CHEM 0089 - CONCEPTS OF CHEMISTRY



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CHEM 0089 - Concepts of Chemistry

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Licensing

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CHAPTER OVERVIEW

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1.3: Significant Figures in Calculations

1.4: The Basic Units of Measurement

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1.1: Expressing Numbers

Learning Objective

- Learn to express numbers properly

Quantities have two parts: the number and the unit. The number tells "how many." It is important to be able to express numbers properly so that the quantities can be communicated properly.

Standard Notation

Standard notation is the straightforward expression of a number. Numbers such as 17, 101.5, and 0.00446 are expressed in standard notation. For relatively small numbers, standard notation is fine. However, for very large numbers, such as 306,000,000, or for very small numbers, such as 0.000000419, standard notation can be cumbersome because of the number of zeros needed to place nonzero numbers in the proper position.

Scientific Notation

Scientific notation is an expression of a number using powers of 10. Powers of 10 are used to express numbers that have many zeros:

Table shows the powers of 10. Left side has 10 to a specific power and right side has the equation for the specified power.

10^0	= 1
10^1	= 10
10^2	= 100 = 10 × 10
10^3	= 1,000 = 10 × 10 × 10
10^4	= 10,000 = 10 × 10 × 10 × 10

and so forth.

The raised number to the right of the 10 indicates the number of factors of 10 in the original number. (Scientific notation is sometimes called *exponential notation*.) The exponent's value is equal to the number of zeros in the number expressed in standard notation.

Small numbers can also be expressed in scientific notation but with negative exponents:

Table shows the powers of 10 with negative exponents. Left side has 10 to a specific power and right side has the equation for the specified power.

10^{-1}	= 0.1 = 1/10
10^{-2}	= 0.01 = 1/100
10^{-3}	= 0.001 = 1/1,000
10^{-4}	= 0.0001 = 1/10,000

and so forth. Again, the value of the exponent is equal to the number of zeros in the denominator of the associated fraction. A negative exponent implies a decimal number less than one.

A number is expressed in scientific notation by writing the first nonzero digit, then a decimal point, and then the rest of the digits. The part of a number in scientific notation that is multiplied by a power of 10 is called the *coefficient*. We determine the power of 10 needed to make that number into the original number and multiply the written number by the proper power of 10. For example, to write 79,345 in scientific notation,

$$79,345 = 7.9345 \times 10,000 = 7.9345 \times 10^4$$

Thus, the number in scientific notation is 7.9345×10^4. For small numbers, the same process is used, but the exponent for the power of 10 is negative:

$$0.000411 = 4.11 \times \frac{1}{10,000} = 4.11 \times 10^{-4}$$

Typically, the extra zero digits at the end or the beginning of a number are not included (Figure 1.1.1).



Figure 1.1.1: "The Blue Marble" is a famous photograph of the Earth taken on December 7, 1972, by the crew of the Apollo 17 spacecraft en route to the Moon at a distance of about 29,000 kilometers. This is 2.9×10^4 *km*. It shows Africa, Antarctica, and the Arabian Peninsula.The earth is about 93,000,000 miles from the sun. In scientific notation, this is 9.3×10^7 *miles*. (Public Domain; NASA/Apollo 17 crew; taken by either Harrison Schmitt or Ron Evans.)

Example 1.1.1: Expressing Numbers in Scientific Notation

Express these numbers in scientific notation.

a. 306,000
b. 0.00884
c. 2,760,000
d. 0.000000559

Solution

a. The number 306,000 is 3.06 times 100,000, or 3.06 times 10^5. In scientific notation, the number is 3.06×10^5.
b. The number 0.00884 is 8.84 times 1/1,000, which is 8.84 times 10^{-3}. In scientific notation, the number is 8.84×10^{-3}.
c. The number 2,760,000 is 2.76 times 1,000,000, which is the same as 2.76 times 10^6. In scientific notation, the number is written as 2.76×10^6. Note that we omit the zeros at the end of the original number.
d. The number 0.000000559 is 5.59 times 1/10,000,000, which is 5.59 times 10^{-7}. In scientific notation, the number is written as 5.59×10^{-7}.

Exercise 1.1.1

Express these numbers in scientific notation.

a. 23,070
b. 0.0009706

Answer a

2.307×10^4

Answer b

9.706×10^{-4}

Another way to determine the power of 10 in scientific notation is to count the number of places you need to move the decimal point to get a numerical value between 1 and 10. The number of places equals the power of 10. This number is positive if you move the decimal point to the right and negative if you move the decimal point to the left:

$$56,900 = 5.69 \times 10^{4} \qquad 0.000028 = 2.8 \times 10^{-5}$$

(4 3 2 1 for 56,900; 1 2 3 4 5 for 0.000028)

56900 can be written as 5.69 times 10 to the fourth power. 0.000028 can be written as 2.8 times 10 to the negative fifth power.

Many quantities in chemistry are expressed in scientific notation. When performing calculations, you may have to enter a number in scientific notation into a calculator. Be sure you know how to correctly enter a number in scientific notation into your calculator. Different models of calculators require different actions for properly entering scientific notation. If in doubt, consult your instructor immediately (Figure **1.1.2**).

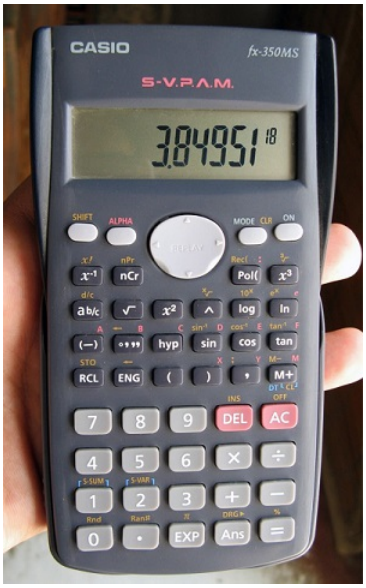


Figure **1.1.2**: This calculator shows only the coefficient and the power of 10 to represent the number in scientific notation. Thus, the number being displayed is $\mathbf{3.84951 \times 10^{18}}$, or $\mathbf{3,849,510,000,000,000,000}$. Source: "Casio" Asim Bijarani is licensed under Creative Commons Attribution 2.0 Generic.

Key Takeaways

- Standard notation expresses a number normally.
- Scientific notation expresses a number as a coefficient times a power of 10.
- The power of 10 is positive for numbers greater than 1 and negative for numbers between 0 and 1.

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1.2: Significant Figures - Writing Numbers to Reflect Precision

Learning Objectives

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

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

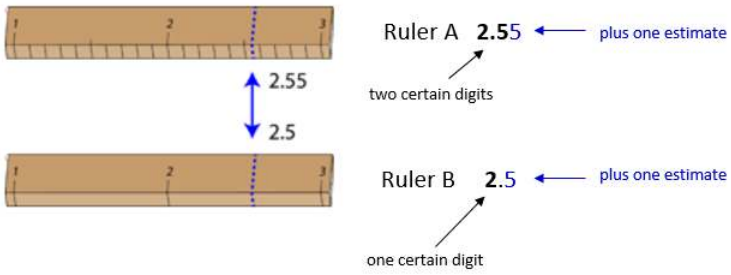


Figure 1.2.1: Measurement with two different rulers. Ruler A's measurement can be rounded to 2.55, with 2 certain digits, while Ruler B's measurement of 2.5 has 1 certain digit

Measurement Uncertainty

Some error or **uncertainty** always exists in any measurement. The amount of uncertainty depends both upon the skill of the measurer and upon the quality of the measuring tool. While some balances are capable of measuring masses only to the nearest $0.1\ \text{g}$, other highly sensitive balances are capable of measuring to the nearest $0.001\ \text{g}$ or even better. Many measuring tools such as rulers and graduated cylinders have small lines which need to be carefully read in order to make a measurement. Figure 1.2.1 shows two rulers making the same measurement of an object (indicated by the blue arrow).

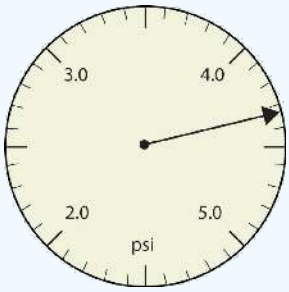
With either ruler, it is clear that the length of the object is between 2 and $3\ \text{cm}$. The bottom ruler contains no millimeter markings. With that ruler, the tenths digit can be estimated and the length may be reported as $2.5\ \text{cm}$. However, another person may judge that the measurement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

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

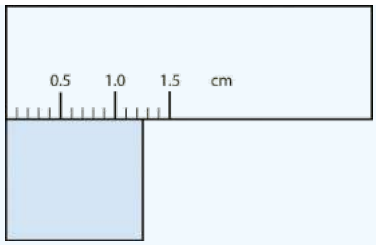
Example 1.2.1: Reporting Measurements to the Proper Number of Significant Figures

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

a.



b.



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

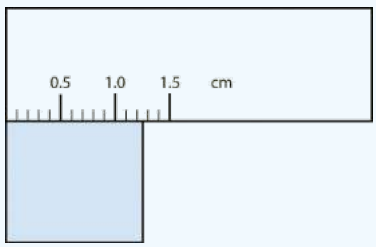
Solutions

Solutions to Example 2.3.1

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

? Exercise 1.2.1

What would be the reported width of this rectangle?



Answer

1.25 cm

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

Table **1.2.1**: Significant Figure Rules

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

Exact Numbers

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

Example 1.2.2

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

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

Solution

Solution to Example 2.3.2

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

? Exercise 1.2.2

Give the number of significant figures in each.

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

Answer a

three significant figures

Answer b

four significant figures

Answer c

four significant figures

Answer d

infinite (exact number)

Answer e

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

Accuracy and Precision

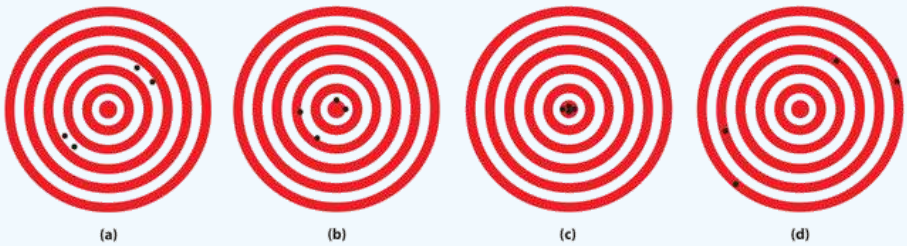
Measurements may be accurate, meaning that the measured value is the same as the true value; they may be precise, meaning that multiple measurements give nearly identical values (i.e., reproducible results); they may be both accurate and precise; or they may be neither accurate nor precise. The goal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



Video **1.2.1**: Difference between precision and accuracy.

Example 1.2.3

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



Which target shows

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

Solution

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

Summary

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

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1.3: Significant Figures in Calculations

Learning Objectives

- Use significant figures correctly in arithmetical operations.

Rounding

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

Consider the measurement **207.518 m**. Right now, the measurement contains six significant figures. How would we successively round it to fewer and fewer significant figures? Follow the process as outlined in Table **1.3.1**.

Table **1.3.1**: Rounding examples

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

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

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

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

Multiplication and Division

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

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

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

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

Example 1.3.1

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

a. 23.096×90.300
b. 125×9.000

Solution

a

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

b

Explanation	Answer
The calculator gives 1,125 as the answer, but we limit it to three significant figures.	$\mathbf{1.13 \times 10^3}$

Addition and Subtraction

How are significant figures handled in calculations? It depends on what type of calculation is being performed. If the calculation is an addition or a subtraction, the rule is as follows: limit the reported answer to the rightmost column that all numbers have significant figures in common. For example, if you were to add 1.2 and 4.71, we note that the first number stops its significant figures in the tenths column, while the second number stops its significant figures in the hundredths column. We therefore limit our answer to the tenths column.

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

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

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

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

Example 1.3.2

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

Solution

a

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

b

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

Exercise 1.3.2

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

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

Answer a:

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

Answer b:

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

Answer c:

$156 = 1.56 \times 10^2$

Answer d:

$2.14 = 2.14 \times 10^0$

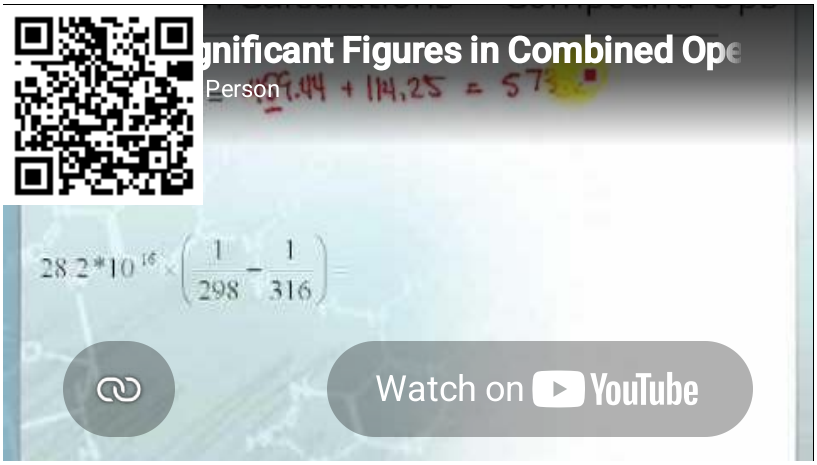
Remember that calculators do not understand significant figures. *You* are the one who must apply the rules of significant figures to a result from your calculator.

Calculations Involving Multiplication/Division and Addition/Subtraction

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



Video 1.3.1: Significant figures in mixed operations (https://www.youtube.com/watch?v=yBntMndXQWA).



Video 1.3.2: https://www.youtube.com/watch?v=__csP0NtlGI

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

Example 1.3.3

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

Solution

a.

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

b.

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

c.

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

Exercise 1.3.3

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

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

Answer a

-5.62 s

Answer b

110.2 cm

Summary

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

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1.4: The Basic Units of Measurement

Learning Objectives

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

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

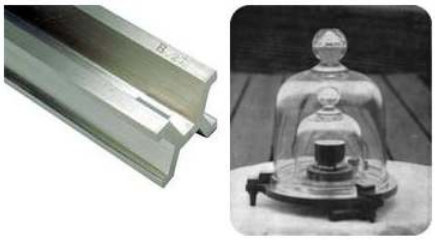


Figure 1.4.1: Meter standard (left) and Kilogram standard (right).

SI Base Units

All measurements depend on the use of units that are well known and understood. The **English system** of measurement units (inches, feet, ounces, etc.) are not used in science because of the difficulty in converting from one unit to another. The **metric system** is used because all metric units are based on multiples of 10, making conversions very simple. The metric system was originally established in France in 1795. **The International System of Units** is a system of measurement based on the metric system. The acronym **SI** is commonly used to refer to this system and stands for the French term, *Le Système International d'Unités*. The SI was adopted by international agreement in 1960 and is composed of seven base units in Table 1.4.1.

Table 1.4.1: SI Base Units of Measurement

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

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

Unfortunately, the Metric System is Not Ubiquitous

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

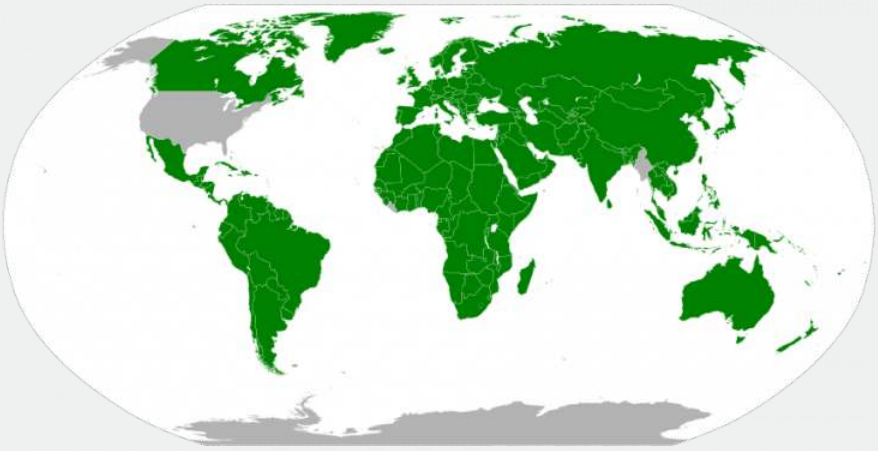


Figure **1.4.1**: Areas of world using metric system (in green). Only a few countries are slow or resistant to adoption including the United States.

Prefix Multipliers

Conversions between metric system units are straightforward because the system is based on powers of ten. For example, meters, centimeters, and millimeters are all metric units of length. There are 10 millimeters in 1 centimeter and 100 centimeters in 1 meter. **Metric prefixes** are used to distinguish between units of different size. These prefixes all derive from either Latin or Greek terms. For example, *mega* comes from the Greek word μεγας, meaning "great". Table **1.4.2** lists the most common metric prefixes and their relationship to the central unit that has no prefix. Length is used as an example to demonstrate the relative size of each prefixed unit.

Table **1.4.2**: SI Prefixes

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

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

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

Example 1.4.1: Unit Abbreviations

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

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

Solutions

Solutions to Example 2.5.1

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

Exercise 1.4.1

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

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

Answer a:

km

Answer b:

mg

Answer c:

ns

Answer d:

cL

Summary

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

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1.5: Problem Solving and Unit Conversions

Learning Objectives

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

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

Converting Between Units with Conversion Factors

A **conversion factor** is a factor used to convert one unit of measurement into another. A simple conversion factor can convert meters into centimeters, or a more complex one can convert miles per hour into meters per second. Since most calculations require measurements to be in certain units, you will find many uses for conversion factors. Always remember that a conversion factor has to represent a fact; this fact can either be simple or more complex. For instance, you already know that 12 eggs equal 1 dozen. A more complex fact is that the speed of light is 1.86×10^5 miles/sec. Either one of these can be used as a conversion factor depending on what type of calculation you are working with (Table 1.5.1).

Table 1.5.1: Conversion Factors from SI units to English Units

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

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

Of course, there are other ratios which are not listed in Table 1.5.1. They may include:

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

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

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

or

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

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

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

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

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

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

Performing Dimensional Analysis

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

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

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

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

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

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

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

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

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

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

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

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

For the answer to be meaningful, we have to *construct the conversion factor in a form that causes the original unit to cancel out*. Figure **1.5.1** shows a concept map for constructing a proper conversion.

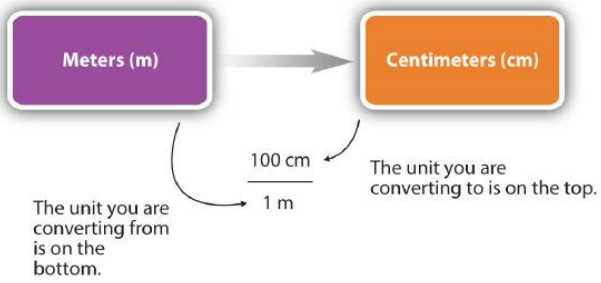


Figure 1.5.1: A Concept Map for Conversions. This is how you construct a conversion factor to convert from one unit to another. Converting meters to centimeters: the unit you are converting is on the bottom of the fraction, and the unit to convert to is on top

General Steps in Performing Dimensional Analysis

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

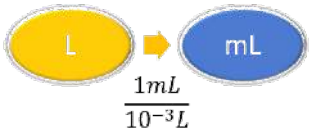
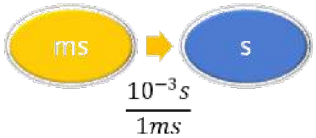
Significant Figures in Conversions

How do conversion factors affect the determination of significant figures?

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

Example 1.5.1

Steps for Problem Solving for Example 2.6.1 and 2.6.2

	Example 1.5.1	Example 1.5.2
Steps for Problem Solving	The average volume of blood in an adult male is 4.7 L. What is this volume in milliliters?	A hummingbird can flap its wings once in 18 ms. How many seconds are in 18 ms?
Identify the "given" information and what the problem is asking you to "find."	Given: 4.7 L Find: mL	Given: 18 ms Find: s
List other known quantities.	$1\,mL = 10^{-3} L$	$1\,ms = 10^{-3} s$
Prepare a concept map and use the proper conversion factor.	 $\frac{1mL}{10^{-3}L}$	 $\frac{10^{-3}s}{1ms}$
Cancel units and calculate.	$4.7 \cancel{L} \times \frac{1\ \text{mL}}{10^{-3}\ \cancel{L}} = 4,700\ \text{mL}$ or $4.7 \cancel{L} \times \frac{1,000\ \text{mL}}{1\ \cancel{L}} = 4,700\ \text{mL}$ or 4.7 x 10^3 2SF, not ambiguous	$18\ \cancel{\text{ms}} \times \frac{10^{-3}\ \text{s}}{1\ \cancel{\text{ms}}} = 0.018\ \text{s}$ or $18\ \cancel{\text{ms}} \times \frac{1\ \text{s}}{1,000\ \cancel{\text{ms}}} = 0.018\ \text{s}$
Think about your result.	The amount in mL should be 1000 times larger than the given amount in L.	The amount in s should be 1/1000 the given amount in ms.

? Exercise 1.5.1

Perform each conversion.

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

Answer a:

$1.01000x10^{-4}s$

Answer b:

$3.208x10^{4}g$

Answer c:

$1.53x10^{2}cg$

Summary

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

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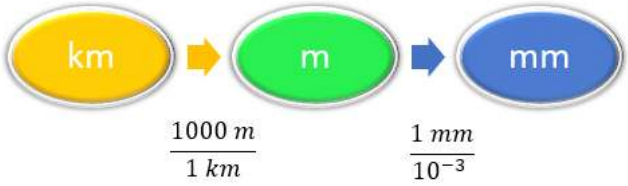
1.6: Solving Multistep Conversion Problems

Multiple Conversions

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

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

Concept Map



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

Calculation

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

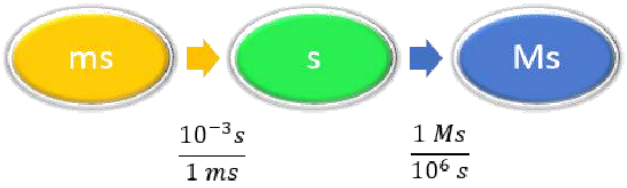
$$= 5.47 \times 10^{7}\ \text{mm}$$

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

Example 1.6.1: Unit Conversion

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

Solution

Steps for Problem Solving	Unit Conversion
Identify the "given" information and what the problem is asking you to "find."	Given: 58.2 ms Find: Ms
List other known quantities	$1ms = 10^{-3}s$ $1Ms = 10^{6}s$
Prepare a concept map.	 Convert milliseconds to seconds to microseconds: use conversion factors 0.001 second per millisecond and 1 microsecond per 1 million seconds
Calculate.	$58.2\ \cancel{ms} \times \frac{10^{-3}\ \cancel{s}}{1\ \cancel{ms}} \times \frac{1\ \text{Ms}}{1,000,000\ \cancel{s}} = 0.0000000582\ \text{Ms} = 5.82 \times 10^{-8}\ \text{Ms}$ Neither conversion factor affects the number of significant figures in the final answer.

Example 1.6.2: Unit Conversion

How many seconds are in a day?

Solution

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

Exercise 1.6.1

Perform each conversion in one multi-step calculation.

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

Answer a

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

Answer b

$83.75\ ft$

Answer c

$19\ km$

Career Focus: Pharmacist

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



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

Summary

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

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CHAPTER OVERVIEW

2: The Structure of Matter

2.1: Density
2.2: Classifying Matter According to Its Composition
2.3: Differences in Matter- Physical and Chemical Properties
2.4: Looking for Patterns - The Periodic Table
2.5: Cutting Alumimun until you get Atoms
2.6: Indivisible - The Atomic Theory
2.7: The Nuclear Atom
2.8: The Properties of Protons, Neutrons, and Electrons
2.9: Elements- Defined by Their Number of Protons
2.10: Isotopes - When the Number of Neutrons Varies
2.11: Atomic Mass- The Average Mass of an Element’s Atoms

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2.1: Density

Learning Objectives

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

Density (ρ) is a physical property found by dividing the mass of an object by its volume. Regardless of the sample size, density is always constant. For example, the density of a pure sample of tungsten is always 19.25 grams per cubic centimeter. This means that whether you have one gram or one kilogram of the sample, the density will never vary. The equation, as we already know, is as follows:

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

or just

$$\rho = \frac{m}{V} \tag{2.1.1}$$

Based on this equation, it's clear that density can, and does, vary from element to element and substance to substance due to differences in the relationship of mass and volume. Pure water, for example, has a density of 0.998 g/cm^3 at 25° C. The average densities of some common substances are in Table **2.1.1**. Notice that corn oil has a lower mass to volume ratio than water. This means that when added to water, corn oil will "float."

Table **2.1.1**: Densities of Common Substances

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

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

Example 2.1.1: Ethyl Alcohol

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

Solution

This is a direct application of Equation **2.1.1**:

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

? Exercise 2.1.1

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

Answer a

$0.274\ kg/L$

Answer b

$1.049\ kg/L$

Density as a Conversion Factor

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

13.6 g mercury = 1 mL mercury

This relationship can be used to construct two conversion factors:

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

and

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

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

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

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

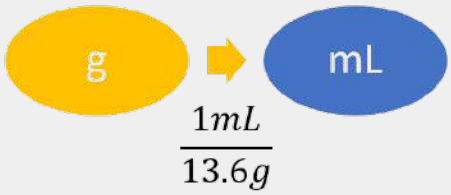
> *Density can be used as a conversion factor between mass and volume.*

✓ Example 2.1.2: Mercury Thermometer Steps for Problem Solving

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

Solution

Solution to Example 2.9.2

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

? Exercise 2.1.2

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

Answer

$77\ L$

Summary

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

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2.2: Classifying Matter According to Its Composition

Learning Objectives

- Explain the difference between a pure substance and a mixture.
- Explain the difference between an element and a compound.
- Explain the difference between a homogeneous mixture and a heterogeneous mixture.

One useful way of organizing our understanding of matter is to think of a hierarchy that extends down from the most general and complex to the simplest and most fundamental (Figure **2.2.1**). Matter can be classified into two broad categories: pure substances and mixtures. A **pure substance** is a form of matter that has a constant composition (meaning that it is the same everywhere) and properties that are constant throughout the sample (meaning that there is only one set of properties such as melting point, color, boiling point, etc. throughout the matter). A material composed of two or more substances is a **mixture**. Elements and compounds are both examples of pure substances. A substance that cannot be broken down into chemically simpler components is an **element**. Aluminum, which is used in soda cans, is an element. A substance that can be broken down into chemically simpler components (because it has more than one element) is a **compound**. For example, water is a compound composed of the elements hydrogen and oxygen. Today, there are about 118 elements in the known universe. In contrast, scientists have identified tens of millions of different compounds to date.

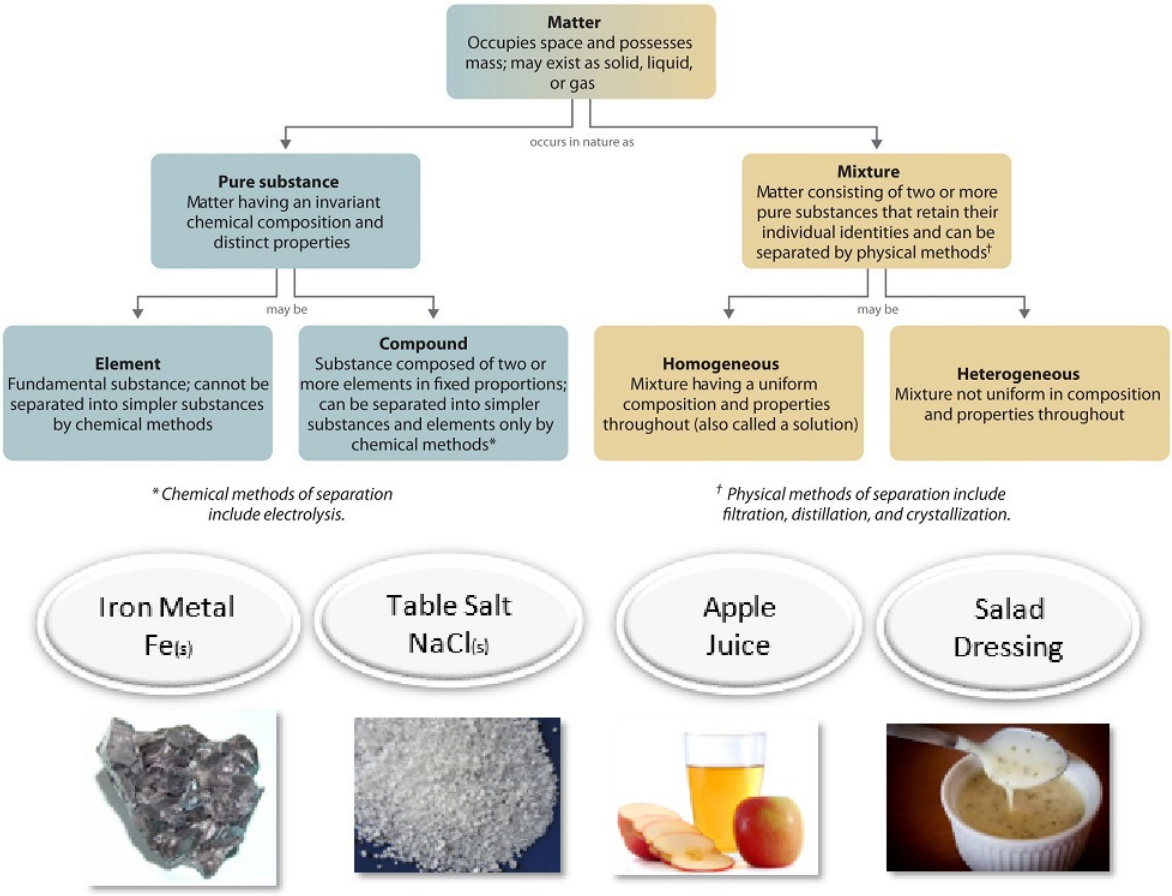


Figure **2.2.1**: Relationships between the Types of Matter and the Methods Used to Separate Mixtures

Ordinary table salt is called sodium chloride. It is considered a **substance** because it has a uniform and definite composition. All samples of sodium chloride are chemically identical. Water is also a pure substance. Salt easily dissolves in water, but salt water cannot be classified as a substance because its composition can vary. You may dissolve a small amount of salt or a large amount into a given amount of water. A mixture is a physical blend of two or more components, each of which retains its own identity and

properties in the **mixture**. Only the form of the salt is changed when it is dissolved into water. It retains its composition and properties.

A **homogeneous** mixture is a mixture in which the composition is uniform throughout the mixture. The salt water described above is homogeneous because the dissolved salt is evenly distributed throughout the entire salt water sample. Often it is easy to confuse a homogeneous mixture with a pure substance because they are both uniform. The difference is that the composition of the substance is always the same. The amount of salt in the salt water can vary from one sample to another. All solutions are considered homogeneous because the dissolved material is present in the same amount throughout the solution.

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

Phase

A phase is any part of a sample that has a uniform composition and properties. By definition, a pure substance or a homogeneous mixture consists of a single phase. A heterogeneous mixture consists of two or more phases. When oil and water are combined, they do not mix evenly, but instead form two separate layers. Each of the layers is called a phase.

Example 2.2.1

Identify each substance as a compound, an element, a heterogeneous mixture, or a homogeneous mixture (solution).

a. filtered tea
b. freshly squeezed orange juice
c. a compact disc
d. aluminum oxide, a white powder that contains a 2:3 ratio of aluminum and oxygen atoms
e. selenium

Given: a chemical substance

Asked for: its classification

Strategy:

A. Decide whether a substance is chemically pure. If it is pure, the substance is either an element or a compound. If a substance can be separated into its elements, it is a compound.
B. If a substance is not chemically pure, it is either a heterogeneous mixture or a homogeneous mixture. If its composition is uniform throughout, it is a homogeneous mixture.

Solution

a. **A)** Tea is a solution of compounds in water, so it is not chemically pure. It is usually separated from tea leaves by filtration.
B) Because the composition of the solution is uniform throughout, it is ***a homogeneous mixture***.
b. **A)** Orange juice contains particles of solid (pulp) as well as liquid; it is not chemically pure.
B) Because its composition is not uniform throughout, orange juice is ***a heterogeneous mixture***.
c. **A)** A compact disc is a solid material that contains more than one element, with regions of different compositions visible along its edge. Hence, a compact disc is not chemically pure.
B) The regions of different composition indicate that a compact disc is ***a heterogeneous mixture.***
d. **A)** Aluminum oxide is a single, chemically ***pure compound***.
e. **A)** Selenium is one of the known ***elements***.

Exercise 2.2.1

Identify each substance as a compound, an element, a heterogeneous mixture, or a homogeneous mixture (solution).

a. white wine
b. mercury
c. ranch-style salad dressing
d. table sugar (sucrose)

Answer a:
homogeneous mixture (solution)

Answer b:
element

Answer c:
heterogeneous mixture

Answer d:
compound

Example 2.2.2

How would a chemist categorize each example of matter?

a. saltwater
b. soil
c. water
d. oxygen

Solution

a. Saltwater acts as if it were a single substance even though it contains two substances—salt and water. Saltwater is a homogeneous mixture, or a solution.
b. Soil is composed of small pieces of a variety of materials, so it is a heterogeneous mixture.
c. Water is a substance. More specifically, because water is composed of hydrogen and oxygen, it is a compound.
d. Oxygen, a substance, is an element.

Exercise 2.2.2

How would a chemist categorize each example of matter?

a. coffee
b. hydrogen
c. an egg

Answer a:
a homogeneous mixture (solution), assuming it is filtered coffee

Answer b:
element

Answer c:
heterogeneous mixture

Summary

Matter can be classified into two broad categories: pure substances and mixtures. A pure substance is a form of matter that has a constant composition and properties that are constant throughout the sample. Mixtures are physical combinations of two or more

elements and/or compounds. Mixtures can be classified as homogeneous or heterogeneous. Elements and compounds are both examples of pure substances. Compounds are substances that are made up of more than one type of atom. Elements are the simplest substances made up of only one type of atom.

Vocabulary

- Element: a substance that is made up of only one type of atom.
- Compound:a substance that is made up of more than one type of atom bonded together.
- Mixture: a combination of two or more elements or compounds which have not reacted to bond together; each part in the mixture retains its own properties.

Contributions & Attributions

-
- Stephen Lower, Professor Emeritus (Simon Fraser U.) Chem1 Virtual Textbook

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2.3: Differences in Matter- Physical and Chemical Properties

Learning Objectives

To separate physical from chemical properties.

All matter has physical and chemical properties. Physical properties are characteristics that scientists can measure without changing the composition of the sample under study, such as mass, color, and volume (the amount of space occupied by a sample). Chemical properties describe the characteristic ability of a substance to react to form new substances; they include its flammability and susceptibility to corrosion. All samples of a pure substance have the same chemical and physical properties. For example, pure copper is always a reddish-brown solid (a physical property) and always dissolves in dilute nitric acid to produce a blue solution and a brown gas (a chemical property).

Physical Property

A *physical property* is a characteristic of a substance that can be observed or measured without changing the identity of the substance. Silver is a shiny metal that conducts electricity very well. It can be molded into thin sheets, a property called malleability. Salt is dull and brittle and conducts electricity when it has been dissolved into water, which it does quite easily. Physical properties of matter include color, hardness, malleability, solubility, electrical conductivity, density, melting point, and boiling point.

For the elements, color does not vary much from one element to the next. The vast majority of elements are colorless, silver, or gray. Some elements do have distinctive colors: sulfur and chlorine are yellow, copper is (of course) copper-colored, and elemental bromine is red. However, density can be a very useful parameter for identifying an element. Of the materials that exist as solids at room temperature, iodine has a very low density compared to zinc, chromium, and tin. Gold has a very high density, as does platinum. Pure water, for example, has a density of 0.998 g/cm^3 at 25°C. The average densities of some common substances are in Table **2.3.1**. Notice that corn oil has a lower mass to volume ratio than water. This means that when added to water, corn oil will "float."

Table **2.3.1**: Densities of Common Substances

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

Hardness helps determine how an element (especially a metal) might be used. Many elements are fairly soft (silver and gold, for example) while others (such as titanium, tungsten, and chromium) are much harder. Carbon is an interesting example of hardness. In graphite, (the "lead" found in pencils) the carbon is very soft, while the carbon in a diamond is roughly seven times as hard.



Figure **2.3.1**: Pencil (left) and Diamond ring (right). Both are a form of carbon, but exhibit very different physical properties.

Melting and boiling points are somewhat unique identifiers, especially of compounds. In addition to giving some idea as to the identity of the compound, important information can be obtained about the purity of the material.

Chemical Properties

Chemical properties of matter describe its potential to undergo some chemical change or reaction by virtue of its composition. The elements, electrons, and bonds that are present give the matter potential for chemical change. It is quite difficult to define a chemical property without using the word "change". Eventually, after studying chemistry for some time, you should be able to look at the formula of a compound and state some chemical property. For example, hydrogen has the potential to ignite and explode given the right conditions—this is a chemical property. Metals in general have the chemical property of reacting with an acid. Zinc reacts with hydrochloric acid to produce hydrogen gas—this is a chemical property.



Figure **2.3.2**: Heavy rust on the links of a chain near the Golden Gate Bridge in San Francisco; it was continuously exposed to moisture and salt spray, causing surface breakdown, cracking, and flaking of the metal. (CC BY-SA 3.0; Marlith).

A chemical property of iron is its capability of combining with oxygen to form iron oxide, the chemical name of rust (Figure **2.3.2**). The more general term for rusting and other similar processes is corrosion. Other terms that are commonly used in descriptions of chemical changes are burn, rot, explode, decompose, and ferment. Chemical properties are very useful in identifying substances. However, unlike physical properties, chemical properties can only be observed as the substance is in the process of being changed into a different substance.

Table **2.3.2**: Contrasting Physical and Chemical Properties

Physical Properties	Chemical Properties
Gallium metal melts at 30 ^{o}C.	Iron metal rusts.
Mercury is a very dense liquid.	A green banana turns yellow when it ripens.
Gold is shiny.	A dry piece of paper burns.

Example 2.3.1

Which of the following is a chemical property of iron?

a. Iron corrodes in moist air.
b. Density = 7.874 g/cm^3
c. Iron is soft when pure.
d. Iron melts at 1808 K.

Solution

"Iron corrodes in moist air" is the only chemical property of iron from the list.

Exercise 2.3.1*A*

Which of the following is a physical property of matter?

a. corrosiveness
b. pH (acidity)
c. density
d. flammability

Answer

c

Exercise 2.3.1*B*

Which of the following is a chemical property?

a. flammability
b. melting point
c. boiling point
d. density

Answer

a

Summary

A physical property is a characteristic of a substance that can be observed or measured without changing the identity of the substance. Physical properties include color, density, hardness, and melting and boiling points. A chemical property describes the ability of a substance to undergo a specific chemical change. To identify a chemical property, we look for a chemical change. A chemical change always produces one or more types of matter that differ from the matter present before the change. The formation of rust is a chemical change because rust is a different kind of matter than the iron, oxygen, and water present before the rust formed.

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2.4: Looking for Patterns - The Periodic Table

Learning Objectives

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

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

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

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

The periodic table is one of the cornerstones of chemistry because it organizes all of the known elements on the basis of their chemical properties. A modern version is shown in Figure **2.4.1**. Most periodic tables provide additional data (such as atomic mass) in a box that contains each element's symbol. The elements are listed in order of atomic number.

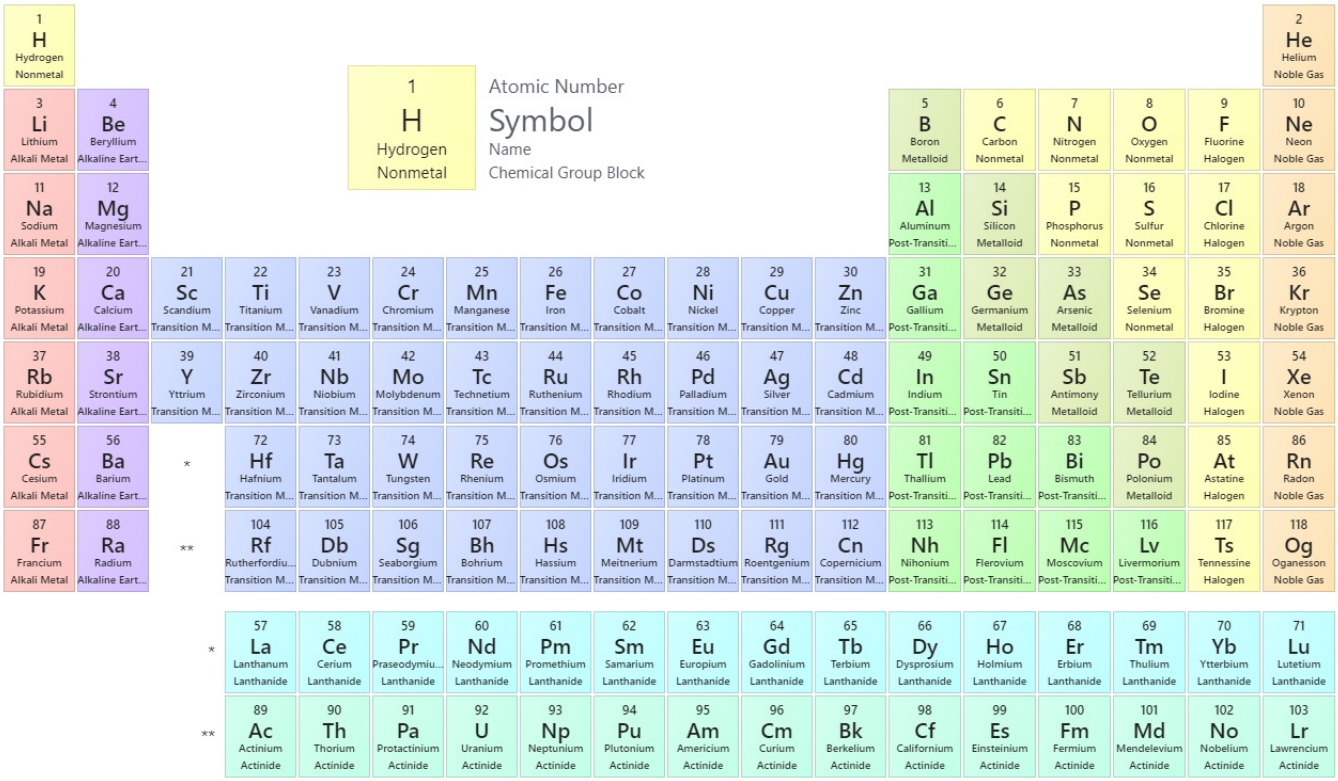


Figure **2.4.1**: A Modern Periodic Table. A modern periodic table lists elements left to right by atomic number. An interactive Periodic table can be found Periodic Table of Elements. (Public Domain; PubChem via NIH)

Features of the Periodic Table

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

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

To Your Health: Radon

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

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

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

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

Certain elemental properties become apparent in a survey of the periodic table as a whole. Every element can be classified as either a metal, a nonmetal, or a metalloid (or semi metal), as shown in Figure **2.4.2**. A **metal** is a substance that is shiny, typically (but not always) silvery in color, and an excellent conductor of electricity and heat. Metals are also malleable (they can be beaten into thin sheets) and ductile (they can be drawn into thin wires). A **nonmetal** is typically dull and a poor conductor of electricity and heat. Solid nonmetals are also very brittle. As shown in Figure **2.4.2**, metals occupy the left three-fourths of the periodic table, while nonmetals (except for hydrogen) are clustered in the upper right-hand corner of the periodic table. The elements with properties intermediate between those of metals and nonmetals are called **metalloids** (or **semi-metals**). Elements adjacent to the bold line in the right-hand portion of the periodic table have semimetal properties.

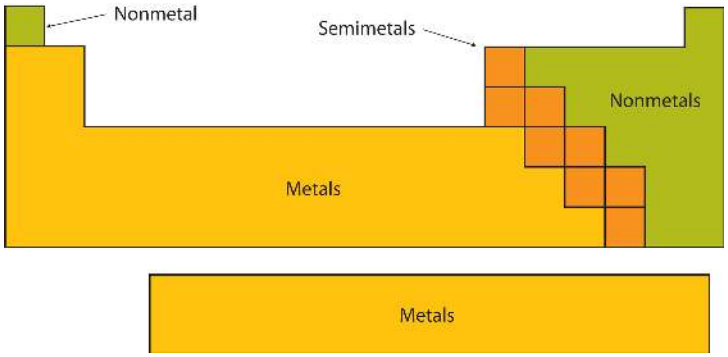


Figure **2.4.2**: Types of Elements. Elements are either metals, nonmetals, or metalloids (or semi metals). Each group is located in a different part of the periodic table. (CC BY-NC-SA; Anonymous by request)

Example 2.4.1

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

a. Se
b. Mg
c. Ge

Solution

a. In Figure **2.4.1**, selenium lies above and to the right of the diagonal line marking the boundary between metals and nonmetals, so it should be a nonmetal.
b. Magnesium lies to the left of the diagonal line marking the boundary between metals and nonmetals, so it should be a metal.
c. Germanium lies within the diagonal line marking the boundary between metals and nonmetals, so it should be a metalloid.

Exercise 2.4.1

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

Answer

Indium is a metal.

Another way to categorize the elements of the periodic table is shown in Figure **2.4.3**. The first two columns on the left and the last six columns on the right are called the main group elements. The ten-column block between these columns contains the **transition metals**. The two rows beneath the main body of the periodic table contain the **inner transition metals**. The elements in these two rows are also referred to as, respectively, the **lanthanide metals** and the **actinide metals**.

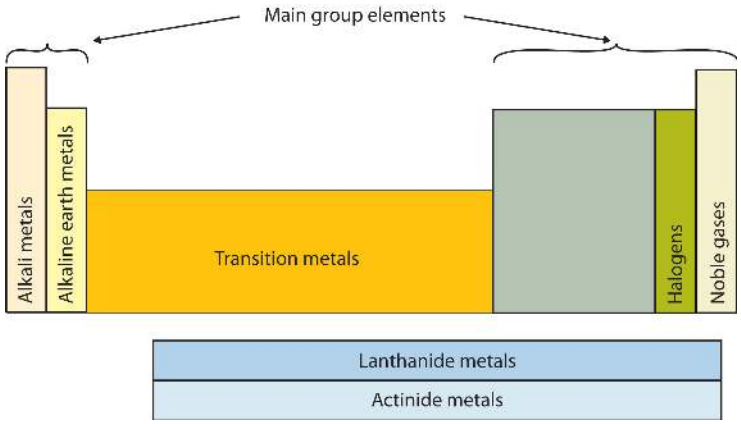


Figure **2.4.3**: Special Names for Sections of the Periodic Table. (CC BY-NC-SA; Anonymous by request)

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

Descriptive Names

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

Group 1: The Alkali Metals

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

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



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

Group 2: The Alkaline Earth Metals

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

Group 17: The Halogens

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

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

Group 18: The Noble Gases

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

Example 2.4.2: Groups

Provide the family or group name of each element.

a. Li
b. Ar
c. Cl

Solution

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

? Exercise 2.4.2: Groups

Provide the family or group name of each element.

a. F
b. Ca
c. Kr

Answer a:

Fluorine is a halogen (Group 17).

Answer b:

Calcium is a alkaline earth metal (Group 2).

Answer c:

Krypton is a noble gas (Group 18).

✓ Example 2.4.3: Classification of Elements

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

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

Solution

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

? Exercise 2.4.3: Classification of Elements

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

a. F
b. U
c. Cu

Answer a:

Fluorine is a nonmetal.

Answer b:

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

Answer c:

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

Summary

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

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

References

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2.5: Cutting Alumimun until you get Atoms

Take some aluminum foil. Cut it in half. Now there are two smaller pieces of aluminum foil. Cut one of the pieces in half again. Cut one of those smaller pieces in half again. Continue cutting, making smaller and smaller pieces of aluminum foil. It should be obvious that the pieces are still aluminum foil; they are just becoming smaller and smaller. But how far can this exercise be taken, at least in theory? Can one continue cutting the aluminum foil into halves forever, making smaller and smaller pieces? Or is there some limit, some absolute smallest piece of aluminum foil? Thought experiments like this—and the conclusions based on them—were debated as far back as the fifth century BC by Democritus and other ancient Greek philosophers (Figure **2.5.1**).

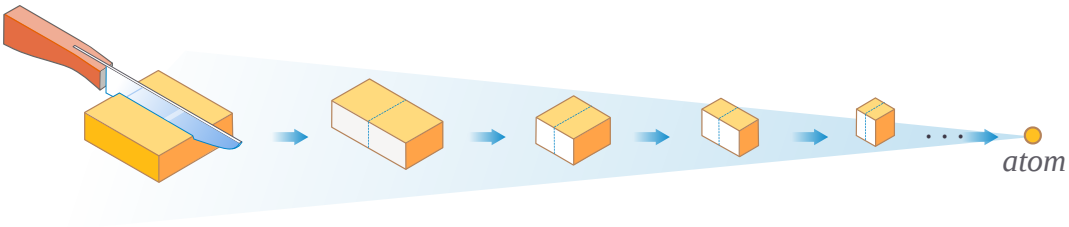


Figure **2.5.1**: Democritus argued that matter, like an aluminum block, cannot be repeatedly cut in half perpetually. At some point, a limit is reached before the substance can no longer be called "aluminum"; this is the atomic limit. (CC BY-NC; Ümit Kaya via LibreTexts)

Most elements in their pure form exist as individual atoms. For example, a macroscopic chunk of iron metal is composed, microscopically, of individual atoms. Some elements, however, exist as groups of atoms called molecules. Several important elements exist as two-atom combinations and are called diatomic molecules. In representing a diatomic molecule, we use the symbol of the element and include the subscript 2 to indicate that two atoms of that element are joined together. The elements that exist as diatomic molecules are hydrogen (H_2), oxygen (O_2), nitrogen (N_2), fluorine (F_2), chlorine (Cl_2), bromine (Br_2), and iodine (I_2).

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2.6: Indivisible - The Atomic Theory

Learning Objectives

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

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

Democritus and the Greek Philosophers

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



Figure **2.6.1**: (left) Democritus by Hendrick ter Brugghen, 1628. Democritus was known as the "laughing philosopher." It was a good thing he liked to laugh, because most other philosophers were laughing at his theories. (right) British physicist and chemist John Dalton (1766-1844). Unlike the Greek philosophers, John Dalton believed in both logical thinking and experimentation.

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

The early Greek philosophers tried to understand the nature of the world through reason and logic, but not through experiment and observation. As a result, they had some very interesting ideas, but they felt no need to justify their ideas based on life experiences. In a lot of ways, you can think of the Greek philosophers as being "all thought and no action." It's truly amazing how much they achieved using their minds, but because they never performed any experiments, they missed or rejected a lot of discoveries that they could have made otherwise. Greek philosophers dismissed Democritus' theory entirely. Sadly, it took over two millennia before the theory of atomos (or "atoms," as they are known today) was fully appreciated.

Greeks: "All Thought and No Action"

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

While it must be assumed that many more scientists, philosophers, and others studied composition of matter after Democritus, a major leap forward in our understanding of the composition of matter took place in the 1800's with the work of the British

scientists John Dalton. He started teaching school at age twelve, and was primarily known as a teacher. In his twenties, he moved to the growing city of Manchester, where he was able to pursue some scientific studies. His work in several areas of science brought him a number of honors. When he died, over 40,000 people in Manchester marched at his funeral.

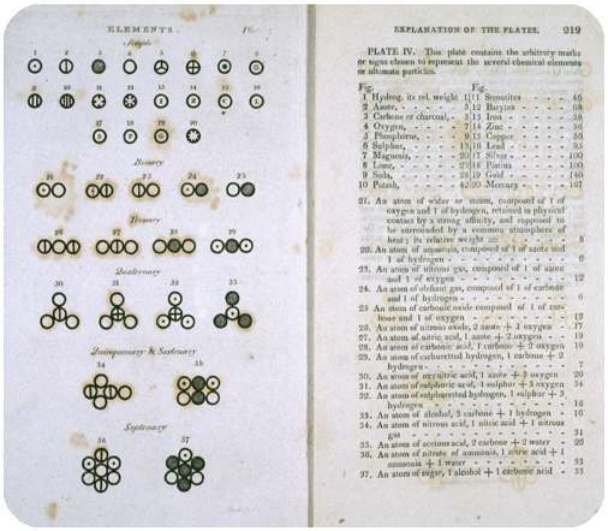
The modern atomic theory, proposed about 1803 by the English chemist John Dalton (Figure **2.6.1**), is a fundamental concept that states that all elements are composed of atoms. Previously, we defined an atom as the smallest part of an element that maintains the identity of that element. Individual atoms are extremely small; even the largest atom has an approximate diameter of only 5.4×10^{-10} m. With that size, it takes over 18 million of these atoms, lined up side by side, to equal the width of your little finger (about 1 cm).

Dalton studied the weights of various elements and compounds. He noticed that matter always combined in fixed ratios based on weight, or volume in the case of gases. Chemical compounds always contain the same proportion of elements by mass, regardless of amount, which provided further support for Proust's law of definite proportions. Dalton also observed that there could be more than one combination of two elements.

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

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

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


ELEMENTS. PL.

EXPLANATION OF THE PLATES. 219

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

Figure **2.6.2**: Dalton's symbols from his text "A New System of Chemical Philosophy."

The evidence for atoms is so great that few doubt their existence. In fact, individual atoms are now routinely observed with state-of-the art technologies. Moreover, they can even be used for making pretty images; or as IBM research demonstrates in Video **2.6.1**, control of individual atoms can be use used create animations.



Video **2.6.1**: A Boy And His Atom: The World's Smallest Movie.

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

Summary

- 2,500 years ago, Democritus suggested that all matter in the universe was made up of tiny, indivisible, solid objects he called "atomos." However, other Greek philosophers disliked Democritus' "atomos" theory because they felt it was illogical.
- Dalton's Atomic Theory is the first scientific theory to relate chemical changes to the structure, properties, and behavior of the atom. The general tenets of this theory are:
  - All matter is composed of extremely small particles called atoms.
  - Atoms of a given element are identical in size, mass, and other properties. Atoms of different elements differ in size, mass, and other properties.
  - Atoms cannot be subdivided, created, or destroyed.
  - Atoms of different elements can combine in simple whole number ratios to form chemical compounds.
  - In chemical reactions, atoms are combined, separated, or rearranged.

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2.7: The Nuclear Atom

Learning Objectives

- Explain the observations that led to Thomson's discovery of the electron.
- Describe Thomson's "plum pudding" model of the atom and the evidence for it.
- Draw a diagram of Thomson's "plum pudding" model of the atom and explain why it has this name.
- Describe Rutherford's gold foil experiment and explain how this experiment altered the "plum pudding" model.
- Draw a diagram of the Rutherford model of the atom and label the nucleus and the electron cloud.

Dalton's Atomic Theory held up well to a lot of the different chemical experiments that scientists performed to test it. In fact, for almost 100 years, it seemed as if Dalton's Atomic Theory was the whole truth. However, in 1897, a scientist named J. J. Thomson conducted some research that suggested that Dalton's Atomic Theory was not the entire story. He suggested that the small, negatively charged particles making up the cathode ray were actually pieces of atoms. He called these pieces "corpuscles," although today we know them as **electrons**. Thanks to his clever experiments and careful reasoning, J. J. Thomson is credited with the discovery of the electron.



Figure **2.7.1**: J. J. Thomson (center) concluded experiments that suggested that Dalton's (left) atomic theory was not telling the entire story. Ernest Rutherford (right) later built on Thomson's work to argue for the model nuclear atom.

Electrons and Plums

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

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

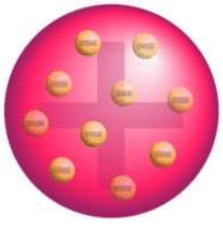


Figure **2.7.2**: The "plum pudding" model.

However, this model of the atom soon gave way to a new model developed by New Zealander Ernest Rutherford (1871-1937) about five years later. Thomson did still receive many honors during his lifetime, including being awarded the Nobel Prize in Physics in 1906 and a knighthood in 1908.

Atoms and Gold

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

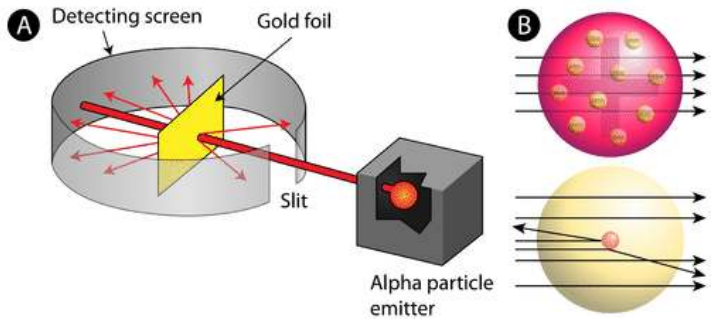


Figure **2.7.3**: (A) The experimental setup for Rutherford's gold foil experiment: A radioactive element that emitted alpha particles was directed toward a thin sheet of gold foil that was surrounded by a screen which would allow detection of the deflected particles. (B) According to the plum pudding model (top), all of the alpha particles should have passed through the gold foil with little or no deflection. Rutherford found that a small percentage of alpha particles were deflected at large angles, which could be explained by an atom with a very small, dense, positively-charged nucleus at its center (bottom).

According to the accepted atomic model, in which an atom's mass and charge are uniformly distributed throughout the atom, the scientists expected that all of the alpha particles would pass through the gold foil with only a slight deflection or none at all. Surprisingly, while most of the alpha particles were indeed not deflected, a very small percentage (about 1 in 8000 particles) bounced off the gold foil at very large angles. Some were even redirected back toward the source. No prior knowledge had prepared them for this discovery. In a famous quote, Rutherford exclaimed that it was "as if you had fired a 15-inch [artillery] shell at a piece of tissue and it came back and hit you."

Rutherford needed to come up with an entirely new model of the atom in order to explain his results. Because the vast majority of the alpha particles had passed through the gold, he reasoned that most of the atom was empty space. In contrast, the particles that were highly deflected must have experienced a tremendously powerful force within the atom. He concluded that all of the positive charge and the majority of the mass of the atom must be concentrated in a very small space in the atom's interior, which he called the nucleus. The **nucleus** is the tiny, dense, central core of the atom and is composed of protons and neutrons.

Rutherford's atomic model became known as the **nuclear model**. In the nuclear atom, the protons and neutrons, which comprise nearly all of the mass of the atom, are located in the nucleus at the center of the atom. The electrons are distributed around the nucleus and occupy most of the volume of the atom. It is worth emphasizing just how small the nucleus is compared to the rest of the atom. If we could blow up an atom to be the size of a large professional football stadium, the nucleus would be about the size of a marble.

Rutherford's model proved to be an important step towards a full understanding of the atom. However, it did not completely address the nature of the electrons and the way in which they occupy the vast space around the nucleus. It was not until some years later that a full understanding of the electron was achieved. This proved to be the key to understanding the chemical properties of elements.

Atomic Nucleus

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

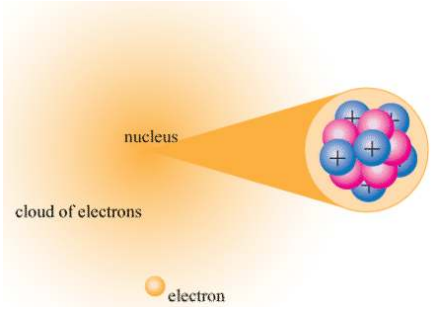


Figure **2.7.4**: The nuclear atom.

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

Holding it all Together

Particles with opposite electric charges attract each other. This explains why negative electrons orbit the positive nucleus. Particles with the same electric charge repel each other. This means that the positive protons in the nucleus push apart from one another. So why doesn't the nucleus fly apart? An even stronger force—called the **strong nuclear force**—holds protons and neutrons together in the nucleus.

Summary

- Atoms are the ultimate building blocks of all matter.
- The modern atomic theory establishes the concepts of atoms and how they compose matter.
- Bombardment of gold foil with alpha particles showed that some particles were deflected.
- The nuclear model of the atom consists of a small and dense positively charged interior surrounded by a cloud of electrons.

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2.8: The Properties of Protons, Neutrons, and Electrons

Learning Objectives

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

Dalton's Atomic Theory explained a lot about matter, chemicals, and chemical reactions. Nevertheless, it was not entirely accurate, because contrary to what Dalton believed, atoms can, in fact, be broken apart into smaller subunits or subatomic particles. We have been talking about the electron in great detail, but there are two other particles of interest to us: protons and neutrons. We already learned that J. J. Thomson discovered a negatively charged particle, called the **electron**. Rutherford proposed that these electrons orbit a positive nucleus. In subsequent experiments, he found that there is a smaller positively charged particle in the nucleus, called a **proton**. There is also a third subatomic particle, known as a neutron.

Electrons

Electrons are one of three main types of particles that make up atoms. Unlike protons and neutrons, which consist of smaller, simpler particles, electrons are fundamental particles that do not consist of smaller particles. They are a type of fundamental particle called leptons. All leptons have an electric charge of -1 or 0. Electrons are extremely small. The mass of an electron is only about 1/2000 the mass of a proton or neutron, so electrons contribute virtually nothing to the total mass of an atom. Electrons have an electric charge of -1, which is equal but opposite to the charge of a proton, which is $+1$. All atoms have the same number of electrons as protons, so the positive and negative charges "cancel out", making atoms electrically neutral.

Unlike protons and neutrons, which are located inside the nucleus at the center of the atom, electrons are found outside the nucleus. Because opposite electric charges attract one another, negative electrons are attracted to the positive nucleus. This force of attraction keeps electrons constantly moving through the otherwise empty space around the nucleus. The figure below is a common way to represent the structure of an atom. It shows the electron as a particle orbiting the nucleus, similar to the way that planets orbit the sun. However, this is an incorrect perspective, as quantum mechanics demonstrates that electrons are more complicated.



Figure **2.8.1**: Electrons are much smaller than protons or neutrons. If an electron was the mass of a penny, a proton or a neutron would have the mass of a large bowling ball!

Protons

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

Neutrons

Atoms of all elements—except for most atoms of hydrogen—have neutrons in their nucleus. Unlike protons and electrons, which are electrically charged, neutrons have no charge—they are electrically neutral. That's why the neutrons in the diagram above are labeled n^0. The zero stands for "zero charge". The mass of a neutron is slightly greater than the mass of a proton, which is 1 atomic

mass unit (amu). (An atomic mass unit equals about 1.67×10^{-27} kilograms.) A neutron also has about the same diameter as a proton, or 1.7×10^{-15} meters.

