molecule. Correspondingly, making a bond **always** releases energy.*

Molecules with three or more atoms have two or more bonds. The sum of all bond energies in such a molecule is equal to the standard enthalpy change for the endothermic reaction that breaks all the bonds in the molecule. For example, the sum of the four C–H bond energies in CH₄, 1660 kJ, is equal to the standard enthalpy change of the reaction:



A reaction is shown with Lewis structures. The first structure shows a carbon atom single bonded to four hydrogen atoms with the symbol, “(g)” written next to it. A right-facing arrow points to the letter “C” and the symbol “(g),” which is followed by a plus sign. Next is the number 4, the letter “H” and the symbol, “(g).” To the right of this equation is another equation: capital delta H superscript degree symbol equals 1660 k J.

The average C–H bond energy, D_{C-H} , is $1660/4 = 415$ kJ/mol because there are four moles of C–H bonds broken per mole of the reaction. Although the four C–H bonds are equivalent in the original molecule, they do not each require the same energy to break; once the first bond is broken (which requires 439 kJ/mol), the remaining bonds are easier to break. The 415 kJ/mol value is the average, not the exact value required to break any one bond.

The strength of a bond between two atoms increases as the number of electron pairs in the bond increases. Generally, as the bond strength increases, the bond length decreases. Thus, we find that triple bonds are stronger and shorter than double bonds between the same two atoms; likewise, double bonds are stronger and shorter than single bonds between the same two atoms. Average bond energies for some common bonds appear in Table 8.2.2, and a comparison of bond lengths and bond strengths for some common bonds appears in Table 8.2.2. When one atom bonds to various atoms in a group, the bond strength typically decreases as we move down the group. For example, C–F is 439 kJ/mol, C–Cl is 330 kJ/mol, and C–Br is 275 kJ/mol.

Table 8.2.1: Bond Energies (kJ/mol)

Bond	Bond Energy		Bond	Bond Energy		Bond	Bond Energy
H-H	436		C-S	260		F-Cl	255
H-C	415		C-Cl	330		F-Br	235
H-N	390		C-Br	275		Si-Si	230
H-O	464		C-I	240		Si-P	215
H-F	569		N-N	160		Si-S	225
H-Si	395		N = N	418		Si-Cl	359
H-P	320		N $\equiv$ N	946		Si-Br	290
H-S	340		N-O	200		Si-I	215
H-Cl	432		N-F	270		P-P	215
H-Br	370		N-P	210		P-S	230
H-I	295		N-Cl	200		P-Cl	330
C-C	345		N-Br	245		P-Br	270
C = C	611		O-O	140		P-I	215
C $\equiv$ C	837		O = O	498		S-S	215
C-N	290		O-F	160		S-Cl	250
C = N	615		O-Si	370		S-Br	215
C $\equiv$ N	891		O-P	350		Cl-Cl	243
C-O	350		O-Cl	205		Cl-Br	220
C = O	741		O-I	200		Cl-I	210
C $\equiv$ O	1080		F-F	160		Br-Br	190
C-F	439		F-Si	540		Br-I	180
C-Si	360		F-P	489		I-I	150
C-P	265		F-S	285			

Table 8.2.2: Average Bond Lengths and Bond Energies for Some Common Bonds

Bond	Bond Length (Å)	Bond Energy (kJ/mol)
C–C	1.54	345
C = C	1.34	611
C ≡ C	1.20	837
C–N	1.43	290
C = N	1.38	615
C ≡ N	1.16	891
C–O	1.43	350
C = O	1.23	741
C ≡ O	1.13	1080

We can use bond energies to calculate approximate enthalpy changes for reactions where enthalpies of formation are not available. Calculations of this type will also tell us whether a reaction is exothermic or endothermic.

- An **exothermic reaction** (ΔH negative, heat produced) results when the bonds in the products are stronger than the bonds in the reactants.
- An **endothermic reaction** (ΔH positive, heat absorbed) results when the bonds in the products are weaker than those in the reactants.

The enthalpy change, ΔH , for a chemical reaction is approximately equal to the sum of the energy required to break all bonds in the reactants (energy “in”, positive sign) plus the energy released when all bonds are formed in the products (energy “out,” negative sign). This can be expressed mathematically in the following way:

$$\Delta H = \sum D_{\text{bonds broken}} - \sum D_{\text{bonds formed}} \quad (8.2.3)$$

In this expression, the symbol Σ means “the sum of” and D represents the bond energy in kilojoules per mole, which is always a positive number. The bond energy is obtained from a table and will depend on whether the particular bond is a single, double, or triple bond. Thus, in calculating enthalpies in this manner, it is important that we consider the bonding in all reactants and products. Because D values are typically averages for one type of bond in many different molecules, this calculation provides a rough estimate, not an exact value, for the enthalpy of reaction.

Consider the following reaction:



or



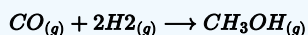
To form two moles of HCl, one mole of H–H bonds and one mole of Cl–Cl bonds must be broken. The energy required to break these bonds is the sum of the bond energy of the H–H bond (436 kJ/mol) and the Cl–Cl bond (243 kJ/mol). During the reaction, two moles of H–Cl bonds are formed (bond energy = 432 kJ/mol), releasing 2×432 kJ; or 864 kJ. Because the bonds in the products are stronger than those in the reactants, the reaction releases more energy than it consumes:

$$\begin{aligned} \Delta H &= \sum D_{\text{bonds broken}} - \sum D_{\text{bonds formed}} \\ &= [D_{\text{H}-\text{H}} + D_{\text{Cl}-\text{Cl}}] - 2D_{\text{H}-\text{Cl}} \\ &= [436 + 243] - 2(432) = -185 \text{ kJ} \end{aligned}$$

This excess energy is released as heat, so the reaction is exothermic. Table T2 gives a value for the standard molar enthalpy of formation of HCl(g) , ΔH_f° , of -92.307 kJ/mol . Twice that value is -184.6 kJ , which agrees well with the answer obtained earlier for the formation of two moles of HCl .

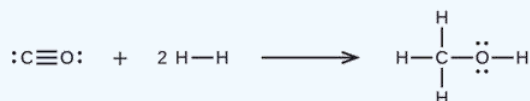
✓ Example 8.2.1: Using Bond Energies to Approximate Enthalpy Changes

Methanol, CH_3OH , may be an excellent alternative fuel. The high-temperature reaction of steam and carbon produces a mixture of the gases carbon monoxide, CO , and hydrogen, H_2 , from which methanol can be produced. Using the bond energies in Table 8.2.2, calculate the approximate enthalpy change, ΔH , for the reaction here:



Solution

First, we need to write the Lewis structures of the reactants and the products:



A set of Lewis diagrams show a chemical reaction. The first structure shows a carbon atom with a lone pair of electrons triple bonded to an oxygen with a lone pair of electrons. To the right of this structure is a plus sign, then the number 2 followed by a hydrogen atom single bonded to a hydrogen atom. To the right of this structure is a right-facing arrow followed by a hydrogen atom single bonded to a carbon atom that is single bonded to two hydrogen atoms and an oxygen atom with two lone pairs of electrons. The oxygen atom is also single bonded to a hydrogen atom.

From this, we see that ΔH for this reaction involves the energy required to break a C–O triple bond and two H–H single bonds, as well as the energy produced by the formation of three C–H single bonds, a C–O single bond, and an O–H single bond. We can express this as follows (via Equation 8.2.3):

$$\begin{aligned} \Delta H &= \sum D_{\text{bonds broken}} - \sum D_{\text{bonds formed}} \\ \Delta H &= [D_{\text{C}\equiv\text{O}} + 2(D_{\text{H}-\text{H}})] - [3(D_{\text{C}-\text{H}}) + D_{\text{C}-\text{O}} + D_{\text{O}-\text{H}}] \end{aligned}$$

Using the bond energy values in Table 8.2.2, we obtain:

$$\begin{aligned} \Delta H &= [1080 + 2(436)] - [3(415) + 350 + 464] \\ &= -107 \text{ kJ} \end{aligned}$$

We can compare this value to the value calculated based on ΔH_f° data from Appendix G:

$$\begin{aligned} \Delta H &= [\Delta H_f^\circ \text{CH}_3\text{OH(g)}] - [\Delta H_f^\circ \text{CO(g)} + 2 \times \Delta H_f^\circ \text{H}_2] \\ &= [-201.0] - [-110.52 + 2 \times 0] \\ &= -90.5 \text{ kJ} \end{aligned}$$

Note that there is a fairly significant gap between the values calculated using the two different methods. This occurs because D values are the *average* of different bond strengths; therefore, they often give only rough agreement with other data.

? Exercise 8.2.1

Ethyl alcohol, $\text{CH}_3\text{CH}_2\text{OH}$, was one of the first organic chemicals deliberately synthesized by humans. It has many uses in industry, and it is the alcohol contained in alcoholic beverages. It can be obtained by the fermentation of sugar or synthesized by the hydration of ethylene in the following reaction:



A set of Lewis structures show a chemical reaction. The first structure shows two carbon atoms that are double bonded together and are each single bonded to two hydrogen atoms. This structure is followed by a plus sign, then an oxygen atom with two lone pairs of electrons single bonded to two hydrogen atoms. A right-facing arrow leads to a carbon atom single bonded to three hydrogen atoms and a second carbon atom. The second carbon atom is single bonded to two hydrogen atoms and an oxygen atom with two lone pairs of electrons. The oxygen atom is single bonded to a hydrogen atom as well.

Using the bond energies in Table 8.2.2, calculate an approximate enthalpy change, ΔH , for this reaction.

Answer

−35 kJ

Ionic Bond Strength and Lattice Energy

An ionic compound is stable because of the electrostatic attraction between its positive and negative ions. The lattice energy of a compound is a measure of the strength of this attraction. The lattice energy ($\Delta H_{\text{lattice}}$) of an ionic compound is defined as the energy required to separate one mole of the solid into its component gaseous ions. For the ionic solid MX, the lattice energy is the enthalpy change of the process:



Note that we are using the convention where the ionic solid is separated into ions, so our lattice energies will be endothermic (positive values). Some texts use the equivalent but opposite convention, defining lattice energy as the energy released when separate ions combine to form a lattice and giving negative (exothermic) values. Thus, if you are looking up lattice energies in another reference, be certain to check which definition is being used. In both cases, a larger magnitude for lattice energy indicates a more stable ionic compound. For sodium chloride, $\Delta H_{\text{lattice}} = 769$ kJ. Thus, it requires 769 kJ to separate one mole of solid NaCl into gaseous Na^+ and Cl^- ions. When one mole each of gaseous Na^+ and Cl^- ions form solid NaCl, 769 kJ of heat is released.

The lattice energy $\Delta H_{\text{lattice}}$ of an ionic crystal can be expressed by the following equation (derived from Coulomb's law, governing the forces between electric charges):

$$\Delta H_{\text{lattice}} = \frac{C(Z^+)(Z^-)}{R_o} \quad (8.2.7)$$

in which

- C is a constant that depends on the type of crystal structure;
- Z^+ and Z^- are the charges on the ions; and
- R_o is the interionic distance (the sum of the radii of the positive and negative ions).

Thus, the lattice energy of an ionic crystal increases rapidly as the charges of the ions increase and the sizes of the ions decrease. When all other parameters are kept constant, doubling the charge of both the cation and anion quadruples the lattice energy. For example, the lattice energy of LiF (Z^+ and $Z^- = 1$) is 1023 kJ/mol, whereas that of MgO (Z^+ and $Z^- = 2$) is 3900 kJ/mol (R_o is nearly the same—about 200 pm for both compounds).

Different interatomic distances produce different lattice energies. For example, we can compare the lattice energy of MgF_2 (2957 kJ/mol) to that of MgI_2 (2327 kJ/mol) to observe the effect on lattice energy of the smaller ionic size of F^- as compared to I^- .

✓ Example 8.2.2: Lattice Energy Comparisons

The precious gem ruby is aluminum oxide, Al_2O_3 , containing traces of Cr^{3+} . The compound Al_2Se_3 is used in the fabrication of some semiconductor devices. Which has the larger lattice energy, Al_2O_3 or Al_2Se_3 ?

Solution

In these two ionic compounds, the charges Z^+ and Z^- are the same, so the difference in lattice energy will mainly depend upon R_0 . The O^{2-} ion is smaller than the Se^{2-} ion. Thus, Al_2O_3 would have a shorter interionic distance than Al_2Se_3 , and Al_2O_3 would have the larger lattice energy.

? Exercise 8.2.2

Zinc oxide, ZnO, is a very effective sunscreen. How would the lattice energy of ZnO compare to that of NaCl?

Answer

ZnO would have the larger lattice energy because the Z values of both the cation and the anion in ZnO are greater, and the interionic distance of ZnO is smaller than that of NaCl.

The Born-Haber Cycle

It is not possible to measure lattice energies directly. However, the lattice energy can be calculated using the equation given in the previous section or by using a thermochemical cycle. The Born-Haber cycle is an application of Hess's law that breaks down the formation of an ionic solid into a series of individual steps:

- ΔH_f° , the standard enthalpy of formation of the compound
- IE , the ionization energy of the metal
- EA , the electron affinity of the nonmetal
- ΔH_s° , the enthalpy of sublimation of the metal
- D , the bond dissociation energy of the nonmetal
- $\Delta H_{\text{lattice}}$, the lattice energy of the compound

Figure 8.2.1 diagrams the Born-Haber cycle for the formation of solid cesium fluoride.

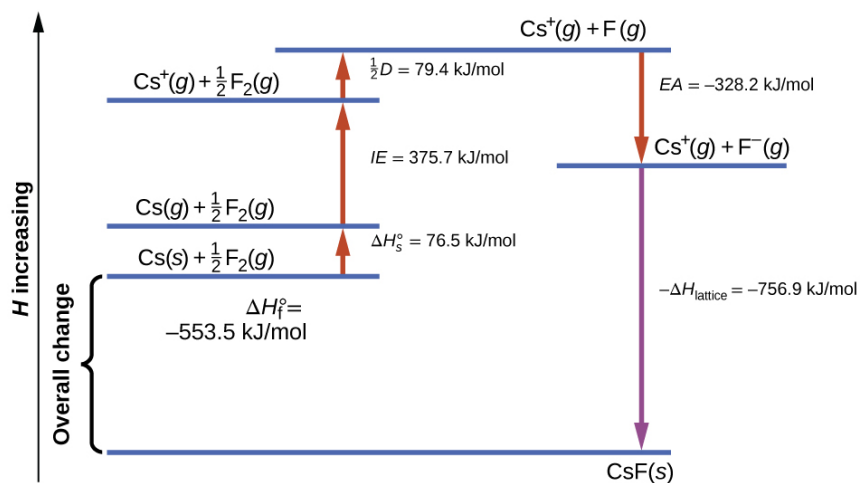


Figure 8.2.1: The Born-Haber cycle shows the relative energies of each step involved in the formation of an ionic solid from the necessary elements in their reference states.

A diagram is shown. An upward facing arrow is drawn to the far left of the chart and is labeled “H increasing.” A horizontal line is drawn at the bottom of the chart. A downward-facing, vertical arrow to the left side of this line is labeled, “Overall change.” Beside this arrow is another label, “capital delta H subscript f, equals negative 553.5 k J per mol, (Enthalpy of formation).” Three horizontal lines, one above the other, and all above the bottom line, are labeled, from bottom to top, as: “C s (s), plus sign, one half F subscript 2, (g),” “C s (g), plus sign, one half F subscript 2, (g),” and “C s, superscript positive sign, (g), plus sign, one half F subscript 2, (g).” Each of these lines is connected by an upward-facing vertical arrow. Each arrow is labeled, “capital delta H subscript 1, equals 76.5 k J per mol, (Enthalpy of sublimation),” “capital delta H subscript 2, equals 375.7 k J per mol, (ionization energy),” and “capital delta H subscript 3 equals 79.4 k J / mol (one half dissociation energy).” Another horizontal line is drawn in the center top portion of the diagram and is labeled “C s, superscript positive sign, (g), plus sign, F, (g).” There is one more horizontal line drawn to the right of the overall diagram and located halfway down the image. An arrow connects the top line to this line and is labeled, “capital delta H equals negative 328.2 k J / mol (electron affinity).” The line is labeled, “C s superscript positive sign (g) plus F superscript negative sign (g).” The arrow connecting this line to the bottom line is labeled, “negative capital delta H subscript lattice equals negative 756.9 k J / mol.” The arrow points to a label on the bottom line which reads, “C s F (s).”

We begin with the elements in their most common states, Cs(s) and F₂(g). The ΔH_s° represents the conversion of solid cesium into a gas, and then the ionization energy converts the gaseous cesium atoms into cations. In the next step, we account for the energy required to break the F–F bond to produce fluorine atoms. Converting one mole of fluorine atoms into fluoride ions is an exothermic process, so this step gives off energy (the electron affinity) and is shown as decreasing along the y-axis. We now have one mole of Cs cations and one mole of F anions. These ions combine to produce solid cesium fluoride. The enthalpy change in this step is the negative of the lattice energy, so it is also an exothermic quantity. The total energy involved in this conversion is equal to the experimentally determined enthalpy of formation, ΔH_f° , of the compound from its elements. In this case, the overall change is exothermic.

Hess’s law can also be used to show the relationship between the enthalpies of the individual steps and the enthalpy of formation. Table 8.2.3 shows this for cesium fluoride, CsF.

Table 8.2.3: Enthalpies of Select Transitions

Enthalpy of sublimation of Cs(s)	$\text{Cs(s)} \rightarrow \text{Cs(g)} \quad \Delta H = \Delta H_s^\circ = 77 \text{ kJ/mol}$
One-half of the bond energy of F ₂	$\frac{1}{2}\text{F}_2(\text{g}) \rightarrow \text{F(g)} \quad \Delta H = \frac{1}{2}D = 79 \text{ kJ/mol}$
Ionization energy of Cs(g)	$\text{Cs(g)} \rightarrow \text{Cs}^+(\text{g}) + \text{e}^- \quad \Delta H = IE = 376 \text{ kJ/mol}$
Negative of the electron affinity of F	$\text{F(g)} + \text{e}^- \rightarrow \text{F}^-(\text{g}) \quad \Delta H = -EA = -328 \text{ kJ/mol}$
Negative of the lattice energy of CsF(s)	$\text{Cs}^+(\text{g}) + \text{F}^-(\text{g}) \rightarrow \text{CsF(s)} \quad \Delta H = -\Delta H_{\text{lattice}} = ?$
Enthalpy of formation of CsF(s), add steps 1–5	$\Delta H = \Delta H_f^\circ = \Delta H_s^\circ + \frac{1}{2}D + IE + (-EA) + (-\Delta H_{\text{lattice}})$ $\text{Cs(s)} + \frac{1}{2}\text{F}_2(\text{g}) \rightarrow \text{CsF(s)} = -554 \text{ kJ/mol}$

Thus, the lattice energy can be calculated from other values. For cesium chloride, using this data, the lattice energy is:

$$\Delta H_{\text{lattice}} = (411 + 109 + 122 + 496 + 368) \text{ kJ} = 770 \text{ kJ}$$

The Born-Haber cycle may also be used to calculate any one of the other quantities in the equation for lattice energy, provided that the remainder is known. For example, if the relevant enthalpy of sublimation ΔH_g° , ionization energy (IE), bond dissociation enthalpy (D), lattice energy $\Delta H_{\text{lattice}}$, and standard enthalpy of formation ΔH_f° are known, the Born-Haber cycle can be used to determine the electron affinity of an atom.

Lattice energies calculated for ionic compounds are typically much larger than bond dissociation energies measured for covalent bonds. Whereas lattice energies typically fall in the range of 600–4000 kJ/mol (some even higher), covalent bond dissociation energies are typically between 150–400 kJ/mol for single bonds. Keep in mind, however, that these are not directly comparable values. For ionic compounds, lattice energies are associated with many interactions, as cations and anions pack together in an extended lattice. For covalent bonds, the bond dissociation energy is associated with the interaction of just two atoms.

Summary

The strength of a covalent bond is measured by its bond dissociation energy, that is, the amount of energy required to break that particular bond in a mole of molecules. Multiple bonds are stronger than single bonds between the same atoms. The enthalpy of a reaction can be estimated based on the energy input required to break bonds and the energy released when new bonds are formed. For ionic bonds, the lattice energy is the energy required to separate one mole of a compound into its gas phase ions. Lattice energy increases for ions with higher charges and shorter distances between ions. Lattice energies are often calculated using the Born-Haber cycle, a thermochemical cycle including all of the energetic steps involved in converting elements into an ionic compound.

Key Equations

- Bond energy for a diatomic molecule: $\text{XY}(g) \rightarrow \text{X}(g) + \text{Y}(g) \quad D_{\text{X-Y}} = \Delta H^\circ$
- Enthalpy change: $\Delta H = \sum D_{\text{bonds broken}} - \sum D_{\text{bonds formed}}$
- Lattice energy for a solid MX: $\text{MX}(s) \rightarrow \text{M}^{n+}(g) + \text{X}^{n-}(g) \quad \Delta H_{\text{lattice}}$
- Lattice energy for an ionic crystal: $\Delta H_{\text{lattice}} = \frac{C(Z^+)(Z^-)}{R_o}$

Footnotes

- This question is taken from the Chemistry Advanced Placement Examination and is used with the permission of the Educational Testing Service.

Glossary

bond energy

(also, bond dissociation energy) energy required to break a covalent bond in a gaseous substance

Born-Haber cycle

thermochemical cycle relating the various energetic steps involved in the formation of an ionic solid from the relevant elements

lattice energy ($\Delta H_{\text{lattice}}$)

energy required to separate one mole of an ionic solid into its component gaseous ions

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8.3: Chemical Formulas

Learning Objectives

- Symbolize the composition of molecules using molecular formulas and empirical formulas
- Represent the bonding arrangement of atoms within molecules using structural formulas

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 8.3.1). 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.

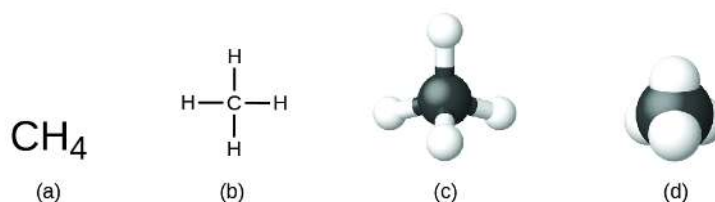


Figure 8.3.1: A methane molecule can be represented as (a) a molecular formula, (b) a structural formula, (c) a ball-and-stick model, and (d) a space-filling model. Carbon and hydrogen atoms are represented by black and white spheres, respectively.

Figure A shows C H subscript 4. Figure B shows a carbon atom that is bonded to four hydrogen atoms at right angles: one above, one to the left, one to the right, and one below. Figure C shows a 3-D, ball-and-stick model of the carbon atom bonded to four hydrogen atoms. Figure D shows a space-filling model of a carbon atom with hydrogen atoms partially embedded into the surface of the carbon atom.

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 8.3.2).

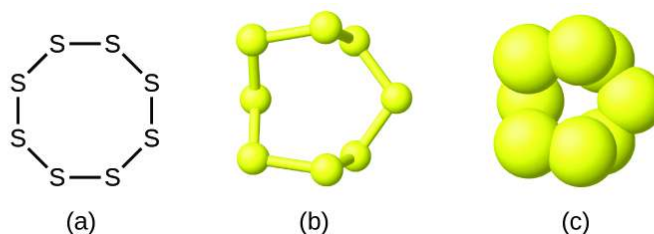


Figure 8.3.2: A molecule of sulfur is composed of eight sulfur atoms and is therefore written as S_8 . It can be represented as (a) a structural formula, (b) a ball-and-stick model, and (c) a space-filling model. Sulfur atoms are represented by yellow spheres.

Figure A shows eight sulfur atoms, symbolized with the letter S, that are bonded to each other to form an octagon. Figure B shows a 3-D, ball-and-stick model of the arrangement of the sulfur atoms. The shape is clearly not octagonal as it is represented in the structural formula. Figure C is a space-filling model that shows each sulfur atom is partially embedded into the sulfur atom it bonds with.

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 8.3.3).

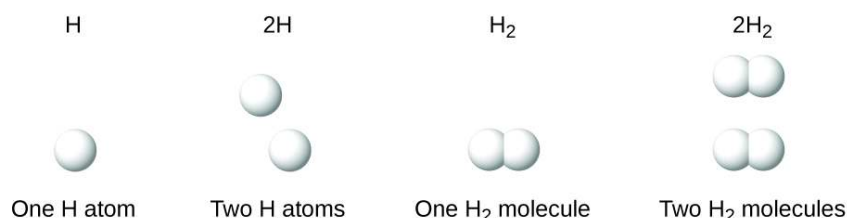


Figure 8.3.3: The symbols H , 2H , H_2 , and 2H_2 represent very different entities.

This figure shows four diagrams. The diagram for H shows a single, white sphere and is labeled one H atom. The diagram for 2H shows two white spheres that are not bonded together. It is labeled 2 H atoms. The diagram for H_2 shows two white spheres bonded together. It is labeled one H subscript 2 molecule. The diagram for 2H_2 shows two sets of bonded, white spheres. It is labeled 2 H subscript 2 molecules.

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 8.3.4).

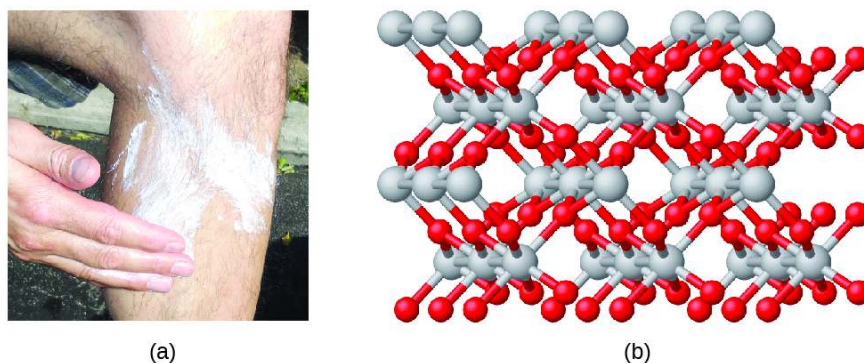


Figure 8.3.4: (a) The white compound titanium dioxide provides effective protection from the sun. (b) A crystal of titanium dioxide, TiO_2 , contains titanium and oxygen in a ratio of 1 to 2. The titanium atoms are gray and the oxygen atoms are red. (credit a: modification of work by "osseous"/Flickr).

Figure A shows a photo of a person applying suntan lotion to his or her lower leg. Figure B shows a 3-D ball-and-stick model of the molecule titanium dioxide, which involves a complicated interlocking of many titanium and oxygen atoms. The titanium atoms in the molecule are shown as silver spheres and the oxygen atoms are shown as red spheres. There are twice as many oxygen atoms as titanium atoms in the molecule.

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 8.3.5).

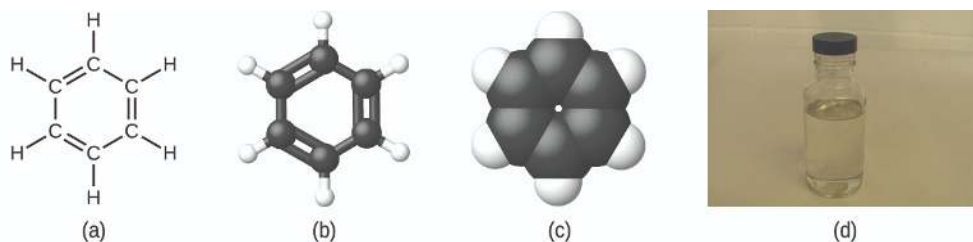


Figure 8.3.5: Benzene, C_6H_6 , is produced during oil refining and has many industrial uses. A benzene molecule can be represented as (a) a structural formula, (b) a ball-and-stick model, and (c) a space-filling model. (d) Benzene is a clear liquid. (credit d: modification of work by Sahar Atwa).

Figure A shows that benzene is composed of six carbons shaped like a hexagon. Every other bond between the carbon atoms is a double bond. Each carbon also has a single bonded hydrogen atom. Figure B shows a 3-D, ball-and-stick drawing of benzene. The six carbon atoms are black spheres while the six hydrogen atoms are smaller, white spheres. Figure C is a space-filling model of benzene which shows that most of the interior space is occupied by the carbon atoms. The hydrogen atoms are embedded in the outside surface of the carbon atoms. Figure d shows a small vial filled with benzene which appears to be clear.

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 8.3.6) 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.

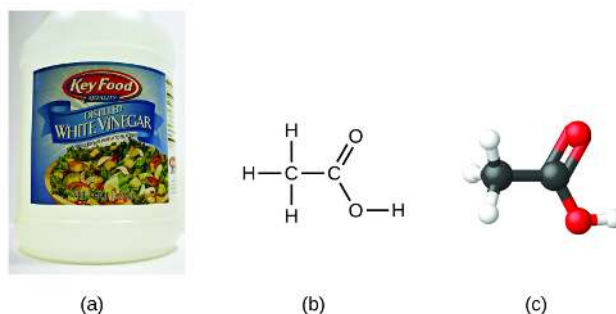


Figure 8.3.6: (a) Vinegar contains acetic acid, $C_2H_4O_2$, which has an empirical formula of CH_2O . It can be represented as (b) a structural formula and (c) as a ball-and-stick model. (credit a: modification of work by "HomeSpot HQ"/Flickr)

Figure A shows a jug of distilled, white vinegar. Figure B shows a structural formula for acetic acid which contains two carbon atoms connected by a single bond. The left carbon atom forms single bonds with three hydrogen atoms. The right carbon atom forms a double bond with an oxygen atom. The right carbon atom also forms a single bond with an oxygen atom. This oxygen forms a single bond with a hydrogen atom. Figure C shows a 3-D ball-and-stick model of acetic acid.

✓ Example 8.3.1: 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 8.3.1

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 8.3.7). 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.

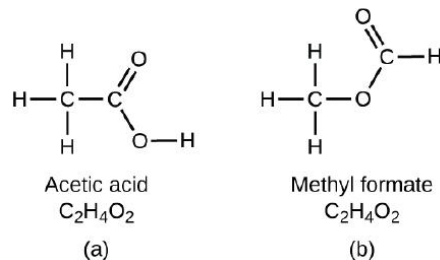


Figure 8.3.7: Molecules of (a) acetic acid and methyl formate (b) are structural isomers; they have the same formula ($C_2H_4O_2$) but different structures (and therefore different chemical properties).

Figure A shows a structural diagram of acetic acid, C subscript 2 H subscript 4 O subscript 2. Acetic acid contains two carbon atoms connected by a single bond. The left carbon atom forms single bonds with three hydrogen atoms. The carbon on the right forms a double bond with an oxygen atom. The right carbon atom also forms a single bond to an oxygen atom which forms a single bond with a hydrogen atom. Figure B shows a structural diagram of methyl formate, C subscript 2 H subscript 4 O subscript 2. This molecule contains a carbon atom which forms single bonds with three hydrogen atoms, and a single bond with an oxygen atom. The oxygen atom forms a single bond with another carbon atom which forms a double bond with another oxygen atom and a single bond with a hydrogen atom.

Many types of isomers exist (Figure 8.3.8). 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.

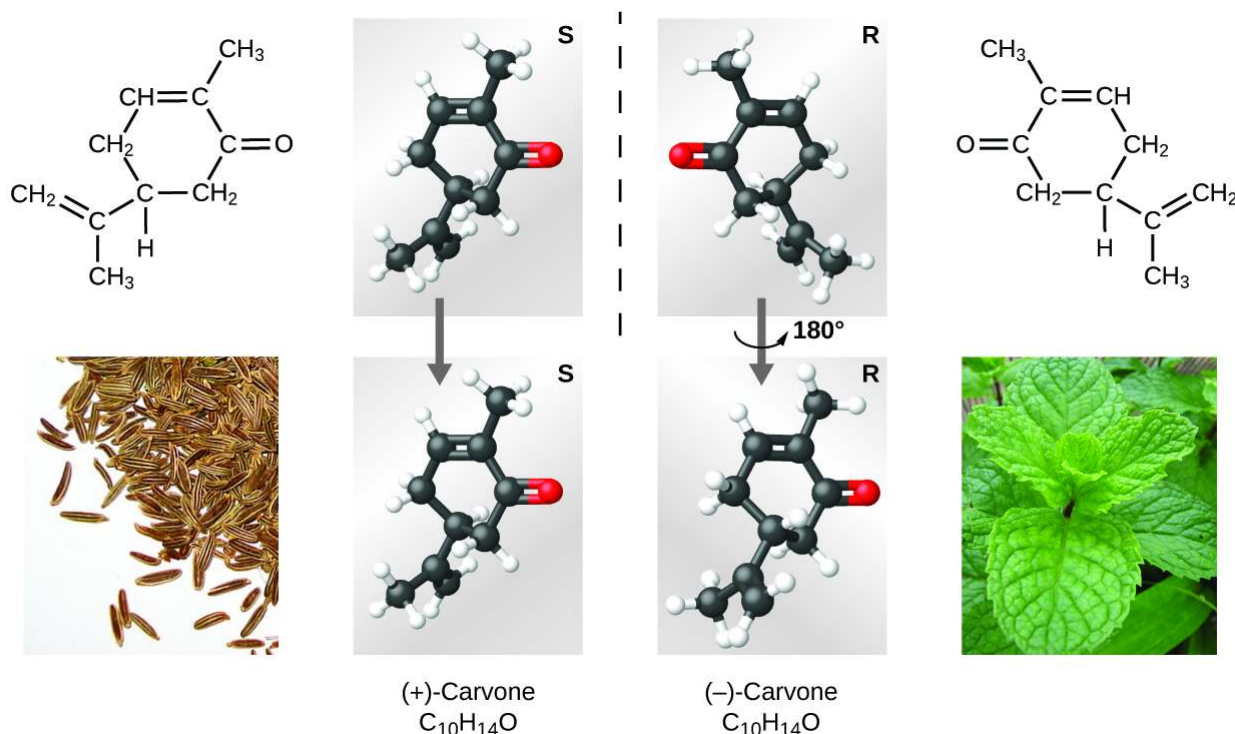


Figure 8.3.8: Molecules of carvone are spatial isomers; they only differ in the relative orientations of the atoms in space. (credit bottom left: modification of work by "Miansari66"/Wikimedia Commons; credit bottom right: modification of work by Forest & Kim Starr)

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

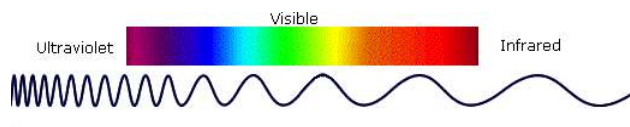
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8.4: Infrared (IR) Spectroscopy

Introduction

Photon energies associated with the infrared (from 1 to 15 kcal/mole) are not large enough to excite electrons, but may induce vibrational excitation of covalently bonded atoms and groups.

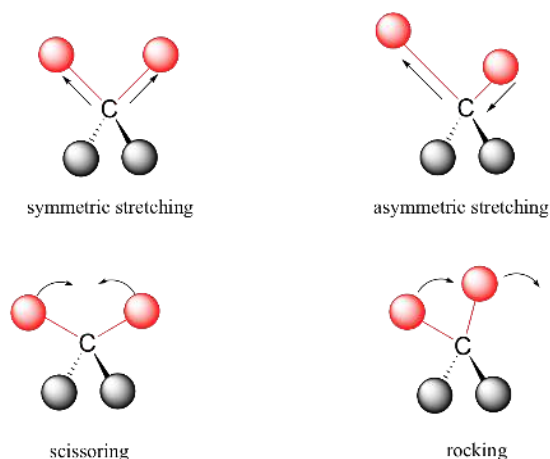


The covalent bonds in molecules are not rigid sticks or rods, such as found in molecular model kits, but are more like stiff springs that can be stretched and bent. The mobile nature of organic molecules was noted in the chapter concerning conformational isomers. We must now recognize that, in addition to the facile rotation of groups about single bonds, molecules experience a wide variety of vibrational motions, characteristic of their component atoms. Consequently, virtually all organic compounds will absorb infrared radiation that corresponds in energy to these vibrations. Infrared spectrometers, similar in principle to the UV-Visible spectrometer described elsewhere, permit chemists to obtain absorption spectra of compounds that are a unique reflection of their molecular structure.

Vibrational Spectroscopy

A molecule composed of n -atoms has $3n$ degrees of freedom, six of which are translations and rotations of the molecule itself. This leaves $3n-6$ degrees of vibrational freedom ($3n-5$ if the molecule is linear). Vibrational modes are often given descriptive names, such as stretching, bending, scissoring, rocking and twisting. The four-atom molecule of formaldehyde, the gas phase spectrum of which is shown below, provides an example of these terms. If a ball & stick model of formaldehyde is not displayed to the right of the spectrum, press the **view ball&stick model** button on the right. We expect six fundamental vibrations (12 minus 6), and these have been assigned to the spectrum absorptions. To see the formaldehyde molecule display a vibration, click one of the buttons under the spectrum, or click on one of the absorption peaks in the spectrum.

Covalent bonds in organic molecules are not rigid sticks – rather, they behave more like springs. At room temperature, organic molecules are always in motion, as their bonds stretch, bend, and twist. These complex vibrations can be broken down mathematically into individual **vibrational modes**, a few of which are illustrated below.

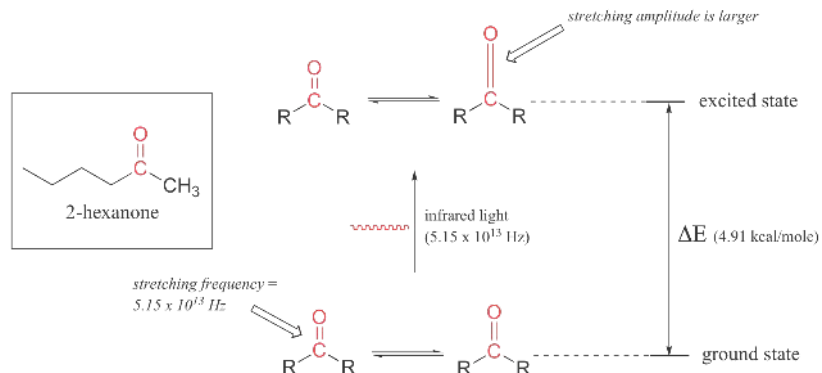


The energy of molecular vibration is *quantized* rather than continuous, meaning that a molecule can only stretch and bend at certain 'allowed' frequencies. If a molecule is exposed to electromagnetic radiation that matches the frequency of one of its vibrational modes, it will in most cases absorb energy from the radiation and jump to a higher vibrational energy state - what this means is that the *amplitude* of the vibration will increase, but the vibrational *frequency* will remain the same. The difference in energy between the two vibrational states is equal to the energy associated with the wavelength of radiation that was absorbed. It turns out that it is

the *infrared* region of the electromagnetic spectrum which contains frequencies corresponding to the vibrational frequencies of organic bonds.

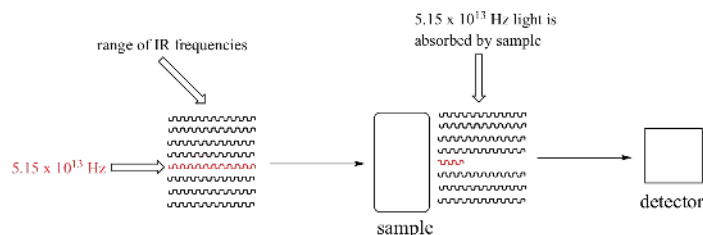
An IR Spectrum

We will use a ketone sample to illustrate this process. The sample is irradiated with infrared light and the carbonyl bond will specifically absorb light with this same frequency, which by equations 4.1 and 4.2 corresponds to a wavelength of 5.83×10^{-6} m and an energy of 4.91 kcal/mol. When the carbonyl bond absorbs this energy, it jumps up to an excited vibrational state.



The value of ΔE - the energy difference between the low energy (ground) and high energy (excited) vibrational states - is equal to 4.91 kcal/mol, the same as the energy associated with the absorbed light frequency. The molecule does not remain in its excited vibrational state for very long, but quickly releases energy to the surrounding environment in form of heat, and returns to the ground state.

With an instrument called an infrared spectrophotometer, we can 'see' this vibrational transition. In the spectrophotometer, infrared light with frequencies ranging from about 10^{13} to 10^{14} Hz is passed through our sample of cyclohexane. Most frequencies pass right through the sample and are recorded by a detector on the other side.

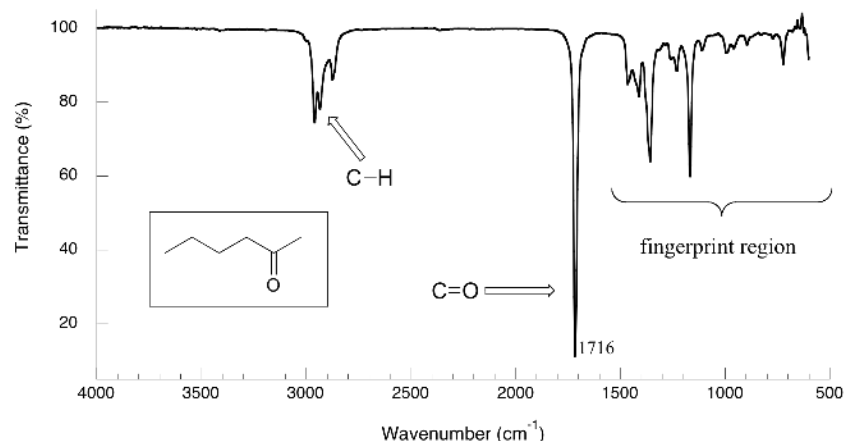


Our 5.15×10^{13} Hz carbonyl stretching frequency, however, is absorbed by the 2-hexanone sample, and so the detector records that the intensity of this frequency, after having passed through the sample, is something less than 100% of its initial intensity.

The vibrations of a 2-hexanone molecule are not, of course, limited to the simple stretching of the carbonyl bond. The various carbon-carbon bonds also stretch and bend, as do the carbon-hydrogen bonds, and all of these vibrational modes also absorb different frequencies of infrared light.

The power of infrared spectroscopy arises from the observation that *different functional groups have different characteristic absorption frequencies*. The carbonyl bond in a ketone, as we saw with our 2-hexanone example, typically absorbs in the range of $5.11 - 5.18 \times 10^{13}$ Hz, depending on the molecule. The carbon-carbon triple bond of an alkyne, on the other hand, absorbs in the range $6.30 - 6.80 \times 10^{13}$ Hz. The technique is therefore very useful as a means of identifying which functional groups are present in a molecule of interest. If we pass infrared light through an unknown sample and find that it absorbs in the carbonyl frequency range but not in the alkyne range, we can infer that the molecule contains a carbonyl group but not an alkyne.

Now, let's look at some actual output from IR spectroscopy experiments. Below is the IR spectrum for 2-hexanone.



There are a number of things that need to be explained in order for you to understand what it is that we are looking at. On the horizontal axis we see IR wavelengths expressed in terms of a unit called **wavenumber** (cm^{-1}), which tells us how many waves fit into one centimeter. On the vertical axis we see '**% transmittance**', which tells us how strongly light was absorbed at each frequency (100% transmittance means no absorption occurred at that frequency). The solid line traces the values of % transmittance for every wavelength – the 'peaks' (which are actually pointing down) show regions of strong absorption. For some reason, it is typical in IR spectroscopy to report wavenumber values rather than wavelength (in meters) or frequency (in Hz). The 'upside down' vertical axis, with absorbance peaks pointing down rather than up, is also a curious convention in IR spectroscopy. We wouldn't want to make things too easy for you!

A calculator for interconverting these frequency and wavelength values is provided on the right. Simply enter the value to be converted in the appropriate box, press "Calculate" and the equivalent number will appear in the empty box.

Infrared spectra may be obtained from samples in all phases (liquid, solid and gaseous). Liquids are usually examined as a thin film sandwiched between two polished salt plates (note that glass absorbs infrared radiation, whereas NaCl is transparent). If solvents are used to dissolve solids, care must be taken to avoid obscuring important spectral regions by solvent absorption. Perchlorinated solvents such as carbon tetrachloride, chloroform and tetrachloroethene are commonly used. Alternatively, solids may either be incorporated in a thin KBr disk, prepared under high pressure, or mixed with a little non-volatile liquid and ground to a paste (or mull) that is smeared between salt plates.

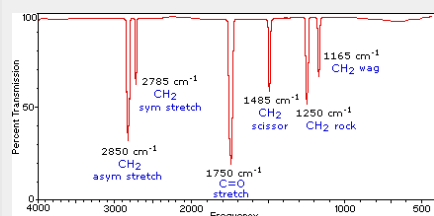
Frequency - Wavelength Converter

Frequency in cm^{-1}

Calculate

Wavelength in μ

Gas Phase Infrared Spectrum of Formaldehyde, $\text{H}_2\text{C}=\text{O}$



1. View CH2 Asymmetric Stretch
 - View CH2 Symmetric Stretch
 - View C=O Stretch
 - View CH2 Scissoring
 - View CH2 Rocking
 - View CH2 Wagging

- ☐ Ball&Stick Model
- ☐ Spacefill Model
- ☐ Stick Model
- ☐ Motion Off

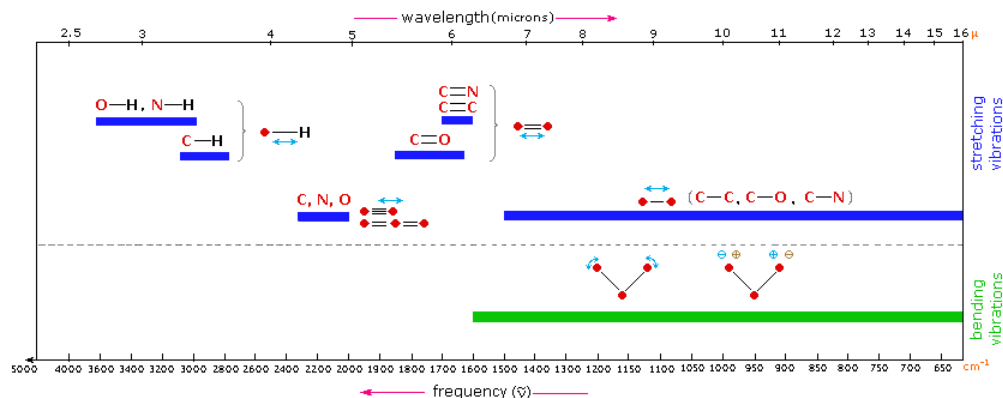
The exact frequency at which a given vibration occurs is determined by the strengths of the bonds involved and the mass of the component atoms. For a more detailed discussion of these factors [Click Here](#). In practice, infrared spectra do not normally display separate absorption signals for each of the $3n-6$ fundamental vibrational modes of a molecule. The number of observed absorptions may be increased by additive and subtractive interactions leading to combination tones and overtones of the fundamental vibrations, in much the same way that sound vibrations from a musical instrument interact. Furthermore, the number of observed absorptions may be decreased by molecular symmetry, spectrometer limitations, and spectroscopic selection rules. One selection rule that influences the intensity of infrared absorptions, is that a change in dipole moment should occur for a vibration to absorb infrared energy. Absorption bands associated with C=O bond stretching are usually very strong because a large change in the dipole takes place in that mode.

Some General Trends:

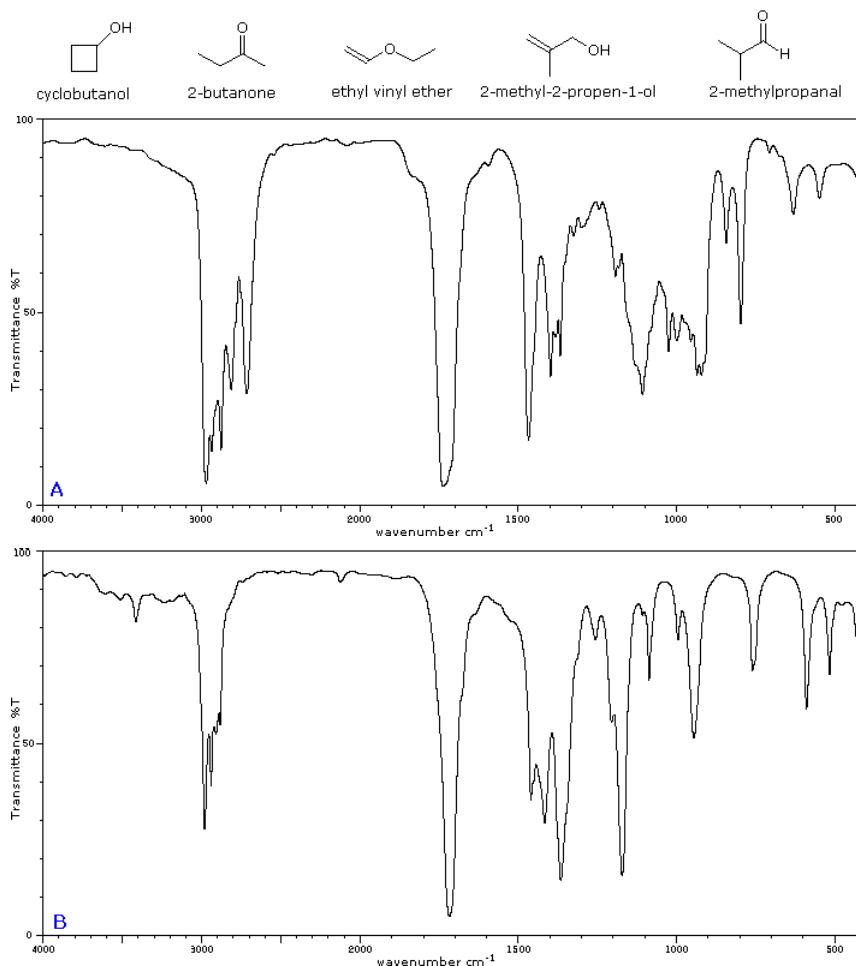
1. **Stretching frequencies are higher than corresponding bending frequencies.** (It is easier to bend a bond than to stretch or compress it.)
2. **Bonds to hydrogen have higher stretching frequencies than those to heavier atoms.**
3. **Triple bonds have higher stretching frequencies than corresponding double bonds, which in turn have higher frequencies than single bonds.** (Except for bonds to hydrogen).

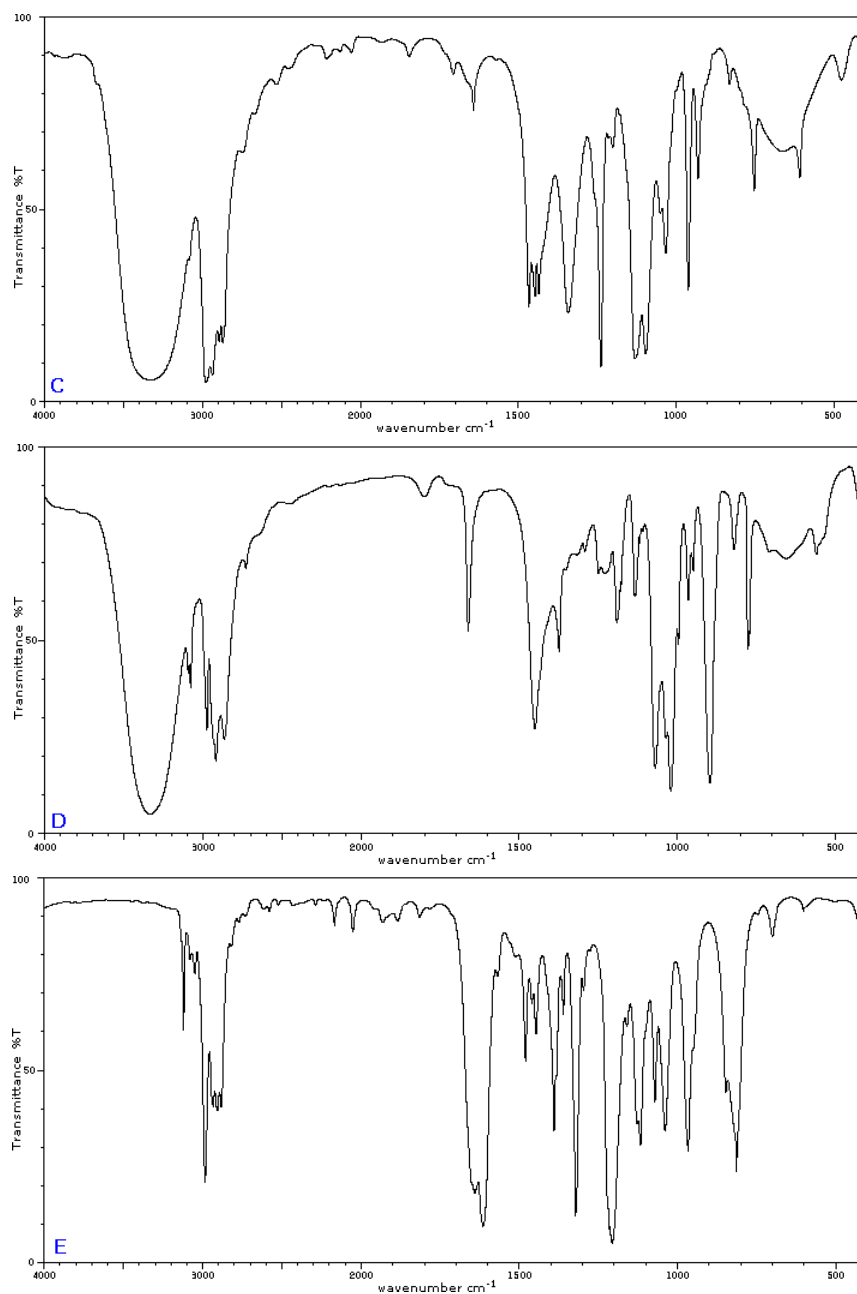
The general regions of the infrared spectrum in which various kinds of vibrational bands are observed are outlined in the following chart. Note that the blue colored sections above the dashed line refer to stretching vibrations, and the green colored band below the

line encompasses bending vibrations. The complexity of infrared spectra in the 1450 to 600 cm^{-1} region makes it difficult to assign all the absorption bands, and because of the unique patterns found there, it is often called the **fingerprint** region. Absorption bands in the 4000 to 1450 cm^{-1} region are usually due to stretching vibrations of diatomic units, and this is sometimes called the **group frequency** region.



