UBC INTRODUCTORY CHEMISTRY

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UBC Introductory Chemistry

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Licensing

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CHAPTER OVERVIEW

1: Units and Measure

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Chemistry, like all sciences, is quantitative. It deals with *quantities*, things that have amounts and units. Dealing with quantities is very important in chemistry, as is relating quantities to each other. In this chapter, we will discuss how we deal with numbers and units, including how they are combined and manipulated.

1.1: Scientific Notation - Writing Large and Small Numbers

🧠 Learning Objectives

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

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

$$N \times 10^n$$

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

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

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

Another way to remember this is to recognize that as the number N decreases in magnitude, the exponent increases and vice versa. The application of this rule is illustrated in Example 1.1.1.

✔ Example 1.1.1: Expressing Numbers in Scientific Notation

Convert each number to scientific notation.

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

Solution

Solutions to Example 2.2.1

	Explanation	Answer
a	To convert 637.8 to a number from 1 to 10, we move the decimal point two places to the left: 637.8 Because the decimal point was moved two places to the left, n = 2.	6.378×10^2
b	To convert 0.0479 to a number from 1 to 10, we move the decimal point two places to the right: 0.0479 Because the decimal point was moved two places to the right, n = −2.	4.79×10^{-2}
c	This is usually expressed simply as 7.86. (Recall that $10^0 = 1$.)	7.86×10^0
d	Because the decimal point was moved four places to the left, n = 4.	1.2378×10^4

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

Addition and Subtraction

Before numbers expressed in scientific notation can be added or subtracted, they must be converted to a form in which all the exponents have the same value. The appropriate operation is then carried out on the values of N. Example 1.1.2 illustrates how to do this.

✔ Example 1.1.2: Expressing Sums and Differences in Scientific Notation

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

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

Solution

Solutions to Example 2.2.2.

	Explanation	Answer
a	Both exponents must have the same value, so these numbers are converted to either $(1.36 \times 10^{2}) + (47.3 \times 10^{2}) =$ $(1.36 + 47.3) \times 10^{2} = 48.66 \times 10^{2}$ or $(0.136 \times 10^{3}) + (4.73 \times 10^{3}) =$ $(0.136 + 4.73) \times 10^{3} = 4.87 \times 10^{3}$. Choosing either alternative gives the same answer, reported to two decimal places. In converting 48.66×10^{2} to scientific notation, n has become more positive by 1 because the value of N has decreased.	4.8
b	Converting the exponents to the same value gives either $(6.923 \times 10^{-3}) - (0.8756 \times 10^{-3}) =$ $(6.923 - 0.8756) \times 10^{-3}$ or $(69.23 \times 10^{-4}) - (8.756 \times 10^{-4}) =$ $(69.23 - 8.756) \times 10^{-4} = 60.474 \times 10^{-4}$. In converting 60.474×10^{-4} to scientific notation, n has become more positive by 1 because the value of N has decreased.	6.0

Multiplication and Division

When multiplying numbers expressed in scientific notation, we multiply the values of N and add together the values of n. Conversely, when dividing, we divide N in the dividend (the number being divided) by N in the divisor (the number by which we are dividing) and then

subtract n in the divisor from n in the dividend. In contrast to addition and subtraction, the exponents do not have to be the same in multiplication and division. Examples of problems involving multiplication and division are shown in Example 1.1.3.

> ✔ **Example 1.1.3: Expressing Products and Quotients in Scientific Notation**
>
> Perform the appropriate operation and express your answer in scientific notation.
>
> a. $(6.022 \times 10^{23})(6.42 \times 10^{-2})$
>
> b. $\dfrac{1.67 \times 10^{-24}}{9.12 \times 10^{-28}}$
>
> c. $\dfrac{(6.63 \times 10^{-34})(6.0 \times 10)}{8.52 \times 10^{-2}}$
>
> **Solution**
>
> Solution to Example 2.2.3
>
> | | Explanation | |
> |---|---|---|
> | **a** | In multiplication, we add the exponents: $(6.022 \times 10^{23})(6.42 \times 10^{-2}) = (6.022)(6.42) \times 10^{[23+(-2)]} = 38.7 \times 10^{21}$ In converting 38.7×10^{21} to scientific notation, n has become more positive by 1 because the value of N has decreased. | 3.87×10^{22} |
> | **b** | In division, we subtract the exponents: $\dfrac{1.67 \times 10^{-24}}{9.12 \times 10^{-28}} = \dfrac{1.67}{9.12} \times 10^{[-24-(-28)]} = 0.183 \times 10^{4}$ In converting 0.183×10^{4} to scientific notation, n has become more negative by 1 because the value of N has increased. | 1.83×10^{3} |
> | **c** | This problem has both multiplication and division: $\dfrac{(6.63 \times 10^{-34})(6.0 \times 10)}{(8.52 \times 10^{-2})} = \dfrac{39.78}{8.52} \times 10^{[-34+1-(-2)]}$ | 4.7×10^{-31} |

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 $2.553\,cm$ as there is no possible way that the thousandths digit could be estimated. The 3 is not significant and would not be reported.
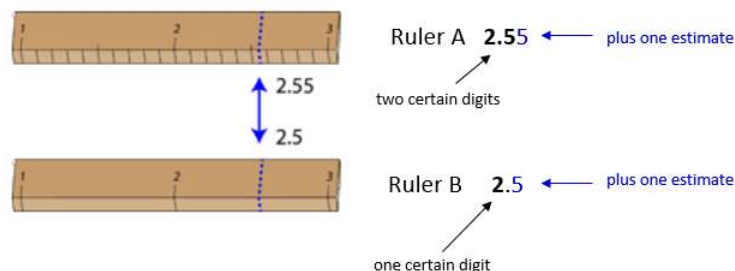
Figure 1.2.1: Measurement with two different rulers.
Ruler A's measurement can be rounded to 2.55, with 2 certain digits, while Ruler B's measurement of 2.5 has 1 certain digit

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 $0.1\,g$, other highly sensitive balances are capable of measuring to the nearest $0.001\,g$ or even better. Many measuring tools such as rulers and graduated cylinders have small lines which need to be carefully read in order to make a measurement. Figure $1.2.1$ shows two rulers making the same measurement of an object (indicated by the blue arrow).

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

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

> **✔ Example 1.2.1: 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.
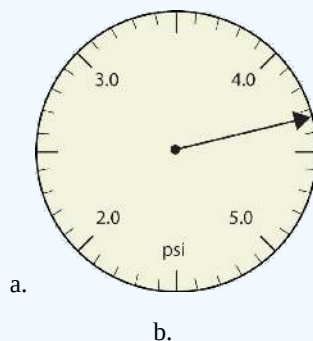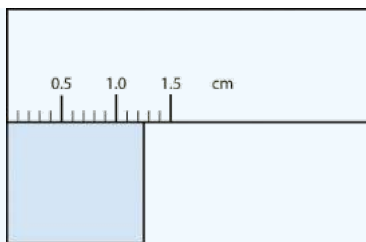
Ruler measuring a rectangle in units of centimeters, with the rectangle's edge between 1.2 and 1.3 cm marks

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?
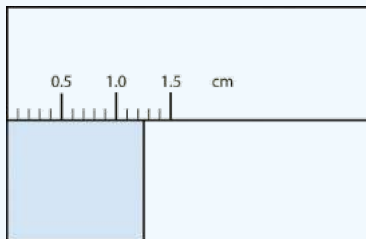
Answer

   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

	Explanation	Answer
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.
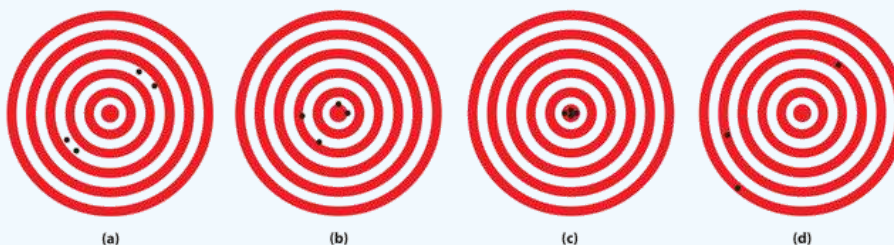
Summary

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:

$$38.65 \times 105.93 = 4{,}094.1945$$

4 sig figs   5 sig figs   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. | 2.0856×10^3 |
>
> b
>
> | Explanation | Answer |
> |---|---|
> | The calculator gives 1,125 as the answer, but we limit it to three significant figures. | 1.13×10^3 |

Addition and Subtraction

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

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

↑ limit final answer to the tenths column: 5.6

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

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.

$$
\begin{array}{r}
77.2 \\
\underline{10.46} \\
87.66
\end{array}
$$

↑ limit final answer to the tenths column and round up: 87.7

> ✔ **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.

$\qquad$ 2 (1.008 g *4 sig figs*) = **2.01<u>6</u> 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.

$\qquad$ **2.01<u>6</u> g** *thousandths place* + 15.9<u>9</u> 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.
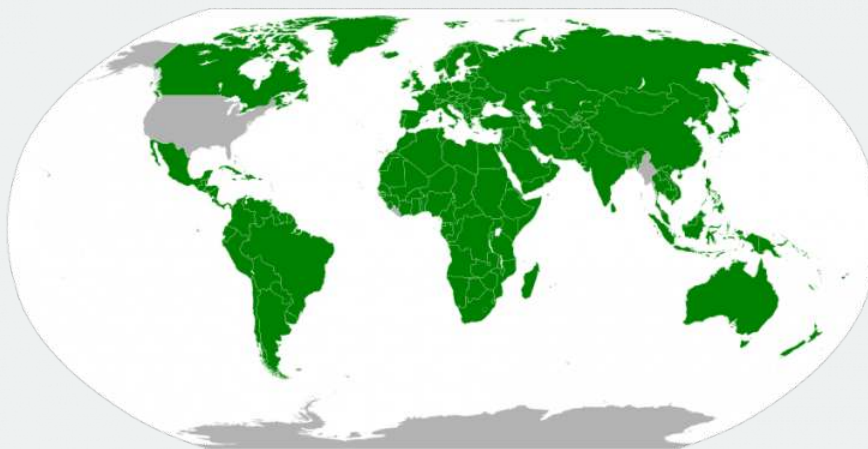
Figure 1.4.1: Areas of world using metric system (in green). Only a few countries are slow or resistant to adoption including the United States.

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 $\mu\varepsilon\gamma\alpha\varsigma$, 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 $(\mathrm{Gm}) = 10^9$ m
mega	M	1,000,000	1 megameter $(\mathrm{Mm}) = 10^6$ m
kilo	k	1,000	1 kilometer $(\mathrm{km}) = 1,000$ m
hecto	h	100	1 hectometer $(\mathrm{hm}) = 100$ m
deka	da	10	1 dekameter $(\mathrm{dam}) = 10$ m
		1	1 meter (m)
deci	d	1/10	1 decimeter $(\mathrm{dm}) = 0.1$ m
centi	c	1/100	1 centimeter $(\mathrm{cm}) = 0.01$ m
milli	m	1/1,000	1 millimeter $(\mathrm{mm}) = 0.001$ m
micro	μ	1/1,000,000	1 micrometer $(\mu\mathrm{m}) = 10^{-6}$ m
nano	n	1/1,000,000,000	1 nanometer $(\mathrm{nm}) = 10^{-9}$ m
pico	p	1/1,000,000,000,000	1 picometer $(\mathrm{pm}) = 10^{-12}$ 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 $\dfrac{100 \text{ cm}}{1 \text{ m}}$ and multiply:

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

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:

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

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

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

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:

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

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 $\dfrac{100 \text{ cm}}{1 \text{ m}}$ as a conversion factor. Does the conversion factor $\dfrac{1 \text{ m}}{100 \text{ cm}}$ 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:

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

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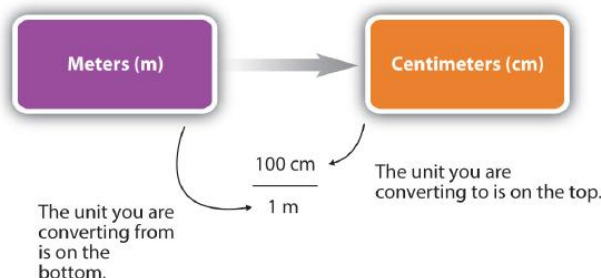
Figure 1.5.1: A Concept Map for Conversions. This is how you construct a conversion factor to convert from one unit to another. Converting meters to centimeters: the unit you are converting is on the bottom of the fraction, and the unit to convert to is on top

📌 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.
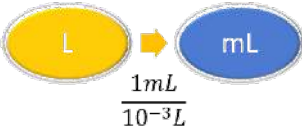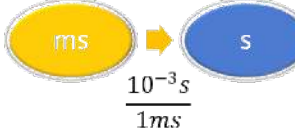
Significant Figures in Conversions

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

Steps for Problem Solving	Example 1.5.1	Example 1.5.2
	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.	L → mL $\dfrac{1mL}{10^{-3}L}$	ms → s $\dfrac{10^{-3}s}{1ms}$
Cancel units and calculate.	$4.7\,\cancel{L} \times \dfrac{1\text{ mL}}{10^{-3}\,\cancel{L}} = 4,700\text{ mL}$ or $4.7\,\cancel{L} \times \dfrac{1,000\text{ mL}}{1\,\cancel{L}} = 4,700\text{ mL}$ or 4.7×10^3 2SF, not ambiguous	$18\,\cancel{ms} \times \dfrac{10^{-3}\text{ s}}{1\,\cancel{ms}} = 0.018\text{ s}$ or $18\,\cancel{ms} \times \dfrac{1\text{ s}}{1,000\,\cancel{ms}} = 0.018\text{ s}$
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:

$1.01000 x 10^{-4} s$

Answer b:

$3.208 x 10^4 g$

Answer c:

$1.53 x 10^2 cg$

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 $1 \text{ mm} = 10^{-3}$ m.

Concept Map
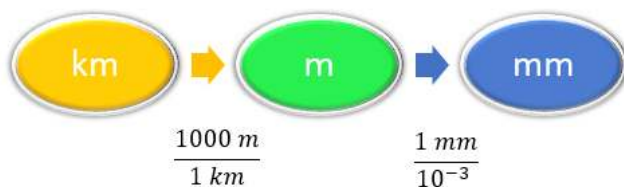
$$\frac{1000 \, m}{1 \, km} \qquad \frac{1 \, mm}{10^{-3}}$$

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

Calculation

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

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

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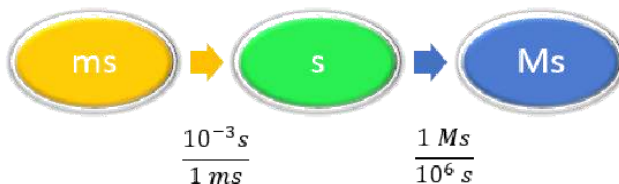
Steps for Problem Solving	Unit Conversion
Identify the "given" information and what the problem is asking you to "find."	Given: 58.2 ms Find: Ms
List other known quantities	$1ms = 10^{-3}s$ $1Ms = 10^{6}s$
Prepare a concept map.	 $$\frac{10^{-3}s}{1 \, ms} \qquad \frac{1 \, Ms}{10^{6} \, s}$$ Convert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

Steps for Problem Solving	Unit Conversion
Calculate.	$58.2 \ \cancel{ms} \times \dfrac{10^{-3} \ \cancel{s}}{1 \ \cancel{ms}} \times \dfrac{1 \ Ms}{1,000,000 \ \cancel{s}} = 0.0000000582 \ Ms$ $= 5.82 \times 10^{-8} \ Ms$ 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.	 $\dfrac{24hr}{1 \ day}$ $\dfrac{60min}{1 \ hr}$ $\dfrac{60 \ s}{1 \ min}$ Convert day to hour to minute to second: use conversion factors 24 hours per day, 60 minutes per hour, and 60 seconds per minute
Calculate.	$1 \ d \times \dfrac{24 \ hr}{1 \ d} \times \dfrac{60 \ min}{1 \ hr} \times \dfrac{60 \ s}{1 \ min} = 86,400 \ s$
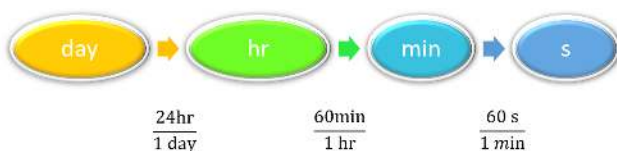
❓ Exercise 1.6.1

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
   $19 \, km$

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

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

Summary

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

1.7: Units Raised to a Power

> **◀▶ Learning Objectives**
>
> - To convert a value reported in one unit raised to a power of 10, to a corresponding value in a different unit raised to the same power of 10, using conversion factors.

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

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

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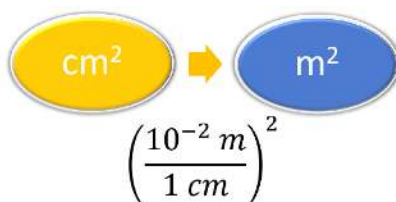
To convert centimeters squared to meters squared, use the conversion factor 0.01 meters per 1 centimeter, squared overall

CALCULATION

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

or

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

or

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

> **✔ Example 1.7.1: Volume of a Sphere**
>
> What is the volume of a sphere (radius 4.30 inches) in cubic cm (cm^3)?
>
> **Solution**
>
> <div align="center">Solution for Example 2.8.1</div>
>
> | Steps for Problem Solving | What is the volume of a sphere (radius 4.30 inches) in cubic cm (cm^3)? |
> |---|---|
> | Identify the "given" information and what the problem is asking you to "find." | Given: radius = 4.30 in
 Find: cm^3 (volume) |
> | Determine other known quantities. | Volume of a sphere: V = $\frac{4}{3} \times \pi \times r^3$
 $= \frac{4}{3} \times 3.1416 \times (4.30\underline{i}n)^3$
 $= 333.04in^3$ |

Steps for Problem Solving	What is the volume of a sphere (radius 4.30 inches) in cubic cm (cm^3)?
Prepare a concept map.	$$\left(\frac{2.54\ cm}{1\ in}\right)^3$$ To convert inches cubed to centimeters cubed, use conversion factor 2.54 centimeters per 1 inch, cubed overall
Calculate.	$333.04\ \cancel{in^3}\left(\dfrac{2.54cm}{1\ \cancel{in}}\right)^3 = 5.46\times10^3\,cm^3$
Think about your result.	A centimeter is a smaller unit than an inch, so the answer in cubic centimeters is larger than the given value in cubic inches.
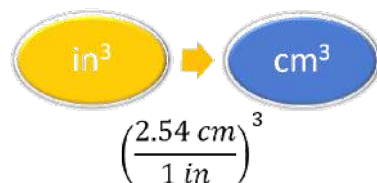
? Exercise 1.7.1

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

Answer

495 km^2

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CHAPTER OVERVIEW

2: Naming and Composition

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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 moleculesThe smallest part of a substance that has the physical and chemical properties of that substance.. 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.

2.1: 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 2.1.1: 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 2.1.1). 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 2.1.1).
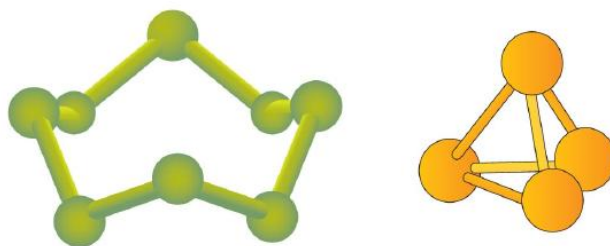
Figure 2.1.1: Molecular Art of S_8 and P_4 Molecules. If each green ball represents a sulfur atom, then the diagram on the left represents an S_8 molecule. The molecule on the right shows that one form of elemental phosphorus exists, as a four-atom molecule.

Figure 2.1.1 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 2.1.1**
>
> 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 2.1.1**
>
> 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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2.2: Writing Formulas for Ionic Compounds

> ### 🧠 Learning Objectives
>
> - Write the correct formula for an ionic compound.
> - Recognize polyatomic ions in chemical formulas.

Ionic compounds do not exist as molecules. In the solid state, ionic compounds are in crystal lattice containing many ions each of the cation and anion. An ionic formula, like $NaCl$, is an empirical formula. This formula merely indicates that sodium chloride is made of an equal number of sodium and chloride ions. Sodium sulfide, another ionic compound, has the formula Na_2S. This formula indicates that this compound is made up of twice as many sodium ions as sulfide ions. This section will teach you how to find the correct ratio of ions, so that you can write a correct formula.

If you know the name of a binary ionic compound, you can write its **chemical formula**. Start by writing the metal ion with its charge, followed by the nonmetal ion with its charge. Because the overall compound must be electrically neutral, decide how many of each ion is needed in order for the positive and negative charges to cancel each other out.

> ### ✔ Example 2.2.1: Aluminum Nitride and Lithium Oxide
>
> Write the formulas for aluminum nitride and lithium oxide.
>
> **Solution**
>
> <div align="center">Solution to Example 5.5.1</div>
>
> | | Write the formula for aluminum nitride | Write the formula for lithium oxide |
> |---|:---:|:---:|
> | 1. Write the symbol and charge of the cation (metal) first and the anion (nonmetal) second. | Al^{3+} N^{3-} | Li^+ O^{2-} |
> | 2. Use a multiplier to make the total charge of the cations and anions equal to each other. | total charge of cations = total charge of anions
1(3+) = 1(3-)
+3 = -3 | total charge of cations = total charge of anions
2(1+) = 1(2-)
+2 = -2 |
> | 3. Use the multipliers as subscript for each ion. | Al_1N_1 | Li_2O_1 |
> | 4. Write the final formula. Leave out all charges and all subscripts that are 1. | AlN | Li_2O |

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

> ### ✔ Example 2.2.2: The Crisscross Method for Lead (IV) Oxide
>
> Write the formula for lead (IV) oxide.
>
> **Solution**
>
> <div align="center">Solution to Example 5.5.2</div>
>
> | Crisscross Method | Write the formula for lead (IV) oxide |
> |---|:---:|
> | 1. Write the symbol and charge of the cation (metal) first and the anion (nonmetal) second. | Pb^{4+} O^{2-} |

Crisscross Method	Write the formula for lead (IV) oxide
2. Transpose only the number of the positive charge to become the subscript of the anion and the number only of the negative charge to become the subscript of the cation.	Pb^{4+} ⟶ O^{2-}
3. Reduce to the lowest ratio.	Pb_2O_4
4. Write the final formula. Leave out all subscripts that are 1.	PbO_2
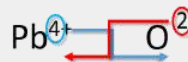
? **Exercise 2.2.2**

Write the chemical formula for an ionic compound composed of each pair of ions.

a. the calcium ion and the oxygen ion
b. the 2+ copper ion and the sulfur ion
c. the 1+ copper ion and the sulfur ion

Answer a:
　CaO
Answer b:
　CuS
Answer c:
　Cu_2S

> *Be aware that ionic compounds are empirical formulas and so must be written as the lowest ratio of the ions.*

✔ **Example 2.2.3: Sulfur Compound**

Write the formula for sodium combined with sulfur.

Solution

Solution to Example 5.5.3

Crisscross Method	Write the formula for sodium combined with sulfur
1. Write the symbol and charge of the cation (metal) first and the anion (nonmetal) second.	Na^+　S^{2-}
2. Transpose only the number of the positive charge to become the subscript of the anion and the number only of the negative charge to become the subscript of the cation.	Na^{1+} ⟶ S^{2-}
3. Reduce to the lowest ratio.	This step is not necessary.
4. Write the final formula. Leave out all subscripts that are 1.	Na_2S
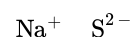
? **Exercise 2.2.3**

Write the formula for each ionic compound.

a. sodium bromide
b. lithium chloride
c. magnesium oxide

Answer a:

NaBr

Answer b:

LiCl

Answer c:

MgO

Polyatomic Ions

Some ions consist of groups of atoms bonded together and have an overall electric charge. Because these ions contain more than one atom, they are called polyatomic ions. Polyatomic ions have characteristic formulas, names, and charges that should be memorized. For example, NO_3^- is the nitrate ion; it has one nitrogen atom and three oxygen atoms and an overall 1− charge. Table 2.2.1 lists the most common polyatomic ions.

Table 2.2.1: Some Polyatomic Ions

Name	Formula
ammonium ion	NH_4^+
acetate ion	$C_2H_3O_2^-$ (also written $CH_3CO_2^-$)
carbonate ion	CO_3^{2-}
chromate ion	CrO_4^{2-}
dichromate ion	$Cr_2O_7^{2-}$
hydrogen carbonate ion (bicarbonate ion)	HCO_3^-
cyanide ion	CN^-
hydroxide ion	OH^-
nitrate ion	NO_3^-
nitrite ion	NO_2^-
permanganate ion	MnO_4^-
phosphate ion	PO_4^{3-}
hydrogen phosphate ion	HPO_4^{2-}
dihydrogen phosphate ion	$H_2PO_4^-$
sulfate ion	SO_4^{2-}
hydrogen sulfate ion (bisulfate ion)	HSO_4^-
sulfite ion	SO_3^{2-}

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

Writing Formulas for Ionic Compounds Containing Polyatomic Ions

Writing a formula for ionic compounds containing polyatomic ions also involves the same steps as for a binary ionic compound. Write the symbol and charge of the cation followed by the symbol and charge of the anion.

✔ Example 2.2.4: Calcium Nitrate

Write the formula for calcium nitrate.

Solution

Solution to Example 5.5.4

Crisscross Method	**Write the formula for calcium nitrate**
1. Write the symbol and charge of the cation (metal) first and the anion (nonmetal) second.	Ca^{2+} NO_3^-
2. Transpose only the number of the positive charge to become the subscript of the anion and the number only of the negative charge to become the subscript of the cation.	Ca^{2+} ⟶ NO_3 ① The 2+ charge on Ca becomes the subscript of NO3 and the 1- charge on NO3 becomes the subscript of Ca.
3. Reduce to the lowest ratio.	$Ca_1(NO_3)_2$
4. Write the final formula. Leave out all subscripts that are 1. If there is only 1 of the polyatomic ion, leave off parentheses.	$Ca(NO_3)_2$

✔ Example 2.2.5

Write the chemical formula for an ionic compound composed of the potassium ion and the sulfate ion.

Solution

Solution to Example 5.5.5

Explanation	**Answer**
Potassium ions have a charge of 1+, while sulfate ions have a charge of 2−. We will need two potassium ions to balance the charge on the sulfate ion, so the proper chemical formula is K_2SO_4.	K_2SO_4

❓ Exercise 2.2.5

Write the chemical formula for an ionic compound composed of each pair of ions.

a. the magnesium ion and the carbonate ion
b. the aluminum ion and the acetate ion

Answer a:
   $MgCO_3$
Answer b:
   $Al(CH_3COO)_3$
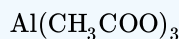
Recognizing Ionic Compounds

There are two ways to recognize ionic compounds.

Method 1

Compounds between metal and nonmetal elements are usually ionic. For example, $CaBr_2$ contains a metallic element (calcium, a group 2 [or 2A] metal) and a nonmetallic element (bromine, a group 17 [or 7A] nonmetal). Therefore, it is most likely an ionic compound (in fact, it *is* ionic). In contrast, the compound NO_2 contains two elements that are both nonmetals (nitrogen, from group 15 [or 5A], and oxygen, from group 16 [or 6A]. It is not an ionic compound; it belongs to the category

of covalent compounds discussed elsewhere. Also note that this combination of nitrogen and oxygen has no electric charge specified, so it is *not* the nitrite ion.

Method 2

Second, if you recognize the formula of a polyatomic ion in a compound, the compound is ionic. For example, if you see the formula $Ba(NO_3)_2$, you may recognize the "NO_3" part as the nitrate ion, NO_3^-. (Remember that the convention for writing formulas for ionic compounds is not to include the ionic charge.) This is a clue that the other part of the formula, Ba, is actually the Ba^{2+} ion, with the 2+ charge balancing the overall 2− charge from the two nitrate ions. Thus, this compound is also ionic.

✔ **Example 2.2.6**

Identify each compound as ionic or not ionic.

a. Na_2O
b. PCl_3
c. NH_4Cl
d. OF_2

Solution

Solution to Example 5.5.6

Explanation	Answer
a. Sodium is a metal, and oxygen is a nonmetal. Therefore, Na_2O is expected to be ionic via method 1.	Na_2O, ionic
b. Both phosphorus and chlorine are nonmetals. Therefore, PCl_3 is not ionic via method 1	PCl_3, not ionic
c. The NH_4 in the formula represents the ammonium ion, NH_4^+, which indicates that this compound is ionic via method 2	NH_4Cl, ionic
d. Both oxygen and fluorine are nonmetals. Therefore, OF_2 is not ionic via method 1	OF_2, not ionic

---

? **Exercise 2.2.6**

Identify each compound as ionic or not ionic.

a. N_2O
b. $FeCl_3$
c. $(NH_4)_3PO_4$
d. $SOCl_2$

Answer a:
  not ionic
Answer b:
  ionic
Answer c:
  ionic
Answer d:
  not ionic

Summary

Formulas for ionic compounds contain the symbols and number of each atom present in a compound in the lowest whole number ratio.

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2.3: Nomenclature- Naming Compounds

Nomenclature is the process of naming chemical compounds so that they can be easily identified as separate chemicals. The primary function of chemical nomenclature is to ensure that a spoken or written chemical name leaves no ambiguity concerning which chemical compound the name refers to—each chemical name should refer to a single substance. A less important aim is to ensure that each substance has a single name, although a limited number of alternative names is acceptable in some cases. Preferably, the name also conveys some information about the structure or chemistry of a compound. A common name will often suffice to identify a chemical compound in a particular set of circumstances. To be more generally applicable, the name should indicate at least the chemical formula. To be more specific still, the three-dimensional arrangement of the atoms may need to be specified.

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2.4: Naming Ionic Compounds

> **◐ Learning Objectives**
>
> - To use the rules for naming ionic compounds.

After learning a few more details about the names of individual ions, you will be one step away from knowing how to name ionic compounds. This section begins the formal study of nomenclature, the systematic naming of chemical compounds.

Naming Ions

The name of a monatomic cation is simply the name of the element followed by the word *ion*. Thus, Na^+ is the sodium ion, Al^{3+} is the aluminum ion, Ca^{2+} is the calcium ion, and so forth.

We have seen that some elements lose different numbers of electrons, producing ions of different charges (Figure 3.3). Iron, for example, can form two cations, each of which, when combined with the same anion, makes a different compound with unique physical and chemical properties. Thus, we need a different name for each iron ion to distinguish Fe^{2+} from Fe^{3+}. The same issue arises for other ions with more than one possible charge.

There are two ways to make this distinction. In the simpler, more modern approach, called the **Stock system**, an ion's positive charge is indicated by a roman numeral in parentheses after the element name, followed by the word *ion*. Thus, Fe^{2+} is called the iron(II) ion, while Fe^{3+} is called the iron(III) ion. This system is used only for elements that form more than one common positive ion. We do not call the Na^+ ion the sodium(I) ion because (I) is unnecessary. Sodium forms only a 1+ ion, so there is no ambiguity about the name *sodium ion*.

Table 2.4.1: The Modern and Common System of Cation Names

Element	Stem	Charge	Modern Name	Common Name
iron	ferr-	2+	iron(II) ion	ferrous ion
		3+	iron(III) ion	ferric ion
copper	cupr-	1+	copper(I) ion	cuprous ion
		2+	copper(II) ion	cupric ion
tin	stann-	2+	tin(II) ion	stannous ion
		4+	tin(IV) ion	stannic ion
lead	plumb-	2+	lead(II) ion	plumbous ion
		4+	lead(IV) ion	plumbic ion
chromium	chrom-	2+	chromium(II) ion	chromous ion
		3+	chromium(III) ion	chromic ion
gold	aur-	1+	gold(I) ion	aurous ion
		3+	gold(III) ion	auric ion

The second system, called the **common system**, is not conventional but is still prevalent and used in the health sciences. This system recognizes that many metals have two common cations. The common system uses two suffixes (*-ic* and *-ous*) that are appended to the stem of the element name. The *-ic* suffix represents the greater of the two cation charges, and the *-ous* suffix represents the lower one. In many cases, the stem of the element name comes from the Latin name of the element. Table 2.4.1 lists the elements that use the common system, along with their respective cation names.

Table 2.4.2: Some Monatomic Anions

Ion	Name

Ion	Name
F^-	fluoride ion
Cl^-	chloride ion
Br^-	bromide ion
I^-	iodide ion
O^{2-}	oxide ion
S^{2-}	sulfide ion
P^{3-}	phosphide ion
N^{3-}	nitride ion

The name of a monatomic anion consists of the stem of the element name, the suffix *-ide*, and then the word *ion*. Thus, as we have already seen, Cl^- is "chlor-" + "-ide ion," or the chloride ion. Similarly, O^{2-} is the oxide ion, Se^{2-} is the selenide ion, and so forth. Table $2.4.2$ lists the names of some common monatomic ions. The polyatomic ions have their own characteristic names, as discussed earlier.

✔ **Example 2.4.1**

Name each ion.

a. Ca^{2+}
b. S^{2-}
c. SO_3^{2-}
d. NH_4^+
e. Cu^+

Solution

a. the calcium ion
b. the sulfide ion
c. the sulfite ion
d. the ammonium ion
e. the copper(I) ion or the cuprous ion

? **Exercise 2.4.1**

Name each ion.

a. Fe^{2+}
b. Fe^{3+}
c. SO_4^{2-}
d. Ba^{2+}
e. HCO_3^-

Answer a:
  iron(II) ion

Answer b:
  iron(III) ion

Answer c:
  sulfate ion

Answer d:
  barium ion

Answer e:

hydrogen carbonate ion or bicarbonate ion

✔ Example 2.4.2

Write the formula for each ion.

a. the bromide ion
b. the phosphate ion
c. the cupric ion
d. the magnesium ion

Solution
a. Br^-
b. PO_4^{3-}
c. Cu^{2+}
d. Mg^{2+}

? Exercise 2.4.2

Write the formula for each ion.

a. the fluoride ion
b. the carbonate ion
c. the stannous ion
d. the potassium ion

Answer a:

F^-

Answer b:

CO_3^{2-}

Answer c:

Sn^{2+}

Answer d:

K^+

Naming Binary Ionic Compounds with a Metal that Forms Only One Type of Cation

A **binary** ionic compound is a compound composed of a **monatomic** metal **cation** and a monatomic nonmetal **anion**. The metal cation is named first, followed by the nonmetal anion as illustrated in Figure 2.4.1 for the compound $BaCl_2$. The word *ion* is dropped from both parts.

Name of cation (metal) + Base name of anion (nonmetal) and -ide

BaCl₂

| Ba²⁺ | | Cl⁻ |
| | | Cl⁻ |

barium ion   chloride ion

Remove the word "ion"

barium + chloride
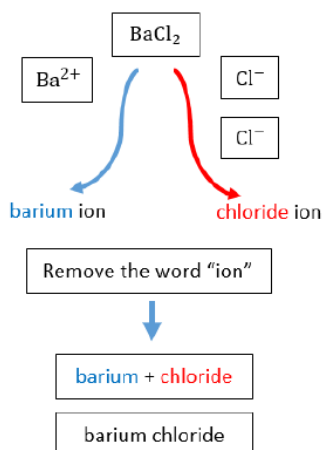
barium chloride

Figure 2.4.1: Naming $BaCl_2$
Naming formula: Name of metal cation + base
name of nonmetal anion + suffix -ide. BaCl2 is named as barium chloride.

Subscripts in the formula do not affect the name.

> **✔ Example 2.4.3: Naming Ionic Compounds**
>
> Name each ionic compound.
>
> a. $CaCl_2$
> b. AlF_3
> c. KCl
>
> **Solution**
> a. Using the names of the ions, this ionic compound is named calcium chloride.
> b. The name of this ionic compound is aluminum fluoride.
> c. The name of this ionic compound is potassium chloride

> **? Exercise 2.4.3**
>
> Name each ionic compound.
>
> a. AgI
> b. MgO
> c. Ca_3P_2
>
> **Answer a:**
>   silver iodide
> **Answer b:**
>   magnesium oxide
> **Answer c:**
>   calcium phosphide

Naming Binary Ionic Compounds with a Metal That Forms More Than One Type of Cation

If you are given a formula for an ionic compound whose cation can have more than one possible charge, you must first determine the charge on the cation before identifying its correct name. For example, consider $FeCl_2$ and $FeCl_3$. In the first compound, the iron ion has a 2+ charge because there are two Cl^- ions in the formula (1− charge on each chloride ion). In the second compound, the

iron ion has a 3+ charge, as indicated by the three Cl^- ions in the formula. These are two different compounds that need two different names. By the Stock system, the names are iron(II) chloride and iron(III) chloride (Figure $2.4.2$).

Table $2.4.3$: Naming the $FeCl_2$ and $FeCl_3$ Compounds in the Modern/Stock System.

Name of cation (metal) + (Roman Numeral in parenthesis) + Base name of anion (nonmetal) and -*ide*

If we were to use the stems and suffixes of the common system, the names would be ferrous chloride and ferric chloride, respectively (Figure $2.4.3$) .

Table $2.4.4$: Naming the $FeCl_2$ and $FeCl_3$ Compounds in the Old/Common System.

"Old" base name of cation (metal) and -*ic or -ous* + Base name of anion (nonmetal) and -*ide*

✔ **Example 2.4.4:**

Name each ionic compound.

a. Co$_2$O$_3$
b. FeCl2

Solution

Solutions to Example 5.7.4

	Explanation	Answer
a	We know that cobalt can have more than one possible charge; we just need to determine what it is. • Oxide always has a 2− charge, so with three oxide ions, we have a total negative charge of 6−. • This means that the two cobalt ions have to contribute 6+, which for two cobalt ions means that each one is 3+. • Therefore, the proper name for this ionic compound is cobalt(III) oxide.	cobalt(III) oxide
b	Iron can also have more than one possible charge. • Chloride always has a 1− charge, so with two chloride ions, we have a total negative charge of 2−. • This means that the one iron ion must have a 2+ charge. • Therefore, the proper name for this ionic compound is iron(II) chloride.	iron(II) chloride

? **Exercise 2.4.4**

Name each ionic compound.

a. AuCl$_3$
b. PbO$_2$
c. CuO

Answer a:
   gold(III) chloride
Answer b:
   lead(IV) oxide
Answer c:
   copper(II) oxide

Naming Ionic Compounds with Polyatomic Ions

The process of naming ionic compounds with polyatomic ions is the same as naming binary ionic compounds. The cation is named first, followed by the anion. One example is the ammonium sulfate compound in Figure 2.4.6.
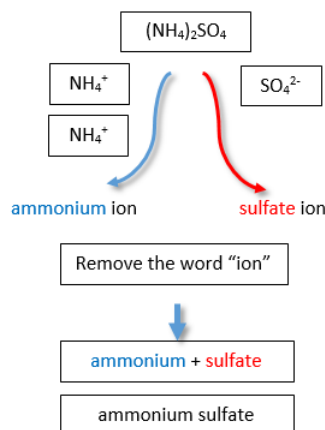
| (NH₄)₂SO₄ |

Figure 2.4.2: Naming Ionic Compounds with Polyatomic Ions

✔ Example 2.4.5: Naming Ionic Compounds

Write the proper name for each ionic compound.

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

Solution

Solutions to Example 5.7.5

Explanation	Answer
a. The ammonium ion has a 1+ charge and the sulfide ion has a 2− charge. Two ammonium ions need to balance the charge on a single sulfide ion. The compound's name is ammonium sulfide.	ammonium sulfide
b. The ions have the same magnitude of charge, one of each (ion) is needed to balance the charges. The name of the compound is aluminum phosphate.	aluminum phosphate
c. Neither charge is an exact multiple of the other, so we have to go to the least common multiple of 6. To get 6+, three iron(II) ions are needed, and to get 6−, two phosphate ions are needed . The compound's name is iron(II) phosphate.	iron(II) phosphate

---

? Exercise 2.4.5A

Write the proper name for each ionic compound.

a. $(NH_4)_3PO_4$
b. $Co(NO_2)_3$

Answer a:

ammonium phosphate

Answer b:

cobalt(III) nitrite

Figure 2.4.1 is a synopsis of how to name simple ionic compounds.
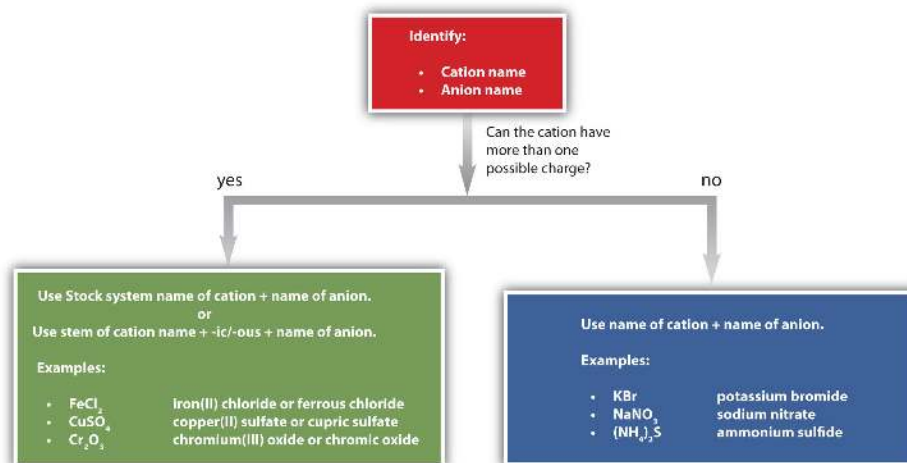
Figure 2.4.3: A Guide to Naming Simple Ionic Compounds.

> **? Exercise 2.4.5B**
>
> Name each ionic compound.
>
> a. $ZnBr_2$
> b. Al_2O_3
> c. $(NH_4)_3PO_4$
> d. AuF_3
> e. AgF
>
> **Answer a:**
>   zinc bromide
>
> **Answer b:**
>   aluminum oxide
>
> **Answer c:**
>   ammonium phosphate
>
> **Answer d:**
>   gold(III) fluoride or auric fluoride
>
> **Answer e:**
>   silver fluoride

Summary

- Ionic compounds are named by stating the cation first, followed by the anion.
- Positive and negative charges must balance.
- Some anions have multiple forms and are named accordingly with the use of roman numerals in parentheses.
- Ternary compounds are composed of three or more elements.

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2.5: Naming Molecular Compounds

> 🔵 **Learning Objectives**
>
> - Determine the name of a simple molecular compound from its chemical formula.

Molecular Compounds

Molecular compounds are inorganic compounds that take the form of discrete **molecules**. Examples include such familiar substances as water (H_2O) and carbon dioxide (CO_2). These compounds are very different from ionic compounds like sodium chloride $(NaCl)$. Ionic compounds are formed when metal atoms lose one or more of their electrons to nonmetal atoms. The resulting cations and anions are electrostatically attracted to each other.

So what holds the atoms of a molecule together? Rather than forming ions, the atoms of a molecule share their **electrons** in such a way that a **bond** forms between a pair of atoms. In a carbon dioxide molecule, there are two of these bonds, each occurring between the carbon atom and one of the two oxygen atoms.

Figure 2.5.1: Carbon dioxide molecules consist of a central carbon atom bonded to 2 oxygen atoms.

Larger molecules can have many, many bonds that serve to keep the molecule together. In a large sample of a given molecular compound, all of the individual molecules are identical.

Naming Binary Molecular Compounds

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

Figure 2.5.2: Nitrogen dioxide (NO_2) is a reddish-brown toxic gas that is a prominent air pollutant produced by internal combustion engines.

Naming *binary* (two-element) molecular compounds is similar to naming simple ionic compounds. The first element in the formula is simply listed using the name of the element. The second element is named by taking the stem of the element name and adding the suffix *-ide*. A system of numerical prefixes is used to specify the number of atoms in a molecule. Table 2.5.1 lists these numerical prefixes.

Table 2.5.1: Numerical Prefixes for Naming Binary Covalent Compounds

Number of Atoms in Compound	Prefix on the Name of the Element
1	mono-*
2	di-
3	tri-
4	tetra-
5	penta-

Number of Atoms in Compound	Prefix on the Name of the Element
6	hexa-
7	hepta-
8	octa-
9	nona-
10	deca-

*This prefix is not used for the first element's name.

dichlorine heptoxide
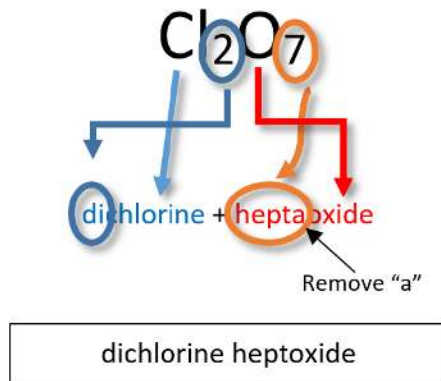
> **📌 Note**
>
> - Generally, the less electronegative element is written first in the formula, though there are a few exceptions. Carbon is always first in a formula and hydrogen is after nitrogen in a formula such as NH_3. The order of common nonmetals in binary compound formulas is C, P, N, H, S, I, Br, Cl, O, F.
> - The *a* or *o* at the end of a prefix is usually dropped from the name when the name of the element begins with a vowel. As an example, four oxygen atoms, is tetr**o**xide instead of tetr**ao**xide.
> - The prefix is "mono" is not added to the first element's name if there is only one atom of the first element in a molecule.

Some examples of molecular compounds are listed in Table $2.5.2$.

<div align="center">Table 2.5.2</div>

Formula	Name
NO	nitrogen monoxide
N_2O	dinitrogen monoxide
S_2Cl_2	disulfur dichloride
Cl_2O_7	dichlorine heptoxide

Notice that the *mono-* prefix is not used with the nitrogen in the first compound, but is used with the oxygen in both of the first two examples. The S_2Cl_2 emphasizes that the formulas for molecular compounds are not reduced to their lowest ratios. The *o* of the *mono-* and the *a* of *hepta-* are dropped from the name when paired with oxide.

> **❓ Exercise 2.5.1**
>
> Write the name for each compound.
>
> a. CF_4
> b. $SeCl_2$

c. SO_3

Answer a:
carbon tetrafluoride
Answer b:
selenium dichloride
Answer c:
sulfur trioxide

Simple molecular compounds with common names

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

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

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

Some Compounds Have Both Covalent and Ionic Bonds

If you recall the introduction of polyatomic ions, you will remember that the bonds that hold the polyatomic ions together are covalent bonds. Once the polyatomic ion is constructed with covalent bonds, it reacts with other substances as an ion. The bond between a polyatomic ion and another ion will be ionic. An example of this type of situation is in the compound sodium nitrate. Sodium nitrate is composed of a sodium ion and a nitrate ion. The nitrate ion is held together by covalent bonds and the nitrate ion is attached to the sodium ion by an ionic bond.

Summary

- A molecular compound is usually composed of two or more nonmetal elements.
- Molecular compounds are named with the first element first and then the second element by using the stem of the element name plus the suffix -ide. Numerical prefixes are used to specify the number of atoms in a molecule.

2.6: Naming Acids

A spot test for gold has been in use for decades. The sample is first treated with nitric acid. Other metals may react or dissolve in this acid, but gold will not. Then the sample is added to a mixture of nitric acid and hydrochloric acid. Gold will only dissolve in this mixture. The term "acid test" arose from the California gold rush in the late 1840's when this combination was used to test for the presence of real gold. It has since come to mean, "tested and approved" in a number of fields.

Acids

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

Figure 2.6.1: (A) Vinegar comes in a variety of types, but all contain acetic acid. (B) Citrus fruits like grapefruit contain citric and ascorbic acids.

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

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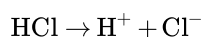
Since acids produce H^+ cations upon dissolving in water, the H of an acid is written first in the formula of an inorganic acid. The remainder of the acid (other than the H) is the anion after the acid dissolves. Organic acids are also an important class of compounds, but will not be discussed here.

Naming Acids

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

Naming Binary acids (in aqueous form)

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

Hydro- and Base name of Non metal and _-ic + acid_

Example: HCl$_{(aq)}$

Cl⁻, chloride ion

hydrochloric acid

Formula for naming acids: Hydro- and Base name of nonmetal and -ic + acid. Example: HCl is hydrochloric acid.

Naming Oxyacids

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

a. Oxyanions with **-ite** ending.

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

Base name of oxyanion and -ous+ acid

Example: $H_2SO_{3(aq)}$

SO_3^{2-}, sulfite ion

sulfurous acid

Formula for naming oxyanions with -ite ending: Base name of oxyanion and -ous + acid. Example: H2SO3 is sulfurous acid.

b. Oxyanions with **-ate** ending.

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

Base name of oxyanion and -ic+ acid

Example: $H_3PO_{4(aq)}$

PO_4^{3-} phosphate ion

phosphoric acid

Formula for naming oxyanions with -ate ending: Base name of oxyanion and -ic + acid. Example: H3PO4 is phosphoric acid.

> 📌 Note
>
> The base name for sulfur containing oxyacid is **sulfur-** instead of just **sulf-**. The same is true for a phosphorus containing oxyacid. The base name is **phosphor-** instead of simply **phosph-**.

Writing Formulas for Acids

Like other compounds that we have studied, acids are electrically neutral. Therefore, the charge of the anion part of the formula must be exactly balanced out by the H^+ ions. Another way to think about writing the correct formula is to utilize the crisscross method, shown below for sulfuric acid.

$$H^{1+} \quad SO_4^{2-}$$
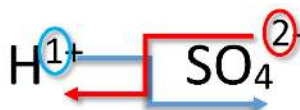
H2SO4: H has +1 charge and SO4 has -2 charge, so there must be 2 H+ and 1 SO4 for the charges to balance out.

Formula: H_2SO_4

***Figure* 2.6.2**: *Crisscross approach to writing formula for sulfuric acid.*

Summary

- Acids are molecular compounds that release hydrogen ions.
- A binary acid consists of hydrogen and one other element.
- Oxyacids contain hydrogen, oxygen, and one other element.
- The name of the acid is based on the anion attached to the hydrogen.

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2.7: Nomenclature Summary

NOMENCLATURE FLOWCHART

IONIC COMPOUNDS
"FORMULA UNITS"
Metal/Nonmetal
Or
Compounds with Polyatomic ions

COVALENT COMPOUNDS
"MOLECULES"
Nonmetal/Nonmetal

H⁺ AND ANION

(Mostly Acids)

1. Name cation first
2. Name ion last
3. **NO PREFIXES**
4. Include variable oxidation state of metal when appropriate – use Roman Numerals in parenthesis

1. Name less electronegative element first
2. Take -ide ending
3. **USE PREFIXES**

Derived from OXYANION

Derived from MONATOMIC ANION

Ex. CO₂ "Not Ions"
Carbon dioxide

From -*ite* ion
_____-ous acid
Ex. HNO₂ (from nitrite ion)
nitrous acid

Aqueous solution
-named as an acid

Hydro-_____-ic acid

Ex. HCl(aq)
hydrochloric acid

OR

From -*ate* ion
_____-ic acid
Ex. HNO₃ (from nitrate ion)
nitric acid

BINARY
Metal/Nonmetal
Monoatomic ion/-*ide* ending
1) **NaCl**
   Na⁺ (with fixed charge) + Cl⁻
   sodium ion + chloride ion
   sodium chloride
2) **FeCl₂**
   Fe²⁺ (with variable charge) + Cl⁻
   iron(II) ion + chloride ion
   iron(II) chloride

WITH POLYATOMIC IONS
Name polyatomic ions "as is"
1) **NH₄NO₃**
   NH₄⁺ + NO₃⁻
   ammonium ion + chloride ion
   ammonium chloride
2) **Fe(NO₃)₂**
   Fe²⁺ (with variable charge) + NO₃⁻
   iron(II) ion + nitrate ion
   iron(II) nitrate

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2.8: Formula Mass- The Mass of a Molecule or Formula Unit

> ◀▶ Learning Objectives
>
> • To determine the formula mass of an ionic or molecular compound.

A necessary skill for future chapters is the ability to determine the mass of the formula of an ionic compound. This quantity is called the formula mass. The formula mass is obtained by adding the masses of each individual atom in the formula of the compound. Because a proper formula is electrically neutral (with no net electrons gained or lost), the ions can be considered atoms for the purpose of calculating the formula mass.

Let us start by calculating the formula mass of sodium chloride (NaCl). This formula mass is the sum of the atomic masses of one sodium atom and one chlorine atom, which we find from the periodic table; here, we use the masses to two decimal places:

<div align="center">

Na: 22.99 amu

Cl: +35.34 amu

Total: 58.44 amu

</div>

To two decimal places, the formula mass of NaCl is 58.44 amu.

When an ionic compound has more than one anion or cation, you must remember to use the proper multiple of the atomic mass for the element in question. For the formula mass of calcium fluoride (CaF_2), we must multiply the mass of the fluorine atom by 2 to account for the two fluorine atoms in the chemical formula:

<div align="center">

Ca: 1 x 40.08 = 40.08 amu

F: 2 x 19.00 = +38.00 amu

Total = 78.08 amu

</div>

The formula mass of CaF_2 is 78.08 amu.

For ionic compounds with polyatomic ions, the sum must include the number and mass of each atom in the formula for the polyatomic ion. For example, potassium nitrate (KNO_3) has one potassium atom, one nitrogen atom, and three oxygen atoms:

<div align="center">

K: 1 x 39.10 = 39.10 amu

N: 1 x 14.00 = +14.00 amu

O: 3 x 16.00 = +48.00 amu

Total = 101.10 amu

</div>

The formula mass of KNO_3 is 101.10 amu.

> Potassium nitrate is a key ingredient in gunpowder and has been used clinically as a diuretic.

When a formula contains more than one polyatomic unit in the chemical formula, as in $Ca(NO_3)_2$, do not forget to multiply the atomic mass of every atom inside of the parentheses by the subscript outside of the parentheses. This is necessary because the subscript refers to the *entire polyatomic ion*. Thus, for $Ca(NO_3)_2$, the subscript 2 implies two complete nitrate ions, so we must sum the masses of two (1 × 2) nitrogen atoms and six (3 × 2) oxygen atoms, along with the mass of a single calcium atom:

<div align="center">

Ca: 1 x 40.08 = 40.08 amu

N: 2 x 14.00 = +28.00 amu

O: 6 x 16.00 = +96.00 amu

Total = 164.08 amu

</div>

The key to calculating the formula mass of an ionic compound is to correctly count each atom in the formula and multiply the atomic masses of its atoms accordingly.

> ✔ **Example 2.8.1**
>
> Use the atomic masses (rounded to two decimal places) to determine the formula mass for each ionic compound.
>
>   a. $FeCl_3$
>   b. $(NH_4)_3PO_4$
>
> **Solution**
>
> a.
>
> $$Fe: 1 \times 55.85 = 55.85 \text{ amu}$$
> $$Cl: 1 \times 35.45 = +106.\underline{3}5 \text{ amu}$$
> $$\rule{4cm}{0.4pt}$$
> $$Total = 162.\underline{2}0 \text{ amu}$$
>
>   The formula mass of $FeCl_3$ is 162.2 amu.
>
> b. When we distribute the subscript 3 through the parentheses containing the formula for the ammonium ion, we see that we have 3 nitrogen atoms and 12 hydrogen atoms. Thus, we set up the sum as follows:
>
> $$N: 3 \times 14.00 = 42.00 \text{ amu}$$
> $$H: 12 \times 1.00 = +12.\underline{0}0 \text{ amu}$$
> $$P: 1 \times 30.97 = +30.97 \text{ amu}$$
> $$\underline{O: 4 \times 16.00 = +64.00 \text{ amu}}$$
> $$Total = 148.\underline{9}7 \text{ amu}$$
>
> The formula mass for $(NH_4)_3PO_4$ is 149.0 amu.

> ❓ **Exercise 2.8.1**
>
> Use the atomic masses (rounded to two decimal places) to determine the formula mass for each ionic compound.
>
>   a. TiO_2
>   b. $AgBr$
>   c. $Au(NO_3)_3$
>   d. $Fe_3(PO_4)_2$
>
> **Answer**
>
>   a. 79.87 amu
>   b. 187.77 amu
>   c. 383.0 amu

> 📌 To Your Health: Hydrates
>
> Some ionic compounds have water (H_2O) incorporated within their formula unit. These compounds, called *hydrates*, have a characteristic number of water units associated with each formula unit of the compound. Hydrates are solids, not liquids or solutions, despite the water they contain.
>
> To write the chemical formula of a hydrate, write the number of water units per formula unit of compound after its chemical formula. The two chemical formulas are separated by a vertically centered dot. The hydrate of copper(II) sulfate has five water units associated with each formula unit, so it is written as $CuSO_4 \cdot 5\,H_2O$. The name of this compound is copper(II) sulfate pentahydrate, with the *penta-* prefix indicating the presence of five water units per formula unit of copper(II) sulfate.

Cast (CC BY-SA 4.0; JanSLWC via Wikipedia).

Hydrates have various uses in the health industry. Calcium sulfate hemihydrate ($CaSO_4 \cdot \frac{1}{2} H_2O$), known as **plaster of Paris**, is used to make casts for broken bones. Epsom salt ($MgSO_4 \cdot 7\,H_2O$) is used as a bathing salt and a laxative. Aluminum chloride hexahydrate is an active ingredient in antiperspirants. Table $2.8.1$ lists some useful hydrates.

Table 2.8.1: Names and Formulas of Some Widely Used Hydrates

Formula	Name	Uses
AlCl$_3$•6H$_2$O	aluminum chloride hexahydrate	antiperspirant
CaSO$_4$•½H$_2$O	calcium sulfate hemihydrate (plaster of Paris)	casts (for broken bones and castings)
CaSO$_4$•2H$_2$O	calcium sulfate dihydrate (gypsum)	drywall component
CoCl$_2$•6H$_2$O	cobalt(II) chloride hexahydrate	drying agent, humidity indicator
CuSO$_4$•5H$_2$O	copper(II) sulfate pentahydrate	fungicide, algicide, herbicide
MgSO$_4$•7H$_2$O	magnesium sulfate heptahydrate (Epsom salts)	laxative, bathing salt
Na$_2$CO$_3$•10H$_2$O	sodium carbonate decahydrate (washing soda)	laundry additive/cleaner

Key Takeaway

- Formula masses of ionic compounds can be determined from the masses of the atoms in their formulas.

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2.9: Counting Atoms by the Gram

> **◑ Learning Objectives**
>
> - Use Avogadro's number to convert to moles and vice versa given the number of particles of an element.
> - Use the molar mass to convert to grams and vice versa given the number of moles of an element.

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

This problem of dealing with things that are too small to operate with as single items also occurs in chemistry. Atoms and molecules are too small to see, let alone to count or measure. Chemists needed to select a group of atoms or molecules that would be convenient to operate with.

Avogadro's Number and Mole

In chemistry, it is impossible to deal with a single atom or molecule because we can't see them, count them, or weigh them. Chemists have selected a number of particles with which to work that is convenient. Since molecules are extremely small, you may suspect this number is going to be very large, and you are right. The number of particles in this group is 6.02×10^{23} particles and the name of this group is the **mole** (the abbreviation for *mole* is mol). One mole of any object is 6.02×10^{23} of those objects. There is a particular reason that this number was chosen and this reason will become clear as we proceed.

When chemists are carrying out chemical reactions, it is important that the relationship between the numbers of particles of each reactant is known. Any readily measurable mass of an element or compound contains an extraordinarily large number of atoms, molecules, or ions, so an extremely large numerical unit is needed to count them. The mole is used for this purpose.

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

It is not obvious why eggs come in dozens rather than 10s or 14s, or why a ream of paper contains 500 sheets rather than 400 or 600. The definition of a mole—that is, the decision to base it on 12 g of carbon-12—is also arbitrary. The important point is that 1 mole of carbon—or of anything else, whether atoms, compact discs, or houses—always has the same number of objects: 6.022×10^{23}.

Converting Between Number of Atoms to Moles and Vice Versa

We can use Avogadro's number as a conversion factor, or ratio, in dimensional analysis problems. If we are given the number of atoms of an element X, we can convert it into moles by using the relationship
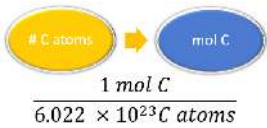
$$1 \text{ mol X} = 6.022 \times 10^{23} \text{ X atoms.}$$

> **✔ Example 2.9.1: Moles of Carbon**
>
> The element carbon exists in two primary forms: graphite and diamond. How many moles of carbon atoms is 4.72×10^{24} atoms of carbon?
>
> **Solution**
>
> <div align="center">Solutions to Example 6.3.1</div>

Steps for Problem Solving	The element carbon exists in two primary forms: graphite and diamond. How many moles of carbon atoms is 4.72×10^{24} atoms of carbon?
Identify the "given" information and what the problem is asking you to "find."	Given: 4.72×10^{24} C atoms Find: mol C
List other known quantities.	$1\,mol = 6.022 \times 10^{23}$ C atoms
Prepare a concept map and use the proper conversion factor.	 $\dfrac{1\,mol\,C}{6.022\,\times\,10^{23}C\,atoms}$
Cancel units and calculate.	4.72×10^{24} ~~C atoms~~ $\times \dfrac{1\,\text{mol C}}{6.02 \times 10^{23}~~\text{C atoms}~~} = 7.84\,\text{mol C}$
Think about your result.	The given number of carbon atoms was greater than Avogadro's number, so the number of moles of C atoms is greater than 1 mole. Since Avogadro's number is a measured quantity with three significant figures, the result of the calculation is rounded to three significant figures.

Molar Mass

Molar mass is defined as the mass of one mole of representative particles of a substance. By looking at a periodic table, we can conclude that the molar mass of the element lithium is 6.94g, the molar mass of zinc is 65.38g, and the molar mass of gold is 196.97g. Each of these quantities contains 6.022×10^{23} atoms of that particular element. The units for molar mass are grams per mole or g/mol. $1.00\,mol$ of carbon-12 atoms has a mass of $12.0\,g$ and contains 6.022×10^{23} atoms. 1.00 mole of any element has a mass numerically equal to its atomic mass in grams and contains 6.022×10^{23} particles. The mass, in grams, of 1 mole of particles of a substance is now called the **molar mass** (mass of 1.00 mole).

Converting Grams to Moles of an Element and Vice Versa

We can also convert back and forth between grams of an element and moles. The conversion factor for this is the molar mass of the substance. The **molar mass** is the ratio giving the number of grams for each one mole of the substance. This ratio is easily found by referring to the atomic mass of the element using the periodic table. This ratio has units of grams per mole or g/mol.

Conversions like this are possible for any substance, as long as the proper atomic mass, formula mass, or molar mass is known (or can be determined) and expressed in grams per mole. Figure 6.4.1 illustrates what conversion factor is needed and two examples are given below.
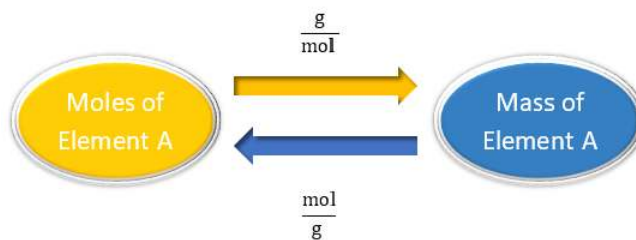

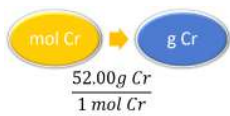Figure 2.9.1: A Simple Flowchart for Converting Between Mass and Moles of an Element.
Flowchart: to convert moles of Element A to mass of Element A, use g/mol, and to convert vice versa, use mol/g.

> ✔ **Example 2.9.2: Chromium**
>
> Chromium metal is used for decorative electroplating of car bumpers and other surfaces. Find the mass of 0.560 moles of chromium.
>
> **Solution**
>
> <div align="center">Solutions to Example 6.3.2</div>
>
> | Steps for Problem Solving | Chromium metal is used for decorative electroplating of car bumpers and other surfaces. Find the mass of 0.560 moles of chromium. |
> |---|---|
> | Identify the "given" information and what the problem is asking you to "find." | Given: 0.560 mol Cr
 Find: g Cr |
> | List other known quantities. | 1 mol Cr = 52.00g Cr |
> | Prepare a concept map and use the proper conversion factor. | mol Cr ➡ g Cr
 $\dfrac{52.00g\ Cr}{1\ mol\ Cr}$ |
> | Cancel units and calculate. | $0.560\ \cancel{mol\ Cr} \times \dfrac{52.00\ \text{g Cr}}{1\ \cancel{mol\ Cr}} = 29.1\ \text{g Cr}$ |
> | Think about your result. | Since the desired amount was slightly more than one half of a mole, the mass should be slightly more than one half of the molar mass. The answer has three significant figures because of the $0.560\,\text{mol}$ |

> ✔ **Example 2.9.3: Silicon**
>
> How many moles are in 107.6g of Si?
>
> **Solution**
>
> <div align="center">Solutions to Example 6.3.3</div>
>
> | Steps for Problem Solving | How many moles are in 107.6g of Si. |
> |---|---|
> | Identify the "given" information and what the problem is asking you to "find." | Given: 107.6g Si
 Find: mol Si |
> | List other known quantities. | 1 mol Si = 28.09g Si |
> | Prepare a concept map and use the proper conversion factor. | g Si ➡ mol Si
 $\dfrac{1\ mol\ Si}{28.09g\ Si}$ |
> | Cancel units and calculate. | $107.6\ \cancel{\text{g Si}} \times \dfrac{1\ \text{mol Si}}{28.09\ \cancel{\text{g Si}}} = 3.83\ \text{mol Si}$ |
> | Think about your result. | Since 1 mol of Si is 28.09g, 107.6 should be about 4 moles. |

? Exercise 2.9.1

  a. How many moles are present in 100.0 g of Al?
  b. What is the mass of 0.552 mol of Ag metal?

Answer a:

   3.706 mol Al

Answer b:

   59.5 g Ag

Summary

- A mole is defined as exactly $6.02214076 \times 10^{23}$ particles, e.g., atoms, molecules, ions or electrons.
- There are $6.02214076 \times 10^{23}$ particles in 1.00 mole. This number is called Avogadro's number.
- The molar mass of an element can be found by referring to the atomic mass on a periodic table with units of g/mol.
- Using dimensional analysis, it is possible to convert between grams, moles, and the number of atoms or molecules.

Further Reading/Supplemental Links

- learner.org/resources/series61.html - The ***learner.org*** website allows users to view streaming videos of the Annenberg series of chemistry videos. You are required to register before you can watch the videos, but there is no charge. The website has one video that relates to this lesson called ***The Mole***.
- Using Avogadro's law, the mass of a substance can be related to the number of particles contained in that mass. The Mole: (www.learner.org/vod/vod_window.html?pid=803)
- Vision Learning tutorial: The Mole http://visionlearning.com/library/mo...p?mid-53&1=&c3=

Contributions & Attributions

-
- Wikipedia

2.10: Counting Molecules by the Gram

> **◗ Learning Objectives**
>
> - Define molecular mass and formula mass.
> - Perform conversions between mass and moles of a compound.
> - Perform conversions between mass and number of particles.

Molecular and Formula Masses

The molecular mass of a substance is the sum of the average masses of the atoms in one molecule of a substance. It is calculated by adding together the atomic masses of the elements in the substance, each multiplied by its subscript (written or implied) in the molecular formula. Because the units of atomic mass are atomic mass units, the units of molecular mass are also atomic mass units. The procedure for calculating molecular masses is illustrated in Example $2.10.1$.

> **✔ Example 2.10.1: Ethanol**
>
> Calculate the molecular mass of ethanol, whose condensed structural formula is CH_3CH_2OH. Among its many uses, ethanol is a fuel for internal combustion engines
>
> **Solution**
>
> <div align="center">Solutions to Example 6.4.1</div>
>
> | Steps for Problem Solving | Calculate the molecular mass of ethanol, whose condensed structural formula is CH_3CH_2OH |
> |---|---|
> | Identify the "given" information and what the problem is asking you to "find." | Given: Ethanol molecule (CH_3CH_2OH)
 Find: molecular mass |
> | Determine the number of atoms of each element in the molecule. | The molecular formula of ethanol may be written in three different ways:
 - CH_3CH_2OH (which illustrates the presence of an ethyl group
 - CH_3CH_2-, and an $-OH$ group)
 - C_2H_5OH, and C_2H_6O;
 All show that ethanol has two carbon atoms, six hydrogen atoms, and one oxygen atom. |
> | Obtain the atomic masses of each element from the periodic table and multiply the atomic mass of each element by the number of atoms of that element. | 1 C atom = 12.011 amu
 1 H atom = 1.0079 amu
 1 O atom = 15.9994 amu |
> | Add the masses together to obtain the molecular mass. | 2C: (2 atoms)(12.011amu/atom) = 24.022 amu
 6H: (6 atoms)(1.0079amu/atom) = 6.0474amu
 +1O: (1 atoms)(15.9994amu/atom) =15.9994amu
 C_2H_6O : molecular mass of ethanol = 46.069amu |

> **? Exercise 2.10.1: Freon**
>
> Calculate the molecular mass of trichlorofluoromethane, also known as Freon-11, which has a condensed structural formula of CCl_3F. Until recently, it was used as a refrigerant. The structure of a molecule of Freon-11 is as follows:
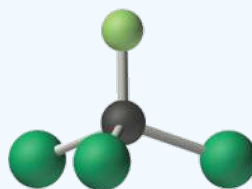
Freon-11, CCl_3F

Figure 2.10.1: Molecular structure of freon-11, CCl_3F.

Answer

137.37 amu

Unlike molecules, which form covalent bonds, ionic compounds do not have a readily identifiable molecular unit. Therefore, for ionic compounds, the **formula mass** (also called the empirical formula mass) of the compound is used instead of the molecular mass. The formula mass is the sum of the atomic masses of all the elements in the empirical formula, each multiplied by its subscript (written or implied). It is directly analogous to the molecular mass of a covalent compound. The units are atomic mass units.

> *Atomic mass, molecular mass, and formula mass all have the same units: atomic mass units.*

✔ Example 2.10.2: Calcium Phosphate

Calculate the formula mass of $Ca_3(PO_4)_2$, commonly called calcium phosphate. This compound is the principal source of calcium found in bovine milk.

Solution

Solutions to Example 6.4.2

Steps for Problem Solving	Calculate the formula mass of $Ca_3(PO_4)_2$, commonly called calcium phosphate.
Identify the "given" information and what the problem is asking you to "find."	Given: Calcium phosphate [$Ca_3(PO_4)_2$] formula unit Find: formula mass
Determine the number of atoms of each element in the molecule.	• The empirical formula—$Ca_3(PO_4)_2$—indicates that the simplest electrically neutral unit of calcium phosphate contains three Ca^{2+} ions and two PO_4^{3-} ions. • The formula mass of this molecular unit is calculated by adding together the atomic masses of three calcium atoms, two phosphorus atoms, and eight oxygen atoms.
Obtain the atomic masses of each element from the periodic table and multiply the atomic mass of each element by the number of atoms of that element.	1 Ca atom = 40.078 amu 1 P atom = 30.973761 amu 1 O atom = 15.9994 amu
Add together the masses to give the formula mass.	3Ca: (3 atoms) (40.078 amu/atom)=120.234amu 2P: (2 atoms) (30.973761amu/atom)=61.947522amu + 8O: (8 atoms)(15.9994amu/atom)=127.9952amu Formula mass of $Ca_3(PO_4)_2$=310.177amu

? Exercise 2.10.2: Silicon Nitride

Calculate the formula mass of Si_3N_4, commonly called silicon nitride. It is an extremely hard and inert material that is used to make cutting tools for machining hard metal alloys.

Figure 2.10.2: Si_3N_4 bearing parts. (Public Domain; David W. Richerson and Douglas W. Freitag; Oak Ridge National Laboratory).

Answer

140.29 amu

Molar Mass

The molar mass of a substance is defined as the mass in grams of 1 mole of that substance. One mole of isotopically pure carbon-12 has a mass of 12 g. For an element, the molar mass is the mass of 1 mol of atoms of that element; for a covalent molecular compound, it is the mass of 1 mol of molecules of that compound; for an ionic compound, it is the mass of 1 mol of formula units. That is, the molar mass of a substance is the mass (in grams per mole) of 6.022×10^{23} atoms, molecules, or formula units of that substance. In each case, the number of grams in 1 mol is the same as the number of atomic mass units that describe the atomic mass, the molecular mass, or the formula mass, respectively.

> *The molar mass of any substance is its atomic mass, molecular mass, or formula mass in grams per mole.*

The periodic table lists the atomic mass of carbon as 12.011 amu; the average molar mass of carbon—the mass of 6.022×10^{23} carbon atoms—is therefore 12.011 g/mol:

Table 2.10.1: Molar Mass of Select Substances

Substance (formula)	Basic Unit	Atomic, Molecular, or Formula Mass (amu)	Molar Mass (g/mol)
carbon (C)	atom	12.011 (atomic mass)	12.011
ethanol (C_2H_5OH)	molecule	46.069 (molecular mass)	46.069
calcium phosphate [$Ca_3(PO_4)_2$]	formula unit	310.177 (formula mass)	310.177

Converting Between Grams and Moles of a Compound

The molar mass of any substance is the mass in grams of one mole of representative particles of that substance. The representative particles can be atoms, molecules, or formula units of ionic compounds. This relationship is frequently used in the laboratory. Suppose that for a certain experiment you need 3.00 moles of calcium chloride ($CaCl_2$). Since calcium chloride is a solid, it would be convenient to use a balance to measure the mass that is needed. Dimensional analysis will allow you to calculate the mass of $CaCl_2$ that you should measure as shown in Example 2.10.3.

✔ Example 2.10.3: Calcium Chloride

Calculate the mass of 3.00 moles of calcium chloride ($CaCl_2$).

Figure 2.10.3: Calcium chloride is used as a drying agent and as a road deicer.

Solution

Solutions to Example 6.4.3

Steps for Problem Solving	Calculate the mass of 3.00 moles of calcium chloride
Identify the "given" information and what the problem is asking you to "find."	Given: 3.00 moles of $CaCl_2$ Find: g $CaCl_2$
List other known quantities.	1 mol $CaCl_2$ = 110.98 g $CaCl_2$
Prepare a concept map and use the proper conversion factor.	 $$\frac{110.98 \; g \; CaCl_2}{1 \; mol \; CaCl_2}$$
Cancel units and calculate.	$$3.00 \; \cancel{mol \; CaCl_2} \times \frac{110.98 \; g \; CaCl_2}{1 \; \cancel{mol \; CaCl_2}} = 333 \; g \; CaCl_2$$
Think about your result.	

? **Exercise 2.10.3: Calcium Oxide**

What is the mass of $7.50 \; mol$ of (calcium oxide) CaO?

Answer

420.60 g

✔ **Example 2.10.4: Water**

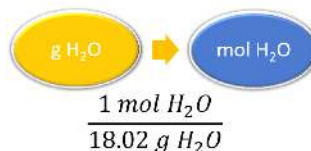How many moles are present in 108 grams of water?

Solution

Solutions to Example 6.4.4

Steps for Problem Solving	How many moles are present in 108 grams of water?
Identify the "given" information and what the problem is asking you to "find."	Given: 108 g H_2O Find: mol H_2O
List other known quantities.	1 mol H_2O = 18.02 g H2O

Steps for Problem Solving	How many moles are present in 108 grams of water?
Prepare a concept map and use the proper conversion factor.	$$\frac{1\ mol\ H_2O}{18.02\ g\ H_2O}$$
Cancel units and calculate.	$108\ \cancel{g\ H_2O} \times \dfrac{1\ mol\ H_2O}{18.02\ \cancel{g\ H_2O}} = 5.99\ mol\ H_2O$
Think about your result.	

? Exercise 2.10.4: Nitrogen Gas

What is the mass of $7.50\ mol$ of Nitrogen gas N_2?

Answer

   210 g

Conversions Between Mass and Number of Particles

In "Conversions Between Moles and Mass", you learned how to convert back and forth between moles and the number of representative particles. Now you have seen how to convert back and forth between moles and mass of a substance in grams. We can combine the two types of problems into one. Mass and number of particles are both related to moles. To convert from mass to number of particles or vice-versa, it will first require a conversion to moles as shown in Figure $2.10.1$ and Example $2.10.5$.
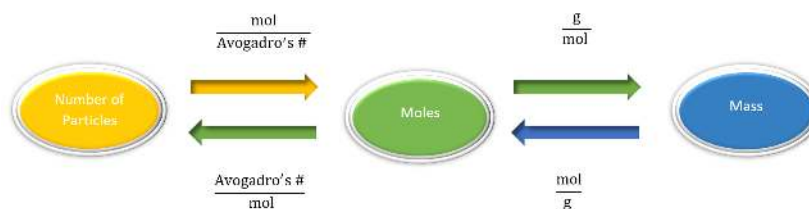

Figure 2.10.4: Conversion from number of particles to mass, or from mass to number of particles, requires two steps. To convert from number of particles to moles, use mol/Avogrado's #, an d to convert from moles to mass, use g/mol.

✔ Example 2.10.5: Chlorine

How many molecules is $20.0\ g$ of chlorine gas, Cl_2?