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

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

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

Table 2.8.1: Properties of Subatomic Particles

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

Table 2.8.1 gives the properties and locations of electrons, protons, and neutrons. The third column shows the masses of the three subatomic particles in "atomic mass units." An **atomic mass unit (amu)** is defined as one-twelfth of the mass of a carbon-12 atom. Atomic mass units (amu) are useful, because, as you can see, the mass of a proton and the mass of a neutron are almost exactly 1 in this unit system.

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

Summary

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

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2.9: Elements- Defined by Their Number of Protons

Learning Objectives

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

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



Figure **2.9.1**: It is difficult to find qualities that differ between each element, and to distinguish one element from another. Each element, however, does have a unique number of protons. Sulfur has 16 protons, silicon has 14 protons, and gold has 79 protons. Images used with permission (public domain for sulfur and silicon, gold is licensed by CC-BY-SA-NC-ND; Alchemist-hp).

Atomic Number

Scientists distinguish between different elements by counting the number of protons in the nucleus (Table **2.9.1**). If an atom has only one proton, we know that it's a hydrogen atom. An atom with two protons is always a helium atom. If scientists count four protons in an atom, they know it's a beryllium atom. An atom with three protons is a lithium atom, an atom with five protons is a boron atom, an atom with six protons is a carbon atom . . . the list goes on.

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

Table **2.9.1**: Atoms of the First Six Elements

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

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

Neutral Atoms

Atoms are neutral in electrical charge because they have the same number of negative electrons as positive protons (Table 2.9.1). Therefore, the atomic number of an atom also tells you how many electrons the atom has. This, in turn, determines many of the atom's chemical properties.

Mass Number

The **mass number** (A) of an atom is the total number of protons and neutrons in its nucleus. The mass of the atom is a unit called the atomic mass unit (amu). One atomic mass unit is the mass of a proton, or about 1.67×10^{-27} kilograms, which is an extremely small mass. A neutron has just a tiny bit more mass than a proton, but its mass is often assumed to be one atomic mass unit as well. Because electrons have virtually no mass, just about all the mass of an atom is in its protons and neutrons. Therefore, the total number of protons and neutrons in an atom determines its mass in atomic mass units (Table 2.9.1).

Consider helium again. Most helium atoms have two neutrons in addition to two protons. Therefore the mass of most helium atoms is 4 atomic mass units (2 amu for the protons + 2 amu for the neutrons). However, some helium atoms have more or less than two neutrons. Atoms with the same number of protons but different numbers of neutrons are called isotopes. Because the number of neutrons can vary for a given element, the mass numbers of different atoms of an element may also vary. For example, some helium atoms have three neutrons instead of two (these are called isotopes and are discussed in detail later on).

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

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

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

Example 4.5.1

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

Solution

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

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

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

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

A **chemical symbol** is a one- or two-letter designation of an element. Some examples of chemical symbols are **O** for oxygen, **Zn** for zinc, and **Fe** for iron. The first letter of a symbol is always capitalized. If the symbol contains two letters, the second letter is lower case. The majority of elements have symbols that are based on their English names. However, some of the elements that have been known since ancient times have maintained symbols that are based on their Latin names, as shown in Table 2.9.2.

Table 2.9.2: *Symbols and Latin Names for Elements*

Chemical Symbol	Name	Latin Name
Na	Sodium	Natrium
K	Potassium	Kalium
Fe	Iron	Ferrum
Cu	Copper	Cuprum
Ag	Silver	Argentum
Sn	Tin	Stannum
Sb	Antimony	Stibium
Au	Gold	Aurum
Pb	Lead	Plumbum

Summary

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

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2.10: Isotopes - When the Number of Neutrons Varies

Learning Objectives

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

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

An Example: Hydrogen Isotopes

Hydrogen is an example of an element that has isotopes. Three isotopes of hydrogen are modeled in Figure **2.10.1**. Most hydrogen atoms have just one proton, one electron, and lack a neutron. These atoms are just called hydrogen. Some hydrogen atoms have one neutron as well. These atoms are the isotope named deuterium. Other hydrogen atoms have two neutrons. These atoms are the isotope named tritium.

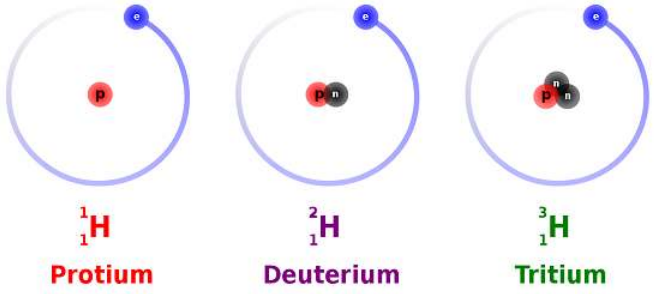


Figure **2.10.1**: The three most stable isotopes of hydrogen: protium (A = 1), deuterium (A = 2), and tritium (A = 3). (CC SA-BY 3.0; Balajijagadesh via Wikipedia).

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

Example 2.10.1: Lithium Isotopes

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

Solution

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

a.

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

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

b.

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

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

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

Stability of Isotopes

Atoms need a certain ratio of neutrons to protons to have a stable nucleus. Having too many or too few neutrons relative to protons results in an unstable, or radioactive, nucleus that will sooner or later break down to a more stable form. This process is called radioactive decay. Many isotopes have radioactive nuclei, and these isotopes are referred to as radioisotopes. When they decay, they release particles that may be harmful. This is why radioactive isotopes are dangerous and why working with them requires special suits for protection. The isotope of carbon known as carbon-14 is an example of a radioisotope. In contrast, the carbon isotopes called carbon-12 and carbon-13 are stable.

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

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

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

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



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

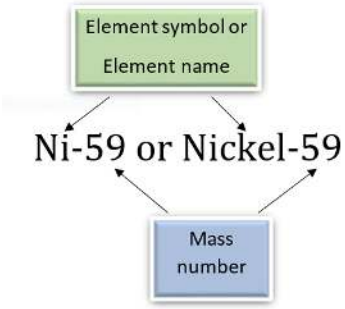
The following nuclear symbols are for a nickel nucleus with 31 neutrons and a uranium nucleus with 146 neutrons.

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

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

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

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



Example 2.10.2: Potassium-40

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

Solution

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

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

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

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

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

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

Example 2.10.3: Zinc-65

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

Solution

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

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

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

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

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

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

Exercise 2.10.3

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

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

Answer a:

27 protons, 27 electrons, 33 neutrons

Answer b:

11 protons, 11 electrons, 13 neutrons

Answer c:

20 protons, 20 electrons, 25 neutrons

Answer d:

38 protons, 38 electrons, 52 neutrons

Summary

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

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2.11: Atomic Mass- The Average Mass of an Element's Atoms

Learning Objectives

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

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

Calculating Atomic Mass

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

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

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

Example 2.11.1: Boron Isotopes

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

Solution

Boron has two isotopes. We will use the equation:

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

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

Substitute these into the equation, and we get:

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

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

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

Example 2.11.2: Neon Isotopes

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

Solution

Neon has three isotopes. We will use the equation:

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

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

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

Substitute these into the equation, and we get:

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

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

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

The periodic table gives the atomic mass of each element. The atomic mass is a number that usually appears below the element's symbol in each square. Notice that the atomic mass of boron (symbol B) is 10.8, which is what we calculated in Example **2.11.1**, and the atomic mass of neon (symbol Ne) is 20.8, which is what we calculated in Example **2.11.2**. Take time to notice that not all periodic tables have the atomic number above the element's symbol and the mass number below it. If you are ever confused, remember that the atomic number should always be the smaller of the two and will be a whole number, while the atomic mass should always be the larger of the two and will be a decimal number.

? Exercise 2.11.1

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

Answer

35.45 amu

Summary

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

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CHAPTER OVERVIEW

3: The Structure of Atoms

3.1: Prelude to Electronic Structure
3.2: Light
3.3: Quantum Numbers for Electrons
3.4: Organization of Electrons in Atoms
3.5: Electronic Structure and the Periodic Table
3.6: Electronic Structure and the Periodic Table
3.7: Periodic Trends

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3.1: Prelude to Electronic Structure

Normal light microscopes can magnify objects up to about 1,500 times. Electron microscopes can magnify objects up to 1,000,000 times. Why can electron microscopes magnify images so much? A microscope's resolution depends on the wavelength of light used. The smaller the wavelength, the more a microscope can magnify. Light is a wave, and as such, it has a wavelength associated with it. The wavelength of visible light, which is detected by the eyes, varies from about 700 nm to about 400 nm.

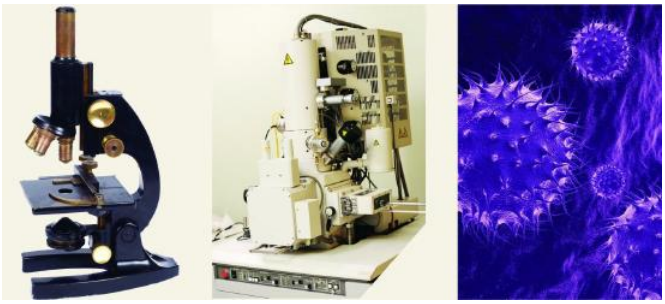


Figure **3.1.1** Microscopes © Thinkstock (a) A simple light microscope can magnify up to 1,500 times. (b) An electron microscope can magnify up to 1,000,000 times. (c) Flu viruses imaged by an electron microscope. The virus is about 100 nm in diameter.

A startling conclusions of modern science is that electrons also act as waves. However, the wavelength of electrons is much, much shorter—about 0.5 to 1 nm. This allows electron microscopes to magnify 600–700 times more than light microscopes. This allows us to see even smaller features in a world that is invisible to the naked eye.

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3.2: Light

Learning Objectives

- Describe light with its frequency and wavelength.
- Describe light as a particle of energy.

What is known as light is more properly called *electromagnetic radiation*. We know from experiments that light acts as a wave. As such, it can be described as having a frequency and a wavelength. The **wavelength** of light is the distance between corresponding points in two adjacent light cycles, and the **frequency** of light is the number of cycles of light that pass a given point in one second. Wavelength is typically represented by λ, the lowercase Greek letter *lambda*, while frequency is represented by ν, the lowercase Greek letter *nu* (although it looks like a Roman "vee," it is actually the Greek equivalent of the letter "en"). Wavelength has units of length (meters, centimeters, etc.), while frequency has units of *per second*, written as s^{-1} and sometimes called a *hertz* (Hz). Figure 3.2.1 - Characteristics of Light Waves, shows how these two characteristics are defined.

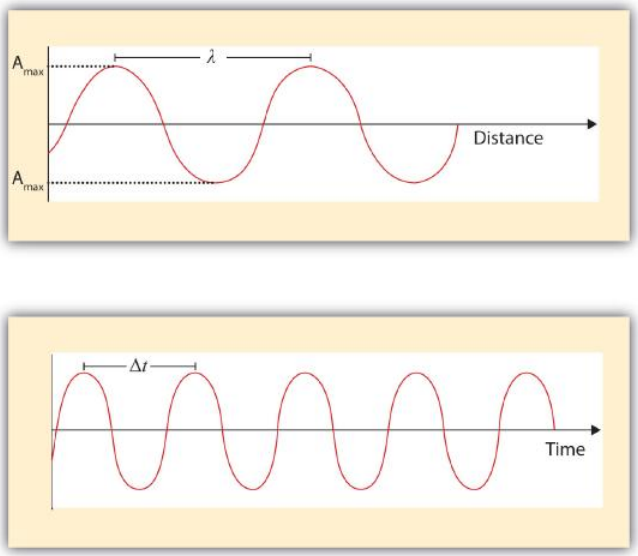


Figure 3.2.1: Characteristics of Light Waves. Light acts as a wave and can be described by a wavelength λ and a frequency ν.

One property of waves is that their speed is equal to their wavelength times their frequency. That means we have

$$speed = \lambda\nu$$

For light, however, speed is actually a universal constant when light is traveling through a vacuum (or, to a very good approximation, air). The measured speed of light (c) in a vacuum is 2.9979×10^8 m/s, or about 3.00×10^8 m/s. Thus, we have

$$c = \lambda\nu$$

Because the speed of light is a constant, the wavelength and the frequency of light are related to each other: as one increases, the other decreases and vice versa. We can use this equation to calculate what one property of light has to be when given the other property.

Example 3.2.1

What is the frequency of light if its wavelength is 5.55×10^{-7} m?

Solution

We use the equation that relates the wavelength and frequency of light with its speed. We have

$$3.00 \times 10^8 m/s = \left(5.55 \times 10^{-7} m\right) \nu$$

We divide both sides of the equation by 5.55×10^{-7} m and get

$$\nu = 5.41 \times 10^{14} s^{-1}$$

Note how the m units cancel, leaving s in the denominator. A unit in a denominator is indicated by a −1 power, s^{-1}, and read as "per second."

? Exercise 3.2.1

What is the wavelength of light if its frequency is 1.55×10^{10} s^{-1}?

Answer

0.0194 m, or 19.4 mm

Light also behaves like a package of energy. It turns out that for light, the energy of the "package" of energy is proportional to its frequency. (For most waves, energy is proportional to wave amplitude, or the height of the wave.) The mathematical equation that relates the energy (E) of light to its frequency is

$$E = h\nu$$

where ν is the frequency of the light, and h is a constant called Planck's constant. Its value is 6.626×10^{-34} J·s—a very small number that is another fundamental constant of our universe, like the speed of light. The units on Planck's constant may look unusual, but these units are required so that the algebra works out.

✓ Example 3.2.2

What is the energy of light if its frequency is 1.55×10^{10} s^{-1}?

Solution

Using the formula for the energy of light, we have

$E = (6.626 \times 10^{-34}$ J·s$)(1.55 \times 10^{10}$ $s^{-1})$

Seconds are in the numerator and the denominator, so they cancel, leaving us with joules, the unit of energy. So

$E = 1.03 \times 10^{-23}$ J

This is an extremely small amount of energy—but this is for only one light wave.

? Exercise 3.2.2

What is the frequency of a light wave if its energy is 4.156×10^{-20} J?

Answer

6.27×10^{13} s^{-1}

Because a light wave behaves like a little particle of energy, light waves have a particle-type name: the photon. It is not uncommon to hear light described as photons.

Wavelengths, frequencies, and energies of light span a wide range; the entire range of possible values for light is called the **electromagnetic spectrum**. We are mostly familiar with visible light, which is light having a wavelength range between about 400 nm and 700 nm. Light can have much longer and much shorter wavelengths than this, with corresponding variations in frequency and energy. Figure **3.2.2** shows the entire electromagnetic spectrum and how certain regions of the spectrum are labeled. You may already be familiar with some of these regions; they are all light—with different frequencies, wavelengths, and energies.

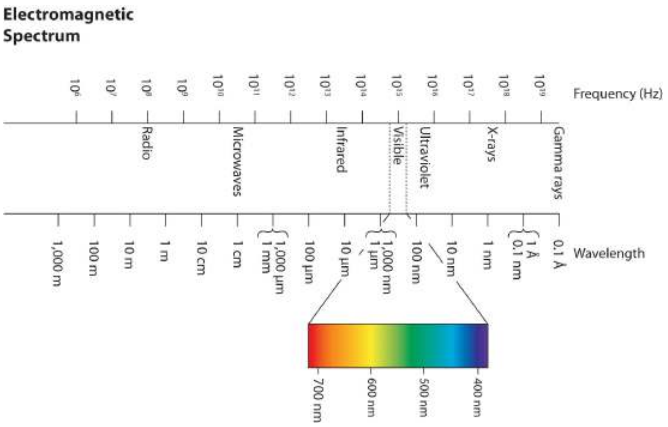


Figure **3.2.2**: The Electromagnetic Spectrum. The electromagnetic spectrum, with its various regions labeled. The borders of each region are approximate.

Summary

Light acts like a wave, with a frequency and a wavelength. The frequency and wavelength of light are related by the speed of light, a constant. Light acts like a particle of energy, whose value is related to the frequency of light.

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3.3: Quantum Numbers for Electrons

Learning Objectives

- Explain what spectra are.
- Learn the quantum numbers that are assigned to electrons.

There are two fundamental ways of generating light: either heat an object up to be so hot that it glows, or pass an electrical current through a sample of matter (usually a gas). Incandescent lights and fluorescent lights generate light via these two methods, respectively.

A hot object gives off a continuum of light. We notice this when the visible portion of the electromagnetic spectrum is passed through a prism: the prism separates light into its constituent colors, and all colors are present in a continuous rainbow (Figure **3.3.1*a*** - Prisms and Light). This image is known as a **continuous spectrum**. However, when electricity is passed through a gas and light is emitted and this light is passed though a prism, we see only certain lines of light in the image (Figure **3.3.1*b***). This image is called a line spectrum. It turns out that every element has its own unique, characteristic line spectrum.



Figure **3.3.1**: Prisms and Light. (a) A glowing object gives off a full rainbow of colors, which are noticed only when light is passed through a prism to make a continuous spectrum. (b) However, when electricity is passed through a gas, only certain colors of light are emitted. Here are the colors of light in the line spectrum of Hg.

Why does the light emitted from an electrically excited gas have only certain colors, while light given off by hot objects has a continuous spectrum? For a long time, it was not well explained. Particularly simple was the spectrum of hydrogen gas, which could be described easily by an equation; no other element has a spectrum that is so predictable (Figure **3.3.2** - Hydrogen Spectrum). Late nineteenth century scientists found that the positions of the lines obeyed a pattern given by the equation

$$\frac{1}{\lambda} = (109,700 cm^{-1})\left(\frac{1}{4} - \frac{1}{n^2}\right)$$

where n = 3, 4, 5, 6, etc. However, they could not explain why this was so.

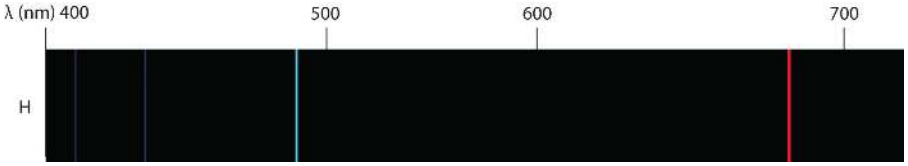


Figure **3.3.2**: Hydrogen Spectrum. The spectrum of hydrogen was particularly simple and could be predicted by a simple mathematical expression.

In 1913, the Danish scientist Niels Bohr suggested a reason why the hydrogen atom spectrum looked this way. He suggested that the electron in a hydrogen atom could not have any random energy, having *only* certain fixed values of energy that were indexed by the number n (the same n in the equation above and now called a **quantum number**). Quantities that have certain specific values are **quantized** values. Bohr suggested that the energy of the electron in hydrogen was quantized because it was in a specific orbit. Because the energies of the electron can have only certain values, the changes in energies can have only certain values (somewhat similar to a staircase—not only are the stair steps set at specific heights, but the height between steps is fixed). Finally, Bohr suggested that the energy of light emitted from electrified hydrogen gas was equal to the energy difference of the electron's energy states:

$$E_{light} = h\nu = \Delta E_{electron}$$

This means that only certain frequencies (and thus, certain wavelengths) of light are emitted. Figure **3.3.3** - Bohr's Model of the Hydrogen Atom, shows a model of the hydrogen atom based on Bohr's ideas.

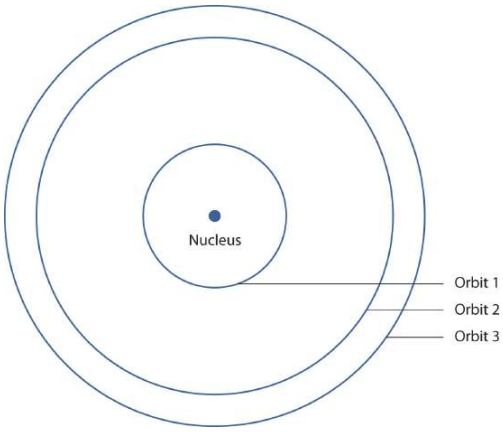


Figure **3.3.3**: Bohr's Model of the Hydrogen Atom. Bohr's description of the hydrogen atom had specific orbits for the electron, which had quantized energies.

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

In the quantum-mechanical model of an atom, the state of an electron is described by four quantum numbers, not just the one predicted by Bohr. The first quantum number is called the **principal quantum number(n).** The principal quantum number largely determines the energy of an electron. Electrons in the same atom that have the same principal quantum number are said to occupy an electron **shell** of the atom. The principal quantum number can be any nonzero positive integer: 1, 2, 3, 4,….

Within a shell, there may be multiple possible values of the next quantum number, the **angular momentum quantum number (ℓ)**. The ℓ quantum number has a minor effect on the energy of the electron but also affects the spatial distribution of the electron in three-dimensional space—that is, the shape of an electron's distribution in space. The value of the ℓ quantum number can be any integer between 0 and $n - 1$: $\ell = 0, 1, 2, \ldots, n - 1$.

Thus, for a given value of n, there are different possible values of ℓ:

Table with two columns and four rows. The first (left) column is labeled "If n equals" and the second (right) column is labeled "ℓ can be". Underneath the columns in the rows are different values. All of the rows have numerical values.

If *n* equals	ℓ can be
1	0
2	0 or 1
3	0, 1, or 2
4	0, 1, 2, or 3

and so forth. Electrons within a shell that have the same value of ℓ are said to occupy a **subshell** in the atom. Commonly, instead of referring to the numerical value of ℓ, a letter represents the value of ℓ (to help distinguish it from the principal quantum number):

Table with two columns and four rows. The first (left) column is labeled "If ℓ equals" and the second (right) column is labeled "The letter is". The rows underneath the left column are numbers and the rows underneath the right column are letters.

If ℓ equals	The letter is
0	*s*
1	*p*
2	*d*
3	*f*

The next quantum number is called the **magnetic quantum number (m_ℓ)**. For any value of ℓ, there are 2ℓ + 1 possible values of m_ℓ, ranging from −ℓ to ℓ:

$$-\ell < m\ell < \ell$$

or

$$|m_\ell| < \ell$$

The following explicitly lists the possible values of m_ℓ for the possible values of ℓ:

Table with two columns and four rows. The first (left) column is labeled "If ℓ equals" and the second (right) column is labeled "The mℓ values can be". The rows underneath the left column are positive numbers and the rows underneath the right column are negative numbers.

If ℓ equals	The m_ℓ values can be
0	0
1	−1, 0, or 1
2	−2, −1, 0, 1, or 2
3	−3, −2, −1, 0, 1, 2, or 3

The particular value of m_ℓ dictates the orientation of an electron's distribution in space. When ℓ is zero, m_ℓ can be only zero, so there is only one possible orientation. When ℓ is 1, there are three possible orientations for an electron's distribution. When ℓ is 2, there are five possible orientations of electron distribution. This goes on and on for other values of ℓ, but we need not consider any higher values of ℓ here. Each value of m_ℓ designates a certain orbital. Thus, there is only one orbital when ℓ is zero, three orbitals when ℓ is 1, five orbitals when ℓ is 2, and so forth. The m_ℓ quantum number has no effect on the energy of an electron unless the electrons are subjected to a magnetic field—hence its name.

The ℓ quantum number dictates the general shape of electron distribution in space (Figure **3.3.4** - Electron Orbitals). Any s orbital is spherically symmetric (Figure **3.3.4*a*** - Electron Orbitals), and there is only one orbital in any s subshell. Any p orbital has a two-lobed, dumbbell-like shape (Figure **3.3.4*b*** - Electron Orbitals); because there are three of them, we normally represent them as pointing along the x-, y-, and z-axes of Cartesian space. The d orbitals are four-lobed rosettes (Figure **3.3.4*c*** - Electron Orbitals) and they are oriented differently in space (the one labeled Math input error has two lobes and a torus instead of four lobes, but it is equivalent to the other orbitals). When there is more than one possible value of m_ℓ, each orbital is labeled with one of the possible values. It should be noted that the diagrams in Figure **3.3.4** are estimates of the electron distribution in space, not surfaces electrons are fixed on.

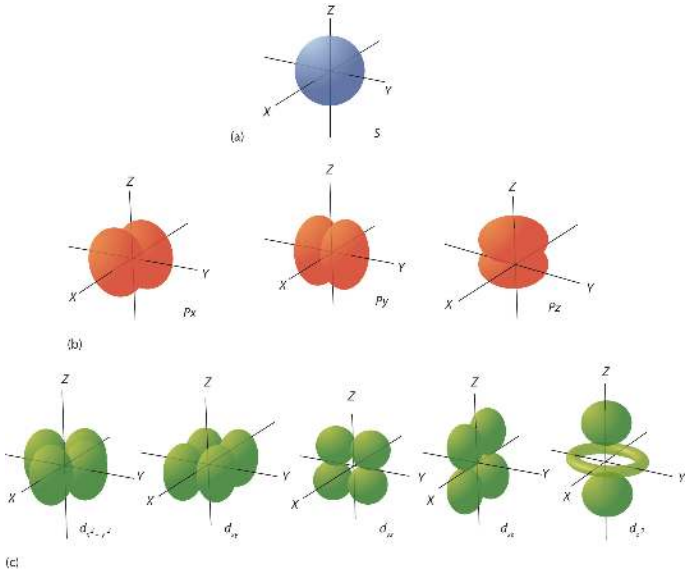


Figure **3.3.4**: Electron Orbitals. (a) The lone s orbital is spherical in distribution. (b) The three p orbitals are shaped like dumbbells, and each one points in a different direction. (c) The five d orbitals are rosette in shape, except for the dz2 orbital, which is a "dumbbell + torus" combination. They are all oriented in different directions.

The final quantum number is the **spin quantum number** (m_S). Electrons and other subatomic particles behave as if they are spinning (we cannot tell if they really are, but they behave as if they are). Electrons themselves have two possible spin states, and because of mathematics, they are assigned the quantum numbers +1/2 and −1/2. These are the only two possible choices for the spin quantum number of an electron.

✔ Example 3.3.1

Of the set of quantum numbers $\{n, \ell, m\ell, m_S\}$, which are possible and which are not allowed?

a. {3, 2, 1, +1/2}
b. {2, 2, 0, −1/2}
c. {3, −1, 0, +1/2}

Solution

a. The principal quantum number n must be an integer, as it is here. The quantum number ℓ must be less than n, which it is. The $m\ell$ quantum number must be between $-\ell$ and ℓ, which it is. The spin quantum number is +1/2, which is allowed. Because this set of quantum numbers follows all restrictions, it is possible.
b. The quantum number n is an integer, but the quantum number ℓ must be less than n, which it is not. Thus, this is not an allowed set of quantum numbers.
c. The principal quantum number n is an integer, but ℓ is not allowed to be negative. Therefore, this is not an allowed set of quantum numbers.

? Exercise 3.3.1

Of the set of quantum numbers $\{n, \ell, m\ell, m_S\}$, which are possible and which are not allowed?

a. {4, 2, −2, 1}
b. {3, 1, 0, −1/2}

Answers

a. Spin must be either +1/2 or −1/2, so this set of quantum number is not allowed.
b. allowed

Chemistry is Everywhere: Neon Lights

A neon light is basically an electrified tube with a small amount of gas in it. Electricity excites electrons in the gas atoms, which then give off light as the electrons go back into a lower energy state. However, many so-called "neon" lights do not contain neon!

Although we know now that a gas discharge gives off only certain colors of light, without a prism or other component to separate the individual light colors, we see a composite of all the colors emitted. It is not unusual for a certain color to predominate. True neon lights, with neon gas in them, have a reddish-orange light due to the large amount of red-, orange-, and yellow-colored light emitted. However, if krypton is used instead of neon, a whitish light is emitted, while using argon yields a blue-purple light. A light filled with nitrogen gas glows purple, as does a helium lamp. Other gases—and mixtures of gases—emit other colors of light. Ironically, despite its importance in the development of modern electronic theory, hydrogen lamps emit little visible light and are rarely used for illumination purposes.



The Human/Need/Desire statue consists of purple "NEED", orange "HUMAN", green "HUMAN", pink "DESIRE", red "HOPE", and blue "DREAM".

Neon lights. The different colors of these "neon" lights are caused by gases other than neon in the discharge tubes. Human/Need/Desire. Neon sculpture by Bruce Nauman (1983), who has been characterized as a conceptual artist. (CC BY-SA 3.0; eschipul).

Key Takeaways

Electrons in atoms have quantized energies. The state of electrons in atoms is described by four quantum numbers.

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3.4: Organization of Electrons in Atoms

Learning Objectives

- Learn how electrons are organized within atoms.
- Represent the organization of electrons by an electron configuration.

Now that you know that electrons have quantum numbers, how are they arranged in atoms? The key to understanding electronic arrangement is summarized in the **Pauli exclusion principle:** no two electrons in an atom can have the same set of four quantum numbers. This dramatically limits the number of electrons that can exist in a shell or a subshell.

Electrons are typically organized around an atom by starting at the lowest possible quantum numbers first, which are the shells-subshells with lower energies. Consider H, an atom with a single electron only. Under normal conditions, the single electron would go into the n = 1 shell, which has only a single s subshell with one orbital (because m_ℓ can equal only 0). The convention is to label the shell-subshell combination with the number of the shell and the letter that represents the subshell. Thus, the electron goes in the 1s shell-subshell combination. It is usually not necessary to specify the m_ℓ or m_s quantum numbers, but for the H atom, the electron has $m_\ell = 0$ (the only possible value) and an m_s of either +1/2 or −1/2.

The He atom has two electrons. The second electron can also go into the 1s shell-subshell combination, but only if its spin quantum number is different from the first electron's spin quantum number. Thus, the sets of quantum numbers for the two electrons are {1, 0, 0, +1/2} and {1, 0, 0, −1/2}. Notice that the overall set is different for the two electrons, as required by the Pauli exclusion principle.

The next atom is Li, with three electrons. However, now the Pauli exclusion principle implies that we cannot put that electron in the 1s shell-subshell because no matter how we try, this third electron would have the same set of four quantum numbers as one of the first two electrons. So this third electron must be assigned to a different shell-subshell combination. However, the n = 1 shell doesn't have another subshell; it is restricted to having just $\ell = 0$, or an s subshell. Therefore, this third electron has to be assigned to the n = 2 shell, which has an s ($\ell = 0$) subshell and a p ($\ell = 1$) subshell. Again, we usually start with the lowest quantum number, so this third electron is assigned to the 2s shell-subshell combination of quantum numbers.

The Pauli exclusion principle has the net effect of limiting the number of electrons that can be assigned a shell-subshell combination of quantum numbers. For example, in any s subshell, no matter what the shell number, there can be a maximum of only two electrons. Once the s subshell is filled up, any additional electrons must go to another subshell in the shell (if it exists), or to a higher-numbered shell. A similar analysis shows that a p subshell can hold a maximum of six electrons. A d subshell can hold a maximum of 10 electrons, while an f subshell can have a maximum of 14 electrons. By limiting subshells to these maxima, we can distribute the available electrons to their shells and subshells.

Example 3.4.1: Carbon Atoms

How would the six electrons for C be assigned to the n and ℓ quantum numbers?

Solution

The first two electrons go into the 1s shell-subshell combination. Two additional electrons can go into the 2s shell-subshell, but now this subshell is filled with the maximum number of electrons. The n = 2 shell also has a p subshell, so the remaining two electrons can go into the 2p subshell. The 2p subshell is not completely full because it can hold a maximum of six electrons.

Exercise 3.4.1: Sodium Atoms

How would the 11 electrons for Na be assigned to the n and ℓ quantum numbers?

Answer

two 1s electrons, two 2s electrons, six 2p electrons, and one 3s electron

Now that we see how electrons are partitioned among the shells and subshells, we need a more concise way of communicating this partitioning. Chemists use an **electron configuration** to represent the organization of electrons in shells and subshells in an atom. An electron configuration simply lists the shell and subshell labels, with a right superscript giving the number of electrons in that subshell. The shells and subshells are listed in the order of filling.

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

$$\text{H: } 1s^1$$

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

$$\text{He: } 1s^2$$

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

$$\text{Li: } 1s^2 2s^1$$

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

$$\text{Be: } 1s^2 2s^2$$

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

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

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

Example 3.4.2: Sodium

What is the electron configuration for Na, which has 11 electrons?

Solution

The first two electrons occupy the 1s subshell. The next two occupy the 2s subshell, while the next six electrons occupy the 2p subshell. This gives us 10 electrons so far, with 1 electron left. This last electron goes into the n = 3 shell, s subshell. Thus, the electron configuration of Na is $1s^2 2s^2 2p^6 3s^1$.

Exercise 3.4.2: Magnesium

What is the electron configuration for Mg, which has 12 electrons?

Answer

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

For larger atoms, the electron arrangement becomes more complicated. This is because after the 3p subshell is filled, filling the 4s subshell first actually leads to a lesser overall energy than filling the 3d subshell. Recall that while the principal quantum number largely dictates the energy of an electron, the angular momentum quantum number also has an impact on energy; by the time we get to the 3d and 4s subshells, we see overlap in the filling of the shells. Thus, after the 3p subshell is completely filled (which occurs for Ar), the next electron for K occupies the 4s subshell, not the 3d subshell:

$$\text{K: } 1s^2 2s^2 2p^6 3s^2 3p^6 4s^1,$$

not

$$\text{K: } 1s^2 2s^2 2p^6 3s^2 3p^6 3d^1$$

For larger and larger atoms, the order of filling the shells and subshells seems to become even more complicated. There are some useful ways to remember the order, like that shown in Figure **3.4.1**. If you follow the arrows in order, they pass through the subshells in the order that they are filled with electrons in larger atoms. Initially, the order is the same as the expected shell-subshell order, but for larger atoms, there is some shifting around of the principal quantum numbers. However, Figure **3.4.1** gives a valid ordering of filling subshells with electrons for most atoms.

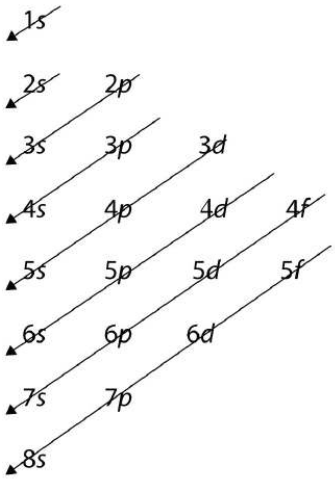


Figure **3.4.1** Electron Shell Filling Order. Starting with the top arrow, follow each arrow. The subshells you reach along each arrow give the ordering of filling of subshells in larger atoms. The n = 5 and higher shells have more subshells, but only those subshells that are needed to accommodate the electrons of the known elements are given.

The electron shell filling order goes as follows: 1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s, 5f, 6d, 7p, then 8s.

✔ Example **3.4.3**: Tin

What is the predicted electron configuration for Sn, which has 50 electrons?

Solution

We will follow the chart in Figure 8.4., until we can accommodate 50 electrons in the subshells in the proper order: Sn: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^2$

Verify by adding the superscripts, which indicate the number of electrons: 2 + 2 + 6 + 2 + 6 + 2 + 10 + 6 + 2 + 10 + 2 = 50, so we have placed all 50 electrons in subshells in the proper order.

? Exercise **3.4.3**: Barium

What is the electron configuration for Ba, which has 56 electrons?

Answer

$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2$

As the previous example demonstrated, electron configurations can get fairly long. An **abbreviated electron configuration** uses one of the elements from the last column of the periodic table, which contains the noble gases, to represent the core of electrons up to that element. Then, the remaining electrons are listed explicitly. For example, the abbreviated electron configuration for Li, which has three electrons, would be

$$\text{Li: [He]}2s^1$$

where [He] represents the two-electron core that is equivalent to He's electron configuration. The square brackets represent the electron configuration of a noble gas. This is not much of an abbreviation. However, consider the abbreviated electron configuration for W, which has 74 electrons:

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

This is a significant simplification over an explicit listing of all 74 electrons. So for larger elements, the abbreviated electron configuration can be a very useful shorthand.

Example 3.4.4: Phosphorus

What is the abbreviated electron configuration for P, which has 15 electrons?

Solution

With 15 electrons, the electron configuration of P is

$$\text{P: } 1s^2 2s^2 2p^6 3s^2 3p^3$$

The first immediate noble gas is Ne, which has an electron configuration of $1s^2 2s^2 2p^6$. Using the electron configuration of Ne to represent the first 10 electrons, the abbreviated electron configuration of P is

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

Exercise 3.4.4: Rubidium

What is the abbreviated electron configuration for Rb, which has 37 electrons?

Answer

$[Kr]5s^1$

There are some exceptions to the rigorous filling of subshells by electrons. In many cases, an electron goes from a higher-numbered shell to a lower-numbered, but later-filled, subshell to fill the later-filled subshell. One example is Ag. With 47 electrons, its electron configuration is predicted to be

$$\text{Ag: [Kr]}5s^2 4d^9$$

However, experiments have shown that the electron configuration is actually

$$\text{Ag: [Kr]}5s^1 4d^{10}$$

This, then, qualifies as an exception to our expectations. At this point, you do not need to memorize the exceptions; but if you come across one, understand that it is an exception to the normal rules of filling subshells with electrons, which can happen.

Summary

The Pauli exclusion principle limits the number of electrons in the subshells and shells. Electrons in larger atoms fill shells and subshells in a regular pattern that can be followed. Electron configurations are a shorthand method of indicating what subshells electrons occupy in atoms. Abbreviated electron configurations are a simpler way of representing electron configurations for larger atoms. Exceptions to the strict filling of subshells with electrons do occur.

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3.5: Electronic Structure and the Periodic Table

Learning Objectives

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

In Chapter 3, we introduced the periodic table as a tool for organizing the known chemical elements. A periodic table is shown in Figure **3.5.1**. The elements are listed by atomic number (the number of protons in the nucleus), and elements with similar chemical properties are grouped together in columns.

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

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

Figure **3.5.1**: The Periodic Table

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

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

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

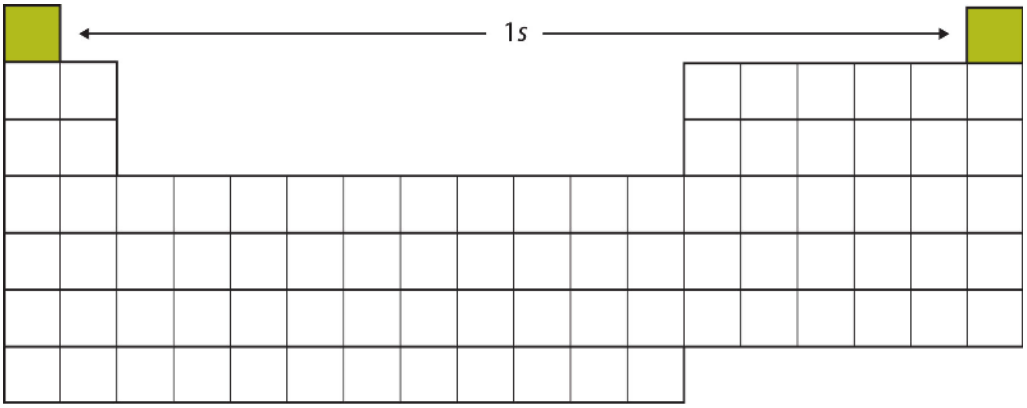


Figure 3.5.2: The 1s Subshell. H and He represent the filling of the 1s subshell.

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

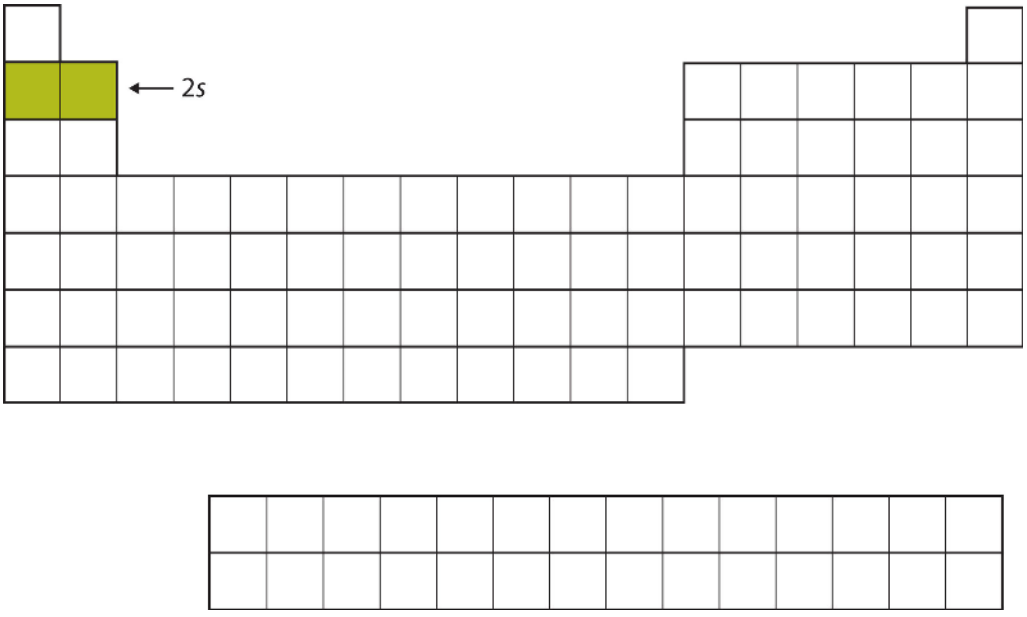


Figure 3.5.3: The 2s Subshell. In Li and Be, the 2s subshell is being filled.

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

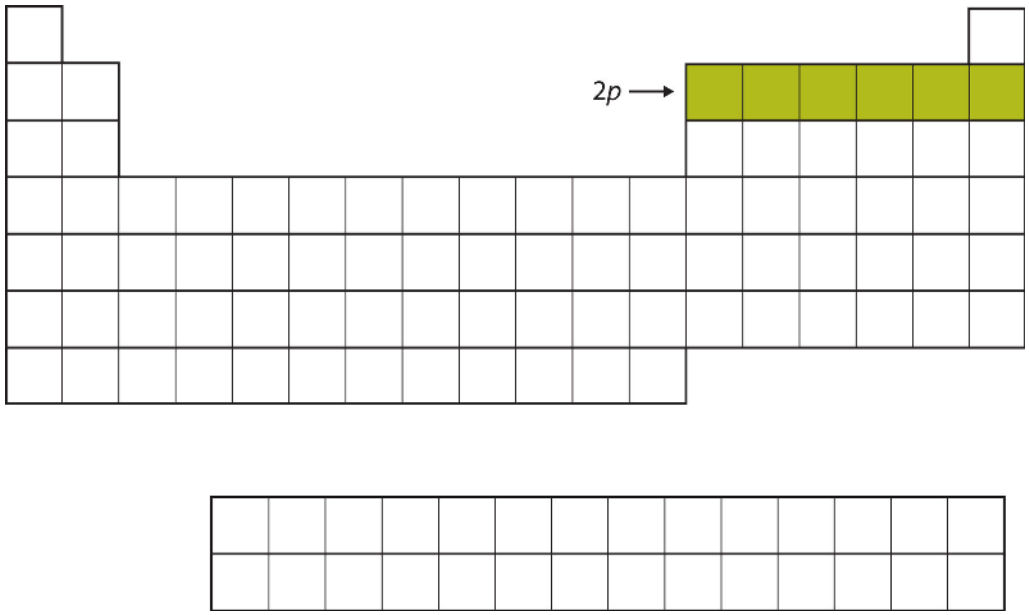


Figure 3.5.4: The 2p Subshell. For B through Ne, the 2p subshell is being occupied.

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

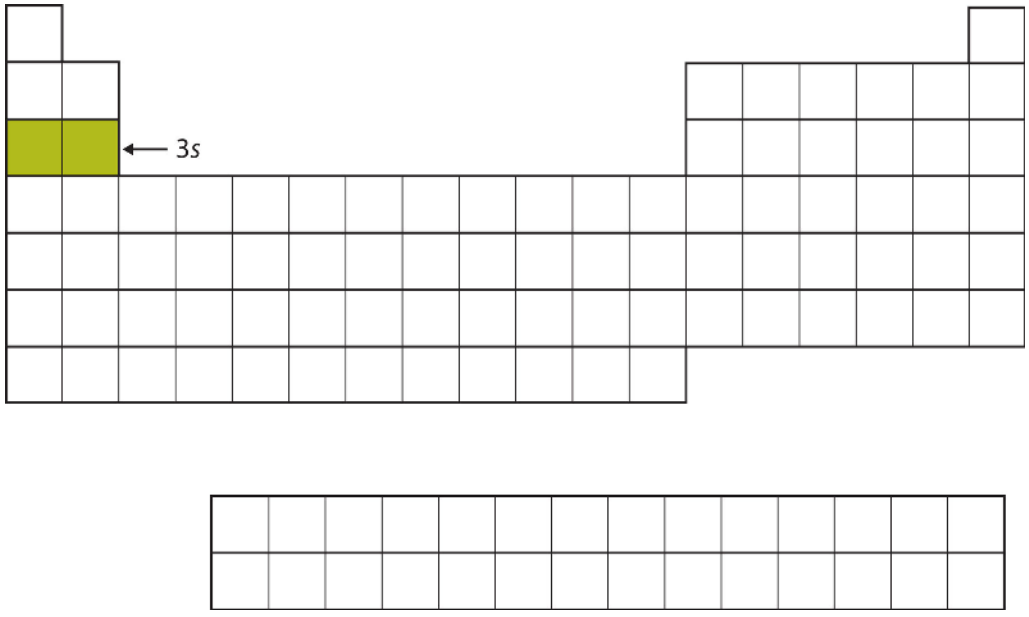


Figure 3.5.5: The 3s Subshell. Now the 3s subshell is being occupied.

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

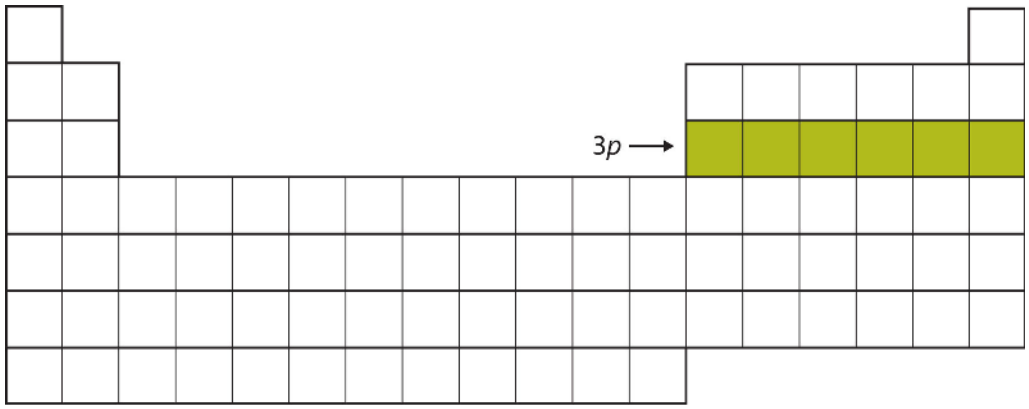


Figure8.5.6: The 3p Subshell. Next, the 3p subshell is filled with electrons.

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

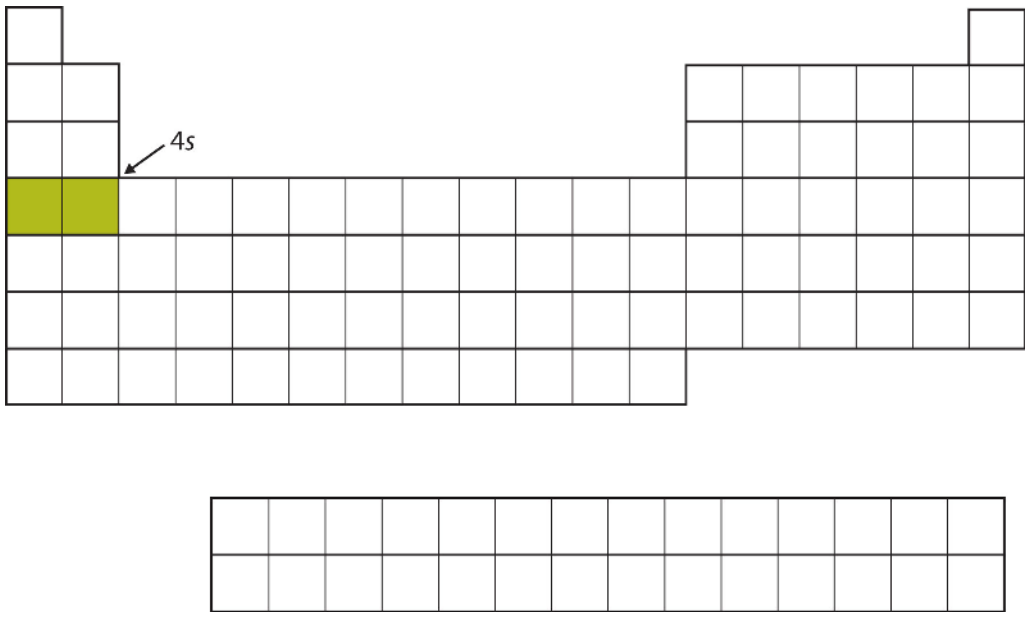


Figure **3.5.7**: The 4s Subshell. The 4s subshell is filled before the 3d subshell. This is reflected in the structure of the periodic table.

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

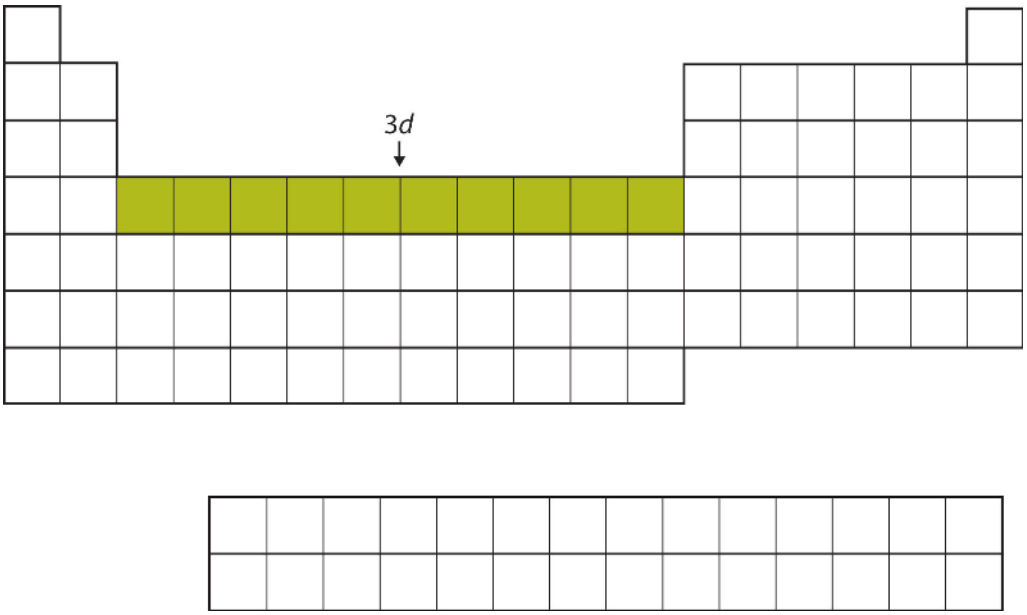


Figure 3.5.8: The 3d Subshell. The 3d subshell is filled in the middle section of the periodic table.

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

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

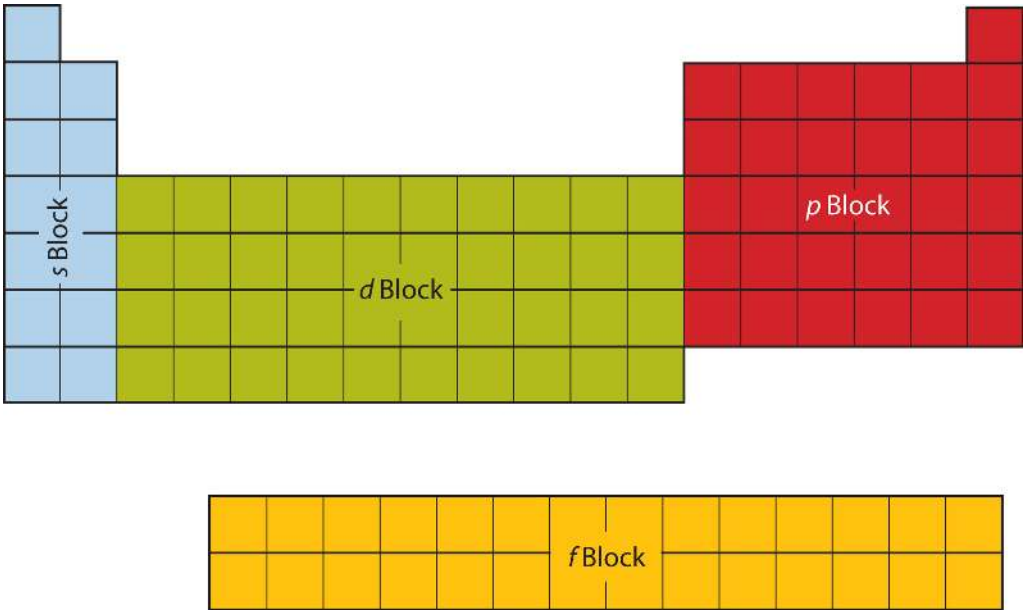


Figure 3.5.9: Blocks on the Periodic Table. The periodic table is separated into blocks depending on which subshell is being filled for the atoms that belong in that section.

Empty periodic table, separated into 4 different colored blocks. S block is blue, d block is green, p block is red and f block is orange.

The electrons in the highest-numbered shell, plus any electrons in the last unfilled subshell, are called **valence electrons**; the highest-numbered shell is called the **valence shell**. (The inner electrons are called *core electrons*.) The valence electrons largely control the chemistry of an atom. If we look at just the valence shell's electron configuration, we find that in each column, the

valence shell's electron configuration is the same. For example, take the elements in the first column of the periodic table: H, Li, Na, K, Rb, and Cs. Their electron configurations (abbreviated for the larger atoms) are as follows, with the valence shell electron configuration highlighted:

Table with two columns and 6 rows. The first column on the left has various elements in the rows underneath. The second column on the right has the different corresponding electron configurations for the specified element in the rows underneath.

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

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

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

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

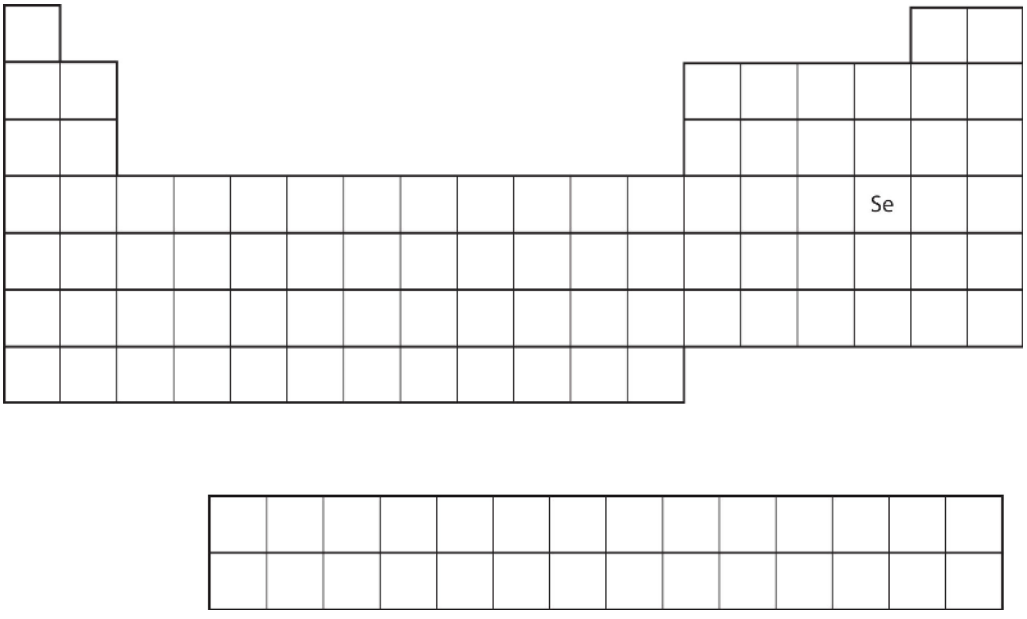


Figure **3.5.10**: Selenium on the Periodic Table

Example 3.5.1

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

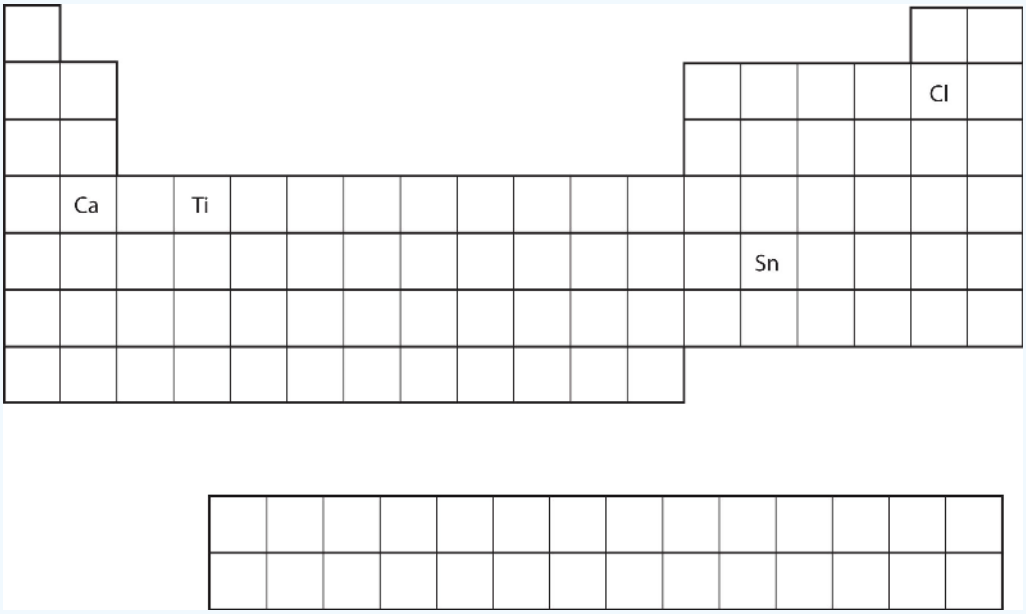


Figure **3.5.11**: Various Elements on the Periodic Table

1. Ca
2. Sn

Solution

1. Ca is located in the second column of the *s* block. We would expect that its electron configuration should end with s^2. Calcium's electron configuration is $[Ar]4s^2$.
2. Sn is located in the second column of the *p* block, so we expect that its electron configuration would end in p^2. Tin's electron configuration is $[Kr]5s^24d^{10}5p^2$.

Exercise 3.5.1

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

a. Ti
b. Cl

Answer a

$[Ar]4s^23d^2$

Answer b

$[Ne]3s^23p^5$

Food and Drink Application: Artificial Colors

The color of objects comes from a different mechanism than the colors of neon and other discharge lights. Although colored lights produce their colors, objects are colored because they preferentially reflect a certain color from the white light that shines on them. A red tomato, for example, is bright red because it reflects red light while absorbing all the other colors of the rainbow.

Many foods, such as tomatoes, are highly colored; in fact, the common statement "you eat with your eyes first" is an implicit recognition that the visual appeal of food is just as important as its taste. But what about processed foods?

Many processed foods have food colorings added to them. There are two types of food colorings: natural and artificial. Natural food colorings include caramelized sugar for brown; annatto, turmeric, and saffron for various shades of orange or yellow; betanin from beets for purple; and even carmine, a deep red dye that is extracted from the cochineal, a small insect that is a parasite on cacti in Central and South America. (That's right—you may be eating bug juice!)

Some colorings are artificial. In the United States, the Food and Drug Administration currently approves only seven compounds as artificial colorings in food, beverages, and cosmetics:

- FD&C Blue #1: Brilliant Blue FCF
- FD&C Blue #2: Indigotine
- FD&C Green #3: Fast Green FCF
- RD&C Red #3: Erythrosine
- FD&C Red #40: Allura Red AC
- FD&C Yellow #5: Tartrazine
- FD&C Yellow #6: Sunset Yellow FCF

Lower-numbered colors are no longer on the market or have been removed for various reasons. Typically, these artificial colorings are large molecules that absorb certain colors of light very strongly, making them useful even at very low concentrations in foods and cosmetics. Even at such low amounts, some critics claim that a small portion of the population (especially children) is sensitive to artificial colorings and urge that their use be curtailed or halted. However, formal studies of artificial colorings and their effects on behavior have been inconclusive or contradictory. Many people continue to enjoy processed foods with artificial coloring (like those shown in the accompanying figure).



Artificial food colorings. Artificial food colorings are found in a variety of food products, such as processed foods, candies, and egg dyes. Even pet foods have artificial food coloring in them. (CC by 2.0, Matthew Bland via Flickr.)

Summary

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

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3.6: Electronic Structure and the Periodic Table

Learning Objectives

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

In Chapter 3, we introduced the periodic table as a tool for organizing the known chemical elements. A periodic table is shown in Figure **3.6.1**. The elements are listed by atomic number (the number of protons in the nucleus), and elements with similar chemical properties are grouped together in columns.