To illustrate the usefulness of infrared absorption spectra, examples for five $\text{C}_4\text{H}_8\text{O}$ isomers are presented below their corresponding structural formulas. Try to associate each spectrum (A - E) with one of the isomers in the row above it.





Answers

Internal Links

- [Organic Chemistry With a Biological Emphasis](#)

Contributors

- William Reusch, Professor Emeritus ([Michigan State U.](#)), [Virtual Textbook of Organic Chemistry](#)

Contributors and Attributions

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- Prof. Steven Farmer ([Sonoma State University](#))
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- [Organic Chemistry With a Biological Emphasis](#) by [Tim Soderberg](#) (University of Minnesota, Morris)
-

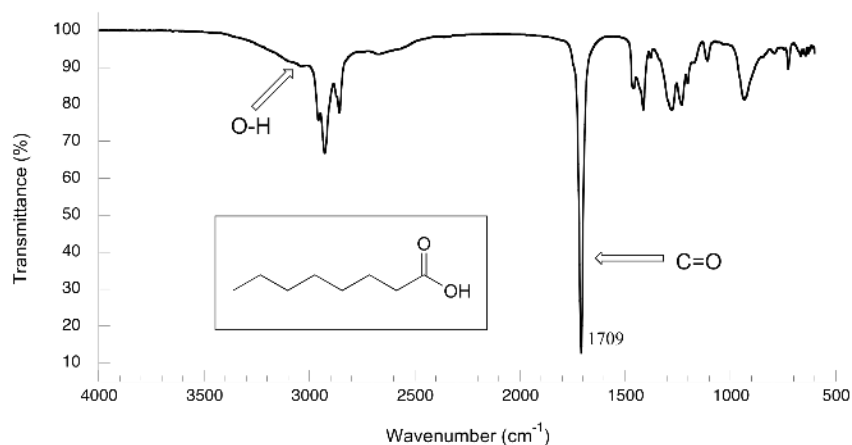
8.4: Infrared (IR) Spectroscopy is shared under a [not declared](#) license and was authored, remixed, and/or curated by LibreTexts.

8.4.1: Interpreting IR Spectra

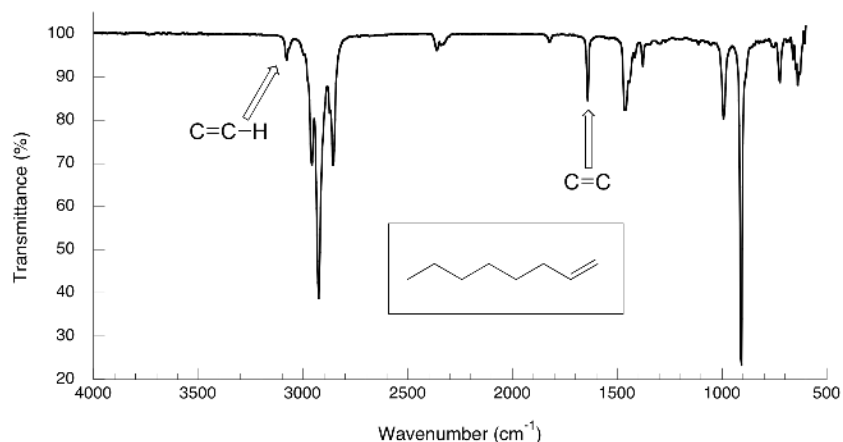
Guided IR Spectrum Interpretation

Now, let's take a look at the IR spectrum for 1-hexanol. There is a very broad 'mountain' centered at about 3400 cm^{-1} . This signal is characteristic of the O-H stretching mode of alcohols, and is a dead giveaway for the presence of an alcohol group. The breadth of this signal is a consequence of hydrogen bonding between molecules.

In the spectrum of octanoic acid we see, as expected, the characteristic carbonyl peak, this time at 1709 cm^{-1} . We also see a low, broad absorbance band that looks like an alcohol, except that it is displaced slightly to the right (long-wavelength) side of the spectrum, causing it to overlap to some degree with the C-H region. This is the characteristic carboxylic acid O-H single bond stretching absorbance.



The spectrum for 1-octene shows two peaks that are characteristic of alkenes: the one at 1642 cm^{-1} is due to stretching of the carbon-carbon double bond, and the one at 3079 cm^{-1} is due to stretching of the s bond between the alkene carbons and their attached hydrogens.



Alkynes have characteristic IR absorbance peaks in the range of $2100\text{--}2250\text{ cm}^{-1}$ due to stretching of the carbon-carbon triple bond, and terminal alkenes can be identified by their absorbance at about 3300 cm^{-1} , due to stretching of the bond between the sp-

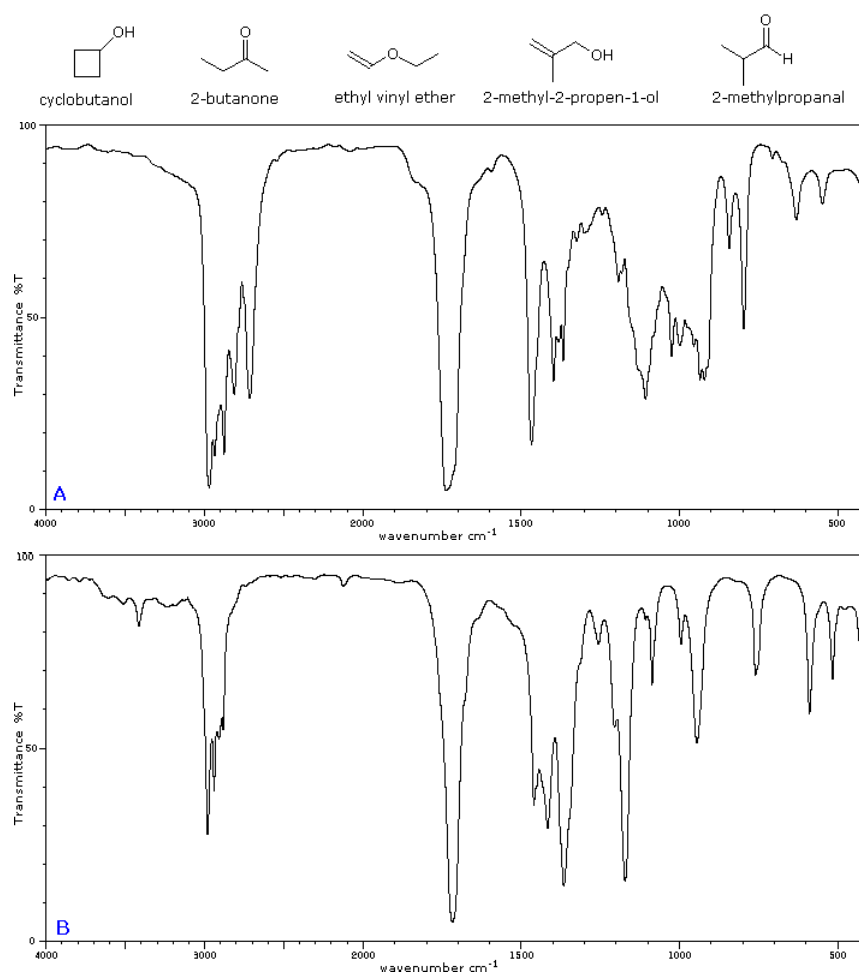
hybridized carbon and the terminal hydrogen.

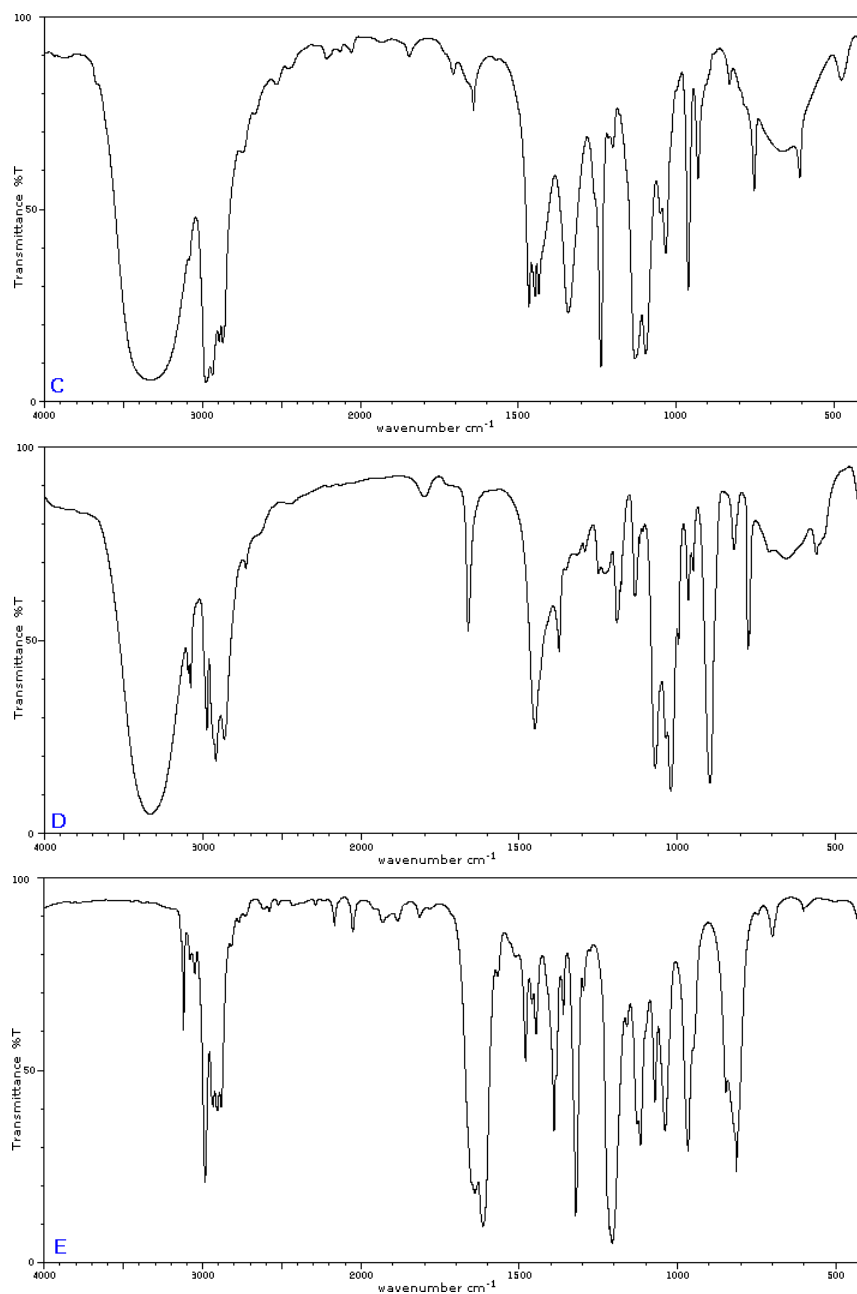
It is possible to identify other functional groups such as amines and ethers, but the characteristic peaks for these groups are considerably more subtle and/or variable, and often are overlapped with peaks from the fingerprint region. For this reason, we will limit our discussion here to the most easily recognized functional groups, which are summarized in this [table](#).

As you can imagine, obtaining an IR spectrum for a compound will not allow us to figure out the complete structure of even a simple molecule, unless we happen to have a reference spectrum for comparison. In conjunction with other analytical methods, however, IR spectroscopy can prove to be a very valuable tool, given the information it provides about the presence or absence of key functional groups. IR can also be a quick and convenient way for a chemist to check to see if a reaction has proceeded as planned. If we were to run a reaction in which we wished to convert cyclohexanone to cyclohexanol, for example, a quick comparison of the IR spectra of starting compound and product would tell us if we had successfully converted the ketone group to an alcohol.

More examples of IR spectra

To illustrate the usefulness of infrared absorption spectra, examples for five C_4H_8O isomers are presented below their corresponding structural formulas. Try to associate each spectrum with one of the isomers in the row above it.





Exercises

Questions

Q12.7.1

What functional groups give the following signals in an IR spectrum?

- A) 1700 cm^{-1}
- B) 1550 cm^{-1}
- C) 1700 cm^{-1} and 2510-3000 cm^{-1}

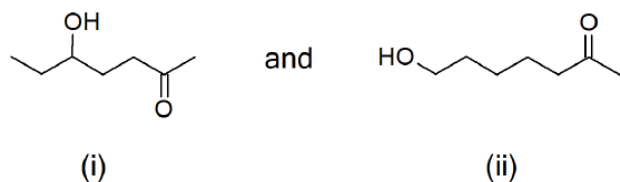
Q12.7.2

How can you distinguish the following pairs of compounds through IR analysis?

- A) CH_3OH (Methanol) and $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$ (Diethylether)

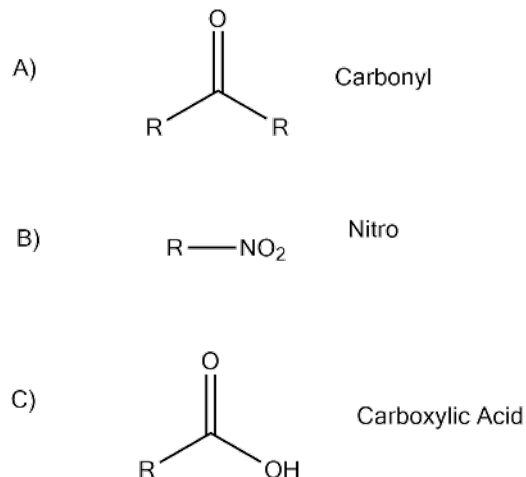
B) Cyclopentane and 1-pentene.

C)



Solutions

S12.7.1



S12.7.2

A) A OH peak will be present around 3300 cm^{-1} for methanol and will be absent in the ether.

B) 1-pentene will have a alkene peak around 1650 cm^{-1} for the C=C and there will be another peak around 3100 cm^{-1} for the sp^2 C-H group on the alkene

C) Cannot distinguish these two isomers. They both have the same functional groups and therefore would have the same peaks on an IR spectra.

Contributors and Attributions

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- **Organic Chemistry With a Biological Emphasis** by [Tim Soderberg](#) (University of Minnesota, Morris)

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8.5: Overview of the IUPAC Naming Strategy

learning objectives

- name alkanes, cycloalkanes, alkenes, alkynes, alkyl halides, ethers, alcohols, amines, benzene and its derivatives, aldehydes, ketones, amines, carboxylic acids, and carboxylic acid derivatives using IUPAC (systematic) and selected common name nomenclature
- draw the structure of alkanes, cycloalkanes, alkenes, alkynes, alkyl halides, ethers, alcohols, amines, benzene and its derivatives, aldehydes, ketones, amines, carboxylic acids, and carboxylic acid derivatives from the IUPAC (systematic) and selected common names

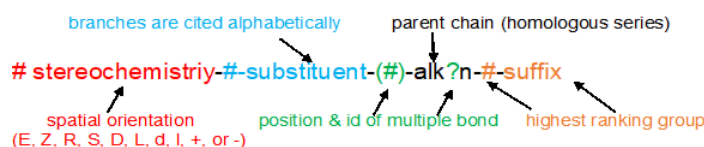
Overview of the IUPAC System for Naming Organic Compounds

The International Union of Pure and Applied Chemistry (IUPAC) has established the rules of nomenclature of all chemical compounds. IUPAC nomenclature can also be called "systematic" nomenclature because there is an overall system and structure to the names. This section provides an overview of the general naming strategy and structure for organic compounds.

Naming organic compounds according to the IUPAC system requires up to four pieces of information

1. recognize & prioritize the functional group(s) present
2. identify & number the longest continuous carbon chain to give the highest ranking group the lowest possible number
3. cite the substituents (branches) alphabetically using the numbering determined above
4. recognize & classify any stereochemistry (E/Z, R/S, cis/trans, etc)

With these four pieces of information, the IUPAC name is written using the format below. This same format applies to **ALL** the organic compounds.



Recognize & Prioritize the Functional Group(s) Present

The IUPAC Rules of Organic Nomenclature assume that the following table is understood and memorized.

Structure	Classification	Suffix Name	Substituent Name
<div style="display: flex; align-items: center;"> <div style="border: 1px solid black; padding: 2px; margin-right: 5px;">higher priority</div> <div style="text-align: center;"> $\text{R}-\text{C}(=\text{O})\text{OH}$ </div> </div>	Carboxylic acid	-oic acid	carboxy-
<div style="display: flex; align-items: center;"> <div style="border: 1px solid black; padding: 2px; margin-right: 5px;">↑</div> <div style="text-align: center;"> $\text{R}-\text{C}(=\text{O})\text{OR}'$ $\text{R}-\text{C}(=\text{O})\text{NH}_2$ </div> </div>	Ester Amide	-oate -amide	alkoxycarbonyl- amido-
<div style="display: flex; align-items: center;"> <div style="border: 1px solid black; padding: 2px; margin-right: 5px;">↑</div> <div style="text-align: center;"> $\text{R}-\text{C}\equiv\text{N}$ </div> </div>	Nitrile	-nitrile	cyano-
<div style="display: flex; align-items: center;"> <div style="border: 1px solid black; padding: 2px; margin-right: 5px;">↑</div> <div style="text-align: center;"> $\text{R}-\text{C}(=\text{O})\text{H}$ </div> </div>	Aldehyde	-al	formyl-
<div style="display: flex; align-items: center;"> <div style="border: 1px solid black; padding: 2px; margin-right: 5px;">↑</div> <div style="text-align: center;"> $\text{R}-\text{C}(=\text{O})\text{R}_1$ </div> </div>	Ketone	-one	oxo-
<div style="display: flex; align-items: center;"> <div style="border: 1px solid black; padding: 2px; margin-right: 5px;">↑</div> <div style="text-align: center;"> $\text{R}-\text{OH}$ </div> </div>	Alcohol	-ol	hydroxy-
<div style="display: flex; align-items: center;"> <div style="border: 1px solid black; padding: 2px; margin-right: 5px;">↑</div> <div style="text-align: center;"> $\text{R}-\text{NH}_2$ </div> </div>	Amine	-amine	amino-
<div style="display: flex; align-items: center;"> <div style="border: 1px solid black; padding: 2px; margin-right: 5px;">↑</div> <div style="text-align: center;"> $\text{R}_2\text{C}=\text{CR}_2$ </div> </div>	Alkene	-ene	alken-
<div style="display: flex; align-items: center;"> <div style="border: 1px solid black; padding: 2px; margin-right: 5px;">↑</div> <div style="text-align: center;"> $\text{RC}\equiv\text{CR}$ </div> </div>	Alkyne	-yne	alkyn-
<div style="display: flex; align-items: center;"> <div style="border: 1px solid black; padding: 2px; margin-right: 5px;">↑</div> <div style="text-align: center;"> R </div> </div>	Alkane*	-ane	alkyl-
<div style="display: flex; align-items: center;"> <div style="border: 1px solid black; padding: 2px; margin-right: 5px;">↑</div> <div style="text-align: center;"> $\text{R}-\text{O}-\text{R}_1$ </div> </div>	Ether*	---	alkoxy-
<div style="display: flex; align-items: center;"> <div style="border: 1px solid black; padding: 2px; margin-right: 5px;">lower priority</div> <div style="text-align: center;"> $\text{R}-\text{X}$ </div> </div>	Alkyl halide*	---	halo-

*Same overall priority, prioritize by structure as described in the appendix

Identify & Number the Longest Continuous Carbon Chain with the Highest Priority Group

The longest continuous carbon chain (parent) is named using the Homologous Series, as well as any carbon branches. The suffixes and location within the name distinguish between the parent and the branches.

When Alkenes and Alkynes have Lower Priority

The hydrocarbon suffixes differ in the letter preceeding the "n". When alkenes and alkynes occur in compounds with higher priority functional groups, then the distinction between hydrocarbons is communicated with a single letter: "e", or "y" for alkenes and alkynes, respectively. An example is shown below to illustrate the application of this rule.



substituents (branches) alphabetically

The major substituents are listed above and need to be memorized. There are a few additional substituents that will introduced later in the text.

Stereochemistry

Distinguishing spatial orientations of atoms (stereochemistry) are communicated at the beginning of the name using the appropriate symbols, such as E/Z, R/S, cis/trans, etc. This nomenclature will be discussed when it is possible for a functional group.

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8.5.1: Hydrocarbons

Learning Objectives

- Explain the importance of hydrocarbons and the reason for their diversity
- Name saturated and unsaturated hydrocarbons, and molecules derived from them
- Describe the reactions characteristic of saturated and unsaturated hydrocarbons
- Identify structural and geometric isomers of hydrocarbons

The largest database¹ of organic compounds lists about 10 million substances, which include compounds originating from living organisms and those synthesized by chemists. The number of potential organic compounds has been estimated² at 10^{60} —an astronomically high number. The existence of so many organic molecules is a consequence of the ability of carbon atoms to form up to four strong bonds to other carbon atoms, resulting in chains and rings of many different sizes, shapes, and complexities.

The simplest organic compounds contain only the elements carbon and hydrogen, and are called hydrocarbons. Even though they are composed of only two types of atoms, there is a wide variety of hydrocarbons because they may consist of varying lengths of chains, branched chains, and rings of carbon atoms, or combinations of these structures. In addition, hydrocarbons may differ in the types of carbon-carbon bonds present in their molecules. Many hydrocarbons are found in plants, animals, and their fossils; other hydrocarbons have been prepared in the laboratory. We use hydrocarbons every day, mainly as fuels, such as natural gas, acetylene, propane, butane, and the principal components of gasoline, diesel fuel, and heating oil. The familiar plastics polyethylene, polypropylene, and polystyrene are also hydrocarbons. We can distinguish several types of hydrocarbons by differences in the bonding between carbon atoms. This leads to differences in geometries and in the hybridization of the carbon orbitals.

Alkanes

Alkanes, or saturated hydrocarbons, contain only single covalent bonds between carbon atoms. Each of the carbon atoms in an alkane has sp^3 hybrid orbitals and is bonded to four other atoms, each of which is either carbon or hydrogen. The Lewis structures and models of methane, ethane, and pentane are illustrated in Figure 8.5.1.1. Carbon chains are usually drawn as straight lines in Lewis structures, but one has to remember that Lewis structures are not intended to indicate the geometry of molecules. Notice that the carbon atoms in the structural models (the ball-and-stick and space-filling models) of the pentane molecule do not lie in a straight line. Because of the sp^3 hybridization, the bond angles in carbon chains are close to 109.5° , giving such chains in an alkane a zigzag shape.

The structures of alkanes and other organic molecules may also be represented in a less detailed manner by condensed structural formulas (or simply, *condensed formulas*). Instead of the usual format for chemical formulas in which each element symbol appears just once, a condensed formula is written to suggest the bonding in the molecule. These formulas have the appearance of a Lewis structure from which most or all of the bond symbols have been removed. Condensed structural formulas for ethane and pentane are shown at the bottom of Figure 8.5.1.1, and several additional examples are provided in the exercises at the end of this chapter.

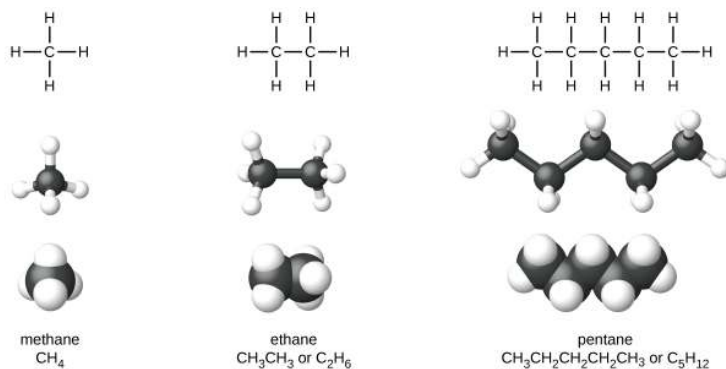


Figure 8.5.1.1: Pictured are the Lewis structures, ball-and-stick models, and space-filling models for molecules of methane, ethane, and pentane.

A common method used by organic chemists to simplify the drawings of larger molecules is to use a skeletal structure (also called a line-angle structure). In this type of structure, carbon atoms are not symbolized with a C, but represented by each end of a line or bend in a line. Hydrogen atoms are not drawn if they are attached to a carbon. Other atoms besides carbon and hydrogen are represented by their elemental symbols. Figure 8.5.1.2 shows three different ways to draw the same structure.

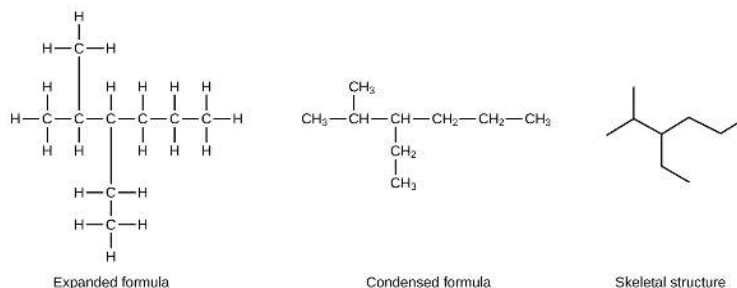
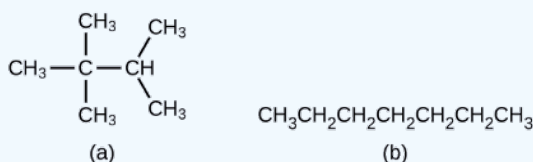


Figure 8.5.1.2: The same structure can be represented three different ways: an expanded formula, a condensed formula, and a skeletal structure.

✓ Example 8.5.1.1

Drawing Skeletal Structures Draw the skeletal structures for these two molecules:



Solution

Each carbon atom is converted into the end of a line or the place where lines intersect. All hydrogen atoms attached to the carbon atoms are left out of the structure (although we still need to recognize they are there):

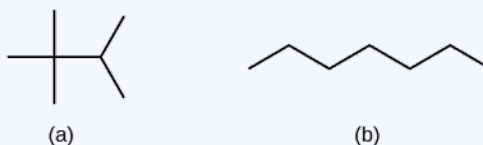


Figure a shows a branched skeleton structure that looks like a plus sign with line segments extending up and to the right and down and to the left of the rightmost point of the plus sign. Figure b appears in a zig zag pattern made with six line segments. The segments rise, fall, rise, fall, rise, and fall moving left to right across the figure.

? Exercise 8.5.1.1

Draw the skeletal structures for these two molecules:

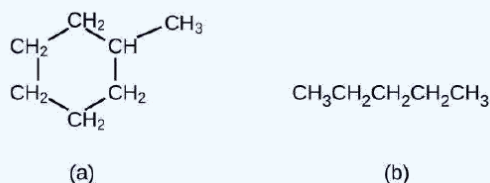
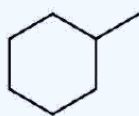


Figure a shows five C H subscript 2 groups and one C H group bonded in a hexagonal ring. A C H subscript 3 group appears above and to the right of the ring, bonded to the ring on the C H group appearing at the upper right portion of the ring. In b, a straight chain molecule composed of C H subscript 3 C H subscript 2 C H subscript 2 C H subscript 2 C H subscript 3 is shown.

Answer



(a)

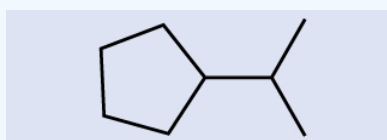


(b)

In a, a hexagon with a vertex at the top is shown. The vertex just to the right has a line segment attached that extends up and to the right. In b, a zigzag pattern is shown in which line segments rise, fall, rise, fall, and rise moving left to right.

✓ Example 8.5.1.2

Interpreting Skeletal Structures Identify the chemical formula of the molecule represented here:

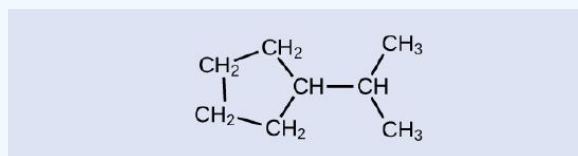


This figure shows a pentagon with a vertex pointing right, from which a line segment extends that has two line segments attached at its right end, one extending up and to the right, and the other extending down and to the right.

Solution

There are eight places where lines intersect or end, meaning that there are eight carbon atoms in the molecule. Since we know that carbon atoms tend to make four bonds, each carbon atom will have the number of hydrogen atoms that are required for four bonds. This compound contains 16 hydrogen atoms for a molecular formula of C_8H_{16} .

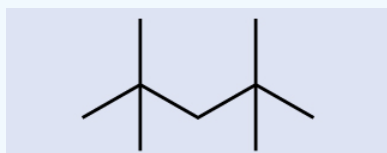
Location of the hydrogen atoms:



In this figure a ring composed of four CH_2 groups and one CH group in a pentagonal shape is shown. From the CH group, which is at the right side of the pentagon, a CH is bonded. From this CH , a CH_3 group is bonded above and to the right and a second is bonded below and to the right.

? Exercise 8.5.1.2

Identify the chemical formula of the molecule represented here:



A skeleton model is shown with a zigzag pattern that rises, falls, rises, and falls again left to right through the center of the molecule. From the two risen points, line segments extend both up and down, creating four branches.

Answer

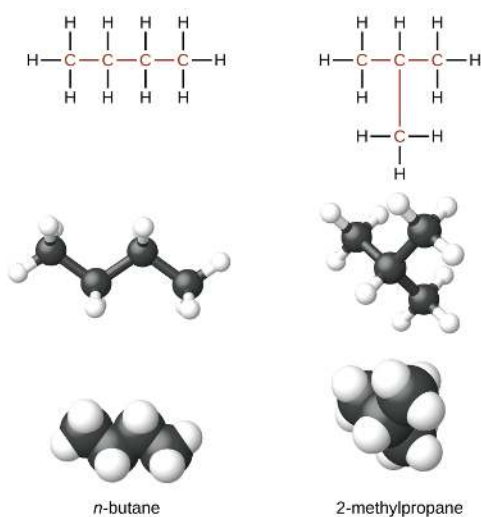


All alkanes are composed of carbon and hydrogen atoms, and have similar bonds, structures, and formulas; noncyclic alkanes all have a formula of C_nH_{2n+2} . The number of carbon atoms present in an alkane has no limit. Greater numbers of atoms in the molecules will lead to stronger intermolecular attractions (dispersion forces) and correspondingly different physical properties of the molecules. Properties such as melting point and boiling point (Table 8.5.1.1) usually change smoothly and predictably as the number of carbon and hydrogen atoms in the molecules change.

Table 8.5.1.1: Properties of Some Alkanes

Alkane	Molecular Formula	Melting Point ($^{\circ}C$)	Boiling Point ($^{\circ}C$)	Phase at STP ⁴	Number of Structural Isomers
methane	CH_4	-182.5	-161.5	gas	1
ethane	C_2H_6	-183.3	-88.6	gas	1
propane	C_3H_8	-187.7	-42.1	gas	1
butane	C_4H_{10}	-138.3	-0.5	gas	2
pentane	C_5H_{12}	-129.7	36.1	liquid	3
hexane	C_6H_{14}	-95.3	68.7	liquid	5
heptane	C_7H_{16}	-90.6	98.4	liquid	9
octane	C_8H_{18}	-56.8	125.7	liquid	18
nonane	C_9H_{20}	-53.6	150.8	liquid	35
decane	$C_{10}H_{22}$	-29.7	174.0	liquid	75
tetradecane	$C_{14}H_{30}$	5.9	253.5	solid	1858
octadecane	$C_{18}H_{38}$	28.2	316.1	solid	60,523

Hydrocarbons with the same formula, including alkanes, can have different structures. For example, two alkanes have the formula C_4H_{10} : They are called *n*-butane and 2-methylpropane (or isobutane), and have the following Lewis structures:



The compounds *n*-butane and 2-methylpropane are structural isomers (the term constitutional isomers is also commonly used). Constitutional isomers have the same molecular formula but different spatial arrangements of the atoms in their molecules. The *n*-butane molecule contains an *unbranched chain*, meaning that no carbon atom is bonded to more than two other carbon atoms. We use the term *normal*, or the prefix *n*, to refer to a chain of carbon atoms without branching. The compound 2-methylpropane has a branched chain (the carbon atom in the center of the Lewis structure is bonded to three other carbon atoms)

Identifying isomers from Lewis structures is not as easy as it looks. Lewis structures that look different may actually represent the same isomers. For example, the three structures in Figure 8.5.1.3 all represent the same molecule, *n*-butane, and hence are not different isomers. They are identical because each contains an unbranched chain of four carbon atoms.

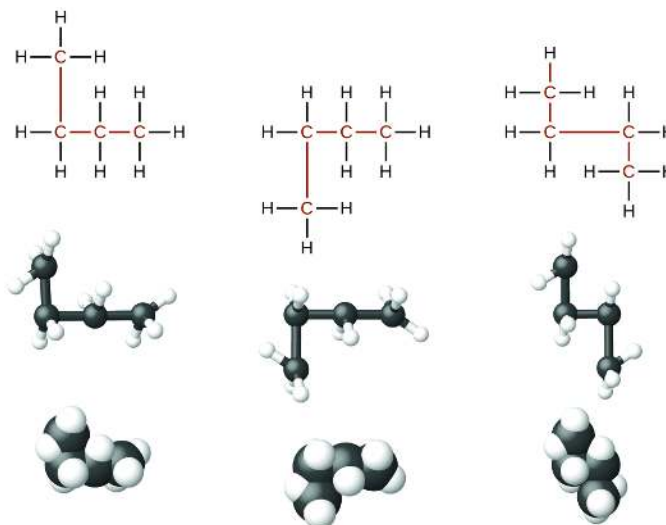
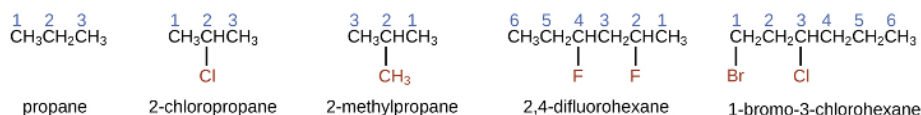


Figure 8.5.1.3: These three representations of the structure of *n*-butane are not isomers because they all contain the same arrangement of atoms and bonds.

The Basics of Organic Nomenclature: Naming Alkanes

The International Union of Pure and Applied Chemistry (IUPAC) has devised a system of nomenclature that begins with the names of the alkanes and can be adjusted from there to account for more complicated structures. The nomenclature for alkanes is based on two rules:

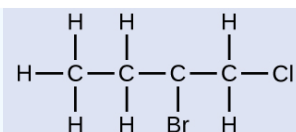
1. To name an alkane, first identify the longest chain of carbon atoms in its structure. A two-carbon chain is called ethane; a three-carbon chain, propane; and a four-carbon chain, butane. Longer chains are named as follows: pentane (five-carbon chain), hexane (6), heptane (7), octane (8), nonane (9), and decane (10). These prefixes can be seen in the names of the alkanes described in Table 8.5.1.1.
2. Add prefixes to the name of the longest chain to indicate the positions and names of substituents. Substituents are branches or functional groups that replace hydrogen atoms on a chain. The position of a substituent or branch is identified by the number of the carbon atom it is bonded to in the chain. We number the carbon atoms in the chain by counting from the end of the chain nearest the substituents. Multiple substituents are named individually and placed in alphabetical order at the front of the name.
- 3.



When more than one substituent is present, either on the same carbon atom or on different carbon atoms, the substituents are listed alphabetically. Because the carbon atom numbering begins at the end closest to a substituent, the longest chain of carbon atoms is numbered in such a way as to produce the lowest number for the substituents. The ending *-o* replaces *-ide* at the end of the name of an electronegative substituent (in ionic compounds, the negatively charged ion ends with *-ide* like chloride; in organic compounds, such atoms are treated as substituents and the *-o* ending is used). The number of substituents of the same type is indicated by the prefixes *di-* (two), *tri-* (three), *tetra-* (four), and so on (for example, *difluoro-* indicates two fluoride substituents).

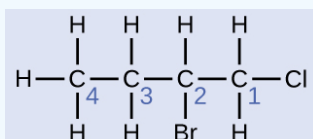
✓ Example 8.5.1.3: Naming Halogen-substituted Alkanes

Name the molecule whose structure is shown here:



This structure shows a C atom bonded to the H atoms and another C atom. This second C atom is bonded to two H atoms and another C atom. This third C atom is bonded to a Br atom and another C atom. This fourth C atom is bonded to two H atoms and a Cl atom.

Solution

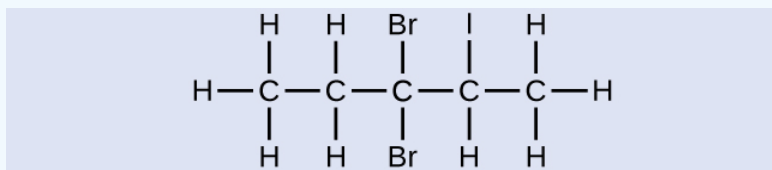


This structure shows a C atom bonded to the H atoms and another C atom. This second C atom is bonded to two H atoms and another C atom. This third C atom is bonded to an H atom, a Br atom, and another C atom. This fourth C atom is bonded to two H atoms and a Cl atom. The C atoms are numbered 4, 3, 2, and 1 from left to right.

The four-carbon chain is numbered from the end with the chlorine atom. This puts the substituents on positions 1 and 2 (numbering from the other end would put the substituents on positions 3 and 4). Four carbon atoms means that the base name of this compound will be butane. The bromine at position 2 will be described by adding 2-bromo-; this will come at the beginning of the name, since bromo- comes before chloro- alphabetically. The chlorine at position 1 will be described by adding 1-chloro-, resulting in the name of the molecule being 2-bromo-1-chlorobutane.

? Exercise 8.5.1.3

Name the following molecule:

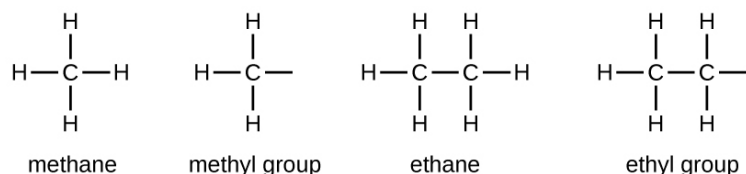


This figure shows a C atom bonded to three H atoms and another C atom. This second C atom is bonded to two H atoms and a third C atom. The third C atom is bonded to two Br atoms and a fourth C atom. This C atom is bonded to an H atom, and I atom, and a fifth C atom. This last C atom is bonded to three H atoms.

Answer

3,3-dibromo-2-iodopentane

We call a substituent that contains one less hydrogen than the corresponding alkane an alkyl group. The name of an alkyl group is obtained by dropping the suffix *-ane* of the alkane name and adding *-yl*:

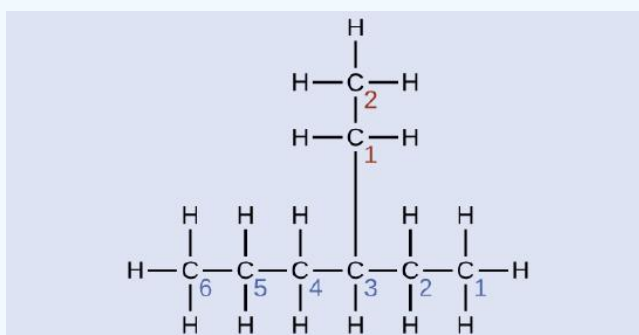


In this figure, methane is named and represented as C with four H atoms bonded above, below, to the left, and to the right of the C. The methyl group is shown, which appears like methane without the right most H. A dash remains at the location where the H was formerly bonded. Ethane is named and represented with two centrally bonded C atoms to which six H atoms are bonded; two above and below each of the two C atoms and to the left and right ends of the linked C atoms. The ethyl group appears as a similar structure with the right-most H atom removed. A dash remains at the location where the H atom was formerly bonded.

The open bonds in the methyl and ethyl groups indicate that these alkyl groups are bonded to another atom.

✓ Example 8.5.1.4 Naming Substituted Alkanes

Name the molecule whose structure is shown here:



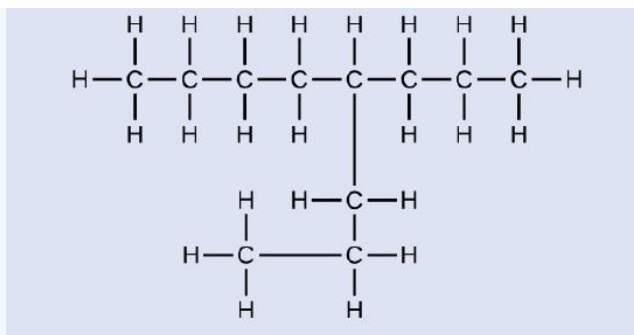
A chain of six carbon atoms, numbered 6, 5, 4, 3, 2, and 1 is shown. Bonded above carbon 3, a chain of two carbons is shown, numbered 1 and 2 moving upward. H atoms are present directly above, below, left and right of all carbon atoms in positions not already taken up in bonding to other carbon atoms.

Solution

The longest carbon chain runs horizontally across the page and contains six carbon atoms (this makes the base of the name hexane, but we will also need to incorporate the name of the branch). In this case, we want to number from right to left (as shown by the blue numbers) so the branch is connected to carbon 3 (imagine the numbers from left to right—this would put the branch on carbon 4, violating our rules). The branch attached to position 3 of our chain contains two carbon atoms (numbered in red)—so we take our name for two carbons *eth-* and attach *-yl* at the end to signify we are describing a branch. Putting all the pieces together, this molecule is 3-ethylhexane.

? Exercise 8.5.1.4

Name the following molecule:



This figure shows a C atom bonded to three H atoms and another C atom. This C atom is bonded to two H atoms and third C atom. The third C atom is bonded to two H atoms and a fourth C atom. The fourth C atom is bonded to two H atoms and a fifth C atom. This C atom is bonded to an H atom, a sixth C atom in the chain, and another C atom which appears to branch off the chain. The C atom in the branch is bonded to two H atoms and another C atom. This C atom is bonded to two H atoms and another C atom. This third C atom appears to the left of the second and is bonded to three H atoms. The sixth C atom in the chain is bonded to two H atoms and a seventh C atom. The seventh C atom is bonded to two H atoms and an eighth C atom. The eighth C atom is bonded to three H atoms.

Answer

4-propyloctane

Some hydrocarbons can form more than one type of alkyl group when the hydrogen atoms that would be removed have different “environments” in the molecule. This diversity of possible alkyl groups can be identified in the following way: The four hydrogen atoms in a methane molecule are equivalent; they all have the same environment. They are equivalent because each is bonded to a carbon atom (the same carbon atom) that is bonded to three hydrogen atoms. (It may be easier to see the equivalency in the ball and stick models in Figure 8.5.1.3. Removal of any one of the four hydrogen atoms from methane forms a methyl group. Likewise, the six hydrogen atoms in ethane are equivalent and removing any one of these hydrogen atoms produces an ethyl group. Each of the six hydrogen atoms is bonded to a carbon atom that is bonded to two other hydrogen atoms and a carbon atom. However, in both propane and 2-methylpropane, there are hydrogen atoms in two different environments, distinguished by the adjacent atoms or groups of atoms:

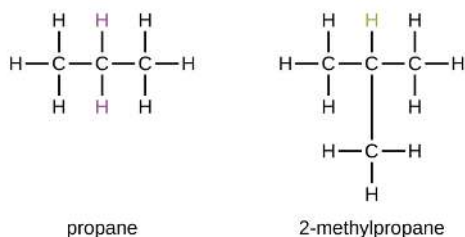
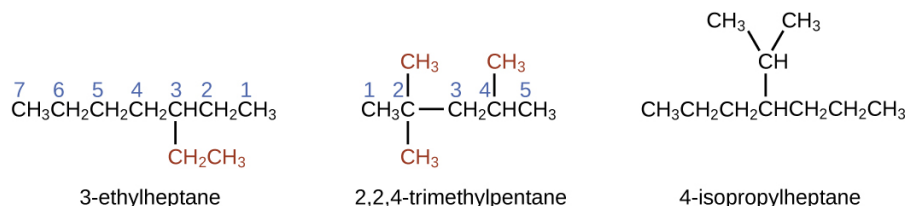


Figure 8.5.1.4.

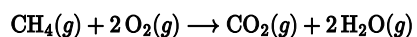
Alkyl Group	Structure
methyl	$\text{CH}_3\text{—}$
ethyl	$\text{CH}_3\text{CH}_2\text{—}$
<i>n</i> -propyl	$\text{CH}_3\text{CH}_2\text{CH}_2\text{—}$
isopropyl	$\begin{array}{c} \\ \text{CH}_3\text{CHCH}_3 \end{array}$
<i>n</i> -butyl	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{—}$
sec-butyl	$\begin{array}{c} \\ \text{CH}_3\text{CH}_2\text{CHCH}_3 \end{array}$
isobutyl	$\begin{array}{c} \text{CH}_3\text{CHCH}_2\text{—} \\ \\ \text{CH}_3 \end{array}$
<i>tert</i> -butyl	$\begin{array}{c} \\ \text{CH}_3\text{CCH}_3 \\ \\ \text{CH}_3 \end{array}$

Figure 8.5.1.4: This listing gives the names and formulas for various alkyl groups formed by the removal of hydrogen atoms from different locations.

Note that alkyl groups do not exist as stable independent entities. They are always a part of some larger molecule. The location of an alkyl group on a hydrocarbon chain is indicated in the same way as any other substituent:



Alkanes are relatively stable molecules, but heat or light will activate reactions that involve the breaking of C–H or C–C single bonds. Combustion is one such reaction:



Alkanes burn in the presence of oxygen, a highly exothermic oxidation-reduction reaction that produces carbon dioxide and water. As a consequence, alkanes are excellent fuels. For example, methane, CH_4 , is the principal component of natural gas. Butane, C_4H_{10} , used in camping stoves and lighters is an alkane. Gasoline is a liquid mixture of continuous- and branched-chain alkanes, each containing from five to nine carbon atoms, plus various additives to improve its performance as a fuel. Kerosene, diesel oil, and fuel oil are primarily mixtures of alkanes with higher molecular masses. The main source of these liquid alkane fuels is crude oil, a complex mixture that is separated by fractional distillation. Fractional distillation takes advantage of differences in the boiling points of the components of the mixture (Figure 8.5.1.5). You may recall that boiling point is a function of intermolecular interactions, which was discussed in the chapter on solutions and colloids.

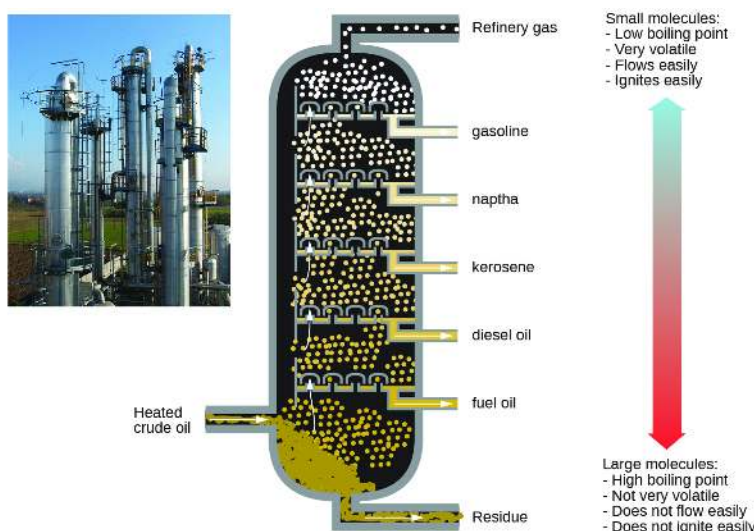
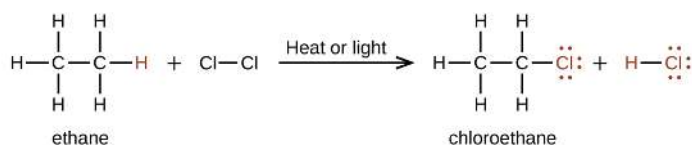


Figure 8.5.1.5: In a column for the fractional distillation of crude oil, oil heated to about 425 °C in the furnace vaporizes when it enters the base of the tower. The vapors rise through bubble caps in a series of trays in the tower. As the vapors gradually cool, fractions of higher, then of lower, boiling points condense to liquids and are drawn off. (credit left: modification of work by Luigi Chiesa)

In a substitution reaction, another typical reaction of alkanes, one or more of the alkane's hydrogen atoms is replaced with a different atom or group of atoms. No carbon-carbon bonds are broken in these reactions, and the hybridization of the carbon atoms does not change. For example, the reaction between ethane and molecular chlorine depicted here is a substitution reaction:



The C–Cl portion of the chloroethane molecule is an example of a functional group, the part or moiety of a molecule that imparts a specific chemical reactivity. The types of functional groups present in an organic molecule are major determinants of its chemical properties and are used as a means of classifying organic compounds as detailed in the remaining sections of this chapter.

Alkenes

Organic compounds that contain one or more double or triple bonds between carbon atoms are described as unsaturated. You have likely heard of unsaturated fats. These are complex organic molecules with long chains of carbon atoms, which contain at least one double bond between carbon atoms. Unsaturated hydrocarbon molecules that contain one or more double bonds are called alkenes. Carbon atoms linked by a double bond are bound together by two bonds, one σ bond and one π bond. Double and triple bonds give rise to a different geometry around the carbon atom that participates in them, leading to important differences in molecular shape and properties. The differing geometries are responsible for the different properties of unsaturated versus saturated fats.

Ethene, C_2H_4 , is the simplest alkene. Each carbon atom in ethene, commonly called ethylene, has a trigonal planar structure. The second member of the series is propene (propylene) (Figure 8.5.1.6); the butene isomers follow in the series. Four carbon atoms in the chain of butene allows for the formation of isomers based on the position of the double bond, as well as a new form of isomerism.

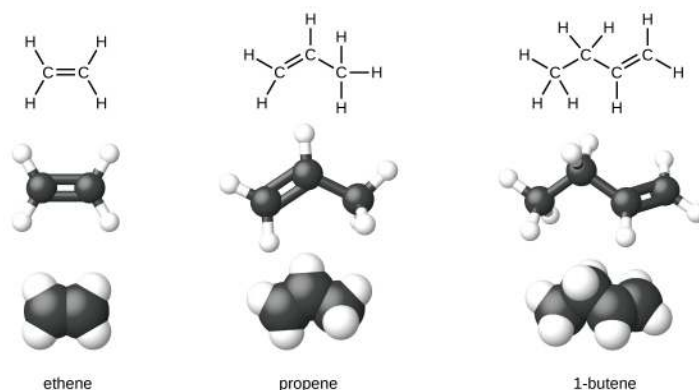


Figure 8.5.1.6: Expanded structures, ball-and-stick structures, and space-filling models for the alkenes ethene, propene, and 1-butene are shown.

Ethylene (the common industrial name for ethene) is a basic raw material in the production of polyethylene and other important compounds. Over 135 million tons of ethylene were produced worldwide in 2010 for use in the polymer, petrochemical, and plastic industries. Ethylene is produced industrially in a process called cracking, in which the long hydrocarbon chains in a petroleum mixture are broken into smaller molecules.

Recycling Plastics

Polymers (from Greek words *poly* meaning “many” and *mer* meaning “parts”) are large molecules made up of repeating units, referred to as monomers. Polymers can be natural (starch is a polymer of sugar residues and proteins are polymers of amino acids) or synthetic [like polyethylene, polyvinyl chloride (PVC), and polystyrene]. The variety of structures of polymers translates into a broad range of properties and uses that make them integral parts of our everyday lives. Adding functional groups to the structure of a polymer can result in significantly different properties (see the discussion about Kevlar later in this chapter).

An example of a polymerization reaction is shown in Figure 8.5.1.7. The monomer ethylene (C₂H₄) is a gas at room temperature, but when polymerized, using a transition metal catalyst, it is transformed into a solid material made up of long chains of –CH₂– units called polyethylene. Polyethylene is a commodity plastic used primarily for packaging (bags and films).

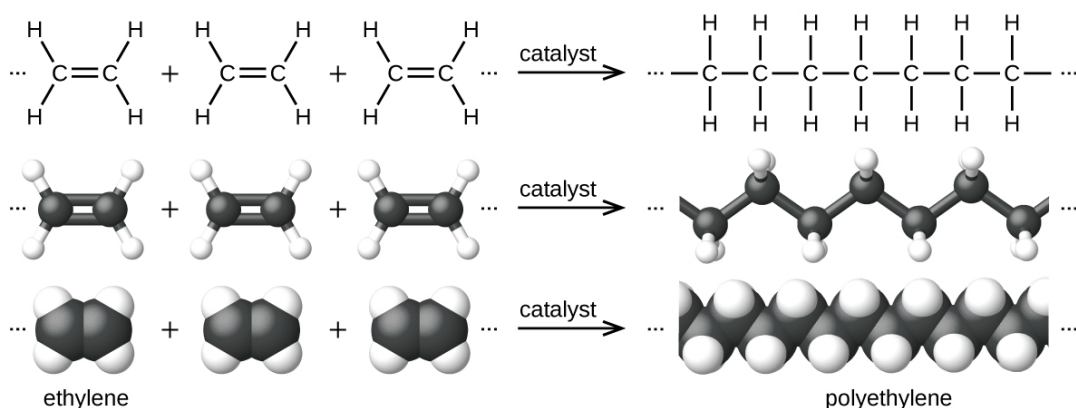


Figure 8.5.1.7: The reaction for the polymerization of ethylene to polyethylene is shown.