Solution

Solutions to Example 6.4.5

Steps for Problem Solving	How many molecules is $20.0\ g$ of chlorine gas, Cl_2?
Identify the "given" information and what the problem is asking you to "find."	Given: 20.0 g Cl_2 Find: # Cl_2 molecules
List other known quantities.	• 1 mol Cl_2 = 70.90 g Cl_2, • 1mol Cl_2 = 6.022×10^{23} Cl_2 molecules

Steps for Problem Solving	How many molecules is 20.0 g of chlorine gas, Cl_2?
Prepare a concept map and use the proper conversion factor.	$$\frac{1 \ mol \ Cl_2}{70.90 \ g \ Cl_2} \qquad \frac{6.022 \times 10^{23} \ Cl_2 \ molecules}{1 \ mol \ Cl_2}$$ The conversion factors are 1 mole Cl_2 over 70.90 grams Cl_2, and 6.022×10^23 Cl_2 molecules over 1 mole Cl_2.
Cancel units and calculate.	$$20.0 \ \cancel{g \ Cl_2} \times \frac{1 \ \cancel{mol \ Cl_2}}{70.90 \ \cancel{g \ Cl_2}} \times \frac{6.02 \times 10^{23} \ molecules \ Cl_2}{1 \ \cancel{mol \ Cl_2}}$$ $$= 1.70 \times 10^{23} \ molecules \ Cl_2$$
Think about your result.	Since the given mass is less than half of the molar mass of chlorine, the resulting number of molecules is less than half of Avogadro's number.
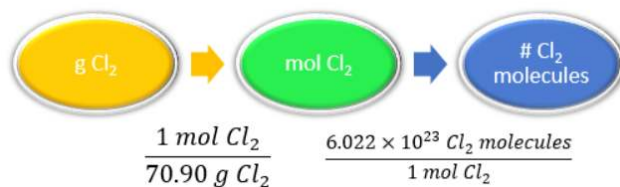
? **Exercise 2.10.5: Calcium Chloride**

How many formula units are in 25.0 g of $CaCl_2$?

Answer

   1.36 x 10^{23} $CaCl_2$ formula units

Summary

- Calculations for formula mass and molecular mass are described.
- Calculations involving conversions between moles of a material and the mass of that material are described.
- Calculations are illustrated for conversions between mass and number of particles.

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2.11: Chemical Formulas as Conversion Factors

> **Learning Objectives**
>
> - Use chemical formulas as conversion factors.

Figure 2.11.1 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.
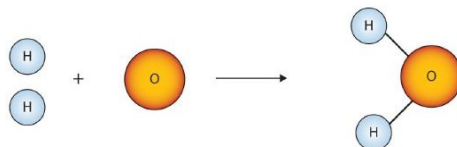

Figure 2.11.1 Water Molecules. The ratio of hydrogen atoms to oxygen atoms used to make water molecules is always 2:1, no matter how many water molecules are being made.
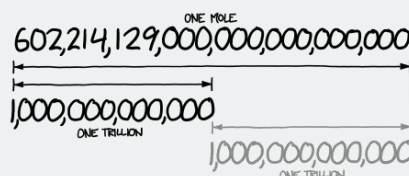
Using formulas to indicate how many atoms of each element we have in a substance, we can relate the number of moles of molecules to the number of moles of atoms. For example, in 1 mol of water (H_2O) we can construct the relationships given in (Table 2.11.1).

Table 2.11.1: 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	$\dfrac{2 \text{ mol H atoms}}{1 \text{ mol H}_2\text{O molecules}}$ or $\dfrac{1 \text{ mol H}_2\text{O molecules}}{2 \text{ mol H atoms}}$
1 O atom	1 mol of O atoms	$\dfrac{1 \text{ mol O atoms}}{1 \text{ mol H}_2\text{O molecules}}$ or $\dfrac{1 \text{ mol H}_2\text{O molecules}}{1 \text{ mol O atoms}}$

> **📌 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 2.11.2: 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	$\dfrac{2 \text{ mol C atoms}}{1 \text{ mol C}_2\text{H}_6\text{O molecules}}$ or $\dfrac{1 \text{ mol C}_2\text{H}_6\text{O molecules}}{2 \text{ mol C atoms}}$
6 H atoms	6 mol of H atoms	$\dfrac{6 \text{ mol H atoms}}{1 \text{ mol C}_2\text{H}_6\text{O molecules}}$ or $\dfrac{1 \text{ mol C}_2\text{H}_6\text{O molecules}}{6 \text{ mol H atoms}}$

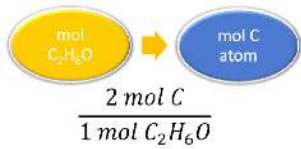| 1 Molecule of C_2H_6O Has	1 Mol of C_2H_6O Has	Molecular and Mass Relationships
1 O atom	1 mol of O atoms	$\dfrac{1 \text{ mol O atoms}}{1 \text{ mol C}_2\text{H}_6\text{O molecules}}$ or $\dfrac{1 \text{ mol C}_2\text{H}_6\text{O molecules}}{1 \text{ mol O atoms}}$
2 (12.01 amu) C 24.02 amu C	2 (12.01 g) C 24.02 g C	$\dfrac{24.02 \text{ g C}}{1 \text{ mol C}_2\text{H}_6\text{O molecules}}$ or $\dfrac{1 \text{ mol C}_2\text{H}_6\text{O molecules}}{24.02 \text{ g C}}$
6 (1.008 amu) H 6.048 amu H	6 (1.008 g) H 6.048 g H	$\dfrac{6.048 \text{ g H}}{1 \text{ mol C}_2\text{H}_6\text{O molecules}}$ or $\dfrac{1 \text{ mol C}_2\text{H}_6\text{O molecules}}{6.048 \text{ g H}}$
1 (16.00 amu) O 16.00 amu O	1 (16.00 g) O 16.00 g O	$\dfrac{16.00 \text{ g O}}{1 \text{ mol C}_2\text{H}_6\text{O molecules}}$ or $\dfrac{1 \text{ mol C}_2\text{H}_6\text{O molecules}}{16.00 \text{ g O}}$

The following example illustrates how we can use the relationships in Table $2.11.2$ as conversion factors.

✔ Example 2.11.1: 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.	$\dfrac{2 \; mol \; C}{1 \; mol \; C_6H_6O}$
Cancel units and calculate.	Note how the unit *mol C_2H_6O molecules* cancels algebraically. $2.5 \; \text{mol C}_2\text{H}_6\text{O molecules} \times \dfrac{2 \text{ mol C atoms}}{1 \; \text{mol C}_2\text{H}_6\text{O molecules}} = 5.0 \text{ mol C atoms}$
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 2.11.1

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

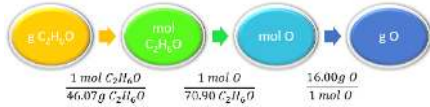 13.5 mol Na atoms, 6.75 mol S atoms, and 27.0 mol O atoms

The fact that 1 mol equals 6.022×10^{23} items can also be used as a conversion factor.

✔ Example 2.11.2: 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.	$75.0 \ \text{g C}_2\text{H}_6\text{O} \times \dfrac{1 \ \text{mol C}_2\text{H}_6\text{O}}{46.07 \ \text{g C}_2\text{H}_6\text{O}} \times \dfrac{1 \ \text{mol O}}{1 \ \text{mol C}_2\text{H}_6\text{O}} \times \dfrac{16.00 \ \text{g O}}{1 \ \text{mol O}} = 26$
Think about your result.	

> **?** **Exercise 2.11.2**
>
> 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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2.12: Mass Percent Composition of Compounds

📖 Learning Objectives

- Determine percent composition of each element in a compound based on mass.

Packaged foods that you eat typically have nutritional information provided on the label. The label on a jar of peanut butter reveals that one serving size is considered to be 32 g. The label also gives the masses of various types of compounds that are present in each serving. One serving contains 7 g of protein, 15 g of fat, and 3 g of sugar. By calculating the fraction of protein, fat, or sugar in one serving size of peanut butter and converting to percent values, we can determine the composition of peanut butter on a percent by mass basis.

Percent Composition

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

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

The sample problem below shows the calculation of the percent composition of a compound based on mass data.

✔ Example 2.12.1: Percent Composition from Mass Data

A certain newly synthesized compound is known to contain the elements zinc and oxygen. When a 20.00 g sample of the compound is decomposed, 16.07 g of zinc remains. Determine the percent composition of the compound.

Solution

Solutions to Example 6.6.1

Steps for Problem Solving	When a 20.00 g sample of the zinc-and-oxygen compound is decomposed, 16.07 g of zinc remains. Determine the percent composition of the compound.
Identify the "given" information and what the problem is asking you to "find."	Given : Mass of compound = 20.00 g Mass of Zn = 16.07 g Find: % Composition (% Zn and %O)
List other known quantities.	Subtract to find the mass of oxygen in the compound. Divide each element's mass by the mass of the compound to find the percent by mass. Mass of oxygen = 20.00 g - 16.07 g = 3.93 g O
Cancel units and calculate.	$$\% \text{ Zn} = \frac{16.07 \text{ g Zn}}{20.00 \text{ g}} \times 100\% = 80.35\% \text{ Zn}$$ $$\% \text{ O} = \frac{3.93 \text{ g O}}{20.00 \text{ g}} \times 100\% = 19.65\% \text{ O}$$ Calculate the percent by mass of each element by dividing the mass of that element by the mass of the compound and multiplying by 100%.
Think about your result.	The calculations make sense because the sum of the two percentages adds up to 100%. By mass, the compound is mostly zinc.

? Exercise 2.12.1

Sulfuric acid, H_2SO_4 is a very useful chemical in industrial processes. If 196.0 g of sulfuric acid contained 64.0g oxygen and 4.0 g of hydrogen, what is the percent composition of the compound?

Answer

    2.04% H, 32.65% S, and 65.3% O

Summary

- Processes are described for calculating the percent composition of a compound based on mass.

2.13: Mass Percent Composition from a Chemical Formula

> ◐ **Learning Objectives**
>
> - Determine the percent composition of each element in a compound from the chemical formula.

The percent composition of a compound can also be determined from the formula of the compound. The subscripts in the formula are first used to calculate the mass of each element in one mole of the compound. This is divided by the molar mass of the compound and multiplied by 100%.

$$\% \text{ by mass} = \frac{\text{mass of element in 1 mol}}{\text{molar mass of compound}} \times 100\%$$

The percent composition of a given compound is always the same, given that the compound is pure.

> ✔ **Example 2.13.1**
>
> Dichlorine heptoxide $\left(Cl_2O_7\right)$ is a highly reactive compound used in some organic synthesis reactions. Calculate the percent composition of dichlorine heptoxide.
>
> **Solution**
>
> <div align="center">Solutions to Example 6.7.1</div>
>
> | Steps for Problem Solving | Calculate the percent composition of dichlorine heptoxide $\left(Cl_2O_7\right)$. |
> |---|---|
> | Identify the "given" information and what the problem is asking you to "find." | Given : Cl_2O_7
 Find: % Composition (% Cl and %O) |
> | List other known quantities. | Mass of Cl in 1 mol Cl_2O_7 , 2 Cl : 2 x 35.45 g = 70.90 g
 Mass of O in 1 mol Cl_2O_7 , 7 O: 7 x 16.00 g = 112.00 g
 Molar mass of Cl_2O_7 = 182.90 g/mol |
> | Cancel units and calculate. | $$\%\,Cl = \frac{70.90 \text{ g Cl}}{182.90 \text{ g}} \times 100\% = 38.76\% \text{ Cl}$$ $$\%\,O = \frac{112.00 \text{ g O}}{182.90 \text{ g}} \times 100\% = 61.24\% \text{ O}$$ Calculate the percent by mass of each element by dividing the mass of that element in 1 mole of the compound by the molar mass of the compound and multiplying by 100%. |
> | Think about your result. | The percentages add up to 100%. |

Percent composition can also be used to determine the mass of a certain element that is contained in any mass of a compound. In the previous sample problem, it was found that the percent composition of dichlorine heptoxide is 38.76% Cl and 61.24% O. Suppose that you needed to know the masses of chlorine and oxygen present in a 12.50 g sample of dichlorine heptoxide. You can set up a conversion factor based on the percent by mass of each element.

$$12.50 \text{ g } Cl_2O_7 \times \frac{38.76 \text{ g Cl}}{100 \text{ g } Cl_2O_7} = 4.845 \text{ g Cl}$$

$$12.50 \text{ g } Cl_2O_7 \times \frac{61.24 \text{ g O}}{100 \text{ g } Cl_2O_7} = 7.655 \text{ g O}$$

The sum of the two masses is 12.50 g the mass of the sample size.

? Exercise 2.13.1

Barium fluoride is a transparent crystal that can be found in nature as the mineral frankdicksonite. Determine the percent composition of barium fluoride.

Answer a:

78.32% Ba and 21.67% F

Summary

- Processes are described for calculating the percent composition of a compound based on the chemical formula.

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2.14: Calculating Empirical Formulas for Compounds

> ◑ **Learning Objectives**
>
> - Define empirical formula.
> - Determine empirical formula from percent composition of a compound.

In the early days of chemistry, there were few tools for the detailed study of compounds. Much of the information regarding the composition of compounds came from the elemental analysis of inorganic materials. The "new" field of organic chemistry (the study of carbon compounds) faced the challenge of not being able to characterize a compound completely. The relative amounts of elements could be determined, but so many of these materials had carbon, hydrogen, oxygen, and possibly nitrogen in simple ratios. We did not know exactly how many of these atoms were actually in a specific molecule.

Determining Empirical Formulas

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

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

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

> ✔ **Example 2.14.1**
>
> A compound of iron and oxygen is analyzed and found to contain 69.94% iron and 30.06% oxygen. Find the empirical formula of the compound.
>
> **Solution**
>
> Solutions to Example 6.8.1
>
> | Steps for Problem Solving | Find the empirical formula of a compound of 69.94% iron and 30.06% oxygen. |
> |---|---|
> | Identify the "given" information and what the problem is asking you to "find." | Given:
% of Fe $= 69.94\%$
% of O $= 30.06\%$
Find: Empirical formula $= Fe_?O_?$ |
> | *Calculate* | |
> | | |

Steps for Problem Solving	Find the empirical formula of a compound of 69.94% iron and 30.06% oxygen.
a. Assume a 100 g sample, convert the same % values to grams.	69.94 g Fe 30.06 g O
b. Convert to moles.	$69.94 \text{ g Fe} \times \dfrac{1 \text{ mol Fe}}{55.85 \text{ g Fe}} = 1.252 \text{ mol Fe}$ $30.06 \text{ g O} \times \dfrac{1 \text{ mol O}}{16.00 \text{ g O}} = 1.879 \text{ mol O}$
c. Divide both moles by the smallest of the results.	$\text{Fe} : \dfrac{1.252 \text{ mol}}{1.252}$ $\text{O} : \dfrac{1.879 \text{ mol}}{1.252}$ The "non-whole number" empirical formula of the compound is $\text{Fe}_1\text{O}_{1.5}$
Multiply each of the moles by the smallest whole number that will convert each into a whole number.	Fe:O = 2 (1:1.5) = 2:3 Since the moles of O is still not a whole number, both moles can be multiplied by 2, while rounding to a whole number.
Write the empirical formula.	The empirical formula of the compound is Fe_2O_3.
Think about your result.	The subscripts are whole numbers and represent the mole ratio of the elements in the compound. The compound is the ionic compound iron (III) oxide.

? Exercise 2.14.1

Mercury forms a compound with chlorine that is 73.9% mercury and 26.1% chlorine by mass. What is the empirical formula?

Answer

HgCl_2

Summary

- A process is described for the calculation of the empirical formula of a compound, based on the percent composition of that compound.

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2.15: Calculating Molecular Formulas for Compounds

> **◖◗ Learning Objectives**
>
> - Understand the difference between empirical formulas and molecular formulas.
> - Determine molecular formula from percent composition and molar mass of a compound.

Below, we see two carbohydrates: glucose and sucrose. Sucrose is almost exactly twice the size of glucose, although their empirical formulas are very similar. Some people can distinguish them on the basis of taste, but it's not a good idea to go around tasting chemicals. The best way to tell glucose and sucrose apart is to determine the molar masses—this approach allows you to easily tell which compound is which.
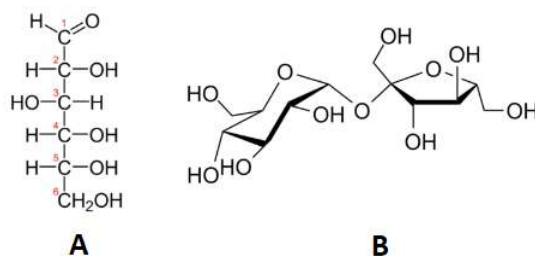
Figure 2.15.1: (A) the molecular structure of glucose and (B) the molecular structure of sucrose.

Molecular Formulas

Molecular formulas give the kind and number of atoms of each element present in the molecular compound. In many cases, the molecular formula is the same as the empirical formula. The chemical formula will always be some *integer multiple* (n) of the empirical formula (i.e. integer multiples of the subscripts of the empirical formula).

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

therefore

$$n = \frac{\text{Molecular Formula}}{\text{Empirical Formula}}$$

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

$$n = \frac{MM(molar\,mass)}{EFM(empirical\,formula\,molar\,mass)}$$

Table 2.15.1 shows the comparison between the empirical and molecular formula of methane, acetic acid, and glucose, and the different values of n. The molecular formula of methane is CH_4 and because it contains only one carbon atom, that is also its empirical formula. Sometimes, however, the molecular formula is a simple whole number multiple of the empirical formula. Acetic acid is an organic acid that is the main component of vinegar. Its molecular formula is $C_2H_4O_2$. Glucose is a simple sugar that cells use as a primary source of energy. Its molecular formula is $C_6H_{12}O_6$. The structures of both molecules are shown in Figure 2.15.2 They are very different compounds, yet both have the same empirical formula of CH_2O.

Table 2.15.1: Molecular Formula and Empirical Formula of Various Compounds.

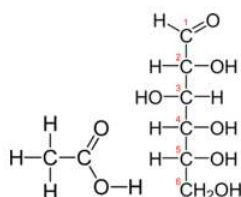| Name of Compound	Molecular Formula	Empirical Formula	n
Methane	CH_4	CH_4	1
Acetic acid	$C_2H_4O_2$	CH_2O	2
Glucose	$C_6H_{12}O_6$	CH_2O	6

Figure 2.15.2: Acetic acid (left) has a molecular formula of $C_2H_4O_2$, while glucose (right) has a molecular formula of $C_6H_{12}O_6$. Both have the empirical formula CH_2O.

Empirical formulas can be determined from the percent composition of a compound as discussed in section 6.8. In order to determine its molecular formula, it is necessary to know the molar mass of the compound. Chemists use an instrument called a mass spectrometer to determine the molar mass of compounds. In order to go from the empirical formula to the molecular formula, follow these steps:

1. Calculate the **empirical formula molar mass (EFM)**.
2. Divide the molar mass of the compound by the empirical formula molar mass. The result should be a whole number or very close to a whole number.
3. Multiply all the subscripts in the empirical formula by the whole number found in step 2. The result is the molecular formula.

✔ **Example 2.15.1**

The empirical formula of a compound of boron and hydrogen is BH_3. Its molar mass is $27.7\ \text{g/mol}$ Determine the molecular formula of the compound.

Solution

Solutions to Example 6.9.1

Steps for Problem Solving	Determine the molecular formula of BH_3.
Identify the "given" information and what the problem is asking you to "find."	Given: Empirical formula $= BH_3$ Molar mass $= 27.7\ \text{g/mol}$ Find: Molecular formula $=?$
Calculate the empirical formula mass (EFM).	Empirical formula molar mass $(\text{EFM}) = 13.84\ \text{g/mol}$
Divide the molar mass of the compound by the empirical formula mass. The result should be a whole number or very close to a whole number.	$\dfrac{\text{molar mass}}{\text{EFM}} = \dfrac{27.7 g/mol}{13.84 g/mol} = 2$
Multiply all the subscripts in the empirical formula by the whole number found in step 2. The result is the molecular formula.	$BH_3 \times 2 = B_2H_6$
Write the molecular formula.	The molecular formula of the compound is B_2H_6.
Think about your result.	The molar mass of the molecular formula matches the molar mass of the compound.

? **Exercise 2.15.1**

Vitamin C (ascorbic acid) contains 40.92 % C, 4.58 % H, and 54.50 % O, by mass. The experimentally determined molecular mass is 176 amu. What are the empirical and chemical formulas for ascorbic acid?

Answer Empirical Formula
    $C_3H_4O_3$
Answer Molecular Formula
    $C_6H_8O_6$

Summary

- A procedure is described that allows the calculation of the exact molecular formula for a compound.

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3: Reactions and Stoichiometry

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3.1: Chemical Equations

> **⟨⟩ Learning Objectives**
>
> - Identify the reactants and products in any chemical reaction.
> - Convert word equations into chemical equations.
> - Use the common symbols, (s), (l), (g), (aq), and $\rightarrow$ appropriately when writing a chemical reaction.

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

Reactants and Products

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

Sometimes when reactants are put into a reaction vessel, a reaction will take place to produce products. Reactants are the starting materials, that is, whatever we have as our initial ingredients. The products are just that—what is produced—or the result of what happens to the reactants when we put them together in the reaction vessel. If we think about baking chocolate chip cookies, our reactants would be flour, butter, sugar, vanilla, baking soda, salt, egg, and chocolate chips. What would be the products? Cookies! The reaction vessel would be our mixing bowl.

$$\underbrace{\text{Flour} + \text{Butter} + \text{Sugar} + \text{Vanilla} + \text{Baking Soda} + \text{Eggs} + \text{Chocolate Chips}}_{\text{Ingredients} = \text{Reactants}} \rightarrow \underbrace{\text{Cookies}}_{\text{Product}}$$

Writing Chemical Equations

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

$$\underbrace{2\,SO_2(g) + O_2(g)}_{\text{Reactants}} \rightarrow \underbrace{2\,SO_3(g)}_{\text{Products}}$$
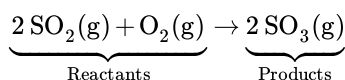
In chemical reactions, the reactants are found before the symbol "$\rightarrow$" and the products are found after the symbol "$\rightarrow$". The general equation for a reaction is:

$$\text{Reactants} \rightarrow \text{Products}$$
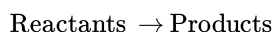
There are a few special symbols that we need to know in order to "talk" in chemical shorthand. In the table below is the summary of the major symbols used in chemical equations. Table $3.1.1$ shows a listing of symbols used in chemical equations.

Table 3.1.1: Symbols Used in Chemical Equations

Symbol	Description	Symbol	Description
$+$	used to separate multiple reactants or products	(s)	reactant or product in the solid state
$\rightarrow$	yield sign; separates reactants from products	(l)	reactant or product in the liquid state
$\rightleftharpoons$	replaces the yield sign for reversible reactions that reach equilibrium	(g)	reactant or product in the gas state

Symbol	Description	Symbol	Description
$\xrightarrow{Pt}$	formula written above the arrow is used as a catalyst in the reaction	(aq)	reactant or product in an aqueous solution (dissolved in water)
$\xrightarrow{\Delta}$	triangle indicates that the reaction is being heated		

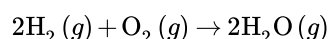Chemists have a choice of methods for describing a chemical reaction.

  1. They could draw a picture of the chemical reaction.
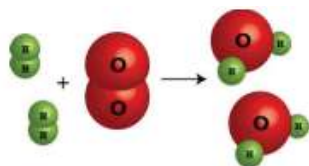
  2. They could write a word equation for the chemical reaction:

"Two molecules of hydrogen gas react with one molecule of oxygen gas to produce two molecules of water vapor."

  3. They could write the equation in chemical shorthand.

$$2H_2\,(g) + O_2\,(g) \rightarrow 2H_2O\,(g)$$

In the symbolic equation, chemical formulas are used instead of chemical names for reactants and products, while symbols are used to indicate the phase of each substance. It should be apparent that the chemical shorthand method is the quickest and clearest method for writing chemical equations.

We could write that an aqueous solution of calcium nitrate is added to an aqueous solution of sodium hydroxide to produce solid calcium hydroxide and an aqueous solution of sodium nitrate. Or in shorthand we could write:

$$Ca(NO_3)_2\,(aq) + 2NaOH\,(aq) \rightarrow Ca(OH)_2\,(s) + 2NaNO_3\,(aq)$$
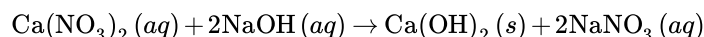
How much easier is that to read? Let's try it in reverse. Look at the following reaction in shorthand and write the word equation for the reaction:

$$Cu\,(s) + AgNO_3\,(aq) \rightarrow Cu(NO_3)_2\,(aq) + Ag\,(s)$$
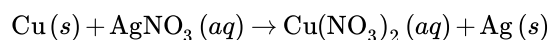
The word equation for this reaction might read something like "solid copper reacts with an aqueous solution of silver nitrate to produce a solution of copper (II) nitrate with solid silver."

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

  1. Identify the reactants and products. This will help you know which symbols go on each side of the arrow and where the $+$ signs go.
  2. Write the correct formulas for all compounds. You will need to use the rules you learned in Chapter 5 (including making all ionic compounds charge balanced).
  3. Write the correct formulas for all elements. Usually this is given straight off of the periodic table. However, there are seven elements that are considered diatomic, meaning that they are always found in pairs in nature. They include those elements listed in the table.

Table 3.1.1*: Diatomic Elements*

Element Name	Hydrogen	Nitrogen	Oxygen	Fluorine	Chlorine	Bromine	Iodine
Formula	H_2	N_2	O_2	F_2	Cl_2	Br_2	I_2

✔ **Example 3.1.1**

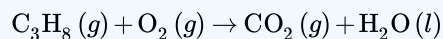Transfer the following symbolic equations into word equations or word equations into symbolic equations.

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

b. Gaseous propane, C_3H_8, burns in oxygen gas to produce gaseous carbon dioxide and liquid water.

c. Hydrogen fluoride gas reacts with an aqueous solution of potassium carbonate to produce an aqueous solution of potassium fluoride, liquid water, and gaseous carbon dioxide.

Solution

a. An aqueous solution of hydrochloric acid reacts with an aqueous solution of sodium hydroxide to produce an aqueous solution of sodium chloride and liquid water.

b. Reactants: propane (C_3H_8) and oxygen (O_2)

Product: carbon dioxide (CO_2) and water (H_2O)

$$C_3H_8\,(g) + O_2\,(g) \rightarrow CO_2\,(g) + H_2O\,(l)$$

c. Reactants: hydrogen fluoride and potassium carbonate

Products: potassium fluoride, water, and carbon dioxide

$$HF\,(g) + K_2CO_3\,(aq) \rightarrow KF\,(aq) + H_2O\,(l) + CO_2\,(g)$$

? **Exercise 3.1.1**

Transfer the following symbolic equations into word equations or word equations into symbolic equations.

a. Hydrogen gas reacts with nitrogen gas to produce gaseous ammonia.

b. $HCl\,(aq) + LiOH\,(aq) \rightarrow LiCl\,(aq) + H_2O\,(l)$

c. Copper metal is heated with oxygen gas to produce solid copper(II) oxide.

Answer a

$$H_2(g) + N_2(g) \rightarrow NH_3(g)$$
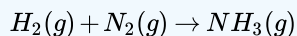
Answer b

An aqueous solution of hydrochloric acid reacts with an aqueous solution of lithium hydroxide to produce an aqueous solution of lithium chloride and liquid water.

Answer c

$$Cu(s) + O_2(g) \rightarrow CuO(s)$$
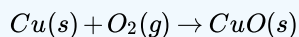
Summary

- A chemical reaction is the process by which one or more substances are changed into one or more new substances.
- Chemical reactions are represented by chemical equations.
- Chemical equations have reactants on the left, an arrow that is read as "yields", and the products on the right.

3.2: How to Write Balanced Chemical Equations

> ◀▶ **Learning Objectives**
>
> - Explain the roles of subscripts and coefficients in chemical equations.
> - Balance a chemical equation when given the unbalanced equation.
> - Explain the role of the Law of Conservation of Mass in a chemical reaction.

Even though chemical compounds are broken up and new compounds are formed during a chemical reaction, atoms in the reactants do not disappear, nor do new atoms appear to form the products. In chemical reactions, atoms are never created or destroyed. The same atoms that were present in the reactants are present in the products—they are merely reorganized into different arrangements. In a complete chemical equation, the two sides of the equation must be present on the reactant and the product sides of the equation.

Coefficients and Subscripts

There are two types of numbers that appear in chemical equations. There are subscripts, which are part of the chemical formulas of the reactants and products; and there are coefficients that are placed in front of the formulas to indicate how many molecules of that substance is used or produced.

$$\text{Cu}_{(s)} + 2\,\text{AgNO}_{3(aq)} \longrightarrow \text{Cu(NO}_3)_{2(aq)} + 2\,\text{Ag}_{(s)}$$
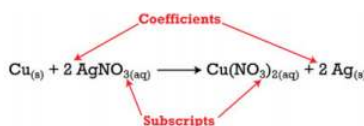
Figure 3.2.1: Balancing Equations. You cannot change subscripts in a chemical formula to balance a chemical equation; you can change only the coefficients. Changing subscripts changes the ratios of atoms in the molecule and the resulting chemical properties. For example, water (H_2O) and hydrogen peroxide (H_2O_2) are chemically distinct substances. H_2O_2 decomposes to H_2O and O_2 gas when it comes in contact with the metal platinum, whereas no such reaction occurs between water and platinum.

The **subscripts** are part of the formulas and once the formulas for the reactants and products are determined, the subscripts may not be changed. The **coefficients** indicate the number of each substance involved in the reaction and may be changed in order to balance the equation. The equation above indicates that one mole of solid copper is reacting with two moles of aqueous silver nitrate to produce one mole of aqueous copper (II) nitrate and two atoms of solid silver.

Balancing a Chemical Equation

Because the identities of the reactants and products are fixed, the equation cannot be balanced by changing the subscripts of the reactants or the products. To do so would change the chemical identity of the species being described, as illustrated in Figure 3.2.1.
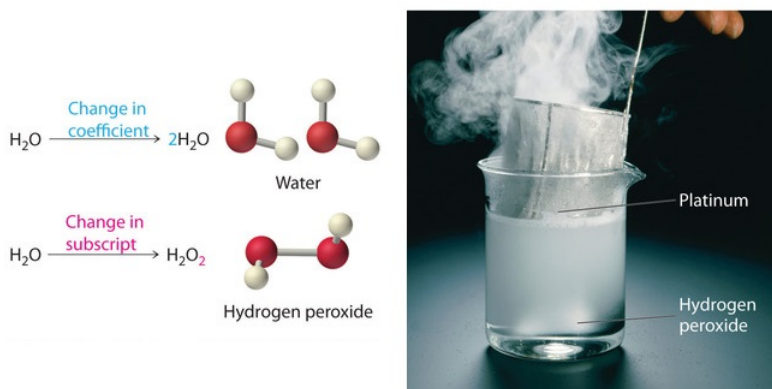
Original molecule H_2O: if the coefficient 2 is added in front, that makes 2 water molecules; but if the subscript 2 is added to make H_2O_2, that's hydrogen peroxide.
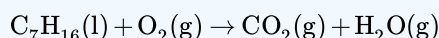
The simplest and most generally useful method for balancing chemical equations is "inspection," better known as trial and error. The following is an efficient approach to balancing a chemical equation using this method.

📌 **Steps in Balancing a Chemical Equation**

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

✔ **Example 3.2.1: Combustion of Heptane**

Balance the chemical equation for the combustion of Heptane (C_7H_{16}).

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

Solution

Solutions to Example 3.2.1

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

✔ **Example 3.2.2: Combustion of Isooctane**

Combustion of Isooctane (C_8H_{18})

$$C_8H_{18}(l) + O_2(g) \longrightarrow CO_2(g) + H_2O(g)$$
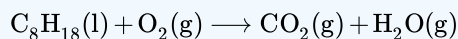
Solution

The assumption that the final balanced chemical equation contains only one molecule or formula unit of the most complex substance is not always valid, but it is a good place to start. The combustion of any hydrocarbon with oxygen produces carbon dioxide and water.

Solutions to Example 7.4.2

Steps	Example
1. **Identify the most complex substance.**	The most complex substance is the one with the largest number of different atoms, which is C_8H_{18}. We will assume initially that the final balanced chemical equation contains 1 molecule or formula unit of this substance.
2. **Adjust the coefficients.**	a. The first element that appears only once in the reactants is carbon: 8 carbon atoms in isooctane means that there must be 8 CO_2 molecules in the products: $$C_8H_{18}(l) + O_2(g) \longrightarrow \underline{8}CO_2(g) + H_2O(g)$$ • 8 carbon atoms on both reactant and product sides b. 18 hydrogen atoms in isooctane means that there must be 9 H_2O molecules in the products: $$C_8H_{18}(l) + O_2(g) \longrightarrow 8\,CO_2(g) + \underline{9}H_2O(g)$$ • 18 hydrogen atoms on both reactant and product sides
3. **Balance polyatomic ions as a unit.**	There are no polyatomic ions to be considered in this reaction.
4. **Balance the remaining atoms.**	The carbon and hydrogen atoms are now balanced, but we have 25 oxygen atoms on the right side and only 2 oxygen atoms on the left. We can balance the least complex substance, O_2, but because there are 2 oxygen atoms per O_2 molecule, we must use a fractional coefficient ($\frac{25}{2}$) to balance the oxygen atoms: $$C_8H_{18}(l) + \underline{\frac{25}{2}}O_2(g) \rightarrow 8\,CO_2(g) + 9\,H_2O(g)$$ • 25 oxygen atoms on both reactant and product sides The equation is now balanced, but we usually write equations with whole number coefficients. We can eliminate the fractional coefficient by multiplying all coefficients on both sides of the chemical equation by **2**: $$\underline{2}C_8H_{18}(l) + \underline{25}O_2(g) \longrightarrow \underline{16}CO_2(g) + \underline{18}H_2O(g)$$

Steps	Example
5. **Check your work.**	The balanced chemical equation has 16 carbon atoms, 36 hydrogen atoms, and 50 oxygen atoms on each side. Balancing equations requires some practice on your part as well as some common sense. If you find yourself using very large coefficients or if you have spent several minutes without success, go back and make sure that you have written the formulas of the reactants and products correctly.

✔ Example 3.2.3: Precipitation of Lead (II) Chloride

Aqueous solutions of lead (II) nitrate and sodium chloride are mixed. The products of the reaction are an aqueous solution of sodium nitrate and a solid precipitate of lead (II) chloride. Write the balanced chemical equation for this reaction.

Solution

Solutions to Example 7.4.3

Steps	Example
1. **Identify the most complex substance.**	The most complex substance is lead (II) chloride. $$\mathrm{Pb(NO_3)_2(aq) + NaCl(aq) \rightarrow NaNO_3(aq) + PbCl_2(s)}$$
2. **Adjust the coefficients.**	There are twice as many chloride ions in the reactants as there are in the products. Place a 2 in front of the NaCl in order to balance the chloride ions. $$\mathrm{Pb(NO_3)_2(aq) + \underline{2}NaCl(aq) \rightarrow NaNO_3(aq) + PbCl_2(s)}$$ • 1 Pb atom on both reactant and product sides • 2 Na atoms on reactant side, 1 Na atom on product side • 2 Cl atoms on both reactant and product sides
3. **Balance polyatomic ions as a unit.**	The nitrate ions are still unbalanced. Place a 2 in front of the NaNO$_3$. The result is: $$\mathrm{Pb(NO_3)_2(aq) + 2\,NaCl(aq) \rightarrow \underline{2}NaNO_3(aq) + PbCl_2(s)}$$ • 1 Pb atom on both reactant and product sides • 2 Na atoms on both reactant and product sides • 2 Cl atoms on both reactant and product sides • 2 NO$_3^-$ atoms on both reactant and product sides
4. **Balance the remaining atoms.**	There is no need to balance the remaining atoms because they are already balanced.
5. **Check your work.**	$$\mathrm{Pb(NO_3)_2(aq) + 2\,NaCl(aq) \rightarrow 2\,NaNO_3(aq) + PbCl_2(s)}$$ • 1 Pb atom on both reactant and product sides • 2 Na atoms on both reactant and product sides • 2 Cl atoms on both reactant and product sides • 2 NO$_3^-$ atoms on both reactant and product sides

? Exercise 3.2.1

Is each chemical equation balanced?

a. $2\,Hg(\ell) + O_2(g) \rightarrow Hg_2O_2(s)$
b. $C_2H_4(g) + 2\,O_2(g) \rightarrow 2\,CO_2(g) + 2\,H_2O(g)$
c. $Mg(NO_3)_2(s) + 2\,Li(s) \rightarrow Mg(s) + 2\,LiNO_3(s)$

Answer a

yes

Answer b

no

Answer c

yes

? Exercise 3.2.2

Balance the following chemical equations.

a. $N_2(g) + O_2(g) \rightarrow NO_2(g)$
b. $Pb(NO_3)_2(aq) + FeCl_3(aq) \rightarrow Fe(NO_3)_3(aq) + PbCl_2(s)$
c. $C_6H_{14}(l) + O_2(g) \rightarrow CO_2(g) + H_2O(g)$

Answer a

$N_2\,(g) + 2O_2\,(g) \rightarrow 2NO_2\,(g)$

Answer b

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

Answer c

$2C_6H_{14}(l) + 19O_2(g) \rightarrow 12CO_2(g) + 14H_2O(g)$
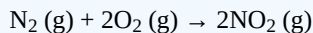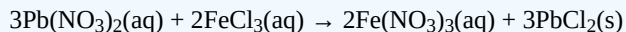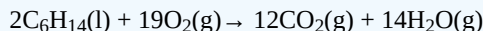
Summary

- To be useful, chemical equations must always be balanced. Balanced chemical equations have the same number and type of each atom on both sides of the equation.
- The coefficients in a balanced equation must be the simplest whole number ratio. Mass is always conserved in chemical reactions.

Vocabulary

- **Chemical reaction -** The process in which one or more substances are changed into one or more new substances.
- **Reactants -** The starting materials in a reaction.
- **Products -** Materials present at the end of a reaction.
- **Balanced chemical equation -** A chemical equation in which the number of each type of atom is equal on the two sides of the equation.
- **Subscripts -** Part of the chemical formulas of the reactants and products that indicate the number of atoms of the preceding element.
- **Coefficient -** A small whole number that appears in front of a formula in a balanced chemical equation.

3.3: Stoichiometry

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

Stoichiometry, by definition, is the calculation of the quantities of reactants or products in a chemical reaction using the relationships found in the balanced chemical equation. The word stoichiometry is actually Greek from two words: $\sigma\tau o\iota\kappa\eta\iota o\nu$, which means "element", and \(\mu \epsilon \tau \rho \omicron \nu), which means "measure".

Interpreting Chemical Equations

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

$$2CuSO_4 + 4KI \rightarrow 2CuI + 2K_2SO_4 + I_2$$
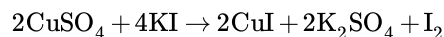
The coefficients used, as we have learned, tell us the relative amounts of each substance in the equation. So for every 2 units of copper (II) sulfate ($CuSO_4$) we have, we need to have 4 units of potassium iodide (KI). For every two dozen copper (II) sulfates, we need 4 dozen potassium iodides. Because the unit "mole" is also a counting unit, we can interpret this equation in terms of moles, as well: For every two moles of copper (II) sulfate, we need 4 moles potassium iodide.

The production of ammonia (NH_3) from nitrogen and hydrogen gases is an important industrial reaction called the Haber process, after German chemist Fritz Haber.

$$N_2\,(g) + 3H_2\,(g) \rightarrow 2NH_3\,(g)$$
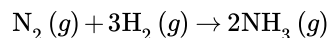
The balanced equation can be analyzed in several ways, as shown in the figure below.

1 molecule **N$_2$**   3 molecules **H$_2$**   2 molecules **NH$_3$**
1 mol **N$_2$**   3 mol **H$_2$**   2 mol **NH$_3$**
28.02 g **N$_2$**   3 x 2.02 g = 6.06 g **H$_2$** 2 x 17.04 g = 34.08 g **NH$_3$**
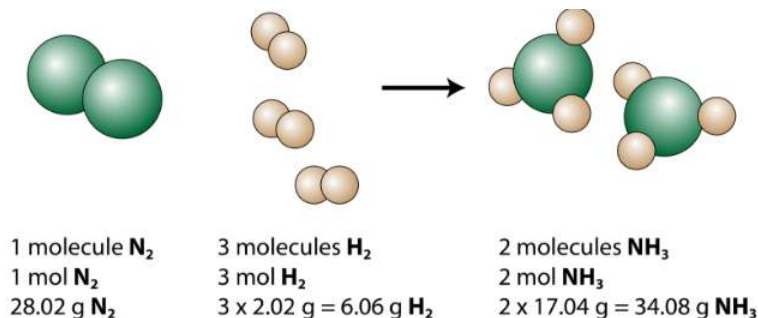
Figure 3.3.1: This representation of the production of ammonia from nitrogen and hydrogen show several ways to interpret the quantitative information of a chemical reaction.

We see that 1 molecule of nitrogen reacts with 3 molecules of hydrogen to form 2 molecules of ammonia. This is the smallest possible relative amount of the reactants and products. To consider larger relative amounts, each coefficient can be multiplied by the same number. For example, 10 molecules of nitrogen would react with 30 molecules of hydrogen to produce 20 molecules of ammonia.

The most useful quantity for counting particles is the mole. So if each coefficient is multiplied by a mole, the balanced chemical equation tells us that 1 mole of nitrogen reacts with 3 moles of hydrogen to produce 2 moles of ammonia. This is the conventional way to interpret any balanced chemical equation.

Finally, if each mole quantity is converted to grams by using the molar mass, we can see that the law of conservation of mass is followed. 1 mol of nitrogen has a mass of $28.02\ g$ while 3 mol of hydrogen has a mass of $6.06\ g$, and 2 mol of ammonia has a mass of $34.08\ g$

$$28.02 \text{ g N}_2 + 6.06 \text{ g H}_2 \rightarrow 34.08 \text{ g NH}_3$$
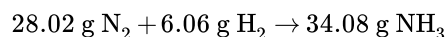
Mass and the number of atoms must be conserved in any chemical reaction. The number of molecules is not necessarily conserved.

✔ **Example 3.3.1**

The equation for the combustion of ethane (C_2H_6) is

$$2C_2H_6 + 7O_2 \rightarrow 4CO_2 + 6H_2O$$
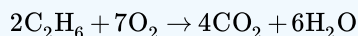
a. Indicate the number of formula units or molecules in the balanced equation.
b. Indicate the number of moles present in the balanced equation.

Solution
a. Two molecules of C_2H_6 plus seven molecules of O_2 yields four molecules of CO_2 plus six molecules of H_2O.
b. Two moles of C_2H_6 plus seven moles of O_2 yields four moles of CO_2 plus six moles of H_2O.

? **Exercise 3.3.1**

For the following equation below, indicate the number of formula units or molecules, and the number of moles present in the balanced equation.

$$KBrO_3 + 6KI + 6HBr \rightarrow 7KBr + 3H_2O$$

Answer

One molecules of $KBrO_3$ plus six molecules of KI plus six molecules of HBr yields seven molecules of KBr plus three molecules of I_2 and three molecules of H_2O. One mole of $KBrO_3$ plus six moles of KI plus six moles of HBr yields seven moles of KBr plus three moles of I_2 plus three moles of H_2O.

Summary

- Stoichiometry is the calculation of the quantities of reactants or products in a chemical reaction using the relationships found in a balanced chemical equation.
- The coefficients in a balanced chemical equation represent the reacting ratios of the substances in the reaction.
- The coefficients of a balanced equation can be used to determine the ratio of moles of all substances in the reaction.

Vocabulary

- **Stoichiometry** - The calculation of quantitative relationships of the reactants and products in a balanced chemical equation.
- **Formula unit** - The empirical formula of an ionic compound.
- **Mole ratio** - The ratio of the moles of one reactant or product to the moles of another reactant or product according to the coefficients in the balanced chemical equation.


# 3.4: 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:

$$2H_2 + O_2 \rightarrow 2H_2O$$
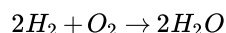
The convention for writing balanced chemical equations is to use the lowest whole-number ratio for the coefficients. However, the equation is balanced as long as the coefficients are in a 2:1:2 ratio. For example, this equation is also balanced if we write it as
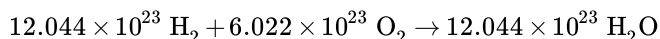
$$4H_2 + 2O_2 \rightarrow 4H_2O$$
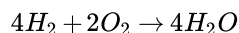
The ratio of the coefficients is 4:2:4, which reduces to 2:1:2. The equation is also balanced if we were to write it as

$$22H_2 + 11O_2 \rightarrow 22H_2O$$
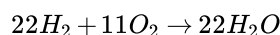
because 22:11:22 also reduces to 2:1:2.

Suppose we want to use larger numbers. Consider the following coefficients:

$$12.044 \times 10^{23} \text{ H}_2 + 6.022 \times 10^{23} \text{ O}_2 \rightarrow 12.044 \times 10^{23} \text{ H}_2O$$

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

$$2 \ mol \text{ H}_2 + 1 \ mol \text{ O}_2 \rightarrow 2 \ mol \text{ H}_2O$$
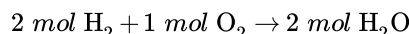
We can leave out the word *mol* and not write the 1 coefficient (as is our habit), so the final form of the equation, still balanced, is

$$2 \text{ H}_2 + O_2 \rightarrow 2 \text{ H}_2O$$
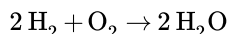
Now we interpret the coefficients as referring to molar amounts, not individual molecules. The lesson? *Balanced chemical equations are balanced not only at the molecular level, but also in terms of molar amounts of reactants and products.* Thus, we can read this reaction as "two moles of hydrogen react 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:

$$\frac{2 \text{ mol H}_2}{1 \text{ mol O}_2} \text{ or } \frac{1 \text{ mol O}_2}{2 \text{ mol H}_2}$$

$$\frac{2 \text{ mol H}_2O}{1 \text{ mol O}_2} \text{ or } \frac{1 \text{ mol O}_2}{2 \text{ mol H}_2O}$$

$$\frac{2 \text{ mol H}_2}{2 \text{ mol H}_2O} \text{ or } \frac{2 \text{ mol H}_2O}{2 \text{ mol H}_2}$$

We can use these 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 3.4.1

How many moles of oxygen react with hydrogen to produce 27.6 mol of H_2O?
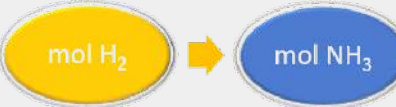
Solution

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.	mol H_2O ➡ mol O_2 $$\dfrac{1\ mol\ O_2}{2\ mol\ H_2O}$$
Cancel units and calculate.	$$27.6\ \cancel{mol\ H_2O} \times \dfrac{1\ mol\ O_2}{2\ \cancel{mol\ H_2O}} = 13.8\ mol\ O_2$$ 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 3.4.2

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: $H_2 = 4.20\ mol$ Find: mol of NH_3
List other known quantities.	3 mol H_2 = 2 mol NH_3
Prepare a concept map and use the proper conversion factor.	mol H_2 ➡ mol NH_3 $$\dfrac{2\ mol\ NH_3}{3\ mol\ H_2}$$

| Steps for Problem Solving	How many moles of ammonia are produced if 4.20 moles of hydrogen are reacted with an excess of nitrogen?
Cancel units and calculate.	$$4.20 \, \cancel{\text{mol } H_2} \times \frac{2 \text{ mol } NH_3}{3 \, \cancel{\text{mol } H_2}} = 2.80 \text{ mol } NH_3$$ The reaction of 4.20 mol of hydrogen with excess nitrogen produces 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 3.4.3

a. Given the following balanced chemical equation:

$$C_5H_{12} + 8\,O_2 \rightarrow 5\,CO_2 + 6\,H_2O$$
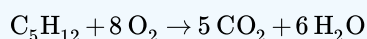
, How many moles of H_2O can be formed if 0.0652 mol of C_5H_{12} were to react?

b. Balance the following unbalanced equation and determine how many moles of H_2O are produced when 1.65 mol of NH_3 react:

$$NH_3 + O_2 \rightarrow N_2 + H_2O$$
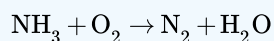
Answer a

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.

3.5: Making Molecules- Mole to Mass (or vice versa) and Mass-to-Mass Conversions

> ◖ Learning Objectives
>
> - Convert from mass or moles of one substance to mass or moles of another substance in a chemical reaction.

Mole to Mass Conversions

We have established that a balanced chemical equation is balanced in terms of moles, as well as atoms or molecules. We have used balanced equations to set up ratios, in terms of moles of materials, that we can use as conversion factors to answer stoichiometric questions—such as how many moles of substance A react with so many moles of reactant B. We can extend this technique even further. Recall that we can relate a molar amount to a mass amount using molar mass. We can use that relation to answer stoichiometry questions in terms of the masses of a particular substance, in addition to moles. We do this using the following sequence:
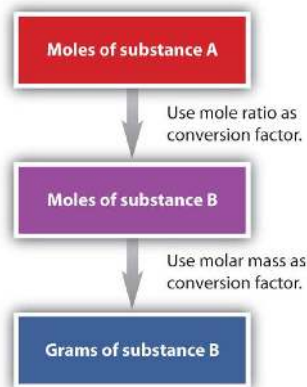
Collectively, these conversions are called mole-mass calculations. Flowchart of mole mass calculations: To convert from moles of substance A to moles of substance B, use the mole ratio conversion factor, and to convert from moles to grams of substance B, use molar mass conversion factor

As an example, consider the balanced chemical equation

$$\mathrm{Fe_2O_3 + 3\,SO_3 \to Fe_2(SO_4)_3} \tag{3.5.1}$$

If we have 3.59 mol of $\mathrm{Fe_2O_3}$, how many grams of $\mathrm{SO_3}$ can react with it? Using the mole-mass calculation sequence, we can determine the required mass of $\mathrm{SO_3}$ in two steps. First, we construct the appropriate molar ratio, determined from the balanced chemical equation, to calculate the number of moles of $\mathrm{SO_3}$ needed. Then, using the molar mass of $\mathrm{SO_3}$ as a conversion factor, we determine the mass that this number of moles of $\mathrm{SO_3}$ has.

As usual, we start with the quantity we were given:

$$3.59 \ \mathrm{mol\,Fe_2O_3} \times \left(\frac{3 \ \mathrm{mol\,SO_3}}{1 \ \mathrm{mol\,Fe_2O_3}} \right) = 10.77 \ \mathrm{mol\,SO_3} \tag{3.5.2}$$

The mol $\mathrm{Fe_2O_3}$ units cancel, leaving mol $\mathrm{SO_3}$ unit. Now, we take this answer and convert it to grams of $\mathrm{SO_3}$, using the molar mass of $\mathrm{SO_3}$ as the conversion factor:

$$10.77 \ \mathrm{mol\,SO_3} \times \left(\frac{80.06 \ \mathrm{g\,SO_3}}{1 \ \mathrm{mol\,SO_3}} \right) = 862 \ \mathrm{g\,SO_3} \tag{3.5.3}$$

Our final answer is expressed to three significant figures. Thus, in a two-step process, we find that 862 g of $\mathrm{SO_3}$ will react with 3.59 mol of $\mathrm{Fe_2O_3}$. Many problems of this type can be answered in this manner.
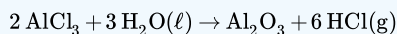
> The same two-step problem can also be worked out in a single line, rather than as two separate steps, as follows:
>
> $$3.59 \ \mathrm{mol\,Fe_2O_3} \times \underbrace{\left(\frac{3 \ \mathrm{mol\,SO_3}}{1 \ \mathrm{mol\,Fe_2O_3}} \right)}_{\text{converts to moles of SO}_3} \times \underbrace{\left(\frac{80.06 \ g\,SO_3}{1 \ \mathrm{mol\,SO_3}} \right)}_{\text{converts to grams of SO}_3} = 862 \ g\,SO_3$$
>
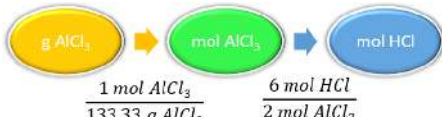> We get exactly the same answer when combining all math steps together.

> ✔ **Example 3.5.1: Generation of Aluminum Oxide**
>
> How many moles of HCl will be produced when 249 g of $AlCl_3$ are reacted according to this chemical equation?
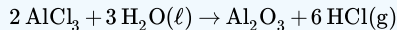>
> $$2\,AlCl_3 + 3\,H_2O(\ell) \rightarrow Al_2O_3 + 6\,HCl(g)$$
>
> **Solution**
>
> Solutions to Example 8.5.1
>
> | Steps for Problem Solving | Example 3.5.1 |
> |---|---|
> | Identify the "given" information and what the problem is asking you to "find." | Given: 249 g AlCl3
 Find: moles HCl |
> | List other known quantities. | 1 mol AlCl3 = 133.33 g AlCl3
 6 mol of HCl to 2 mol AlCl3 |
> | Prepare a concept map and use the proper conversion factor. |
 Flowchart of needed conversion factors: 1 mole AlCl3 to 133.33 grams AlCl3, and 6 moles HCl to 2 moles AlCl3 |
> | Cancel units and calculate. | $249\ g\ AlCl_3 \times \dfrac{1\ mol\ AlCl_3}{133.33\ g\ AlCl_3} \times \dfrac{6\ mol\ HCl}{2\ mol\ AlCl_3} = 5.60\ mol\ HCl$ |
> | Think about your result. | Since 249 g of $AlCl_3$ is less than 266.66 g, the mass for 2 moles of $AlCl_3$ and the relationship is 6 mol of HCl to 2 mol $AlCl_3$, the answer should be less than 6 moles of HCl. |

> ❓ **Exercise 3.5.1: Generation of Aluminum Oxide**
>
> How many moles of Al_2O_3 will be produced when 23.9 g of H_2O are reacted according to this chemical equation?
>
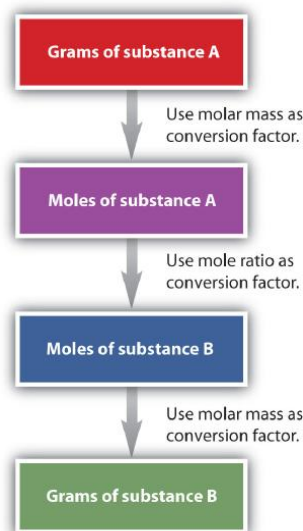> $$2\,AlCl_3 + 3\,H_2O(\ell) \rightarrow Al_2O_3 + 6\,HCl(g)$$
>
> **Answer**
>
> 0.442 mol Al2O3
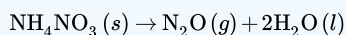
Mass to Mass Conversions

It is a small step from mole-mass calculations to mass-mass calculations. If we start with a known mass of one substance in a chemical reaction (instead of a known number of moles), we can calculate the corresponding masses of other substances in the reaction. The first step in this case is to convert the known mass into moles, using the substance's molar mass as the conversion factor. Then—and only then—we use the balanced chemical equation to construct a conversion factor to convert that quantity to moles of another substance, which in turn can be converted to a corresponding mass. Sequentially, the process is as follows:

Grams of substance A

Use molar mass as conversion factor.

Moles of substance A

Use mole ratio as conversion factor.

Moles of substance B

Use molar mass as conversion factor.

Grams of substance B

This three-part process can be carried out in three discrete steps or combined into a single calculation that contains three conversion factors. The following example illustrates both techniques. Flowchart of mole mass calculations: To convert from grams to moles of substance A, use molar mass conversion factor; To convert from moles of substance A to moles of substance B, use the mole ratio conversion factor, and to convert from moles to grams of substance B, use molar mass conversion factor

> ✔ Example $3.5.2$: Decomposition of Ammonium Nitrate
>
> Ammonium nitrate decomposes to dinitrogen monoxide and water according to the following equation.
>
> $$\mathrm{NH_4NO_3\,(s) \rightarrow N_2O\,(g) + 2H_2O\,(l)}$$
>
> In a certain experiment, $45.7\,\mathrm{g}$ of ammonium nitrate is decomposed. Find the mass of each of the products formed.
>
> Solutions to Example 8.5.2
>
> | Steps for Problem Solving | Example $3.5.2$ |
> |---|---|
> | Identify the "given" information and what the problem is asking you to "find." | Given: 45.7 g $\mathrm{NH_4NO_3}$
 Find:
 Mass $\mathrm{N_2O} =?$ g
 Mass $\mathrm{H_2O} =?$ g |
> | List other known quantities. | 1 mol $\mathrm{NH_4NO_3} = 80.06$ g
 1 mol $\mathrm{N_2O} = 44.02$ g
 1 mol $\mathrm{H_2O} = 18.02$ g
 1 mol $\mathrm{NH_4NO_3}$ to 1 mol $\mathrm{N_2O}$ to 2 mol $\mathrm{H_2O}$ |
> | Prepare two concept maps and use the proper conversion factor. |
 Flowchart of conversion factors: 1 mole NH4NO3 to 80.06 grams NH4NO3, 1 mole N2O to 1 mole NH4NO3, 44.02 grams N2O to 1 mole N2O

 Flowchart of conversion factors: 1 mole NH4NO3 to 80.06 grams NH4NO3, 2 moles H2O to 1 mole NH4NO3, 18.02 grams H2O to 1 mole H2O |
> | Cancel units and calculate. | $45.7 \,\mathrm{g\,NH_4NO_3} \times \dfrac{1\,\mathrm{mol\,NH_4NO_3}}{80.06\,\mathrm{g\,NH_4NO_3}} \times \dfrac{1\,\mathrm{mol\,N_2O}}{1\,\mathrm{mol\,NH_4NO_3}} \times \dfrac{44.02\,\mathrm{g\,N_2O}}{1\,\mathrm{mol\,N_2O}} = 2$
 $45.7 \,\mathrm{g\,NH_4NO_3} \times \dfrac{1\,\mathrm{mol\,NH_4NO_3}}{80.06\,\mathrm{g\,NH_4NO_3}} \times \dfrac{2\,\mathrm{mol\,H_2O}}{1\,\mathrm{mol\,NH_4NO_3}} \times \dfrac{18.02\,\mathrm{g\,H_2O}}{1\,\mathrm{mol\,H_2O}} = 2$ |

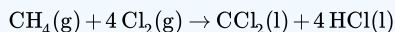| Steps for Problem Solving	Example 3.5.2
Think about your result.	The total mass of the two products is equal to the mass of ammonium nitrate which decomposed, demonstrating the law of conservation of mass. Each answer has three significant figures.

> **?** Exercise 3.5.2: Carbon Tetrachloride
>
> Methane can react with elemental chlorine to make carbon tetrachloride (CCl_4). The balanced chemical equation is as follows:
>
> $$CH_4(g) + 4\,Cl_2(g) \rightarrow CCl_2(l) + 4\,HCl(l)$$
>
> How many grams of HCl are produced by the reaction of 100.0 g of CH_4?
>
> **Answer**
>
> 908.7g HCl

Summary

- Calculations involving conversions between moles of a substance and the mass of that substance can be done using conversion factors.
- A balanced chemical reaction can be used to determine molar and mass relationships between substances.

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3.6: Limiting Reactant and Theoretical Yield

> **◐ Learning Objectives**
>
> - Identify the limiting reactant (limiting reagent) in a given chemical reaction.
> - Calculate how much product will be produced from the limiting reactant.
> - Calculate how much reactant(s) remains when the reaction is complete.

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

Consider a nonchemical example. Assume you have invited some friends for dinner and want to bake brownies for dessert. You find two boxes of brownie mix in your pantry and see that each package requires two eggs. The balanced equation for brownie preparation is:

$$1\,\text{box mix} + 2\,\text{eggs} \rightarrow 1\,\text{batch brownies} \tag{3.6.1}$$

If you have a dozen eggs, which ingredient will determine the number of batches of brownies that you can prepare? Because each box of brownie mix requires two eggs and you have two boxes, you need four eggs. Twelve eggs is eight more eggs than you need. Although the ratio of eggs to boxes is is 2:1, the ratio in your possession is 6:1. Hence the eggs are the ingredient (reactant) present in excess, and the brownie mix is the limiting reactant. Even if you had a refrigerator full of eggs, you could make only two batches of brownies.
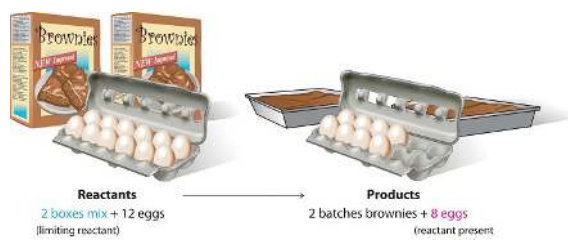

Figure 3.6.1: The Concept of a Limiting Reactant in the Preparation of Brownies. For a chemist, the **balanced** chemical equation is the recipe that must be followed.
2 boxes of brownie mix and 12 eggs results in 2 batches of brownies and 8 eggs; in this case the 8 eggs are reactant present in excess
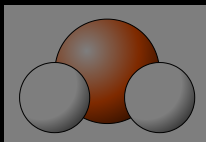
> **📌 PhET Simulation: Reactants, Products and Leftovers**
>
> View this interactive simulation illustrating the concepts of limiting and excess reactants.
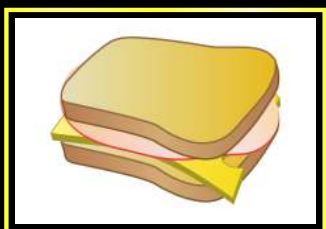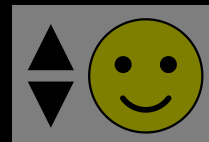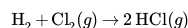

Consider this concept now with regard to a chemical process, the reaction of hydrogen with chlorine to yield hydrogen chloride:

$$\text{H}_2 + \text{Cl}_2(g) \rightarrow 2\,\text{HCl}(g)$$

The balanced equation shows that hydrogen and chlorine react in a 1:1 stoichiometric ratio. If these reactants are provided in any other amounts, one of the reactants will nearly always be entirely consumed, thus limiting the amount of product that may be generated. This substance is the limiting reactant, and the other substance is the excess reactant. Identifying the limiting and excess

reactants for a given situation requires computing the molar amounts of each reactant provided and comparing them to the stoichiometric amounts represented in the balanced chemical equation. For example, imagine combining 3 moles of H_2 and 2 moles of Cl_2. This represents a 3:2 (or 1.5:1) ratio of hydrogen to chlorine present for reaction, which is greater than the stoichiometric ratio of 1:1. Hydrogen, therefore, is present in excess, and chlorine is the limiting reactant. Reaction of all the provided chlorine (2 mol) will consume 2 mol of the 3 mol of hydrogen provided, leaving 1 mol of hydrogen non-reacted.

An alternative approach to identifying the limiting reactant involves comparing the amount of product expected for the complete reaction of each reactant. Each reactant amount is used to separately calculate the amount of product that would be formed per the reaction's stoichiometry. The reactant yielding the lesser amount of product is the limiting reactant. For the example, in the previous paragraph, complete reaction of the hydrogen would yield:

$$\text{mol HCl produced} = 3 \text{ mol } H_2 \times \frac{2 \text{ mol HCl}}{1 \text{ mol } H_2} = 6 \text{ mol HCl}$$

Complete reaction of the provided chlorine would produce:

$$\text{mol HCl produced} = 2 \text{ mol } Cl_2 \times \frac{2 \text{ mol HCl}}{1 \text{ mol } Cl_2} = 4 \text{ mol HCl}$$

The chlorine will be completely consumed once 4 moles of HCl have been produced. Since enough hydrogen was provided to yield 6 moles of HCl, there will be non-reacted hydrogen remaining once this reaction is complete. Chlorine, therefore, is the limiting reactant and hydrogen is the excess reactant (Figure $3.6.2$).
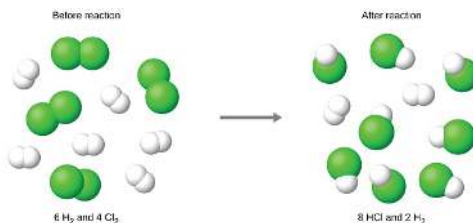

Figure 3.6.2: When H_2 and Cl_2 are combined in nonstoichiometric amounts, one of these reactants will limit the amount of HCl that can be produced. This illustration shows a reaction in which hydrogen is present in excess and chlorine is the limiting reactant. The figure shows a space-filling molecular models reacting. There is a reaction arrow pointing to the right in the middle. To the left of the reaction arrow there are three molecules each consisting of two green spheres bonded together. There are also five molecules each consisting of two smaller, white spheres bonded together. Above these molecules is the label, "Before reaction," and below these molecules is the label, "6 H subscript 2 and 4 C l subscript 2." To the right of the reaction arrow there are eight molecules each consisting of one green sphere bonded to a smaller white sphere. There are also two molecules each consisting of two white spheres bonded together. Above these molecules is the label, "After reaction," and below these molecules is the label, "8 H C l and 2 H subscript 2."

A similar situation exists for many chemical reactions: you usually run out of one reactant before all of the other reactant has reacted. The reactant you run out of is called the limiting reactant; the other reactant or reactants are considered to be *in excess*. A crucial skill in evaluating the conditions of a chemical process is to determine which reactant is the limiting reactant and which is in excess.

> 📌 **How to Identify the Limiting Reactant (Limiting Reagent)**
>
> There are two ways to determine the limiting reactant. One method is to find and compare the mole ratio of the reactants used in the reaction (Approach 1). Another way is to calculate the grams of products produced from the given quantities of reactants; the reactant that produces the **smallest** amount of product is the limiting reactant (Approach 2). This section will focus more on the second method.
>
> **Approach 1 (The "Reactant Mole Ratio Method"):** Find the limiting reactant by looking at the number of moles of each reactant.
>
> 1. Determine the balanced chemical equation for the chemical reaction.
> 2. Convert all given information into moles (most likely, through the use of molar mass as a conversion factor).
> 3. Calculate the mole ratio from the given information. Compare the calculated ratio to the actual ratio.
> 4. Use the amount of limiting reactant to calculate the amount of product produced.
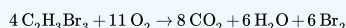> 5. If necessary, calculate how much is left in excess of the non-limiting (excess) reactant.
>
> **Approach 2 (The "The Product Method"):** Find the limiting reactant by calculating and comparing the amount of product that each reactant will produce.
>
> 1. Balance the chemical equation for the chemical reaction.
> 2. Convert the given information into moles.
> 3. Use stoichiometry for each individual reactant to find the mass of product produced.
> 4. The reactant that produces a lesser amount of product is the limiting reactant.
> 5. The reactant that produces a larger amount of product is the excess reactant.
> 6. To find the amount of remaining excess reactant, subtract the mass of excess reactant consumed from the total mass of excess reactant given.

The key to recognizing which reactant is the limiting reactant is based on a mole-mass or mass-mass calculation: whichever reactant gives the *lesser* amount of product is the limiting reactant. What we need to do is determine an amount of one product (either moles or mass) assuming all of each reactant reacts. Whichever reactant gives the least amount of that particular product is the limiting reactant. It does not matter which product we use, as long as we use the same one each time. It does not matter whether we determine the number of moles or grams of that product; however, we will see shortly that knowing the final mass of product can be useful.

> ✔ **Example 3.6.1: Identifying the Limiting Reactant**
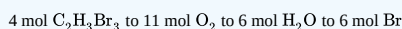>
> As an example, consider the balanced equation
>
> $$4\,C_2H_3Br_3 + 11\,O_2 \rightarrow 8\,CO_2 + 6\,H_2O + 6\,Br_2$$
>
> What is the limiting reactant if 76.4 grams of $C_2H_3Br_3$ reacted with 49.1 grams of O_2?
>
> **Solution**
> Using Approach 1:
>
> **Step 1:** *Balance the chemical equation.*
>   The equation is already balanced with the relationship
>
> $$4 \text{ mol } C_2H_3Br_3 \text{ to } 11 \text{ mol } O_2 \text{ to } 6 \text{ mol } H_2O \text{ to } 6 \text{ mol } Br$$
>
> *Step 2: Convert all given information into moles.*
>
> $$76.4 \text{ g } C_2H_3Br_3 \times \frac{1 \text{ mol } C_2H_3Br_3}{266.72 \text{ g } C_2H_3Br_3} = 0.286 \text{ mol } C_2H_3Br_3$$
>
> $$49.1 \text{ g } O_2 \times \frac{1 \text{ mol } O_2}{32.00 \text{ g } O_2} = 1.53 \text{ mol } O_2$$

Step 3: *Calculate the mole ratio from the given information. Compare the calculated ratio to the actual ratio.*

Assuming that all of the oxygen is used up,

$$1.53 \ \text{mol O}_2 \times \frac{4 \ \text{mol C}_2\text{H}_3\text{Br}_3}{11 \ \text{mol O}_2} = 0.556 \ \text{mol C}_2\text{H}_3\text{Br}_3 \ \text{are required.}$$

Because 0.556 moles of C₂H₃Br₃ required > 0.286 moles of C₂H₃Br₃ available, <u>C₂H₃Br₃ is the limiting reactant</u>.

Using Approach 2:

Step 1: *Balance the chemical equation.*

The equation is already balanced with the relationship

$$4 \ \text{mol C}_2\text{H}_3\text{Br}_3 \ \text{to} \ 11 \ \text{mol O}_2 \ \text{to} \ 6 \ \text{mol H}_2\text{O} \ \text{to} \ 6 \ \text{mol Br}_2$$
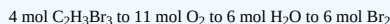
Step 2 and Step 3: *Convert mass to moles and stoichiometry.*

$$76.4 \ \text{g C}_2\text{H}_3\text{Br}_3 \times \frac{1 \ \text{mol C}_2\text{H}_3\text{Br}_3}{266.72 \ \text{g C}_2\text{H}_3\text{Br}_3} \times \frac{8 \ \text{mol CO}_2}{4 \ \text{mol C}_2\text{H}_3\text{Br}_3} \times \frac{44.01 \ \text{g CO}_2}{1 \ \text{mol CO}_2} = 25.2 \ \text{g CO}_2$$

$$49.1 \ \text{g O}_2 \times \frac{1 \ \text{mol O}_2}{32.00 \ \text{g O}_2} \times \frac{8 \ \text{mol CO}_2}{11 \ \text{mol O}_2} \times \frac{44.01 \ \text{g CO}_2}{1 \ \text{mol CO}_2} = 49.1 \ \text{g CO}_2$$

Step 4: *The reactant that produces a smaller amount of product is the limiting reactant.*

Therefore, by either method, $C_2H_3Br_3$ is the limiting reactant.

✔ Example 3.6.2: Identifying the Limiting Reactant and the Mass of Excess Reactant

For example, in the reaction of magnesium metal and oxygen, calculate the mass of magnesium oxide that can be produced if 2.40 g Mg reacts with 10.0 g O_2. Also determine the amount of excess reactant. MgO is the only product in the reaction.

Solution

Following Approach 1:

Step 1: *Balance the chemical equation.*

$$\mathbf{2} \ \text{Mg (s)} + \text{O}_2 \ \text{(g)} \rightarrow \mathbf{2} \ \text{MgO (s)}$$
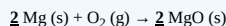
The balanced equation provides the relationship of 2 mol Mg to 1 mol O₂ to 2 mol MgO

Step 2 and Step 3: *Convert mass to moles and stoichiometry.*

$$2.40 \ \text{g Mg} \times \frac{1 \ \text{mol Mg}}{24.31 \ \text{g Mg}} \times \frac{2 \ \text{mol MgO}}{2 \ \text{mol Mg}} \times \frac{40.31 \ \text{g MgO}}{1 \ \text{mol MgO}} = 3.98 \ \text{g MgO}$$

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

Step 4: *The reactant that produces a smaller amount of product is the limiting reactant.*

Mg produces less MgO than does O₂ (3.98 g MgO vs. 25.2 g MgO), therefore Mg is the limiting reactant in this reaction.

Step 5: *The reactant that produces a larger amount of product is the excess reactant.*

O₂ produces more amount of MgO than Mg (25.2g MgO vs. 3.98 MgO), therefore O₂ is the excess reactant in this reaction.

Step 6: *Find the amount of remaining excess reactant by subtracting the mass of the excess reactant consumed from the total mass of excess reactant given.*

Mass of excess reactant calculated using the limiting reactant:

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

OR

Mass of excess reactant calculated using the mass of the product:

$$3.98 \ \text{g MgO} \times \frac{1 \ \text{mol MgO}}{40.31 \ \text{g MgO}} \times \frac{1 \ \text{mol O}_2}{2 \ \text{mol MgO}} \times \frac{32.0 \ \text{g O}_2}{1 \ \text{mol O}_2} = 1.58 \ \text{g O}_2$$
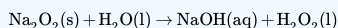
Mass of total excess reactant given – mass of excess reactant consumed in the reaction:

$$10.0\text{g O}_2 - \text{(available) } 1.58\text{g O}_2 \text{ (used)} = 8.42\text{g O}_2 \text{ (excess)}$$

Therefore, O₂ is in excess.

✔ Example 3.6.3: Limiting Reactant

What is the limiting reactant if 78.0 grams of Na₂O₂ were reacted with 29.4 grams of H₂O? The unbalanced chemical equation is

$$\text{Na}_2\text{O}_2(\text{s}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{NaOH}(\text{aq}) + \text{H}_2\text{O}_2(\text{l})$$

Solution

Solutions to Example 8.4.3

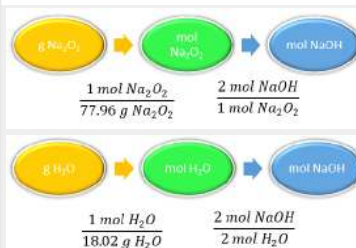| Steps for Problem Solving- The Product Method	Example 3.6.1
Identify the "given" information and what the problem is asking you to "find."	Given: 78.0 grams of Na₂O₂ 29.4 g H₂O Find: limiting reactant
List other known quantities.	1 mol Na₂O₂= 77.96 g/mol 1 mol H₂O = 18.02 g/mol Since the amount of product in grams is not required, only the molar mass of the reactants is needed.

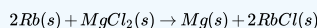| Steps for Problem Solving- The Product Method	Example 3.6.1
Balance the equation.	Na_2O_2 (s) + **2**H_2O (l) → **2**NaOH (aq) + H_2O_2 (l) The balanced equation provides the relationship of 1 mol Na_2O_2 to 2 mol H_2O 2mol NaOH to 1 mol H_2O_2
Prepare a concept map and use the proper conversion factor.	 $$\frac{1 \text{ mol } Na_2O_2}{77.96 \text{ g } Na_2O_2} \qquad \frac{2 \text{ mol } NaOH}{1 \text{ mol } Na_2O_2}$$ $$\frac{1 \text{ mol } H_2O}{18.02 \text{ g } H_2O} \qquad \frac{2 \text{ mol } NaOH}{2 \text{ mol } H_2O}$$ Because the question only asks for the limiting reactant, we can perform two **mass-mole** calculations and determine which amount is less.
Cancel units and calculate.	$$78.0 \text{ g } Na_2O_2 \times \frac{1 \text{ mol } Na_2O_2}{77.96 \text{ g } Na_2O_2} \times \frac{2 \text{ mol } NaOH}{1 \text{ mol } Na_2O_2} \times \frac{40 \text{ g } NaOH}{1 \text{ mol } NaOH} = 2.00 \text{ mol } NaOH$$ $$29.4 \text{ g } H_2O \times \frac{1 \text{ mol } H_2O}{18.02 \text{ g } H_2O} \times \frac{2 \text{ mol } NaOH}{2 \text{ mol } Na_2O_2} \times \frac{40 \text{ g } NaOH}{1 \text{ mol } NaOH} = 1.63 \text{ mol } NaOH$$ Therefore, H_2O is the *limiting reactant*.

Think about your result.

✔ Example 3.6.4: Limiting Reactant and Mass of Excess Reactant

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 remaining reactant is left over?