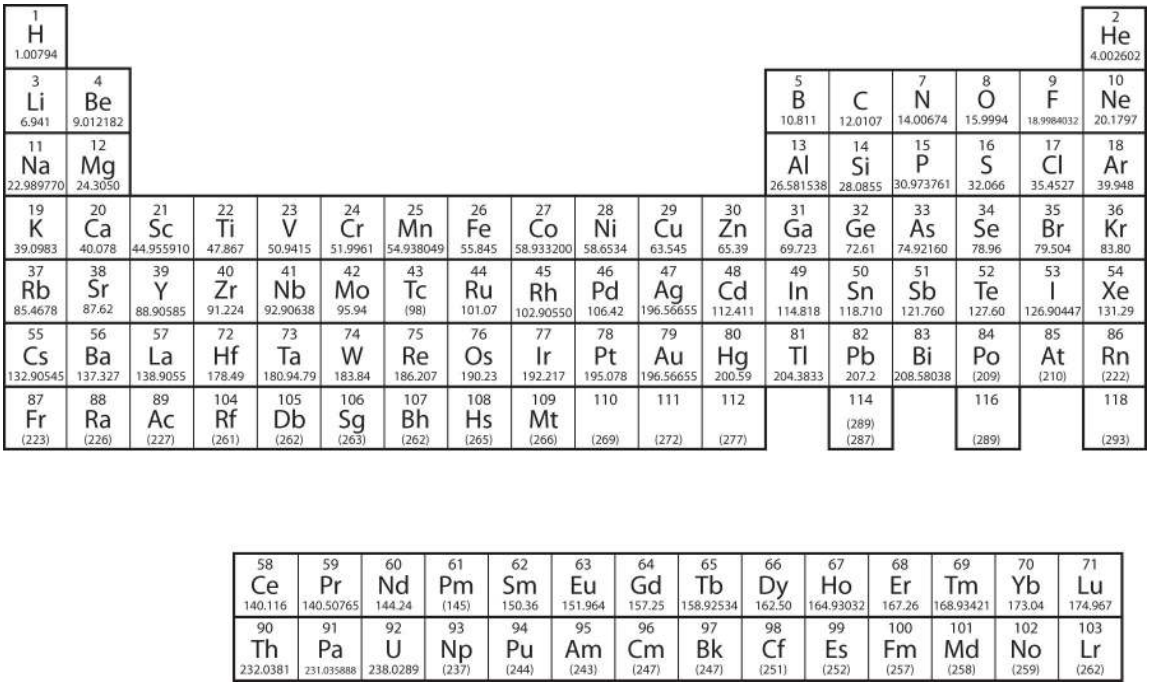


Figure **3.6.1**: The Periodic Table

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

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

Let us start with H and He. Their electron configurations are $1s^1$ and $1s^2$, respectively; with He, the $n = 1$ shell is filled. These two elements make up the first row of the periodic table (Figure **3.6.2**)

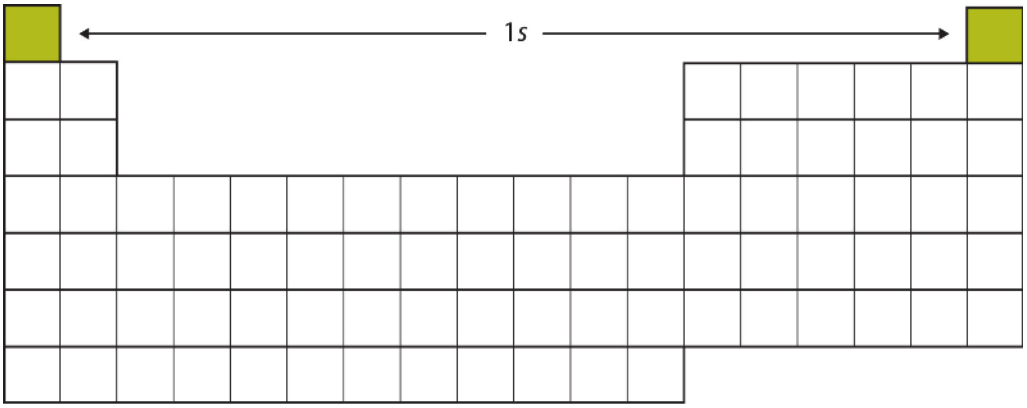


Figure **3.6.2**: The 1s Subshell. H and He represent the filling of the 1s subshell.

The next two electrons, for Li and Be, would go into the 2*s* subshell. Figure **3.6.3** shows that these two elements are adjacent on the periodic table.

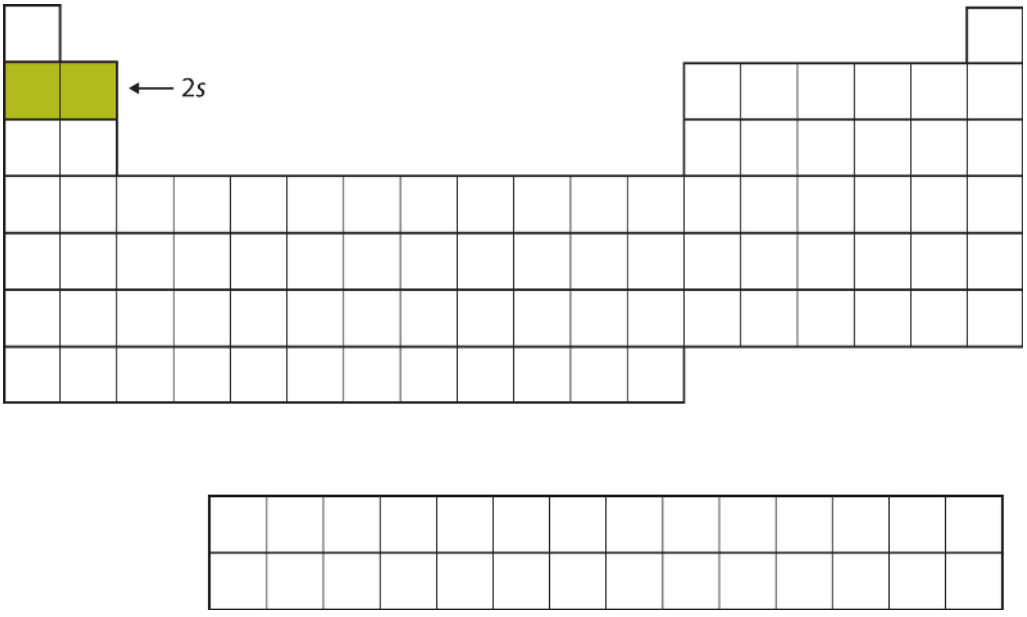


Figure **3.6.3**: The 2s Subshell. In Li and Be, the 2s subshell is being filled.

For the next six elements, the 2*p* subshell is being occupied with electrons. On the right side of the periodic table, these six elements (B through Ne) are grouped together (Figure **3.6.4**).

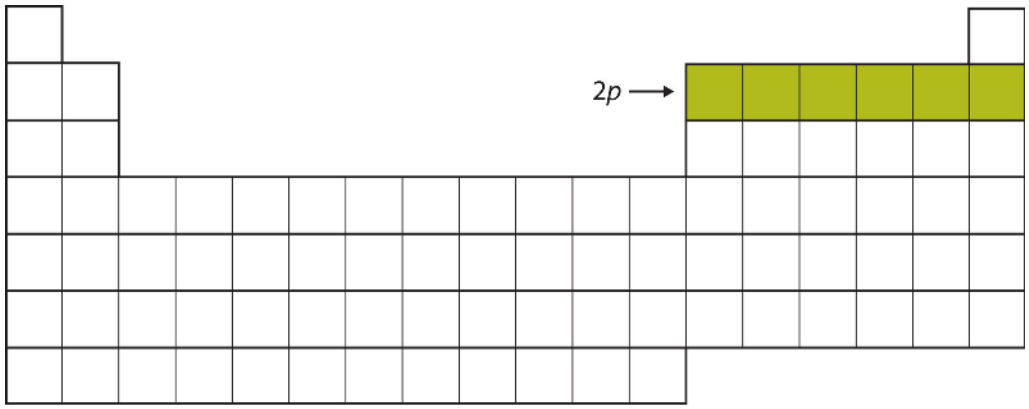


Figure 3.6.4: The 2p Subshell. For B through Ne, the 2p subshell is being occupied.

The next subshell to be filled is the 3*s* subshell. The elements coinciding this subshell being filled, Na and Mg, are back on the left side of the periodic table (Figure 3.6.5).

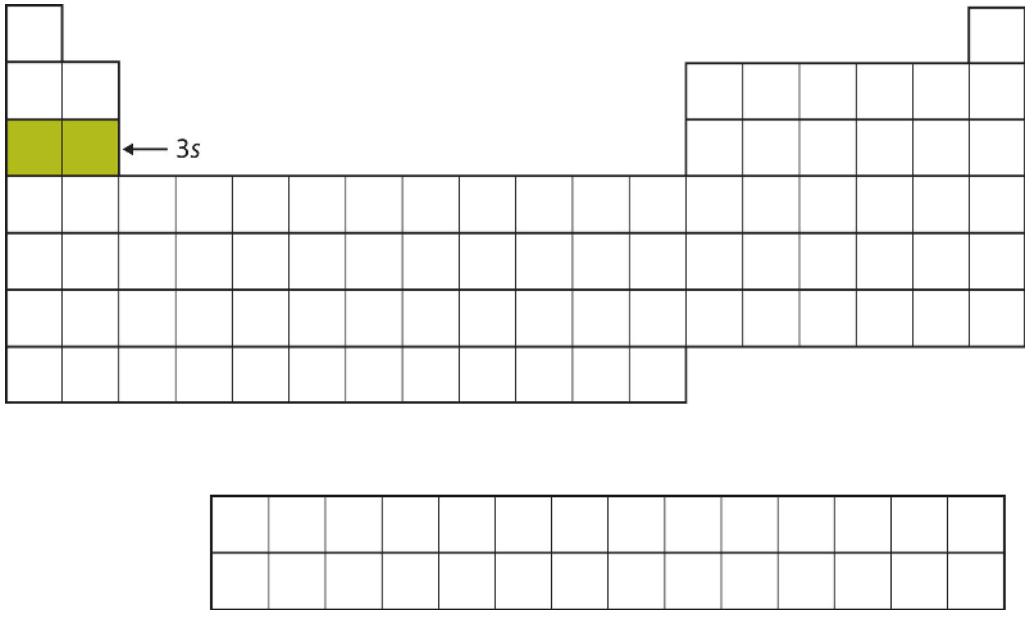


Figure 3.6.5: The 3s Subshell. Now the 3s subshell is being occupied.

Next, the 3*p* subshell is filled with the next six elements (Figure 3.6.6).

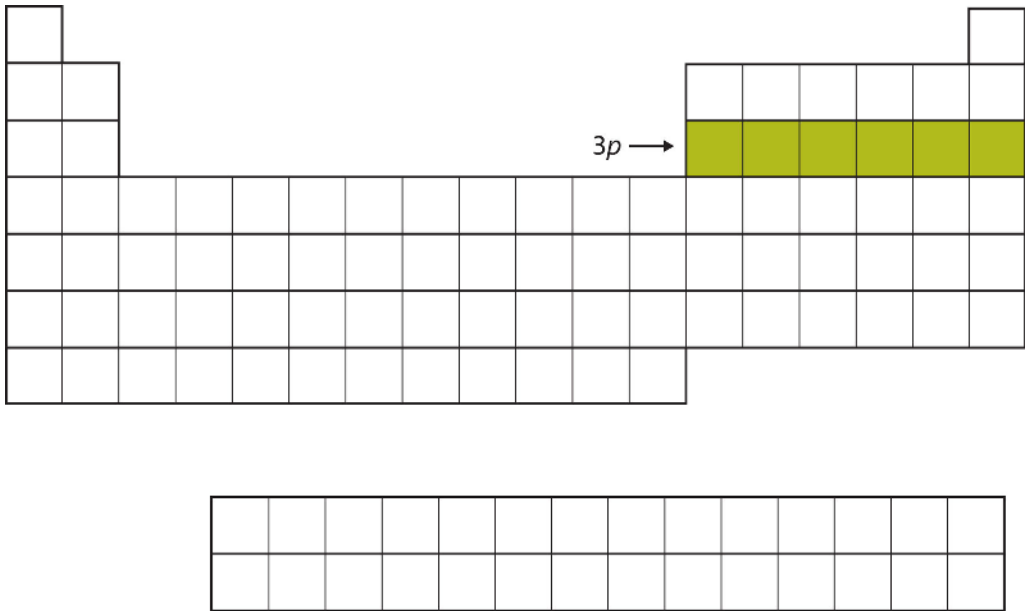


Figure8.5.6: The 3p Subshell. Next, the 3p subshell is filled with electrons.

Instead of filling the 3*d* subshell next, electrons go into the 4*s* subshell (Figure **3.6.7**).

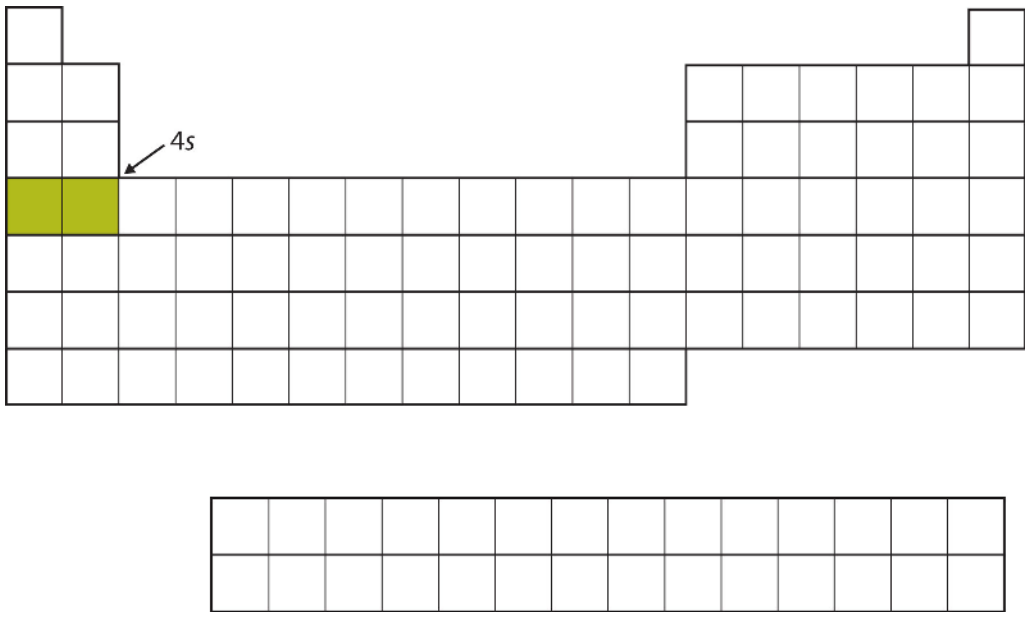


Figure **3.6.7**: The 4s Subshell. The 4s subshell is filled before the 3d subshell. This is reflected in the structure of the periodic table.

After the 4*s* subshell is filled, the 3*d* subshell is filled with up to 10 electrons. This explains the section of 10 elements in the middle of the periodic table (Figure **3.6.8**).

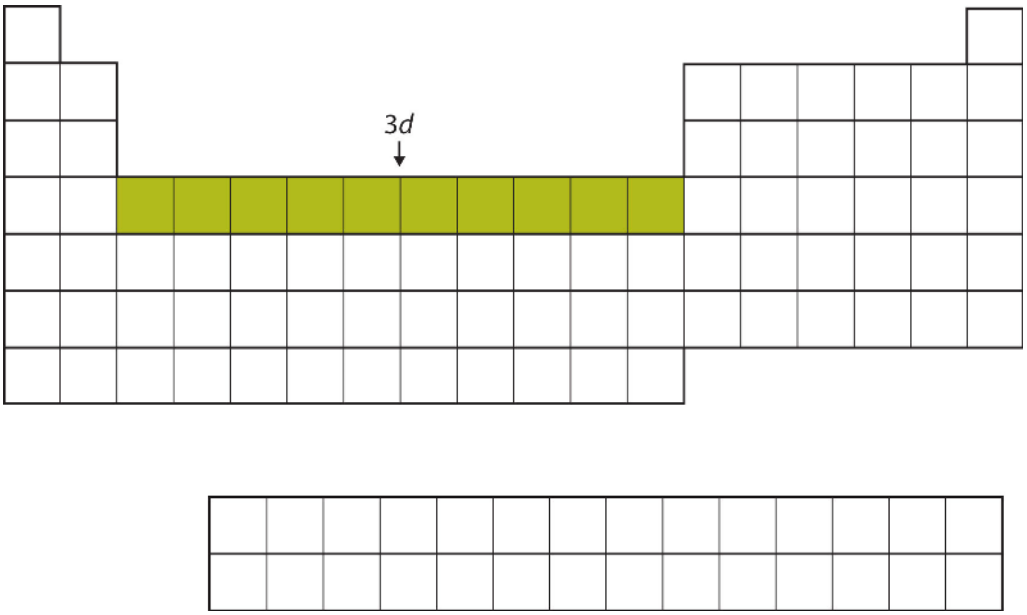


Figure 3.6.8: The 3d Subshell. The 3d subshell is filled in the middle section of the periodic table.

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

The first two columns on the left side of the periodic table are where the *s* subshells are being occupied. Because of this, the first two rows of the periodic table are labeled the **s block**. Similarly, the **p block** is the right-most six columns of the periodic table, the **d block** is the middle 10 columns of the periodic table, while the **f block** is the 14-column section that is normally depicted as detached from the main body of the periodic table. It could be part of the main body, but then the periodic table would be rather long and cumbersome. Figure 3.6.9 shows the blocks of the periodic table.

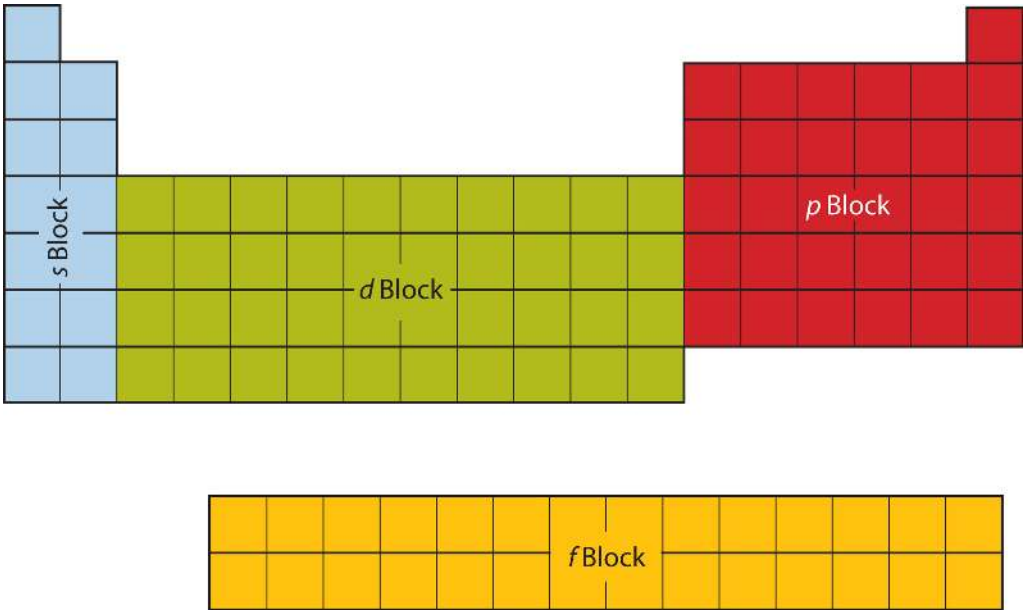


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Empty periodic table, separated into 4 different colored blocks. S block is blue, d block is green, p block is red and f block is orange.

The electrons in the highest-numbered shell, plus any electrons in the last unfilled subshell, are called **valence electrons**; the highest-numbered shell is called the **valence shell**. (The inner electrons are called *core electrons*.) The valence electrons largely control the chemistry of an atom. If we look at just the valence shell's electron configuration, we find that in each column, the

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Similarity of valence shell electron configuration implies that we can determine the electron configuration of an atom solely by its position on the periodic table. Consider Se, as shown in Figure **3.6.10**. It is in the fourth column of the *p* block. This means that its electron configuration should end in a p^4 electron configuration. Indeed, the electron configuration of Se is $[Ar]4s^2 3d^{10} 4p^4$, as expected.

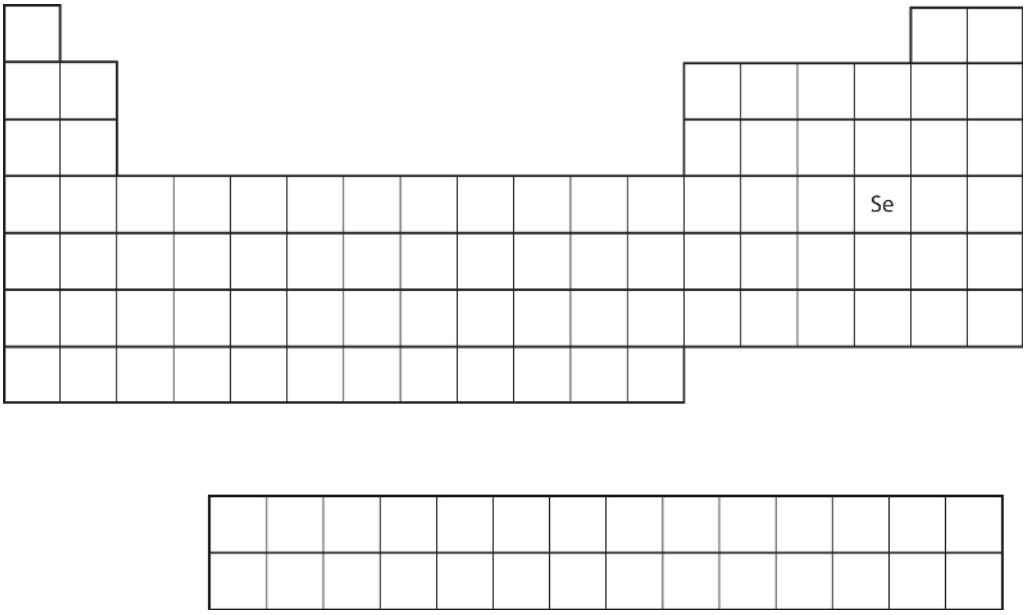


Figure **3.6.10**: Selenium on the Periodic Table

Example 3.6.1

From the element's position on the periodic table, predict the valence shell electron configuration for each atom (Figure **3.6.11**).

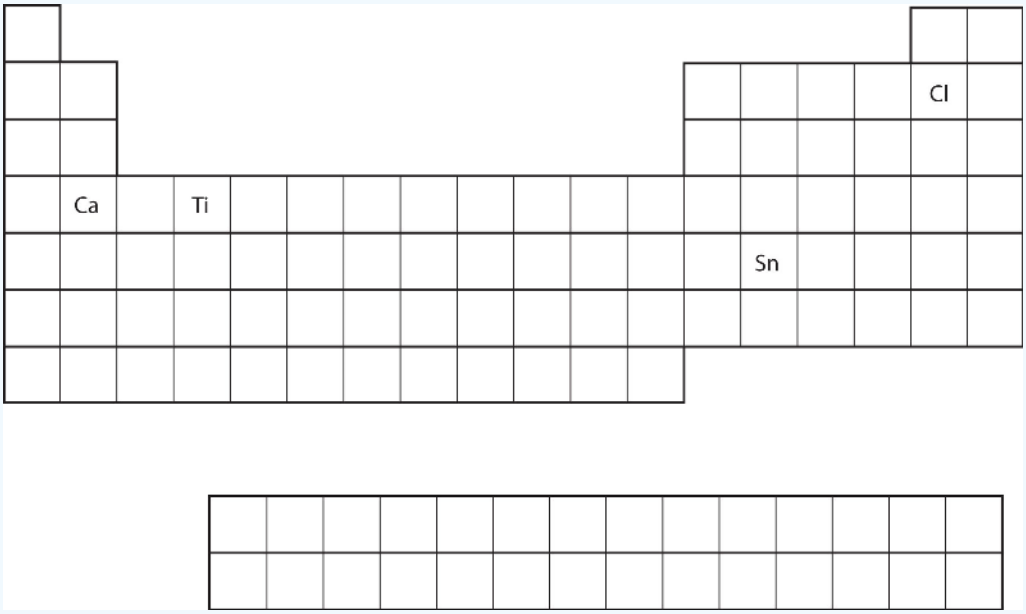


Figure **3.6.11**: Various Elements on the Periodic Table

1. Ca
2. Sn

Solution

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Answer b

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Summary

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3.7: Periodic Trends

Learning Objective

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

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

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

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

\[as\downarrow PT,atomic\; radius \uparrow\nonumber \]

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

$$as \rightarrow PT, atomic\ radius \downarrow$$

Figure **3.7.1** shows spheres representing the atoms of the *s* and *p* blocks from the periodic table to scale, showing the two trends for the atomic radius.

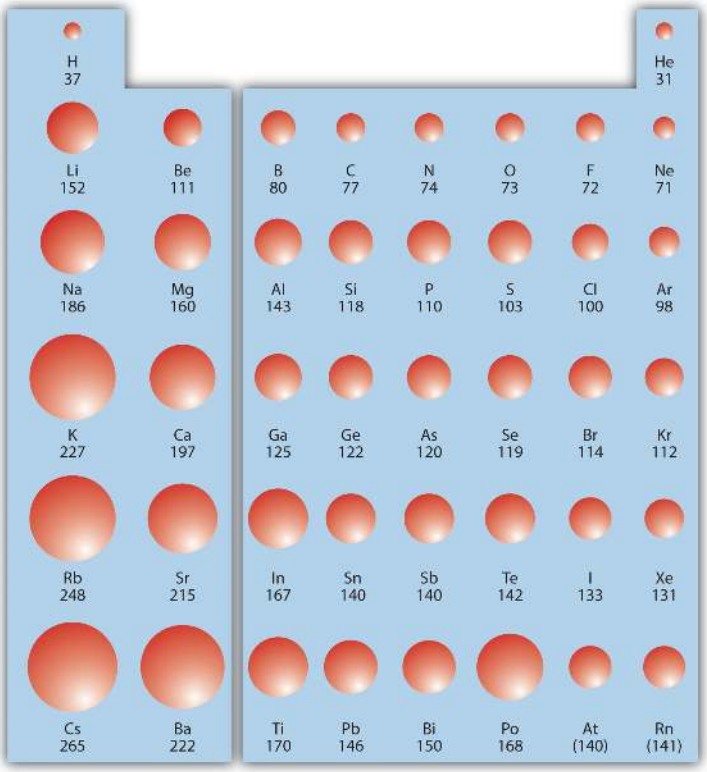


Figure 3.7.1: Atomic Radii Trends on the Periodic Table. Although there are some reversals in the trend (e.g., see Po in the bottom row), atoms generally get smaller as you go across the periodic table and larger as you go down any one column. Numbers are the radii in pm.

Example 3.7.1: Atomic Radii

Referring only to a periodic table and not to Figure **3.7.1**, which atom is larger in each pair?

a. Si or S
b. S or Te

Solution

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

Exercise 3.7.1: Atomic Radii

Referring only to a periodic table and not to Figure **3.7.1**, which atom is smaller, Ca or Br?

Answer

Br

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

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

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

$$as \downarrow PT,\ IE \downarrow$$

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

$$as \rightarrow PT,\ IE \uparrow$$

Figure **3.7.2** shows values of IE versus position on the periodic table. Again, the trend isn't absolute, but the general trends going across and down the periodic table should be obvious.

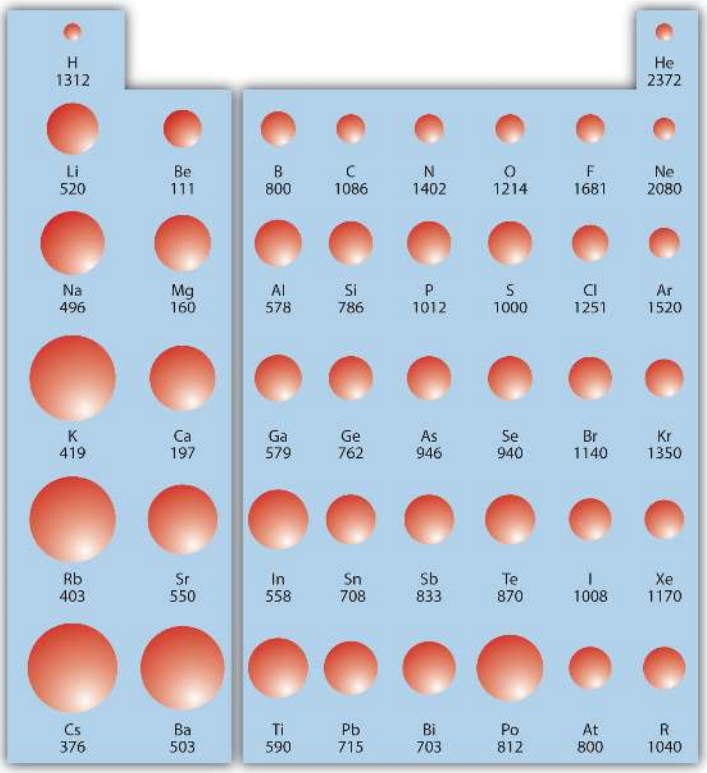


Figure **3.7.2**: Ionization Energy on the Periodic Table. Values are in kJ/mol.

IE also shows an interesting trend within a given atom. This is because more than one IE can be defined by removing successive electrons (if the atom has them to begin with):

- First Ionization Energy (IE_1):

$$A(g) \rightarrow A^+(g) + e^-$$

- Second Ionization Energy (IE_2):

$$A^+(g) \rightarrow A^{2+}(g) + e^-$$

- Third Ionization Energy (IE_3):

$$A^{2+}(g) \rightarrow A^{3+}(g) + e^-$$

and so forth.

Each successive IE is larger than the previous because an electron is being removed from an atom with a progressively larger positive charge. However, IE takes a large jump when a successive ionization goes down into a new shell. For example, the following are the first three IEs for Mg, whose electron configuration is $1s^2 2s^2 2p^6 3s^2$:

First Ionization Energy (IE_1) = 738 kJ/mol:

$$Mg(g) \rightarrow Mg^+(g) + e^-$$

Second Ionization Energy (IE_2) = 1,450 kJ/mol:

$$Mg^{+}(g) \rightarrow Mg^{2+}(g) + e^{-}$$

Third Ionization Energy (IE_3) = 7,734 kJ/mol:

$$Mg^{2+}(g) \rightarrow Mg^{3+}(g) + e^{-}$$

The second IE is twice the first, which is not a surprise: the first IE involves removing an electron from a neutral atom, while the second one involves removing an electron from a positive ion. The third IE, however, is over *five times* the previous one. Why is it so much larger? Because the first two electrons are removed from the 3*s* subshell, but the third electron has to be removed from the n = 2 shell (specifically, the 2*p* subshell, which is lower in energy than the n = 3 shell). Thus, it takes much more energy than just overcoming a larger ionic charge would suggest. Trends like this one demonstrate that electrons within atoms are organized in groups.

Example 3.7.2: Ionization Energies

Which atom in each pair has the larger first ionization energy?

a. Ca or Sr
b. K or K^+

Solution

a. Because Sr is below Ca on the periodic table, it is easier to remove an electron from it; thus, Ca has the higher IE.
b. Because K^+ has a positive charge, it will be harder to remove another electron from it, so its IE is larger than that of K. Indeed, it will be significantly larger because the next electron in K^+ to be removed comes from another shell.

Exercise 3.7.2: Ionization Energies

Which atom has the lower ionization energy, C or F?

Answer

C

The opposite of IE is described by **electron affinity (EA),** which is the energy change when a gas-phase atom accepts an electron:

$$A(g) + e^{-} \rightarrow A^{-}(g) \quad \Delta H \equiv EA$$

EA is also usually expressed in kJ/mol. EA also demonstrates some periodic trends, although they are less obvious than the other periodic trends discussed previously. Generally, as you go across the periodic table, EA increases its magnitude:

$$as \rightarrow PT,\ EA \uparrow$$

There is not a definitive trend as you go down the periodic table; sometimes EA increases, sometimes it decreases. Figure **3.7.3** shows EA values versus position on the periodic table for the *s*- and *p*-block elements. The trend isn't absolute, especially considering the large positive EA values for the second column. However, the general trend going across the periodic table should be obvious.

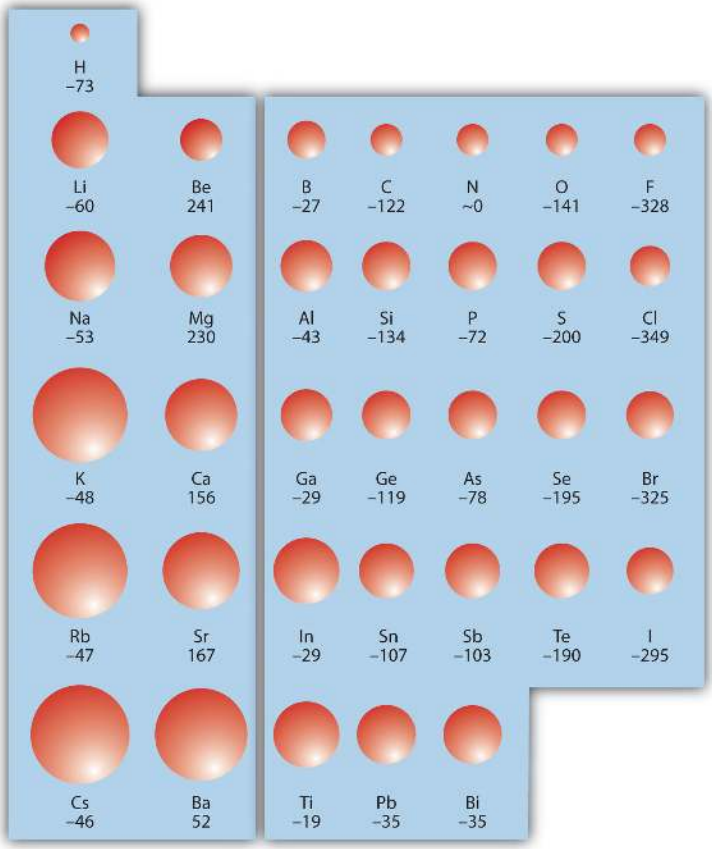


Figure **3.7.3**: Electron Affinity on the Periodic Table. Values are in kJ/mol.

✔ Example 3.7.3: Electron Affinities

Predict which atom in each pair will have the highest magnitude of Electron Affinity.

a. C or F
b. Na or S

Solution

a. C and F are in the same row on the periodic table, but F is farther to the right. Therefore, F should have the larger magnitude of EA.
b. Na and S are in the same row on the periodic table, but S is farther to the right. Therefore, S should have the larger magnitude of EA.

? Exercise 3.7.3: Electron Affinities

Predict which atom will have the highest magnitude of Electron Affinity: As or Br.

Answer

Br

Summary

Certain properties—notably atomic radius, ionization energies, and electron affinities—can be qualitatively understood by the positions of the elements on the periodic table.

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CHAPTER OVERVIEW

4: Chemical Compounds

4.1: Ions and Ionic Compounds

4.2: A Molecular View of Elements and Compounds

4.3: Molecules and Chemical Nomenclature

4.4: Acids

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4.1: Ions and Ionic Compounds

Learning Objectives

- Know how ions form.
- Learn the characteristic charges that ions have.
- Construct a proper formula for an ionic compound.
- Generate a proper name for an ionic compound.

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

Individual atoms can gain or lose electrons. When they do, they become *monatomic* ions. When atoms gain or lose electrons, they usually gain or lose a characteristic number of electrons and so take on a characteristic overall charge. Table **4.1.1** lists some common ions in terms of how many electrons they lose (making cations) or gain (making anions). There are several things to notice about the ions in Table **4.1.1**. First, each element that forms a cation is a metal, except for one (hydrogen), while each element that forms an anion is a nonmetal. This is actually one of the chemical properties of metals and nonmetals: metals tend to form cations, while nonmetals tend to form anions. Second, most atoms form ions of a single characteristic charge. When sodium atoms form ions, they always form a 1+ charge, never a 2+ or 3+ or even 1− charge. Thus, if you commit the information in Table **4.1.1** to memory, you will always know what charges most atoms form.

Table **4.1.1**: Monatomic Ions of Various Charges

Ions formed by losing a single electron	H^+
Na^+	
K^+	
Rb^+	
Ag^+	
Au^+	
Ions formed by losing two electrons	Mg^{2+}
	Ca^{2+}
	Sr^{2+}
	Fe^{2+}
	Co^{2+}
	Ni^{2+}
	Cu^{2+}
	Zn^{2+}
	Sn^{2+}
	Hg^{2+}
	Pb^{2+}
Ions formed by losing three electrons	Sc^{3+}
	Fe^{3+}
	Co^{3+}
	Ni^{3+}
	Au^{3+}
	Al^{3+}
	Cr^{3+}
Ions formed by losing four electrons	Ti^{4+}
	Sn^{4+}
	Pb^{4+}
Ions formed by gaining a single electron	F^-
	Cl^-
	Br^-
	I^-
Ions formed by gaining two electrons	O^{2-}
	S^{2-}
	Se^{2-}
Ions formed by gaining three electrons	N^{3-}
	P^{3-}

Third, there are some exceptions to the previous point. A few elements, all of which are metals, can form more than one possible charge. For example, iron atoms can form 2+ cations or 3+ cations. Cobalt is another element that can form more than one possible charged ion (2+ and 3+), while lead can form 2+ or 4+ cations. Unfortunately, there is little understanding which two charges a metal atom may take, so it is best to just memorize the possible charges a particular element can have.

Note the convention for indicating an ion. The magnitude of the charge is listed as a right superscript next to the symbol of the element. If the charge is a single positive or negative one, the number 1 is not written; if the magnitude of the charge is greater than 1, then the number is written *before* the + or − sign. An element symbol without a charge written next to it is assumed to be the uncharged atom.

Naming an ion is straightforward. For a cation, simply use the name of the element and add the word *ion* (or if you want to be more specific, add *cation*) after the element's name. So Na^+ is the sodium ion; Ca^{2+} is the calcium ion. If the element has more than one possible charge, the value of the charge comes after the element name and before the word *ion*. Thus, Fe^{2+} is the iron two ion, while Fe^{3+} is the iron three ion. In print, we use roman numerals in parentheses to represent the charge on the ion; so these two iron ions would be represented as the iron(II) cation and the iron(III) cation, respectively.

For a monatomic anion, use the stem of the element name and append the suffix *-ide* to it, and then add *ion*. This is similar to how we named molecular compounds. Thus, Cl^- is the chloride ion, and N^{3-} is the nitride ion.

Example 4.1.1

Name each species.

a. O^{2-}
b. Co
c. Co^{2+}

Solution

a. This species has a 2− charge on it, so it is an anion. Anions are named using the stem of the element name with the suffix *-ide* added. This is the oxide anion.
b. Because this species has no charge, it is an atom in its elemental form. This is cobalt.
c. In this case, there is a 2+ charge on the atom, so it is a cation. We note from Table **4.1.1** that cobalt cations can have two possible charges, so the name of the ion must specify which charge the ion has. This is the cobalt(II) cation.

Exercise 4.1.1

Name each species.

a. P^{3-}
b. Sr^{2+}

Answers

a. the phosphide anion
b. the strontium cation

Ionic Formulas

Chemical formulas for ionic compounds are called ionic formulas. A proper ionic formula has a cation and an anion in it; an ionic compound is never formed between two cations only or two anions only. The key to writing proper ionic formulas is simple: the total positive charge must balance the total negative charge. Because the charges on the ions are characteristic, sometimes we have to have more than one of a cation or an anion to balance the overall positive and negative charges. It is conventional to use the lowest ratio of ions that are needed to balance the charges.

For example, consider the ionic compound between Na^+ and Cl^-. Each ion has a single charge, one positive and one negative, so we need only one ion of each to balance the overall charge. When writing the ionic formula, we follow two additional conventions: (1) write the formula for the cation first and the formula for the anion second, but (2) do not write the charges on the ions. Thus, for

the compound between Na^+ and Cl^-, we have the ionic formula NaCl (Figure **4.1.1**). The formula Na_2Cl_2 also has balanced charges, but the convention is to use the lowest ratio of ions, which would be one of each. (Remember from our conventions for writing formulas that we do not write a 1 subscript if there is only one atom of a particular element present.) For the ionic compound between magnesium cations (Mg^{2+}) and oxide anions (O^{2-}), again we need only one of each ion to balance the charges. By convention, the formula is MgO.



Figure **4.1.1**: The ionic compound **NaCl** is table salt and is very common. (Public Domain; Pexels.)

For the ionic compound between Mg^{2+} ions and Cl^- ions, we now consider the fact that the charges have different magnitudes: 2+ on the magnesium ion and 1− on the chloride ion. To balance the charges with the lowest number of ions possible, we need to have two chloride ions to balance the charge on the one magnesium ion. Rather than write the formula MgClCl, we combine the two chloride ions and write it with a 2 subscript: $MgCl_2$.

What is the formula $MgCl_2$ telling us? There are two chloride ions in the formula. Although chlorine as an element is a diatomic molecule, Cl_2, elemental chlorine is not part of this ionic compound. The chlorine is in the form of a negatively charged *ion*, not the neutral *element*. The 2 subscript is in the ionic formula because we need two Cl^- ions to balance the charge on one Mg^{2+} ion.

Example 4.1.2

Write the proper ionic formula for each of the two given ions.

a. Ca^{2+} and Cl^-
b. Al^{3+} and F^-
c. Al^{3+} and O^{2-}

Solution

a. We need two Cl^- ions to balance the charge on one Ca^{2+} ion, so the proper ionic formula is $CaCl_2$.
b. We need three F^- ions to balance the charge on the Al^{3+} ion, so the proper ionic formula is AlF_3.
c. With Al^{3+} and O^{2-}, note that neither charge is a perfect multiple of the other. This means we have to go to a least common multiple, which in this case will be six. To get a total of 6+, we need two Al^{3+} ions; to get 6−, we need three O^{2-} ions. Hence the proper ionic formula is Al_2O_3.

Exercise 4.1.2

Write the proper ionic formulas for each of the two given ions.

a. Fe^{2+} and S^{2-}
b. Fe^{3+} and S^{2-}

Answers

a. FeS
b. Fe_2S_3

Naming ionic compounds is simple: combine the name of the cation and the name of the anion, in both cases omitting the word *ion*. *Do not use numerical prefixes if there is more than one ion necessary to balance the charges.* NaCl is sodium chloride, a combination of the name of the cation (sodium) and the anion (chloride). MgO is magnesium oxide. $MgCl_2$ is magnesium chloride—*not* magnesium dichloride.

When naming ionic compounds whose cations can have more than one possible charge, we must also include the charge, in parentheses and in roman numerals, as part of the name. Hence FeS is iron(II) sulfide, while Fe_2S_3 is iron(III) sulfide. Again, no numerical prefixes appear in the name. The number of ions in the formula is dictated by the need to balance the positive and negative charges.

Example 4.1.3

Name each ionic compound.

a. $CaCl_2$
b. AlF_3
c. Co_2O_3

Solution

a. Using the names of the ions, this ionic compound is named calcium chloride. It is *not* calcium(II) chloride, because calcium forms only one cation when it forms an ion, and it has a characteristic charge of 2+.
b. The name of this ionic compound is aluminum fluoride.
c. We know that cobalt can have more than one possible charge; we just need to determine what it is. Oxide always has a 2− charge, so with three oxide ions, we have a total negative charge of 6−. This means that the two cobalt ions have to contribute 6+, which for two cobalt ions means that each one is 3+. Therefore, the proper name for this ionic compound is cobalt(III) oxide.

Exercise 4.1.3

Name each ionic compound.

a. Sc_2O_3
b. AgCl

Answers

a. scandium oxide
b. silver chloride

How do you know whether a formula—and by extension, a name—is for a molecular compound or for an ionic compound? Molecular compounds form between nonmetals and nonmetals, while ionic compounds form between metals and nonmetals. The periodic table can be used to determine which elements are metals and nonmetals.

There also exists a group of ions that contain more than one atom. These are called **polyatomic ions**. Table 4.1.2 lists the formulas, charges, and names of some common polyatomic ions. Only one of them, the ammonium ion, is a cation; the rest are anions. Most of them also contain oxygen atoms, so sometimes they are referred to as ***oxyanions***. Some of them, such as nitrate and nitrite, and sulfate and sulfite, have very similar formulas and names, so care must be taken to get the formulas and names correct. Note that the -ite polyatomic ion has one less oxygen atom in its formula than the -ate ion but with the same ionic charge.

Table 4.1.2: Common Polyatomic Ions

Name	Formula and Charge		Name	Formula and Charge
ammonium	NH_4^+		hydroxide	OH^-
acetate	$C_2H_3O_2^-$, or CH_3COO^-		nitrate	NO_3^-
bicarbonate (hydrogen carbonate)	HCO_3^-		nitrite	NO_2^-
bisulfate (hydrogen sulfate)	HSO_4^-		peroxide	O_2^{2-}
carbonate	CO_3^{2-}		perchlorate	ClO_4^-
chlorate	ClO_3^-		phosphate	PO_4^{3-}
chromate	CrO_4^{2-}		sulfate	SO_4^{2-}
cyanide	CN^-		sulfite	SO_3^{2-}
dichromate	$Cr_2O_7^{2-}$		triiodide	I_3^-

The naming of ionic compounds that contain polyatomic ions follows the same rules as the naming for other ionic compounds: simply combine the name of the cation and the name of the anion. Do not use numerical prefixes in the name if there is more than one polyatomic ion; the only exception to this is if the name of the ion itself contains a numerical prefix, such as dichromate or triiodide.

Writing the formulas of ionic compounds has one important difference. If more than one polyatomic ion is needed to balance the overall charge in the formula, enclose the formula of the polyatomic ion in parentheses and write the proper numerical subscript to the right and *outside* of the parentheses. Thus, the formula between calcium ions, Ca^{2+}, and nitrate ions, NO_3^-, is properly written $Ca(NO_3)_2$, not $CaNO_{32}$ or CaN_2O_6. Use parentheses where required. The name of this ionic compound is simply calcium nitrate.

Example 4.1.4

Write the proper formula and give the proper name for each ionic compound formed between the two listed ions.

a. NH_4^+ and S^{2-}
b. Al^{3+} and PO_4^{3-}
c. Fe^{2+} and PO_4^{3-}

Solution

a. Because the ammonium ion has a 1+ charge and the sulfide ion has a 2− charge, we need two ammonium ions to balance the charge on a single sulfide ion. Enclosing the formula for the ammonium ion in parentheses, we have $(NH_4)_2S$. The compound's name is ammonium sulfide.
b. Because the ions have the same magnitude of charge, we need only one of each to balance the charges. The formula is $AlPO_4$, and the name of the compound is aluminum phosphate.
c. Neither charge is an exact multiple of the other, so we have to go to the least common multiple of 6. To get 6+, we need three iron(II) ions, and to get 6−, we need two phosphate ions. The proper formula is $Fe_3(PO_4)_2$, and the compound's name is iron(II) phosphate.

Exercise 4.1.4

Write the proper formula and give the proper name for each ionic compound formed between the two listed ions.

a. NH_4^+ and PO_4^{3-}
b. Co^{3+} and NO_2^-

Answers

a. $(NH_4)_3PO_4$, ammonium phosphate

b. $Co(NO_2)_3$, cobalt(III) nitrite

Food and Drink Application: Sodium in Your Food

The element sodium, at least in its ionic form as Na^+, is a necessary nutrient for humans to live. In fact, the human body is approximately 0.15% sodium, with the average person having one-twentieth to one-tenth of a kilogram in their body at any given time, mostly in fluids outside cells and in other bodily fluids.

Sodium is also present in our diet. The common table salt we use on our foods is an ionic sodium compound. Many processed foods also contain significant amounts of sodium added to them as a variety of ionic compounds. Why are sodium compounds used so much? Usually sodium compounds are inexpensive, but, more importantly, most ionic sodium compounds dissolve easily. This allows processed food manufacturers to add sodium-containing substances to food mixtures and know that the compound will dissolve and distribute evenly throughout the food. Simple ionic compounds such as sodium nitrite ($NaNO_2$) are added to cured meats, such as bacon and deli-style meats, while a compound called sodium benzoate is added to many packaged foods as a preservative. Table **4.1.3** is a partial list of some sodium additives used in food. Some of them you may recognize after reading this chapter. Others you may not recognize, but they are all ionic sodium compounds with some negatively charged ion also present.

Table **4.1.3**: Some Sodium Compounds Added to Food

Sodium Compound	Use in Food
Sodium acetate	preservative, acidity regulator
Sodium adipate	food acid
Sodium alginate	thickener, vegetable gum, stabilizer, gelling agent, emulsifier
Sodium aluminum phosphate	acidity regulator, emulsifier
Sodium aluminosilicate	anti-caking agent
Sodium ascorbate	antioxidant
Sodium benzoate	preservative
Sodium bicarbonate	mineral salt
Sodium bisulfite	preservative, antioxidant
Sodium carbonate	mineral salt
Sodium carboxymethylcellulose	emulsifier
Sodium citrates	food acid
Sodium dehydroacetate	preservative
Sodium erythorbate	antioxidant
Sodium erythorbin	antioxidant
Sodium ethyl para-hydroxybenzoate	preservative
Sodium ferrocyanide	anti-caking agent
Sodium formate	preservative
Sodium fumarate	food acid
Sodium gluconate	stabilizer
Sodium hydrogen acetate	preservative, acidity regulator
Sodium hydroxide	mineral salt
Sodium lactate	food acid
Sodium malate	food acid
Sodium metabisulfite	preservative, antioxidant, bleaching agent
Sodium methyl para-hydroxybenzoate	preservative
Sodium nitrate	preservative, color fixative
Sodium nitrite	preservative, color fixative
Sodium orthophenyl phenol	preservative
Sodium propionate	preservative
Sodium propyl para-hydroxybenzoate	preservative
Sodium sorbate	preservative
Sodium stearoyl lactylate	emulsifier

Sodium Compound	Use in Food
Sodium succinates	acidity regulator, flavor enhancer
Sodium salts of fatty acids	emulsifier, stabilizer, anti-caking agent
Sodium sulfite	mineral salt, preservative, antioxidant
Sodium sulfite	preservative, antioxidant
Sodium tartrate	food acid
Sodium tetraborate	preservative

The use of so many sodium compounds in prepared and processed foods has alarmed some physicians and nutritionists. They argue that the average person consumes too much sodium from his or her diet. The average person needs only about 500 mg of sodium every day; most people consume more than this—up to 10 times as much. Some studies have implicated increased sodium intake with high blood pressure; newer studies suggest that the link is questionable. However, there has been a push to reduce the amount of sodium most people ingest every day: avoid processed and manufactured foods, read labels on packaged foods (which include an indication of the sodium content), avoid oversalting foods, and use other herbs and spices besides salt in cooking.



Figure **4.1.2**: Food labels include the amount of sodium per serving. This particular label shows that there are 75 mg of sodium in one serving of this particular food item.

Key Takeaways

- Ions form when atoms lose or gain electrons.
- Ionic compounds have positive ions and negative ions.
- Ionic formulas balance the total positive and negative charges.
- Ionic compounds have a simple system of naming.
- Groups of atoms can have an overall charge and make ionic compounds.

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4.2: A Molecular View of Elements and Compounds

Learning Objectives

- Classify substances as atomic elements, molecular elements, molecular compounds, or ionic compounds.

Atomic Elements

Most elements exist with **individual atoms** as their basic unit. It is assumed that there is only one atom in a formula if there is no numerical subscript on the right side of an element's symbol.

Molecular Elements

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

Table **4.2.1**: Elements That Exist as Diatomic Molecules

Hydrogen, H	Oxygen	Nitrogen	Fluorine	Chlorine	Bromine	Iodine

Some elements exist naturally as molecules. For example, hydrogen and oxygen exist as two-atom molecules. Other elements also exist naturally as diatomic molecules—a molecule with only two atoms (Table **4.2.1**). As with any molecule, these elements are labeled with a **molecular formula**, a formal listing of what and how many atoms are in a molecule. (Sometimes only the word *formula* is used, and its meaning is inferred from the context.) For example, the molecular formula for elemental hydrogen is H_2, with H being the symbol for hydrogen and the subscript 2 implying that there are two atoms of this element in the molecule. Other diatomic elements have similar formulas: O_2, N_2, and so forth. Other elements exist as molecules—for example, sulfur normally exists as an eight-atom molecule, S_8, while phosphorus exists as a four-atom molecule, P_4 (Figure **4.2.1**).

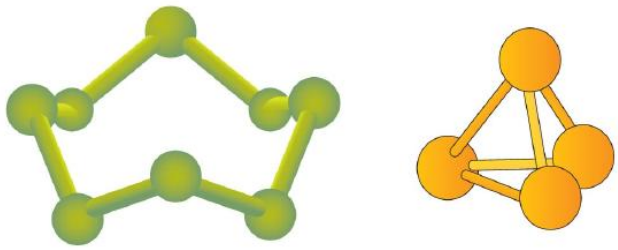


Figure **4.2.1**: Molecular Art of S_8 and P_4 Molecules. If each green ball represents a sulfur atom, then the diagram on the left represents an S_8 molecule. The molecule on the right shows that one form of elemental phosphorus exists, as a four-atom molecule.

Figure **4.2.1** shows two examples of how molecules will be represented in this text. An atom is represented by a small ball or sphere, which generally indicates where the nucleus is in the molecule. A cylindrical line connecting the balls represents the connection between the atoms that make this collection of atoms a molecule. This connection is called a chemical bond.

Ionic Compounds

The elements in the periodic table are divided into specific groupings; the metals, the non-metals, the semi-metals, and so on. These groupings are largely based on physical properties and on the tendency of the various elements to bond with other elements by forming either an ionic or a covalent bond. As a general rule of thumb, compounds that involve a metal binding with either a non-metal or a semi-metal will display ionic bonding. Thus, the compound formed from sodium and chlorine will be ionic (a metal and a non-metal). The basic unit of ionic compounds is the **formula unit**.

Molecular Compounds

Compounds that are composed of only non-metals or semi-metals with non-metals will display covalent bonding and will be classified as molecular compounds. Nitrogen monoxide (NO) will be a covalently bound molecule (two non-metals) and silicon dioxide (SiO_2) will also be a covalently bound molecule (a semi-metal and a non-metal). The basic unit of molecular compounds is the **molecule**.

Example 4.2.1

Provide the classification (i.e. atomic element, molecular element, molecular compound, or ionic compound) of each substance.

a. Fe
b. PCl_3
c. LiBr
d. P_4
e. oxygen gas

Solution

a. **Fe** (iron) is an element that is represented with no subscript, so it is an **atomic element**.
b. **PCl_3** is made up of two nonmetals, so it is a **molecular compound**.
c. **LiBr** is made up of lithium, a metal, and bromine, a nonmetal, so it is an **ionic compound**.
d. **P_4** is a substance that is made up of four atoms of the same element, so it is a **molecular element**.
e. The formula for **oxygen gas** is **O_2** so it is a molecular element.

Exercise 4.2.1

Provide the classification (i.e. atomic element, molecular element, molecular compound, or ionic compound) of each substance.

a. I_2
b. He
c. H_2O
d. Al
e. CuCl

Answer a:
molecular element

Answer b:
atomic element

Answer c:
molecular compound

Answer d:
atomic element

Answer e:
ionic compound

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4.3: Molecules and Chemical Nomenclature

Learning Objectives

- Define *molecule*.
- Name simple molecules based on their formulas.
- Determine a formula of a molecule based on its name.

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

Table **4.3.1**: Elements That Exist as Diatomic Molecules

Hydrogen ($\mathbf{H_2}$)	Oxygen ($\mathbf{O_2}$)	Nitrogen ($\mathbf{N_2}$)	Fluorine ($\mathbf{F_2}$)
Chlorine ($\mathbf{Cl_2}$)	Bromine ($\mathbf{Br_2}$)	Iodine ($\mathbf{I_2}$)	

Some elements exist naturally as molecules. For example, hydrogen and oxygen exist as two-atom molecules. Other elements also exist naturally as diatomic molecules (Table **4.3.1**). As with any molecule, these elements are labeled with a molecular formula, a formal listing of what and how many atoms are in a molecule. (Sometimes only the word *formula* is used, and its meaning is inferred from the context.) For example, the molecular formula for elemental hydrogen is H_2, with H being the symbol for hydrogen and the subscript 2 implying that there are two atoms of this element in the molecule. Other diatomic elements have similar formulas: O_2, N_2, and so forth. Other elements exist as molecules—for example, sulfur normally exists as an eight-atom molecule, S_8, while phosphorus exists as a four-atom molecule, P_4 (Figure **4.3.1**). Otherwise, we will assume that elements exist as individual atoms, rather than molecules. It is assumed that there is only one atom in a formula if there is no numerical subscript on the right side of an element's symbol.

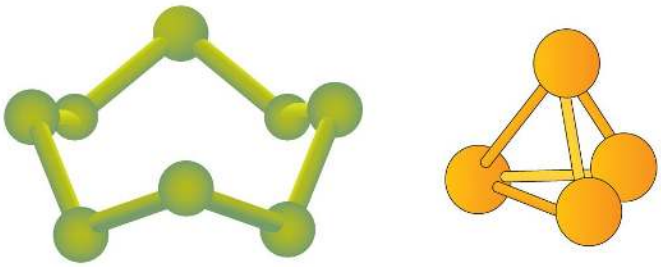


Figure **4.3.1**: Molecular Art of S_8 and P_4 Molecules. If each green ball represents a sulfur atom, then the diagram on the left represents an S_8 molecule. The molecule on the right shows that one form of elemental phosphorus exists, as a four-atom molecule.

Figure **4.3.1** shows two examples of how we will be representing molecules in this text. An atom is represented by a small ball or sphere, which generally indicates where the nucleus is in the molecule. A cylindrical line connecting the balls represents the connection between the atoms that make this collection of atoms a molecule. This connection is called a chemical bond and is the connection between two atoms in a molecule.

Many compounds exist as molecules. In particular, when nonmetals connect with other nonmetals, the compounds typically exist as molecules. (Compounds between a metal and a nonmetal are different and will be considered in Section 3.4.) In some cases, there are many different kinds of molecules that can be formed between any given elements, with all the different molecules having different chemical and physical properties. How do we tell them apart?

The answer is a very specific system of naming compounds, called *chemical nomenclature*. By following the rules of nomenclature, each and every compound has its own unique name, and each name refers to one and only one compound. Here, we will start with relatively simple molecules that have only two elements in them, the so-called *binary compounds*:

1. Identify the elements in the molecule from its formula.

2. Begin the name with the element name of the first element. If there is more than one atom of this element in the molecular formula, use a numerical prefix to indicate the number of atoms, as listed in Table **4.3.2**. *Do not use the prefix* mono- *if there is only one atom of the first element.*
3. Name the second element by using three pieces:
   - a numerical prefix indicating the number of atoms of the second element, plus
   - the stem of the element name (e.g., *ox* for oxygen, *chlor* for chlorine, etc.), plus
   - the suffix *-ide*
4. Combine the two words, leaving a space between them.

Table **4.3.2**: Numerical Prefixes Used in Naming Molecular Compounds

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

Let us see how these steps work for a molecule whose molecular formula is SO_2, which has one sulfur atom and two oxygen atoms—this completes step 1. According to step 2, we start with the name of the first element—sulfur. Remember, we do not use the *mono-* prefix for the first element. Now for step 3, we combine the numerical prefix *di-* (see Table **4.3.2**) with the stem *ox-* and the suffix *-ide*, to make *dioxide*. Bringing these two words together, we have the unique name for this compound—sulfur dioxide.

Why all this trouble? There is another common compound consisting of sulfur and oxygen whose molecular formula is SO_3, so the compounds need to be distinguished. SO_3 has three oxygen atoms in it, so it is a different compound with different chemical and physical properties. The system of chemical nomenclature is designed to *give this compound its own unique name*. Its name, if you go through all the steps, is sulfur trioxide. Different compounds have different names.

In some cases, when a prefix ends in *a* or *o;* and the element name begins with *o*, we drop the *a* or *o* on the prefix. So we see *monoxide* or *pentoxide*, rather than *monooxide* or *pentaoxide* in molecule names.

Example 4.3.1

Name each molecule.

a. PF_3
b. CO
c. Se_2Br_2

Solution

a. A molecule with a single phosphorus atom and three fluorine atoms is called phosphorus trifluoride.
b. A compound with one carbon atom and one oxygen atom is properly called carbon monoxide, not carbon monooxide.
c. There are two atoms of each element, selenium and bromine. According to the rules, the proper name here is *diselenium dibromide*.

Exercise 4.3.1

Name each molecule.

a. SF_4
b. P_2S_5

Answer a

sulfur tetrafluoride

Answer b

diphosphorus pentasulfide

One great thing about this system is that it works both ways. From the name of a compound, you should be able to determine its molecular formula. Simply list the element symbols, with a numerical subscript if there is more than one atom of that element, in the order of the name (we do not use the subscript 1 if there is only one atom of the element present; 1 is implied). From the name *nitrogen trichloride*, you should be able to get NCl_3 as the formula for this molecule. From the name *diphosphorus pentoxide*, you should be able to get the formula P_2O_5 (note the numerical prefix on the first element, indicating there is more than one atom of phosphorus in the formula).

Example 4.3.2

Give the formula for each molecule.

a. carbon tetrachloride
b. silicon dioxide
c. trisilicon tetranitride

Solution

a. The name *carbon tetrachloride* implies one carbon atom and four chlorine atoms, so the formula is CCl_4.
b. The name *silicon dioxide* implies one silicon atom and two oxygen atoms, so the formula is SiO_2.
c. We have a name that has numerical prefixes on both elements. *Tri-* means three, and *tetra-* means four, so the formula of this compound is Si_3N_4.

Exercise 4.3.2

Give the formula for each molecule.

a. disulfur difluoride
b. iodine pentabromide

Answer a

S_2F_2

Answer b

IBr_5

Some simple molecules have common names that we use as part of the formal system of chemical nomenclature. For example, H_2O is given the name *water*, not *dihydrogen monoxide*. NH_3 is called *ammonia*, while CH_4 is called *methane*. We will occasionally see other molecules that have common names; we will point them out as they occur.

Key Takeaways

- Molecules are groups of atoms that behave as a single unit.
- Some elements exist as molecules: hydrogen, oxygen, sulfur, and so forth.
- There are rules that can express a unique name for any given molecule, and a unique formula for any given name.

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4.4: Acids

Learning Objectives

- Define *acid*.
- Name a simple acid.

There is one other group of compounds that is important to us—acids—and these compounds have interesting chemical properties. Initially, we will define an acid as an ionic compound of the H^+ cation dissolved in water. To indicate that something is dissolved in water, we will use the phase label (aq) next to a chemical formula (where aq stands for "aqueous," a word that describes something dissolved in water). If the formula does not have this label, then the compound is treated as a molecular compound rather than an acid.

Acids have their own nomenclature system. If an acid is composed of only hydrogen and one other element, the name is *hydro-* + the stem of the other element + *-ic acid*. For example, the compound HCl(aq) is hydrochloric acid, while H_2S(aq) is hydrosulfuric acid. If these acids were not dissolved in water, the compounds would be called hydrogen chloride and hydrogen sulfide, respectively. Both of these substances are well known as molecular compounds; when dissolved in water, however, they are treated as acids.