This diagram has three rows, showing ethylene reacting to form polyethylene. In the first row, Lewis structural formulas show three molecules of ethylene being added together, which are each composed of two doubly bonded C atoms, each with two bonded H atoms. Ellipses, or three dots, are present before and after the molecule structures, which in turn are followed by an arrow pointing right. On the right side of the arrow, the ellipses or dots again appear to the left of a dash that connects to a chain of 7 C atoms, each with H atoms connected above and below. A dash appears at the end of the chain, which in turn is followed by ellipses or dots. The reaction diagram is repeated in the second row using ball-and-stick models for the structures. In these representations, single bonds are represented with sticks, double bonds are represented with two parallel sticks, and elements are represented with balls. Carbon atoms are black and hydrogen atoms are white in this image. In the third row, space-filling models are shown. In these models, atoms are enlarged spheres which are pushed together, without sticks to represent bonds.

Polyethylene is a member of one subset of synthetic polymers classified as plastics. Plastics are synthetic organic solids that can be molded; they are typically organic polymers with high molecular masses. Most of the monomers that go into common plastics

(ethylene, propylene, vinyl chloride, styrene, and ethylene terephthalate) are derived from petrochemicals and are not very biodegradable, making them candidate materials for recycling. Recycling plastics helps minimize the need for using more of the petrochemical supplies and also minimizes the environmental damage caused by throwing away these nonbiodegradable materials.

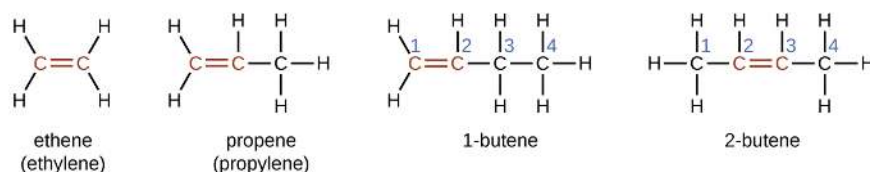
Plastic recycling is the process of recovering waste, scrap, or used plastics, and reprocessing the material into useful products. For example, polyethylene terephthalate (soft drink bottles) can be melted down and used for plastic furniture, in carpets, or for other applications. Other plastics, like polyethylene (bags) and polypropylene (cups, plastic food containers), can be recycled or reprocessed to be used again. Many areas of the country have recycling programs that focus on one or more of the commodity plastics that have been assigned a recycling code (Figure 8.5.1.8). These operations have been in effect since the 1970s and have made the production of some plastics among the most efficient industrial operations today.

	polyethylene terephthalate (PETE)	Soda bottles and oven-ready food trays
	high-density polyethylene (HDPE)	Bottles for milk and dishwashing liquids
	polyvinyl chloride (PVC)	Food trays, plastic wrap, bottles for mineral water and shampoo
	low density polyethylene (LDPE)	Shopping bags and garbage bags
	polypropylene (PP)	Margarine tubs, microwaveable food trays
	polystyrene (PS)	Yogurt tubs, foam meat trays, egg cartons, vending cups, plastic cutlery, packaging for electronics and toys
	any other plastics (OTHER)	Plastics that do not fall into any of the above categories One example is melamine resin (plastic plates, plastic cups)

Figure 8.5.1.8: Each type of recyclable plastic is imprinted with a code for easy identification.

This table shows recycling symbols, names, and uses of various types of plastics. Symbols are shown with three arrows in a triangular shape surrounding a number. Number 1 is labeled P E T E. The related plastic, polyethylene terephthalate (P E T E), is used in soda bottles and oven-ready food trays. Number 2 is labeled H D P E. The related plastic is high-density polyethylene (H D P E), which is used in bottles for milk and dishwashing liquids. Number 3 is labeled V. The related plastic is polyvinyl chloride or (P V C). This plastic is used in food trays, plastic wrap, and bottles for mineral water and shampoo. Number 4 is labeled L D P E. This plastic is low density polyethylene (L D P E). It is used in shopping bags and garbage bags. Number 5 is labeled P P. The related plastic is polypropylene (P P). It is used in margarine tubs and microwaveable food trays. Number 6 is labeled P S. The related plastic is polystyrene (P S). It is used in yogurt tubs, foam meat trays, egg cartons, vending cups, plastic cutlery, and packaging for electronics and toys. Number 7 is labeled other for any other plastics. Items in this category include those plastic materials that do not fit any other category. Melamine used in plastic plates and cups is an example.

The name of an alkene is derived from the name of the alkane with the same number of carbon atoms. The presence of the double bond is signified by replacing the suffix *-ane* with the suffix *-ene*. The location of the double bond is identified by naming the smaller of the numbers of the carbon atoms participating in the double bond:



Four structural formulas and names are shown. The first shows two red C atoms connected by a red double bond illustrated with two parallel line segments. H atoms are bonded above and below to the left of the left-most C atom. Two more H atoms are similarly bonded to the right of the C atom on the right. Beneath this structure the name ethene and alternate name ethylene are shown. The second shows three C atoms bonded together with a red double bond between the red first and second C atoms moving left to right across the three-carbon chain. H atoms are bonded above and below to the left of the C atom to the left. A single H is bonded above the middle C atom. Three more H atoms are bonded above, below, and to the right of the third C atom. Beneath this structure the name propene and alternate name propylene is shown. The third shows four C atoms bonded together, numbered one through four moving left to right with a red double bond between the red first and second carbon in the chain. H atoms are bonded above and below to the left of the C atom to the left. A single H is bonded above the second C atom. H atoms are bonded above and below the third C atom. Three more H atoms are bonded above, below, and to the right of the fourth C atom. Beneath this structure the name 1 dash butene is shown. The fourth shows four C atoms bonded together, numbered one through four moving left to right with a red double bond between the red second and third C atoms in the chain. H atoms are bonded above, below, and to the left of the left-most C atom. A single H atom is bonded above the second C atom. A single H atom is bonded above the third C atom. Three more H atoms are bonded above, below, and to the right of the fourth C atom. Beneath this structure the name 2 dash butene is shown.

Isomers of Alkenes

Molecules of 1-butene and 2-butene are structural isomers; the arrangement of the atoms in these two molecules differs. As an example of arrangement differences, the first carbon atom in 1-butene is bonded to two hydrogen atoms; the first carbon atom in 2-butene is bonded to three hydrogen atoms.

The compound 2-butene and some other alkenes also form a second type of isomer called a geometric isomer. In a set of geometric isomers, the same types of atoms are attached to each other in the same order, but the geometries of the two molecules differ. Geometric isomers of alkenes differ in the orientation of the groups on either side of a $C = C$ bond.

Carbon atoms are free to rotate around a single bond but not around a double bond; a double bond is rigid. This makes it possible to have two isomers of 2-butene, one with both methyl groups on the same side of the double bond and one with the methyl groups on opposite sides. When structures of butene are drawn with 120° bond angles around the sp^2 -hybridized carbon atoms participating in the double bond, the isomers are apparent. The 2-butene isomer in which the two methyl groups are on the same side is called a *cis*-isomer; the one in which the two methyl groups are on opposite sides is called a *trans*-isomer (Figure 8.5.1.9). The different geometries produce different physical properties, such as boiling point, that may make separation of the isomers possible:

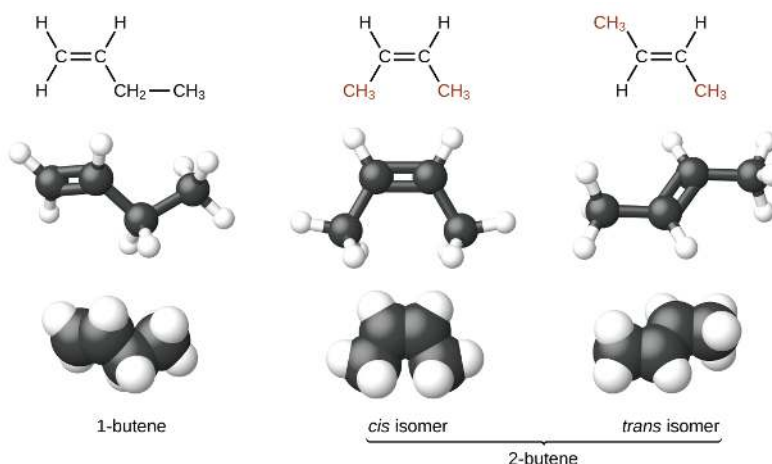
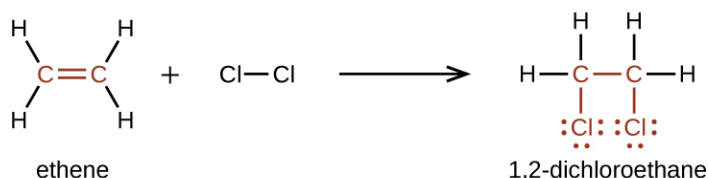


Figure 8.5.1.9: These molecular models show the structural and geometric isomers of butene.

The figure illustrates three ways to represent isomers of butene. In the first row of the figure, Lewis structural formulas show carbon and hydrogen element symbols and bonds between the atoms. The first structure in this row shows a C atom with a double bond to another C atom which is bonded down and to the right to C H subscript 2 which, in turn, is bonded to C H subscript 3. The first C atom, moving from left to right, has two H atoms bonded to it and the second C atom has one H atom bonded to it. The second structure in the row shows a C atom with a double bond to another C atom. The first C atom is bonded to an H atom up and to the left and C H subscript 3 down and to the left. The second C atom is bonded to an H atom up and to the right and C H subscript 3 down and to the right. Both C H subscript 3 structures appear in red. The third structure shows a C atom with a double bond to another C atom. The first C atom from the left is bonded up to the left to C H subscript 3 which appears in red. It is also bonded down and to the left to an H atom. The second C atom is bonded up and to the right to an H atom and down and to the left to C H subscript 3 which appears in red. In the second row, ball-and-stick models for the structures are shown. In these representations, single bonds are represented with sticks, double bonds are represented with two parallel sticks, and elements are represented with balls. C atoms are black and H atoms are white in this image. In the third row, space-filling models are shown. In these models, atoms are enlarged and pushed together, without sticks to represent bonds. In the final row, names are provided. The molecule with the double bond between the first and second carbons is named 1 dash butene. The two molecules with the double bond between the second and third carbon atoms is called 2 dash butene. The first model, which has both C H subscript 3 groups beneath the double bond is called the cis isomer. The second which has the C H subscript 3 groups on opposite sides of the double bond is named the trans isomer.

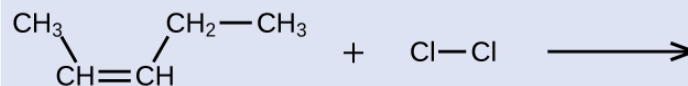
Alkenes are much more reactive than alkanes because the $\text{C}=\text{C}$ moiety is a reactive functional group. A π bond, being a weaker bond, is disrupted much more easily than a σ bond. Thus, alkenes undergo a characteristic reaction in which the π bond is broken and replaced by two σ bonds. This reaction is called an addition reaction. The hybridization of the carbon atoms in the double bond in an alkene changes from sp^2 to sp^3 during an addition reaction. For example, halogens add to the double bond in an alkene instead of replacing hydrogen, as occurs in an alkane:



This diagram illustrates the reaction of ethene and C l subscript 2 to form 1 comma 2 dash dichloroethane. In this reaction, the structural formula of ethane is shown. It has a double bond between the two C atoms with two H atoms bonded to each C atom plus C l bonded to C l. This is shown on to the left of an arrow. The two C atoms and the double bond between them are shown in red. To the right of the arrow, the 1 comma 2 dash dichloroethane molecule is shown. It has only single bonds and each C atom has a C l with three pairs of electron dots bonded beneath it. The C and C l atoms, single bond between them, and electron pairs are shown in red. Each C atom also has two H atoms bonded to it.

✓ Example 8.5.1.5: Alkene Reactivity and Naming

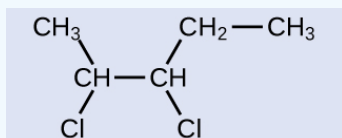
Provide the IUPAC names for the reactant and product of the halogenation reaction shown here:



The left side of a reaction and arrow are shown with an empty product side. On the left, C H subscript 3 is bonded down and to the right to C H which has a double bond to another C H. The second C H is bonded up and to the right to C H subscript 2 which is also bonded to C H subscript 3. A plus sign is shown with a C l atom bonded to a C l atom following it. This is also followed by a reaction arrow.

Solution

The reactant is a five-carbon chain that contains a carbon-carbon double bond, so the base name will be pentene. We begin counting at the end of the chain closest to the double bond—in this case, from the left—the double bond spans carbons 2 and 3, so the name becomes 2-pentene. Since there are two carbon-containing groups attached to the two carbon atoms in the double bond—and they are on the same side of the double bond—this molecule is the *cis*-isomer, making the name of the starting alkene *cis*-2-pentene. The product of the halogenation reaction will have two chlorine atoms attached to the carbon atoms that were a part of the carbon-carbon double bond:

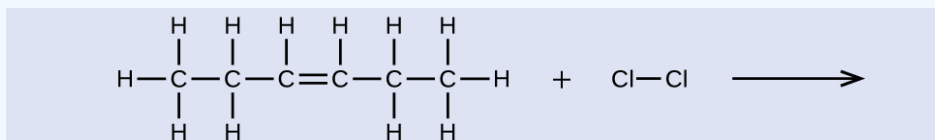


C H subscript 3 is bonded down and to the right to C H which is bonded down and to the left to C l. C H is also bonded to another C H which is bonded down and to the right to C l and up and to the right to C H subscript 2. C H subscript 2 is also bonded to C H subscript 3.

This molecule is now a substituted alkane and will be named as such. The base of the name will be pentane. We will count from the end that numbers the carbon atoms where the chlorine atoms are attached as 2 and 3, making the name of the product 2,3-dichloropentane.

? Exercise 8.5.1.5

Provide names for the reactant and product of the reaction shown:



This shows a C atom bonded to three H atoms and another C atom. This second C atom is bonded to two H atoms and a third C atom. This third C atom is bonded to one H atom and also forms a double bond with a fourth C atom. This fourth C atom is bonded to one H atom and a fifth C atom. This fifth C atom is bonded to two H atoms and a sixth C atom. This sixth C atom is bonded to three H atoms. There is a plus sign followed by a C l atom bonded to another C l atom. There is a reaction arrow. no products are shown.

Answer

reactant: *cis*-3-hexene, product: 3,4-dichlorohexane

Alkynes

Hydrocarbon molecules with one or more triple bonds are called alkynes; they make up another series of unsaturated hydrocarbons. Two carbon atoms joined by a triple bond are bound together by one σ bond and two π bonds. The *sp*-hybridized carbons involved in the triple bond have bond angles of 180° , giving these types of bonds a linear, rod-like shape.

The simplest member of the alkyne series is ethyne, C_2H_2 , commonly called acetylene. The Lewis structure for ethyne, a linear molecule, is:



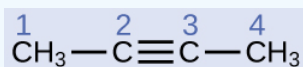
ethyne (acetylene)

The structural formula and name for ethyne, also known as acetylene, are shown. In red, two C atoms are shown with a triple bond illustrated by three horizontal line segments between them. Shown in black at each end of the structure, a single H atom is bonded.

The IUPAC nomenclature for alkynes is similar to that for alkenes except that the suffix *-yne* is used to indicate a triple bond in the chain. For example, $\text{CH}_3\text{CH}_2\text{C}\equiv\text{CH}$ is called 1-butyne.

✓ Example 8.5.1.6: Structure of Alkynes

Describe the geometry and hybridization of the carbon atoms in the following molecule:



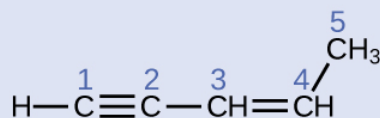
A structural formula is shown with C H subscript 3 bonded to a C atom which is triple bonded to another C atom which is bonded to C H subscript 3. Each C atom is labeled 1, 2, 3, and 4 from left to right.

Solution

Carbon atoms 1 and 4 have four single bonds and are thus tetrahedral with sp^3 hybridization. Carbon atoms 2 and 3 are involved in the triple bond, so they have linear geometries and would be classified as sp hybrids.

? Exercise 8.5.1.6

Identify the hybridization and bond angles at the carbon atoms in the molecule shown:

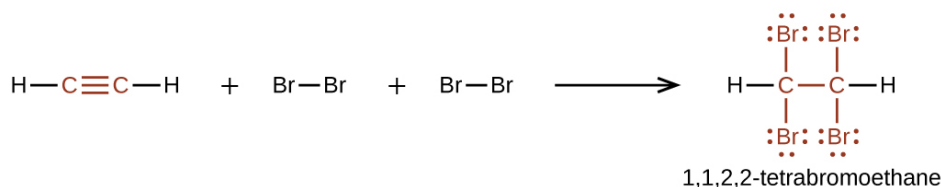


A structural formula is shown with an H atom bonded to a C atom. The C atom has a triple bond with another C atom which is also bonded to C H. The C H has a double bond with another C H which is also bonded up and to the right to C H subscript 3. Each C atom is labeled 1, 2, 3, 4, or 5 from left to right.

Answer

carbon 1: sp , 180° ; carbon 2: sp , 180° ; carbon 3: sp^2 , 120° ; carbon 4: sp^2 , 120° ; carbon 5: sp^3 , 109.5°

Chemically, the alkynes are similar to the alkenes. Since the $\text{C}\equiv\text{C}$ functional group has two π bonds, alkynes typically react even more readily, and react with twice as much reagent in addition reactions. The reaction of acetylene with bromine is a typical example:



This diagram illustrates the reaction of ethyne and two molecules of Br₂ to form 1,1,2,2-tetrabromoethane. In this reaction, the structural formula of ethyne, an H atom bonded to a red C atom with a red triple bond to another red C atom bonded to a black H atom, plus Br bonded to Br plus Br bonded to Br is shown to the left of an arrow. On the right, the 1,1,2,2-tetrabromoethane molecule is shown. It has an H atom bonded to a C atom which is bonded to another C atom which is bonded to an H atom. Each C atom is bonded above and below to a Br atom. Each Br atom has three pairs of electron dots. The C and Br atoms, single bond between them, and electron pairs are shown in red.

Acetylene and the other alkynes also burn readily. An acetylene torch takes advantage of the high heat of combustion for acetylene.

Aromatic Hydrocarbons

Benzene, C₆H₆, is the simplest member of a large family of hydrocarbons, called aromatic hydrocarbons. These compounds contain ring structures and exhibit bonding that must be described using the resonance hybrid concept of valence bond theory or the delocalization concept of molecular orbital theory. (To review these concepts, refer to the earlier chapters on chemical bonding). The resonance structures for benzene, C₆H₆, are:

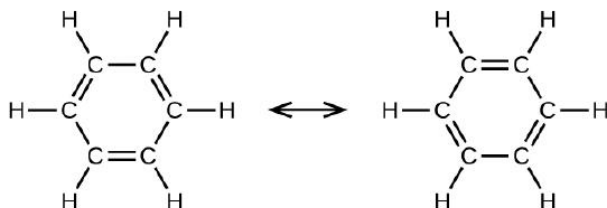


Figure 8.5.1.10.

This structural formula shows a six carbon hydrocarbon ring. On the left side there are six C atoms. The C atom on top and to the left forms a single bond to the C atom on the top and to the right. The C atom has a double bond to another C atom which has a single bond to a C atom. That C atom has a double bond to another C atom which has a single bond to a C atom. That C atom forms a double bond with another C atom. Each C atom has a single bond to an H atom. There is a double sided arrow and the structure on the right is almost identical to the structure on the left. The structure on the right shows double bonds where the structure on the left showed single bonds. The structure on the right shows single bonds where the structure on the left showed double bonds.

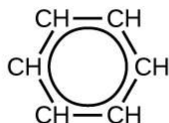
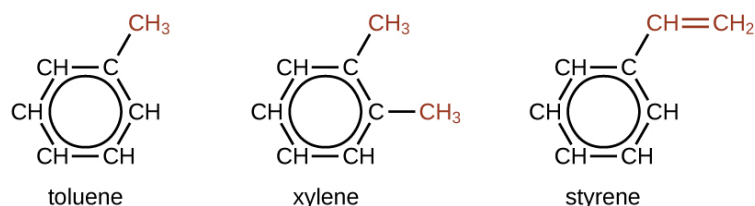


Figure 8.5.1.10: This condensed formula shows the unique bonding structure of benzene.

A six carbon hydrocarbon ring structural formula is shown. Each C atom is bonded to only one H atom. A circle is at the center of the ring.

There are many derivatives of benzene. The hydrogen atoms can be replaced by many different substituents. Aromatic compounds more readily undergo substitution reactions than addition reactions; replacement of one of the hydrogen atoms with another substituent will leave the delocalized double bonds intact. The following are typical examples of substituted benzene derivatives:

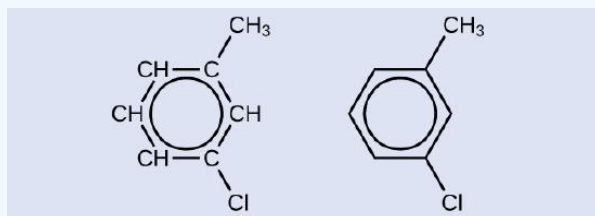


Three structural formulas are shown. The first is labeled toluene. This molecule has a six carbon hydrocarbon ring in which five of the C atoms are each bonded to only one H atom. At the upper right of the ring, the C atom that does not have a bonded H atom has a red C H subscript 3 group attached. A circle is at the center of the ring. The second is labeled xylene. This molecule has a six carbon hydrocarbon ring in which four of the C atoms are each bonded to only one H atom. At the upper right and right of the ring, the two C atoms that do not have bonded H atoms have C H subscript 3 groups attached. These C H subscript 3 groups appear in red. A circle is at the center of the ring. The third is labeled styrene. This molecule has a six carbon hydrocarbon ring in which five of the carbon atoms are each bonded to only one H atom. At the upper right of the ring, the carbon that does not have a bonded H atom has a red C H double bond C H subscript 2 group attached. A circle is at the center of the ring.

Toluene and xylene are important solvents and raw materials in the chemical industry. Styrene is used to produce the polymer polystyrene.

✓ Example 8.5.1.7: Structure of Aromatic Hydrocarbons

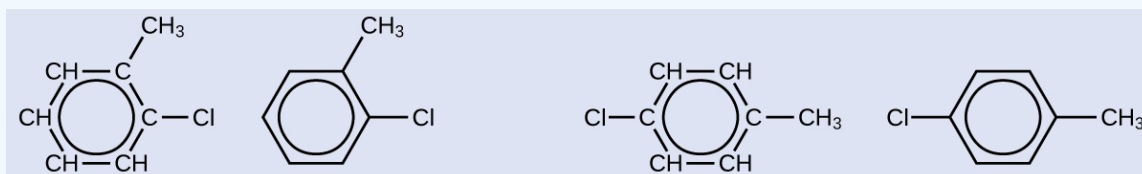
One possible isomer created by a substitution reaction that replaces a hydrogen atom attached to the aromatic ring of toluene with a chlorine atom is shown here. Draw two other possible isomers in which the chlorine atom replaces a different hydrogen atom attached to the aromatic ring:



Two structural formulas are shown. The first has a six carbon hydrocarbon ring in which four of the carbon atoms are each bonded to only one H atom. At the upper right of the ring, the carbon that does not have a bonded H atom has a C H subscript 3 group attached. The C to the lower right has a C l atom attached. A circle is at the center of the ring. The second molecule has a hexagon with a circle inside. From a vertex of the hexagon at the upper right a C H subscript 3 group is attached. From the vertex at the lower right, a C l atom is attached.

Solution

Since the six-carbon ring with alternating double bonds is necessary for the molecule to be classified as aromatic, appropriate isomers can be produced only by changing the positions of the chloro-substituent relative to the methyl-substituent:

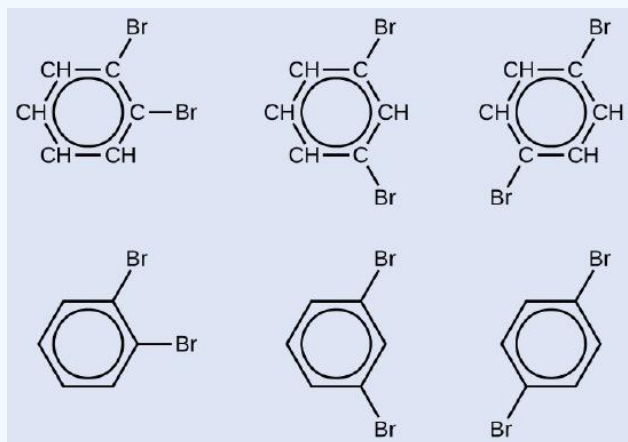


Two pairs of structural formulas are shown. The first has a six carbon hydrocarbon ring in which four of the C atoms are each bonded to only one H atom. At the upper right of the ring, the C atom that does not have a bonded H atom has a C H subscript 3 group attached. The C atom to the right has a C l atom attached. A circle is at the center of the ring. The second molecule in the first pair has a hexagon with a circle inside. From a vertex of the hexagon at the upper right a C H subscript 3 group is attached. From the vertex at the right, a C l atom is attached. The second pair first shows a six carbon hydrocarbon ring in which four of the C atoms are each bonded to only one H atom. A C l atom is attached to the left-most C atom and a C H subscript 3 group is attached to the right-most C atom. A circle is at the center of the ring. The second molecule in the pair has a hexagon with a circle inside. A C H subscript 3 group is attached to a vertex on the right side of the hexagon and to a vertex on the left side, a C l atom is bonded.

? Exercise 8.5.1.7

Draw three isomers of a six-membered aromatic ring compound substituted with two bromines.

Answer



Three pairs of structural formulas are shown. The first has a six carbon hydrocarbon ring in which four of the C atoms are each bonded to only one H atom. At the upper right and right of the ring, the two C atoms that do not have bonded H atoms have one Br atom bonded each. A circle is at the center of the ring. Beneath this structure, a similar structure is shown which has a hexagon with a circle inside. From vertices of the hexagon at the upper right and right single Br atoms are attached. The second has a six carbon hydrocarbon ring in which four of the C atoms are each bonded to only one H atom. At the upper right and lower right of the ring, the two C atoms that do not have bonded H atoms have a single Br atom bonded each. A circle is at the center of the ring. Beneath this structure, a similar structure is shown which has a hexagon with a circle inside. From vertices of the hexagon at the upper right and lower right single Br atoms are attached. The third has a six carbon hydrocarbon ring in which four of the C atoms are each bonded to only one H atom. At the upper right and lower left of the ring, the two C atoms that do not have bonded H atoms have Br atoms bonded. A circle is at the center of the ring. Beneath this structure, a similar structure is shown which has a hexagon with a circle inside. From vertices of the hexagon at the upper right and lower left, single Br atoms are attached.

Summary

Strong, stable bonds between carbon atoms produce complex molecules containing chains, branches, and rings. The chemistry of these compounds is called organic chemistry. Hydrocarbons are organic compounds composed of only carbon and hydrogen. The alkanes are saturated hydrocarbons—that is, hydrocarbons that contain only single bonds. Alkenes contain one or more carbon-carbon double bonds. Alkynes contain one or more carbon-carbon triple bonds. Aromatic hydrocarbons contain ring structures with delocalized π electron systems.

Footnotes

1. This is the Beilstein database, now available through the Reaxys site (www.elsevier.com/online-tools/reaxys).
2. Peplow, Mark. "Organic Synthesis: The Robo-Chemist," *Nature* 512 (2014): 20–2.
3. Physical properties for C_4H_{10} and heavier molecules are those of the *normal isomer*, *n*-butane, *n*-pentane, etc.
4. STP indicates a temperature of 0 °C and a pressure of 1 atm.

Glossary

addition reaction

reaction in which a double carbon-carbon bond forms a single carbon-carbon bond by the addition of a reactant. Typical reaction for an alkene.

alkane

molecule consisting of only carbon and hydrogen atoms connected by single (σ) bonds

alkene

molecule consisting of carbon and hydrogen containing at least one carbon-carbon double bond

alkyl group

substituent, consisting of an alkane missing one hydrogen atom, attached to a larger structure

alkyne

molecule consisting of carbon and hydrogen containing at least one carbon-carbon triple bond

aromatic hydrocarbon

cyclic molecule consisting of carbon and hydrogen with delocalized alternating carbon-carbon single and double bonds, resulting in enhanced stability

functional group

part of an organic molecule that imparts a specific chemical reactivity to the molecule

organic compound

natural or synthetic compound that contains carbon

saturated hydrocarbon

molecule containing carbon and hydrogen that has only single bonds between carbon atoms

skeletal structure

shorthand method of drawing organic molecules in which carbon atoms are represented by the ends of lines and bends in between lines, and hydrogen atoms attached to the carbon atoms are not shown (but are understood to be present by the context of the structure)

substituent

branch or functional group that replaces hydrogen atoms in a larger hydrocarbon chain

substitution reaction

reaction in which one atom replaces another in a molecule

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8.5.2: Alcohols and Ethers

Learning Objectives

- Describe the structure and properties of alcohols
- Describe the structure and properties of ethers
- Name and draw structures for alcohols and ethers

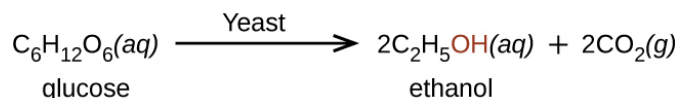
In this section, we will learn about alcohols and ethers.

Alcohols

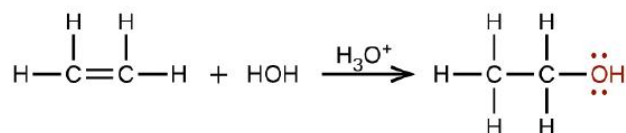
Incorporation of an oxygen atom into carbon- and hydrogen-containing molecules leads to new functional groups and new families of compounds. When the oxygen atom is attached by single bonds, the molecule is either an alcohol or ether.

Alcohols are derivatives of hydrocarbons in which an -OH group has replaced a hydrogen atom. Although all alcohols have one or more hydroxyl (-OH) functional groups, they do not behave like bases such as NaOH and KOH . NaOH and KOH are ionic compounds that contain OH^- ions. Alcohols are covalent molecules; the -OH group in an alcohol molecule is attached to a carbon atom by a covalent bond.

Ethanol, $\text{CH}_3\text{CH}_2\text{OH}$, also called ethyl alcohol, is a particularly important alcohol for human use. Ethanol is the alcohol produced by some species of yeast that is found in wine, beer, and distilled drinks. It has long been prepared by humans harnessing the metabolic efforts of yeasts in fermenting various sugars:

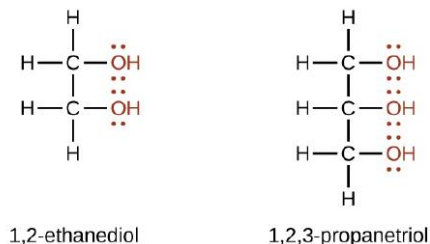


Large quantities of ethanol are synthesized from the addition reaction of water with ethylene using an acid as a catalyst:



This reaction shows two carbons connected by a double bond, each with two bonded H atoms plus H O H arrow labeled “H subscript 3 O superscript plus” followed by two carbon atoms connected with a single bond with 5 bonded H atoms and an O H group shown in red at the right end of the molecule. The O of this group is shown with 2 pairs of electron dots.

Alcohols containing two or more hydroxyl groups can be made. Examples include 1,2-ethanediol (ethylene glycol, used in antifreeze) and 1,2,3-propanetriol (glycerine, used as a solvent for cosmetics and medicines):

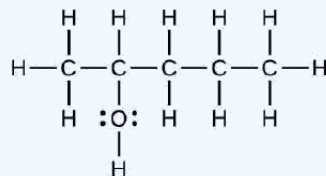


Naming Alcohols

The name of an alcohol comes from the hydrocarbon from which it was derived. The final -e in the name of the hydrocarbon is replaced by -ol , and the carbon atom to which the -OH group is bonded is indicated by a number placed before the name.¹

✓ Example 8.5.2.1: Naming Alcohols

Consider the following example. How should it be named?

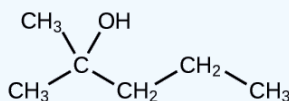


Solution

The carbon chain contains five carbon atoms. If the hydroxyl group was not present, we would have named this molecule pentane. To address the fact that the hydroxyl group is present, we change the ending of the name to *-ol*. In this case, since the -OH is attached to carbon 2 in the chain, we would name this molecule 2-pentanol.

? Exercise 8.5.2.1

Name the following molecule:



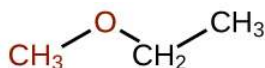
The structure shown has a C H subscript 3 group bonded up and to the right to a C atom. The C atom is bonded down and to the right to a C H subscript 2 group. The C H subscript 2 group is bonded up and to the right to a C H subscript 2 group. The C H subscript 2 group is bonded down and to the right to a C H subscript 3 group. The second C atom (from left to right) is bonded to a C H subscript 3 group and an O H group.

Answer

2-methyl-2-pentanol

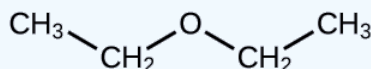
Ethers

Ethers are compounds that contain the functional group -O- . Ethers do not have a designated suffix like the other types of molecules we have named so far. In the IUPAC system, the oxygen atom and the smaller carbon branch are named as an alkoxy substituent and the remainder of the molecule as the base chain, as in alkanes. As shown in the following compound, the red symbols represent the smaller alkyl group and the oxygen atom, which would be named “methoxy.” The larger carbon branch would be ethane, making the molecule methoxyethane. Many ethers are referred to with common names instead of the IUPAC system names. For common names, the two branches connected to the oxygen atom are named separately and followed by “ether.” The common name for the compound shown in below is ethylmethyl ether:



✓ Example 8.5.2.2: Naming Ethers

Provide the IUPAC and common name for the ether shown here:



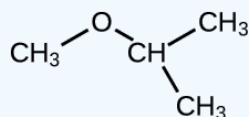
Solution

- IUPAC name: The molecule is made up of an ethoxy group attached to an ethane chain, so the IUPAC name would be ethoxyethane.

- Common name: The groups attached to the oxygen atom are both ethyl groups, so the common name would be diethyl ether.

? Exercise 8.5.2.2

Provide the IUPAC and common name for the ether shown:

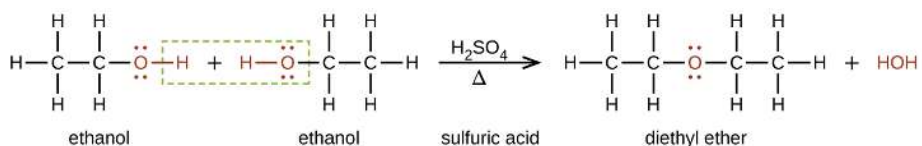


A molecular structure shows a C H subscript 3 group bonded up and to the right to an O atom. The O atom is bonded down and to the right to a C H group. The C H group is bonded up and to the right to a C H subscript 3 group. The C H group is also bonded down and to the right to another C H subscript 3 group.

Answer

IUPAC: 2-methoxypropane; common: isopropylmethyl ether

Ethers can be obtained from alcohols by the elimination of a molecule of water from two molecules of the alcohol. For example, when ethanol is treated with a limited amount of sulfuric acid and heated to 140 °C, diethyl ether and water are formed:



In the general formula for ethers, R—O—R, the hydrocarbon groups (R) may be the same or different. Diethyl ether, the most widely used compound of this class, is a colorless, volatile liquid that is highly flammable. It was first used in 1846 as an anesthetic, but better anesthetics have now largely taken its place. Diethyl ether and other ethers are presently used primarily as solvents for gums, fats, waxes, and resins. *Tertiary*-butyl methyl ether, C₄H₉OCH₃ (abbreviated MTBE—italicized portions of names are not counted when ranking the groups alphabetically—so butyl comes before methyl in the common name), is used as an additive for gasoline. MTBE belongs to a group of chemicals known as oxygenates due to their capacity to increase the oxygen content of gasoline.

📌 Carbohydrates and Diabetes

Carbohydrates are large biomolecules made up of carbon, hydrogen, and oxygen. The dietary forms of carbohydrates are foods rich in these types of molecules, like pastas, bread, and candy. The name “carbohydrate” comes from the formula of the molecules, which can be described by the general formula C_m(H₂O)_n, which shows that they are in a sense “carbon and water” or “hydrates of carbon.” In many cases, *m* and *n* have the same value, but they can be different. The smaller carbohydrates are generally referred to as “sugars,” the biochemical term for this group of molecules is “saccharide” from the Greek word for sugar (Figure 8.5.2.1). Depending on the number of sugar units joined together, they may be classified as monosaccharides (one sugar unit), disaccharides (two sugar units), oligosaccharides (a few sugars), or polysaccharides (the polymeric version of sugars—polymers were described in the feature box earlier in this chapter on recycling plastics). The scientific names of sugars can be recognized by the suffix *-ose* at the end of the name (for instance, fruit sugar is a monosaccharide called “fructose” and milk sugar is a disaccharide called lactose composed of two monosaccharides, glucose and galactose, connected together). Sugars contain some of the functional groups we have discussed: Note the alcohol groups present in the structures and how monosaccharide units are linked to form a disaccharide by formation of an ether.

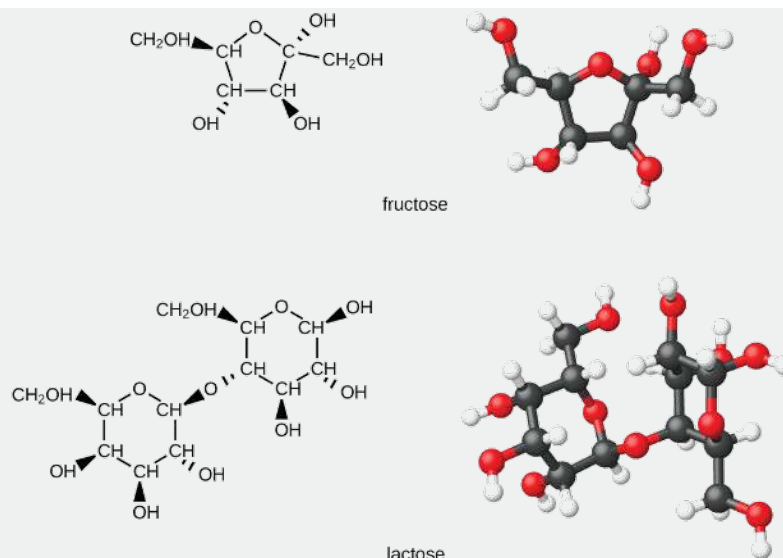


Figure 8.5.2.1: The illustrations show the molecular structures of fructose, a five-carbon monosaccharide, and of lactose, a disaccharide composed of two isomeric, six-carbon sugars.

Organisms use carbohydrates for a variety of functions. Carbohydrates can store energy, such as the polysaccharides glycogen in animals or starch in plants. They also provide structural support, such as the polysaccharide cellulose in plants and the modified polysaccharide chitin in fungi and animals. The sugars ribose and deoxyribose are components of the backbones of RNA and DNA, respectively. Other sugars play key roles in the function of the immune system, in cell-cell recognition, and in many other biological roles.

Diabetes is a group of metabolic diseases in which a person has a high sugar concentration in their blood (Figure 8.5.2.2). Diabetes may be caused by insufficient insulin production by the pancreas or by the body's cells not responding properly to the insulin that is produced. In a healthy person, insulin is produced when it is needed and functions to transport glucose from the blood into the cells where it can be used for energy. The long-term complications of diabetes can include loss of eyesight, heart disease, and kidney failure.



Figure 8.5.2.2: Diabetes is a disease characterized by high concentrations of glucose in the blood. Treating diabetes involves making lifestyle changes, monitoring blood-sugar levels, and sometimes insulin injections. (credit: "Blausen Medical Communications"/Wikimedia Commons)

In 2013, it was estimated that approximately 3.3% of the world's population (~380 million people) suffered from diabetes, resulting in over a million deaths annually. Prevention involves eating a healthy diet, getting plenty of exercise, and maintaining a normal body weight. Treatment involves all of these lifestyle practices and may require injections of insulin.

Summary

Many organic compounds that are not hydrocarbons can be thought of as derivatives of hydrocarbons. A hydrocarbon derivative can be formed by replacing one or more hydrogen atoms of a hydrocarbon by a functional group, which contains at least one atom of an element other than carbon or hydrogen. The properties of hydrocarbon derivatives are determined largely by the functional group. The -OH group is the functional group of an alcohol. The -R-O-R- group is the functional group of an ether.

Footnotes

1. The IUPAC adopted new nomenclature guidelines in 2013 that require this number to be placed as an “infix” rather than a prefix. For example, the new name for 2-propanol would be propan-2-ol. Widespread adoption of this new nomenclature will take some time, and students are encouraged to be familiar with both the old and new naming protocols.

Glossary

alcohol

organic compound with a hydroxyl group (-OH) bonded to a carbon atom

ether

organic compound with an oxygen atom that is bonded to two carbon atoms

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8.5.3: Aldehydes, Ketones, Carboxylic Acids, and Esters

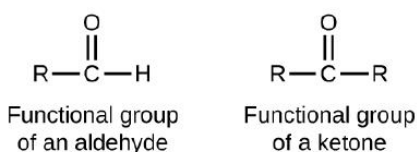
Learning Objectives

- Describe the structure and properties of aldehydes, ketones, carboxylic acids and esters

Another class of organic molecules contains a carbon atom connected to an oxygen atom by a double bond, commonly called a carbonyl group. The trigonal planar carbon in the carbonyl group can attach to two other substituents leading to several subfamilies (aldehydes, ketones, carboxylic acids and esters) described in this section.

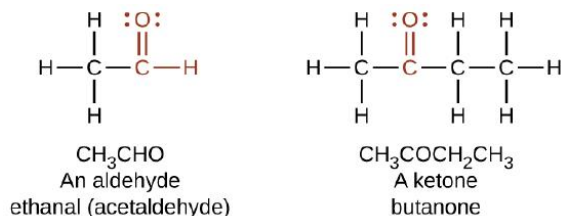
Aldehydes and Ketones

Both aldehydes and ketones contain a carbonyl group, a functional group with a carbon-oxygen double bond. The names for aldehyde and ketone compounds are derived using similar nomenclature rules as for alkanes and alcohols, and include the class-identifying suffixes *-al* and *-one*, respectively.



Five structures are shown. The first is a C atom with an R group bonded to the left and an H atom to the right. An O atom is double bonded above the C atom. This structure is labeled, "Functional group of an aldehyde." The second structure shows a C atom with R groups bonded to the left and right. An O atom is double bonded above the C atom. This structure is labeled, "Functional group of a ketone." The third structure looks exactly like the functional group of a ketone. The fourth structure is labeled C H subscript 3 C H O. It is also labeled, "An aldehyde," and "ethanal (acetaldehyde)." This structure has a C atom to which 3 H atoms are bonded above, below, and to the left. In red to the right of this C atom, a C atom is attached which has an O atom double bonded above and an H atom bonded to the right. The O atom has two sets of electron dots. The fifth structure is labeled C H subscript 3 C O C H subscript 2 C H subscript 3. It is also labeled, "A ketone," and "butanone." This structure has a C atom to which 3 H atoms are bonded above, below, and to the left. To the right of this in red is a C atom to which an O atom is double bonded above. The O atom has two sets of electron dots. Attached to the right of this red C atom in black is a two carbon atom chain with H atoms attached above, below, and to the right.

In an aldehyde, the carbonyl group is bonded to at least one hydrogen atom. In a ketone, the carbonyl group is bonded to two carbon atoms. As text, an aldehyde group is represented as $-\text{CHO}$; a ketone is represented as $-\text{C}(\text{O})-$ or $-\text{CO}-$.



In both aldehydes and ketones, the geometry around the carbon atom in the carbonyl group is trigonal planar; the carbon atom exhibits sp^2 hybridization. Two of the sp^2 orbitals on the carbon atom in the carbonyl group are used to form σ bonds to the other carbon or hydrogen atoms in a molecule. The remaining sp^2 hybrid orbital forms a σ bond to the oxygen atom. The unhybridized p orbital on the carbon atom in the carbonyl group overlaps a p orbital on the oxygen atom to form the π bond in the double bond.

Like the $\text{C}=\text{O}$ bond in carbon dioxide, the $\text{C}=\text{O}$ bond of a carbonyl group is polar (recall that oxygen is significantly more electronegative than carbon, and the shared electrons are pulled toward the oxygen atom and away from the carbon atom). Many of the reactions of aldehydes and ketones start with the reaction between a Lewis base and the carbon atom at the positive end of the polar $\text{C}=\text{O}$ bond to yield an unstable intermediate that subsequently undergoes one or more structural rearrangements to form the final product (Figure 8.5.3.1).

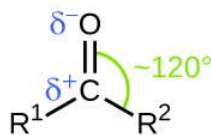
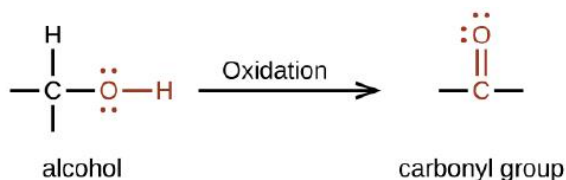


Figure 8.5.3.1: The carbonyl group is polar, and the geometry of the bonds around the central carbon is trigonal planar.

This structure shows a central C atom to which an O atom is double bonded above. To the lower left, R superscript 1 is bonded and to the lower right, R superscript 2 is bonded. A Greek lowercase delta superscript plus appears to the left of the C and just above the bond with R superscript 1. Similarly, a Greek lowercase delta superscript negative sign appears to the left of the O atom. An arc is drawn from the double bond that links the C atom and the O atom to the bond that links the C atom to the R superscript 2 group. This arc is labeled approximately 120 degrees.

The importance of molecular structure in the reactivity of organic compounds is illustrated by the reactions that produce aldehydes and ketones. We can prepare a carbonyl group by oxidation of an alcohol—for organic molecules, oxidation of a carbon atom is said to occur when a carbon-hydrogen bond is replaced by a carbon-oxygen bond. The reverse reaction—replacing a carbon-oxygen bond by a carbon-hydrogen bond—is a reduction of that carbon atom. Recall that oxygen is generally assigned a -2 oxidation number unless it is elemental or attached to a fluorine. Hydrogen is generally assigned an oxidation number of $+1$ unless it is attached to a metal. Since carbon does not have a specific rule, its oxidation number is determined algebraically by factoring the atoms it is attached to and the overall charge of the molecule or ion. In general, a carbon atom attached to an oxygen atom will have a more positive oxidation number and a carbon atom attached to a hydrogen atom will have a more negative oxidation number. This should fit nicely with your understanding of the polarity of C–O and C–H bonds. The other reagents and possible products of these reactions are beyond the scope of this chapter, so we will focus only on the changes to the carbon atoms:



A reaction is shown. On the left appears an alcohol and on the right, a carbonyl group. Above the reaction arrow appears the word “oxidation.” The alcohol is represented as a C atom with dashes to the left and below, an H atom bonded above, and an O atom bonded to an H atom in red connected to the right. The O atom has two sets of electron dots. The carbonyl group is indicated in red with a C atom to which an O atom is double bonded above. Dashes appear left and right of the C atom in black. The O atom has two sets of electron dots.

✓ Example 8.5.3.1: Oxidation and Reduction in Organic Chemistry

Methane represents the completely reduced form of an organic molecule that contains one carbon atom. Sequentially replacing each of the carbon-hydrogen bonds with a carbon-oxygen bond would lead to an alcohol, then an aldehyde, then a carboxylic acid (discussed later), and, finally, carbon dioxide:



What are the oxidation numbers for the carbon atoms in the molecules shown here?

Solution

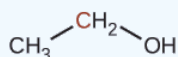
In this example, we can calculate the oxidation number (review the chapter on oxidation-reduction reactions if necessary) for the carbon atom in each case (note how this would become difficult for larger molecules with additional carbon atoms and hydrogen atoms, which is why organic chemists use the definition dealing with replacing C–H bonds with C–O bonds described).

- For CH_4 , the carbon atom carries a -4 oxidation number (the hydrogen atoms are assigned oxidation numbers of $+1$ and the carbon atom balances that by having an oxidation number of -4)
- For the alcohol (in this case, methanol), the carbon atom has an oxidation number of -2 (the oxygen atom is assigned -2 , the four hydrogen atoms each are assigned $+1$, and the carbon atom balances the sum by having an oxidation number of -2 ; note that compared to the carbon atom in CH_4 , this carbon atom has lost two electrons so it was oxidized)

- For the aldehyde, the carbon atom's oxidation number is 0 (–2 for the oxygen atom and +1 for each hydrogen atom already balances to 0, so the oxidation number for the carbon atom is 0)
- For the carboxylic acid, the carbon atom's oxidation number is +2 (two oxygen atoms each at –2 and two hydrogen atoms at +1)
- For carbon dioxide, the carbon atom's oxidation number is +4 (here, the carbon atom needs to balance the –4 sum from the two oxygen atoms).

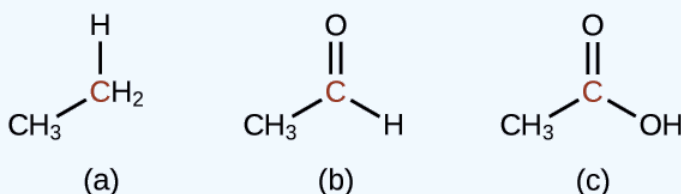
? Exercise 8.5.3.1

Indicate whether the marked carbon atoms in the three molecules here are oxidized or reduced relative to the marked carbon atom in ethanol:



A molecular structure is shown. A C H subscript 3 group is bonded up and to the right to a C H subscript 2 group. Bonded to the C H subscript 2 group down and to the right is an O H group.

There is no need to calculate oxidation states in this case; instead, just compare the types of atoms bonded to the marked carbon atoms:



Three molecular structures are shown, each with a red central C atom. In a, a C H subscript 3 group is bonded to the lower left, an H atom is bonded above, and H subscript 2 appears to the right of the central C atom. In b, an O atom is double bonded above the central C atom, a C H subscript 3 group is bonded to the lower left, and an H atom is bonded to the lower right. In c, an O atom is double bonded above the central C atom, a C H subscript 3 group is bonded to the lower left, and an O H group is bonded to the lower right.

Answer a

reduced (bond to oxygen atom replaced by bond to hydrogen atom);

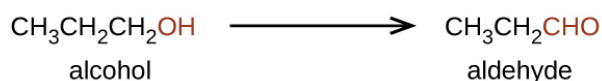
Answer b

oxidized (one bond to hydrogen atom replaced by one bond to oxygen atom);

Answer c

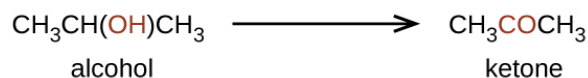
oxidized (2 bonds to hydrogen atoms have been replaced by bonds to an oxygen atom)

Aldehydes are commonly prepared by the oxidation of alcohols whose –OH functional group is located on the carbon atom at the end of the chain of carbon atoms in the alcohol:



A reaction is shown. An alcohol appears on the left and an aldehyde on the right of the reaction arrow. The alcohol is shown as C H subscript 3 C H subscript 2 C H subscript 2 O H, and the aldehyde is shown as C H subscript 3 C H subscript 2 C H O. The O H group at the right end of the alcohol structure and the C H O group at the right end of the aldehyde structure are in red.

Alcohols that have their -OH groups in the middle of the chain are necessary to synthesize a ketone, which requires the carbonyl group to be bonded to two other carbon atoms:



A reaction is shown. An alcohol appears on the left and a ketone on the right of the reaction arrow. The alcohol is shown as $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$ and the ketone is shown as CH_3COCH_3 . The OH group in the alcohol structure and the CO group at the center of the ketone structure are in red.

An alcohol with its -OH group bonded to a carbon atom that is bonded to no or one other carbon atom will form an aldehyde. An alcohol with its -OH group attached to two other carbon atoms will form a ketone. If three carbons are attached to the carbon bonded to the -OH , the molecule will not have a C-H bond to be replaced, so it will not be susceptible to oxidation.

Formaldehyde, an aldehyde with the formula HCHO , is a colorless gas with a pungent and irritating odor. It is sold in an aqueous solution called formalin, which contains about 37% formaldehyde by weight. Formaldehyde causes coagulation of proteins, so it kills bacteria (and any other living organism) and stops many of the biological processes that cause tissue to decay. Thus, formaldehyde is used for preserving tissue specimens and embalming bodies. It is also used to sterilize soil or other materials. Formaldehyde is used in the manufacture of Bakelite, a hard plastic having high chemical and electrical resistance.