Solution

Solutions to Example 8.4.10

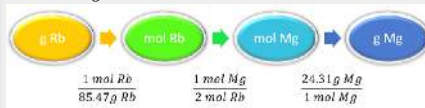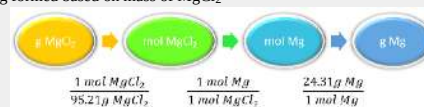| Steps for Problem Solving- The Product Method	Example 3.6.2
Steps for Problem Solving	A 5.00 g quantity of Rb is combined with 3.44 g of $MgCl_2$ according to this chemical reaction: $$2Rb(s) + MgCl_2(s) \rightarrow Mg(s) + 2RbCl(s)$$ What mass of Mg is formed, and what mass of remaining reactant is left over?
Identify the "given" information and what the problem is asking you to "find."	Given: 5.00g Rb, 2.44g MgCl2 Find: mass of Mg formed, mass of remaining reactant
List other known quantities.	• molar mass: Rb = 85.47 g/mol • molar mass: $MgCl_2$ = 95.21 g/mol • molar mass: Mg = 24.31 g/mol
Prepare concept maps and use the proper conversion factor.	Find mass Mg formed based on mass of Rb $$\frac{1 \text{ mol } Rb}{85.47 \text{ g } Rb} \qquad \frac{1 \text{ mol } Mg}{2 \text{ mol } Rb} \qquad \frac{24.31 \text{ g } Mg}{1 \text{ mol } Mg}$$ Find mass of Mg formed based on mass of $MgCl_2$ $$\frac{1 \text{ mol } MgCl_2}{95.21 \text{ g } MgCl_2} \qquad \frac{1 \text{ mol } Mg}{1 \text{ mol } MgCl_2} \qquad \frac{24.31 \text{ g } Mg}{1 \text{ mol } Mg}$$ Conversion factors: 1 mole MgCl2 to 95.21 grams MgCl2, 1 mole Mg to 1 mole MgCl2, 24.31 grams Mg to 1 mole Mg Use limiting reactant to determine amount of excess reactant consumed $$\frac{1 \text{ mol } Rb}{85.47 \text{ g } Rb} \qquad \frac{1 \text{ mol } MgCl_2}{2 \text{ mol } Rb} \qquad \frac{95.21 \text{ g } MgCl_2}{1 \text{ mol } MgCl_2}$$ Conversion factors: 1 mole Rb to 85.47 grams Rb, 1 mole MgCl2 to 2 moles Rb, 95.21 grams MgCl2 to 1 mole MgCl2
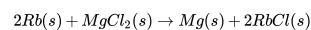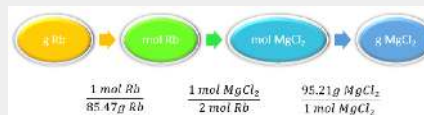
Steps for Problem Solving- The Product Method	Example 3.6.2
	Because the question asks what mass of magnesium is formed, we can perform two mass-mass calculations and determine which amount is less.
	$$5.00 \, g \, Rb \times \frac{1 \, mol \, Rb}{85.47 \, g \, Rb} \times \frac{1 \, mol \, Mg}{2 \, mol \, Rb} \times \frac{24.31 \, g \, Mg}{1 \, mol \, Mg} = 0.711 \, g \, Mg$$
	$$3.44 \, g \, MgCl_2 \times \frac{1 \, mol \, MgCl_2}{95.21 \, g \, MgCl_2} \times \frac{1 \, mol \, Mg}{1 \, mol \, MgCl_2} \times \frac{24.31 \, g \, Mg}{1 \, mol \, Mg} = 0.878 \, g \, Mg$$
Cancel units and calculate.	The 0.711 g of Mg is the lesser quantity, so the associated reactant—5.00 g of Rb—is the limiting reactant. To determine how much of the other reactant is left, we have to do one more mass-mass calculation to determine what mass of $MgCl_2$ reacted with the 5.00 g of Rb, and then subtract the amount reacted from the original amount.
	$$5.00 \, g \, Rb \times \frac{1 \, mol \, Rb}{85.47 \, g \, Rb} \times \frac{1 \, mol \, MgCl_2}{2 \, mol \, Rb} \times \frac{95.21 \, g \, MgCl_2}{1 \, mol \, MgCl_2} = 2.78 \, g \, MgCl_2 \;\, reacted$$
	Because we started with 3.44 g of $MgCl_2$, we have
	3.44 g $MgCl_2$ − 2.78 g $MgCl_2$ reacted = 0.66 g $MgCl_2$ left
Think about your result.	It usually is not possible to determine the limiting reactant using just the initial masses, as the reagents have different molar masses and coefficients.

? Exercise 3.6.1

Given the initial amounts listed, what is the limiting reactant, and what is the mass of the leftover reactant?

$$\underbrace{22.7 \, g}_{MgO(s)} + \underbrace{17.9 \, g}_{H_2S} \to MgS(s) + H_2O(l)$$
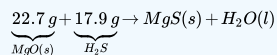
Answer

H$_2$S is the limiting reagent; 1.5 g of MgO are left over.

3.7: Limiting Reactant, Theoretical Yield, and Percent Yield from Initial Masses of Reactants

> ◖ **Learning Objectives**
>
> - Calculate percentage or actual yields from known amounts of reactants.

The world of pharmaceutical production is an expensive one. Many drugs have several steps in their synthesis and use costly chemicals. A great deal of research takes place to develop better ways to make drugs faster and more efficiently. Studying how much of a compound is produced in any given reaction is an important part of cost control.

Percent Yield

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

To compute the percent yield, it is first necessary to determine how much of the product should be formed based on stoichiometry. This is called the **theoretical yield**, the maximum amount of product that can be formed from the given amounts of reactants. The **actual yield** is the amount of product that is actually formed when the reaction is carried out in the laboratory. The **percent yield** is the ratio of the actual yield to the theoretical yield, expressed as a percentage.
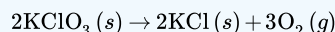
$$\text{Percent Yield} = \frac{\text{Actual Yield}}{\text{Theoretical Yield}} \times 100\%$$

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

Typically, percent yields are understandably less than 100% because of the reasons indicated earlier. However, percent yields greater than 100% are possible if the measured product of the reaction contains impurities that cause its mass to be greater than it actually would be if the product was pure. When a chemist synthesizes a desired chemical, he or she is always careful to purify the products of the reaction. Example $3.7.1$ illustrates the steps for determining percent yield.

> ✔ **Example 3.7.1: Decomposition of Potassium Chlorate**
>
> Potassium chlorate decomposes upon slight heating in the presence of a catalyst, according to the reaction below:
>
> $$2KClO_3\,(s) \rightarrow 2KCl\,(s) + 3O_2\,(g)$$
>
> In a certain experiment, $40.0\ g\ KClO_3$ is heated until it completely decomposes. The experiment is performed and the oxygen gas is collected and its mass is found to be $14.9\ g$.
>
> a. What is the theoretical yield of oxygen gas?
> b. What is the percent yield for the reaction?
>
> **Solution**
> a. Calculation of theoretical yield
>
> First, we will calculate the theoretical yield based on the stoichiometry.
>
> **Step 1: Identify the "given" information and what the problem is asking you to "find".**
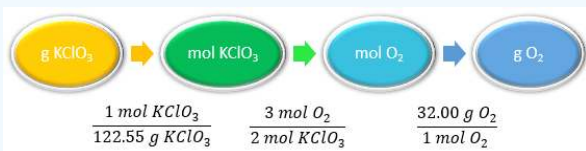> Given: Mass of $KClO_3 = 40.0\ g$
>
> Mass of O_2 collected = 14.9g
>
> Find: Theoretical yield, g O_2
>
> **Step 2: List other known quantities and plan the problem.**
> 1 mol KClO₃ = 122.55 g/mol
>
> 1 mol O₂ = 32.00 g/mol
>
> **Step 3: Apply stoichiometry to convert from the mass of a reactant to the mass of a product:**
>
>
>
> **Step 4: Solve.**

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

The theoretical yield of O_2 is 15.7 g, 15.$\underline{6}$7 g unrounded.

Step 5: Think about your result.

The mass of oxygen gas must be less than the 40.0 g of potassium chlorate that was decomposed.

b. Calculation of percent yield

Now we will use the actual yield and the theoretical yield to calculate the percent yield.

Step 1: Identify the "given" information and what the problem is asking you to "find".

Given: Theoretical yield =15.$\underline{6}$7 g, use the un-rounded number for the calculation.

Actual yield = 14.9g

Find: Percent yield, % Yield

Step 2: List other known quantities and plan the problem.
No other quantities needed.
Step 3: Use the percent yield equation below.

$$\text{Percent Yield} = \frac{\text{Actual Yield}}{\text{Theoretical Yield}} \times 100\%$$

Step 4: Solve.

$$\text{Percent Yield} = \frac{14.9 \ \text{g}}{15.\underline{6}7 \ \text{g}} \times 100\% = 94.9\%$$

Step 5: Think about your result.

Since the actual yield is slightly less than the theoretical yield, the percent yield is just under 100%.

✔ Example 3.7.2: Oxidation of Zinc

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

$$\text{CuSO}_4(aq) + \text{Zn}(s) \rightarrow \text{Cu}(s) + \text{ZnSO}_4(aq)$$
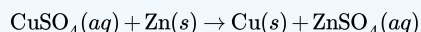
What is the percent yield?

Solution

Solutions to Example 8.6.2

Steps for Problem Solving-The Product Method	Example 3.7.1
Identify the "given" information and what the problem is asking you to "find."	Given: 1.274 g CuSO4 Actual yield = 0.392 g Cu Find: Percent yield
List other known quantities.	1 mol CuSO4= 159.62 g/mol 1 mol Cu = 63.55 g/mol Since the amount of product in grams is not required, only the molar mass of the reactants is needed.
Balance the equation.	The chemical equation is already balanced. The balanced equation provides the relationship of 1 mol CuSO4 to 1 mol Zn to 1 mol Cu to 1 mol ZnSO4.
Prepare a concept map and use the proper conversion factor.	 The provided information identifies copper sulfate as the limiting reactant, and so the theoretical yield (g Cu) is found by performing **mass-mass** calculation based on the initial amount of $CuSO_4$.

Steps for Problem Solving-The Product Method	Example 3.7.1
Cancel units and calculate.	$1.274 \ \text{g} \ \cancel{\text{CuSO}_4} \times \dfrac{1 \ \text{mol} \ \cancel{\text{CuSO}_4}}{159.62 \ \text{g} \ \cancel{\text{CuSO}_4}} \times \dfrac{1 \ \text{mol} \ \cancel{\text{Cu}}}{1 \ \text{mol} \ \cancel{\text{CuSO}_4}} \times \dfrac{63.55 \ \text{g Cu}}{1 \ \text{mol} \ \cancel{\text{Cu}}} = 0.$ Using this theoretical yield and the provided value for actual yield, the percent yield is calculated to be: $\text{percent yield} = \left(\dfrac{\text{actual yield}}{\text{theoretical yield}} \right) \times 100$ $= \left(\dfrac{0.392 \, g \, \text{Cu}}{0.5072 \, g \, \text{Cu}} \right) \times 100$ $= 77.3\%$
Think about your result.	Since the actual yield is slightly less than the theoretical yield, the percent yield is just under 100%.

? Exercise 3.7.1

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

$$CCl_4 + 2\,HF \rightarrow CF_2Cl_2 + 2\,HCl$$
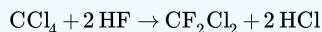
Answer

    48.3%

Summary

Theoretical yield is calculated based on the stoichiometry of the chemical equation. The actual yield is experimentally determined. The percent yield is determined by calculating the ratio of actual yield to theoretical yield.

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3.8: Enthalpy Change is a Measure of the Heat Evolved or Absorbed

When physical or chemical changes occur, they are generally accompanied by a transfer of energy. The **law of conservation of energy** states that in any physical or chemical process, energy is neither created nor destroyed. In other words, the entire energy in the universe is conserved. In order to better understand the energy changes taking place during a reaction, we need to define two parts of the universe, called the system and the surroundings. The **system** is the specific portion of matter in a given space that is being studied during an experiment or an observation. The **surroundings** are everything in the universe that is not part of the system. In practical terms for a laboratory chemist, the system is the particular chemicals being reacted, while the surroundings is the immediate vicinity within the room. During most processes, energy is exchanged between the system and the surroundings. If the system loses a certain amount of energy, that same amount of energy is gained by the surroundings. If the system gains a certain amount of energy, that energy is supplied by the surroundings.

A chemical reaction or physical change is **endothermic** if heat is absorbed by the system from the surroundings. In the course of an endothermic process, the system gains heat from the surroundings and so the temperature of the surroundings decreases. The quantity of heat for a process is represented by the letter q. The sign of q for an endothermic process is positive because the system is gaining heat. A chemical reaction or physical change is **exothermic** if heat is released by the system into the surroundings. Because the surroundings are gaining heat from the system, the temperature of the surroundings increases. The sign of q for an exothermic process is negative because the system is losing heat.
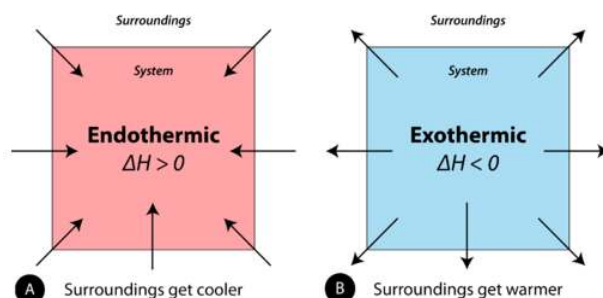

Figure 3.8.1: (A) Endothermic reaction. (B) Exothermic reaction.

Enthalpy

Heat changes in chemical reactions are often measured in the laboratory under conditions in which the reacting system is open to the atmosphere. In that case, the system is at a constant pressure. **Enthalpy** (H) is the heat content of a system at constant pressure. Chemists routinely measure changes in enthalpy of chemical systems as reactants are converted into products. The heat that is absorbed or released by a reaction at constant pressure is the same as the enthalpy change, and is given the symbol ΔH. Unless otherwise specified, all reactions in this material are assumed to take place at constant pressure.

The change in enthalpy of a reaction is a measure of the differences in enthalpy of the reactants and products. The enthalpy of a system is determined by the energies needed to break chemical bonds and the energies needed to form chemical bonds. Energy needs to be put into the system in order to break chemical bonds, as they do not come apart spontaneously in most cases. Bond formation to produce products will involve release of energy. The change in enthalpy shows the trade-offs made in these two processes. Does it take more energy to break bonds than that needed to form bonds? If so, the reaction is endothermic and the enthalpy change is positive. If more energy is produced in bond formation than that needed for bond breaking, the reaction is exothermic and the enthalpy is negative.

Several factors influence the enthalpy of a system. Enthalpy is an extensive property, determined in part by the amount of material we work with. The state of reactants and products (solid, liquid, or gas) influences the enthalpy value for a system. The direction of the reaction affects the enthalpy value. A reaction that takes place in the opposite direction has the same numerical enthalpy value, but the opposite sign.

Thermochemical Equation

When methane gas is combusted, heat is released, making the reaction exothermic. Specifically, the combustion of $1 \, \text{mol}$ of methane releases 890.4 kilojoules of heat energy. This information can be shown as part of the balanced equation:

$$CH_4 \, (g) + 2O_2 \, (g) \rightarrow CO_2 \, (g) + 2H_2O \, (l) + 890.4 \, \text{kJ}$$
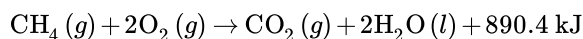
The equation tells us that 1 mol of methane combines with 2 mol of oxygen to produce 1 mol of carbon dioxide and 2 mol of water. In the process, 890.4 kJ is released and so it is written as a product of the reaction. A **thermochemical equation** is a chemical equation that includes the enthalpy change of the reaction. The process in the above thermochemical equation can be shown visually in Figure 3.8.2.
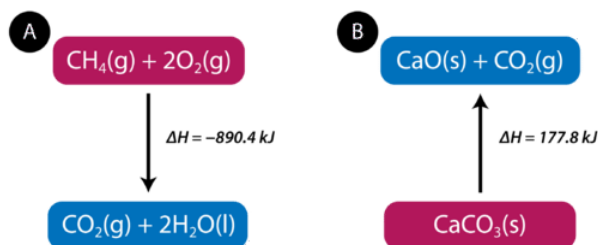

Figure 3.8.2: (A) As reactants are converted to products in an exothermic reaction, enthalpy is released into the surroundings. The enthalpy change of the reaction is negative. (B) As reactants are converted to products in an endothermic reaction, enthalpy is absorbed from the surroundings. The enthalpy change of the reaction is positive.

In the combustion of methane example, the enthalpy change is negative because heat is being released by the system. Therefore, the overall enthalpy of the system decreases. The **heat of reaction** is the enthalpy change for a chemical reaction. In the case above, the heat of reaction is -890.4 kJ. The thermochemical reaction can also be written in this way:

$$CH_4\,(g) + 2O_2\,(g) \to CO_2\,(g) + 2H_2O\,(l) \quad \Delta H = -890.4\text{ kJ}$$
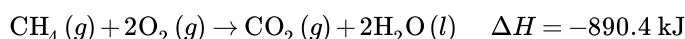
Heats of reaction are typically measured in kilojoules. It is important to include the physical states of the reactants and products in a thermochemical equation as the value of the ΔH depends on those states.

Endothermic reactions absorb energy from the surroundings as the reaction occurs. When 1 mol of calcium carbonate decomposes into 1 mol of calcium oxide and 1 mol of carbon dioxide, 177.8 kJ of heat is absorbed. The process is shown visually in Figure 3.8.2B. The thermochemical reaction is shown below.

$$CaCO_3\,(s) + 177.8\text{ kJ} \to CaO\,(s) + CO_2\,(g)$$
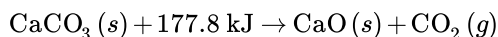
Because the heat is absorbed by the system, the 177.8 kJ is written as a reactant. The heat of reaction is positive for an endothermic reaction.

$$CaCO_3\,(s) \to CaO\,(s) + CO_2\,(g) \quad \Delta H = 177.8\text{ kJ}$$

The way in which a reaction is written influences the value of the enthalpy change for the reaction. Many reactions are reversible, meaning that the product(s) of the reaction are capable of combining and reforming the reactant(s). If a reaction is written in the reverse direction, the sign of the ΔH changes. For example, we can write an equation for the reaction of calcium oxide with carbon dioxide to form calcium carbonate.

$$CaO\,(s) + CO_2\,(g) \to CaCO_3\,(s) + 177.8\text{ kJ}$$
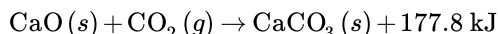
The reaction is exothermic and thus the sign of the enthalpy change is negative.

$$CaO\,(s) + CO_2\,(g) \to CaCO_3\,(s) \quad \Delta H = -177.8\text{ kJ}$$

Stoichiometric Calculations and Enthalpy Changes

Chemistry problems that involve enthalpy changes can be solved by techniques similar to stoichiometry problems. Refer again to the combustion reaction of methane. Since the reaction of 1 mol of methane released 890.4 kJ, the reaction of 2 mol of methane would release $2 \times 890.4\text{ kJ} = 1781\text{ kJ}$. The reaction of 0.5 mol of methane would release $\dfrac{890,4\text{ kJ}}{2} = 445.2\text{ kJ}$. As with other stoichiometry problems, the moles of a reactant or product can be linked to mass or volume.

> ✔ Example 3.8.1
>
> Sulfur dioxide gas reacts with oxygen to form sulfur trioxide in an exothermic reaction, according to the following thermochemical equation.
>
> $$2SO_2\,(g) + O_2\,(g) \to 2SO_3\,(g) + 198\text{ kJ}$$
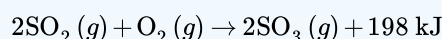
Calculate the enthalpy change that occurs when $58.0\,\mathrm{g}$ of sulfur dioxide is reacted with excess oxygen.

Solution

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

- Mass $SO_2 = 58.0$ g
- Molar mass $SO_2 = 64.07$ g/mol
- $\Delta H = -198$ kJ for the reaction of 2 mol SO_2

Unknown

- $\Delta H = ?$ kJ

The calculation requires two steps. The mass of SO_2 is converted to moles. Then the moles of SO_2 is multiplied by the conversion factor of $\left(\dfrac{-198\ \mathrm{kJ}}{2\ \mathrm{mol}\ SO_2}\right)$.

Step 2: Solve.

$$\Delta H = 58.0\ \mathrm{g}\ SO_2 \times \frac{1\ \mathrm{mol}\ SO_2}{64.07\ \mathrm{g}\ SO_2} \times \frac{-198\ \mathrm{kJ}}{2\ \mathrm{mol}\ SO_2} = 89.6\ \mathrm{kJ}$$

Step 3: Think about your result.

The mass of sulfur dioxide is slightly less than 1 mol. Since 198 kJ is released for every 2 mol of SO_2 that reacts, the heat released when about 1 mol reacts is one half of 198. The 89.6 kJ is slightly less than half of 198. The sign of ΔH is negative because the reaction is exothermic.

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4: Gases

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Of the three basic phases of matter—solids, liquids, and gases—only one of them has predictable physical properties: gases. In fact, the study of the properties of gases was the beginning of the development of modern chemistry from its alchemical roots. The interesting thing about some of these properties is that they are independent of the identity of the gas. That is, it doesn't matter if the gas is helium gas, oxygen gas, or sulfur vapors; some of their behavior is predictable and, as we will find, very similar. In this chapter, we will review some of the common behaviors of gases. Gases have no definite shape or volume; they tend to fill whatever container they are in. They can compress and expand, sometimes to a great extent. Gases have extremely low densities, one-thousandth or less the density of a liquid or solid. Combinations of gases tend to mix together spontaneously; that is, they form solutions. Air, for example, is a solution of mostly nitrogen and oxygen. Any understanding of the properties of gases must be able to explain these characteristics.

4.1: Kinetic Molecular Theory- A Model for Gases

> **Learning Objectives**
>
> - State the major concepts behind the kinetic theory of gases.
> - Relate the general properties of gases to the kinetic theory.

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

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

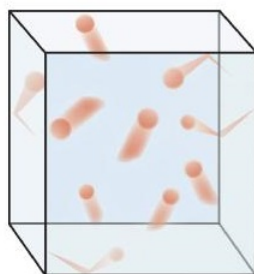Figure 4.1.1 shows a representation of how we mentally picture the gas phase.

Figure 4.1.1: The Kinetic Theory of Gases. The kinetic theory of gases describes this state of matter as composed of tiny particles in constant motion with a lot of distance between the particles.

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

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

- The physical behavior of gases is explained by the kinetic theory of gases.
- An ideal gas adheres exactly to the kinetic theory of gases.

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4.2: Pressure- The Result of Constant Molecular Collisions

> ◑ **Learning Objectives**
>
> - Define *pressure*.
> - Learn the units of pressure and how to convert between them.

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

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

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

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

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

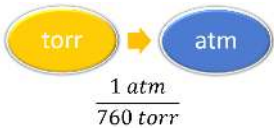$$1 \text{ atm} = 760 \text{ mmHg} = 760 \text{ torr}$$

We can use these equivalents as with any equivalence—to perform conversions from one unit to another. Relating these to the formal SI unit of pressure, 1 atm = 101,325 Pa.

> ✔ **Example 4.2.1: Pressure Conversion**
>
> How many atmospheres are there in 595 torr?
>
> **Solution**
>
> Solutions to Example 11.3.1
>
> | Steps for Problem Solving | Unit Conversion |
> |---|---|
> | Identify the "given" information and what the problem is asking you to "find." | Given: 595 torr
 Find: ? atm |
> | List other known quantities. | 1 atm = 760 torr |
> | Prepare a concept map. | $\dfrac{1\,atm}{760\,torr}$ |
> | Cancel units and calculate. | $595\ \cancel{torr} \times \dfrac{1\,atm}{760\ \cancel{torr}} = 0.783\,atm$ |
> | Think about your result. | 595 torr is less than 760 torr so the final answer should be less than 1 atm. |

? Exercise 4.2.1
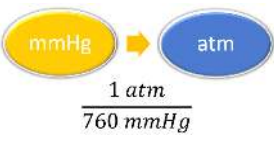
How many atmospheres are there in 1,022 torr?

Answer

1.345 atm

✔ Example 4.2.2: Mars

The atmosphere on Mars is largely CO_2 at a pressure of 6.01 mmHg. What is this pressure in atmospheres?

Solution

Solutions to Example 11.3.2

Steps for Problem Solving	Unit Conversion
Identify the "given" information and what the problem is asking you to "find."	Given: 6.01mmHg Find: ? atm
List other known quantities.	1 atm = 760 mmHg
Prepare a concept map.	 $\dfrac{1\ atm}{760\ mmHg}$
Cancel units and calculate.	$6.01\ \cancel{mmHg} \times \dfrac{1\ atm}{760\ \cancel{mmHg}} = 0.00791\ atm = 7.91 \times 10^{-3} atm$
Think about your result.	6.01 is a very small number relative to 760 mmHg, just like the value in atmospheres.

? Exercise 4.2.2

Atmospheric pressure is low in the eye of a hurricane. In a 1979 hurricane in the Pacific Ocean, a pressure of 0.859 atm was reported inside the eye. What is this pressure in torr?

Answer

652 torr

Summary

- Pressure is a force exerted over an area.
- Pressure has several common units that can be converted.

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4.3: Boyle's Law- Pressure and Volume

> **◑ Learning Objectives**
>
> - Learn what is meant by the term *gas laws*.
> - Learn and apply Boyle's Law.

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

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

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

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

$$P_1 V_1 = \text{constant} = P_2 V_2$$

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

$$P_1 V_1 = P_2 V_2 \text{ at constant n and T}$$

This equation is an example of a gas law. A **gas law** is a simple mathematical formula that allows you to model, or predict, the behavior of a gas. This particular gas law is called **Boyle's Law**, after the English scientist Robert Boyle, who first announced it in 1662. Figure $4.3.1$ shows two representations of how Boyle's Law works.
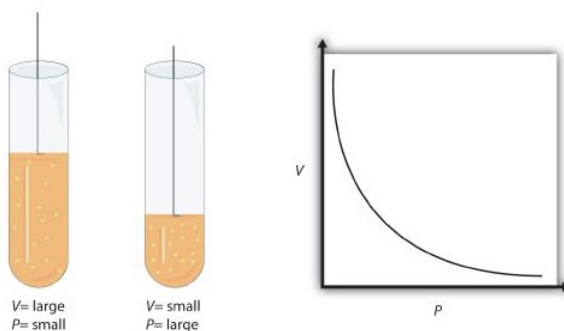

Figure 4.3.1: Boyle's Law. A piston having a certain pressure and volume (left piston) will have half the volume when its pressure is twice as much (right piston). One can also plot *P* versus *V* for a given amount of gas at a certain temperature; such a plot will look like the graph on the right.

Boyle's Law is an example of a second type of mathematical problem we see in chemistry—one based on a mathematical formula. Tactics for working with mathematical formulas are different from tactics for working with conversion factors. First, most of the questions you will have to answer using formulas are word-type questions, so the first step is to identify what quantities are known and assign them to variables. Second, in most formulas, some mathematical rearrangements (i.e., algebra) must be performed to solve for an unknown variable. The rule is that to find the value of the unknown variable, you must mathematically isolate the unknown variable *by itself and in the numerator* of one side of the equation. Finally, units must be consistent. For example, in Boyle's Law there are two pressure variables; they must have the same unit. There are also two volume variables; they also must have the same unit. In most cases, it won't matter *what* the unit is, but the unit must be the *same* on both sides of the equation.

✔ Example 4.3.1

A sample of gas has an initial pressure of 2.44 atm and an initial volume of 4.01 L. Its pressure changes to 1.93 atm. What is the new volume if temperature and amount are kept constant?

Solution

Solutions to Example 11.8.1

Steps for Problem Solving	
Identify the "given" information and what the problem is asking you to "find."	Given: P_1 = 2.44 atm and V_1 = 4.01 L P_2 = 1.93 atm Find: V_2 = ? L
List other known quantities.	none
Plan the problem.	First, rearrange the equation algebraically to solve for V_2. $$V_2 = \frac{P_1 \times V_1}{P_2}$$
Cancel units and calculate.	Now substitute the known quantities into the equation and solve. $$V_2 = \frac{2.44 \ \cancel{\text{atm}} \times 4.01 \text{ L}}{1.93 \ \cancel{atm}} = 5.07 \text{ L}$$
Think about your result.	We know that pressure and volume are inversely related; as one decreases, the other increases. Pressure is decreasing (from 2.44 atm to 1.93 atm), so volume should be increasing to compensate, and it is (from 4.01 L to 5.07 L). So the answer makes sense based on Boyle's Law.

? Exercise 4.3.1

If P_1 = 334 torr, V_1 = 37.8 mL, and P_2 = 102 torr, what is V_2?

Answer

   124 mL

As mentioned, you can use any units for pressure and volume, but both pressures must be expressed in the same units, and both volumes must be expressed in the same units.

✔ Example 4.3.2:

A sample of gas has an initial pressure of 722 torr and an initial volume of 88.8 mL. Its volume changes to 0.663 L. What is the new pressure?

Solution

Solutions to Example 11.8.2

Steps for Problem Solving	
Identify the "given" information and what the problem is asking you to "find."	Given: P_1 = 722 torr and V_1 = 88.8 mL V_2 = 0.633 L Find: P_2 = ? torr
List other known quantities.	1 L = 1000 mL to have the same units for volume.

Steps for Problem Solving	
Plan the problem.	1. Perform the conversion of the second volume unit from L to mL. 2. Rearrange the equation algebraically to solve for P_2. $$P_2 = \frac{P_1 \times V_1}{V_2}$$
Cancel units and calculate.	1. $$0.663 \; \cancel{L} \times \frac{1000 \, ml}{1 \; \cancel{L}} = 663 \, ml$$ 2. Substitute the known quantities into the equation and solve. $$P_2 = \frac{722 \, \text{torr} \times 88.8 \; \cancel{mL}}{663 \; \cancel{mL}} = 96.7 \, \text{torr}$$
Think about your result.	When the volume increased, the pressure decreased, which is as expected for Boyle's Law.

? Exercise 4.3.2

If V_1 = 456 mL, P_1 = 308 torr, and P_2 = 1.55 atm, what is V_2?

Answer

119 mL

Summary

- The behavior of gases can be modeled with gas laws.
- Boyle's Law relates the pressure and volume of a gas at constant temperature and amount.

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4.4: 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.
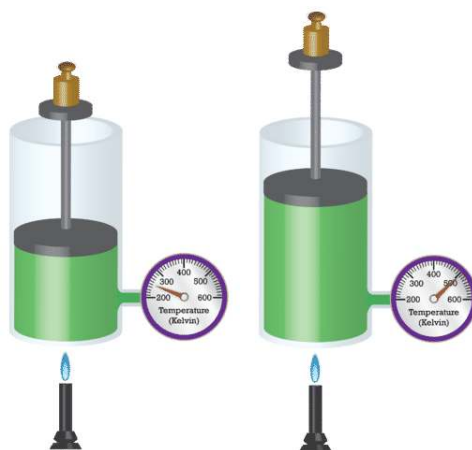
Figure 4.4.1: As a container of confined gas is heated, its molecules increase in kinetic energy and push the movable piston outward, resulting in an increase in volume.

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 4.4.1: Temperature-Volume Data

Temperature (K)	Volume (mL)	$\frac{V}{T} = k \left(\frac{mL}{K} \right)$
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.
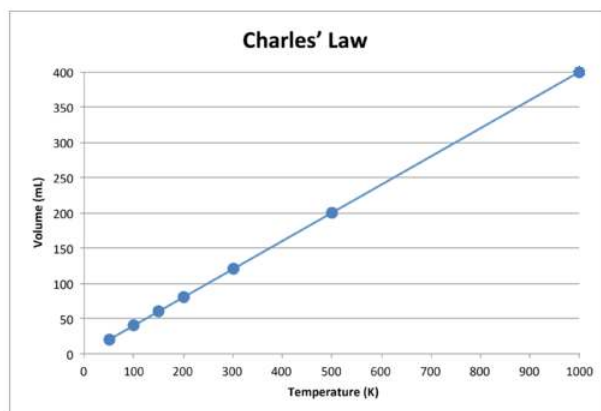
Figure 4.4.2:The volume of a gas increases as the Kelvin temperature increases.

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 $K = {}^{\circ}C + 273$.

✔ **Example 4.4.1:**

A balloon is filled to a volume of 2.20 L at a temperature of $22^{\circ}C$. The balloon is then heated to a temperature of $71^{\circ}C$. 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: $V_1 = 2.20$ L and $T_1 = 22^{\circ}C = 295$ K $T_2 = 71^{\circ}C = 344$ 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. $$V_2 = \frac{2.20\text{ L} \times 344\ \cancel{K}}{295\ \cancel{K}} = 2.57\text{ L}$$

Steps for Problem Solving	
Think about your result.	The volume increases as the temperature increases. The result has three significant figures.

? Exercise 4.4.1

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 4.4.2:

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 4.4.2

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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4.5: Gay-Lussac's Law- Temperature and Pressure

> **◑ Learning Objectives**
>
> - Explain Gay-Lussac's Law.

Propane tanks are widely used with barbeque grills. But it's not fun to find out halfway through grilling that you have run out of gas. You can buy gauges that measure the pressure inside the tank to see how much is left. The gauge measures pressure and will register a higher pressure on a hot day than it will on a cold day. So you need to take the air temperature into account when you decide whether or not to refill the tank before your next cook-out.

Gay-Lussac's Law

When the temperature of a sample of gas in a rigid container is increased, the pressure of the gas increases as well. The increase in kinetic energy results in the molecules of gas striking the walls of the container with more force, resulting in a greater pressure. The French chemist Joseph Gay-Lussac (1778-1850) discovered the relationship between the pressure of a gas and its absolute temperature. **Gay-Lussac's Law** states that the pressure of a given mass of gas varies directly with the absolute temperature of the gas, when the volume is kept constant. Gay-Lussac's Law is very similar to Charles's Law, with the only difference being the type of container. Whereas the container in a Charles's Law experiment is flexible, it is rigid in a Gay-Lussac's Law experiment.

Figure 4.5.1: Joseph Gay-Lussac.

The mathematical expressions for Gay-Lussac's Law are likewise similar to those of Charles's Law:

$$\frac{P}{T} \quad \text{and} \quad \frac{P_1}{T_1} = \frac{P_2}{T_2}$$

A graph of pressure vs. temperature also illustrates a direct relationship. As a gas is cooled at constant volume, its pressure continually decreases until the gas condenses to a liquid.

> **✔ Example 4.5.1**
>
> The gas in an aerosol can is under a pressure of $3.00 \, \text{atm}$ at a temperature of 25°C. It is dangerous to dispose of an aerosol can by incineration. What would the pressure in the aerosol can be at a temperature of 845°C?
>
> **Solution**
>
> Solutions to Example 11.10.1
>
> | Steps for Problem Solving | |
> |---|---|
> | Identify the "given" information and what the problem is asking you to "find." | Given:
$P_1 = 3.00 \, \text{atm}$
$T_1 = 25^\circ\text{C} = 298 \, \text{K}$
$T_2 = 845^\circ\text{C} = 1118 \, \text{K}$
Find: $P_2 = ? \, \text{atm}$ |
> | List other known quantities. | The temperatures have first been converted to Kelvin. |
> | Plan the problem. | First, rearrange the equation algebraically to solve for P_2.

$$P_2 = \frac{P_1 \times T_2}{T_1}$$ |

Steps for Problem Solving	
Calculate.	Now substitute the known quantities into the equation and solve. $$P_2 = \frac{3.00 \, \text{atm} \times 1118 \; \cancel{K}}{298 \; \cancel{K}} = 11.3 \, \text{atm}$$
Think about your result.	The pressure increases dramatically due to a large increase in temperature.

Summary

- Pressure and temperature at constant volume are directly proportional.

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4.6: The Combined Gas Law- Pressure, Volume, and Temperature

> **Learning Objectives**
>
> - Learn and apply the Combined Gas Law.

One thing we notice about all the gas laws is that, collectively, volume and pressure are always in the numerator, and temperature is always in the denominator. This suggests that we can propose a gas law that combines pressure, volume, and temperature. This gas law is known as the **Combined Gas Law**, and its mathematical form is

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \quad at \; constant \; n$$

This allows us to follow changes in all three major properties of a gas. Again, the usual warnings apply about how to solve for an unknown algebraically (isolate it on one side of the equation in the numerator), units (they must be the same for the two similar variables of each type), and units of temperature must be in Kelvin.

> ✔ **Example 4.6.1:**
>
> A sample of gas at an initial volume of 8.33 L, an initial pressure of 1.82 atm, and an initial temperature of 286 K simultaneously changes its temperature to 355 K and its volume to 5.72 L. What is the final pressure of the gas?
>
> **Solution**
>
> Solutions to Example 11.4.1
>
> | **Steps for Problem Solving** | |
> |---|---|
> | Identify the "given" information and what the problem is asking you to "find." | Given:
 V_1 = 8.33 L, P_1 = 1.82 atm, and T_1 = 286 K
 V2 = 5.72 L and T_2 = 355 K
 Find: P_2 = ? atm |
> | List other known quantities. | none |
> | Plan the problem. | First, rearrange the equation algebraically to solve for V_2. $$P_2 = \frac{P_1 V_1 T_2}{T_1 V_2}$$ |
> | Calculate. | Now substitute the known quantities into the equation and solve. $$P_2 = \frac{(1.82 \, atm)(8.33 \, \cancel{L})(355 \, \cancel{K})}{(286 \, \cancel{K})(5.72 \, \cancel{L})} = 3.22 atm$$ |
> | Think about your result. | Ultimately, the pressure increased, which would have been difficult to predict because two properties of the gas were changing. |

> **?** **Exercise 4.6.1**
>
> If P_1 = 662 torr, V_1 = 46.7 mL, T_1 = 266 K, P_2 = 409 torr, and T_2 = 371 K, what is V_2?
>
> **Answer**
>
> 105 mL

As with other gas laws, if you need to determine the value of a variable in the denominator of the combined gas law, you can either cross-multiply all the terms or just take the reciprocal of the combined gas law. Remember, the variable you are solving for must be in the numerator and all by itself on one side of the equation.

Summary

- The Combined Gas Law relates pressure, volume, and temperature of a gas.

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4.7: 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 4.7.1
>
> 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 4.7.1
>
> 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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4.8: The Ideal Gas Law- Pressure, Volume, Temperature, and Moles

> **Learning Objectives**
>
> - Explain the Ideal Gas Law.

There are a number of chemical reactions that require ammonia. In order to carry out the reaction efficiently, we need to know how much ammonia we have for stoichiometric purposes. Using gas laws, we can determine the number of moles present in the tank if we know the volume, temperature, and pressure of the system.

Ideal Gas Law

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

$$\frac{P_1 \times V_1}{T_1 \times n_1} = \frac{P_2 \times V_2}{T_2 \times n_2}$$

As with the other gas laws, we can also say that $\dfrac{(P \times V)}{(T \times n)}$ is equal to a constant. The constant can be evaluated provided that the gas being described is considered to be ideal.

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

$$\frac{P \times V}{T \times n} = R$$

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

$$PV = nRT$$

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

Evaluating the Ideal Gas Constant

The value of R, the ideal gas constant, depends on the units chosen for pressure, temperature, and volume in the ideal gas equation. It is necessary to use Kelvin for the temperature and it is conventional to use the SI unit of liters for the volume. However, pressure is commonly measured in one of three units: kPa, atm, or mm Hg. Therefore, R can have three different values.

We will demonstrate how R is calculated when the pressure is measured in kPa. The volume of $1.00\,\text{mol}$ of any gas at STP (Standard temperature, 273.15 K and pressure, 1 atm) is measured to be $22.414\,\text{L}$ We can substitute $101.325\,\text{kPa}$ for pressure, $22.414\,\text{L}$ for volume, and $273.15\,\text{K}$ for temperature into the ideal gas equation and solve for R.

$$R = \frac{PV}{nT}$$
$$= \frac{101.325\,\text{kPa} \times 22.414\,\text{L}}{1.000\,\text{mol} \times 273.15\,\text{K}}$$
$$= 8.314\,\text{kPa} \cdot \text{L}/\text{K} \cdot \text{mol}$$

This is the value of R that is to be used in the ideal gas equation when the pressure is given in kPa. The table below shows a summary of this and the other possible values of R. It is important to choose the correct value of R to use for a given problem.

Table 4.8.1: Values of the Ideal Gas Constant

Unit of P	Unit of V	Unit of n	Unit of T	Value and Unit of R
kPa	L	mol	K	$8.314\,\text{J}/\text{K} \cdot \text{mol}$
atm	L	mol	K	$0.08206\,\text{L} \cdot \text{atm}/\text{K} \cdot \text{mol}$
mm Hg	L	mol	K	$62.36\,\text{L} \cdot \text{mm Hg}/\text{K} \cdot \text{mol}$

Notice that the unit for R when the pressure is in kPa has been changed to $\text{J/K} \cdot \text{mol}$. A kilopascal multiplied by a liter is equal to the SI unit for energy, a joule (J).

✔ **Example 4.8.1 Oxygen Gas**

What volume is occupied by 3.76 g of oxygen gas at a pressure of 88.4 kPa and a temperature of 19°C? Assume the oxygen is ideal.

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: • $P = 88.4 \text{ kPa}$ • $T = 19^{\circ}\text{C} = 292 \text{ K}$ Mass $O_2 = 3.76 \text{ g}$ Find: $V = ? \text{ L}$
List other known quantities.	$O_2 = 32.00 \text{ g/mol}$ $R = 8.314 \text{ J/K} \cdot \text{mol}$
Plan the problem.	1. First, determine the number of moles of O_2 from the given mass and the molar mass. 2. Then, rearrange the equation algebraically to solve for V $$V = \frac{nRT}{P}$$
Calculate.	1. $$3.76 \text{ g} \times \frac{1 \text{ mol } O_2}{32.00 \text{ g } O_2} = 0.1175 \text{ mol } O_2$$ 2. Now substitute the known quantities into the equation and solve. $$V = \frac{nRT}{P} = \frac{0.1175 \text{ mol} \times 8.314 \text{ J/K} \cdot \text{mol} \times 292 \text{ K}}{88.4 \text{ kPa}} = 3.23 \text{ L}$$
Think about your result.	The number of moles of oxygen is far less than one mole, so the volume should be fairly small compared to molar volume (22.4 L/mol) since the pressure and temperature are reasonably close to standard. The result has three significant figures because of the values for T and P. Since a joule $(\text{J}) = \text{kPa} \cdot \text{L}$, the units cancel out correctly, leaving a volume in liters.

✔ **Example 4.8.2: Argon Gas**

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

Solutions to Example 11.5.2

Steps for Problem Solving	
Identify the "given" information and what the problem is asking you to "find."	Given: n = 4.22 mol P = 1.21 atm T = 34°C Find: $V = ? \text{ L}$
List other known quantities.	none

Steps for Problem Solving	
Plan the problem.	1. The first step is to convert temperature to Kelvin. 2. Then, rearrange the equation algebraically to solve for V $$V = \frac{nRT}{P}$$
Calculate.	1. 34 + 273 = 307 K 2. Now substitute the known quantities into the equation and solve. $$V = \frac{(4.22 \; \cancel{mol})(0.08205\frac{L. \; atm}{\cancel{mol.K}})(307 \; \cancel{K})}{1.21 \; \cancel{atm}}$$ $$= 87.9 \, L$$
Think about your result.	The number of moles of Ar is large so the expected volume should also be large.

? Exercise 4.8.1

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

? Exercise 4.8.2

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

Summary

- The Ideal Gas Law is a single equation which relates the pressure, volume, temperature, and number of moles of an ideal gas.

4.9: Mixtures of Gases - Why Deep-Sea Divers Breathe a Mixture of Helium and Oxygen

> **◑ Learning Objectives**
>
> - Explain Dalton's Law of Partial Pressures.

The atmosphere of Venus is markedly different from that of Earth. The gases in the Venusian atmosphere are 96.5% carbon dioxide and 3% nitrogen. The atmospheric pressure on Venus is roughly 92 times that of Earth, so the amount of nitrogen on Venus would contribute a pressure well over $2700 \mathrm{~mm~Hg}$. And there is no oxygen present, so we couldn't breathe there. Not that we would want to go to Venus, as the surface temperature is usually over $460^{\circ}\mathrm{C}$.

Dalton's Law of Partial Pressures

Gas pressure results from collisions between gas particles and the inside walls of their container. If more gas is added to a rigid container, the gas pressure increases. The identities of the two gases do not matter. John Dalton, the English chemist who proposed the atomic theory, also studied mixtures of gases. He found that each gas in a mixture exerts a pressure independently of every other gas in the mixture. For example, our atmosphere is composed of about 78% nitrogen and 21% oxygen, with smaller amounts of several other gases making up the rest. Since nitrogen makes up 78% of the gas particles in a given sample of air, it exerts 78% of the pressure. If the overall atmospheric pressure is $1.00 \mathrm{~atm}$, then the pressure of just the nitrogen in the air is $0.78 \mathrm{~atm}$. The pressure of the oxygen in the air is $0.21 \mathrm{~atm}$.

The **partial pressure** of a gas is the contribution that gas makes to the total pressure when the gas is part of a mixture. The partial pressure of nitrogen is represented by P_{N_2}. **Dalton's Law of Partial Pressures** states that the total pressure of a mixture of gases is equal to the sum of all of the partial pressures of the component gases. Dalton's Law can be expressed with the following equation:

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

The figure below shows two gases that are in separate, equal-sized containers at the same temperature and pressure. Each exerts a different pressure, P_1 and P_2, reflective of the number of particles in the container. On the right, the two gases are combined into the same container, with no volume change. The total pressure of the gas mixture is equal to the sum of the individual pressures. If $P_1 = 300 \mathrm{~mm~Hg}$ and $P_2 = 500 \mathrm{~mm~Hg}$, then $P_{\text{total}} = 800 \mathrm{~mm~Hg}$.
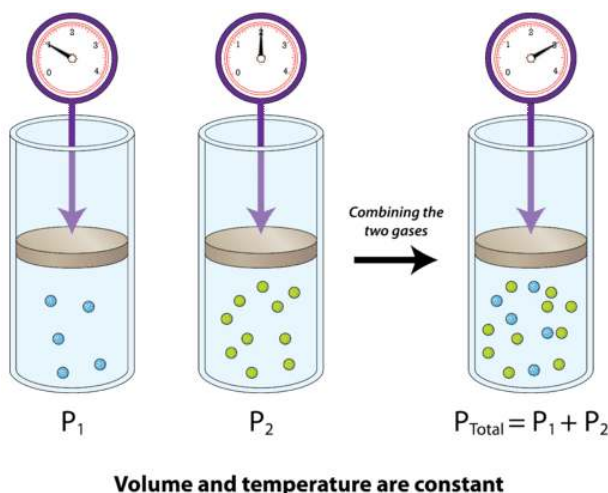
Figure 4.9.1: Dalton's Law states that the pressure of a gas mixture is equal to the partial pressures of the combining gases.

Collecting Gases Over Water

You need to do a lab experiment where hydrogen gas is generated. In order to calculate the yield of gas, you have to know the pressure inside the tube where the gas is collected. But how can you get a barometer in there? Very simple: you don't. All you need

is the atmospheric pressure in the room. As the gas pushes out the water, it is pushing against the atmosphere, so the pressure inside is equal to the pressure outside.

Gas Collection by Water Displacement

Gases that are produced in laboratory experiments are often collected by a technique called **water displacement** (Figure 4.9.2). A bottle is filled with water and placed upside-down in a pan of water. The reaction flask is fitted with rubber tubing, which is then fed under the bottle of water. As the gas is produced in the reaction flask, it exits through the rubber tubing and displaces the water in the bottle. When the bottle is full of the gas, it can be sealed with a lid.

Figure 4.9.2: A gas produced in a chemical reaction can be collected by water displacement.

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

$$P_{\text{Total}} = P_g + P_{H_2O}$$

where P_g is the pressure of the desired gas, which can be solved for:

$$P_g = P_{Total} - P_{H_2O}$$

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

Table 4.9.1: Vapor Pressure of Water (mm Hg) at Selected Temperatures $(^\circ\text{C})$

0	5	10	15	20	25	30	35	40	45	50	55	60
4.58	6.54	9.21	12.79	17.54	23.76	31.82	42.18	55.32	71.88	92.51	118.04	149.38

✔ Example 14.14.1

A certain experiment generates $2.58\ \text{L}$ of hydrogen gas, which is collected over water. The temperature is 20°C and the atmospheric pressure is $98.60\ \text{kPa}$. Find the volume that the dry hydrogen would occupy at STP.

Solution

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

Known
- $V_{\text{Total}} = 2.58\ \text{L}$
- $T = 20^\circ\text{C} = 293\ \text{K}$
- $P_{\text{Total}} = 98.60\ \text{kPa} = 739.7\ \text{mm Hg}$

Unknown
- V_{H_2} at STP $= ?\ \text{L}$

The atmospheric pressure is converted from kPa to mm Hg in order to match units with the table. The sum of the pressures of the hydrogen and the water vapor is equal to the atmospheric pressure. The pressure of the hydrogen is found by subtraction. Then, the volume of the gas at STP can be calculated by using the combined gas law.

Step 2: Solve.

$$
\begin{aligned}
P_{H_2} &= P_{\text{Total}} - P_{H_2O} \\
&= 739,7\ \text{mm Hg} - 17.54\ \text{mm Hg} \\
&= 722.2\ \text{mm Hg}
\end{aligned}
$$

Now the combined gas law is used, solving for V_2, the volume of hydrogen at STP.

$$V_2 = \frac{P_1 \times V_1 \times T_2}{P_2 \times T_1}$$

$$= \frac{722.2 \text{ mm Hg} \times 2.58 \text{ L} \times 273 \text{ K}}{760 \text{ mm Hg} \times 293 \text{ K}}$$

$$= 2.28 \text{ L H}_2$$

Step 3: Think about your result.

If the hydrogen gas were to be collected at STP and without the presence of the water vapor, its volume would be 2.28 L. This is less than the actual collected volume because some of that is water vapor. The conversion using STP is useful for stoichiometry purposes.

Summary

- Dalton's Law of Partial Pressures states that the total pressure in a system is equal to the sum of the partial pressures of the gases present.
- The vapor pressure due to water in a sample can be corrected for, in order to get the true value for the pressure of the gas.

CHAPTER OVERVIEW

5: Solutions

Template:HideTOC

Solutions play a very important role in many biological, laboratory, and industrial applications of chemistry. Of particular importance are solutions involving substances dissolved in water, or aqueous solutions. Solutions represent equilibrium systems, and the lessons learned in our last unit will be of particular importance again. Quantitative measurements of solutions are another key component of this unit. Solutions can involve all physical states - gases dissolved in gases (the air around us), solids dissolved in solids (metal alloys), liquids dissolved in solids (amalgams - liquid mercury dissolved in another metal such as silver, tin or copper). In this unit we will almost exclusively be concerned with aqueous solutions - substances dissolved in water.

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5.1: 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 5.1.1).
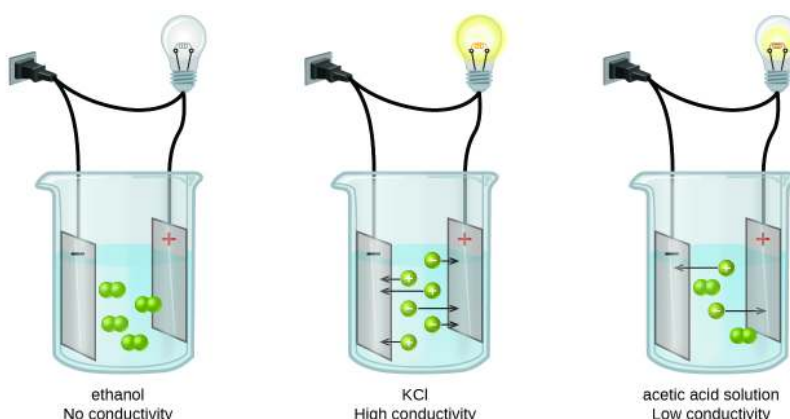
Figure 5.1.1: Solutions of nonelectrolytes, such as ethanol, do not contain dissolved ions and cannot conduct electricity. Solutions of electrolytes contain ions that permit the passage of electricity. The conductivity of an electrolyte solution is related to the strength of the electrolyte. This diagram 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 5.1.2. 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.
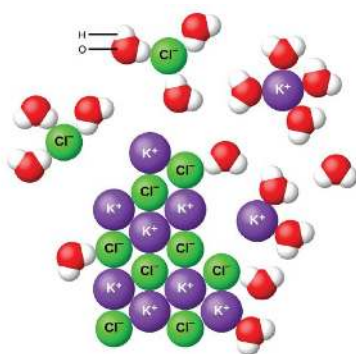
Figure 5.1.2: As potassium chloride (KCl) dissolves in water, the ions are hydrated. The polar water molecules are attracted by the charges on the K^+ and Cl^- ions. Water molecules in front of and behind the ions are not shown. The diagram shows eight purple spheres labeled K superscript plus and eight 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 5.1.2 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 5.1.1 and 5.1.2).

Table 5.1.1: 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 5.1.2: Solubility Rules for Sparingly Soluble Substances

5.1.2

https://chem.libretexts.org/@go/page/329760

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.

$$Cs^+ \, (aq) + Br^- \, (aq) + Pb^{2+} \, (aq) + 2NO_3^- \, (aq) \rightarrow ?$$
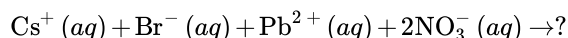
The potential precipitates from a double-replacement reaction are cesium nitrate and lead (II) bromide. According to the solubility rules table, cesium nitrate is soluble because all compounds containing the nitrate ion, as well as all compounds containing the alkali metal ions, are soluble. Most compounds 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:

$$Pb^{2+} \, (aq) + 2Br^- \, (aq) \rightarrow PbBr_2 \, (s)$$
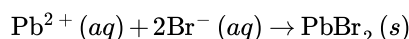
✔ **Example 5.1.1: Solubility**

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 5.1.1: 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

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

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5.2: 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.

$$\mathrm{AgNO_3(aq) + K_2Cr_2O_7(aq) \rightarrow Ag_2Cr_2O_7(s) + KNO_3(aq)} \qquad (5.2.1)$$
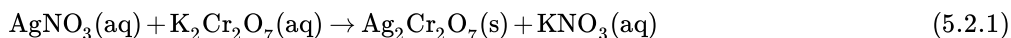
This unbalanced equation has the general form of an exchange reaction:

$$\mathrm{AC + BD \rightarrow \underset{insoluble}{AD} + BC} \qquad (5.2.2)$$

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 5.2.1).

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 5.2.1), 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.

KBr(aq)   NaCl(aq)
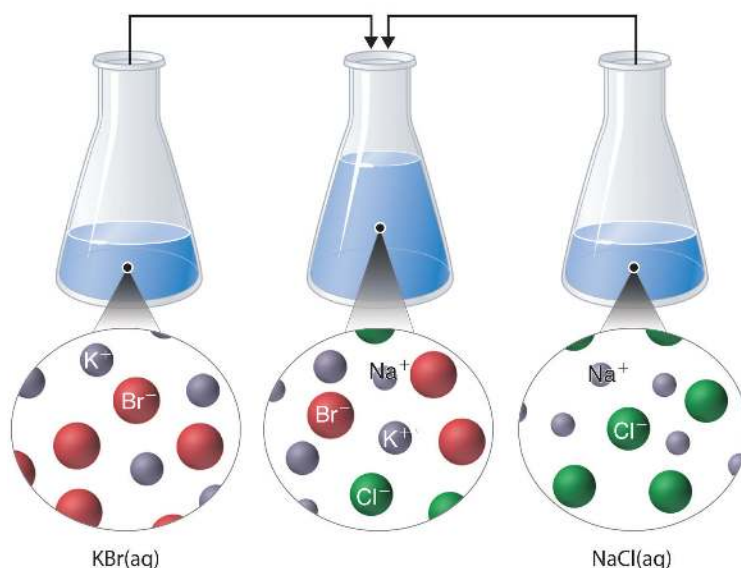
Figure 5.2.1: The Effect of Mixing Aqueous KBr and NaCl Solutions. Because no net reaction occurs, the only effect is to dilute each solution with the other. (Water molecules are omitted from molecular views of the solutions for clarity.)

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):

$$\mathrm{BaCl_{2(aq)}} + \mathrm{Li_2SO_{4(aq)}} \rightarrow \mathrm{BaSO_4} + \mathit{LiCl}$$
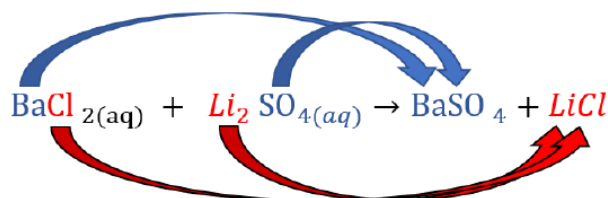
Chemical equation of the reactants barium chloride and lithium sulfate forming the products barium sulfate and lithium chloride.

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.
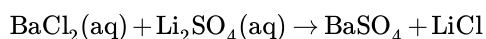
$$\mathrm{BaCl_2(aq) + Li_2SO_4(aq) \rightarrow BaSO_4 + LiCl}$$

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

$$\mathrm{BaCl_2(aq) + Li_2SO_4(aq) \rightarrow BaSO_4(s) + LiCl(aq)}$$
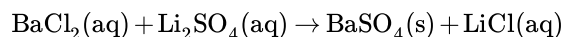
Table 7.5.1 from the previous section shows that $LiCl$ is soluble in water, but $BaSO_4$ is not soluble in water.

Balance the equation:

$$\mathrm{BaCl_2(aq) + Li_2SO_4(aq) \rightarrow BaSO_4(s) + 2\,LiCl(aq)}$$
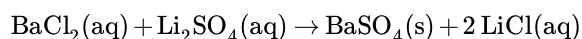
Although soluble barium salts are toxic, $BaSO_4$ is so insoluble that it can be used to diagnose stomach and intestinal problems without being absorbed into tissues. An outline of the digestive organs appears on x-rays of patients who have been given a "barium milkshake" or a "barium enema"—a suspension of very fine $BaSO_4$ particles in water.

Figure 5.2.2: 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 BaSO₄ particles in water; the high atomic mass of barium makes it opaque to x-rays. (Public Domain; Glitzy queen00 via Wikipedia).

✔ Example 5.2.1

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.	$RbOH(aq) + CoCl_2(aq) \rightarrow RbCl + Co(OH)_2$
Refer to the solubility rules table to determine insoluble products which will therefore form a precipitate.	$RbOH(aq) + CoCl_2(aq) \rightarrow RbCl(aq) + Co(OH)_2(s)$
Balance the equation.	Coefficients already balanced. $RbOH(aq) + CoCl_2(aq) \rightarrow RbCl(aq) + Co(OH)_2(s)$
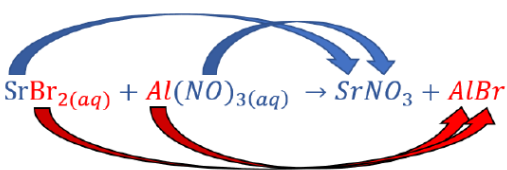
✔ Example 5.2.2

Predict what will happen if aqueous solutions of strontium bromide and aluminum nitrate are mixed.

Solution

Solutions for Example 7.6.2

Steps	Example

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.	$SrBr_2(aq) + Al(NO_3)_3(aq) \rightarrow Sr(NO_3)_2 + AlBr_3$
Refer to the solubility rules table to determine insoluble products which will therefore form a precipitate.	$SrBr_2(aq) + Al(NO_3)_3(aq) \rightarrow Sr(NO_3)_2(aq) + AlBr_3(aq)$ According to Table 7.5.1 from the previous section, both $AlBr_3$ (rule 4) and $Sr(NO_3)_2$ (rule 2) are soluble.
If all possible products are soluble, then no net reaction will occur.	$SrBr_2(aq) + Al(NO_3)_3(aq) \rightarrow$ **NO REACTION**

? Exercise $5.2.2$

Using the information in Table 7.5.1 from the previous section, predict what will happen in each case involving strong electrolytes.

 a. An aqueous solution of strontium hydroxide is added to an aqueous solution of iron(II) chloride.
 b. Solid potassium phosphate is added to an aqueous solution of mercury(II) perchlorate.
 c. Solid sodium fluoride is added to an aqueous solution of ammonium formate.
 d. Aqueous solutions of calcium bromide and cesium carbonate are mixed.

Answer a

   $Fe(OH)_2$ precipitate is formed.

Answer b

   $Hg_3(PO_4)_2$ precipitate is formed.

Answer c

   No Reaction.

Answer d

   $CaCO_3$ is precipitate formed.

Summary

In a **precipitation reaction**, a subclass of exchange reactions, an insoluble material (a **precipitate**) forms when two electrolyte solutions are mixed. To predict the product of a precipitation reaction, all species initially present in the solutions are identified, as are any combinations likely to produce an insoluble salt.

Contributions & Attributions

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5.3: 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.

$$\underbrace{\mathrm{BaCl_2(aq) + Na_2SO_4(aq) \longrightarrow BaSO_4(s) + 2\,NaCl(aq)}}_{\text{Complete Chemical Equation}} \qquad (5.3.1)$$
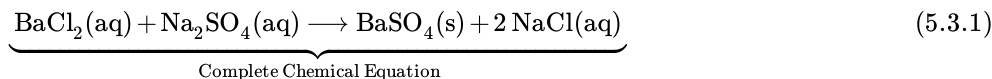
However, Equation 5.3.1 does not really represent the microscopic particles (that is, the ions) present in the solution. Below is the complete ionic equation:

$$\underbrace{\mathrm{Ba^{2+}(aq) + \overbrace{2\,Cl^-(aq)}^{\text{spectator}} + \overbrace{2\,Na^+(aq)}^{\text{spectator}} + SO_4^{2-}(aq) \longrightarrow BaSO_4(s) + \overbrace{2\,Na^+(aq)}^{\text{spectator}} + \overbrace{Cl^-(aq)}^{\text{spectator}}}}_{\text{Complete Ionic Equation}} \qquad (5.3.2)$$
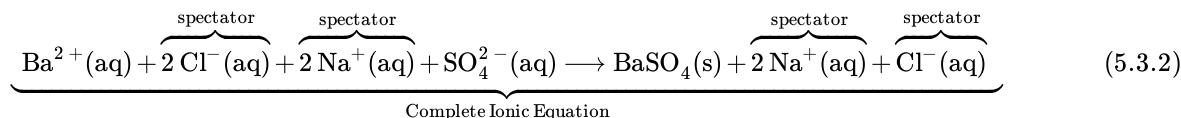
Equation 5.3.2 is rather cumbersome and includes so many different ions that it may be confusing. In any case, we are often interested in the independent behavior of ions, not the specific compound from which they came. A precipitate of $\mathrm{BaSO_4(s)}$ will form when *any* solution containing $\mathrm{Ba^{2+}(aq)}$ 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 5.3.2. 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

$$\underbrace{\mathrm{Ba^{2+}(aq) + SO_4^{2-}(aq) \longrightarrow BaSO_4(s)}}_{\text{Net Ionic Equation}} \qquad (5.3.3)$$
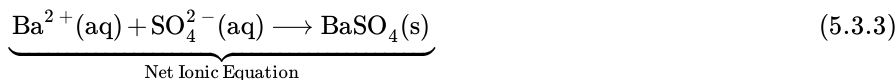
> ✔ **Example 5.3.1**
>
> a. When a solution of $\mathrm{AgNO_3}$ is added to a solution of $\mathrm{CaCl_2}$, insoluble AgCl precipitates. Write three equations (complete chemical equation, complete ionic equation, and net ionic equation) that describe this process.
> b. Write the balanced net ionic 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 **5.3.1***a* | Example **5.3.1***b* |
> |---|---|---|
> | Complete Chemical Equation | $\mathrm{2\,AgNO_3(aq) + CaCl_2(aq) \longrightarrow}$ $\mathrm{2\,AgCl(s) + Ca(NO_3)_2(aq)}$ The proper states and formulas of all products are written and the chemical equation is balanced. | $\mathrm{Na_2SO_4(aq) + 2\,NH_4I(aq) \longrightarrow}$ $\mathrm{2\,NaI(aq) + (NH_4)_2SO_4(aq)}$ Both products are aqueous so there is no net ionic equation that can be written. |
> | Complete Ionic Equation | $\mathrm{2\,Ag^+(aq) + 2\,NO_3^-(aq) + Ca^{2+}(aq) + 2\,Cl^-(aq) \longrightarrow}$ $\mathrm{2\,AgCl(s) + Ca^{2+}(aq) + 2\,NO_3^-(aq)}$ AgCl is a solid so it does not break up into ions in solution. | |
> | Net Ionic Equation | $\mathrm{Ag^+(aq) + Cl^-(aq) \longrightarrow AgCl(s)}$ All spectator ions are removed. 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 5.3.1: 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 5.3.1). 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 5.3.1**
>
> 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**
>
> $$Ba^{2+}(aq) + SO_4^{2-}(aq) \longrightarrow Ba(SO_4)(s)$$
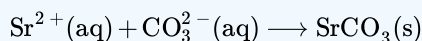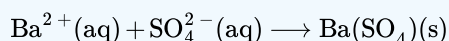
Precipitates are also used for quantitative analysis of solutions, that is, to determine the amount of solute or the mass of solute in a given solution. For this purpose it is often convenient to use the first of the three types of equations described above. Then the rules of stoichiometry may be applied.

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.

5.4: Solution Concentration- Molarity

> 🧠 **Learning Objectives**
>
> - Use molarity to determine quantities in chemical reactions.
> - Use molarity as a conversion factor in calculations.

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

$$\text{molarity} = \frac{\text{number of moles of solute}}{\text{number of liters of solution}} \qquad (5.4.1)$$

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

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

$$\frac{1.5 \text{ mol NaCl}}{0.500 \text{ L solution}} = 3.0 \text{ M NaCl}$$

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

> Be sure to note that molarity is calculated as the total volume of the **entire** solution, not just volume of solvent! The solute contributes to total volume.

If the quantity of the solute is given in mass units, you must convert mass units to mole units before using the definition of molarity to calculate concentration. For example, what is the molar concentration of a solution of 22.4 g of HCl dissolved in 1.56 L?

Step 1: First, convert the mass of solute to moles using the molar mass of HCl (36.5 g/mol):

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

Step 2: Now we can use the definition of molarity to determine a concentration:

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

Before a molarity concentration can be calculated, the amount of the solute must be expressed in moles, and the volume of the solution must be expressed in liters, as demonstrated in the following example.
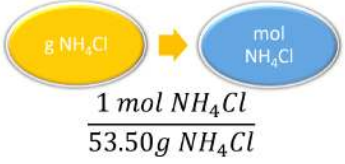
> ✔ **Example 5.4.1**
>
> A solution is prepared by dissolving $42.23 \; g$ of NH_4Cl into enough water to make $500.0 \; mL$ of solution. Calculate its molarity.
>
> **Solution**
>
> Solutions to Example 13.6.1
>
> | Steps for Problem Solving | |
> |---|---|
> | Identify the "given" information and what the problem is asking you to "find." | Given:
Mass $= 42.23 \text{ g } NH_4Cl$
Volume solution $= 500.0 \text{ mL} = 0.5000 \text{ L}$
Find: Molarity = ? M |
> | List other known quantities. | Molar mass $NH_4Cl = 53.50 \text{ g/mol}$ |
> | | |

Steps for Problem Solving	
Plan the problem.	1. The mass of the ammonium chloride is first converted to moles. $$\frac{1\ mol\ NH_4Cl}{53.50g\ NH_4Cl}$$ 2. Then the molarity is calculated by dividing by liters. Note the given volume has been converted to liters. $$M = \frac{mol\ NH_4Cl}{L\ solution}$$
Cancel units and calculate.	Now substitute the known quantities into the equation and solve. $$42.23\ \cancel{g\ NH_4Cl} \times \frac{1\ mol\ NH_4Cl}{53.50\ \cancel{g\ NH_4Cl}} = 0.7893\ mol\ NH_4Cl$$ $$\frac{0.7893\ mol\ NH_4Cl}{0.5000\ L\ solution} = 1.579\ M$$
Think about your result.	The molarity is 1.579 M, meaning that a liter of the solution would contain 1.579 mol NH_4Cl. Four significant figures are appropriate.

> **? Exercise $5.4.1A$**
>
> What is the molarity of a solution made when 66.2 g of $C_6H_{12}O_6$ are dissolved to make 235 mL of solution?
>
> **Answer**
>
> 1.57 M $C_6H_{12}O_6$

> **? Exercise $5.4.1B$**
>
> What is the concentration, in mol/L, where $137\ g$ of $NaCl$ has been dissolved in enough water to make $500\ mL$ of solution?
>
> **Answer**
>
> 4.69 M NaCl

Using Molarity in Calculations
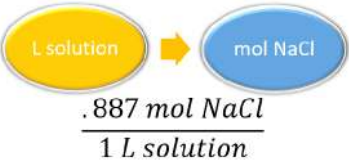
Concentration can be a conversion factor between the amount of solute and the amount of solution or solvent (depending on the definition of the concentration unit). As such, concentrations can be useful in a variety of stoichiometry problems. In many cases, it is best to use the original definition of the concentration unit; it is that definition that provides the conversion factor.

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

> **✔ Example $5.4.2$: Determining Moles of Solute, Given the Concentration and Volume of a Solution**
>
> For example, suppose we ask how many moles of solute are present in 0.108 L of a 0.887 M NaCl solution. Because 0.887 M means 0.887 mol/L, we can use this second expression for the concentration as a conversion factor:
>
> **Solution**
>
>
>
> $$\frac{.887\ mol\ NaCl}{1\ L\ solution}$$
>
> $$0.108\ \cancel{L\ solution} \times \frac{0.887\ mol\ NaCl}{1L\ \cancel{solution}} = 0.0958\ mol\ NaCl$$
>
> If we used the definition approach, we get the same answer, but now we are using conversion factor skills.

Like any other conversion factor that relates two different types of units, the reciprocal of the concentration can be also used as a conversion factor.

✔ **Example 5.4.3: Determining Volume of a Solution, Given the Concentration and Moles of Solute**

Using concentration as a conversion factor, how many liters of 2.35 M $CuSO_4$ are needed to obtain 4.88 mol of $CuSO_4$?

Solution

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

$$\frac{1\ L\ solution}{2.35\ mol\ CuSO_4}$$
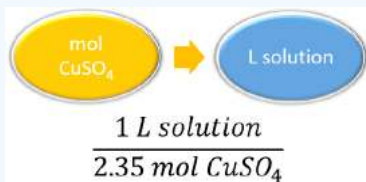
$$4.88\ mol\ CuSO_4 \times \frac{1\ L\ solution}{2.35\ mol\ CuSO_4} = 2.08\ L\ of\ solution$$

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

✔ **Example 5.4.4**

A chemist needs to prepare $3.00\ L$ of a $0.250\ M$ solution of potassium permanganate $(KMnO_4)$. What mass of $KMnO_4$ does she need to make the solution?

Solution

Solutions to Example 13.6.4

Steps for Problem Solving	
Identify the "given" information and what the problem is asking you to "find."	Given: Molarity $= 0.250\ M$ Volume $= 3.00\ L$ Find: Mass $KMnO_4 = ?\ g$
List other known quantities.	Molar mass $KMnO_4 = 158.04\ g/mol$ 0.250 mol $KMnO_4$ to 1 L of $KMnO_4$ solution
Plan the problem.	 $\frac{.250\ mol\ KMnO_4}{1\ L\ solution}$ $\frac{158.04g\ KMnO_4}{1\ mol\ KMnO_4}$
Cancel units and calculate.	Now substitute the known quantities into the equation and solve. $mol\ KMnO_4 = 0.250\ M\ KMnO_4 \times 3.00\ L = 0.750\ mol$ $3.00\ L\ solution \times \frac{0.250\ mol\ KMnO_4}{1\ L\ solution} \times \frac{158.04\ g\ KMnO_4}{1\ mol\ KMnO_4} = 119\ g\ KM$
Think about your result.	When 119 g of potassium permanganate is dissolved into water to make $3.00\ L$ of solution, the molarity is $0.250\ M$.

? **Exercise 5.4.4A**

Using concentration as a conversion factor, how many liters of 0.0444 M CH_2O are needed to obtain 0.0773 mol of CH_2O?

Answer

1.74 L

? Exercise 5.4.4B

Answer the problems below using concentration as a conversion factor.

a. What mass of solute is present in 1.08 L of 0.0578 M H_2SO_4?
b. What volume of 1.50 M HCl solution contains 10.0 g of hydrogen chloride?

Answer a

6.12 g

Answer b

183 mL or 0.183L

📌 How to Indicate Concentration

- Square brackets are often used to represent concentration, e.g., [NaOH] = 0.50 M.
- Use the capital letter M for molarity, not a lower case m (this is a different concentration unit called *molality*).

Watch as the Flinn Scientific Tech Staff demonstrates "How To Prepare Solutions."

It is important to note that there are many different ways you can set up and solve your chemistry equations. Some students prefer to answer multi-step calculations in one long step, while others prefer to work out each step individually. Neither method is necessarily better or worse than the other method—whichever makes the most sense to *you* is the one that you should use. In this text, we will typically use unit analysis (also called dimension analysis or factor analysis).

Contributors and Attributions

- Peggy Lawson (Oxbow Prairie Heights School). Funded by Saskatchewan Educational Technology Consortium.

5.5: Solution Dilution

> **◗ Learning Objectives**
>
> - Explain how concentrations can be changed in the lab.
> - Understand how stock solutions are used in the laboratory.

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

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

These two terms do not provide any quantitative information (actual numbers), but they are often useful in comparing solutions in a more general sense. These terms also do not tell us whether or not the solution is saturated or unsaturated, or whether the solution is "strong" or "weak". These last two terms will have special meanings when we discuss acids and bases, so be careful not to confuse them.

Stock Solutions

It is often necessary to have a solution with a concentration that is very precisely known. Solutions containing a precise mass of solute in a precise volume of solution are called **stock (or standard) solutions.** To prepare a standard solution, a piece of lab equipment called a volumetric flask should be used. These flasks range in size from 10 mL to 2000 mL and are carefully calibrated to a single volume. On the narrow stem is a **calibration mark**. The precise mass of solute is dissolved in a bit of the solvent, and this is added to the flask. Then, enough solvent is added to the flask until the level reaches the calibration mark.

Often, it is convenient to prepare a series of solutions of known concentrations by first preparing a single **stock solution**, as described in the previous section. **Aliquots** (carefully measured volumes) of the stock solution can then be diluted to any desired volume. In other cases, it may be inconvenient to weigh a small mass of sample accurately enough to prepare a small volume of a dilute solution. Each of these situations requires that a solution be diluted to obtain the desired concentration.

Dilutions of Stock (or Standard) Solutions

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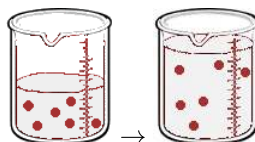
Before Dilution and After Dilution

The molarity of solution 1 is

$$M_1 = \frac{\text{moles}_1}{\text{liter}_1}$$

and the molarity of solution 2 is

$$M_2 = \frac{\text{moles}_2}{\text{liter}_2}$$

rearrange the equations to find moles:

$$\text{moles}_1 = M_1 \text{liter}_1$$

and

$$\text{moles}_2 = M_2 \text{liter}_2$$

What stayed the same and what changed between the two solutions? By adding more water, we changed the volume of the solution. Doing so also changed its concentration. **However, the number of moles of solute did not change.** So,

$$moles_1 = moles_2$$

Therefore

$$\boxed{M_1 V_1 = M_2 V_2} \tag{5.5.1}$$

where

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

Preparing dilutions is a common activity in the chemistry lab and elsewhere. Once you understand the above relationship, the calculations are simple.

Suppose that you have $100.\ \text{mL}$ of a $2.0\ \text{M}$ solution of HCl. You dilute the solution by adding enough water to make the solution volume $500.\ \text{mL}$. The new molarity can easily be calculated by using the above equation and solving for M_2.

$$M_2 = \frac{M_1 \times V_1}{V_2} = \frac{2.0\ \text{M} \times 100.\ \text{mL}}{500.\ \text{mL}} = 0.40\ \text{M HCl}$$

The solution has been diluted by one-fifth since the new volume is five times as great as the original volume. Consequently, the molarity is one-fifth of its original value.

Another common dilution problem involves calculating what amount of a highly concentrated solution is required to make a desired quantity of solution of lesser concentration. The highly concentrated solution is typically referred to as the stock solution.

✔ Example 5.5.1: Diluting Nitric Acid

Nitric acid (HNO_3) is a powerful and corrosive acid. When ordered from a chemical supply company, its molarity is $16\ \text{M}$. How much of the stock solution of nitric acid needs to be used to make $8.00\ \text{L}$ of a $0.50\ \text{M}$ solution?

Solution

Solutions to Example13.7.1

Steps for Problem Solving	
Identify the "given" information and what the problem is asking you to "find."	Given: M_1, Stock $\text{HNO}_3 = 16\ \text{M}$ $V_2 = 8.00\ \text{L}$ $M_2 = 0.50\ \text{M}$ Find: Volume stock $\text{HNO}_3\ (V_1) =?\ \text{L}$
List other known quantities.	none
Plan the problem.	First, rearrange the equation algebraically to solve for V_1. $$V_1 = \frac{M_2 \times V_2}{M_1}$$
Calculate and cancel units.	Now substitute the known quantities into the equation and solve. $$V_1 = \frac{0.50\ \text{M} \times 8.00\ \text{L}}{16\ \text{M}} = 0.25\ \text{L} \tag{5.5.2}$$
Think about your result.	$0.25\ \text{L}\ (250\ \text{mL})$ of the stock HNO_3 needs to be diluted with water to a final volume of $8.00\ \text{L}$. The dilution is by a factor of 32 to go from $16\ \text{M}$ to $0.5\ \text{M}$.

? Exercise 5.5.1

A 0.885 M solution of KBr with an initial volume of 76.5 mL has more water added until its concentration is 0.500 M. What is the new volume of the solution?