If a compound is composed of hydrogen ions and a polyatomic anion, then the name of the acid is derived from the stem of the polyatomic ion's name. Typically, if the anion name ends in -ate, the name of the acid is the stem of the anion name plus *-ic acid*; if the related anion's name ends in -ite, the name of the corresponding acid is the stem of the anion name plus *-ous acid*. Table **4.4.1** lists the formulas and names of a variety of acids that you should be familiar with. You should recognize most of the anions in the formulas of the acids.

Table **4.4.1** Names and Formulas of Acids

Formula	Name
$HC_2H_3O_2$	acetic acid
$HClO_3$	chloric acid
HCl	hydrochloric acid
HBr	hydrobromic acid
HI	hydriodic acid
HF	hydrofluoric acid
HNO_3	nitric acid
$H_2C_2O_4$	oxalic acid
$HClO_4$	perchloric acid
H_3PO_4	phosphoric acid
H_2SO_4	sulfuric acid
H_2SO_3	sulfurous acid

Note: The "aq" label is omitted for clarity.

Example 4.4.1

Name each acid without consulting Table 3.9.

1. HBr

2. H_2SO_4

Solution

1. As a binary acid, the acid's name is *hydro-* + stem name + *-ic acid*. Because this acid contains a bromine atom, the name is hydrobromic acid.
2. Because this acid is derived from the sulfate ion, the name of the acid is the stem of the anion name + *-ic acid*. The name of this acid is sulfuric acid.

? Exercise 4.4.1

Name each acid.

a. HF
b. HNO_2

Answer a

hydrofluoric acid

Answer b

nitrous acid

All acids have some similar properties. For example, acids have a sour taste; in fact, the sour taste of some of our foods, such as citrus fruits and vinegar, is caused by the presence of acids in food. Many acids react with some metallic elements to form metal ions and elemental hydrogen. Acids make certain plant pigments change colors; indeed, the ripening of some fruits and vegetables is caused by the formation or destruction of excess acid in the plant. In Chapter 12, we will explore the chemical behavior of acids.

Acids are very prevalent in the world around us. We have already mentioned that citrus fruits contain acid; among other compounds, they contain citric acid, $H_3C_6H_5O_7(aq)$. Oxalic acid, $H_2C_2O_4(aq)$, is found in spinach and other green leafy vegetables. Hydrochloric acid not only is found in the stomach (stomach acid), but also can be bought in hardware stores as a cleaner for concrete and masonry. Phosphoric acid is an ingredient in some soft drinks.

Key Takeaways

- An acid is a compound of the H^+ ion dissolved in water.
- Acids have their own naming system.
- Acids have certain chemical properties that distinguish them from other compounds.

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CHAPTER OVERVIEW

5: Chemical Reactions

5.1: Prelude to Chemical Reactions
5.2: The Chemical Equation
5.3: Classifying Chemical Reactions
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5.5: Aqueous Solutions and Solubility - Compounds Dissolved in Water
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5.1: Prelude to Chemical Reactions

The space shuttle—and any other rocket-based system—uses chemical reactions to propel itself into space and maneuver itself when it gets into orbit. The rockets that lift the orbiter are of two different types. The three main engines are powered by reacting liquid hydrogen with liquid oxygen to generate water. Then there are the two solid rocket boosters, which use a solid fuel mixture that contains mainly ammonium perchlorate and powdered aluminum. The chemical reaction between these substances produces aluminum oxide, water, nitrogen gas, and hydrogen chloride. Although the solid rocket boosters each have a significantly lower mass than the liquid oxygen and liquid hydrogen tanks, they provide over 80% of the lift needed to put the shuttle into orbit—all because of chemical reactions.



Figure 5.1.1 The Space Shuttle. (Public Domain; NASA).

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5.2: The Chemical Equation

Learning Objectives

- Define *chemical equation*.
- Identify the parts of a chemical equation.

A chemical reaction expresses a chemical change. For example, one chemical property of hydrogen is that it will react with oxygen to make water. We can write that as follows:

$$\textbf{hydrogen reacts with oxygen to make water}$$

We can represent this chemical change more succinctly as:

$$\textbf{hydrogen} + \textbf{oxygen} \rightarrow \textbf{water}$$

where the + sign means that the two substances interact chemically with each other and the → symbol implies that a chemical reaction takes place. But substances can also be represented by chemical formulas. Remembering that hydrogen and oxygen both exist as diatomic molecules, we can rewrite our chemical change as:

$$\mathrm{H_2 + O_2 \longrightarrow H_2O}$$

This is an example of a chemical equation, which is a concise way of representing a **chemical reaction**. The initial substances are called **reactants** and the final substances are called **products**.

Unfortunately, it is also an *incomplete* chemical equation. The law of conservation of matter says that matter cannot be created or destroyed. In chemical equations, the number of atoms of each element in the reactants must be the same as the number of atoms of each element in the products. If we count the number of hydrogen atoms in the reactants and products, we find two hydrogen atoms. But if we count the number of oxygen atoms in the reactants and products, we find that there are two oxygen atoms in the reactants, but only one oxygen atom in the products.

What can we do? Can we change the subscripts in the formula for water so that it has two oxygen atoms in it? No—you *cannot* change the formulas of individual substances, because the chemical formula for a given substance is characteristic of that substance. What you *can* do, however, is to change the number of molecules that react or are produced. We do this one element at a time, going from one side of the reaction to the other, changing the number of molecules of a substance until all elements have the same number of atoms on each side.

To accommodate the two oxygen atoms as reactants, let us assume that we have two water molecules as products:

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

The 2 in front of the formula for water is called a **coefficient**. Now there are the same number of oxygen atoms in the reactants as there are in the product. But in satisfying the need for the same number of oxygen atoms on both sides of the reaction, we have also changed the number of hydrogen atoms on the product side, so the number of hydrogen atoms is no longer equal. No problem, simply go back to the reactant side of the equation, and add a coefficient in front of the H_2. The coefficient that works is 2:

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

There are now four hydrogen atoms in the reactants and also four atoms of hydrogen in the product. There are two oxygen atoms in the reactants and two atoms of oxygen in the product. The law of conservation of matter has been satisfied. When the reactants and products of a chemical equation have the same number of atoms of all elements present, we say that an equation is **balanced**. All proper chemical equations are balanced. If a substance does not have a coefficient written in front of it, it is assumed to be 1. Also, the convention is to use all whole numbers when balancing chemical equations. This sometimes makes us do a bit more "back and forth" work when balancing a chemical equation.

Example 5.2.1

Write and balance the chemical equation for each given chemical reaction.

1. Hydrogen and chlorine react to make HCl
2. Ethane, $\mathrm{C_2H_6}$, reacts with oxygen to make carbon dioxide and water.

Solution

1. Let us start by simply writing a chemical equation in terms of the formulas of the substances, remembering that both elemental hydrogen and chlorine are diatomic:

$$\mathrm{H_2 + Cl_2 \longrightarrow HCl}$$

There are two hydrogen atoms and two chlorine atoms in the reactants and one of each atom in the product. We can fix this by including the coefficient 2 on the product side:

$$\mathrm{H_2 + Cl_2 \longrightarrow 2\,HCl}$$

Now there are two hydrogen atoms and two chlorine atoms on both sides of the chemical equation, so it is balanced.

2. Start by writing the chemical equation in terms of the substances involved:

$$\mathrm{C_2H_6 + O_2 \longrightarrow CO_2 + H_2O}$$

We have two carbon atoms on the left, so we need two carbon dioxide molecules on the product side, so that each side has two carbon atoms; that element is balanced. We have six hydrogen atoms in the reactants, so we need six hydrogen atoms in the products. We can get this by having three water molecules:

$$\mathrm{C_2H_6 + O_2 \longrightarrow 2\,CO_2 + 3\,H_2O}$$

Now we have seven oxygen atoms in the products (four from the CO_2 and three from the H_2O). This means we need seven oxygen atoms in the reactants. However, because oxygen is a diatomic molecule, we can only get an even number of oxygen atoms at a time. We can achieve this by multiplying the other coefficients by 2:

$$\mathrm{2\,C_2H_6 + O_2 \longrightarrow 4\,CO_2 + 6\,H_2O}$$

By multiplying everything else by 2, we do not unbalance the other elements, and we now get an even number of oxygen atoms in the product—14. We can get 14 oxygen atoms on the reactant side by having 7 oxygen molecules:

$$\mathrm{2\,C_2H_6 + 7\,O_2 \longrightarrow 4\,CO_2 + 6\,H_2O}$$

As a check, recount everything to determine that each side has the same number of atoms of each element. This chemical equation is now balanced.

Exercise 5.2.1

Write and balance the chemical equation that represents nitrogen and hydrogen reacting to produce ammonia, NH_3.

Answer

\[\ce{N2 + 3H2 → 2NH3 \nonumber \nonumber \]

Many chemical equations also include phase labels for the substances: (s) for solid, (ℓ) for liquid, (g) for gas, and (aq) for aqueous (i.e., dissolved in water). Special conditions, such as temperature, may also be listed above the arrow. For example,

$$\mathrm{2\,NaHCO_3\,(s) \overset{200^\circ C}{\rightarrow} Na_2CO_3\,(s) + CO_2\,(g) + H_2O\,(l)}$$

Key Takeaways

- A chemical equation is a concise description of a chemical reaction.
- Proper chemical equations are balanced.

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5.3: Classifying Chemical Reactions

Learning Objectives

- Classify a chemical reaction as a synthesis, decomposition, single replacement, double replacement, or a combustion reaction.
- Predict the products of simple reactions.

The chemical reactions we have described are only a tiny sampling of the infinite number of chemical reactions possible. How do chemists cope with this overwhelming diversity? How do they predict which compounds will react with one another and what products will be formed? The key to success is to find useful ways to categorize reactions. Familiarity with a few basic types of reactions will help you to predict the products that form when certain kinds of compounds or elements come in contact.

Most chemical reactions can be classified into one or more of five basic types: acid–base reactions, exchange reactions, condensation reactions (and the reverse, cleavage reactions), and oxidation–reduction reactions. The general forms of these five kinds of reactions are summarized in Table **5.3.1**, along with examples of each. It is important to note, however, that many reactions can be assigned to more than one classification, as you will see in our discussion.

Table **5.3.1:** *Basic Types of Chemical Reactions*

Name of Reaction	General Form	Examples
Oxidation–Reduction (redox)	oxidant + reductant → reduced oxidant + oxidized reductant	$C_7H_{16}(l) + 11O_2(g) \rightarrow 7CO_2(g) + 8H_2O(g)$
Acid–Base	acid + base → salt	$NaOH(aq) + HNO_3(aq) \rightarrow NaNO_3(aq) + H_2O(l)$
Exchange: Single Replacement	AB + C → AC + B	$ZnCl_2(aq) + Mg(s) \rightarrow MgCl_2(aq) + Zn(s)$
Exchange: Double Replacement	AB + CD → AD + CB	$BaCl_2(aq) + Na_2SO_4(aq) \rightarrow BaSO_4(s) + 2NaCl(aq)$
Combination (Synthesis)	A + B → AB	$CO_2(g) + H_2O(l) \rightarrow H_2CO_3(aq)$ $N_2(g) + 2O_2(g) \rightarrow 2NO_2(g)$
Decomposition	AB → A + B	$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$

The classification scheme is only for convenience; the same reaction can be classified in different ways, depending on which of its characteristics is most important. Oxidation–reduction reactions, in which there is a net transfer of electrons from one atom to another, and condensation reactions are discussed in this section. Acid–base reactions are one kind of exchange reaction—the formation of an insoluble salt, such as barium sulfate, when solutions of two soluble salts are mixed together.

Combination Reactions

A **combination reaction** is a reaction in which two or more substances combine to form a single new substance. Combination reactions can also be called synthesis reactions. The general form of a combination reaction is:

$$\mathbf{A + B \rightarrow AB}$$

One combination reaction is two elements combining to form a compound. Solid sodium metal reacts with chlorine gas to produce solid sodium chloride.

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

Notice that in order to write and balance the equation correctly, it is important to remember the seven elements that exist in nature as diatomic molecules ($\mathbf{H_2}$, $\mathbf{N_2}$, $\mathbf{O_2}$, $\mathbf{F_2}$, $\mathbf{Cl_2}$, $\mathbf{Br_2}$, and $\mathbf{I_2}$).

One type of combination reaction that occurs frequently is the reaction of an element with oxygen to form an oxide. Metals and nonmetals both react readily with oxygen under most conditions. Magnesium reacts rapidly and dramatically when ignited, combining with oxygen from the air to produce a fine powder of magnesium oxide:

$$2Mg\,(s) + O_2\,(g) \rightarrow 2MgO\,(s)$$

Sulfur reacts with oxygen to form sulfur dioxide:

$$S\,(s) + O_2\,(g) \rightarrow SO_2\,(g)$$

When nonmetals react with one another, the product is a molecular compound. Often, the nonmetal reactants can combine in different ratios and produce different products. Sulfur can also combine with oxygen to form sulfur trioxide:

$$2S\,(s) + 3O_2\,(g) \rightarrow 2SO_3\,(g)$$

Transition metals are capable of adopting multiple positive charges within their ionic compounds. Therefore, most transition metals are capable of forming different products in a combination reaction. Iron reacts with oxygen to form both iron (II) oxide and iron (III) oxide:

$$2Fe\,(s) + O_2\,(g) \rightarrow 2FeO\,(s)$$

$$4Fe\,(s) + 3O_2\,(g) \rightarrow 2Fe_2O_3\,(s)$$

Example 5.3.1: Combustion of Solid Potassium

Potassium is a very reactive alkali metal that must be stored under oil in order to prevent it from reacting with air. Write the balanced chemical equation for the combination reaction of potassium with oxygen.

Solution

Solutions to Example 7.10.1

Steps	Example Solution
Plan the problem.	Make sure formulas of all reactants and products are correct before balancing the equation. Oxygen gas is a diatomic molecule. Potassium oxide is an ionic compound and so its formula is constructed by the crisscross method. Potassium as an ion becomes K^+, while the oxide ion is O^{2-}.
Solve.	The skeleton (unbalanced) equation: $$K\,(s) + O_2\,(g) \rightarrow K_2O\,(s)$$ The equation is then easily balanced with coefficients. $$4K\,(s) + O_2\,(g) \rightarrow 2K_2O\,(s)$$
Think about your result.	Formulas are correct and the resulting combination reaction is balanced.

Combination reactions can also take place when an element reacts with a compound to form a new compound composed of a larger number of atoms. Carbon monoxide reacts with oxygen to form carbon dioxide according to the equation:

$$2CO\,(g) + O_2\,(g) \rightarrow 2CO_2\,(g)$$

Two compounds may also react to form a more complex compound. A very common example is the reactions of oxides with water. Calcium oxide reacts readily with water to produce an aqueous solution of calcium hydroxide:

$$CaO\,(s) + H_2O\,(l) \rightarrow Ca(OH)_2\,(aq)$$

Sulfur trioxide gas reacts with water to form sulfuric acid. This is an unfortunately common reaction that occurs in the atmosphere in some places where oxides of sulfur are present as pollutants. The acid formed in the reaction falls to the ground as acid rain.

$$SO_3\,(g) + H_2O\,(l) \rightarrow H_2SO_4\,(aq)$$



Figure 5.3.1: Acid rain has severe consequences on both natural and manmade objects. Acid rain degrades marble statues like the one on the left (A). The trees in the forest on the right (B) have been killed by acid rain.

? Exercise 5.3.1

a. Write the chemical equation for the synthesis of silver bromide, $AgBr$.
b. Predict the products for the following reaction: $CO_2\,(g) + H_2O\,(l)$

Answer a:

$$2Ag + Br_2 \rightarrow 2AgBr$$

Answer b:

$$CO_2\,(g) + H_2O\,(l) \rightarrow H_2CO_3$$

Decomposition Reactions

A **decomposition reaction** is a reaction in which a compound breaks down into two or more simpler substances. The general form of a decomposition reaction is:

$$AB \rightarrow A + B$$

Most decomposition reactions require an input of energy in the form of heat, light, or electricity.

Binary compounds are compounds composed of just two elements. The simplest kind of decomposition reaction is when a binary compound decomposes into its elements. Mercury (II) oxide, a red solid, decomposes when heated to produce mercury and oxygen gas:

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



***Video* 5.3.2:** *Mercury (II) oxide is a red solid. When it is heated, it decomposes into mercury metal and oxygen gas.*

A reaction is also considered to be a decomposition reaction even when one or more of the products are still compounds. A metal carbonate decomposes into a metal oxide and carbon dioxide gas. For example, calcium carbonate decomposes into calcium oxide and carbon dioxide:

$$CaCO_3\,(s) \rightarrow CaO\,(s) + CO_2\,(g)$$

Metal hydroxides decompose on heating to yield metal oxides and water. Sodium hydroxide decomposes to produce sodium oxide and water:

$$2NaOH\,(s) \rightarrow Na_2O\,(s) + H_2O\,(g)$$

Some unstable acids decompose to produce nonmetal oxides and water. Carbonic acid decomposes easily at room temperature into carbon dioxide and water:

$$H_2CO_3\,(aq) \rightarrow CO_2\,(g) + H_2O\,(l)$$

Example 5.3.2: Electrolysis of Water

When an electric current is passed through pure water, it decomposes into its elements. Write a balanced equation for the decomposition of water.

Solution

Solutions to Example 7.10.2

Steps	Example Solution
Plan the problem.	Water is a binary compound composed of hydrogen and oxygen. The hydrogen and oxygen gases produced in the reaction are both diatomic molecules.
Solve.	The skeleton (unbalanced) equation: $$H_2O\,(l) \xrightarrow{elec} H_2\,(g) + O_2\,(g)$$ Note the abbreviation "**elec**" above the arrow to indicate the passage of an electric current to initiate the reaction. Balance the equation. $$2H_2O\,(l) \xrightarrow{elec} 2H_2\,(g) + O_2\,(g)$$
Think about your result.	The products are elements and the equation is balanced.

Exercise 5.3.2

Write the chemical equation for the decomposition of:

a. Al_2O_3
b. Ag_2S

Answer a

$$2Al_2O_3 \rightarrow 4Al + 3O_2$$

Answer b

$$Ag_2S \rightarrow 2Ag + S$$

Single Replacement Reactions

A third type of reaction is the single replacement reaction, in which one element replaces a similar element in a compound. The general form of a single-replacement (also called single-displacement) reaction is:

$$A + BC \rightarrow AC + B$$

In this general reaction, element **A** is a metal and replaces element **B**, also a metal, in the compound. When the element that is doing the replacing is a nonmetal, it must replace another nonmetal in a compound, and the general equation becomes:

$$\mathbf{Y + XZ \rightarrow XY + Z}$$

where **Y** is a nonmetal and replaces the nonmetal **Z** in the compound with **X**.

Metal Replacement

Magnesium is a more reactive metal than copper. When a strip of magnesium metal is placed in an aqueous solution of copper (II) nitrate, it replaces the copper. The products of the reaction are aqueous magnesium nitrate and solid copper metal.

$$\mathbf{Mg\,(\mathit{s}) + Cu(NO_3)_2\,(\mathit{aq}) \rightarrow Mg(NO_3)_2\,(\mathit{aq}) + Cu\,(\mathit{s})}$$

This subcategory of single-replacement reactions is called a metal replacement reaction because it is a metal that is being replaced (copper).

Hydrogen Replacement

Many metals react easily with acids and when they do so, one of the products of the reaction is hydrogen gas. Zinc reacts with hydrochloric acid to produce aqueous zinc chloride and hydrogen (figure below).

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

In a hydrogen replacement reaction, the hydrogen in the acid is replaced by an active metal. Some metals are so reactive that they are capable of replacing the hydrogen in water. The products of such a reaction are the metal hydroxide and hydrogen gas. All Group 1 metals undergo this type of reaction. Sodium reacts vigorously with water to produce aqueous sodium hydroxide and hydrogen (see figure below).

$$\mathbf{2Na\,(\mathit{s}) + 2H_2O\,(\mathit{l}) \rightarrow 2NaOH\,(\mathit{aq}) + H_2\,(\mathit{g})}$$



Figure **5.3.2**: (First image) Zinc metal reacts with hydrochloric acid to give off hydrogen gas in a single-displacement reaction. (Second image) Sodium metal reacts vigorously with water, giving off hydrogen gas. A large piece of sodium will often generate so much heat that the hydrogen will ignite.

Halogen Replacement

The element chlorine reacts with an aqueous solution of sodium bromide to produce aqueous sodium chloride and elemental bromine:

$$\mathbf{Cl_2\,(\mathit{g}) + 2NaBr\,(\mathit{aq}) \rightarrow 2NaCl\,(\mathit{aq}) + Br_2\,(\mathit{l})}$$

The reactivity of the halogen group (group 17) decreases from top to bottom within the group. Fluorine is the most reactive halogen, while iodine is the least. Since chlorine is above bromine, it is more reactive than bromine and can replace it in a halogen replacement reaction.

Example 5.3.3

What are the products of the reaction between solid aluminum (**Al**) and iron (III) oxide ($\mathbf{Fe_2O_3}$)?

Solution

Solutions to Example 7.10.3

Steps	Example Solution
Plan the problem.	To predict the products, we need to know that aluminum will replace iron and form aluminum oxide (the metal will replace the metal ion in the compound). Aluminum has a charge of $+3$ and oxygen has a charge of -2. The compound formed between aluminum and oxygen, therefore, will be Al_2O_3. Since iron is replaced in the compound by aluminum, the iron will now be the single element in the products.
Solve.	The unbalanced equation will be: $$Al + Fe_2O_3 \rightarrow Al_2O_3 + Fe$$ and the balanced equation will be: $$2Al + Fe_2O_3 \rightarrow Al_2O_3 + 2Fe$$
Think about your result.	This is a single replacement reaction, and when balanced the coefficients accurately reflect that the iron and aluminum have the same charge in this reaction.

? Exercise 5.3.3

a. Write the chemical equation for the single replacement reaction between zinc solid and lead (II) nitrate solution to produce zinc nitrate solution and solid lead. (Note that zinc forms ions with a $+2$ charge.)

b. Predict the products for the following reaction: $Fe + CuSO_4$. (In this reaction, assume iron forms ions with a $+2$ charge.)

Answer a

$$Zn + Pb(NO_3)_2 \rightarrow Pb + Zn(NO_3)_2$$

Answer b

$$Fe + CuSO_4 \rightarrow Cu + FeSO_4$$

Double Replacement Reactions

A **double-replacement reaction** is a reaction in which the positive and negative ions of two ionic compounds exchange places to form two new compounds. The general form of a double-replacement (also called double-displacement) reaction is:

$$AB + CD \rightarrow AD + BC$$

In this reaction, A and C are positively-charged cations, while B and D are negatively-charged anions. Double-replacement reactions generally occur between substances in aqueous solution. In order for a reaction to occur, one of the products is usually a solid precipitate, a gas, or a molecular compound such as water.

Formation of a Precipitate

A precipitate forms in a double-replacement reaction when the cations from one of the reactants combine with the anions from the other reactant to form an insoluble ionic compound. When aqueous solutions of potassium iodide and lead (II) nitrate are mixed, the following reaction occurs:

$$2KI\,(aq) + Pb(NO_3)_2\,(aq) \rightarrow 2KNO_3\,(aq) + PbI_2\,(s) \tag{5.3.1}$$

There are very strong attractive forces that occur between Pb^{2+} and I^- ions and the result is a brilliant yellow precipitate (Figure 5.3.3). The other product of the reaction, potassium nitrate, remains soluble.



Figure **5.3.3**: Lead (II) iodide precipitates when potassium iodide is mixed with lead (II) nitrate (Equation **5.3.1**). (CC BY-SA 3.0; PRHaney).

Formation of a Gas

Some double-replacement reactions produce a gaseous product which then bubbles out of the solution and escapes into the air. When solutions of sodium sulfide and hydrochloric acid are mixed, the products of the reaction are aqueous sodium chloride and hydrogen sulfide gas:

$$\mathrm{Na_2S}\,(aq) + 2\mathrm{HCl}\,(aq) \rightarrow 2\mathrm{NaCl}\,(aq) + \mathrm{H_2S}\,(g)$$

Formation of a Molecular Compound

Another kind of double-replacement reaction is one that produces a molecular compound as one of its products. Many examples in this category are reactions that produce water. When aqueous hydrochloric acid is reacted with aqueous sodium hydroxide, the products are aqueous sodium chloride and water:

$$\mathrm{HCl}\,(aq) + \mathrm{NaOH}\,(aq) \rightarrow \mathrm{NaCl}\,(aq) + \mathrm{H_2O}\,(l)$$

Example 5.3.4

Write a complete and balanced chemical equation for the double-replacement reaction $\mathrm{NaCN}\,(aq) + \mathrm{HBr}\,(aq) \rightarrow$ (hydrogen cyanide gas is formed).

Solution

Solutions to Example 7.10.4

Steps	Example Solution
Plan the problem.	The production of a gas drives the reaction.
Solve.	The cations of both reactants are $+1$ charged ions, while the anions are -1 charged ions. After exchanging partners, the balanced equation is: $\mathrm{NaCN}\,(aq) + \mathrm{HBr}\,(aq) \rightarrow \mathrm{NaBr}\,(aq) + \mathrm{HCN}\,(g)$
Think about your result.	This is a double replacement reaction. All formulas are correct and the equation is balanced.

Exercise 5.3.4

Write a complete and balanced chemical equation for the double-replacement reaction $(\mathrm{NH_4})_2\mathrm{SO_4}\,(aq) + \mathrm{Ba(NO_3)_2}\,(aq) \rightarrow$ (a precipitate of barium sulfate forms).

Answer a:

$$(\mathrm{NH_4})_2\mathrm{SO_4}\,(aq) + \mathrm{Ba(NO_3)_2}\,(aq) \rightarrow 2\mathrm{NH_4NO_3}\,(aq) + \mathrm{BaSO_4}\,(s)$$

Occasionally, a reaction will produce both a gas and a molecular compound. The reaction of a sodium carbonate solution with hydrochloric acid produces aqueous sodium chloride, carbon dioxide gas, and water:

$$\mathrm{Na_2CO_3}\,(aq) + \mathrm{2HCl}\,(aq) \rightarrow 2\ \mathrm{NaCl}\,(aq) + \mathrm{CO_2}\,(g) + \mathrm{H_2O}\,(l)$$

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5.4: Composition, Decomposition, and Combustion Reactions

Learning Objectives

- Recognize composition, decomposition, and combustion reactions.
- Predict the products of a combustion reaction.

Three classifications of chemical reactions will be reviewed in this section. Predicting the products in some of them may be difficult, but the reactions are still easy to recognize.

A **composition reaction** (sometimes also called a *combination reaction* or a *synthesis reaction*) produces a single substance from multiple reactants. A single substance as a product is the key characteristic of the composition reaction. There may be a coefficient other than one for the substance, but if the reaction has only a single substance as a product, it can be called a composition reaction. In the reaction

$$2\,H_2\,(g) + O_2\,(g) \longrightarrow 2\,H_2O(\ell)$$

water is produced from hydrogen and oxygen. Although there are two molecules of water being produced, there is only one substance—water—as a product. So this is a composition reaction.

A **decomposition reaction** starts from a single substance and produces more than one substance; that is, it decomposes. The key characteristics of a decomposition reaction are: one substance as a reactant and more than one substance as the products. For example, in the decomposition of sodium hydrogen carbonate (also known as sodium bicarbonate):

$$2\,NaHCO_3\,(s) \longrightarrow Na_2CO_3\,(s) + CO_2\,(g) + H_2O(\ell)$$

sodium carbonate, carbon dioxide, and water are produced from the single substance sodium hydrogen carbonate.

Composition and decomposition reactions are difficult to predict; however, they should be easy to recognize.

Example 5.4.1: Identifying Reactions

Identify each equation as a composition reaction, a decomposition reaction, or neither.

a. $Fe_2O_3 + 3\,SO_3 \longrightarrow Fe_2(SO_4)_3$
b. $NaCl + AgNO_3 \longrightarrow AgCl + NaNO_3$
c. $(NH_4)_2Cr_2O_7 \longrightarrow Cr_2O_3 + 4\,H_2O + N_2$

Solution

a. In this equation, two substances combine to make a single substance. This is a composition reaction.
b. Two different substances react to make two new substances. This does not fit the definition of either a composition reaction or a decomposition reaction, so it is neither. In fact, you may recognize this as a double-replacement reaction.
c. A single substance reacts to make multiple substances. This is a decomposition reaction.

Exercise 5.4.1

Identify the equation as a composition reaction, a decomposition reaction, or neither.

$$C_3H_8 \longrightarrow C_3H_4 + 2\,H_2$$

Answer

decomposition

A **combustion reaction** occurs when a reactant combines with oxygen, many times from the atmosphere, to produce oxides of all other elements as products; any nitrogen in the reactant is converted to elemental nitrogen, N_2. Many reactants, called *fuels*,

contain mostly carbon and hydrogen atoms, reacting with oxygen to produce CO_2 and H_2O. For example, the balanced chemical equation for the combustion of methane, CH_4, is as follows:

$$\mathrm{CH_4 + 2\,O_2 \longrightarrow CO_2 + 2\,H_2O}$$

Kerosene can be approximated with the formula $\mathrm{C_{12}H_{26}}$, and its combustion equation is:

$$\mathrm{2\,C_{12}H_{26} + 37\,O_2 \longrightarrow 24\,CO\text{-}2 + 26\,H_2O}$$

Sometimes fuels contain oxygen atoms, which must be counted when balancing the chemical equation. One common fuel is ethanol, $\mathrm{C_2H_5OH}$, whose combustion equation is:

$$\mathrm{C_2H_5OH + 3\,O_2 \longrightarrow 2\,CO_2 + 3\,H_2O}$$

If nitrogen is present in the original fuel, it is converted to $\mathrm{N_2}$, not to a nitrogen-oxygen compound. Thus, for the combustion of the fuel dinitroethylene, whose formula is $\mathrm{C_2H_2N_2O_4}$, we have:

$$\mathrm{2\,C_2H_2N_2O_4 + O_2 \longrightarrow 4\,CO_2 + 2\,H_2O + 2\,N_2}$$

Example 5.4.2: Combustion Reactions

Complete and balance each combustion equation.

1. the combustion of propane ($\mathrm{C_3H_8}$)
2. the combustion of ammonia ($\mathrm{NH_3}$)

Solution

1. The products of the reaction are CO_2 and H_2O, so our unbalanced equation is

   $$\mathrm{C_3H_8 + O_2 \longrightarrow CO_2 + H_2O}$$

   Balancing (and you may have to go back and forth a few times to balance this), we get

   $$\mathrm{C_3H_8 + 5\,O_2 \longrightarrow 3\,CO_2 + 4\,H_2O}$$

2. The nitrogen atoms in ammonia will react to make N_2, while the hydrogen atoms will react with O_2 to make H_2O:

   $$\mathrm{NH_3 + O_2 \longrightarrow N_2 + H_2O}$$

   To balance this equation without fractions (which is the convention), we get

   $$\mathrm{4\,NH_3 + 3\,O_2 \longrightarrow 2\,N_2 + 6\,H_2O}$$

Exercise 5.4.2

Complete and balance the combustion equation for cyclopropanol (\ce{C3H6O}\)).

Answer

$$\mathrm{C_3H_6O + 4\,O_2 \longrightarrow 3\,CO_2 + 3\,H_2O}$$



Figure **5.4.1** A 20 lb (9.1 kg) steel propane cylinder.

Key Takeaways

- A composition reaction produces a single substance from multiple reactants.
- A decomposition reaction produces multiple products from a single reactant.
- Combustion reactions are the combination of some compound with oxygen to make oxides of the other elements as products (although nitrogen atoms react to make N_2).

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5.5: Aqueous Solutions and Solubility - Compounds Dissolved in Water

Learning Objectives

- Define and give examples of electrolytes.

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

Substances may be identified as strong, weak, or nonelectrolytes by measuring the electrical conductance of an aqueous solution containing the substance. To conduct electricity, a substance must contain freely mobile, charged species. Most familiar is the conduction of electricity through metallic wires, in which case the mobile, charged entities are electrons. Solutions may also conduct electricity if they contain dissolved ions, with conductivity increasing as ion concentration increases. Applying a voltage to electrodes immersed in a solution permits assessment of the relative concentration of dissolved ions, either quantitatively, by measuring the electrical current flow, or qualitatively, by observing the brightness of a light bulb included in the circuit (Figure 5.5.1).

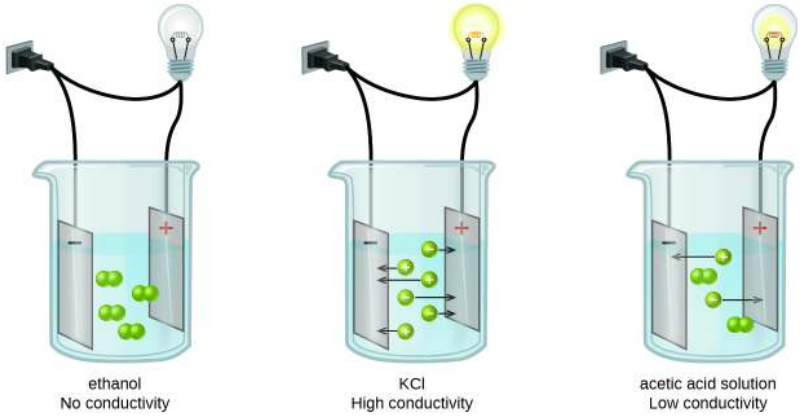


Figure 5.5.1: Solutions of nonelectrolytes, such as ethanol, do not contain dissolved ions and cannot conduct electricity. Solutions of electrolytes contain ions that permit the passage of electricity. The conductivity of an electrolyte solution is related to the strength of the electrolyte. This diagram shows three separate beakers. Each has a wire plugged into a wall outlet. In each case, the wire leads from the wall to the beaker and is split resulting in two ends. One end leads to a light bulb and continues on to a rectangle labeled with a plus sign. The other end leads to a rectangle labeled with a minus sign. The rectangles are in a solution. In the first beaker, labeled “Ethanol No Conductivity,” four pairs of linked small green spheres suspended in the solution between the rectangles. In the second beaker, labeled “K C l Strong Conductivity,” six individual green spheres, three labeled plus and three labeled minus are suspended in the solution. Each of the six spheres has an arrow extending from it pointing to the rectangle labeled with the opposite sign. In the third beaker, labeled “Acetic acid solution Weak conductivity,” two pairs of joined green spheres and two individual spheres, one labeled plus and one labeled minus are shown suspended between the two rectangles. The plus labeled sphere has an arrow pointing to the rectangle labeled minus and the minus labeled sphere has an arrow pointing to the rectangle labeled plus.

Ionic Electrolytes

Water and other polar molecules are attracted to ions, as shown in Figure 5.5.2. The electrostatic attraction between an ion and a molecule with a dipole is called an ion-dipole attraction. These attractions play an important role in the dissolution of ionic compounds in water.

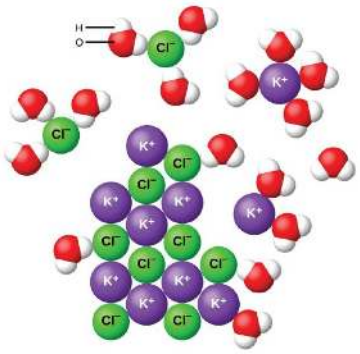


Figure 5.5.2: As potassium chloride (KCl) dissolves in water, the ions are hydrated. The polar water molecules are attracted by the charges on the K^+ and Cl^- ions. Water molecules in front of and behind the ions are not shown. The diagram shows eight purple spheres labeled K superscript plus and eight green spheres labeled C l superscript minus mixed and touching near the center of the diagram. Outside of this cluster of spheres are seventeen clusters of three spheres, which include one red and two white spheres. A red sphere in one of these clusters is labeled O. A white sphere is labeled H. Two of the green C l superscript minus spheres are surrounded by three of the red and white clusters, with the red spheres closer to the green spheres than the white spheres. One of the K superscript plus purple spheres is surrounded by four of the red and white clusters. The white spheres of these clusters are closest to the purple spheres.

When ionic compounds dissolve in water, the ions in the solid separate and disperse uniformly throughout the solution because water molecules surround and solvate the ions, reducing the strong electrostatic forces between them. This process represents a physical change known as dissociation. Under most conditions, ionic compounds will dissociate nearly completely when dissolved, and so they are classified as strong electrolytes.

Let us consider what happens at the microscopic level when we add solid KCl to water. Ion-dipole forces attract the positive (hydrogen) end of the polar water molecules to the negative chloride ions at the surface of the solid, and they attract the negative (oxygen) ends to the positive potassium ions. The water molecules penetrate between individual K^+ and Cl^- ions and surround them, reducing the strong interionic forces that bind the ions together and letting them move off into solution as solvated ions, as Figure 5.5.2 shows. The reduction of the electrostatic attraction permits the independent motion of each hydrated ion in a dilute solution, resulting in an increase in the disorder of the system, as the ions change from their fixed and ordered positions in the crystal to mobile and much more disordered states in solution. This increased disorder is responsible for the dissolution of many ionic compounds, including KCl, which dissolve with absorption of heat.

In other cases, the electrostatic attractions between the ions in a crystal are so large, or the ion-dipole attractive forces between the ions and water molecules are so weak, that the increase in disorder cannot compensate for the energy required to separate the ions, and the crystal is insoluble. Such is the case for compounds such as calcium carbonate (limestone), calcium phosphate (the inorganic component of bone), and iron oxide (rust).

Solubility Rules

Some combinations of aqueous reactants result in the formation of a solid precipitate as a product. However, some combinations will not produce such a product. If solutions of sodium nitrate and ammonium chloride are mixed, no reaction occurs. One could write a molecular equation showing a double-replacement reaction, but both products, sodium chloride and ammonium nitrate, are soluble and would remain in the solution as ions. Every ion is a spectator ion and there is no net ionic equation at all. It is useful to be able to predict when a precipitate will occur in a reaction. To do so, you can use a set of guidelines called the **solubility rules** (Tables 5.5.1 and 5.5.2).

Table 5.5.1: Solubility Rules for Soluble Substances

Soluble in Water	Important Exceptions (Insoluble)
All Group IA and NH_4^+ salts	none
All nitrates, chlorates, perchlorates and acetates	none
All sulfates	$CaSO_4$, $BaSO_4$, $SrSO_4$, $PbSO_4$
All chlorides, bromides, and iodides	AgX, Hg_2X_2, PbX_2 (X= Cl, Br, or I)

Table 5.5.2: Solubility Rules for Sparingly Soluble Substances

Sparingly Soluble in Water	Important Exceptions (Soluble)
All carbonates and phosphates	Group IA and NH_4^+ salts
All hydroxides	Group IA and NH_4^+ salts; Ba^{2+}, Sr^{2+}, Ca^{2+} sparingly soluble
All sulfides	Group IA, IIA and NH_4^+ salts; MgS, CaS, BaS sparingly soluble
All oxalates	Group IA and NH_4^+ salts
Special note: The following electrolytes are of only moderate solubility in water: CH_3COOAg, Ag_2SO_4, $KClO_4$. They will precipitate only if rather concentrated solutions are used.	

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

$$Cs^+(aq) + Br^-(aq) + Pb^{2+}(aq) + 2NO_3^-(aq) \rightarrow ?$$

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

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

✔ Example 5.5.1: Solubility

Classify each compound as soluble or insoluble

a. $Zn(NO_3)_2$
b. $PbBr_2$
c. $Sr_3(PO_4)_2$

Solution

a. All nitrates are soluble in water, so $Zn(NO_3)_2$ is soluble.
b. All bromides are soluble in water, except those combined with Pb^{2+}, so $PbBr_2$ is insoluble.
c. All phosphates are insoluble, so $Sr_3(PO_4)_2$ is insoluble.

? Exercise 5.5.1: Solubility

Classify each compound as soluble or insoluble.

a. $Mg(OH)_2$
b. KBr
c. $Pb(NO_3)_2$

Answer a

insoluble

Answer b

soluble

Answer c

soluble

Summary

Substances that dissolve in water to yield ions are called electrolytes. Nonelectrolytes are substances that do not produce ions when dissolved in water. Solubility rules allow prediction of what products will be insoluble in water.

Contributions & Attributions

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5.6: Precipitation Reactions

Learning Objectives

- To identify a precipitation reaction and predict solubility.

A precipitation reaction is a reaction that yields an insoluble product—a precipitate—when two solutions are mixed. When a colorless solution of silver nitrate is mixed with a yellow-orange solution of potassium dichromate, a reddish precipitate of silver dichromate is produced.

$$\mathrm{AgNO_3\,(aq) + K_2Cr_2O_7\,(aq) \rightarrow Ag_2Cr_2O_7\,(s) + KNO_3\,(aq)} \tag{5.6.1}$$

This unbalanced equation has the general form of an exchange reaction:

$$\mathrm{AC + BD \rightarrow \underset{insoluble}{AD} + BC} \tag{5.6.2}$$

Thus precipitation reactions are a subclass of exchange reactions that occur between ionic compounds when one of the products is insoluble. Because both components of each compound change partners, such reactions are sometimes called **double-displacement reactions**. Precipitation reactions are used to isolate metals that have been extracted from their ores, and to recover precious metals for recycling.



Video: Mixing potassium dichromate and silver nitrate together to initiate a precipitation reaction (Equation 5.6.1).

Just as important as predicting the product of a reaction is knowing when a chemical reaction will *not* occur. Simply mixing solutions of two different chemical substances does *not* guarantee that a reaction will take place. For example, if 500 mL of aqueous NaCl solution is mixed with 500 mL of aqueous KBr solution, the final solution has a volume of 1.00 L and contains $\mathrm{Na^+\,(aq)}$, $\mathrm{Cl^-\,(aq)}$, $\mathrm{K^+\,(aq)}$, and $\mathrm{Br^-\,(aq)}$. As you will see in (Figure 5.6.1), none of these species reacts with any of the others. When these solutions are mixed, the only effect is to dilute each solution with the other.

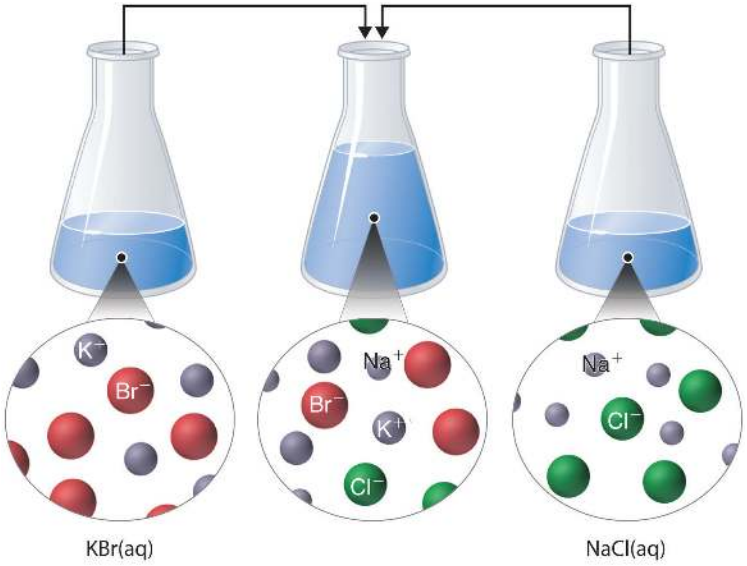


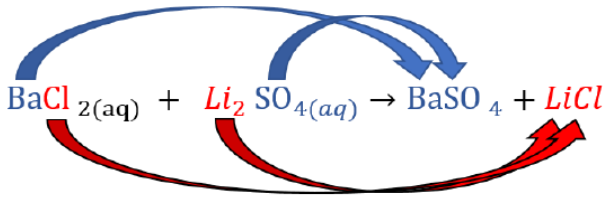
Figure 5.6.1: The Effect of Mixing Aqueous **KBr** and **NaCl** Solutions. Because no net reaction occurs, the only effect is to dilute each solution with the other. (Water molecules are omitted from molecular views of the solutions for clarity.)

Predicting Precipitation Reactions

A precipitation reaction occurs when a solid precipitate forms after mixing two strong electrolyte solutions. As stated previously, if none of the species in the solution reacts then no net reaction occurred.

Predict what will happen when aqueous solutions of barium chloride and lithium sulfate are mixed.

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



Chemical equation of the reactants barium chloride and lithium sulfate forming the products barium sulfate and lithium chloride.

Because barium chloride and lithium sulfate are strong electrolytes, each dissociates completely in water to give a solution that contains the constituent anions and cations. Mixing the two solutions *initially* gives an aqueous solution that contains Ba^{2+}, Cl^-, Li^+, and SO_4^{2-} ions. The only possible exchange reaction is to form **LiCl** and **$BaSO_4$**.

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

No need to correct the formula as both compounds already have their charges balanced.

$$BaCl_2\,(aq) + Li_2SO_4\,(aq) \rightarrow BaSO_4 + LiCl$$

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

$$BaCl_2\,(aq) + Li_2SO_4\,(aq) \rightarrow BaSO_4\,(s) + LiCl\,(aq)$$

Table 7.5.1 from the previous section shows that **LiCl** is soluble in water, but **$BaSO_4$** is not soluble in water.

Balance the equation:

$$BaCl_2\,(aq) + Li_2SO_4\,(aq) \rightarrow BaSO_4\,(s) + 2\,LiCl\,(aq)$$

Although soluble barium salts are toxic, **$BaSO_4$** is so insoluble that it can be used to diagnose stomach and intestinal problems without being absorbed into tissues. An outline of the digestive organs appears on x-rays of patients who have been given a "barium milkshake" or a "barium enema"—a suspension of very fine **$BaSO_4$** particles in water.



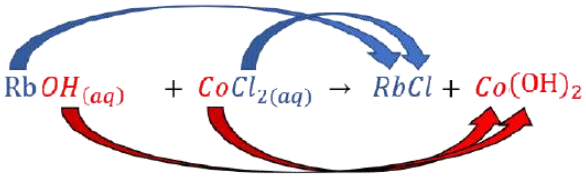
Figure 5.6.2: An x-ray of the digestive organs of a patient who has swallowed a “barium milkshake.” A barium milkshake is a suspension of very fine $BaSO_4$ particles in water; the high atomic mass of barium makes it opaque to x-rays. (Public Domain; Glitzy queen00 via Wikipedia).

Example 5.6.1

Predict what will happen if aqueous solutions of rubidium hydroxide and cobalt(II) chloride are mixed.

Solution

Solutions to Example 7.6.1

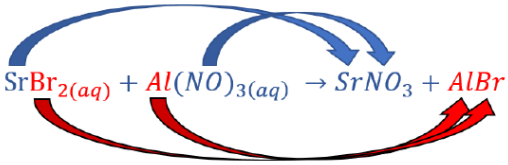
Steps	Example
Change the partners of the anions and cations on the reactant side to form new compounds (products).	 Chemical equation of the reactants rubidium hydroxide and cobalt(II) chloride forming the products rubidium chloride and cobalt hydroxide.
Correct the formulas of the products based on the charges of the ions.	$\mathrm{RbOH\,(aq) + CoCl_2\,(aq) \rightarrow RbCl + Co(OH)_2}$
Refer to the solubility rules table to determine insoluble products which will therefore form a precipitate.	$\mathrm{RbOH\,(aq) + CoCl_2\,(aq) \rightarrow RbCl\,(aq) + Co(OH)_2\,(s)}$
Balance the equation.	Coefficients already balanced. $\mathrm{RbOH\,(aq) + CoCl_2\,(aq) \rightarrow RbCl\,(aq) + Co(OH)_2\,(s)}$

Example 5.6.2

Predict what will happen if aqueous solutions of strontium bromide and aluminum nitrate are mixed.

Solution

Solutions for Example 7.6.2

Steps	Example
Change the partners of the anions and cations on the reactant side to form new compounds (products).	 Chemical equation of the reactants strontium bromide and aluminum nitrate forming the products strontium nitrate and aluminum bromide.
Correct the formulas of the products based on the charges of the ions.	$\mathbf{SrBr_2\,(aq) + Al(NO_3)_3\,(aq) \rightarrow Sr(NO_3)_2 + AlBr_3}$
Refer to the solubility rules table to determine insoluble products which will therefore form a precipitate.	$\mathbf{SrBr_2\,(aq) + Al(NO_3)_3\,(aq) \rightarrow Sr(NO_3)_2\,(aq) + AlBr_3\,(aq)}$ According to Table 7.5.1 from the previous section, both $\mathbf{AlBr_3}$ (rule 4) and $\mathbf{Sr(NO_3)_2}$ (rule 2) are soluble.
If all possible products are soluble, then no net reaction will occur.	$\mathbf{SrBr_2\,(aq) + Al(NO_3)_3\,(aq) \rightarrow}$ **NO REACTION**

? Exercise 5.6.2

Using the information in Table 7.5.1 from the previous section, predict what will happen in each case involving strong electrolytes.

a. An aqueous solution of strontium hydroxide is added to an aqueous solution of iron(II) chloride.
b. Solid potassium phosphate is added to an aqueous solution of mercury(II) perchlorate.
c. Solid sodium fluoride is added to an aqueous solution of ammonium formate.
d. Aqueous solutions of calcium bromide and cesium carbonate are mixed.

Answer a

$Fe(OH)_2$ precipitate is formed.

Answer b

$Hg_3(PO_4)_2$ precipitate is formed.

Answer c

No Reaction.

Answer d

$CaCO_3$ is precipitate formed.

Summary

In a **precipitation reaction**, a subclass of exchange reactions, an insoluble material (a **precipitate**) forms when two electrolyte solutions are mixed. To predict the product of a precipitation reaction, all species initially present in the solutions are identified, as are any combinations likely to produce an insoluble salt.

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5.7: Writing Chemical Equations for Reactions in Solution- Molecular, Complete Ionic, and Net Ionic Equations

A typical precipitation reaction occurs when an aqueous solution of barium chloride is mixed with one containing sodium sulfate. The **complete chemical equation** can be written to describe what happens, and such an equation is useful in making chemical calculations.

$$\underbrace{\mathrm{BaCl_2\,(aq) + Na_2SO_4\,(aq) \longrightarrow BaSO_4\,(s) + 2\,NaCl\,(aq)}}_{\text{Complete Chemical Equation}} \tag{5.7.1}$$

However, Equation 5.7.1 does not really represent the microscopic particles (that is, the ions) present in the solution. Below is the complete ionic equation:

$$\underbrace{\mathrm{Ba^{2+}\,(aq) + \overbrace{2Cl^-(aq)}^{\text{spectator}} + \overbrace{2Na^+(aq)}^{\text{spectator}} + SO_4{}^{2-}\,(aq) \longrightarrow BaSO_4\,(s) + \overbrace{2Na^+(aq)}^{\text{spectator}} + \overbrace{Cl^-(aq)}^{\text{spectator}}}}_{\text{Complete Ionic Equation}} \tag{5.7.2}$$

Equation 5.7.2 is rather cumbersome and includes so many different ions that it may be confusing. In any case, we are often interested in the independent behavior of ions, not the specific compound from which they came. A precipitate of $\mathrm{BaSO_4\,(s)}$ will form when *any* solution containing $\mathrm{Ba^{2+}\,(aq)}$ is mixed with *any* solution containing $\mathrm{SO_4{}^{2-}\,(aq)}$ (provided concentrations are not extremely small). This happens independently of the $\mathrm{Cl^-\,(aq)}$ and $\mathrm{Na^+\,(aq)}$ ions in Equation 5.7.2. These ions are called **spectator ions** because they do not participate in the reaction. When we want to emphasize the independent behavior of ions, a **net ionic equation** is written, omitting the spectator ions. For precipitation of $\mathrm{BaSO_4}$ the net ionic equation is

$$\underbrace{\mathrm{Ba^{2+}\,(aq) + SO_4{}^{2-}\,(aq) \longrightarrow BaSO_4\,(s)}}_{\text{Net Ionic Equation}} \tag{5.7.3}$$

Example 5.7.1

a. When a solution of $\mathrm{AgNO_3}$ is added to a solution of $\mathrm{CaCl_2}$, insoluble AgCl precipitates. Write three equations (complete chemical equation, complete ionic equation, and net ionic equation) that describe this process.

b. Write the balanced net ionic equation to describe any reaction that occurs when the solutions of $\mathrm{Na_2SO_4}$ and $\mathrm{NH_4I}$ are mixed.

Solution

Solutions to Example 7.7.1

Equation Type	Example 5.7.1*a*	Example 5.7.1*b*
Complete Chemical Equation	$\mathrm{2\,AgNO_3\,(aq) + CaCl_2\,(aq) \longrightarrow 2\,AgCl\,(s) + Ca(NO_3)_2\,(aq)}$ The proper states and formulas of all products are written and the chemical equation is balanced.	$\mathrm{Na_2SO_4\,(aq) + 2\,NH_4I\,(aq) \longrightarrow 2\,NaI\,(aq) + (NH_4)_2SO_4\,(aq)}$ Both products are aqueous so there is no net ionic equation that can be written.
Complete Ionic Equation	$\mathrm{2\,Ag^+\,(aq) + 2\,NO_3{}^-\,(aq) + Ca^{2+}\,(aq) + 2\,Cl^-\,(aq) \longrightarrow 2\,AgCl\,(s) + Ca^{2+}\,(aq) + 2\,NO_3{}^-\,(aq)}$ AgCl is a solid so it does not break up into ions in solution.	
Net Ionic Equation	$\mathrm{Ag^+\,(aq) + Cl^-\,(aq) \longrightarrow AgCl\,(s)}$ All spectator ions are removed. The chemical equation is written using the lowest common coefficients.	NaI and $\mathrm{(NH_4)_2SO_4}$ are both soluble. No net ionic equation. There is no reaction.

The occurrence or nonoccurrence of precipitates can be used to detect the presence or absence of various species in solution. A $BaCl_2$ solution, for instance, is often used as a test for the presence of $SO_4^{2-}(aq)$ ions. There are several insoluble salts of Ba, but they all dissolve in dilute acid except for $BaSO_4$. Thus, if $BaCl_2$ solution is added to an unknown solution which has previously been acidified, the occurrence of a white precipitate is proof of the presence of the SO_4^{2-} ion.



Figure 5.7.1: The three common silver halide precipitates: AgI, AgBr and AgCl (left to right). The silver halides precipitate out of solution, but often form suspensions before settling. (CC BY-SA 3.0; Cychr).

$AgNO_3$ solutions are often used in a similar way to test for halide ions. If $AgNO_3$ solution is added to an acidified unknown solution, a white precipitate indicates the presence of Cl^- ions, a cream-colored precipitate indicates the presence of Br^- ions, and a yellow precipitate indicates the presence of I^- ions (Figure 5.7.1). Further tests can then be made to see whether perhaps a mixture of these ions is present. When $AgNO_3$ is added to tap water, a white precipitate is almost always formed. The Cl^- ions in tap water usually come from the Cl_2 which is added to municipal water supplies to kill microorganisms.

? Exercise 5.7.1

Write balanced net ionic equations to describe any reaction that occurs when the following solutions are mixed.

a. $K_2CO_3 + SrCl_2$
b. $FeSO_4 + Ba(NO_3)_2$

Answer a

$$Sr^{2+}(aq) + CO_3^{2-}(aq) \longrightarrow SrCO_3(s)$$

Answer b

$$Ba^{2+}(aq) + SO_4^{2-}(aq) \longrightarrow Ba(SO_4)(s)$$

Precipitates are also used for quantitative analysis of solutions, that is, to determine the amount of solute or the mass of solute in a given solution. For this purpose it is often convenient to use the first of the three types of equations described above. Then the rules of stoichiometry may be applied.

Contributions & Attributions

- Ed Vitz (Kutztown University), John W. Moore (UW-Madison), Justin Shorb (Hope College), Xavier Prat-Resina (University of Minnesota Rochester), Tim Wendorff, and Adam Hahn.

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5.8: Oxidation–Reduction Reactions

Learning Objectives

- Define *oxidation* and *reduction*.
- Assign oxidation numbers to atoms in simple compounds.
- Recognize a reaction as an oxidation-reduction reaction.

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

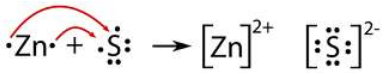


Figure 5.8.1: Reaction between zinc and sulfur.

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

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

$$\underbrace{Zn \longrightarrow Zn_2^{2+} + e^-}_{\text{Oxidation}} \tag{5.8.1}$$

$$\underbrace{S^+ \, 2e^- \longrightarrow S^{2-}}_{\text{Reduction}} \tag{5.8.2}$$

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

Another example of an oxidation-reduction reaction involving electron transfer is the well-known combination of metallic sodium and chlorine gas to form sodium chloride:

$$2\,Na^+Cl_2 \longrightarrow 2\,NaCl \tag{5.8.3}$$

The half reactions are as follows:

$$\underbrace{2\,Na \longrightarrow 2\,Na^+ + 2\,e^-}_{\text{Oxidation}} \tag{5.8.4}$$

$$\underbrace{Cl_2 + 2\,e^- \longrightarrow 2\,Cl^-}_{\text{Reduction}} \tag{5.8.5}$$

We will concern ourselves with the balancing of these equations at another time.

Oxidation Numbers

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

Assigning Oxidation Numbers

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

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

In H_2, both H atoms have an oxidation number of 0.

2. Atoms in monatomic (i.e., one-atom) ions are assigned an oxidation number equal to their charge. Oxidation numbers are usually written with the sign first, then the magnitude, to differentiate them from charges.

In $MgCl_2$, magnesium has an oxidation number of +2, while chlorine has an oxidation number of −1.

3. In compounds, fluorine is assigned a −1 oxidation number; oxygen is usually assigned a −2 oxidation number (except in peroxide compounds [where it is −1] and in binary compounds with fluorine [where it is positive]); and hydrogen is usually assigned a +1 oxidation number [except when it exists as the hydride ion (H^-), in which case rule 2 prevails].

In H_2O, the H atoms each have an oxidation number of +1, while the O atom has an oxidation number of −2, even though hydrogen and oxygen do not exist as ions in this compound (rule 3). By contrast, by rule 3, each H atom in hydrogen peroxide (H_2O_2) has an oxidation number of +1, while each O atom has an oxidation number of −1.

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

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

Example 5.8.1: Assigning Oxidation States

Assign oxidation numbers to the atoms in each substance.

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

Solution

a. Cl_2 is the elemental form of chlorine. Rule 1 states that each atom has an oxidation number of 0.
b. By rule 3, oxygen is normally assigned an oxidation number of −2. For the sum of the oxidation numbers to equal the charge on the species (zero), the Ge atom is assigned an oxidation number of +4.
c. $Ca(NO_3)_2$ can be separated into two parts: the Ca^{2+} ion and the NO_3^- ion. Considering these separately, the Ca^{2+} ion has an oxidation number of +2 by rule 2. Now consider the NO_3^- ion. Oxygen is assigned an oxidation number of −2, and there are three of them. According to rule 4, the sum of the oxidation numbers on all atoms must equal the charge on the species, so we have the simple algebraic equation

$$x + 3(-2) = -1$$

where x is the oxidation number of the N atom and the −1 represents the charge on the species. Evaluating for x,

$$x + (-6) = -1 \quad x = +5$$

Thus the oxidation number on the N atom in the NO_3^- ion is +5.

Exercise 5.8.1: Assigning Oxidation States

Assign oxidation numbers to the atoms in the following:

a. H_3PO_4
b. MgO

Answer a

H: +1; O: −2; P: +5

Answer b

Mg: +2, O: −2

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

Example 5.8.2: Formation of Sodium Bromide

Identify what is being oxidized and reduced in the following redox reaction.

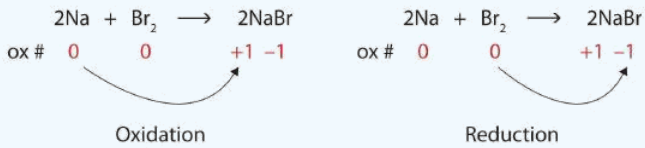
$$2\,Na + Br_2 \longrightarrow 2\,NaBr$$

Solution

Both reactants are the elemental forms of their atoms, so the Na and Br atoms have oxidation numbers of 0. In the ionic product, the Na^+ ions have an oxidation number of +1, while the Br^- ions have an oxidation number of −1.

$$\overset{0}{2Na} + \overset{0}{Br_2} \rightarrow \overset{+1-1}{2NaBr}$$

Sodium is increasing its oxidation number from 0 to +1, so it is being oxidized; bromine is decreasing its oxidation number from 0 to −1, so it is being reduced:



Equation of sodium and bromine reacting, labeled with sodium's oxidation number change from 0 to +1 and bromine's oxidation number change from 0 to -1

Because oxidation numbers are changing, this is a redox reaction. The total number of electrons being lost by sodium (two, one lost from each Na atom) is gained by bromine (two, one gained for each Br atom).

Exercise 5.8.2: Oxidation of Carbon

Identify what is being oxidized and reduced in this redox reaction.

$$C + O_2 \rightarrow CO_2$$

Answer

C is being oxidized from 0 to +4; O is being reduced from 0 to −2

Oxidation reactions can become quite complex, as attested by the following redox reaction:

$$6H^+(aq) + 2\overset{+7}{MnO_4^-}(aq) + 5\overset{-1}{H_2O_2}(l) \rightarrow 2\overset{+2}{Mn^{2+}}(aq) + 5\overset{0}{O_2}(g) + 8H_2O(l)$$

To demonstrate that this is a redox reaction, the oxidation numbers of the species being oxidized and reduced are listed; can you determine what is being oxidized and what is being reduced? This is also an example of a net ionic reaction; spectator ions that do not change oxidation numbers are not displayed in the equation. Eventually, we will need to learn techniques for writing correct (i.e., balanced) redox reactions.

Combustion Reactions

A **combustion reaction** is a reaction in which a substance reacts with oxygen gas, releasing energy in the form of light and heat. Combustion reactions must involve $\mathbf{O_2}$ as one reactant. The combustion of hydrogen gas produces water vapor.

$$\mathbf{2H_2}\,(g) + \mathbf{O_2}\,(g) \rightarrow \mathbf{2H_2O}\,(g) \tag{5.8.6}$$

Notice that this reaction also qualifies as a combination reaction.