Dimethyl ketone, CH_3COCH_3 , commonly called acetone, is the simplest ketone. It is made commercially by fermenting corn or molasses, or by oxidation of 2-propanol. Acetone is a colorless liquid. Among its many uses are as a solvent for lacquer (including fingernail polish), cellulose acetate, cellulose nitrate, acetylene, plastics, and varnishes; as a paint and varnish remover; and as a solvent in the manufacture of pharmaceuticals and chemicals.

Carboxylic Acids and Esters

The odor of vinegar is caused by the presence of acetic acid, a carboxylic acid, in the vinegar. The odor of ripe bananas and many other fruits is due to the presence of esters, compounds that can be prepared by the reaction of a carboxylic acid with an alcohol. Because esters do not have hydrogen bonds between molecules, they have lower vapor pressures than the alcohols and carboxylic acids from which they are derived (Figure 8.5.3.2).

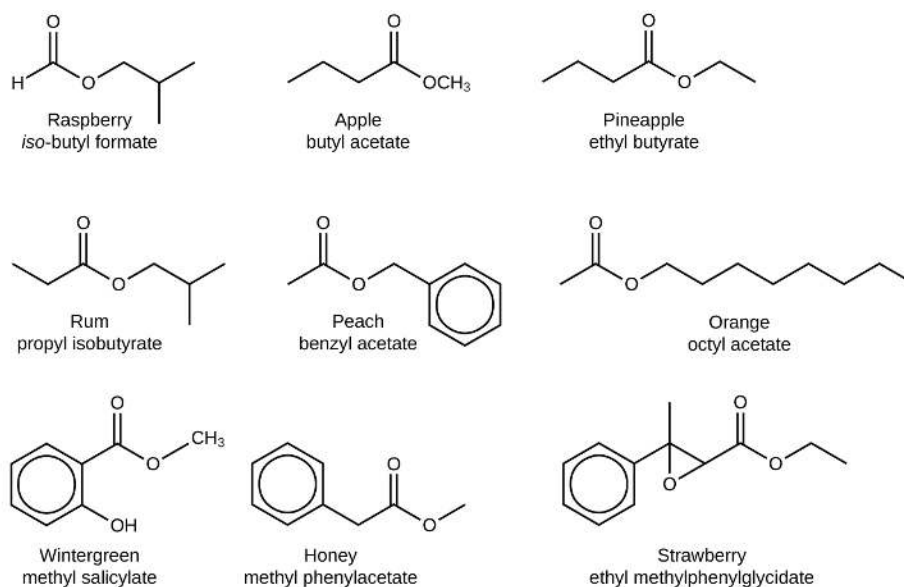
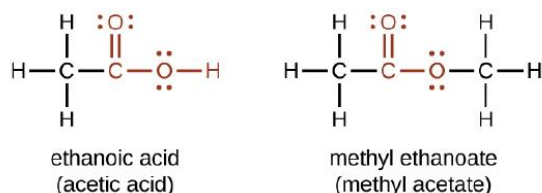


Figure 8.5.3.2: Esters are responsible for the odors associated with various plants and their fruits.

There are nine structures represented in this figure. The first is labeled, “raspberry,” and, “iso-butyl formate.” It shows an H atom with a line going up and to the right which then goes down and to the right. It goes up and to the right again and down and to the right and up and to the right. At the first peak is a double bond to an O atom. At the first trough is an O atom. At the second trough, there is a line going straight down. The second is labeled, “apple,” and, “butyl acetate.” There is a line that goes up and to the right, down and to the right, up and to the right, and down and to the right. At the second peak is a double bond to an O atom. At the end, on the right is O C H subscript 3. The third is labeled, “pineapple,” and, “ethyl butyrate.” It is a line that goes up and to the right, down and to the right, up and to the right, down and to the right, up and to the right, and down and to the right. At the second peak is a double bond to an O atom and at the second trough is an O atom. The fourth is labeled, “rum,” and “propyl isobutyrate.” It shows a line that goes down and to the right, up and to the right, down and to the right, up and to the right, down and to the right and up and to the right. The first complete peak has a double bond to an O atom and the second trough has an O atom. The fifth is labeled, “peach,” and “benzyl acetate.” It shows a line that goes up and to the right, down and to the right, up and to the right and down and to the right. This line connects to a hexagon with a circle inside it. The first peak has a double bond to an O atom and the first trough has an O atom. The sixth is labeled, “orange,” and, “octyl acetate.” It shows a line that goes up and to the right and down and to the right and up and to the right and down and to the right and up and to the right and down and to the right and up and to the right and down and to the right. The first peak has a double bond to an O atom and the first complete trough has an O atom. The seventh is labeled, “wintergreen,” and “methyl salicylate.” It shows a hexagon with a circle inside of it. On the right, is a bond down and to the right to an O H group. On the right is a bond to a line that goes up and to the right and down and two the right and up and to the right. At the first peak is a double bond to an O atom, the next trough shows an O atom and at the end of the line is a C H subscript 3 group. The eighth is labeled, “honey,” and “methyl phenylacetate.” It shows a hexagon with a circle inside of it. It shows it connecting to a line on the right that goes down and to the right then up and to the right and down and to the right and up and to the right. At the first peak that is not part of the hexagon is a double bond to an O atom. At the last trough is an O atom. The ninth is labeled, “strawberry,” and “ethyl methylphenylglycidate.” This shows a hexagon with a circle inside of it. On the right, it connects to a line that goes up and to the right and down and to the right and up and to the right and down and to the right and up and to the right and down and to the right. At the first peak is a line that extends above and below. Below, it connects to an O atom. At the next trough, the line extends down and to the left to the same O atom. At the next peak is a double bond to an O atom and at the next trough is an O atom.

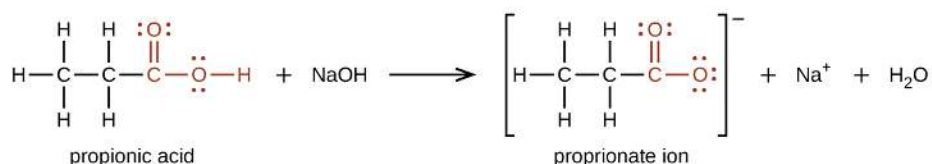
Both carboxylic acids and esters contain a carbonyl group with a second oxygen atom bonded to the carbon atom in the carbonyl group by a single bond. In a carboxylic acid, the second oxygen atom also bonds to a hydrogen atom. In an ester, the second oxygen atom bonds to another carbon atom. The names for carboxylic acids and esters include prefixes that denote the lengths of the carbon chains in the molecules and are derived following nomenclature rules similar to those for inorganic acids and salts (see these examples):



Two structures are shown. The first structure is labeled, “ethanoic acid,” and, “acetic acid.” This structure indicates a C atom to which H atoms are bonded above, below and to the left. To the right of this in red is a bonded group comprised of a C atom to which an O atom is double bonded above. To the right of the red C atom, an O atom is bonded which has an H atom bonded to its right. Both O atoms have two sets of electron dots. The second structure is labeled, “methyl ethanoate,” and, “methyl acetate.” This structure indicates a C atom to which H atoms are bonded above, below and to the left. In red, bonded to the right is a C atom with a double bonded O atom above and a single bonded O atom to the right. To the right of this last O atom in black is another C atom to which H atoms are bonded above, below and to the right. Both O atoms have two pairs of electron dots.

The functional groups for an acid and for an ester are shown in red in these formulas.

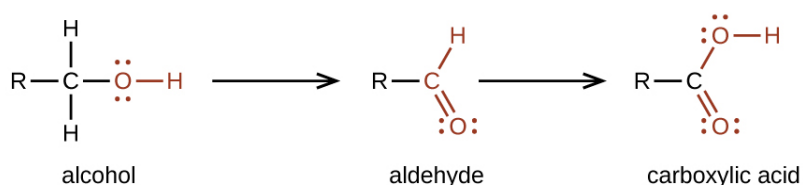
The hydrogen atom in the functional group of a carboxylic acid will react with a base to form an ionic salt:



A chemical reaction is shown. On the left, a structure of propionic acid is indicated. This structure includes a 2 carbon hydrocarbon group on the left end in black. Above, below, and to the left, H atoms are bonded. This group is bonded to a red group comprised of a C atom to which an O atom is double bonded above. To the right of the red C atom, an O atom is connected with a single bond. To the right of the O atom, an H atom is bonded. To the right of this structure appears a plus and N a O H. Following the reaction arrow, the propionate ion is shown. This structure is in brackets. Appearing inside the brackets, is a 2 carbon hydrocarbon group on the left end. Above, below, and to the left, H atoms are bonded. To the right of this group, a group in red is attached comprised of a C atom to which an O atom is double bonded above and a second O atom is single bonded to the right. Outside the brackets appears a superscript minus symbol. This is followed by a plus sign, N a superscript plus another plus sign and H subscript 2 O. The singly bonded O atom in the propionate ion structure has 3 pairs of electron dots. All other O atoms have two pairs of electron dots.

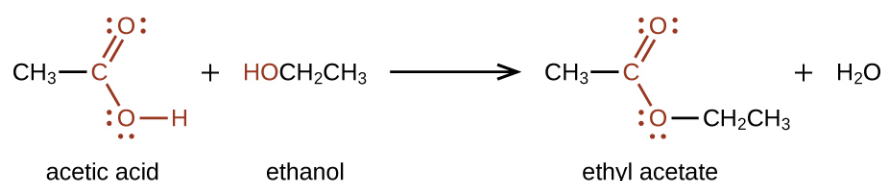
Carboxylic acids are weak acids, meaning they are not 100% ionized in water. Generally only about 1% of the molecules of a carboxylic acid dissolved in water are ionized at any given time. The remaining molecules are undissociated in solution.

We prepare carboxylic acids by the oxidation of aldehydes or alcohols whose –OH functional group is located on the carbon atom at the end of the chain of carbon atoms in the alcohol:



A chemical reaction with two arrows is shown. On the left, an alcohol, indicated with a C atom to which an R group is bonded to the left, H atoms are bonded above and below, and in red, a single bonded O atom with an H atom bonded to the right is shown. Following the first reaction arrow, an aldehyde is shown. This structure is represented with an R group bonded to a red C atom to which an H atom is bonded above and to the right, and an O atom is double bonded below and to the right. Appearing to the right of the second arrow, is a carboxylic acid comprised of an R group bonded to a C atom to which, in red, an O atom is single bonded with an H atom bonded to its right side. A red O is double bonded below and to the right. All O atoms have two pairs of electron dots.

Esters are produced by the reaction of acids with alcohols. For example, the ester ethyl acetate, $\text{CH}_3\text{CO}_2\text{CH}_2\text{CH}_3$, is formed when acetic acid reacts with ethanol:



A chemical reaction is shown. On the left, a C H subscript 3 group bonded to a red C atom. The C atom forms a double bond with an O atom which is also in red. The C atom is also bonded to an O atom which is bonded to an H atom, also in red. A plus sign is shown, which is followed by H O C H subscript 2 C H subscript 3. The H O group is in red. Following a reaction arrow, a C H subscript 3 group is shown which is bonded to a red C atom with a double bonded O atom and a single bonded O. To the right of this single bonded O atom, a C H subscript 2 C H subscript 3 group is attached and shown in black. This structure is followed by a plus sign and H subscript 2 O. The O atoms in the first structure on the left and the structure following the reaction arrow have two pairs of electron dots.

The simplest carboxylic acid is formic acid, HCO_2H , known since 1670. Its name comes from the Latin word *formicus*, which means “ant”; it was first isolated by the distillation of red ants. It is partially responsible for the pain and irritation of ant and wasp stings, and is responsible for a characteristic odor of ants that can be sometimes detected in their nests.

Acetic acid, $\text{CH}_3\text{CO}_2\text{H}$, constitutes 3–6% vinegar. Cider vinegar is produced by allowing apple juice to ferment without oxygen present. Yeast cells present in the juice carry out the fermentation reactions. The fermentation reactions change the sugar present in the juice to ethanol, then to acetic acid. Pure acetic acid has a penetrating odor and produces painful burns. It is an excellent solvent for many organic and some inorganic compounds, and it is essential in the production of cellulose acetate, a component of many synthetic fibers such as rayon.

The distinctive and attractive odors and flavors of many flowers, perfumes, and ripe fruits are due to the presence of one or more esters (Figure 8.5.3.3). Among the most important of the natural esters are fats (such as lard, tallow, and butter) and oils (such as linseed, cottonseed, and olive oils), which are esters of the trihydroxyl alcohol glycerine, $\text{C}_3\text{H}_5(\text{OH})_3$, with large carboxylic acids, such as palmitic acid, $\text{CH}_3(\text{CH}_2)_{14}\text{CO}_2\text{H}$, stearic acid, $\text{CH}_3(\text{CH}_2)_{16}\text{CO}_2\text{H}$, and oleic acid, $\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{CO}_2\text{H}$. Oleic acid is an unsaturated acid; it contains a $\text{C}=\text{C}$ double bond. Palmitic and stearic acids are saturated acids that contain no double or triple bonds.



Figure 8.5.3.3: Over 350 different volatile molecules (many members of the ester family) have been identified in strawberries. (credit: Rebecca Siegel)

Summary

Functional groups related to the carbonyl group include the $-\text{CHO}$ group of an aldehyde, the $-\text{CO}-$ group of a ketone, the $-\text{CO}_2\text{H}$ group of a carboxylic acid, and the $-\text{CO}_2\text{R}$ group of an ester. The carbonyl group, a carbon-oxygen double bond, is the key structure in these classes of organic molecules: Aldehydes contain at least one hydrogen atom attached to the carbonyl carbon atom, ketones contain two carbon groups attached to the carbonyl carbon atom, carboxylic acids contain a hydroxyl group attached to the carbonyl carbon atom, and esters contain an oxygen atom attached to another carbon group connected to the carbonyl carbon atom. All of these compounds contain oxidized carbon atoms relative to the carbon atom of an alcohol group.

Glossary

aldehyde

organic compound containing a carbonyl group bonded to two hydrogen atoms or a hydrogen atom and a carbon substituent

carbonyl group

carbon atom double bonded to an oxygen atom

carboxylic acid

organic compound containing a carbonyl group with an attached hydroxyl group

ester

organic compound containing a carbonyl group with an attached oxygen atom that is bonded to a carbon substituent

ketone

organic compound containing a carbonyl group with two carbon substituents attached to it

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9.1: Valence Bond Theory

Learning Objectives

- Describe the formation of covalent bonds in terms of atomic orbital overlap
- Define and give examples of σ and π bonds

As we know, a scientific theory is a strongly supported explanation for observed natural laws or large bodies of experimental data. For a theory to be accepted, it must explain experimental data and be able to predict behavior. For example, VSEPR theory has gained widespread acceptance because it predicts three-dimensional molecular shapes that are consistent with experimental data collected for thousands of different molecules. However, VSEPR theory does not provide an explanation of chemical bonding.

There are successful theories that describe the electronic structure of atoms. We can use quantum mechanics to predict the specific regions around an atom where electrons are likely to be located: A spherical shape for an s orbital, a dumbbell shape for a p orbital, and so forth. However, these predictions only describe the orbitals around free atoms. When atoms bond to form molecules, atomic orbitals are not sufficient to describe the regions where electrons will be located in the molecule. A more complete understanding of electron distributions requires a model that can account for the electronic structure of molecules. One popular theory holds that a covalent bond forms when a pair of electrons is shared by two atoms and is simultaneously attracted by the nuclei of both atoms. In the following sections, we will discuss how such bonds are described by valence bond theory and hybridization.

Valence bond theory describes a covalent bond as the overlap of half-filled atomic orbitals (each containing a single electron) that yield a pair of electrons shared between the two bonded atoms. We say that orbitals on two different atoms overlap when a portion of one orbital and a portion of a second orbital occupy the same region of space. According to valence bond theory, a covalent bond results when two conditions are met:

1. an orbital on one atom overlaps an orbital on a second atom and
2. the single electrons in each orbital combine to form an electron pair.

The mutual attraction between this negatively charged electron pair and the two atoms' positively charged nuclei serves to physically link the two atoms through a force we define as a covalent bond. The strength of a covalent bond depends on the extent of overlap of the orbitals involved. Orbitals that overlap extensively form bonds that are stronger than those that have less overlap.

The energy of the system depends on how much the orbitals overlap. Figure 9.1.1 illustrates how the sum of the energies of two hydrogen atoms (the colored curve) changes as they approach each other. When the atoms are far apart there is no overlap, and by convention we set the sum of the energies at zero. As the atoms move together, their orbitals begin to overlap. Each electron begins to feel the attraction of the nucleus in the other atom. In addition, the electrons begin to repel each other, as do the nuclei. While the atoms are still widely separated, the attractions are slightly stronger than the repulsions, and the energy of the system decreases. (A bond begins to form.) As the atoms move closer together, the overlap increases, so the attraction of the nuclei for the electrons continues to increase (as do the repulsions among electrons and between the nuclei). At some specific distance between the atoms, which varies depending on the atoms involved, the energy reaches its lowest (most stable) value. This optimum distance between the two bonded nuclei is the bond distance between the two atoms. The bond is stable because at this point, the attractive and repulsive forces combine to create the lowest possible energy configuration. If the distance between the nuclei were to decrease further, the repulsions between nuclei and the repulsions as electrons are confined in closer proximity to each other would become stronger than the attractive forces. The energy of the system would then rise (making the system destabilized), as shown at the far left of Figure 9.1.1.

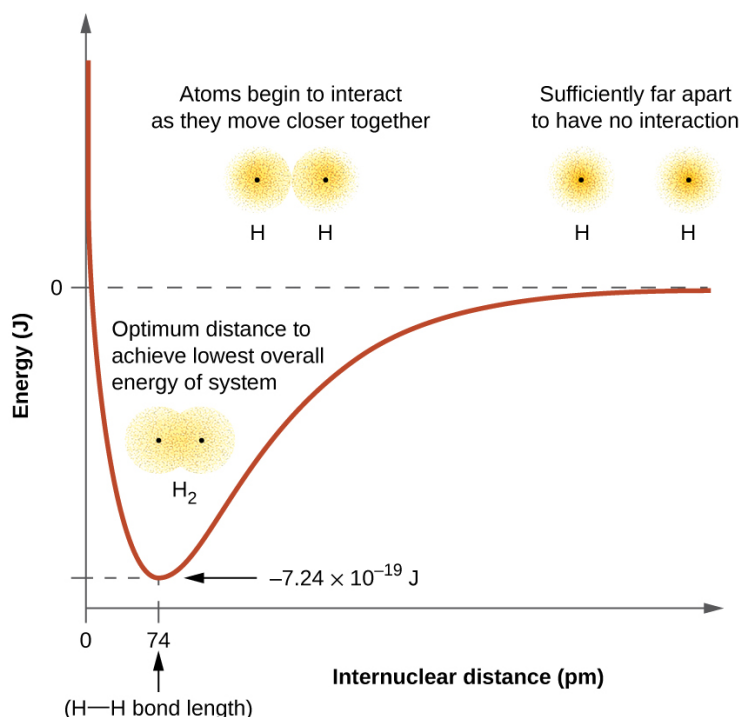


Figure 9.1.1: The interaction of two hydrogen atoms changes as a function of distance. The energy of the system changes as the atoms interact. The lowest (most stable) energy occurs at a distance of 74 pm, which is the bond length observed for the H_2 molecule.

A pair of diagrams are shown and labeled “a” and “b”. Diagram a shows three consecutive images. The first image depicts two separated blurry circles, each labeled with a positive sign and the term “H atom.” The phrase written under them reads, “Sufficiently far apart to have no interaction.” The second image shows the same two circles, but this time they are much closer together and are labeled, “Atoms begin to interact as they move closer together.” The third image shows the two circles overlapping, labeled, “ H_2 ,” and, “Optimum distance to achieve lowest overall energy of system.” Diagram b shows a graph on which the y-axis is labeled “Energy (J),” and the x-axis is labeled, “Internuclear distance (p m).” The midpoint of the y-axis is labeled as zero. The curve on the graph begins at zero p m and high on the y-axis. The graph slopes downward steeply to a point far below the zero joule line on the y-axis and the lowest point reads “0.74 p m” and “H bonded to H bond length.” It is also labeled “ negative 7.24 times 10 superscript negative 19 J.” The graph then rises again to zero J. The graph is accompanied by the same images from diagram a; the first image correlates to the point in the graph where it crosses the zero point on the y-axis, the third image where the graph is lowest.

The bond energy is the difference between the energy minimum (which occurs at the bond distance) and the energy of the two separated atoms. This is the quantity of energy released when the bond is formed. Conversely, the same amount of energy is required to break the bond. For the H_2 molecule shown in Figure 9.1.1, at the bond distance of 74 pm the system is $7.24 \times 10^{-19} \text{ J}$ lower in energy than the two separated hydrogen atoms. This may seem like a small number. However, we know from our earlier description of thermochemistry that bond energies are often discussed on a per-mole basis. For example, it requires $7.24 \times 10^{-19} \text{ J}$ to break one H–H bond, but it takes $4.36 \times 10^5 \text{ J}$ to break 1 mole of H–H bonds. A comparison of some bond lengths and energies is shown in Table 9.1.1. We can find many of these bonds in a variety of molecules, and this table provides average values. For example, breaking the first C–H bond in CH_4 requires 439.3 kJ/mol, while breaking the first C–H bond in $\text{H}-\text{CH}_2\text{C}_6\text{H}_5$ (a common paint thinner) requires 375.5 kJ/mol.

Table 9.1.1: Representative Bond Energies and Lengths

Bond	Length (pm)	Energy (kJ/mol)	Bond	Length (pm)	Energy (kJ/mol)
H-H	74	436	C-O	140.1	358
H-C	106.8	413	C = O	119.7	745
H-N	101.5	391	C ≡ O	113.7	1072
H-O	97.5	467	H-Cl	127.5	431
C-C	150.6	347	H-Br	141.4	366
C = C	133.5	614	H-I	160.9	298
C ≡ C	120.8	839	O-O	148	146
C-N	142.1	305	O = O	120.8	498
C = N	130.0	615	F-F	141.2	159
C ≡ N	116.1	891	Cl-Cl	198.8	243

In addition to the distance between two orbitals, the orientation of orbitals also affects their overlap (other than for two *s* orbitals, which are spherically symmetric). Greater overlap is possible when orbitals are oriented such that they overlap on a direct line between the two nuclei. Figure 9.1.2 illustrates this for two *p* orbitals from different atoms; the overlap is greater when the orbitals overlap end to end rather than at an angle.

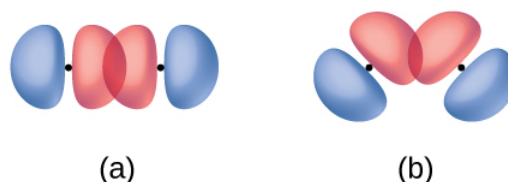


Figure 9.1.2: (a) The overlap of two *p* orbitals is greatest when the orbitals are directed end to end. (b) Any other arrangement results in less overlap. The dots indicate the locations of the nuclei.

The overlap of two *s* orbitals (as in H_2), the overlap of an *s* orbital and a *p* orbital (as in HCl), and the end-to-end overlap of two *p* orbitals (as in Cl_2) all produce sigma bonds (σ bonds), as illustrated in Figure 9.1.3. A σ bond is a covalent bond in which the electron density is concentrated in the region along the internuclear axis; that is, a line between the nuclei would pass through the center of the overlap region. Single bonds in Lewis structures are described as σ bonds in valence bond theory.

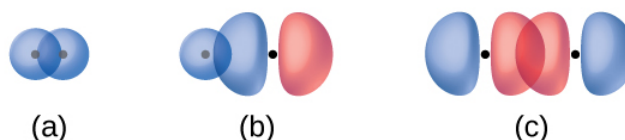


Figure 9.1.3: Sigma (σ) bonds form from the overlap of the following: (a) two *s* orbitals, (b) an *s* orbital and a *p* orbital, and (c) two *p* orbitals. The dots indicate the locations of the nuclei.

Three diagrams are shown and labeled “a,” “b,” and “c.” Diagram a shows two spherical orbitals lying side by side and overlapping. Diagram b shows one spherical and one peanut-shaped orbital lying near one another so that the spherical orbital overlaps with one end of the peanut-shaped orbital. Diagram c shows two peanut-shaped orbitals lying end to end so that one end of each orbital overlaps the other.

A pi bond (π bond) is a type of covalent bond that results from the side-by-side overlap of two *p* orbitals, as illustrated in Figure 9.1.4. In a π bond, the regions of orbital overlap lie on opposite sides of the internuclear axis. Along the axis itself, there is a node, that is, a plane with no probability of finding an electron.

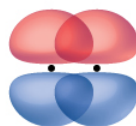
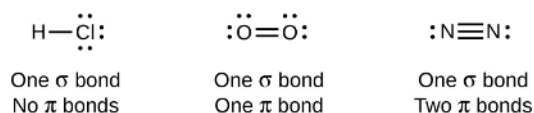


Figure 9.1.4: Pi (π) bonds form from the side-by-side overlap of two p orbitals. The dots indicate the location of the nuclei.

While all single bonds are σ bonds, multiple bonds consist of both σ and π bonds. As the Lewis structures suggest, O_2 contains a double bond, and N_2 contains a triple bond. The double bond consists of one σ bond and one π bond, and the triple bond consists of one σ bond and two π bonds. Between any two atoms, the first bond formed will always be a σ bond, but there can only be one σ bond in any one location. In any multiple bond, there will be one σ bond, and the remaining one or two bonds will be π bonds. These bonds are described in more detail later in this chapter.

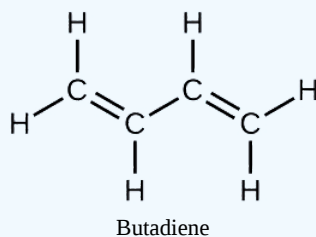


A diagram contains three Lewis structures. The left most structure shows an H atom bonded to a Cl atom by a single bond. The Cl atom has three lone pairs of electrons. The phrase “One sigma bond No pi bonds” is written below the drawing. The center structure shows two O atoms bonded by a double bond. The O atoms each have two lone pairs of electrons. The phrase “One sigma bond One pi bond” is written below the drawing. The right most structure shows two N atoms bonded by a triple bond. Each N atom has a lone pairs of electrons. The phrase “One sigma bond Two pi bonds” is written below the drawing.

As seen in Table 9.1.1, an average carbon-carbon single bond is 347 kJ/mol, while in a carbon-carbon double bond, the π bond increases the bond strength by 267 kJ/mol. Adding an additional π bond causes a further increase of 225 kJ/mol. We can see a similar pattern when we compare other σ and π bonds. Thus, each individual π bond is generally weaker than a corresponding σ bond between the same two atoms. In a σ bond, there is a greater degree of orbital overlap than in a π bond.

✓ Example 9.1.1: Counting σ and π Bonds

Butadiene, C_4H_6 , is used to make synthetic rubber. Identify the number of σ and π bonds contained in this molecule.



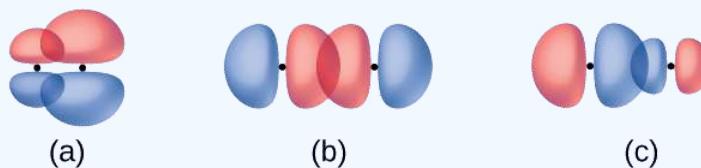
Solution

There are six σ C–H bonds and one σ C–C bond, for a total of seven from the single bonds. There are two double bonds that each have a π bond in addition to the σ bond. This gives a total nine σ and two π bonds overall.

? Exercise 9.1.1

Identify each illustration as depicting a σ or π bond:

- side-by-side overlap of a $4p$ and a $2p$ orbital
- end-to-end overlap of a $4p$ and $4p$ orbital
- end-to-end overlap of a $4p$ and a $2p$ orbital



Answer

(a) is a π bond with a node along the axis connecting the nuclei while (b) and (c) are σ bonds that overlap along the axis.

Summary

Valence bond theory describes bonding as a consequence of the overlap of two separate atomic orbitals on different atoms that creates a region with one pair of electrons shared between the two atoms. When the orbitals overlap along an axis containing the nuclei, they form a σ bond. When they overlap in a fashion that creates a node along this axis, they form a π bond.

Glossary

overlap

coexistence of orbitals from two different atoms sharing the same region of space, leading to the formation of a covalent bond

node

plane separating different lobes of orbitals, where the probability of finding an electron is zero

pi bond (π bond)

covalent bond formed by side-by-side overlap of atomic orbitals; the electron density is found on opposite sides of the internuclear axis

sigma bond (σ bond)

covalent bond formed by overlap of atomic orbitals along the internuclear axis

valence bond theory

description of bonding that involves atomic orbitals overlapping to form σ or π bonds, within which pairs of electrons are shared

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9.2: Hybrid Atomic Orbitals

Learning Objectives

- Explain the concept of atomic orbital hybridization
- Determine the hybrid orbitals associated with various molecular geometries

Thinking in terms of overlapping atomic orbitals is one way for us to explain how chemical bonds form in diatomic molecules. However, to understand how molecules with more than two atoms form stable bonds, we require a more detailed model. As an example, let us consider the water molecule, in which we have one oxygen atom bonding to two hydrogen atoms. Oxygen has the electron configuration $1s^2 2s^2 2p^4$, with two unpaired electrons (one in each of the two $2p$ orbitals). Valence bond theory would predict that the two O–H bonds form from the overlap of these two $2p$ orbitals with the $1s$ orbitals of the hydrogen atoms. If this were the case, the bond angle would be 90° , as shown in Figure 9.2.1, because p orbitals are perpendicular to each other. Experimental evidence shows that the bond angle is 104.5° , not 90° . The prediction of the valence bond theory model does not match the real-world observations of a water molecule; a different model is needed.

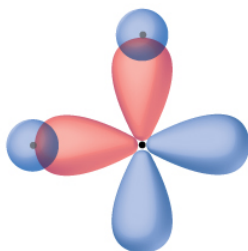


Figure 9.2.1: The hypothetical overlap of two of the $2p$ orbitals on an oxygen atom (red) with the $1s$ orbitals of two hydrogen atoms (blue) would produce a bond angle of 90° . This is not consistent with experimental evidence.¹

Two peanut-shaped orbitals lie perpendicular to one another. They overlap with spherical orbitals to the left and top of the diagram.

Quantum-mechanical calculations suggest why the observed bond angles in H_2O differ from those predicted by the overlap of the $1s$ orbital of the hydrogen atoms with the $2p$ orbitals of the oxygen atom. The mathematical expression known as the wave function, ψ , contains information about each orbital and the wavelike properties of electrons in an isolated atom. When atoms are bound together in a molecule, the wave functions combine to produce new mathematical descriptions that have different shapes. This process of combining the wave functions for atomic orbitals is called hybridization and is mathematically accomplished by the *linear combination of atomic orbitals*, LCAO, (a technique that we will encounter again later). The new orbitals that result are called hybrid orbitals. The valence orbitals in an *isolated* oxygen atom are a $2s$ orbital and three $2p$ orbitals. The valence orbitals in an oxygen atom in a water molecule differ; they consist of four equivalent hybrid orbitals that point approximately toward the corners of a tetrahedron (Figure 9.2.2). Consequently, the overlap of the O and H orbitals should result in a tetrahedral bond angle (109.5°). The observed angle of 104.5° is experimental evidence for which quantum-mechanical calculations give a useful explanation: Valence bond theory must include a hybridization component to give accurate predictions.

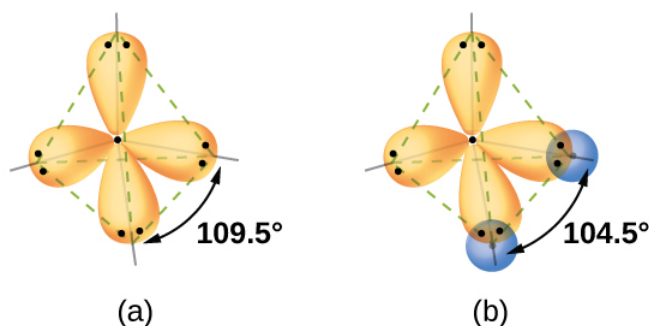


Figure 9.2.2: (a) A water molecule has four regions of electron density, so VSEPR theory predicts a tetrahedral arrangement of hybrid orbitals. (b) Two of the hybrid orbitals on oxygen contain lone pairs, and the other two overlap with the 1s orbitals of hydrogen atoms to form the O–H bonds in H_2O . This description is more consistent with the experimental structure.

Two diagrams are shown and labeled “a” and “b.” Diagram a shows two peanut-shaped orbitals lying in a tetrahedral arrangement around the letter “O.” Diagram b shows the same two orbitals, but they now overlap to the top and to the left with two spherical orbitals, each labeled “H.” A pair of electrons occupies each lobe of the peanut-shaped orbitals.

The following ideas are important in understanding hybridization:

1. Hybrid orbitals do not exist in isolated atoms. They are formed only in covalently bonded atoms.
2. Hybrid orbitals have shapes and orientations that are very different from those of the atomic orbitals in isolated atoms.
3. A set of hybrid orbitals is generated by combining atomic orbitals. The number of hybrid orbitals in a set is equal to the number of atomic orbitals that were combined to produce the set.
4. All orbitals in a set of hybrid orbitals are equivalent in shape and energy.
5. The type of hybrid orbitals formed in a bonded atom depends on its electron-pair geometry as predicted by the VSEPR theory.
6. Hybrid orbitals overlap to form σ bonds. Unhybridized orbitals overlap to form π bonds.

In the following sections, we shall discuss the common types of hybrid orbitals.

sp Hybridization

The beryllium atom in a gaseous BeCl_2 molecule is an example of a central atom with no lone pairs of electrons in a linear arrangement of three atoms. There are two regions of valence electron density in the BeCl_2 molecule that correspond to the two covalent Be–Cl bonds. To accommodate these two electron domains, two of the Be atom’s four valence orbitals will mix to yield two hybrid orbitals. This hybridization process involves mixing of the valence s orbital with one of the valence p orbitals to yield two equivalent sp hybrid orbitals that are oriented in a linear geometry (Figure 9.2.3). In this figure, the set of sp orbitals appears similar in shape to the original p orbital, but there is an important difference. The number of atomic orbitals combined always equals the number of hybrid orbitals formed. The p orbital is one orbital that can hold up to two electrons. The sp set is two equivalent orbitals that point 180° from each other. The two electrons that were originally in the s orbital are now distributed to the two sp orbitals, which are half filled. In gaseous BeCl_2 , these half-filled hybrid orbitals will overlap with orbitals from the chlorine atoms to form two identical σ bonds.

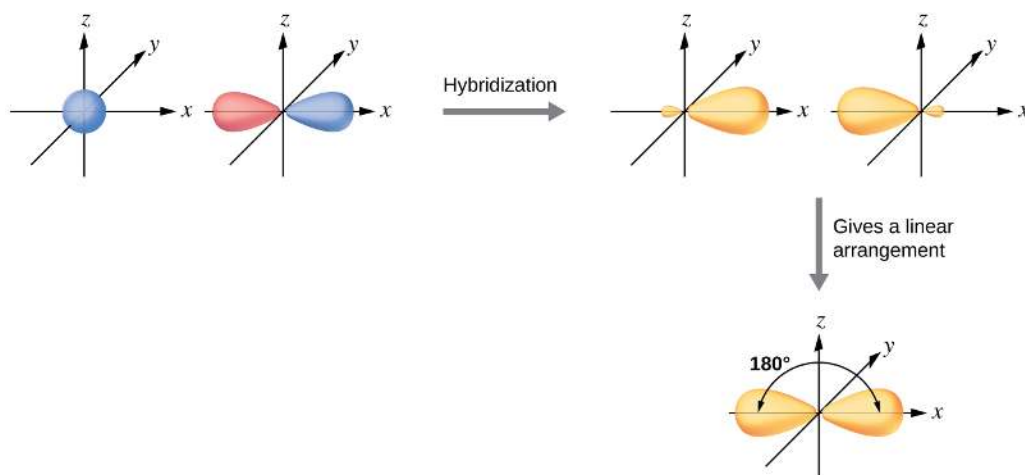


Figure 9.2.3: Hybridization of an s orbital (blue) and a p orbital (red) of the same atom produces two sp hybrid orbitals (yellow). Each hybrid orbital is oriented primarily in just one direction. Note that each sp orbital contains one lobe that is significantly larger than the other. The set of two sp orbitals are oriented at 180° , which is consistent with the geometry for two domains.

A series of three diagrams connected by a right-facing arrow that is labeled, “Hybridization,” and a downward-facing arrow labeled, “Gives a linear arrangement,” are shown. The first diagram shows a blue spherical orbital and a red, peanut-shaped orbital, each placed on an X, Y, Z axis system. The second diagram shows the same two orbitals, but they are now purple and have one enlarged lobe and one smaller lobe. Each lies along the x-axis in the drawing. The third diagram shows the same two orbitals, but their smaller lobes now overlap along the x-axis while their larger lobes are located at and labeled as “180 degrees” from one another.

We illustrate the electronic differences in an isolated Be atom and in the bonded Be atom in the orbital energy-level diagram in Figure 9.2.4. These diagrams represent each orbital by a horizontal line (indicating its energy) and each electron by an arrow. Energy increases toward the top of the diagram. We use one upward arrow to indicate one electron in an orbital and two arrows (up and down) to indicate two electrons of opposite spin.

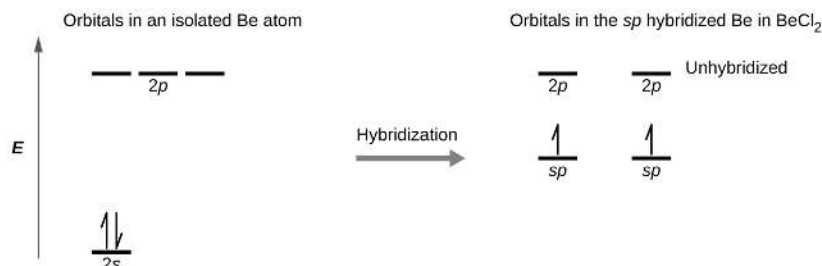


Figure 9.2.4: This orbital energy-level diagram shows the sp hybridized orbitals on Be in the linear BeCl_2 molecule. Each of the two sp hybrid orbitals holds one electron and is thus half filled and available for bonding via overlap with a Cl 3p orbital.

A diagram is shown in two parts, connected by a right facing arrow labeled, “Hybridization.” The left diagram shows an up-facing arrow labeled, “E.” To the lower right of the arrow is a short, horizontal line labeled, “2 s,” that has two vertical half-arrows facing up and down on it. To the upper right of the arrow are a series of three short, horizontal lines labeled, “2 p.” Above these two sets of lines is the phrase, “Orbitals in an isolated B e atom.” The right side of the diagram shows two short, horizontal lines placed halfway up the space and each labeled, “s p.” An upward-facing half arrow is drawn vertically on each line. Above these lines are two other short, horizontal lines, each labeled, “2 p.” Above these two sets of lines is the phrase, “Orbitals in the s p hybridized B e in B e C l subscript 2.”

When atomic orbitals hybridize, the valence electrons occupy the newly created orbitals. The Be atom had two valence electrons, so each of the sp orbitals gets one of these electrons. Each of these electrons pairs up with the unpaired electron on a chlorine atom when a hybrid orbital and a chlorine orbital overlap during the formation of the Be–Cl bonds. Any central atom surrounded by just two regions of valence electron density in a molecule will exhibit sp hybridization. Other examples include the mercury atom in the linear HgCl_2 molecule, the zinc atom in $\text{Zn}(\text{CH}_3)_2$, which contains a linear C–Zn–C arrangement, and the carbon atoms in HCCH and CO_2 .

sp^2 Hybridization

The valence orbitals of a central atom surrounded by three regions of electron density consist of a set of three sp^2 hybrid orbitals and one unhybridized p orbital. This arrangement results from sp^2 hybridization, the mixing of one s orbital and two p orbitals to produce three identical hybrid orbitals oriented in a trigonal planar geometry (Figure 9.2.5).

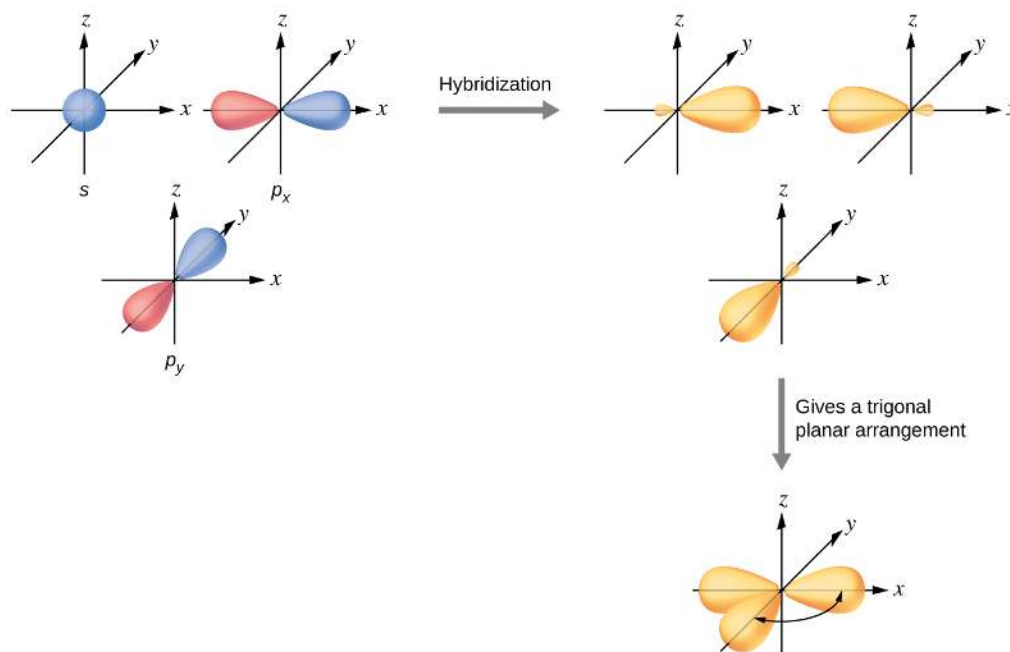


Figure 9.2.5: The hybridization of an s orbital (blue) and two p orbitals (red) produces three equivalent sp^2 hybridized orbitals (yellow) oriented at 120° with respect to each other. The remaining unhybridized p orbital is not shown here, but is located along the z axis.

A series of three diagrams connected by a right-facing arrow that is labeled, “Hybridization,” and a downward-facing arrow labeled, “Gives a trigonal planar arrangement,” are shown. The first diagram shows a blue spherical orbital and two red, peanut-shaped orbitals, each placed on an X , Y , Z axis system. The two red orbitals are located on the x and z axes, respectively. The second diagram shows the same three orbitals, but they are now purple and have one enlarged lobe and one smaller lobe. Each lies in a different axis in the drawing. The third diagram shows the same three orbitals, but their smaller lobes now overlap while their larger lobes are located at and labeled as “ 120° ” from one another.

Although quantum mechanics yields the “plump” orbital lobes as depicted in Figure 9.2.5, sometimes for clarity these orbitals are drawn thinner and without the minor lobes, as in Figure 9.2.6, to avoid obscuring other features of a given illustration. We will use these “thinner” representations whenever the true view is too crowded to easily visualize.

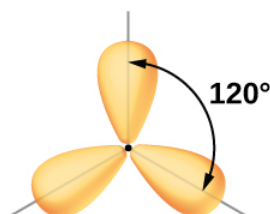


Figure 9.2.6: This alternate way of drawing the trigonal planar sp^2 hybrid orbitals is sometimes used in more crowded figures. Three balloon-like orbitals are shown, and connect together near their narrower ends in one plane. The angle between a pair of lobes is labeled, “ 120° .”

The observed structure of the borane molecule, BH_3 , suggests sp^2 hybridization for boron in this compound. The molecule is trigonal planar, and the boron atom is involved in three bonds to hydrogen atoms (Figure 9.2.7).

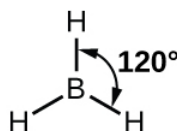


Figure 9.2.7: BH_3 is an electron-deficient molecule with a trigonal planar structure.

A boron atom is shown connected to three hydrogen atoms, which are arranged around it like a pyramid. The angle from one line connecting the boron atom to a hydrogen atom to another line connecting the boron atom to a hydrogen atom is labeled, “120 degrees.”

We can illustrate the comparison of orbitals and electron distribution in an isolated boron atom and in the bonded atom in BH_3 as shown in the orbital energy level diagram in Figure 9.2.8. We redistribute the three valence electrons of the boron atom in the three sp^2 hybrid orbitals, and each boron electron pairs with a hydrogen electron when B–H bonds form.

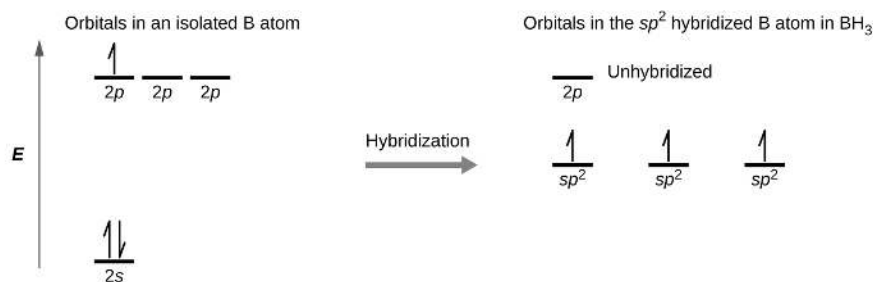


Figure 9.2.8: In an isolated B atom, there are one 2s and three 2p valence orbitals. When boron is in a molecule with three regions of electron density, three of the orbitals hybridize and create a set of three sp^2 orbitals and one unhybridized 2p orbital. The three half-filled hybrid orbitals each overlap with an orbital from a hydrogen atom to form three σ bonds in BH_3 .

A diagram is shown in two parts, connected by a right facing arrow labeled, “Hybridization.” The left diagram shows an up-facing arrow labeled “E.” To the lower right of the arrow is a short, horizontal line labeled, “2 s,” that has two vertical half-arrows facing up and down on it. To the upper right of the arrow are a series of three short, horizontal lines labeled, “2 p.” Above both sets of these lines is the phrase, “Orbitals in an isolated B atom.” One of the lines has a vertical, up-facing arrow drawn on it. The right side of the diagram shows three short, horizontal lines placed halfway up the space and each labeled, “s p superscript 2.” An upward-facing half arrow is drawn vertically on each line. Above these lines is one other short, horizontal line, labeled, “2 p.” Above both sets of lines is the phrase, “Orbitals in the s p superscript 2 hybridized B atom in B H subscript 3.”

Any central atom surrounded by three regions of electron density will exhibit sp^2 hybridization. This includes molecules with a lone pair on the central atom, such as ClNO (Figure 9.2.9), or molecules with two single bonds and a double bond connected to the central atom, as in formaldehyde, CH_2O , and ethene, H_2CCH_2 .

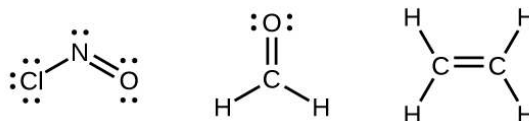


Figure 9.2.9: The central atom(s) in each of the structures shown contain three regions of electron density and are sp^2 hybridized. As we know from the discussion of VSEPR theory, a region of electron density contains all of the electrons that point in one direction. A lone pair, an unpaired electron, a single bond, or a multiple bond would each count as one region of electron density.

Three Lewis structures are shown. The left-hand structure shows a chlorine atom surrounded by three lone pairs of electrons single bonded to a nitrogen atom with one lone pair of electrons and double bonded to an oxygen atom with two lone pairs of electrons. The middle structure shows a carbon atom single bonded to two hydrogen atoms and double bonded to an oxygen atom that has two lone pairs of electrons. The right-hand structure shows two carbon atoms, double bonded to one another and each single bonded to two hydrogen atoms.

sp^3 Hybridization

The valence orbitals of an atom surrounded by a tetrahedral arrangement of bonding pairs and lone pairs consist of a set of four sp^3 hybrid orbitals. The hybrids result from the mixing of one s orbital and all three p orbitals that produces four identical sp^3 hybrid orbitals (Figure 9.2.10). Each of these hybrid orbitals points toward a different corner of a tetrahedron.

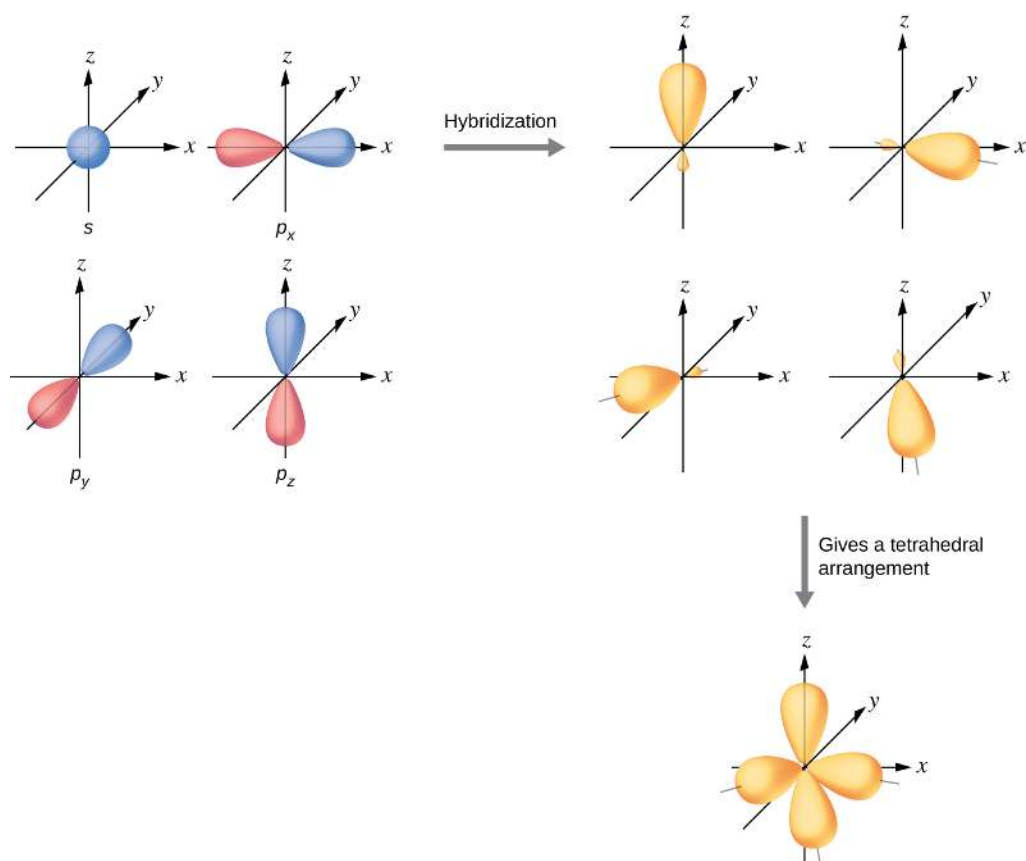


Figure 9.2.10: The hybridization of an s orbital (blue) and three p orbitals (red) produces four equivalent sp^3 hybridized orbitals (yellow) oriented at 109.5° with respect to each other.

A series of three diagrams connected by a right-facing arrow that is labeled, "Hybridization," and a downward-facing arrow labeled, "Gives a tetrahedral arrangement," are shown. The first diagram shows a blue spherical orbital and three red, peanut-shaped orbitals, each placed on an x, y, z axis system. The three red orbitals are located on the x, y and z axes, respectively. The second diagram shows the same four orbitals, but they are now purple and have one enlarged lobe and one smaller lobe. Each lies in a different axis in the drawing. The third diagram shows the same four orbitals, but their smaller lobes now overlap to form a tetrahedral structure.

A molecule of methane, CH_4 , consists of a carbon atom surrounded by four hydrogen atoms at the corners of a tetrahedron. The carbon atom in methane exhibits sp^3 hybridization. We illustrate the orbitals and electron distribution in an isolated carbon atom and in the bonded atom in CH_4 in Figure 9.2.11. The four valence electrons of the carbon atom are distributed equally in the hybrid orbitals, and each carbon electron pairs with a hydrogen electron when the C–H bonds form.

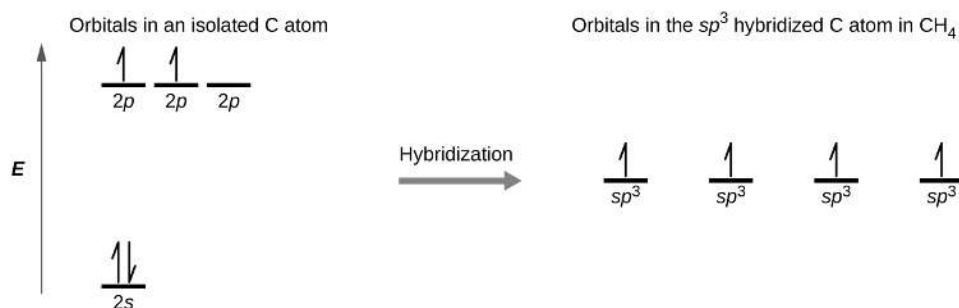


Figure 9.2.11: The four valence atomic orbitals from an isolated carbon atom all hybridize when the carbon bonds in a molecule like CH_4 with four regions of electron density. This creates four equivalent sp^3 hybridized orbitals. Overlap of each of the hybrid orbitals with a hydrogen orbital creates a C–H σ bond.