Answer

135.4 mL

Note that the calculated volume will have the same dimensions as the input volume, and dimensional analysis tells us that in this case we don't need to convert to liters, since L cancels when we divide M (mol/L) by M (mol/L).

Diluting and Mixing Solutions

Diluting and Mixing Solutions

How to Dilute a Solution by CarolinaBiological
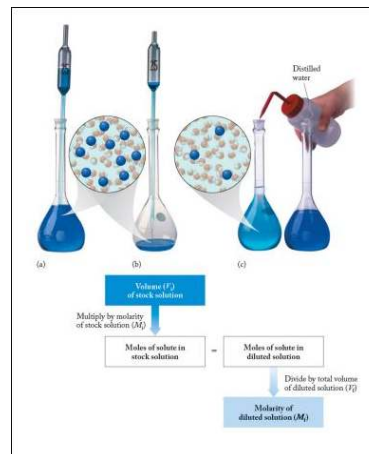
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5.6: Solution Stoichiometry

> **Learning Objectives**
> - Determine amounts of reactants or products in aqueous solutions.

As we learned previously, double replacement reactions involve the reaction between ionic compounds in solution and, in the course of the reaction, the ions in the two reacting compounds are "switched" (they *replace* each other). Because these reactions occur in aqueous solution, we can use the concept of molarity to directly calculate the number of moles of reactants or products that will be formed, and therefore their amounts (i.e. volume of solutions or mass of precipitates).
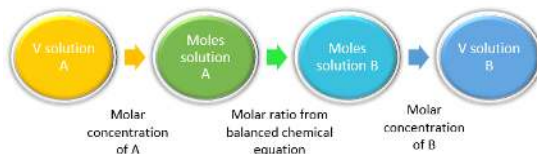
As an example, lead (II) nitrate and sodium chloride react to form sodium nitrate and the *insoluble* compound, lead (II) chloride.

$$Pb(NO_3)_2(aq) + 2\,NaCl(aq) \rightarrow PbCl_2(s) + 2\,NaNO_3(aq) \tag{5.6.1}$$

In the reaction shown above, if we mixed 0.123 L of a 1.00 M solution of NaCl with 1.50 M solution of $Pb(NO_3)_2$, we could calculate the volume of $Pb(NO_3)_2$ solution needed to completely precipitate the Pb^{2+} ions.

The molar concentration can also be expressed as the following:

$$1.00\,M\,NaCl = \frac{1.00\,mol\,NaCl}{1\,L\,NaCl\,solution}$$

and

$$1.50\,M\,Pb(NO_3)_2 = \frac{1.50\,mol\,Pb(NO_3)_2}{1\,L\,Pb(NO_3)_2 solution}$$

First, we must examine the reaction stoichiometry in the balanced reaction (Equation 5.6.1). In this reaction, one mole of $Pb(NO_3)_2$ reacts with two moles of NaCl to give one mole of $PbCl_2$ precipitate. Thus, the concept map utilizing the stoichiometric ratios is:

so the volume of lead (II) nitrate that reacted is calculated as:

$$0.123\,L\,NaCl\,solution \times \frac{1.00\,mol\,NaCl}{1\,L\,NaCl\,solution} \times \frac{1\,mol\,Pb(NO_3)_2}{2\,mol\,NaCl} \times \frac{1\,L\,Pb(NO_3)_2\,solution}{1.5\,mol\,Pb(NO_3)_2} = 0.041\,Pb(NO_3)_2$$
$$L\,solution$$

This volume makes intuitive sense for two reasons: (1) the number of moles of $Pb(NO_3)_2$ required is half of the number of moles of NaCl, based off of the stoichiometry in the balanced reaction (Equation 5.6.1); (2) the concentration of $Pb(NO_3)_2$ solution is 50% greater than the NaCl solution, so less volume is needed.

> **✔ Example 5.6.1**
>
> What volume (in L) of 0.500 M sodium sulfate will react with 275 mL of 0.250 M barium chloride to completely precipitate all Ba^{2+} in the solution?
>
> **Solution**
>
> Solutions to Example 13.8.1
>
> | Steps for Problem Solving | Example 5.6.1 |
> |---|---|
> | Identify the "given" information and what the problem is asking you to "find." | Given: 275 mL $BaCl_2$
 0.250 M $BaCl_2$ or $\dfrac{0.250\,mol\,BaCl_2}{1\,L\,BaCl_2\,solution}$
 0.500 M Na_2SO_4 or $\dfrac{0.500\,mol\,Na_2SO_4}{1\,L\,Na_2SO_4\,solution}$
 Find: Volume Na_2SO_4 solution. |
> | Set up and balance the chemical equation. | $Na_2SO_4(aq) + BaCl_2(aq) \longrightarrow BaSO_4(s) + 2NaCl(aq)$
 An insoluble product is formed after the reaction. |
> | List other known quantities. | 1 mol of Na_2SO_4 to 1 mol $BaCl_2$
 1000 mL = 1 L |
> | Prepare a concept map and use the proper conversion factor. | |
> | Cancel units and calculate. | $275\,mL\,BaCl_2\,solution \times \dfrac{1\,L}{1000\,mL} \times \dfrac{0.250\,mol\,BaCl_2}{1\,L\,BaCl_2\,solution} \times \dfrac{1\,mol\,Na_2S}{1\,mol\,BaCl}$
 = 0.1375 L sodium sulfate |

Steps for Problem Solving	Example 5.6.1
Think about your result.	The lesser amount (almost half) of sodium sulfate is to be expected as it is more concentrated than barium chloride. Also, the units are correct.

? Exercise 5.6.1

What volume of 0.250 M lithium hydroxide will completely react with 0.500 L of 0.250 M of sulfuric acid solution?

Answer

   0.250 L LiOH solution

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CHAPTER OVERVIEW

6: Atomic Structure and Periodic Trends

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6.1: 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 6.1.1: 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 6.1.1: 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 6.1.1 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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6.2: 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 6.2.1: 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 6.2.1). 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 6.2.1: 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 6.2.1). 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 6.2.1).

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 6.2.2.

Table 6.2.2: *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

Chemical Symbol	Name	Latin Name
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.

![LibreTexts logo]

6.3: 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 6.3.1. 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 6.3.1: 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 $6.3.2$. 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 $6.3.2$, 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.
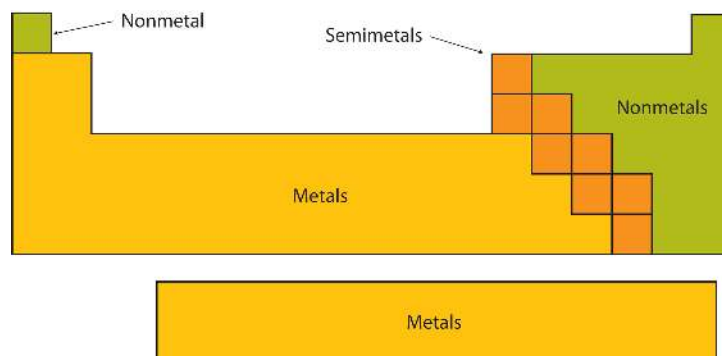
Figure $6.3.2$: Types of Elements. Elements are either metals, nonmetals, or metalloids (or semi metals). Each group is located in a different part of the periodic table. (CC BY-NC-SA; Anonymous by request)

✔ Example 6.3.1

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 6.3.1, 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 6.3.1

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 6.3.3. 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**.
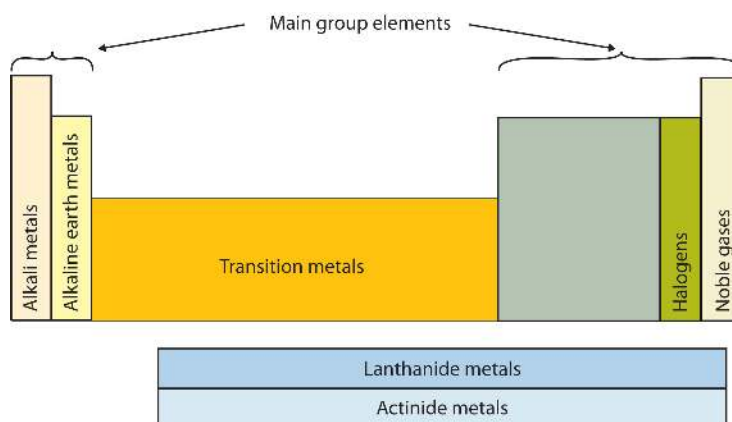
Figure 6.3.3: Special Names for Sections of the Periodic Table. (CC BY-NC-SA; Anonymous by request)

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 6.3.2: 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 6.3.2: 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 6.3.3: 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 6.3.3: 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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Contributions & Attributions

6.4: Ions - Losing and Gaining Electrons

> **◐ Learning Objectives**
>
> - Define the two types of ions.

Atoms tend to lose, gain, or share some valance electrons, making bonds to acquire the electron configuration of the nearest noble gas, i.e., usually eight valence electrons for the main group elements, called an octet. Most atoms do not have eight electrons in their valence electron shell. Some atoms have only a few electrons in their outer shell, while others lack only one or two electrons to have an octet. In cases where an atom has three or fewer valence electrons, the atom may lose those valence electrons quite easily until what remains is a lower shell that contains an octet. Atoms that lose electrons acquire a positive charge because they are left with fewer negatively charged electrons to balance the positive charges of the protons in the nucleus. Positively charged ions are called **cations**. Most metals become cations when they make ionic compounds.

Cations

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

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

The cation produced in this way, Na^+, is called the sodium ion to distinguish it from the element. The outermost shell of the sodium ion is the second electron shell, which has eight electrons in it. The octet rule has been satisfied. Figure 6.4.1 is a graphical depiction of this process.
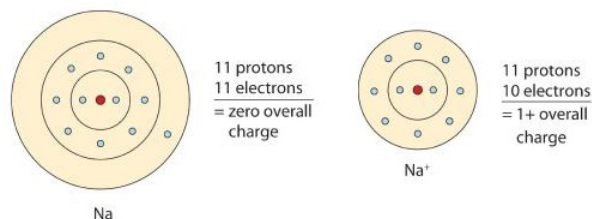
Figure 6.4.1: The Formation of a Sodium Ion. On the left, a sodium atom has 11 electrons. On the right, the sodium ion only has 10 electrons and a 1+ charge. Neutral sodium atom on left has 11 protons and 11 electrons. Sodium ion on right has 11 protons and 10 electrons, with a +1 overall charge.

Anions

Some atoms have nearly eight electrons in their valence shell and can gain additional valence electrons until they have an octet. When these atoms gain electrons, they acquire a negative charge because they now possess more electrons than protons. Negatively charged ions are called **anions**. Most nonmetals become anions when they make ionic compounds.

A neutral chlorine atom has seven electrons in its outermost shell. Only one more electron is needed to achieve an octet in chlorine's valence shell. (In table salt, this electron comes from the sodium atom.)

$$e^- + Cl \longrightarrow Cl^-$$
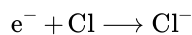
In this case, the ion has the same outermost shell as the original atom, but now that shell has eight electrons in it. Once again, the octet rule has been satisfied. The resulting anion, Cl^-, is called the chloride ion; note the slight change in the suffix (-*ide* instead of -*ine*) to create the name of this anion. Figure 6.4.2 is a graphical depiction of this process.
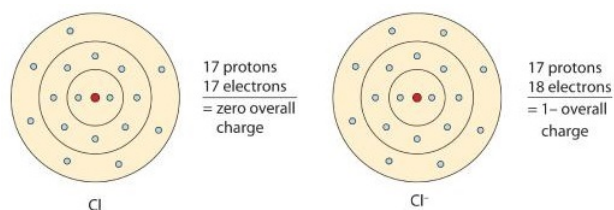
Figure 6.4.2: The Formation of a Chlorine Ion. On the left, the chlorine atom has 17 electrons. On the right, the chloride ion has 18 electrons and has a 1− charge. Neutral chlorine atom on left has 17 protons and 17 electrons. Sodium ion on right has 17 protons and 18 electrons, with a -1 overall charge.

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

In many cases, elements that belong to the same group (vertical column) on the periodic table form ions with the same charge because they have the same number of valence electrons. Thus, the periodic table becomes a tool for remembering the charges on many ions. For example, all ions made from alkali metals, the first column on the periodic table, have a 1+ charge. Ions made from alkaline earth metals, the second group on the periodic table, have a 2+ charge. On the other side of the periodic table, the next-to-last column, the halogens, form ions having a 1− charge. Figure $6.4.3$ shows how the charge on many ions can be predicted by the location of an element on the periodic table. Note the convention of first writing the number and then the sign on a ion with multiple charges. The barium cation is written Ba^{2+}, not Ba^{+2}.

Figure 6.4.3: Predicting Ionic Charges. The charge that an atom acquires when it becomes an ion is related to the structure of the periodic table. Within a group (family) of elements, atoms form ions of a certain charge.

6.5: 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 $6.5.1$. 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.
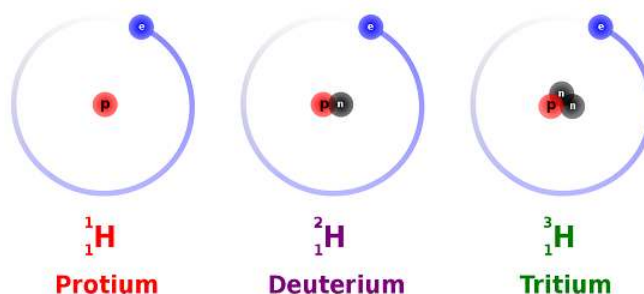
Figure $6.5.1$: The three most stable isotopes of hydrogen: protium (A = 1), deuterium (A = 2), and tritium (A = 3). (CC SA-BY 3.0; Balajijagadesh via Wikipedia).

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 6.5.1: 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.
>
> $$\text{atomic number} = (\text{number of protons}) = 3$$
> $$(\text{number of neutrons}) = 3$$
>
> $$\text{mass number} = (\text{number of protons}) + (\text{number of neutrons})$$
> $$\text{mass number} = 3 + 3$$
> $$= 6$$
>
> b.
>
> $$\text{atomic number} = (\text{number of protons}) = 3$$
> $$(\text{number of neutrons}) = 4$$

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

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:

$$\underset{\text{atomic number}}{\overset{\text{mass number}}{}} \;\; {}^{4}_{2}\text{He} \;\; \leftarrow \text{element symbol}$$

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.

Element symbol or
Element name

Ni-59 or Nickel-59

Mass
number
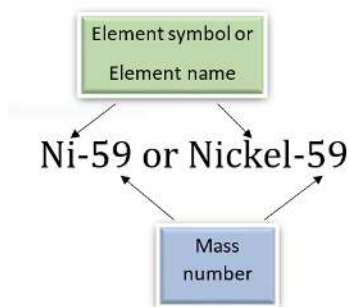
✔ **Example 6.5.2: Potassium-40**

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

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 6.5.3: 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 6.5.3**

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

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

Answer a:

27 protons, 27 electrons, 33 neutrons

Answer b:

11 protons, 11 electrons, 13 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.

6.5: Isotopes - When the Number of Neutrons Varies is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

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6.6: 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 6.6.1: 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 amu. The other 80% of the atoms are B-11, which is an isotope of boron with 6 neutrons and a mass of 11 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 amu.

> **✔ Example 6.6.2: 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 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 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 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** 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 6.6.1, and the atomic mass of neon (symbol Ne) is 20.8, which is what we calculated in Example 6.6.2. 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 6.6.1**
>
> Chlorine has two naturally occurring isotopes. In a sample of chlorine, 75.77% of the atoms are Cl-35, with a mass of 34.97 amu Another 24.23% of the atoms are Cl-37, with a mass of 36.97 amu What is the atomic mass of chlorine?
>
> **Answer**
>
> 35.45 amu

Summary

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

6.7: The Quantum-Mechanical Model- Atoms with Orbitals

> **⊕ Learning Objectives**
>
> - Define quantum mechanics
> - Differentiate between an orbit and an orbital.

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

Quantum Mechanics

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

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

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

Erwin Schrödinger.

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

Summary

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

6.8: Quantum-Mechanical Orbitals and Electron Configurations

> ◀▶ **Learning Objectives**
>
> - Represent the organization of electrons by an electron configuration and orbital diagram.

The flight path of a commercial airliner is carefully regulated by the Federal Aviation Administration. Each airplane must maintain a distance of five miles from another plane flying at the same altitude and 2,000 feet above and below another aircraft (1,000 feet if the altitude is less than 29,000 feet). So, each aircraft only has certain positions it is allowed to maintain while it flies. As we explore quantum mechanics, we see that electrons have similar restrictions on their locations.

Orbitals

We can apply our knowledge of quantum numbers to describe the arrangement of electrons for a given atom. We do this with something called **electron configurations**. They are effectively a map of the electrons for a given atom. We look at the four quantum numbers for a given electron and then assign that electron to a specific orbital below.

s Orbitals

For any value of n, a value of $l = 0$ places that electron in an s **orbital**. This orbital is spherical in shape:
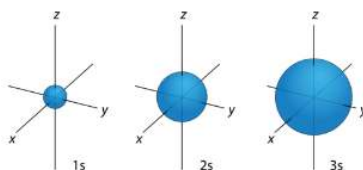
Figure 6.8.1: s orbitals have no orientational preference and resemble spheres.

p Orbitals

For the table below, we see that we can have three possible orbitals when $l = 1$. These are designated as p **orbitals** and have dumbbell shapes. Each of the p orbitals has a different orientation in three-dimensional space.
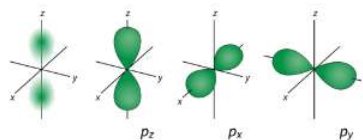
Figure 6.8.2: p orbitals have an orientational preference and resemble dumbbells.

d Orbitals

When $l = 2$, m_l values can be -2, -1, 0, $+1$, $+2$ for a total of five d **orbitals**. Note that all five of the orbitals have specific three-dimensional orientations.
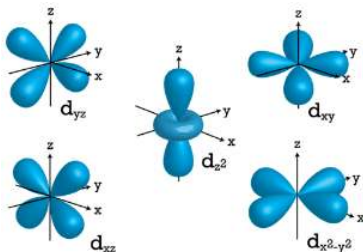
Figure 6.8.3: d orbitals have an orientational preference and exhibit complex structures.

f Orbitals

The most complex set of orbitals are the f **orbitals**. When $l = 3$, m_l values can be -3, -2, -1, 0, $+1$, $+2$, $+3$ for a total of seven different orbital shapes. Again, note the specific orientations of the different f orbitals.
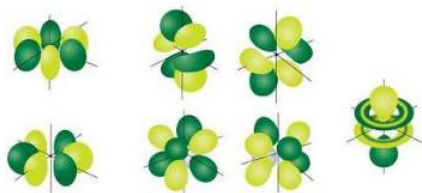
Figure 6.8.4: f orbitals have an orientational preference and exhibit quite complex structures.

Orbitals that have the same value of the principal quantum number form a **shell**. Orbitals within a shell are divided into **subshells** that have the same value of the angular quantum number. Some of the allowed combinations of quantum numbers are compared in Table 6.8.1.

Table 6.8.1: Electron Arrangement Within Energy Levels

Principal Quantum Number (n)	Allowable Sublevels	Number of Orbitals per Sublevel	Number of Orbitals per Principal Energy Level	Number of Electrons per Sublevel	Number of Electrons per Principal Energy Level
1	s	1	1	2	2
2	s	1	4	2	8
	p	3		6	
3	s	1	9	2	18
	p	3		6	
	d	5		10	
4	s	1	16	2	32
	p	3		6	
	d	5		10	
	f	7		14	

Electron Configurations

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

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

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

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

$$\text{He}: 1s^2$$
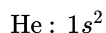
The three electrons for Li are arranged in the 1s subshell (two electrons) and the 2s subshell (one electron). The electron configuration of Li is

$$\text{Li}: 1s^2 2s^1$$
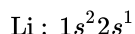
Be has four electrons, two in the 1s subshell and two in the 2s subshell. Its electron configuration is
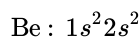
$$\text{Be}: 1s^2 2s^2$$

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.

Second Period Elements

Periods refer to the horizontal rows of the periodic table. Looking at a periodic table you will see that the first period contains only the elements hydrogen and helium. This is because the first principal energy level consists of only the s sublevel and so only two electrons are required in order to fill the entire principal energy level. Each time a new principal energy level begins, as with the third element lithium, a new period is started on the periodic table. As one moves across the second period, electrons are successively added. With beryllium $(Z = 4)$, the $2s$ sublevel is complete and the $2p$ sublevel begins with boron $(Z = 5)$. Since there are three $2p$ orbitals and each orbital holds two electrons, the $2p$ sublevel is filled after six elements. Table 6.8.1 shows the electron configurations of the elements in the second period.

Table 6.8.2: Electron Configurations of Second-Period Elements

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

Aufbau Principle

Construction of a building begins at the bottom. The foundation is laid and the building goes up step by step. You obviously cannot start with the roof since there is no place to hang it. The building goes from the lowest level to the highest level in a systematic way. In order to create ground state electron configurations for any element, it is necessary to know the way in which the atomic sublevels are organized in order of increasing energy. Figure 6.8.5 shows the order of increasing energy of the sublevels.

The lowest energy sublevel is always the $1s$ sublevel, which consists of one orbital. The single electron of the hydrogen atom will occupy the $1s$ orbital when the atom is in its ground state. As we proceed with atoms with multiple electrons, those electrons are added to the next lowest sublevel: $2s$, $2p$, $3s$, and so on. The **Aufbau principle** states that an electron occupies orbitals in order from lowest energy to highest. The Aufbau (German: "building up, construction") principle is sometimes referred to as the "building up" principle. It is worth noting that in reality atoms are not built by adding protons and electrons one at a time, and that this method is merely an aid for us to understand the end result.
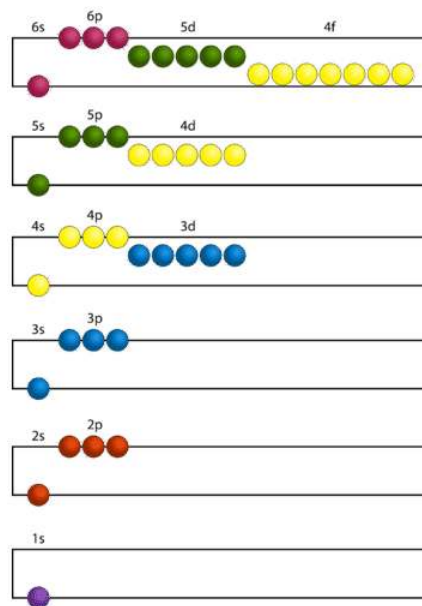
Figure 6.8.5: Electrons are added to atomic orbitals in order from low energy (bottom of the graph) to high (top of the graph) according to the Aufbau principle. Principle energy levels are color coded, while sublevels are grouped together and each circle represents an orbital capable of holding two electrons.

As seen in the figure above, the energies of the sublevels in different principal energy levels eventually begin to overlap. After the $3p$ sublevel, it would seem logical that the $3d$ sublevel should be the next lowest in energy. However, the $4s$ sublevel is slightly lower in energy than the $3d$ sublevel and thus fills first. Following the filling of the $3d$ sublevel is the $4p$, then the $5s$ and the $4d$. Note that the $4f$ sublevel does not fill until just after the $6s$ sublevel. Figure 6.8.6 is a useful and simple aid for keeping track of the order of fill of the atomic sublevels.
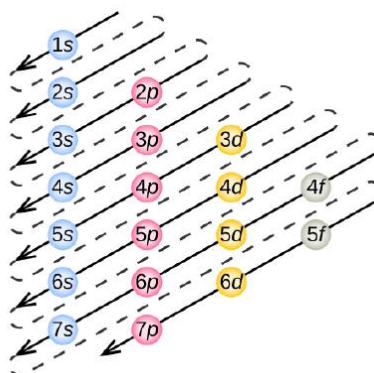
Figure 6.8.6: The arrow leads through each subshell in the appropriate filling order for electron configurations. This chart is straightforward to construct. Simply make a column for all the s orbitals with each n shell on a separate row. Repeat for p, d, and f. Be sure to only include orbitals allowed by the quantum numbers (no 1p or 2d, and so forth). Finally, draw diagonal lines from top to bottom as shown.

Video 6.8.1: Energy levels, sublevels and orbitals.

> ✔ Example 6.8.1: Nitrogen Atoms
>
> Nitrogen has 7 electrons. Write the electron configuration for nitrogen.
>
> **Solution**:
>
> Take a close look at Figure 6.8.5, and use it to figure out how many electrons go into each sublevel, and also the order in which the different sublevels get filled.
>
> 1. Begin by filling up the 1s sublevel. **This gives 1s^2**. Now all of the orbitals in the red n = 1 block are filled.
>
>   Since we used 2 electrons, there are 7 − 2 = **5 electrons left**
>
> 2. Next, fill the 2s sublevel. This gives **1$s^2$2s^2**. Now all of the orbitals in the s sublevel of the orange n = 2 block are filled.
>
>   Since we used another 2 electrons, there are 5 − 2 = **3 electrons left**
>
> 3. Notice that we haven't filled the entire n = 2 block yet… there are still the p orbitals!
>
>   The final 3 electrons go into the 2p sublevel. This gives **1$s^2$2$s^2$2p^3**
>
> The overall electron configuration is: **1$s^2$2$s^2$2p^3**.

> ✔ Example 6.8.2: Potassium Atoms
>
> Potassium has 19 electrons. Write the electron configuration code for potassium.
>
> **Solution**
>
> This time, take a close look at Figure 6.8.5.
>
> 1. Begin by filling up the 1s sublevel. **This gives 1s^2**. Now the n = 1 level is filled.
>
>   Since we used 2 electrons, there are 19 − 2 = **17 electrons left**
>
> 2. Next, fill the 2s sublevel. **This gives 1$s^2$2s^2**
>
>   Since we used another 2 electrons, there are 17 − 2 = **15 electrons left**
>
> 3. Next, fill the 2p sublevel. **This gives 1$s^2$2$s^2$2p^6.** Now the n = 2 level is filled.
>
>   Since we used another 6 electrons, there are 15 − 6 = **9 electrons left**
>
> 4. Next, fill the 3s sublevel. **This gives 1$s^2$2$s^2$2$p^6$3s^2**

Since we used another 2 electrons, there are $9 - 2 =$ **<u>7 electrons left</u>**

5. Next, fill the 3p sublevel. **This gives $1s^2 2s^2 2p^6 3s^2 3p^6$**

Since we used another 6 electrons, there are $7 - 6 =$ **<u>1 electron left</u>**

Here's where we have to be careful – right after 3p^6!

Remember, 4s comes before 3d

6. The final electron goes into the 4s sublevel. **This gives $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$**

The overall electron configuration is: **$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$**

? Exercise 6.8.1: Magnesium and Sodium Atoms

What is the electron configuration for Mg and Na?

Answer Mg

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

Answer Na

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

Pauli Exclusion Principle

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

For the hydrogen atom, there is no problem since there is only one electron in the H atom. However, when we get to helium we see that the first three quantum numbers for the two electrons are the same: same energy level, same spherical shape. What differentiates the two helium electrons is their spin. One of the electrons has a $+\frac{1}{2}$ spin while the other electron has a $-\frac{1}{2}$ spin. So the two electrons in the 1s orbital are each unique and distinct from one another because their spins are different. This observation leads to the **Pauli exclusion principle**, which states that no two electrons in an atom can have the same set of four quantum numbers. The energy of the electron is specified by the principal, angular momentum, and magnetic quantum numbers. If those three numbers are identical for two electrons, the spin numbers must be different in order for the two electrons to be differentiated from one another. The two values of the spin quantum number allow each orbital to hold two electrons. Figure 6.8.7 shows how the electrons are indicated in a diagram.
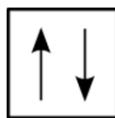
Figure 6.8.7: In an orbital filling diagram, a square represents an orbital, while arrows represent electrons. An arrow pointing upward represents one spin direction, while an arrow pointing downward represents the other spin direction.

Hund's Rule

The last of the three rules for constructing electron arrangements requires electrons to be placed one at a time in a set of orbitals within the same sublevel. This minimizes the natural repulsive forces that one electron has for another. **Hund's rule** states that orbitals of equal energy are each occupied by one electron before any orbital is occupied by a second electron and that each of the single electrons must have the same spin. The figure below shows how a set of three p orbitals is filled with one, two, three, and four electrons.
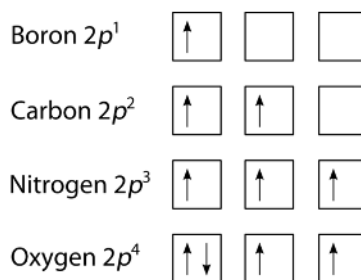
Figure 6.8.8: The $2p$ sublevel, for the elements boron $(Z = 5)$, carbon $(Z = 6)$, nitrogen $(Z = 7)$, and oxygen $(Z = 8)$. According to Hund's rule, as electrons are added to a set of orbitals of equal energy, one electron enters each orbital before any orbital receives a second electron.

Orbital Filling Diagrams

An **orbital filling diagram** is the more visual way to represent the arrangement of all the electrons in a particular atom. In an orbital filling diagram, the individual orbitals are shown as circles (or squares) and orbitals within a sublevel are drawn next to each other horizontally. Each sublevel is labeled by its principal energy level and sublevel. Electrons are indicated by arrows inside of the circles. An arrow pointing upwards indicates one spin direction, while a downward pointing arrow indicates the other direction. The orbital filling diagrams for hydrogen, helium, and lithium are shown in the figure below.
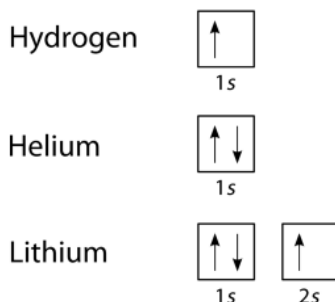
Figure 6.8.9: Orbital filling diagrams for hydrogen, helium, and lithium.

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

The filling diagram for carbon is shown in Figure 6.8.10. There are two $2p$ electrons for carbon and each occupies its own $2p$ orbital.
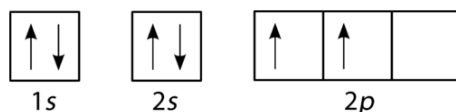
Figure 6.8.10: Orbital filling diagram for carbon.

Oxygen has four $2p$ electrons. After each $2p$ orbital has one electron in it, the fourth electron can be placed in the first $2p$ orbital with a spin opposite that of the other electron in that orbital.
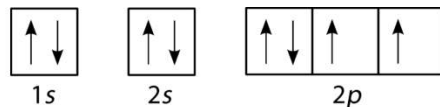
Figure 6.8.11: Orbital filling diagram for oxygen.

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

✔ **Example 6.8.3: Carbon Atoms**

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

Solution

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

Known
- Atomic number of carbon, Z=6

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

Step 2: Construct the diagram.
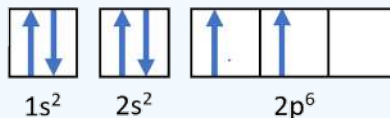
$1s^2 \quad 2s^2 \qquad 2p^6$

Orbital filling diagram for carbon.

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

Step 3: Think about your result.

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

? **Exercise 6.8.2: Electronic Configurations**

Write the electron configurations and orbital diagrams for

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

Answer a:

Potassium: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$

$1s^2 \quad 2s^2 \qquad 2p^6 \qquad 3s^2 \qquad 3p^6 \qquad 4s^1$
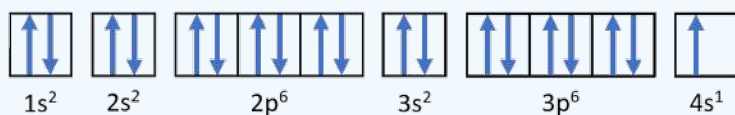
Answer b:

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

$1s^2 \quad 2s^2 \qquad 2p^6 \qquad 3s^2 \qquad 3p^6 \qquad 4s^2 \qquad\qquad 3d^{10} \qquad\qquad 4p^3$
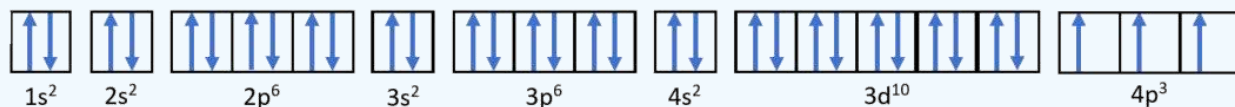
Answer c:

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

$1s^2 \quad 2s^2 \qquad 2p^6 \qquad 3s^2 \qquad 3p^3$
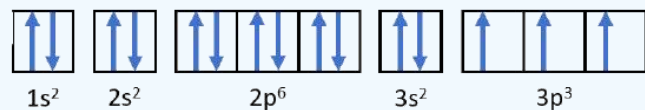
Figure 6.8.12: The atom neighborhood. Source: Dr. Binh Dao, Sacramento City College.

Summary

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

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

Vocabulary

principal quantum number (n)

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

quantum numbers

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

Contributions & Attributions

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

6.9: Electron Configurations and the Periodic Table

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

Previously, we introduced the periodic table as a tool for organizing the known chemical elements. A periodic table is shown in Figure 6.9.1. 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 6.9.1: 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 6.9.2)

Figure 6.9.2: The 1s Subshell. H and He represent the filling of the 1s subshell.
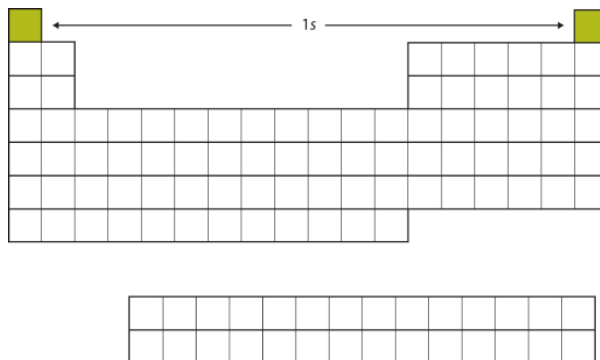
The next two electrons, for Li and Be, would go into the 2s subshell. Figure 6.9.3 shows that these two elements are adjacent on the periodic table.
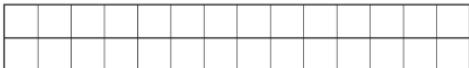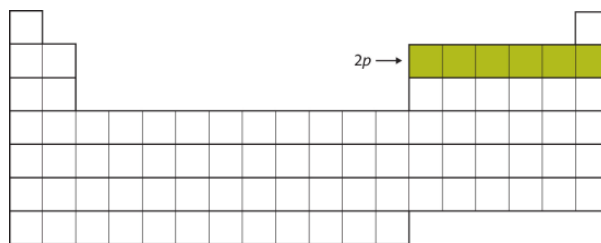
Figure $6.9.3$: The 2s Subshell. In Li and Be, the 2s subshell is being filled.

For the next six elements, the 2p subshell is being occupied with electrons. On the right side of the periodic table, these six elements (B through Ne) are grouped together (Figure $6.9.4$).
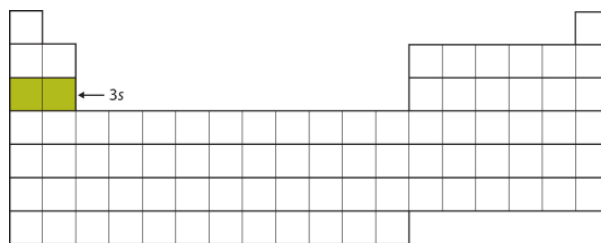
Figure $6.9.4$: The 2p Subshell. For B through Ne, the 2p subshell is being occupied.

The next subshell to be filled is the 3s subshell. The elements when this subshell is being filled, Na and Mg, are back on the left side of the periodic table (Figure $6.9.5$).

Figure $6.9.5$: The 3s Subshell. Now the 3s subshell is being occupied.

Next, the 3p subshell is filled with the next six elements (Figure $6.9.6$).
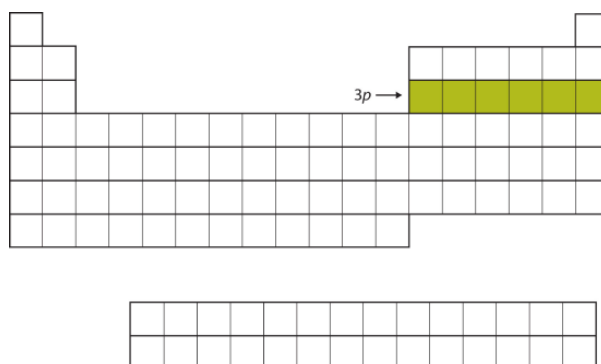
Figure 6.9.6: The 3*p* Subshell. Next, the 3*p* subshell is filled with electrons.

Instead of filling the 3*d* subshell next, electrons go into the 4*s* subshell (Figure 6.9.7).
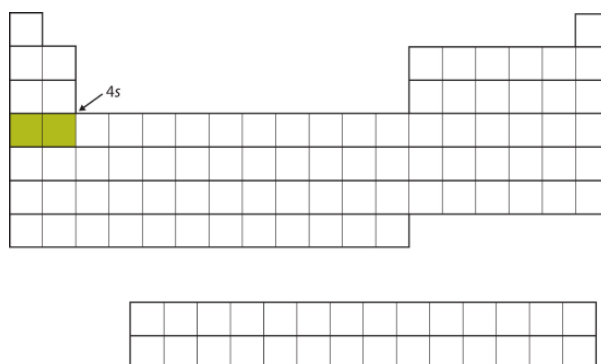
Figure 6.9.7: The 4*s* Subshell. The 4*s* subshell is filled before the 3*d* subshell. This is reflected in the structure of the periodic table.

After the 4*s* subshell is filled, the 3*d* subshell is filled with up to 10 electrons. This explains the section of 10 elements in the middle of the periodic table (Figure 6.9.8).
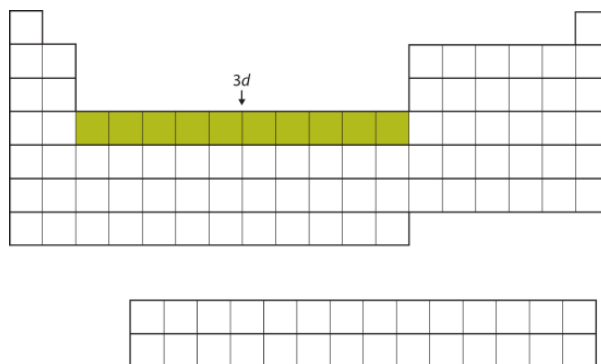
Figure 6.9.8: The 3*d* Subshell. The 3*d* subshell is filled in the middle section of the periodic table.

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

The first two columns on the left side of the periodic table are where the *s* subshells are being occupied. Because of this, the first two rows of the periodic table are labeled the **s block**. Similarly, the **p block** are the right-most six columns of the periodic table, the **d block** is the middle 10 columns of the periodic table, while the **f block** is the 14-column section that is normally depicted as detached from the main body of the periodic table. It could be part of the main body, but then the periodic table would be rather long and cumbersome. Figure 6.9.9 shows the blocks of the periodic table.
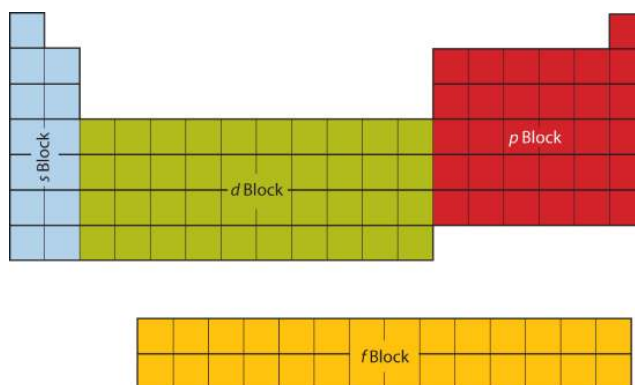
Figure 6.9.9: Blocks on the Periodic Table. The periodic table is separated into blocks depending on which subshell is being filled for the atoms that belong in that section.

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

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

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

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 6.9.10. 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.
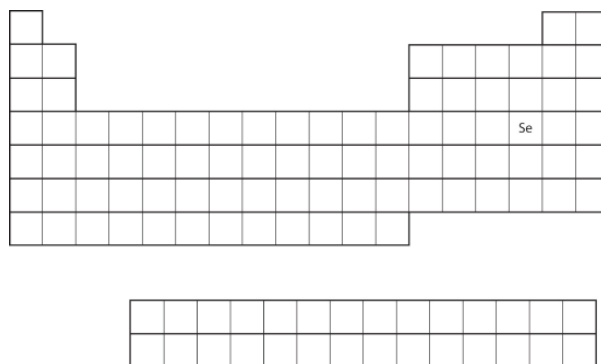
Figure 6.9.10: Selenium on the Periodic Table

✔ Example 6.9.1: Predicting Electron Configurations

From the element's position on the periodic table, predict the valence shell electron configuration for each atom (Figure 6.9.11).
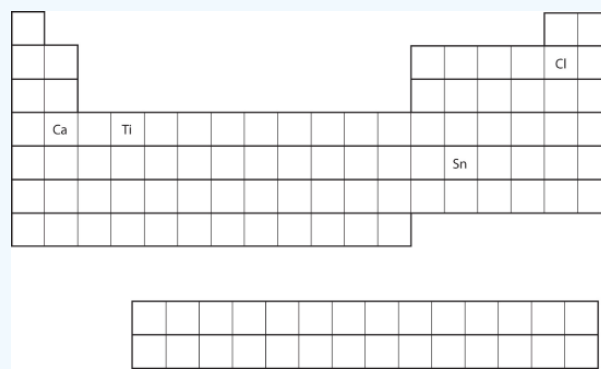
Figure 6.9.11: Various Elements on the Periodic Table

a. Ca
b. Sn

Solution

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

? Exercise 6.9.1

From the element's position on the periodic table, predict the valence shell electron configuration for each atom. Figure 6.9.11.

a. Ti
b. Cl

Answer a

$[Ar]4s^2 3d^2$

Answer b

$[Ne]3s^2 3p^5$
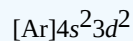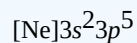
Summary

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

6.10: The Explanatory Power of the Quantum-Mechanical Model

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

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

Families of the Periodic Table

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

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

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

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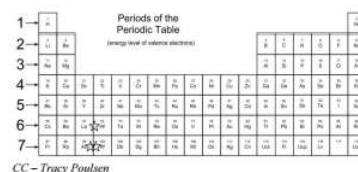
Families of the periodic table.
CC – Tracy Poulsen

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

Periods of the Periodic Table

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

CC – Tracy Poulsen

Summary

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

Vocabulary

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

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

> ◖◗ **Learning Objectives**
>
> - Be able to state how certain properties of atoms vary based on their relative position on the periodic table.

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

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

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

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

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

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

Figure 6.11.1 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.
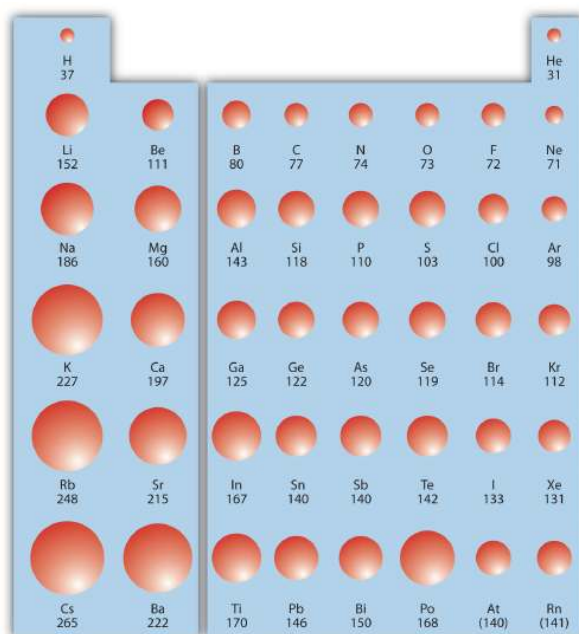
Figure 6.11.1: Atomic Radii Trends on the Periodic Table. Although there are some reversals in the trend (e.g., see Po in the bottom row), atoms generally get smaller as you go across the periodic table and larger as you go down any one column. Numbers are the radii in pm.

✔ Example 6.11.1: Atomic Radii

Referring only to a periodic table and not to Figure 6.11.1, which atom is larger in each pair?

a. Si or S
b. S or Te

Solution
a. Si is to the left of S on the periodic table; it is larger because as you go across the row, the atoms get smaller.
b. S is above Te on the periodic table; Te is larger because as you go down the column, the atoms get larger.
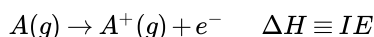
? Exercise 6.11.1: Atomic Radii

Referring only to a periodic table and not to Figure 6.11.1, which atom is smaller, Ca or Br?

Answer

Br

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

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

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 6.11.2 shows values of IE versus position on the periodic table. Again, the trend is not absolute, but the general trends going across and down the periodic table should be obvious.
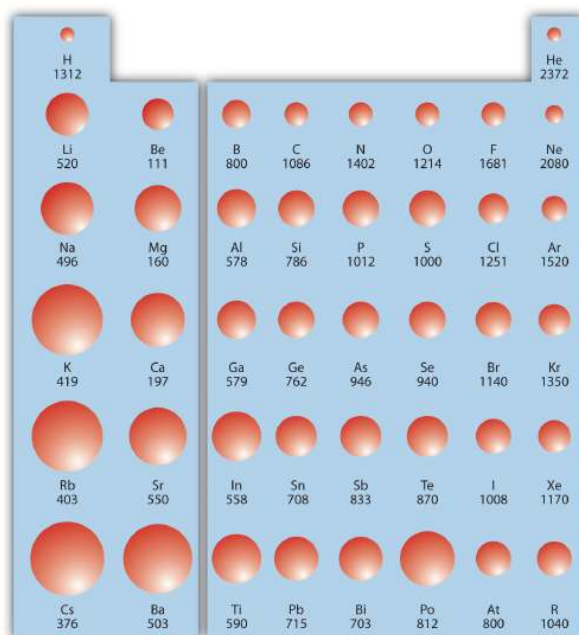
Figure 6.11.2: Ionization Energy on the Periodic Table. Values are in kJ/mol.

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$_2$):

$$A^+(g) \rightarrow A^{2+}(g) + e^-$$
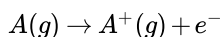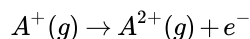
- Third Ionization Energy (IE$_3$):

$$A^{2+}(g) \rightarrow A^{3+}(g) + e^-$$
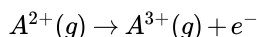
and so forth.

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:

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

- Second Ionization Energy (IE$_2$) = 1,450 kJ/mol:

$$Mg^+(g) \longrightarrow Mg^{2+}(g) + e-$$
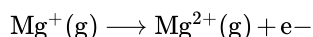
- Third Ionization Energy (IE$_3$) = 7,734 kJ/mol:

$$Mg^{2+}(g) \longrightarrow Mg^{3+}(g) + e-$$
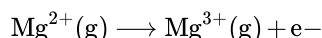
The second IE is twice the first, which is not a surprise: the first IE involves removing an electron from a neutral atom, while the second one involves removing an electron from a positive ion. The third IE, however, is over *five times* the previous one. Why is it so much larger? Because the first 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. It is trends like this that demonstrate that electrons within atoms are organized in groups.

> ✔ Example 6.11.2: 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.
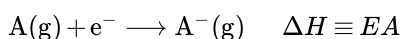
> ❓ Exercise 6.11.2: Ionization Energies
>
> Which atom has the lower ionization energy, C or F?
>
> **Answer**
>
> C

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

$$A(g) + e^- \longrightarrow A^-(g) \quad \Delta H \equiv EA$$

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 6.11.3 shows EA values versus position on the periodic table for the *s*- and *p*-block elements. The trend is not absolute, especially considering the large positive EA values for the second column. However, the general trend going across the periodic table should be obvious.
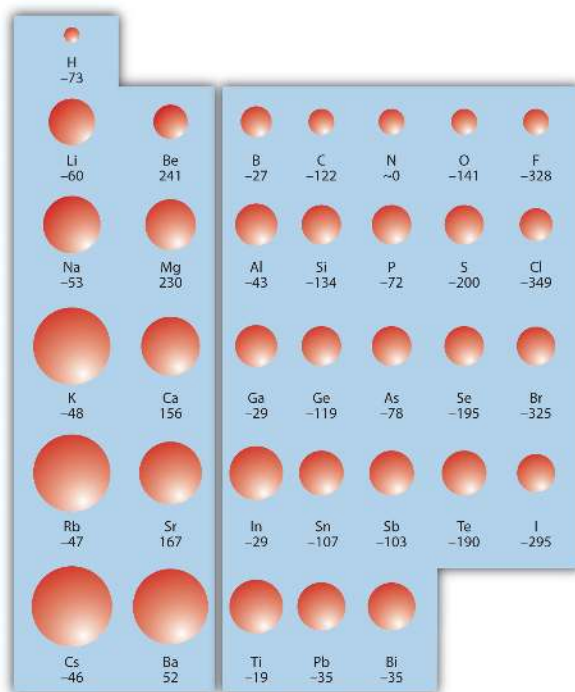
Figure 6.11.3: Electron Affinity on the Periodic Table. Values are in kJ/mol.

✔ **Example 6.11.3: 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 6.11.3: Electron Affinities**

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

Answer

  Br

Metallic Character

The metallic character is used to define the chemical properties that metallic elements present. Generally, metals tend to lose electrons to form cations. Nonmetals tend to gain electrons to form anions. They also have a high oxidation potential—therefore they are easily oxidized and are strong reducing agents. Metals also form basic oxides; the more basic the oxide, the higher the metallic character.
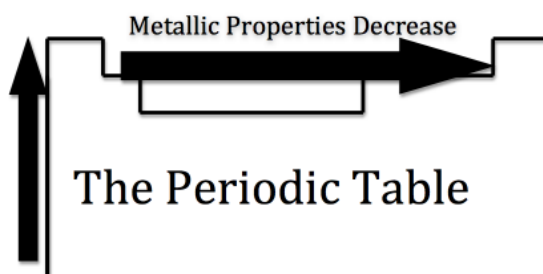
Figure 6.11.4: Courtesy of Jessica Thornton (UCD)

As you move across the table from left to right, the metallic character decreases, because the elements easily accept electrons to fill their valance shells. Therefore, these elements take on the nonmetallic character of forming anions. As you move up the table, the metallic character decreases, due to the greater pull that the nucleus has on the outer electrons. This greater pull makes it harder for the atoms to lose electrons and form cations.

📌 Uses of the Periodic Properties of Elements

1. Predict greater or smaller atomic size and radial distribution in neutral atoms and ions.
2. Measure and compare ionization energies.
3. Compare electron affinities and electronegativities.

- Predict redox potential.
- Compare metallic character with other elements; ability to form cations.
- Predict reactions that may or may not occur due to the trends.
- Determine greater cell potential (sum of oxidation and reduction potential) between reactions.
- Complete chemical reactions according to trends.

Summary

- Certain properties—notably atomic radius, ionization energies, and electron affinities—can be qualitatively understood by the positions of the elements on the periodic table. The major trends are summarized in the figure below.
- There are three factors that help in the prediction of the trends in the Periodic Table: number of protons in the nucleus, number of shells, and shielding effect.
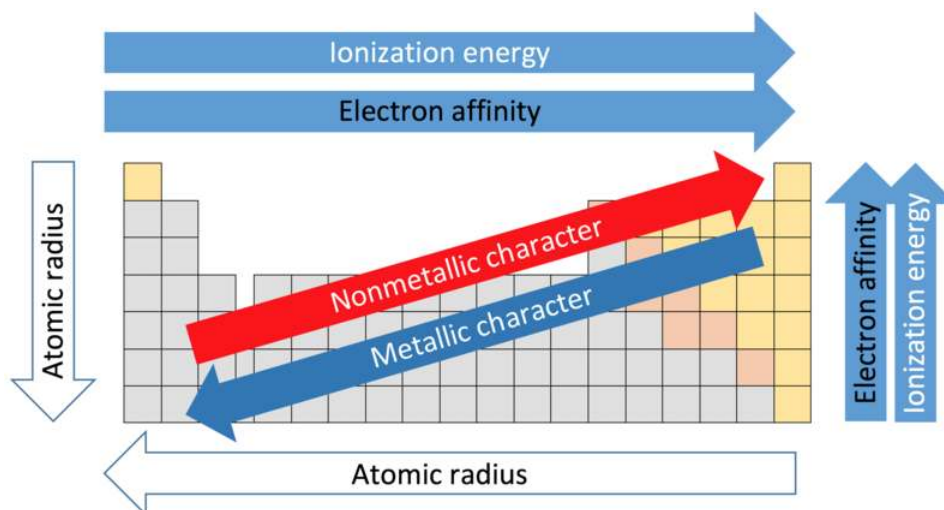
Various periodic trends (CC BY-SA 4.0; Sandbh via Wikipedia)

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CHAPTER OVERVIEW

7: Bonding and Intermolecular Forces

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How do atoms make compounds? Typically they join together in such a way that they lose their identities as elements and adopt a new identity as a compound. These joins are called *chemical bonds*. But how do atoms join together? Ultimately, it all comes down to electrons. Before we discuss how electrons interact, we need to introduce a tool to simply illustrate electrons in an atom.

7.1: Representing Valence Electrons with Dots

> **◐ Learning Objective**
>
> - Draw a Lewis electron dot diagram for an atom or a monatomic ion.

In almost all cases, chemical bonds are formed by interactions of valence electrons in atoms. To facilitate our understanding of how valence electrons interact, a simple way of representing those valence electrons would be useful.

A **Lewis electron dot diagram** (or electron dot diagram, or a Lewis diagram, or a Lewis structure) is a representation of the valence electrons of an atom that uses dots around the symbol of the element. The number of dots equals the number of valence electrons in the atom. These dots are arranged to the right and left and above and below the symbol, with no more than two dots on a side. (The order in which the positions are used does not matter.) For example, the Lewis electron dot diagram for hydrogen is simply

$$\mathbf{H}\cdot$$

Because the side is not important, the Lewis electron dot diagram could also be drawn as follows:

$$\dot{\mathbf{H}} \quad or \ \cdot\mathbf{H} \quad or \quad \underset{\cdot}{\mathbf{H}}$$
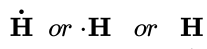
The electron dot diagram for helium, with two valence electrons, is as follows:

$$\mathbf{He}\mathbf{:}$$

By putting the two electrons together on the same side, we emphasize the fact that these two electrons are both in the 1s subshell; this is the common convention we will adopt, although there will be exceptions later. The next atom, lithium, has an electron configuration of $1s^2 2s^1$, 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 2s shell, so its electron dot diagram is like that of helium:

$$\mathbf{Be}\mathbf{:}$$

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:

$$\dot{\mathbf{B}}\mathbf{:}$$

Again, it does not matter on which sides of the symbol the electron dots are positioned.

For carbon, there are four valence electrons, two in the 2s subshell and two in the 2p subshell. As usual, we will draw two dots together on one side, to represent the 2s 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:

$$\cdot\underset{\cdot}{\dot{\mathbf{N}}}\mathbf{:}$$

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 each side has no more than two electrons.

$$\cdot\underset{\cdot}{\ddot{\mathbf{O}}}\mathbf{:}$$

Fluorine and neon have seven and eight dots, respectively:

$$\mathbf{:}\underset{\cdot}{\ddot{\mathbf{F}}}\mathbf{:}$$

$$:\overset{\displaystyle\cdot\cdot}{\underset{\displaystyle\cdot\cdot}{N}}e:$$

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 7.1.1: Lewis Dot Diagrams**

What is the Lewis electron dot diagram for each element?

a. aluminum
b. selenium

Solution

a. The valence electron configuration for aluminum is $3s^2 3p^1$. So it would have three dots around the symbol for aluminum, two of them paired to represent the $3s$ electrons:

$$\overset{\displaystyle\cdot}{Al}:$$

2. The valence electron configuration for selenium is $4s^2 4p^4$. In the highest-numbered shell, the $n = 4$ shell, there are six electrons. Its electron dot diagram is as follows:

$$\cdot\overset{\displaystyle\cdot}{\underset{\displaystyle\cdot\cdot}{S}}e:$$

❓ **Exercise 7.1.1**

What is the Lewis electron dot diagram for each element?

a. phosphorus
b. argon

Answer a

$$\cdot\overset{\displaystyle\cdot}{\underset{\displaystyle\cdot}{P}}:$$

Answer b

$$:\overset{\displaystyle\cdot\cdot}{\underset{\displaystyle\cdot\cdot}{A}}r:$$

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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7.2: Lewis Structures of Ionic Compounds- Electrons Transferred

> **◑ Learning Objectives**
>
> - State the octet rule.
> - Define *ionic bond*.
> - Draw Lewis structures for ionic compounds.

In Section 4.7, we demonstrated that ions are formed by losing electrons to make cations, or by gaining electrons to form anions. The astute reader may have noticed something: many of the ions that form have eight electrons in their valence shell. Either atoms gain enough electrons to have eight electrons in the valence shell and become the appropriately charged anion, or they lose the electrons in their original valence shell; the *lower* shell, now the valence shell, has eight electrons in it, so the atom becomes positively charged. For whatever reason, having eight electrons in a valence shell is a particularly energetically stable arrangement of electrons. The **octet rule** explains the favorable trend of atoms having eight electrons in their valence shell. When atoms form compounds, the octet rule is not always satisfied for all atoms at all times, but it is a very good rule of thumb for understanding the kinds of bonding arrangements that atoms can make.

It is not impossible to violate the octet rule. Consider sodium: in its elemental form, it has one valence electron and is stable. It is rather reactive, however, and does not require a lot of energy to remove that electron to make the Na^+ ion. We *could* remove another electron by adding even more energy to the ion, to make the Na^{2+} ion. However, that requires much more energy than is normally available in chemical reactions, so sodium stops at a 1+ charge after losing a single electron. It turns out that the Na^+ ion has a complete octet in its new valence shell, the $n = 2$ shell, which satisfies the octet rule. The octet rule is a result of trends in energies and is useful in explaining why atoms form the ions that they do.

Now consider an Na atom in the presence of a Cl atom. The two atoms have these Lewis electron dot diagrams and electron configurations:

$$\mathbf{Na}\cdot \qquad \cdot\overset{\displaystyle ..}{\underset{\displaystyle ..}{\mathbf{Cl}}}:$$

$$[Ne]\,3s^1 \qquad [Ne]\,3s^2 3p^5$$
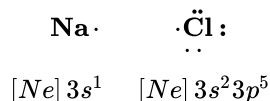
For the Na atom to obtain an octet, it must lose an electron; for the Cl atom to gain an octet, it must gain an electron. An electron transfers from the Na atom to the Cl atom:

$$\mathbf{Na}\cdot \curvearrowright \cdot\overset{\displaystyle ..}{\underset{\displaystyle ..}{\mathbf{Cl}}}:$$
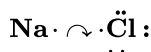
resulting in two ions—the Na^+ ion and the Cl^- ion:

$$\mathbf{Na}^+ \qquad :\overset{\displaystyle ..}{\underset{\displaystyle ..}{\mathbf{Cl}}}:^-$$

$$[Ne] \qquad [Ne]\,3s^2 3p^6$$
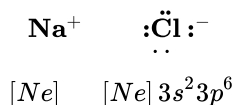
Both species now have complete octets, and the electron shells are energetically stable. From basic physics, we know that opposite charges attract. This is what happens to the Na^+ and Cl^- ions:

$$\mathbf{Na}^+ \;+\; :\overset{\displaystyle ..}{\underset{\displaystyle ..}{\mathbf{Cl}}}:^- \rightarrow Na^+Cl^- \;\; or \;\; NaCl$$
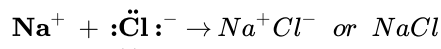
where we have written the final formula (the formula for sodium chloride) as per the convention for ionic compounds, without listing the charges explicitly. The attraction between oppositely charged ions is called an **ionic bond,** and it is one of the main types of chemical bonds in chemistry. Ionic bonds are caused by electrons *transferring* from one atom to another.

In electron transfer, the number of electrons lost must equal the number of electrons gained. We saw this in the formation of NaCl. A similar process occurs between Mg atoms and O atoms, except in this case two electrons are transferred:

The two ions each have octets as their valence shell, and the two oppositely charged particles attract, making an ionic bond:

$$\mathbf{Mg}^{2+} + \left[:\ddot{\mathbf{O}}: \right]^{2-} \quad Mg^{2+}O^{2-} \text{ or } MgO$$
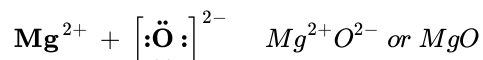
Remember, in the final formula for the ionic compound, we do not write the charges on the ions.

What about when an Na atom interacts with an O atom? The O atom needs two electrons to complete its valence octet, but the Na atom supplies only one electron:

$$\mathbf{Na} \cdot \curvearrowright \cdot \ddot{\mathbf{O}} :$$
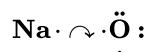
The O atom still does not have an octet of electrons. What we need is a second Na atom to donate a second electron to the O atom:

These three ions attract each other to give an overall neutral-charged ionic compound, which we write as Na$_2$O. The need for the number of electrons lost being equal to the number of electrons gained explains why ionic compounds have the ratio of cations to anions that they do. This is required by the law of conservation of matter as well.

✔ Example 7.2.1: Synthesis of Calcium Chloride from Elements

With arrows, illustrate the transfer of electrons to form calcium chloride from Ca atoms and Cl atoms.

Solution

A Ca atom has two valence electrons, while a Cl atom has seven electrons. A Cl atom needs only one more to complete its octet, while Ca atoms have two electrons to lose. Thus we need two Cl atoms to accept the two electrons from one Ca atom. The transfer process looks as follows:
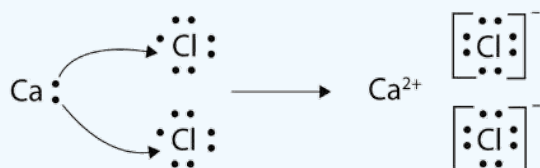
The oppositely charged ions attract each other to make CaCl$_2$.

? Exercise 7.2.1

With arrows, illustrate the transfer of electrons to form potassium sulfide from K atoms and S atoms.

Answer
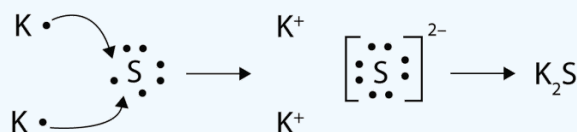
Summary

- The tendency to form species that have eight electrons in the valence shell is called the octet rule.
- The attraction of oppositely charged ions caused by electron transfer is called an ionic bond.
- The strength of ionic bonding depends on the magnitude of the charges and the sizes of the ions.

7.3: Covalent Lewis Structures- Electrons Shared

> **◖◗ Learning Objectives**
>
> - Define *covalent bond*.
> - Illustrate covalent bond formation with Lewis electron dot diagrams.

Ionic bonding typically occurs when it is easy for one atom to lose one or more electrons and another atom to gain one or more electrons. However, some atoms won't give up or gain electrons easily. Yet they still participate in compound formation. How? There is another mechanism for obtaining a complete valence shell: *sharing* electrons. When electrons are shared between two atoms, they make a bond called a **covalent bond**.

Let us illustrate a covalent bond by using H atoms, with the understanding that H atoms need only two electrons to fill the 1*s* subshell. Each H atom starts with a single electron in its valence shell:

$$\mathbf{H} \cdot \qquad \cdot \mathbf{H}$$

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:

2 electrons on this H   2 electrons on this H
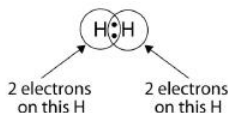
Because each H atom has a filled valence shell, this bond is stable, and we have made a diatomic hydrogen molecule. (This explains why hydrogen is one of the diatomic elements.) For simplicity's sake, it is not unusual to represent the covalent bond with a dash, instead of with two dots:

$$\text{H–H}$$

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:

8 electrons on this F   8 electrons on this F
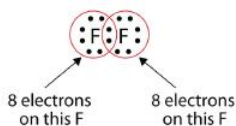
We can also write this using a dash to represent the shared electron pair:

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:

$$H\cdot \qquad \cdot\ddot{F}\!:$$

The two atoms can share their unpaired electrons to make a covalent bond:

$$H\!:\!\ddot{F}\!: \quad \text{or} \quad H\!-\!\ddot{F}\!:$$
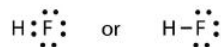
We note that the H atom has a full valence shell with two electrons, while the F atom has a complete octet of electrons.
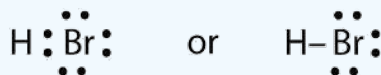
✔ **Example 7.3.1:**

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:

$$H\cdot \qquad \cdot\ddot{Br}\!:$$

The two atoms can share their unpaired electron:

$$H\!:\!\ddot{Br}\!: \quad \text{or} \quad H\!-\!\ddot{Br}\!:$$

? **Exercise 7.3.1**

Use Lewis electron dot diagrams to illustrate the covalent bond formation in Cl_2.

Answer

$$:\!\ddot{Cl}\!-\!\ddot{Cl}\!:$$
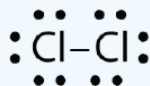
When working with covalent structures, it sometimes looks like you have leftover electrons. You apply the rules you learned so far, and there are still some electrons that remain unattached. You can't just leave them there. So where do you put them?

Multiple Covalent Bonds

Some molecules are not able to satisfy the octet rule by making only single covalent bonds between the atoms. Consider the compound ethene, which has a molecular formula of C_2H_4. The carbon atoms are bonded together, with each carbon also bonded to two hydrogen atoms.

$$\text{two C atoms} = 2 \times 4 = 8 \text{ valence electrons}$$
$$\text{four H atoms} = 4 \times 1 = 4 \text{ valence electrons}$$
$$\text{total of 12 valence electrons in the molecule}$$

If the Lewis electron dot structure was drawn with a single bond between the carbon atoms and with the octet rule followed, it would look like this:
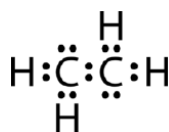
H:C:C:H structure

Figure 7.3.1: Incorrect dot structure of ethene. (CK12 License)

This Lewis structure is incorrect because it contains a total of 14 electrons. However, the Lewis structure can be changed by eliminating the lone pairs on the carbon atoms and having to share two pairs instead of only one pair.
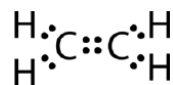
Figure 7.3.2: Correct dot structure for ethene. (CK12 License)

A **double covalent bond** is a covalent bond formed by atoms that share two pairs of electrons. The double covalent bond that occurs between the two carbon atoms in ethane can also be represented by a structural formula and with a molecular model as shown in the figure below.
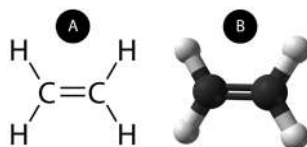
Figure 7.3.3: (A) The structural model for C_2H_4 consists of a double covalent bond between the two carbon atoms and single bonds to the hydrogen atoms. (B) Molecular model of C_2H_4.

A **triple covalent bond** is a covalent bond formed by atoms that share three pairs of electrons. The element nitrogen is a gas that composes the majority of Earth's atmosphere. A nitrogen atom has five valence electrons, which can be shown as one pair and three single electrons. When combining with another nitrogen atom to form a diatomic molecule, the three single electrons on each atom combine to form three shared pairs of electrons.
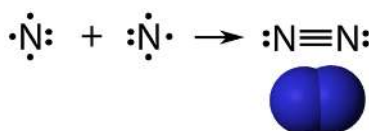
Figure 7.3.4: Triple bond in N_2.

Each nitrogen atom follows the octet rule with one lone pair of electrons, and six electrons that are shared between the atoms.

Summary

- Covalent bonds are formed when atoms share electrons.
- Lewis electron dot diagrams can be drawn to illustrate covalent bond formation.
- Double bonds or triple bonds between atoms may be necessary to properly illustrate the bonding in some molecules.

Contributions & Attributions

-
- Anonymous by request

7.4: Writing Lewis Structures for Covalent Compounds

💡 Learning Objectives

- Draw Lewis structures for covalent compounds.

The following procedure can be used to construct Lewis electron structures for more complex molecules and ions.

📌 How-to: Constructing Lewis electron structures

1. Determine the total number of valence electrons in the molecule or ion.

- Add together the valence electrons from each atom. (Recall that the number of valence electrons is indicated by the position of the element in the periodic table.)
- If the species is a polyatomic ion, remember to add or subtract the number of electrons necessary to give the total charge on the ion.

  For CO_3^{2-}, for example, we add two electrons to the total because of the -2 charge.

2. Arrange the atoms to show specific connections.

- When there is a central atom, it is usually the least electronegative element in the compound. Chemists usually list this central atom first in the chemical formula (as in CCl_4 and CO_3^{2-}, which both have C as the central atom), which is another clue to the compound's structure.
- Hydrogen and the halogens are almost always connected to only one other atom, so they are usually *terminal* rather than central.

3. Place a bonding pair of electrons between each pair of adjacent atoms to give a single bond.

- In H_2O, for example, there is a bonding pair of electrons between oxygen and each hydrogen.

4. Beginning with the terminal atoms, add enough electrons to each atom to give each atom an octet (two for hydrogen).

- These electrons will usually be lone pairs.

5. If any electrons are left over, place them on the central atom.

- We will explain later that some atoms are able to accommodate more than eight electrons.

6. If the central atom has fewer electrons than an octet, use lone pairs from terminal atoms to form multiple (double or triple) bonds to the central atom to achieve an octet.

- This will not change the number of electrons on the terminal atoms.

7. Final check

- Always make sure all valence electrons are accounted for and that each atom has an octet of electrons, except for hydrogen (with two electrons).
- The central atom is usually the least electronegative element in the molecule or ion; hydrogen and the halogens are usually terminal.

Now let's apply this procedure to some particular compounds, beginning with one we have already discussed.

✔ Example 7.4.1: Water

Write the Lewis Structure for H_2O.

Solution

Solutions to Example 10.4.1

Steps for Writing Lewis Structures	Example 7.4.1
1. Determine the total number of valence electrons in the molecule or ion.	Each H atom (group 1) has 1 valence electron, and the O atom (group 16) has 6 valence electrons, for a total of 8 valence electrons.

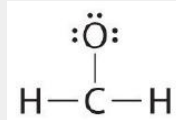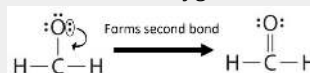| Steps for Writing Lewis Structures	Example 7.4.1
2. Arrange the atoms to show specific connections.	H O H Because H atoms are almost always terminal, the arrangement within the molecule must be <u>HOH.</u>
3. Place a bonding pair of electrons between each pair of adjacent atoms to give a single bond. 4. Beginning with the terminal atoms, add enough electrons to each atom to give each atom an octet (two for hydrogen).	Placing one bonding pair of electrons between the O atom and each H atom gives H -O- H with 4 electrons left over. Each H atom has a full valence shell of 2 electrons.
5. If any electrons are left over, place them on the central atom.	Adding the remaining 4 electrons to the oxygen (as two lone pairs) gives the following structure: H:Ö:H
6. If the central atom has fewer electrons than an octet, use lone pairs from terminal atoms to form multiple (double or triple) bonds to the central atom to achieve an octet.	Not necessary.
7. Final check.	The Lewis structure gives oxygen an octet and each hydrogen 2 electrons.

✔ Example 7.4.2

Write the Lewis structure for the CH_2O molecule

Solution

Solutions to Example 10.4.2

Steps for Writing Lewis Structures	Example 7.4.2
1. Determine the total number of valence electrons in the molecule or ion.	Each hydrogen atom (group 1) has 1 valence electron, carbon (group 14) has 4 valence electrons, and oxygen (group 16) has 6 valence electrons, for a total of [(2)(1) + 4 + 6] = <u>12 valence electrons.</u>
2. Arrange the atoms to show specific connections.	O H C H Because carbon is less electronegative than oxygen and hydrogen is normally terminal, C must be the central atom.
3. Place a bonding pair of electrons between each pair of adjacent atoms to give a single bond.	Placing a bonding pair of electrons between each pair of bonded atoms gives the following: O | H—C—H 6 electrons are used, and 6 are left over.
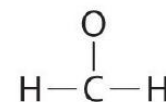
Steps for Writing Lewis Structures	Example 7.4.2
	Adding all 6 remaining electrons to oxygen (as three lone pairs) gives the following:
4. Beginning with the terminal atoms, add enough electrons to each atom to give each atom an octet (two for hydrogen).	$:\ddot{O}:$ $\vert$ $H—C—H$ Although oxygen now has an octet and each hydrogen has 2 electrons, carbon has only 6 electrons.
5. If any electrons are left over, place them on the central atom.	Not necessary. There are no electrons left to place on the central atom.
6. If the central atom has fewer electrons than an octet, use lone pairs from terminal atoms to form multiple (double or triple) bonds to the central atom to achieve an octet.	To give carbon an octet of electrons, we use one of the lone pairs of electrons on oxygen to form a carbon–oxygen double bond: $:\ddot{O}:$ Forms second bond $:O:$ $\vert$ $\vert\vert$ $H—C—H$ $\longrightarrow$ $H—C—H$
7. Final check	Both the oxygen and the carbon now have an octet of electrons, so this is an acceptable Lewis electron structure. The O has two bonding pairs and two lone pairs, and C has four bonding pairs. This is the structure of formaldehyde, which is used in embalming fluid.

? Exercise 7.4.1

Write Lewis electron structures for CO_2 and SCl_2, a vile-smelling, unstable red liquid that is used in the manufacture of rubber.

Answer CO_2

$\ddot{O}=C=\ddot{O}$

Carbon dioxide

Answer SCl_2

$:\ddot{Cl}—\ddot{S}—\ddot{Cl}:$

Sulfur dichloride
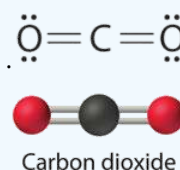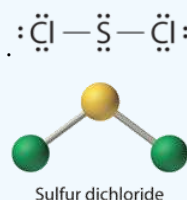
The United States Supreme Court has the unenviable task of deciding what the law is. This responsibility can be a major challenge when there is no clear principle involved or where there is a new situation not encountered before. Chemistry faces the same challenge in extending basic concepts to fit a new situation. Drawing of Lewis structures for polyatomic ions uses the same approach, but tweaks the process a little to fit a somewhat different set of circumstances.

Writing Lewis Structures for Polyatomic Ions (CK-12)

Recall that a polyatomic ion is a group of atoms that are covalently bonded together and which carry an overall electrical charge. The ammonium ion, NH_4^+, is formed when a hydrogen ion (H^+) attaches to the lone pair of an ammonia (NH_3) molecule in a coordinate covalent bond.

$$H^+ \ + \ :\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{N}}\!:\!H \ \rightarrow \ \left[H\!:\!\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{N}}\!:\!H \right]^+$$
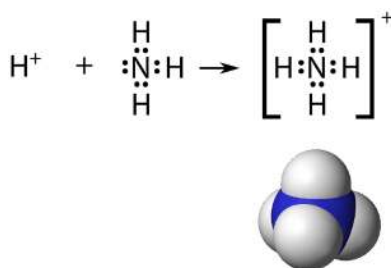
Figure 7.4.3: The ammonium ion. (CK12 License)

When drawing the Lewis structure of a polyatomic ion, the charge of the ion is reflected in the number of total valence electrons in the structure. In the case of the ammonium ion:

$$1 \text{ N atom} = 5 \text{ valence electrons}$$

$$4 \text{ H atoms} = 4 \times 1 = 4 \text{ valence electrons}$$

$$\text{subtract 1 electron for the } 1+ \text{ charge of the ion}$$

$$\text{total of 8 valence electrons in the ion}$$

It is customary to put the Lewis structure of a polyatomic ion into a large set of brackets, with the charge of the ion as a superscript outside of the brackets.

> ✔ Exercise 7.4.2
>
> Draw the Lewis electron dot structure for the sulfate ion.
>
> **Answer (CK12 License)**
>
> $$\left[\begin{array}{c} :\ddot{O}: \\ :\ddot{O}\!:\!\ddot{S}\!:\!\ddot{O}: \\ :\ddot{O}: \end{array} \right]^{2-}$$
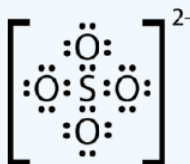
Exceptions to the Octet Rule (BC Campus)

As important and useful as the octet rule is in chemical bonding, there are some well-known violations. This does not mean that the octet rule is useless—quite the contrary. As with many rules, there are exceptions, or violations.

There are three violations to the octet rule. Odd-electron molecules represent the first violation to the octet rule. Although they are few, some stable compounds have an odd number of electrons in their valence shells. With an odd number of electrons, at least one atom in the molecule will have to violate the octet rule. Examples of stable odd-electron molecules are NO, NO_2, and ClO_2. The Lewis electron dot diagram for NO is as follows:

$$.\ddot{N}\!::\!\ddot{O}.$$

Although the O atom has an octet of electrons, the N atom has only seven electrons in its valence shell. Although NO is a stable compound, it is very chemically reactive, as are most other odd-electron compounds.