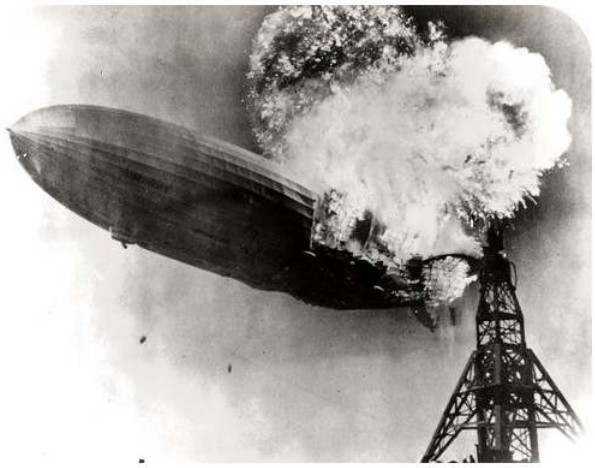


Figure 5.8.2: Explosion of the Hindenberg.

The *Hindenberg* was a hydrogen-filled airship that suffered an accident upon its attempted landing in New Jersey in 1937. The hydrogen immediately combusted in a huge fireball, destroying the airship and killing 36 people. The chemical reaction was a simple one: hydrogen combining with oxygen to produce water (Equation 5.8.6).

Many combustion reactions occur with a hydrocarbon, a compound made up solely of carbon and hydrogen. The products of the combustion of hydrocarbons are carbon dioxide and water. Many hydrocarbons are used as fuel because their combustion releases very large amounts of heat energy. Propane ($\mathbf{C_3H_8}$) is a gaseous hydrocarbon that is commonly used as the fuel source in gas grills.

$$\mathbf{C_3H_8}\,(g) + \mathbf{5O_2}\,(g) \rightarrow \mathbf{3CO_2}\,(g) + \mathbf{4H_2O}\,(g)$$

Example 5.8.3: Combustion of Ethanol

Ethanol can be used as a fuel source in an alcohol lamp. The formula for ethanol is $\mathbf{C_2H_5OH}$. Write the balanced equation for the combustion of ethanol.

Solution

Solutions to Example 7.9.3

Steps	Example Solution
Write the unbalanced reaction.	$\mathbf{C_2H_5OH}\,(l) + \mathbf{O_2}\,(g) \rightarrow \mathbf{CO_2}\,(g) + \mathbf{H_2O}\,(g)$ Ethanol and atmospheric oxygen are the reactants. As with a hydrocarbon, the products of the combustion of an alcohol are carbon dioxide and water.
Balance the equation.	$\mathbf{C_2H_5OH}\,(l) + \mathbf{3O_2}\,(g) \rightarrow \mathbf{2CO_2}\,(g) + \mathbf{3H_2O}\,(g)$
Think about your result.	Combustion reactions must have oxygen as a reactant. Note that the water produced is in the gas state, rather than the liquid state, because of the high temperatures that accompany a combustion reaction.

Exercise 5.8.3: Combustion of Hexane

Write the balanced equation for the combustion of hexane, C_6H_{14}

Answer

$$2\,C_6H_{14}\,(\ell) + 19\,O_2\,(g) \longrightarrow 12\,CO_2\,(g) + 14\,H_2O(\ell)$$

Contributors & Affiliations

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CHAPTER OVERVIEW

6: Stoichiometry

6.1: The Mole
6.2: Chemical Formulas as Conversion Factors
6.3: Stoichiometry
6.4: Mole-Mass and Mass-Mass Calculations
6.5: Mole-to-Mole Conversions
6.6: Limiting Reagents
6.7: Yields

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6.1: The Mole

Learning Objectives

- Describe the unit *mole*.
- Relate the mole quantity of substance to its mass.

So far, we have been talking about chemical substances in terms of individual atoms and molecules. Yet we do not typically deal with substances an atom or a molecule at a time; we work with millions, billions, and trillions of atoms and molecules at a time. We need a way to deal with macroscopic, rather than microscopic, amounts of matter. We need a unit of amount that relates quantities of substances on a scale that we can interact with.

Chemistry uses a unit called mole. A **mole** (mol) is a number of things equal to the number of atoms in exactly 12 g of carbon-12. Experimental measurements have determined that this number is very large:

$$1 \text{ mol} = 6.02214179 \times 10^{23} \text{ things}$$

Understand that a mole means a specific number of things, just like a dozen means a certain number of things—twelve, in the case of a dozen. But a mole is a much larger number of things. These things can be atoms, or molecules, or eggs; however, in chemistry, we usually use the mole to refer to the amounts of atoms or molecules. Although the number of things in a mole is known to eight decimal places, it is usually fine to use only two or three decimal places in calculations. The numerical value of things in a mole is often called *Avogadro's number* (N_A). *Avogadro's number* is also known as the *Avogadro constant*, after Amadeo Avogadro, an Italian chemist who first proposed its importance.

Example 6.1.1

How many molecules are present in 2.76 mol of H_2O? How many atoms is this?

Solution

The definition of a mole is an equality that can be used to construct a conversion factor. Also, because we know that there are three atoms in each molecule of H_2O, we can also determine the number of atoms in the sample.

$$2.76 \cancel{\text{ mol } H_2O} \times \frac{6.022 \times 10^{23} \text{ molecules } H_2O}{\cancel{\text{mol } H_2O}} = 1.66 \times 10^{24} \text{ molecules } H_2O$$

To determine the total number of atoms, we have

$$1.66 \times 10^{24} \cancel{\text{ molecules } H_2O} \times \frac{3 \text{ atoms}}{1 \text{ molecule}} = 4.99 \times 10^{24} \text{ atoms}$$

Exercise 6.1.1

How many molecules are present in 4.61×10^{-2} mol of O_2?

Answer

2.78×10^{22} molecules

How big is a mole? It is very large. Suppose you had a mole of dollar bills that need to be counted. If everyone on earth (about 6 billion people) counted one bill per second, it would take about 3.2 million years to count all the bills. A mole of sand would fill a cube about 32 km on a side. A mole of pennies stacked on top of each other would have about the same diameter as our galaxy, the Milky Way. A mole is a lot of things—but atoms and molecules are very tiny. One mole of carbon atoms would make a cube that is 1.74 cm on a side, small enough to carry in your pocket.

Why is the mole unit so important? It represents the link between the microscopic and the macroscopic, especially in terms of mass. *A mole of a substance has the same mass in grams as one unit (atom or molecules) has in atomic mass units*. The mole unit

allows us to express amounts of atoms and molecules in visible amounts that we can understand.

For example, we already know that, by definition, a mole of carbon has a mass of exactly 12 g. This means that exactly 12 g of C has 6.022×10^{23} atoms:

$$12 \text{ g C} = 6.022 \times 10^{23} \text{ atoms C}$$

We can use this equality as a conversion factor between the number of atoms of carbon and the number of grams of carbon. How many grams are there, say, in 1.50×10^{25} atoms of carbon? This is a one-step conversion:

$$1.50 \times 10^{25} \cancel{\text{ atoms C}} \times \frac{12.0000\, g\, C}{6.022 \times 10^{23} \cancel{\text{ atoms C}}} = 299\, g\, C$$

But it also goes beyond carbon. Previously we defined atomic and molecular masses as the number of atomic mass units per atom or molecule. Now we can do so in terms of grams. The atomic mass of an element is the number of grams in 1 mol of atoms of that element, while the molecular mass of a compound is the number of grams in 1 mol of molecules of that compound. Sometimes these masses are called **molar masses** to emphasize the fact that they are the mass for 1 mol of things. (The term *molar* is the adjective form of mole and has nothing to do with teeth.)

Here are some examples. The mass of a hydrogen atom is 1.0079 u; the mass of 1 mol of hydrogen atoms is 1.0079 g. Elemental hydrogen exists as a diatomic molecule, H_2. One molecule has a mass of 1.0079 + 1.0079 = 2.0158 u, while 1 mol H_2 has a mass of 2.0158 g. A molecule of H_2O has a mass of about 18.01 u; 1 mol H_2O has a mass of 18.01 g. A single unit of NaCl has a mass of 58.45 u; NaCl has a molar mass of 58.45 g. In each of these moles of substances, there are 6.022×10^{23} units: 6.022×10^{23} atoms of H, 6.022×10^{23} molecules of H_2 and H_2O, 6.022×10^{23} units of NaCl ions. These relationships give us plenty of opportunities to construct conversion factors for simple calculations.

Example 6.1.2: Sugar

What is the molar mass of sugar ($C_6H_{12}O_6$)?

Solution

To determine the molar mass, we simply add the atomic masses of the atoms in the molecular formula; but express the total in grams per mole, not atomic mass units. The masses of the atoms can be taken from the periodic table.

Solutions to Example 5.3.2

6 C = 6 × 12.011	= 72.066
12 H = 12 × 1.0079	= 12.0948
6 O = 6 × 15.999	= 95.994
TOTAL	= 180.155 g/mol

Per convention, the unit *grams per mole* is written as a fraction.

Exercise 6.1.2

What is the molar mass of $AgNO_3$?

Answer

169.87 g/mol

Knowing the molar mass of a substance, we can calculate the number of moles in a certain mass of a substance and vice versa, as these examples illustrate. The molar mass is used as the conversion factor.

Example 6.1.3

What is the mass of 3.56 mol of $HgCl_2$? The molar mass of $HgCl_2$ is 271.49 g/mol.

Solution

Use the molar mass as a conversion factor between moles and grams. Because we want to cancel the mole unit and introduce the gram unit, we can use the molar mass as given:

$$3.56 \cancel{mol\ HgCl_2} \times \frac{271.49\ g\ HgCl_2}{\cancel{mol\ HgCl_2}} = 967\ g\ HgCl_2$$

Exercise 6.1.3

What is the mass of 33.7 mol of $\mathbf{H_2O}$?

Answer

607 g

Example 6.1.4

How many moles of H_2O are present in 240.0 g of water (about the mass of a cup of water)?

Solution

Use the molar mass of H_2O as a conversion factor from mass to moles. The molar mass of water is

$$(1.0079 + 1.0079 + 15.999) = 18.015\ g/mol.$$

However, because we want to cancel the gram unit and introduce moles, we need to take the reciprocal of this quantity, or 1 mol/18.015 g:

$$240.0\ \cancel{g\ H_2O} \times \frac{1\ mol\ H_2O}{18.015\ \cancel{g\ H_2O}} = 13.32\ mol\ H_2O$$

Exercise 6.1.4

How many moles are present in 35.6 g of H_2SO_4 (molar mass = 98.08 g/mol)?

Answer

0.363 mol

Other conversion factors can be combined with the definition of mole—density, for example.

Example 6.1.5

The density of ethanol is 0.789 g/mL. How many moles are in 100.0 mL of ethanol? The molar mass of ethanol is 46.08 g/mol.

Solution

Here, we use density to convert from volume to mass and then use the molar mass to determine the number of moles.

$$100\ \cancel{ml}\ ethanol \times \frac{0.789\ g}{\cancel{ml}} \times \frac{1\ mol}{46.08\ \cancel{g}} = 1.71\ mol\ ethanol$$

Exercise 6.1.5

If the density of benzene, C_6H_6, is 0.879 g/mL, how many moles are present in 17.9 mL of benzene?

Answer

0.201 mol

Summary

The mole is a key unit in chemistry. The molar mass of a substance, in grams, is numerically equal to one atom's or molecule's mass in atomic mass units.

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6.2: Chemical Formulas as Conversion Factors

Learning Objectives

- Use chemical formulas as conversion factors.

Figure **6.2.1** shows that we need 2 hydrogen atoms and 1 oxygen atom to make one water molecule. If we want to make two water molecules, we will need 4 hydrogen atoms and 2 oxygen atoms. If we want to make five molecules of water, we need 10 hydrogen atoms and 5 oxygen atoms. The ratio of atoms we will need to make any number of water molecules is the same: 2 hydrogen atoms to 1 oxygen atom.

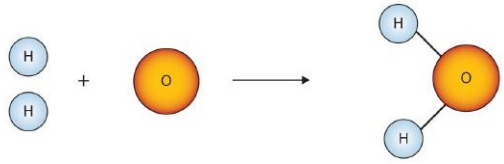


Figure **6.2.1** Water Molecules. The ratio of hydrogen atoms to oxygen atoms used to make water molecules is always 2:1, no matter how many water molecules are being made.

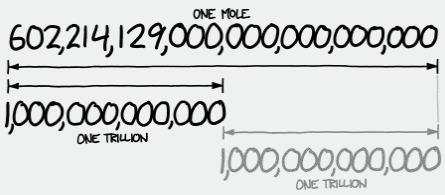
Using formulas to indicate how many atoms of each element we have in a substance, we can relate the number of moles of molecules to the number of moles of atoms. For example, in 1 mol of water (H_2O) we can construct the relationships given in (Table **6.2.1**).

Table **6.2.1**: Molecular Relationships for Water

1 Molecule of H_2O Has	1 Mol of H_2O Has	Molecular Relationships
2 H atoms	2 mol of H atoms	$\frac{2\text{ mol H atoms}}{1\text{ mol }H_2O\text{ molecules}}$ or $\frac{1\text{ mol }H_2O\text{ molecules}}{2\text{ mol H atoms}}$
1 O atom	1 mol of O atoms	$\frac{1\text{ mol O atoms}}{1\text{ mol }H_2O\text{ molecules}}$ or $\frac{1\text{ mol }H_2O\text{ molecules}}{1\text{ mol O atoms}}$

The Mole is big

A mole represents a very large number! The number 602,214,129,000,000,000,000,000 looks about twice as long as a trillion, which means it's about a trillion trillion.



(CC BY-SA NC; what if? [what-if.xkcd.com]).

A trillion trillion kilograms is how much a planet weighs. If 1 mol of quarters were stacked in a column, it could stretch back and forth between Earth and the sun *6.8 billion* times.

Table **6.2.2**: Molecular and Mass Relationships for Ethanol

1 Molecule of C_2H_6O Has	1 Mol of C_2H_6O Has	Molecular and Mass Relationships
2 C atoms	2 mol of C atoms	$\frac{2\text{ mol C atoms}}{1\text{ mol }C_2H_6O\text{ molecules}}$ or $\frac{1\text{ mol }C_2H_6O\text{ molecules}}{2\text{ mol C atoms}}$
6 H atoms	6 mol of H atoms	$\frac{6\text{ mol H atoms}}{1\text{ mol }C_2H_6O\text{ molecules}}$ or $\frac{1\text{ mol }C_2H_6O\text{ molecules}}{6\text{ mol H atoms}}$
1 O atom	1 mol of O atoms	$\frac{1\text{ mol O atoms}}{1\text{ mol }C_2H_6O\text{ molecules}}$ or $\frac{1\text{ mol }C_2H_6O\text{ molecules}}{1\text{ mol O atoms}}$
2 (12.01 amu) C 24.02 amu C	2 (12.01 g) C 24.02 g C	$\frac{24.02\text{ g C}}{1\text{ mol }C_2H_6O\text{ molecules}}$ or $\frac{1\text{ mol }C_2H_6O\text{ molecules}}{24.02\text{ g C}}$
6 (1.008 amu) H 6.048 amu H	6 (1.008 g) H 6.048 g H	$\frac{6.048\text{ g H}}{1\text{ mol }C_2H_6O\text{ molecules}}$ or $\frac{1\text{ mol }C_2H_6O\text{ molecules}}{6.048\text{ g H}}$
1 (16.00 amu) O 16.00 amu O	1 (16.00 g) O 16.00 g O	$\frac{16.00\text{ g O}}{1\text{ mol }C_2H_6O\text{ molecules}}$ or $\frac{1\text{ mol }C_2H_6O\text{ molecules}}{16.00\text{ g O}}$

The following example illustrates how we can use the relationships in Table **6.2.2** as conversion factors.

Example 6.2.1: Ethanol

If a sample consists of 2.5 mol of ethanol (C_2H_6O), how many moles of carbon atoms does it have?

Solution

Solutions to Example 6.5.1

Steps for Problem Solving	If a sample consists of 2.5 mol of ethanol (C_2H_6O), how many moles of carbon atoms does it have?
Identify the "given" information and what the problem is asking you to "find."	Given: 2.5 mol C_2H_6O Find: mol C atoms
List other known quantities.	1 mol C_2H_6O = 2 mol C
Prepare a concept map and use the proper conversion factor.	mol C_2H_6O → mol C atom $\frac{2\ mol\ C}{1\ mol\ C_2H_6O}$
Cancel units and calculate.	Note how the unit *mol C_2H_6O molecules* cancels algebraically. $2.5\ \cancel{\text{mol }C_2H_6O\text{ molecules}} \times \frac{2\text{ mol C atoms}}{1\ \cancel{\text{mol }C_2H_6O\text{ molecules}}} = 5.0\text{ mol C atoms}$
Think about your result.	There are twice as many C atoms in one C_2H_6O molecule, so the final amount should be double.

Exercise 6.2.1

If a sample contains 6.75 mol of Na_2SO_4, how many moles of sodium atoms, sulfur atoms, and oxygen atoms does it have?

Answer

13.5 mol Na atoms, 6.75 mol S atoms, and 27.0 mol O atoms

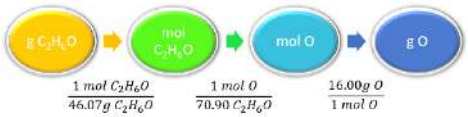
The fact that 1 mol equals 6.022×10^{23} items can also be used as a conversion factor.

Example 6.2.2: Oxygen Mass

Determine the mass of Oxygen in 75.0g of C_2H_6O.

Solution

Solutions to Example 6.5.2

Steps for Problem Solving	Determine the mass of Oxygen in 75.0g of C_2H_6O
Identify the "given" information and what the problem is asking you to "find."	Given: 75.0g C_2H_6O Find: g O
List other known quantities.	1 mol O = 16.0g O 1 mol C_2H_6O = 1 mol O 1 mol C_2H_6O = 46.07g C_2H_6O
Prepare a concept map and use the proper conversion factor.	 The conversion factors are 1 mol C2H6O over 46.07 g C2H6O, 1 mol O over 1 mol C2H6O, and 16.00 g O over 1 mole O.
Cancel units and calculate.	$75.0\ \cancel{g\ C_2H_6O} \times \frac{1\ \cancel{mol\ C_2H_6O}}{46.07\ \cancel{g\ C_2H_6O}} \times \frac{1\ \cancel{mol\ O}}{1\ \cancel{mol\ C_2H_6O}} \times \frac{16.00\ g\ O}{1\ \cancel{mol\ O}} = 26.0\ g$
Think about your result.	

Exercise 6.2.2

a. How many molecules are present in 16.02 mol of C_4H_{10}? How many C atoms are in 16.02 mol?
b. How many moles of each type of atom are in 2.58 mol of Na_2SO_4?

Answer a:

9.647×10^{24} C_4H_{10} molecules and 3.859×10^{25} C atoms

Answer b:

5.16 mol Na atoms, 2.58 mol S atoms, and 10.3 mol O atoms

Summary

In any given formula, the ratio of the number of moles of molecules (or formula units) to the number of moles of atoms can be used as a conversion factor.

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6.3: Stoichiometry

Learning Objectives

- Define *stoichiometry*.
- Relate quantities in a balanced chemical reaction on a molecular basis.

Consider a classic recipe for pound cake: 1 pound of eggs, 1 pound of butter, 1 pound of flour, and 1 pound of sugar. (That's why it's called "pound cake.") If you have 4 pounds of butter, how many pounds of sugar, flour, and eggs do you need? You would need 4 pounds each of sugar, flour, and eggs.

Now suppose you have 1.00 g H_2. If the chemical reaction follows the balanced chemical equation

$$2\,H_2\,(g) + O_2\,(g) \longrightarrow 2\,H_2O(\ell)$$

then what mass of oxygen do you need to make water?

Curiously, this chemical reaction question is very similar to the pound cake question. Both of them involve relating a quantity of one substance to a quantity of another substance or substances. The relating of one chemical substance to another using a balanced chemical reaction is called **stoichiometry**. Using stoichiometry is a fundamental skill in chemistry; it greatly broadens your ability to predict what will occur and, more importantly, how much is produced.

Let us consider a more complicated example. A recipe for pancakes calls for 2 cups (c) of pancake mix, 1 egg, and 1/2 c of milk. We can write this in the form of a chemical equation:

2 c mix + 1 egg + 1/2 c milk → 1 batch of pancakes

If you have 9 c of pancake mix, how many eggs and how much milk do you need? It might take a little bit of work, but eventually you will find you need 4½ eggs and 2¼ c milk.

How can we formalize this? We can make a conversion factor using our original recipe and use that conversion factor to convert from a quantity of one substance to a quantity of another substance. This is similar to the way we constructed a conversion factor between feet and yards in Chapter 2. Because one recipe's worth of pancakes requires 2 c of pancake mix, 1 egg, and 1/2 c of milk, we actually have the following mathematical relationships that relate these quantities:

2 c pancake mix ⇔ 1 egg ⇔ 1/2 c milk

where ⇔ is the mathematical symbol for "is equivalent to." This does not mean that 2 c of pancake mix equal 1 egg. However, *as far as this recipe is concerned*, these are the equivalent quantities needed for a single recipe of pancakes. So, any possible quantities of two or more ingredients must have the same numerical ratio as the ratios in the equivalence.

We can deal with these equivalences in the same way we deal with equalities in unit conversions: we can make conversion factors that essentially equal 1. For example, to determine how many eggs we need for 9 c of pancake mix, we construct the conversion factor:

$$\frac{1\,egg}{2\,c\,pancake\,mix}$$

This conversion factor is, in a strange way, equivalent to 1 because the recipe relates the two quantities. Starting with our initial quantity and multiplying by our conversion factor,

$$9\,\cancel{c\,pancake\,mix} \times \frac{1\,egg}{2\,\cancel{c\,pancake\,mix}} = 4.5\,eggs$$

Note how the units *cups pancake mix* canceled, leaving us with units of *eggs*. This is the formal, mathematical way of getting our amounts to mix with 9 c of pancake mix. We can use a similar conversion factor for the amount of milk:

$$9\,\cancel{c\,pancake\,mix} \times \frac{\frac{1}{2}\,c\,milk}{2\,\cancel{c\,pancake\,mix}} = 2.25\,c\,milk$$

Again, units cancel, and new units are introduced.

A balanced chemical equation is nothing more than *a recipe for a chemical reaction*. The difference is that a balanced chemical equation is written in terms of atoms and molecules, not cups, pounds, and eggs.

For example, consider the following chemical equation:

$$2\,H_2\,(g) + O_2\,(g) \longrightarrow 2\,H_2O(\ell)$$

We can interpret this as, literally, "two hydrogen molecules react with one oxygen molecule to make two water molecules." That interpretation leads us directly to some equivalencies, just as our pancake recipe did:

$$2H_2 \text{ molecules} \Leftrightarrow 1O_2 \text{ molecule} \Leftrightarrow 2H_2O \text{ molecules}$$

These equivalences allow us to construct conversion factors:

$$\frac{2\,molecules\,H_2}{1\,molecule\,O_2} \quad \frac{2\,molecules\,H_2}{2\,molecules\,H_2O} \quad \frac{1\,molecule\,H_2}{2\,molecules\,H_2O}$$

and so forth. These conversions can be used to relate quantities of one substance to quantities of another. For example, suppose we need to know how many molecules of oxygen are needed to react with 16 molecules of H_2. As we did with converting units, we start with our given quantity and use the appropriate conversion factor:

$$\cancel{16\,molecules\,H_2} \times \frac{1\,molecules\,O_2}{\cancel{2\,molecules\,H_2}} = 8\,molecules\,O_2$$

Note how the unit *molecules H2* cancels algebraically, just as any unit does in a conversion like this. The conversion factor came directly from the coefficients in the balanced chemical equation. This is another reason why a properly balanced chemical equation is important.

Example 6.3.1

How many molecules of SO_3 are needed to react with 144 molecules of Fe_2O_3 given this balanced chemical equation?

$$Fe_2O_3 + 3\,SO_3 \longrightarrow Fe_2(SO_4)_3$$

Solution

We use the balanced chemical equation to construct a conversion factor between Fe_2O_3 and SO_3. The number of molecules of Fe_2O_3 goes on the bottom of our conversion factor so it cancels with our given amount, and the molecules of SO_3 go on the top. Thus, the appropriate conversion factor is

$$\frac{3\,molecules\,SO_3}{1\,molecule\,Fe_2O_3}$$

Starting with our given amount and applying the conversion factor, the result is

$$144\ \cancel{molecules}\ Fe_2O_3 \times \frac{3\,molecules\,SO_3}{1\ \cancel{molecule}\ Fe_2O_3} = 432\,molecules\,SO_3$$

We need 432 molecules of SO_3 to react with 144 molecules of Fe_2O_3.

Exercise 6.3.1

How many molecules of H_2 are needed to react with 29 molecules of N_2 to make ammonia if the balanced chemical equation is:

$$N_2 + 3\,H_2 \longrightarrow 2\,NH_3?$$

Answer

87 molecules

Chemical equations also allow us to make conversions regarding the number of atoms in a chemical reaction, because a chemical formula lists the number of atoms of each element in a compound. The formula H_2O indicates that there are two hydrogen atoms and one oxygen atom in each molecule, and these relationships can be used to make conversion factors:

$$\frac{2\,atoms\,H}{1\,molecule\,H_2O} \quad \frac{1\,molecule\,H_2O}{1\,atom\,O}$$

Conversion factors like this can also be used in stoichiometry calculations.

Example 6.3.2

How many molecules of NH_3 can you make if you have 228 atoms of H_2?

Solution

From the formula, we know that one molecule of NH_3 has three H atoms. Use that fact as a conversion factor:

$$228\ \cancel{atoms\,H} \times \frac{1\,molecule\,NH_3}{3\ \cancel{atoms\,H}} = 76\,NH_3$$

Exercise 6.3.2

How many molecules of $Fe_2(SO_4)_3$ can you make from 777 atoms of S?

Answer

259 molecules

Summary

Quantities of substances can be related to each other using balanced chemical equations.

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6.4: Mole-Mass and Mass-Mass Calculations

Learning Objectives

- From a given number of moles of a substance, calculate the mass of another substance involved using the balanced chemical equation.
- From a given mass of a substance, calculate the moles of another substance involved using the balanced chemical equation.
- From a given mass of a substance, calculate the mass of another substance involved using the balanced chemical equation.

Mole-mole calculations are not the only type of calculations that can be performed using balanced chemical equations. Recall that the molar mass can be determined from a chemical formula and used as a conversion factor. We can add that conversion factor as another step in a calculation to make a **mole-mass calculation**, where we start with a given number of moles of a substance and calculate the mass of another substance involved in the chemical equation, or vice versa.

For example, suppose we have the balanced chemical equation

$$2Al + 3Cl_2 \rightarrow 2AlCl_3$$

Suppose we know we have 123.2 g of Cl_2. How can we determine how many moles of $AlCl_3$ we will get when the reaction is complete? First and foremost, *chemical equations are not balanced in terms of grams; they are balanced in terms of moles*. So to use the balanced chemical equation to relate an amount of Cl_2 to an amount of $AlCl_3$, we need to convert the given amount of Cl_2 into moles. We know how to do this by simply using the molar mass of Cl_2 as a conversion factor. The molar mass of Cl_2 (which we get from the atomic mass of Cl from the periodic table) is 70.90 g/mol. We must invert this fraction so that the units cancel properly:

$$123.2\ \cancel{g\,Cl_2} \times \frac{1\,mol\,Cl_2}{70.90\ \cancel{g\,Cl_2}} = 1.738\ mol\,Cl_2$$

Now that we have the quantity in moles, we can use the balanced chemical equation to construct a conversion factor that relates the number of moles of Cl_2 to the number of moles of $AlCl_3$. The numbers in the conversion factor come from the coefficients in the balanced chemical equation:

$$\frac{2\,mol\,AlCl_3}{3\,mol\,Cl_2}$$

Using this conversion factor with the molar quantity we calculated above, we get

$$1.738\ \cancel{mol\,Cl_2} \times \frac{2\,mol\,AlCl_3}{3\ \cancel{mol\,Cl_2}} = 1.159\,mol\,AlCl_3$$

So, we will get 1.159 mol of $AlCl_3$ if we react 123.2 g of Cl_2.

In this last example, we did the calculation in two steps. However, it is mathematically equivalent to perform the two calculations sequentially on one line:

$$123.2\ \cancel{g\,Cl_2} \times \frac{1\,mol\,Cl_2}{70.90\ \cancel{g\,Cl_2}} \times \frac{2\,mol\,AlCl_3}{3\ \cancel{mol\,Cl_2}} = 1.159\,mol\,AlCl_3$$

The units still cancel appropriately, and we get the same numerical answer in the end. Sometimes the answer may be slightly different from doing it one step at a time because of rounding of the intermediate answers, but the final answers should be effectively the same.

Example 6.4.1

How many moles of HCl will be produced when 249 g of $AlCl_3$ are reacted according to this chemical equation?

$$2AlCl_3 + 3H_2O(\ell) \rightarrow Al_2O_3 + 6HCl(g)$$

Solution

We will do this in two steps: convert the mass of $AlCl_3$ to moles and then use the balanced chemical equation to find the number of moles of HCl formed. The molar mass of $AlCl_3$ is 133.33 g/mol, which we have to invert to get the appropriate conversion factor:

$$249\ \cancel{g\ AlCl_3} \times \frac{1\ mol\ AlCl_3}{133.33\ \cancel{g\ AlCl_3}} = 1.87\ mol\ AlCl_3$$

Now we can use this quantity to determine the number of moles of HCl that will form. From the balanced chemical equation, we construct a conversion factor between the number of moles of $AlCl_3$ and the number of moles of HCl:

$$frac6\ mol\ HCl2\ \cancel{mol\ AlCl_3}$$

Applying this conversion factor to the quantity of $AlCl_3$, we get

$$1.87\ \cancel{mol\ AlCl_3} \times \frac{6\ mol\ HCl}{2\ \cancel{mol\ AlCl_3}} = 5.61\ mol\ HCl$$

Alternatively, we could have done this in one line:

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

The last digit in our final answer is slightly different because of rounding differences, but the answer is essentially the same.

Exercise 6.4.1

How many moles of Al_2O_3 will be produced when 23.9 g of H_2O are reacted according to this chemical equation?

$$2AlCl_3 + 3H_2O(\ell) \rightarrow Al_2O_3 + 6HCl(g)$$

Answer

0.442 mol

A variation of the mole-mass calculation is to start with an amount in moles and then determine an amount of another substance in grams. The steps are the same but are performed in reverse order.

Example 6.4.2

How many grams of NH_3 will be produced when 33.9 mol of H_2 are reacted according to this chemical equation?

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

Solution

The conversions are the same, but they are applied in a different order. Start by using the balanced chemical equation to convert to moles of another substance and then use its molar mass to determine the mass of the final substance. In two steps, we have

$$33.9\ \cancel{mol\ H_2} \times \frac{2\ mol\ NH_3}{3\ \cancel{mol\ H_2}} = 22.6\ mol\ NH_3$$

Now, using the molar mass of NH_3, which is 17.03 g/mol, we get

$$22.6\ \cancel{mol\ NH_3} \times \frac{17.03\ g\ NH_3}{1\ \cancel{mol\ NH_3}} = 385\ g\ NH_3$$

? Exercise 6.4.2

How many grams of N_2 are needed to produce 2.17 mol of NH_3 when reacted according to this chemical equation?

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

Answer

30.4 g (Note: here we go from a product to a reactant, showing that mole-mass problems can begin and end with any substance in the chemical equation.)

It should be a trivial task now to extend the calculations to **mass-mass calculations**, in which we start with a mass of some substance and end with the mass of another substance in the chemical reaction. For this type of calculation, the molar masses of two different substances must be used—be sure to keep track of which is which. Again, however, it is important to emphasize that before the balanced chemical reaction is used, the mass quantity must first be converted to moles. Then the coefficients of the balanced chemical reaction can be used to convert to moles of another substance, which can then be converted to a mass.

For example, let us determine the number of grams of SO_3 that can be produced by the reaction of 45.3 g of SO_2 and O_2:

$$2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$$

First, we convert the given amount, 45.3 g of SO_2, to moles of SO_2 using its molar mass (64.06 g/mol):

$$45.3\ g\,SO_2 \times \frac{1\ mol\ SO_2}{64.06\ g\,SO_2} = 0.707\ mol\ SO_2$$

Second, we use the balanced chemical reaction to convert from moles of SO_2 to moles of SO_3:

$$0.707\ mol\,SO_2 \times \frac{2\ mol\ SO_3}{2\ mol\,SO_2} = 0.707\ mol\ SO_3$$

Finally, we use the molar mass of SO_3 (80.06 g/mol) to convert to the mass of SO_3:

$$0.707\ mol\,SO_3 \times \frac{80.06\ g\ SO_3}{1\ mol\,SO_3} = 56.6\ g\ SO_3$$

We can also perform all three steps sequentially, writing them on one line as

$$45.3\ g\,SO_2 \times \frac{1\ mol\ SO_2}{64.06\ g\,SO_2} \times \frac{2\ mol\ SO_3}{2\ mol\,SO_2} \times \frac{80.06\ g\ SO_3}{1\ mol\,SO_3} = 56.6\ g\ SO_3$$

We get the same answer. Note how the initial and all the intermediate units cancel, leaving grams of SO_3, which is what we are looking for, as our final answer.

✓ Example 6.4.3

What mass of Mg will be produced when 86.4 g of K are reacted?

$$\mathrm{MgCl_2\,(s) + 2\,K\,(s) \longrightarrow Mg\,(s) + 2\,KCl\,(s)}$$

Solution

We will simply follow the steps

mass K → mol K → mol Mg → mass Mg

In addition to the balanced chemical equation, we need the molar masses of K (39.09 g/mol) and Mg (24.31 g/mol). In one line,

$$86.4\ g\,K \times \frac{1\ mol\ K}{39.09\ g\,K} \times \frac{1\ mol\,Mg}{2\ mol\,K} \times \frac{24.31\ g\ Mg}{1\ mol\,Mg} = 26.87\ g\ Mg$$

? Exercise 6.4.3

What mass of H_2 will be produced when 122 g of Zn are reacted?

$$\mathrm{Zn\,(s) + 2\,HCl\,(aq) \longrightarrow ZnCl_2\,(aq) + H_2\,(g)}$$

Answer

3.77 g

Summary

- Mole quantities of one substance can be related to mass quantities using a balanced chemical equation.
- Mass quantities of one substance can be related to mass quantities using a balanced chemical equation.
- In all cases, quantities of a substance must be converted to moles before the balanced chemical equation can be used to convert to moles of another substance.

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6.5: Mole-to-Mole Conversions

/;Learning Objectives

- Use a balanced chemical equation to determine molar relationships between substances.

Previously, you learned to balance chemical equations by comparing the numbers of each type of atom in the reactants and products. The coefficients in front of the chemical formulas represent the numbers of molecules or formula units (depending on the type of substance). As follows, we will extend the meaning of the coefficients in a chemical equation.

Consider the simple chemical equation:

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

The convention for writing balanced chemical equations is to use the lowest whole-number ratio for the coefficients. However, the equation is balanced as long as the coefficients are in a 2:1:2 ratio. For example, this equation is also balanced if we write it as

$$4H_2 + 2O_2 \rightarrow 4H_2O$$

The ratio of the coefficients is 4:2:4, which reduces to 2:1:2. The equation is also balanced if we were to write it as

$$22H_2 + 11O_2 \rightarrow 22H_2O$$

because 22:11:22 also reduces to 2:1:2.

Suppose we want to use larger numbers. Consider the following coefficients:

$$12.044 \times 10^{23}\ \mathrm{H_2} + 6.022 \times 10^{23}\ \mathrm{O_2} \rightarrow 12.044 \times 10^{23}\ \mathrm{H_2O}$$

These coefficients also have the ratio 2:1:2 (check it and see), so this equation is balanced. But 6.022×10^{23} is 1 mol, while 12.044×10^{23} is 2 mol (and the number is written that way to make this more obvious), so we can simplify this version of the equation by writing it as

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

We can leave out the word *mol* and not write the 1 coefficient (as is our habit), so the final form of the equation, still balanced, is

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

Now we interpret the coefficients as referring to molar amounts, not individual molecules. The lesson? *Balanced chemical equations are balanced not only at the molecular level, but also in terms of molar amounts of reactants and products.* Thus, we can read this reaction as “two moles of hydrogen react with one mole of oxygen to produce two moles of water.”

By the same token, the ratios we constructed to describe a molecular reaction can also be constructed in terms of moles rather than molecules. For the reaction in which hydrogen and oxygen combine to make water, for example, we can construct the following ratios:

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

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

$$\frac{2\ \mathrm{mol\ H_2}}{2\ \mathrm{mol\ H_2O}} \text{ or } \frac{2\ \mathrm{mol\ H_2O}}{2\ \mathrm{mol\ H_2}}$$

We can use these ratios to determine what amount of a substance, in moles, will react with or produce a given number of moles of a different substance. The study of the numerical relationships between the reactants and the products in balanced chemical reactions is called *stoichiometry*.

Example 6.5.1

How many moles of oxygen react with hydrogen to produce 27.6 mol of H_2O?

Solution

Solutions to Example 8.3.1

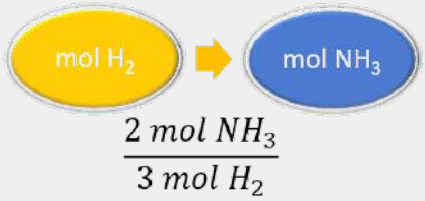
Steps for Problem Solving	How many moles of oxygen react with hydrogen to produce 27.6 mol of H_2O?
Find a balanced equation that describes the reaction.	Unbalanced: $H_2 + O_2 \rightarrow H_2O$ Balanced: $\underline{2}H_2 + O_2 \rightarrow \underline{2}H_2O$
Identify the "given" information and what the problem is asking you to "find."	Given: moles H_2O Find: moles oxygen
List other known quantities.	1 mol O_2 = 2 mol H_2O
Prepare a concept map and use the proper conversion factor.	 $\frac{1\ mol\ O_2}{2\ mol\ H_2O}$
Cancel units and calculate.	$\cancel{27.6\ mol\ H_2O} \times \frac{1\ mol\ O_2}{\cancel{2\ mol\ H_2O}} = 13.8\ mol\ O_2$ To produce 27.6 mol of H_2O, 13.8 mol of O_2 react.
Think about your result.	Since each mole of oxygen produces twice as many moles of water, it makes sense that the produced amount is greater than the reactant amount

Example 6.5.2

How many moles of ammonia are produced if 4.20 moles of hydrogen are reacted with an excess of nitrogen?

Solution

Solutions to Example 8.3.2

Steps for Problem Solving	How many moles of ammonia are produced if 4.20 moles of hydrogen are reacted with an excess of nitrogen?
Find a balanced equation that describes the reaction.	Unbalanced: $N_2 + H_2 \rightarrow NH_3$ Balanced: $N_2 + \underline{3}H_2 \rightarrow \underline{2}NH_3$
Identify the "given" information and what the problem is asking you to "find."	Given: $\mathbf{H_2 = 4.20\ mol}$ Find: **mol** of $\mathbf{NH_3}$
List other known quantities.	3 mol H_2 = 2 mol NH_3
Prepare a concept map and use the proper conversion factor.	 $\frac{2\ mol\ NH_3}{3\ mol\ H_2}$
Cancel units and calculate.	$\cancel{4.20\ mol\ H_2} \times \frac{2\ mol\ NH_3}{\cancel{3\ mol\ H_2}} = 2.80\ mol\ NH_3$ The reaction of $\mathbf{4.20\ mol}$ of hydrogen with excess nitrogen produces $\mathbf{2.80\ mol}$ of ammonia.
Think about your result.	The result corresponds to the 3:2 ratio of hydrogen to ammonia from the balanced equation.

Exercise 6.5.3

a. Given the following balanced chemical equation:

$$\mathbf{C_5H_{12} + 8\,O_2 \longrightarrow 5\,CO_2 + 6\,H_2O}$$

, How many moles of $\mathbf{H_2O}$ can be formed if 0.0652 mol of $\mathbf{C_5H_{12}}$ were to react?

b. Balance the following unbalanced equation and determine how many moles of $\mathbf{H_2O}$ are produced when 1.65 mol of NH_3 react:

$$\mathbf{NH_3 + O_2 \longrightarrow N_2 + H_2O}$$

Answer a

0.391 mol H_2O

Answer b

$4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O$; 2.48 mol H_2O

Summary

- The balanced chemical reaction can be used to determine molar relationships between substances.

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6.6: Limiting Reagents

Learning Objectives

- Identify a limiting reagent from a set of reactants.
- Calculate how much product will be produced from the limiting reagent.
- Calculate how much reactant(s) remains when the reaction is complete.

In addition to the assumption that reactions proceed all the way to completion, one additional assumption we have made about chemical reactions is that all the reactants are present in the proper quantities to react to products; this is not always the case. In Figure **6.6.2** we are taking hydrogen atoms and oxygen atoms (left) to make water molecules (right). However, there are not enough oxygen atoms to use up all the hydrogen atoms. We run out of oxygen atoms and cannot make any more water molecules, so the process stops when we run out of oxygen atoms.

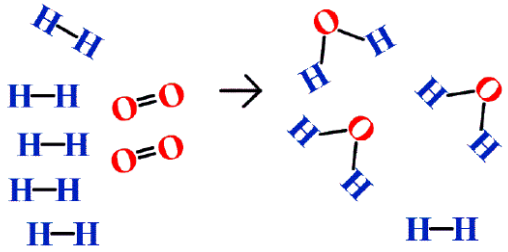


Figure **6.6.2**: Making Water. In this scenario for making water molecules, we run out of O atoms before we use up all the H atoms. Similar situations exist for many chemical reactions when one reactant runs out before the other.

A similar situation exists for many chemical reactions: you usually run out of one reactant before all of the other reactant has reacted. The reactant you run out of is called the limiting reagent; the other reactant or reactants are considered to be *in excess*. A crucial skill in evaluating the conditions of a chemical process is to determine which reactant is the limiting reagent and which is in excess.

The key to recognizing which reactant is the limiting reagent is based on a mole-mass or mass-mass calculation: whichever reactant gives the *lesser* amount of product is the limiting reagent. What we need to do is determine an amount of one product (either moles or mass), assuming all of each reactant reacts. Whichever reactant gives the least amount of that particular product is the limiting reagent. It does not matter which product we use, as long as we use the same one each time. It does not matter whether we determine the number of moles or grams of that product; however, we will see shortly that knowing the final mass of product can be useful.

For example, consider this reaction:

$$4As(s) + 3O_2(g) \rightarrow 2As_2O_3(s)$$

Suppose we start a reaction with 50.0 g of As and 50.0 g of O_2. Which one is the limiting reagent? We need to perform two mole-mass calculations, each assuming that each reactant reacts completely. Then we compare the amount of the product produced by each and determine which is less.

The calculations are as follows:

$$50.0\ \cancel{g\,As} \times \frac{1\ \cancel{mol\,As}}{74.92\ \cancel{g\,As}} \times \frac{2\,mol\,As_2O_3}{4\ \cancel{mol\,As}} = 0.334\,mol\,As_2O_3$$

$$50.0\ \cancel{g\,O_2} \times \frac{1\ \cancel{mol\,O_2}}{32.00\ \cancel{g\,O_2}} \times \frac{2\,mol\,As_2O_3}{3\ \cancel{mol\,O_2}} = 1.04\,mol\,As_2O_3$$

Comparing these two answers, it is clear that 0.334 mol of As_2O_3 is less than 1.04 mol of As_2O_3, so arsenic is the limiting reagent. If this reaction is performed under these initial conditions, the arsenic will run out before the oxygen runs out. We say that the oxygen is "in excess."

Identifying the limiting reagent, then, is straightforward. However, there are usually two associated questions: (1) what mass of product (or products) is then actually formed? and (2) what mass of what reactant is left over? The first question is straightforward to answer: simply perform a conversion from the number of moles of product formed to its mass, using its molar mass. For As_2O_3, the molar mass is 197.84 g/mol; knowing that we will form 0.334 mol of As_2O_3 under the given conditions, we will get

$$0.334\ \cancel{mol\ As_2O_3} \times \frac{197.84\ g\ As_2}{1\ \cancel{mol\ As_2O_3}} = 66.1\ g\ As_2O_3$$

The second question is somewhat more convoluted to answer. First, we must do a mass-mass calculation relating the limiting reagent (here, As) to the other reagent (O_2). Once we determine the mass of O_2 that reacted, we subtract that from the original amount to determine the amount left over. According to the mass-mass calculation,

$$50.0\ \cancel{g\ As} \times \frac{1\ \cancel{mol\ As}}{74.92\ \cancel{g\ As}} \times \frac{3\ \cancel{mol\ O_2}}{4\ \cancel{mol\ As}} \times \frac{32.00\ g\ O_2}{1\ \cancel{mol\ O_2}} = 16.0\ g\ O_2\ reacted$$

Because we reacted 16.0 g of our original O_2, we subtract that from the original amount, 50.0 g, to get the mass of O_2 remaining:

50.0 g O_2 − 16.0 g O_2 reacted = 34.0 g O_2 left over

You must remember to perform this final subtraction to determine the amount remaining; a common error is to report the 16.0 g as the amount remaining.

Example 6.6.1

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

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

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

Solution

Because the question asks what mass of magnesium is formed, we can perform two mass-mass calculations and determine which amount is less.

$$5.00\ \cancel{g\ Rb} \times \frac{1\ \cancel{mol\ Rb}}{85.47\ \cancel{g\ Rb}} \times \frac{1\ \cancel{mol\ Mg}}{2\ \cancel{mol\ Rb}} \times \frac{24.31\ g\ Mg}{1\ \cancel{mol\ Mg}} = 0.711\ g\ Mg$$

$$3.44\ \cancel{g\ MgCl_2} \times \frac{1\ \cancel{mol\ MgCl_2}}{95.21\ \cancel{g\ MgCl_2}} \times \frac{1\ \cancel{mol\ Mg}}{1\ \cancel{mol\ MgCl_2}} \times \frac{24.31\ g\ Mg}{1\ \cancel{mol\ Mg}} = 0.878\ g\ Mg$$

The 0.711 g of Mg is the lesser quantity, so the associated reactant—5.00 g of Rb—is the limiting reagent. To determine how much of the other reactant is left, we have to do one more mass-mass calculation to determine what mass of MgCl2 reacted with the 5.00 g of Rb, and then subtract the amount reacted from the original amount.

$$5.00\ \cancel{g\ Rb} \times \frac{1\ \cancel{mol\ Rb}}{85.47\ \cancel{g\ Rb}} \times \frac{1\ \cancel{mol\ MgCl_2}}{2\ \cancel{mol\ Rb}} \times \frac{95.21\ g\ Mg}{1\ \cancel{mol\ MgCl_2}} = 2.78\ g\ MgCl_2\ reacted$$

Because we started with 3.44 g of MgCl2, we have

3.44 g MgCl2 − 2.78 g MgCl2 reacted = 0.66 g MgCl2 left

Exercise 6.6.1

Given the initial amounts listed, what is the limiting reagent, and what is the mass of the leftover reagent?

$$\underbrace{22.7\ g}_{MgO(s)} + \underbrace{17.9\ g}_{H_2S} \rightarrow MgS(s) + H_2O(l)$$

Answer

H_2S is the limiting reagent; 1.5 g of MgO are left over.

Summary

The limiting reagent is the reactant that produces the least amount of product. Mass-mass calculations can determine how much product is produced and how much of the other reactants remain.

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6.7: Yields

Learning Objective

- Define and determine theoretical yields, actual yields, and percent yields.

In all the previous calculations we have performed involving balanced chemical equations, we made two assumptions:

1. The reaction goes exactly as written.
2. The reaction proceeds completely.

In reality, such things as side reactions occur that make some chemical reactions rather messy. For example, in the actual combustion of some carbon-containing compounds, such as methane, some CO is produced as well as CO_2. However, we will continue to ignore side reactions, unless otherwise noted. The second assumption, that the reaction proceeds completely, is more troublesome. Many chemical reactions do not proceed to completion as written, for a variety of reasons (some of which we will consider in Chapter 13). When we calculate an amount of product assuming that all the reactant reacts, we calculate the **theoretical yield**, an amount that is theoretically produced as calculated using the balanced chemical reaction.

In many cases, however, this is not what really happens. In many cases, less—sometimes, much less—of a product is made during the course of a chemical reaction. The amount that is actually produced in a reaction is called the **actual yield**. By definition, the actual yield is less than or equal to the theoretical yield. If it is not, then an error has been made.

Both theoretical yields and actual yields are expressed in units of moles or grams. It is also common to see something called a percent yield. The **percent yield** is a comparison between the actual yield and the theoretical yield and is defined as

$$\text{percent yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100\% \tag{6.7.1}$$

It does not matter whether the actual and theoretical yields are expressed in moles or grams, as long as they are expressed in the same units. However, the percent yield always has units of percent. Proper percent yields are between 0% and 100%. Again, if percent yield is greater than 100%, an error has been made.

Example 6.7.1

A worker reacts 30.5 g of Zn with nitric acid and evaporates the remaining water to obtain 65.2 g of $Zn(NO_3)_2$. What are the theoretical yield, the actual yield, and the percent yield?

$$\mathrm{Zn\,(s) + 2\,HNO_3\,(aq) \longrightarrow Zn(NO_3)_2\,(aq) + H_2\,(g)}$$

Solution

A mass-mass calculation can be performed to determine the theoretical yield. We need the molar masses of Zn (65.39 g/mol) and $Zn(NO_3)_2$ (189.41 g/mol). In three steps, the mass-mass calculation is:

$$30.5\ g\ Zn \times \frac{1\ mol\ Zn}{65.39\ g\ Zn} \times \frac{1\ mol\ Zn(NO_3)_2}{1\ mol\ Zn} \times \frac{189.41\ g\ Zn(NO_3)_2}{1\ mol\ Zn(NO_3)_2} = 88.3\ g\ Zn(NO_3)_2$$

Thus, the theoretical yield is 88.3 g of $Zn(NO_3)_2$. The actual yield is the amount that was actually made, which was 65.2 g of $Zn(NO_3)_2$. To calculate the percent yield, we take the actual yield and divide it by the theoretical yield and multiply by 100 (Equation 6.7.1):

$$\frac{65.2\ g\ Zn(NO_3)_2}{88.3\ g\ Zn(NO_3)_2} \times 100\% = 73.8\%$$

The worker achieved almost three-fourths of the possible yield.

Exercise 6.7.1

A synthesis produced 2.05 g of NH_3 from 16.5 g of N_2. What is the theoretical yield and the percent yield?

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

*Technically, this is a reversible reaction (with double arrows), but for this exercise consider it irreversible (single arrow).

Answer

theoretical yield = 20.1 g; percent yield = 10.2%

Chemistry is Everywhere: Actual Yields in Drug Synthesis and Purification

Many drugs are the product of several steps of chemical synthesis. Each step typically occurs with less than 100% yield, so the overall percent yield might be very small. The general rule is that the overall percent yield is the product of the percent yields of the individual synthesis steps. For a drug synthesis that has many steps, the overall percent yield can be very tiny, which is one factor in the huge cost of some drugs. For example, if a 10-step synthesis has a percent yield of 90% for each step, the overall yield for the entire synthesis is only 35%. Many scientists work every day trying to improve percent yields of the steps in the synthesis to decrease costs, improve profits, and minimize waste.

Even purifications of complex molecules into drug-quality purity are subject to percent yields. Consider the purification of impure albuterol. Albuterol ($C_{13}H_{21}NO_2$; accompanying figure) is an inhaled drug used to treat asthma, bronchitis, and other obstructive pulmonary diseases. It is synthesized from norepinephrine, a naturally occurring hormone and neurotransmitter. Its initial synthesis makes very impure albuterol that is purified in five chemical steps. The details of the steps do not concern us; only the percent yields do:

A child using an albuterol inhaler, a container of albuterol medication, and a molecular model of albuterol are shown in three combined images.

impure albuterol → intermediate A	percent yield = 70%
intermediate A → intermediate B	percent yield = 100%
intermediate B → intermediate C	percent yield = 40%
intermediate C → intermediate D	percent yield = 72%
intermediate D → purified albuterol	percent yield = 35%
overall percent yield = 70% × 100% × 40% × 72% × 35% = 7.5%	

That is, only about *one-fourteenth* of the original material was turned into the purified drug. This demonstrates one reason why some drugs are so expensive—a lot of material is lost in making a high-purity pharmaceutical.



Figure 6.7.1 A child using an albuterol inhaler, the container of albuterol medication, and a molecular model of the albuterol molecule. Source: Photo on far left © Thinkstock. Photo in center courtesy of Intropin, http://commons.wikimedia.org/wiki/Fi...te_%281%29.JPG.

Summary

Theoretical yield is the calculated yield using the balanced chemical reaction. Actual yield is what is actually obtained in a chemical reaction. Percent yield is a comparison of the actual yield with the theoretical yield.

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CHAPTER OVERVIEW

7: Chemical Bonding

7.1: Prelude to Chemical Bonds
7.2: Lewis Electron Dot Diagrams
7.3: Covalent Bonds
7.4: Molecular Shapes
7.5: Electronegativity and Polarity - Why Oil and Water Don’t Mix
7.6: Interactions between Molecules
7.7: Water - A Remarkable Molecule

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7.1: Prelude to Chemical Bonds

Diamond is the hardest natural material known on Earth. Yet diamond is just pure carbon. What is special about this element that makes diamond so hard? Bonds. Chemical bonds.

In a perfect diamond crystal, each C atom makes four connections—bonds—to four other C atoms in a three-dimensional matrix. Four is the greatest number of bonds that is commonly made by atoms, so C atoms maximize their interactions with other atoms. This three-dimensional array of connections extends throughout the diamond crystal, making it essentially one large molecule. Breaking a diamond means breaking every bond at once. Also, the bonds are moderately strong. There are stronger interactions known, but the carbon-carbon connection is fairly strong itself. Not only does a person have to break many connections at once, but the bonds are also strong connections from the start.



Diamond is the hardest known natural substance and is composed solely of the element carbon. (CC SA-BY 3.0; Mario Sarto).

There are other substances that have bonding arrangements similar to diamond. Silicon dioxide and boron nitride have some similarities, but neither of them comes close to the ultimate hardness of diamond.

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7.2: Lewis Electron Dot Diagrams

Learning Objective

- Draw a Lewis electron dot diagram for an atom or a monatomic ion.

In almost all cases, chemical bonds are formed by interactions of valence electrons in atoms. To facilitate our understanding of how valence electrons interact, a simple way of representing those valence electrons would be useful.

A **Lewis electron dot diagram** (or electron dot diagram, or a Lewis diagram, or a Lewis structure) is a representation of the valence electrons of an atom that uses dots around the symbol of the element. The number of dots equals the number of valence electrons in the atom. These dots are arranged to the right and left and above and below the symbol, with no more than two dots on a side. (The order in which the positions are used does not matter.) For example, the Lewis electron dot diagram for hydrogen is simply

$$\mathbf{H}\cdot$$

Because the side is not important, the Lewis electron dot diagram could also be drawn as follows:

$$\dot{\mathbf{H}} \quad \textit{or} \quad \cdot\mathbf{H} \quad \textit{or} \quad \underset{\cdot}{\mathbf{H}}$$

The electron dot diagram for helium, with two valence electrons, is as follows:

$$\mathbf{He:}$$

By putting the two electrons together on the same side, we emphasize the fact that these two electrons are both in the 1*s* subshell; this is the common convention we will adopt, although there will be exceptions later. The next atom, lithium, has an electron configuration of $1s^2 2s^1$, so it has only one electron in its valence shell. Its electron dot diagram resembles that of hydrogen, except the symbol for lithium is used:

$$\mathbf{Li}\cdot$$

Beryllium has two valence electrons in its 2*s* shell, so its electron dot diagram is like that of helium:

$$\mathbf{Be:}$$

The next atom is boron. Its valence electron shell is $2s^2 2p^1$, so it has three valence electrons. The third electron will go on another side of the symbol:

$$\dot{\mathbf{B}}\mathbf{e:}$$

Again, it does not matter on which sides of the symbol the electron dots are positioned.

For carbon, there are four valence electrons, two in the 2*s* subshell and two in the 2*p* subshell. As usual, we will draw two dots together on one side, to represent the 2*s* electrons. However, conventionally, we draw the dots for the two *p* electrons on different sides. As such, the electron dot diagram for carbon is as follows:

$$\cdot\dot{\mathbf{C}}\mathbf{:}$$

With N, which has three *p* electrons, we put a single dot on each of the three remaining sides:

$$\cdot\dot{\underset{\cdot}{\mathbf{N}}}\mathbf{:}$$

For oxygen, which has four *p* electrons, we now have to start doubling up on the dots on one other side of the symbol. When doubling up electrons, make sure that a side has no more than two electrons.

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

Fluorine and neon have seven and eight dots, respectively:





With the next element, sodium, the process starts over with a single electron because sodium has a single electron in its highest-numbered shell, the $n = 3$ shell. By going through the periodic table, we see that the Lewis electron dot diagrams of atoms will never have more than eight dots around the atomic symbol.

Example 7.2.1

What is the Lewis electron dot diagram for each element?

a. aluminum
b. selenium

Solution

a. The valence electron configuration for aluminum is $3s^2 3p^1$. So it would have three dots around the symbol for aluminum, two of them paired to represent the 3*s* electrons:



2. The valence electron configuration for selenium is $4s^2 4p^4$. In the highest-numbered shell, the $n = 4$ shell, there are six electrons. Its electron dot diagram is as follows:



Exercise 7.2.1

What is the Lewis electron dot diagram for each element?

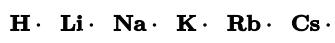
a. phosphorus
b. argon

Answer



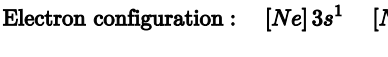


Elements in the same column of the periodic table have similar Lewis electron dot diagrams because they have the same valence shell electron configuration. The electron dot diagrams for the first column of elements are as follows:



Monatomic ions are atoms that have either lost (for cations) or gained (for anions) electrons. Electron dot diagrams for ions are the same as for atoms, except that some electrons have been removed for cations, while some electrons have been added for anions. Thus, in comparing the electron configurations and electron dot diagrams for the Na atom and the Na^+ ion, we note that the Na atom has a single valence electron in its Lewis diagram, while the Na^+ ion has lost that one valence electron:





Technically, the valence shell of the Na^+ ion is now the $n = 2$ shell, which has eight electrons in it. So why do we not put eight dots around Na^+? Conventionally, when we show electron dot diagrams for ions, we show the original valence shell of the atom, which in this case is the $n = 3$ shell and empty in the Na^+ ion.

In making cations, electrons are first lost from the *highest numbered shell*, not necessarily the last subshell filled. For example, in going from the neutral Fe atom to the Fe^{2+} ion, the Fe atom loses its two 4*s* electrons first, not its 3*d* electrons, despite the fact that the 3*d* subshell is the last subshell being filled. Thus, we have

$$\textbf{Lewis dot diagram :} \quad \textbf{Fe} : \quad Fe^{2+}$$

$$\textbf{Electron configuration :} \quad [Ar]\,4s^2 3d^6 \quad [Ar]\,3d^6$$

Anions have extra electrons when compared to the original atom. Here is a comparison of the Cl atom with the Cl^- ion:

$$\textbf{Lewis dot diagram :} \quad :\ddot{\underset{\cdot\cdot}{\text{Cl}}}\cdot \quad :\ddot{\underset{\cdot\cdot}{\text{Cl}}}:^-$$

$$\textbf{Electron configuration :} \quad [Ne]\,3s^2 3p^5 \quad [Ne]\,3s^2 3p^6$$

Example 7.2.2

What is the Lewis electron dot diagram for each ion?

a. Ca^{2+}
b. O^{2-}

Solution

a. Having lost its two original valence electrons, the Lewis electron dot diagram is simply: Ca^{2+}
b. The O^{2-} ion has gained two electrons in its valence shell, so its Lewis electron dot diagram is as follows:

$$:\ddot{\underset{\cdot\cdot}{\text{O}}}:^{2-}$$

Exercise 7.2.2

The electronic configuration of the thallium ion is $6s^2 4f^{14} 5d^{10}$. What is the Lewis electron dot diagram for the Tl^+ ion?

Answer

$$\textbf{Tl} :^+$$

Summary

- Lewis electron dot diagrams use dots to represent valence electrons around an atomic symbol.
- Lewis electron dot diagrams for ions have less (for cations) or more (for anions) dots than the corresponding atom.

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7.3: Covalent Bonds

Learning Objectives

- Define *covalent bond*.
- Illustrate covalent bond formation with Lewis electron dot diagrams.

Ionic bonding typically occurs when it is easy for one atom to lose one or more electrons, and for another atom to gain one or more electrons. However, some atoms will not give up or gain electrons easily. Yet they still participate in compound formation. How? There is another mechanism for obtaining a complete valence shell: *sharing* electrons. When electrons are shared between two atoms, they form a **covalent bond**.

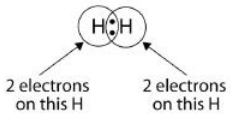
Let us illustrate a covalent bond by using H atoms, with the understanding that H atoms need only two electrons to fill the 1*s* subshell. Each H atom starts with a single electron in its valence shell:

$$\mathbf{H}\cdot \quad \cdot\mathbf{H}$$

The two H atoms can share their electrons:

$$\mathbf{H:H}$$

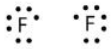
We can use circles to show that each H atom has two electrons around the nucleus, completely filling each atom's valence shell:



Because each H atom has a filled valence shell, this bond is stable, and we have made a diatomic hydrogen molecule. (This explains why hydrogen is one of the diatomic elements.) For simplicity's sake, it is not unusual to represent the covalent bond with a dash, instead of with two dots:

H–H

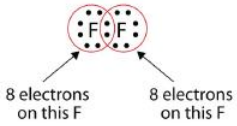
Because two atoms are sharing one pair of electrons, this covalent bond is called a **single bond**. As another example, consider fluorine. F atoms have seven electrons in their valence shell:



These two atoms can do the same thing that the H atoms did; they share their unpaired electrons to make a covalent bond.



Note that each F atom has a complete octet around it now:



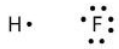
We can also write this using a dash to represent the shared electron pair:



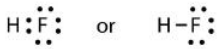
There are two different types of electrons in the fluorine diatomic molecule. The **bonding electron pair** makes the covalent bond. Each F atom has three other pairs of electrons that do not participate in the bonding; they are called **lone pair electrons**. Each F

atom has one bonding pair and three lone pairs of electrons.

Covalent bonds can be made between different elements as well. One example is HF. Each atom starts out with an odd number of electrons in its valence shell:



The two atoms can share their unpaired electrons to make a covalent bond:



Note that the H atom has a full valence shell with two electrons, while the F atom has a complete octet of electrons.