A diagram is shown in two parts, connected by a right facing arrow labeled, “Hybridization.” The left diagram shows an up-facing arrow labeled “E.” To the lower right of the arrow is a short, horizontal line labeled, “2 s,” that has two vertical half-arrows facing up and down on it. To the upper right of the arrow are a series of three short, horizontal lines labeled, “2 p.” Two of the lines have a vertical, up-facing arrow drawn on them. Above both sets of lines is the phrase, “Orbitals in an isolated C atom.” The right side of the diagram shows four short, horizontal lines placed halfway up the space and each labeled, “s p superscript 3.” An upward-facing half arrow is drawn vertically on each line. Above these lines is the phrase, “Orbitals in the s p superscript 3 hybridized C atom in C H subscript 4.”

In a methane molecule, the 1s orbital of each of the four hydrogen atoms overlaps with one of the four sp^3 orbitals of the carbon atom to form a sigma (σ) bond. This results in the formation of four strong, equivalent covalent bonds between the carbon atom and each of the hydrogen atoms to produce the methane molecule, CH_4 .

The structure of ethane, C_2H_6 , is similar to that of methane in that each carbon in ethane has four neighboring atoms arranged at the corners of a tetrahedron—three hydrogen atoms and one carbon atom (Figure 9.2.10). However, in ethane an sp^3 orbital of one carbon atom overlaps end to end with an sp^3 orbital of a second carbon atom to form a σ bond between the two carbon atoms. Each of the remaining sp^3 hybrid orbitals overlaps with an s orbital of a hydrogen atom to form carbon–hydrogen σ bonds. The structure and overall outline of the bonding orbitals of ethane are shown in Figure 9.2.12. The orientation of the two CH_3 groups is not fixed relative to each other. Experimental evidence shows that rotation around σ bonds occurs easily.

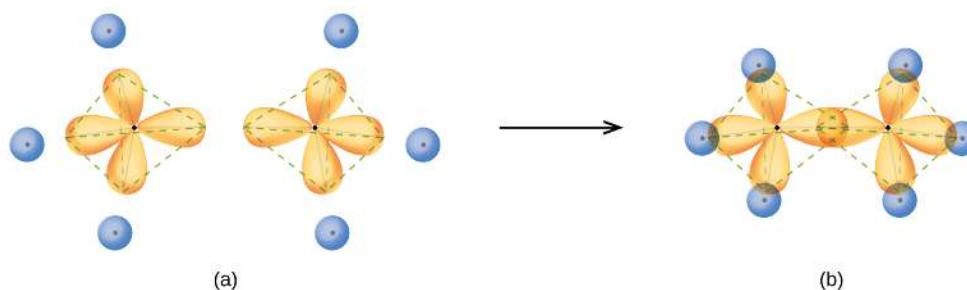


Figure 9.2.12: (a) In the ethane molecule, C_2H_6 , each carbon has four sp^3 orbitals. (b) These four orbitals overlap to form seven σ bonds.

Two diagrams are shown and labeled “a” and “b.” Diagram a shows two carbon atoms, each surrounded by their four s p subscript three hybridized orbitals in a three dimensional arrangement. Each of the orbitals is shown overlapping with a spherical hydrogen atom. Diagram b shows the same general arrangement, but the hydrogen atoms are just represented by an, “H” and their spherical orbitals are not shown.

An sp^3 hybrid orbital can also hold a lone pair of electrons. For example, the nitrogen atom in ammonia is surrounded by three bonding pairs and a lone pair of electrons directed to the four corners of a tetrahedron. The nitrogen atom is sp^3 hybridized with one hybrid orbital occupied by the lone pair.

The molecular structure of water is consistent with a tetrahedral arrangement of two lone pairs and two bonding pairs of electrons. Thus we say that the oxygen atom is sp^3 hybridized, with two of the hybrid orbitals occupied by lone pairs and two by bonding pairs. Since lone pairs occupy more space than bonding pairs, structures that contain lone pairs have bond angles slightly distorted from the ideal. Perfect tetrahedra have angles of 109.5° , but the observed angles in ammonia (107.3°) and water (104.5°) are slightly smaller. Other examples of sp^3 hybridization include CCl_4 , PCl_3 , and NCl_3 .

sp^3d and sp^3d^2 Hybridization

To describe the five bonding orbitals in a trigonal bipyramidal arrangement, we must use five of the valence shell atomic orbitals (the s orbital, the three p orbitals, and one of the d orbitals), which gives five sp^3d hybrid orbitals. With an octahedral arrangement of six hybrid orbitals, we must use six valence shell atomic orbitals (the s orbital, the three p orbitals, and two of the d orbitals in its valence shell), which gives six sp^3d^2 hybrid orbitals. These hybridizations are only possible for atoms that have d orbitals in their valence subshells (that is, not those in the first or second period).

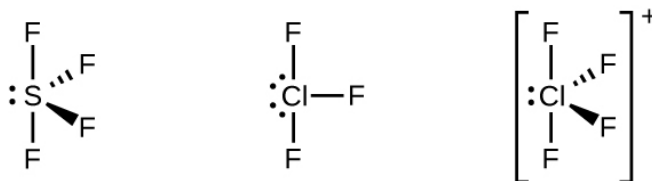


Figure 9.2.13: The three compounds pictured exhibit sp^3d hybridization in the central atom and a trigonal bipyramid form. SF_4 and ClF_4^+ have one lone pair of electrons on the central atom, and ClF_3 has two lone pairs giving it the T-shape shown.

Three Lewis structures are shown along with designations of molecular shape. The left image shows a sulfur atom singly bonded to four fluorine atoms. The sulfur atom has one lone pair of electrons while each fluorine has three. Two fluorine atoms are drawn vertically up and down from the sulfur while the other two are shown going into and out of the page. The second structure shows one chlorine atom singly bonded to three fluorine atoms. The chlorine has two lone pairs of electrons while each fluorine has three. Two fluorine atoms are drawn vertically up and down from the sulfur while the other is shown horizontally. The right structure shows a chlorine atom singly bonded to four fluorine atoms. The chlorine atom has one lone pair of electrons and a superscript plus sign, while each fluorine has three lone pairs of electrons. Two fluorine atoms are drawn vertically up and down from the sulfur while the other two are shown going into and out of the page.

In a molecule of phosphorus pentachloride, PCl_5 , there are five P–Cl bonds (thus five pairs of valence electrons around the phosphorus atom) directed toward the corners of a trigonal bipyramid. We use the $3s$ orbital, the three $3p$ orbitals, and one of the $3d$ orbitals to form the set of five sp^3d hybrid orbitals (Figure 9.2.14) that are involved in the P–Cl bonds. Other atoms that exhibit sp^3d hybridization include the sulfur atom in SF_4 and the chlorine atoms in ClF_3 and in ClF_4^+ . (The electrons on fluorine atoms are omitted for clarity.)

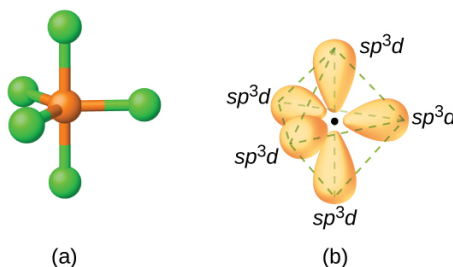


Figure 9.2.14: (a) The five regions of electron density around phosphorus in PCl_5 require five hybrid sp^3d orbitals. (b) These orbitals combine to form a trigonal bipyramidal structure with each large lobe of the hybrid orbital pointing at a vertex. As before, there are also small lobes pointing in the opposite direction for each orbital (not shown for clarity).

Two images are shown and labeled “a” and “b.” Image a depicts a ball-and-stick model in a trigonal bipyramidal arrangement. Image b depicts the hybrid orbitals in the same arrangement and each is labeled, “ sp^3d .”

The sulfur atom in sulfur hexafluoride, SF_6 , exhibits sp^3d^2 hybridization. A molecule of sulfur hexafluoride has six bonding pairs of electrons connecting six fluorine atoms to a single sulfur atom. There are no lone pairs of electrons on the central atom. To bond six fluorine atoms, the $3s$ orbital, the three $3p$ orbitals, and two of the $3d$ orbitals form six equivalent sp^3d^2 hybrid orbitals, each directed toward a different corner of an octahedron. Other atoms that exhibit sp^3d^2 hybridization include the phosphorus atom in PCl_6^- , the iodine atom in the interhalogens IF_6^+ , IF_5 , ICl_4^- , IF_4^- and the xenon atom in XeF_4 .

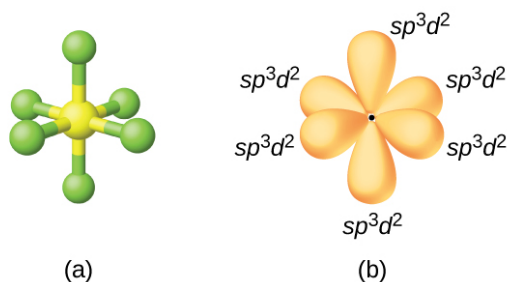


Figure 9.2.15: (a) Sulfur hexafluoride, SF_6 , has an octahedral structure that requires sp^3d^2 hybridization. (b) The six sp^3d^2 orbitals form an octahedral structure around sulfur. Again, the minor lobe of each orbital is not shown for clarity.

Two images are shown and labeled “a” and “b.” Image a depicts a ball-and-stick model in an octahedral arrangement. Image b depicts the hybrid orbitals in the same arrangement and each is labeled, “s p superscript three d superscript two.”

Assignment of Hybrid Orbitals to Central Atoms

The hybridization of an atom is determined based on the number of regions of electron density that surround it. The geometrical arrangements characteristic of the various sets of hybrid orbitals are shown in Figure 9.2.16. These arrangements are identical to those of the electron-pair geometries predicted by VSEPR theory. VSEPR theory predicts the shapes of molecules, and hybrid orbital theory provides an explanation for how those shapes are formed. To find the hybridization of a central atom, we can use the following guidelines:

1. Determine the Lewis structure of the molecule.
2. Determine the number of regions of electron density around an atom using VSEPR theory, in which single bonds, multiple bonds, radicals, and lone pairs each count as one region.
3. Assign the set of hybridized orbitals from Figure 9.2.16 that corresponds to this geometry.

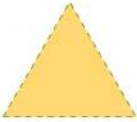
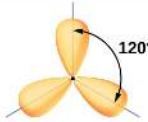
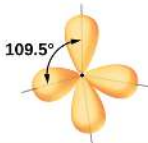
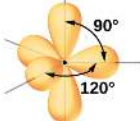
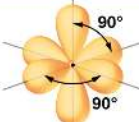
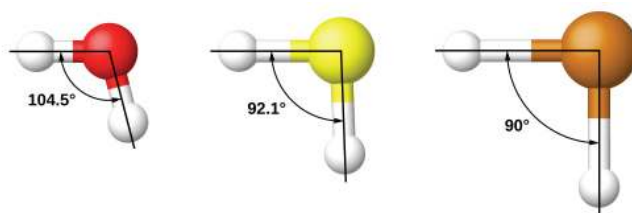
Regions of Electron Density	Arrangement		Hybridization	
2		linear	sp	
3		trigonal planar	sp^2	
4		tetrahedral	sp^3	
5		trigonal bipyramidal	sp^3d	
6		octahedral	sp^3d^2	

Figure 9.2.16: The shapes of hybridized orbital sets are consistent with the electron-pair geometries. For example, an atom surrounded by three regions of electron density is sp^2 hybridized, and the three sp^2 orbitals are arranged in a trigonal planar fashion. A table is shown that is composed of five columns and six rows. The header row contains the phrases, "Regions of electron density," "Arrangement," (which has two columns below it), and "Hybridization," (which has two columns below it). The first column contains the numbers "2," "3," "4," "5," and "6." The second column contains images of a line, a triangle, a three sided pyramid, a trigonal bipyramid, and an eight-faced octahedron. The third column contains the terms, "Linear," "Trigonal planar," "Tetrahedral," "Trigonal bipyramidal," and "Octahedral." The fourth column contains the terms " sp ," " sp^2 ," " sp^3 ," " sp^3d ," and " sp^3d^2 ." The last column contains drawings of the molecules beginning with a peanut-shaped structure marked with an angle of "180 degrees." The second structure is made up of three equal-sized, rounded structures connected at one point with an angle of "120 degrees," while the third structure is a three-dimensional arrangement of four equal-sized, rounded structures labeled as "109.5 degrees." The fourth structure is made up of five equal-sized, rounded structures connected at "120 and 90 degrees," while the fifth structure has six equal-sized, rounded structures connected at "90 degrees."

It is important to remember that hybridization was devised to rationalize experimentally observed molecular geometries, not the other way around.

The model works well for molecules containing small central atoms, in which the valence electron pairs are close together in space. However, for larger central atoms, the valence-shell electron pairs are farther from the nucleus, and there are fewer repulsions. Their compounds exhibit structures that are often not consistent with VSEPR theory, and hybridized orbitals are not necessary to explain the observed data.



Three Lewis structures are shown. The left structure shows an oxygen atom with two lone pairs of electrons single bonded to two hydrogen atoms. The middle structure is made up of a sulfur atom with two lone pairs of electrons single bonded to two hydrogen atoms. The right structure is made up of a tellurium atom with two lone pairs of electrons single bonded to two hydrogen atoms. From left to right, the bond angles of each molecule decrease.

For example, we have discussed the H–O–H bond angle in H_2O , 104.5° , which is more consistent with sp^3 hybrid orbitals (109.5°) on the central atom than with $2p$ orbitals (90°). Sulfur is in the same group as oxygen, and H_2S has a similar Lewis structure. However, it has a much smaller bond angle (92.1°), which indicates much less hybridization on sulfur than oxygen. Continuing down the group, tellurium is even larger than sulfur, and for H_2Te , the observed bond angle (90°) is consistent with overlap of the $5p$ orbitals, without invoking hybridization. We invoke hybridization where it is necessary to explain the observed structures.

✓ Example 9.2.1: Assigning Hybridization

Ammonium sulfate is important as a fertilizer. What is the hybridization of the sulfur atom in the sulfate ion, SO_4^{2-} ?

Solution

The Lewis structure of sulfate shows there are four regions of electron density.

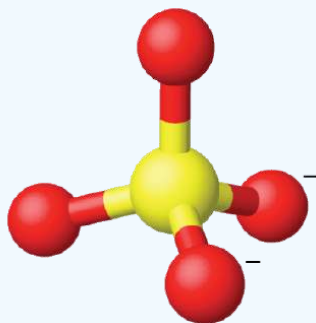


Figure 9.2.16).

A structure is shown in which a sulfur atom is bonded to four oxygen atoms in a tetrahedral arrangement. Two of the oxygen atoms have a negative charge.

? Exercise 9.2.1

What is the hybridization of the selenium atom in SeF_4 ?



A Lewis structure is shown in which four fluorine atoms are each attached to one sulfur atom. Two of the attached fluorine atoms are vertically attached up and down, while two are attached into and out of the page to the right. The sulfur also has one lone pair of electrons attached to the left of the structure.

Answer

The selenium atom is sp^3d hybridized.

✓ Example 9.2.2: Assigning Hybridization

Urea, $\text{NH}_2\text{C}(\text{O})\text{NH}_2$, is sometimes used as a source of nitrogen in fertilizers. What is the hybridization of each nitrogen and carbon atom in urea?

Solution

The Lewis structure of urea is

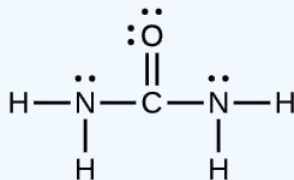


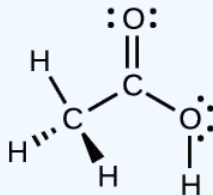
Figure 9.2.16). This is the hybridization of the nitrogen atoms in urea.

A Lewis structure is shown in which a carbon atom is double bonded to an oxygen atom that has two lone pairs of electrons. The carbon atom forms single bonds to two nitrogen atoms. Each nitrogen is single bonded to two hydrogen atoms, and each nitrogen atoms has one lone pair of electrons.

The carbon atom is surrounded by three regions of electron density, positioned in a trigonal planar arrangement. The hybridization in a trigonal planar electron pair geometry is sp^2 (Figure 9.2.16), which is the hybridization of the carbon atom in urea.

? Exercise 9.2.1

Acetic acid, $\text{H}_3\text{CC}(\text{O})\text{OH}$, is the molecule that gives vinegar its odor and sour taste. What is the hybridization of the two carbon atoms in acetic acid?



A Lewis structure is shown in which a carbon atom is double bonded to an oxygen atom that has two lone pairs of electrons and single bonded to another oxygen atom that is single bonded to a hydrogen atom. This second oxygen atom has two lone pairs of electrons. The carbon is also single bonded to a carbon atom that is single bonded to three hydrogen atoms.

Answer

H_3C , sp^3 ; $\text{C}(\text{O})\text{OH}$, sp^2

Summary

We can use hybrid orbitals, which are mathematical combinations of some or all of the valence atomic orbitals, to describe the electron density around covalently bonded atoms. These hybrid orbitals either form sigma (σ) bonds directed toward other atoms of the molecule or contain lone pairs of electrons. We can determine the type of hybridization around a central atom from the geometry of the regions of electron density about it. Two such regions imply sp hybridization; three, sp^2 hybridization; four, sp^3 hybridization; five, sp^3d hybridization; and six, sp^3d^2 hybridization. Pi (π) bonds are formed from unhybridized atomic orbitals (p or d orbitals).

Footnotes

1. Note that orbitals may sometimes be drawn in an elongated “balloon” shape rather than in a more realistic “plump” shape in order to make the geometry easier to visualize.

Glossary

hybrid orbital

orbital created by combining atomic orbitals on a central atom

hybridization

model that describes the changes in the atomic orbitals of an atom when it forms a covalent compound

sp hybrid orbital

one of a set of two orbitals with a linear arrangement that results from combining one s and one p orbital

sp^2 hybrid orbital

one of a set of three orbitals with a trigonal planar arrangement that results from combining one s and two p orbitals

sp^3 hybrid orbital

one of a set of four orbitals with a tetrahedral arrangement that results from combining one s and three p orbitals

sp^3d hybrid orbital

one of a set of five orbitals with a trigonal bipyramidal arrangement that results from combining one s , three p , and one d orbital

sp^3d^2 hybrid orbital

one of a set of six orbitals with an octahedral arrangement that results from combining one s , three p , and two d orbitals

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9.3: Multiple Bonds

Learning Objectives

- Describe multiple covalent bonding in terms of atomic orbital overlap
- Relate the concept of resonance to π -bonding and electron delocalization

The hybrid orbital model appears to account well for the geometry of molecules involving single covalent bonds. Is it also capable of describing molecules containing double and triple bonds? We have already discussed that multiple bonds consist of σ and π bonds. Next we can consider how we visualize these components and how they relate to hybrid orbitals. The Lewis structure of ethene, C_2H_4 , shows us that each carbon atom is surrounded by one other carbon atom and two hydrogen atoms.

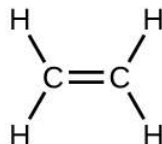


Figure 9.3.2).

A Lewis structure is shown in which two carbon atoms are bonded together by a double bond. Each carbon atom is bonded to two hydrogen atoms by a single bond.

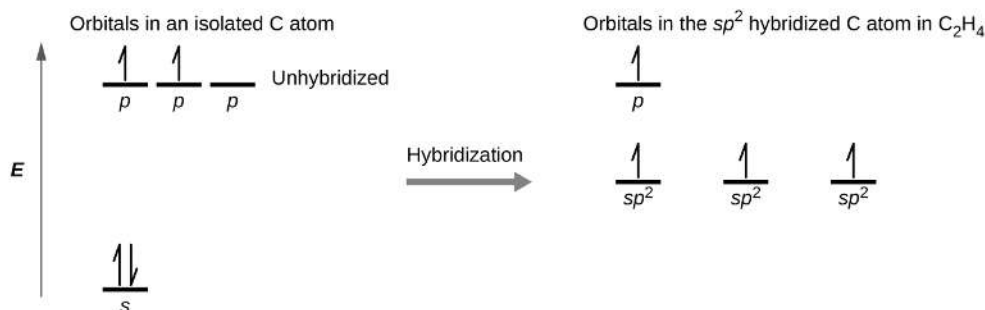


Figure 9.3.1: In ethene, each carbon atom is sp^2 hybridized, and the sp^2 orbitals and the p orbital are singly occupied. The hybrid orbitals overlap to form σ bonds, while the p orbitals on each carbon atom overlap to form a π bond.

A diagram is shown in two parts, connected by a right facing arrow labeled, "Hybridization." The left diagram shows an up-facing arrow labeled, "E." To the lower right of the arrow is a short, horizontal line labeled, "2 s," that has two vertical half-arrows facing up and down on it. To the upper right of the arrow are a series of three short, horizontal lines labeled, "2 p." Above both sets of lines is the phrase, "Orbitals in an isolated C atom." Two of the lines have vertical, up-facing arrows drawn on them. The right side of the diagram shows three short, horizontal lines placed halfway up the space and each labeled, "s p superscript 2." An upward-facing half arrow is drawn vertically on each line. Above these lines is one other short, horizontal line, labeled, "p." Above both sets of lines is the phrase, "Orbitals in the s p superscript 2 hybridized C atom in C subscript 2 H subscript 4."

The π bond in the $C=C$ double bond results from the overlap of the third (remaining) $2p$ orbital on each carbon atom that is not involved in hybridization. This unhybridized p orbital (lobes shown in red and blue in Figure 9.3.2) is perpendicular to the plane of the sp^2 hybrid orbitals. Thus the unhybridized $2p$ orbitals overlap in a side-by-side fashion, above and below the internuclear axis and form a π bond.

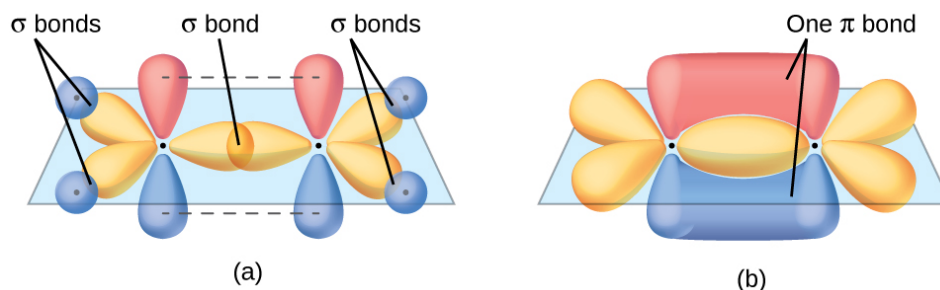
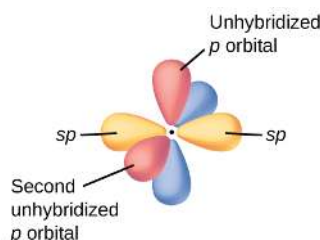


Figure 9.3.2: In the ethene molecule, C_2H_4 , there are (a) five σ bonds. One C–C σ bond results from overlap of sp^2 hybrid orbitals on the carbon atom with one sp^2 hybrid orbital on the other carbon atom. Four C–H bonds result from the overlap between the C atoms' sp^2 orbitals with s orbitals on the hydrogen atoms. (b) The π bond is formed by the side-by-side overlap of the two unhybridized p orbitals in the two carbon atoms. The two lobes of the π bond are above and below the plane of the σ system.

Two diagrams are shown labeled, “a” and “b.” Diagram a shows two carbon atoms with three purple balloon-like orbitals arranged in a plane around them and two red balloon-like orbitals arranged vertically and perpendicularly to the plane. There is an overlap of two of the purple orbitals in between the two carbon atoms, and the other four purple orbitals that face the outside of the molecule are shown interacting with spherical blue orbitals from four hydrogen atoms. Diagram b depicts a similar image to diagram a, but the red, vertical orbitals are interacting above and below the plane of the molecule to form two areas labeled, “One pi bond.”

In an ethene molecule, the four hydrogen atoms and the two carbon atoms are all in the same plane. If the two planes of sp^2 hybrid orbitals tilted relative to each other, the p orbitals would not be oriented to overlap efficiently to create the π bond. The planar configuration for the ethene molecule occurs because it is the most stable bonding arrangement. This is a significant difference between σ and π bonds; rotation around single (σ) bonds occurs easily because the end-to-end orbital overlap does not depend on the relative orientation of the orbitals on each atom in the bond. In other words, rotation around the internuclear axis does not change the extent to which the σ bonding orbitals overlap because the bonding electron density is symmetric about the axis. Rotation about the internuclear axis is much more difficult for multiple bonds; however, this would drastically alter the off-axis overlap of the π bonding orbitals, essentially breaking the π bond.



A diagram of a carbon atom with two balloon-like purple orbitals labeled, “sp” arranged in a linear fashion around it is shown. Four red balloon-like orbitals are aligned in pairs in the y and z axes around the carbon and are labeled, “unhybridized p orbital,” and, “Second unhybridized p orbital.”

Figure 9.3.3: Diagram of the two linear sp hybrid orbitals of a carbon atom, which lie in a straight line, and the two unhybridized p orbitals at perpendicular angles.

In molecules with sp hybrid orbitals, two unhybridized p orbitals remain on the atom (Figure 9.3.3). We find this situation in acetylene, $H-C\equiv C-H$, which is a linear molecule. The sp hybrid orbitals of the two carbon atoms overlap end to end to form a σ bond between the carbon atoms (Figure 9.3.4). The remaining sp orbitals form σ bonds with hydrogen atoms. The two unhybridized p orbitals per carbon are positioned such that they overlap side by side and, hence, form two π bonds. The two carbon atoms of acetylene are thus bound together by one σ bond and two π bonds, giving a triple bond.

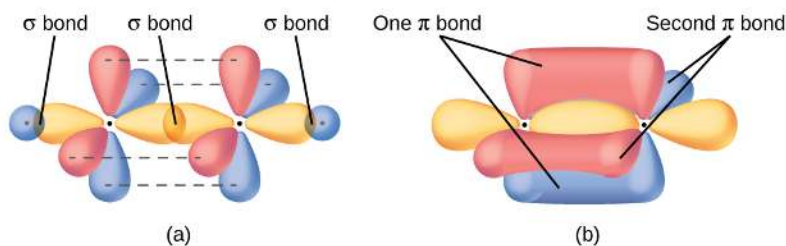
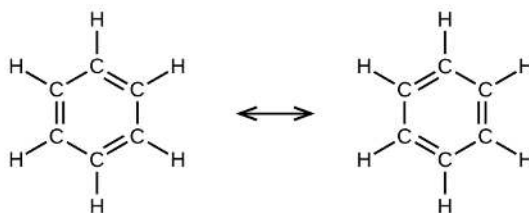


Figure 9.3.4: (a) In the acetylene molecule, C_2H_2 , there are two $C-H$ σ bonds and a $C\equiv C$ triple bond involving one $C-C$ σ bond and two $C-C$ π bonds. The dashed lines, each connecting two lobes, indicate the side-by-side overlap of the four unhybridized p orbitals. (b) This shows the overall outline of the bonds in C_2H_2 . The two lobes of each of the π bonds are positioned across from each other around the line of the $C-C$ σ bond.

Two diagrams are shown and labeled, “a” and “b.” Diagram a shows two carbon atoms with two purple balloon-like orbitals arranged in a plane around each of them, and four red balloon-like orbitals arranged along the y and z axes perpendicular to the plane of the molecule. There is an overlap of two of the purple orbitals in between the two carbon atoms. The other two purple orbitals that face the outside of the molecule are shown interacting with spherical blue orbitals from two hydrogen atoms. Diagram b depicts a similar image to diagram a, but the red, vertical orbitals are interacting above and below and to the front and back of the plane of the molecule to form two areas labeled, “One π bond,” and, “Second π bond,” each respectively.

Hybridization involves only σ bonds, lone pairs of electrons, and single unpaired electrons (radicals). Structures that account for these features describe the correct hybridization of the atoms. However, many structures also include resonance forms. Remember that resonance forms occur when various arrangements of π bonds are possible. Since the arrangement of π bonds involves only the unhybridized orbitals, resonance does not influence the assignment of hybridization.

For example, molecule benzene has two resonance forms (Figure 9.3.5). We can use either of these forms to determine that each of the carbon atoms is bonded to three other atoms with no lone pairs, so the correct hybridization is sp^2 . The electrons in the unhybridized p orbitals form π bonds. Neither resonance structure completely describes the electrons in the π bonds. They are not located in one position or the other, but in reality are delocalized throughout the ring. Valence bond theory does not easily address delocalization. Bonding in molecules with resonance forms is better described by molecular orbital theory.



A diagram is shown that is made up of two Lewis structures connected by a double ended arrow. The left image shows six carbon atoms bonded together with alternating double and single bonds to form a six-sided ring. Each carbon is also bonded to a hydrogen atom by a single bond. The right image shows the same structure, but the double and single bonds in between the carbon atoms have changed positions.

Figure 9.3.5: Each carbon atom in benzene, C_6H_6 , is sp^2 hybridized, independently of which resonance form is considered. The electrons in the π bonds are not located in one set of p orbitals or the other, but rather delocalized throughout the molecule.

✓ Example 9.3.1: Assignment of Hybridization Involving Resonance

Some acid rain results from the reaction of sulfur dioxide with atmospheric water vapor, followed by the formation of sulfuric acid. Sulfur dioxide, SO_2 , is a major component of volcanic gases as well as a product of the combustion of sulfur-containing coal. What is the hybridization of the S atom in SO_2 ?

Solution

The resonance structures of SO_2 are



Two Lewis structures connected by a double-ended arrow are shown. The left structure shows a sulfur atom with one lone pair of electrons and a positive sign which is single bonded on one side to an oxygen atom with three lone pairs of electrons and a negative sign. The sulfur atom is double bonded on the other side to another oxygen atom with two lone pairs of electrons. The right-hand structure is the same as the left except that the position of the double bonded oxygen atom is switched. In both structures the attached oxygen atoms form an acute angle in terms of the sulfur atom.

The sulfur atom is surrounded by two bonds and one lone pair of electrons in either resonance structure. Therefore, the electron-pair geometry is trigonal planar, and the hybridization of the sulfur atom is sp^2 .

? Exercise 9.3.1

Another acid in acid rain is nitric acid, HNO_3 , which is produced by the reaction of nitrogen dioxide, NO_2 , with atmospheric water vapor. What is the hybridization of the nitrogen atom in NO_2 ? (Note: the lone electron on nitrogen occupies a hybridized orbital just as a lone pair would.)

Answer

sp^2

Summary

Multiple bonds consist of a σ bond located along the axis between two atoms and one or two π bonds. The σ bonds are usually formed by the overlap of hybridized atomic orbitals, while the π bonds are formed by the side-by-side overlap of unhybridized orbitals. Resonance occurs when there are multiple unhybridized orbitals with the appropriate alignment to overlap, so the placement of π bonds can vary.

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CHAPTER OVERVIEW

10: Resonance. So 1 bond is 2 electrons, right? Right?

Topic hierarchy

[10.1: Formal Charges and Resonance](#)

[10.2: Resonance](#)

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10.1: Formal Charges and Resonance

Learning Objectives

- Compute formal charges for atoms in any Lewis structure
- Use formal charges to identify the most reasonable Lewis structure for a given molecule
- Explain the concept of resonance and draw Lewis structures representing resonance forms for a given molecule

Previously, we discussed how to write Lewis structures for molecules and polyatomic ions. In some cases, however, there is seemingly more than one valid structure for a molecule. We can use the concept of formal charges to help us predict the most appropriate Lewis structure when more than one is reasonable.

Calculating Formal Charge

The formal charge of an atom in a molecule is the *hypothetical* charge the atom would have if we could redistribute the electrons in the bonds evenly between the atoms. Another way of saying this is that formal charge results when we take the number of valence electrons of a neutral atom, subtract the nonbonding electrons, and then subtract the number of bonds connected to that atom in the Lewis structure.

Thus, we calculate formal charge as follows:

Misplaced '#'

We can double-check formal charge calculations by determining the sum of the formal charges for the whole structure. The sum of the formal charges of all atoms in a molecule must be zero; the sum of the formal charges in an ion should equal the charge of the ion.

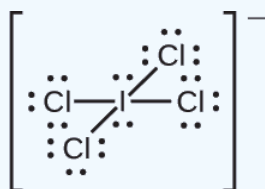
We must remember that the formal charge calculated for an atom is not the *actual* charge of the atom in the molecule. Formal charge is only a useful bookkeeping procedure; it does not indicate the presence of actual charges.

✓ Example 10.1.1: Calculating Formal Charge from Lewis Structures

Assign formal charges to each atom in the interhalogen ion ICl_4^- .

Solution

We divide the bonding electron pairs equally for all $\text{I}-\text{Cl}$ bonds:



We assign lone pairs of electrons to their atoms. Each Cl atom now has seven electrons assigned to it, and the I atom has eight.

Subtract this number from the number of valence electrons for the neutral atom:

- I: $7 - 8 = -1$
- Cl: $7 - 7 = 0$

The sum of the formal charges of all the atoms equals -1 , which is identical to the charge of the ion (-1).

? Exercise 10.1.1

Calculate the formal charge for each atom in the carbon monoxide molecule:



Answer

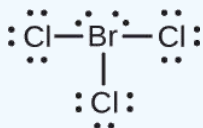
C -1, O +1

✓ Example 10.1.2: Calculating Formal Charge from Lewis Structures

Assign formal charges to each atom in the interhalogen molecule BrCl_3 .

Solution

Assign one of the electrons in each Br–Cl bond to the Br atom and one to the Cl atom in that bond:



Assign the lone pairs to their atom. Now each Cl atom has seven electrons and the Br atom has seven electrons.

Subtract this number from the number of valence electrons for the neutral atom. This gives the formal charge:

- Br: $7 - 7 = 0$
- Cl: $7 - 7 = 0$

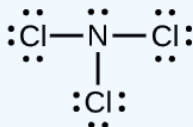
All atoms in BrCl_3 have a formal charge of zero, and the sum of the formal charges totals zero, as it must in a neutral molecule.

? Exercise 10.1.2

Determine the formal charge for each atom in NCl_3 .

Answer

N: 0; all three Cl atoms: 0



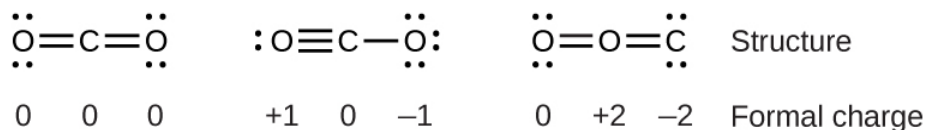
Using Formal Charge to Predict Molecular Structure

The arrangement of atoms in a molecule or ion is called its molecular structure. In many cases, following the steps for writing Lewis structures may lead to more than one possible molecular structure—different multiple bond and lone-pair electron placements or different arrangements of atoms, for instance. A few guidelines involving formal charge can be helpful in deciding which of the possible structures is most likely for a particular molecule or ion.

📌 Predicting Molecular Structure Guidelines

1. A molecular structure in which all formal charges are zero is preferable to one in which some formal charges are not zero.
2. If the Lewis structure must have nonzero formal charges, the arrangement with the smallest nonzero formal charges is preferable.
3. Lewis structures are preferable when adjacent formal charges are zero or of the opposite sign.
4. When we must choose among several Lewis structures with similar distributions of formal charges, the structure with the negative formal charges on the more electronegative atoms is preferable.

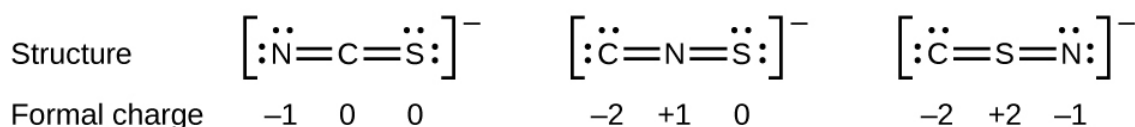
To see how these guidelines apply, let us consider some possible structures for carbon dioxide, CO_2 . We know from our previous discussion that the less electronegative atom typically occupies the central position, but formal charges allow us to understand *why* this occurs. We can draw three possibilities for the structure: carbon in the center and double bonds, carbon in the center with a single and triple bond, and oxygen in the center with double bonds:



Three Lewis structures are shown. The left and right structures show a carbon atom double bonded to two oxygen atoms, each of which has two lone pairs of electrons. The center structure shows a carbon atom that is triple bonded to an oxygen atom with one lone pair of electrons and single bonded to an oxygen atom with three lone pairs of electrons. The third structure shows an oxygen atom double bonded to another oxygen atom with two lone pairs of electrons. The first oxygen atom is also double bonded to a carbon atom with two lone pairs of electrons.

Comparing the three formal charges, we can definitively identify the structure on the left as preferable because it has only formal charges of zero (Guideline 1).

As another example, the thiocyanate ion, an ion formed from a carbon atom, a nitrogen atom, and a sulfur atom, could have three different molecular structures: CNS^- , NCS^- , or CSN^- . The formal charges present in each of these molecular structures can help us pick the most likely arrangement of atoms. Possible Lewis structures and the formal charges for each of the three possible structures for the thiocyanate ion are shown here:

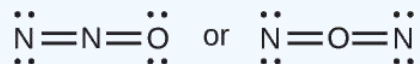


Two rows of structures and numbers are shown. The top row is labeled, "Structure" and depicts three Lewis structures and the bottom row is labeled, "Formal charge." The left structure shows a carbon atom double bonded to a nitrogen atom with two lone electron pairs on one side and double bonded to a sulfur atom with two lone electron pairs on the other. The structure is surrounded by brackets and has a superscripted negative sign. Below this structure are the numbers negative one, zero, and zero. The middle structure shows a carbon atom with two lone pairs of electrons double bonded to a nitrogen atom that is double bonded to a sulfur atom with two lone electron pairs. The structure is surrounded by brackets and has a superscripted negative sign. Below this structure are the numbers negative two, positive one, and zero. The right structure shows a carbon atom with two lone electron pairs double bonded to a sulfur atom that is double bonded to a nitrogen atom with two lone electron pairs. The structure is surrounded by brackets and has a superscripted negative sign. Below this structure are the numbers negative two, positive two, and one.

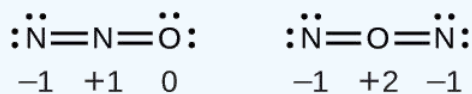
Note that the sum of the formal charges in each case is equal to the charge of the ion (-1). However, the first arrangement of atoms is preferred because it has the lowest number of atoms with nonzero formal charges (Guideline 2). Also, it places the least electronegative atom in the center, and the negative charge on the more electronegative element (Guideline 4).

✓ Example 10.1.3: Using Formal Charge to Determine Molecular Structure

Nitrous oxide, N_2O , commonly known as laughing gas, is used as an anesthetic in minor surgeries, such as the routine extraction of wisdom teeth. Which is the likely structure for nitrous oxide?



Solution Determining formal charge yields the following:



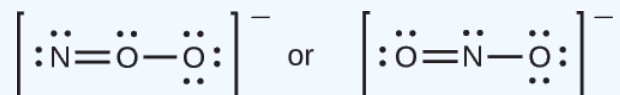
The structure with a terminal oxygen atom best satisfies the criteria for the most stable distribution of formal charge:



The number of atoms with formal charges are minimized (Guideline 2), and there is no formal charge larger than one (Guideline 2). This is again consistent with the preference for having the less electronegative atom in the central position.

? Exercise 10.1.3

Which is the most likely molecular structure for the nitrite (NO_2^-) ion?



Answer



Resonance

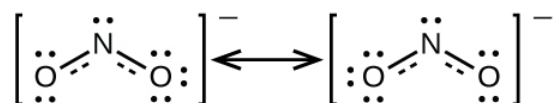
You may have noticed that the nitrite anion in Example 10.1.3 can have two possible structures with the atoms in the same positions. The electrons involved in the N–O double bond, however, are in different positions:



Two Lewis structures are shown. The left structure shows an oxygen atom with three lone pairs of electrons single bonded to a nitrogen atom with one lone pair of electrons that is double bonded to an oxygen with two lone pairs of electrons. Brackets surround this structure, and there is a superscripted negative sign. The right structure shows an oxygen atom with two lone pairs of electrons double bonded to a nitrogen atom with one lone pair of electrons that is single bonded to an oxygen atom with three lone pairs of electrons. Brackets surround this structure, and there is a superscripted negative sign.

If nitrite ions do indeed contain a single and a double bond, we would expect for the two bond lengths to be different. A double bond between two atoms is shorter (and stronger) than a single bond between the same two atoms. Experiments show, however, that both N–O bonds in NO_2^- have the same strength and length, and are identical in all other properties.

It is not possible to write a single Lewis structure for NO_2^- in which nitrogen has an octet and both bonds are equivalent. Instead, we use the concept of resonance: if two or more Lewis structures with the same arrangement of atoms can be written for a molecule or ion, the actual distribution of electrons is an *average* of that shown by the various Lewis structures. The actual distribution of electrons in each of the nitrogen-oxygen bonds in NO_2^- is the average of a double bond and a single bond. We call the individual Lewis structures resonance forms. The actual electronic structure of the molecule (the average of the resonance forms) is called a resonance hybrid of the individual resonance forms. A double-headed arrow between Lewis structures indicates that they are resonance forms. Thus, the electronic structure of the NO_2^- ion is shown as:

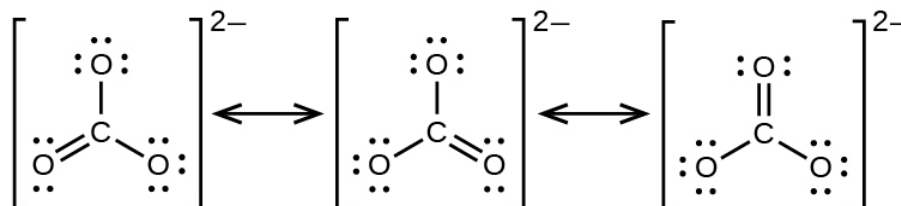


Two Lewis structures are shown with a double headed arrow drawn between them. The left structure shows an oxygen atom with two lone pairs of electrons double bonded to a nitrogen atom with one lone pair of electrons that is single bonded to an oxygen atom with three lone pairs of electrons. Brackets surround this structure, and there is a superscripted negative sign. The right structure shows an oxygen atom with three lone pairs of electrons single bonded to a nitrogen atom with one lone pair of electrons that is double bonded to an oxygen atom with two lone pairs of electrons. Brackets surround this structure, and there is a superscripted negative sign.

We should remember that a molecule described as a resonance hybrid *never* possesses an electronic structure described by either resonance form. It does not fluctuate between resonance forms; rather, the actual electronic structure is *always* the average of that

shown by all resonance forms. George Wheland, one of the pioneers of resonance theory, used a historical analogy to describe the relationship between resonance forms and resonance hybrids. A medieval traveler, having never before seen a rhinoceros, described it as a hybrid of a dragon and a unicorn because it had many properties in common with both. Just as a rhinoceros is neither a dragon sometimes nor a unicorn at other times, a resonance hybrid is neither of its resonance forms at any given time. Like a rhinoceros, it is a real entity that experimental evidence has shown to exist. It has some characteristics in common with its resonance forms, but the resonance forms themselves are convenient, imaginary images (like the unicorn and the dragon).

The carbonate anion, CO_3^{2-} , provides a second example of resonance:



Three Lewis structures are shown with double headed arrows in between. Each structure is surrounded by brackets, and each has a superscripted two negative sign. The left structure depicts a carbon atom bonded to three oxygen atoms. It is single bonded to two of these oxygen atoms, each of which has three lone pairs of electrons, and double bonded to the third, which has two lone pairs of electrons. The double bond is located between the lower left oxygen atom and the carbon atom. The central and right structures are the same as the first, but the position of the double bonded oxygen has moved to the lower right oxygen in the central structure and to the top oxygen in the right structure.

One oxygen atom must have a double bond to carbon to complete the octet on the central atom. All oxygen atoms, however, are equivalent, and the double bond could form from any one of the three atoms. This gives rise to three resonance forms of the carbonate ion. Because we can write three identical resonance structures, we know that the actual arrangement of electrons in the carbonate ion is the average of the three structures. Again, experiments show that all three C–O bonds are exactly the same.

Summary

In a Lewis structure, formal charges can be assigned to each atom by treating each bond as if one-half of the electrons are assigned to each atom. These hypothetical formal charges are a guide to determining the most appropriate Lewis structure. A structure in which the formal charges are as close to zero as possible is preferred. Resonance occurs in cases where two or more Lewis structures with identical arrangements of atoms but different distributions of electrons can be written. The actual distribution of electrons (the resonance hybrid) is an average of the distribution indicated by the individual Lewis structures (the resonance forms).

Key Equations

- Misplaced '#'

Glossary

formal charge

charge that would result on an atom by taking the number of valence electrons on the neutral atom and subtracting the nonbonding electrons and the number of bonds (one-half of the bonding electrons)

molecular structure

arrangement of atoms in a molecule or ion

resonance

situation in which one Lewis structure is insufficient to describe the bonding in a molecule and the average of multiple structures is observed

resonance forms

two or more Lewis structures that have the same arrangement of atoms but different arrangements of electrons

resonance hybrid

average of the resonance forms shown by the individual Lewis structures

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10.2: Resonance

Resonance is a mental exercise within the [Valence Bond Theory](#) of bonding that describes the delocalization of electrons within molecules. It involves constructing multiple Lewis structures that, when combined, represent the full electronic structure of the molecule. **Resonance structures** are used when a single Lewis structure cannot fully describe the bonding; the combination of possible resonance structures is defined as a **resonance hybrid**, which represents the overall delocalization of electrons within the molecule. In general, molecules with multiple resonance structures will be more stable than one with fewer and some resonance structures contribute more to the stability of the molecule than others - formal charges aid in determining this.

Introduction

Resonance is a way of describing delocalized electrons within certain molecules or polyatomic ions where the bonding cannot be expressed by a single Lewis formula. A molecule or ion with such delocalized electrons is represented by several resonance structures. The nuclear skeleton of the Lewis Structure of these resonance structures remains the same, only the electron locations differ. Such is the case for [ozone](#) (O_3), an allotrope of oxygen with a V-shaped structure and an O–O–O angle of 117.5° . Let's motivate the discussion by building the Lewis structure for ozone.

1. We know that ozone has a V-shaped structure, so one O atom is central:

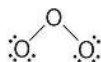


2. Each O atom has 6 valence electrons, for a total of 18 valence electrons.
3. Assigning one bonding pair of electrons to each oxygen–oxygen bond gives



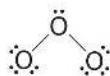
with 14 electrons left over.

4. If we place three lone pairs of electrons on each terminal oxygen, we obtain

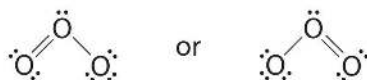


and have 2 electrons left over.

5. At this point, both terminal oxygen atoms have octets of electrons. We therefore place the last 2 electrons on the central atom:

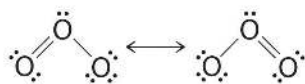


6. The central oxygen has only 6 electrons. We must convert one lone pair on a terminal oxygen atom to a bonding pair of electrons—but which one? Depending on which one we choose, we obtain either



Which is correct? In fact, neither is correct. Both predict one O–O single bond and one O=O double bond. As you will learn, if the bonds were of different types (one single and one double, for example), they would have different lengths. It turns out, however, that both O–O bond distances are identical, 127.2 pm, which is shorter than a typical O–O single bond (148 pm) and longer than the O=O double bond in O_2 (120.7 pm).

Equivalent Lewis dot structures, such as those of ozone, are called **resonance structures**. The position of the *atoms* is the same in the various resonance structures of a compound, but the position of the *electrons* is different. Double-headed arrows link the different resonance structures of a compound:



The double-headed arrow indicates that the actual electronic structure is an *average* of those shown, not that the molecule oscillates between the two structures.

When it is possible to write more than one equivalent resonance structure for a molecule or ion, the actual structure is the average of the resonance structures.

The electrons appear to "shift" between different resonance structures and while not strictly correct as each resonance structure is just a limitation of using the Lewis structure perspective to describe these molecules. A more accurate description of the electron structure of the molecule requires considering multiple resonance structures simultaneously.

Delocalization and Resonance Structures Rules

1. Resonance structures should have the same number of electrons, do not add or subtract any electrons. (check the number of electrons by simply counting them).
2. Each resonance structures follows the rules of writing [Lewis Structures](#).
3. The hybridization of the structure must stay the same.
4. The skeleton of the structure can not be changed (only the electrons move).
5. Resonance structures must also have the same number of lone pairs.

"Pick the Correct Arrow for the Job"

Most arrows in chemistry cannot be used interchangeably and care must be given to selecting the correct arrow for the job.

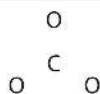
- $\longleftrightarrow$: A double headed arrow on both ends of the arrow between Lewis structures is used to show resonance
- $\rightleftharpoons$: Double harpoons are used to designate equilibria
- $\rightarrow$: A single harpoon on one end indicates the movement of **one** electron
- $\rightarrow$: A double headed arrow on one end is used to indicate the movement of **two** electrons

✓ Example 10.2.2: Carbonate Ion

Identify the resonance structures for the carbonate ion: CO_3^{2-} .

Solution

1. Because carbon is the least electronegative element, we place it in the central position:

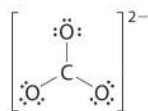


2. Carbon has 4 valence electrons, each oxygen has 6 valence electrons, and there are 2 more for the -2 charge. This gives $4 + (3 \times 6) + 2 = 24$ valence electrons.

3. Six electrons are used to form three bonding pairs between the oxygen atoms and the carbon:

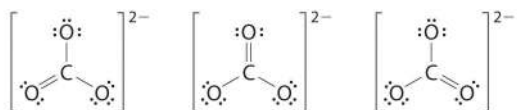


4. We divide the remaining 18 electrons equally among the three oxygen atoms by placing three lone pairs on each and indicating the -2 charge:

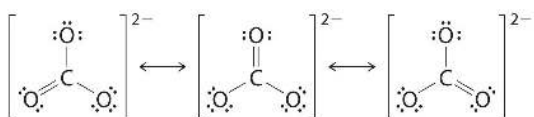


5. No electrons are left for the central atom.

6. At this point, the carbon atom has only 6 valence electrons, so we must take one lone pair from an oxygen and use it to form a carbon–oxygen double bond. In this case, however, there are *three* possible choices:



As with ozone, none of these structures describes the bonding exactly. Each predicts one carbon–oxygen double bond and two carbon–oxygen single bonds, but experimentally all C–O bond lengths are identical. We can write resonance structures (in this case, three of them) for the carbonate ion:



The actual structure is an average of these three resonance structures.

Like ozone, the electronic structure of the carbonate ion cannot be described by a single Lewis electron structure. Unlike O₃, though, the actual structure of CO₃^{2−} is an average of *three* resonance structures.

Using Formal Charges to Identify viable Resonance Structures

While each resonance structure contributes to the total electronic structure of the molecule, they may not contribute equally. Assigning **Formal charges** to atoms in the molecules is one mechanism to identify the viability of a resonance structure and determine its relative magnitude among other structures. The formal charge on an atom in a covalent species is the net charge the atom would bear if the electrons in all the bonds to the atom were equally shared. Alternatively the formal charge on an atom in a covalent species is the net charge the atom would bear if all bonds to the atom were nonpolar covalent bonds. To determine the formal charge on a given atom in a covalent species, use the following formula:

$$\text{Formal Charge} = (\text{number of valence electrons in free orbital}) - (\text{number of lone-pair electrons}) - \frac{1}{2}(\text{number bond pair electrons}) \quad (10.2.1)$$

📌 Rules for estimating stability of resonance structures

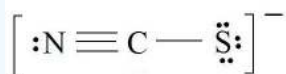
1. The **greater the number of covalent bonds**, the greater the stability since more atoms will have complete octets
2. The structure with the **least number of formal charges** is more stable
3. The structure with the **least separation of formal charge** is more stable
4. A structure with a **negative charge on the more electronegative atom** will be more stable
5. **Positive charges on the least electronegative atom** (most electropositive) is more stable
6. Resonance forms that are equivalent have no difference in stability and contribute equally (eg. benzene)

✓ Example 10.2.3: Thiocyanate Ion

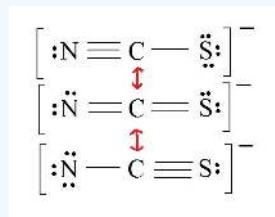
Consider the thiocyanate (CNS[−]) ion.

Solution

1. Find the Lewis Structure of the molecule. (Remember the Lewis Structure rules.)



2. Resonance: All elements want an octet, and we can do that in multiple ways by moving the terminal atom's electrons around (bonds too).

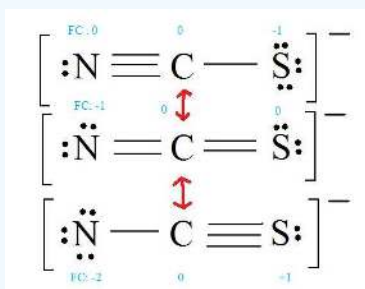


3. Assign Formal Charges via Equation 10.2.1.

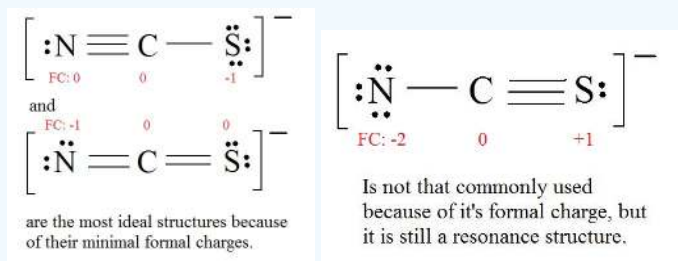
Formal Charge = (number of valence electrons in free orbital) - (number of lone-pair electrons) - ($\frac{1}{2}$ number bond pair electrons)

Remember to determine the number of valence electron each atom has before assigning Formal Charges

C = 4 valence e^{-} , N = 5 valence e^{-} , S = 6 valence e^{-} , also add an extra electron for the (-1) charge. The total of valence electrons is 16.