Electron-deficient molecules represent the second violation to the octet rule. These stable compounds have less than eight electrons around an atom in the molecule. The most common examples are the covalent compounds of beryllium and boron. For example, beryllium can form two covalent bonds, resulting in only four electrons in its valence shell:

$$:\ddot{Cl}\!-\!Be\!-\!\ddot{Cl}:$$
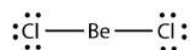
Boron commonly makes only three covalent bonds, resulting in only six valence electrons around the B atom. A well-known example is BF_3:
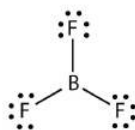
The third violation to the octet rule is found in those compounds with more than eight electrons assigned to their valence shell. These are called expanded valence shell molecules. Such compounds are formed only by central atoms in the third row of the periodic table or beyond that have empty d orbitals in their valence shells that can participate in covalent bonding. One such compound is PF_5. The only reasonable Lewis electron dot diagram for this compound has the P atom making five covalent bonds:
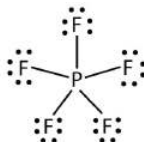
Formally, the P atom has 10 electrons in its valence shell.

> ✔ Example 7.4.3: Octet Violations
>
> Identify each violation to the octet rule by drawing a Lewis electron dot diagram.
>
>   a. ClO
>   b. SF_6
>
> **Solution**
>
> a. With one Cl atom and one O atom, this molecule has $6 + 7 = 13$ valence electrons, so it is an odd-electron molecule. A Lewis electron dot diagram for this molecule is as follows:
>
> b. In SF_6, the central S atom makes six covalent bonds to the six surrounding F atoms, so it is an expanded valence shell molecule. Its Lewis electron dot diagram is as follows:
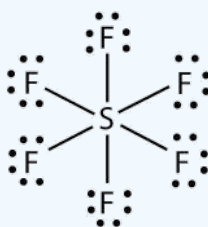
> ? Exercise 7.4.3: Xenon Difluoride
>
> Identify the violation to the octet rule in XeF_2 by drawing a Lewis electron dot diagram.
>
> **Answer**
>
> The Xe atom has an expanded valence shell with more than eight electrons around it.

Summary

Lewis dot symbols provide a simple rationalization of why elements form compounds with the observed stoichiometries. A plot of the overall energy of a covalent bond as a function of internuclear distance is identical to a plot of an ionic pair because both result from attractive and repulsive forces between charged entities. In Lewis electron structures, we encounter **bonding pairs**, which are shared by two atoms, and **lone pairs**, which are not shared between atoms. Lewis structures for polyatomic ions follow the same rules as those for other covalent compounds. There are three violations to the octet rule: odd-electron molecules, electron-deficient molecules, and expanded valence shell molecules.

7.5: Resonance - Equivalent Lewis Structures for the Same Molecule

> **◀▶ Learning Objectives**
>
> - Explain the concept of resonance and how it works with within molecules.

Resonance

There are some cases in which more than one viable Lewis structure can be drawn for a molecule. An example is the ozone (O_3) molecule in Figure $7.5.1$. There are a total of 18 electrons in the structure and so the following two structures are possible.

Figure $7.5.1$: Resonance forms of ozone. Note the use of the double-headed arrow.

The structure on the left $(7.5.1)$ can be converted to the structure on the right by a shifting of electrons without altering the positions of the atoms.

It was once thought that the structure of a molecule such as O_3 consisted of one single bond and one double bond which then shifted back and forth as shown above. However, further studies showed that the two bonds are identical. Any double covalent bond between two given atoms is typically shorter than a single covalent bond. Studies of the O_3 and other similar molecules showed that the bonds were identical in length. Interestingly, the length of the bond is in between the lengths expected for an $O-O$ single bond and a double bond.

Resonance is the use of two or more Lewis structures to represent the covalent bonding in a molecule. One of the valid structures is referred to as a resonance structure. It is now understood that the true structure of a molecule which displays resonance is that of an average or a hybrid of all the resonance structures. In the case of the O_3 molecule, each of the covalent bonds between O atoms are best thought of as being "one and a half" bonds, as opposed to either a pure single bond or a pure double bond. This "half-bond" can be shown as a dotted line in both the Lewis structure and the molecular model (Figure $7.5.2$).

Figure $7.5.2$: "Half-bond" model of ozone molecule. This is a better description of the electronic structure of ozone than either of the resonance structures in Figure $7.5.1$.

Many polyatomic ions also display resonance. In some cases, the true structure may be an average of three valid resonance structures, as in the case of the nitrate ion, NO_3^- in Figure $7.5.3$.
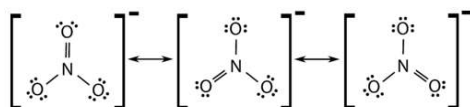

Figure $7.5.3$: Resonance structure of nitrate anion.

The bond lengths between the central N atom and each O atom are identical and the bonds can be approximated as being equal to one and one-third bonds.

Summary

- Resonance structures are averages of different Lewis structure possibilities.
- Bond lengths are intermediate between covalent bonds and covalent double bonds.

7.6: Predicting the Shapes of Molecules

> **◖◗ Learning Objective**
>
> - Determine the shape of simple molecules.

Molecules have shapes. There is an abundance of experimental evidence to that effect—from their physical properties to their chemical reactivity. Small molecules—molecules with a single central atom—have shapes that can be easily predicted. The basic idea in molecular shapes is called **valence shell electron pair repulsion (VSEPR).** VSEPR says that electron pairs, being composed of negatively charged particles, repel each other to get as far away from one another as possible. VSEPR makes a distinction between *electron group geometry*, which expresses how electron groups (bonds and nonbonding electron pairs) are arranged, and *molecular geometry*, which expresses how the atoms in a molecule are arranged. However, the two geometries are related.

There are two types of **electron groups**: any type of bond—single, double, or triple—and lone electron pairs. When applying VSEPR to simple molecules, the first thing to do is to count the number of electron groups around the central atom. Remember that a multiple bond counts as only *one* electron group.

Any molecule with only two atoms is linear. A molecule whose central atom contains only two electron groups orients those two groups as far apart from each other as possible—180° apart. When the two electron groups are 180° apart, the atoms attached to those electron groups are also 180° apart, so the overall molecular shape is linear. Examples include BeH_2 and CO_2:

Figure 7.6.1: Beryllium hydride and carbon dioxide bonding.

The two molecules, shown in the figure below in a "ball and stick" model.

Figure 7.6.2: Beryllium hydride and carbon dioxide models. (CK12 Licence)

A molecule with three electron groups orients the three groups as far apart as possible. They adopt the positions of an equilateral triangle—120° apart and in a plane. The shape of such molecules is *trigonal planar*. An example is BF_3:
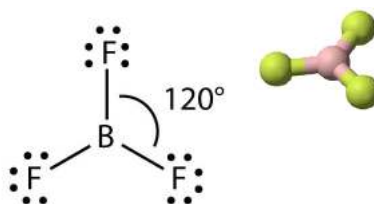

Figure 7.6.3: Boron trifluoride bonding. (CK12 Licence)

Some substances have a trigonal planar electron group distribution but have atoms bonded to only two of the three electron groups. An example is GeF_2:
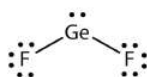

Figure 7.6.4: Germanium difluoride bonding.

From an electron group geometry perspective, GeF_2 has a trigonal planar shape, but its real shape is dictated by the positions of the atoms. This shape is called *bent* or *angular*.

A molecule with four electron groups about the central atom orients the four groups in the direction of a tetrahedron, as shown in Figure 7.6.1 Tetrahedral Geometry. If there are four atoms attached to these electron groups, then the molecular shape is also
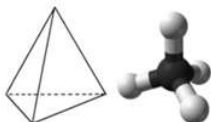
tetrahedral. Methane (CH$_4$) is an example.

Figure 7.6.5: Tetrahedral structure of methane. (CK12 Licence)

This diagram of CH$_4$ illustrates the standard convention of displaying a three-dimensional molecule on a two-dimensional surface. The straight lines are in the plane of the page, the solid wedged line is coming out of the plane toward the reader, and the dashed wedged line is going out of the plane away from the reader.
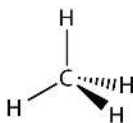

Figure 7.6.6: Methane bonding. (CK12 Licence)

NH$_3$ is an example of a molecule whose central atom has four electron groups, but only three of them are bonded to surrounding atoms.
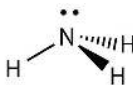
Figure 7.6.7: Ammonia bonding. (CK12 Licence)

Although the electron groups are oriented in the shape of a tetrahedron, from a molecular geometry perspective, the shape of NH$_3$ is *trigonal pyramidal*.

H$_2$O is an example of a molecule whose central atom has four electron groups, but only two of them are bonded to surrounding atoms.

Figure 7.6.8: Water bonding.

Although the electron groups are oriented in the shape of a tetrahedron, the shape of the molecule is *bent* or *angular*. A molecule with four electron groups about the central atom, but only one electron group bonded to another atom, is linear because there are only two atoms in the molecule.

Double or triple bonds count as a single electron group. The Lewis electron dot diagram of formaldehyde (CH$_2$O) is shown in Figure 7.6.9.

Figure 7.6.9: Lewis Electron Dot Diagram of Formaldehyde.

The central C atom has three electron groups around it because the double bond counts as one electron group. The three electron groups repel each other to adopt a trigonal planar shape.
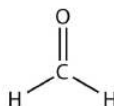

Figure 7.6.10: Formaldehyde bonding.

(The lone electron pairs on the O atom are omitted for clarity.) The molecule will not be a perfect equilateral triangle because the C–O double bond is different from the two C–H bonds, but both planar and triangular describe the appropriate approximate shape of this molecule.

Table 7.6.1 summarizes the shapes of molecules based on the number of electron groups and surrounding atoms.

Table 7.6.1: Summary of Molecular Shapes

| Number of Electron Groups on Central Atom	Number of Bonding Groups	Number of Lone Pairs	Electron Geometry	Molecular Shape
2	2	0	linear	linear
3	3	0	trigonal planar	trigonal planar
3	2	1	trigonal planar	bent
4	4	0	tetrahedral	tetrahedral
4	3	1	tetrahedral	trigonal pyramidal
4	2	2	tetrahedral	bent

✔ **Example 7.6.1**

What is the approximate shape of each molecule?

  a. PCl3
  b. NOF

Solution

The first step is to draw the Lewis structure of the molecule.

For PCl_3, the electron dot diagram is as follows:
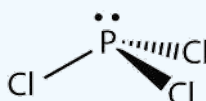
The lone electron pairs on the Cl atoms are omitted for clarity. The P atom has four electron groups with three of them bonded to surrounding atoms, so the molecular shape is trigonal pyramidal.

The electron dot diagram for NOF is as follows:
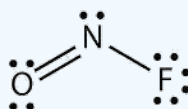
The N atom has three electron groups on it, two of which are bonded to other atoms. The molecular shape is bent.

? **Exercise 7.6.1**

What is the approximate molecular shape of CH_2Cl_2?

Answer

    Tetrahedral

? **Exercise 7.6.2**

Ethylene (C_2H_4) has two central atoms. Determine the geometry around each central atom and the shape of the overall molecule. (Hint: hydrogen is a terminal atom.)

Answer

    Trigonal planar about both central C atoms.

Summary

The approximate shape of a molecule can be predicted from the number of electron groups and the number of surrounding atoms.

7.6: Predicting the Shapes of Molecules is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

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7.7: 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 $7.7.1$.
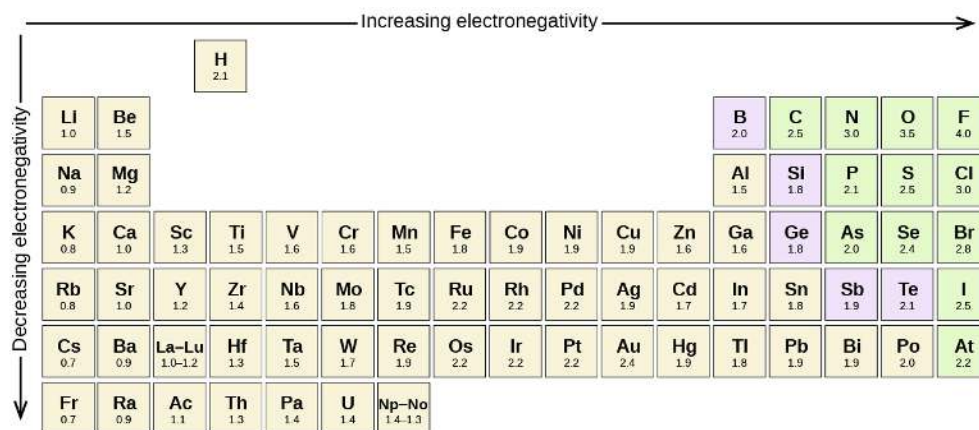

Figure 7.7.1: Electronegativities of the Elements. Electronegativities are used to determine the polarity of covalent bonds.

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.
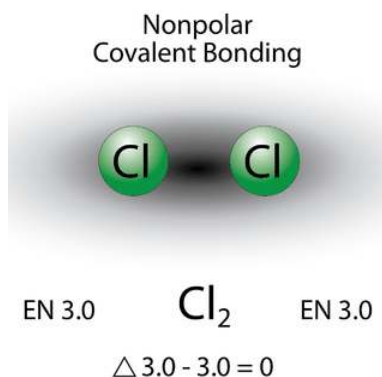
Nonpolar
Covalent Bonding

EN 3.0 Cl_2 EN 3.0

$\triangle 3.0 - 3.0 = 0$

Figure $7.7.2$: 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 Cl_2 molecule is symmetrical. Also note that molecules in which the electronegativity difference is very small (<0.5) are also considered nonpolar covalent. An example would be a bond between chlorine and bromine ($\Delta EN = 3.0 - 2.8 = 0.2$).

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.
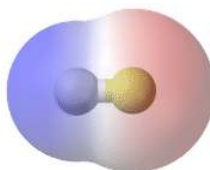
Figure $7.7.3$: In the polar covalent bond of HF, the electron density is unevenly distributed. There is a higher density (red) near the fluorine atom, and a lower density (blue) near the hydrogen atom.

An easy way to illustrate the uneven electron distribution in a polar covalent bond is to use the Greek letter delta (δ).

$$\overset{\delta+}{H}—\overset{\delta-}{\underset{\cdot\cdot}{\overset{\cdot\cdot}{F}}}:$$

Figure $7.7.4$: 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.

$$H—\underset{\cdot\cdot}{\overset{\cdot\cdot}{F}}:$$

Figure $7.7.5$: 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 7.7.1: Bond Polarity**

What is the polarity of each bond?

a. C–H
b. O–H

Solution

Using Figure $7.7.1$, 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 7.7.1**

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 7.7.6: 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.
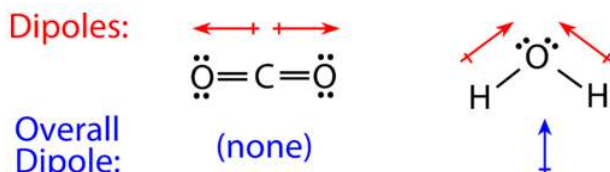
Figure 7.7.7: The molecular geometry of a molecule affects its polarity. Each CO bond has a dipole moment, but they point in opposite directions so that the net CO2 molecule is nonpolar. In contrast, water is polar because the OH bond moments do not cancel out.

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.
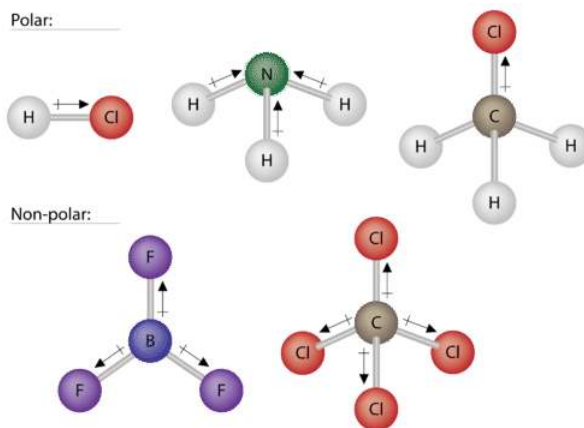

Figure 7.7.8: Some examples of polar and nonpolar molecules based on molecular geometry.

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 7.7.14). 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.
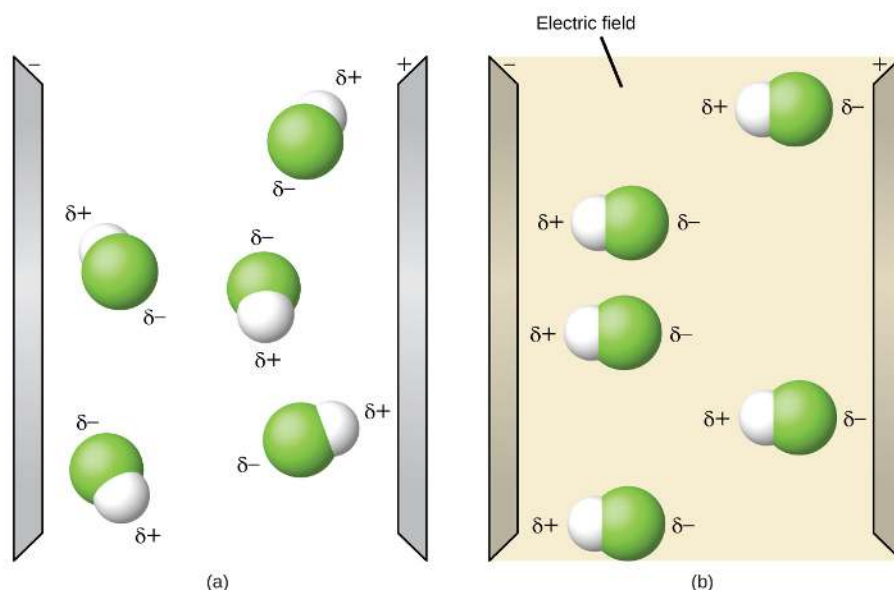
Figure 7.7.9: (a) Molecules are always randomly distributed in the liquid state in the absence of an electric field. (b) When an electric field is applied, polar molecules like HF will align to the dipoles with the field direction. (OpenStax CC-BY-SA);

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 7.7.2:**
>
> Label each of the following as polar or nonpolar.
>
> a. Water, H_2O:
>
> b. Methanol, CH_3OH:
>
> c. Hydrogen Cyanide, HCN:
>
> d. Oxygen, O_2:
>
> e. Propane, C_3H_8:
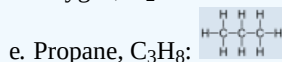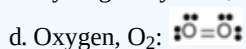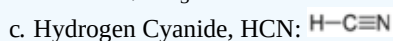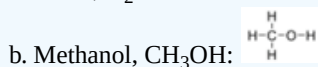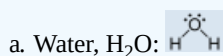
Solution

a. Water is polar. Any molecule with lone pairs of electrons around the central atom is polar.

b. Methanol is polar. This is not a symmetric molecule. The $-$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 7.7.2

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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7.8: 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.
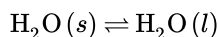
Melting Point

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 $801^{\circ}C$. 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 7.8.1: 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 $0^{\circ}C$.

$$H_2O\,(s) \rightleftharpoons H_2O\,(l)$$

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 7.8.1: Melting Points of Common Materials

Materials	Melting Point (°C)
Hydrogen	-259
Oxygen	-219
Diethyl ether	-116
Ethanol	-114
Water	0
Pure silver	961

Materials	Melting Point (°C)
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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7.9: Evaporation and Condensation

> **◑ Learning Objectives**
>
> - Explain how intermolecular forces affect rates of vaporization, evaporation, and condensation.

On the roof of the house in the picture below is a device known as a "swamp cooler". This piece of equipment traces its origin back to the ancient Egyptians who hung wet blankets across the doors of their homes. As the warm air passed through the blankets, water would evaporate and cool the air. The royalty went one step further and had servants fan wet cloths over jugs of water to get more evaporation and cooling.

Figure 7.9.1: A home with a swamp cooler attached to the roof.

The origin of the term "swamp cooler" is not known - they certainly don't work in a swamp. Best conditions for cooling include a high temperature (over 80^oF) and a low humidity (preferably less than 30%). These coolers work well in desert areas, but don't provide any cooling in the humid areas of the country.

Evaporation

A puddle of water left undisturbed eventually disappears. The liquid molecules escape into the gas phase, becoming water vapor. **Vaporization** is the process in which a liquid is converted to a gas. **Evaporation** is the conversion of a liquid to its vapor below the boiling temperature of the liquid. If the water is instead kept in a closed container, the water vapor molecules do not have a chance to escape into the surroundings and so the water level does not change. As some water molecules become vapor, an equal number of water vapor molecules condense back into the liquid state. **Condensation** is the change of state from a gas to a liquid.
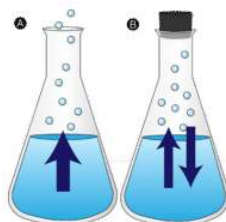

Figure 7.9.2: Evaporation (A) and condensation (B).

In order for a liquid molecule to escape into the gas state, the molecule must have enough kinetic energy to overcome the intermolecular attractive forces in the liquid. Recall that a given liquid sample will have molecules with a wide range of kinetic energies. Liquid molecules that have this certain threshold kinetic energy escape the surface and become vapor. As a result, the liquid molecules that remain now have lower kinetic energy. As evaporation occurs, the temperature of the remaining liquid decreases. You have observed the effects of evaporative cooling. On a hot day, the water molecules in your perspiration absorb body heat and evaporate from the surface of your skin. The evaporating process leaves the remaining perspiration cooler, which in turn absorbs more heat from your body.

A given liquid will evaporate more quickly when it is heated. This is because the heating process results in a greater fraction of the liquid's molecules having the necessary kinetic energy to escape the surface of the liquid. The figure below shows the kinetic energy distribution of liquid molecules at two temperatures. The numbers of molecules that have the required kinetic energy to

evaporate are shown in the shaded area under the curve at the right. The higher temperature liquid (T_2) has more molecules that are capable of escaping into the vapor phase than the lower temperature liquid (T_1).
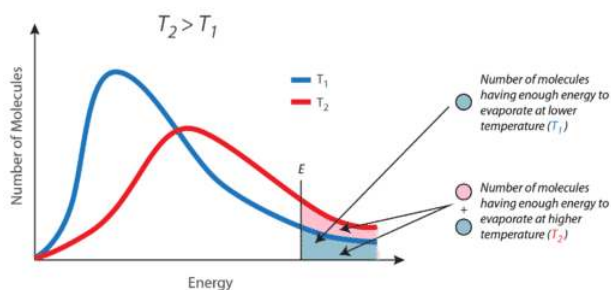

Figure 7.9.3: Kinetic energy distribution curves for a liquid at two temperatures T_1 and T_2. The shaded area represents the molecules with enough kinetic energy to escape the liquid and become vapor.

At 29,029 feet (8848 m), Mount Everest in the Himalayan range on the border between China and Nepal is the highest point on the earth. Its altitude presents many practical problems to climbers. The oxygen content of the air is much lower than at sea level, making it necessary to bring oxygen tanks along (although a few climbers have reached the peak without oxygen). One other problem is that of boiling water for cooking food. Although water boils at 100°C at sea level, the boiling point on top of Mount Everest is only about 70°C. This difference makes it very difficult to get a decent cup of tea (which definitely frustrated some of the British climbers).

Boiling

As a liquid is heated, the average kinetic energy of its particles increases. The rate of evaporation increases as more and more molecules are able to escape the liquid's surface into the vapor phase. Eventually a point is reached when the molecules all throughout the liquid have enough kinetic energy to **vaporize**. At this point the liquid begins to boil. The **boiling point** is the temperature at which the vapor pressure of a liquid is equal to the external pressure. The figure below illustrates the boiling of liquid.
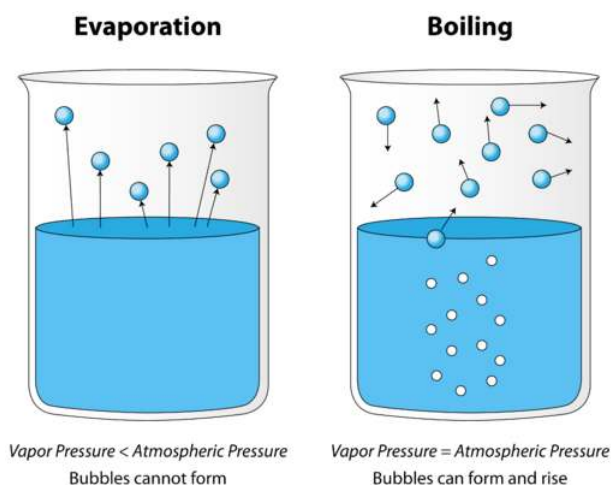

Figure 7.9.4: Comparison between evaporation and boiling.

In the picture on the left, the liquid is below its boiling point, yet some of the liquid evaporates. On the right, the temperature has been increased until bubbles begin to form in the body of the liquid. When the vapor pressure inside the bubble is equal to the external atmospheric pressure, the bubbles rise to the surface of the liquid and burst. The temperature at which this process occurs is the boiling point of the liquid.

The normal boiling point is the temperature at which the vapor pressure of the liquid is equal to standard pressure. Because atmospheric pressure can change based on location, the boiling point of a liquid changes with the external pressure. The normal boiling point is a constant because it is defined relative to the standard atmospheric pressure of $760\,\text{mm}\,\text{Hg}$ (or $1\,\text{atm}$ or $101.3\,\text{kPa}$).
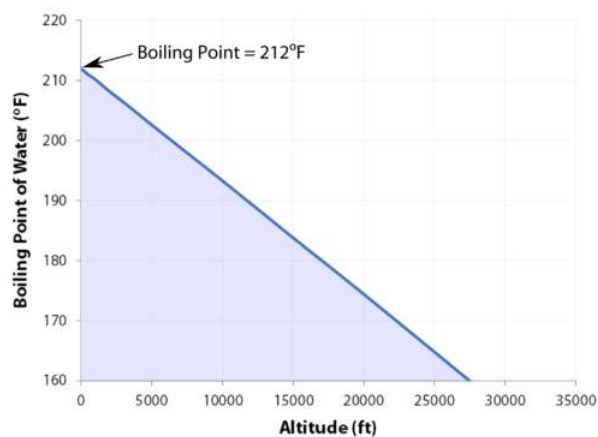
Figure 7.9.5: Influence of altitude on the boiling point of water.

Summary

- The boiling point is the temperature at which the vapor pressure of a liquid is equal to the external pressure.
- As the altitude increases, the boiling point decreases.
- Evaporation is the conversion of a liquid to its vapor below the boiling temperature of the liquid.
- Condensation is the change of state from a gas to a liquid.
- As the temperature increases, the rate of evaporation increases.

7.10: Melting, Freezing, and Sublimation

> **◖ Learning Objectives**
>
> - Define melting, freezing, and sublimation.

Depending on the surrounding conditions, normal matter usually exists as one of three *phases*: solid, liquid, or gas.

A phase change is a physical process in which a substance goes from one phase to another. Usually the change occurs when adding or removing heat at a particular temperature, known as the melting point or the boiling point of the substance. The melting point is the temperature at which the substance goes from a solid to a liquid (or from a liquid to a solid). The boiling point is the temperature at which a substance goes from a liquid to a gas (or from a gas to a liquid). The nature of the phase change depends on the direction of the heat transfer. Heat going *into* a substance changes it from a solid to a liquid, or a liquid to a gas. Removing heat *from* a substance changes a gas to a liquid, or a liquid to a solid.

Two key points are worth emphasizing. First, at a substance's melting point or boiling point, two phases can exist simultaneously. Take water (H_2O) as an example. On the Celsius scale, H_2O has a melting point of 0°C and a boiling point of 100°C. At 0°C, both the solid and liquid phases of H_2O can coexist. However, if heat is added, some of the solid H_2O will melt and turn into liquid H_2O. If heat is removed, the opposite happens: some of the liquid H_2O turns into solid H_2O. A similar process can occur at 100°C: adding heat increases the amount of gaseous H_2O, while removing heat increases the amount of liquid H_2O (Figure 7.10.1).

Figure 7.10.1: The Boiling Point of Water. Nucleate boiling of water over a kitchen stove burner. (Source: Wikipedia). Water is a good substance to use as an example because many people are already familiar with it. Other substances have melting points and boiling points as well.

Second, the temperature of a substance does not change as the substance goes from one phase to another. In other words, phase changes are isothermal (isothermal means "constant temperature"). Again, consider H_2O as an example. Solid water (ice) can exist at 0°C. If heat is added to ice at 0°C, some of the solid changes phase to make liquid, which is also at 0°C. Remember, the solid and liquid phases of H_2O can coexist at 0°C. Only after all of the solid has melted into liquid does the addition of heat change the temperature of the substance.

For each phase change of a substance, there is a characteristic quantity of heat needed to perform the phase change per gram (or per mole) of material. The heat of fusion (ΔH_{fus}) is the amount of heat per gram (or per mole) required for a phase change that occurs at the melting point. The heat of vaporization (ΔH_{vap}) is the amount of heat per gram (or per mole) required for a phase change that occurs at the boiling point. If you know the total number of grams or moles of material, you can use the ΔH_{fus} or the ΔH_{vap} to determine the total heat being transferred for melting or solidification using these expressions:

$$\text{heat} = n \times \Delta H_{fus} \tag{7.10.1}$$

where n is the number of moles and ΔH_{fus} is expressed in energy/mole or

$$\text{heat} = m \times \Delta H_{fus} \tag{7.10.2}$$

where m is the mass in grams and ΔH_{fus} is expressed in energy/gram.

For the boiling or condensation, use these expressions:

$$\text{heat} = n \times \Delta H_{vap} \tag{7.10.3}$$

where n is the number of moles) and ΔH_{vap} is expressed in energy/mole or

$$\text{heat} = m \times \Delta H_{vap} \qquad (7.10.4)$$

where m is the mass in grams and ΔH_{vap} is expressed in energy/gram.

Remember that a phase change depends on the direction of the heat transfer. If heat transfers in, solids become liquids, and liquids become solids at the melting and boiling points, respectively. If heat transfers out, liquids solidify, and gases condense into liquids.

> ✔ **Example 7.10.1**
>
> How much heat is necessary to melt 55.8 g of ice (solid H_2O) at 0°C? The heat of fusion of H_2O is 79.9 cal/g.
>
> **Solution**
>
> We can use the relationship between heat and the heat of fusion (Eq. 7.10.1b) to determine how many joules of heat are needed to melt this ice:
>
> $$\text{heat} = m \times \Delta H_{fus}$$
>
> $$= (55.8 \ \cancel{g}) \left(\frac{79.9 \, cal}{\cancel{g}} \right)$$
>
> $$= 4,460 \, cal$$

> ? **Exercise 7.10.1**
>
> How much heat is necessary to vaporize 685 g of H_2O at 100°C? The heat of vaporization of H_2O is 540 cal/g.

Table 7.10.1 lists the heats of fusion and vaporization for some common substances. Note the units on these quantities; when you use these values in problem solving, make sure that the other variables in your calculation are expressed in units consistent with the units in the specific heats, or the heats of fusion and vaporization.

Table 7.10.1: Heats of Fusion and Vaporization for Selected Substances

Substance	ΔH_{fus} (cal/g)	ΔH_{vap} (cal/g)
aluminum (Al)	94.0	2,602
gold (Au)	15.3	409
iron (Fe)	63.2	1,504
water (H_2O)	79.9	540
sodium chloride (NaCl)	123.5	691
ethanol (C_2H_5OH)	45.2	200.3
benzene (C_6H_6)	30.4	94.1

Looking Closer: Sublimation

There is also a phase change where a solid goes directly to a gas:

$$\text{solid} \rightarrow \text{gas} \qquad (7.10.5)$$
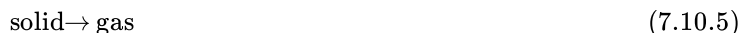
This phase change is called *sublimation*. Each substance has a characteristic heat of sublimation associated with this process. For example, the heat of sublimation (ΔH_{sub}) of H_2O is 620 cal/g.

We encounter sublimation in several ways. You may already be familiar with dry ice, which is simply solid carbon dioxide (CO_2). At −78.5°C (−109°F), solid carbon dioxide sublimes, changing directly from the solid phase to the gas phase:

$$CO_2(s) \xrightarrow{-78.5°C} CO_2(g) \qquad (7.10.6)$$

Solid carbon dioxide is called dry ice because it does not pass through the liquid phase. Instead, it goes directly to the gas phase. (Carbon dioxide *can* exist as liquid but only under high pressure.) Dry ice has many practical uses, including the long-term preservation of medical samples.

Even at temperatures below 0°C, solid H_2O will slowly sublime. For example, a thin layer of snow or frost on the ground may slowly disappear as the solid H_2O sublimes, even though the outside temperature may be below the freezing point of water. Similarly, ice cubes in a freezer may get smaller over time. Although frozen, the solid water slowly sublimes, redepositing on the colder cooling elements of the freezer, which necessitates periodic defrosting (frost-free freezers minimize this redeposition). Lowering the temperature in a freezer will reduce the need to defrost as often.

Under similar circumstances, water will also sublime from frozen foods (e.g., meats or vegetables), giving them an unattractive, mottled appearance called freezer burn. It is not really a "burn," and the food has not necessarily gone bad, although it looks unappetizing. Freezer burn can be minimized by lowering a freezer's temperature and by wrapping foods tightly so water does not have any space to sublime into.

Melting Point

Solids are similar to liquids in that both are condensed states, with particles that are far closer together than those of a gas. However, while liquids are fluid, solids are not. The particles of most solids are packed tightly together in an orderly arrangement. The motion of individual atoms, ions, or molecules in a solid is restricted to **vibrational motion** about a fixed point. Solids are almost completely **incompressible** and are the most dense of the three states of matter.

As a solid is heated, its particles vibrate more rapidly as the solid absorbs kinetic energy. Eventually, the organization of the particles within the solid structure begins to break down and the solid starts to melt. The **melting point** is the temperature at which a solid changes into a liquid. At its melting point, the disruptive vibrations of the particles of the solid overcome the attractive forces operating within the solid. As with boiling points, the melting point of a solid is dependent on the strength of those attractive forces. Sodium chloride ($NaCl$) is an ionic compound that consists of a multitude of strong ionic bonds. Sodium chloride melts at 801^oC. Ice (solid H_2O) is a molecular compound composed of molecules that are held together by hydrogen bonds. Though hydrogen bonds are the strongest of the intermolecular forces, the strength of hydrogen bonds is much less than that of ionic bonds. The melting point of ice is 0^oC.

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^oC.

$$H_2O\,(s) \rightleftharpoons H_2O\,(l)$$
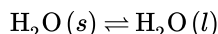
We tend to think of solids as those materials that are solid at room temperature. However, all materials have melting points of some sort. Gases become solids at extremely low temperatures, and liquids will also become solid if the temperature is low enough. The table below gives the melting points of some common materials.

Table $7.10.2$: Melting Points of Common Materials

Materials	Melting Point (ºC)
Hydrogen	-259
Oxygen	-219
Diethyl ether	-116
Ethanol	-114
Water	0
Pure silver	961
Pure gold	1063
Iron	1538

> **? Exercise 7.10.2**
>
> a. Explain what happens when heat flows into or out of a substance at its melting point or boiling point.
> b. How does the amount of heat required for a phase change relate to the mass of the substance?
>
> **Answer a**
>
> The energy goes into changing the phase, not the temperature.
>
> **Answer b**
>
> The amount of heat is a constant per gram of substance.

Summary

- There is an energy change associated with any phase change.
- Sublimation is the change of state from a solid to a gas, without passing through the liquid state.
- Deposition is the change of state from a gas to a solid.
- Carbon dioxide is an example of a material that easily undergoes sublimation.
- The melting point is the temperature at which a solid changes into a liquid.
- Intermolecular forces have a strong influence on melting point.

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7.11: Intermolecular Forces- Dispersion, Dipole–Dipole, Hydrogen Bonding, and Ion-Dipole

> **◑ Learning Objectives**
>
> - To describe the intermolecular forces in liquids.

The properties of liquids are intermediate between those of gases and solids, but are more similar to solids. In contrast to *intra*molecular forces, such as the covalent bonds that hold atoms together in molecules and polyatomic ions, *inter*molecular forces hold molecules together in a liquid or solid. Intermolecular forces are generally much weaker than covalent bonds. For example, it requires 927 kJ to overcome the intramolecular forces and break both O–H bonds in 1 mol of water, but it takes only about 41 kJ to overcome the intermolecular attractions and convert 1 mol of liquid water to water vapor at 100°C. (Despite this seemingly low value, the intermolecular forces in liquid water are among the strongest such forces known!) Given the large difference in the strengths of intra- and intermolecular forces, changes between the solid, liquid, and gaseous states almost invariably occur for molecular substances *without breaking covalent bonds*.

> *The properties of liquids are intermediate between those of gases and solids, but are more similar to solids.*

Intermolecular forces determine bulk properties, such as the melting points of solids and the boiling points of liquids. Liquids boil when the molecules have enough thermal energy to overcome the intermolecular attractive forces that hold them together, thereby forming bubbles of vapor within the liquid. Similarly, solids melt when the molecules acquire enough thermal energy to overcome the intermolecular forces that lock them into place in the solid.

Intermolecular forces are electrostatic in nature; that is, they arise from the interaction between positively and negatively charged species. Like covalent and ionic bonds, intermolecular interactions are the sum of both attractive and repulsive components. Because electrostatic interactions fall off rapidly with increasing distance between molecules, intermolecular interactions are most important for solids and liquids, where the molecules are close together. These interactions become important for gases only at very high pressures, where they are responsible for the observed deviations from the ideal gas law at high pressures.

In this section, we explicitly consider three kinds of intermolecular interactions. There are two additional types of electrostatic interaction that you are already familiar with: the ion–ion interactions that are responsible for ionic bonding, and the ion–dipole interactions that occur when ionic substances dissolve in a polar substance such as water. The first two are often described collectively as van der Waals forces.

Dipole–Dipole Interactions

Polar covalent bonds behave as if the bonded atoms have localized fractional charges that are equal but opposite (i.e., the two bonded atoms generate a *dipole*). If the structure of a molecule is such that the individual bond dipoles do not cancel one another, then the molecule has a net dipole moment. Molecules with net dipole moments tend to align themselves so that the positive end of one dipole is near the negative end of another and vice versa, as shown in Figure $7.11.1a$.
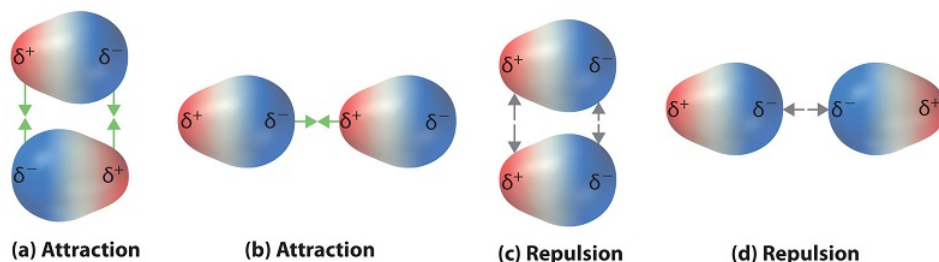

Figure 7.11.1: Attractive and Repulsive Dipole–Dipole Interactions. (a and b) Molecular orientations in which the positive end of one dipole (δ^+) is near the negative end of another (δ^-) (and vice versa) produce attractive interactions. (c and d) Molecular orientations that juxtapose the positive or negative ends of the dipoles on adjacent molecules produce repulsive interactions. (CC BY-SA-NC; anonymous)

These arrangements are more stable than arrangements in which two positive or two negative ends are adjacent (Figure $7.11.1c$). Hence dipole–dipole interactions, such as those in Figure $7.11.1b$, are *attractive intermolecular interactions*, whereas those in

Figure $7.11.1d$ are *repulsive intermolecular interactions*. Because molecules in a liquid move freely and continuously, molecules always experience both attractive and repulsive dipole–dipole interactions simultaneously, as shown in Figure $7.11.2$ On average, however, the attractive interactions dominate.
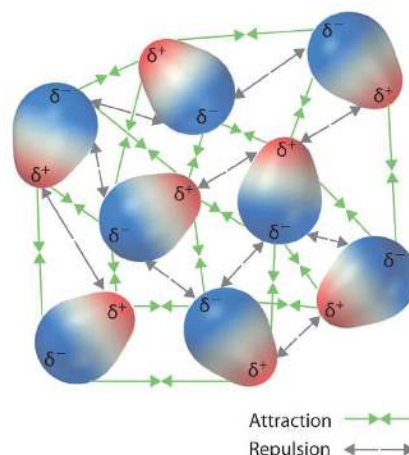

Figure $7.11.2$: Both attractive and repulsive dipole–dipole interactions occur in a liquid sample with many molecules. (CC BY-SA-NC; anonymous)

The green arrows pointing towards each other represent attraction. The gray arrows pointing away from each other represent repulsion

Because each end of a dipole possesses only a fraction of the charge of an electron, dipole–dipole interactions are substantially weaker than the interactions between two ions, each of which has a charge of at least ±1, or between a dipole and an ion, in which one of the species has at least a full positive or negative charge. In addition, the attractive interaction between dipoles falls off much more rapidly with increasing distance than do the ion–ion interactions. Recall that the attractive energy between two ions is proportional to $1/r$, where r is the distance between the ions. Doubling the distance ($r \rightarrow 2r$) decreases the attractive energy by one-half. In contrast, the energy of the interaction of two dipoles is proportional to $1/r^3$, so doubling the distance between the dipoles decreases the strength of the interaction by 2^3, or 8-fold. Thus a substance such as HCl, which is partially held together by dipole–dipole interactions, is a gas at room temperature and 1 atm pressure. Conversely, $NaCl$, which is held together by interionic interactions, is a high-melting-point solid. Within a series of compounds of similar molar mass, the strength of the intermolecular interactions increases as the dipole moment of the molecules increases, as shown in Table $7.11.1$.

Table $7.11.1$: Relationships Between the Dipole Moment and the Boiling Point for Organic Compounds of Similar Molar Mass

Compound	Molar Mass (g/mol)	Dipole Moment (D)	Boiling Point (K)
C_3H_6 (cyclopropane)	42	0	240
CH_3OCH_3 (dimethyl ether)	46	1.30	248
CH_3CN (acetonitrile)	41	3.9	355

> *The attractive energy between two ions is proportional to 1/r, whereas the attractive energy between two dipoles is proportional to 1/r6.*
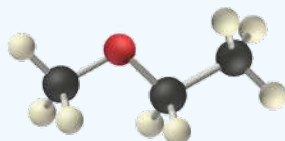
Video Discussing Dipole Intermolecular Forces. Source: Dipole Intermolecular Force, YouTube(opens in new window) [youtu.be]
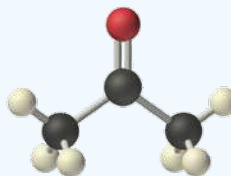
> ✔ **Example 7.11.1**
>
> Arrange ethyl methyl ether ($CH_3OCH_2CH_3$), 2-methylpropane [isobutane, ($CH_3)_2CHCH_3$], and acetone (CH_3COCH_3) in order of increasing boiling points. Their structures are as follows:
>
>
>
> 2-Methylpropane   Ethyl methyl ether   Acetone
>
> **Given:** compounds.
>
> **Asked for:** order of increasing boiling points.
>
> **Strategy:**
>
> Compare the molar masses and the polarities of the compounds. Compounds with higher molar masses and that are polar will have the highest boiling points.
>
> **Solution:**
>
> The three compounds have essentially the same molar mass (58–60 g/mol), so we must look at differences in polarity to predict the strength of the intermolecular dipole–dipole interactions and thus the boiling points of the compounds.
>
> The first compound, 2-methylpropane, contains only C–H bonds, which are not very polar because C and H have similar electronegativities. It should therefore have a very small (but nonzero) dipole moment and a very low boiling point.
>
> Ethyl methyl ether has a structure similar to H_2O; it contains two polar C–O single bonds oriented at about a 109° angle to each other, in addition to relatively nonpolar C–H bonds. As a result, the C–O bond dipoles partially reinforce one another and generate a significant dipole moment that should give a moderately high boiling point.
>
> Acetone contains a polar C=O double bond oriented at about 120° to two methyl groups with nonpolar C–H bonds. The C–O bond dipole therefore corresponds to the molecular dipole, which should result in both a rather large dipole moment and a high boiling point.
>
> Thus we predict the following order of boiling points:
>
> ***2-methylpropane < ethyl methyl ether < acetone***

This result is in good agreement with the actual data: 2-methylpropane, boiling point = −11.7°C, and the dipole moment (μ) = 0.13 D; methyl ethyl ether, boiling point = 7.4°C and μ = 1.17 D; acetone, boiling point = 56.1°C and μ = 2.88 D.

> **? Exercise 7.11.1**
>
> Arrange carbon tetrafluoride (CF_4), ethyl methyl sulfide ($CH_3SC_2H_5$), dimethyl sulfoxide [$(CH_3)_2S{=}O$], and 2-methylbutane [isopentane, $(CH_3)_2CHCH_2CH_3$] in order of decreasing boiling points.
>
> **Answer**
>
> dimethyl sulfoxide (boiling point = 189.9°C) > ethyl methyl sulfide (boiling point = 67°C) > 2-methylbutane (boiling point = 27.8°C) > carbon tetrafluoride (boiling point = −128°C)

London Dispersion Forces

Thus far, we have considered only interactions between polar molecules. Other factors must be considered to explain why many nonpolar molecules, such as bromine, benzene, and hexane, are liquids at room temperature; why others, such as iodine and naphthalene, are solids. Even the noble gases can be liquefied or solidified at low temperatures, high pressures, or both (Table 7.11.2).

What kind of attractive forces can exist between nonpolar molecules or atoms? This question was answered by Fritz London (1900–1954), a German physicist who later worked in the United States. In 1930, London proposed that temporary fluctuations in the electron distributions within atoms and nonpolar molecules could result in the formation of short-lived instantaneous dipole moments, which produce attractive forces called London dispersion forces between otherwise nonpolar substances.

Table 7.11.2: Normal Melting and Boiling Points of Some Elements and Nonpolar Compounds

Substance	Molar Mass (g/mol)	Melting Point (°C)	Boiling Point (°C)
Ar	40	−189.4	−185.9
Xe	131	−111.8	−108.1
N_2	28	−210	−195.8
O_2	32	−218.8	−183.0
F_2	38	−219.7	−188.1
I_2	254	113.7	184.4
CH_4	16	−182.5	−161.5

Consider a pair of adjacent He atoms, for example. On average, the two electrons in each He atom are uniformly distributed around the nucleus. Because the electrons are in constant motion, however, their distribution in one atom is likely to be asymmetrical at any given instant, resulting in an instantaneous dipole moment. As shown in part (a) in Figure 7.11.3, the instantaneous dipole moment on one atom can interact with the electrons in an adjacent atom, pulling them toward the positive end of the instantaneous dipole or repelling them from the negative end. The net effect is that the first atom causes the temporary formation of a dipole, called an induced dipole, in the second. Interactions between these temporary dipoles cause atoms to be attracted to one another. These attractive interactions are weak and fall off rapidly with increasing distance. London was able to show with quantum mechanics that the attractive energy between molecules due to temporary dipole–induced dipole interactions falls off as $1/r^6$. Doubling the distance therefore decreases the attractive energy by 2^6, or 64-fold.
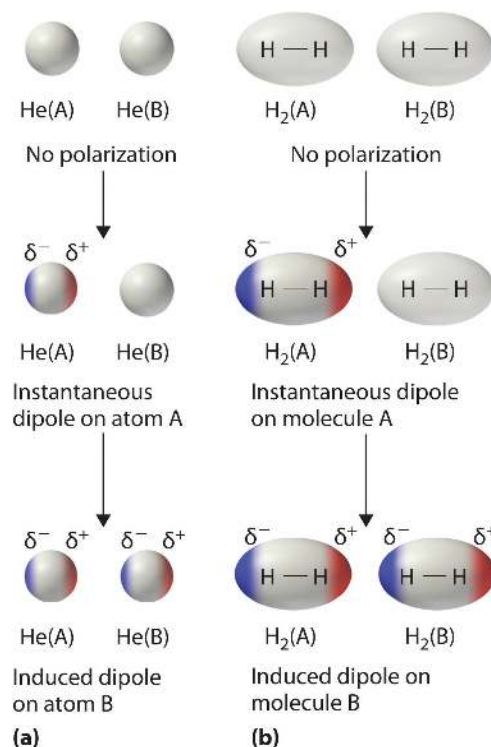
Figure 7.11.3: Instantaneous Dipole Moments. The formation of an instantaneous dipole moment on one He atom (a) or an H_2 molecule (b) results in the formation of an induced dipole on an adjacent atom or molecule.

Instantaneous dipole–induced dipole interactions between nonpolar molecules can produce intermolecular attractions just as they produce interatomic attractions in monatomic substances like Xe. This effect, illustrated for two H_2 molecules in part (b) in Figure 7.11.3, tends to become more pronounced as atomic and molecular masses increase (Table 7.11.2). For example, Xe boils at −108.1°C, whereas He boils at −269°C. The reason for this trend is that the strength of London dispersion forces is related to the ease with which the electron distribution in a given atom can be perturbed. In small atoms such as He, the two 1s electrons are held close to the nucleus in a very small volume, and electron–electron repulsions are strong enough to prevent significant asymmetry in their distribution. In larger atoms such as Xe, however, the outer electrons are much less strongly attracted to the nucleus because of filled intervening shells. As a result, it is relatively easy to temporarily deform the electron distribution to generate an instantaneous or induced dipole. The ease of deformation of the electron distribution in an atom or molecule is called its polarizability. Because the electron distribution is more easily perturbed in large, heavy species than in small, light species, we say that heavier substances tend to be much more *polarizable* than lighter ones.

> *For similar substances, London dispersion forces get stronger with increasing molecular size.*

The polarizability of a substance also determines how it interacts with ions and species that possess permanent dipoles. Thus, London dispersion forces are responsible for the general trend toward higher boiling points with increased molecular mass and greater surface area in a homologous series of compounds, such as the alkanes (part (a) in Figure 7.11.4). The strengths of London dispersion forces also depend significantly on molecular shape because shape determines how much of one molecule can interact with its neighboring molecules at any given time. For example, part (b) in Figure 7.11.4 shows 2,2-dimethylpropane (neopentane) and *n*-pentane, both of which have the empirical formula C_5H_{12}. Neopentane is almost spherical, with a small surface area for intermolecular interactions, whereas *n*-pentane has an extended conformation that enables it to come into close contact with other *n*-pentane molecules. As a result, the boiling point of neopentane (9.5°C) is more than 25°C lower than the boiling point of *n*-pentane (36.1°C).
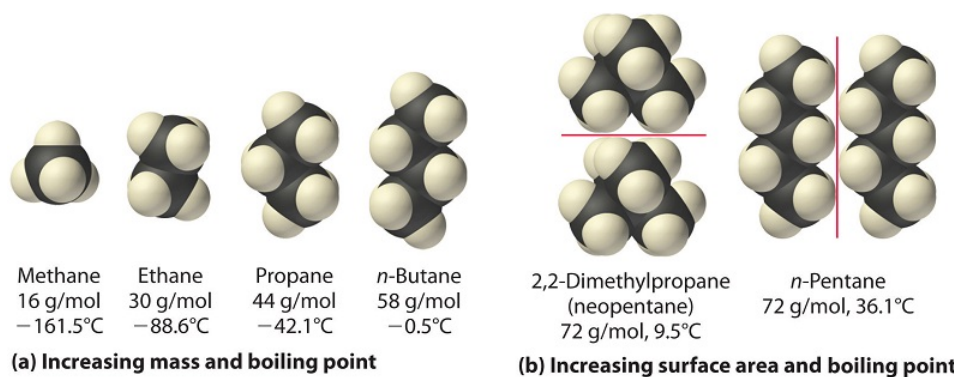
Figure 7.11.4: Mass and Surface Area Affect the Strength of London Dispersion Forces. (a) In this series of four simple alkanes, larger molecules have stronger London forces between them than smaller molecules do, and consequently have higher boiling points. (b) Linear *n*-pentane molecules have a larger surface area and stronger intermolecular forces than spherical neopentane molecules. As a result, neopentane is a gas at room temperature, whereas *n*-pentane is a volatile liquid.

All molecules, whether polar or nonpolar, are attracted to one another by London dispersion forces in addition to any other attractive forces that may be present. In general, however, dipole–dipole interactions in small polar molecules are significantly stronger than London dispersion forces, so the former predominate.
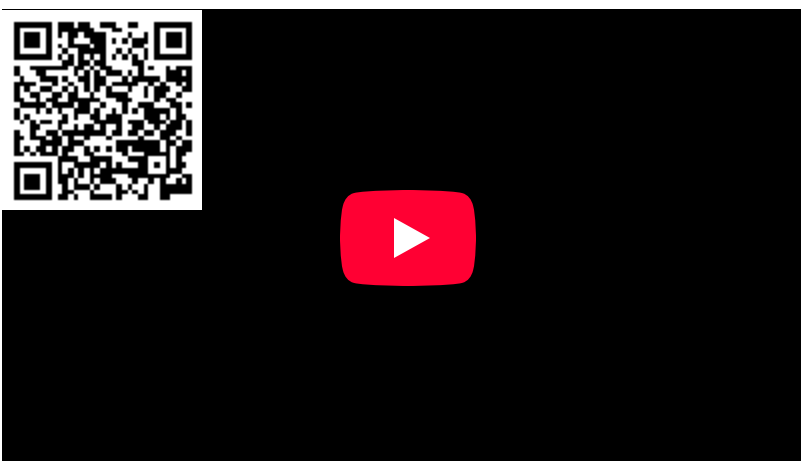
Video Discussing London/Dispersion Intermolecular Forces. Source: Dispersion Intermolecular Force, YouTube(opens in new window) [youtu.be]

✔ Example 7.11.2

Arrange *n*-butane, propane, 2-methylpropane [isobutene, $(CH_3)_2CHCH_3$], and *n*-pentane in order of increasing boiling points.

Given: compounds

Asked for: order of increasing boiling points

Strategy:
Determine the intermolecular forces in the compounds, and then arrange the compounds according to the strength of those forces. The substance with the weakest forces will have the lowest boiling point.

Solution:
The four compounds are alkanes and nonpolar, so London dispersion forces are the only important intermolecular forces. These forces are generally stronger with increasing molecular mass, so propane should have the lowest boiling point and *n*-pentane should have the highest, with the two butane isomers falling in between. Of the two butane isomers, 2-methylpropane is more compact, and *n*-butane has the more extended shape. Consequently, we expect intermolecular interactions for *n*-butane to be stronger due to its larger surface area, resulting in a higher boiling point. The overall order is thus as follows, with actual boiling points in parentheses: propane (−42.1°C) < 2-methylpropane (−11.7°C) < *n*-butane (−0.5°C) < *n*-pentane (36.1°C).

> **? Exercise 7.11.2**
>
> Arrange GeH_4, $SiCl_4$, SiH_4, CH_4, and $GeCl_4$ in order of decreasing boiling points.
>
> **Answer**
>
> $GeCl_4$ (87°C) > $SiCl_4$ (57.6°C) > GeH_4 (−88.5°C) > SiH_4 (−111.8°C) > CH_4 (−161°C)

Hydrogen Bonds

Molecules with hydrogen atoms bonded to electronegative atoms such as O, N, and F (and to a much lesser extent, Cl and S) tend to exhibit unusually strong intermolecular interactions. These result in much higher boiling points than are observed for substances in which London dispersion forces dominate, as illustrated for the covalent hydrides of elements of groups 14–17 in Figure 7.11.5. Methane and its heavier congeners in group 14 form a series whose boiling points increase smoothly with increasing molar mass. This is the expected trend in nonpolar molecules, for which London dispersion forces are the exclusive intermolecular forces. In contrast, the hydrides of the lightest members of groups 15–17 have boiling points that are more than 100°C greater than predicted on the basis of their molar masses. The effect is most dramatic for water: if we extend the straight line connecting the points for H_2Te and H_2Se to the line for period 2, we obtain an estimated boiling point of −130°C for water! Imagine the implications for life on Earth if water boiled at −130°C rather than 100°C.
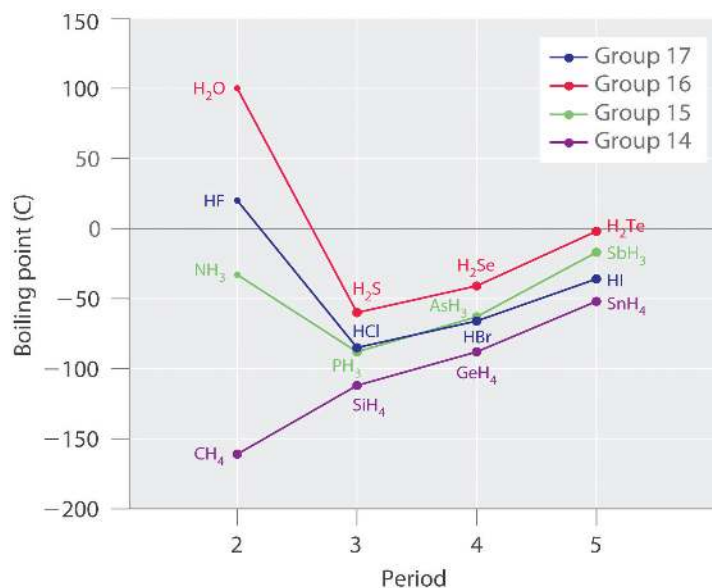
Figure 7.11.5: The Effects of Hydrogen Bonding on Boiling Points. These plots of the boiling points of the covalent hydrides of the elements of groups 14–17 show that the boiling points of the lightest members of each series for which hydrogen bonding is possible (HF, NH_3, and H_2O) are anomalously high for compounds with such low molecular masses.
Group 14 is in purple, group 15 is in green, group 16 is red, and group 17 is blue. Graph of boiling point against period.

Why do strong intermolecular forces produce such anomalously high boiling points and other unusual properties, such as high enthalpies of vaporization and high melting points? The answer lies in the highly polar nature of the bonds between hydrogen and very electronegative elements such as O, N, and F. The large difference in electronegativity results in a large partial positive charge on hydrogen and a correspondingly large partial negative charge on the O, N, or F atom. Consequently, H–O, H–N, and H–F bonds have very large bond dipoles that can interact strongly with one another. Because a hydrogen atom is so small, these dipoles can also approach one another more closely than most other dipoles. The combination of large bond dipoles and short dipole–dipole distances results in very strong dipole–dipole interactions called hydrogen bonds, as shown for ice in Figure 7.11.6. A hydrogen bond is usually indicated by a dotted line between the hydrogen atom attached to O, N, or F (the *hydrogen bond donor*) and the atom that has the lone pair of electrons (the *hydrogen bond acceptor*). Because each water molecule contains two hydrogen atoms and two lone pairs, a tetrahedral arrangement maximizes the number of hydrogen bonds that can be formed. In the structure of ice, each oxygen atom is surrounded by a distorted tetrahedron of hydrogen atoms that form bridges to the oxygen atoms of adjacent water molecules. The bridging hydrogen atoms are *not* equidistant from the two oxygen atoms they connect, however. Instead, each hydrogen atom is 101 pm from one oxygen and 174 pm from the other. In contrast, each oxygen atom is bonded to two H atoms at

the shorter distance and two at the longer distance, corresponding to two O–H covalent bonds and two O⋯H hydrogen bonds from adjacent water molecules, respectively. The resulting open, cagelike structure of ice means that the solid is actually slightly less dense than the liquid, which explains why ice floats on water, rather than sinks.
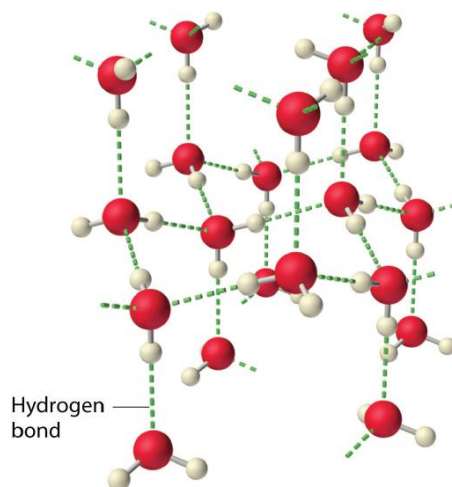

Figure 7.11.6: The Hydrogen-Bonded Structure of Ice

Each water molecule accepts two hydrogen bonds from two other water molecules and donates two hydrogen atoms to form hydrogen bonds with two more water molecules, producing an open, cage like structure. The structure of liquid water is very similar, but in the liquid, the hydrogen bonds are continually broken and formed because of rapid molecular motion.

> *Hydrogen bond formation requires both a hydrogen bond donor and a hydrogen bond acceptor.*

Because ice is less dense than liquid water, rivers, lakes, and oceans freeze from the top down. In fact, the ice forms a protective surface layer that insulates the rest of the water, allowing fish and other organisms to survive in the lower levels of a frozen lake or sea. If ice were denser than the liquid, the ice formed at the surface in cold weather would sink as fast as it formed. Bodies of water would freeze from the bottom up, which would be lethal for most aquatic creatures. The expansion of water when freezing also explains why automobile or boat engines must be protected by "antifreeze" and why unprotected pipes in houses break if they are allowed to freeze.

Video Discussing Hydrogen Bonding Intermolecular Forces. Source: Hydrogen Bonding Intermolecular Force, YouTube(opens in new window) [youtu.be]

✔ Example 7.11.3

Considering CH_3OH, C_2H_6, Xe, and $(CH_3)_3N$, which can form hydrogen bonds with themselves? Draw the hydrogen-bonded structures.

Given: compounds

Asked for: formation of hydrogen bonds and structure

Strategy:
A. Identify the compounds with a hydrogen atom attached to O, N, or F. These are likely to be able to act as hydrogen bond donors.
B. Of the compounds that can act as hydrogen bond donors, identify those that also contain lone pairs of electrons, which allow them to be hydrogen bond acceptors. If a substance is both a hydrogen donor and a hydrogen bond acceptor, draw a structure showing the hydrogen bonding.

Solution:
A. Of the species listed, xenon (Xe), ethane (C_2H_6), and trimethylamine [$(CH_3)_3N$] do not contain a hydrogen atom attached to O, N, or F; hence they cannot act as hydrogen bond donors.

B. The one compound that can act as a hydrogen bond donor, methanol (CH_3OH), contains both a hydrogen atom attached to O (making it a hydrogen bond donor) and two lone pairs of electrons on O (making it a hydrogen bond acceptor); methanol can thus form hydrogen bonds by acting as either a hydrogen bond donor or a hydrogen bond acceptor. The hydrogen-bonded structure of methanol is as follows:
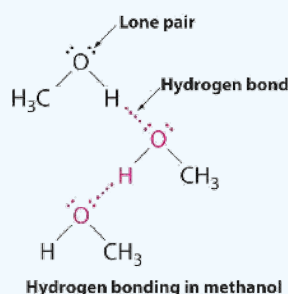
Hydrogen bonding in methanol

Considering CH_3CO_2H, $(CH_3)_3N$, NH_3, and CH_3F, which can form hydrogen bonds with themselves? Draw the hydrogen-bonded structures.

Answer

 CH_3CO_2H and NH_3;
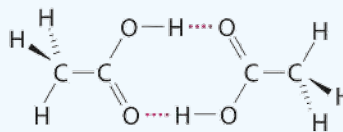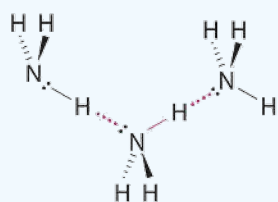
Hydrogen bonding in ammonia between nitrogen and hydrogen. hydrogen bonding in acetic acid is between oxygen and hydrogen.

Although hydrogen bonds are significantly weaker than covalent bonds, with typical dissociation energies of only 15–25 kJ/mol, they have a significant influence on the physical properties of a compound. Compounds such as HF can form only two hydrogen bonds at a time as can, on average, pure liquid NH_3. Consequently, even though their molecular masses are similar to that of water, their boiling points are significantly lower than the boiling point of water, which forms *four* hydrogen bonds at a time.

✔ Example 7.11.4: Buckyballs

Arrange C_{60} (buckminsterfullerene, which has a cage structure), NaCl, He, Ar, and N_2O in order of increasing boiling points.

Given: compounds.

Asked for: order of increasing boiling points.

Strategy:
Identify the intermolecular forces in each compound and then arrange the compounds according to the strength of those forces. The substance with the weakest forces will have the lowest boiling point.

Solution
Electrostatic interactions are strongest for an ionic compound, so we expect NaCl to have the highest boiling point. To predict the relative boiling points of the other compounds, we must consider their polarity (for dipole–dipole interactions), their ability to form hydrogen bonds, and their molar mass (for London dispersion forces). Helium is nonpolar and by far the lightest, so it should have the lowest boiling point. Argon and N_2O have very similar molar masses (40 and 44 g/mol, respectively), but N_2O is polar while Ar is not. Consequently, N_2O should have a higher boiling point. A C_{60} molecule is nonpolar, but its molar mass is 720 g/mol, much greater than that of Ar or N_2O. Because the boiling points of nonpolar substances increase rapidly with molecular mass, C_{60} should boil at a higher temperature than the other nonionic substances. The predicted order is thus as follows, with actual boiling points in parentheses:

$$He (-269°C) < Ar (-185.7°C) < N_2O (-88.5°C) < C_{60} (>280°C) < NaCl (1465°C).$$
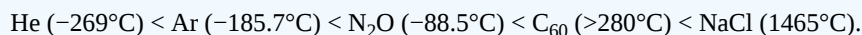
❓ Exercise 7.11.4

Arrange 2,4-dimethylheptane, Ne, CS_2, Cl_2, and KBr in order of decreasing boiling points.

Answer

KBr (1435°C) > 2,4-dimethylheptane (132.9°C) > CS_2 (46.6°C) > Cl_2 (−34.6°C) > Ne (−246°C)
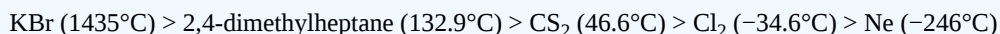
✔ Example 7.11.5

Identify the most significant intermolecular force in each substance.

a. C_3H_8
b. CH_3OH
c. H_2S

Solution
a. Although C–H bonds are polar, they are only minimally polar. The most significant intermolecular force for this substance would be dispersion forces.
b. This molecule has an H atom bonded to an O atom, so it will experience hydrogen bonding.
c. Although this molecule does not experience hydrogen bonding, the Lewis electron dot diagram and VSEPR indicate that it is bent, so it has a permanent dipole. The most significant force in this substance is dipole-dipole interaction.

❓ Exercise 7.11.6

Identify the most significant intermolecular force in each substance.

a. HF
b. HCl

Answer a

hydrogen bonding

Answer b

Summary

Intermolecular forces are electrostatic in nature and include van der Waals forces and hydrogen bonds. Molecules in liquids are held to other molecules by intermolecular interactions, which are weaker than the intramolecular interactions that hold the atoms together within molecules and polyatomic ions. Transitions between the solid and liquid, or the liquid and gas phases, are due to changes in intermolecular interactions, but do not affect intramolecular interactions. The three major types of intermolecular interactions are dipole–dipole interactions, London dispersion forces (these two are often referred to collectively as **van der Waals forces**), and hydrogen bonds. **Dipole–dipole interactions** arise from the electrostatic interactions of the positive and negative ends of molecules with permanent dipole moments; their strength is proportional to the magnitude of the dipole moment and to $1/r^3$, where r is the distance between dipoles. **London dispersion forces** are due to the formation of **instantaneous dipole moments** in polar or nonpolar molecules as a result of short-lived fluctuations of electron charge distribution, which in turn cause the temporary formation of an **induced dipole** in adjacent molecules; their energy falls off as $1/r^6$. Larger atoms tend to be more **polarizable** than smaller ones, because their outer electrons are less tightly bound and are therefore more easily perturbed. **Hydrogen bonds** are especially strong dipole–dipole interactions between molecules that have hydrogen bonded to a highly electronegative atom, such as O, N, or F. The resulting partially positively charged H atom on one molecule (the *hydrogen bond donor*) can interact strongly with a lone pair of electrons of a partially negatively charged O, N, or F atom on adjacent molecules (the *hydrogen bond acceptor*). Because of strong O···H hydrogen bonding between water molecules, water has an unusually high boiling point, and ice has an open, cage like structure that is less dense than liquid water.

CHAPTER OVERVIEW

8: Organic Chemistry

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8.1: Drawing Chemical Structures

> ### 📖 Objectives
>
> After completing this section, you should be able to
>
> 1. propose one or more acceptable Kekulé structures (structural formulas) for any given molecular formula
> 2. write the molecular formula of a compound, given its Kekulé structure.
> 3. draw the shorthand structure of a compound, given its Kekulé structure.
> 4. interpret shorthand structures and convert them to Kekulé structures.
> 5. write the molecular formula of a compound, given its shorthand structure.

> ### 📌 Study Notes
>
> When drawing the structure of a neutral organic compound, you will find it helpful to remember that
>
> - each carbon atom has four bonds.
> - each nitrogen atom has three bonds.
> - each oxygen atom has two bonds.
> - each hydrogen atom has one bond.

Through general chemistry, you may have already experienced looking at molecular structures using Lewis structures. Because organic chemistry can involve large molecules it would be beneficial if Lewis structures could be abbreviated. The three different ways to draw organic molecules include **Kekulé Formulas**, **Condensed Formulas**, and **Skeletal structures** (also called line-bond structures or line formulas). During this course, you will view molecules written in all three forms. It will be more helpful if you become comfortable going from one style of drawing to another, and look at drawings and understanding what they represent. Developing the ability to convert between different types of formulas requires practice, and in most cases the aid of molecular models. Many kinds of model kits are available to students and professional chemists, and the beginning student is encouraged to obtain one.

Simplification of structural formulas may be achieved without any loss of the information they convey. Kekule formulas is just organic chemistry's term for Lewis structures you have previously encountered. In **condensed structural formulas**, the bonds to each carbon are omitted, but each distinct structural unit (group) is written with subscript numbers designating multiple substituents, including the hydrogens. **Line formulas** omit the symbols for carbon and hydrogen entirely (unless the hydrogen is bonded to an atom other than carbon). Each straight line segment represents a bond, the ends and intersections of the lines are carbon atoms, and the correct number of hydrogens is calculated from the tetravalency of carbon. Non-bonding valence shell electrons are omitted in these formulas.

Kekulé (a.k.a. Lewis Structures)

A Kekulé Formula or structural formula displays the atoms of the molecule in the order they are bonded. It also depicts how the atoms are bonded to one another, for example single, double, and triple covalent bond. Covalent bonds are shown using lines. The number of dashes indicate whether the bond is a single, double, or triple covalent bond. All atom labels are shown and all lone pairs are shown.

A	B	C
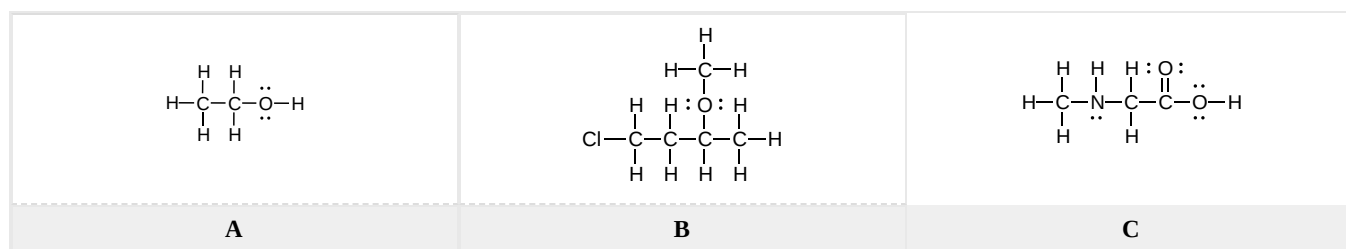
Condensed Formula

A condensed formula is made up of the elemental symbols. Condensed structural formulas show the order of atoms like a structural formula but are written in a single line to save space and make it more convenient and faster to write out. The order of the atoms suggests the connectivity in the molecule. Condensed structural formulas are also helpful when showing that a group of atoms is connected to a single atom in a compound. When this happens, parenthesis are used around the group of atoms to show they are together. Also, if more than one of the same substituent is attached to a given atom, it is show with a subscript number. An example is CH_4, which represents four hydrogens attached to the same carbon. Condensed formulas can be read from either direction and H_3C is the same as CH_3, although the latter is more common.
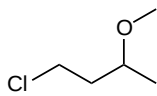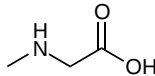
Look at the examples below and match them with their identical molecule under the Kekulé structures and the line formulas.

CH_3CH_2OH	$ClCH_2CH_2CH(OCH_3)CH_3$	CH_3NHCH_2COOH
A	**B**	**C**

Let's look closely at example B. As you go through a condensed formula, you want to focus on the carbons and other elements that aren't hydrogen. The hydrogen's are important, but are usually there to complete octets. Also, notice the $-OCH_3$ is in written in parentheses which tell you that it not part of the main chain of carbons. As you read through a a condensed formula, if you reach an atom that doesn't have a complete octet by the time you reach the next hydrogen, then it's possible that there are double or triple bonds. In example C, the carbon is double bonded to oxygen and single bonded to another oxygen. Notice how COOH means $C(=O)-O-H$ instead of $CH_3-C-O-O-H$ because carbon does not have a complete octet and oxygens.
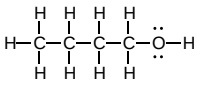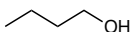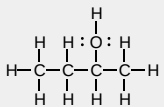
Line Formula
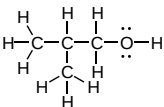
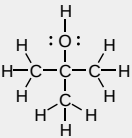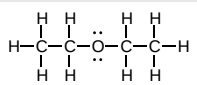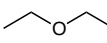Because organic compounds can be complex at times, line-angle formulas are used to write carbon and hydrogen atoms more efficiently by replacing the letter "C" with lines. A carbon atom is present wherever a line intersects another line. Hydrogen atoms are omitted but are assumed to be present to complete each of carbon's four bonds. Hydrogens that are attached to elements other than carbon are shown. Atom labels for all other elements are shown. Lone pair electrons are usually omitted. They are assumed to be present to complete the octet of non-carbon atoms. Line formulas help show the structure and order of the atoms in a compound.

A	**B**	**C**

These molecules correspond to the exact same molecules depicted for Kekulé structures and condensed formulas. Notice how the carbons are no longer drawn in and are replaced by the ends and bends of a lines. In addition, the hydrogens have been omitted, but could be easily drawn in (see practice problems). Although we do not usually draw in the H's that are bonded to carbon, we do draw them in if they are connected to other atoms besides carbon (example is the OH group above in example A) . This is done because it is not always clear if the non-carbon atom is surrounded by lone pairs or hydrogens. Also in example A, notice how the OH is drawn with a bond to the second carbon, but it does not mean that there is a third carbon at the end of that bond/ line.

Table 8.1.1: Structural Formulas for $C_4H_{10}O$ isomers

| Kekulé Formula	Condensed Formula	Line Formula
	$CH_3(CH_2)_3OH$	
	$CH_3CH_2CH(OH)CH_3$	

Kekulé Formula	Condensed Formula	Line Formula
	$(CH_3)_2CHCH_2OH$	
	$(CH_3)_3COH$	
	$CH_3CH_2OCH_2CH_3$	

## Example: Converting between Structural Formulas

It is helpful to convert compounds into different structural formulas (Kekule, Line, and Condensed) depending on the type of question that is asked. Standardized exams frequently include a high percentage of condensed formulas because it is easier and cheaper to type letters and numbers than to import figures. Initially, it can be difficult writing a Line structure directly from a condensed formula. First, write the Kekule structure from the condensed formula and then draw the Line structure from the Kekule.

a) The condensed formula for propanal is CH_3CH_2CHO. Draw the Kekule structure.

The Kekule structure for propanal is shown below. Remember that every carbon will have four bonds and oxygens octet is filled with lone pairs.
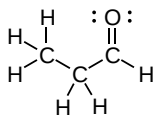
The bond-line structure for propanal is shown below. First, remove hydrogens. The hydrogen attached to the aldehyde group remains because it is part of a functional group. The remove the "C" labels from the structure and keep the lines in place. Lastly, remove any lone pairs.
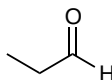

All three structures represent the same compound, propanal.
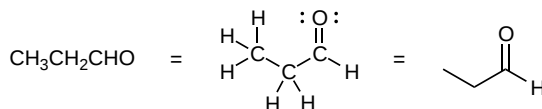
b) The following is the line structure of the molecule trimethyl amine.

To convert it to a Kekule structure first identify the carbons in the molecule. The will be at the corners and ends of line without an atom label. Trimethyl amine has three carbons. Next, add hydrogens to the carbons until four bonds are present. Each carbon in trimethyl amine is singly bonded to nitrogen. This means each carbon will need three additional C-H bonds to create its octet. Lastly, add lone pairs to other elements to fill their octets. The nitrogen in trimethyl amine is bonded to three carbons. This means it will require one of lone pair electrons to complete its octet.
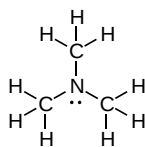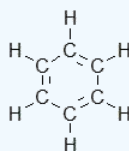
Exercise 8.1.1

How many carbons are in the following drawing? How many hydrogens?