Example 7.3.1

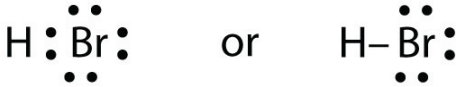
Use Lewis electron dot diagrams to illustrate the covalent bond formation in HBr.

Solution

HBr is very similar to HF, except that it has Br instead of F. The atoms are as follows:



The two atoms can share their unpaired electron:



Exercise 7.3.1

Use Lewis electron dot diagrams to illustrate the covalent bond formation in Cl_2.

Answer



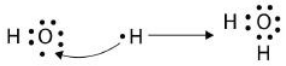
More than two atoms can participate in covalent bonding, although any given covalent bond will be between two atoms only. Consider H and O atoms:



The H and O atoms can share an electron to form a covalent bond:



The H atom has a complete valence shell. However, the O atom has only seven electrons around it, which is not a complete octet. This can be fixed by including a second H atom, whose single electron will make a second covalent bond with the O atom:



(It does not matter what side the second H atom is positioned on.) Now the O atom has a complete octet around it, and each H atom has two electrons, filling its valence shell. This is how a water molecule, H_2O, is made.

Example 7.3.2

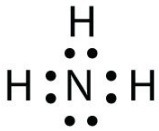
Use a Lewis electron dot diagram to show the covalent bonding in NH_3.

Solution

The N atom has the following Lewis electron dot diagram:



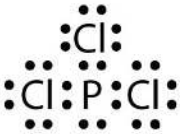
It has three unpaired electrons, each of which can make a covalent bond by sharing electrons with an H atom. The electron dot diagram of NH_3 is as follows:



Exercise 7.3.2

Use a Lewis electron dot diagram to show the covalent bonding in PCl_3.

Answer



There is a simple set of steps for determining the Lewis electron dot diagram of a simple molecule. First, you must identify the central atom and the surrounding atoms. The **central atom** is the atom in the center of the molecule, while the **surrounding atoms** are the atoms making bonds to the central atom. The central atom is usually written first in the formula of the compound (H_2O is the notable exception). After the central and surrounding atoms have been identified, follow these steps:

1. Count the total number of valence electrons. Add extra if the species has negative charges and remove some for every positive charge on the species.
2. Write the central atom and surround it with the surrounding atoms.
3. Put a pair of electrons between the central atom and each surrounding atom.
4. Complete the octets around the surrounding atoms (except for H).
5. Put remaining electrons, if any, around the central atom.
6. Check that every atom has a full valence shell.

Let us try these steps to determine the electron dot diagram for BF_4^-. The B atom is the central atom, and the F atoms are the surrounding atoms. There is a negative sign on the species, so we have an extra electron to consider.

1. **Count the total number of electrons.** B has 3, each F has 7, and there is one extra electron: 3 + 7 + 7 + 7 + 7 + 1 = 32.

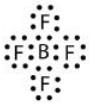
2. **Write the central atom surrounded by surrounding atoms.**



3. **Put a pair of electrons between the central atom and each surrounding atom.** This uses up eight electrons, so we have 32 − 8 = 24 electrons left.



4. **Complete the octets around the surrounding atoms (except for H).** This uses up 24 more electrons, leaving 24 − 24 = 0 electrons left.



5. **Put remaining electrons, if any, around the central atom.** There are no additional electrons to add to the central atom.

6. **Check.** The B atom has eight electrons around it, as does each F atom. Each atom has a complete octet. This is a good Lewis electron dot diagram for BF_4^-.

Sometimes, however, these steps do not work. If we were to follow these steps for the compound formaldehyde (CH_2O), we would get the following:



The H and O atoms have the proper number of electrons, but the C atom only has six electrons around it, not the eight electrons for an octet. How do we fix this?

We fix this by recognizing that two atoms can share more than one pair of electrons. In the case of CH_2O, the O and C atoms share two pairs of electrons, with the following Lewis electron dot diagram as a result:



By circling the electrons around each atom, we can now see that the O and C atoms have octets, while each H atom has two electrons:



Each valence shell is full, so this is an acceptable Lewis electron dot diagram. If we were to use lines to represent the bonds, we would use two lines between the C and O atoms:



The bond between the C and O atoms is a **double bond** and represents two bonding pairs of electrons between the atoms. If the rules for drawing Lewis electron dot diagrams do not work as written, a double bond may be required.

Example 7.3.3: Carbon Dioxide

What is the proper Lewis electron dot diagram for CO_2?

Solution

The central atom is a C atom, with O atoms as surrounding atoms. We have a total of 4 + 6 + 6 = 16 valence electrons. Following the rules for Lewis electron dot diagrams for compounds gives us



The O atoms have complete octets around them, but the C atom only has four electrons around it. The way to solve this dilemma is to make a double bond between carbon and *each* O atom:



Each O atom still has eight electrons around it, but now the C atom also has a complete octet. This is an acceptable Lewis electron dot diagram for CO_2.

Exercise 7.3.3

What is the proper Lewis electron dot diagram for carbonyl sulfide (COS)?

Answer



It is also possible to have a **triple bond,** in which there are three pairs of electrons between two atoms. Good examples of this are elemental nitrogen (N_2) and acetylene (C_2H_2):



Acetylene is an interesting example of a molecule with two central atoms, which are both C atoms. Polyatomic ions are bonded together with covalent bonds. Because they are ions, however, they participate in ionic bonding with other ions. So both major types of bonding can occur at the same time.

Food and Drink Application: Vitamins and Minerals

Vitamins are nutrients that our bodies need in small amounts but cannot synthesize; therefore, they must be obtained from the diet. The word *vitamin* comes from "vital amine" because it was once thought that all these compounds had an amine group (NH_2) in it. This is not actually true, but the name stuck anyway.

All vitamins are covalently bonded molecules. Most of them are commonly named with a letter, although all of them also have formal chemical names. Thus vitamin A is also called retinol, vitamin C is called ascorbic acid, and vitamin E is called tocopherol. There is no single vitamin B; there is a group of substances called the *B complex vitamins* that are all water soluble and participate in cell metabolism. If a diet is lacking in a vitamin, diseases such as scurvy or rickets develop. Luckily, all vitamins are available as supplements, so any dietary deficiency in a vitamin can be easily corrected.

A mineral is any chemical element other than carbon, hydrogen, oxygen, or nitrogen that is needed by the body. Minerals that the body needs in quantity include sodium, potassium, magnesium, calcium, phosphorus, sulfur, and chlorine. Essential minerals that the body needs in tiny quantities (so-called *trace elements*) include manganese, iron, cobalt, nickel, copper, zinc, molybdenum, selenium, and iodine. Minerals are also obtained from the diet. Interestingly, most minerals are consumed in ionic form, rather than as elements or from covalent molecules. Like vitamins, most minerals are available in pill form, so any deficiency can be compensated for by taking supplements.



Supplement Facts

Serving Size 1 Tablet

Each Tablet Contains	% Daily Value
Vitamin A 5000 I.U (50% as Beta Carotene)	100%
Vitamin C 60 mg	100%
Vitamin D 400 I.U.	100%
Vitamin E 30 I.U.	100%
Vitamin K 25 mcg	31%
Thiamin (Vitamin B1) 1.5 mg	100%
Riboflavin (Vitamin B2) 1.7 mg	100%
Niacin 20 mg	100%
Vitamin B6 2 mg	100%
Folic Acid 400 mcg	100%
Vitamin B12 6 mcg	100%
Biotin 30 mcg	10%
Pantothenic Acid 10 mg	100%
Calcium 160 mg	16%
Iron 18 mg	100%
Phosphorus 110 mg	11%
Iodine 150 mcg	100%
Magnesium 100 mg	25%
Zinc 15 mg	100%
Selenium 20 mcg	29%
Copper 2 mg	100%
Manganese 2 mg	100%
Chromium 120 mcg	100%
Molybdenum 75 mcg	100%
Chloride 72 mg	2%
Potassium 80 mg	2%
Boron 150 mcg	*
Nickel 5 mcg	*
Silicon 2 mg	*
Tin 10 mcg	*
Vanadium 10 mcg	*
Lutein 250 mcg	*

* Daily Value (DV) not stablished

Figure 7.3.1: Vitamin and Mineral supplements. Every entry down through pantothenic acid is a vitamin, and everything from calcium and below is a mineral.

Summary

- Covalent bonds are formed when atoms share electrons.
- Lewis electron dot diagrams can be drawn to illustrate covalent bond formation.
- Double bonds or triple bonds between atoms may be necessary to properly illustrate the bonding in some molecules.

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7.4: Molecular Shapes

Learning Objective

- Determine the shape of simple molecules.

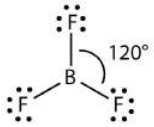
Molecules have shapes. There is an abundance of experimental evidence to that effect, from their physical properties to their chemical reactivity. Small molecules—molecules with a single central atom—have shapes that can be easily predicted. The basis of molecular shapes is called **valence shell electron pair repulsion (VSEPR).** VSEPR says that electron pairs, being composed of negatively charged particles, repel each other to get as far away from each other as possible. VSEPR makes a distinction between *electron group geometry*, which expresses how electron groups (bonds and nonbonding electron pairs) are arranged, and *molecular geometry*, which expresses how the atoms in a molecule are arranged. However, the two geometries are related.

There are two types of **electron groups**: any type of bond—single, double, or triple—and lone electron pairs. When applying VSEPR to simple molecules, the first thing to do is to count the number of electron groups around the central atom. Remember that a multiple bond counts as only *one* electron group.

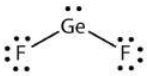
Any molecule with only two atoms is linear. A molecule whose central atom contains only two electron groups orients those two groups as far apart from each other as possible—180° apart. When the two electron groups are 180° apart, the atoms attached to those electron groups are also 180° apart, so the overall molecular shape is linear. Examples include BeH_2 and CO_2:



A molecule with three electron groups orients the three groups as far apart as possible. They adopt the positions of an equilateral triangle—120° apart and in a plane. The shape of such molecules is *trigonal planar*. An example is BF_3:



Some substances have a trigonal planar electron group distribution, but have atoms bonded to only two of the three electron groups. An example is GeF_2:



From an electron group geometry perspective, GeF_2 has a trigonal planar shape, but its real shape is dictated by the positions of the atoms. This shape is called *bent* or *angular*.

A molecule with four electron groups about the central atom orients the four groups in the direction of a tetrahedron, as shown in Figure **7.4.1**: Tetrahedral Geometry. If there are four atoms attached to these electron groups, then the molecular shape is also *tetrahedral*. Methane (CH_4) is an example.

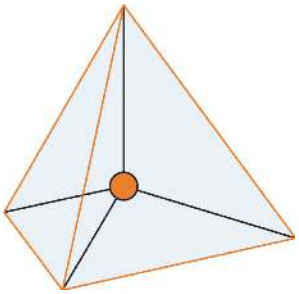
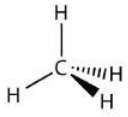
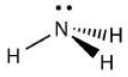


Figure **7.4.1**: Tetrahedral Geometry. Four electron groups orient themselves in the shape of a tetrahedron.

This diagram of CH_4 illustrates the standard convention of displaying a three-dimensional molecule on a two-dimensional surface. The straight lines are in the plane of the page, the solid wedged line is coming out of the plane toward the reader, and the dashed wedged line is going out of the plane away from the reader.



NH_3 is an example of a molecule whose central atom has four electron groups, but only three of them are bonded to surrounding atoms.



Although the electron groups are oriented in the shape of a tetrahedron, from a molecular geometry perspective, the shape of NH_3 is *trigonal pyramidal*.

H_2O is an example of a molecule whose central atom has four electron groups, but only two of them are bonded to surrounding atoms.

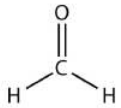


Although the electron groups are oriented in the shape of a tetrahedron, the shape of the molecule is *bent* or *angular*. A molecule with four electron groups about the central atom, but only one electron group bonded to another atom is linear because there are only two atoms in the molecule.

Double or triple bonds count as a single electron group. CH_2O has the following Lewis electron dot diagram.



The central C atom has three electron groups around it because the double bond counts as one electron group. The three electron groups repel each other to adopt a trigonal planar shape:



(The lone electron pairs on the O atom are omitted for clarity.) The molecule will not be a perfect equilateral triangle because the C–O double bond is different from the two C–H bonds, but both planar and triangular describe the appropriate approximate shape of this molecule.

Example 7.4.1

What is the approximate shape of each molecule?

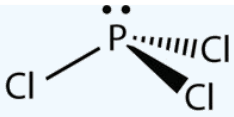
a. $\mathbf{PCl_3}$
b. **NOF**

Solution

The first step is to draw the Lewis electron dot diagram of the molecule.

a:

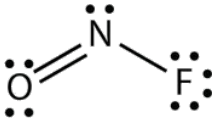
For PCl_3, the electron dot diagram is as follows:



The lone electron pairs on the Cl atoms are omitted for clarity. The P atom has four electron groups with three of them bonded to surrounding atoms, so the molecular shape is trigonal pyramidal.

b:

The electron dot diagram for NOF is as follows:



The N atom has three electron groups on it, two of which are bonded to other atoms. The molecular shape is bent.

? Exercise 7.4.1

What is the approximate molecular shape of CH_2Cl_2?

Answer

Tetrahedral

Table **7.4.1** summarizes the shapes of molecules based on their number of electron groups and surrounding atoms.

Table **7.4.1**: Summary of Molecular Shapes

Number of Electron Groups on Central Atom	Number of Surrounding Atoms	Molecular Shape
any	1	linear
2	2	linear
3	3	trigonal planar
3	2	bent
4	4	tetrahedral
4	3	trigonal pyramidal
4	2	bent

Summary

The approximate shape of a molecule can be predicted from the number of electron groups and the number of surrounding atoms.

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7.5: Electronegativity and Polarity - Why Oil and Water Don't Mix

Learning Objectives

- Explain how polar compounds differ from nonpolar compounds.
- Determine if a molecule is polar or nonpolar.
- Given a pair of compounds, predict which would have a higher melting or boiling point.

Bond Polarity

The ability of an atom in a molecule to attract shared electrons is called **electronegativity**. When two atoms combine, the difference between their electronegativities is an indication of the type of bond that will form. If the difference between the electronegativities of the two atoms is small, neither atom can take the shared electrons completely away from the other atom, and the bond will be covalent. If the difference between the electronegativities is large, the more electronegative atom will take the bonding electrons completely away from the other atom (electron transfer will occur), and the bond will be ionic. This is why metals (low electronegativities) bonded with nonmetals (high electronegativities) typically produce ionic compounds.

A bond may be so polar that an electron actually transfers from one atom to another, forming a true ionic bond. How do we judge the degree of polarity? Scientists have devised a scale called **electronegativity**, a scale for judging how much atoms of any element attract electrons. Electronegativity is a unitless number; the higher the number, the more an atom attracts electrons. A common scale for electronegativity is shown in Figure **7.5.1**.

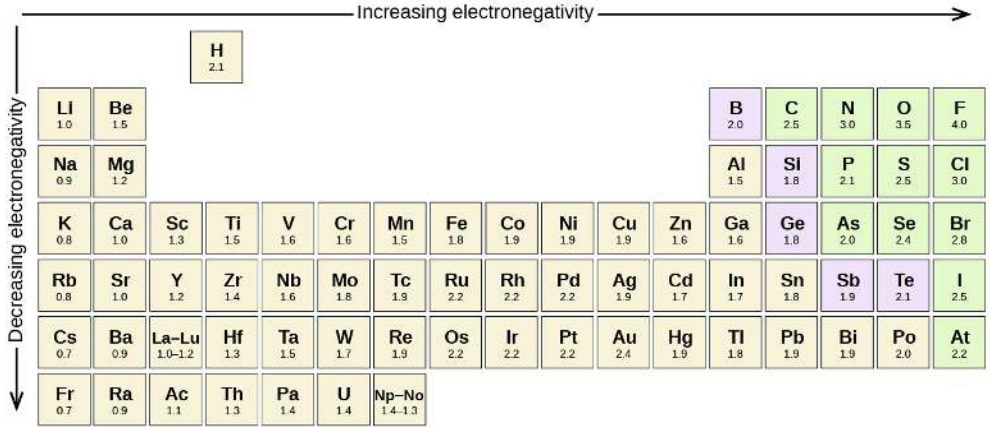


Figure **7.5.1**: Electronegativities of the Elements. Electronegativities are used to determine the polarity of covalent bonds.

The polarity of a covalent bond can be judged by determining the *difference* of the electronegativities of the two atoms involved in the covalent bond, as summarized in the following table:

difference of the electronegativities of the two atoms involved in the covalent bond

Electronegativity Difference	Bond Type
0–0.4	pure covalent
0.5–2.0	polar covalent
>2.0	likely ionic

Nonpolar Covalent Bonds

A bond in which the electronegativity difference is less than 1.9 is considered to be mostly covalent in character. However, at this point we need to distinguish between two general types of covalent bonds. A **nonpolar covalent bond** is a covalent bond in which the bonding electrons are shared equally between the two atoms. In a nonpolar covalent bond, the distribution of electrical charge is balanced between the two atoms.

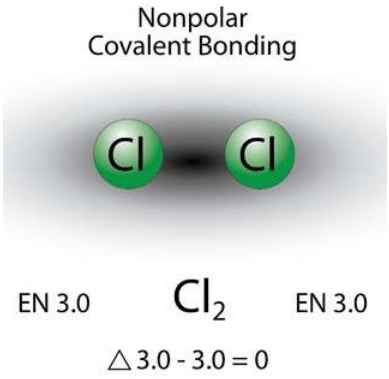


Figure **7.5.2**: A nonpolar covalent bond is one in which the distribution of electron density between the two atoms is equal.

The two chlorine atoms share the pair of electrons in the single covalent bond equally, and the electron density surrounding the $\mathbf{Cl_2}$ molecule is symmetrical. Also note that molecules in which the electronegativity difference is very small (<0.5) are also considered nonpolar covalent. An example would be a bond between chlorine and bromine ($\mathbf{\Delta EN = 3.0 - 2.8 = 0.2}$).

Polar Covalent Bonds

A bond in which the electronegativity difference between the atoms is between 0.5 and 2.0 is called a polar covalent bond. A **polar covalent bond** is a covalent bond in which the atoms have an unequal attraction for electrons and so the sharing is unequal. In a polar covalent bond, sometimes simply called a polar bond, the distribution of electrons around the molecule is no longer symmetrical.

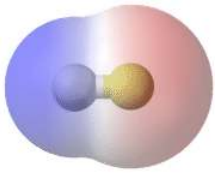


Figure **7.5.3**: In the polar covalent bond of **HF**, the electron density is unevenly distributed. There is a higher density (red) near the fluorine atom, and a lower density (blue) near the hydrogen atom.

An easy way to illustrate the uneven electron distribution in a polar covalent bond is to use the Greek letter delta (δ).

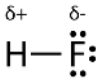
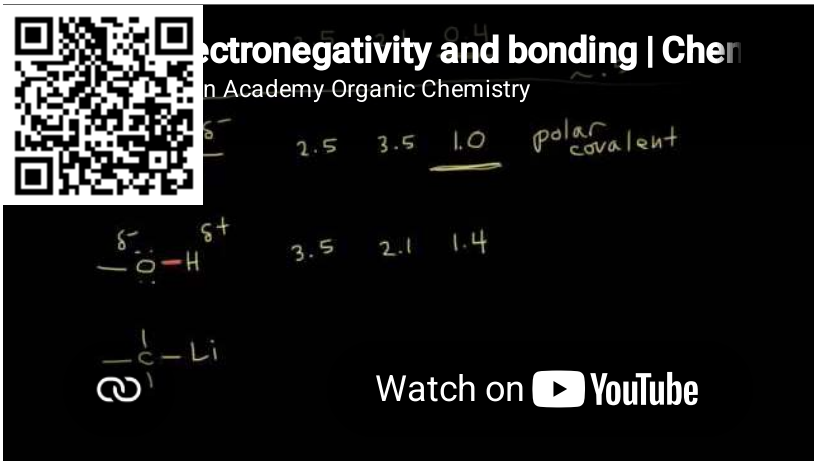


Figure **7.5.4**: Use of δ to indicate partial charge.

The atom with the greater electronegativity acquires a partial negative charge, while the atom with the lesser electronegativity acquires a partial positive charge. The delta symbol is used to indicate that the quantity of charge is less than one. A crossed arrow can also be used to indicate the direction of greater electron density.



Figure **7.5.5**: Use of crossed arrow to indicate polarity.



Electronegativity differences in bonding using Pauling scale. Differences in electronegativity classify bonds as covalent, polar covalent, or ionic.

Example 7.5.1: Bond Polarity

What is the polarity of each bond?

a. C–H
b. O–H

Solution

Using Figure 7.5.1, we can calculate the difference of the electronegativities of the atoms involved in the bond.

a. For the C–H bond, the difference in the electronegativities is 2.5 − 2.1 = 0.4. Thus we predict that this bond will be nonpolar covalent.
b. For the O–H bond, the difference in electronegativities is 3.5 − 2.1 = 1.4, so we predict that this bond will be polar covalent.

Exercise 7.5.1

What is the polarity of each bond?

a. Rb–F
b. P–Cl

Answer a

likely ionic

Answer b

polar covalent

Molecular Polarity

To determine if a molecule is polar or nonpolar, it is generally useful to look at Lewis structures. **Nonpolar compounds** will be symmetric, meaning all of the sides around the central atom are identical—bonded to the same element with no unshared pairs of electrons. **Polar molecules** are asymmetric, either containing lone pairs of electrons on a central atom or having atoms with different electronegativities bonded. This works pretty well, as long as you can visualize the molecular geometry. That's the hard part. To know how the bonds are oriented in space, you have to have a strong grasp of Lewis structures and VSEPR theory. Assuming that you do, you can look at the structure of each one and decide if it is polar or not, *whether or not you know the individual atom's electronegativity*. This is because you know that all bonds between dissimilar elements are polar, and in these particular examples, it doesn't matter which direction the dipole moment vectors are pointing (out or in).

A **polar molecule** is a molecule in which one end of the molecule is slightly positive, while the other end is slightly negative. A diatomic molecule that consists of a polar covalent bond, such as **HF**, is a polar molecule. The two electrically charged regions on either end of the molecule are called poles, similar to a magnet having a north and a south pole. A molecule with two poles is called a **dipole** (see figure below). Hydrogen fluoride is a dipole.



Figure **7.5.6**: A dipole is any molecule with a positive end and a negative end, resulting from unequal distribution of electron density throughout the molecule.

For molecules with more than two atoms, the molecular geometry must also be taken into account when determining if the molecule is polar or nonpolar. The figure below shows a comparison between carbon dioxide and water. Carbon dioxide (CO_2) is a linear molecule. The oxygen atoms are more electronegative than the carbon atom, so there are two individual dipoles pointing outward from the **C** atom to each **O** atom. However, since the dipoles are of equal strength and are oriented this way, they cancel out and the overall molecular polarity of CO_2 is zero.

Water is a bent molecule because of the two lone pairs on the central oxygen atom. The individual dipoles point from the **H** atoms toward the **O** atom. Because of the shape, the dipoles do not cancel each other out and the water molecule is polar. In the figure below, the net dipole is shown in blue and points upward.

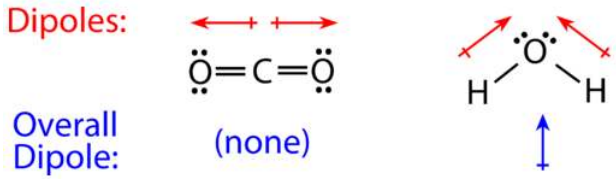


Figure **7.5.7**: The molecular geometry of a molecule affects its polarity. Each CO bond has a dipole moment, but they point in opposite directions so that the net CO2 molecule is nonpolar. In contrast, water is polar because the OH bond moments do not cancel out.

Some other molecules are shown in the figure below. Notice that a tetrahedral molecule such as CH_4 is nonpolar. However, if one of the peripheral **H** atoms is replaced with another atom that has a different electronegativity, the molecule becomes polar. A trigonal planar molecule (BF_3) may be nonpolar if all three peripheral atoms are the same, but a trigonal pyramidal molecule (NH_3) is polar.

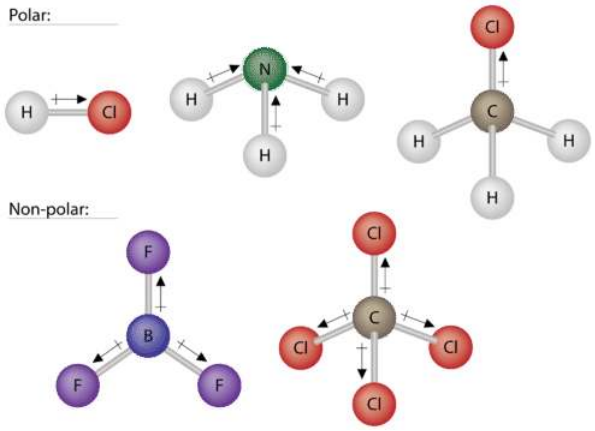


Figure **7.5.8**: Some examples of polar and nonpolar molecules based on molecular geometry.

To summarize, to be polar, a molecule must:

1. Contain at least one polar covalent bond.
2. Have a molecular structure such that the sum of the vectors of each bond dipole moment do not cancel.

Steps to Identify Polar Molecules

1. Draw the Lewis structure.
2. Figure out the geometry (using VSEPR theory).
3. Visualize or draw the geometry.
4. Find the net dipole moment (you don't have to actually do calculations if you can visualize it).
5. If the net dipole moment is zero, it is non-polar. Otherwise, it is polar.

Properties of Polar Molecules

Polar molecules tend to align when placed in an electric field with the positive end of the molecule oriented toward the negative plate and the negative end toward the positive plate (Figure **7.5.14**). 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.

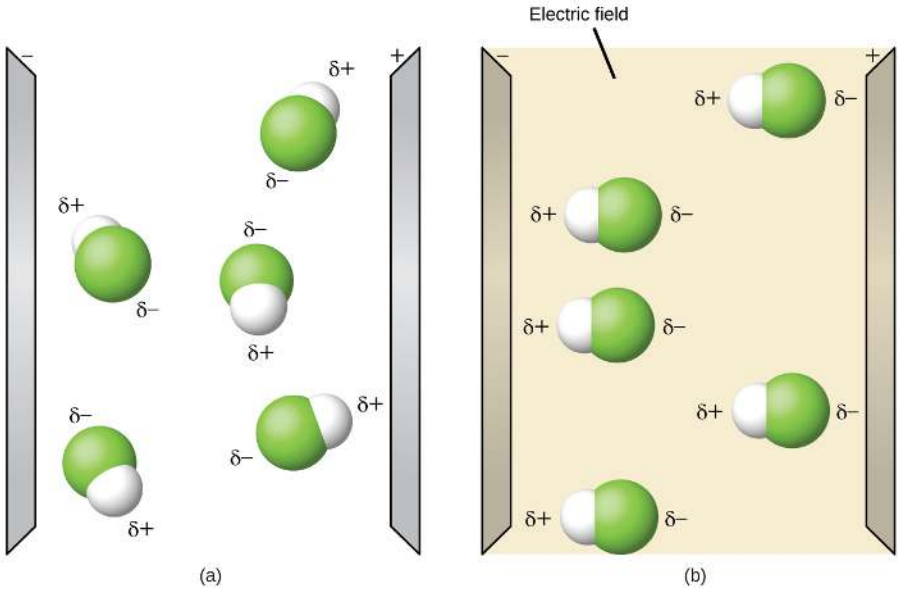


Figure **7.5.9**: (a) Molecules are always randomly distributed in the liquid state in the absence of an electric field. (b) When an electric field is applied, polar molecules like HF will align to the dipoles with the field direction. (OpenStax CC-BY-SA);

While molecules can be described as "polar covalent" or "ionic", it must be noted that this is often a relative term, with one molecule simply being *more polar* or *less polar* than another. However, the following properties are typical of such molecules. Polar molecules tend to:

- have higher melting points than nonpolar molecules
- have higher boiling points than nonpolar molecules
- be more soluble in water (dissolve better) than nonpolar molecules
- have lower vapor pressures than nonpolar molecules

Example 7.5.2:

Label each of the following as polar or nonpolar.

a. Water, H_2O:

b. Methanol, CH_3OH:

c. Hydrogen Cyanide, HCN: H–C≡N

d. Oxygen, O_2:

e. Propane, C_3H_8: 

Solution

a. Water is polar. Any molecule with lone pairs of electrons around the central atom is polar.
b. Methanol is polar. This is not a symmetric molecule. The $-OH$ side is different from the other 3 $-H$ sides.
c. Hydrogen cyanide is polar. The molecule is not symmetric. The nitrogen and hydrogen have different electronegativities, creating an uneven pull on the electrons.
d. Oxygen is nonpolar. The molecule is symmetric. The two oxygen atoms pull on the electrons by exactly the same amount.
e. Propane is nonpolar, because it is symmetric, with H atoms bonded to every side around the central atoms and no unshared pairs of electrons.

? Exercise 7.5.2

Label each of the following as polar or nonpolar.

a. SO_3
b. NH_3

Answer a

nonpolar

Answer b

polar

Contributions & Attributions

- StackExchange (thomij).

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7.6: Interactions between Molecules

In the winter, many people find the snow and ice beautiful; they enjoy getting out to ski or ice-skate. When the snow melts, however, the roads get very sloppy and messy. Some people look forward to spring, when the ice and snow are gone and the weather is warmer. All of these events and factors are dependent on the melting point of a solid and the freezing point of a liquid.

Melting Point

Solids are similar to liquids in that both are condensed states, with particles that are far closer together than those of a gas. However, while liquids are fluid, solids are not. The particles of most solids are packed tightly together in an orderly arrangement. The motion of individual atoms, ions, or molecules in a solid is restricted to **vibrational motion** about a fixed point. Solids are almost completely **incompressible** and are the densest of the three states of matter.

As a solid is heated, its particles vibrate more rapidly as it absorbs kinetic energy. Eventually, the organization of the particles within the solid structure begins to break down and the solid starts to melt. The **melting point** is the temperature at which a solid changes into a liquid. At its melting point, the disruptive vibrations of the particles of the solid overcome the attractive forces operating within the solid. As with boiling points, the melting point of a solid is dependent on the strength of those attractive forces. Sodium chloride ($NaCl$) is an ionic compound that consists of a multitude of strong ionic bonds. Sodium chloride melts at $801°C$. Ice (solid H_2O) is a molecular compound of molecules that are held together by hydrogen bonds. Though hydrogen bonds are the strongest of the intermolecular forces, the strength of hydrogen bonds is much less than that of ionic bonds. The melting point of ice is 0 °C.



Figure **7.6.1**: Melting ice cubes illustrate the process of this phase transition. (Public Domain; Moussa).

The melting point of a solid is the same as the **freezing point** of the liquid. At that temperature, the solid and liquid states of the substance are in equilibrium. For water, this equilibrium occurs at $0°C$.

$$H_2O\,(s) \rightleftharpoons H_2O\,(l)$$

We tend to think of solids as those materials that are solid at room temperature. However, all materials have melting points of some sort. Gases become solids at extremely low temperatures, and liquids will also become solid if the temperature is low enough. The table below gives the melting points of some common materials.

Table **7.6.1**: Melting Points of Common Materials

Materials	Melting Point (°C)
Hydrogen	-259
Oxygen	-219
Diethyl ether	-116
Ethanol	-114
Water	0
Pure silver	961
Pure gold	1063
Iron	1538

Summary

The melting point is the temperature at which a solid changes into a liquid. Intermolecular forces have a strong influence on melting point.

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7.7: Water - A Remarkable Molecule

Learning Objectives

- Interpret the unique properties of water in terms of a phase diagram.

Earth is the only known body in our solar system that has liquid water existing freely on its surface; life on Earth would not be possible without the presence of liquid water. Water has several properties that make it a unique substance among substances. It is an excellent solvent; it dissolves many other substances and allows those substances to react when in solution. In fact, water is sometimes called the *universal solvent* because of this ability. Water has unusually high melting and boiling points (0°C and 100°C, respectively) for such a small molecule. The boiling points for similar-sized molecules, such as methane (BP = −162°C) and ammonia (BP = −33°C), are more than 100° lower. Though a liquid at normal temperatures, water molecules experience a relatively strong intermolecular interaction that allows them to maintain the liquid phase at higher temperatures than expected.

Unlike most substances, the solid form of water is less dense than its liquid form, which allows ice to float on water. In colder weather, lakes and rivers freeze from the top, allowing animals and plants to continue to live underneath. Water also requires an unusually large amount of energy to change temperature. While 100 J of energy will change the temperature of 1 g of Fe by 230°C, this same amount of energy will change the temperature of 1 g of H_2O by only 100°C. Thus, water changes its temperature slowly as heat is added or removed. This has a major impact on weather, as storm systems like hurricanes can be impacted by the amount of heat that ocean water can store. Water's influence on the world around us is affected by these properties. Isn't it fascinating that such a small molecule can have such a big impact?

Phase Diagram for Water

Water is a unique substance in many ways. One of these special properties is the fact that solid water (ice) is less dense than liquid water just above the freezing point. The phase diagram for water is shown in the figure below.

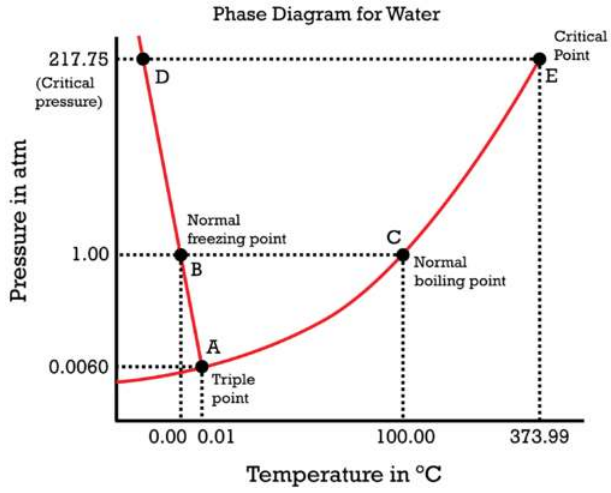


Figure 7.7.1: Phase diagram for water.

Notice one key difference between the general phase diagram and the phase diagram for water. In water's diagram, the slope of the line between the solid and liquid states is negative rather than positive. The reason for this is that water is an unusual substance, as its solid state is less dense than the liquid state. Ice floats in liquid water. Therefore, a pressure change has the opposite effect on those two phases. If ice is relatively near its melting point, it can be changed into liquid water by the application of pressure. The water molecules are actually closer together in the liquid phase than they are in the solid phase.

Refer again to water's phase diagram (figure above). Notice point ***E***, labeled the **critical point**. What does that mean? At **373.99°C**, particles of water in the gas phase are moving very, very rapidly. At any temperature higher than that, the gas phase cannot be made to liquefy, no matter how much pressure is applied to the gas. The **critical pressure** (P_C) is the pressure that must be applied to the gas at the critical temperature in order to turn it into a liquid. For water, the critical pressure is very high, **217.75 atm**. The critical point is the intersection point of the **critical temperature** and the critical pressure.

Summary

- Solid water is less dense than liquid water just above the freezing point.
- The critical temperature (T_C) of a substance is the highest temperature at which the substance can possibly exist as a liquid.
- The critical pressure (P_C) is the pressure that must be applied to the gas at the critical temperature in order to turn it into a liquid.
- The critical point is the intersection point of the critical temperature and the critical pressure.

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CHAPTER OVERVIEW

8: Gases

8.1: Charles’s Law- Volume and Temperature

8.2: Avogadro’s Law- Volume and Moles

8.3: Pressure

8.4: The Ideal Gas Law and Some Applications

8.5: Gas Mixtures

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8.1: Charles's Law- Volume and Temperature

Learning Objectives

- Learn and apply Charles's Law.

Everybody enjoys the smell and taste of freshly-baked bread. It is light and fluffy as a result of the action of yeast on sugar. The yeast converts the sugar to carbon dioxide, which at high temperatures causes the dough to expand. The end result is an enjoyable treat, especially when covered with melted butter.

Charles's Law

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

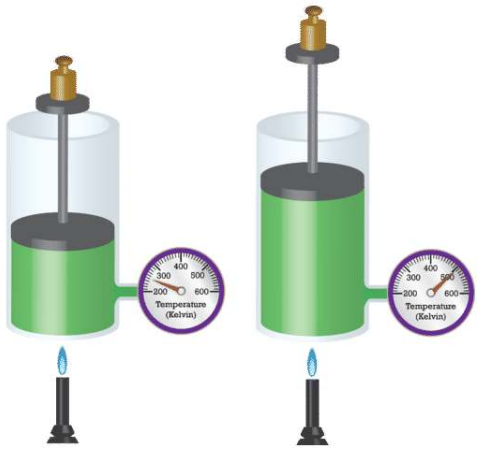


Figure 8.1.1: As a container of confined gas is heated, its molecules increase in kinetic energy and push the movable piston outward, resulting in an increase in volume.

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

$$\frac{V}{T} = k$$

As with Boyle's Law, k is constant only for a given gas sample. The table below shows temperature and volume data for a set amount of gas at a constant pressure. The third column is the constant for this particular data set and is always equal to the volume divided by the Kelvin temperature.

Table 8.1.1: Temperature-Volume Data

Temperature (K)	Volume (mL)	$\frac{V}{T} = k \left(\frac{\text{mL}}{\text{K}}\right)$
50	20	0.40
100	40	0.40
150	60	0.40
200	80	0.40
300	120	0.40
500	200	0.40
1000	400	0.40

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

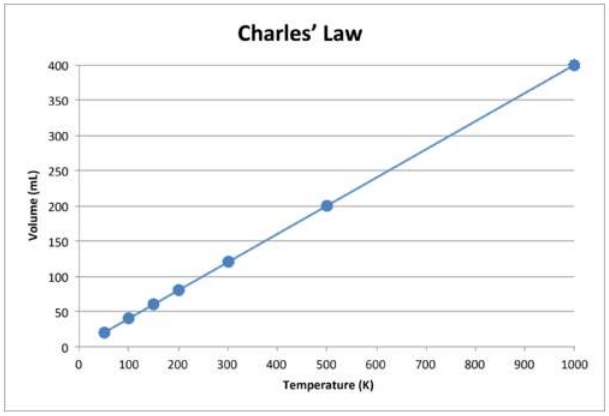


Figure 8.1.2:The volume of a gas increases as the Kelvin temperature increases.

Notice that the line goes exactly toward the origin, meaning that as the absolute temperature of the gas approaches zero, its volume approaches zero. However, when a gas is brought to extremely cold temperatures, its molecules would eventually condense into the liquid state before reaching absolute zero. The temperature at which this change into the liquid state occurs varies for different gases.

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

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

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

Example 8.1.1:

A balloon is filled to a volume of $2.20\ \mathrm{L}$ at a temperature of $22^{\circ}\mathrm{C}$. The balloon is then heated to a temperature of $71^{\circ}\mathrm{C}$. Find the new volume of the balloon.

Solution

Solutions to Example 11.5.1

Steps for Problem Solving	
Identify the "given" information and what the problem is asking you to "find."	Given: $V_1 = 2.20\ \text{L}$ and $T_1 = 22°\text{C} = 295\ \text{K}$ $T_2 = 71°\text{C} = 344\ \text{K}$ Find: V_2 = ? L
List other known quantities.	The temperatures have first been converted to Kelvin.
Plan the problem.	First, rearrange the equation algebraically to solve for V_2. $$V_2 = \frac{V_1 \times T_2}{T_1}$$
Cancel units and calculate.	Now substitute the known quantities into the equation and solve. $$V_2 = \frac{2.20\ \text{L} \times 344\ \cancel{\text{K}}}{295\ \cancel{\text{K}}} = 2.57\ \text{L}$$
Think about your result.	The volume increases as the temperature increases. The result has three significant figures.

? Exercise 8.1.1

If V_1 = 3.77 L and T_1 = 255 K, what is V_2 if T_2 = 123 K?

Answer

1.82 L

✔ Example 8.1.2:

A sample of a gas has an initial volume of 34.8 L and an initial temperature of −67°C. What must be the temperature of the gas for its volume to be 25.0 L?

Solution

Solutions to Example 11.5.2

Steps for Problem Solving	
Identify the "given" information and what the problem is asking you to "find."	Given: Given:T_1 = -27°C and V_1 = 34.8 L V_2 = 25.0 L Find: T_2 = ? K
List other known quantities.	K = -27°C + 273
Plan the problem.	1. Convert the initial temperature to Kelvin 2. Rearrange the equation algebraically to solve for T_2. $$T_2 = \frac{V_2 \times T_1}{V_1}$$
Cancel units and calculate.	1. −67°C + 273 = 206 K 2. Substitute the known quantities into the equation and solve. $$T_2 = \frac{25.0 \cancel{L} \times 206\ \text{K}}{34.8 \cancel{L}} = 148\ \text{K}$$
Think about your result.	This is also equal to −125°C. As temperature decreases, volume decreases—which it does in this example.

? Exercise 8.1.2

If V_1 = 623 mL, T_1 = 255°C, and V_2 = 277 mL, what is T_2?

Answer

235 K, or −38°C

Summary

- Charles's Law relates the volume and temperature of a gas at constant pressure and amount.

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8.2: Avogadro’s Law- Volume and Moles

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

Avogadro's Law

You have learned about Avogadro's hypothesis: equal volumes of any gas at the same temperature and pressure contain the same number of molecules. It follows that the volume of a gas is directly proportional to the number of moles of gas present in the sample. **Avogadro's Law** states that the volume of a gas is directly proportional to the number of moles (or number of particles) of gas when the temperature and pressure are held constant. The mathematical expression of Avogadro's Law is:

$$V = k \times n$$

or

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

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

If the container holding the gas is rigid rather than flexible, pressure can be substituted for volume in Avogadro's Law. Adding gas to a rigid container makes the pressure increase.

Example 8.2.1

A balloon has been filled to a volume of $1.90\ \text{L}$ with $0.0920\ \text{mol}$ of helium gas. If $0.0210\ \text{mol}$ of additional helium is added to the balloon while the temperature and pressure are held constant, what is the new volume of the balloon?

Solution

Solutions to Example 11.11.1

Steps for Problem Solving	
Identify the "given" information and what the problem is asking you to "find."	Given: $V_1 = 1.90\ \text{L}$ $n_1 = 0.0920\ \text{mol}$ Find: $V_2 = ?\ \text{L}$
List other known quantities.	Note that the final number of moles has to be calculated by adding the original number of moles to the moles of added helium. $n_2 = 0.0920 + 0.0210 = 0.1130\ \text{mol}$
Plan the problem.	First, rearrange the equation algebraically to solve for V_2. $V_2 = \frac{V_1 \times n_2}{n_1}$
Calculate.	Now substitute the known quantities into the equation and solve. $V_2 = \frac{1.90\ \text{L} \times 0.1130\ \cancel{\text{mol}}}{0.0920\ \cancel{\text{mol}}} = 2.33\ \text{L}$
Think about your result.	Since a relatively small amount of additional helium was added to the balloon, its volume increases slightly.

Exercise 8.2.1

A 12.8 L volume of gas contains .000498 moles of oxygen gas. At constant temperature and pressure, what volume does .0000136 moles of the gas fill?

Answer

0.350 L

Summary

- Calculations for relationships between volume and number of moles of a gas can be performed using Avogadro's Law.

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8.3: Pressure

Learning Objectives

- Define *pressure*.
- Learn the units of pressure and how to convert between them.

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

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

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

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

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

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

We can use these equivalencies as with any equivalencies—to perform conversions from one unit to another. Relating these to the formal SI unit of pressure, 1 atm = 101,325 Pa.

Example 8.3.1: Pressure Conversion

How many atmospheres are there in 595 torr?

Solution

Using the pressure equivalencies, we construct a conversion factor between torr and atmospheres:

$$\frac{1\,atm}{760\,torr}$$

$$595\ \cancel{torr} \times \frac{1\,atm}{760\ \cancel{torr}} = 0.783\,atm$$

Because the numbers in the conversion factor are exact, the number of significant figures in the final answer is determined by the initial value of pressure.

Exercise 8.3.1

How many atmospheres are there in 1,022 torr?

Answer

1.345 atm

Example 8.3.2: Mars

The atmosphere on Mars is largely CO_2 at a pressure of 6.01 mmHg. What is this pressure in atmospheres?

Solution

Use the pressure equivalencies to construct the proper conversion factor between millimeters of mercury and atmospheres.

$$6.01\ \cancel{mmHg} \times \frac{1\ atm}{760\ \cancel{mmHg}} = 0.00791\ atm = 7.91 \times 10^{-3} atm$$

At the end, we expressed the answer in scientific notation.

Exercise 8.3.2

Atmospheric pressure is low in the eye of a hurricane. In a 1979 hurricane in the Pacific Ocean, a pressure of 0.859 atm was reported inside the eye. What is this pressure in torr?

Answer

652 torr

Summary

- Pressure is a force exerted over an area.
- Pressure has several common units that can be converted.

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8.4: The Ideal Gas Law and Some Applications

Learning Objectives

- Learn the ideal gas law.
- Apply the ideal gas law to any set of conditions of a gas.
- Apply the ideal gas law to molar volumes, density, and stoichiometry problems.

So far, the gas laws we have considered have all required that the gas change its conditions; then we predict a resulting change in one of its properties. Are there any gas laws that relate the physical properties of a gas at any given time? Consider a further extension of the combined gas law to include *n*. By analogy to Avogadro's law, *n* is positioned in the denominator of the fraction, opposite the volume. So,

$$\frac{PV}{nT} = constant$$

Because pressure, volume, temperature, and amount are the only four independent physical properties of a gas, the constant in the above equation is truly a constant. Indeed, because we do not need to specify the identity of a gas to apply the gas laws, this constant is the same for all gases. We define this constant with the symbol *R*, so the previous equation is written as

$$\frac{PV}{nT} = R$$

which is usually rearranged as

$$PV = nRT$$

This equation is called the **ideal gas law**. It relates the four independent properties of a gas at any time. The constant \(*R*\) is called the **ideal gas law constant**. Its value depends on the units used to express pressure and volume.

Table **8.4.1**: Values of the Ideal Gas Law Constant lists the numerical values of ***R***.

Numerical Value	Units
0.08205	$\frac{L.atm}{mol.K}$
62.36	$\frac{L.torr}{mol.K} = \frac{L.mmHg}{mol.K}$
8.314	$\frac{J}{mol.K}$

The ideal gas law is used like any other gas law, with attention paid to the unit and expression of the temperature in kelvin. However, *the ideal gas law does not require a change in the conditions of a gas sample*. The ideal gas law implies that if you know any three of the physical properties of a gas, you can calculate the fourth property.

Example 8.4.1

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

Solution

The first step is to convert temperature to kelvins:

$$34 + 273 = 307\,\mathrm{K}$$

Now we can substitute the conditions into the ideal gas law:

$$(1.21atm)(V) = (4.22\,mol)\left(0.08205\frac{L.atm}{mol.K}\right)(307\,K)$$

The *atm* unit is in the numerator of both sides, so it cancels. On the right side of the equation, the *mol* and *K* units appear in the numerator and the denominator, so they cancel as well. The only unit remaining is *L*, which is the unit of volume that we are

looking for. We isolate the volume variable by dividing both sides of the equation by 1.21:

$$V = \frac{(4.22)(0.08205)(307)}{1.21} L$$

Then solving for volume, we get V = 87.9 L

? Exercise 8.4.1

A 0.0997 mol sample of O_2 has a pressure of 0.692 atm and a temperature of 333 K. What is its volume?

Answer

3.94 L

✓ Example 8.4.2

At a given temperature, 0.00332 g of Hg in the gas phase has a pressure of 0.00120 mmHg and a volume of 435 L. What is its temperature?

Solution

We are not given the number of moles of Hg directly, but we are given a mass. We can use the molar mass of Hg to convert to the number of moles.

$$0.00332\,\cancel{g\,Hg} \times \frac{1\,mol\,Hg}{200.59\,\cancel{g\,Hg}} = 0.0000165\,mol = 1.65 \times 10^{-5} mol$$

Pressure is given in units of millimeters of mercury. We can either convert this to atmospheres or use the value of the ideal gas constant that includes the mmHg unit. We will take the second option. Substituting into the ideal gas law,

$$(0.00332\,mm\,Hg)(435\,L) = (1.65 \times 10^{-5} mol)(62.36 \frac{L.mmHg}{mol.K})T$$

The mmHg, L, and mol units cancel, leaving the K unit, the unit of temperature. Isolating T on one side, we get

$$T = \frac{(0.00332)(435)}{(1.65 \times 10^{-5})(62.36)} K$$

Then solving for K, we get T = 1,404 K.

? Exercise 8.4.2

For a 0.00554 mol sample of H_2, P = 23.44 torr and T = 557 K. What is its volume?

Answer

8.21 L

The ideal gas law can also be used in stoichiometry problems.

✓ Example 8.4.3

What volume of H_2 is produced at 299 K and 1.07 atm when 55.8 g of Zn metal react with excess HCl?

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

Solution

Here we have a stoichiometry problem where we need to find the number of moles of H_2 produced. Then we can use the ideal gas law, with the given temperature and pressure, to determine the volume of gas produced. First, the number of moles of H_2 is

calculated:

$$55.8\,\cancel{g\,Zn} \times \frac{1\,\cancel{mol\,Zn}}{65.41\,\cancel{g\,Zn}} \times \frac{1\,mol\,H_2}{1\,\cancel{mol\,Zn}} = 0.853\,H_2$$

Now that we know the number of moles of gas, we can use the ideal gas law to determine the volume, given the other conditions:

$$(1.07atm)V = (0.853\,mol)\left(0.08205\frac{L.atm}{mol.K}\right)(299\,K)$$

All the units cancel except for L, for volume, which means V = 19.6 L

? Exercise 8.4.3

What pressure of **HCl** is generated if 3.44 g of Cl_2 are reacted in 4.55 L at 455 K?

$$H_2(g) + Cl_2(g) \longrightarrow 2\,HCl(g)$$

Answer

0.796 atm

It should be obvious by now that some physical properties of gases depend strongly on the conditions. What we need is a set of standard conditions so that properties of gases can be properly compared to each other. **Standard Temperature and Pressure (STP)** is defined as exactly 100 kPa of pressure (0.986 atm) and 273 K (0°C). For simplicity, we will use 1 atm as standard pressure. Defining STP allows us to more directly compare the properties of gases that differ from one another.

One property shared among gases is a molar volume. The **molar volume** is the volume of 1 mol of a gas. At STP, the molar volume of a gas can be easily determined by using the ideal gas law:

$$(1\,atm)V = (1\,mol)\left(0.08205\frac{L.atm}{mol.K}\right)(273\,K)$$

All the units cancel except for L, the unit of volume. So V = 22.4 L

Note that we have not specified the identity of the gas; we have specified only that the pressure is 1 atm and the temperature is 273 K. This makes for a very useful approximation: *any gas at STP has a volume of 22.4 L per mole of gas*; that is, the molar volume at STP is 22.4 L/mol (Figure 8.4.1). This molar volume makes a useful conversion factor in stoichiometry problems if the conditions are at STP. If the conditions are not at STP, a molar volume of 22.4 L/mol is not applicable. However, if the conditions are at STP, the combined gas law can be used to calculate what the volume of the gas would be if at STP; then the 22.4 L/mol molar volume can be used.

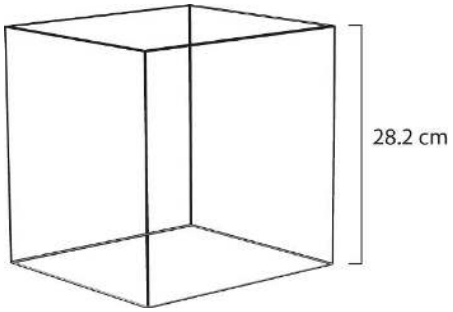


Figure 8.4.1: Molar Volume. A mole of gas at STP occupies 22.4 L, the volume of a cube that is 28.2 cm on a side.

✓ Example 8.4.4

How many moles of **Ar** are present in 38.7 L at STP?

Solution

We can use the molar volume, 22.4 L/mol, as a conversion factor, but we need to reverse the fraction so that the L units cancel and mol units are introduced. It is a one-step conversion:

$$38.7 \cancel{L} \times \frac{1\,mol}{22.4\,\cancel{L}} = 1.73\,mol$$

? Exercise 8.4.4

What volume does 4.87 mol of $\mathbf{Kr}$ have at STP?

Answer

109 L

✓ Example 8.4.5

What volume of $\mathbf{H_2}$ is produced at STP when 55.8 g of $\mathbf{Zn}$ metal react with excess $\mathbf{HCl}$?

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

Solution

This is a stoichiometry problem with a twist: we need to use the molar volume of a gas at STP to determine the final answer. The first part of the calculation is the same as in a previous example:

$$55.8\,\cancel{g\,Zn} \times \frac{1\,\cancel{mol\,Zn}}{65.41\,\cancel{g\,Zn}} \times \frac{1\,mol\,H_2}{1\,\cancel{mol\,Zn}} = 0.853\,H_2$$

Now we can use the molar volume, 22.4 L/mol, because the gas is at STP:

$$0.853\,\cancel{mol\,H_2} \times \frac{22.4\,L}{1\,\cancel{mol\,H_2}} = 19.1\,L\,H_2$$

Alternatively, we could have applied the molar volume as a third conversion factor in the original stoichiometry calculation.

? Exercise 8.4.5

What volume of $\mathbf{HCl}$ is generated if 3.44 g of $\mathbf{Cl_2}$ are reacted at STP?

$$\mathbf{H_2\,(g) + Cl_2\,(g) \longrightarrow 2\,HCl\,(g)}$$

Answer

2.17 L

The ideal gas law can also be used to determine the density of gases. Density, recall, is defined as the mass of a substance divided by its volume:

$$d = \frac{m}{V} \tag{8.4.1}$$

Assume that you have exactly 1 mol of a gas. If you know the identity of the gas, you can determine the molar mass of the substance. Using the ideal gas law, you can also determine the volume of that mole of gas, using whatever the temperature and pressure conditions are. Then you can calculate the density of the gas by using

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

Example 8.4.6

What is the density of $\mathbf{N_2}$ at 25°C and 0.955 atm?

Solution

First, we must convert the temperature into kelvin:

$$25 + 273 = 298\,\mathrm{K}$$

If we assume exactly 1 mol of $\mathbf{N_2}$, then we know its mass: 28.0 g. Using the ideal gas law, we can calculate the volume:

$$(0.955\,atm)V = (1\,mol)\left(0.08205\frac{L.atm}{mol.K}\right)(298\,K)$$

All the units cancel except for L, the unit of volume. So $V = 25.6\,\mathrm{L}$

Knowing the molar mass and the molar volume, we can determine the density of $\mathbf{N_2}$ under these conditions using Equation 8.4.1:

$$d = \frac{28.0\,g}{25.6\,L} = 1.09\,g/L$$

Exercise 8.4.6

What is the density of $\mathbf{CO_2}$ at a pressure of 0.0079 atm and 227 K? (These are the approximate atmospheric conditions on Mars.)

Answer

0.019 g/L

Chemistry is Everywhere: Breathing

Breathing (more properly called *respiration*) is the process by which we draw air into our lungs so that our bodies can take up oxygen from the air. Let us apply the gas laws to breathing.

Start by considering pressure. We draw air into our lungs because the diaphragm, a muscle underneath the lungs, moves down to reduce pressure in the lungs, causing external air to rush in to fill the lower-pressure volume. We expel air by the diaphragm pushing against the lungs, increasing pressure inside the lungs and forcing the high-pressure air out. What are the pressure changes involved? A quarter of an atmosphere? A tenth of an atmosphere? Actually, under normal conditions, it's only 1 or 2 torr of pressure difference that makes us breathe in and out.

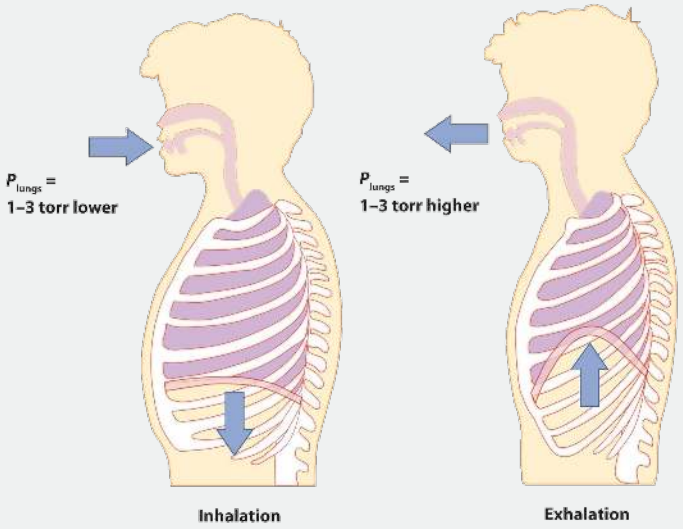


Figure **8.4.2**: Breathing Mechanics. Breathing involves pressure differences between the inside of the lungs and the air outside. The pressure differences are only a few torr.

A normal breath is about 0.50 L. If room temperature is about 22°C, then the air has a temperature of about 295 K. With normal pressure being 1.0 atm, how many moles of air do we take in for every breath? The ideal gas law gives us an answer:

$$(1.0\,atm)(0.50\,L) = n\left(0.08205\frac{L.atm}{mol.K}\right)(295\,K)$$

Solving for the number of moles, we get

$$n = 0.021\,\text{mol air}$$

This ends up being about 0.6 g of air per breath—not much, but enough to keep us alive.

Summary

- The ideal gas law relates the four independent physical properties of a gas at any time.
- The ideal gas law can be used in stoichiometry problems with chemical reactions that involve gases.
- Standard temperature and pressure (STP) are a useful set of benchmark conditions to compare other properties of gases.
- At STP, gases have a volume of 22.4 L per mole.
- The ideal gas law can be used to determine the density of gases.

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8.5: Gas Mixtures

Learning Objective

- Learn Dalton's law of partial pressures.

One of the properties of gases is that they mix with each other. When they do so, they become a solution—a homogeneous mixture. Some of the properties of gas mixtures are easy to determine if we know the composition of the gases in the mix.

In gas mixtures, each component in the gas phase can be treated separately. Each component of the mixture shares the same temperature and volume. (Remember that gases expand to fill the volume of their container; gases in a mixture continue to do that as well.) However, each gas has its own pressure. The **partial pressure** of a gas, P_i, is the pressure that an individual gas in a mixture has. Partial pressures are expressed in torr, millimeters of mercury, or atmospheres like any other gas pressure; however, we use the term *pressure* when talking about pure gases and the term *partial pressure* when we are talking about the individual gas components in a mixture.

Dalton's law of partial pressures states that the total pressure of a gas mixture, P_{tot}, is equal to the sum of the partial pressures of the components, P_i:

$$\begin{aligned} P_{tot} &= P_1 + P_2 + P_3 + \ldots \\ &= \sum_i P_i \end{aligned} \tag{8.5.1}$$

where i counts over all gases in mixture.

Although this law may seem trivial, it reinforces the idea that gases behave independently of each other.

Example 8.5.1

A mixture of H_2 at 2.33 atm and N_2 at 0.77 atm is in a container. What is the total pressure in the container?

Solution

Dalton's law of partial pressures (Equation 8.5.1) states that the total pressure is equal to the sum of the partial pressures. We simply add the two pressures together:

P_{tot} = 2.33 atm + 0.77 atm = 3.10 atm

Exercise 8.5.1

N_2 and O_2. In 760 torr of air, the partial pressure of N_2 is 608 torr. What is the partial pressure of O_2?

Answer

152 torr

Example 8.5.2

A 2.00 L container with 2.50 atm of H_2 is connected to a 5.00 L container with 1.90 atm of O_2 inside. The containers are opened, and the gases mix. What is the final pressure inside the containers?

Solution

Because gases act independently of each other, we can determine the resulting final pressures using Boyle's law and then add the two resulting pressures together to get the final pressure. The total final volume is 2.00 L + 5.00 L = 7.00 L. First, we use Boyle's law to determine the final pressure of H_2:

$$(2.50 \text{ atm})(2.00 \text{ L}) = P_2(7.00 \text{ L})$$

Solving for P_2, we get $P_2 = 0.714$ atm = partial pressure of H_2.

Now we do that same thing for the O_2:

$$(1.90 \text{ atm})(5.00 \text{ L}) = P_2(7.00 \text{ L}) P_2 = 1.36 \text{ atm} = \text{partial pressure of } O_2$$

The total pressure is the sum of the two resulting partial pressures:

$$P_{tot} = 0.714 \text{ atm} + 1.36 \text{ atm} = 2.07 \text{ atm}$$

? Exercise 8.5.2

If 0.75 atm of He in a 2.00 L container is connected to a 3.00 L container with 0.35 atm of Ne and the containers are opened, what is the resulting total pressure?

Answer

0.51 atm

One of the reasons we have to deal with Dalton's law of partial pressures is because gases are frequently collected by bubbling through water. As we will see in Chapter 10, liquids are constantly evaporating into a vapor until the vapor achieves a partial pressure characteristic of the substance and the temperature. This partial pressure is called a **vapor pressure**. Table 8.5.1 lists the vapor pressures of H_2O versus temperature. Note that if a substance is normally a gas under a given set of conditions, the term *partial pressure* is used; the term *vapor pressure* is reserved for the partial pressure of a vapor when the liquid is the normal phase under a given set of conditions.

Table 8.5.1: Vapor Pressure of Water versus Temperature

Temperature (°C)	Vapor Pressure (torr)	Temperature (°C)	Vapor Pressure (torr)
5	6.54	30	31.84
10	9.21	35	42.20
15	12.79	40	55.36
20	17.54	50	92.59
21	18.66	60	149.5
22	19.84	70	233.8
23	21.08	80	355.3
24	22.39	90	525.9
25	23.77	100	760.0

Any time a gas is collected over water, the total pressure is equal to the partial pressure of the gas *plus* the vapor pressure of water. This means that the amount of gas collected will be less than the total pressure suggests.

✓ Example 8.5.3

Hydrogen gas is generated by the reaction of nitric acid and elemental iron. The gas is collected in an inverted 2.00 L container immersed in a pool of water at 22°C. At the end of the collection, the partial pressure inside the container is 733 torr. How many moles of H_2 gas were generated?