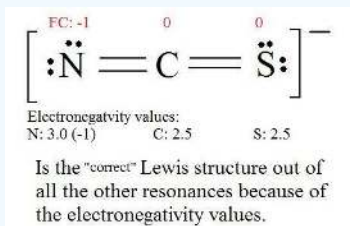


4. Find the most ideal resonance structure. (Note: It is the one with the least formal charges that adds up to zero or to the molecule's overall charge.)



5. Now we have to look at electronegativity for the "Correct" Lewis structure.

The most electronegative atom usually has the negative formal charge, while the least electronegative atom usually has the positive formal charges.



It is useful to combine the resonance structures into a single structure called the **Resonance Hybrid** that describes the bonding of the molecule. The general approach is described below:

1. Draw the Lewis Structure & Resonance for the molecule (using solid lines for bonds).
2. Where there **can** be a double or triple bond, draw a dotted line (-----) for the bond.
3. Draw only the lone pairs found in all resonance structures, do not include the lone pairs that are not on all of the resonance structures.

✓ Example 10.2.4: Benzene

Benzene is a common organic solvent that was previously used in gasoline; it is no longer used for this purpose, however, because it is now known to be a carcinogen. The benzene molecule (C_6H_6) consists of a regular hexagon of carbon atoms, each of which is also bonded to a hydrogen atom. Use resonance structures to describe the bonding in benzene.

Given: molecular formula and molecular geometry

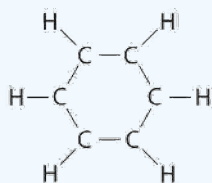
Asked for: resonance structures

Strategy:

- A. Draw a structure for benzene illustrating the bonded atoms. Then calculate the number of valence electrons used in this drawing.
- B. Subtract this number from the total number of valence electrons in benzene and then locate the remaining electrons such that each atom in the structure reaches an octet.
- C. Draw the resonance structures for benzene.

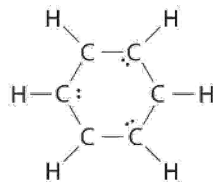
Solution:

A Each hydrogen atom contributes 1 valence electron, and each carbon atom contributes 4 valence electrons, for a total of $(6 \times 1) + (6 \times 4) = 30$ valence electrons. If we place a single bonding electron pair between each pair of carbon atoms and between each carbon and a hydrogen atom, we obtain the following:



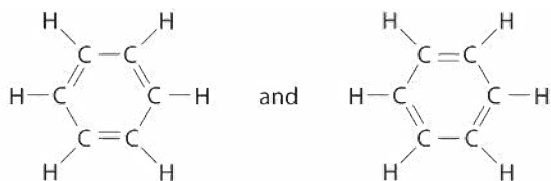
Each carbon atom in this structure has only 6 electrons and has a formal charge of +1, but we have used only 24 of the 30 valence electrons.

B If the 6 remaining electrons are uniformly distributed pairwise on alternate carbon atoms, we obtain the following:

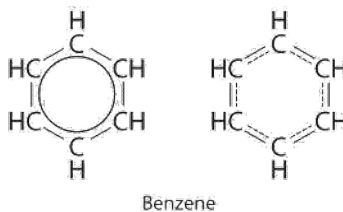


Three carbon atoms now have an octet configuration and a formal charge of -1, while three carbon atoms have only 6 electrons and a formal charge of +1. We can convert each lone pair to a bonding electron pair, which gives each atom an octet of electrons and a formal charge of 0, by making three C=C double bonds.

C There are, however, two ways to do this:



Each structure has alternating double and single bonds, but experimentation shows that each carbon–carbon bond in benzene is identical, with bond lengths (139.9 pm) intermediate between those typically found for a C–C single bond (154 pm) and a C=C double bond (134 pm). We can describe the bonding in benzene using the two resonance structures, but the actual electronic structure is an average of the two. The existence of multiple resonance structures for aromatic hydrocarbons like benzene is often indicated by drawing either a circle or dashed lines inside the hexagon:

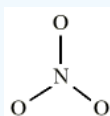


✓ Example 10.2.5: Nitrate Ion

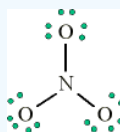
Draw the possible resonance structures for the Nitrate ion NO_3^- .

Solution

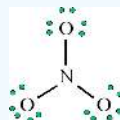
1. Count up the valence electrons: $(1 \times 5) + (3 \times 6) + 1(\text{ion}) = 24$ electrons
2. Draw the bond connectivities:



3. Add octet electrons to the atoms bonded to the center atom:

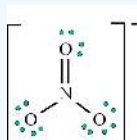


4. Place any leftover electrons $(24 - 24 = 0)$ on the center atom:



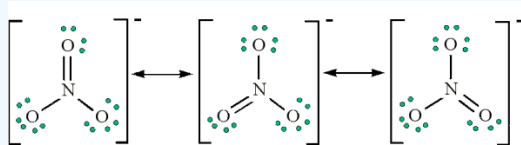
5. Does the central atom have an octet?

- **NO**, it has 6 electrons
- Add a multiple bond (first try a double bond) to see if the central atom can achieve an octet:



6. Does the central atom have an octet?

- YES
- Are there possible resonance structures? YES



Note: We would expect that the bond lengths in the NO_3^- ion to be somewhat shorter than a single bond.

References

1. Petrucci, Ralph H., et al. *General Chemistry: Principles and Modern Applications*. New Jersey: Pearson Prentice Hall, 2007.
2. Ahmad, Wan-Yacob and Zakaria, Mat B. "Drawing Lewis Structures from Lewis Symbols: A Direct Electron Pairing Approach." *Journal of Chemical Education*: Journal 77.3.

Problems

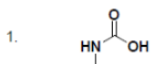
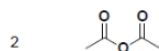
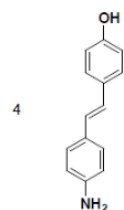
1. True or False, The picture below is a resonance structure?

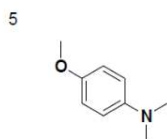


2. Draw the Lewis Dot Structure for SO_4^{2-} and all possible resonance structures. Which of the following resonance structure is not favored among the Lewis Structures? Explain why. Assign Formal Charges.
3. Draw the Lewis Dot Structure for CH_3COO^- and all possible resonance structures. Assign Formal Charges. Choose the most favorable Lewis Structure.
4. Draw the Lewis Dot Structure for HPO_3^{2-} and all possible resonance structures. Assign Formal Charges.
5. Draw the Lewis Dot Structure for CHO_2^{1-} and all possible resonance structures. Assign Formal Charges.
6. Draw the Resonance Hybrid Structure for PO_4^{3-} .
7. Draw the Resonance Hybrid Structure for NO_3^- .

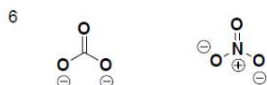
Problems #2

Problems: Draw the resonance forms for the following structures





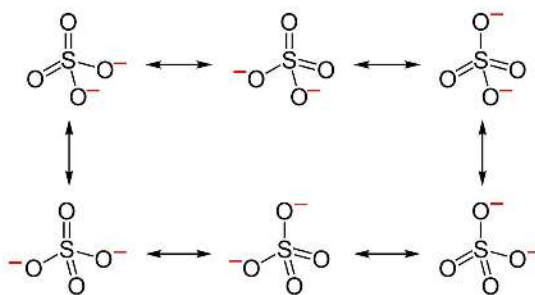
Based on resonance conformation which structure is more stable?



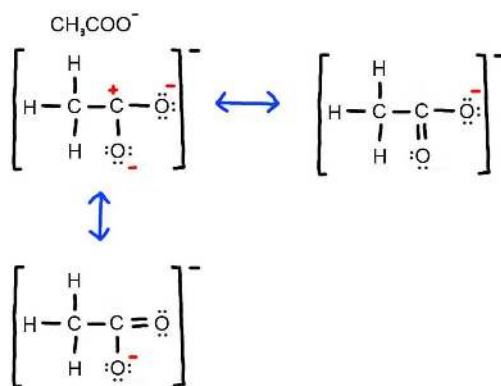
Answers

1. False, because the electrons were not moved around, only the atoms (this violates the Resonance Structure Rules).

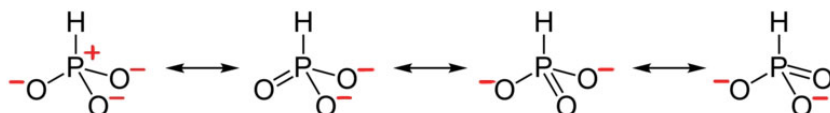
2. Below are the all Lewis dot structure with formal charges (in red) for Sulfate (SO_4^{2-}). There isn't a most favorable resonance of the Sulfate ion because they are all identical in charge and there is no change in Electronegativity between the Oxygen atoms.



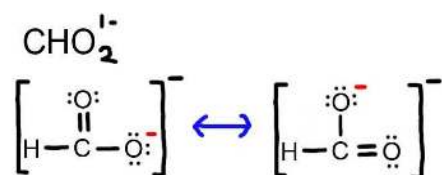
3. Below is the resonance for CH_3COO^- , formal charges are displayed in red. The Lewis Structure with the most formal charges is not desirable, because we want the Lewis Structure with the least formal charge.



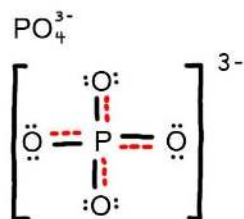
4. The resonance for HPO_3^{2-} , and the formal charges (in red).



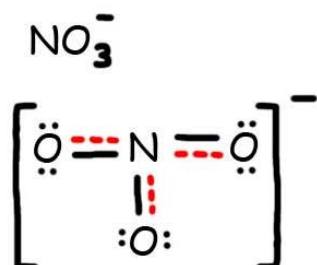
5. The resonance for CHO_2^{1-} , and the formal charges (in red).



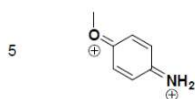
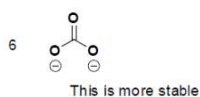
6. The resonance hybrid for PO_4^{3-} , hybrid bonds are in red.



7. The resonance hybrid for NO_3^- , hybrid bonds are in red.



Problems #2



Contributors and Attributions

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11.1: Molecular Structure and Polarity

Learning Objectives

- Predict the structures of small molecules using valence shell electron pair repulsion (VSEPR) theory
- Explain the concepts of polar covalent bonds and molecular polarity
- Assess the polarity of a molecule based on its bonding and structure

Thus far, we have used two-dimensional Lewis structures to represent molecules. However, molecular structure is actually three-dimensional, and it is important to be able to describe molecular bonds in terms of their distances, angles, and relative arrangements in space (Figure 11.1.1). A bond angle is the angle between any two bonds that include a common atom, usually measured in degrees. A bond distance (or bond length) is the distance between the nuclei of two bonded atoms along the straight line joining the nuclei. Bond distances are measured in Ångstroms ($1 \text{ Å} = 10^{-10} \text{ m}$) or picometers ($1 \text{ pm} = 10^{-12} \text{ m}$, $100 \text{ pm} = 1 \text{ Å}$).

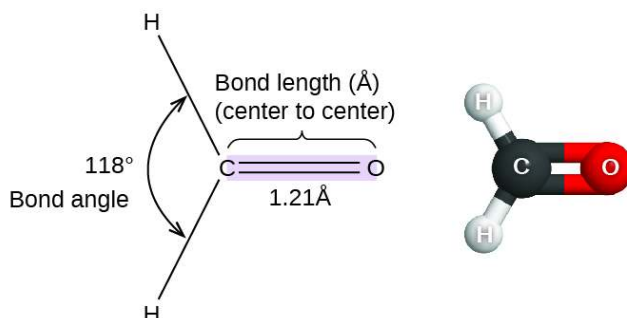


Figure 11.1.1: Bond distances (lengths) and angles are shown for the formaldehyde molecule, H_2CO .

A pair of images are shown. The left image shows a carbon atom with three atoms bonded in a triangular arrangement around it. There are two hydrogen atoms bonded on the left side of the carbon and the angle between them is labeled, "118 degrees" and, "Bond angle." The carbon is also double bonded to an oxygen atom. The double bond is shaded and there is a bracket which labels the bond, "Bond length (angstrom), (center to center)," and, "1.21 angstrom." The right image shows a ball-and-stick model of the same elements. The hydrogen atoms are white, the carbon atom is black, and the oxygen atom is red."

VSEPR Theory

Valence shell electron-pair repulsion theory (VSEPR theory) enables us to predict the molecular structure, including approximate bond angles around a central atom, of a molecule from an examination of the number of bonds and lone electron pairs in its Lewis structure. The VSEPR model assumes that electron pairs in the valence shell of a central atom will adopt an arrangement that minimizes repulsions between these electron pairs by maximizing the distance between them. The electrons in the valence shell of a central atom form either bonding pairs of electrons, located primarily between bonded atoms, or lone pairs. The electrostatic repulsion of these electrons is reduced when the various regions of high electron density assume positions as far from each other as possible.

VSEPR theory predicts the arrangement of electron pairs around each central atom and, usually, the correct arrangement of atoms in a molecule. We should understand, however, that the theory only considers electron-pair repulsions. Other interactions, such as nuclear-nuclear repulsions and nuclear-electron attractions, are also involved in the final arrangement that atoms adopt in a particular molecular structure.

As a simple example of VSEPR theory, let us predict the structure of a gaseous BeF_2 molecule. The Lewis structure of BeF_2 (Figure 11.1.2) shows only two electron pairs around the central beryllium atom. With two bonds and no lone pairs of electrons on the central atom, the bonds are as far apart as possible, and the electrostatic repulsion between these regions of high electron density is reduced to a minimum when they are on opposite sides of the central atom. The bond angle is 180° (Figure 11.1.2).

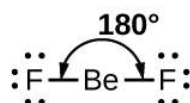


Figure 11.1.2: The BeF₂ molecule adopts a linear structure in which the two bonds are as far apart as possible, on opposite sides of the Be atom.

A Lewis structure is shown. A fluorine atom with three lone pairs of electrons is single bonded to a beryllium atom which is single bonded to a fluorine atom with three lone pairs of electrons. The angle of the bonds between the two fluorine atoms and the beryllium atom is labeled, “180 degrees.”

Figure 11.1.3 illustrates this and other electron-pair geometries that minimize the repulsions among regions of high electron density (bonds and/or lone pairs). Two regions of electron density around a central atom in a molecule form a linear geometry; three regions form a trigonal planar geometry; four regions form a tetrahedral geometry; five regions form a trigonal bipyramidal geometry; and six regions form an octahedral geometry.

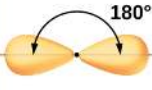
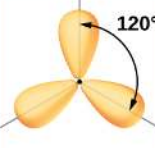
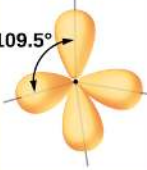
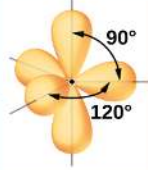
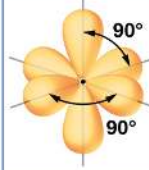
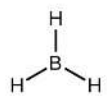
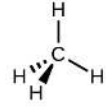
Number of regions	Two regions of high electron density (bonds and/or unshared pairs)	Three regions of high electron density (bonds and/or unshared pairs)	Four regions of high electron density (bonds and/or unshared pairs)	Five regions of high electron density (bonds and/or unshared pairs)	Six regions of high electron density (bonds and/or unshared pairs)
Spatial arrangement					
Line-dash-wedge notation	$\text{H}-\text{Be}-\text{H}$				
Electron pair geometry	Linear; 180° angle	Trigonal planar; all angles 120°	Tetrahedral; all angles 109.5°	Trigonal bipyramidal; angles of 90° or 120° An attached atom may be equatorial (in the plane of the triangle) or axial (above or below the plane of the triangle).	Octahedral; all angles 90° or 180°

Figure 11.1.3: The basic electron-pair geometries predicted by VSEPR theory maximize the space around any region of electron density (bonds or lone pairs).

A table with four rows and six columns is shown. The header column contains the phrases, “Number of regions,” “Spatial arrangement,” “Wedge/dash Notation,” and “Electron pair Geometry.” The first row reads: “Two regions of high electron density (bonds and/or unshared pairs),” “Three regions of high electron density (bonds and/or unshared pairs),” “Four regions of high electron density (bonds and/or unshared pairs),” and “Six regions of high electron density (bonds and/or unshared pairs).” The second row shows diagrams of orbitals. The first image shows two oval-shaped orbs with an arrow indicating an angle of 180 degrees. The second image shows three oval-shaped orbs with an arrow indicating an angle of 120 degrees. The third image shows four oval-shaped orbs with an arrow indicating an angle of 109.5 degrees. The fourth image shows five oval-shaped orbs with an arrow indicating an angle of 90 and 120 degrees. The fifth image shows six oval-shaped orbs with an arrow indicating an angle of 90 degrees. The third row contains Lewis structures. The first structure shows a beryllium atom single bonded to two hydrogen atoms. The second structure shows a boron atom single bonded to three hydrogen atoms. The third structure shows a carbon atom single bonded to four hydrogen atoms. The fourth structure shows a phosphorus atom single bonded to five fluorine atoms. The fifth structure shows a sulfur atom single bonded to six fluorine atoms. The fourth row contains the phrases “Linear; 180 degree angle,” “Trigonal Planar; all angles 120 degrees,” “Tetrahedral; all angles 109.5 degrees,” “Trigonal bipyramidal; angles of 90 degrees and 120 degrees. An attached atom may be equatorial, (in the plane of the triangle), or axial, (above the plane of the triangle),” and “Octahedral; 90 degrees or 180 degrees.”

Electron-pair Geometry versus Molecular Structure

It is important to note that electron-pair geometry around a central atom is *not* the same thing as its molecular structure. The electron-pair geometries shown in Figure 11.1.3 describe all regions where electrons are located, bonds as well as lone pairs. Molecular structure describes the location of the *atoms*, not the electrons.

We differentiate between these two situations by naming the geometry that includes *all* electron pairs the electron-pair geometry. The structure that includes only the placement of the atoms in the molecule is called the molecular structure. The electron-pair geometries will be the same as the molecular structures when there are no lone electron pairs around the central atom, but they will be different when there are lone pairs present on the central atom.

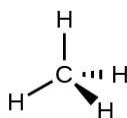


Figure 11.1.4: The molecular structure of the methane molecule, CH_4 , is shown with a tetrahedral arrangement of the hydrogen atoms. VSEPR structures like this one are often drawn using the wedge and dash notation, in which solid lines represent bonds in the plane of the page, solid wedges represent bonds coming up out of the plane, and dashed lines represent bonds going down into the plane.

A Lewis structure shows a carbon atom single bonded to four hydrogen atoms. This structure uses wedges and dashes to give it a three dimensional appearance.

For example, the methane molecule, CH_4 , which is the major component of natural gas, has four bonding pairs of electrons around the central carbon atom; the electron-pair geometry is tetrahedral, as is the molecular structure (Figure 11.1.4). On the other hand, the ammonia molecule, NH_3 , also has four electron pairs associated with the nitrogen atom, and thus has a tetrahedral electron-pair geometry. One of these regions, however, is a lone pair, which is not included in the molecular structure, and this lone pair influences the shape of the molecule (Figure 11.1.5).

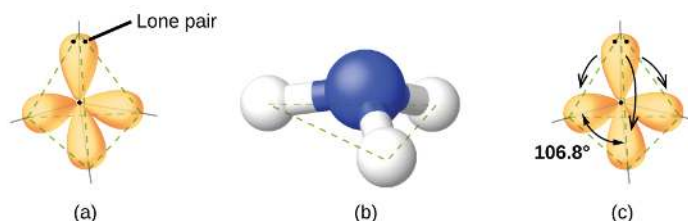
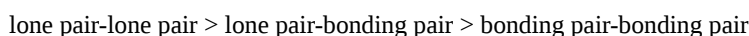


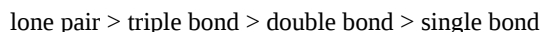
Figure 11.1.5: (a) The electron-pair geometry for the ammonia molecule is tetrahedral with one lone pair and three single bonds. (b) The trigonal pyramidal molecular structure is determined from the electron-pair geometry. (c) The actual bond angles deviate slightly from the idealized angles because the lone pair takes up a larger region of space than do the single bonds, causing the HNH angle to be slightly smaller than 109.5° .

Three images are shown and labeled, “a,” “b,” and “c.” Image a shows a nitrogen atom single bonded to three hydrogen atoms. There are four oval-shaped orbs that surround each hydrogen and one facing away from the rest of the molecule. These orbs are located in a tetrahedral arrangement. Image b shows a ball-and-stick model of the nitrogen single bonded to the three hydrogen atoms. Image c is the same as image a, but there are four curved, double headed arrows that circle the molecule and are labeled, “ 106.8° degrees.”

Small distortions from the ideal angles in Figure 11.1.5 can result from differences in repulsion between various regions of electron density. VSEPR theory predicts these distortions by establishing an order of repulsions and an order of the amount of space occupied by different kinds of electron pairs. The order of electron-pair repulsions from greatest to least repulsion is:



This order of repulsions determines the amount of space occupied by different regions of electrons. A lone pair of electrons occupies a larger region of space than the electrons in a triple bond; in turn, electrons in a triple bond occupy more space than those in a double bond, and so on. The order of sizes from largest to smallest is:



Consider formaldehyde, H_2CO , which is used as a preservative for biological and anatomical specimens. This molecule has regions of high electron density that consist of two single bonds and one double bond. The basic geometry is trigonal planar with 120° bond angles, but we see that the double bond causes slightly larger angles (121°), and the angle between the single bonds is slightly smaller (118°).

In the ammonia molecule, the three hydrogen atoms attached to the central nitrogen are not arranged in a flat, trigonal planar molecular structure, but rather in a three-dimensional trigonal pyramid (Figure 11.1.6) with the nitrogen atom at the apex and the three hydrogen atoms forming the base. The ideal bond angles in a trigonal pyramid are based on the tetrahedral electron pair geometry. Again, there are slight deviations from the ideal because lone pairs occupy larger regions of space than do bonding electrons. The H–N–H bond angles in NH_3 are slightly smaller than the 109.5° angle in a regular tetrahedron (Figure 11.1.6) because the lone pair-bonding pair repulsion is greater than the bonding pair-bonding pair repulsion. The ideal molecular structures are predicted based on the electron-pair geometries for various combinations of lone pairs and bonding pairs.

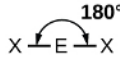
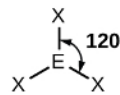
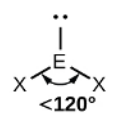
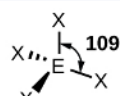
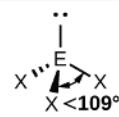
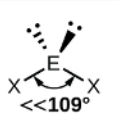
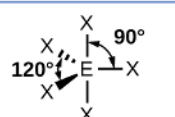
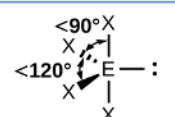
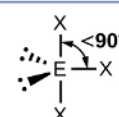
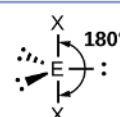
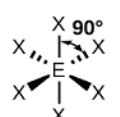
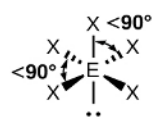
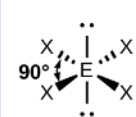
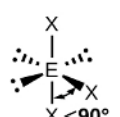
Number of electron pairs	Electron pair geometries: 0 lone pair	1 lone pair	2 lone pairs	3 lone pairs	4 lone pairs
2	 Linear				
3	 Trigonal planar	 Bent or angular			
4	 Tetrahedral	 Trigonal pyramid	 Bent or angular		
5	 Trigonal bipyramid	 Sawhorse or seesaw	 T-shape	 Linear	
6	 Octahedral	 Square pyramid	 Square planar	 T-shape	 Linear

Figure 11.1.6: The molecular structures are identical to the electron-pair geometries when there are no lone pairs present (first column). For a particular number of electron pairs (row), the molecular structures for one or more lone pairs are determined based on modifications of the corresponding electron-pair geometry.

A table is shown that is comprised of six rows and six columns. The header row reads: "Number of Electron Pairs," "Electron pair geometries; 0 lone pair," "1 lone pair," "2 lone pairs," "3 lone pairs," and "4 lone pairs." The first column contains the numbers 2, 3, 4, 5, and 6. The first space in the second column contains a structure in which the letter E is single bonded to the letter X on each side. The angle of the bonds is labeled with a curved, double headed arrow and the value, "180 degrees." The structure is labeled, "Linear." The second space in the second column contains a structure in which the letter E is single bonded to the letter X on three sides. The angle between the bonds is labeled with a curved, double headed arrow and the value, "120 degrees." The structure is labeled, "Trigonal planar." The third space in the second column contains a structure in which the letter E is single bonded to the letter X four times. The angle between the bonds is labeled with a curved, double headed arrow and the value, "109 degrees." The structure is labeled, "Tetrahedral." The fourth space in the second column contains a structure in which the letter E is single bonded to the letter X on five sides. The angle between the bonds is labeled with a curved, double headed arrow and the values "90 and 120 degrees." The structure is labeled, "Trigonal bipyramid." The fifth space in the second column contains a structure in which the letter E is single bonded to the letter X on six sides. The angle between the bonds is labeled with a curved, double headed arrow and the value, "90 degrees." The structure is labeled, "Octahedral." The first space in the third column is empty while the second contains a structure in which the letter E is single bonded to the letter X on each side and has a lone pair of electrons. The angle between the bonds is labeled with a curved, double headed arrow and the value, "less than 120 degrees." The structure is labeled, "Bent or angular." The third space in the third column contains a structure in which the letter E is single bonded to the letter X three times and to a lone pair of electrons. It is labeled with a curved, double headed arrow and the value, "less than 109 degrees." The structure is labeled, "Trigonal pyramid." The fourth space in the third column contains a structure in which the letter E is single bonded to the letter X on four sides and has a lone pair of electrons. The bond angle is labeled with a curved, double headed arrow and the values, "less than 90 and less than 120 degrees." The structure is labeled, "Sawhorse or seesaw." The fifth space in the third column contains a structure in which the letter E is single bonded to the letter X on five sides and has a lone pair of electrons. The bond angle is labeled with a curved, double headed arrow and the value, "less than 90 degrees." The structure is labeled, "Square pyramidal." The first and second spaces in the fourth column are empty while the third contains a structure in which the letter E is single bonded to the letter X on each side and has two lone pairs of electrons. The bond angle is labeled with a curved, double headed arrow and the value, "less than less than 109 degrees." The structure is labeled, "Bent or angular." The fourth space in the fourth column contains a structure in which the letter E is single bonded to the letter X three times and to two lone pairs of electrons. The bond angle is labeled with a curved, double headed arrow and the value, "less than 90 degrees." The structure is labeled, "T - shape." The fifth space in the fourth column contains a structure in which the letter E is single bonded to the letter X on four sides and has two lone pairs of electrons. The bond angle is labeled with a curved, double headed arrow and the value "90 degrees." The structure is labeled, "Square planar." The first, second and third spaces in the fifth column are empty while the fourth contains a structure in which the letter E is single bonded to the letter X on each side and has three lone pairs of electrons. The bond angle is labeled with a curved, double headed arrow and the value, "180 degrees." The structure is labeled, "Linear." The fifth space in the fifth column contains a structure in which the letter E is single bonded to the letter X three times and to three lone pairs of electrons. The bond angle is labeled with a curved, double headed arrow and the value, "less than 90 degrees." The structure is labeled, "T - shape." The first, second, third, and fourth spaces in the sixth column are empty while the fifth contains a structure in which the letter E is single bonded to the letter X on each side and has four lone pairs of electrons. The bond angle is labeled with a curved, double headed arrow and the value "180 degrees." The structure is labeled, "Linear." All the structures use wedges and dashes to give them three dimensional appearances.

According to VSEPR theory, the terminal atom locations (Xs in Figure 11.1.7) are equivalent within the linear, trigonal planar, and tetrahedral electron-pair geometries (the first three rows of the table). It does not matter which X is replaced with a lone pair because the molecules can be rotated to convert positions. For trigonal bipyramidal electron-pair geometries, however, there are two distinct X positions (Figure 11.1.7a): an axial position (if we hold a model of a trigonal bipyramid by the two axial positions, we have an axis around which we can rotate the model) and an equatorial position (three positions form an equator around the middle of the molecule). The axial position is surrounded by bond angles of 90° , whereas the equatorial position has more space available because of the 120° bond angles. In a trigonal bipyramidal electron-pair geometry, lone pairs always occupy equatorial positions because these more spacious positions can more easily accommodate the larger lone pairs.

Theoretically, we can come up with three possible arrangements for the three bonds and two lone pairs for the ClF_3 molecule (Figure 11.1.7). The stable structure is the one that puts the lone pairs in equatorial locations, giving a T-shaped molecular structure.

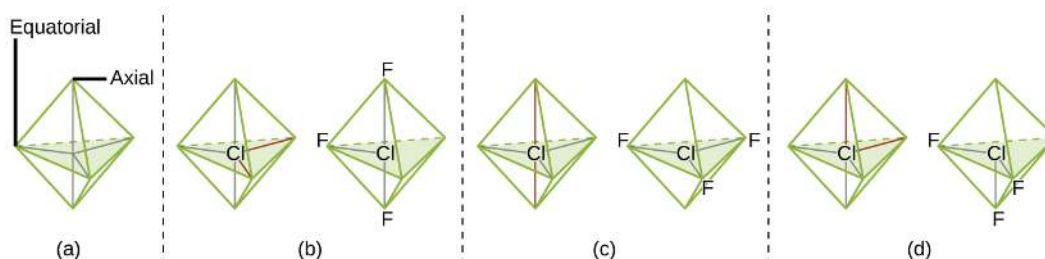


Figure 11.1.7: (a) In a trigonal bipyramid, the two axial positions are located directly across from one another, whereas the three equatorial positions are located in a triangular arrangement. (b–d) The two lone pairs (red lines) in ClF_3 have several possible arrangements, but the T-shaped molecular structure (b) is the one actually observed, consistent with the larger lone pairs both occupying equatorial positions.

Four sets of images are shown and labeled, “a,” “b,” “c,” and “d.” Each image is separated by a dashed vertical line. Image a shows a six-faced, bi-pyramidal structure where the central vertical axis is labeled, “Axial,” and the horizontal plane is labeled, “Equatorial.” Image b shows a pair of diagrams in the same shape as image a, but in these diagrams, the left has a chlorine atom in the center while the right has a chlorine atom in the center, two fluorine atoms on the upper and lower ends, and one fluorine in the left horizontal position. Image c shows a pair of diagrams in the same shape as image a, but in these diagrams, the left has a chlorine atom in the center while the right has a chlorine atom in the center and three fluorine atoms in each horizontal position. Image d shows a pair of diagrams in the same shape as image a, but in these diagrams, the left has a chlorine atom in the center while the right has a chlorine atom in the center, two fluorine atoms in the horizontal positions, and one in the axial bottom position.

When a central atom has two lone electron pairs and four bonding regions, we have an octahedral electron-pair geometry. The two lone pairs are on opposite sides of the octahedron (180° apart), giving a square planar molecular structure that minimizes lone pair-lone pair repulsions.

✚ Predicting Electron Pair Geometry and Molecular Structure

The following procedure uses VSEPR theory to determine the electron pair geometries and the molecular structures:

1. Write the Lewis structure of the molecule or polyatomic ion.
2. Count the number of regions of electron density (lone pairs and bonds) around the central atom. A single, double, or triple bond counts as one region of electron density.
3. Identify the electron-pair geometry based on the number of regions of electron density: linear, trigonal planar, tetrahedral, trigonal bipyramidal, or octahedral (Figure 11.1.7, first column).
4. Use the number of lone pairs to determine the molecular structure (Figure 11.1.7). If more than one arrangement of lone pairs and chemical bonds is possible, choose the one that will minimize repulsions, remembering that lone pairs occupy more space than multiple bonds, which occupy more space than single bonds. In trigonal bipyramidal arrangements, repulsion is minimized when every lone pair is in an equatorial position. In an octahedral arrangement with two lone pairs, repulsion is minimized when the lone pairs are on opposite sides of the central atom.

The following examples illustrate the use of VSEPR theory to predict the molecular structure of molecules or ions that have no lone pairs of electrons. In this case, the molecular structure is identical to the electron pair geometry.

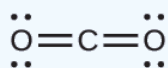
✓ Example 11.1.1: Predicting Electron-pair Geometry and Molecular Structure

Predict the electron-pair geometry and molecular structure for each of the following:

- a. carbon dioxide, CO_2 , a molecule produced by the combustion of fossil fuels
- b. boron trichloride, BCl_3 , an important industrial chemical

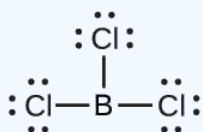
Solution

(a) We write the Lewis structure of CO_2 as:

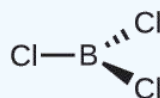


This shows us two regions of high electron density around the carbon atom—each double bond counts as one region, and there are no lone pairs on the carbon atom. Using VSEPR theory, we predict that the two regions of electron density arrange themselves on opposite sides of the central atom with a bond angle of 180° . The electron-pair geometry and molecular structure are identical, and CO_2 molecules are linear.

(b) We write the Lewis structure of BCl_3 as:



Thus we see that BCl_3 contains three bonds, and there are no lone pairs of electrons on boron. The arrangement of three regions of high electron density gives a trigonal planar electron-pair geometry. The B–Cl bonds lie in a plane with 120° angles between them. BCl_3 also has a trigonal planar molecular structure.



The electron-pair geometry and molecular structure of BCl_3 are both trigonal planar. Note that the VSEPR geometry indicates the correct bond angles (120°), unlike the Lewis structure shown above.

? Exercise 11.1.1

Carbonate, CO_3^{2-} , is a common polyatomic ion found in various materials from eggshells to antacids. What are the electron-pair geometry and molecular structure of this polyatomic ion?

Answer

The electron-pair geometry is trigonal planar and the molecular structure is trigonal planar. Due to resonance, all three C–O bonds are identical. Whether they are single, double, or an average of the two, each bond counts as one region of electron density.

✓ Example 11.1.2: Predicting Electron-pair Geometry and Molecular Structure

Two of the top 50 chemicals produced in the United States, ammonium nitrate and ammonium sulfate, both used as fertilizers, contain the ammonium ion. Predict the electron-pair geometry and molecular structure of the NH_4^+ cation.

Solution

We write the Lewis structure of NH_4^+ as:

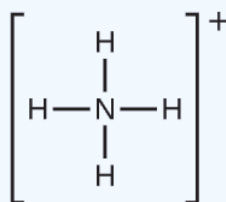


Figure 11.1.7).

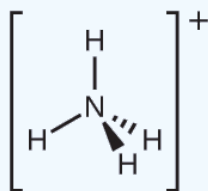


Figure 11.1.8: The ammonium ion displays a tetrahedral electron-pair geometry as well as a tetrahedral molecular structure.

? Exercise 11.1.2

Identify a molecule with trigonal bipyramidal molecular structure.

Answer

Any molecule with five electron pairs around the central atoms including no lone pairs will be trigonal bipyramidal. PF_5 is a common example

The next several examples illustrate the effect of lone pairs of electrons on molecular structure.

✓ Example 11.1.3: Lone Pairs on the Central Atom

Predict the electron-pair geometry and molecular structure of a water molecule.

Solution

The Lewis structure of H_2O indicates that there are four regions of high electron density around the oxygen atom: two lone pairs and two chemical bonds:

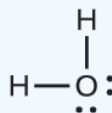


Figure 11.1.9. Thus, the electron-pair geometry is tetrahedral and the molecular structure is bent with an angle slightly less than 109.5° . In fact, the bond angle is 104.5° .

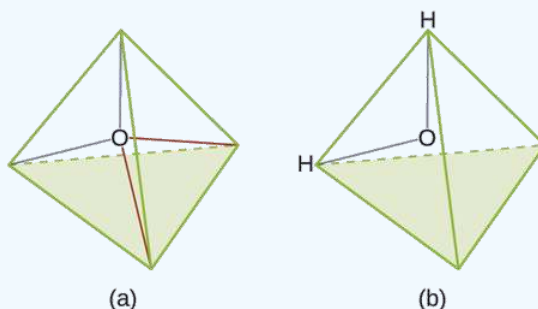


Figure 11.1.9: (a) H_2O has four regions of electron density around the central atom, so it has a tetrahedral electron-pair geometry. (b) Two of the electron regions are lone pairs, so the molecular structure is bent.

? Exercise 11.1.3

The hydronium ion, H_3O^+ , forms when acids are dissolved in water. Predict the electron-pair geometry and molecular structure of this cation.

Answer

electron pair geometry: tetrahedral; molecular structure: trigonal pyramidal

✓ Example 11.1.4: SF₄ Sulfur tetrafluoride,

Predicting Electron-pair Geometry and Molecular Structure: SF₄, is extremely valuable for the preparation of fluorine-containing compounds used as herbicides (i.e., SF₄ is used as a fluorinating agent). Predict the electron-pair geometry and molecular structure of a SF₄ molecule.

Solution

The Lewis structure of SF₄ indicates five regions of electron density around the sulfur atom: one lone pair and four bonding pairs:

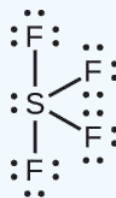


Figure 11.1.10).

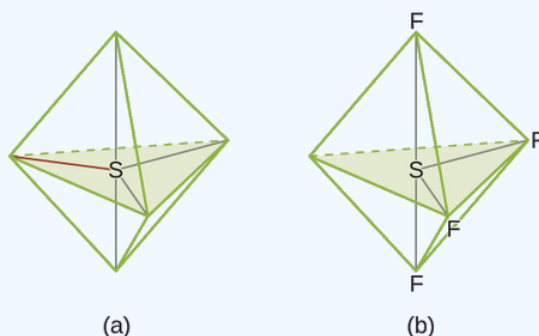


Figure 11.1.10: (a) SF₄ has a trigonal bipyramidal arrangement of the five regions of electron density. (b) One of the regions is a lone pair, which results in a seesaw-shaped molecular structure.

? Exercise 11.1.4

Predict the electron pair geometry and molecular structure for molecules of XeF₂.

Answer

The electron-pair geometry is trigonal bipyramidal. The molecular structure is linear.

✓ Example 11.1.4: XeF₄

Of all the noble gases, xenon is the most reactive, frequently reacting with elements such as oxygen and fluorine. Predict the electron-pair geometry and molecular structure of the XeF₄ molecule.

Solution

The Lewis structure of XeF₄ indicates six regions of high electron density around the xenon atom: two lone pairs and four bonds:

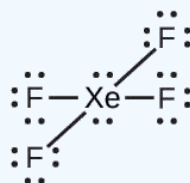


Figure 11.1.11: The five atoms are all in the same plane and have a square planar molecular structure.

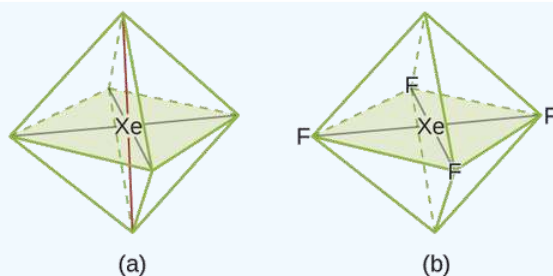


Figure 11.1.11: (a) XeF₄ adopts an octahedral arrangement with two lone pairs (red lines) and four bonds in the electron-pair geometry. (b) The molecular structure is square planar with the lone pairs directly across from one another.

? Exercise 11.1.4

In a certain molecule, the central atom has three lone pairs and two bonds. What will the electron pair geometry and molecular structure be?

Answer

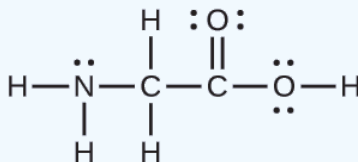
electron pair geometry: trigonal bipyramidal; molecular structure: linear

Molecular Structure for Multicenter Molecules

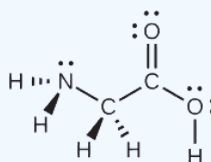
When a molecule or polyatomic ion has only one central atom, the molecular structure completely describes the shape of the molecule. Larger molecules do not have a single central atom, but are connected by a chain of interior atoms that each possess a “local” geometry. The way these local structures are oriented with respect to each other also influences the molecular shape, but such considerations are largely beyond the scope of this introductory discussion. For our purposes, we will only focus on determining the local structures.

✓ Example 11.1.5: Predicting Structure in Multicenter Molecules

The Lewis structure for the simplest amino acid, glycine, H₂NCH₂CO₂H, is shown here. Predict the local geometry for the nitrogen atom, the two carbon atoms, and the oxygen atom with a hydrogen atom attached:



Solution



Consider each central atom independently. The electron-pair geometries:

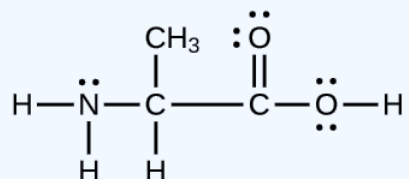
- nitrogen—four regions of electron density; tetrahedral
- carbon (CH₂)—four regions of electron density; tetrahedral
- carbon (CO₂)—three regions of electron density; trigonal planar
- oxygen (OH)—four regions of electron density; tetrahedral

The local structures:

- nitrogen—three bonds, one lone pair; trigonal pyramidal
- carbon (CH_2)—four bonds, no lone pairs; tetrahedral
- carbon (CO_2)—three bonds (double bond counts as one bond), no lone pairs; trigonal planar
- oxygen (OH)—two bonds, two lone pairs; bent (109°)

? Exercise 11.1.5

Another amino acid is alanine, which has the Lewis structure shown here. Predict the electron-pair geometry and local structure of the nitrogen atom, the three carbon atoms, and the oxygen atom with hydrogen attached:



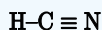
Answer

electron-pair geometries: nitrogen—tetrahedral; carbon (CH)—tetrahedral; carbon (CH_3)—tetrahedral; carbon (CO_2)—trigonal planar; oxygen (OH)—tetrahedral; local structures: nitrogen—trigonal pyramidal; carbon (CH)—tetrahedral; carbon (CH_3)—tetrahedral; carbon (CO_2)—trigonal planar; oxygen (OH)—bent (109°)

✓ Example 11.1.6: Molecular Simulation

Using this molecular shape simulator allows us to control whether bond angles and/or lone pairs are displayed by checking or unchecking the boxes under “Options” on the right. We can also use the “Name” checkboxes at bottom-left to display or hide the electron pair geometry (called “electron geometry” in the simulator) and/or molecular structure (called “molecular shape” in the simulator).

Build the molecule HCN in the simulator based on the following Lewis structure:



Click on each bond type or lone pair at right to add that group to the central atom. Once you have the complete molecule, rotate it to examine the predicted molecular structure. What molecular structure is this?

Solution

The molecular structure is linear.

? Exercise 11.1.6

Build a more complex molecule in the simulator. Identify the electron-group geometry, molecular structure, and bond angles. Then try to find a chemical formula that would match the structure you have drawn.

Answer

Answers will vary. For example, an atom with four single bonds, a double bond, and a lone pair has an octahedral electron-group geometry and a square pyramidal molecular structure. XeOF_4 is a molecule that adopts this structure.

Molecular Polarity and Dipole Moment

As discussed previously, polar covalent bonds connect two atoms with differing electronegativities, leaving one atom with a partial positive charge (δ^+) and the other atom with a partial negative charge (δ^-), as the electrons are pulled toward the more electronegative atom. This separation of charge gives rise to a bond dipole moment. The magnitude of a bond dipole moment is represented by the Greek letter mu (μ) and is given by

$$\mu = Qr \quad (11.1.1)$$

where

- Q is the magnitude of the partial charges (determined by the electronegativity difference) and
- r is the distance between the charges:

This bond moment can be represented as a vector, a quantity having both direction and magnitude (Figure 11.1.12). Dipole vectors are shown as arrows pointing along the bond from the less electronegative atom toward the more electronegative atom. A small plus sign is drawn on the less electronegative end to indicate the partially positive end of the bond. The length of the arrow is proportional to the magnitude of the electronegativity difference between the two atoms.

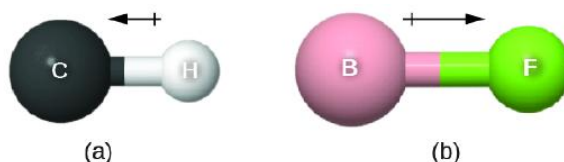


Figure 11.1.12: (a) There is a small difference in electronegativity between C and H, represented as a short vector. (b) The electronegativity difference between B and F is much larger, so the vector representing the bond moment is much longer.

A whole molecule may also have a separation of charge, depending on its molecular structure and the polarity of each of its bonds. If such a charge separation exists, the molecule is said to be a polar molecule (or dipole); otherwise the molecule is said to be nonpolar. The dipole moment measures the extent of net charge separation in the molecule as a whole. We determine the dipole moment by adding the bond moments in three-dimensional space, taking into account the molecular structure.

For diatomic molecules, there is only one bond, so its bond dipole moment determines the molecular polarity. Homonuclear diatomic molecules such as Br_2 and N_2 have no difference in electronegativity, so their dipole moment is zero. For heteronuclear molecules such as CO , there is a small dipole moment. For HF , there is a larger dipole moment because there is a larger difference in electronegativity.

When a molecule contains more than one bond, the geometry must be taken into account. If the bonds in a molecule are arranged such that their bond moments cancel (vector sum equals zero), then the molecule is nonpolar. This is the situation in CO_2 (Figure 11.1.13A). Each of the bonds is polar, but the molecule as a whole is nonpolar. From the Lewis structure, and using VSEPR theory, we determine that the CO_2 molecule is linear with polar $\text{C}=\text{O}$ bonds on opposite sides of the carbon atom. The bond moments cancel because they are pointed in opposite directions. In the case of the water molecule (Figure 11.1.13B), the Lewis structure again shows that there are two bonds to a central atom, and the electronegativity difference again shows that each of these bonds has a nonzero bond moment. In this case, however, the molecular structure is bent because of the lone pairs on O, and the two bond moments do not cancel. Therefore, water does have a net dipole moment and is a polar molecule (dipole).

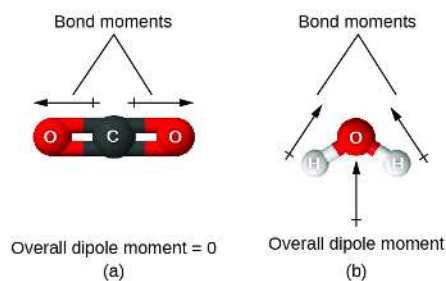
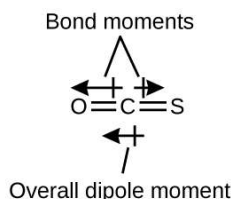


Figure 11.1.13: The overall dipole moment of a molecule depends on the individual bond dipole moments and how they are arranged. (a) Each CO bond has a bond dipole moment, but they point in opposite directions so that the net CO_2 molecule is nonpolar. (b) In contrast, water is polar because the OH bond moments do not cancel out.

The OCS molecule has a structure similar to CO_2 , but a sulfur atom has replaced one of the oxygen atoms. To determine if this molecule is polar, we draw the molecular structure. VSEPR theory predicts a linear molecule:

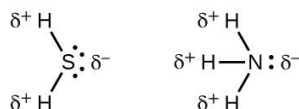


The C–O bond is considerably polar. Although C and S have very similar electronegativity values, S is slightly more electronegative than C, and so the C–S bond is just slightly polar. Because oxygen is more electronegative than sulfur, the oxygen end of the molecule is the negative end.

Chloromethane, CH_3Cl , is another example of a polar molecule. Although the polar C–Cl and C–H bonds are arranged in a tetrahedral geometry, the C–Cl bonds have a larger bond moment than the C–H bond, and the bond moments do not completely cancel each other. All of the dipoles have a upward component in the orientation shown, since carbon is more electronegative than hydrogen and less electronegative than chlorine:



When we examine the highly symmetrical molecules BF_3 (trigonal planar), CH_4 (tetrahedral), PF_5 (trigonal bipyramidal), and SF_6 (octahedral), in which all the polar bonds are identical, the molecules are nonpolar. The bonds in these molecules are arranged such that their dipoles cancel. However, just because a molecule contains identical bonds does not mean that the dipoles will always cancel. Many molecules that have identical bonds and lone pairs on the central atoms have bond dipoles that do not cancel. Examples include H_2S and NH_3 . A hydrogen atom is at the positive end and a nitrogen or sulfur atom is at the negative end of the polar bonds in these molecules:



To summarize, to be polar, a molecule must:

1. Contain at least one polar covalent bond.
2. Have a molecular structure such that the sum of the vectors of each bond dipole moment does not cancel.

Properties of Polar Molecules

Polar molecules tend to align when placed in an electric field with the positive end of the molecule oriented toward the negative plate and the negative end toward the positive plate (Figure 11.1.14). We can use an electrically charged object to attract polar molecules, but nonpolar molecules are not attracted. Also, polar solvents are better at dissolving polar substances, and nonpolar solvents are better at dissolving nonpolar substances.

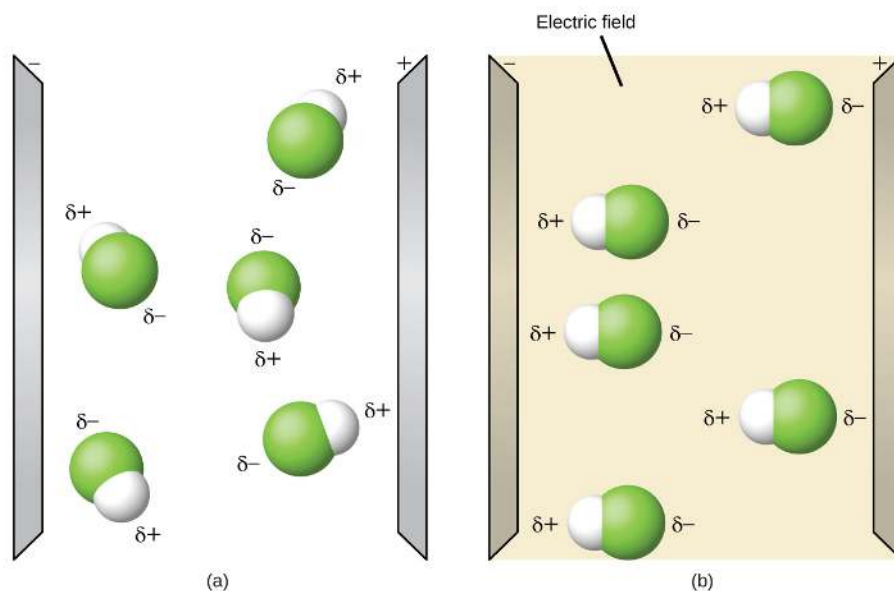


Figure 11.1.14: (a) Molecules are always randomly distributed in the liquid state in the absence of an electric field. (b) When an electric field is applied, polar molecules like HF will align to the dipoles with the field direction.

✓ Example 11.1.7: Polarity Simulations

Open the [molecule polarity simulation](#) and select the “Three Atoms” tab at the top. This should display a molecule ABC with three electronegativity adjusters. You can display or hide the bond moments, molecular dipoles, and partial charges at the right. Turning on the Electric Field will show whether the molecule moves when exposed to a field, similar to Figure 11.1.14.

Use the electronegativity controls to determine how the molecular dipole will look for the starting bent molecule if:

- A and C are very electronegative and B is in the middle of the range.
- A is very electronegative, and B and C are not.

Solution

- Molecular dipole moment points immediately between A and C.
- Molecular dipole moment points along the A–B bond, toward A.

? Exercise 11.1.7

Determine the partial charges that will give the largest possible bond dipoles.

Answer

The largest bond moments will occur with the largest partial charges. The two solutions above represent how unevenly the electrons are shared in the bond. The bond moments will be maximized when the electronegativity difference is greatest. The controls for A and C should be set to one extreme, and B should be set to the opposite extreme. Although the magnitude of the bond moment will not change based on whether B is the most electronegative or the least, the direction of the bond moment will.

Summary

VSEPR theory predicts the three-dimensional arrangement of atoms in a molecule. It states that valence electrons will assume an electron-pair geometry that minimizes repulsions between areas of high electron density (bonds and/or lone pairs). Molecular structure, which refers only to the placement of atoms in a molecule and not the electrons, is equivalent to electron-pair geometry only when there are no lone electron pairs around the central atom. A dipole moment measures a separation of charge. For one

bond, the bond dipole moment is determined by the difference in electronegativity between the two atoms. For a molecule, the overall dipole moment is determined by both the individual bond moments and how these dipoles are arranged in the molecular structure. Polar molecules (those with an appreciable dipole moment) interact with electric fields, whereas nonpolar molecules do not.