Answer

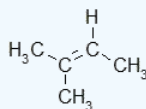Remember the octet rule and how many times carbons and hydrogens are able to bond to other atoms.

Exercise 8.1.2

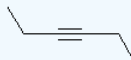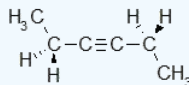How many carbons are in the following drawing? How many hydrogens?

Answer

Exercise 8.1.3

How many carbons are in the following drawing? How many hydrogens?
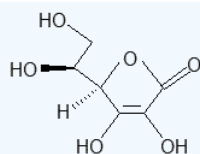
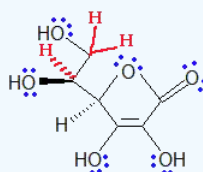**Answer**

Exercise 8.1.4

Look at the following molecule of vitamin A and draw in the hidden hydrogens and electron pairs.

Hint: Do all of the carbons have 4 bonds? Do all the oxygens have a full octet?
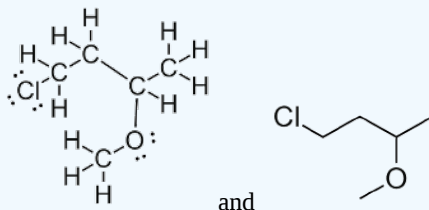
Answer

Electron pairs drawn in blue and hydrogens draw in red.

? Exercise 8.1.5

Draw $ClCH_2CH_2CH(OCH_3)CH_3$ in Kekulé and line form.

Answer

and

? Exercise 8.1.6

Write down the molecular formula for each of the compounds shown here.
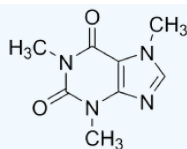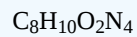

A   B   C   D
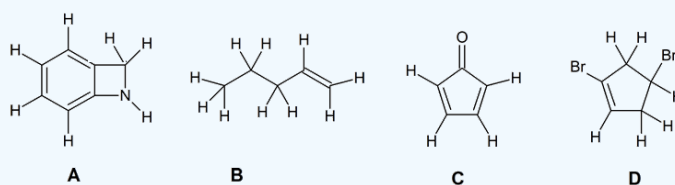
Answer

  a. C_7H_7N
  b. C_5H_{10}
  c. C_5H_4O
  d. $C_5H_6Br_2$

? Exercise 8.1.7

Below is the molecule for caffeine. Give the molecular formula for it.

Answer

$C_8H_{10}O_2N_4$

8.2: Alkanes- Saturated Hydrocarbons

> ### Learning Objectives
>
> To identify and name simple (straight-chain) alkanes given formulas and write formulas for straight-chain alkanes given their names.

We begin our study of organic chemistry with the hydrocarbons, the simplest organic compounds, which are composed of carbon and hydrogen atoms only. As we noted, there are several different kinds of hydrocarbons. They are distinguished by the types of bonding between carbon atoms and the properties that result from that bonding. Hydrocarbons with only carbon-to-carbon single bonds (C–C) and existing as a continuous chain of carbon atoms also bonded to hydrogen atoms are called alkanes (or saturated hydrocarbons). *Saturated*, in this case, means that each carbon atom is bonded to four other atoms (hydrogen or carbon)—the most possible; there are no double or triple bonds in the molecules.

> The word *saturated* has the same meaning for hydrocarbons as it does for the dietary fats and oils: the molecule has no carbon-to-carbon double bonds (C=C).

We previously introduced the three simplest alkanes—methane (CH_4), ethane (C_2H_6), and propane (C_3H_8) and they are shown again in Figure 8.2.1.
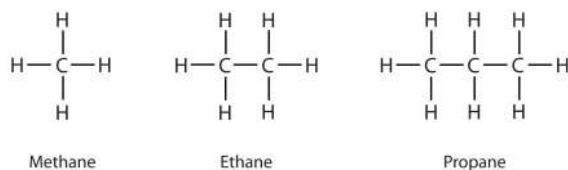

Figure 8.2.1: The Three Simplest Alkanes

The flat representations shown do not accurately portray bond angles or molecular geometry. Methane has a tetrahedral shape that chemists often portray with wedges indicating bonds coming out toward you and dashed lines indicating bonds that go back away from you. An ordinary solid line indicates a bond in the plane of the page. Recall that the VSEPR theory correctly predicts a tetrahedral shape for the methane molecule (Figure 8.2.2).
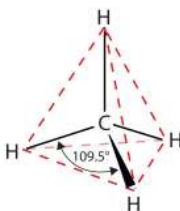
Figure 8.2.2: The Tetrahedral Methane Molecule

Methane (CH_4), ethane (C_2H_6), and propane (C_3H_8) are the beginning of a series of compounds in which any two members in a sequence differ by one carbon atom and two hydrogen atoms—namely, a CH_2 unit. The first 10 members of this series are given in Table 8.2.1.

Table 8.2.1: The First 10 Straight-Chain Alkanes

Name	Molecular Formula (C_nH_{2n+2})	Condensed Structural Formula	Number of Possible Isomers
methane	CH_4	CH_4	—
ethane	C_2H_6	CH_3CH_3	—
propane	C_3H_8	$CH_3CH_2CH_3$	—
butane	C_4H_{10}	$CH_3CH_2CH_2CH_3$	2
pentane	C_5H_{12}	$CH_3CH_2CH_2CH_2CH_3$	3

Name	Molecular Formula (C_nH_{2n+2})	Condensed Structural Formula	Number of Possible Isomers
hexane	C_6H_{14}	$CH_3CH_2CH_2CH_2CH_2CH_3$	5
heptane	C_7H_{16}	$CH_3CH_2CH_2CH_2CH_2CH_2CH_3$	9
octane	C_8H_{18}	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3$	18
nonane	C_9H_{20}	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$	35
decane	$C_{10}H_{22}$	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$	75

Consider the series in Figure 8.2.3. The sequence starts with C_3H_8, and a CH_2 unit is added in each step moving up the series. Any family of compounds in which adjacent members differ from each other by a definite factor (here a CH_2 group) is called a homologous series. The members of such a series, called *homologs*, have properties that vary in a regular and predictable manner. The principle of *homology* gives organization to organic chemistry in much the same way that the periodic table gives organization to inorganic chemistry. Instead of a bewildering array of individual carbon compounds, we can study a few members of a homologous series and from them deduce some of the properties of other compounds in the series.
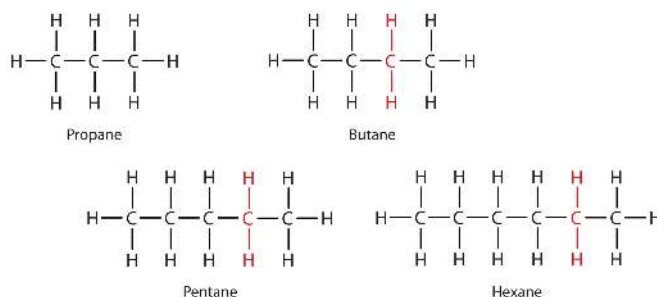
Figure 8.2.3: Members of a Homologous Series. Each succeeding formula incorporates one carbon atom and two hydrogen atoms more than the previous formula.

The principle of homology allows us to write a general formula for alkanes: C_nH_{2n+2}. Using this formula, we can write a molecular formula for any alkane with a given number of carbon atoms. For example, an alkane with eight carbon atoms has the molecular formula $C_8H_{(2 \times 8)+2} = C_8H_{18}$.

Key Takeaway

- Simple alkanes exist as a homologous series, in which adjacent members differ by a CH_2 unit.

8.3: Alkenes and Alkynes

> **Learning Objectives**
>
> - To name alkenes given formulas and write formulas for alkenes given names.

As noted before, alkenes are hydrocarbons with carbon-to-carbon double bonds ($R_2C=CR_2$) and alkynes are hydrocarbons with carbon-to-carbon triple bonds ($R–C\equiv C–R$). Collectively, they are called unsaturated hydrocarbons because they have fewer hydrogen atoms than does an alkane with the same number of carbon atoms, as is indicated in the following general formulas:

Some representative alkenes—their names, structures, and physical properties—are given in Table 8.3.1.
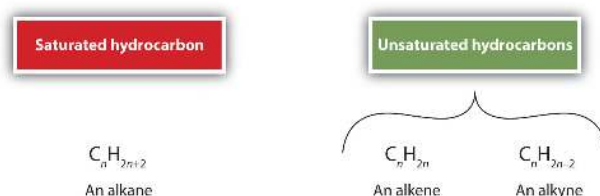
Table 8.3.1: Physical Properties of Some Selected Alkenes

IUPAC Name	Molecular Formula	Condensed Structural Formula	Melting Point (°C)	Boiling Point (°C)
ethene	C_2H_4	$CH_2=CH_2$	−169	−104
propene	C_3H_6	$CH_2=CHCH_3$	−185	−47
1-butene	C_4H_8	$CH_2=CHCH_2CH_3$	−185	−6
1-pentene	C_5H_{10}	$CH_2=CH(CH_2)_2CH_3$	−138	30
1-hexene	C_6H_{12}	$CH_2=CH(CH_2)_3CH_3$	−140	63
1-heptene	C_7H_{14}	$CH_2=CH(CH_2)_4CH_3$	−119	94
1-octene	C_8H_{16}	$CH_2=CH(CH_2)_5CH_3$	−102	121

We used only condensed structural formulas in Table 8.3.1. Thus, $CH_2=CH_2$ stands for
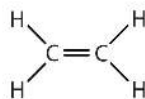
The double bond is shared by the two carbons and does not involve the hydrogen atoms, although the condensed formula does not make this point obvious. Note that the molecular formula for ethene is C_2H_4, whereas that for ethane is C_2H_6.

The first two alkenes in Table 8.3.1, ethene and propene, are most often called by their common names—ethylene and propylene, respectively (Figure 8.3.1). Ethylene is a major commercial chemical. The US chemical industry produces about 25 billion kilograms of ethylene annually, more than any other synthetic organic chemical. More than half of this ethylene goes into the manufacture of polyethylene, one of the most familiar plastics. Propylene is also an important industrial chemical. It is converted to plastics, isopropyl alcohol, and a variety of other products.
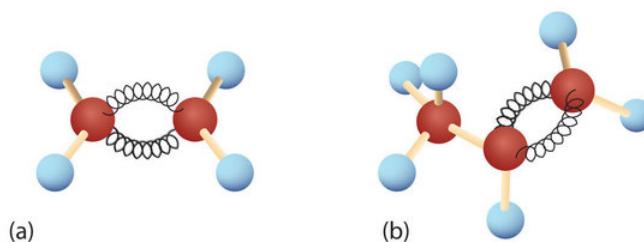
Figure 8.3.1: Ethene and Propene. The ball-and-spring models of ethene/ethylene (a) and propene/propylene (b) show their respective shapes, especially bond angles.

> Although there is only one alkene with the formula C_2H_4 (ethene) and only one with the formula C_3H_6 (propene), there are several alkenes with the formula C_4H_8.

Here are some basic rules for naming alkenes from the International Union of Pure and Applied Chemistry (IUPAC):

1. The longest chain of carbon atoms *containing the double bond* is considered the parent chain. It is named using the same stem as the alkane having the same number of carbon atoms but ends in *-ene* to identify it as an alkene. Thus the compound $CH_2{=}CHCH_3$ is *propene*.
2. If there are four or more carbon atoms in a chain, we must indicate the position of the double bond. The carbons atoms are numbered so that the first of the two that are doubly bonded is given the lower of the two possible numbers. The compound $CH_3CH{=}CHCH_2CH_3$, for example, has the double bond between the second and third carbon atoms. Its name is 2-pentene (not 3-pentene).
3. Substituent groups are named as with alkanes, and their position is indicated by a number. Thus, the structure below is 5-methyl-2-hexene. Note that the numbering of the parent chain is always done in such a way as to give the double bond the lowest number, even if that causes a substituent to have a higher number. *The double bond always has priority in numbering.*
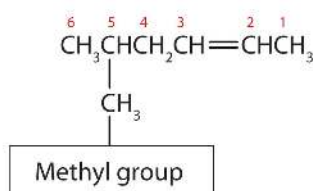
✔ Example 8.3.1

Name each compound.

a.

b.
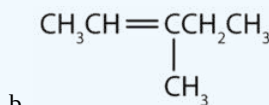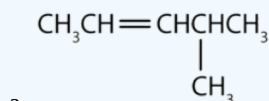
Solution

a. The longest chain containing the double bond has five carbon atoms, so the compound is a *pentene* (rule 1). To give the first carbon atom of the double bond the lowest number (rule 2), we number from the left, so the compound is a 2-pentene. There is a methyl group on the fourth carbon atom (rule 3), so the compound's name is 4-methyl-2-pentene.
b. The longest chain containing the double bond has five carbon atoms, so the parent compound is a *pentene* (rule 1). To give the first carbon atom of the double bond the lowest number (rule 2), we number from the left, so the compound is a 2-pentene. There is a methyl group on the third carbon atom (rule 3), so the compound's name is 3-methyl-2-pentene.

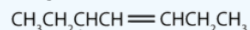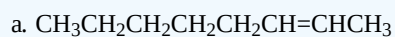### ? Exercise 8.3.1

Name each compound.

a. $CH_3CH_2CH_2CH_2CH_2CH=CHCH_3$

b. $CH_3CH_2CHCH=CHCH_2CH_3$
   $\quad\quad\quad\quad |$
   $\quad\quad\quad CH_3$

Answer

Just as there are cycloalkanes, there are *cycloalkenes*. These compounds are named like alkenes, but with the prefix *cyclo-* attached to the beginning of the parent alkene name.

✔ Example 8.3.2

Draw the structure for each compound.

a. 3-methyl-2-pentene
b. cyclohexene
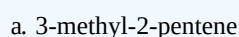
Solution

a.

First write the parent chain of five carbon atoms: C–C–C–C–C. Then add the double bond between the second and third carbon atoms:

$$\overset{1}{C}-\overset{2}{C}=\overset{3}{C}-\overset{4}{C}-\overset{5}{C}$$
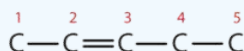
Now place the methyl group on the third carbon atom and add enough hydrogen atoms to give each carbon atom a total of four bonds.

$$CH_3CH=CCH_2CH_3$$
$$\quad\quad\quad |$$
$$\quad\quad\quad CH_3$$
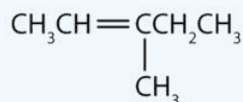
b

First, consider what each of the three parts of the name means. *Cyclo* means a ring compound, *hex* means 6 carbon atoms, and -*ene* means a double bond.
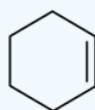
? Exercise 8.3.2

Draw the structure for each compound.

a. 2-ethyl-1-hexene
b. cyclopentene
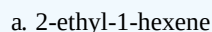
Key Takeaway

- Alkenes are hydrocarbons with a carbon-to-carbon double bond.

8.3: Alkenes and Alkynes is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

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8.4: Hydrocarbon Reactions

> **◐ Learning Objectives**
>
> - To identify the main chemical properties of alkanes.

Alkane molecules are nonpolar and therefore generally do not react with ionic compounds such as most laboratory acids, bases, oxidizing agents, or reducing agents. Consider butane as an example:

$$CH_3CH_2CH_2CH_3 + OH^- \longrightarrow \text{no reaction}$$
$$\text{butane}$$

$$+ H^+ \longrightarrow \text{no reaction}$$
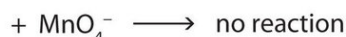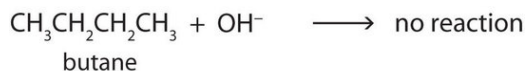
$$+ MnO_4^- \longrightarrow \text{no reaction}$$

Butane plus O H superscript negative sign yields no reaction. There is also no reaction of butane with H superscript positive sign and Mn O subscript 4 superscript negative sign.

Neither positive ions nor negative ions are attracted to a nonpolar molecule. In fact, the alkanes undergo so few reactions that they are sometimes called *paraffins*, from the Latin *parum affinis*, meaning "little affinity."

Two important reactions that the alkanes do undergo are combustion and halogenation. Nothing happens when alkanes are merely mixed with oxygen (O_2) at room temperature, but when a flame or spark provides the activation energy, a highly exothermic combustion reaction proceeds vigorously. For methane (CH_4), the reaction is as follows:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O + \text{heat} \tag{8.4.1}$$

If the reactants are adequately mixed and there is sufficient oxygen, the only products are carbon dioxide (CO_2), water (H_2O), and heat—heat for cooking foods, heating homes, and drying clothes. Because conditions are rarely ideal, however, other products are frequently formed. When the oxygen supply is limited, carbon monoxide (CO) is a by-product:

$$2CH_4 + 3O_2 \rightarrow 2CO + 4H_2O \tag{8.4.2}$$

This reaction is responsible for dozens of deaths each year from unventilated or improperly adjusted gas heaters. (Similar reactions with similar results occur with kerosene heaters.)

Alkanes also react with the halogens chlorine (Cl_2) and bromine (Br_2) in the presence of ultraviolet light or at high temperatures to yield chlorinated and brominated alkanes. For example, chlorine reacts with excess methane (CH_4) to give methyl chloride (CH_3Cl).

$$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl \tag{8.4.3}$$

With more chlorine, a mixture of products is obtained: CH$_3$Cl, CH$_2$Cl$_2$, CHCl$_3$, and CCl$_4$. Fluorine (F_2), the lightest halogen, combines explosively with most hydrocarbons. Iodine (I_2) is relatively unreactive. Fluorinated and iodinated alkanes are produced by indirect methods.

Key Takeaway

- Alkanes react with oxygen (combustion) and with halogens (halogenation).

8.5: Aromatic Hydrocarbons

Benzene, C_6H_6, is the simplest member of a large family of hydrocarbons, called aromatic hydrocarbons. These compounds contain ring structures and exhibit bonding that must be described using the resonance hybrid concept of valence bond theory or the delocalization concept of molecular orbital theory. (To review these concepts, refer to the earlier chapters on chemical bonding). The resonance structures for benzene, C_6H_6, are:
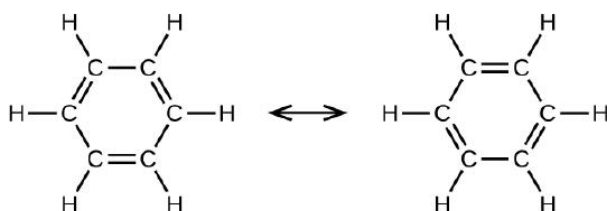
Benzene is shown as a hexagonal ring. There are three double bonds in total. The left structure shows double bonds occupying three sides of the hexagon. A double sided arrow points to the right structure which has three double bonds which occupy the three previously unoccupied sides on the left.

Valence bond theory describes the benzene molecule and other planar aromatic hydrocarbon molecules as hexagonal rings of sp^2-hybridized carbon atoms with the unhybridized p orbital of each carbon atom perpendicular to the plane of the ring. Three valence electrons in the sp^2 hybrid orbitals of each carbon atom and the valence electron of each hydrogen atom form the framework of σ bonds in the benzene molecule. The fourth valence electron of each carbon atom is shared with an adjacent carbon atom in their unhybridized p orbitals to yield the π bonds. Benzene does not, however, exhibit the characteristics typical of an alkene. Each of the six bonds between its carbon atoms is equivalent and exhibits properties that are intermediate between those of a C–C single bond and a $C = C$ double bond. To represent this unique bonding, structural formulas for benzene and its derivatives are typically drawn with single bonds between the carbon atoms and a circle within the ring as shown in Figure $8.5.10$.
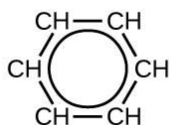
Figure 8.5.10: This condensed formula shows the unique bonding structure of benzene.

A six carbon hexagonal ring structural formula is shown. Each C has an H atom beside it. A circle is at the center of the ring.

There are many derivatives of benzene. The hydrogen atoms can be replaced by many different substituents. Aromatic compounds more readily undergo substitution reactions than addition reactions; replacement of one of the hydrogen atoms with another substituent will leave the delocalized double bonds intact. The following are typical examples of substituted benzene derivatives:
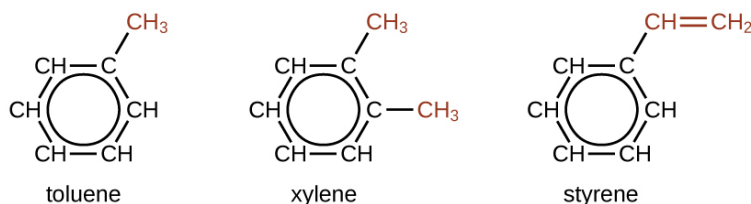
Toluene has one of the H replaced by C H subscript 3 molecule. Xylene has 2 of the H atoms replaced by two C H subscript 3 molecules respectively. Styrene has one of the H atom replaced C H double bond C H subscript 2.

Toluene and xylene are important solvents and raw materials in the chemical industry. Styrene is used to produce the polymer polystyrene.

Structure of Aromatic Hydrocarbons

One possible isomer created by a substitution reaction that replaces a hydrogen atom attached to the aromatic ring of toluene with a chlorine atom is shown here. Draw two other possible isomers in which the chlorine atom replaces a different hydrogen atom attached to the aromatic ring:
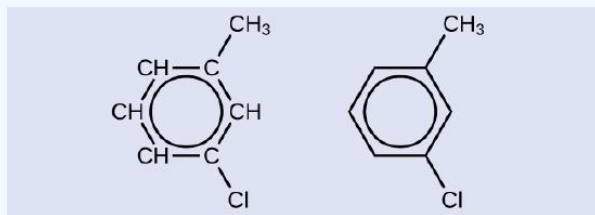
A hexagonal structure of benzene is shown with one of the H replaced by a chlorine atom and another H replaced by C H subscript 3. These two substitutions are apart by 1 carbon atom. Two structures are shown, one shows all the C and H in the ring written out, while the other omits it.

Solution

Since the six-carbon ring with alternating double bonds is necessary for the molecule to be classified as aromatic, appropriate isomers can be produced only by changing the positions of the chloro-substituent relative to the methyl-substituent:
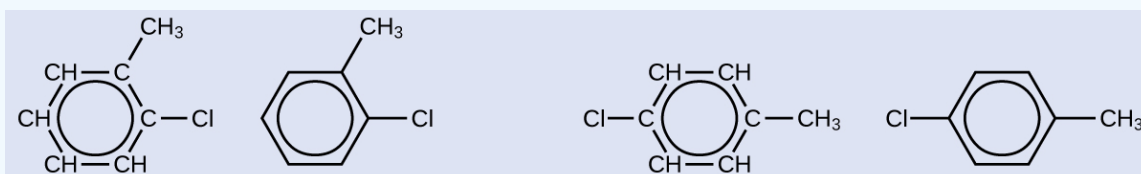
A hexagonal structure of benzene is shown with one of the H replaced by a chlorine atom and another H replaced by C H subscript 3. There are two of these isomers. The first isomer has these two substitutions adjacent to one another while the other are apart by 2 carbons. Two structures are shown for each isomer, one shows all the C and H in the ring written out, while the other omits it.

Exercise 8.5.7

Draw three isomers of a six-membered aromatic ring compound substituted with two bromines.

Answer
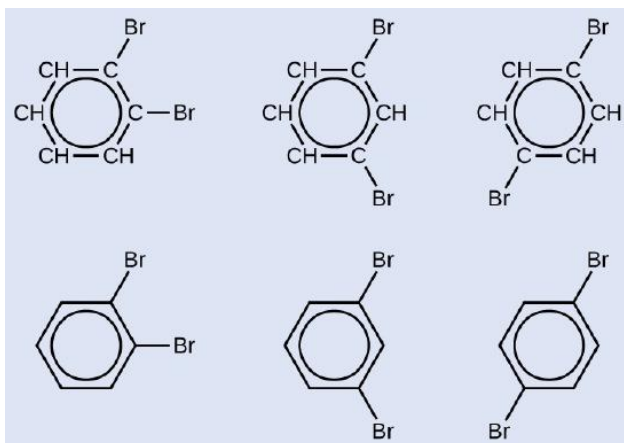
A hexagonal structure of benzene is shown with two of the H replaced by two bromine atoms. Three of these isomers are shown. The first isomer has these two substitutions adjacent to one another, the next isomer has these two bromines 1 carbon apart and the final isomer has two bromines that are two carbons apart. Two structures are shown for each isomer, one shows all the C and H in the ring written out, while the other omits it.

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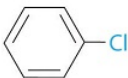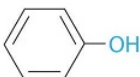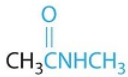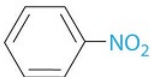
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8.6: Functional Groups

> **◑ Learning Objectives**
>
> - To know the major classes of organic compounds and identify important functional groups.

You were previously introduced to several structural units that chemists use to classify organic compounds and predict their reactivities. These functional groups, which determine the chemical reactivity of a molecule under a given set of conditions, can consist of a single atom (such as Cl) or a group of atoms (such as CO_2H). The major families of organic compounds are characterized by their functional groups. Figure 8.6.1 summarizes five families introduced in earlier chapters, gives examples of compounds that contain each functional group, and lists the suffix or prefix used in the systematic nomenclature of compounds that contain each functional group.

Class	General Formula	Example	Common Name (Systematic Name)	Common Suffix/Prefix (Systematic)
Hydrocarbons				
Alkanes	RH	CH_3CH_3	ethane	-ane
Alkenes	$RR'C{=}CR''R'''$	$H_2C{=}CH_2$	ethylene (ethene)	-ene
Alkynes	$RC{\equiv}CR'$	$HC{\equiv}CH$	acetylene (ethyne)	(-yne)
Arenes	ArH[a]		benzene	-ene
Halogen-Containing Compounds				
Alkyl halides	RX	CH_3CH_2Cl	ethyl chloride (chloroethane)	halide (halo-)
Aryl halides	ArX[a]		chlorobenzene	halo-
Oxygen-Containing Compounds				
Alcohols	ROH[a]	CH_3CH_2OH	ethyl alcohol (ethanol)	-ol
Phenols	ArOH[b]		phenol	-ol
Ethers	ROR'	$H_3CH_2COCH_2CH_3$	diethyl ether	ether
Aldehydes	RCHO		acetaldehyde (ethanal)	-aldehyde (-al)
Ketones	$RR'C{=}O$		acetone (2-propanone)	-one
Carboxylic acids	RCO_2H		acetic acid (ethanoic acid)	-ic acid (-oic acid)
Carboxylic Acid Derivatives				
Esters	RCO_2R'		methyl acetate (methyl ethanoate)	-ate (-oate)
Amides	RCONHR'		N-methylacetamide	-amide
Nitrogen-Containing Compounds				
Amines	RNH_2, RNHR', RNR'R''	$CH_3CH_2NH_2$	ethylamine	-amine
Nitriles	$RC{\equiv}N$	$H_3CC{\equiv}N$	acetonitrile	-nitrile
Nitro compounds	$ArNO_2$[a]		nitrobenzene	nitro-

Figure 8.6.1: Major Classes of Organic Compounds

The first family listed in Figure 8.6.1 is the hydrocarbons. These include alkanes, with the general molecular formula C_nH_{2n+2} where n is an integer; alkenes, represented by C_nH_{2n}; alkynes, represented by C_nH_{2n-2}; and arenes. Halogen-substituted alkanes, alkenes, and arenes form a second major family of organic compounds, which include the alkyl halides and the aryl halides. Oxygen-containing organic compounds, a third family, may be divided into two main types: those that contain at least one C–O bond, which include alcohols, phenols (derivatives of benzene), and ethers, and those that contain a carbonyl group (C=O), which include aldehydes, ketones, and carboxylic acids. Carboxylic acid derivatives, the fourth family listed, are compounds in which the OH of the –CO_2H functional group is replaced by either an alkoxy (–OR) group, producing an ester, or by an amido (–NRR′, where R and R′ can be H and/or alkyl groups), forming an amide. Nitrogen-containing organic compounds, the fifth family, include amines; nitriles, which have a C≡N bond; and nitro compounds, which contain the –NO_2 group.

The systematic nomenclature of organic compounds indicates the positions of substituents using the lowest numbers possible to identify their locations in the carbon chain of the parent compound. If two compounds have the same systematic name, then they are the same compound. Although systematic names are preferred because they are unambiguous, many organic compounds are known by their common names rather than their systematic names. Common nomenclature uses the prefix form—for a compound that contains no carbons other than those in the functional group, and acet—for those that have one carbon atom in addition [two in the case of acetone, $(CH_3)_2$C=O]. Thus methanal and ethanal, respectively, are the systematic names for formaldehyde and acetaldehyde.
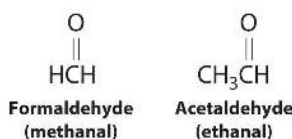
Recall that in the systematic nomenclature of aromatic compounds, the positions of groups attached to the aromatic ring are indicated by numbers, starting with 1 and proceeding around the ring in the direction that produces the lowest possible numbers. For example, the position of the first CH_3 group in dimethyl benzene is indicated with a 1, but the second CH_3 group, which can be placed in any one of three positions, produces 1,2-dimethylbenzene, 1,3-dimethylbenzene, or 1,4-dimethylbenzene (Figure 8.6.2). In common nomenclature, in contrast, the prefixes ortho-, meta-, and para- are used to describe the relative positions of groups attached to an aromatic ring. If the CH_3 groups in dimethylbenzene, whose common name is xylene, are adjacent to each other, the compound is commonly called ortho-xylene, abbreviated o-xylene. If they are across from each other on the ring, the compound is commonly called para-xylene or p-xylene. When the arrangement is intermediate between those of ortho- and para- compounds, the name is meta-xylene or m-xylene.

Figure 8.6.2: Common Nomenclature for Aromatic Ring Substitutions

We begin our discussion of the structure and reactivity of organic compounds by exploring structural variations in the simple saturated hydrocarbons known as alkanes. These compounds serve as the scaffolding to which the various functional groups are most often attached.

Summary

Functional groups determine the chemical reactivity of an organic molecule. Functional groups are structural units that determine the chemical reactivity of a molecule under a given set of conditions. Organic compounds are classified into several major categories based on the functional groups they contain. In the systematic names of organic compounds, numbers indicate the positions of functional groups in the basic hydrocarbon framework. Many organic compounds also have common names, which use the prefix form—for a compound that contains no carbons other than those in the functional group and acet—for those that have one additional carbon atom.

Conceptual Problems

1. Can two substances have the same systematic name and be different compounds?
2. Is a carbon–carbon multiple bond considered a functional group?

8.7: Alcohols

> ◗ **Learning Objectives**
>
> - Identify the general structure for an alcohol.
> - Identify the structural feature that classifies alcohols as primary, secondary, or tertiary.
> - Name alcohols with both common names and IUPAC names

An alcohol is an organic compound with a hydroxyl (OH) functional group on an aliphatic carbon atom. Because OH is the functional group of all alcohols, we often represent alcohols by the general formula ROH, where R is an alkyl group. Alcohols are common in nature. Most people are familiar with ethyl alcohol (ethanol), the active ingredient in alcoholic beverages, but this compound is only one of a family of organic compounds known as alcohols. The family also includes such familiar substances as cholesterol and the carbohydrates. Methanol (CH_3OH) and ethanol (CH_3CH_2OH) are the first two members of the homologous series of alcohols.

Nomenclature of Alcohols

Alcohols with one to four carbon atoms are frequently called by common names, in which the name of the alkyl group is followed by the word *alcohol*:

CH_3OH CH_3CH_2OH $CH_3CH_2CH_2OH$ CH_3CHOH
                                                                                    |
                                                                                  CH_3

Methyl alcohol   Ethyl alcohol   Propyl alcohol   Isopropyl alcohol
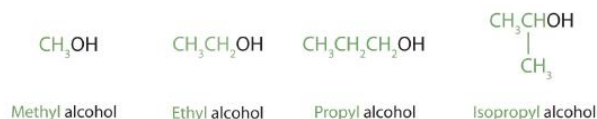
Structural formula of methyl alcohol, ethyl alcohol, propyl alcohol, and isopropyl alcohol with the methyl, ethyl propyl, and isopropyl groups highlighted in green.

According to the International Union of Pure and Applied Chemistry (IUPAC), alcohols are named by changing the ending of the parent alkane name to *-ol*. Here are some basic IUPAC rules for naming alcohols:

1. The longest continuous chain (LCC) of carbon atoms containing the OH group is taken as the parent compound—an alkane with the same number of carbon atoms. The chain is numbered from the end nearest the OH group.
2. The number that indicates the position of the OH group is prefixed to the name of the parent hydrocarbon, and the *-e* ending of the parent alkane is replaced by the suffix *-ol*. (In cyclic alcohols, the carbon atom bearing the OH group is designated C1, but the 1 is not used in the name.) Substituents are named and numbered as in alkanes.
3. If more than one OH group appears in the same molecule (polyhydroxy alcohols), suffixes such as *-diol* and *-triol* are used. In these cases, the *-e* ending of the parent alkane is retained.

Figure $8.7.1$ shows some examples of the application of these rules.

Structures of 2 methylbutan-2-ol, 3 5-dimethylhexan-1-ol, 6 methylheptan-3-ol, 2 bromo 5 chlorocyclopentanol are shown to highlight rules 1 and 2. 1 2 ethanediol and propane 1 2 3 triol are shown to highlight rule 3
Figure 8.7.1: IUPAC Rules for Alcohols. The names and structures of some alcohols demonstrate the use of IUPAC rules.

> ✔ **Example 8.7.1**
>
> Give the IUPAC name for each compound.
>
> a.
> $CH_3CH_2CHCH_2CHCH_2CH_2CHCH_2CH_3$
> | | |
> CH_3 CH_3 OH
>
> From left to right, there are ten carbon on the alkane straight chain with methyl groups emerging from carbon 3 and 5 and a hydroxyl group on carbon 8.
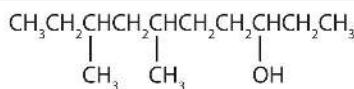
- $HOCH_2CH_2CH_2CH_2CH_2OH$

Solution

a. Ten carbon atoms in the LCC makes the compound a derivative of decane (rule 1), and the OH on the third carbon atom makes it a 3-decanol (rule 2).

$$\overset{10}{C}H_3\overset{9}{C}H_2\overset{8}{C}H\overset{7}{C}H_2\overset{6}{C}H\overset{5}{C}H_2\overset{4}{C}H_2\overset{3}{C}H\overset{2}{C}H_2\overset{1}{C}H_3$$

with CH₃ on C8, CH₃ on C6, and OH on C3.
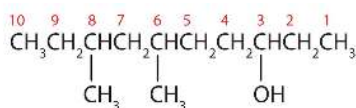
The carbon atoms are numbered from the end closest to the OH group. That fixes the two methyl (CH₃) groups at the sixth and eighth positions. The name is 6,8-dimethyl-3-decanol (not 3,5-dimethyl-8-decanol).

b. Five carbon atoms in the LCC make the compound a derivative of pentane. Two OH groups on the first and fifth carbon atoms make the compound a diol and give the name 1,5-pentanediol (rule 3).

$$\overset{1}{H}OC H_2\overset{2}{C}H_2\overset{3}{C}H_2\overset{4}{C}H_2\overset{5}{C}H_2OH$$
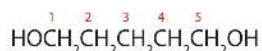
? Exercise 8.7.1

Give the IUPAC name for each compound.

a.
$$CH_3CHCH_2OH$$
with OH on the middle carbon.

-
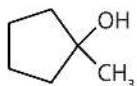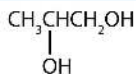
✔ Example 8.7.2

Draw the structure for each compound.

a. 2-hexanol
b. 3-methyl-2-pentanol

Solution

a. The ending *-ol* indicates an alcohol (the OH functional group), and the *hex-* stem tells us that there are six carbon atoms in the LCC. We start by drawing a chain of six carbon atoms: –C–C–C–C–C–C–.

The 2 indicates that the OH group is attached to the second carbon atom.

$$-C-C-C-C-C-C-$$
with OH on the second carbon.
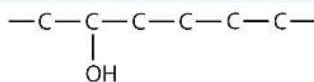
Finally, we add enough hydrogen atoms to give each carbon atom four bonds.

$$CH_3CHCH_2CH_2CH_2CH_3$$
with OH on the second carbon.
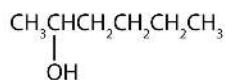
- The numbers indicate that there is a methyl (CH₃) group on the third carbon atom and an OH group on the second carbon atom.

$$CH_3CH-CHCH_2CH_3$$
with OH and CH₃.
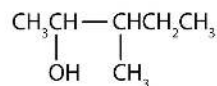
? Exercise 8.7.2

Draw the structure for each compound.

a. 3-heptanol

- 2-methyl-3-hexanol

Classification of Alcohols

Some of the properties of alcohols depend on the number of carbon atoms attached to the specific carbon atom that is attached to the OH group. Alcohols can be grouped into three classes on this basis.

- A primary (1°) alcohol is one in which the carbon atom (in red) with the OH group is attached to *one* other carbon atom (in blue). Its general formula is RCH_2OH.

$$R - \overset{\displaystyle H}{\underset{\displaystyle H}{C}} - OH$$

- A secondary (2°) alcohol is one in which the carbon atom (in red) with the OH group is attached to *two* other carbon atoms (in blue). Its general formula is R_2CHOH.

$$R - \overset{\displaystyle R}{\underset{\displaystyle H}{C}} - OH$$
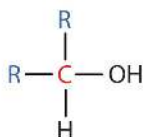
- A tertiary (3°) alcohol is one in which the carbon atom (in red) with the OH group is attached to *three* other carbon atoms (in blue). Its general formula is R_3COH.

$$R - \overset{\displaystyle R}{\underset{\displaystyle R}{C}} - OH$$
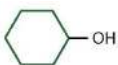
Table 8.7.1 names and classifies some of the simpler alcohols. Some of the common names reflect a compound's classification as secondary (*sec-*) or tertiary (*tert-*). These designations are not used in the IUPAC nomenclature system for alcohols. Note that there are four butyl alcohols in the table, corresponding to the four butyl groups: the butyl group ($CH_3CH_2CH_2CH_2$) discussed before, and three others:

$$CH_3CHCH_2- \atop {\underset{\displaystyle CH_3}{|}} \qquad CH_3CHCH_2CH_3 \atop {\underset{\displaystyle |}{}} \qquad CH_3C- \atop {\overset{\displaystyle |}{\underset{\displaystyle CH_3}{}}{}^{\overset{\displaystyle CH_3}{|}}}$$

Isobutyl group   *Sec*-butyl group   *Tert*-butyl group

Table 8.7.1: Classification and Nomenclature of Some Alcohols

Condensed Structural Formula	Class of Alcohol	Common Name	IUPAC Name
CH_3OH	—	methyl alcohol	methanol
CH_3CH_2OH	primary	ethyl alcohol	ethanol
$CH_3CH_2CH_2OH$	primary	propyl alcohol	1-propanol
$(CH_3)_2CHOH$	secondary	isopropyl alcohol	2-propanol
$CH_3CH_2CH_2CH_2OH$	primary	butyl alcohol	1-butanol

Condensed Structural Formula	Class of Alcohol	Common Name	IUPAC Name
$CH_3CH_2CHOHCH_3$	secondary	*sec*-butyl alcohol	2-butanol
$(CH_3)_2CHCH_2OH$	primary	isobutyl alcohol	2-methyl-1-propanol
$(CH_3)_3COH$	tertiary	*tert*-butyl alcohol	2-methyl-2-propanol
⬡—OH	secondary	cyclohexyl alcohol	cyclohexanol

Summary

In the IUPAC system, alcohols are named by changing the ending of the parent alkane name to *-ol*. Alcohols are classified according to the number of carbon atoms attached to the carbon atom that is attached to the OH group.

> **Learning Objectives**
> - Explain why the boiling points of alcohols are higher than those of ethers and alkanes of similar molar masses.
> - Explain why alcohols and ethers of four or fewer carbon atoms are soluble in water while comparable alkanes are not soluble.

Alcohols can be considered derivatives of water (H_2O; also written as HOH).

Like the H–O–H bond in water, the R–O–H bond is bent, and alcohol molecules are polar. This relationship is particularly apparent in small molecules and reflected in the physical and chemical properties of alcohols with low molar mass. Replacing a hydrogen atom from an alkane with an OH group allows the molecules to associate through hydrogen bonding (Figure 8.7.1).
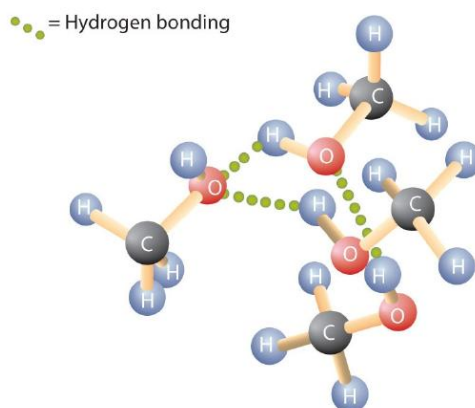
Figure 8.7.1: Intermolecular Hydrogen Bonding in Methanol. The OH groups of alcohol molecules make hydrogen bonding possible.

Recall that physical properties are determined to a large extent by the type of intermolecular forces. Table 8.7.1 lists the molar masses and the boiling points of some common compounds. The table shows that substances with similar molar masses can have quite different boiling points.

Table 8.7.1: Comparison of Boiling Points and Molar Masses

Formula	Name	Molar Mass	Boiling Point (°C)
CH_4	methane	16	−164
HOH	water	18	100

Formula	Name	Molar Mass	Boiling Point (°C)
C_2H_6	ethane	30	–89
CH_3OH	methanol	32	65
C_3H_8	propane	44	–42
CH_3CH_2OH	ethanol	46	78
C_4H_{10}	butane	58	–1
$CH_3CH_2CH_2OH$	1-propanol	60	97

Alkanes are nonpolar and are thus associated only through relatively weak dispersion forces. Alkanes with one to four carbon atoms are gases at room temperature. In contrast, even methanol (with one carbon atom) is a liquid at room temperature. Hydrogen bonding greatly increases the boiling points of alcohols compared to hydrocarbons of comparable molar mass. The boiling point is a rough measure of the amount of energy necessary to separate a liquid molecule from its nearest neighbors. If the molecules interact through hydrogen bonding, a relatively large quantity of energy must be supplied to break those intermolecular attractions. Only then can the molecule escape from the liquid into the gaseous state.

Alcohols can also engage in hydrogen bonding with water molecules (Figure 8.7.2). Thus, whereas the hydrocarbons are insoluble in water, alcohols with one to three carbon atoms are completely soluble. As the length of the chain increases, however, the solubility of alcohols in water decreases; the molecules become more like hydrocarbons and less like water. The alcohol 1-decanol ($CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2OH$) is essentially insoluble in water. We frequently find that the borderline of solubility in a family of organic compounds occurs at four or five carbon atoms.
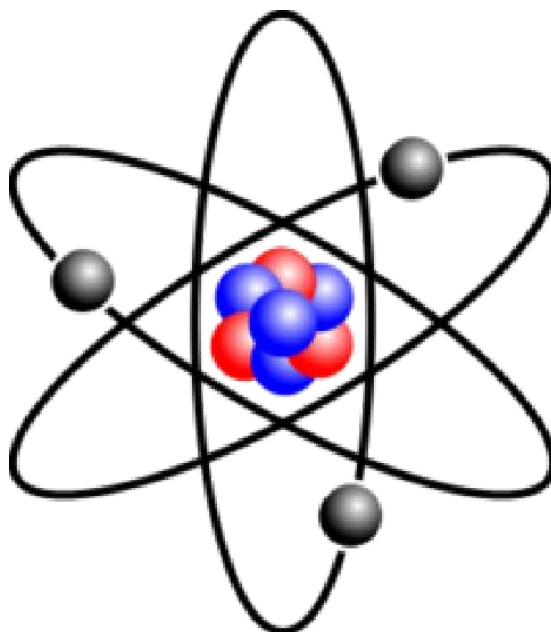
Figure 8.7.2: Hydrogen Bonding between Methanol Molecules and Water Molecules. Hydrogen bonding between the OH of methanol and water molecules accounts for the solubility of methanol in water.

Summary

Alcohols have higher boiling points than do ethers and alkanes of similar molar masses because the OH group allows alcohol molecules to engage in hydrogen bonding. Alcohols of four or fewer carbon atoms are soluble in water because the alcohol molecules engage in hydrogen bonding with water molecules; comparable alkane molecules cannot engage in hydrogen bonding.

> **◐ Learning Objectives**
>
> 1. Give two major types of reactions of alcohols.
> 2. Describe the result of the oxidation of a primary alcohol.
> 3. Describe the result of the oxidation of a secondary alcohol.

Chemical reactions in alcohols occur mainly at the functional group, but some involve hydrogen atoms attached to the OH-bearing carbon atom or to an adjacent carbon atom. Of the three major kinds of alcohol reactions, which are summarized in Figure 8.7.1, two—dehydration and oxidation—are considered here. The third reaction type—esterification—is covered elsewhere.
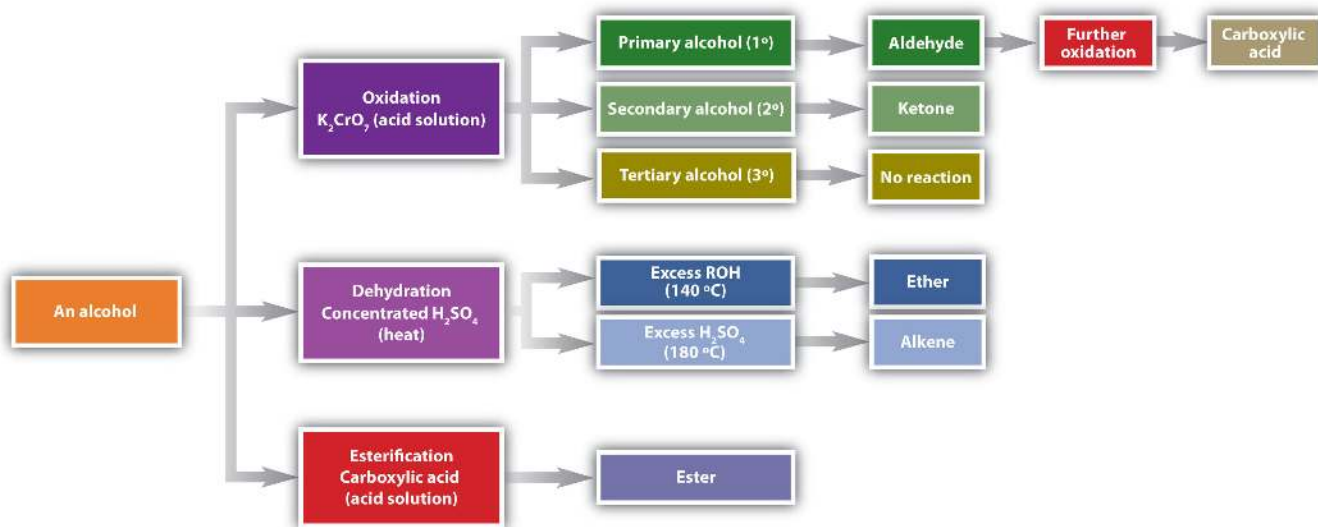
Figure 8.7.1: Reactions of Alcohols. Oxidation and dehydration of alcohols are considered here.

A flow diagram of three possible reactions of an alcohol. The final products of the reactions are also shown at the end of the flow diagram.

Dehydration

As noted in Figure 8.7.1, an alcohol undergoes dehydration in the presence of a catalyst to form an alkene and water. The reaction removes the OH group from the alcohol carbon atom and a hydrogen atom from an adjacent carbon atom in the same molecule:
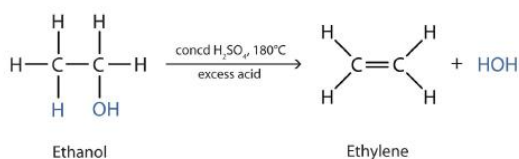
Structural formula of ethanol dehydrating under excess concentrated sulfuric acid at 180 degrees celsius. The products are ethylene and a side product of a water molecule.

Under the proper conditions, it is possible for the dehydration to occur between *two* alcohol molecules. The entire OH group of one molecule and only the hydrogen atom of the OH group of the second molecule are removed. The two ethyl groups attached to an oxygen atom form an ether molecule.
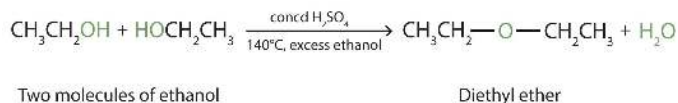
Two molecules of ethanol are dehydrated under concentrated sulfuric acid at 140 degrees celsius and excess ethanol to give a diethyl ether and a water molecule.

([Ethers are discussed in elsewhere](#)) Thus, depending on conditions, one can prepare either alkenes or ethers by the dehydration of alcohols.

Both dehydration and hydration reactions occur continuously in cellular metabolism, with enzymes serving as catalysts and at a temperature of about 37°C. The following reaction occurs in the "Embden–Meyerhof" pathway

2-Phosphoglycerate   Phosphoenolpyruvate
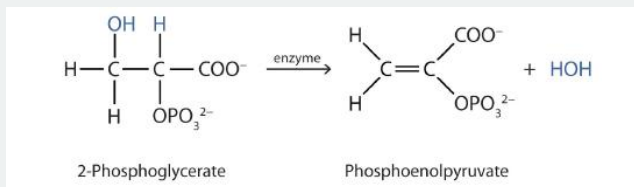
Structural formula of 2 phosphoglycerate forming phosphoenolpyruvate and a water molecule with the aid of enzymes.

Although the participating compounds are complex, the reaction is the same: elimination of water from the starting material. The idea is that if you know the chemistry of a particular functional group, you know the chemistry of hundreds of different compounds.

Oxidation

Primary and secondary alcohols are readily oxidized. We saw earlier how methanol and ethanol are oxidized by liver enzymes to form aldehydes. Because a variety of oxidizing agents can bring about oxidation, we can indicate an oxidizing agent without specifying a particular one by writing an equation with the symbol [O] above the arrow. For example, we write the oxidation of ethanol—a primary alcohol—to form acetaldehyde—an aldehyde—as follows:

Ethanol   Acetaldehyde
(a primary alcohol)   (an aldehyde)
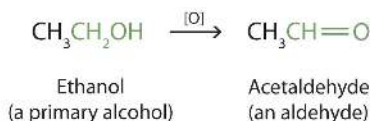
Formula of ethanol reacting to form acetaldehyde with an O in a bracket above the right pointing arrow.

We shall see that aldehydes are even more easily oxidized than alcohols and yield carboxylic acids. Secondary alcohols are oxidized to *ketones*. The oxidation of isopropyl alcohol by potassium dichromate ($K_2Cr_2O_7$) gives acetone, the simplest ketone:

Isopropyl alcohol   Acetone
(a secondary alcohol)   (a ketone)
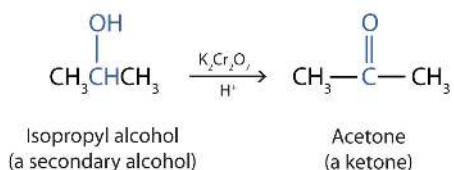
Unlike aldehydes, ketones are relatively resistant to further oxidation, so no special precautions are required to isolate them as they form. Note that in oxidation of both primary (RCH_2OH) and secondary (R_2CHOH) alcohols, two hydrogen atoms are removed from the alcohol molecule, one from the OH group and other from the carbon atom that bears the OH group.

These reactions can also be carried out in the laboratory with chemical oxidizing agents. One such oxidizing agent is potassium dichromate. The balanced equation (showing only the species involved in the reaction) in this case is as follows:

$$8\,H^= + Cr_2O_7^{2-} + 3\,CH_3CH_2OH \longrightarrow 3\,CH_3CHO + 2\,Cr^{3+} + 7\,H_2O$$
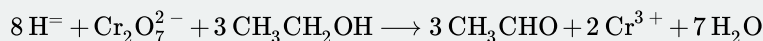
Alcohol oxidation is important in living organisms. Enzyme-controlled oxidation reactions provide the energy cells need to do useful work. One step in the metabolism of carbohydrates involves the oxidation of the secondary alcohol group in isocitric acid to a ketone group:

Isocitrate   enzyme →   Oxalosuccinate
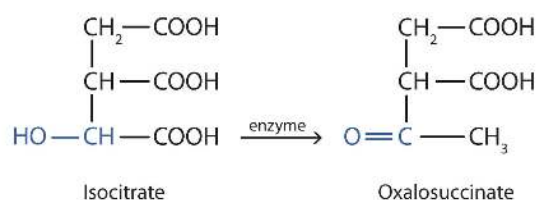
The overall type of reaction is the same as that in the conversion of isopropyl alcohol to acetone.

Tertiary alcohols (R_3COH) are resistant to oxidation because the carbon atom that carries the OH group does not have a hydrogen atom attached but is instead bonded to other carbon atoms. The oxidation reactions we have described involve the formation of a carbon-to-oxygen double bond. Thus, the carbon atom bearing the OH group must be able to release one of its attached atoms to form the double bond. The carbon-to-hydrogen bonding is easily broken under oxidative conditions, but carbon-to-carbon bonds are not. Therefore tertiary alcohols are not easily oxidized.

✔ **Example 8.7.1**

Write an equation for the oxidation of each alcohol. Use [O] above the arrow to indicate an oxidizing agent. If no reaction occurs, write "no reaction" after the arrow.

a. $CH_3CH_2CH_2CH_2CH_2OH$
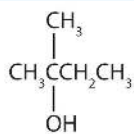
b.

From left to right, there are four carbons on the alkane straight chain with a methyl and hydroxyl group on carbon 2.
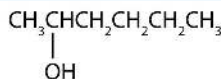
c.

From left to right, there are six carbons on the alkane straight chain with a hydroxyl group on carbon 2.

Solution

The first step is to recognize the class of each alcohol as primary, secondary, or tertiary.

a. This alcohol has the OH group on a carbon atom that is attached to only *one* other carbon atom, so it is a primary alcohol. Oxidation forms first an aldehyde and further oxidation forms a carboxylic acid.
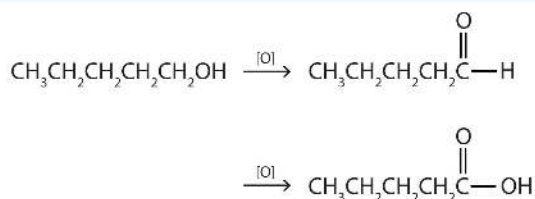
b. This alcohol has the OH group on a carbon atom that is attached to three other carbon atoms, so it is a tertiary alcohol. No
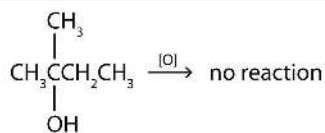
reaction occurs.

c. This alcohol has the OH group on a carbon atom that is attached to two other carbon atoms, so it is a secondary alcohol;
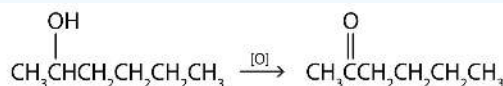
oxidation gives a ketone.

? Exercise 8.7.1

Write an equation for the oxidation of each alcohol. Use [O] above the arrow to indicate an oxidizing agent. If no reaction occurs, write "no reaction" after the arrow.

a.

$$\underset{\underset{CH_3}{|}}{\overset{\overset{OH}{|}}{CH_3CH_2CCH_2CH_2CH_3}}$$
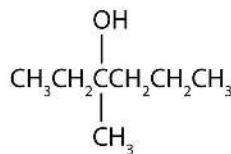
From left to right, there are six carbons on the alkane straight chain with a hydroxyl group and methyl group on carbon 3.

b.
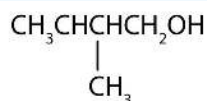
$$\underset{\underset{CH_3}{|}}{CH_3CHCHCH_2OH}$$

From left to right, there are four carbons on the alkane straight chain with a methyl group on carbon 3 as well as a hydroxyl group on carbon 4.

c.
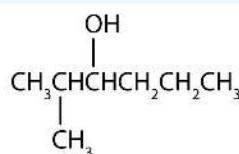
$$\underset{\underset{CH_3}{|}}{\overset{\overset{OH}{|}}{CH_3CHCHCH_2CH_2CH_3}}$$

From left to right, there are six carbons on the alkane straight chain with a methyl group on carbon 2 and a hydroxyl group on carbon 3.

Summary

Alcohols can be dehydrated to form either alkenes (higher temperature, excess acid) or ethers (lower temperature, excess alcohol). Primary alcohols are oxidized to form aldehydes. Secondary alcohols are oxidized to form ketones. Tertiary alcohols are not readily oxidized.

8.8: Aldehydes and Ketones

> ### ◑ Learning Objectives
>
> - Identify the general structure for an aldehyde and a ketone.
> - Use common names to name aldehydes and ketones.
> - Use the IUPAC system to name aldehydes and ketones.

The next functional group we consider, the carbonyl group, has a carbon-to-oxygen double bond.

$$\overset{\displaystyle O}{\underset{\displaystyle }{\underset{|}{\overset{\|}{-C-}}}}$$

Carbonyl groups define two related families of organic compounds: the aldehydes and the ketones.

> *The carbonyl group is ubiquitous in biological compounds. It is found in carbohydrates, fats, proteins, nucleic acids, hormones, and vitamins—organic compounds critical to living systems.*

In a ketone, two carbon groups are attached to the carbonyl carbon atom. The following general formulas, in which R represents an alkyl group and Ar stands for an aryl group, represent ketones.

$$R-\overset{O}{\overset{\|}{C}}-R \qquad Ar-\overset{O}{\overset{\|}{C}}-R \qquad Ar-\overset{O}{\overset{\|}{C}}-Ar$$

In an aldehyde, at least one of the attached groups must be a hydrogen atom. The following compounds are aldehydes:

$$H-\overset{O}{\overset{\|}{C}}-H \qquad R-\overset{O}{\overset{\|}{C}}-H \qquad Ar-\overset{O}{\overset{\|}{C}}-H$$

In condensed formulas, we use CHO to identify an aldehyde rather than COH, which might be confused with an alcohol. This follows the general rule that in condensed structural formulas H comes after the atom it is attached to (usually C, N, or O).

$$—CHO \qquad\qquad\qquad —CO—$$

An aldehyde A ketone

The carbon-to-oxygen double bond is not shown but understood to be present. Because they contain the same functional group, aldehydes and ketones share many common properties, but they still differ enough to warrant their classification into two families.

Naming Aldehydes and Ketones

Both common and International Union of Pure and Applied Chemistry (IUPAC) names are frequently used for aldehydes and ketones, with common names predominating for the lower homologs. The common names of aldehydes are taken from the names of the acids into which the aldehydes can be converted by *oxidation*.

$$H-\overset{\displaystyle O}{\overset{\|}{C}}-H \xrightarrow{[O]} H-\overset{\displaystyle O}{\overset{\|}{C}}-OH$$

Formaldehyde   Formic acid

$$CH_3-\overset{\displaystyle O}{\overset{\|}{C}}-H \xrightarrow{[O]} CH_3-\overset{\displaystyle O}{\overset{\|}{C}}-OH$$

Acetaldehyde   Acetic acid
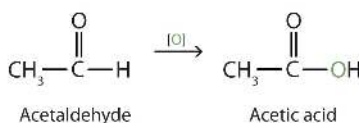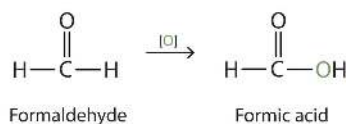
The stems for the common names of the first four aldehydes are as follows:

- 1 carbon atom: *form-*
- 2 carbon atoms: *acet-*
- 3 carbon atoms: *propion-*
- 4 carbon atoms: *butyr-*

Because the carbonyl group in a ketone must be attached to two carbon groups, the simplest ketone has three carbon atoms. It is widely known as *acetone*, a unique name unrelated to other common names for ketones.

$$CH_3-\overset{\displaystyle O}{\overset{\|}{C}}-CH_3$$
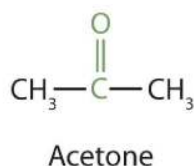
Acetone

Generally, the common names of ketones consist of the names of the groups attached to the carbonyl group, followed by the word *ketone*. (Note the similarity to the naming of ethers.) Another name for acetone, then, is *dimethyl ketone*. The ketone with four carbon atoms is ethyl methyl ketone.

$$CH_3-\overset{\displaystyle O}{\overset{\|}{C}}-CH_2CH_3$$

Ethyl methyl ketone
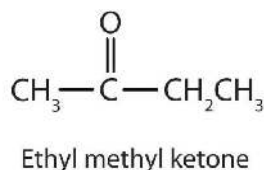
✔ **Example 8.8.1**

Classify each compound as an aldehyde or a ketone. Give the common name for each ketone.

a. $CH_3CH_2CH_2-\overset{\displaystyle O}{\overset{\|}{C}}-H$

b. $CH_3CH_2CH_2-\overset{\displaystyle O}{\overset{\|}{C}}-CH_2CH_2CH_3$

c. $CH_3-\overset{\displaystyle O}{\overset{\|}{C}}-\overset{\displaystyle CH_3}{\overset{|}{C}HCH_3}$

Solution
a. This compound has the carbonyl group on an end carbon atom, so it is an aldehyde.
b. This compound has the carbonyl group on an interior carbon atom, so it is a ketone. Both alkyl groups are propyl groups. The name is therefore dipropyl ketone.

c. This compound has the carbonyl group between two alkyl groups, so it is a ketone. One alkyl group has three carbon atoms and is attached by the middle carbon atom; it is an isopropyl group. A group with one carbon atom is a methyl group. The name is therefore isopropyl methyl ketone.

? Exercise 8.8.1

Classify each compound as an aldehyde or a ketone. Give the common name for each ketone.

1. $CH_3CH_2CH_2 - \overset{\overset{\displaystyle O}{\|}}{C} - CH_2CH_3$

2. $CH_3CH_2\overset{\overset{\displaystyle CH_3}{|}}{CH} - \overset{\overset{\displaystyle O}{\|}}{C} - H$

3. (cyclobutyl)$- \overset{\overset{\displaystyle O}{\|}}{C} - CH_3$
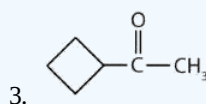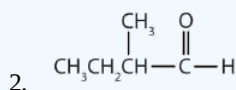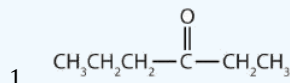
Here are some simple IUPAC rules for naming aldehydes and ketones:

- The stem names of aldehydes and ketones are derived from those of the parent alkanes, defined by the longest continuous chain (LCC) of carbon atoms that contains the functional group.
- For an aldehyde, drop the *-e* from the alkane name and add the ending *-al*. Methanal is the IUPAC name for formaldehyde, and ethanal is the name for acetaldehyde.
- For a ketone, drop the *-e* from the alkane name and add the ending *-one*. Propanone is the IUPAC name for acetone, and butanone is the name for ethyl methyl ketone.
- To indicate the position of a substituent on an aldehyde, the carbonyl carbon atom is always considered to be C1; it is unnecessary to designate this group by number.
- To indicate the position of a substituent on a ketone, number the chain in the manner that gives the carbonyl carbon atom the lowest possible number. In cyclic ketones, it is understood that the carbonyl carbon atom is C1.

✔ Example 8.8.2

Give the IUPAC name for each compound.

a. $CH_3CH_2CH_2\overset{\overset{\displaystyle CH_3}{|}}{CH} - \overset{\overset{\displaystyle O}{\|}}{C} - H$

b. $CH_3\overset{\overset{\displaystyle CH_3}{|}}{CH} - \overset{\overset{\displaystyle O}{\|}}{C} - \overset{\overset{\displaystyle CH_3}{|}}{CH}CH_3$

c. (cyclohexane ring)$=O$
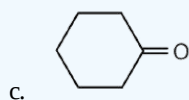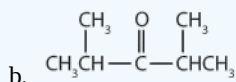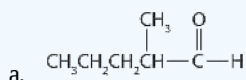
Solution

a. There are five carbon atoms in the LCC. The methyl group (CH_3) is a substituent on the second carbon atom of the chain; the aldehyde carbon atom is always C1. The name is derived from pentane. Dropping the *-e* and adding the ending *-al* gives pentanal. The methyl group on the second carbon atom makes the name 2-methylpentanal.

b. There are five carbon atoms in the LCC. The carbonyl carbon atom is C3, and there are methyl groups on C2 and C4. The IUPAC name is 2,4-dimethyl-3-pentanone.

c. There are six carbon atoms in the ring. The compound is cyclohexanone. No number is needed to indicate the position of the carbonyl group because all six carbon atoms are equivalent.

? Exercise

Give the IUPAC name for each compound.

a.
$$CH_3CCH_2C-H$$
with CH_3 and O above, CH_3 below

b.
$$CH_3CH-C-CH_2CH_2CH_3$$
with CH_3 and O above

c.
(cyclobutane ring with =O)
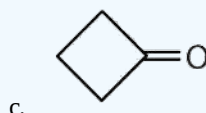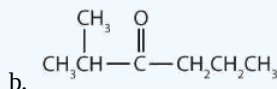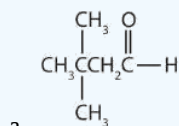
✔ Example 8.8.3

Draw the structure for each compound.

a. 7-chlorooctanal
b. 4-methyl–3-hexanone

Solution

a. The *octan-* part of the name tells us that the LCC has eight carbon atoms. There is a chlorine (Cl) atom on the seventh carbon atom; numbering from the carbonyl group and counting the carbonyl carbon atom as C1, we place the Cl atom on the seventh carbon atom.

$$CH_3CHCH_2CH_2CH_2CH_2CH_2CHO$$
with Cl below
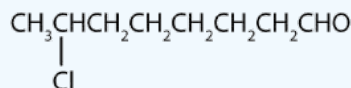
b. The *hexan-* part of the name tells us that the LCC has six carbon atoms. The 3 means that the carbonyl carbon atom is C3 in this chain, and the 4 tells us that there is a methyl (CH_3) group at C4:

$$CH_3CH_2-C-CHCH_2CH_3$$
with O and CH_3 above
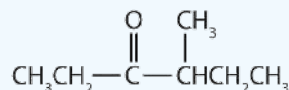
? Exercise 8.8.3

Draw the structure for each compound.

a. 5-bromo-3-iodoheptanal
b. 5-bromo-4-ethyl-2-heptanone

Summary

The common names of aldehydes are taken from the names of the corresponding carboxylic acids: formaldehyde, acetaldehyde, and so on. The common names of ketones, like those of ethers, consist of the names of the groups attached to the carbonyl group, followed by the word *ketone*. Stem names of aldehydes and ketones are derived from those of the parent alkanes, using an *-al* ending for an aldehydes and an *-one* ending for a ketone.

The carbon-to-oxygen double bond is quite polar, more polar than a carbon-to-oxygen single bond. The electronegative oxygen atom has a much greater attraction for the bonding electron pairs than does the carbon atom. The carbon atom has a partial positive charge, and the oxygen atom has a partial negative charge:
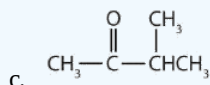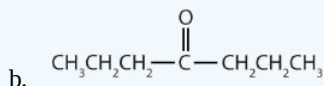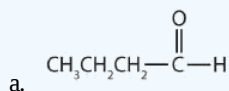
$$\begin{array}{c} R \\ \diagdown \\ \delta + \ C = O \ \delta - \\ \diagup \\ R \end{array}$$
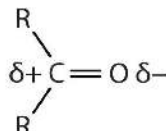
In aldehydes and ketones, this charge separation leads to dipole-dipole interactions that are great enough to significantly affect the boiling points. Table 8.8.1 shows that the polar single bonds in ethers have little such effect, whereas hydrogen bonding between alcohol molecules is even stronger.

Table 8.8.1: Boiling Points of Compounds Having Similar Molar Masses but Different Types of Intermolecular Forces

Compound	Family	Molar Mass	Type of Intermolecular Forces	Boiling Point (°C)
$CH_3CH_2CH_2CH_3$	alkane	58	dispersion only	−1
$CH_3OCH_2CH_3$	ether	60	weak dipole	6
CH_3CH_2CHO	aldehyde	58	strong dipole	49
$CH_3CH_2CH_2OH$	alcohol	60	hydrogen bonding	97

Formaldehyde is a gas at room temperature. Acetaldehyde boils at 20°C; in an open vessel, it boils away in a warm room. Most other common aldehydes are liquids at room temperature.

Although the lower members of the homologous series have pungent odors, many higher aldehydes have pleasant odors and are used in perfumes and artificial flavorings. As for the ketones, acetone has a pleasant odor, but most of the higher homologs have rather bland odors.

The oxygen atom of the carbonyl group engages in hydrogen bonding with a water molecule.

$$\begin{array}{ccc} R & & H \\ | & & | \\ R - C = O \cdots H - O \end{array}$$
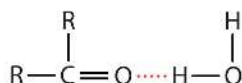
The solubility of aldehydes is therefore about the same as that of alcohols and ethers. Formaldehyde, acetaldehyde, and acetone are soluble in water. As the carbon chain increases in length, solubility in water decreases. The borderline of solubility occurs at about four carbon atoms per oxygen atom. All aldehydes and ketones are soluble in organic solvents and, in general, are less dense than water.

Oxidation of Aldehydes and Ketones

Aldehydes and ketones are much alike in many of their reactions, owing to the presence of the carbonyl functional group in both. They differ greatly, however, in one most important type of reaction: oxidation. Aldehydes are readily oxidized to carboxylic acids, whereas ketones resist oxidation.

An aldehyde → A carboxylic acid

A ketone → no reaction
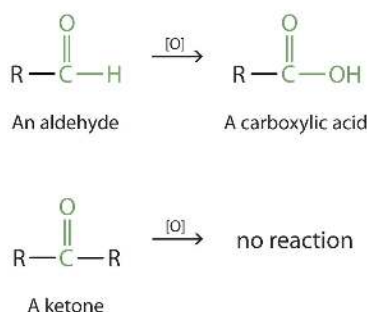
The aldehydes are, in fact, among the most easily oxidized of organic compounds. They are oxidized by oxygen (O_2) in air to carboxylic acids.

$$2\,RCHO + O_2 \longrightarrow 2\,RCOOH$$
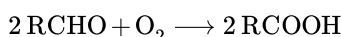
The ease of oxidation helps chemists identify aldehydes. A sufficiently mild oxidizing agent can distinguish aldehydes not only from ketones but also from alcohols. Tollens' reagent, for example, is an alkaline solution of silver (Ag^+) ion complexed with ammonia (NH_3), which keeps the Ag^+ ion in solution.

$$H_3N{-\!\!-}Ag^+{-\!\!-}NH_3$$
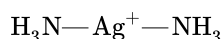
When Tollens' reagent oxidizes an aldehyde, the Ag^+ ion is reduced to free silver (Ag).

$$\underbrace{RCHO(aq)}_{\text{an aldehyde}} + 2\,Ag(NH_3)_2^+(aq) \longrightarrow RCOO^- + \underbrace{2\,Ag(s)}_{\text{free silver}} + 4\,NH_3(aq) + 2\,H_2O$$
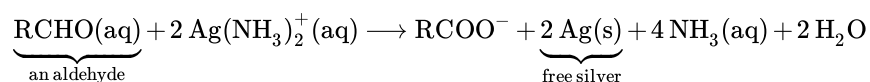
Deposited on a clean glass surface, the silver produces a mirror (Figure 8.8.1). Ordinary ketones do not react with Tollens' reagent.
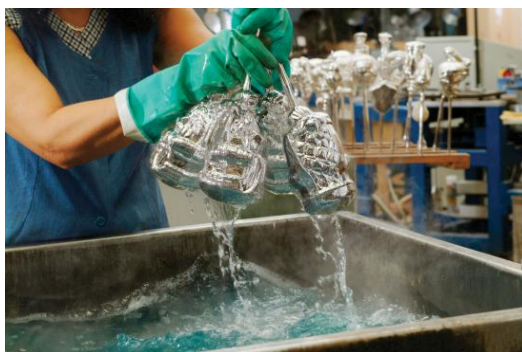
Figure 8.8.1: Aldehyde Reactions. A reaction related to the Tollens' reaction is often used to silver mirrors. These ornaments were silvered by such a reaction. Glucose, a simple sugar with an aldehyde functional group, is used as the reducing agent. Source: Photo courtesy of Krebs Glas Lauscha, commons.wikimedia.org/wiki/File:Silvering.jpg.

A person wearing gloves is holding a bunch of ornaments that she has just lifted from a basin containing a solution.

Although ketones resist oxidation by ordinary laboratory oxidizing agents, they undergo combustion, as do aldehydes.

Some Common Carbonyl Compounds

Formaldehyde has an irritating odor. Because of its reactivity, it is difficult to handle in the gaseous state. For many uses, it is therefore dissolved in water and sold as a 37% to 40% aqueous solution called *formalin*. Formaldehyde denatures proteins, rendering them insoluble in water and resistant to bacterial decay. For this reason, formalin is used in embalming solutions and in preserving biological specimens.

Aldehydes are the active components in many other familiar substances. Large quantities of formaldehyde are used to make phenol-formaldehyde resins for gluing the wood sheets in plywood and as adhesives in other building materials. Sometimes the formaldehyde escapes from the materials and causes health problems in some people. While some people seem unaffected, others experience coughing, wheezing, eye irritation, and other symptoms.

> *The odor of green leaves is due in part to a carbonyl compound, cis-3-hexenal, which with related compounds is used to impart a "green" herbal odor to shampoos and other products.*

Acetaldehyde is an extremely volatile, colorless liquid. It is a starting material for the preparation of many other organic compounds. Acetaldehyde is formed as a metabolite in the fermentation of sugars and in the detoxification of alcohol in the liver. Aldehydes are the active components of many other familiar materials (Figure 8.8.2).
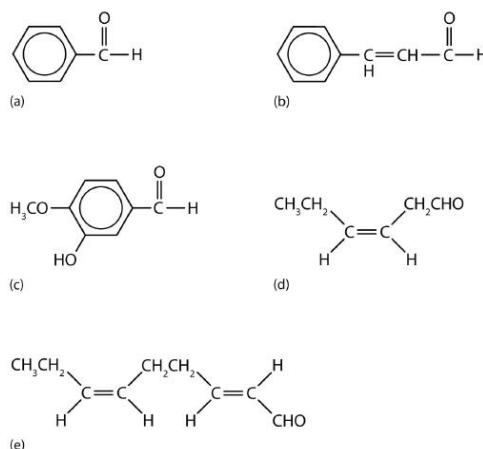
Figure 8.8.2 Some Interesting Aldehydes. (a) Benzaldehyde is an oil found in almonds; (b) cinnamaldehyde is oil of cinnamon; (c) vanillin gives vanilla its flavor; (d) *cis*-3-hexenal provides an herbal odor; and (e) *trans*-2-*cis*-6-nonadienal gives a cucumber odor.

Acetone is the simplest and most important ketone. Because it is miscible with water as well as with most organic solvents, its chief use is as an industrial solvent (for example, for paints and lacquers). It is also the chief ingredient in some brands of nail polish remover.

⚎ To Your Health: Acetone in Blood, Urine, and Breath

Acetone is formed in the human body as a by-product of lipid metabolism. Normally, acetone does not accumulate to an appreciable extent because it is oxidized to carbon dioxide and water. The normal concentration of acetone in the human body is less than 1 mg/100 mL of blood. In certain disease states, such as uncontrolled diabetes mellitus, the acetone concentration rises to higher levels. It is then excreted in the urine, where it is easily detected. In severe cases, its odor can be noted on the breath.

Ketones are also the active components of other familiar substances, some of which are noted in the accompanying figure.
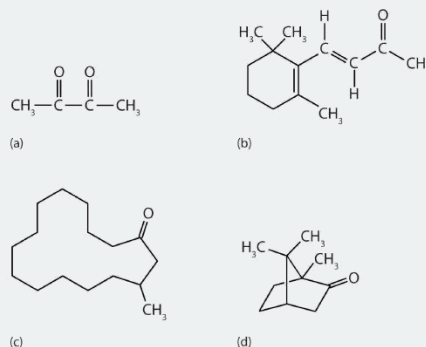
Some ketones have interesting properties: (a) Butter flavoring comes from 2,3-butanedione; (b) β-ionone is responsible for the odor of violets; (c) muscone is musk oil, an ingredient in perfumes; and (d) camphor is used in some insect repellents.

Certain steroid hormones have the ketone functional group as a part of their structure. Two examples are progesterone, a hormone secreted by the ovaries that stimulates the growth of cells in the uterine wall and prepares it for attachment of a fertilized egg, and testosterone, the main male sex hormone. These and other sex hormones affect our development and our lives in fundamental ways.

Summary

The polar carbon-to-oxygen double bond causes aldehydes and ketones to have higher boiling points than those of ethers and alkanes of similar molar masses but lower than those of comparable alcohols that engage in intermolecular hydrogen bonding. Aldehydes are readily oxidized to carboxylic acids, whereas ketones resist oxidation.