Solution

We need to take into account that the total pressure includes the vapor pressure of water. According to Table 8.5.1, the vapor pressure of water at 22°C is 19.84 torr. According to Dalton's law of partial pressures (Equation 8.5.1), the total pressure equals the sum of the pressures of the individual gases, so

$$733\,torr = P_{H_2} + P_{H_2O} = P_{H_2} + 19.84\,torr$$

We solve by subtracting:

$$P_{H_2} = 713\,torr$$

Now we can use the ideal gas law to determine the number of moles (remembering to convert temperature to kelvins, making it 295 K):

$$(713\,torr)(2.00\,L) = n\left(62.36\frac{L.atm}{mol.K}\right)(295\,K)$$

All the units cancel except for mol, which is what we are looking for.

Therefore $n = 0.0775\,mol\,H_2$ collected

? Exercise 8.5.1

CO_2, generated by the decomposition of $CaCO_3$, is collected in a 3.50 L container over water. If the temperature is 50°C and the total pressure inside the container is 833 torr, how many moles of CO_2 were generated?

Answer

0.129 mol

Finally, we introduce a new unit that can be useful, especially for gases: the mole fraction. The ratio of the number of moles of a component in a mixture divided by the total number of moles in the sample, χ_i, is the ratio of the number of moles of component *i* in a mixture divided by the total number of moles in the sample:

$$\chi_i = \frac{\text{moles of component i}}{\text{total number of moles}}$$

(χ is the lowercase Greek letter *chi*.) Note that mole fraction is *not* a percentage; its values range from 0 to 1. For example, consider the combination of 4.00 g of He and 5.0 g of Ne. Converting both to moles, we get

$$4.00\,\cancel{g\,He} \times \frac{1\,mol\,He}{4.00\,\cancel{g\,He}} = 1.00\,mol\,He$$

and

$$5.0\,\cancel{g\,Ne} \times \frac{1\,mol\,Ne}{20.0\,\cancel{g\,Ne}} = 0.25\,mol\,Ne$$

The total number of moles is the sum of the two mole amounts:

$$\text{total moles} = 1.00\,mol + 0.025\,mol = 1.25\,mol$$

The mole fractions are simply the ratio of each mole amount and the total number of moles, 1.25 mol:

$$\chi_{He} = \frac{1.00\,\cancel{mol}}{1.25\,\cancel{mol}} = 0.800$$

$$\chi_{Ne} = \frac{0.25\,\cancel{mol}}{1.25\,\cancel{mol}} = 0.200$$

The sum of the mole fractions equals exactly 1.

$$\chi_{He} + \chi_{Ne} = 0.800 + 0.200 = 1$$

For gases, there is another way to determine the mole fraction. When gases have the same volume and temperature (as they would in a mixture of gases), the number of moles is proportional to partial pressure, so the mole fractions for a gas mixture can be determined by taking the ratio of partial pressure to total pressure:

$$\chi_i = \frac{P_i}{P_{tot}}$$

This expression allows us to determine mole fractions without calculating the moles of each component directly.

Example 8.5.4

A container has a mixture of He at 0.80 atm and Ne at 0.60 atm. What are the mole fractions of each component?

Solution

According to Dalton's law, the total pressure is the sum of the partial pressures:

$$P_{tot} = 0.80\,atm + 0.60\,atm = 1.40\,atm$$

The mole fractions are the ratios of the partial pressure of each component and the total pressure:

$$\chi_{He} = \frac{0.80\,atm}{1.40\,atm} = 0.57$$

$$\chi_{Ne} = \frac{0.60\,atm}{1.40\,atm} = 0.43$$

Again, the sum of the mole fractions is exactly 1.

Exercise 8.5.4

What are the mole fractions when 0.65 atm of O_2 and 1.30 atm of N_2 are mixed in a container?

Food and Drink Application: Carbonated Beverages

Carbonated beverages—sodas, beer, sparkling wines—have one thing in common: they have CO_2 gas dissolved in them in such sufficient quantities that it affects the drinking experience. Most people find the drinking experience pleasant—indeed, in the United States alone, over 1.5×10^9 gal of soda are consumed each year, which is almost 50 gal per person! This figure does not include other types of carbonated beverages, so the total consumption is probably significantly higher.

All carbonated beverages are made in one of two ways. First, the flat beverage is subjected to a high pressure of CO_2 gas, which forces the gas into solution. The carbonated beverage is then packaged in a tightly-sealed package (usually a bottle or a can) and sold. When the container is opened, the CO_2 pressure is released, resulting in the well-known *hiss* of an opening container, and CO_2 bubbles come out of solution. This must be done with care: if the CO_2 comes out too violently, a mess can occur!



Figure 8.5.1: Carbonated beverage. If you are not careful opening a container of a carbonated beverage, you can make a mess, as the CO_2 comes out of solution suddenly. (Unsplash License; Tina Vanhove via Unsplash)

The second way a beverage can become carbonated is by the ingestion of sugar by yeast, which then generates CO_2 as a digestion product. This process is called *fermentation*. The overall reaction is

$$C_6H_{12}O_6\,(aq) \longrightarrow 2\,C_2H_5OH\,(aq) + 2\,CO_2\,(aq)$$

When this process occurs in a closed container, the CO_2 produced dissolves in the liquid, only to be released from solution when the container is opened. Most fine sparkling wines and champagnes are turned into carbonated beverages this way. Less-expensive sparkling wines are made like sodas and beer, with exposure to high pressures of CO_2 gas.

Summary

- The pressure of a gas in a gas mixture is termed the *partial pressure*.
- Dalton's law of partial pressure says that the total pressure in a gas mixture is the sum of the individual partial pressures.
- Collecting gases over water requires that we take the vapor pressure of water into account.
- Mole fraction is another way to express the amount of each component in a mixture.

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CHAPTER OVERVIEW

9: Solutions

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9.2: Definitions
9.3: Solutions of Gases in Water
9.4: Quantitative Units of Concentration
9.5: Concentrations as Conversion Factors
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9.1: Prelude to Solutions

More than 70% of the earth's surface is covered by a very important solution—seawater. It is likely that without seawater, no life would exist on Earth.

At its simplest, seawater is mostly H_2O. However, about 3.5% of seawater is dissolved solids—mostly NaCl—but other ions as well. Table **9.1.1** lists the percentage by mass of the various ions in seawater. Because it is highly likely that life on Earth originated in the oceans, it should not be surprising that many bodily fluids resemble seawater, especially blood. Table **9.1.1** also lists the percentage by mass of ions in a typical sample of blood.

Table **9.1.1**: Percentage by Mass of Ions in Seawater and Blood

Ion	Percentage in Seawater	Percentage in Blood
Na^+	2.36	0.322
Cl^-	1.94	0.366
Mg^{2+}	0.13	0.002
SO_4^{2-}	0.09	-
K^+	0.04	0.016
Ca^{2+}	0.04	0.0096
HCO_3^-	0.002	0.165
HPO_4^{2-}, $H_2PO_4^-$	-	0.01

Most ions are more abundant in seawater than they are in blood, with some notable exceptions. There is far more hydrogen carbonate ion (HCO_3^-) in blood than in seawater; indeed, it is the third most common ion in blood. This difference is significant because the HCO_3^- ion and some related species [CO_3^{2-}, $CO_2(aq)$] have an important role in controlling the acid-base properties of blood. Although there is a negligible amount of the two hydrogen phosphate ions (HPO_4^{2-} and $H_2PO_4^-$) in seawater, there is a small amount in blood, where these ions affect acid-base properties. Another notable difference is that blood has a negligible amount of the sulfate ion (SO_4^{2-}), but this ion is present in seawater. Gold is present in seawater—but only a tiny amount. A current estimate of the amount of gold is about 1 part per every 1×10^{13} parts of seawater, which makes the extraction of gold from seawater unfeasible. However, it does mean that there are about 1.4×10^{14} g of gold in the world's oceans!



Figure **9.1.1**: Gold in the Ocean. There are approximately 1.4×10^{14} g of gold in the oceans, but extracting it effectively is beyond current technologies. (CC SA-BY; Evgeni Dinev, Flickr.)

A solution is a *homogeneous mixture*: a mixture of two or more substances that are so intimately mixed that the mixture behaves in many ways like a single substance. Many chemical reactions occur when the reactants are dissolved in solution. In this chapter, we will introduce concepts that are applicable to solutions and the chemical reactions that occur in them.

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9.2: Definitions

Learning Objective

- Learn some terminology involving solutions.
- Recognize which terminology is qualitative and which terminology is quantitative.
- Explain why certain substances dissolve in other substances.

The major component of a solution is called the **solvent.** The minor component of a solution is called the **solute**. "Major" and "minor" indicate which component has the greater or lesser presence by mass or moles, respectively. Sometimes this becomes confusing, especially when considering substances with very different molar masses. We will confine the discussion here to solutions for which the major component and the minor component are obvious.

Solutions exist for every possible phase of the solute and the solvent. Salt water, for example, is a solution of solid NaCl in liquid water; soda water is a solution of gaseous CO_2 in liquid water, while air is a solution of a gaseous solute (O_2) in a gaseous solvent (N_2). In all cases, however, the overall phase of the solution is the same phase as the solvent.

Example 9.2.1: Sugar Water

A solution is made by dissolving 1.00 g of sucrose ($C_{12}H_{22}O_{11}$) in 100.0 g of liquid water. Identify the solvent and solute in the resulting solution.

Solution

Either by mass or by moles, the obvious minor component is sucrose, so it is the solute. Water—the majority component—is the solvent. The fact that the resulting solution is the same phase as water also suggests that water is the solvent.

Exercise 9.2.1

A solution is made by dissolving 3.33 g of HCl(g) in 40.0 g of liquid methyl alcohol (CH_3OH). Identify the solvent and solute in the resulting solution.

Answer

solute: HCl(g); solvent: CH_3OH

One important concept of solutions is in defining how much solute is dissolved in a given amount of solvent. This concept is called **concentration**. Various words are used to describe the relative amounts of solute. **Dilute** describes a solution that has very little solute, while **concentrated** describes a solution that has a lot of solute. One problem is that these terms are qualitative; they describe more or less but not exactly how much.

In most cases, only a certain maximum amount of solute can be dissolved in a given amount of solvent. This maximum amount is called the **solubility** of the solute. It is usually expressed in terms of the amount of solute that can dissolve in 100 g of the solvent at a given temperature. Table **9.2.1** lists the solubilities of some simple ionic compounds. These solubilities vary widely: NaCl can dissolve up to 31.6 g per 100 g of H_2O, while AgCl can dissolve only 0.00019 g per 100 g of H_2O.

Table **9.2.1**: Solubilities of Some Ionic Compounds

Solute	Solubility (g per 100 g of H_2O at 25°C)
AgCl	0.00019
$CaCO_3$	0.0006
KBr	70.7
NaCl	36.1
$NaNO_3$	94.6

When the maximum amount of solute has been dissolved in a given amount of solvent, we say that the solution is **saturated** with solute. When less than the maximum amount of solute is dissolved in a given amount of solute, the solution is **unsaturated**. These terms are also qualitative terms because each solute has its own solubility. A solution of 0.00019 g of AgCl per 100 g of H_2O may be saturated, but with so little solute dissolved, it is also rather dilute. A solution of 36.1 g of NaCl in 100 g of H_2O is also saturated but rather concentrated. Ideally, we need more precise ways of specifying the amount of solute in a solution. We will introduce such ways in Section 11.3.

In some circumstances, it is possible to dissolve more than the maximum amount of a solute in a solution. Usually, this happens by heating the solvent, dissolving more solute than would normally dissolve at regular temperatures, and letting the solution cool down slowly and carefully. Such solutions are called **supersaturated** solutions and are not stable; given an opportunity (such as dropping a crystal of solute in the solution), the excess solute will precipitate from the solution.

It should be obvious that some solutes dissolve in certain solvents but not others. NaCl, for example, dissolves in water but not in vegetable oil. Beeswax dissolves in liquid hexane but not water. What is it that makes a solute soluble in some solvents but not others?

The answer is intermolecular interactions. The intermolecular interactions include London dispersion forces, dipole-dipole interactions, and hydrogen bonding (as described in Chapter 10). From experimental studies, it has been determined that if molecules of a solute experience the same intermolecular forces that the solvent does, the solute will likely dissolve in that solvent. So, NaCl—a very polar substance because it is composed of ions—dissolves in water, which is very polar, but not in oil, which is generally nonpolar. Nonpolar wax dissolves in nonpolar hexane but not in polar water. This concept leads to the general rule that "like dissolves like" for predicting whether a solute is soluble in a given solvent. However, this is a general rule, not an absolute statement, so it must be applied with care.

✔ Example 9.2.2: Polar and Nonpolar Solvents

Would I_2 be more soluble in CCl_4 or H_2O? Explain your answer.

Solution

I_2 is nonpolar. Of the two solvents, CCl_4 is nonpolar and H_2O is polar, so I_2 would be expected to be more soluble in CCl_4.

? Exercise 9.2.2

Would C_3H_7OH be more soluble in CCl_4 or H_2O? Explain your answer.

Answer

H_2O because both experience hydrogen bonding

Summary

- Solutions are composed of a solvent (major component) and a solute (minor component).
- Concentration is the expression of the amount of solute in a given amount of solvent and can be described by several qualitative terms.
- Solubility is a specific amount of solute that can dissolve in a given amount of solvent.

- "Like dissolves like" is a useful rule for deciding if a solute will be soluble in a solvent.

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9.3: Solutions of Gases in Water

Learning Objectives

- Explain how temperature and pressure affect the solubility of gases.

In an earlier module of this chapter, the effect of intermolecular attractive forces on solution formation was discussed. The chemical structures of the solute and solvent dictate the types of forces possible and, consequently, are important factors in determining solubility. For example, under similar conditions, the water solubility of oxygen is approximately three times greater than that of helium, but 100 times less than the solubility of chloromethane, $CHCl_3$. Considering the role of the solvent's chemical structure, note that the solubility of oxygen in the liquid hydrocarbon hexane, C_6H_{14}, is approximately 20 times greater than it is in water.

Other factors also affect the solubility of a given substance in a given solvent. Temperature is one such factor, with gas solubility typically decreasing as temperature increases (Figure **9.3.1**). This is one of the major impacts resulting from the thermal pollution of natural bodies of water.

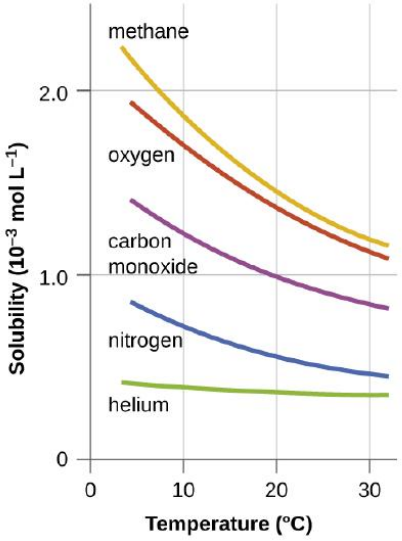


Figure **9.3.1**: The solubilities of these gases in water decrease as the temperature increases. All solubilities were measured with a constant pressure of 101.3 kPa (1 atm) of gas above the solutions.

When the temperature of a river, lake, or stream is raised abnormally high, usually due to the discharge of hot water from some industrial process, the solubility of oxygen in the water is decreased. Decreased levels of dissolved oxygen may have serious consequences for the health of the water's ecosystems and, in severe cases, can result in large-scale fish kills (Figure **9.3.2**).



(a) (b)

Figure 9.3.2: (a) The small bubbles of air in this glass of chilled water formed when the water warmed to room temperature and the solubility of its dissolved air decreased. (b) The decreased solubility of oxygen in natural waters subjected to thermal pollution can result in large-scale fish kills. (Credit a: modification of work by Liz West; credit b: modification of work by U.S. Fish and Wildlife Service.)

The solubility of a gaseous solute is also affected by the partial pressure of solute in the gas to which the solution is exposed. Gas solubility increases as the pressure of the gas increases. Carbonated beverages provide a nice illustration of this relationship. The carbonation process involves exposing the beverage to a relatively high pressure of carbon dioxide gas and then sealing the beverage container, thus saturating the beverage with CO_2 at this pressure. When the beverage container is opened, a familiar hiss is heard as the carbon dioxide gas pressure is released, and some of the dissolved carbon dioxide is typically seen leaving solution in the form of small bubbles (Figure 9.3.3). At this point, the beverage is *supersaturated* with carbon dioxide and, with time, the dissolved carbon dioxide concentration will decrease to its equilibrium value and the beverage will become "flat."

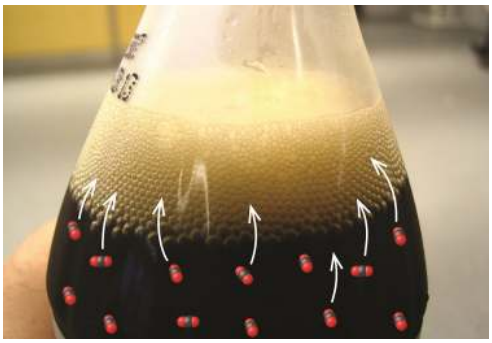


Figure 9.3.3: Opening the bottle of carbonated beverage reduces the pressure of the gaseous carbon dioxide above the beverage. The solubility of CO_2 is thus lowered, and some dissolved carbon dioxide may be seen leaving the solution as small gas bubbles. A dark brown liquid is shown in a clear, colorless container. A thick layer of beige bubbles appear at the surface of the liquid. In the liquid, thirteen small clusters of single black spheres with two red spheres attached to the left and right are shown. Red spheres represent oxygen atoms and black represent carbon atoms. Seven white arrows point upward in the container from these clusters to the bubble layer at the top of the liquid. (Credit: modification of work by Derrick Coetzee.)

"Fizz"

The dissolution in a liquid, also known as fizz, usually involves carbon dioxide under high pressure. When the pressure is reduced, the carbon dioxide is released from the solution as small bubbles, which causes the solution to become effervescent, or fizzy. A common example is the dissolving of carbon dioxide in water, resulting in carbonated water.

Carbon dioxide is weakly soluble in water, therefore it separates into a gas when the pressure is released. This process is generally represented by the following reaction, where a pressurized dilute solution of carbonic acid in water releases gaseous carbon dioxide at decompression:

$$\mathrm{H_2CO_3\,(aq) \longrightarrow H_2O\,(l) + CO_2\,(g)}$$

In simple terms, it is the result of the chemical reaction occurring in the liquid which produces a gaseous product.

For many gaseous solutes, the relation between solubility, C_g, and partial pressure, P_g, is a proportional one:

$$C_g = kP_g$$

where k is a proportionality constant that depends on the identities of the gaseous solute and solvent, and on the solution temperature. This is a mathematical statement of Henry's law: *The quantity of an ideal gas that dissolves in a definite volume of liquid is directly proportional to the pressure of the gas.*

Example 9.3.1: Application of Henry's Law

At 20 °C, the concentration of dissolved oxygen in water exposed to gaseous oxygen at a partial pressure of 101.3 kPa (760 torr) is 1.38×10^{-3} mol L^{-1}. Use Henry's law to determine the solubility of oxygen when its partial pressure is 20.7 kPa (155 torr), the approximate pressure of oxygen in earth's atmosphere.

Solution

According to Henry's law, for an ideal solution the solubility, C_g, of a gas (1.38×10^{-3} mol L^{-1}, in this case) is directly proportional to the pressure, P_g, of the undissolved gas above the solution (101.3 kPa, or 760 torr, in this case). Because we know both C_g and P_g, we can rearrange this expression to solve for k.

$$\begin{aligned} C_g &= kP_g \\ k &= \frac{C_g}{P_g} \\ &= \frac{1.38 \times 10^{-3}\ \text{mol L}^{-1}}{101.3\ \text{kPa}} \\ &= 1.36 \times 10^{-5}\ \text{mol L}^{-1}\ \text{kPa}^{-1} \\ &\quad (1.82 \times 10^{-6}\ \text{mol L}^{-1}\ \text{torr}^{-1}) \end{aligned}$$

Now we can use k to find the solubility at the lower pressure.

$$C_g = kP_g$$

$$\begin{aligned} &1.36 \times 10^{-5}\ \text{mol L}^{-1}\ \text{kPa}^{-1} \times 20.7\ \text{kPa} \\ &(\text{or } 1.82 \times 10^{-6}\ \text{mol L}^{-1}\ \text{torr}^{-1} \times 155\ \text{torr}) \\ &= 2.82 \times 10^{-4}\ \text{mol L}^{-1} \end{aligned}$$

Note that various units may be used to express the quantities involved in these sorts of computations. Any combination of units that yield to the constraints of dimensional analysis are acceptable.

Exercise 9.3.1

A 100.0 mL sample of water at 0 °C to an atmosphere containing a gaseous solute at 20.26 kPa (152 torr) resulted in the dissolution of 1.45×10^{-3} g of the solute. Use Henry's law to determine the solubility of this gaseous solute when its pressure is 101.3 kPa (760 torr).

Answer

7.25×10^{-3} g

Case Study: Decompression Sickness ("The Bends")

Decompression sickness (DCS), or "the bends," is an effect of the increased pressure of the air inhaled by scuba divers when swimming underwater at considerable depths. In addition to the pressure exerted by the atmosphere, divers are subjected to additional pressure due to the water above them, experiencing an increase of approximately 1 atm for each 10 m of depth. Therefore, the air inhaled by a diver while submerged contains gases at the corresponding higher ambient pressure, and the concentrations of the gases dissolved in the diver's blood are proportionally higher per Henry's law.

As the diver ascends to the surface of the water, the ambient pressure decreases and the dissolved gases becomes less soluble. If the ascent is too rapid, the gases escaping from the diver's blood may form bubbles that can cause a variety of symptoms ranging from rashes and joint pain to paralysis and death. To avoid DCS, divers must ascend from depths at relatively slow

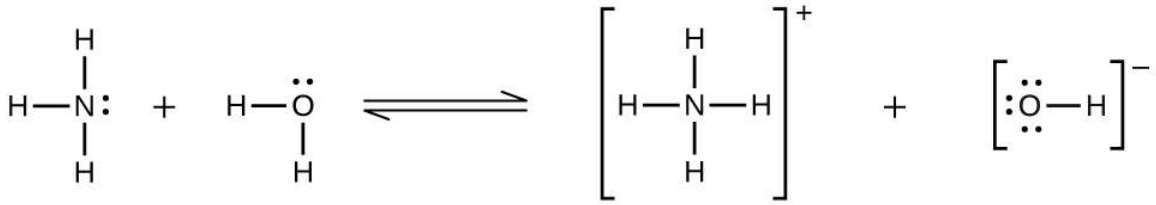
speeds (10 or 20 m/min) or otherwise make several decompression stops, pausing for several minutes at given depths during the ascent. When these preventative measures are unsuccessful, divers with DCS are often provided hyperbaric oxygen therapy in pressurized vessels called decompression (or recompression) chambers (Figure **9.3.4**).



(a) (b)

Figure **9.3.4**: (a) US Navy divers undergo training in a recompression chamber. (b) Divers receive hyperbaric oxygen therapy. Two photos are shown. The first shows two people seated in a steel chamber on benches that run length of the chamber on each side. The chamber has a couple of small circular windows and an open hatch-type door. One of the two people is giving a thumbs up gesture. The second image provides a view through a small, circular window. Inside the two people can be seen with masks over their mouths and noses. The people appear to be reading.

Deviations from Henry's law are observed when a chemical reaction takes place between the gaseous solute and the solvent. Thus, for example, the solubility of ammonia in water does not increase as rapidly with increasing pressure as predicted by the law because ammonia, being a base, reacts to some extent with water to form ammonium ions and hydroxide ions.



This reaction diagram shows three H atoms bonded to an N atom above, below, and two the left of the N. A single pair of dots is present on the right side of the N. This is followed by a plus, then two H atoms bonded to an O atom to the left and below the O. Two pairs of dots are present on the O, one above and the other to the right of the O. A double arrow, with a top arrow pointing right and a bottom arrow pointing left follows. To the right of the double arrow, four H atoms are shown bonded to a central N atom. These 5 atoms are enclosed in brackets with a superscript plus outside. A plus follows, then an O atom linked by a bond to an H atom on its right. The O atom has pairs of dots above, to the left, and below the atom. The linked O and H are enclosed in brackets with superscript minus outside.

Gases can form supersaturated solutions. If a solution of a gas in a liquid is prepared either at low temperature or under pressure (or both), then as the solution warms or as the gas pressure is reduced, the solution may become supersaturated.

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9.4: Quantitative Units of Concentration

Learning Objective

- Learn to determine specific concentrations with several common units.

Rather than qualitative terms (Section 11.2 - Definitions), we need quantitative ways to express the amount of solute in a solution; that is, we need specific units of concentration. In this section, we will introduce several common and useful units of concentration.

Molarity (M) is defined as the number of moles of solute divided by the number of liters of solution:

$$molarity = \frac{moles\ of\ solute}{liters\ of\ solution}$$

which can be simplified as

$$M = \frac{mol}{L},\ or\ mol/L$$

As with any mathematical equation, if you know any two quantities, you can calculate the third, unknown, quantity.

For example, suppose you have 0.500 L of solution that has 0.24 mol of NaOH dissolved in it. The concentration of the solution can be calculated as follows:

$$molarity = \frac{0.24\ mol\ NaOH}{0.500 L} = 0.48\ M\ NaOH$$

The concentration of the solution is 0.48 M, which is spoken as "zero point forty-eight molarity" or "zero point forty-eight molar." If the quantity of the solute is given in mass units, you must convert mass units to mole units before using the definition of molarity to calculate concentration. For example, what is the molar concentration of a solution of 22.4 g of HCl dissolved in 1.56 L? First, convert the mass of solute to moles using the molar mass of HCl (36.5 g/mol):

$$22.4\ \cancel{g HCl} \times \frac{1\ mol\ Hcl}{36.5\ \cancel{g HCl}} = 0.614\ M\ HCl$$

Now we can use the definition of molarity to determine a concentration:

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

Example 9.4.1

What is the molarity of a solution made when 32.7 g of NaOH are dissolved to make 445 mL of solution?

Solution

To use the definition of molarity, both quantities must be converted to the proper units. First, convert the volume units from milliliters to liters:

$$445\ \cancel{mL} \times \frac{1\ L}{1000\ \cancel{mL}} = 0.445\ L$$

Now we convert the amount of solute to moles, using the molar mass of NaOH, which is 40.0 g/mol:

$$32.7\ \cancel{g NaOH} \times \frac{1\ mol\ NaOH}{40.0\ \cancel{g NaOH}} = 0.818\ mol\ NaOH$$

Now we can use the definition of molarity to determine the molar concentration:

$$M = \frac{0.818\ mol\ NaOH}{0.445 L} = 1.84\ M\ NaOH$$

Exercise 9.4.1

What is the molarity of a solution made when 66.2 g of $C_6H_{12}O_6$ are dissolved to make 235 mL of solution?

Answer

1.57 M

The definition of molarity can be used to determine the amount of solute or the volume of solution, if the other information is given. Example 4 illustrates this situation.

Example 9.4.2

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

Solution

We know the volume and the molarity; we can use the definition of molarity to mathematically solve for the amount in moles. Substituting the quantities into the definition of molarity:

$$0.887\,M = \frac{mol\ NaCl}{0.108 L}$$

We multiply the 0.108 L over to the other side of the equation and multiply the units together; "molarity × liters" equals moles, according to the definition of molarity. So

mol NaCl = (0.887 M)(0.108 L) = 0.0958 mol

Exercise 9.4.2

How many moles of solute are present in 225 mL of a 1.44 M $CaCl_2$ solution?

Answer

0.324 mol

If you need to determine volume, remember the rule that the unknown quantity must be by itself and in the numerator to determine the correct answer. Thus, rearrangement of the definition of molarity is required.

Example 9.4.3

What volume of a 2.33 M $NaNO_3$ solution is needed to obtain 0.222 mol of solute?

Solution

Using the definition of molarity, we have

$$2.33\,M = \frac{0.222 mol}{L}$$

To solve for the number of liters, we bring the 2.33 M over to the right into the denominator, and the number of liters over to the left in the numerator. We now have

$$L = \frac{0.222 mol}{2.33\,M}$$

Dividing, **the volume is 0.0953 L = 95.3 mL.**

? Exercise 9.4.3

What volume of a 0.570 M K_2SO_4 solution is needed to obtain 0.872 mol of solute?

Answer

1.53 L

A similar unit of concentration is **molality** (*m*), which is defined as the number of moles of solute per kilogram of solvent, not per liter of solution:

$$molality = \frac{moles\ solute}{kilograms\ solvent}$$

Mathematical manipulation of molality is the same as with molarity.

Another way to specify an amount is **percentage composition by mass** (or *mass percentage*, % m/m). It is defined as follows:

$$\%m/m = \frac{mass\ of\ solute}{mass\ of\ entire\ sample} \times 100\%$$

It is not uncommon to see this unit used on commercial products (see Figure **9.4.1** - Concentration in Commercial Applications).



Figure **9.4.1** Concentration in Commercial Applications © Thinkstock. *The percentage of urea in this package is 5% m/m, meaning that there are 5 g of urea per 100 g of product.*

✓ Example 9.4.4

What is the mass percentage of Fe in a piece of metal with 87.9 g of Fe in a 113 g sample?

Solution

Using the definition of mass percentage, we have

$$\%m/m = \frac{87.9\,g\,Fe}{113\,g\,sample} \times 100\% = 77.8\%\,Fe$$

Exercise 9.4.4

What is the mass percentage of H_2O_2 in a solution with 1.67 g of H_2O_2 in a 55.5 g sample?

Answer

3.01%

Related concentration units are **parts per thousand (ppth), parts per million (ppm)** and **parts per billion (ppb).** Parts per thousand is defined as follows:

$$ppth = \frac{mass\ of\ solute}{mass\ of\ sample} \times 1000$$

There are similar definitions for parts per million and parts per billion:

$$ppm = \frac{mass\ of\ solute}{mass\ of\ sample} \times 1,000,000$$

and

$$ppb = \frac{mass\ of\ solute}{mass\ of\ sample} \times 1,000,000,000$$

Each unit is used for progressively lower and lower concentrations. The two masses must be expressed in the same unit of mass, so conversions may be necessary.

Example 9.4.5

If there are 0.6 g of Pb present in 277 g of solution, what is the Pb concentration in parts per thousand?

Solution

Use the definition of parts per thousand to determine the concentration. Substituting

$$\frac{0.6g\ Pb}{277g\ solution} \times 1000 = 2.17\ ppth$$

Exercise 9.4.5

If there are 0.551 mg of As in 348 g of solution, what is the As concentration in ppm?

Answer

1.58 ppm

As with molarity and molality, algebraic rearrangements may be necessary to answer certain questions.

Example 9.4.6

The concentration of Cl^- ion in a sample of H_2O is 15.0 ppm. What mass of Cl^- ion is present in 240.0 mL of H_2O, which has a density of 1.00 g/mL?

Solution

First, use the density of H_2O to determine the mass of the sample:

$$240.0\ \cancel{mL} \times \frac{1.00\ g}{\cancel{mL}} = 240.0\ g$$

Now we can use the definition of ppm:

$$15.0\,ppm = \frac{mass\ of\ solute}{240.0\ g\ solution} \times 1,000,000$$

Rearranging to solve for the mass of solute,

$$mass\ solute = \frac{(15.0\,ppm)(240.0\ g\ solution)}{1,000,000} = 0.0036g = 3.6\,mg$$

Exercise 9.4.6

The concentration of Fe^{3+} ion in a sample of H_2O is 335.0 ppm. What mass of Fe^{3+} ion is present in 3,450 mL of H_2O, which has a density of 1.00 g/mL?

Answer

1.16 g

For ionic solutions, we need to differentiate between the concentration of the salt versus the concentration of each individual ion. Because the ions in ionic compounds go their own way when a compound is dissolved in a solution, the resulting concentration of the ion may be different from the concentration of the complete salt. For example, if 1 M NaCl were prepared, the solution could also be described as a solution of 1 M $Na^+(aq)$ and 1 M $Cl^-(aq)$ because there is one Na^+ ion and one Cl^- ion per formula unit of the salt. However, if the solution were 1 M $CaCl_2$, there are two $Cl^-(aq)$ ions for every formula unit dissolved, so the concentration of $Cl^-(aq)$ would be 2 M, not 1 M.

In addition, the total ion concentration is the sum of the individual ion concentrations. Thus for the 1 M NaCl, the total ion concentration is 2 M; for the 1 M $CaCl_2$, the total ion concentration is 3 M.

Key Takeaway

- Quantitative units of concentration include molarity, molality, mass percentage, parts per thousand (ppth), parts per million (ppm), and parts per billion (ppb).

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9.5: Concentrations as Conversion Factors

Learning Objective

- Apply concentration units as conversion factors.

Concentration can be a conversion factor between the amount of solute and the amount of solution or solvent (depending on the definition of the concentration unit). As such, concentrations can be useful in a variety of stoichiometry problems. In many cases, it is best to use the original definition of the concentration unit; it is that definition that provides the conversion factor.

A simple example of using a concentration unit as a conversion factor is one in which we use the definition of the concentration unit and rearrange; we can do the calculation again as a unit conversion, rather than as a definition. For example, suppose we ask how many moles of solute are present in 0.108 L of a 0.887 M NaCl solution. Because 0.887 M means 0.887 mol/L, we can use this second expression for the concentration as a conversion factor:

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

(There is an understood 1 in the denominator of the conversion factor.) If we used the definition approach, we get the same answer, but now we are using conversion factor skills. Like any other conversion factor that relates two different types of units, the reciprocal of the concentration can be also used as a conversion factor.

Example 9.5.1

Using concentration as a conversion factor, how many liters of 2.35 M $CuSO_4$ are needed to obtain 4.88 mol of $CuSO_4$?

Solution

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

$$4.88\ \cancel{mol\ CuSO_4} \times \frac{1\ L}{2.35\ \cancel{mol}} = 2.08\ L\ of\ solution$$

Exercise 9.5.1

Using concentration as a conversion factor, how many liters of 0.0444 M CH_2O are needed to obtain 0.0773 mol of CH_2O?

Answer:

1.74 L

Of course, once quantities in moles are available, another conversion can give the mass of the substance, using molar mass as a conversion factor.

Example 9.5.2

What mass of solute is present in 0.765 L of 1.93 M NaOH?

Solution

This is a two-step conversion, first using concentration as a conversion factor to determine the number of moles and then the molar mass of NaOH (40.0 g/mol) to convert to mass:

$$0.765\ \cancel{L} \times \frac{1.93\ \cancel{mol\ NaOH}}{\cancel{L\ solution}} \times \frac{40.0\ g\ NaOH}{1\ \cancel{mol\ NaOH}} = 59.1\ g\ NaOH$$

Exercise 9.5.2

What mass of solute is present in 1.08 L of 0.0578 M H_2SO_4?

Answer

6.12 g

More complex stoichiometry problems using balanced chemical reactions can also use concentrations as conversion factors. For example, suppose the following equation represents a chemical reaction:

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

If we wanted to know what volume of 0.555 M $CaCl_2$ would react with 1.25 mol of $AgNO_3$, we first use the balanced chemical equation to determine the number of moles of $CaCl_2$ that would react and then use concentration to convert to liters of solution:

$$1.25\ \cancel{mol\ AgNO_3} \times \frac{1\ \cancel{mol\ CaCl_2}}{2\ \cancel{mol\ AgNO_3}} \times \frac{1L\ solution}{0.555\ \cancel{mol\ CaCl_2}} = 1.13\,L\,CaCl_2$$

This can be extended by starting with the mass of one reactant, instead of moles of a reactant.

Example 9.5.3

What volume of 0.0995 M $Al(NO_3)_3$ will react with 3.66 g of Ag according to the following chemical equation?

$$3\,Ag\,(s) + Al(NO_3)_3\,(aq) \longrightarrow 3\,AgNO_3 + Al\,(s)$$

Solution

Here, we first must convert the mass of Ag to moles before using the balanced chemical equation and then the definition of molarity as a conversion factor:

$$3.66\ \cancel{g\ Ag} \times \frac{1\ \cancel{mol\ Ag}}{107.97\ \cancel{g\ Ag}} \times \frac{1\ \cancel{mol\ Al(NO_3)_3}}{3\ \cancel{mol\ Ag}} \times \frac{1L\ solution}{0.0995\ \cancel{mol\ Al(NO_3)_3}} = 0.114\,L$$

The strikeouts show how the units cancel.

Exercise 9.5.3

What volume of 0.512 M NaOH will react with 17.9 g of $H_2C_2O_4(s)$ according to the following chemical equation?

$$H_2C_2O_4\,(s) + 2\,NaOH\,(aq) \longrightarrow Na_2C_2O_4\,(aq) + 2\,H_2O(\ell)$$

Answer:

0.777 L

We can extend our skills even further by recognizing that we can relate quantities of one solution to quantities of another solution. Knowing the volume and concentration of a solution containing one reactant, we can determine how much of another solution of another reactant will be needed using the balanced chemical equation.

Example 9.5.4

A student takes a precisely measured sample, called an *aliquot*, of 10.00 mL of a solution of $FeCl_3$. The student carefully adds 0.1074 M $Na_2C_2O_4$ until all the $Fe^{3+}(aq)$ has precipitated as $Fe_2(C_2O_4)_3(s)$. Using a precisely measured tube called a burette, the student finds that 9.04 mL of the $Na_2C_2O_4$ solution was added to completely precipitate the $Fe^{3+}(aq)$. What was the concentration of the $FeCl_3$ in the original solution? (A precisely measured experiment like this, which is meant to determine the amount of a substance in a sample, is called a *titration*.) The balanced chemical equation is as follows:

$$2\,FeCl_3\,(aq) + 3\,Na_2C_2O_4\,(aq) \longrightarrow Fe_2(C_2O_4)_3\,(s) + 6\,NaCl\,(aq)$$

Solution

First we need to determine the number of moles of $Na_2C_2O_4$ that reacted. We will convert the volume to liters and then use the concentration of the solution as a conversion factor:

$$9.04\,\cancel{mL} \times \frac{1\,\cancel{L}}{1000\,\cancel{mL}} \times \frac{0.1074 mol\,Na_2C_2O_4}{\cancel{L}} = 0.000971\,mol\,Na_2C_2O_4$$

Now we will use the balanced chemical equation to determine the number of moles of Fe^{3+}(aq) that were present in the initial aliquot:

$$0.000971\,\cancel{mol\,Na_2C_2O_4} \times \frac{2 mol\,FeCl_3}{3\,\cancel{mol Na_2C_2O_4}} = 0.000647 mol\,FeCl_3$$

Then we determine the concentration of $FeCl_3$ in the original solution. Converting 10.00 mL into liters (0.01000 L), we use the definition of molarity directly:

$$M = \frac{mol}{L} = \frac{0.000647 mol\,FeCl_3}{0.01000 L} = 0.0647 M\,FeCl_3$$

Exercise 9.5.4

A student titrates 25.00 mL of H_3PO_4 with 0.0987 M KOH. She uses 54.06 mL to complete the chemical reaction. What is the concentration of H_3PO_4?

$$H_3PO_4\,(aq) + 3\,KOH\,(aq) \longrightarrow K_3PO_4\,(aq) + 3\,H_2O$$

Answer:

0.0711 M



Figure **9.5.1** Titration © Thinkstock. When a student performs a titration, a measured amount of one solution is added to another reactant.

We have used molarity exclusively as the concentration of interest, but that will not always be the case. The next example shows a different concentration unit being used.

Example 9.5.5

H_2O_2 is used to determine the amount of Mn according to this balanced chemical equation:

$$2\,MnO_4^-(aq) + 5\,H_2O_2(aq) + 6\,H^+(aq) \longrightarrow 2\,Mn_2^+(aq) + 5\,O_2(g) + 8\,H_2O(\ell)$$

What mass of 3.00% m/m H_2O_2 solution is needed to react with 0.355 mol of MnO_4^-(aq)?

Solution

Because we are given an initial amount in moles, all we need to do is use the balanced chemical equation to determine the number of moles of H_2O_2 and then convert to find the mass of H_2O_2. Knowing that the H_2O_2 solution is 3.00% by mass, we can determine the mass of solution needed:

$$0.355\ \cancel{mol\ MnO_4^-} \times \frac{5\ \cancel{mol\ H_2O_2}}{2\ \cancel{mol\ MnO_4^-}} \times \frac{34.02\ \cancel{g\ H_2O_2}}{\cancel{mol\ H_2O_2}} \times \frac{100 g\ solution}{3\ \cancel{g\ H_2O_2}} = 1006 g\ sol$$

The first conversion factor comes from the balanced chemical equation, the second conversion factor is the molar mass of H_2O_2, and the third conversion factor comes from the definition of percentage concentration by mass.

Exercise 9.5.5

Use the balanced chemical reaction for MnO_4^- and H_2O_2 to determine what mass of O_2 is produced if 258 g of 3.00% m/m H_2O_2 is reacted with MnO_4^-.

Answer

7.28 g

Summary

Know how to apply concentration units as conversion factors.

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9.6: Dilutions and Concentrations

Learning Objective

- Learn how to dilute and concentrate solutions.

Often, a worker will need to change the concentration of a solution by changing the amount of solvent. **Dilution** is the addition of solvent, which decreases the concentration of the solute in the solution. **Concentration** is the removal of solvent, which increases the concentration of the solute in the solution. (Do not confuse the two uses of the word *concentration* here!)

In both dilution and concentration, the amount of solute stays the same. This gives us a way to calculate what the new solution volume must be for the desired concentration of solute. From the definition of molarity,

$$\text{molarity} = \frac{\text{moles of solute}}{\text{liters of solution}}$$

we can solve for the number of moles of solute:

moles of solute = (molarity)(liters of solution)

A simpler way of writing this is to use M to represent molarity and V to represent volume. So the equation becomes

moles of solute = MV

Because this quantity does not change before and after the change in concentration, the product MV must be the same before and after the concentration change. Using numbers to represent the initial and final conditions, we have

$$M_1V_1 = M_2V_2$$

as the **dilution equation**. The volumes must be expressed in the same units. Note that this equation gives only the initial and final conditions, not the amount of the change. The amount of change is determined by subtraction.

Example 9.6.1

If 25.0 mL of a 2.19 M solution are diluted to 72.8 mL, what is the final concentration?

Solution

It does not matter which set of conditions is labeled 1 or 2, as long as the conditions are paired together properly. Using the dilution equation, we have

$$(2.19\text{ M})(25.0\text{ mL}) = M_2(72.8\text{ mL})$$

Solving for the second concentration (noting that the milliliter units cancel),

$$M_2 = 0.752\text{ M}$$

The concentration of the solution has decreased. In going from 25.0 mL to 72.8 mL, 72.8 − 25.0 = 47.8 mL of solvent must be added.

Exercise 9.6.1

A 0.885 M solution of KBr whose initial volume is 76.5 mL has more water added until its concentration is 0.500 M. What is the new volume of the solution?

Answer

135.4 mL

Concentrating solutions involves removing solvent. Usually this is done by evaporating or boiling, assuming that the heat of boiling does not affect the solute. The dilution equation is used in these circumstances as well.

Chemistry is Everywhere: Preparing IV Solutions

In a hospital emergency room, a physician orders an intravenous (IV) delivery of 100 mL of 0.5% KCl for a patient suffering from hypokalemia (low potassium levels). Does an aide run to a supply cabinet and take out an IV bag containing this concentration of KCl?

Not likely. It is more probable that the aide must make the proper solution from an IV bag of sterile solution and a more concentrated, sterile solution, called a *stock solution*, of KCl. The aide is expected to use a syringe to draw up some stock solution and inject it into the waiting IV bag and dilute it to the proper concentration. Thus the aide must perform a dilution calculation.



Figure **9.6.1** Preparing IV Solution © Thinkstock. Medical personnel commonly must perform dilutions for IV solutions.

If the stock solution is 10.0% KCl and the final volume and concentration need to be 100 mL and 0.50%, respectively, then it is easy to calculate how much stock solution to use:

$$(10\%)V_1 = (0.50\%)(100\text{ mL})V_1 = 5\text{ mL}$$

Of course, the addition of the stock solution affects the total volume of the diluted solution, but the final concentration is likely close enough even for medical purposes.

Medical and pharmaceutical personnel are constantly dealing with dosages that require concentration measurements and dilutions. It is an important responsibility: calculating the *wrong* dose can be useless, harmful, or even fatal!

Summary

- Molarity and volume are used to determine dilutions and concentrations of solutions.

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CHAPTER OVERVIEW

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10.1: Chemical Reaction Rate

Drag racing is a sport that involves two cars starting from a dead stop, and driving as fast as they can down a quarter-mile strip. At the end of the strip are timers that determine both elapsed time (how long it took for the cars to cover the quarter mile) and top speed (how fast they were going as they went through the timer chute). Both pieces of data are important. One car may accelerate faster and get ahead that way, while the other car may be slower off the line, but can get up to a higher top speed at the end of the run.

Chemical Reaction Rate

Chemical reactions vary widely in terms of the speed with which they occur. Some reactions occur very quickly. If a lit match is brought in contact with lighter fluid or another flammable liquid, it erupts into flames instantly and burns fast. Other reactions occur very slowly. A container of milk in the refrigerator will be good to drink for weeks before it begins to turn sour. Millions of years were required for dead plants under Earth's surface to accumulate and eventually turn into fossil fuels such as coal and oil.

Chemists need to be concerned with the rates at which chemical reactions occur. Rate is another word for speed. If a sprinter takes $11.0\ \text{s}$ to run a $100\ \text{m}$ dash, his rate is given by the distance traveled divided by the time.

$$\text{speed} = \frac{\text{distance}}{\text{time}} = \frac{100\ \text{m}}{11.0\ \text{s}} = 9.09\ \text{m/s}$$

The sprinter's average running rate for the race is $9.09\ \text{m/s}$. We say that it is his average rate because he did not run at that speed for the entire race. At the very beginning of the race, while coming from a standstill, his rate must be slower until he is able to get up to his top speed. His top speed must then be greater than $9.09\ \text{m/s}$ so that, taken over the entire race, the average ends up at $9.09\ \text{m/s}$.



Figure 10.1.1: Runner. (CC BY-NC; CK-12)

Chemical reactions can't be measured in units of meters per second, as that would not make any sense. A **reaction rate** is the change in concentration of a reactant or product with time. Suppose that a simple reaction were to take place in which a $1.00\ \text{M}$ aqueous solution of substance A was converted to substance B.

$$\text{A}\,(aq) \rightarrow \text{B}\,(aq)$$

Suppose that after 20.0 seconds, the concentration of A had dropped from $1.00\ \text{M}$ to $0.72\ \text{M}$ as A was slowly being converted to B. We can express the rate of this reaction as the change in concentration of A divided by time.

$$\text{rate} = -\frac{\Delta\,[\text{A}]}{\Delta t} = -\frac{[\text{A}]_{\text{final}} - [\text{A}]_{\text{initial}}}{\Delta t}$$

A bracket around a symbol or formula means the concentration in molarity of that substance. The change in concentration of A is its final concentration minus its initial concentration. Because the concentration of A is decreasing over time, the negative sign is used. Thus, the rate for the reaction is positive and the units are molarity per second or M/s.

$$\text{rate} = -\frac{0.72\ \text{M} - 1.00\ \text{M}}{20.0\ \text{s}} = -\frac{-0.28\ \text{M}}{20.0\ \text{s}} = 0.014\ \text{M/s}$$

The molarity of A decreases by an average rate of $0.014\ \text{M}$ every second. In summary, the rate of a chemical reaction is measured by the change in concentration over time for a reactant or product. The unit of measurement for a reaction rate is molarity per second (M/s).

Summary

- Chemists need to be concerned with the rates at which chemical reactions occur.
- The reaction rate indicates how fast the reaction proceeds.

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10.2: Collision Theory

Car damage can be very expensive, especially if the driver who did the damage does not have car insurance. Many people have had the experience of backing up while parallel parking and hearing that "bump". Fortunately, cars are often not going fast enough to do any damage. Every once in a while, though, there is a rearrangement of the body parts of a car when it is hit with sufficient speed; then things need to be fixed.

Collision Theory

The behavior of the atoms, molecules, or ions that comprise the reactants is responsible for the rates of a given chemical reaction. **Collision theory** is a set of principles that states that the reacting particles can form products when they collide with one another, provided those collisions have enough kinetic energy and the correct orientation. Particles that lack the necessary kinetic energy may collide, but the particles will simply bounce off one another unchanged. The figure below illustrates the difference. In the first collision, the particles bounce off one another, and no rearrangement of atoms has occurred. The second collision occurs with greater kinetic energy, and so the bond between the two red atoms breaks. One red atom bonds with the other molecule as one product, while the single red atom is the other product. The first collision is called an **ineffective collision**, while the second collision is called an **effective collision**.

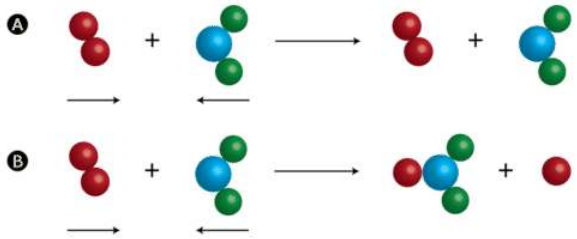


Figure **10.2.1**: An ineffective collision (A) is one that does not result in product formation. An effective collision (B) is one in which chemical bonds are broken and a product is formed. (CC BY-NC; CK-12)

Summary

- Collision theory explains how materials can collide and become new materials.
- Effective collisions result in product formation.
- Ineffective collisions do not result in product formation.

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10.3: Activation Energy

The sight of fireworks cascading across the night sky is a hallmark of special occasions. These materials, invented hundreds of years ago, can be dangerous if not handled properly. The chemicals do not react until the fuse burns down and heat is applied to the system. Then, the rocket is launched and explodes high in the sky.

Activation Energy



Figure **10.3.1**: Calcium metal stored in an argon atmosphere. (CC BY-NC; CK-12)

Why do some chemical reactions occur readily while others require input of heat in order to take place? If we mix metallic sodium with water, a reaction occurs immediately, releasing a great deal of heat (enough to ignite the hydrogen gas that is formed). Group II metals, such as calcium, react at a much slower rate. Unlike the extremely vigorous reaction with sodium, the reaction with calcium is slow enough that we can trap the hydrogen gas released.

Supplying reactant particles with energy causes the bonds between the atoms to vibrate with a greater frequency. This increase in vibrational energy makes a chemical bond more likely to break, and a chemical reaction more likely to occur, when those particles collide with other particles. The **activation energy** for a reaction is the minimum energy that colliding particles must have in order to undergo a reaction. Some reactions occur readily at room temperature because the reacting particles already have the requisite activation energy at that temperature. Other reactions only occur when heated because the particles do not have enough energy unless an external source of heat provides the particles with more kinetic energy.

Summary

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10.4: Potential Energy Diagrams

Sisyphus was a mythological being who was a very evil king. As a punishment for his misdoings, he was supposed to roll a large stone up to the top of a long hill. A spell had been placed on the stone so that it would roll back down before reaching the top, never to complete the task. Sisyphus was condemned to an eternity of trying to get to the top of the hill, but never succeeding.

Potential Energy Diagrams

The energy changes that occur during a chemical reaction can be shown in a diagram called a potential energy diagram, or sometimes called a reaction progress curve. A **potential energy diagram** shows the change in potential energy of a system as reactants are converted into products. The figure below shows basic potential energy diagrams for an endothermic (A) and an exothermic (B) reaction. Recall that the enthalpy change (ΔH) is positive for an endothermic reaction and negative for an exothermic reaction. This can be seen in the potential energy diagrams. The total potential energy of the system increases for the endothermic reaction as the system absorbs energy from the surroundings. The total potential energy of the system decreases for the exothermic reaction as the system releases energy to the surroundings.

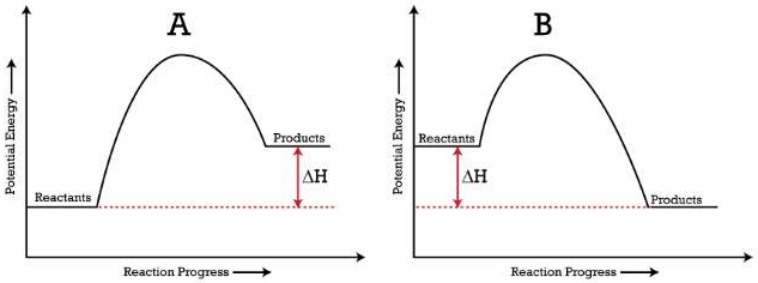


Figure **10.4.1**: A potential energy diagram shows the total potential energy of a reacting system as the reaction proceeds. (A) In an endothermic reaction, the energy of the products is greater than the energy of the reactants and ΔH is positive. (B) In an exothermic reaction, the energy of the products is lower than the energy of the reactants and ΔH is negative. (CC BY-NC; CK-12)

The activation energy for a reaction is illustrated in the potential energy diagram by the height of the hill between the reactants and the products. For this reason, the activation energy of a reaction is sometimes referred to as the activation energy barrier. Reacting particles must have enough energy so that when they collide, they can overcome that barrier (see figure below).

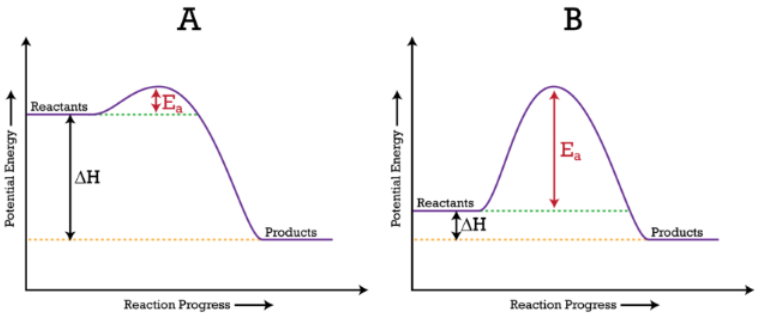


Figure **10.4.2**: The activation energy (E_a) of a reaction is the barrier that must be overcome for the reactants to be able to become products. (A) The activation energy is low, meaning that the reaction is likely to be fast. (B) The activation energy is high, meaning that the reaction is likely to be slow. (CC BY-NC; CK-12)

Summary

- A potential energy diagram shows the change in potential energy of a system as reactants are converted into products.
- Potential energy diagrams for endothermic and exothermic reactions are described.
- Diagrams of activation energy and reaction progress are given.

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10.5: Activated Complex

Velcro is a synthetic material that allows fabric (among other things) to stick together. Another, more unusual, use for Velcro is the sport of "Velcro-jumping". The participant wears clothing made of Velcro and jumps at a Velcro-covered wall. Sometimes the collision with the wall will result in the person sticking to the wall. Other times, the person simply bounces off the wall and does not connect.

Activated Complex

Reactant particles sometimes collide with one another and remain unchanged by the collision. Other times, the collision leads to the formation of products. The state of the particles that is in between the reactants and products is called the activated complex. An **activated complex** is an unstable arrangement of atoms that exists momentarily at the peak of the activation energy barrier. Because of its high energy, the activated complex exists for an extremely short period of time (about 10^{-13} s). There is equal likelihood that the activated complex either reforms the original reactants or goes on to form products. The figure below shows the formation of a possible activated complex between colliding hydrogen and oxygen molecules. Because of their unstable nature and brief existence, very little is known about the exact structures of many activated complexes.

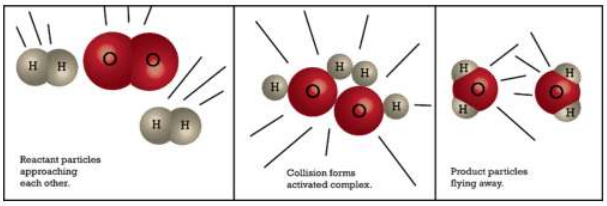


Figure **10.5.1**: An activated complex is a short-lived state in which the colliding particles are at the peak of the potential energy curve. (CC BY-NC; CK-12)

Summary

- An activated complex is an unstable arrangement of atoms that exists momentarily at the peak of the activation energy barrier.
- The role of the activated complex in reactions is described.

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10.6: Factors Affecting Reaction Rate

Driving on a crowded freeway can be stressful. Lots of cars, drivers who aren't paying attention, people who speed or who drive too slow—the chances of a collision are rather high. A lot of cars in a particular amount of space means a high car concentration and many opportunities for unwanted connections with other cars.

Factors Affecting Reaction Rates

According to their nature, some reactions occur very quickly, while others are very slow. However, certain changes in the reacting conditions can have an effect on the rate of a given chemical reaction. Collision theory can be utilized to explain these rate effects.

Concentration

An increase in the concentration of one or more reacting substances results in an increase in the rate of reaction. When more particles are present in a given amount of space, a greater number of collisions will naturally occur between those particles. Since the rate of a reaction is dependent on the number of collisions occurring between reactants, the rate increases as the concentration increases.

Pressure

When the pressure of a gas is increased, its particles are forced closer together, decreasing the amount of empty space between the particles. Therefore, an increase in the pressure of a gas is also an increase in the concentration of the gas. For gaseous reactions, an increase in pressure increases the rate of reaction due to a greater number of collisions between reacting particles.

Surface Area

A large log placed in a fire will burn relatively slowly. If the same mass of wood were added to the fire in the form of small twigs, the twigs would burn much more quickly. This is because the twigs provide a greater surface area than the log does. An increase in the surface area of a reactant increases the rate of a reaction. Surface area is larger when a given amount of a solid is present as smaller particles. A powdered reactant has a greater surface area than the same reactant as a solid chunk. In order to increase the surface area of a substance, it may be ground into smaller particles or dissolved into a liquid. In solution, the dissolved particles are separated from each other and will react more quickly with other reactants.

Temperature

Raising the temperature of a chemical reaction usually results in a higher rate of reaction. When the reactant particles are heated, they move faster and faster. This results in a greater frequency of collisions. A more important effect of the temperature increase is that the collisions occur with a greater force, and are thus more likely to surmount the activation energy barrier and go on to form products. Increasing the temperature of a reaction increases the number of effective collisions between reacting particles, so the reaction rate increases.

Summary

- Factors that affect (and generally increase) reaction rate are:
  - Concentration of reactants
  - Pressure (in the case of a gas)
  - Surface area
  - Temperature

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10.7: Catalysts

Gasoline-powered vehicles emit various harmful materials. Nitrogen oxides are formed when atmospheric nitrogen reacts with oxygen at the high temperatures found in a car engine. Carbon monoxide is a by-product of the incomplete combustion of hydrocarbons. Evaporated and unused fuel releases volatile hydrocarbons into the atmosphere to help form smog. The presence of a catalytic converter in the exhaust system of the car causes these materials to react and be changed into less harmful products.

Catalysts

Sometimes a particular substance added to a chemical reaction will cause that reaction to undergo a dramatic increase in rate. Hydrogen peroxide is used as a disinfectant for scrapes and cuts, and is found in many medicine cabinets as a 3% aqueous solution. Hydrogen peroxide naturally decomposes to produce water and oxygen gas, but the reaction is very slow. A bottle of hydrogen peroxide will last for several years before it needs to be replaced. However, the addition of just a small amount of manganese (IV) oxide to hydrogen peroxide will cause it to decompose completely in just a matter of minutes. A **catalyst** is a substance that increases the rate of a chemical reaction by lowering the activation energy without being used up in the reaction. After the reaction occurs, a catalyst returns to its original state; so catalysts can be used over and over again. Because it is neither a reactant nor a product, a catalyst is shown in a chemical equation by being written above the yield arrow.

$$\mathrm{H_2O_2\,(aq)} \xrightarrow{\mathrm{MnO_2}} \mathrm{2H_2O\,(l) + O_2\,(g)}$$

A catalyst works by changing the specific way in which the reaction occurs, called its mechanism. The important outcome from the use of a catalyst is that the overall activation energy of the reaction is lowered (see figure below). With a lower activation energy barrier, a greater percentage of reactant molecules are able to have effective collisions, and the reaction rate increases.

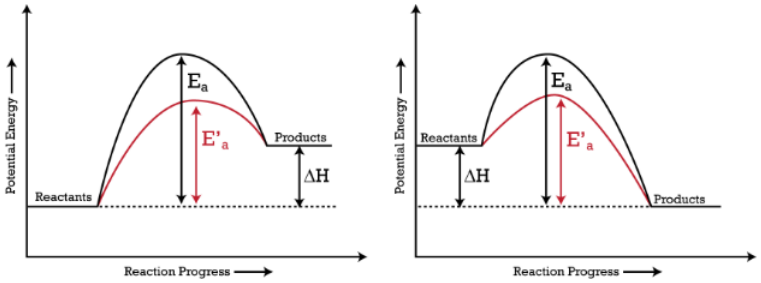


Figure **10.7.1**: The addition of a catalyst to a reaction lowers the activation energy, increasing the rate of the reaction. The activation energy of the uncatalyzed reaction is shown by E_a, while the catalyzed reaction is shown by E'_a. The heat of reaction (ΔH) is unchanged by the presence of the catalyst. (CC BY-NC; CK-12)

Catalysts are an extremely important part of many chemical reactions. Enzymes in your body acts as nature's catalysts, allowing important biochemical reactions to occur at reasonable rates. Chemical companies constantly search for new and better catalysts to make reactions go faster and thus make the company more profitable.

Summary

- A catalyst is a substance that increases the rate of a chemical reaction by lowering the activation energy without being used up in the reaction.
- Catalysts are an important part of many chemical reactions.

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10.8: Rate Law and Specific Rate Constant

Where are people moving from and where are they moving to? How fast is the population changing in different areas? These are important considerations for those individuals or companies who decide where to build schools or hospitals, or where to open new businesses. If an area is growing rapidly, action needs to be taken quickly to accommodate the growth. Rates of change affect many decisions.

Rate Law and Specific Rate Constant

Consider a simple chemical reaction in which reactant **A** is converted into product **B**, according to the equation below.

$$\mathbf{A} \rightarrow \mathbf{B}$$

The rate of reaction is given by the change in concentration of **A** as a function of time. The rate of disappearance of **A** is also proportional to the concentration of **A**.

$$-\frac{\Delta[\mathbf{A}]}{\Delta t} \propto [\mathbf{A}]$$

Since the rate of a reaction generally depends upon collision frequency, it stands to reason that as the concentration of **A** increases, the rate of reaction increases. Likewise, as the concentration of **A** decreases, the rate of reaction decreases. The expression for the rate of the reaction can be shown as follows:

$$\text{rate} = -\frac{\Delta[\mathbf{A}]}{\Delta t} \quad \text{or} \quad \text{rate} = k[\mathbf{A}]$$

The proportionality between the rate and $[\mathbf{A}]$ becomes an equal sign by the insertion of a constant (k). A **rate law** is an expression showing the relationship of the reaction rate to the concentrations of each reactant. The **specific rate constant** (k) is the proportionality constant relating the rate of the reaction to the concentrations of reactants. The rate law and the specific rate constant for any chemical reaction must be determined experimentally. The value of the rate constant is temperature dependent. A large value of the rate constant means that the reaction is relatively fast, while a small value of the rate constant means that the reaction is relatively slow.