Glossary

axial position

location in a trigonal bipyramidal geometry in which there is another atom at a 180° angle and the equatorial positions are at a 90° angle

bond angle

angle between any two covalent bonds that share a common atom

bond distance

(also, bond length) distance between the nuclei of two bonded atoms

bond dipole moment

separation of charge in a bond that depends on the difference in electronegativity and the bond distance represented by partial charges or a vector

dipole moment

property of a molecule that describes the separation of charge determined by the sum of the individual bond moments based on the molecular structure

electron-pair geometry

arrangement around a central atom of all regions of electron density (bonds, lone pairs, or unpaired electrons)

equatorial position

one of the three positions in a trigonal bipyramidal geometry with 120° angles between them; the axial positions are located at a 90° angle

linear

shape in which two outside groups are placed on opposite sides of a central atom

molecular structure

structure that includes only the placement of the atoms in the molecule

octahedral

shape in which six outside groups are placed around a central atom such that a three-dimensional shape is generated with four groups forming a square and the other two forming the apex of two pyramids, one above and one below the square plane

polar molecule

(also, dipole) molecule with an overall dipole moment

tetrahedral

shape in which four outside groups are placed around a central atom such that a three-dimensional shape is generated with four corners and 109.5° angles between each pair and the central atom

trigonal bipyramidal

shape in which five outside groups are placed around a central atom such that three form a flat triangle with 120° angles between each pair and the central atom, and the other two form the apex of two pyramids, one above and one below the triangular plane

trigonal planar

shape in which three outside groups are placed in a flat triangle around a central atom with 120° angles between each pair and the central atom

valence shell electron-pair repulsion theory (VSEPR)

theory used to predict the bond angles in a molecule based on positioning regions of high electron density as far apart as possible to minimize electrostatic repulsion

vector

quantity having magnitude and direction

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11.2: Intermolecular Forces

Learning Objectives

- Describe the types of intermolecular forces possible between atoms or molecules in condensed phases (dispersion forces, dipole-dipole attractions, and hydrogen bonding)
- Identify the types of intermolecular forces experienced by specific molecules based on their structures
- Explain the relation between the intermolecular forces present within a substance and the temperatures associated with changes in its physical state

As was the case for gaseous substances, the kinetic molecular theory may be used to explain the behavior of solids and liquids. In the following description, the term *particle* will be used to refer to an atom, molecule, or ion. Note that we will use the popular phrase “intermolecular attraction” to refer to attractive forces between the particles of a substance, regardless of whether these particles are molecules, atoms, or ions.

Consider these two aspects of the molecular-level environments in solid, liquid, and gaseous matter:

- Particles in a solid are tightly packed together and often arranged in a regular pattern; in a liquid, they are close together with no regular arrangement; in a gas, they are far apart with no regular arrangement.
- Particles in a solid vibrate about fixed positions and do not generally move in relation to one another; in a liquid, they move past each other but remain in essentially constant contact; in a gas, they move independently of one another except when they collide.

The differences in the properties of a solid, liquid, or gas reflect the strengths of the attractive forces between the atoms, molecules, or ions that make up each phase. The phase in which a substance exists depends on the relative extents of its intermolecular forces (IMFs) and the kinetic energies (KE) of its molecules. IMFs are the various forces of attraction that may exist between the atoms and molecules of a substance due to electrostatic phenomena, as will be detailed in this module. These forces serve to hold particles close together, whereas the particles’ KE provides the energy required to overcome the attractive forces and thus increase the distance between particles. Figure 11.2.1 illustrates how changes in physical state may be induced by changing the temperature, hence, the average KE, of a given substance.

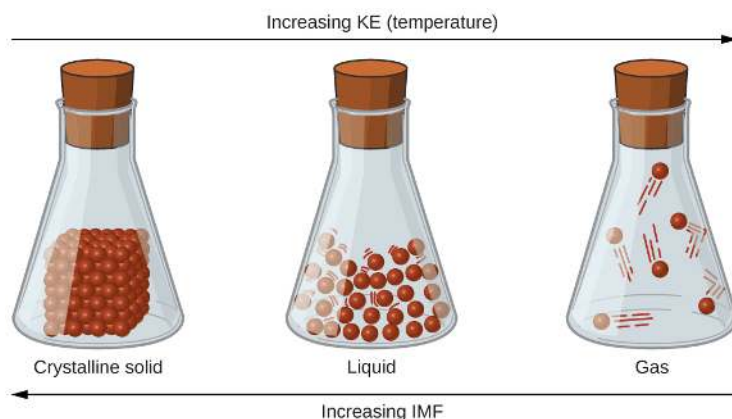


Figure 11.2.1: Transitions between solid, liquid, and gaseous states of a substance occur when conditions of temperature or pressure favor the associated changes in intermolecular forces. (Note: The space between particles in the gas phase is much greater than shown.)

Three sealed flasks are labeled, “Crystalline solid,” “Liquid,” and “Gas,” from left to right. The first flask holds a cube composed of small spheres sitting on the bottom while the second flask shows a lot of small spheres in the bottom that are spaced a small distance apart from one another and have lines around them to indicate motion. The third flask shows a few spheres spread far from one another with larger lines to indicate motion. There is a right-facing arrow that spans the top of all three flasks. The arrow is labeled, “Increasing K E (temperature).” There is a left-facing arrow that spans the bottom of all three flasks. The arrow is labeled, “Increasing I M F.”

As an example of the processes depicted in this figure, consider a sample of water. When gaseous water is cooled sufficiently, the attractions between H_2O molecules will be capable of holding them together when they come into contact with each other; the gas

condenses, forming liquid H_2O . For example, liquid water forms on the outside of a cold glass as the water vapor in the air is cooled by the cold glass, as seen in Figure 11.2.2.



Figure 11.2.2: Condensation forms when water vapor in the air is cooled enough to form liquid water, such as (a) on the outside of a cold beverage glass or (b) in the form of fog. (credit a: modification of work by Jenny Downing; credit b: modification of work by Cory Zanker)

Image a shows a brown colored beverage in a glass with condensation on the outside. Image b shows a body of water with fog hovering above the surface of the water.

We can also liquefy many gases by compressing them, if the temperature is not too high. The increased pressure brings the molecules of a gas closer together, such that the attractions between the molecules become strong relative to their KE. Consequently, they form liquids. Butane, C_4H_{10} , is the fuel used in disposable lighters and is a gas at standard temperature and pressure. Inside the lighter's fuel compartment, the butane is compressed to a pressure that results in its condensation to the liquid state, as shown in Figure 11.2.3.



Figure 11.2.3: Gaseous butane is compressed within the storage compartment of a disposable lighter, resulting in its condensation to the liquid state. (credit: modification of work by "Sam-Cat"/Flickr)

Finally, if the temperature of a liquid becomes sufficiently low, or the pressure on the liquid becomes sufficiently high, the molecules of the liquid no longer have enough KE to overcome the IMF between them, and a solid forms. A more thorough discussion of these and other changes of state, or phase transitions, is provided in a later module of this chapter.

Forces between Molecules

Under appropriate conditions, the attractions between all gas molecules will cause them to form liquids or solids. This is due to intermolecular forces, not *intramolecular* forces. *Intramolecular* forces are those *within* the molecule that keep the molecule

together, for example, the bonds between the atoms. *Intermolecular forces* are the attractions *between* molecules, which determine many of the physical properties of a substance. Figure 11.2.4 illustrates these different molecular forces. The strengths of these attractive forces vary widely, though usually the IMFs between small molecules are weak compared to the intramolecular forces that bond atoms together within a molecule. For example, to overcome the IMFs in one mole of liquid HCl and convert it into gaseous HCl requires only about 17 kilojoules. However, to break the covalent bonds between the hydrogen and chlorine atoms in one mole of HCl requires about 25 times more energy—430 kilojoules.

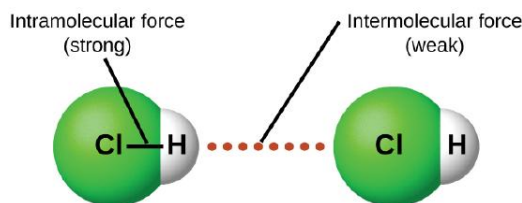


Figure 11.2.4: Intramolecular forces keep a molecule intact. Intermolecular forces hold multiple molecules together and determine many of a substance's properties.

An image is shown in which two molecules composed of a green sphere labeled "Cl" connected on the right to a white sphere labeled "H" are near one another with a dotted line labeled "Intermolecular force (weak)" drawn between them. A line connects the two spheres in each molecule and the line is labeled "Intramolecular force (strong)."

All of the attractive forces between neutral atoms and molecules are known as van der Waals forces, although they are usually referred to more informally as intermolecular attraction. We will consider the various types of IMFs in the next three sections of this module.

Dispersion Forces

One of the three van der Waals forces is present in all condensed phases, regardless of the nature of the atoms or molecules composing the substance. This attractive force is called the London dispersion force in honor of German-born American physicist Fritz London who, in 1928, first explained it. This force is often referred to as simply the dispersion force. Because the electrons of an atom or molecule are in constant motion (or, alternatively, the electron's location is subject to quantum-mechanical variability), at any moment in time, an atom or molecule can develop a temporary, instantaneous dipole if its electrons are distributed asymmetrically. The presence of this dipole can, in turn, distort the electrons of a neighboring atom or molecule, producing an induced dipole. These two rapidly fluctuating, temporary dipoles thus result in a relatively weak electrostatic attraction between the species—a so-called dispersion force like that illustrated in Figure 11.2.5.

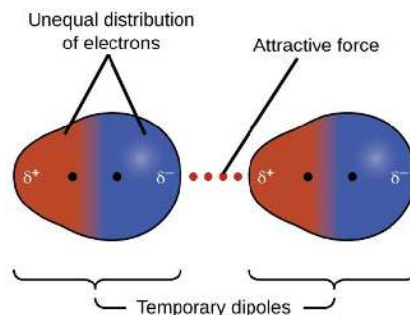


Figure 11.2.5: Dispersion forces result from the formation of temporary dipoles, as illustrated here for two nonpolar diatomic molecules.

Two pairs of molecules are shown where each molecule has one larger blue side labeled "delta sign, negative sign" and a smaller red side labeled "delta sign, positive sign." Toward the middle of the both molecules, but still on each distinct side, is a black dot. Between the two images is a dotted line labeled, "Attractive force." In the first image, the red and blue sides are labeled, "Unequal distribution of electrons." Below both images are brackets. The brackets are labeled, "Temporary dipoles."

Dispersion forces that develop between atoms in different molecules can attract the two molecules to each other. The forces are relatively weak, however, and become significant only when the molecules are very close. Larger and heavier atoms and molecules exhibit stronger dispersion forces than do smaller and lighter atoms and molecules. F_2 and Cl_2 are gases at room temperature

(reflecting weaker attractive forces); Br_2 is a liquid, and I_2 is a solid (reflecting stronger attractive forces). Trends in observed melting and boiling points for the halogens clearly demonstrate this effect, as seen in Table 11.2.1.

Table 11.2.1: Melting and Boiling Points of the Halogens

Halogen	Molar Mass	Atomic Radius	Melting Point	Boiling Point
fluorine, F_2	38 g/mol	72 pm	53 K	85 K
chlorine, Cl_2	71 g/mol	99 pm	172 K	238 K
bromine, Br_2	160 g/mol	114 pm	266 K	332 K
iodine, I_2	254 g/mol	133 pm	387 K	457 K
astatine, At_2	420 g/mol	150 pm	575 K	610 K

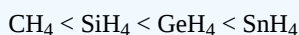
The increase in melting and boiling points with increasing atomic/molecular size may be rationalized by considering how the strength of dispersion forces is affected by the electronic structure of the atoms or molecules in the substance. In a larger atom, the valence electrons are, on average, farther from the nuclei than in a smaller atom. Thus, they are less tightly held and can more easily form the temporary dipoles that produce the attraction. The measure of how easy or difficult it is for another electrostatic charge (for example, a nearby ion or polar molecule) to distort a molecule's charge distribution (its electron cloud) is known as polarizability. A molecule that has a charge cloud that is easily distorted is said to be very polarizable and will have large dispersion forces; one with a charge cloud that is difficult to distort is not very polarizable and will have small dispersion forces.

✓ Example 11.2.1: London Forces and Their Effects

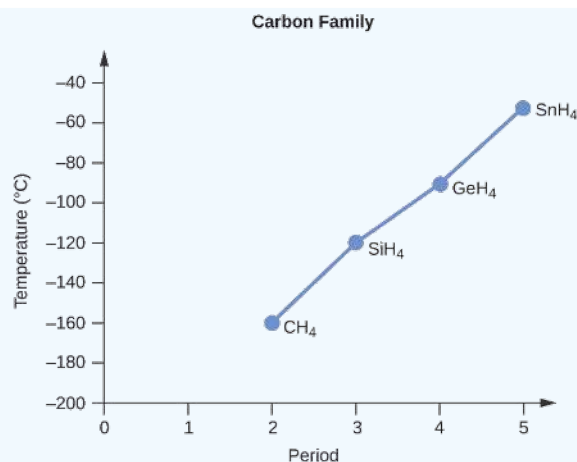
Order the following compounds of a group 14 element and hydrogen from lowest to highest boiling point: CH_4 , SiH_4 , GeH_4 , and SnH_4 . Explain your reasoning.

Solution

Applying the skills acquired in the chapter on chemical bonding and molecular geometry, all of these compounds are predicted to be nonpolar, so they may experience only dispersion forces: the smaller the molecule, the less polarizable and the weaker the dispersion forces; the larger the molecule, the larger the dispersion forces. The molar masses of CH_4 , SiH_4 , GeH_4 , and SnH_4 are approximately 16 g/mol, 32 g/mol, 77 g/mol, and 123 g/mol, respectively. Therefore, CH_4 is expected to have the lowest boiling point and SnH_4 the highest boiling point. The ordering from lowest to highest boiling point is expected to be



A graph of the actual boiling points of these compounds versus the period of the group 14 elements shows this prediction to be correct:



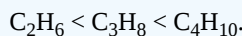
A line graph, titled “Carbon Family,” is shown where the y-axis is labeled “Temperature, (degree sign C)” and has values of “negative 200” to “negative 40” from bottom to top in increments of 20. The x-axis is labeled “Period” and has values of “0” to “5” in increments of 1. The first point on the graph is labeled “C H subscript 4” and is at point “2, negative 160.” The second point on the graph is labeled “S i H subscript 4” and is at point “3, negative 120” while the third point on the graph is labeled “G e H subscript 4” and is at point “4, negative 100.” The fourth point on the graph is labeled “S n H subscript 4” and is at point “5, negative 60.”

? Exercise 11.2.1

Order the following hydrocarbons from lowest to highest boiling point: C₂H₆, C₃H₈, and C₄H₁₀.

Answer

All of these compounds are nonpolar and only have London dispersion forces: the larger the molecule, the larger the dispersion forces and the higher the boiling point. The ordering from lowest to highest boiling point is therefore



The shapes of molecules also affect the magnitudes of the dispersion forces between them. For example, boiling points for the isomers *n*-pentane, isopentane, and neopentane (shown in Figure 11.2.6) are 36 °C, 27 °C, and 9.5 °C, respectively. Even though these compounds are composed of molecules with the same chemical formula, C₅H₁₂, the difference in boiling points suggests that dispersion forces in the liquid phase are different, being greatest for *n*-pentane and least for neopentane. The elongated shape of *n*-pentane provides a greater surface area available for contact between molecules, resulting in correspondingly stronger dispersion forces. The more compact shape of isopentane offers a smaller surface area available for intermolecular contact and, therefore, weaker dispersion forces. Neopentane molecules are the most compact of the three, offering the least available surface area for intermolecular contact and, hence, the weakest dispersion forces. This behavior is analogous to the connections that may be formed between strips of VELCRO brand fasteners: the greater the area of the strip’s contact, the stronger the connection.

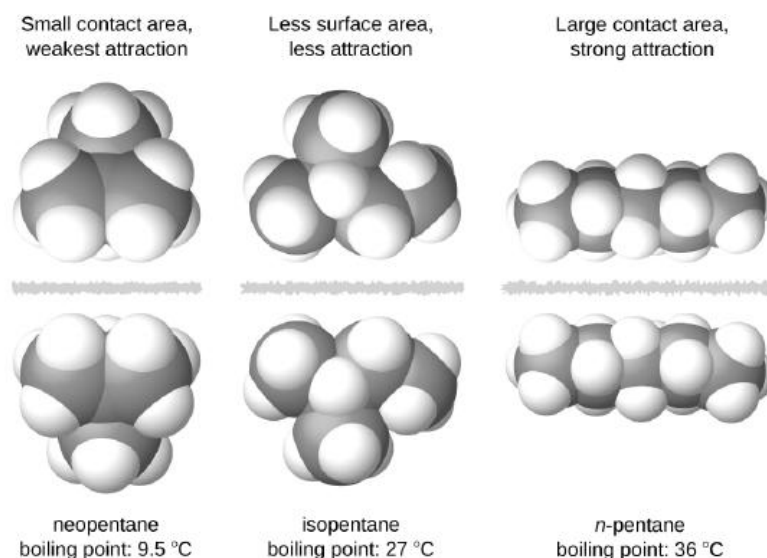


Figure 11.2.6: The strength of the dispersion forces increases with the contact area between molecules, as demonstrated by the boiling points of these pentane isomers.

Three images of molecules are shown. The first shows a cluster of large, gray spheres each bonded together and to several smaller, white spheres. There is a gray, jagged line and then the mirror image of the first cluster of spheres is shown. Above these two clusters is the label, “Small contact area, weakest attraction,” and below is the label, “neopentane boiling point: 9.5 degrees C.” The second shows a chain of three gray spheres bonded by the middle sphere to a fourth gray sphere. Each gray sphere is bonded to several smaller, white spheres. There is a jagged, gray line and then the mirror image of the first chain appears. Above these two chains is the label, “Less surface area, less attraction,” and below is the label, “isopentane boiling point: 27 degrees C.” The third image shows a chain of five gray spheres bonded together and to several smaller, white spheres. There is a jagged gray line and then the mirror image of the first chain appears. Above these chains is the label, “Large contact area, strong attraction,” and below is the label, “n-pentane boiling point 36 degrees C.”

Applications: Geckos and Intermolecular Forces

Geckos have an amazing ability to adhere to most surfaces. They can quickly run up smooth walls and across ceilings that have no toe-holds, and they do this without having suction cups or a sticky substance on their toes. And while a gecko can lift its feet easily as it walks along a surface, if you attempt to pick it up, it sticks to the surface. How are geckos (as well as spiders and some other insects) able to do this? Although this phenomenon has been investigated for hundreds of years, scientists only recently uncovered the details of the process that allows geckos’ feet to behave this way.

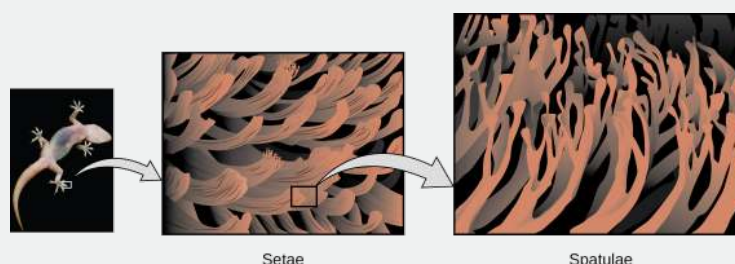


Figure 11.2.7: Geckos’ toes contain large numbers of tiny hairs (setae), which branch into many triangular tips (spatulae). Geckos adhere to surfaces because of van der Waals attractions between the surface and a gecko’s millions of spatulae. By changing how the spatulae contact the surface, geckos can turn their stickiness “on” and “off.” (credit photo: modification of work by “JC*+A!”/Flickr)

Three figures are shown. The first is a photo of the bottom of a gecko’s foot. The second is bigger version which shows the setae. The third is a bigger version of the setae and shows the spatulae.

Geckos’ toes are covered with hundreds of thousands of tiny hairs known as *setae*, with each seta, in turn, branching into hundreds of tiny, flat, triangular tips called *spatulae*. The huge numbers of spatulae on its setae provide a gecko, shown in Figure 11.2.7, with a large total surface area for sticking to a surface. In 2000, Kellar Autumn, who leads a multi-institutional gecko research team, found that geckos adhered equally well to both polar silicon dioxide and nonpolar gallium arsenide. This proved that geckos stick to surfaces because of dispersion forces—weak intermolecular attractions arising from temporary,

synchronized charge distributions between adjacent molecules. Although dispersion forces are very weak, the total attraction over millions of spatulae is large enough to support many times the gecko's weight.

In 2014, two scientists developed a model to explain how geckos can rapidly transition from “sticky” to “non-sticky.” Alex Greaney and Congcong Hu at Oregon State University described how geckos can achieve this by changing the angle between their spatulae and the surface. Geckos’ feet, which are normally nonsticky, become sticky when a small shear force is applied. By curling and uncurling their toes, geckos can alternate between sticking and unsticking from a surface, and thus easily move across it. Further investigations may eventually lead to the development of better adhesives and other applications.



Watch this video to learn more about Kellar Autumn's research that determined that van der Waals forces are responsible for a gecko's ability to cling and climb.

Dipole-Dipole Attractions

Recall from the chapter on chemical bonding and molecular geometry that *polar* molecules have a partial positive charge on one side and a partial negative charge on the other side of the molecule—a separation of charge called a *dipole*. Consider a polar molecule such as hydrogen chloride, HCl. In the HCl molecule, the more electronegative Cl atom bears the partial negative charge, whereas the less electronegative H atom bears the partial positive charge. An attractive force between HCl molecules results from the attraction between the positive end of one HCl molecule and the negative end of another. This attractive force is called a dipole-dipole attraction—the electrostatic force between the partially positive end of one polar molecule and the partially negative end of another, as illustrated in Figure 11.2.8.

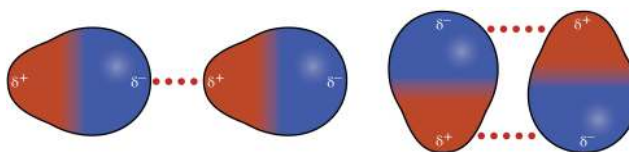


Figure 11.2.8: This image shows two arrangements of polar molecules, such as HCl, that allow an attraction between the partial negative end of one molecule and the partial positive end of another.

Two pairs of molecules are shown where each molecule has one larger blue side labeled “delta sign, negative sign” and a smaller red side labeled “delta sign, positive sign. In the first pair, the red sides of the two molecules both face to the left and the blue side to the right. A horizontal dotted line lies in between the two. In the second pair, the molecules face up and down, with the red and blue ends aligning. A horizontal dotted line lies between the red and blue ends facing upward and another lies between the red and blue ends facing downward.

The effect of a dipole-dipole attraction is apparent when we compare the properties of HCl molecules to nonpolar F₂ molecules. Both HCl and F₂ consist of the same number of atoms and have approximately the same molecular mass. At a temperature of 150 K, molecules of both substances would have the same average KE. However, the dipole-dipole attractions between HCl molecules are sufficient to cause them to “stick together” to form a liquid, whereas the relatively weaker dispersion forces between nonpolar F₂ molecules are not, and so this substance is gaseous at this temperature. The higher normal boiling point of HCl (188 K) compared to F₂ (85 K) is a reflection of the greater strength of dipole-dipole attractions between HCl molecules, compared to the

attractions between nonpolar F_2 molecules. We will often use values such as boiling or freezing points, or enthalpies of vaporization or fusion, as indicators of the relative strengths of IMFs of attraction present within different substances.

✓ Example 11.2.2: Dipole-Dipole Forces and Their Effects

Predict which will have the higher boiling point: N_2 or CO . Explain your reasoning.

Solution

CO and N_2 are both diatomic molecules with masses of about 28 amu, so they experience similar London dispersion forces. Because CO is a polar molecule, it experiences dipole-dipole attractions. Because N_2 is nonpolar, its molecules cannot exhibit dipole-dipole attractions. The dipole-dipole attractions between CO molecules are comparably stronger than the dispersion forces between nonpolar N_2 molecules, so CO is expected to have the higher boiling point.

A common method for preparing oxygen is the decomposition

? Exercise 11.2.2

Predict which will have the higher boiling point: ICl or Br_2 . Explain your reasoning.

Answer

ICl . ICl and Br_2 have similar masses (~ 160 amu) and therefore experience similar London dispersion forces. ICl is polar and thus also exhibits dipole-dipole attractions; Br_2 is nonpolar and does not. The relatively stronger dipole-dipole attractions require more energy to overcome, so ICl will have the higher boiling point.

Hydrogen Bonding

Nitrosyl fluoride (ONF , molecular mass 49 amu) is a gas at room temperature. Water (H_2O , molecular mass 18 amu) is a liquid, even though it has a lower molecular mass. We clearly cannot attribute this difference between the two compounds to dispersion forces. Both molecules have about the same shape and ONF is the heavier and larger molecule. It is, therefore, expected to experience more significant dispersion forces. Additionally, we cannot attribute this difference in boiling points to differences in the dipole moments of the molecules. Both molecules are polar and exhibit comparable dipole moments. The large difference between the boiling points is due to a particularly strong dipole-dipole attraction that may occur when a molecule contains a hydrogen atom bonded to a fluorine, oxygen, or nitrogen atom (the three most electronegative elements). The very large difference in electronegativity between the H atom (2.1) and the atom to which it is bonded (4.0 for an F atom, 3.5 for an O atom, or 3.0 for a N atom), combined with the very small size of a H atom and the relatively small sizes of F, O, or N atoms, leads to *highly concentrated partial charges* with these atoms. Molecules with F-H, O-H, or N-H moieties are very strongly attracted to similar moieties in nearby molecules, a particularly strong type of dipole-dipole attraction called hydrogen bonding. Examples of hydrogen bonds include $HF \cdots HF$, $H_2O \cdots HOH$, and $H_3N \cdots HNH_2$, in which the hydrogen bonds are denoted by dots. Figure 11.2.9 illustrates hydrogen bonding between water molecules.

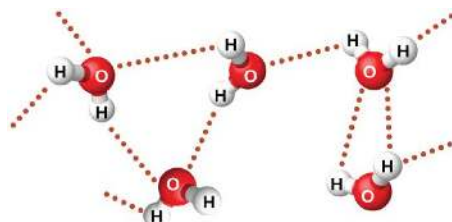


Figure 11.2.9: Water molecules participate in multiple hydrogen-bonding interactions with nearby water molecules.

Five water molecules are shown near one another, but not touching. A dotted line lies between many of the hydrogen atoms on one molecule and the oxygen atom on another molecule.

Despite use of the word “bond,” keep in mind that hydrogen bonds are *intermolecular* attractive forces, not *intramolecular* attractive forces (covalent bonds). Hydrogen bonds are much weaker than covalent bonds, only about 5 to 10% as strong, but are

generally much stronger than other dipole-dipole attractions and dispersion forces.

Hydrogen bonds have a pronounced effect on the properties of condensed phases (liquids and solids). For example, consider the trends in boiling points for the binary hydrides of group 15 (NH_3 , PH_3 , AsH_3 , and SbH_3), group 16 hydrides (H_2O , H_2S , H_2Se , and H_2Te), and group 17 hydrides (HF , HCl , HBr , and HI). The boiling points of the heaviest three hydrides for each group are plotted in Figure 11.2.10. As we progress down any of these groups, the polarities of the molecules decrease slightly, whereas the sizes of the molecules increase substantially. The effect of increasingly stronger dispersion forces dominates that of increasingly weaker dipole-dipole attractions, and the boiling points are observed to increase steadily. For the group 15, 16, and 17 hydrides, the boiling points for each class of compounds increase with increasing molecular mass for elements in periods 3, 4, and 5.

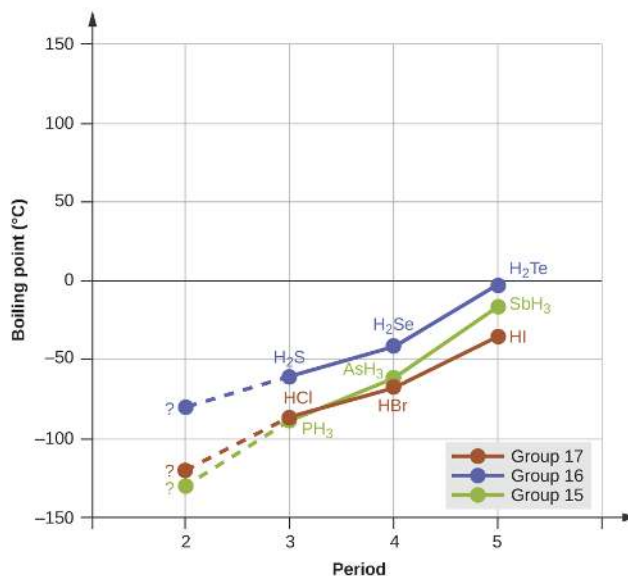


Figure 11.2.10: In comparison to periods 3–5, the binary hydrides of period 2 elements in groups 17, 16 and 15 (F, O and N, respectively) exhibit anomalously high boiling points due to hydrogen bonding.

A line graph is shown where the y-axis is labeled “Boiling point (, degree sign, C)” and has values of “negative 150” to “150” from bottom to top in increments of 50. The x-axis is labeled “Period” and has values of “0” to “5” in increments of 1. Three lines are shown on the graph and are labeled in the legend. The red line is labeled as “halogen family,” the blue is “oxygen family” and the green is “nitrogen family.” The first point on the red line is labeled “question mark” and is at point “2, negative 120.” The second point on the line is labeled “H C l” and is at point “3, negative 80” while the third point on the line is labeled “H B r” and is at point “4, negative 60.” The fourth point on the line is labeled “H I” and is at point “5, negative 40.” The first point on the green line is labeled “question mark” and is at point “2, negative 125.” The second point on the line is labeled “P H, subscript 3” and is at point “3, negative 80” while the third point on the line is labeled “A s H, subscript 3” and is at point “4, negative 55.” The fourth point on the line is labeled “S b H, subscript 3” and is at point “5, negative 10.” The first point on the blue line is labeled “question mark” and is at point “2, negative 80.” The second point on the line is labeled “H, subscript 2, S” and is at point “3, negative 55” while the third point on the line is labeled “H, subscript 2, S e” and is at point “4, negative 45.” The fourth point on the line is labeled “H, subscript 2, T e” and is at point “5, negative 3.”

If we use this trend to predict the boiling points for the lightest hydride for each group, we would expect NH_3 to boil at about -120°C , H_2O to boil at about -80°C , and HF to boil at about -110°C . However, when we measure the boiling points for these compounds, we find that they are dramatically higher than the trends would predict, as shown in Figure 11.2.10. The stark contrast between our naïve predictions and reality provides compelling evidence for the strength of hydrogen bonding.

✓ Example 11.2.3: Effect of Hydrogen Bonding on Boiling Points

Consider the compounds dimethylether (CH_3OCH_3), ethanol ($\text{CH}_3\text{CH}_2\text{OH}$), and propane ($\text{CH}_3\text{CH}_2\text{CH}_3$). Their boiling points, not necessarily in order, are -42.1°C , -24.8°C , and 78.4°C . Match each compound with its boiling point. Explain your reasoning.

Solution

The VSEPR-predicted shapes of CH_3OCH_3 , $\text{CH}_3\text{CH}_2\text{OH}$, and $\text{CH}_3\text{CH}_2\text{CH}_3$ are similar, as are their molar masses (46 g/mol, 46 g/mol, and 44 g/mol, respectively), so they will exhibit similar dispersion forces. Since $\text{CH}_3\text{CH}_2\text{CH}_3$ is nonpolar, it may

exhibit *only* dispersion forces. Because CH_3OCH_3 is polar, it will also experience dipole-dipole attractions. Finally, $\text{CH}_3\text{CH}_2\text{OH}$ has an $-\text{OH}$ group, and so it will experience the uniquely strong dipole-dipole attraction known as hydrogen bonding. So the ordering in terms of strength of IMFs, and thus boiling points, is $\text{CH}_3\text{CH}_2\text{CH}_3 < \text{CH}_3\text{OCH}_3 < \text{CH}_3\text{CH}_2\text{OH}$. The boiling point of propane is $-42.1\text{ }^\circ\text{C}$, the boiling point of dimethylether is $-24.8\text{ }^\circ\text{C}$, and the boiling point of ethanol is $78.5\text{ }^\circ\text{C}$.

? Exercise 11.2.3

Ethane (CH_3CH_3) has a melting point of $-183\text{ }^\circ\text{C}$ and a boiling point of $-89\text{ }^\circ\text{C}$. Predict the melting and boiling points for methylamine (CH_3NH_2). Explain your reasoning.

Answer

The melting point and boiling point for methylamine are predicted to be significantly greater than those of ethane. CH_3CH_3 and CH_3NH_2 are similar in size and mass, but methylamine possesses an $-\text{NH}$ group and therefore may exhibit hydrogen bonding. This greatly increases its IMFs, and therefore its melting and boiling points. It is difficult to predict values, but the known values are a melting point of $-93\text{ }^\circ\text{C}$ and a boiling point of $-6\text{ }^\circ\text{C}$.

Hydrogen Bonding and DNA

Deoxyribonucleic acid (DNA) is found in every living organism and contains the genetic information that determines the organism's characteristics, provides the blueprint for making the proteins necessary for life, and serves as a template to pass this information on to the organism's offspring. A DNA molecule consists of two (anti-)parallel chains of repeating nucleotides, which form its well-known double helical structure, as shown in Figure 11.2.10.

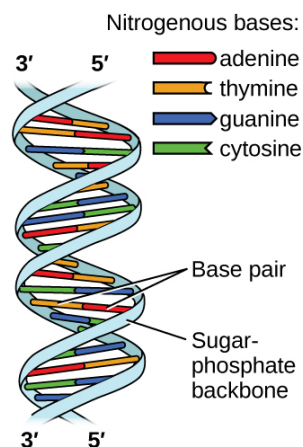


Figure 11.2.11: Two separate DNA molecules form a double-stranded helix in which the molecules are held together via hydrogen bonding. (credit: modification of work by Jerome Walker, Dennis Myts)

Two images are shown. The first lies on the left side of the page and shows a helical structure like a twisted ladder where the rungs of the ladder, labeled “Base pair” are red, yellow, green and blue paired bars. The red and yellow bars, which are always paired together, are labeled in the legend, which is titled “Nitrogenous bases” as “adenine” and “thymine,” respectively. The blue and green bars, which are always paired together, are labeled in the legend as “guanine” and “cytosine,” respectively. At the top of the helical structure, the left-hand side rail, or “Sugar, dash, phosphate backbone,” is labeled as “3, prime” while the right is labeled as “5, prime.” These labels are reversed at the bottom of the helix. To the right of the page is a large Lewis structure. The top left corner of this structure, labeled “5, prime,” shows a phosphorus atom single bonded to three oxygen atoms, one of which has a superscripted negative charge, and double bonded to a fourth oxygen atom. One of the single bonded oxygen atoms is single bonded to the left corner of a five-membered ring with an oxygen atom at its top point and which is single bonded to an oxygen atom on the bottom left. This oxygen atom is single bonded to a phosphorus atom that is single bonded to two other hydrogen atoms and double bonded to a fourth oxygen atom. The lower left of these oxygen atoms is single bonded to another oxygen atom that is single bonded to a five-membered ring with an oxygen in the upper bonding site. The bottom left of this ring has a hydroxyl group attached to it while the upper right carbon is single bonded to a nitrogen atom that is part of a five-membered ring bonded to a six-membered ring. Both of these rings have points of unsaturation and nitrogen atoms bonded into their structures. On the right side of the six-membered ring are two single bonded amine groups and a double bonded oxygen. Three separate dotted lines extend from these sites to corresponding sites on a second six-membered ring. This ring has points of unsaturation and a nitrogen atom in the bottom right bonding position that is single bonded to a five-membered ring on the right side of the image. This ring is single bonded to a carbon that is single bonded to an oxygen that is single bonded to a phosphorus. The phosphorus is single bonded to two other oxygen atoms and double bonded to a fourth oxygen atom. This group is labeled “5, prime.” The five-membered ring is also bonded on the top side to an oxygen that is bonded to a phosphorus single bonded to two other oxygen atoms and double bonded to a fourth oxygen atom. The upper left oxygen of this group is single bonded to a carbon that is single bonded to a five-membered ring with an oxygen in the bottom bonding position. This ring has a hydroxyl group on its upper right side that is labeled “3, prime” and is bonded on the left side to a nitrogen that is a member of a five-membered ring. This ring is bonded to a six-membered ring and both have points of unsaturation. This ring has a nitrogen on the left side, as well as an amine group, that have two dotted lines leading from them to an oxygen and amine group on a six membered ring. These dotted lines are labeled “Hydrogen bonds.” The six membered ring also has a double bonded oxygen on its lower side and a nitrogen atom on its left side that is single bonded to a five-membered ring. This ring connects to the two phosphate groups mentioned at the start of this to form a large circle. The name “guanine” is written below the lower left side of this image while the name “cytosine” is written on the lower right. The name “thymine” is written above the right side of the image and “adenine” is written on the top right. Three sections are indicated below the images where the left is labeled “Sugar, dash, phosphate backbone,” the middle is labeled “Bases” and the right is labeled “Sugar, dash, phosphate backbone.”

Each nucleotide contains a (deoxyribose) sugar bound to a phosphate group on one side, and one of four nitrogenous bases on the other. Two of the bases, cytosine (C) and thymine (T), are single-ringed structures known as pyrimidines. The other two, adenine (A) and guanine (G), are double-ringed structures called purines. These bases form complementary base pairs consisting of one purine and one pyrimidine, with adenine pairing with thymine, and cytosine with guanine. Each base pair is held together by hydrogen bonding. A and T share two hydrogen bonds, C and G share three, and both pairings have a similar shape and structure

Figure 11.2.12

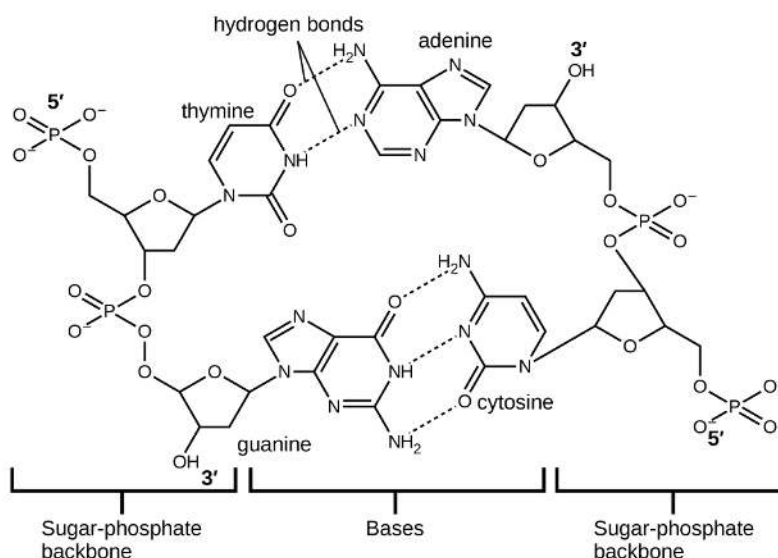


Figure 11.2.12: The geometries of the base molecules result in maximum hydrogen bonding between adenine and thymine (AT) and between guanine and cytosine (GC), so-called “complementary base pairs.”

A large Lewis structure is shown. The top left corner of this structure, labeled “5, prime,” shows a phosphorus atom single bonded to three oxygen atoms, one of which has a superscripted negative charge, and double bonded to a fourth oxygen atom. One of the single bonded oxygen atoms is single bonded to the left corner of a five-membered ring with an oxygen atom at its top point and which is single bonded to an oxygen atom on the bottom left. This oxygen atom is single bonded to a phosphorus atom that is single bonded to two other hydrogen atoms and double bonded to a fourth oxygen atom. The lower left of these oxygen atoms is single bonded to another oxygen atom that is single bonded to a five-membered ring with an oxygen in the upper bonding site. The bottom left of this ring has a hydroxyl group attached to it while the upper right carbon is single bonded to a nitrogen atom that is part of a five-membered ring bonded to a six-membered ring. Both of these rings have points of unsaturation and nitrogen atoms bonded into their structures. On the right side of the six-membered ring are two single bonded amine groups and a double bonded oxygen. Three separate dotted lines extend from these sites to corresponding sites on a second six-membered ring. This ring has points of unsaturation and a nitrogen atom in the bottom right bonding position that is single bonded to a five-membered ring on the right side of the image. This ring is single bonded to a carbon that is single bonded to an oxygen that is single bonded to a phosphorus. The phosphorus is single bonded to two other oxygen atoms and double bonded to a fourth oxygen atom. This group is labeled “5, prime.” The five-membered ring is also bonded on the top side to an oxygen that is bonded to a phosphorus single bonded to two other oxygen atoms and double bonded to a fourth oxygen atom. The upper left oxygen of this group is single bonded to a carbon that is single bonded to a five-membered ring with an oxygen in the bottom bonding position. This ring has a hydroxyl group on its upper right side that is labeled “3, prime” and is bonded on the left side to a nitrogen that is a member of a five-membered ring. This ring is bonded to a six-membered ring and both have points of unsaturation. This ring has a nitrogen on the left side, as well as an amine group, that have two dotted lines leading from them to an oxygen and amine group on a six membered ring. These dotted lines are labeled “Hydrogen bonds.” The six membered ring also has a double bonded oxygen on its lower side and a nitrogen atom on its left side that is single bonded to a five-membered ring. This ring connects to the two phosphate groups mentioned at the start of this to form a large circle. The name “guanine” is written below the lower left side of this image while the name “cytosine” is written on the lower right. The name “thymine” is written above the right side of the image and “adenine” is written on the top right. Three sections are indicated below the images where the left is labeled “Sugar, dash, phosphate backbone,” the middle is labeled “Bases” and the right is labeled “Sugar, dash, phosphate backbone.”

The cumulative effect of millions of hydrogen bonds effectively holds the two strands of DNA together. Importantly, the two strands of DNA can relatively easily “unzip” down the middle since hydrogen bonds are relatively weak compared to the covalent bonds that hold the atoms of the individual DNA molecules together. This allows both strands to function as a template for replication.

Summary

The physical properties of condensed matter (liquids and solids) can be explained in terms of the kinetic molecular theory. In a liquid, intermolecular attractive forces hold the molecules in contact, although they still have sufficient kinetic energy to move past each other. Intermolecular attractive forces, collectively referred to as van der Waals forces, are responsible for the behavior of liquids and solids and are electrostatic in nature. Dipole-dipole attractions result from the electrostatic attraction of the partial negative end of one dipolar molecule for the partial positive end of another. The temporary dipole that results from the motion of the electrons in an atom can induce a dipole in an adjacent atom and give rise to the London dispersion force. London forces

increase with increasing molecular size. Hydrogen bonds are a special type of dipole-dipole attraction that results when hydrogen is bonded to one of the three most electronegative elements: F, O, or N.

Glossary

dipole-dipole attraction

intermolecular attraction between two permanent dipoles

dispersion force

(also, London dispersion force) attraction between two rapidly fluctuating, temporary dipoles; significant only when particles are very close together

hydrogen bonding

occurs when exceptionally strong dipoles attract; bonding that exists when hydrogen is bonded to one of the three most electronegative elements: F, O, or N

induced dipole

temporary dipole formed when the electrons of an atom or molecule are distorted by the instantaneous dipole of a neighboring atom or molecule

instantaneous dipole

temporary dipole that occurs for a brief moment in time when the electrons of an atom or molecule are distributed asymmetrically

intermolecular force

noncovalent attractive force between atoms, molecules, and/or ions

polarizability

measure of the ability of a charge to distort a molecule's charge distribution (electron cloud)

van der Waals force

attractive or repulsive force between molecules, including dipole-dipole, dipole-induced dipole, and London dispersion forces; does not include forces due to covalent or ionic bonding, or the attraction between ions and molecules

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CHAPTER OVERVIEW

12: Gases. Answering essential questions like how we breathe and whose peep will explode first

Topic hierarchy

12.1: Relating Pressure, Volume, Amount, and Temperature- The Ideal Gas Law

12.2: Stoichiometry of Gaseous Substances, Mixtures, and Reactions

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12.1: Relating Pressure, Volume, Amount, and Temperature- The Ideal Gas Law

Learning Objectives

- Identify the mathematical relationships between the various properties of gases
- Use the ideal gas law, and related gas laws, to compute the values of various gas properties under specified conditions

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 12.1.1), 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.

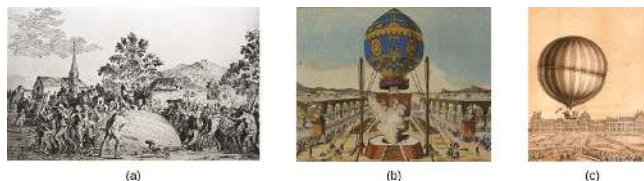


Figure 12.1.1: In 1783, the first (a) hydrogen-filled balloon flight, (b) manned hot air balloon flight, and (c) manned hydrogen-filled balloon flight occurred. When the hydrogen-filled balloon depicted in (a) landed, the frightened villagers of Gonesse reportedly destroyed it with pitchforks and knives. The launch of the latter was reportedly viewed by 400,000 people in Paris.

This figure includes three images. Image a is a black and white image of a hydrogen balloon apparently being deflated by a mob of people. In image b, a blue, gold, and red balloon is being held to the ground with ropes while positioned above a platform from which smoke is rising beneath the balloon. In c, an image is shown in grey on a peach-colored background of an inflated balloon with vertical striping in the air. It appears to have a basket attached to its lower side. A large stately building appears in the background.

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 12.1.2) and the pressure increases.

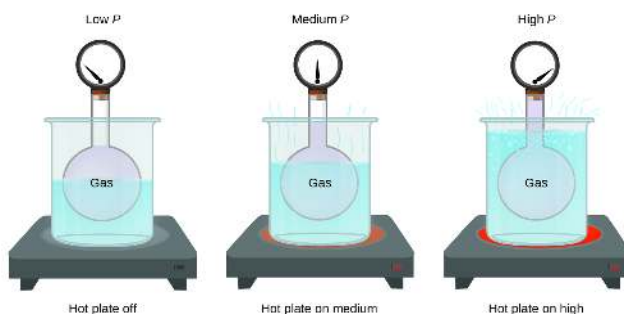


Figure 12.1.2: The effect of temperature on gas pressure: When the hot plate is off, the pressure of the gas in the sphere is relatively low. As the gas is heated, the pressure of the gas in the sphere increases.

This figure includes three similar diagrams. In the first diagram to the left, a rigid spherical container of a gas to which a pressure gauge is attached at the top is placed in a large beaker of water, indicated in light blue, atop a hot plate. The needle on the pressure gauge points to the far left on the gauge. The diagram is labeled "low P" above and "hot plate off" below. The second similar diagram also has the rigid spherical container of gas placed in a large beaker from which light blue wavy line segments extend from the top of the liquid in the beaker. The beaker is situated on top of a slightly reddened circular area. The needle on the pressure gauge points straight up, or to the middle on the gauge. The diagram is labeled "medium P" above and "hot plate on medium" below. The third diagram also has the rigid spherical container of gas placed in a large beaker in which bubbles appear near the liquid surface and several wavy light blue line segments extend from the surface out of the beaker. The beaker is situated on top of a bright red circular area. The needle on the pressure gauge points to the far right on the gauge. The diagram is labeled "high P" above and "hot plate on high" below.

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 12.1.3. 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.

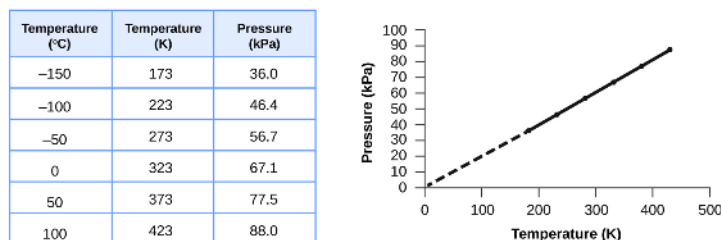


Figure 12.1.3: For a constant volume and amount of air, the pressure and temperature are directly proportional, provided the temperature is in kelvin. (Measurements cannot be made at lower temperatures because of the condensation of the gas.) When this line is extrapolated to lower pressures, it reaches a pressure of 0 at -273°C , which is 0 on the kelvin scale and the lowest possible temperature, called absolute zero.

This figure includes a table and a graph. The table has 3 columns and 7 rows. The first row is a header, which labels the columns "Temperature, degrees C," "Temperature, K," and "Pressure, kPa." The first column contains the values from top to bottom negative 150, negative 100, negative 50, 0, 50, and 100. The second column contains the values from top to bottom 173, 223, 273, 323, 373, and 423. The third column contains the values 36.0, 46.4, 56.7, 67.1, 77.5, and 88.0. A graph appears to the right of the table. The horizontal axis is labeled "Temperature (K)," with markings and labels provided for multiples of 100 beginning at 0 and ending at 500. The vertical axis is labeled "Pressure (kPa)" with markings and labels provided for multiples of 10, beginning at 0 and ending at 100. Six data points from the table are plotted on the graph with black dots. These dots are connected with a solid black line. A dashed line extends from the data point furthest to the left to the origin. The graph shows a positive linear trend.

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:

$$P \propto T \text{ or } P = \text{constant} \times T \text{ or } P = k \times T$$

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 12.1.1: Predicting Change in Pressure with Temperature

A can of hair spray is used until it is empty except for the propellant, isobutane gas.

- On the can is the warning “Store only at temperatures below 120 °F (48.8 °C). Do not incinerate.” Why?
- 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

- 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.)
- 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:

$$\frac{P_1}{T_1} = \frac{P_2}{T_2} \text{ which means that } \frac{360 \text{ kPa}}{297 \text{ K}} = \frac{P_2}{323 \text{ K}}$$

Rearranging and solving gives:

$$P_2 = \frac{360 \text{ kPa} \times 323 \text{ K}}{297 \text{ K}} = 390 \text{ kPa}$$

? Exercise 12.1.1

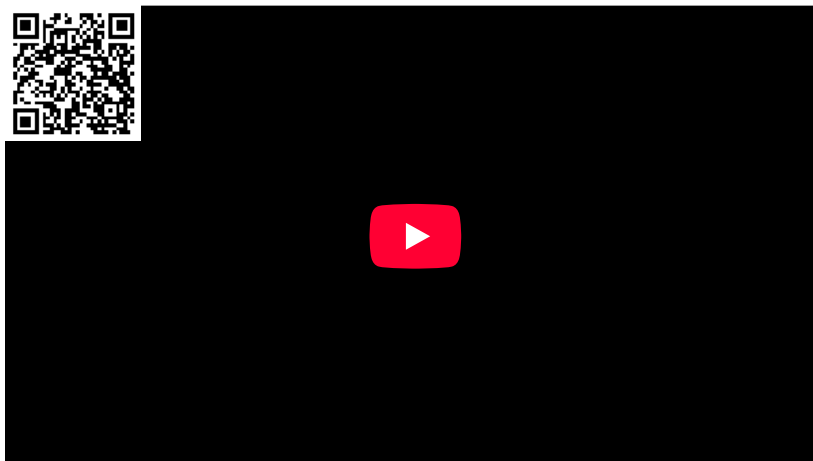
A sample of nitrogen, N_2 , occupies 45.0 mL at 27 °C and 600 torr. What pressure will it have if cooled to –73 °C while the volume remains constant?

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.



Video 12.1.1: 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 12.1.2.

Temperature (°C)	Temperature (K)	Volume (L)
-3	270	22
-23	250	21
-53	220	18
-162	111	9

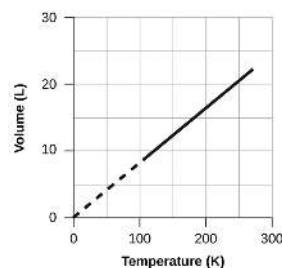


Figure 12.1.4: The volume and temperature are linearly related for 1 mole of methane gas at a constant pressure of 1 atm. If the temperature is in kelvin, volume and temperature are directly proportional. The line stops at 111 K because methane liquefies at this temperature; when extrapolated, it intersects the graph's origin, representing a temperature of absolute zero. This figure includes a table and a graph. The table has 3 columns and 6 rows. The first row is a header, which labels the columns "Temperature, degrees C," "Temperature, K," and "Pressure, k P a." The first column contains the values from top to bottom negative 100, negative 50, 0, 100, and 200. The second column contains the values from top to bottom 173, 223, 273, 373, and 473. The third column contains the values 14.10, 18.26, 22.40, 30.65, and 38.88. A graph appears to the right of the table. The horizontal axis is labeled "Temperature (K)." with markings and labels provided for multiples of 100 beginning at 0 and ending at 300. The vertical axis is labeled "Volume (L)" with marking and labels provided for multiples of 10, beginning at 0 and ending at 30. Five data points from the table are plotted on the graph with black dots. These dots are connected with a solid black line. The graph shows a positive linear trend.

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:

$$V \propto T \text{ or } V = \text{constant} \cdot T \text{ or } V = k \cdot T$$

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 12.1.2: 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: $V_2 = \frac{0.300 \text{ L} \times 303 \text{ K}}{283 \text{ K}} = 0.321 \text{ L}$

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 12.1.2

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 12.1.3: 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:

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \text{ which means that } \frac{150.0 \text{ cm}^3}{273.15 \text{ K}} = \frac{131.7 \text{ cm}^3}{T_2}$$

Rearrangement gives $T_2 = \frac{131.7 \text{ cm}^3 \times 273.15 \text{ K}}{150.0 \text{ cm}^3} = 239.8 \text{ K}$

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 12.1.3

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 12.1.5.

Figure 12.1.5: 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.