8.9: Carboxylic Acids and Esters

Aldehydes and Ketones

There are a number of functional groups that contain a carbon-oxygen double bond, which is commonly referred to as a **carbonyl**. **Ketones** and **aldehydes** are two closely related carbonyl-based functional groups that react in very similar ways. In a ketone, the carbon atom of a carbonyl is bonded to two other carbons. In an aldehyde, the carbonyl carbon is bonded on one side to a hydrogen, and on the other side to a carbon. The exception to this definition is formaldehyde, in which the carbonyl carbon has bonds to two hydrogens.
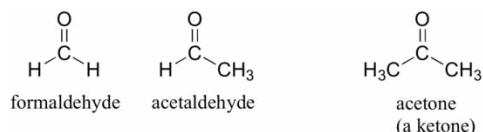
Molecules with carbon-nitrogen double bonds are called **imines**, or **Schiff bases**.
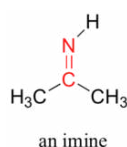
Carboxylic acids and acid derivatives

If a carbonyl carbon is bonded on one side to a carbon (or hydrogen) and on the other side to a **heteroatom** (in organic chemistry, this term generally refers to oxygen, nitrogen, sulfur, or one of the halogens), the functional group is considered to be one of the '**carboxylic acid derivatives**', a designation that describes a grouping of several functional groups. The eponymous member of this grouping is the **carboxylic acid** functional group, in which the carbonyl is bonded to a hydroxyl (OH) group.
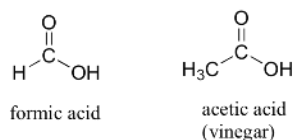
As the name implies, carboxylic acids are acidic, meaning that they are readily deprotonated to form the conjugate base form, called a **carboxylate** (much more about carboxylic acids in the acid-base chapter!).
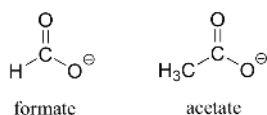
In **amides**, the carbonyl carbon is bonded to a nitrogen. The nitrogen in an amide can be bonded either to hydrogens, to carbons, or to both. Another way of thinking of an amide is that it is a carbonyl bonded to an amine.
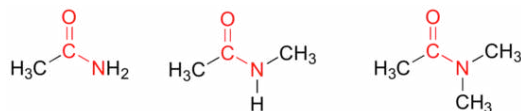
In **esters**, the carbonyl carbon is bonded to an oxygen which is itself bonded to another carbon. Another way of thinking of an ester is that it is a carbonyl bonded to an alcohol. **Thioesters** are similar to esters, except a sulfur is in place of the oxygen.
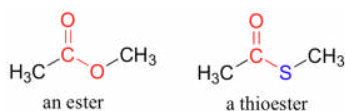
In an **acyl phosphate**, the carbonyl carbon is bonded to the oxygen of a phosphate, and in an **acid chloride**, the carbonyl carbon is bonded to a chlorine.
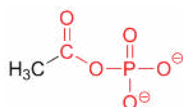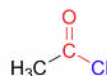
an acyl phosphate   an acid chloride

Finally, in a **nitrile** group, a carbon is triple-bonded to a nitrogen. Nitriles are also often referred to as **cyano** groups.

$$H_3C-C\equiv N$$

a nitrile

A single compound often contains several functional groups. The six-carbon sugar molecules glucose and fructose, for example, contain aldehyde and ketone groups, respectively, and both contain five alcohol groups (a compound with several alcohol groups is often referred to as a '**polyol'**).
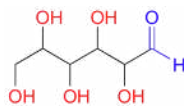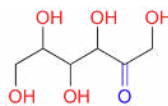
glucose   fructose

Capsaicin, the compound responsible for the heat in hot peppers, contains phenol, ether, amide, and alkene functional groups.
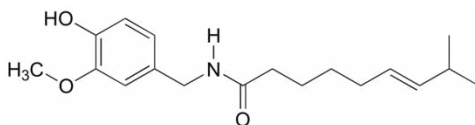
capsiacin

The male sex hormone testosterone contains ketone, alkene, and secondary alcohol groups, while acetylsalicylic acid (aspirin) contains aromatic, carboxylic acid, and ester groups.
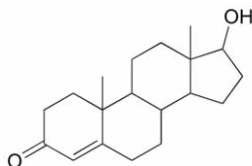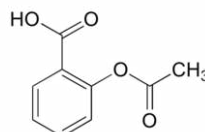
testosterone   acetylsalicylic acid (aspirin)

While not in any way a complete list, this section has covered most of the important functional groups that we will encounter in biological and laboratory organic chemistry. The table on the inside back cover provides a summary of all of the groups listed in this section, plus a few more that will be introduced later in the text.

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8.10: Ethers

> 🌓 **Learning Objectives**
>
> - Describe the structural difference between an alcohol and an ether that affects physical characteristics and reactivity of each.
> - Name simple ethers.
> - Describe the structure and uses of some ethers.

With the general formula ROR′, an ether may be considered a derivative of water in which both hydrogen atoms are replaced by alkyl or aryl groups. It may also be considered a derivative of an alcohol (ROH) in which the hydrogen atom of the OH group is been replaced by a second alkyl or aryl group:

$$\text{HOH} \xrightarrow[\text{H atoms}]{\text{replace both}} \text{ROR}' \xleftarrow[\text{of OH group}]{\text{replace H atom}} \text{ROH}$$
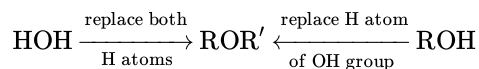
Simple ethers have simple common names, formed from the names of the groups attached to oxygen atom, followed by the generic name *ether*. For example, CH_3–O–$CH_2CH_2CH_3$ is methyl propyl ether. If both groups are the same, the group name should be preceded by the prefix *di-*, as in dimethyl ether (CH_3–O–CH_3) and diethyl ether CH_3CH_2–O–CH_2CH_3.

Ether molecules have no hydrogen atom on the oxygen atom (that is, no OH group). Therefore there is no intermolecular hydrogen bonding between ether molecules, and ethers therefore have quite low boiling points for a given molar mass. Indeed, ethers have boiling points about the same as those of alkanes of comparable molar mass and much lower than those of the corresponding alcohols (Table 8.10.1).

Table 8.10.1: Comparison of Boiling Points of Alkanes, Alcohols, and Ethers

Condensed Structural Formula	Name	Molar Mass	Boiling Point (°C)	Intermolecular Hydrogen Bonding in Pure Liquid?
$CH_3CH_2CH_3$	propane	44	–42	no
CH_3OCH_3	dimethyl ether	46	–25	no
CH_3CH_2OH	ethyl alcohol	46	78	yes
$CH_3CH_2CH_2CH_2CH_3$	pentane	72	36	no
$CH_3CH_2OCH_2CH_3$	diethyl ether	74	35	no
$CH_3CH_2CH_2CH_2OH$	butyl alcohol	74	117	yes

Ether molecules do have an oxygen atom, however, and engage in hydrogen bonding with water molecules. Consequently, an ether has about the same solubility in water as the alcohol that is isomeric with it. For example, dimethyl ether and ethanol (both having the molecular formula C_2H_6O) are completely soluble in water, whereas diethyl ether and 1-butanol (both $C_4H_{10}O$) are barely soluble in water (8 g/100 mL of water).

> ✔ **Example 8.10.1**
>
> What is the common name for each ether?
>
> a. $CH_3CH_2CH_2OCH_2CH_2CH_3$
>
> b. CH_3CHOCH_3 with CH_3 attached
>
> **Solution**
> a. The carbon groups on either side of the oxygen atom are propyl ($CH_3CH_2CH_2$) groups, so the compound is dipropyl ether.
> b. The three-carbon group is attached by the middle carbon atom, so it is an isopropyl group. The one-carbon group is a methyl group. The compound is isopropyl methyl ether.

> **? Exercise 8.10.1**
>
> What is the common name for each ether?
>
> a. $CH_3CH_2CH_2CH_2OCH_2CH_2CH_2CH_3$
>
> b. [structure: cyclobutane ring]—OCH_2CH_3
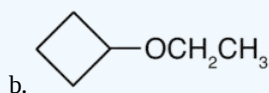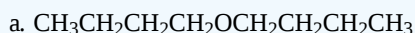
⚲ To Your Health: Ethers as General Anesthetics

A *general anesthetic* acts on the brain to produce unconsciousness and a general insensitivity to feeling or pain. Diethyl ether ($CH_3CH_2OCH_2CH_3$) was the first general anesthetic to be used.
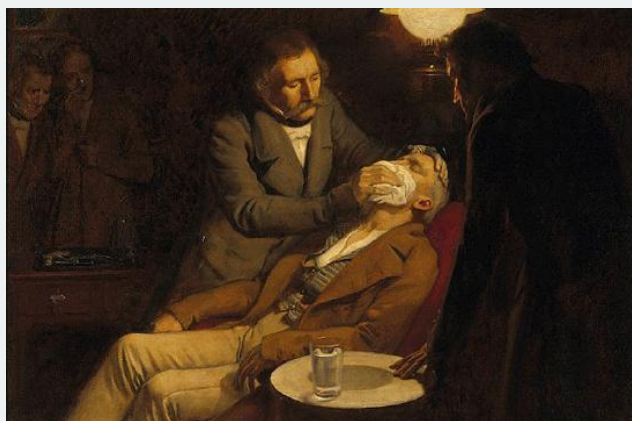
William Morton, a Boston dentist, introduced diethyl ether into surgical practice in 1846. This painting shows an operation in Boston in 1846 in which diethyl ether was used as an anesthetic. Inhalation of ether vapor produces unconsciousness by depressing the activity of the central nervous system. Source: Painting of William Morton by Ernest Board.

Diethyl ether is relatively safe because there is a fairly wide gap between the dose that produces an effective level of anesthesia and the lethal dose. However, because it is highly flammable and has the added disadvantage of causing nausea, it has been replaced by newer inhalant anesthetics, including the fluorine-containing compounds halothane, enflurane, and isoflurane. Unfortunately, the safety of these compounds for operating room personnel has been questioned. For example, female operating room workers exposed to halothane suffer a higher rate of miscarriages than women in the general population.
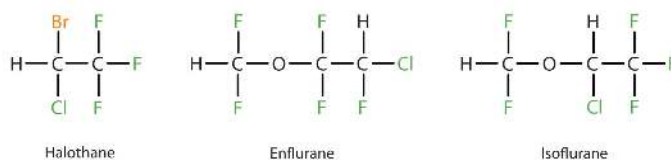
These three modern, inhalant, halogen-containing, anesthetic compounds are less flammable than diethyl ether.

Summary

To give ethers common names, simply name the groups attached to the oxygen atom, followed by the generic name *ether*. If both groups are the same, the group name should be preceded by the prefix *di-*. Ether molecules have no OH group and thus no intermolecular hydrogen bonding. Ethers therefore have quite low boiling points for a given molar mass. Ether molecules have an oxygen atom and can engage in hydrogen bonding with water molecules. An ether molecule has about the same solubility in water as the alcohol that is isomeric with it.

8.11: Amines

> **◖◗ Learning Objectives**
>
> - Name the typical reactions that take place with amines.
> - Describe heterocyclic amines.

Recall that ammonia (NH_3) acts as a base because the nitrogen atom has a lone pair of electrons that can accept a proton. Amines also have a lone electron pair on their nitrogen atoms and can accept a proton from water to form substituted ammonium (NH_4^+) ions and hydroxide (OH^-) ions:

As a specific example, methylamine reacts with water to form the methylammonium ion and the OH^- ion.

$$CH_3NH_2(aq) + H_2O \rightleftharpoons CH_3NH_3^+(aq) + OH^-(aq)$$

Methylamine   Methylammonium ion

Nearly all amines, including those that are not very soluble in water, will react with strong acids to form salts soluble in water.

$$CH_3(CH_2)_6NH_2(l) + HNO_3(aq) \longrightarrow CH_3(CH_2)_6NH_3^+NO_3^-(aq)$$

Octylamine (insoluble)   Octylammonium nitrate (soluble)

Amine salts are named like other salts: the name of the cation is followed by the name of the anion.

> **✔ Example 8.11.1**
>
> What are the formulas of the acid and base that react to form $[CH_3NH_2CH_2CH_3]^+CH_3COO^-$?
>
> **Solution**
>
> The cation has two groups—methyl and ethyl—attached to the nitrogen atom. It comes from ethylmethylamine ($CH_3NHCH_2CH_3$). The anion is the acetate ion. It comes from acetic acid (CH_3COOH).

> **? Exercise 8.11.1**
>
> What are the formulas of the acid and base that react to form $(CH_3CH_2CH_2)_3NH^+I^-$?

> **⚷ To Your Health: Amine Salts as Drugs**
>
> Salts of aniline are properly named as *anilinium* compounds, but an older system, still in use for naming drugs, identifies the salt of aniline and hydrochloric acid as "aniline hydrochloride." These compounds are ionic—they are salts—and the properties of the compounds (solubility, for example) are those characteristic of salts. Many drugs that are amines are converted to hydrochloride salts to increase their solubility in aqueous solution.

Heterocyclic Amines

Looking back at the various cyclic hydrocarbons discussed previously, we see that all the atoms in the rings of these compounds are carbon atoms. In other cyclic compounds, called **heterocyclic compounds** (Greek *heteros*, meaning "other"), nitrogen, oxygen, sulfur, or some other atom is incorporated in the ring. Many heterocyclic compounds are important in medicine and biochemistry. Some compose part of the structure of the nucleic acids, which in turn compose the genetic material of cells and direct protein synthesis.

Many heterocyclic amines occur naturally in plants. Like other amines, these compounds are basic. Such a compound is an **alkaloid**, a name that means "like alkalis." Many alkaloids are physiologically active, including the familiar drugs caffeine, nicotine, and cocaine.

📌 To Your Health: Three Well-Known Alkaloids

Caffeine is a stimulant found in coffee, tea, and some soft drinks. Its mechanism of action is not well understood, but it is thought to block the activity of adenosine, a heterocyclic base that acts as a neurotransmitter, a substance that carries messages across a tiny gap (synapse) from one nerve cell (neuron) to another cell. The effective dose of caffeine is about 200 mg, corresponding to about two cups of strong coffee or tea.
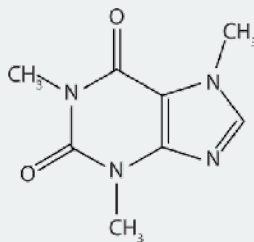
Caffeine

Nicotine acts as a stimulant by a different mechanism; it probably mimics the action of the neurotransmitter acetylcholine. People ingest this drug by smoking or chewing tobacco. Its stimulant effect seems transient, as this initial response is followed by depression. Nicotine is highly toxic to animals. It is especially deadly when injected; the lethal dose for a human is estimated to be about 50 mg. Nicotine has also been used in agriculture as a contact insecticide.
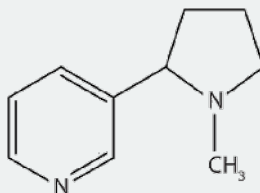
Nicotine

Cocaine acts as a stimulant by preventing nerve cells from taking up dopamine, another neurotransmitter, from the synapse. High levels of dopamine are therefore available to stimulate the pleasure centers of the brain. The enhancement of dopamine action is thought to be responsible for cocaine's "high" and its addictive properties. After the binge, dopamine is depleted in less than an hour. This leaves the user in a pleasureless state and (often) craving more cocaine.
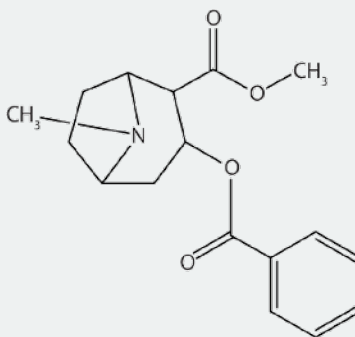
Cocaine

Cocaine is used as the salt cocaine hydrochloride and in the form of broken lumps of the free (unneutralized) base, which is called *crack cocaine*.

$$\underbrace{C_{17}H_{21}O_4N}_{\text{cocaine (freebase)}} + HCl \longrightarrow \underbrace{C_{17}H_{21}O_4NH^+Cl^-}_{\text{cocaine hydrochloride}}$$
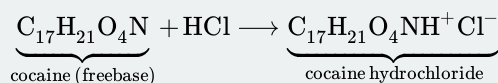
> Because it is soluble in water, cocaine hydrochloride is readily absorbed through the watery mucous membranes of the nose when it is snorted. Crack cocaine is more volatile than cocaine hydrochloride. It vaporizes at the temperature of a burning cigarette. When smoked, cocaine reaches the brain in 15 s.

Summary

Amines are bases; they react with acids to form salts. Salts of aniline are properly named as *anilinium* compounds, but an older system is used to name drugs: the salts of amine drugs and hydrochloric acid are called "hydrochlorides." Heterocyclic amines are cyclic compounds with one or more nitrogen atoms in the ring.

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8.12: Isomers

As we get more into the complexities of organic chemistry, we will see how molecular shape affects reactions. One common reaction for alkenes is the addition of hydrogen across the double bond to form the corresponding alkane. Because of the geometry of the reaction, the different 2-butene shapes have different heats of reaction. These differences are important both from a theoretical standpoint as well as from the point of view of industrial applications. Greater energy requirements mean a higher cost and a more expensive product.

Isomers

One of the interesting aspects of organic chemistry is that it is three-dimensional. A molecule can have a shape in space that may contribute to its properties. Molecules can differ in the way the atoms are arranged - the same combination of atoms can be assembled in more than one way. These compounds are known as **isomers**. Isomers are molecules with the same molecular formulas, but different arrangements of atoms. We will look at some isomer possibilities for alkanes and alkenes.

Structural Isomers

A **structural isomer** is one in which two or more organic compounds have the same molecular formulas but different structures. The two pentane molecules below differ only in the location of the methyl group.
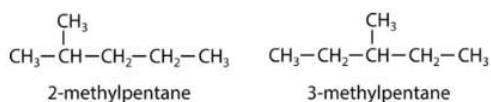
Alkenes can also demonstrate structural isomerism. In alkenes, there are multiple structural isomers based on where in the chain the double bond occurs. The condensed structural formulas of 1-butene and 2-butene show this.

The number in the name of the alkene refers to the lowest numbered carbon in the chain that is part of the double bond.

Geometric Isomers

With a molecule such as 2-butene, a different type of isomerism called geometric isomerism can be observed. **Geometric isomers** are isomers in which the order of atom bonding is the same but the arrangement of atoms in space is different. The double bond in an alkene is not free to rotate because of the nature of the pi bond. Therefore, there are two different ways to construct the 2-butene molecule. The image below shows the two geometric isomers, called *cis*-2-butene and *trans*-2-butene.
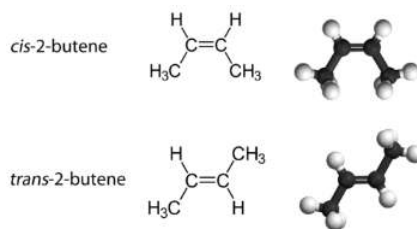
The *cis* isomer has the two single hydrogen atoms on the same side of the molecule, while the *trans* isomer has them on opposite sides of the molecule. In both molecules, the bonding order of the atoms is the same. In order for geometric isomers to exist, there must be a rigid structure in the molecule to prevent free rotation around a bond. If the double bond in an alkene was capable of rotating, the two geometric isomers above would not exist. In addition, the two carbon atoms must each have two different groups attached in order for there to be geometric isomers. Propene has no geometric isomers because one of the carbon atoms has two single hydrogens bonded to it.
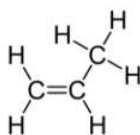
Physical and chemical properties of geometric isomers are generally different. While *cis*-2-butene is a polar molecule, *trans*-2-butene is nonpolar. Heat or irradiation with light can be used to bring about the conversion of one geometric isomer to another. The input of energy must be large enough to break the pi bond between the two carbon atoms, which is weaker than the sigma bond. At that point, the now single bond is free to rotate and the isomers can interconvert.

As with alkenes, alkynes display structural isomerism beginning with 1-butyne and 2-butyne. However, there are no geometric isomers with alkynes because there is only one other group bonded to the carbon atoms that are involved in the triple bond.

Summary

- Structural and geometric isomers are defined.
- Examples of alkane and alkene isomers are given.

Contributors

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CHAPTER OVERVIEW

9: Reaction Kinetics

9.1: Rate of a Chemical Reaction

> **◑ Learning Objectives**
>
> - To determine the reaction rate of a reaction.

Reaction rates are usually expressed as the concentration of reactant consumed or the concentration of product formed per unit time. The units are thus moles per liter per unit time, written as M/s, M/min, or M/h. To measure reaction rates, chemists initiate the reaction, measure the concentration of the reactant or product at different times as the reaction progresses, perhaps plot the concentration as a function of time on a graph, and then calculate the change in the concentration per unit time.
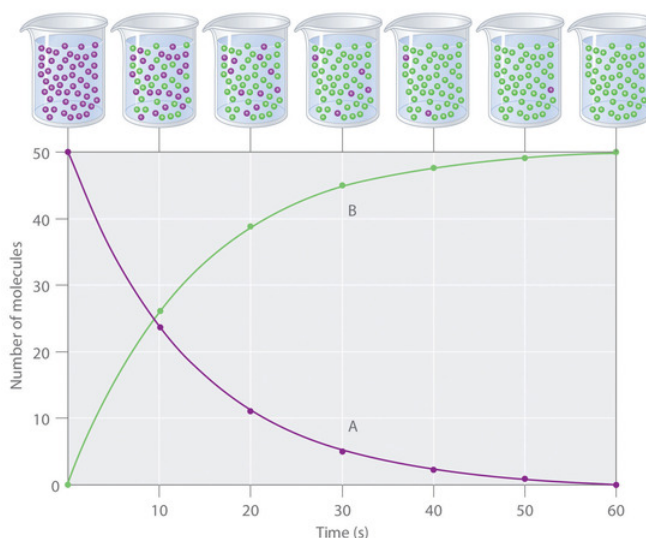
Figure 9.1.1: The Progress of a Simple Reaction (A → B). The mixture initially contains only A molecules (purple). Over time, the number of A molecules decreases and more B molecules (green) are formed (top). The graph shows the change in the number of A and B molecules in the reaction as a function of time over a 1 min period (bottom).

The progress of a simple reaction (A → B) is shown in Figure 9.1.1; the beakers are snapshots of the composition of the solution at 10 s intervals. The number of molecules of reactant (A) and product (B) are plotted as a function of time in the graph. Each point in the graph corresponds to one beaker in Figure 9.1.1. The reaction rate is the change in the concentration of either the reactant or the product over a period of time. The concentration of A decreases with time, while the concentration of B increases with time.

$$\text{rate} = \frac{\Delta[\text{B}]}{\Delta t} = -\frac{\Delta[\text{A}]}{\Delta t} \tag{9.1.1}$$

Square brackets indicate molar concentrations, and the capital Greek delta (Δ) means "change in." Because chemists follow the convention of expressing all reaction rates as positive numbers, however, a negative sign is inserted in front of Δ[A]/Δt to convert that expression to a positive number. The reaction rate calculated for the reaction A → B using Equation 9.1.1 is different for each interval (this is not true for every reaction, as shown below). A greater change occurs in [A] and [B] during the first 10 s interval, for example, than during the last, meaning that the reaction rate is greatest at first.

> *Reaction rates generally decrease with time as reactant concentrations decrease.*

A Video Discussing Average Reaction Rates. Video Link: Introduction to Chemical Reaction Kinetics(opens in new window) [youtu.be] (opens in new window)

Determining the Reaction Rate of Hydrolysis of Aspirin

We can use Equation 9.1.1 to determine the reaction rate of hydrolysis of aspirin, probably the most commonly used drug in the world (more than 25,000,000 kg are produced annually worldwide). Aspirin (acetylsalicylic acid) reacts with water (such as water in body fluids) to give salicylic acid and acetic acid, as shown in Figure 9.1.2.
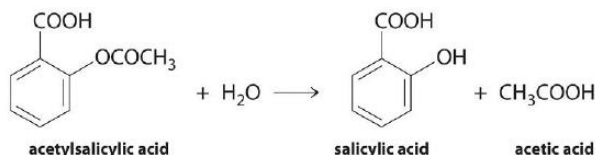
Figure 9.1.2: Hydrolysis of Aspirin reaction.

Because salicylic acid is the actual substance that relieves pain and reduces fever and inflammation, a great deal of research has focused on understanding this reaction and the factors that affect its rate. Data for the hydrolysis of a sample of aspirin are in Table 9.1.1 and are shown in the graph in Figure 9.1.3.

Table 9.1.1: Data for Aspirin Hydrolysis in Aqueous Solution at pH 7.0 and 37°C*

Time (h)	[Aspirin] (M)	[Salicylic Acid] (M)
0	5.55×10^{-3}	0
2.0	5.51×10^{-3}	0.040×10^{-3}
5.0	5.45×10^{-3}	0.10×10^{-3}
10	5.35×10^{-3}	0.20×10^{-3}
20	5.15×10^{-3}	0.40×10^{-3}
30	4.96×10^{-3}	0.59×10^{-3}
40	4.78×10^{-3}	0.77×10^{-3}
50	4.61×10^{-3}	0.94×10^{-3}
100	3.83×10^{-3}	1.72×10^{-3}
200	2.64×10^{-3}	2.91×10^{-3}
300	1.82×10^{-3}	3.73×10^{-3}

*The reaction at pH 7.0 is very slow. It is much faster under acidic conditions, such as those found in the stomach.

The data in Table 9.1.1 were obtained by removing samples of the reaction mixture at the indicated times and analyzing them for the concentrations of the reactant (aspirin) and one of the products (salicylic acid).
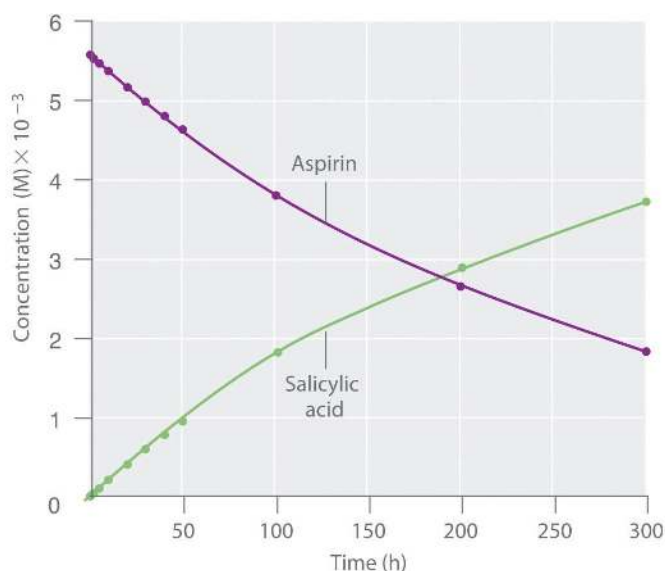
Figure 9.1.3: The Hydrolysis of Aspirin. This graph shows the concentrations of aspirin and salicylic acid as a function of time, based on the hydrolysis data in Table 14.1. The time dependence of the concentration of the other product, acetate, is not shown, but based on the stoichiometry of the reaction, it is identical to the data for salicylic acid.

Graph of concentration against time in hours. The purple line is aspirin. The green line is salicylic acid.

The **average reaction rate** for a given time interval can be calculated from the concentrations of either the reactant or one of the products at the beginning of the interval (time = t_0) and at the end of the interval (t_1). Using salicylic acid, the reaction rate for the interval between t = 0 h and t = 2.0 h (recall that change is always calculated as final minus initial) is calculated as follows:

$$\text{rate}_{(t=0-2.0\,\text{h})} = \frac{[\text{salicyclic acid}]_2 - [\text{salicyclic acid}]_0}{2.0\,\text{h} - 0\,\text{h}}$$
$$= \frac{0.040 \times 10^{-3}\,\text{M} - 0\,\text{M}}{2.0\,\text{h}} = 2.0 \times 10^{-5}\,\text{M/h}$$

The reaction rate can also be calculated from the concentrations of aspirin at the beginning and the end of the same interval, remembering to insert a negative sign, because its concentration decreases:

$$\text{rate}_{(t=0-2.0\,\text{h})} = -\frac{[\text{aspirin}]_2 - [\text{aspirin}]_0}{2.0\,\text{h} - 0\,\text{h}}$$
$$= -\frac{(5.51 \times 10^{-3}\,\text{M}) - (5.55 \times 10^{-3}\,\text{M})}{2.0\,\text{h}}$$
$$= 2 \times 10^{-5}\,\text{M/h}$$

If the reaction rate is calculated during the last interval given in Table 9.1.1(the interval between 200 h and 300 h after the start of the reaction), the reaction rate is significantly slower than it was during the first interval (t = 0–2.0 h):

$$\text{rate}_{(t=200-300\text{h})} = \frac{[\text{salicyclic acid}]_{300} - [\text{salicyclic acid}]_{200}}{300\,\text{h} - 200\,\text{h}}$$
$$= -\frac{(3.73 \times 10^{-3}\,\text{M}) - (2.91 \times 10^{-3}\,\text{M})}{100\,\text{h}}$$
$$= 8.2 \times 10^{-6}\,\text{M/h}$$

Calculating the Reaction Rate of Fermentation of Sucrose

In the preceding example, the stoichiometric coefficients in the balanced chemical equation are the same for all reactants and products; that is, the reactants and products all have the coefficient 1. Consider a reaction in which the coefficients are not all the same, the fermentation of sucrose to ethanol and carbon dioxide:

$$C_{12}H_{22}O_{11}(aq) + H_2O(l) \rightarrow 4C_2H_5OH(aq) + 4CO_2(g) \tag{9.1.2}$$
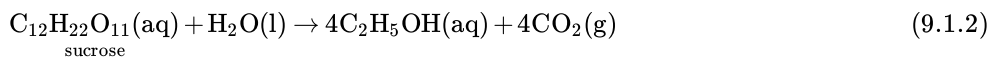
sucrose

The coefficients indicate that the reaction produces four molecules of ethanol and four molecules of carbon dioxide for every one molecule of sucrose consumed. As before, the reaction rate can be found from the change in the concentration of any reactant or product. In this particular case, however, a chemist would probably use the concentration of either sucrose or ethanol because gases are usually measured as volumes and, as explained in Chapter 10, the volume of CO_2 gas formed depends on the total volume of the solution being studied and the solubility of the gas in the solution, not just the concentration of sucrose. The coefficients in the balanced chemical equation tell us that the reaction rate at which ethanol is formed is always four times faster than the reaction rate at which sucrose is consumed:

$$\frac{\Delta[C_2H_5OH]}{\Delta t} = -\frac{4\Delta[\text{sucrose}]}{\Delta t} \tag{9.1.3}$$

The concentration of the reactant—in this case sucrose—*decreases* with time, so the value of Δ[sucrose] is negative. Consequently, a minus sign is inserted in front of Δ[sucrose] in Equation 9.1.3 so the rate of change of the sucrose concentration is expressed as a positive value. Conversely, the ethanol concentration *increases* with time, so its rate of change is automatically expressed as a positive value.

Often the reaction rate is expressed in terms of the reactant or product with the smallest coefficient in the balanced chemical equation. The smallest coefficient in the sucrose fermentation reaction (Equation 9.1.2) corresponds to sucrose, so the reaction rate is generally defined as follows:

$$\text{rate} = -\frac{\Delta[\text{sucrose}]}{\Delta t} = \frac{1}{4}\left(\frac{\Delta[C_2H_5OH]}{\Delta t}\right) \tag{9.1.4}$$

✔ **Example 9.1.1: Decomposition Reaction I**

Consider the thermal decomposition of gaseous N_2O_5 to NO_2 and O_2 via the following equation:

$$2N_2O_5(g) \xrightarrow{\Delta} 4NO_2(g) + O_2(g)$$
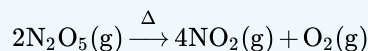
Write expressions for the reaction rate in terms of the rates of change in the concentrations of the reactant and each product with time.

Given: balanced chemical equation

Asked for: reaction rate expressions

Strategy:
 A. Choose the species in the equation that has the smallest coefficient. Then write an expression for the rate of change of that species with time.
 B. For the remaining species in the equation, use molar ratios to obtain equivalent expressions for the reaction rate.

Solution

A Because O_2 has the smallest coefficient in the balanced chemical equation for the reaction, define the reaction rate as the rate of change in the concentration of O_2 and write that expression.

B The balanced chemical equation shows that 2 mol of N_2O_5 must decompose for each 1 mol of O_2 produced and that 4 mol of NO_2 are produced for every 1 mol of O_2 produced. The molar ratios of O_2 to N_2O_5 and to NO_2 are thus 1:2 and 1:4, respectively. This means that the rate of change of $[N_2O_5]$ and $[NO_2]$ must be divided by its stoichiometric coefficient to obtain equivalent expressions for the reaction rate. For example, because NO_2 is produced at four times the rate of O_2, the rate of production of NO_2 is divided by 4. The reaction rate expressions are as follows:

$$\text{rate} = \frac{\Delta[O_2]}{\Delta t} = \frac{\Delta[NO_2]}{4\Delta t} = -\frac{\Delta[N_2O_5]}{2\Delta t}$$

> **? Exercise 9.1.1: Contact Process I**
>
> The contact process is used in the manufacture of sulfuric acid. A key step in this process is the reaction of SO_2 with O_2 to produce SO_3.
>
> $$2SO_{2(g)} + O_{2(g)} \rightarrow 2SO_{3(g)}$$
>
> Write expressions for the reaction rate in terms of the rate of change of the concentration of each species.
>
> **Answer**
>
> $$\text{rate} = -\frac{\Delta[O_2]}{\Delta t} = -\frac{\Delta[SO_2]}{2\Delta t} = \frac{\Delta[SO_3]}{2\Delta t}$$
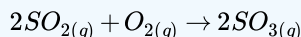
Instantaneous Rates of Reaction

The **instantaneous rate** of a reaction is the reaction rate at any given point in time. As the period of time used to calculate an average rate of a reaction becomes shorter and shorter, the average rate approaches the instantaneous rate. Comparing this to calculus, the instantaneous rate of a reaction at a given time corresponds to the slope of a line tangent to the concentration-versus-time curve at that point—that is, the derivative of concentration with respect to time.

The distinction between the instantaneous and average rates of a reaction is similar to the distinction between the actual speed of a car at any given time on a trip and the average speed of the car for the entire trip. Although the car may travel for an extended period at 65 mph on an interstate highway during a long trip, there may be times when it travels only 25 mph in construction zones or 0 mph if you stop for meals or gas. The average speed on the trip may be only 50 mph, whereas the instantaneous speed on the interstate at a given moment may be 65 mph. Whether the car can be stopped in time to avoid an accident depends on its instantaneous speed, not its average speed. There are important differences between the speed of a car during a trip and the speed of a chemical reaction, however. The speed of a car may vary unpredictably over the length of a trip, and the initial part of a trip is often one of the slowest. In a chemical reaction, the initial interval typically has the fastest rate (though this is not always the case), and the reaction rate generally changes smoothly over time.

> *Chemical kinetics generally focuses on one particular instantaneous rate, which is the initial reaction rate, t = 0. Initial rates are determined by measuring the reaction rate at various times and then extrapolating a plot of rate versus time to t = 0.*

> **✔ Example 9.1.2: Decomposition Reaction II**
>
> Using the reaction shown in Example 9.1.1, calculate the reaction rate from the following data taken at 56°C:
>
> $$2N_2O_{5(g)} \rightarrow 4NO_{2(g)} + O_{2(g)}$$
>
> calculate the reaction rate from the following data taken at 56°C:
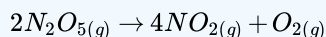
Time (s)	[N₂O₅] (M)	[NO₂] (M)	[O₂] (M)
240	0.0388	0.0314	0.00792
600	0.0197	0.0699	0.0175

Given: balanced chemical equation and concentrations at specific times

Asked for: reaction rate

Strategy:

A. Using the equations in Example 9.1.1, subtract the initial concentration of a species from its final concentration and substitute that value into the equation for that species.

B. Substitute the value for the time interval into the equation. Make sure your units are consistent.

Solution

A Calculate the reaction rate in the interval between t_1 = 240 s and t_2 = 600 s. From Example 9.1.1, the reaction rate can be evaluated using any of three expressions:

$$\text{rate} = \frac{\Delta[\text{O}_2]}{\Delta t} = \frac{\Delta[\text{NO}_2]}{4\Delta t} = -\frac{\Delta[\text{N}_2\text{O}_5]}{2\Delta t}$$

Subtracting the initial concentration from the final concentration of N_2O_5 and inserting the corresponding time interval into the rate expression for N_2O_5,

$$\text{rate} = -\frac{\Delta[\text{N}_2\text{O}_5]}{2\Delta t} = -\frac{[\text{N}_2\text{O}_5]_{600} - [\text{N}_2\text{O}_5]_{240}}{2(600 \text{ s} - 240 \text{ s})}$$

B Substituting actual values into the expression,

$$\text{rate} = -\frac{0.0197 \text{ M} - 0.0388 \text{ M}}{2(360 \text{ s})} = 2.65 \times 10^{-5} \text{ M/s}$$

Similarly, NO_2 can be used to calculate the reaction rate:

$$\text{rate} = \frac{\Delta[\text{NO}_2]}{4\Delta t} = \frac{[\text{NO}_2]_{600} - [\text{NO}_2]_{240}}{4(600 \text{ s} - 240 \text{ s})} = \frac{0.0699 \text{ M} - 0.0314 \text{ M}}{4(360 \text{ s})} = 2.67 \times 10^{-5} \text{ M/s}$$

Allowing for experimental error, this is the same rate obtained using the data for N_2O_5. The data for O_2 can also be used:

$$\text{rate} = \frac{\Delta[\text{O}_2]}{\Delta t} = \frac{[\text{O}_2]_{600} - [\text{O}_2]_{240}}{600 \text{ s} - 240 \text{ s}} = \frac{0.0175 \text{ M} - 0.00792 \text{ M}}{360 \text{ s}} = 2.66 \times 10^{-5} \text{ M/s}$$

Again, this is the same value obtained from the N_2O_5 and NO_2 data. Thus, the reaction rate does not depend on which reactant or product is used to measure it.

? Exercise 9.1.2: Contact Process II

Using the data in the following table, calculate the reaction rate of $SO_2(g)$ with $O_2(g)$ to give $SO_3(g)$.

$$2SO_{2(g)} + O_{2(g)} \rightarrow 2SO_{3(g)}$$
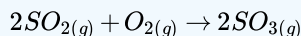
calculate the reaction rate of $SO_2(g)$ with $O_2(g)$ to give $SO_3(g)$.

Time (s)	[SO₂] (M)	[O₂] (M)	[SO₃] (M)
300	0.0270	0.0500	0.0072
720	0.0194	0.0462	0.0148

Answer:

9.0×10^{-6} M/s

Summary

In this Module, the quantitative determination of a reaction rate is demonstrated. Reaction rates can be determined over particular time intervals or at a given point in time. A rate law describes the relationship between reactant rates and reactant concentrations. Reaction rates are reported as either the average rate over a period of time or as the instantaneous rate at a single time. Reaction rates can be determined over particular time intervals or at a given point in time.

- General definition of rate for A → B:

$$\text{rate} = \frac{\Delta[\text{B}]}{\Delta t} = -\frac{\Delta[\text{A}]}{\Delta t}$$

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9.2: The Rate Law- The Effect of Concentration on Reaction Rate

> ◐ **Learning Objectives**
>
> - To understand the meaning of the rate law.

The factors that affect the reaction rate of a chemical reaction, which may determine whether a desired product is formed. In this section, we will show you how to quantitatively determine the reaction rate.

Rate Laws

Typically, reaction rates decrease with time because reactant concentrations decrease as reactants are converted to products. Reaction rates generally increase when reactant concentrations are increased. This section examines mathematical expressions called **rate laws**, which describe the relationships between reactant rates and reactant concentrations. Rate laws are mathematical descriptions of experimentally verifiable data.

Rate laws may be written from either of two different but related perspectives. A **differential rate law** expresses the reaction rate in terms of changes in the concentration of one or more reactants ($\Delta[R]$) over a specific time interval (Δt). In contrast, an **integrated rate law** describes the reaction rate in terms of the initial concentration ($[R]_0$) and the measured concentration of one or more reactants ($[R]$) after a given amount of time (t); integrated rate laws are discussed in more detail later. The integrated rate law is derived by using calculus to integrate the differential rate law. Whether using a differential rate law or integrated rate law, always make sure that the rate law gives the proper units for the reaction rate, usually moles per liter per second (M/s).

Reaction Orders

For a reaction with the general equation:

$$aA + bB \rightarrow cC + dD \tag{9.2.1}$$

the experimentally determined rate law usually has the following form:

$$\text{rate} = k[A]^m[B]^n \tag{9.2.2}$$

The proportionality constant (k) is called the **rate constant**, and its value is characteristic of the reaction and the reaction conditions. A given reaction has a particular rate constant value under a given set of conditions, such as temperature, pressure, and solvent; varying the temperature or the solvent usually changes the value of the rate constant. The numerical value of k, however, does not change as the reaction progresses under a given set of conditions.

> *Under a given set of conditions, the value of the rate constant does **not** change as the reaction progresses.*

The reaction rate thus depends on the rate constant for the given set of reaction conditions and the concentration of A and B raised to the powers m and n, respectively. The values of m and n are derived from experimental measurements of the changes in reactant concentrations over time and indicate the **reaction order**, the degree to which the reaction rate depends on the concentration of each reactant; m and n need not be integers. For example, Equation 9.2.2 tells us that Equation 9.2.1 is m^{th} order in reactant A and n^{th} order in reactant B. It is important to remember that n and m are not related to the stoichiometric coefficients a and b in the balanced chemical equation and must be determined **experimentally**. The overall reaction order is the sum of all the exponents in the rate law: $m + n$.

> *The orders of the reactions (e.g. n and m) are **not** related to the stoichiometric coefficients in the balanced chemical (e.g., a and b).*

To illustrate how chemists interpret a differential rate law, consider the experimentally derived rate law for the hydrolysis of t-butyl bromide in 70% aqueous acetone.

t-butanol   methyl bromide
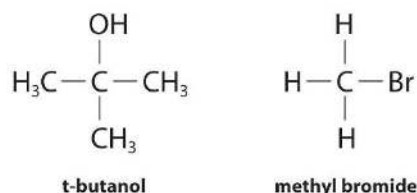
This reaction produces *t*-butanol according to the following equation:

$$(CH_3)_3CBr_{(soln)} + H_2O_{(soln)} \rightarrow (CH_3)_3COH_{(soln)} + HBr_{(soln)} \tag{9.2.3}$$
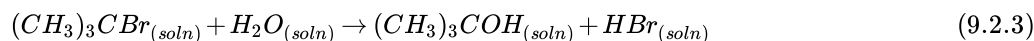
Combining the rate expression in Equation 9.2.2 with the definition of average reaction rate

$$\text{rate} = -\frac{\Delta[A]}{\Delta t}$$

gives a general expression for the differential rate law:

$$\text{rate} = -\frac{\Delta[A]}{\Delta t} = k[A]^m[B]^n \tag{9.2.4}$$

Inserting the identities of the reactants into Equation 9.2.4 gives the following expression for the differential rate law for the reaction:

$$\text{rate} = -\frac{\Delta[(CH_3)_3CBr]}{\Delta t} = k[(CH_3)_3CBr]^m[H_2O]^n \tag{9.2.5}$$

Experiments to determine the rate law for the hydrolysis of *t*-butyl bromide show that the reaction rate is directly proportional to the concentration of $(CH_3)_3CBr$ but is independent of the concentration of water. Therefore, m and n in Equation 9.2.4 are 1 and 0, respectively, and,

$$\text{rate} = k[(CH_3)_3CBr]^1[H_2O]^0 = k[(CH_3)_3CBr] \tag{9.2.6}$$

Because the exponent for the reactant is 1, the reaction is first order in $(CH_3)_3CBr$. It is zeroth order in water because the exponent for $[H_2O]$ is 0. (Recall that anything raised to the zeroth power equals 1.) Thus, the overall reaction order is 1 + 0 = 1. The reaction orders state in practical terms that doubling the concentration of $(CH_3)_3CBr$ doubles the reaction rate of the hydrolysis reaction, halving the concentration of $(CH_3)_3CBr$ halves the reaction rate, and so on. Conversely, increasing or decreasing the concentration of water has no effect on the reaction rate. (Again, when working with rate laws, there is no simple correlation between the stoichiometry of the reaction and the rate law. The values of *k*, *m*, and *n* in the rate law must be determined experimentally.) Experimental data show that *k* has the value 5.15×10^{-4} s^{-1} at 25°C. The rate constant has units of reciprocal seconds (s^{-1}) because the reaction rate is defined in units of concentration per unit time (M/s). The units of a rate constant depend on the rate law for a particular reaction.

Under conditions identical to those for the *t*-butyl bromide reaction, the experimentally derived differential rate law for the hydrolysis of methyl bromide (CH_3Br) is as follows:

$$\text{rate} = -\frac{\Delta[CH_3Br]}{\Delta t} = k'[CH_3Br] \tag{9.2.7}$$

This reaction also has an overall reaction order of 1, but the rate constant in Equation 9.2.7 is approximately 10^6 times smaller than that for *t*-butyl bromide. Thus, methyl bromide hydrolyzes about 1 million times more slowly than *t*-butyl bromide, and this information tells chemists how the reactions differ on a molecular level.

Frequently, changes in reaction conditions also produce changes in a rate law. In fact, chemists often alter reaction conditions to study the mechanics of a reaction. For example, when *t*-butyl bromide is hydrolyzed in an aqueous acetone solution containing OH^- ions rather than in aqueous acetone alone, the differential rate law for the hydrolysis reaction does not change. In contrast, for methyl bromide, the differential rate law becomes

$$\text{rate} = k''[CH_3Br][OH^-]$$

with an overall reaction order of 2. Although the two reactions proceed similarly in neutral solution, they proceed very differently in the presence of a base, providing clues as to how the reactions differ on a molecular level.

✔ **Example 9.2.1: Writing Rate Laws from Reaction Orders**

An experiment shows that the reaction of nitrogen dioxide with carbon monoxide:

$$NO_2(g) + CO(g) \longrightarrow NO(g) + CO_2(g)$$
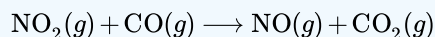
is second order in NO_2 and zero order in CO at 100 °C. What is the rate law for the reaction?

Solution

The reaction will have the form:

$$rate = k[NO_2]^m[CO]^n$$

The reaction is second order in NO_2; thus $m = 2$. The reaction is zero order in CO; thus $n = 0$. The rate law is:

$$rate = k[NO_2]^2[CO]^0 = k[NO_2]^2$$

Remember that a number raised to the zero power is equal to 1, thus $[CO]^0 = 1$, which is why we can simply drop the concentration of CO from the rate equation: the rate of reaction is solely dependent on the concentration of NO_2. When we consider rate mechanisms later in this chapter, we will explain how a reactant's concentration can have no effect on a reaction despite being involved in the reaction.

? **Exercise $9.2.1A$**

The rate law for the reaction:

$$H_2(g) + 2\,NO(g) \longrightarrow N_2O(g) + H_2O(g)$$
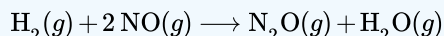
has been experimentally determined to be $rate = k[NO]^2[H_2]$. What are the orders with respect to each reactant, and what is the overall order of the reaction?

Answer

- order in NO = 2
- order in H_2 = 1
- overall order = 3

? **Exercise $9.2.1B$**

In a transesterification reaction, a triglyceride reacts with an alcohol to form an ester and glycerol. Many students learn about the reaction between methanol (CH_3OH) and ethyl acetate ($CH_3CH_2OCOCH_3$) as a sample reaction before studying the chemical reactions that produce biodiesel:

$$CH_3OH + CH_3CH_2OCOCH_3 \longrightarrow CH_3OCOCH_3 + CH_3CH_2OH$$
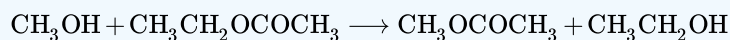
The rate law for the reaction between methanol and ethyl acetate is, under certain conditions, experimentally determined to be:

$$rate = k[CH_3OH]$$

What is the order of reaction with respect to methanol and ethyl acetate, and what is the overall order of reaction?

Answer

- order in CH_3OH = 1
- order in $CH_3CH_2OCOCH_3$ = 0
- overall order = 1

✔ Example 9.2.2: Differential Rate Laws

Below are three reactions and their experimentally determined differential rate laws. For each reaction, give the units of the rate constant, give the reaction order with respect to each reactant, give the overall reaction order, and predict what happens to the reaction rate when the concentration of the first species in each chemical equation is doubled.

a.

$$2HI(g) \xrightarrow{Pt} H_2(g) + I_2(g)$$
$$\text{rate} = -\frac{1}{2}\left(\frac{\Delta[HI]}{\Delta t}\right) = k[HI]^2$$

b.

$$2N_2O(g) \xrightarrow{\Delta} 2N_2(g) + O_2(g)$$
$$\text{rate} = -\frac{1}{2}\left(\frac{\Delta[N_2O]}{\Delta t}\right) = k$$

c.

$$\text{cyclopropane}(g) \rightarrow \text{propane}(g)$$
$$\text{rate} = -\frac{\Delta[\text{cyclopropane}]}{\Delta t} = k[\text{cyclopropane}]$$
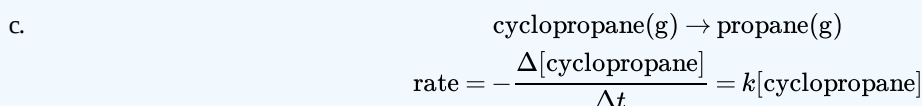
Given: balanced chemical equations and differential rate laws

Asked for: units of rate constant, reaction orders, and effect of doubling reactant concentration

Strategy:
  A. Express the reaction rate as moles per liter per second [mol/(L·s), or M/s]. Then determine the units of each chemical species in the rate law. Divide the units for the reaction rate by the units for all species in the rate law to obtain the units for the rate constant.
  B. Identify the exponent of each species in the rate law to determine the reaction order with respect to that species. Add all exponents to obtain the overall reaction order.
  C. Use the mathematical relationships as expressed in the rate law to determine the effect of doubling the concentration of a single species on the reaction rate.

Solution
  1. **A** $[HI]^2$ will give units of (moles per liter)^2. For the reaction rate to have units of moles per liter per second, the rate constant must have reciprocal units [1/(M·s)]:

$$k M^2 = \frac{M}{s} \quad k = \frac{M/s}{M^2} = \frac{1}{M \cdot s} = M^{-1} \cdot s^{-1}$$

  B The exponent in the rate law is 2, so the reaction is second order in HI. Because HI is the only reactant and the only species that appears in the rate law, the reaction is also second order overall.

  C If the concentration of HI is doubled, the reaction rate will increase from $k[HI]_0^2$ to $k(2[HI])_0^2 = 4k[HI]_0^2$. The reaction rate will therefore quadruple.

  2. **A** Because no concentration term appears in the rate law, the rate constant must have M/s units for the reaction rate to have M/s units.

  B The rate law tells us that the reaction rate is constant and independent of the N_2O concentration. That is, the reaction is zeroth order in N_2O and zeroth order overall.

  C Because the reaction rate is independent of the N_2O concentration, doubling the concentration will have no effect on the reaction rate.

  3. **A** The rate law contains only one concentration term raised to the first power. Hence the rate constant must have units of reciprocal seconds (s^{-1}) to have units of moles per liter per second for the reaction rate: $M \cdot s^{-1} = M/s$.

  B The only concentration in the rate law is that of cyclopropane, and its exponent is 1. This means that the reaction is first order in cyclopropane. Cyclopropane is the only species that appears in the rate law, so the reaction is also first order overall.

C Doubling the initial cyclopropane concentration will increase the reaction rate from $k[\text{cyclopropane}]_0$ to $2k[\text{cyclopropane}]_0$. This doubles the reaction rate.

? Exercise 9.2.2

Given the following two reactions and their experimentally determined differential rate laws: determine the units of the rate constant if time is in seconds, determine the reaction order with respect to each reactant, give the overall reaction order, and predict what will happen to the reaction rate when the concentration of the first species in each equation is doubled.

a.
$$\text{CH}_3\text{N}=\text{NCH}_3(\text{g}) \rightarrow \text{C}_2\text{H}_6(\text{g}) + \text{N}_2(\text{g}) \quad \text{rate} = -\frac{\Delta[\text{CH}_3\text{N}=\text{NCH}_3]}{\Delta t} \tag{9.2.8}$$
$$= k[\text{CH}_3\text{N}=\text{NCH}_3] \tag{9.2.9}$$
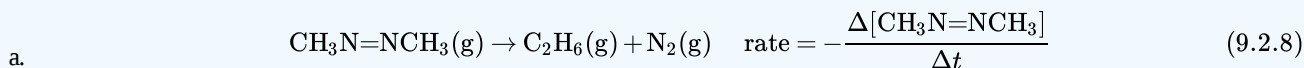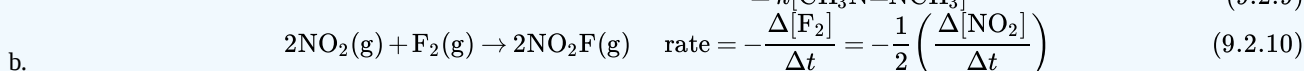
b.
$$2\text{NO}_2(\text{g}) + \text{F}_2(\text{g}) \rightarrow 2\text{NO}_2\text{F}(\text{g}) \quad \text{rate} = -\frac{\Delta[\text{F}_2]}{\Delta t} = -\frac{1}{2}\left(\frac{\Delta[\text{NO}_2]}{\Delta t}\right) \tag{9.2.10}$$
$$= k[\text{NO}_2][\text{F}_2] \tag{9.2.11}$$

Answer a

s^{-1}; first order in $\text{CH}_3\text{N}=\text{NCH}_3$; first order overall; doubling $[\text{CH}_3\text{N}=\text{NCH}_3]$ will double the reaction rate.

Answer b

$M^{-1}\cdot s^{-1}$; first order in NO_2, first order in F_2; second order overall; doubling $[\text{NO}_2]$ will double the reaction rate.

Determining the Rate Law of a Reaction

The number of fundamentally different mechanisms (sets of steps in a reaction) is actually rather small compared to the large number of chemical reactions that can occur. Thus understanding **reaction mechanisms** can simplify what might seem to be a confusing variety of chemical reactions. The first step in discovering the reaction mechanism is to determine the reaction's rate law. This can be done by designing experiments that measure the concentration(s) of one or more reactants or products as a function of time. For the reaction $A + B \rightarrow products$, for example, we need to determine k and the exponents m and n in the following equation:

$$\text{rate} = k[A]^m[B]^n \tag{9.2.12}$$

To do this, we might keep the initial concentration of B constant while varying the initial concentration of A and calculating the initial reaction rate. This information would permit us to deduce the reaction order with respect to A. Similarly, we could determine the reaction order with respect to B by studying the initial reaction rate when the initial concentration of A is kept constant while the initial concentration of B is varied. In earlier examples, we determined the reaction order with respect to a given reactant by comparing the different rates obtained when only the concentration of the reactant in question was changed. An alternative way of determining reaction orders is to set up a proportion using the rate laws for two different experiments. Rate data for a hypothetical reaction of the type $A + B \rightarrow products$ are given in Table 9.2.1.

Table 9.2.1: Rate Data for a Hypothetical Reaction of the Form $A + B \rightarrow products$

Experiment	[A] (M)	[B] (M)	Initial Rate (M/min)
1	0.50	0.50	8.5×10^{-3}
2	0.75	0.50	19×10^{-3}
3	1.00	0.50	34×10^{-3}
4	0.50	0.75	8.5×10^{-3}
5	0.50	1.00	8.5×10^{-3}

The general rate law for the reaction is given in Equation 9.2.12. We can obtain m or n directly by using a proportion of the rate laws for two experiments in which the concentration of one reactant is the same, such as Experiments 1 and 3 in Table 9.2.3.

$$\frac{\text{rate}_1}{\text{rate}_3} = \frac{k[\mathrm{A}_1]^m[\mathrm{B}_1]^n}{k[\mathrm{A}_3]^m[\mathrm{B}_3]^n}$$

Inserting the appropriate values from Table 9.2.3,

$$\frac{8.5 \times 10^{-3}\ \mathrm{M/min}}{34 \times 10^{-3}\ \mathrm{M/min}} = \frac{k[0.50\ \mathrm{M}]^m[0.50\ \mathrm{M}]^n}{k[1.00\ \mathrm{M}]^m[0.50\ \mathrm{M}]^n}$$

Because 1.00 to any power is 1, $[1.00\ \mathrm{M}]^m = 1.00\ \mathrm{M}$. We can cancel like terms to give $0.25 = [0.50]^m$, which can also be written as $1/4 = [1/2]^m$. Thus we can conclude that $m = 2$ and that the reaction is second order in A. By selecting two experiments in which the concentration of B is the same, we were able to solve for m.

Conversely, by selecting two experiments in which the concentration of A is the same (e.g., Experiments 5 and 1), we can solve for n.

$$\frac{\text{rate}_1}{\text{rate}_5} = \frac{k[\mathrm{A}_1]^m[\mathrm{B}_1]^n}{k[\mathrm{A}_5]^m[\mathrm{B}_5]^n}$$

Substituting the appropriate values from Table 9.2.3,

$$\frac{8.5 \times 10^{-3}\ \mathrm{M/min}}{8.5 \times 10^{-3}\ \mathrm{M/min}} = \frac{k[0.50\ \mathrm{M}]^m[0.50\ \mathrm{M}]^n}{k[0.50\ \mathrm{M}]^m[1.00\ \mathrm{M}]^n}$$

Canceling leaves $1.0 = [0.50]^n$, which gives $n = 0$; that is, the reaction is zeroth order in B. The experimentally determined rate law is therefore

$$\text{rate} = k[\mathrm{A}]^2[\mathrm{B}]^0 = k[\mathrm{A}]^2$$

We can now calculate the rate constant by inserting the data from any row of Table 9.2.3 into the experimentally determined rate law and solving for k. Using Experiment 2, we obtain

$$19 \times 10^{-3}\ \mathrm{M/min} = k(0.75\ \mathrm{M})^2$$

$$3.4 \times 10^{-2}\ \mathrm{M^{-1} \cdot min^{-1}} = k$$

You should verify that using data from any other row of Table 9.2.1 gives the same rate constant. This must be true as long as the experimental conditions, such as temperature and solvent, are the same.

> ✔ **Example 9.2.3**
>
> Nitric oxide is produced in the body by several different enzymes and acts as a signal that controls blood pressure, long-term memory, and other critical functions. The major route for removing NO from biological fluids is via reaction with O_2 to give NO_2, which then reacts rapidly with water to give nitrous acid and nitric acid:
>
> $$2NO + O_2 \longrightarrow 2NO_2 \xrightarrow{\ H_2O\ } HNO_2 + HNO_3$$
>
> These reactions are important in maintaining steady levels of NO. The following table lists kinetics data for the reaction of NO with O_2 at 25°C:
>
> $$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$
>
> Determine the rate law for the reaction and calculate the rate constant.
>
> rate law for the reaction and calculate the rate constant.
>
> | Experiment | $[NO]_0$ (M) | $[O_2]_0$ (M) | Initial Rate (M/s) |
> | --- | --- | --- | --- |
> | 1 | 0.0235 | 0.0125 | 7.98×10^{-3} |
> | 2 | 0.0235 | 0.0250 | 15.9×10^{-3} |
> | 3 | 0.0470 | 0.0125 | 32.0×10^{-3} |
> | 4 | 0.0470 | 0.0250 | 63.5×10^{-3} |
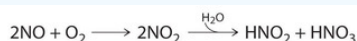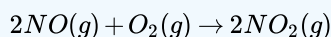
Given: balanced chemical equation, initial concentrations, and initial rates

Asked for: rate law and rate constant

Strategy:
A. Compare the changes in initial concentrations with the corresponding changes in rates of reaction to determine the reaction order for each species. Write the rate law for the reaction.
B. Using data from any experiment, substitute appropriate values into the rate law. Solve the rate equation for k.

Solution

A Comparing Experiments 1 and 2 shows that as $[O_2]$ is doubled at a constant value of $[NO_2]$, the reaction rate approximately doubles. Thus the reaction rate is proportional to $[O_2]^1$, so the reaction is first order in O_2. Comparing Experiments 1 and 3 shows that the reaction rate essentially quadruples when [NO] is doubled and $[O_2]$ is held constant. That is, the reaction rate is proportional to $[NO]^2$, which indicates that the reaction is second order in NO. Using these relationships, we can write the rate law for the reaction:

$$\text{rate} = k[NO]^2[O_2]$$

B The data in any row can be used to calculate the rate constant. Using Experiment 1, for example, gives

$$k = \frac{\text{rate}}{[NO]^2[O_2]} = \frac{7.98 \times 10^{-3} \text{ M/s}}{(0.0235 \text{ M})^2(0.0125 \text{ M})} = 1.16 \times 10^3 \text{ M}^{-2} \cdot \text{s}^{-1}$$

Alternatively, using Experiment 2 gives

$$k = \frac{\text{rate}}{[NO]^2[O_2]} = \frac{15.9 \times 10^{-3} \text{ M/s}}{(0.0235 \text{ M})^2(0.0250 \text{ M})} = 1.15 \times 10^3 \text{ M}^{-2} \cdot \text{s}^{-1}$$

The difference is minor and associated with significant digits and likely experimental error in making the table.

The overall reaction order $(m+n) = 3$, so this is a third-order reaction whose rate is determined by three reactants. The units of the rate constant become more complex as the overall reaction order increases.

? Exercise 9.2.3

The peroxydisulfate ion ($S_2O_8{}^{2-}$) is a potent oxidizing agent that reacts rapidly with iodide ion in water:

$$S_2O_{8(aq)}^{2-} + 3I_{(aq)}^- \rightarrow 2SO_{4(aq)}^{2-} + I_{3(aq)}^-$$
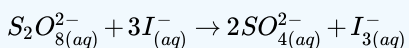
The following table lists kinetics data for this reaction at 25°C. Determine the rate law and calculate the rate constant.

kinetics data for this reaction at 25°C.

Experiment	$[S_2O_8{}^{2-}]_0$ (M)	$[I^-]_0$ (M)	Initial Rate (M/s)
1	0.27	0.38	2.05
2	0.40	0.38	3.06
3	0.40	0.22	1.76

Answer:

rate = $k[S_2O_8{}^{2-}][I^-]$; k = 20 M^{-1}·s^{-1}

A Video Discussing Initial Rates and Rate Law Expressions. Video Link: Initial Rates and Rate Law Expressions(opens in new window) [youtu.be]

Summary

The rate law for a reaction is a mathematical relationship between the reaction rate and the concentrations of species in solution. Rate laws can be expressed either as a differential rate law, describing the change in reactant or product concentrations as a function of time, or as an integrated rate law, describing the actual concentrations of reactants or products as a function of time. The rate constant (k) of a rate law is a constant of proportionality between the reaction rate and the reactant concentration. The exponent to which a concentration is raised in a rate law indicates the reaction order, the degree to which the reaction rate depends on the concentration of a particular reactant.

9.3: The Integrated Rate Law- The Dependence of Concentration on Time

> ◀▶ **Learning Objectives**
>
> - To apply rate laws to zeroth, first and second order reactions.

Either the differential rate law or the integrated rate law can be used to determine the reaction order from experimental data. Often, the exponents in the rate law are the positive integers: 1 and 2 or even 0. Thus the reactions are zeroth, first, or second order in each reactant. The common patterns used to identify the reaction order are described in this section, where we focus on characteristic types of differential and integrated rate laws and how to determine the reaction order from experimental data. The learning objective of this Module is to know how to determine the reaction order from experimental data.

Zeroth-Order Reactions

A **zeroth-order reaction** is one whose rate is independent of concentration; its differential rate law is

$$\text{rate} = k.$$

We refer to these reactions as zeroth order because we could also write their rate in a form such that the exponent of the reactant in the rate law is 0:

$$\text{rate} = -\frac{\Delta[A]}{\Delta t} = k[\text{reactant}]^0 = k(1) = k \tag{9.3.1}$$

Because rate is independent of reactant concentration, a graph of the concentration of any reactant as a function of time is a straight line with a slope of $-k$. The value of k is negative because the concentration of the reactant decreases with time. Conversely, a graph of the concentration of any product as a function of time is a straight line with a slope of k, a positive value.
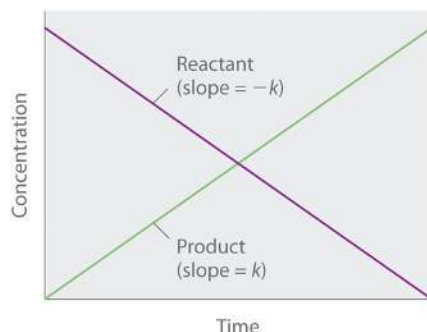
Figure $9.3.1$: The graph of a zeroth-order reaction. The change in concentration of reactant and product with time produces a straight line.

Graph of concentration against time. The reactant is in purple and has a slope of minus k. The product is in green and has a slope of positive k.

The integrated rate law for a zeroth-order reaction also produces a straight line and has the general form

$$[A] = [A]_0 - kt \tag{9.3.2}$$

where $[A]_0$ is the initial concentration of reactant A. Equation $9.3.2$ has the form of the algebraic equation for a straight line,

$$y = mx + b,$$

with $y = [A]$, $mx = -kt$, and $b = [A]_0$.)

> 📌 **Units**
>
> In a zeroth-order reaction, the rate constant must have the same units as the reaction rate, typically moles per liter per second.

Although it may seem counterintuitive for the reaction rate to be independent of the reactant concentration(s), such reactions are rather common. They occur most often when the reaction rate is determined by available surface area. An example is the

decomposition of N_2O on a platinum (Pt) surface to produce N_2 and O_2, which occurs at temperatures ranging from 200°C to 400°C:

$$2N_2O(g) \xrightarrow{\text{Pt}} 2N_2(g) + O_2(g) \tag{9.3.3}$$

Without a platinum surface, the reaction requires temperatures greater than 700°C, but between 200°C and 400°C, the only factor that determines how rapidly N_2O decomposes is the amount of Pt surface available (not the amount of Pt). As long as there is enough N_2O to react with the entire Pt surface, doubling or quadrupling the N_2O concentration will have no effect on the reaction rate. At very low concentrations of N_2O, where there are not enough molecules present to occupy the entire available Pt surface, the reaction rate is dependent on the N_2O concentration. The reaction rate is as follows:

$$\text{rate} = -\frac{1}{2}\left(\frac{\Delta[N_2O]}{\Delta t}\right) = \frac{1}{2}\left(\frac{\Delta[N_2]}{\Delta t}\right) = \frac{\Delta[O_2]}{\Delta t} = k[N_2O]^0 = k \tag{9.3.4}$$

Thus the rate at which N_2O is consumed and the rates at which N_2 and O_2 are produced are independent of concentration. As shown in Figure 9.3.2, the change in the concentrations of all species with time is linear. Most important, the exponent (0) corresponding to the N_2O concentration in the experimentally derived rate law is not the same as the reactant's stoichiometric coefficient in the balanced chemical equation (2). For this reaction, as for all others, the rate law must be determined experimentally.
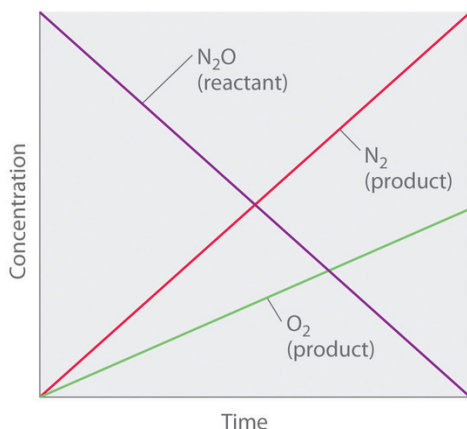
Figure 9.3.2: A Zeroth-Order Reaction. This graph shows the concentrations of reactants and products versus time for the zeroth-order catalyzed decomposition of N_2O to N_2 and O_2 on a Pt surface. The change in the concentrations of all species with time is linear.

Graph of concentration against time. N2O is the reactant is graphed in purple. O2 is one of the products and is graphed in green. The second product is N2 which is graphed in red

A zeroth-order reaction that takes place in the human liver is the oxidation of ethanol (from alcoholic beverages) to acetaldehyde, catalyzed by the **enzyme** alcohol dehydrogenase. At high ethanol concentrations, this reaction is also a zeroth-order reaction. The overall reaction equation is

Figure 9.3.2

where \ce{NAD^{+}}\) (nicotinamide adenine dinucleotide) and NADH (reduced nicotinamide adenine dinucleotide) are the oxidized and reduced forms, respectively, of a species used by all organisms to transport electrons. When an alcoholic beverage is consumed, the ethanol is rapidly absorbed into the blood. Its concentration then decreases at a constant rate until it reaches zero (Figure 9.3.3a). An average 70 kg person typically takes about 2.5 h to oxidize the 15 mL of ethanol contained in a single 12 oz can of beer, a 5 oz glass of wine, or a shot of distilled spirits (such as whiskey or brandy). The actual rate, however, varies a great deal from person to person, depending on body size and the amount of alcohol dehydrogenase in the liver. The reaction rate does not increase if a greater quantity of alcohol is consumed over the same period of time because the reaction rate is determined only by the amount of enzyme present in the liver. Contrary to popular belief, the caffeine in coffee is ineffective at catalyzing the oxidation of ethanol. When the ethanol has been completely oxidized and its concentration drops to essentially zero, the rate of oxidation also drops rapidly (part (b) in Figure 9.3.3).
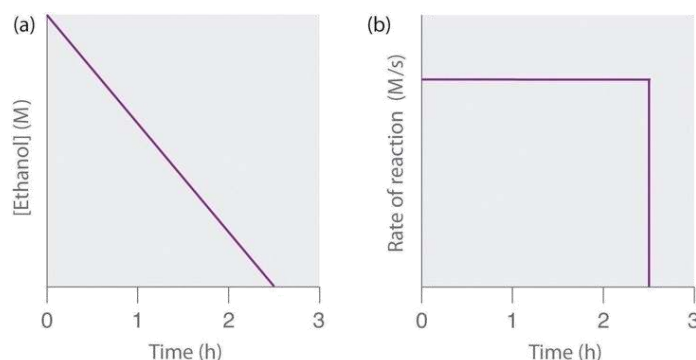
Figure 9.3.3: The Catalyzed Oxidation of Ethanol (a) The concentration of ethanol in human blood decreases linearly with time, which is typical of a zeroth-order reaction. (b) The rate at which ethanol is oxidized is constant until the ethanol concentration reaches essentially zero, at which point the reaction rate drops to zero.

These examples illustrate two important points:

1. In a zeroth-order reaction, the reaction rate does not depend on the reactant concentration.
2. A linear change in concentration with time is a clear indication of a zeroth-order reaction.

First-Order Reactions

In a **first-order reaction**, the reaction rate is directly proportional to the concentration of one of the reactants. First-order reactions often have the general form A → products. The differential rate for a first-order reaction is as follows:

$$\text{rate} = -\frac{\Delta[\text{A}]}{\Delta t} = k[\text{A}] \tag{9.3.5}$$

If the concentration of A is doubled, the reaction rate doubles; if the concentration of A is increased by a factor of 10, the reaction rate increases by a factor of 10, and so forth. Because the units of the reaction rate are always moles per liter per second, the units of a first-order rate constant are reciprocal seconds (s^{-1}).

The integrated rate law for a first-order reaction can be written in two different ways: one using exponents and one using logarithms. The exponential form is as follows:

$$[A] = [A]_0 e^{-kt} \tag{9.3.6}$$

where $[A]_0$ is the initial concentration of reactant A at $t = 0$; k is the rate constant; and e is the base of the natural logarithms, which has the value 2.718 to three decimal places. Recall that an integrated rate law gives the relationship between reactant concentration and time. Equation 9.3.6 predicts that the concentration of A will decrease in a smooth exponential curve over time. By taking the natural logarithm of each side of Equation 9.3.6 and rearranging, we obtain an alternative logarithmic expression of the relationship between the concentration of A and t:

$$\ln[A] = \ln[A]_0 - kt \tag{9.3.7}$$

Because Equation 9.3.7 has the form of the algebraic equation for a straight line,

$$y = mx + b,$$

with $y = \ln[A]$ and $b = \ln[A]_0$, a plot of $\ln[A]$ versus t for a first-order reaction should give a straight line with a slope of $-k$ and an intercept of $\ln[A]_0$. Either the differential rate law (Equation 9.3.5) or the integrated rate law (Equation 9.3.7) can be used to determine whether a particular reaction is first order.
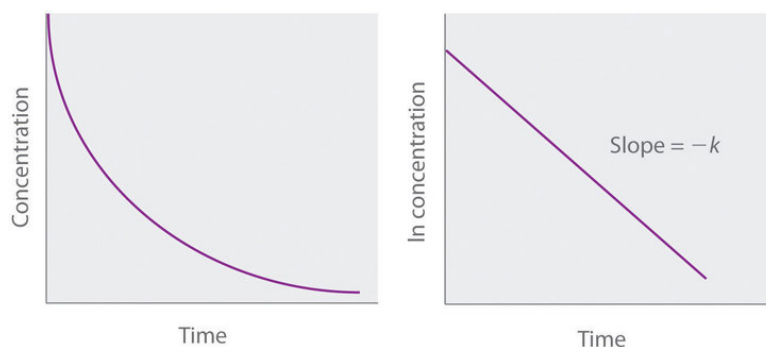
Figure 9.3.4: Graphs of a first-order reaction. The expected shapes of the curves for plots of reactant concentration versus time (top) and the natural logarithm of reactant concentration versus time (bottom) for a first-order reaction.

First-order reactions are very common. One reaction that exhibits apparent first-order kinetics is the hydrolysis of the anticancer drug cisplatin. Cisplatin, the first "inorganic" anticancer drug to be discovered, is unique in its ability to cause complete remission of the relatively rare, but deadly cancers of the reproductive organs in young adults. The structures of cisplatin and its hydrolysis product are as follows:
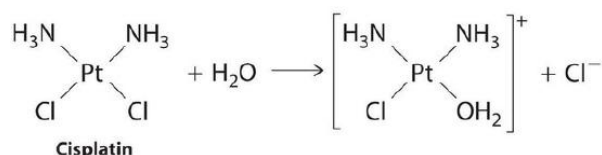
Figure 9.3.5: Cis-platin reaction with water.

Both platinum compounds have four groups arranged in a square plane around a Pt(II) ion. The reaction shown in Figure 9.3.5 is important because cisplatin, the form in which the drug is administered, is not the form in which the drug is active. Instead, at least one chloride ion must be replaced by water to produce a species that reacts with deoxyribonucleic acid (DNA) to prevent cell division and tumor growth. Consequently, the kinetics of the reaction in Figure 9.3.4 have been studied extensively to find ways of maximizing the concentration of the active species.

> *If a plot of reactant concentration versus time is not linear but a plot of the natural logarithm of reactant concentration versus time is linear, then the reaction is first order.*

The rate law and reaction order of the hydrolysis of cisplatin are determined from experimental data, such as those displayed in Table 9.3.1. The table lists initial rate data for four experiments in which the reaction was run at pH 7.0 and 25°C but with different initial concentrations of cisplatin.

Table 9.3.1: Rates of Hydrolysis of Cisplatin as a Function of Concentration at pH 7.0 and 25°C

Experiment	[Cisplatin]$_0$ (M)	Initial Rate (M/min)
1	0.0060	9.0×10^{-6}
2	0.012	1.8×10^{-5}
3	0.024	3.6×10^{-5}
4	0.030	4.5×10^{-5}

Because the reaction rate increases with increasing cisplatin concentration, we know this cannot be a zeroth-order reaction. Comparing Experiments 1 and 2 in Table 9.3.1 shows that the reaction rate doubles [$(1.8 \times 10^{-5}$ M/min) $\div (9.0 \times 10^{-6}$ M/min) $= 2.0$] when the concentration of cisplatin is doubled (from 0.0060 M to 0.012 M). Similarly, comparing Experiments 1 and 4 shows that the reaction rate increases by a factor of 5 [$(4.5 \times 10^{-5}$ M/min) $\div (9.0 \times 10^{-6}$ M/min) $= 5.0$] when the concentration of cisplatin is increased by a factor of 5 (from 0.0060 M to 0.030 M). Because the reaction rate is directly proportional to the concentration of the reactant, the exponent of the cisplatin concentration in the rate law must be 1, so the rate law is rate $= k$[cisplatin]^1. Thus the reaction is first order. Knowing this, we can calculate the rate constant using the differential rate law for a first-order reaction and the data in any row of Table 9.3.1. For example, substituting the values for Experiment 3 into Equation 9.3.5,

$$3.6 \times 10^{-5} \text{ M/min} = k(0.024 \text{ M})$$
$$1.5 \times 10^{-3} \text{ min}^{-1} = k$$

Knowing the rate constant for the hydrolysis of cisplatin and the rate constants for subsequent reactions that produce species that are highly toxic enables hospital pharmacists to provide patients with solutions that contain only the desired form of the drug.