Summary

- A rate law is an expression showing the relationship of the reaction rate to the concentrations of each reactant.
- The specific rate constant (k) is the proportionality constant relating the rate of the reaction to the concentrations of reactants.
- The rate law and the specific rate constant for any chemical reaction must be determined experimentally.

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10.9: Order of Reaction

Forest fires cause extensive damage; both plant and animal life are harmed. The severity of a forest fire depends on how much plant life is available to burn—the more available dry plant material, the more serious the fire, and the more rapidly it will spread.

Order of Reaction

In the reaction $\mathbf{A} \rightarrow \mathbf{B}$, the rate of the reaction is directly proportional to the concentration of $\mathbf{A}$ raised to the first power. That is to say, $[\mathbf{A}] = [\mathbf{A}]^1$. A **first-order reaction** is a reaction in which the rate is proportional to the concentration of only one reactant. As a first-order reaction proceeds, the rate of reaction decreases because the concentration of the reactant decreases (see figure below). The graph of concentration versus time is curved. The reaction rate $\left(\frac{\Delta[\mathrm{A}]}{\Delta t}\right)$ can be determined graphically by the slope of a tangent to the curve at any point. The rate of the reaction at the time shown with the red triangle is given by:

$$\text{rate} = -\frac{[\mathrm{A}]_{\text{final}} - [\mathrm{A}]_{\text{initial}}}{\Delta t} = -\frac{0.35\ \mathrm{M} - 0.63\ \mathrm{M}}{3.0\ \mathrm{s} - 1.0\ \mathrm{s}} = 0.14\ \mathrm{M/s}$$

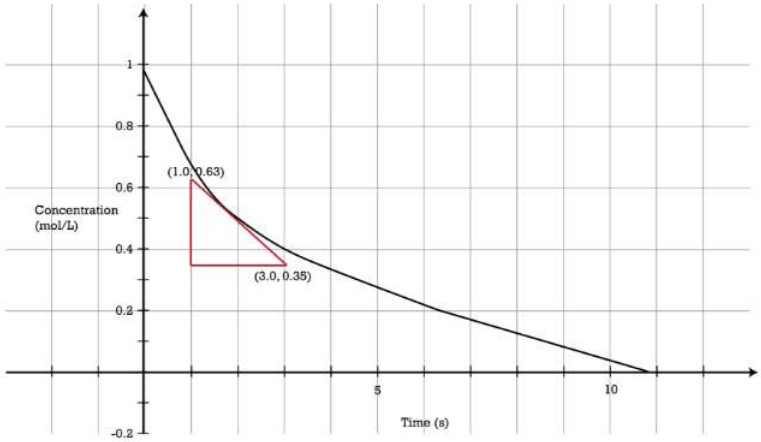


Figure 10.9.1: This graph shows how the concentration of a reactant changes as a reaction proceeds. The rate of the reaction is determined at any point by measuring the slope of a tangent to the curve. (CC BY-NC; CK-12)

The rates of some reactions depend on the concentrations of more than one reactant. Consider a reaction in which a molecule of $\mathbf{A}$ collides with a molecule of $\mathbf{B}$ to form product $\mathbf{C}$.

$$\mathbf{A} + \mathbf{B} \rightarrow \mathbf{C}$$

Doubling the concentration of $\mathbf{A}$ alone would double the reaction rate. Likewise, doubling the concentration of $\mathbf{B}$ alone would also double the rate. The rate law must reflect the rate dependence on both reactants.

$$\text{rate} = k\,[\mathrm{A}]\,[\mathrm{B}]$$

This reaction is said to be first order with respect to $\mathbf{A}$ and first order with respect to $\mathbf{B}$. Overall, it is a second-order reaction. The rate law and the order of a reaction must be determined experimentally.

Summary

- A first-order reaction is a reaction in which the rate is proportional to the concentration of only one reactant.
- As a first-order reaction proceeds, the rate of reaction decreases because the concentration of the reactant decreases (see figure below).

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10.10: Reversible Reaction

A solution of cobalt chloride in water is pink due to the presence of the solvated Co^{2+} ion. If sufficient HCl is added, the solution turns blue as the $CoCl_4^{2-}$ ion forms. The reaction can be shifted back to the pink form if more water is added to the solution.



Figure 10.10.1: Cobalt chloride in various stages of equilibrium with hydrochloric acid. (Public Domain; Chemicalinterest via wikipedia)

Chemical Reversibility

Up until this point, we have written the equations for chemical reactions in a way that would seem to indicate that all reactions proceed completely until all the reactants have been converted into products. In reality, a great many chemical reactions do not proceed entirely to completion. A **reversible reaction** is a reaction in which the conversion of reactants to products and the conversion of products to reactants occur simultaneously. One example of a reversible reaction is the reaction of hydrogen gas and iodine vapor to form hydrogen iodide. The forward and reverse reactions can be written as follows.

$$\text{Forward reaction: } \ H_2\,(g) + I_2\,(g) \rightarrow 2HI\,(g)$$

$$\text{Reverse reaction: } \ 2HI\,(g) \rightarrow H_2\,(g) + I_2\,(g)$$

In the forward reaction, hydrogen and iodine combine to form hydrogen iodide. In the reverse reaction, hydrogen iodide decomposes back into hydrogen and iodine. The two reactions can be combined into one equation by the use of a double arrow:

$$H_2\,(g) + I_2\,(g) \rightleftharpoons 2HI\,(g)$$

The double arrow is the indication that the reaction is reversible.

When hydrogen and iodine gases are mixed in a sealed container, they begin to react and form hydrogen iodide. At first, only the forward reaction occurs because no HI is present. As the forward reaction proceeds, it begins to slow down as the concentrations of the H_2 and the I_2 decrease. As soon as some HI has formed, it begins to decompose back into H_2 and I_2. The rate of the reverse reaction starts out slow because the concentration of HI is low. Gradually, the rate of the forward reaction decreases while the rate of the reverse reaction increases. Eventually the rate of combination of H_2 and I_2 to produce HI becomes equal to the rate of decomposition of HI into H_2 and I_2. When the rates of the forward and reverse reactions have become equal to one another, the reaction has achieved a state of balance.

Summary

- A reversible reaction is defined.

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10.11: Chemical Equilibrium

A tug of war involves two teams at the ends of a rope. The goal is to pull the other team over a line in the middle. At first, there is a great deal of tension on the rope, but no apparent movement. A bystander might think that there is nothing happening. In reality, there is a great deal of tension on the rope as the two teams pull in opposite directions at the same time.

Chemical Equilibrium

Hydrogen and iodine gases react to form hydrogen iodide, according to the following reaction:

$$\mathrm{H_2}\,(g) + \mathrm{I_2}\,(g) \rightleftharpoons 2\mathrm{HI}\,(g)$$

$$\textbf{Forward reaction:}\quad \mathrm{H_2}\,(g) + \mathrm{I_2}\,(g) \rightarrow 2\mathrm{HI}\,(g)$$

$$\textbf{Reverse reaction:}\quad 2\mathrm{HI}\,(g) \rightarrow \mathrm{H_2}\,(g) + \mathrm{I_2}\,(g)$$

Initially, only the forward reaction occurs because no $\mathbf{HI}$ is present. As soon as some $\mathbf{HI}$ has formed, it begins to decompose back into $\mathbf{H_2}$ and $\mathbf{I_2}$. Gradually, the rate of the forward reaction decreases while the rate of the reverse reaction increases. Eventually, the rate of combination of $\mathbf{H_2}$ and $\mathbf{I_2}$ to produce $\mathbf{HI}$ becomes equal to the rate of decomposition of $\mathbf{HI}$ into $\mathbf{H_2}$ and $\mathbf{I_2}$. When the rates of the forward and reverse reactions have become equal to one another, the reaction has achieved a state of balance. **Chemical equilibrium** is the state of a system in which the rate of the forward reaction is equal to the rate of the reverse reaction.

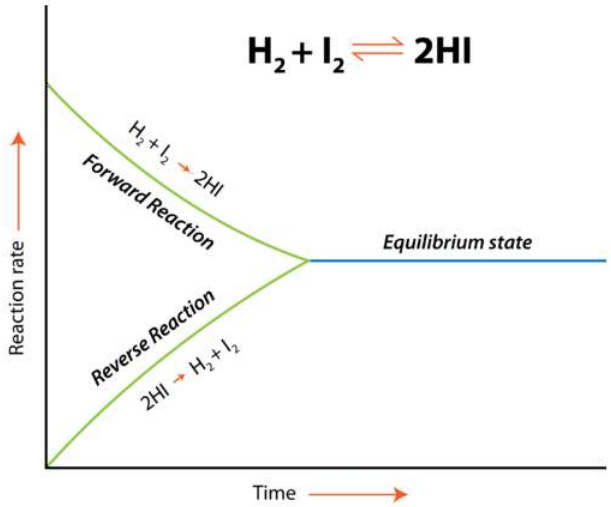


Figure **10.11.1**: Equilibrium in reaction: $\mathrm{H_2}\,(g) + \mathrm{I_2}\,(g) \rightleftharpoons 2\mathrm{HI}\,(g)$.

Chemical equilibrium can be attained whether the reaction begins with all reactants and no products, all products and no reactants, or some of both. The figure below shows changes in concentration of $\mathbf{H_2}$, $\mathbf{I_2}$, and $\mathbf{HI}$ for two different reactions. In the reaction depicted by the graph on the left (A), the reaction begins with only $\mathbf{H_2}$ and $\mathbf{I_2}$ present. There is no $\mathbf{HI}$ initially. As the reaction proceeds toward equilibrium, the concentrations of the $\mathbf{H_2}$ and $\mathbf{I_2}$ gradually decrease, while the concentration of the $\mathbf{HI}$ gradually increases. When the curve levels out and the concentrations all become constant, equilibrium has been reached. At equilibrium, concentrations of all substances are constant. In reaction B, the process begins with only $\mathbf{HI}$ and no $\mathbf{H_2}$ or $\mathbf{I_2}$. In this case, the concentration of $\mathbf{HI}$ gradually decreases while the concentrations of $\mathbf{H_2}$ and $\mathbf{I_2}$ gradually increase until equilibrium is again reached. Notice that in both cases, the relative position of equilibrium is the same, as shown by the relative concentrations of reactants and products. The concentration of $\mathbf{HI}$ at equilibrium is significantly higher than the concentrations of $\mathbf{H_2}$ and $\mathbf{I_2}$. This is true whether the reaction began with all reactants or all products. The position of equilibrium is a property of the particular reversible reaction and does not depend upon how equilibrium was achieved.

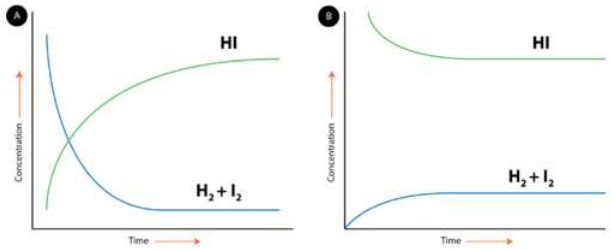


Figure **10.11.2**: Equilibrium between reactants and products.

Conditions for Equilibrium

It may be tempting to think that once equilibrium has been reached, the reaction stops. Chemical equilibrium is a dynamic process. The forward and reverse reactions continue to occur even after equilibrium has been reached. However, because the rates of the reactions are the same, there is no change in the relative concentrations of reactants and products for a reaction that is at equilibrium. The conditions and properties of a system at equilibrium are summarized below.

1. The system must be closed, meaning no substances can enter or leave the system.
2. Equilibrium is a dynamic process. Even though we don't necessarily see the reactions, both the forward and reverse reactions are taking place.
3. The rates of the forward and reverse reactions must be equal.
4. The amount of reactants and products do not have to be equal. However, after equilibrium is attained, the amounts of reactants and products will be constant.

The description of equilibrium in this concept refers primarily to equilibrium between reactants and products in a chemical reaction. Other types of equilibrium include phase equilibrium and solution equilibrium. A **phase equilibrium** occurs when a substance is in equilibrium between two states. For example, a stoppered flask of water attains equilibrium when the rate of evaporation is equal to the rate of condensation. A **solution equilibrium** occurs when a solid substance is in a saturated solution. At this point, the rate of dissolution is equal to the rate of recrystallization. Although these are all different types of transformations, most of the rules regarding equilibrium apply to any situation in which a process occurs reversibly.

Summary

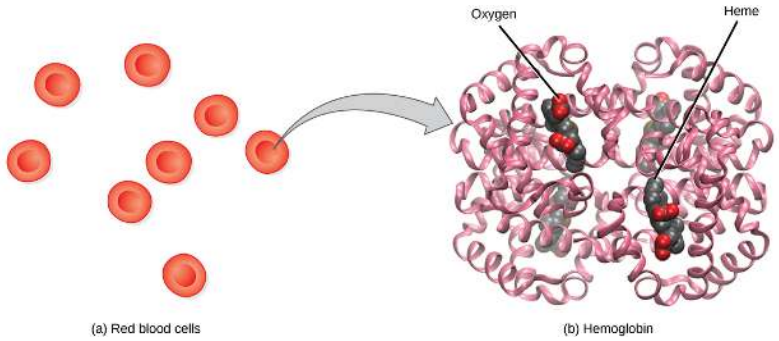
- Chemical equilibrium is the state of a system in which the rate of the forward reaction is equal to the rate of the reverse reaction.
- Conditions for chemical equilibrium are listed.
- A phase equilibrium occurs when a substance is in equilibrium between two states.
- A solution equilibrium occurs when a solid substance is in a saturated solution.

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10.12: Equilibrium Constant

Red blood cells transport oxygen to tissues so that they can function. In the absence of oxygen, cells cannot carry out their biochemical responsibilities. Oxygen moves to the cells attached to hemoglobin, a protein found in red blood cells.



The protein inside (a) red blood cells that carries oxygen to cells and carbon dioxide to the lungs is (b) hemoglobin. Hemoglobin is made up of four symmetrical subunits and four heme groups. Iron associated with the heme binds oxygen. It is the iron in hemoglobin that gives blood its red color. (CC_BY Openstax)

In cases of carbon monoxide poisoning, $\mathbf{CO}$ binds much more strongly to the hemoglobin, blocking oxygen attachment and lowering the amount of oxygen reaching the cells. Treatment involves the patient breathing pure oxygen to displace the carbon monoxide. The equilibrium reaction shown below illustrates the shift toward the right when excess oxygen is added to the system:

$$\mathbf{Hb(CO)_4}\,(aq) + \mathbf{4O_2}\,(g) \rightleftharpoons \mathbf{Hb(O_2)_4}\,(aq) + \mathbf{4CO}\,(g)$$

Equilibrium Constant

Consider the hypothetical reversible reaction in which reactants $\mathbf{A}$ and $\mathbf{B}$ react to form products $\mathbf{C}$ and $\mathbf{D}$. This equilibrium can be shown as demonstrated below, where the lower case letters represent the coefficients of each substance.

$$a\mathbf{A} + b\mathbf{B} \rightleftharpoons c\mathbf{C} + d\mathbf{D}$$

As we have established, the rates of the forward and reverse reactions are the same at equilibrium, and so the concentrations of all of the substances are constant. Since that is the case, it stands to reason that a ratio of the concentrations for any given reaction at equilibrium maintains a constant value. The **equilibrium constant** (K_{eq}) is the ratio of the mathematical product of the concentrations of the products of a reaction to the mathematical product of the concentrations of the reactants of the reaction. Each concentration is raised to the power of its coefficient in the balanced chemical equation. For the general reaction above, the equilibrium constant expression is written as follows:

$$K_{eq} = \frac{[\mathrm{C}]^c\,[\mathrm{D}]^d}{[\mathrm{A}]^a\,[\mathrm{B}]^b}$$

The concentrations of each substance, indicated by the square brackets around the formula, are measured in molarity units ($\mathbf{mol/L}$).

The value of the equilibrium constant for any reaction is only determined by experiment. As detailed in the previous section, the position of equilibrium for a given reaction does not depend on the starting concentrations, and so the value of the equilibrium constant is truly constant. It does, however, depend on the temperature of the reaction. This is because equilibrium is defined as a condition resulting from the rates of forward and reverse reactions being equal. If the temperature changes, the corresponding change in those reaction rates will alter the equilibrium constant. For any reaction in which a K_{eq} is given, the temperature should be specified.

Summary

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10.13: Calculations with Equilibrium Constants

Iron is an important component of red blood cells. Patients who have low iron will usually be anemic and have a lower than normal number of red blood cells. One way to assess serum iron concentration is with the use of Ferrozine, a complex organic molecule. Ferrozine forms a product with $\mathbf{Fe^{3+}}$, producing a pink color. In order to determine factors affecting the reaction, we need to measure the equilibrium constant. If the equilibrium does not lie far in the direction of products, precautions need to be taken when using this material to measure iron in serum.

Calculations with Equilibrium Constants

The general value of the equilibrium constant gives us information about whether the reactants or the products are favored at equilibrium. Since the product concentrations are in the numerator of the equilibrium expression, a $K_{eq} > 1$ means that the products are favored over the reactants. A $K_{eq} < 1$ means that the reactants are favored over the products.

Though it would often seem that the K_{eq} value would have various units depending on the values of the exponents in the expression, the general rule is that any units are dropped. All K_{eq} values will be reported as having no units.

Example 10.13.1

Equilibrium occurs when nitrogen monoxide gas reacts with oxygen gas to form nitrogen dioxide gas:

$$2NO\,(g) + O_2\,(g) \rightleftharpoons 2NO_2\,(g)$$

At equilibrium at $230°C$, the concentrations are measured to be $[NO] = 0.0542\ M$, $[O_2] = 0.127\ M$, and $[NO_2] = 15.5\ M$. Calculate the equilibrium constant at this temperature.

Solution:

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

Known

- $[NO] = 0.0542\ M$
- $[O_2] = 0.127\ M$
- $[NO_2] = 15.5\ M$

Unknown

The equilibrium expression is first written according to the general form in the text. The equilibrium values are substituted into the expression and the value calculated.

Step 2: Solve.

$$K_{eq} = \frac{[NO_2]^2}{[NO]^2\,[O_2]}$$

Substituting in the concentrations at equilibrium:

$$K_{eq} = \frac{(15.5)^2}{(0.0542)^2\,(0.127)} = 6.44 \times 10^5$$

Step 3: Think about your result.

The equilibrium concentration of the product NO_2 is significantly higher than the concentrations of the reactants NO and O_2. As a result, the K_{eq} value is much larger than 1, an indication that the product is favored at equilibrium.

The equilibrium expression only shows those substances whose concentrations are variable during the reaction. A pure solid or a pure liquid does not have a concentration that will vary during a reaction. Therefore, an equilibrium expression omits pure solids and liquids, and only shows the concentrations of gases and aqueous solutions. The decomposition of mercury (II) oxide can be shown by the following equation, followed by its equilibrium expression.

$$2HgO\,(s) \rightleftharpoons 2Hg\,(l) + O_2\,(g) \quad K_{eq} = [O_2]$$

The stoichiometry of an equation can also be used in a calculation of an equilibrium constant. At $40°C$, solid ammonium carbamate decomposes to ammonia and carbon dioxide gases.

$$NH_4CO_2NH_2\,(s) \rightleftharpoons 2NH_3\,(g) + CO_2\,(g)$$

At equilibrium, the $[CO_2]$ is found to be $4.71 \times 10^{-3}\ M$. Can the K_{eq} value be calculated from that information alone? Because the ammonium carbamate is a solid, it is not present in the equilibrium expression.

$$K_{eq} = [NH_3]^2\,[CO_2]$$

The stoichiometry of the chemical equation indicates that as the ammonium carbamate decomposes, $2\ mol$ of ammonia gas is produced for every $1\ mol$ of carbon dioxide. Therefore, at equilibrium, the concentration of the ammonia will be twice the concentration of carbon dioxide. So,

$$[NH_3] = 2 \times \left(4.71 \times 10^{-3}\right) = 9.42 \times 10^{-3}\ M$$

Substituting these values into the K_{eq} expression:

$$K_{eq} = \left(9.42 \times 10^{-3}\right)^2 \left(4.71 \times 10^{-3}\right) = 4.18 \times 10^{-7}$$

Using Equilibrium Constants

The equilibrium constants are known for a great many reactions. Hydrogen and bromine gases combine to form hydrogen bromide gas. At $730°C$, the equation and K_{eq} are given below.

$$H_2\,(g) + Br_2\,(g) \rightleftharpoons 2HBr\,(g) \qquad K_{eq} = 2.18 \times 10^6$$

A certain reaction is begun with only HBr. When the reaction mixture reaches equilibrium at $730°C$, the concentration of bromine gas is measured to be $0.00243\ M$. What is the concentration of the H_2 and the HBr at equilibrium?

Since the reaction begins with only HBr and the mole ratio of H_2 to Br_2 is 1:1, the concentration of H_2 at equilibrium is also $0.00243\ M$. The equilibrium expression can be rearranged to solve for the concentration of HBr at equilibrium:

$$K_{eq} = \frac{[HBr]^2}{[H_2]\,[Br_2]}$$

$$[HBr] = \sqrt{K_{eq}\,[H_2]\,[Br_2]}$$

$$= \sqrt{2.18 \times 10^6\,(0.00243)\,(0.00243)} = 3.59\ M$$

Since the value of the equilibrium constant is very high, the concentration of HBr is much greater than that of H_2 and Br_2 at equilibrium.

Summary

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10.14: Le Châtelier's Principle

There are some who enjoy going up in an airplane, strapping on a parachute, and diving out the door to free-fall before opening the chute, and dropping to the ground. This stressful activity (so they say) relieves the stress of everyday life. The release of adrenaline caused by this stressful behavior is said to promote a mood enhancement that helps you deal better with other stresses in your daily life.

Le Chatelier's Principle

Chemical equilibrium was studied by French chemist Henri Le Chatelier (1850-1936) and his description of how a system responds to a stress on equilibrium has become known as **Le Chatelier's principle:** When a chemical system that is at equilibrium is disturbed by a stress, the system will respond in order to relieve the stress. Stresses to a chemical system involve changes in the concentration of reactants or products, changes in the temperature of the system, or changes in the pressure of the system. We will discuss each of these stresses separately. The change to the equilibrium position in every case is either a favoring of the forward reaction or a favoring of the reverse reaction. When the forward reaction is favored, the concentrations of products increase, while the concentrations of reactants decrease. When the reverse reaction is favored, the concentrations of products decrease, while the concentrations of reactants increase.

Le Chatelier's Principle

Table 10.14.1

Original Equilibrium	Favored Reaction	Result
$\mathbf{A} \rightleftharpoons \mathbf{B}$	Forward: $\mathbf{A} \rightarrow \mathbf{B}$	[A] decreases; [B] increases
$\mathbf{A} \rightleftharpoons \mathbf{B}$	Reverse: $\mathbf{A} \leftarrow \mathbf{B}$	[A] increases; [B] decreases



Figure **10.14.1**: Henri Le Chatelier.

Summary

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10.15: Ion-Product of Water

At one time, you could take the little caps off the top of a car battery and check the condition of the sulfuric acid inside. If it got low, you could add more acid. But, sulfuric acid is hazardous stuff, so the batteries are now sealed to protect people. Because of the acid's dangerous nature, it is not a good idea to cut into a battery to see what it looks like—you could get acid burns.

The Ion-Product of Water

The **self-ionization of water** (the process in which water ionizes to hydronium ions and hydroxide ions) occurs to a very limited extent. When two molecules of water collide, there can be a transfer of a hydrogen ion from one molecule to the other. The products are a positively charged hydronium ion and a negatively charged hydroxide ion.

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

We often use the simplified form of the reaction:

$$\mathrm{H_2O}\,(l) \rightleftharpoons \mathrm{H^+}\,(aq) + \mathrm{OH^-}\,(aq)$$

The equilibrium constant for the self-ionization of water is referred to as the ion-product for water and is given the symbol K_w.

$$K_\mathrm{w} = [\mathrm{H^+}]\,[\mathrm{OH^-}]$$

The **ion-product of water** (K_w) is the mathematical product of the concentration of hydrogen ions and hydroxide ions. Note that $\mathrm{H_2O}$ is not included in the ion-product expression because it is a pure liquid. The value of K_w is very small, in accordance with a reaction that favors the reactants. At $25°\mathrm{C}$, the experimentally determined value of K_w in pure water is 1.0×10^{-14}.

$$K_\mathrm{w} = [\mathrm{H^+}]\,[\mathrm{OH^-}] = 1.0 \times 10^{-14}$$

In pure water, the concentrations of hydrogen and hydroxide ions are equal to one another. Pure water or any other aqueous solution in which this ratio holds is said to be neutral. To find the molarity of each ion, the square root of K_w is taken.

$$[\mathrm{H_+}] = [\mathrm{OH^-}] = 1.0 \times 10^{-7}$$

An **acidic solution** is a solution in which the concentration of hydrogen ions is greater than the concentration of hydroxide ions. For example, hydrogen chloride ionizes to produce $\mathrm{H^+}$ and $\mathrm{Cl^-}$ ions upon dissolving in water.

$$\mathrm{HCl}\,(g) \rightarrow \mathrm{H^+}\,(aq) + \mathrm{Cl^-}\,(aq)$$

This increases the concentration of $\mathrm{H^+}$ ions in the solution. According to Le Chatelier's principle, the equilibrium represented by $\mathrm{H_2O}\,(l) \rightleftharpoons \mathrm{H^+}\,(aq) + \mathrm{OH^-}\,(aq)$ is forced to the left, towards the reactant. As a result, the concentration of the hydroxide ion decreases.

A **basic solution** is a solution in which the concentration of hydroxide ions is greater than the concentration of hydrogen ions. Solid potassium hydroxide dissociates in water to yield potassium ions and hydroxide ions.

$$\mathrm{KOH}\,(s) \rightarrow \mathrm{K^+}\,(aq) + \mathrm{OH^-}\,(aq)$$

The increase in concentration of the $\mathrm{OH^-}$ ions causes a decrease in the concentration of the $\mathrm{H^+}$ ions and the ion-product of $[\mathrm{H^+}]\,[\mathrm{OH^-}]$ remains constant.

Example 10.15.1

Hydrochloric acid (HCl) is a strong acid, meaning it is 100% ionized in solution. What is the $[\mathrm{H^+}]$ and the $[\mathrm{OH^-}]$ in a solution of $2.0 \times 10^{-3}\ \mathrm{M\ HCl}$?

Solution

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

Known

- $[\mathrm{HCl}] = 2.0 \times 10^{-3}\ \mathrm{M}$
- $K_\mathrm{w} = 1.0 \times 10^{-14}$

Unknown

- $[H^+] = ?\ M$
- $[OH^-] = ?\ M$

Because HCl is 100% ionized, the concentration of H^+ ions in solution will be equal to the original concentration of HCl. Each HCl molecule that was originally present ionizes into one H^+ ion and one Cl^- ion. The concentration of OH^- can then be determined from the $[H^+]$ and K_w.

Step 2: Solve.

$$[H^+] = 2.0 \times 10^{-3}\ M$$

$$K_w = [H^+]\,[OH^-] = 1.0 \times 10^{-14}$$

$$[OH^-] = \frac{K_w}{[H^+]} = \frac{1.0 \times 10^{-14}}{2.0 \times 10^{-3}} = 5.0 \times 10^{-12}\ M$$

Step 3: Think about your result.

The $[H^+]$ is much higher than the $[OH^-]$ because the solution is acidic. As with other equilibrium constants, the unit for K_w is customarily omitted.

Summary

- The self-ionization of water is described and an ionization constant for the process is stated.
- Acidic and basic solutions are defined.
- Calculations using K_w are illustrated.

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10.16: The pH Scale

Grapefruit juice has a pH of somewhere between 2.9 and 3.3, depending on the specific product. Excessive exposure to this juice can cause erosion of tooth enamel and can lead to tooth damage. The acids in grapefruit juice are carbon-based, with citric acid being one of the major constituents. This compound has three ionizable hydrogens on each molecule which contribute to the relatively low pH of the juice. Another component of grapefruit juice is malic acid, containing two ionizable hydrogens per molecule.

The pH Scale

Expressing the acidity of a solution by using the molarity of the hydrogen ion is cumbersome because the quantities are generally very small. Danish scientist Søren Sørensen (1868-1939) proposed an easier system for indicating the concentration of $\mathbf{H^+}$ called the pH scale. The letters pH stand for the power of the hydrogen ion. The **pH** of a solution is the negative logarithm of the hydrogen-ion concentration:

$$\mathbf{pH = -\log\ [H^+]}$$

In pure water or a neutral solution, the $\mathbf{[H^+] = 1.0 \times 10^{-7}\ M}$. Substituting into the pH expression:

$$\mathbf{pH = -\log\left[1.0 \times 10^{-7}\right] = -(-7.00) = 7.00}$$

The pH of pure water or any neutral solution is thus 7.00. For recording purposes, the numbers to the right of the decimal point in the pH value are the significant figures. Since $\mathbf{1.0 \times 10^{-7}}$ has two significant figures, the pH can be reported as 7.00.

A logarithmic scale condenses the range of acidity to numbers that are easy to use. Consider a solution with $\mathbf{[H^+] = 1.0 \times 10^{-4}\ M}$. That is a hydrogen-ion concentration that is 1000 times higher than the concentration in pure water. The pH of such a solution is 4.00, a difference of just 3 pH units. Notice that when the $\mathbf{[H^+]}$ is written in scientific notation and the coefficient is 1, the pH is simply the exponent with the sign changed. The pH of a solution with $\mathbf{[H^+] = 1 \times 10^{-2}\ M}$ is 2 and the pH of a solution with $\mathbf{[H^+] = 1 \times 10^{-10}\ M}$ is 10.

As we saw earlier, a solution with $\mathbf{[H^+]}$ higher than $\mathbf{1.0 \times 10^{-7}}$ is acidic, while a solution with $\mathbf{[H^+]}$ lower than $\mathbf{1.0 \times 10^{-7}}$ is basic. Consequently, solutions with a pH of less than 7 are acidic, while those with a pH higher than 7 are basic. Figure **10.16.1** illustrates this relationship, along with some examples of various solutions.

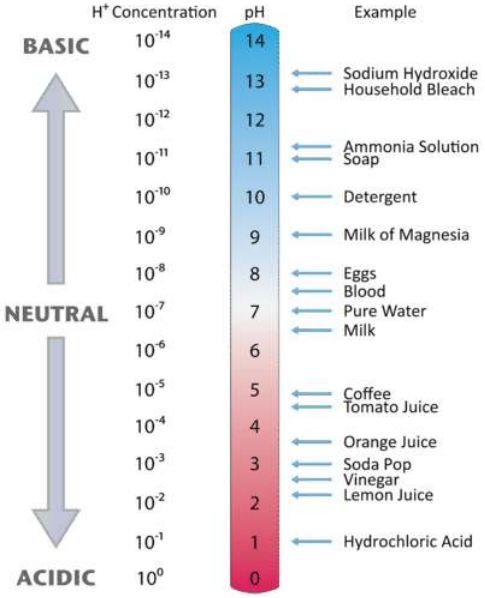


Figure **10.16.1**: The pH values for several common materials. (CC BY-NC; CK-12)

Summary

- The pH of a solution is the negative logarithm of the hydrogen-ion concentration.
- Solutions with a pH of less than 7 are acidic, while those with a pH higher than 7 are basic.
- pH values for several common materials are listed.

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10.17: Calculating pH of Acids and Bases

It's not uncommon to see a tropical fish tank in homes or businesses. These brightly-colored creatures are relaxing to watch, but do require a certain amount of maintenance in order for them to survive. Tap water is usually too alkaline when it comes out of the faucet, so some adjustments need to be made. The pH of the water will change over time while it is in the tank, which means it needs to be tested every so often. Any fish tank caretaker has a chance to be a chemist for their fish!

Calculating pH of Acids and Bases

Calculation of pH is simple when there is a $1 \times 10^{\text{power}}$ problem. However, in real life, this is rarely the situation. If the coefficient is not equal to 1, a calculator must be used to find the pH. For example, the pH of a solution with $[\text{H}^+] = 2.3 \times 10^{-5}\ \text{M}$ can be found as shown below.

$$\text{pH} = -\log\left[2.3 \times 10^{-5}\right] = 4.64$$

When the pH of a solution is known, the concentration of the hydrogen ion can be calculated. The inverse of the logarithm (or antilog) is the 10^x key on a calculator.

$$[\text{H}^+] = 10^{-\text{pH}}$$

For example, suppose that you have a solution with a pH of 9.14. To find the $[\text{H}^+]$ use the 10^x key.

$$[\text{H}^+] = 10^{-\text{pH}} = 10^{-9.14} = 7.24 \times 10^{-10}\ \text{M}$$

Hydroxide Ion Concentration and pH

As we saw earlier, the hydroxide ion concentration of any aqueous solution is related to the hydrogen ion concentration through the value of K_w. We can use that relationship to calculate the pH of a solution of a base.

Example 10.17.1

Sodium hydroxide is a strong base. Find the pH of a solution prepared by dissolving $1.0\ \text{g}$ of NaOH into enough water to make $1.0\ \text{L}$ of solution.

Solution

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

Known

- Mass $\text{NaOH} = 1.0\ \text{g}$
- Molar mass $\text{NaOH} = 40.00\ \text{g/mol}$
- Volume solution $= 1.0\ \text{L}$
- $K_\text{w} = 1.0 \times 10^{-14}$

Unknown

First, convert the mass of NaOH to moles. Second, calculate the molarity of the NaOH solution. Because NaOH is a strong base and is soluble, the $[\text{OH}^-]$ will be equal to the concentration of the NaOH. Third, use K_w to calculate the $[\text{H}^+]$ in the solution. Lastly, calculate the pH.

Step 2: Solve.

$$1.00\ \cancel{\text{g NaOH}} \times \frac{1\ \text{mol NaOH}}{40.00\ \cancel{\text{g NaOH}}} = 0.025\ \text{mol NaOH}$$

$$\text{Molarity} = \frac{0.025\ \text{mol NaOH}}{1.00\ \text{L}} = 0.025\ \text{M NaOH} = 0.025\ \text{M OH}^-$$

$$[\text{H}^+] = \frac{K_\text{w}}{[\text{OH}^-]} = \frac{1.0 \times 10^{-14}}{0.025\ \text{M}} = 4.0 \times 10^{-13}\ \text{M}$$

$$\text{pH} = -\log[\text{H}^+] = -\log\left(4.0 \times 10^{-13}\right) = 12.40$$

Step 3: Think about your result.

The solution is basic and so its pH is greater than 7. The reported pH is rounded to two decimal places because the original mass and volume has two significant figures.

Summary

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10.18: The pOH Concept

Soap Lake has a long history as a healing place. Indian tribes would put aside their rivalries when they came to the lake to enjoy the high mineral content of the water. In the days before good antibiotics, thousands of visitors would come and enjoy the soothing waters of the lake. Soap Lake is alkaline, with water quality though to be similar to that of the moons of the planet Jupiter.

The pOH Concept

As with the hydrogen-ion concentration, the concentration of the hydroxide ion can be expressed logarithmically by the pOH. The **pOH** of a solution is the negative logarithm of the hydroxide-ion concentration:

$$\text{pOH} = -\log\left[\text{OH}^-\right]$$

The pH of a solution can be related to the pOH. Consider a solution with a pH $= 4.0$. The $[\text{H}^+]$ of the solution would be 1.0×10^{-4} M. Dividing K_w by this yields a $[\text{OH}^-]$ of 1.0×10^{-10} M. Finally the pOH of the solution equals $-\log\left(1.0 \times 10^{-10}\right) = 10$. This example illustrates the following relationship.

$$\text{pH} + \text{pOH} = 14$$

The pOH scale is similar to the pH scale in that a pOH of 7 is indicative of a neutral solution. A basic solution has a pOH less than 7, while an acidic solution has a pOH of greater than 7. The pOH is convenient to use when finding the hydroxide ion concentration from a solution with a known pH.

Example 10.18.1

Find the hydroxide concentration of a solution with a pH of 4.42.

Solution

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

Known

- pH $= 4.42$
- pH + pOH $= 14$

Unknown

First, the pOH is calculated, followed by the $[\text{OH}^-]$.

Step 2: Solve.

$$\text{pOH} = 14 - \text{pH} = 14 - 4.42 = 9.58$$
$$\left[\text{OH}^-\right] = 10^{-\text{pOH}} = 10^{-9.58} = 2.6 \times 10^{-10}\ \text{M}$$

Step 3: Think about your result.

The pH is that of an acidic solution, and the resulting hydroxide-ion concentration is less than 1×10^{-7} M. The answer has two significant figures because the given pH has two decimal places.

The diagram below shows all of the interrelationships between $[\text{H}^+]$, $[\text{OH}^-]$, pH, and pOH.

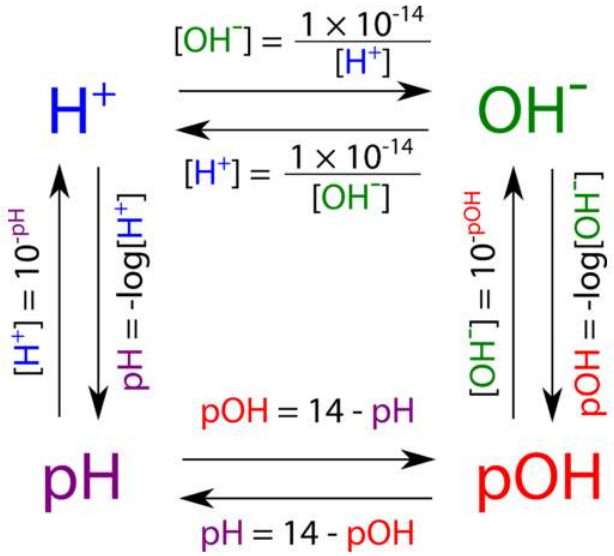


Figure 10.18.1: Relationships between hydrogen ion concentration, hydroxide ion concentration, pH and pOH. (CC BY-NC; CK-12)

Summary

- The pOH of a solution is the negative logarithm of the hydroxide-ion concentration.
- Calculations involving pOH are described.

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10.19: Strong and Weak Acids and Acid Ionization Constant (K a)

The etching of glass is a slow process that can produce beautiful artwork. Traditionally, the glass has been treated with dilute hydrofluoric acid which gradually dissolves the glass under it. Parts of the piece that should not be etched are covered with wax or some other non-reactive material. In more recent times, compounds such as ammonium bifluoride have been used. Whichever chemical is employed, the artist must be very careful not to get any on their skin.

Strong and Weak Acids and Acid Ionization Constant

Acids are classified as either strong or weak, based on their ionization in water. A **strong acid** is an acid which is completely ionized in an aqueous solution. Hydrogen chloride (HCl) ionizes completely into hydrogen ions and chloride ions in water.

$$\mathrm{HCl}\,(g) \rightarrow \mathrm{H^+}\,(aq) + \mathrm{Cl^-}\,(aq)$$

A **weak acid** is an acid that ionizes only slightly in an aqueous solution. Acetic acid (found in vinegar) is a very common weak acid. Its ionization is shown below.

$$\mathrm{CH_3COOH}\,(aq) \rightleftharpoons \mathrm{H^+}\,(aq) + \mathrm{CH_3COO^-}\,(aq)$$

The ionization of acetic acid is incomplete, and so the equation is shown with a double arrow. The extent of ionization of weak acids varies, but is generally less than 10%. A $0.10\ \mathrm{M}$ solution of acetic acid is only about 1.3% ionized, meaning that the equilibrium strongly favors the reactants.

Weak acids, like strong acids, ionize to yield the $\mathrm{H^+}$ ion and a conjugate base. Because HCl is a strong acid, its conjugate base ($\mathrm{Cl^-}$) is extremely weak. The chloride ion is incapable of accepting the $\mathrm{H^+}$ ion and becoming HCl again. In general, the stronger the acid, the weaker its conjugate base. Likewise, the weaker the acid, the stronger its conjugate base.

Table 10.19.1: Relative Strengths of Acids and their Conjugate Bases

Acid	Conjugate Base
Strong Acids	
HCl (hydrochloric acid) (strongest)	$\mathrm{Cl^-}$ (chloride ion) (weakest)
$\mathrm{H_2SO_4}$ (sulfuric acid)	$\mathrm{HSO_4^-}$ (hydrogen sulfate ion)
$\mathrm{HNO_3}$ (nitric acid)	$\mathrm{NO_3^-}$ (nitrate ion)
Weak Acids	
$\mathrm{H_3PO_4}$ (phosphoric acid)	$\mathrm{H_2PO_4^-}$ (dihydrogen phosphate ion)
$\mathrm{CH_3COOH}$ (acetic acid)	$\mathrm{CH_3COO^-}$ (acetate ion)
$\mathrm{H_2CO_3}$ (carbonic acid)	$\mathrm{HCO_3^-}$ (hydrogen carbonate ion)
HCN (hydrocyanic acid) (weakest)	$\mathrm{CN^-}$ (cyanide ion) (strongest)

Strong acids are 100% ionized in solution. Weak acids are only slightly ionized. Phosphoric acid is stronger than acetic acid, and so is ionized to a greater extent. Acetic acid is stronger than carbonic acid, and so on.

The Acid Ionization Constant, K_a

The ionization for a general weak acid, HA, can be written as follows:

$$\mathrm{HA}\,(aq) \rightarrow \mathrm{H^+}\,(aq) + \mathrm{A^-}\,(aq)$$

Because the acid is weak, an equilibrium expression can be written. An **acid ionization constant** (K_a) is the equilibrium constant for the ionization of an acid.

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

The acid ionization represents the fraction of the original acid that has been ionized in solution. Therefore, the numerical value of K_a is a reflection of the strength of the acid. Weak acids with relatively higher K_a values are stronger than acids with relatively lower K_a values. Because strong acids are essentially **100%** ionized, the concentration of the acid in the denominator is nearly zero and the K_a value approaches infinity. For this reason, K_a values are generally reported for weak acids only.

The table below is a listing of acid ionization constants for several acids. Note that polyprotic acids have a distinct ionization constant for each ionization step, with each successive ionization constant being smaller than the previous one.

Table **10.19.2**: Acid Ionization Constants at **25°C**

Name of Acid	Ionization Equation	K_a
Sulfuric acid	$H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$ $HSO_4 \rightleftharpoons H^+ + SO_4^{2-}$	very large 1.3×10^{-2}
Oxalic acid	$H_2C_2O_4 \rightleftharpoons H^+ + HC_2O_4^-$ $HC_2O_4 \rightleftharpoons H^+ + C_2O_4^{2-}$	6.5×10^{-2} 6.1×10^{-5}
Phosphoric acid	$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^-$ $H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2--}$ $HPO_4^{2-} \rightleftharpoons H^+ + PO_4^{3-}$	7.5×10^{-3} 6.2×10^{-8} 4.8×10^{-13}
Hydrofluoric acid	$HF \rightleftharpoons H^+ + F^-$	7.1×10^{-4}
Nitrous acid	$HNO_2 \rightleftharpoons H^+ + NO_2^-$	4.5×10^{-4}
Benzoic acid	$C_6H_5COOH \rightleftharpoons H^+ + C_6H_5COO^-$	6.5×10^{-5}
Acetic acid	$CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$	1.8×10^{-5}
Carbonic acid	$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$ $HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$	4.2×10^{-7} 4.8×10^{-11}
Hydrocyanic acid	$HCN \rightleftharpoons H^+ + CN^-$	4.9×10^{-10}

Summary

- A strong acid is an acid which is completely ionized in an aqueous solution.
- A weak acid is an acid that ionizes only slightly in an aqueous solution.
- The acid ionization constant (K_a) is defined.

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10.20: Strong and Weak Bases and Base Ionization Constant (K b)

All the complex electronics and apparatuses in a space shuttle generate heat, as do the astronauts. The shuttles have a complex arrangement of systems to dissipate that heat into outer space. One of the components of this system is a series of coils filled with ammonia that are located on the outside of the shuttle. Ammonia absorbs the heat and then releases it into space as the gas circulates through the coils. This approach is both inexpensive and effective.

Strong and Weak Bases and Base Ionization Constant, K_b

As with acids, bases can either be strong or weak, depending on the extent of their ionization. A **strong base** is a base that ionizes completely in an aqueous solution. The most common strong bases are soluble metal hydroxide compounds such as potassium hydroxide. Some metal hydroxides are not as strong, simply because they are not as soluble. Calcium hydroxide is only slightly soluble in water, but the portion that does dissolve also dissociates into ions.

A **weak base** is a base that ionizes only slightly in an aqueous solution. Recall that a base can be defined as a substance that accepts a hydrogen ion from another substance. When a weak base such as ammonia is dissolved in water, it accepts an H^+ ion from water, forming the hydroxide ion and the conjugate acid of the base, the ammonium ion.

$$NH_3\,(aq) + H_2O\,(l) \rightleftharpoons NH_4{}^+\,(aq) + OH^-\,(aq)$$

The equilibrium greatly favors the reactants and the extent of ionization of the ammonia molecule is very small.

An equilibrium expression can be written for the reactions of weak bases with water. Because the concentration of water is extremely large and virtually constant, the water is not included in the expression. A **base ionization constant** (K_b) is the equilibrium constant for the ionization of a base. For ammonia, the expression is:

$$K_b = \frac{[NH_4{}^+]\,[OH^-]}{[NH_3]}$$

The numerical value of K_b is a reflection of the strength of the base. Weak bases with relatively high K_b values are stronger than bases with relatively low K_b values. The table below is a listing of base ionization constants for several weak bases.

Table 10.20.1: Base Ionization Constants at 25°C

Name of Base	Ionization Equation	K_b
Methylamine	$CH_3NH_2 + H_2O \rightleftharpoons CH_3NH_3{}^+ + OH^-$	5.6×10^{-4}
Ammonia	$NH_3 + H_2O \rightleftharpoons NH_4{}^+ + OH^-$	1.8×10^{-5}
Pyridine	$C_5H_5N + H_2O \rightleftharpoons C_5H_5NH^+ + OH^-$	1.7×10^{-9}
Acetate ion	$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$	5.6×10^{-10}
Fluoride ion	$F^- + H_2O \rightleftharpoons HF + OH^-$	1.4×10^{-11}
Urea	$H_2NCONH_2 + H_2O \rightleftharpoons H_2NCONH_3{}^+ + OH^-$	1.5×10^{-14}

Notice that the conjugate base of a weak acid is also a strong base. For example, the acetate ion has a small tendency to accept a hydrogen ion from water to form acetic acid and the hydroxide ion.

Summary

- A strong base is a base that ionizes completely in an aqueous solution.
- A weak base is a base that ionizes only slightly in an aqueous solution.
- A base ionization constant (K_b) is the equilibrium constant for the ionization of a base.
- The conjugate base of a weak acid is also a strong base.

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10.21: Solubility Product Constant (K sp)

At one time, a major analytical technique was gravimetric analysis. Gravimetric analysis involves an ion being precipitated out of solution, purified, and weighed to determine the amount of that ion in the original material. As an example, measurement of $\mathrm{Ca^{2+}}$ involved dissolving the sample in water, precipitating the calcium as calcium oxalate, purifying the precipitate, drying it, and weighing the final product. Although this approach can be very accurate (atomic weights for many elements were determined this way), the process is slow, tedious, and prone to a number of errors in technique. Newer methods are now available that measure minute amounts of calcium ions in solution without the long, involved gravimetric approach.

Solubility Product Constant

Ionic compounds have widely differing solubilities. Sodium chloride has a solubility of about $\mathrm{360\ g}$ per liter of water at $\mathrm{25°C}$. Salts of alkali metals tend to be quite soluble. On the other end of the spectrum, the solubility of zinc hydroxide is only $\mathrm{4.2 \times 10^{-4} g/L}$ of water at the same temperature. Many ionic compounds containing hydroxide are relatively insoluble.

Most ionic compounds that are considered to be insoluble will still dissolve to a small extent in water. These "mostly insoluble" compounds are considered to be strong electrolytes, because the portion of the compound that dissolves also dissociates. As an example, silver chloride dissociates to a small extent into silver ions and chloride ions upon being added to water.

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

The process is written as an equilibrium because the dissociation occurs only to a small extent. Therefore, an equilibrium expression can be written for the process. Keep in mind that the solid silver chloride does not have a variable concentration, and so is not included in the expression.

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

This equilibrium constant is called the **solubility product constant** (K_{sp}) and is equal to the mathematical product of the ions each raised to the power of the coefficient of the ion in the dissociation equation.

The stoichiometry of the formula of the ionic compound dictates the form of the K_{sp} expression. For example, the formula of calcium phosphate is $\mathrm{Ca_3(PO_4)_2}$. The dissociation equation and K_{sp} expression are shown below:

$$\mathrm{Ca_3(PO_4)_2}\,(s) \rightleftharpoons \mathrm{3Ca^{2+}}\,(aq) + \mathrm{2PO_4^{3-}}\,(aq) \quad K_{\mathrm{sp}} = [\mathrm{Ca^{2+}}]^3\,[\mathrm{PO_4^{3-}}]^2$$

The table below lists solubility product constants for some common nearly insoluble ionic compounds.

Solubility Product Constants $(\mathrm{25°C})$

Table 10.21.1: Solubility Product Constants $(\mathrm{25°C})$

Compound	K_{sp}	Compound	K_{sp}
AgBr	$\mathrm{5.0 \times 10^{-13}}$	CuS	$\mathrm{8.0 \times 10^{-37}}$
AgCl	$\mathrm{1.8 \times 10^{-10}}$	$\mathrm{Fe(OH)_2}$	$\mathrm{7.9 \times 10^{-16}}$
$\mathrm{Al(OH)_3}$	$\mathrm{3.0 \times 10^{-34}}$	$\mathrm{Mg(OH)_2}$	$\mathrm{7.1 \times 10^{-12}}$
$\mathrm{BaCO_3}$	$\mathrm{5.0 \times 10^{-9}}$	$\mathrm{PbCl_2}$	$\mathrm{1.7 \times 10^{-5}}$
$\mathrm{BaSO_4}$	$\mathrm{1.1 \times 10^{-10}}$	$\mathrm{PbCO_3}$	$\mathrm{7.4 \times 10^{-14}}$
$\mathrm{CaCO_3}$	$\mathrm{4.5 \times 10^{-9}}$	$\mathrm{PbI_2}$	$\mathrm{7.1 \times 10^{-9}}$
$\mathrm{Ca(OH)_2}$	$\mathrm{6.5 \times 10^{-6}}$	$\mathrm{PbSO_4}$	$\mathrm{6.3 \times 10^{-7}}$
$\mathrm{Ca_3(PO_4)_2}$	$\mathrm{1.2 \times 10^{-26}}$	$\mathrm{Zn(OH)_2}$	$\mathrm{3.0 \times 10^{-16}}$
$\mathrm{CaSO_4}$	$\mathrm{2.4 \times 10^{-5}}$	ZnS	$\mathrm{3.0 \times 10^{-23}}$

Summary

- The solubility product constant is equal to the mathematical product of ions each raised to the power of their coefficients in a dissociation equation.
- Calculations using solubility product constants are illustrated.

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10.22: Conversion of Solubility to K sp

Baking soda (sodium bicarbonate) is prepared by bubbling carbon dioxide gas through a solution of ammonia and sodium chloride. Ammonium carbonate is first formed, which then reacts with the $\mathbf{NaCl}$ to form sodium bicarbonate and ammonium chloride. The sodium bicarbonate is less soluble than the other materials, so it will precipitate out of solution.

Conversion of Solubility to K_{sp}

Solubility is normally expressed in $\mathbf{g/L}$ of saturated solution. However, solubility can also be expressed in moles per liter. Molar solubility is the number of moles of solute in one liter of saturated solution. In other words, the molar solubility of a given compound represents the highest molarity solution that is possible for that compound. The molar mass of a compound is the conversion factor between solubility and molar solubility. Given that the solubility of $\mathbf{Zn(OH)_2}$ is $\mathbf{4.2 \times 10^{-4}\ g/L}$, the molar solubility can be calculated as shown below:

$$\frac{4.2 \times 10^{-4}\ \cancel{g}}{\text{L}} \times \frac{1\ \text{mol}}{99.41\ \cancel{g}} = 4.2 \times 10^{-6}\ \text{mol/L (M)}$$

Solubility data can be used to calculate the K_{sp} for a given compound. The following steps need to be taken.

1. Convert from solubility to molar solubility.
2. Use the dissociation equation to determine the concentration of each of the ions in $\mathbf{mol/L}$.
3. Apply the K_{sp} equation.

Example **10.22.1**

The solubility of lead (II) fluoride is found experimentally to be $\mathbf{0.533\ g/L}$. Calculate the K_{sp} for lead (II) fluoride.

Solution

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

Known

- Solubility of $\mathbf{PbF_2} = 0.533\ \mathbf{g/L}$
- Molar mass $= 245.20\ \mathbf{g/mol}$

Unknown

The dissociation equation for $\mathbf{PbF_2}$ and the corresponding K_{sp} expression:

$$\mathrm{PbF_2}\,(s) \rightleftharpoons \mathrm{Pb^{2+}}\,(aq) + 2\mathrm{F^-}\,(aq) \quad K_{sp} = \left[\mathrm{Pb^{2+}}\right]\left[\mathrm{F^-}\right]^2$$

The steps above will be followed to calculate the K_{sp} for $\mathbf{PbF_2}$.

Step 2: Solve.

$$\text{molar solubility} = \frac{0.533\ \cancel{g}}{\text{L}} \times \frac{1\ \text{mol}}{245.20\ \cancel{g}} = 2.17 \times 10^{-3}\ \text{M}$$

The dissociation equation shows that for every mole of $\mathbf{PbF_2}$ that dissociates, $\mathbf{1\ mol}$ of $\mathbf{Pb^{2+}}$ and $\mathbf{2\ mol}$ of $\mathbf{F^-}$ are produced. Therefore, at equilibrium, the concentrations of the ions are:

$$\left[\mathrm{Pb^{2+}}\right] = 2.17 \times 10^{-3}\ \text{M} \text{ and } \left[\mathrm{F^-}\right] = 2 \times 2.17 \times 10^{-3} = 4.35 \times 10^{-3}\ \text{M}$$

Substitute into the expression and solve for the K_{sp}.

$$K_{sp} = \left(2.17 \times 10^{-3}\right)\left(4.35 \times 10^{-3}\right)^2 = 4.11 \times 10^{-8}$$

Step 3: Think about your result.

The solubility product constant is significantly less than 1 for a nearly insoluble compound such as $\mathbf{PbF_2}$.

Summary

- Molar solubility calculations are described.
- Calculations of K_{sp} using molar solubility are described.

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10.23: Predicting Precipitates

The invention of the x-ray machine radically improved medical diagnosis and treatment. For the first time, it was possible to see inside a person's body to detect broken bones, tumors, obstructions, and other problems. Barium sulfate is often used to examine patients with problems of the esophagus, stomach, and intestines. This insoluble compound coats the inside of the tissues and absorbs x-rays, allowing a clear picture of the interior structure of these organs.

Predicting Precipitates

Knowledge of K_{sp} values will allow you to be able to predict whether or not a precipitate will form when two solutions are mixed together. For example, suppose that a known solution of barium chloride is mixed with a known solution of sodium sulfate. Barium sulfate is a mostly insoluble compound, and so could potentially precipitate from the mixture. However, it is first necessary to calculate the **ion product**, $[Ba^{2+}]\,[SO_4{}^{2-}]$, for the solution. If the value of the ion product is less than the value of the K_{sp}, then the solution will remain unsaturated; no precipitate will form because the concentrations are not high enough to begin the precipitation process. If the value of the ion product is greater than the value of the K_{sp}, then a precipitate will form. The formation of the precipitate lowers the concentration of each of the ions until the ion product is exactly equal to the K_{sp}, at which point precipitation ceases.



Figure 10.23.1: Barium sulfate is used as a component of white pigment for paints and as an agent in certain x-ray imaging processes.

Example 10.23.1

Will a precipitate of barium sulfate form when $10.0\ \text{mL}$ of $0.0050\ \text{M}\ BaCl_2$ is mixed with $20.0\ \text{mL}$ of $0.0020\ \text{M}\ Na_2SO_4$?

Solution

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

Known

- Concentration of $BaCl_2 = 0.0050\ \text{M}$
- Volume of $BaCl_2 = 10.0\ \text{mL}$
- Concentration of $Na_2SO_4 = 0.0020\ \text{M}$
- Volume of $Na_2SO_4 = 20.0\ \text{mL}$
- K_{sp} of $BaSO_4 = 1.1 \times 10^{-10}$

Unknown

- Ion product $= [Ba^{2+}]\,[SO_4{}^{2-}]$
- If a precipitate forms.

The concentration and volume of each solution that is mixed together must be used to calculate the $[Ba^{2+}]$ and the $[SO_4{}^{2-}]$. Each individual solution is diluted when they are mixed together. The ion product is calculated and compared to the K_{sp} to determine if a precipitate forms.

Step 2: Solve.

The moles of each ion from the original solutions are calculated by multiplying the molarity by the volume in liters.

$$\text{mol}\ Ba^{2+} = 0.0050\ \text{M} \times 0.010\ \text{L} = 5.0 \times 10^{-5}\ \text{mol}\ Ba^{2+}$$

$$\text{mol}\ SO_4{}^{2-} = 0.0020\ \text{M} \times 0.020\ \text{L} = 4.0 \times 10^{-5}\ \text{mol}\ SO_4{}^{2-}$$

The concentration of each ion after dilution is then calculated by dividing the moles by the final solution volume of $0.030\ \text{L}$.

$$[\text{Ba}^{2+}] = \frac{5.0 \times 10^{-5}\ \text{mol}}{0.030\ \text{L}} = 1.7 \times 10^{-3}\ \text{M}$$

$$[\text{SO}_4{}^{2-}] = \frac{4.0 \times 10^{-5}\ \text{mol}}{0.030\ \text{L}} = 1.3 \times 10^{-3}\ \text{M}$$

Now, the ion product is calculated.

$$[\text{Ba}^{2+}]\,[\text{SO}_4{}^{2-}] = \left(1.7 \times 10^{-3}\right)\left(1.3 \times 10^{-3}\right) = 2.2 \times 10^{-6}$$

Since the ion product is greater than the K_{sp}, a precipitate of barium sulfate will form.

Step 3: Think about your result.

Two significant figures are appropriate for the calculated value of the ion product.

Summary

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10.24: Common Ion Effect

Lithium carbonate is an essential component of lithium batteries, which tend to be longer-lasting than regular alkaline batteries. The material is obtained from lithium ores by adding $\mathrm{CO_2}$ under high pressure to form the more soluble $\mathrm{LiHCO_3}$. The mixture is then de-pressurized to remove the carbon dioxide, and the lithium carbonate precipitates out of solution.

Common Ion Effect

In a saturated solution of calcium sulfate, an equilibrium exists between the solid calcium sulfate and its ions in solution:

$$\mathrm{CaSO_4}\,(s) \rightleftharpoons \mathrm{Ca^{2+}}\,(aq) + \mathrm{SO_4^{2-}}\,(aq) \quad K_{sp} = 2.4 \times 10^{-5}$$

Suppose that some calcium nitrate was added to this saturated solution. Immediately, the concentration of the calcium ion in the solution would increase. As a result, the ion product of the $[\mathrm{Ca^{2+}}]$ times the $[\mathrm{SO_4^{2-}}]$ would increase and now be greater than the K_{sp}. According to Le Chatelier's principle, the equilibrium above would shift to the left in order to relieve the stress of the added calcium ion. Additional calcium sulfate would precipitate out of the solution until the ion product once again becomes equal to the K_{sp}. Note that in the new equilibrium, the concentrations of the calcium ion and the sulfate ion would no longer be equal to each other. The calcium ion concentration would be larger than the sulfate ion concentration.

This situation describes the common ion effect. A **common ion** is an ion that is in common to both salts in a solution. In the above example, the common ion is $\mathrm{Ca^{2+}}$. The **common ion effect** is a decrease in the solubility of an ionic compound as a result of the addition of a common ion. Adding calcium ion to the saturated solution of calcium sulfate causes additional $\mathrm{CaSO_4}$ to precipitate from the solution, lowering its solubility. The addition of a solution containing sulfate ion, such as potassium sulfate, would result in the same common ion effect.

Example 10.24.1

What is the concentration of zinc ion in $1.00\,\mathrm{L}$ of a saturated solution of zinc hydroxide to which $0.040\,\mathrm{mol}$ of NaOH has been added?

Solution

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

Known

- $K_{sp} = 3.0 \times 10^{-16}$ (from table in "Conversion of K_{sp} to Solubility")
- Moles of added $\mathrm{NaOH} = 0.040\,\mathrm{mol}$
- Volume of solution $= 1.00\,\mathrm{L}$

Unknown

Express the concentrations of the two ions relative to the variable s. The concentration of the zinc ion will be equal to s, while the concentration of the hydroxide ion will be equal to $0.040 + 2s$.

Step 2: Solve.

The K_{sp} expression can be written in terms of the variable s.

$$K_{sp} = [\mathrm{Zn^{2+}}]\,[\mathrm{OH^-}]^2 = (s)\,(0.040 + 2s)^2$$

Because the value of the K_{sp} is so small, we can make the assumption that the value of s will be very small compared to 0.040. This simplifies the mathematics involved in solving for s.

$$K_{sp} = (s)\,(0.040)^2 = 0.0016s = 3.0 \times 10^{-16}$$
$$s = \frac{K_{sp}}{[\mathrm{OH^-}]^2} = \frac{3.0 \times 10^{-16}}{0.0016} = 1.9 \times 10^{-13}\,\mathrm{M}$$

The concentration of the zinc ion is equal to s and so $[\mathrm{Zn^{2+}}] = 1.9 \times 10^{-13}\,\mathrm{M}$.

Step 3: Think about your result.

The relatively high concentration of the common ion, OH^-, results in a very low concentration of zinc ion. The molar solubility of the zinc hydroxide is less in the presence of the common ion than it would be in water.

Summary

- The common ion is an ion that is in common to both salts in a solution.
- The common ion effect is a decrease in the solubility of an ionic compound as a result of the addition of a common ion.
- Calculations involving the common ion effect are described.

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