This figure contains a diagram and two graphs. The diagram shows a syringe labeled with a scale in mL or cc 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 mL or cc. The first graph is labeled " V (mL)" on the horizontal axis and " P (psi)" on the vertical axis. Points are labeled at 5, 10, 15, 20, and 25 mL with corresponding values of 39.0, 19.5, 13.0, 9.8, and 6.5 psi. The points are connected with a smooth curve that is declining at a decreasing rate of change. The second graph is labeled " V (mL)" on the horizontal axis and " 1 divided by P (psi)" on the vertical axis. The horizontal axis is labeled at multiples of 5, beginning at zero and extending up to 35 mL. 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.

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:

$$P \propto \frac{1}{V}$$

or

$$P = k \cdot \frac{1}{V}$$

or

$$PV = k$$

or

$$P_1V_1 = P_2V_2$$

with k being a constant. Graphically, this relationship is shown by the straight line that results when plotting the inverse of the pressure ($\frac{1}{P}$) versus the volume (V), or the inverse of volume ($\frac{1}{V}$) 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 12.1.6).

Figure 12.1.6: 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.

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.

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 12.1.4: 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:

- the P - V graph in Figure 12.1.6a
- the $\frac{1}{P}$ vs. V graph in Figure 12.1.6b
- the Boyle's law equation

Comment on the likely accuracy of each method.

Solution

- Estimating from the P - V graph gives a value for P somewhere around 27 psi.
- Estimating from the $\frac{1}{P}$ vs. V graph give a value of about 26 psi.
- 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:

$$P_1V_1 = P_2V_2 \text{ or } 13.0 \text{ psi} \times 15.0 \text{ mL} = P_2 \times 7.5 \text{ mL}$$

Solving:

$$P_2 = \frac{13.0 \text{ psi} \times 15.0 \text{ mL}}{7.5 \text{ mL}} = 26 \text{ psi}$$

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 12.1.4

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:

- the P - V graph in Figure 12.1.6a
- the $\frac{1}{P}$ vs. V graph in Figure 12.1.6b
- 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 12.1.7).

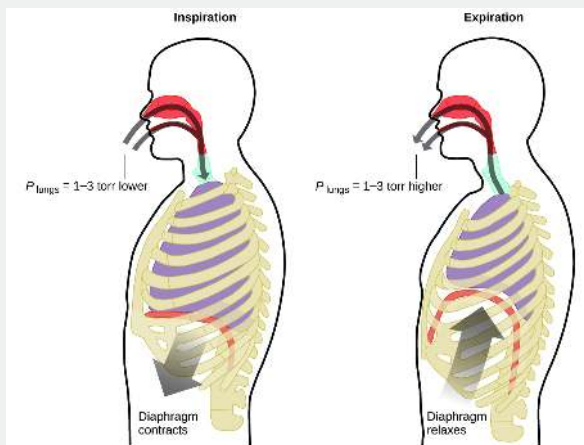


Figure 12.1.7: Breathing occurs because expanding and contracting lung volume creates small pressure differences between your lungs and your surroundings, causing air to be drawn into and forced out of your lungs.

This figure contains two diagrams of a cross section of the human head and torso. The first diagram on the left is labeled "Inspiration." It shows curved arrows in gray proceeding through the nasal passages and mouth to the lungs. An arrow points downward from the diaphragm, which is relatively flat, just beneath the lungs. This arrow is labeled "Diaphragm contracts." At the entrance to the mouth and nasal passages, a label of P_{lungs} equals 1 dash 3 torr lower" is provided. The second, similar diagram, which is labeled "Expiration," reverses the direction of both arrows. Arrows extend from the lungs out through the nasal passages and mouth. Similarly, an arrow points up to the diaphragm, showing a curved diaphragm and lungs reduced in size from the previous image. This arrow is labeled "Diaphragm relaxes." At the entrance to the mouth and nasal passages, a label of P_{lungs} equals 1 dash 3 torr higher" is provided.

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:

$$V \propto n \text{ or } V = k \times n \text{ or } \frac{V_1}{n_1} = \frac{V_2}{n_2}$$

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: $PV = \text{constant}$ at constant T and n
- Amontons's law: $\frac{P}{T} = \text{constant}$ at constant V and n
- Charles's law: $\frac{V}{T} = \text{constant}$ at constant P and n
- Avogadro's law: $\frac{V}{n} = \text{constant}$ 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:

$$PV = nRT$$

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 $0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1}$ and $8.3145 \text{ kPa L mol}^{-1} \text{ K}^{-1}$.

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 12.1.5: 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

? Exercise 12.1.5

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: $\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$ 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 12.1.6: 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 12.1.8). 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 12.1.8: Scuba divers use compressed air to breathe while underwater. (credit: modification of work by Mark Goodchild)
This photograph shows a scuba diver underwater with a tank on his or her back and bubbles ascending from the breathing apparatus.

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:

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \rightarrow \frac{(153 \text{ atm})(13.2 \text{ L})}{(300 \text{ K})} = \frac{(3.13 \text{ atm})(V_2)}{(310 \text{ K})}$$

Solving for V_2 :

$$V_2 = \frac{(153 \text{ atm})(13.2 \text{ L})(310 \text{ K})}{(300 \text{ K})(3.13 \text{ atm})} = 667 \text{ L}$$

(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 12.1.6

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 12.1.9) or in the Caribbean, divers must understand how pressure affects a number of issues related to their comfort and safety.



Figure 12.1.9: 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)

This picture shows colorful underwater corals and anemones in hues of yellow, orange, green, and brown, surrounded by water that appears blue in color.

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 12.1.10).

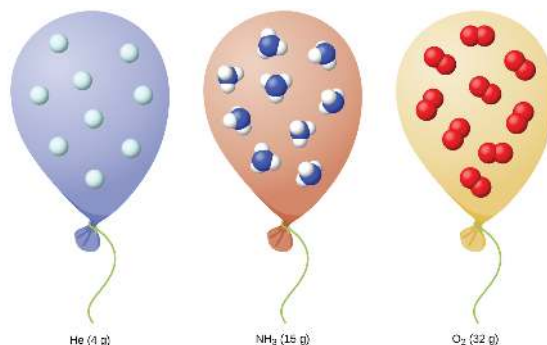


Figure 12.1.10: Since the number of moles in a given volume of gas varies with pressure and temperature changes, chemists use standard temperature and pressure (273.15 K and 1 atm or 101.325 kPa) to report properties of gases.

This figure shows three balloons each filled with He, N H subscript 2, and O subscript 2 respectively. Beneath the first balloon is the label “4 g of He” Beneath the second balloon is the label, “16 g of N H subscript 2.” Beneath the third balloon is the label “32 g of O subscript 2.” Each balloon contains the same number of molecules of their respective gases.

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

- $PV = nRT$

Summary

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 $R = 0.08226 \text{ L atm mol}^{-1} \text{ K}^{-1}$ or $8.314 \text{ L kPa mol}^{-1} \text{ K}^{-1}$

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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12.2: Stoichiometry of Gaseous Substances, Mixtures, and Reactions

Learning Objectives

- Use the ideal gas law to compute gas densities and molar masses
- Perform stoichiometric calculations involving gaseous substances
- State Dalton's law of partial pressures and use it in calculations involving gaseous mixtures

The study of the chemical behavior of gases was part of the basis of perhaps the most fundamental chemical revolution in history. French nobleman Antoine Lavoisier, widely regarded as the “father of modern chemistry,” changed chemistry from a qualitative to a quantitative science through his work with gases. He discovered the law of conservation of matter, discovered the role of oxygen in combustion reactions, determined the composition of air, explained respiration in terms of chemical reactions, and more. He was a casualty of the French Revolution, guillotined in 1794. Of his death, mathematician and astronomer Joseph-Louis Lagrange said, “It took the mob only a moment to remove his head; a century will not suffice to reproduce it.”

As described in an earlier chapter of this text, we can turn to chemical stoichiometry for answers to many of the questions that ask “How much?” We can answer the question with masses of substances or volumes of solutions. However, we can also answer this question another way: with volumes of gases. We can use the ideal gas equation to relate the pressure, volume, temperature, and number of moles of a gas. Here we will combine the ideal gas equation with other equations to find gas density and molar mass. We will deal with mixtures of different gases, and calculate amounts of substances in reactions involving gases. This section will not introduce any new material or ideas, but will provide examples of applications and ways to integrate concepts we have already discussed.

Density of a Gas

Recall that the density of a gas is its mass to volume ratio, $\rho = \frac{m}{V}$. Therefore, if we can determine the mass of some volume of a gas, we will get its density. The density of an unknown gas can be used to determine its molar mass and thereby assist in its identification. The ideal gas law, $PV = nRT$, provides us with a means of deriving such a mathematical formula to relate the density of a gas to its volume in the proof shown in Example 12.2.1.

✓ Example 12.2.1: Derivation of a Density Formula from the Ideal Gas Law

Use $PV = nRT$ to derive a formula for the density of gas in g/L

Solution

$$PV = nRT$$

Rearrange to get (mol/L):

$$\frac{n}{V} = \frac{P}{RT}$$

Multiply each side of the equation by the molar mass, $\mathcal{M}$. When moles are multiplied by $\mathcal{M}$ in g/mol, g are obtained:

$$(\mathcal{M}) \left(\frac{n}{V} \right) = \left(\frac{P}{RT} \right) (\mathcal{M})$$

$$\mathcal{M}/V = \rho = \frac{P\mathcal{M}}{RT}$$

? Exercise 12.2.1

A gas was found to have a density of 0.0847 g/L at 17.0 °C and a pressure of 760 torr. What is its molar mass? What is the gas?

Answer

$$\rho = \frac{PM}{RT}$$

$$0.0847 \text{ g/L} = 760 \cancel{\text{ torr}} \times \frac{1 \cancel{\text{ atm}}}{760 \cancel{\text{ torr}}} \times \frac{M}{0.0821 \text{ L atm/mol K}} \times 290 \text{ K}$$

$M = 2.02 \text{ g/mol}$; therefore, the gas must be hydrogen (H_2 , 2.02 g/mol)

We must specify both the temperature and the pressure of a gas when calculating its density because the number of moles of a gas (and thus the mass of the gas) in a liter changes with temperature or pressure. Gas densities are often reported at STP.

✓ Example 12.2.2: Empirical/Molecular Formula Problems

Using the Ideal Gas Law and Density of a Gas Cyclopropane, a gas once used with oxygen as a general anesthetic, is composed of 85.7% carbon and 14.3% hydrogen by mass. Find the empirical formula. If 1.56 g of cyclopropane occupies a volume of 1.00 L at 0.984 atm and 50 °C, what is the molecular formula for cyclopropane?

Solution

Strategy:

First solve the empirical formula problem using methods discussed earlier. Assume 100 g and convert the percentage of each element into grams. Determine the number of moles of carbon and hydrogen in the 100-g sample of cyclopropane. Divide by the smallest number of moles to relate the number of moles of carbon to the number of moles of hydrogen. In the last step, realize that the smallest whole number ratio is the empirical formula:

$$85.7 \text{ g C} \times \frac{1 \text{ mol C}}{12.01 \text{ g C}} = 7.136 \text{ mol C} \quad \frac{7.136}{7.136} = 1.00 \text{ mol C}$$

$$14.3 \text{ g H} \times \frac{1 \text{ mol H}}{1.01 \text{ g H}} = 14.158 \text{ mol H} \quad \frac{14.158}{7.136} = 1.98 \text{ mol H}$$

Empirical formula is CH_2 [empirical mass (EM) of 14.03 g/empirical unit].

Next, use the density equation related to the ideal gas law to determine the molar mass:

$$d = \frac{PM}{RT} \quad \frac{1.56 \text{ g}}{1.00 \text{ L}} = 0.984 \text{ atm} \times \frac{M}{0.0821 \text{ L atm/mol K}} \times 323 \text{ K}$$

$$M = 42.0 \text{ g/mol}, \quad \frac{M}{EM} = \frac{42.0}{14.03} = 2.99, \text{ so } (3)(\text{CH}_2) = \text{C}_3\text{H}_6 \text{ (molecular formula)}$$

? Exercise 12.2.2

Acetylene, a fuel used welding torches, is comprised of 92.3% C and 7.7% H by mass. Find the empirical formula. If 1.10 g of acetylene occupies a volume of 1.00 L at 1.15 atm and 59.5 °C, what is the molecular formula for acetylene?

Answer

Empirical formula, CH ; Molecular formula, C_2H_2

Molar Mass of a Gas

Another useful application of the ideal gas law involves the determination of molar mass. By definition, the molar mass of a substance is the ratio of its mass in grams, m , to its amount in moles, n :

$$M = \frac{\text{grams of substance}}{\text{moles of substance}} = \frac{m}{n}$$

The ideal gas equation can be rearranged to isolate n :

$$n = \frac{PV}{RT}$$

and then combined with the molar mass equation to yield:

$$\mathcal{M} = \frac{mRT}{PV}$$

This equation can be used to derive the molar mass of a gas from measurements of its pressure, volume, temperature, and mass.

✓ Example 12.2.3: Determining the Molar Mass of a Volatile Liquid

The approximate molar mass of a volatile liquid can be determined by:

1. Heating a sample of the liquid in a flask with a tiny hole at the top, which converts the liquid into gas that may escape through the hole
2. Removing the flask from heat at the instant when the last bit of liquid becomes gas, at which time the flask will be filled with only gaseous sample at ambient pressure
3. Sealing the flask and permitting the gaseous sample to condense to liquid, and then weighing the flask to determine the sample's mass (Figure 12.2.1)

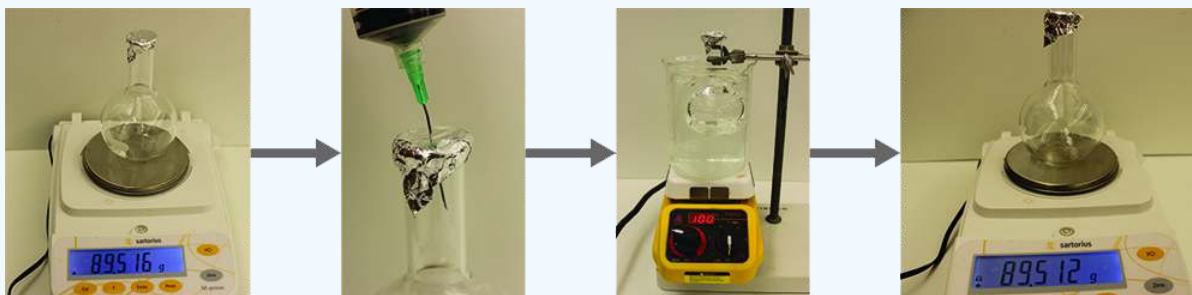


Figure 12.2.1: When the volatile liquid in the flask is heated past its boiling point, it becomes gas and drives air out of the flask. At $t_{l \rightarrow g}$, the flask is filled with volatile liquid gas at the same pressure as the atmosphere. If the flask is then cooled to room temperature, the gas condenses and the mass of the gas that filled the flask, and is now liquid, can be measured. (credit: modification of work by Mark Ott)

Using this procedure, a sample of chloroform gas weighing 0.494 g is collected in a flask with a volume of 129 cm³ at 99.6 °C when the atmospheric pressure is 742.1 mm Hg. What is the approximate molar mass of chloroform?

Solution

Since

$$\mathcal{M} = \frac{m}{n}$$

and

$$n = \frac{PV}{RT}$$

substituting and rearranging gives

$$\mathcal{M} = \frac{mRT}{PV}$$

then

$$\mathcal{M} = \frac{mRT}{PV} = \frac{(0.494 \text{ g}) \times 0.08206 \text{ L} \cdot \text{atm/mol K} \times 372.8 \text{ K}}{0.976 \text{ atm} \times 0.129 \text{ L}} = 120 \text{ g/mol}$$

? Exercise 12.2.3

A sample of phosphorus that weighs 3.243×10^{-2} g exerts a pressure of 31.89 kPa in a 56.0-mL bulb at 550 °C. What are the molar mass and molecular formula of phosphorus vapor?

Answer

The Pressure of a Mixture of Gases: Dalton's Law

Unless they chemically react with each other, the individual gases in a mixture of gases do not affect each other's pressure. Each individual gas in a mixture exerts the same pressure that it would exert if it were present alone in the container (Figure 12.2.2). The pressure exerted by each individual gas in a mixture is called its partial pressure. This observation is summarized by Dalton's law of partial pressures: *The total pressure of a mixture of ideal gases is equal to the sum of the partial pressures of the component gases:*

$$P_{Total} = P_A + P_B + P_C + \dots = \sum_i P_i$$

In the equation P_{Total} is the total pressure of a mixture of gases, P_A is the partial pressure of gas A; P_B is the partial pressure of gas B; P_C is the partial pressure of gas C; and so on.

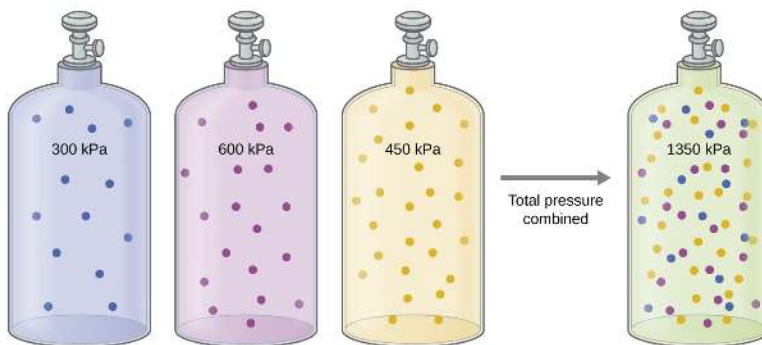


Figure 12.2.2: If equal-volume cylinders containing gas A at a pressure of 300 kPa, gas B at a pressure of 600 kPa, and gas C at a pressure of 450 kPa are all combined in the same-size cylinder, the total pressure of the mixture is 1350 kPa.

This figure includes images of four gas-filled cylinders or tanks. Each has a valve at the top. The interior of the first cylinder is shaded blue. This region contains 5 small blue circles that are evenly distributed. The label “300 k P a” is on the cylinder. The second cylinder is shaded lavender. This region contains 8 small purple circles that are evenly distributed. The label “600 k P a” is on the cylinder. To the right of these cylinders is a third cylinder. Its interior is shaded pale yellow. This region contains 12 small yellow circles that are evenly distributed. The label “450 k P a” is on this region of the cylinder. An arrow labeled “Total pressure combined” appears to the right of these three cylinders. This arrow points to a fourth cylinder. The interior of this cylinder is shaded a pale green. It contains evenly distributed small circles in the following quantities and colors; 5 blue, 8 purple, and 12 yellow. This cylinder is labeled “1350 k P a.”

The partial pressure of gas A is related to the total pressure of the gas mixture via its mole fraction (X), a unit of concentration defined as the number of moles of a component of a solution divided by the total number of moles of all components:

$$P_A = X_A \times P_{Total} \quad \text{where} \quad X_A = \frac{n_A}{n_{Total}}$$

where P_A , X_A , and n_A are the partial pressure, mole fraction, and number of moles of gas A, respectively, and n_{Total} is the number of moles of all components in the mixture.

✓ Example 12.2.2: The Pressure of a Mixture of Gases

A 10.0-L vessel contains 2.50×10^{-3} mol of H₂, 1.00×10^{-3} mol of He, and 3.00×10^{-4} mol of Ne at 35 °C.

- What are the partial pressures of each of the gases?
- What is the total pressure in atmospheres?

Solution

The gases behave independently, so the partial pressure of each gas can be determined from the ideal gas equation, using $P = \frac{nRT}{V}$:

$$P_{\text{H}_2} = \frac{(2.50 \times 10^{-3} \text{ mol})(0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1})(308 \text{ K})}{10.0 \text{ L}} = 6.32 \times 10^{-3} \text{ atm}$$

$$P_{\text{He}} = \frac{(1.00 \times 10^{-3} \text{ mol})(0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1})(308 \text{ K})}{10.0 \text{ L}} = 2.53 \times 10^{-3} \text{ atm}$$

$$P_{\text{Ne}} = \frac{(3.00 \times 10^{-4} \text{ mol})(0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1})(308 \text{ K})}{10.0 \text{ L}} = 7.58 \times 10^{-4} \text{ atm}$$

The total pressure is given by the sum of the partial pressures:

$$P_{\text{T}} = P_{\text{H}_2} + P_{\text{He}} + P_{\text{Ne}} = (0.00632 + 0.00253 + 0.00076) \text{ atm} = 9.61 \times 10^{-3} \text{ atm}$$

? Exercise 12.2.2

A 5.73-L flask at 25 °C contains 0.0388 mol of N₂, 0.147 mol of CO, and 0.0803 mol of H₂. What is the total pressure in the flask in atmospheres?

Answer

1.137 atm

Here is another example of this concept, but dealing with mole fraction calculations.

✓ Example 12.2.3: The Pressure of a Mixture of Gases

A gas mixture used for anesthesia contains 2.83 mol oxygen, O₂, and 8.41 mol nitrous oxide, N₂O. The total pressure of the mixture is 192 kPa.

- What are the mole fractions of O₂ and N₂O?
- What are the partial pressures of O₂ and N₂O?

Solution

The mole fraction is given by

$$X_A = \frac{n_A}{n_{\text{Total}}}$$

and the partial pressure is

$$P_A = X_A \times P_{\text{Total}}$$

For O₂,

$$X_{\text{O}_2} = \frac{n_{\text{O}_2}}{n_{\text{Total}}} = \frac{2.83 \text{ mol}}{(2.83 + 8.41) \text{ mol}} = 0.252$$

and

$$P_{\text{O}_2} = X_{\text{O}_2} \times P_{\text{Total}} = 0.252 \times 192 \text{ kPa} = 48.4 \text{ kPa}$$

For N₂O,

$$X_{\text{N}_2\text{O}} = \frac{n_{\text{N}_2\text{O}}}{n_{\text{Total}}} = \frac{8.41 \text{ mol}}{(2.83 + 8.41) \text{ mol}} = 0.748$$

and

$$P_{\text{N}_2\text{O}} = X_{\text{N}_2\text{O}} \times P_{\text{Total}} = (0.748) \times 192 \text{ kPa} = 143.6 \text{ kPa}$$

? Exercise 12.2.3

What is the pressure of a mixture of 0.200 g of H_2 , 1.00 g of N_2 , and 0.820 g of Ar in a container with a volume of 2.00 L at 20 °C?

Answer

1.87 atm

Collection of Gases over Water

A simple way to collect gases that do not react with water is to capture them in a bottle that has been filled with water and inverted into a dish filled with water. The pressure of the gas inside the bottle can be made equal to the air pressure outside by raising or lowering the bottle. When the water level is the same both inside and outside the bottle (Figure 12.2.3), the pressure of the gas is equal to the atmospheric pressure, which can be measured with a barometer.

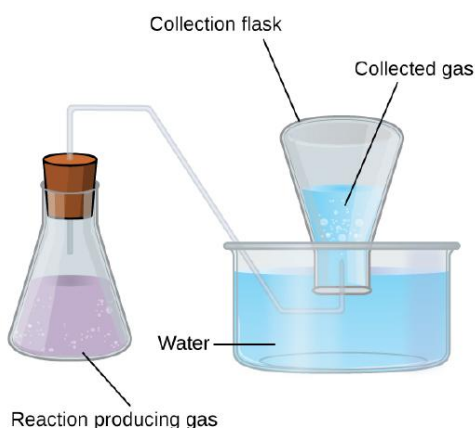


Figure 12.2.3: When a reaction produces a gas that is collected above water, the trapped gas is a mixture of the gas produced by the reaction and water vapor. If the collection flask is appropriately positioned to equalize the water levels both within and outside the flask, the pressure of the trapped gas mixture will equal the atmospheric pressure outside the flask (see the earlier discussion of manometers).

This figure shows a diagram of equipment used for collecting a gas over water. To the left is an Erlenmeyer flask. It is approximately two thirds full of a lavender colored liquid. Bubbles are evident in the liquid. The label “Reaction Producing Gas” appears below the flask. A line segment connects this label to the liquid in the flask. The flask has a stopper in it through which a single glass tube extends from the open region above the liquid in the flask up, through the stopper, to the right, then angles down into a pan that is nearly full of light blue water. This tube again extends right once it is well beneath the water’s surface. It then bends up into an inverted flask which is labeled “Collection Flask.” This collection flask is positioned with its mouth beneath the surface of the light blue water and appears approximately half full. Bubbles are evident in the water in the inverted flask. The open space above the water in the inverted flask is labeled “collected gas.”

However, there is another factor we must consider when we measure the pressure of the gas by this method. Water evaporates and there is always gaseous water (water vapor) above a sample of liquid water. As a gas is collected over water, it becomes saturated with water vapor and the total pressure of the mixture equals the partial pressure of the gas plus the partial pressure of the water vapor. The pressure of the pure gas is therefore equal to the total pressure minus the pressure of the water vapor—this is referred to as the “dry” gas pressure, that is, the pressure of the gas only, without water vapor.

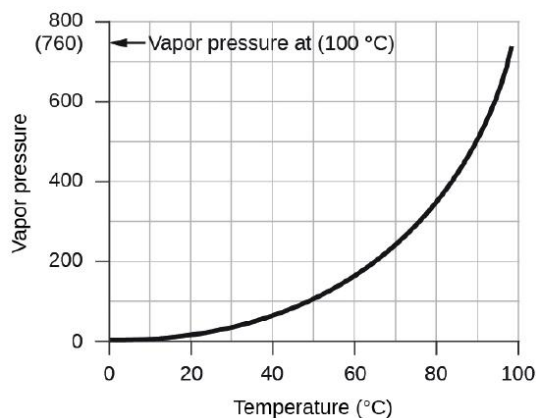


Figure 12.2.4: This graph shows the vapor pressure of water at sea level as a function of temperature.

A graph is shown. The horizontal axis is labeled “Temperature (degrees C)” with markings and labels provided for multiples of 20 beginning at 0 and ending at 100. The vertical axis is labeled “Vapor pressure (torr)” with marking and labels provided for multiples of 200, beginning at 0 and ending at 800. A smooth solid black curve extends from the origin up and to the right across the graph. The graph shows a positive trend with an increasing rate of change. On the vertical axis is (7 60) and an arrow pointing to it. The arrow is labeled, “Vapor pressure at (100 degrees C).”

The vapor pressure of water, which is the pressure exerted by water vapor in equilibrium with liquid water in a closed container, depends on the temperature (Figure 12.2.4); more detailed information on the temperature dependence of water vapor can be found in Table 12.2.1, and vapor pressure will be discussed in more detail in the next chapter on liquids.

Table 12.2.1: Vapor Pressure of Ice and Water in Various Temperatures at Sea Level

Temperature (°C)	Pressure (torr)	Temperature (°C)	Pressure (torr)	Temperature (°C)	Pressure (torr)
–10	1.95	18	15.5	30	31.8
–5	3.0	19	16.5	35	42.2
–2	3.9	20	17.5	40	55.3
0	4.6	21	18.7	50	92.5
2	5.3	22	19.8	60	149.4
4	6.1	23	21.1	70	233.7
6	7.0	24	22.4	80	355.1
8	8.0	25	23.8	90	525.8
10	9.2	26	25.2	95	633.9
12	10.5	27	26.7	99	733.2
14	12.0	28	28.3	100.0	760.0
16	13.6	29	30.0	101.0	787.6

✓ Example 12.2.4: Pressure of a Gas Collected Over Water

If 0.200 L of argon is collected over water at a temperature of 26 °C and a pressure of 750 torr in a system like that shown in Figure 12.2.3, what is the partial pressure of argon?

Solution

According to Dalton’s law, the total pressure in the bottle (750 torr) is the sum of the partial pressure of argon and the partial pressure of gaseous water:

$$P_T = P_{Ar} + P_{H_2O}$$

Rearranging this equation to solve for the pressure of argon gives:

$$P_{Ar} = P_T - P_{H_2O}$$

The pressure of water vapor above a sample of liquid water at 26 °C is 25.2 torr (Appendix E), so:

$$P_{Ar} = 750 \text{ torr} - 25.2 \text{ torr} = 725 \text{ torr}$$

? Exercise 12.2.4

A sample of oxygen collected over water at a temperature of 29.0 °C and a pressure of 764 torr has a volume of 0.560 L. What volume would the dry oxygen have under the same conditions of temperature and pressure?

Answer

0.583 L

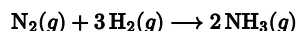
Chemical Stoichiometry and Gases

Chemical stoichiometry describes the quantitative relationships between reactants and products in chemical reactions. We have previously measured quantities of reactants and products using masses for solids and volumes in conjunction with the molarity for solutions; now we can also use gas volumes to indicate quantities. If we know the volume, pressure, and temperature of a gas, we can use the ideal gas equation to calculate how many moles of the gas are present. If we know how many moles of a gas are involved, we can calculate the volume of a gas at any temperature and pressure.

Avogadro's Law Revisited

Sometimes we can take advantage of a simplifying feature of the stoichiometry of gases that solids and solutions do not exhibit: All gases that show ideal behavior contain the same number of molecules in the same volume (at the same temperature and pressure). Thus, the ratios of volumes of gases involved in a chemical reaction are given by the coefficients in the equation for the reaction, provided that the gas volumes are measured at the same temperature and pressure.

We can extend Avogadro's law (that the volume of a gas is directly proportional to the number of moles of the gas) to chemical reactions with gases: Gases combine, or react, in definite and simple proportions by volume, provided that all gas volumes are measured at the same temperature and pressure. For example, since nitrogen and hydrogen gases react to produce ammonia gas according to



a given volume of nitrogen gas reacts with three times that volume of hydrogen gas to produce two times that volume of ammonia gas, if pressure and temperature remain constant.

The explanation for this is illustrated in Figure 12.2.4. According to Avogadro's law, equal volumes of gaseous N_2 , H_2 , and NH_3 , at the same temperature and pressure, contain the same number of molecules. Because one molecule of N_2 reacts with three molecules of H_2 to produce two molecules of NH_3 , the volume of H_2 required is three times the volume of N_2 , and the volume of NH_3 produced is two times the volume of N_2 .

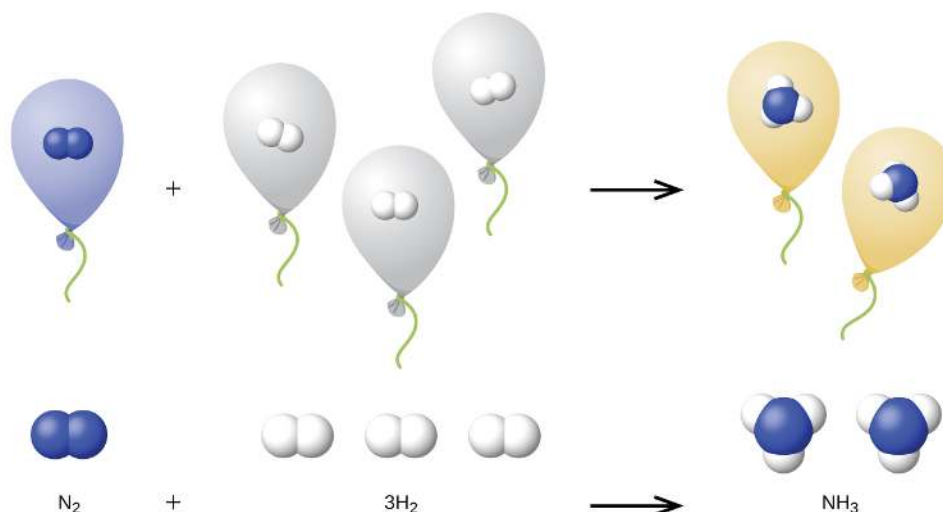


Figure 12.2.5: One volume of N_2 combines with three volumes of H_2 to form two volumes of NH_3 .

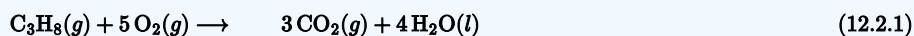
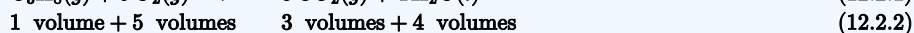
This diagram provided models the chemical reaction written with formulas across the bottom of the figure. The reaction is written; N subscript 2 plus 3 H subscript 2 followed by an arrow pointing right to N H subscript 3. Just above the formulas, space-filling models are provided. Above N H subscript 2, two blue spheres are bonded. Above 3 H subscript 2, three pairs of two slightly smaller white spheres are bonded. Above N H subscript 3, two molecules are shown composed each of a central blue sphere to which three slightly smaller white spheres are bonded. Across the top of the diagram, the reaction is illustrated with balloons. To the left is a light blue balloon which is labeled “N subscript 2”. This balloon contains a single space-filling model composed of two bonded blue spheres. This balloon is followed by a plus sign, then three grey balloons which are each labeled “H subscript 2.” Each of these balloons similarly contain a single space-filling model composed of two bonded white spheres. These white spheres are slightly smaller than the blue spheres. An arrow follows which points right to two light green balloons which are each labeled “N H subscript 3.” Each light green balloon contains a space-filling model composed of a single central blue sphere to which three slightly smaller white spheres are bonded.

✓ Example 12.2.5: Reaction of Gases

Propane, $C_3H_8(g)$, is used in gas grills to provide the heat for cooking. What volume of $O_2(g)$ measured at 25 °C and 760 torr is required to react with 2.7 L of propane measured under the same conditions of temperature and pressure? Assume that the propane undergoes complete combustion.

Solution

The ratio of the volumes of C_3H_8 and O_2 will be equal to the ratio of their coefficients in the balanced equation for the reaction:



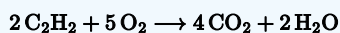
From the equation, we see that one volume of C_3H_8 will react with five volumes of O_2 :

$$2.7 \text{ L } C_3H_8 \times \frac{5 \text{ L } O_2}{1 \text{ L } C_3H_8} = 13.5 \text{ L } O_2$$

A volume of 13.5 L of O_2 will be required to react with 2.7 L of C_3H_8 .

? Exercise 12.2.5

An acetylene tank for an oxyacetylene welding torch provides 9340 L of acetylene gas, C_2H_2 , at 0 °C and 1 atm. How many tanks of oxygen, each providing 7.00×10^3 L of O_2 at 0 °C and 1 atm, will be required to burn the acetylene?

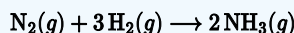


Answer

3.34 tanks (2.34×10^4 L)

✓ Example 12.2.6: Volumes of Reacting Gases

Ammonia is an important fertilizer and industrial chemical. Suppose that a volume of 683 billion cubic feet of gaseous ammonia, measured at 25 °C and 1 atm, was manufactured. What volume of $\text{H}_2(g)$, measured under the same conditions, was required to prepare this amount of ammonia by reaction with N_2 ?



Solution

Because equal volumes of H_2 and NH_3 contain equal numbers of molecules and each three molecules of H_2 that react produce two molecules of NH_3 , the ratio of the volumes of H_2 and NH_3 will be equal to 3:2. Two volumes of NH_3 , in this case in units of billion ft^3 , will be formed from three volumes of H_2 :

$$\cancel{683 \text{ billion ft}^3 \text{ NH}_3} \times \frac{3 \text{ billion ft}^3 \text{ H}_2}{2 \cancel{\text{ billion ft}^3 \text{ NH}_3}} = 1.02 \times 10^3 \text{ billion ft}^3 \text{ H}_2$$

The manufacture of 683 billion ft^3 of NH_3 required 1020 billion ft^3 of H_2 . (At 25 °C and 1 atm, this is the volume of a cube with an edge length of approximately 1.9 miles.)

? Exercise 12.2.6

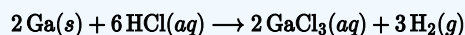
What volume of $\text{O}_2(g)$ measured at 25 °C and 760 torr is required to react with 17.0 L of ethylene, $\text{C}_2\text{H}_4(g)$, measured under the same conditions of temperature and pressure? The products are CO_2 and water vapor.

Answer

51.0 L

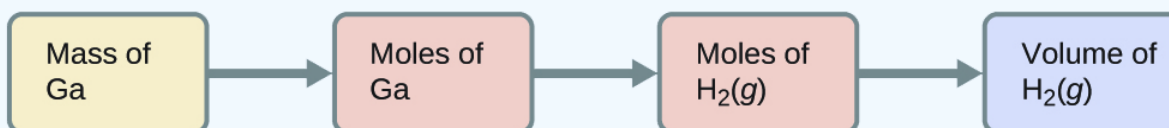
✓ Example 12.2.7: Volume of Gaseous Product

What volume of hydrogen at 27 °C and 723 torr may be prepared by the reaction of 8.88 g of gallium with an excess of hydrochloric acid?



Solution

To convert from the mass of gallium to the volume of $\text{H}_2(g)$, we need to do something like this:



The first two conversions are:

$$8.88 \cancel{\text{ g Ga}} \times \frac{1 \cancel{\text{ mol Ga}}}{69.723 \cancel{\text{ g Ga}}} \times \frac{3 \text{ mol H}_2}{2 \cancel{\text{ mol Ga}}} = 0.191 \text{ mol H}_2$$

Finally, we can use the ideal gas law:

$$V_{\text{H}_2} = \left(\frac{nRT}{P} \right)_{\text{H}_2} = \frac{0.191 \cancel{\text{ mol}} \times 0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1} \times 300 \text{ K}}{0.951 \text{ atm}} = 4.94 \text{ L}$$

? Exercise 12.2.7

Sulfur dioxide is an intermediate in the preparation of sulfuric acid. What volume of SO_2 at $343\text{ }^\circ\text{C}$ and 1.21 atm is produced by burning 1.00 kg of sulfur in oxygen?

Answer

$$1.30 \times 10^3\text{ L}$$

📌 Greenhouse Gases and Climate Change

The thin skin of our atmosphere keeps the earth from being an ice planet and makes it habitable. In fact, this is due to less than 0.5% of the air molecules. Of the energy from the sun that reaches the earth, almost $\frac{1}{3}$ is reflected back into space, with the rest absorbed by the atmosphere and the surface of the earth. Some of the energy that the earth absorbs is re-emitted as infrared (IR) radiation, a portion of which passes back out through the atmosphere into space. However, most of this IR radiation is absorbed by certain substances in the atmosphere, known as greenhouse gases, which re-emit this energy in all directions, trapping some of the heat. This maintains favorable living conditions—without atmosphere, the average global average temperature of $14\text{ }^\circ\text{C}$ ($57\text{ }^\circ\text{F}$) would be about $-19\text{ }^\circ\text{C}$ ($-2\text{ }^\circ\text{F}$). The major greenhouse gases (GHGs) are water vapor, carbon dioxide, methane, and ozone. Since the Industrial Revolution, human activity has been increasing the concentrations of GHGs, which have changed the energy balance and are significantly altering the earth's climate (Figure 12.2.6).

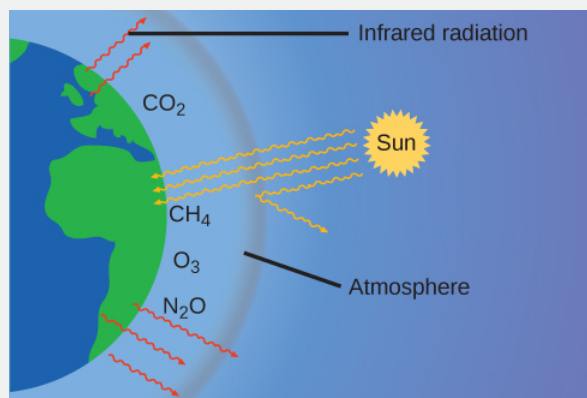
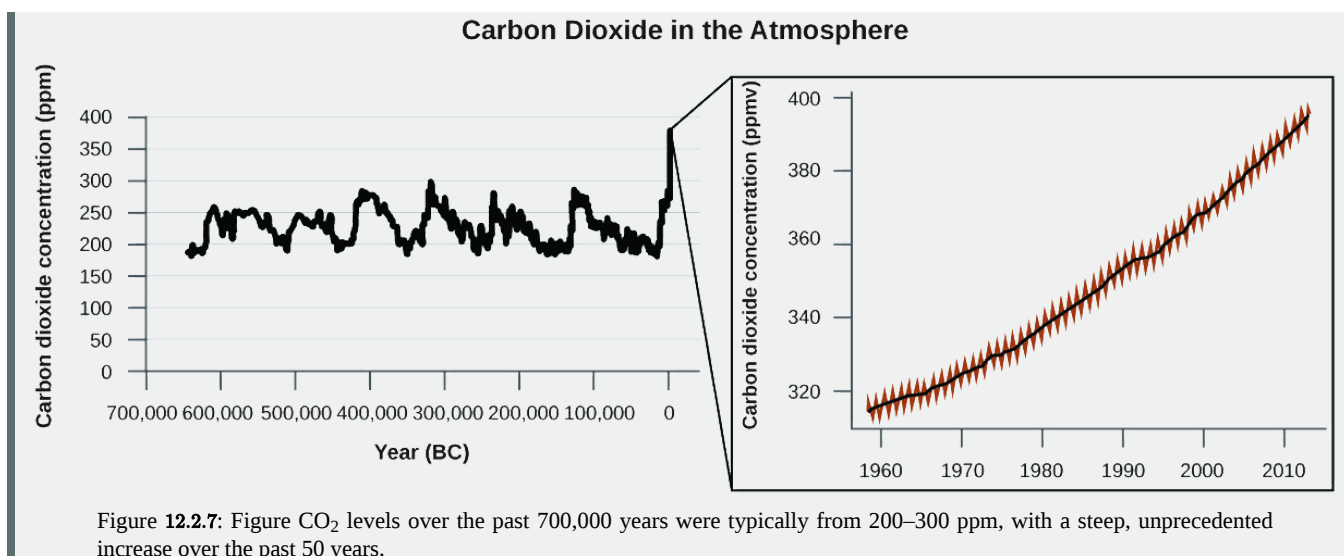


Figure 12.2.6: Greenhouse gases trap enough of the sun's energy to make the planet habitable—this is known as the greenhouse effect. Human activities are increasing greenhouse gas levels, warming the planet and causing more extreme weather events.

There is strong evidence from multiple sources that higher atmospheric levels of CO_2 are caused by human activity, with fossil fuel burning accounting for about $\frac{3}{4}$ of the recent increase in CO_2 . Reliable data from ice cores reveals that CO_2 concentration in the atmosphere is at the highest level in the past 800,000 years; other evidence indicates that it may be at its highest level in 20 million years. In recent years, the CO_2 concentration has increased from historical levels of below 300 ppm to almost 400 ppm today (Figure 12.2.7).



Summary

The ideal gas law can be used to derive a number of convenient equations relating directly measured quantities to properties of interest for gaseous substances and mixtures. Appropriate rearrangement of the ideal gas equation may be made to permit the calculation of gas densities and molar masses. Dalton's law of partial pressures may be used to relate measured gas pressures for gaseous mixtures to their compositions. Avogadro's law may be used in stoichiometric computations for chemical reactions involving gaseous reactants or products.

Key Equations

- $P_{Total} = P_A + P_B + P_C + \dots = \sum_i P_i$
- $P_A = X_A P_{Total}$
- $X_A = \frac{n_A}{n_{Total}}$

Footnotes

1. "Quotations by Joseph-Louis Lagrange," last modified February 2006, accessed February 10, 2015, www-history.mcs.st-andrews.ac.uk/Lagrange.html

Summary

Dalton's law of partial pressures

total pressure of a mixture of ideal gases is equal to the sum of the partial pressures of the component gases.

mole fraction (X)

concentration unit defined as the ratio of the molar amount of a mixture component to the total number of moles of all mixture components

partial pressure

pressure exerted by an individual gas in a mixture

vapor pressure of water

pressure exerted by water vapor in equilibrium with liquid water in a closed container at a specific temperature

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13: Interleaved problems

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SECTION OVERVIEW

13.1: Problems

Topic hierarchy

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[13.1.1.2: Strontium isotopes treat bone cancer pain](#)

[13.1.1.2.1: Strontium treats bone cancer pain- Solutions](#)

13.1.2: Mechanical problems

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13.1.1: Advanced problems

Advanced Problems require application of the knowledge you gained in the Mechanical Problems for this topic to a previously unseen situation. These problems test how deeply you understand the material and provide the challenge you need to grow intellectually. While doing these problems, push yourself. Try completing the problems without looking at the solutions until your next study session. Remember, your brain will keep working while you take a hard-earned break! When you come to an Advanced Problem that you are stuck on, use the solutions—which model how to think about the problems—to try to explain how to do the problem and identify why/how you were stuck. These are great problems to discuss with your classmates and Q&SC tutors. Explaining how to do these complicated problems out loud will really help you assess what you do and don't understand.

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13.1.1.1: All about phosphorous

THE CHEMISTRY OF MATCHES

How Matches Work

The composition of matches varies depending on type, but safety matches are the most commonly used. They contain a strong oxidizing agent in the match head, and red phosphorus in the striking surface. Striking the match causes small amounts of the oxidizer and phosphorus to combine, and the heat generated by the friction of the striking causes them to ignite.

Prior to the 1900s, white phosphorus was the active ingredient in most matches, but this could cause phossy jaw and bone disorders, and was also toxic, so was replaced.

The Match

POTASSIUM CHLORATE
Main ingredient (40-50%) in heads of safety matches.

PHOSPHORUS SESQUI SULFIDE
Compounds in the heads of "strike anywhere" matches.

ANTIMONY (III) SULFIDE
Added to some matches to make them burn more vigorously.

Additionally, the matches contain ammonium phosphates to prevent afterglow, glue to bind materials, and paraffin wax to ease of burning.

The Match Box

The striking surface of safety match boxes contains red phosphorus and an abrasive substance. When struck, a small amount of white phosphorus is produced, which ignites.

Red Phosphorus (above); White Phosphorus (below).

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- Phosphorous (P) is interesting! Here are some questions related to phosphorous in the human body, based on [the following information I found on Wikipedia](#):
 - An average adult human contains about 0.7 kg of phosphorus, about 90% in bones and teeth in the form of apatite, and the remainder in soft tissues and extracellular fluids (~1%). The phosphorus content increases from about 0.5 weight% in infancy to 0.65–1.1 weight% in adults. Average phosphorus concentration in the blood is about 0.4 g/L, about 70% of that is organic and 30% inorganic phosphates. An adult with healthy diet consumes and excretes about 1–3 grams of phosphorus per day, with consumption in the form of inorganic phosphate and phosphorus-containing biomolecules such as nucleic acids and phospholipids; and excretion almost exclusively in the form of phosphate ions.
 - How many atoms of phosphorous are in the bones and teeth of an average adult?
 - Given a typical volume of blood is 5 L, how many atoms of phosphorous are present in the blood stream in the form of inorganic phosphates?
- Phosphorous is essential for healthy body function, but too much is poisonous. "Phossy jaw" is a horrible bone necrosis in the jaw that resulted when people breathed in gaseous phosphorous. It was prevalent in matchstick factory workers in the late 1800's and early 1900's until the match making process started to use red phosphorous rather than white phosphorous (shown in the graphic above). The dangerous white phosphorous contains 4 P atoms chemically bound together. Red phosphorous contains many more P atoms in a chain and therefore is not as easily turned into breathable gas. The Occupational Safety and Health Administration (OSHA) currently sets an inhalation exposure limit for white phosphorus in the workplace during an 8-hour workday at 0.1 milligram per cubic meter of air (mg/m³). Matchstick factory workers who got phossy jaw would typically contract this illness after working ~13 hours/day, 7 days/week (the weekend was not implemented in the US until later in the 1900's!), for 5 years (say 260 weeks).
 - How many hours were workers exposed to phosphorous before getting sick?
 - If these workers breath in 35 L of air per hour and worked in a factory that followed OSHA guidelines, how many moles of phosphorous would they breath over this five year period? Note that 1 m³ = 1000 L.
 - Assuming that matchstick workers were exposed to 100x greater levels than those required by OSHA, how many more atoms of phosphorous would they breath over that 5 year period compared to workers in an OSHA-approved factory?

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13.1.1.2: Strontium isotopes treat bone cancer pain

The element strontium (Sr) is right underneath calcium (Ca) on the periodic table, which means that they tend to have similar chemical behavior and Sr can easily bind to bones in the same places Ca would. This can be useful—Sr is used in Sensodyne toothpaste to minimize tooth sensitivity and ^{89}Sr (isotopic mass = 88.907 g/mol) is used to treat pain in bone cancer patients. The radioactive ^{90}Sr (isotopic mass = 89.908 g/mol) released by the Chernobyl disaster, however, is extremely dangerous for this same reason.

1. Use the following information about the 3 naturally occurring isotopes of Sr to calculate its average atomic mass. Does your calculation match that on the periodic table? Why are we calculating the average atomic mass using only these three isotopes when we mentioned above that ^{89}Sr and ^{90}Sr exist?

Isotope	Isotopic abundance (%)	Isotopic mass (g/mol)
^{86}Sr	?	85.90926
^{87}Sr	7.00%	86.90888
^{88}Sr	82.58%	87.90561

2. I would like to know how many moles of ^{89}Sr are administered to a cancer patient who weighs 16 kg. A radiation dose of 1.5 MBq/kg of body mass using ^{89}Sr will decrease pain [in 80% of bone cancer patients without significant toxicity](#). Note that Bq are a unit of radiation and MBq is “mega” Bq. ^{89}Sr is delivered as a drug called Metastron™ that delivers 37 MBq/mL. Each mL of Metastron contains 15 mg of the drug, which is 55% ^{89}Sr by mass.

Solutions

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13.1.1.2.1: Strontium treats bone cancer pain- Solutions

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1. Use the following information about the 3 naturally occurring isotopes of Sr to calculate its average atomic mass. Does your calculation match that on the periodic table?

Isotope	Isotopic abundance (%)	Isotopic mass (g/mol)
^{86}Sr	?	85.90926
^{87}Sr	7.00%	86.90888
^{88}Sr	82.58%	87.90561

I have the isotopic abundance for 2 of the 3 naturally occurring isotopes, so I can find the 3rd given that the percentages must add up to 100%.

Isotopic abundance of ^{86}Sr is $100.00 - 7.00 - 82.58\% = 10.44\%$. Wait, but you said that ^{89}Sr and ^{90}Sr exist, too? Why don't I have to include them? The question asked you to focus on the 3 *naturally occurring isotopes* of Sr. ^{89}Sr and ^{90}Sr are highly radioactive elements that are man-made. They occur in such small quantities they don't change the average atomic mass of Sr.

Now that I know the fractional isotopic abundances and isotopic masses for each naturally occurring isotope, I can find the average atomic mass using the following equation:

NEEDS equation

$$\text{Average} = 0.8256 \times 87.90561 \text{ g/mol}$$

$$0.0700 \times 86.90888 \text{ g/mol}$$

$$+ 0.1044 \times 85.90926 \text{ g/mol}$$

$$87.6 \text{ g/mol}$$

This is the same value as the periodic table given that the 3 significant figures from $0.0700 \times 86.90888 \text{ g/mol}$ limit the outcome to 3 sig figs.

2. I would like to know how many moles of ^{89}Sr are administered to a cancer patient who weighs 16 kg. A radiation dose of 1.5 MBq/kg of body mass using ^{89}Sr will decrease pain in 80% of bone cancer patients without significant toxicity. Note that Bq are a unit of radiation and MBq is “mega” Bq. ^{89}Sr is delivered as a drug called MetastronTM that delivers 37 MBq/mL. Each mL of Metastron contains 15 mg of the drug, which is 55% ^{89}Sr by mass.

Soooo many conversions to do....

What I know:

Patient mass = 16 kg

Dose = 1.5 MBq/kg

Dose delivered by Metastron = 37 MBq/mL

Metastron contains 15 mg of drug/mL

Metastron is 55% ^{89}Sr by mass

isotopic mass of ^{89}Sr = 88.907 g/mol

Thought process

I am going to do a problem-solving bottom-up strategy, starting with recognizing that the answer I need is in terms of moles of ^{89}Sr . I see a whole bunch of information above, but the two things involving ^{89}Sr are the isotopic mass and the fact that Metastron is 55% ^{89}Sr by mass. So, if I can figure out the mass of Metastron delivered, I will know the mass of ^{89}Sr and I can convert that to moles. I see that there are 15 mg of Metastron/mL, so if I can figure out the volume delivered I can get the mass of Metastron. The dose of the medicine is 37 MBq/mL, so if I get the total radiation in MBq needed, I can get the volume. And lastly, I have the dose required (1.5 MBq/kg), so I can use this plus the mass to get the total radiation. Here is the process:

Step 1: Use the patient mass to get how much radiation we need.

$$16 \text{ kg} \times 1.5 \text{ MBq/kg} = 24 \text{ MBq}$$

Step 2: Use the total radiation needed to find out what volume of the drug we need.

$$24 \text{ MBq} (1 \text{ mL}/37 \text{ MBq}) = 0.65 \text{ mL}$$

Step 3: Use the volume of the drug to find out the mass needed.

$$0.65 \text{ mL} \times 15 \text{ mg/mL} = 975 \text{ mg}$$

Step 4: Use the mass of Metastron to get the mass of ^{89}Sr

$$0.975 \text{ g Metastron} \times 0.55 \text{ g } ^{89}\text{Sr}/\text{g Metastron} = 0.536 \text{ g } ^{89}\text{Sr}$$

Step 5: Convert the mass of ^{89}Sr to moles of ^{89}Sr

$$0.536 \text{ g } ^{89}\text{Sr} \times 1 \text{ mol}/88.907 \text{ g } ^{89}\text{Sr} = 6.0 \times 10^{-3} \text{ mol } ^{89}\text{Sr}$$

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