✔ Example 9.3.1

At high temperatures, ethyl chloride produces HCl and ethylene by the following reaction:

$$CH_3CH_2Cl(g) \xrightarrow{\Delta} HCl(g) + C_2H_4(g)$$
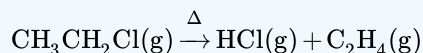
Using the rate data for the reaction at 650°C presented in the following table, calculate the reaction order with respect to the concentration of ethyl chloride and determine the rate constant for the reaction.

data for the reaction at 650°C

Experiment	$[CH_3CH_2Cl]_0$ (M)	Initial Rate (M/s)
1	0.010	1.6×10^{-8}
2	0.015	2.4×10^{-8}
3	0.030	4.8×10^{-8}
4	0.040	6.4×10^{-8}

Given: balanced chemical equation, initial concentrations of reactant, and initial rates of reaction

Asked for: reaction order and rate constant

Strategy:
A. Compare the data from two experiments to determine the effect on the reaction rate of changing the concentration of a species.
B. Compare the observed effect with behaviors characteristic of zeroth- and first-order reactions to determine the reaction order. Write the rate law for the reaction.
C Use measured concentrations and rate data from any of the experiments to find the rate constant.

Solution

The reaction order with respect to ethyl chloride is determined by examining the effect of changes in the ethyl chloride concentration on the reaction rate.

A Comparing Experiments 2 and 3 shows that doubling the concentration doubles the reaction rate, so the reaction rate is proportional to $[CH_3CH_2Cl]$. Similarly, comparing Experiments 1 and 4 shows that quadrupling the concentration quadruples the reaction rate, again indicating that the reaction rate is directly proportional to $[CH_3CH_2Cl]$.

B This behavior is characteristic of a first-order reaction, for which the rate law is rate = $k[CH_3CH_2Cl]$.

C We can calculate the rate constant (k) using any row in the table. Selecting Experiment 1 gives the following:

$$1.60 \times 10^{-8} \text{ M/s} = k(0.010 \text{ M})$$
$$1.6 \times 10^{-6} \text{ s}^{-1} = k$$

? Exercise 9.3.1

Sulfuryl chloride (SO_2Cl_2) decomposes to SO_2 and Cl_2 by the following reaction:

$$SO_2Cl_2(g) \rightarrow SO_2(g) + Cl_2(g)$$

Data for the reaction at 320°C are listed in the following table. Calculate the reaction order with regard to sulfuryl chloride and determine the rate constant for the reaction.

Data for the reaction at 320°C		
Experiment	**$[SO_2Cl_2]_0$ (M)**	**Initial Rate (M/s)**
1	0.0050	1.10×10^{-7}
2	0.0075	1.65×10^{-7}
3	0.0100	2.20×10^{-7}
4	0.0125	2.75×10^{-7}

Answer

first order; $k = 2.2 \times 10^{-5}$ s^{-1}

We can also use the integrated rate law to determine the reaction rate for the hydrolysis of cisplatin. To do this, we examine the change in the concentration of the reactant or the product as a function of time at a single initial cisplatin concentration. Figure $9.3.6a$ shows plots for a solution that originally contained 0.0100 M cisplatin and was maintained at pH 7 and 25°C.

(a)   **(b)**
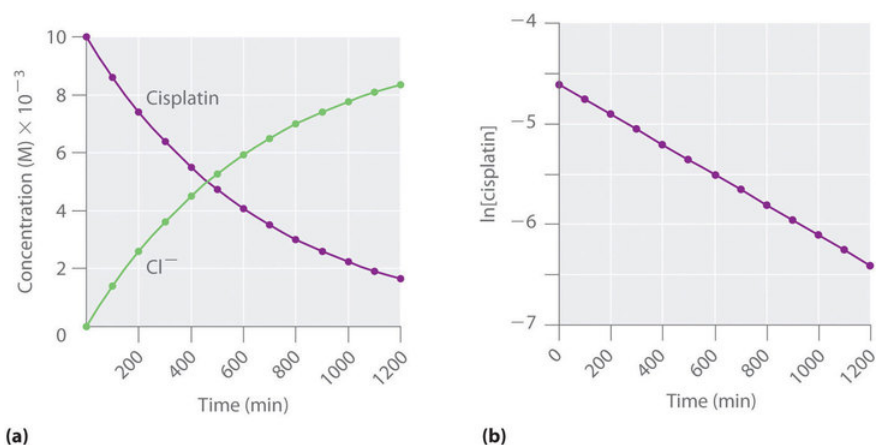
Figure $9.3.6$: The Hydrolysis of Cisplatin, a First-Order Reaction. These plots show hydrolysis of cisplatin at pH 7.0 and 25°C as (a) the experimentally determined concentrations of cisplatin and chloride ions versus time and (b) the natural logarithm of the cisplatin concentration versus time. The straight line in (b) is expected for a first-order reaction.

The concentration of cisplatin decreases smoothly with time, and the concentration of chloride ion increases in a similar way. When we plot the natural logarithm of the concentration of cisplatin versus time, we obtain the plot shown in part (b) in Figure $9.3.6$. The straight line is consistent with the behavior of a system that obeys a first-order rate law. We can use any two points on the line to calculate the slope of the line, which gives us the rate constant for the reaction. Thus taking the points from part (a) in Figure $9.3.6$ for $t = 100$ min ([cisplatin] = 0.0086 M) and $t = 1000$ min ([cisplatin] = 0.0022 M),

$$\text{slope} = \frac{\ln[\text{cisplatin}]_{1000} - \ln[\text{cisplatin}]_{100}}{1000 \text{ min} - 100 \text{ min}}$$

$$-k = \frac{\ln 0.0022 - \ln 0.0086}{1000 \text{ min} - 100 \text{ min}} = \frac{-6.12 - (-4.76)}{900 \text{ min}} = -1.51 \times 10^{-3} \text{ min}^{-1}$$

$$k = 1.5 \times 10^{-3} \text{ min}^{-1}$$

The slope is negative because we are calculating the rate of disappearance of cisplatin. Also, the rate constant has units of min^{-1} because the times plotted on the horizontal axes in parts (a) and (b) in Figure $9.3.6$ are in minutes rather than seconds.

The reaction order and the magnitude of the rate constant we obtain using the integrated rate law are exactly the same as those we calculated earlier using the differential rate law. This must be true if the experiments were carried out under the same conditions.

Video Example Using the First-Order Integrated Rate Law Equation:

Example Using the First-Order Integrated Rate Law Equation(opens in new window) [youtu.be]

✔ **Example 9.3.2**

If a sample of ethyl chloride with an initial concentration of 0.0200 M is heated at 650°C, what is the concentration of ethyl chloride after 10 h? How many hours at 650°C must elapse for the concentration to decrease to 0.0050 M ($k = 1.6 \times 10^{-6}$ s^{-1}) ?

Given: initial concentration, rate constant, and time interval

Asked for: concentration at specified time and time required to obtain particular concentration

Strategy:
A. Substitute values for the initial concentration ($[A]_0$) and the calculated rate constant for the reaction (k) into the integrated rate law for a first-order reaction. Calculate the concentration ($[A]$) at the given time t.
B. Given a concentration $[A]$, solve the integrated rate law for time t.

Solution

The exponential form of the integrated rate law for a first-order reaction (Equation 9.3.6) is $[A] = [A]_0 e^{-kt}$.

A Having been given the initial concentration of ethyl chloride ($[A]_0$) and having the rate constant of $k = 1.6 \times 10^{-6}$ s^{-1}, we can use the rate law to calculate the concentration of the reactant at a given time t. Substituting the known values into the integrated rate law,

$$[CH_3CH_2Cl]_{10\ h} = [CH_3CH_2Cl]_0 e^{-kt}$$
$$= 0.0200\ M(e^{-(1.6 \times 10^{-6}\ s^{-1})[(10\ h)(60\ min/h)(60\ s/min)]})$$
$$= 0.0189\ M$$

We could also have used the logarithmic form of the integrated rate law (Equation 9.3.7):

$$\ln[CH_3CH_2Cl]_{10\ h} = \ln[CH_3CH_2Cl]_0 - kt$$
$$= \ln 0.0200 - (1.6 \times 10^{-6}\ s^{-1})[(10\ h)(60\ min/h)(60\ s/min)]$$
$$= -3.912 - 0.0576 = -3.970$$
$$[CH_3CH_2Cl]_{10\ h} = e^{-3.970}\ M$$
$$= 0.0189\ M$$

B To calculate the amount of time required to reach a given concentration, we must solve the integrated rate law for t. Equation 9.3.7 gives the following:

$$\ln[\mathrm{CH_3CH_2Cl}]_t = \ln[\mathrm{CH_3CH_2Cl}]_0 - kt$$

$$kt = \ln[\mathrm{CH_3CH_2Cl}]_0 - \ln[\mathrm{CH_3CH_2Cl}]_t = \ln\frac{[\mathrm{CH_3CH_2Cl}]_0}{[\mathrm{CH_3CH_2Cl}]_t}$$

$$t = \frac{1}{k}\left(\ln\frac{[\mathrm{CH_3CH_2Cl}]_0}{[\mathrm{CH_3CH_2Cl}]_t}\right) = \frac{1}{1.6\times10^{-6}\ \mathrm{s^{-1}}}\left(\ln\frac{0.0200\ \mathrm{M}}{0.0050\ \mathrm{M}}\right)$$

$$= \frac{\ln 4.0}{1.6\times10^{-6}\ \mathrm{s^{-1}}} = 8.7\times10^5\ \mathrm{s} = 240\ \mathrm{h} = 2.4\times10^2\ \mathrm{h}$$

? Exercise 9.3.2

In the exercise in Example 9.3.1, you found that the decomposition of sulfuryl chloride (SO_2Cl_2) is first order, and you calculated the rate constant at 320°C.

a. Use the form(s) of the integrated rate law to find the amount of SO_2Cl_2 that remains after 20 h if a sample with an original concentration of 0.123 M is heated at 320°C.
b. How long would it take for 90% of the SO_2Cl_2 to decompose?

Answer a

0.0252 M

Answer b

29 h

Second-Order Reactions

The simplest kind of **second-order reaction** is one whose rate is proportional to the square of the concentration of one reactant. These generally have the form
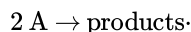
$$2\,\mathrm{A} \rightarrow \mathrm{products}\cdot$$

A second kind of second-order reaction has a reaction rate that is proportional to the product of the concentrations of two reactants. Such reactions generally have the form A + B → products. An example of the former is a dimerization reaction, in which two smaller molecules, each called a monomer, combine to form a larger molecule (a dimer).

The differential rate law for the simplest second-order reaction in which 2A → products is as follows:

$$\mathrm{rate} = -\frac{\Delta[\mathrm{A}]}{2\Delta t} = k[\mathrm{A}]^2 \tag{9.3.8}$$

Consequently, doubling the concentration of A quadruples the reaction rate. For the units of the reaction rate to be moles per liter per second (M/s), the units of a second-order rate constant must be the inverse ($\mathrm{M^{-1}\cdot s^{-1}}$). Because the units of molarity are expressed as mol/L, the unit of the rate constant can also be written as L(mol·s).

For the reaction 2A → products, the following integrated rate law describes the concentration of the reactant at a given time:

$$\frac{1}{[\mathrm{A}]} = \frac{1}{[\mathrm{A}]_0} + kt \tag{9.3.9}$$

Because Equation 9.3.9 has the form of an algebraic equation for a straight line, $y = mx + b$, with $y = 1/[\mathrm{A}]$ and $b = 1/[\mathrm{A}]_0$, a plot of $1/[\mathrm{A}]$ versus t for a simple second-order reaction is a straight line with a slope of k and an intercept of $1/[\mathrm{A}]_0$.

Second-order reactions generally have the form 2A → products or A + B → products.

Video Discussing the Second-Order Integrated Rate Law Equation: Second-Order Integrated Rate Law Equation(opens in new window) [youtu.be]

Simple second-order reactions are common. In addition to dimerization reactions, two other examples are the decomposition of NO_2 to NO and O_2 and the decomposition of HI to I_2 and H_2. Most examples involve simple inorganic molecules, but there are organic examples as well. We can follow the progress of the reaction described in the following paragraph by monitoring the decrease in the intensity of the red color of the reaction mixture.

Many cyclic organic compounds that contain two carbon–carbon double bonds undergo a dimerization reaction to give complex structures. One example is as follows:
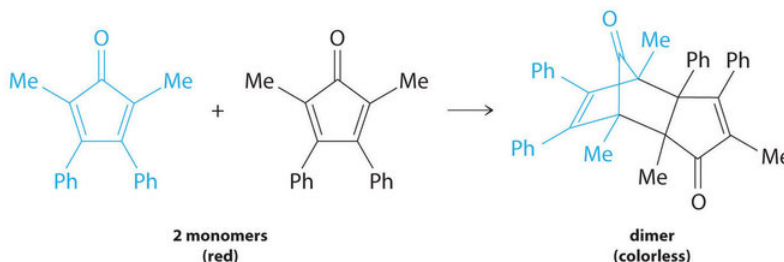
Figure $9.3.7$

For simplicity, we will refer to this reactant and product as "monomer" and "dimer," respectively. The systematic name of the monomer is 2,5-dimethyl-3,4-diphenylcyclopentadienone. The systematic name of the dimer is the name of the monomer followed by "dimer." Because the monomers are the same, the general equation for this reaction is 2A → product. This reaction represents an important class of organic reactions used in the pharmaceutical industry to prepare complex carbon skeletons for the synthesis of drugs. Like the first-order reactions studied previously, it can be analyzed using either the differential rate law (Equation $9.3.8$) or the integrated rate law (Equation $9.3.9$).

Table $9.3.2$: Rates of Reaction as a Function of Monomer Concentration for an Initial Monomer Concentration of 0.0054 M

Time (min)	[Monomer] (M)	Instantaneous Rate (M/min)
10	0.0044	8.0×10^{-5}
26	0.0034	5.0×10^{-5}
44	0.0027	3.1×10^{-5}
70	0.0020	1.8×10^{-5}
120	0.0014	8.0×10^{-6}

To determine the differential rate law for the reaction, we need data on how the reaction rate varies as a function of monomer concentrations, which are provided in Table $9.3.2$. From the data, we see that the reaction rate is not independent of the monomer

concentration, so this is not a zeroth-order reaction. We also see that the reaction rate is not proportional to the monomer concentration, so the reaction is not first order. Comparing the data in the second and fourth rows shows that the reaction rate decreases by a factor of 2.8 when the monomer concentration decreases by a factor of 1.7:

$$\frac{5.0 \times 10^{-5} \text{ M/min}}{1.8 \times 10^{-5} \text{ M/min}} = 2.8 \quad \text{and} \quad \frac{3.4 \times 10^{-3} \text{ M}}{2.0 \times 10^{-3} \text{ M}} = 1.7$$

Because $(1.7)^2 = 2.9 \approx 2.8$, the reaction rate is approximately proportional to the square of the monomer concentration.

$$\text{rate} \propto [\text{monomer}]^2$$

This means that the reaction is second order in the monomer. Using Equation 9.3.8 and the data from any row in Table 9.3.2, we can calculate the rate constant. Substituting values at time 10 min, for example, gives the following:

$$\text{rate} = k[\text{A}]^2 \tag{9.3.10}$$
$$8.0 \times 10^{-5} \text{ M/min} = k(4.4 \times 10^{-3} \text{ M})^2 \tag{9.3.11}$$
$$4.1 \text{ M}^{-1} \cdot \text{min}^{-1} = k \tag{9.3.12}$$

We can also determine the reaction order using the integrated rate law. To do so, we use the decrease in the concentration of the monomer as a function of time for a single reaction, plotted in Figure 9.3.8a. The measurements show that the concentration of the monomer (initially 5.4×10^{-3} M) decreases with increasing time. This graph also shows that the reaction rate decreases smoothly with increasing time. According to the integrated rate law for a second-order reaction, a plot of 1/[monomer] versus t should be a straight line, as shown in Figure 9.3.8b. Any pair of points on the line can be used to calculate the slope, which is the second-order rate constant. In this example, $k = 4.1$ M^{-1}·min^{-1}, which is consistent with the result obtained using the differential rate equation. Although in this example the stoichiometric coefficient is the same as the reaction order, this is not always the case. The reaction order must always be determined experimentally.
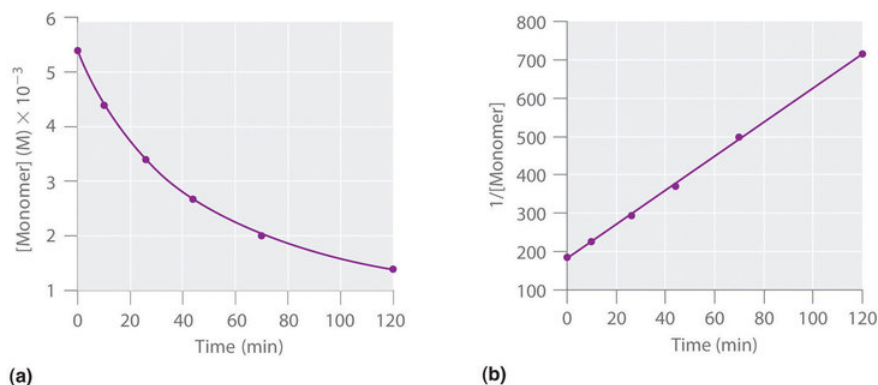
Figure 9.3.8: Dimerization of a Monomeric Compound, a Second-Order Reaction. These plots correspond to dimerization of the monomer in Figure 14.4.6 as (a) the experimentally determined concentration of monomer versus time and (b) 1/[monomer] versus time. The straight line in (b) is expected for a simple second-order reaction.

For two or more reactions of the same order, the reaction with the largest rate constant is the fastest. Because the units of the rate constants for zeroth-, first-, and second-order reactions are different, however, we cannot compare the magnitudes of rate constants for reactions that have different orders.

✔ Example 9.3.3

At high temperatures, nitrogen dioxide decomposes to nitric oxide and oxygen.

$$2NO_2(g) \xrightarrow{\Delta} 2NO(g) + O_2(g)$$
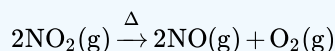
Experimental data for the reaction at 300°C and four initial concentrations of NO_2 are listed in the following table:

Experimental data for the reaction at 300°C and four initial concentrations of NO2

Experiment	$[NO_2]_0$ (M)	Initial Rate (M/s)
1	0.015	1.22×10^{-4}

Experiment	$[NO_2]_0$ (M)	Initial Rate (M/s)
2	0.010	5.40×10^{-5}
3	0.0080	3.46×10^{-5}
4	0.0050	1.35×10^{-5}

Determine the reaction order and the rate constant.

Given: balanced chemical equation, initial concentrations, and initial rates

Asked for: reaction order and rate constant

Strategy:
A. From the experiments, compare the changes in the initial reaction rates with the corresponding changes in the initial concentrations. Determine whether the changes are characteristic of zeroth-, first-, or second-order reactions.
B. Determine the appropriate rate law. Using this rate law and data from any experiment, solve for the rate constant (k).

Solution

A We can determine the reaction order with respect to nitrogen dioxide by comparing the changes in NO_2 concentrations with the corresponding reaction rates. Comparing Experiments 2 and 4, for example, shows that doubling the concentration quadruples the reaction rate [$(5.40 \times 10^{-5}) \div (1.35 \times 10^{-5}) = 4.0$], which means that the reaction rate is proportional to $[NO_2]^2$. Similarly, comparing Experiments 1 and 4 shows that tripling the concentration increases the reaction rate by a factor of 9, again indicating that the reaction rate is proportional to $[NO_2]^2$. This behavior is characteristic of a second-order reaction.

B We have rate = $k[NO_2]^2$. We can calculate the rate constant (k) using data from any experiment in the table. Selecting Experiment 2, for example, gives the following:

$$\text{rate} = k[NO_2]^2$$
$$5.40 \times 10^{-5} \text{ M/s} = k(0.010 \text{ M})^2$$
$$0.54 \text{ M}^{-1} \cdot \text{s}^{-1} = k$$

? Exercise 9.3.3

When the highly reactive species HO_2 forms in the atmosphere, one important reaction that then removes it from the atmosphere is as follows:

$$2HO_{2(g)} \rightarrow H_2O_{2(g)} + O_{2(g)}$$
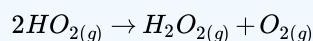
The kinetics of this reaction have been studied in the laboratory, and some initial rate data at 25°C are listed in the following table:

Some initial rate data at 25°C

Experiment	$[HO_2]_0$ (M)	Initial Rate (M/s)
1	1.1×10^{-8}	1.7×10^{-7}
2	2.5×10^{-8}	8.8×10^{-7}
3	3.4×10^{-8}	1.6×10^{-6}
4	5.0×10^{-8}	3.5×10^{-6}

Determine the reaction order and the rate constant.

Answer

second order in HO_2; $k = 1.4 \times 10^9$ M^{-1}·s^{-1}

If a plot of reactant concentration versus time is **not** linear, but a plot of 1/(reactant concentration) versus time is linear, then the reaction is second order.

> ✔ **Example 9.3.4**
>
> If a flask that initially contains 0.056 M NO_2 is heated at 300°C, what will be the concentration of NO_2 after 1.0 h? How long will it take for the concentration of NO_2 to decrease to 10% of the initial concentration? Use the integrated rate law for a second-order reaction (Equation 9.3.9) and the rate constant calculated above.
>
> **Given:** balanced chemical equation, rate constant, time interval, and initial concentration
>
> **Asked for:** final concentration and time required to reach specified concentration
>
> **Strategy:**
> A. Given k, t, and $[A]_0$, use the integrated rate law for a second-order reaction to calculate $[A]$.
> B. Setting $[A]$ equal to 1/10 of $[A]_0$, use the same equation to solve for t.
>
> **Solution**
>
> **A** We know k and $[NO_2]_0$, and we are asked to determine $[NO_2]$ at t = 1 h (3600 s). Substituting the appropriate values into Equation 9.3.9,
>
> $$\frac{1}{[NO_2]_{3600}} = \frac{1}{[NO_2]_0} + kt$$
> $$= \frac{1}{0.056 \text{ M}} + [(0.54 \text{ M}^{-1} \cdot \text{s}^{-1})(3600 \text{ s})]$$
> $$= 2.0 \times 10^3 \text{ M}^{-1}$$

Thus $[NO_2]_{3600}$ = 5.1 × 10^{-4} M.

> **B** In this case, we know k and $[NO_2]_0$, and we are asked to calculate at what time $[NO_2]$ = 0.1$[NO_2]_0$ = 0.1(0.056 M) = 0.0056 M. To do this, we solve Equation 9.3.9 for t, using the concentrations given.
>
> $$t = \frac{(1/[NO_2]) - (1/[NO_2]_0)}{k}$$
> $$= \frac{(1/0.0056 \text{ M}) - (1/0.056 \text{ M})}{0.54 \text{ M}^{-1} \cdot \text{s}^{-1}}$$
> $$= 3.0 \times 10^2 \text{ s} = 5.0 \text{ min}$$

NO_2 decomposes very rapidly; under these conditions, the reaction is 90% complete in only 5.0 min.

> ? **Exercise 9.3.4**
>
> In the previous exercise, you calculated the rate constant for the decomposition of HO_2 as k = 1.4 × 10^9 M^{-1}·s^{-1}. This high rate constant means that HO_2 decomposes rapidly under the reaction conditions given in the problem. In fact, the HO_2 molecule is so reactive that it is virtually impossible to obtain in high concentrations. Given a 0.0010 M sample of HO_2, calculate the concentration of HO_2 that remains after 1.0 h at 25°C. How long will it take for 90% of the HO_2 to decompose? Use the integrated rate law for a second-order reaction (Equation 9.3.9) and the rate constant calculated in the exercise in Example 9.3.3.
>
> **Answer**
>   2.0 × 10^{-13} M; 6.4 × 10^{-6} s

In addition to the simple second-order reaction and rate law we have just described, another very common second-order reaction has the general form $A + B \rightarrow products$, in which the reaction is first order in A and first order in B. The differential rate law for this reaction is as follows:

$$\text{rate} = -\frac{\Delta[\text{A}]}{\Delta t} = -\frac{\Delta[\text{B}]}{\Delta t} = k[\text{A}][\text{B}]$$

Because the reaction is first order both in A and in B, it has an overall reaction order of 2. (The integrated rate law for this reaction is rather complex, so we will not describe it.) We can recognize second-order reactions of this sort because the reaction rate is proportional to the concentrations of each reactant.

Summary

The reaction rate of a zeroth-order reaction is independent of the concentration of the reactants. The reaction rate of a first-order reaction is directly proportional to the concentration of one reactant. The reaction rate of a simple second-order reaction is proportional to the square of the concentration of one reactant. Knowing the rate law of a reaction gives clues to the reaction mechanism.

- **zeroth-order reaction:**

$$\text{rate} = -\frac{\Delta[\text{A}]}{\Delta t} = k$$

$$[A] = [A]_0 - kt$$

- **first-order reaction**:

$$\text{rate} = -\frac{\Delta[\text{A}]}{\Delta t} = k[\text{A}]$$

$$[A] = [A]_0 e^{-kt}$$

$$\ln[A] = \ln[A]_0 - kt$$

- **second-order reaction:**

$$\text{rate} = -\frac{\Delta[\text{A}]}{\Delta t} = k[\text{A}]^2$$

$$\frac{1}{[\text{A}]} = \frac{1}{[\text{A}]_0} + kt$$

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9.4: The Effect of Temperature on Reaction Rate

> **◑ Learning Objectives**
>
> - To understand why and how chemical reactions occur.

It is possible to use kinetics studies of a chemical system, such as the effect of changes in reactant concentrations, to deduce events that occur on a microscopic scale, such as collisions between individual particles. Such studies have led to the collision model of chemical kinetics, which is a useful tool for understanding the behavior of reacting chemical species. The collision model explains why chemical reactions often occur more rapidly at higher temperatures. For example, the reaction rates of many reactions that occur at room temperature approximately double with a temperature increase of only 10°C. In this section, we will use the collision model to analyze this relationship between temperature and reaction rates. Before delving into the relationship between temperature and reaction rate, we must discuss three microscopic factors that influence the observed macroscopic reaction rates.

Microscopic Factor 1: Collisional Frequency

Central to collision model is that a chemical reaction can occur only when the reactant molecules, atoms, or ions collide. Hence, the observed rate is influence by the frequency of collisions between the reactants. The **collisional frequency** is the average rate in which two reactants collide for a given system and is used to express the average number of collisions per unit of time in a defined system. While deriving the collisional frequency (Z_{AB}) between two species in a gas is straightforward, it is beyond the scope of this text and the equation for collisional frequency of A and B is the following:

$$Z_{AB} = N_A N_B (r_A + r_B)^2 \sqrt{\frac{8\pi k_B T}{\mu_{AB}}}$$

(9.4.1)

with

- N_A and N_B are the numbers of A and B molecules in the system, respectively
- r_a and r_b are the radii of molecule A and B, respectively
- k_B is the Boltzmann constant $k_B = 1.380 \times 10^{-23}$ Joules Kelvin
- T is the temperature in Kelvin
- μ_{AB} is calculated via $\mu_{AB} = \frac{m_A m_B}{m_A + m_B}$

The specifics of Equation 9.4.1 are not important for this conversation, but it is important to identify that Z_{AB} increases with increasing density (i.e., increasing N_A and N_B), with increasing reactant size (r_a and r_b), with increasing velocities (predicted via Kinetic Molecular Theory), and with increasing temperature (although weakly because of the square root function).


A Video Discussing Collision Theory of Kinetics: Collusion Theory of Kinetics (opens in new window) [youtu.be]

Microscopic Factor 2: Activation Energy

Previously, we discussed the kinetic molecular theory of gases, which showed that the average kinetic energy of the particles of a gas increases with increasing temperature. Because the speed of a particle is proportional to the square root of its kinetic energy, increasing the temperature will also increase the number of collisions between molecules per unit time. What the kinetic molecular theory of gases does not explain is why the reaction rate of most reactions approximately doubles with a 10°C temperature increase. This result is surprisingly large considering that a 10°C increase in the temperature of a gas from 300 K to 310 K increases the kinetic energy of the particles by only about 4%, leading to an increase in molecular speed of only about 2% and a correspondingly small increase in the number of bimolecular collisions per unit time.

The collision model of chemical kinetics explains this behavior by introducing the concept of **activation energy** (E_a). We will define this concept using the reaction of NO with ozone, which plays an important role in the depletion of ozone in the ozone layer:

$$NO(g) + O_3(g) \rightarrow NO_2(g) + O_2(g)$$
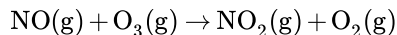
Increasing the temperature from 200 K to 350 K causes the rate constant for this particular reaction to increase by a factor of more than 10, whereas the increase in the frequency of bimolecular collisions over this temperature range is only 30%. Thus something other than an increase in the collision rate must be affecting the reaction rate.

Experimental rate law for this reaction is

$$rate = k[NO][O_3]$$

and is used to identify how the reaction rate (not the rate constant) vares with concentration. The rate constant, however, does vary with temperature. Figure 9.4.1 shows a plot of the rate constant of the reaction of NO with O_3 at various temperatures. The relationship is not linear but instead resembles the relationships seen in graphs of vapor pressure versus temperature (e.g, the Clausius-Claperyon equation). In all three cases, the shape of the plots results from a distribution of kinetic energy over a population of particles (electrons in the case of conductivity; molecules in the case of vapor pressure; and molecules, atoms, or ions in the case of reaction rates). Only a fraction of the particles have sufficient energy to overcome an energy barrier.
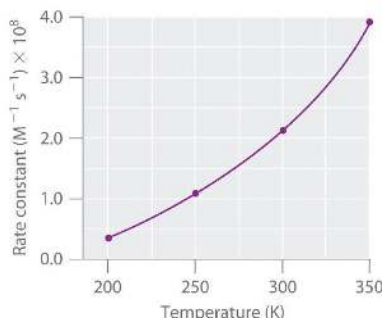
Figure 9.4.1: Rate Constant versus Temperature for the Reaction of NO with O_3 The nonlinear shape of the curve is caused by a distribution of kinetic energy over a population of molecules. Only a fraction of the particles have enough energy to overcome an energy barrier, but as the temperature is increased, the size of that fraction increases. (CC BY-SA-NC; anonymous)

In the case of vapor pressure, particles must overcome an energy barrier to escape from the liquid phase to the gas phase. This barrier corresponds to the energy of the intermolecular forces that hold the molecules together in the liquid. In conductivity, the barrier is the energy gap between the filled and empty bands. In chemical reactions, the energy barrier corresponds to the amount of energy the particles must have to react when they collide. This energy threshold, called the **activation energy**, was first postulated in 1888 by the Swedish chemist Svante Arrhenius (1859–1927; Nobel Prize in Chemistry 1903). It is the minimum amount of energy needed for a reaction to occur. Reacting molecules must have enough energy to overcome electrostatic repulsion, and a minimum amount of energy is required to break chemical bonds so that new ones may be formed. Molecules that collide with less than the threshold energy bounce off one another chemically unchanged, with only their direction of travel and their speed altered by the collision. Molecules that are able to overcome the energy barrier are able to react and form an arrangement of atoms called the **activated complex** or the **transition state** of the reaction. The activated complex is not a reaction intermediate; it does not last long enough to be detected readily.

> *Any phenomenon that depends on the distribution of thermal energy in a population of particles has a nonlinear temperature dependence.*

We can graph the energy of a reaction by plotting the potential energy of the system as the reaction progresses. Figure $9.4.2$ shows a plot for the NO–O_3 system, in which the vertical axis is potential energy and the horizontal axis is the reaction coordinate, which indicates the progress of the reaction with time. The activated complex is shown in brackets with an asterisk. The overall change in potential energy for the reaction (ΔE) is negative, which means that the reaction releases energy. (In this case, ΔE is −200.8 kJ/mol.) To react, however, the molecules must overcome the energy barrier to reaction (E_a is 9.6 kJ/mol). That is, 9.6 kJ/mol must be put into the system as the activation energy. Below this threshold, the particles do not have enough energy for the reaction to occur.
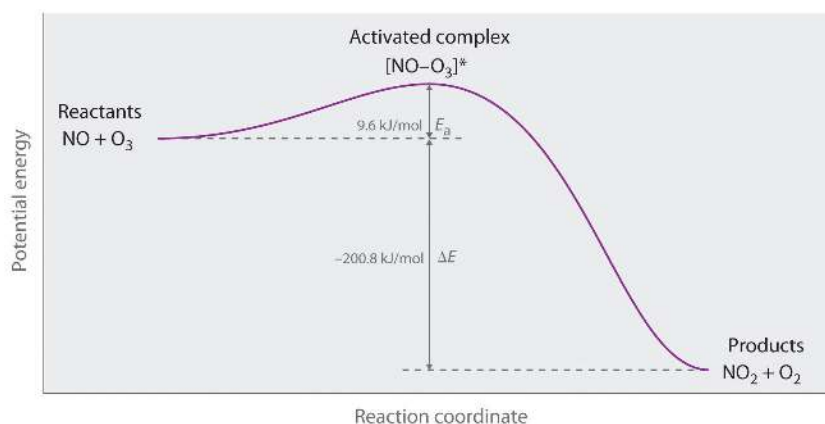
Figure $9.4.2$: Energy of the Activated Complex for the NO–O_3 System. The diagram shows how the energy of this system varies as the reaction proceeds from reactants to products. Note the initial increase in energy required to form the activated complex. (CC BY-SA-NC; anonymous)

Figure $9.4.3a$ illustrates the general situation in which the products have a lower potential energy than the reactants. In contrast, Figure $9.4.3b$ illustrates the case in which the products have a higher potential energy than the reactants, so the overall reaction requires an input of energy; that is, it is energetically uphill, and \($\Delta E > 0$\). Although the energy changes that result from a reaction can be positive, negative, or even zero, in most cases an energy barrier must be overcome before a reaction can occur. This means that the activation energy is almost always positive; there is a class of reactions called barrierless reactions, but those are discussed elsewhere.
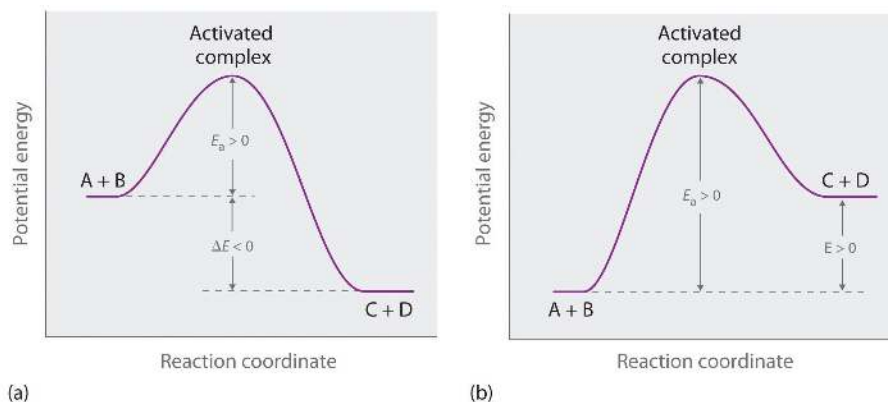
Figure $9.4.3$: Differentiating between E_a and ΔE. The potential energy diagrams for a reaction with (a) ΔE < 0 and (b) ΔE > 0 illustrate the change in the potential energy of the system as reactants are converted to products. In both cases, E_a is positive. For a reaction such as the one shown in (b), E_a must be greater than ΔE. (CC BY-SA-NC; anonymous)

> *For similar reactions under comparable conditions, the one with the smallest E_a will occur most rapidly.*

Whereas ΔE is related to the tendency of a reaction to occur spontaneously, E_a gives us information about the reaction rate and how rapidly the reaction rate changes with temperature. For two similar reactions under comparable conditions, the reaction with

the smallest E_a will occur more rapidly.

Figure 9.4.4 shows both the kinetic energy distributions and a potential energy diagram for a reaction. The shaded areas show that at the lower temperature (300 K), only a small fraction of molecules collide with kinetic energy greater than E_a; however, at the higher temperature (500 K) a much larger fraction of molecules collide with kinetic energy greater than E_a. Consequently, the reaction rate is much slower at the lower temperature because only a relatively few molecules collide with enough energy to overcome the potential energy barrier.
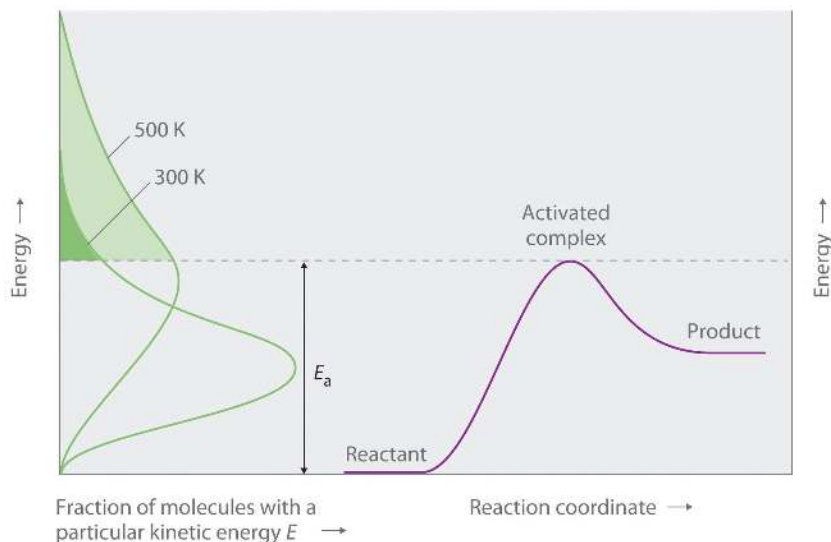
Figure 9.4.4: Surmounting the Energy Barrier to a Reaction. This chart juxtaposes the energy distributions of lower-temperature (300 K) and higher-temperature (500 K) samples of a gas against the potential energy diagram for a reaction. Only those molecules in the shaded region of the energy distribution curve have E > E_a and are therefore able to cross the energy barrier separating reactants and products. The fraction of molecules with $E > E_a$ is much greater at 500 K than at 300 K, so the reaction will occur much more rapidly at 500 K. (CC BY-SA-NC; anonymous)

Energy is on the y axis while reaction coordinate and fraction of molecules with a particular kinetic energy E are on the x axis.

Video Discussing Transition State Theory: Transition State Theory(opens in new window) [youtu.be]

Microscopic Factor 3: Sterics

Even when the energy of collisions between two reactant species is greater than E_a, most collisions do not produce a reaction. The probability of a reaction occurring depends not only on the collision energy but also on the spatial orientation of the molecules when they collide. For NO and O_3 to produce NO_2 and O_2, a terminal oxygen atom of O_3 must collide with the nitrogen atom of NO at an angle that allows O_3 to transfer an oxygen atom to NO to produce NO_2 (Figure 9.4.4). All other collisions produce no reaction. Because fewer than 1% of all possible orientations of NO and O_3 result in a reaction at kinetic energies greater than E_a, most collisions of NO and O_3 are unproductive. The fraction of orientations that result in a reaction is called the **steric factor** (ρ) and its value can range from $\rho = 0$ (no orientations of molecules result in reaction) to $\rho = 1$ (all orientations result in reaction).
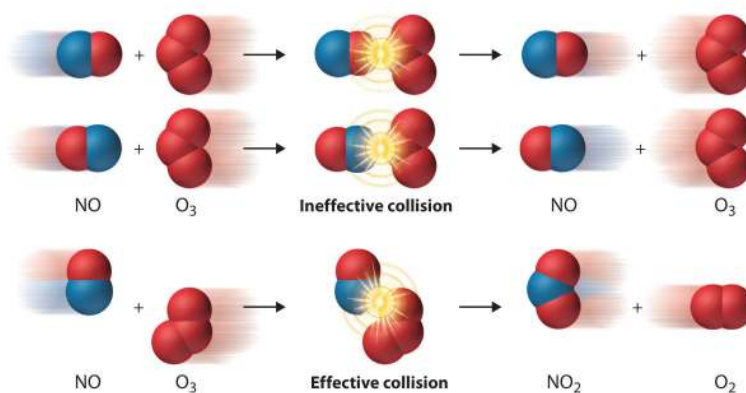
Figure 9.4.4: The Effect of Molecular Orientation on the Reaction of NO and O_3. Most collisions of NO and O_3 molecules occur with an incorrect orientation for a reaction to occur. Only those collisions in which the N atom of NO collides with one of the terminal O atoms of O_3 are likely to produce NO_2 and O_2, even if the molecules collide with $E > E_a$. (CC BY-SA-NC; anonymous)

Macroscopic Behavior: The Arrhenius Equation

The collision model explains why most collisions between molecules do not result in a chemical reaction. For example, nitrogen and oxygen molecules in a single liter of air at room temperature and 1 atm of pressure collide about 10^{30} times per second. If every collision produced two molecules of NO, the atmosphere would have been converted to NO and then NO_2 a long time ago. Instead, in most collisions, the molecules simply bounce off one another without reacting, much as marbles bounce off each other when they collide.

For an $A + B$ elementary reaction, all three microscopic factors discussed above that affect the reaction rate can be summarized in a single relationship:

$$\text{rate} = (\text{collision frequency}) \times (\text{steric factor}) \times (\text{fraction of collisions with } E > E_a)$$

where

$$\text{rate} = k[A][B] \tag{9.4.2}$$

Arrhenius used these relationships to arrive at an equation that relates the magnitude of the rate constant for a reaction to the temperature, the activation energy, and the constant, A, called the **frequency factor**:

$$k = Ae^{-Ea/RT} \tag{9.4.3}$$

The frequency factor is used to convert concentrations to collisions per second (scaled by the steric factor). Because the frequency of collisions depends on the temperature, A is actually not constant (Equation 9.4.1). Instead, A increases slightly with temperature as the increased kinetic energy of molecules at higher temperatures causes them to move slightly faster and thus undergo more collisions per unit time.

Equation 9.4.3 is known as the **Arrhenius equation** and summarizes the collision model of chemical kinetics, where T is the absolute temperature (in K) and R is the ideal gas constant [8.314 J/(K·mol)]. E_a indicates the sensitivity of the reaction to changes in temperature. The reaction rate with a large E_a increases rapidly with increasing temperature, whereas the reaction rate with a smaller E_a increases much more slowly with increasing temperature.

If we know the reaction rate at various temperatures, we can use the Arrhenius equation to calculate the activation energy. Taking the natural logarithm of both sides of Equation 9.4.3,

$$\ln k = \ln A + \left(-\frac{E_a}{RT}\right) \tag{9.4.4}$$

$$= \ln A + \left[\left(-\frac{E_a}{R}\right)\left(\frac{1}{T}\right)\right] \tag{9.4.5}$$

Equation 9.4.5 is the equation of a straight line,

$$y = mx + b$$

where $y = \ln k$ and $x = 1/T$. This means that a plot of $\ln k$ versus $1/T$ is a straight line with a slope of $-E_a/R$ and an intercept of $\ln A$. In fact, we need to measure the reaction rate at only two temperatures to estimate E_a.

Knowing the E_a at one temperature allows us to predict the reaction rate at other temperatures. This is important in cooking and food preservation, for example, as well as in controlling industrial reactions to prevent potential disasters. The procedure for determining E_a from reaction rates measured at several temperatures is illustrated in Example 9.4.1.

A Video Discussing The Arrhenius Equation: The Arrhenius Equation(opens in new window) [youtu.be]

✔ Example 9.4.1: Chirping Tree Crickets

Many people believe that the rate of a tree cricket's chirping is related to temperature. To see whether this is true, biologists have carried out accurate measurements of the rate of tree cricket chirping (f) as a function of temperature (T). Use the data in the following table, along with the graph of ln[chirping rate] versus $1/T$ to calculate E_a for the biochemical reaction that controls cricket chirping. Then predict the chirping rate on a very hot evening, when the temperature is 308 K (35°C, or 95°F).

Chirping Tree Crickets Frequency Table

Frequency (f; chirps/min)	ln f	T (K)	1/T (K)
200	5.30	299	3.34×10^{-3}
179	5.19	298	3.36×10^{-3}
158	5.06	296	3.38×10^{-3}
141	4.95	294	3.40×10^{-3}
126	4.84	293	3.41×10^{-3}
112	4.72	292	3.42×10^{-3}
100	4.61	290	3.45×10^{-3}
89	4.49	289	3.46×10^{-3}
79	4.37	287	3.48×10^{-3}

Given: chirping rate at various temperatures

Asked for: activation energy and chirping rate at specified temperature

Strategy:
A. From the plot of $\ln f$ versus $1/T$, calculate the slope of the line ($-E_a/R$) and then solve for the activation energy.
B. Express Equation 9.4.5 in terms of k_1 and T_1 and then in terms of k_2 and T_2.
C. Subtract the two equations; rearrange the result to describe k_2/k_1 in terms of T_2 and T_1.

D. Using measured data from the table, solve the equation to obtain the ratio k_2/k_1. Using the value listed in the table for k_1, solve for k_2.

Solution

A If cricket chirping is controlled by a reaction that obeys the Arrhenius equation, then a plot of $\ln f$ versus $1/T$ should give a straight line (Figure 9.4.6).
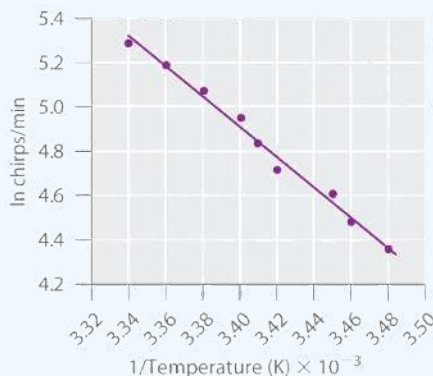
Figure 9.4.6: Graphical Determination of E_a for Tree Cricket Chirping. When the natural logarithm of the rate of tree cricket chirping is plotted versus 1/T, a straight line results. The slope of the line suggests that the chirping rate is controlled by a single reaction with an E_a of 55 kJ/mol. (CC BY-SA-NC; anonymous)

Also, the slope of the plot of $\ln f$ versus $1/T$ should be equal to $-E_a/R$. We can use the two endpoints in Figure 9.4.6 to estimate the slope:

$$\text{slope} = \frac{\Delta \ln f}{\Delta(1/T)}$$

$$= \frac{5.30 - 4.37}{3.34 \times 10^{-3}\ \text{K}^{-1} - 3.48 \times 10^{-3}\ \text{K}^{-1}}$$

$$= \frac{0.93}{-0.14 \times 10^{-3}\ \text{K}^{-1}}$$

$$= -6.6 \times 10^3\ \text{K}$$

A computer best-fit line through all the points has a slope of -6.67×10^3 K, so our estimate is very close. We now use it to solve for the activation energy:

$$E_a = -(\text{slope})(R)$$

$$= -(-6.6 \times 10^3\ \text{K}) \left(\frac{8.314\ \text{J}}{\text{K} \cdot \text{mol}} \right) \left(\frac{1\ \text{KJ}}{1000\ \text{J}} \right)$$

$$= \frac{55\ \text{kJ}}{\text{mol}}$$

B If the activation energy of a reaction and the rate constant at one temperature are known, then we can calculate the reaction rate at any other temperature. We can use Equation 9.4.5 to express the known rate constant (k_1) at the first temperature (T_1) as follows:

$$\ln k_1 = \ln A - \frac{E_a}{RT_1}$$

Similarly, we can express the unknown rate constant (k_2) at the second temperature (T_2) as follows:

$$\ln k_2 = \ln A - \frac{E_a}{RT_2}$$

C These two equations contain four known quantities (E_a, T_1, T_2, and k_1) and two unknowns (A and k_2). We can eliminate A by subtracting the first equation from the second:

$$\ln k_2 - \ln k_1 = \left(\ln A - \frac{E_a}{RT_2}\right) - \left(\ln A - \frac{E_a}{RT_1}\right)$$

$$= -\frac{E_a}{RT_2} + \frac{E_a}{RT_1}$$

Then

$$\ln \frac{k_2}{k_1} = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

D To obtain the best prediction of chirping rate at 308 K (T_2), we try to choose for T_1 and k_1 the measured rate constant and corresponding temperature in the data table that is closest to the best-fit line in the graph. Choosing data for T_1 = 296 K, where f = 158, and using the E_a calculated previously,

$$\ln \frac{k_{T_2}}{k_{T_1}} = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$= \frac{55 \text{ kJ/mol}}{8.314 \text{ J/(K}\cdot\text{mol)}}\left(\frac{1000 \text{ J}}{1 \text{ kJ}}\right)\left(\frac{1}{296 \text{ K}} - \frac{1}{308 \text{ K}}\right)$$

$$= 0.87$$

Thus k_{308}/k_{296} = 2.4 and k_{308} = (2.4)(158) = 380, and the chirping rate on a night when the temperature is 308 K is predicted to be 380 chirps per minute.

? Exercise 9.4.1A

The equation for the decomposition of NO_2 to NO and O_2 is second order in NO_2:

$$2\,NO_2(g) \rightarrow 2\,NO(g) + O_2(g)$$
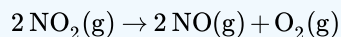
Data for the reaction rate as a function of temperature are listed in the following table. Calculate E_a for the reaction and the rate constant at 700 K.

Data for the reaction rate as a function of temperature

T (K)	k ($M^{-1}\cdot s^{-1}$)
592	522
603	755
627	1700
652	4020
656	5030

Answer

E_a = 114 kJ/mol; k_{700}= 18,600 $M^{-1}\cdot s^{-1}$ = 1.86 × 10^4 $M^{-1}\cdot s^{-1}$.

? Exercise 9.4.1B

What E_a results in a doubling of the reaction rate with a 10°C increase in temperature from 20° to 30°C?

Answer

about 51 kJ/mol

A Video Discussing Graphing Using the Arrhenius Equation: Graphing Using the Arrhenius Equation (opens in new window)
[youtu.be] (opens in new window)

Summary

For a chemical reaction to occur, an energy threshold must be overcome, and the reacting species must also have the correct spatial orientation. The Arrhenius equation is $k = Ae^{-Ea/RT}$. A minimum energy (activation energy, vE_a) is required for a collision between molecules to result in a chemical reaction. Plots of potential energy for a system versus the reaction coordinate show an energy barrier that must be overcome for the reaction to occur. The arrangement of atoms at the highest point of this barrier is the activated complex, or transition state, of the reaction. At a given temperature, the higher the E_a, the slower the reaction. The fraction of orientations that result in a reaction is the steric factor. The frequency factor, steric factor, and activation energy are related to the rate constant in the Arrhenius equation: $k = Ae^{-Ea/RT}$. A plot of the natural logarithm of k versus $1/T$ is a straight line with a slope of $-E_a/R$.

9.5: Reaction Mechanisms

One of the major reasons for studying chemical kinetics is to use measurements of the macroscopic properties of a system, such as the rate of change in the concentration of reactants or products with time, to discover the sequence of events that occur at the molecular level during a reaction. This molecular description is the mechanism of the reaction; it describes how individual atoms, ions, or molecules interact to form particular products. The stepwise changes are collectively called the reaction mechanism.

In an internal combustion engine, for example, isooctane reacts with oxygen to give carbon dioxide and water:

$$2\,C_8H_{18}(l) + 25\,O_2(g) \longrightarrow 16\,CO_2(g) + 18\,H_2O(g) \tag{9.5.1}$$
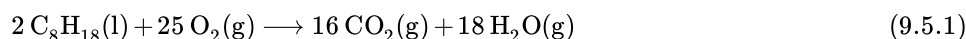
For this reaction to occur in a single step, 25 dioxygen molecules and 2 isooctane molecules would have to collide simultaneously and be converted to 34 molecules of product, which is very unlikely. It is more likely that a complex series of reactions takes place in a stepwise fashion. Each individual reaction, which is called an **elementary reaction**, involves one, two, or (rarely) three atoms, molecules, or ions. The overall sequence of elementary reactions is the **mechanism** of the reaction. The sum of the individual steps, or elementary reactions, in the mechanism must give the balanced chemical equation for the overall reaction.

> *The overall sequence of elementary reactions is the mechanism of the reaction.*

Molecularity and the Rate-Determining Step

To demonstrate how the analysis of elementary reactions helps us determine the overall reaction mechanism, we will examine the much simpler reaction of carbon monoxide with nitrogen dioxide.

$$NO_2(g) + CO(g) \longrightarrow NO(g) + CO_2(g) \tag{9.5.2}$$
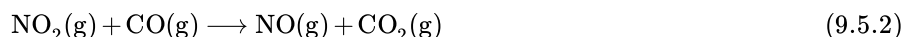
From the balanced chemical equation, one might expect the reaction to occur via a collision of one molecule of NO_2 with a molecule of CO that results in the transfer of an oxygen atom from nitrogen to carbon. The experimentally determined rate law for the reaction, however, is as follows:

$$rate = k[NO_2]^2 \tag{9.5.3}$$

The fact that the reaction is second order in $[NO_2]$ and independent of $[CO]$ tells us that it does not occur by the simple collision model outlined previously. If it did, its predicted rate law would be

$$rate = k[NO_2][CO].$$

The following two-step mechanism is consistent with the rate law if step 1 is much slower than step 2:

<div align="center">two-step mechanism</div>

step 1	$NO_2 + NO_2 \xrightarrow{\text{slow}} NO_3 + NO$	elementary reaction
step 2	$\underline{NO_3 + CO \rightarrow NO_2 + CO_2}$	elementary reaction
sum	$NO_2 + CO \rightarrow NO + CO_2$	overall reaction

According to this mechanism, the overall reaction occurs in two steps, or elementary reactions. Summing steps 1 and 2 and canceling on both sides of the equation gives the overall balanced chemical equation for the reaction. The NO_3 molecule is an **intermediate** in the reaction, a species that does not appear in the balanced chemical equation for the overall reaction. It is formed as a product of the first step but is consumed in the second step.

> *The sum of the elementary reactions in a reaction mechanism **must** give the overall balanced chemical equation of the reaction.*

Using Molecularity to Describe a Rate Law

The **molecularity** of an elementary reaction is the number of molecules that collide during that step in the mechanism. If there is only a single reactant molecule in an elementary reaction, that step is designated as **unimolecular**; if there are two reactant molecules, it is **bimolecular**; and if there are three reactant molecules (a relatively rare situation), it is **termolecular**. Elementary reactions that involve the simultaneous collision of more than three molecules are highly improbable and have never been observed experimentally. (To understand why, try to make three or more marbles or pool balls collide with one another simultaneously!)
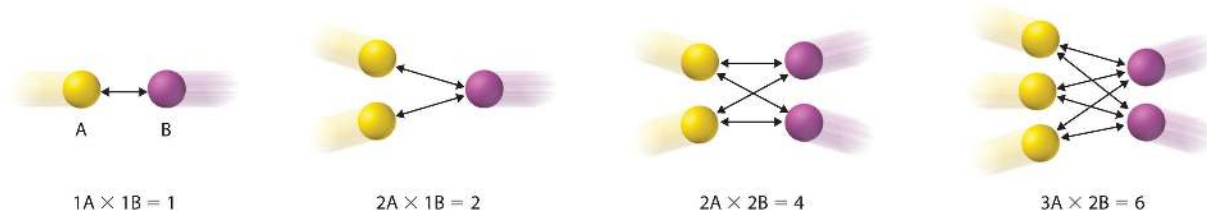
Figure 9.5.1: The Basis for Writing Rate Laws of Elementary Reactions. This diagram illustrates how the number of possible collisions per unit time between two reactant species, A and B, depends on the number of A and B particles present. The number of collisions between A and B particles increases as the product of the number of particles, not as the sum. This is why the rate law for an elementary reaction depends on the product of the concentrations of the species that collide in that step. (CC BY-NC-SA; anonymous)

Writing the rate law for an elementary reaction is straightforward because we know how many molecules must collide simultaneously for the elementary reaction to occur; hence the order of the elementary reaction is the same as its molecularity (Table 9.5.1). In contrast, the rate law for the reaction cannot be determined from the balanced chemical equation for the overall reaction. The general rate law for a unimolecular elementary reaction (A → products) is

$$rate = k[A].$$

For bimolecular reactions, the reaction rate depends on the number of collisions per unit time, which is proportional to the product of the concentrations of the reactants, as shown in Figure 9.5.1. For a bimolecular elementary reaction of the form A + B → products, the general rate law is

$$rate = k[A][B].$$

Table 9.5.1: Common Types of Elementary Reactions and Their Rate Laws

Elementary Reaction	Molecularity	Rate Law	Reaction Order
A → products	unimolecular	rate = $k[A]$	first
2A → products	bimolecular	rate = $k[A]^2$	second
A + B → products	bimolecular	rate = $k[A][B]$	second
2A + B → products	termolecular	rate = $k[A]^2[B]$	third
A + B + C → products	termolecular	rate = $k[A][B][C]$	third

> *For elementary reactions, the order of the elementary reaction is the same as its molecularity. In contrast, the rate law **cannot** be determined from the balanced chemical equation for the overall reaction (unless it is a single step mechanism and is therefore also an elementary step).*

Identifying the Rate-Determining Step

Note the important difference between writing rate laws for elementary reactions and the balanced chemical equation of the overall reaction. Because the balanced chemical equation does not necessarily reveal the individual elementary reactions by which the reaction occurs, we cannot obtain the rate law for a reaction from the overall balanced chemical equation alone. In fact, it is the rate law for the slowest overall reaction, which is the same as the rate law for the slowest step in the reaction mechanism, the **rate-determining step**, that must give the experimentally determined rate law for the overall reaction. This statement is true if one step is substantially slower than all the others, typically by a factor of 10 or more. If two or more slow steps have comparable rates, the

experimentally determined rate laws can become complex. Our discussion is limited to reactions in which one step can be identified as being substantially slower than any other. The reason for this is that any process that occurs through a sequence of steps can take place no faster than the slowest step in the sequence. In an automotive assembly line, for example, a component cannot be used faster than it is produced. Similarly, blood pressure is regulated by the flow of blood through the smallest passages, the capillaries. Because movement through capillaries constitutes the rate-determining step in blood flow, blood pressure can be regulated by medications that cause the capillaries to contract or dilate. A chemical reaction that occurs via a series of elementary reactions can take place no faster than the slowest step in the series of reactions.

Rate-determining step. The phenomenon of a rate-determining step can be compared to a succession of funnels. The smallest-diameter funnel controls the rate at which the bottle is filled, whether it is the first or the last in the series. Pouring liquid into the first funnel faster than it can drain through the smallest results in an overflow. (CC BY-NC-SA; anonymous)

Look at the rate laws for each elementary reaction in our example as well as for the overall reaction.

rate laws for each elementary reaction in our example as well as for the overall reaction.

step 1	$NO_2 + NO_2 \xrightarrow{k_1} NO_3 + NO$	rate $= k_1[NO_2]^2$ (predicted)
step 2	$\underline{NO_3 + CO \xrightarrow{k_2} NO_2 + CO_2}$	rate $= k_2[NO_3][CO]$ (predicted)
sum	$NO_2 + CO \xrightarrow{k} NO + CO_2$	rate $= k[NO_2]^2$ (observed)

The experimentally determined rate law for the reaction of NO_2 with CO is the same as the predicted rate law for step 1. This tells us that the first elementary reaction is the rate-determining step, so k for the overall reaction must equal k_1. That is, NO_3 is formed slowly in step 1, but once it is formed, it reacts very rapidly with CO in step 2.

Sometimes chemists are able to propose two or more mechanisms that are consistent with the available data. If a proposed mechanism predicts the wrong experimental rate law, however, the mechanism must be incorrect.

> ### ✔ Example 9.5.1: A Reaction with an Intermediate
>
> In an alternative mechanism for the reaction of NO_2 with CO with N_2O_4 appearing as an intermediate.
>
> alternative mechanism for the reaction of NO_2 with CO with N_2O_4 appearing as an intermediate.
>
> | step 1 | $NO_2 + NO_2 \xrightarrow{k_1} N_2O_4$ |
> |---|---|
> | step 2 | $\underline{N_2O_4 + CO \xrightarrow{k_2} NO + NO_2 + CO_2}$ |
> | sum | $NO_2 + CO \rightarrow NO + CO_2$ |
>
> Write the rate law for each elementary reaction. Is this mechanism consistent with the experimentally determined rate law (rate = $k[NO_2]^2$)?

Given: elementary reactions

Asked for: rate law for each elementary reaction and overall rate law

Strategy:
 A. Determine the rate law for each elementary reaction in the reaction.
 B. Determine which rate law corresponds to the experimentally determined rate law for the reaction. This rate law is the one for the rate-determining step.

Solution

A The rate law for step 1 is rate = $k_1[NO_2]^2$; for step 2, it is rate = $k_2[N_2O_4][CO]$.

B If step 1 is slow (and therefore the rate-determining step), then the overall rate law for the reaction will be the same: rate = $k_1[NO_2]^2$. This is the same as the experimentally determined rate law. Hence this mechanism, with N_2O_4 as an intermediate, and the one described previously, with NO_3 as an intermediate, are kinetically indistinguishable. In this case, further experiments are needed to distinguish between them. For example, the researcher could try to detect the proposed intermediates, NO_3 and N_2O_4, directly.

? Exercise 9.5.1

Iodine monochloride (ICl) reacts with H_2 as follows:

$$2\,ICl(l) + H_2(g) \rightarrow 2\,HCl(g) + I_2(s)$$
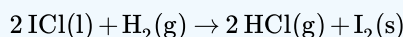
The experimentally determined rate law is $rate = k[ICl][H_2]$. Write a two-step mechanism for this reaction using only bimolecular elementary reactions and show that it is consistent with the experimental rate law. (Hint: HI is an intermediate.)

Answer

Solutions to Exercise 14.6.1

step 1	$ICl + H_2 \xrightarrow{k_1} HCl + HI$	rate = $k_1[ICl][H_2]$ (slow)
step 2	$\underline{HI + ICl \xrightarrow{k_2} HCl + I_2}$	rate = $k_2[HI][ICl]$ (fast)
sum	$2ICl + H_2 \rightarrow 2HCl + I_2$	

This mechanism is consistent with the experimental rate law if the first step is the rate-determining step.

✔ Example 9.5.2 : Nitrogen Oxide Reacting with Molecular Hydrogen

Assume the reaction between NO and H_2 occurs via a three-step process:

the reaction between NO and H_2 occurs via a three-step process

step 1	$NO + NO \xrightarrow{k_1} N_2O_2$	(fast)
step 2	$N_2O_2 + H_2 \xrightarrow{k_2} N_2O + H_2O$	(slow)
step 3	$N_2O + H_2 \xrightarrow{k_3} N_2 + H_2O$	(fast)

Write the rate law for each elementary reaction, write the balanced chemical equation for the overall reaction, and identify the rate-determining step. Is the rate law for the rate-determining step consistent with the experimentally derived rate law for the overall reaction:

$$rate = k[NO]^2[H_2]? \hspace{2cm} \text{(observed)}$$

Answer
- Step 1: $rate = k_1[NO]^2$
- Step 2: $rate = k_2[N_2O_2][H_2]$

- Step 3: $rate = k_3[\text{N}_2\text{O}][\text{H}_2]$

The overall reaction is then

$$2\,\text{NO(g)} + 2\,\text{H}_2\text{(g)} \longrightarrow \text{N}_2\text{(g)} + 2\,\text{H}_2\text{O(g)}$$
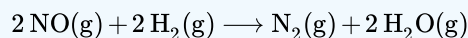
- Rate Determining Step : #2
- Yes, because the rate of formation of $[\text{N}_2\text{O}_2] = k_1[\text{NO}]^2$. Substituting $k_1[\text{NO}]^2$ for $[\text{N}_2\text{O}_2]$ in the rate law for step 2 gives the experimentally derived rate law for the overall chemical reaction, where $k = k_1 k_2$.

Reaction Mechanism (Slow step followed by fast step): Reaction Mechanism (Slow step Followed by Fast Step)(opens in new window) [youtu.be] (opens in new window)

Summary

A balanced chemical reaction does not necessarily reveal either the individual elementary reactions by which a reaction occurs or its rate law. A reaction mechanism is the microscopic path by which reactants are transformed into products. Each step is an elementary reaction. Species that are formed in one step and consumed in another are intermediates. Each elementary reaction can be described in terms of its *molecularity*, the number of molecules that collide in that step. The slowest step in a reaction mechanism is the rate-determining step.

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9.6: Catalysis

> ### ◑ Learning Objectives
>
> - To understand how catalysts increase the reaction rate and the selectivity of chemical reactions.

Catalysts are substances that increase the reaction rate of a chemical reaction without being consumed in the process. A catalyst, therefore, does not appear in the overall stoichiometry of the reaction it catalyzes, but it must appear in at least one of the elementary reactions in the mechanism for the catalyzed reaction. The catalyzed pathway has a lower E_a, but the net change in energy that results from the reaction (the difference between the energy of the reactants and the energy of the products) is not affected by the presence of a catalyst (Figure 9.6.1). Nevertheless, because of its lower E_a, the reaction rate of a catalyzed reaction is faster than the reaction rate of the uncatalyzed reaction at the same temperature. Because a catalyst decreases the height of the energy barrier, its presence increases the reaction rates of both the forward and the reverse reactions by the same amount. In this section, we will examine the three major classes of catalysts: heterogeneous catalysts, homogeneous catalysts, and enzymes.
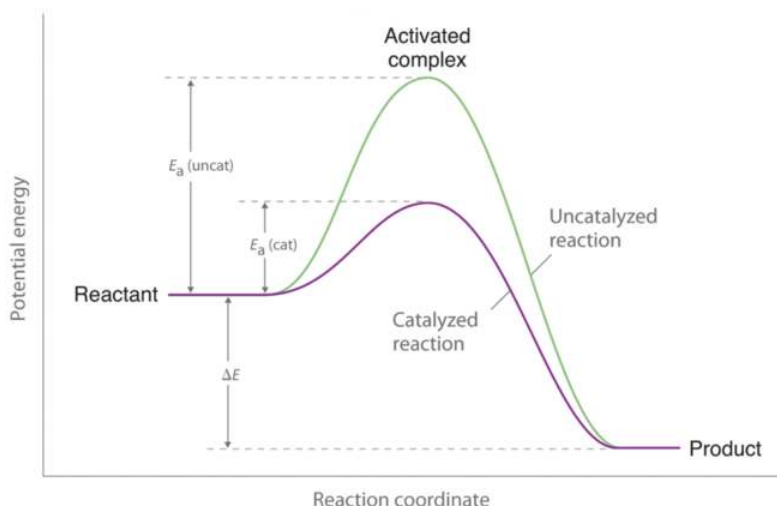
Figure 9.6.1: Lowering the Activation Energy of a Reaction by a Catalyst. This graph compares potential energy diagrams for a single-step reaction in the presence and absence of a catalyst. The only effect of the catalyst is to lower the activation energy of the reaction. The catalyst does not affect the energy of the reactants or products (and thus does not affect ΔE). (CC BY-NC-SA; anonymous)

The green line represents the uncatalyzed reaction. The purple line represent the catalyzed reaction .

> *A catalyst affects E_a, not ΔE.*

Heterogeneous Catalysis

In **heterogeneous catalysis**, the catalyst is in a different phase from the reactants. At least one of the reactants interacts with the solid surface in a physical process called adsorption in such a way that a chemical bond in the reactant becomes weak and then breaks. Poisons are substances that bind irreversibly to catalysts, preventing reactants from adsorbing and thus reducing or destroying the catalyst's efficiency.

An example of heterogeneous catalysis is the interaction of hydrogen gas with the surface of a metal, such as Ni, Pd, or Pt. As shown in part (a) in Figure 9.6.2, the hydrogen–hydrogen bonds break and produce individual adsorbed hydrogen atoms on the surface of the metal. Because the adsorbed atoms can move around on the surface, two hydrogen atoms can collide and form a molecule of hydrogen gas that can then leave the surface in the reverse process, called desorption. Adsorbed H atoms on a metal surface are substantially more reactive than a hydrogen molecule. Because the relatively strong H–H bond (dissociation energy = 432 kJ/mol) has already been broken, the energy barrier for most reactions of H_2 is substantially lower on the catalyst surface.
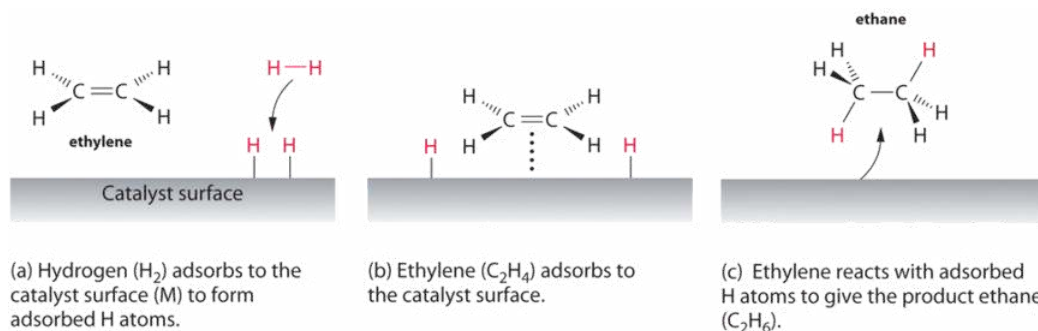
Figure 9.6.2: Hydrogenation of Ethylene on a Heterogeneous Catalyst. When a molecule of hydrogen adsorbs to the catalyst surface, the H–H bond breaks, and new M–H bonds are formed. The individual H atoms are more reactive than gaseous H_2. When a molecule of ethylene interacts with the catalyst surface, it reacts with the H atoms in a stepwise process to eventually produce ethane, which is released. (CC BY-NC-SA; anonymous)

Figure 9.6.2 shows a process called *hydrogenation*, in which hydrogen atoms are added to the double bond of an alkene, such as ethylene, to give a product that contains C–C single bonds, in this case ethane. Hydrogenation is used in the food industry to convert vegetable oils, which consist of long chains of alkenes, to more commercially valuable solid derivatives that contain alkyl chains. Hydrogenation of some of the double bonds in polyunsaturated vegetable oils, for example, produces margarine, a product with a melting point, texture, and other physical properties similar to those of butter.

Several important examples of industrial heterogeneous catalytic reactions are in Table 9.6.1. Although the mechanisms of these reactions are considerably more complex than the simple hydrogenation reaction described here, they all involve adsorption of the reactants onto a solid catalytic surface, chemical reaction of the adsorbed species (sometimes via a number of intermediate species), and finally desorption of the products from the surface.

Table 9.6.1: Some Commercially Important Reactions that Employ Heterogeneous Catalysts

Commercial Process	Catalyst	Initial Reaction	Final Commercial Product
contact process	V_2O_5 or Pt	$2SO_2 + O_2 \rightarrow 2SO_3$	H_2SO_4
Haber process	Fe, K_2O, Al_2O_3	$N_2 + 3H_2 \rightarrow 2NH_3$	NH_3
Ostwald process	Pt and Rh	$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$	HNO_3
water–gas shift reaction	Fe, Cr_2O_3, or Cu	$CO + H_2O \rightarrow CO_2 + H_2$	H_2 for NH_3, CH_3OH, and other fuels
steam reforming	Ni	$CH_4 + H_2O \rightarrow CO + 3H_2$	H_2
methanol synthesis	ZnO and Cr_2O_3	$CO + 2H_2 \rightarrow CH_3OH$	CH_3OH
Sohio process	bismuth phosphomolybdate	$CH_2{=}CHCH_3 + NH_3 + \frac{3}{2}O_2 \rightarrow CH_2{=}CHCN + 3H_2O$ acrylonitrile	$CH_2{=}CHCN$
catalytic hydrogenation	Ni, Pd, or Pt	$RCH{=}CHR' + H2 \rightarrow RCH_2{-}CH_2R'$	partially hydrogenated oils for margarine, and so forth

Homogeneous Catalysis

In **homogeneous catalysis**, the catalyst is in the same phase as the reactant(s). The number of collisions between reactants and catalyst is at a maximum because the catalyst is uniformly dispersed throughout the reaction mixture. Many homogeneous catalysts in industry are transition metal compounds (Table 9.6.2), but recovering these expensive catalysts from solution has been a major challenge. As an added barrier to their widespread commercial use, many homogeneous catalysts can be used only at relatively low temperatures, and even then they tend to decompose slowly in solution. Despite these problems, a number of commercially viable processes have been developed in recent years. High-density polyethylene and polypropylene are produced by homogeneous catalysis.

Table 9.6.2: Some Commercially Important Reactions that Employ Homogeneous Catalysts

Commercial Process	Catalyst	Reactants	Final Product

Commercial Process	Catalyst	Reactants	Final Product
Union Carbide	$[Rh(CO)_2I_2]^-$	$CO + CH_3OH$	CH_3CO_2H
hydroperoxide process	Mo(VI) complexes	$CH_3CH=CH_2 + R–O–O–H$	propylene oxide + ROH
hydroformylation	Rh/PR_3 complexes	$RCH=CH_2 + CO + H_2$	RCH_2CH_2CHO
adiponitrile process	Ni/PR_3 complexes	$2HCN + CH_2=CHCH=CH_2$	$NCCH_2CH_2CH_2CH_2CN$ used to synthesize nylon
olefin polymerization	$(RC_5H_5)_2ZrCl_2$	$CH_2=CH_2$	$–(CH_2CH_2–)_n$: high-density polyethylene

Enzymes

Enzymes, catalysts that occur naturally in living organisms, are almost all protein molecules with typical molecular masses of 20,000–100,000 amu. Some are homogeneous catalysts that react in aqueous solution within a cellular compartment of an organism. Others are heterogeneous catalysts embedded within the membranes that separate cells and cellular compartments from their surroundings. The reactant in an enzyme-catalyzed reaction is called a **substrate**.

Because enzymes can increase reaction rates by enormous factors (up to 10^{17} times the uncatalyzed rate) and tend to be very specific, typically producing only a single product in quantitative yield, they are the focus of active research. At the same time, enzymes are usually expensive to obtain, they often cease functioning at temperatures greater than 37 °C, have limited stability in solution, and have such high specificity that they are confined to turning one particular set of reactants into one particular product. This means that separate processes using different enzymes must be developed for chemically similar reactions, which is time-consuming and expensive. Thus far, enzymes have found only limited industrial applications, although they are used as ingredients in laundry detergents, contact lens cleaners, and meat tenderizers. The enzymes in these applications tend to be proteases, which are able to cleave the amide bonds that hold amino acids together in proteins. Meat tenderizers, for example, contain a protease called papain, which is isolated from papaya juice. It cleaves some of the long, fibrous protein molecules that make inexpensive cuts of beef tough, producing a piece of meat that is more tender. Some insects, like the bombadier beetle, carry an enzyme capable of catalyzing the decomposition of hydrogen peroxide to water (Figure 9.6.3).

Figure 9.6.3: A Catalytic Defense Mechanism. The scalding, foul-smelling spray emitted by this bombardier beetle is produced by the catalytic decomposition of H_2O_2.

Enzyme inhibitors cause a decrease in the reaction rate of an enzyme-catalyzed reaction by binding to a specific portion of an enzyme and thus slowing or preventing a reaction from occurring. Irreversible inhibitors are therefore the equivalent of poisons in heterogeneous catalysis. One of the oldest and most widely used commercial enzyme inhibitors is aspirin, which selectively inhibits one of the enzymes involved in the synthesis of molecules that trigger inflammation. The design and synthesis of related molecules that are more effective, more selective, and less toxic than aspirin are important objectives of biomedical research.

Summary

Catalysts participate in a chemical reaction and increase its rate. They do not appear in the reaction's net equation and are not consumed during the reaction. Catalysts allow a reaction to proceed via a pathway that has a lower activation energy than the uncatalyzed reaction. In heterogeneous catalysis, catalysts provide a surface to which reactants bind in a process of adsorption. In homogeneous catalysis, catalysts are in the same phase as the reactants. Enzymes are biological catalysts that produce large

increases in reaction rates and tend to be specific for certain reactants and products. The reactant in an enzyme-catalyzed reaction is called a substrate. Enzyme inhibitors cause a decrease in the reaction rate of an enzyme-catalyzed reaction.

CHAPTER OVERVIEW

10: Acids and Bases

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Acids and bases are common substances found in many every day items, from fruit juices and soft drinks to soap. In this unit we'll examine what the properties are of acids and bases, and learn about the chemical nature of these important compounds. You'll learn what pH is and how to calculate the pH of a solution.

10.1: Acids- Properties and Examples

◑ Learning Objectives

- Examine properties of acids.

Many people enjoy drinking coffee. A cup first thing in the morning helps start the day. But keeping the coffee maker clean can be a problem. Lime deposits build up after a while and slow down the brewing process. The best cure for this is to put vinegar (dilute acetic acid) in the pot and run it through the brewing cycle. The vinegar dissolves the deposits and cleans the maker, which will speed up the brewing process back to its original rate. Just be sure to run water through the brewing process after the vinegar, or you will get some really horrible coffee.

Acids

Acids are very common in some of the foods that we eat. Citrus fruits such as oranges and lemons contain citric acid and ascorbic acid, which is better known as vitamin C. Carbonated sodas contain phosphoric acid. Vinegar contains acetic acid. Your own stomach utilizes hydrochloric acid to digest food. Acids are a distinct class of compounds because of the properties of their aqueous solutions as outlined below:

1. Aqueous solutions of acids are electrolytes, meaning that they conduct electrical current. Some acids are strong electrolytes because they ionize completely in water, yielding a great many ions. Other acids are weak electrolytes that exist primarily in a non-ionized form when dissolved in water.
2. Acids have a sour taste. Lemons, vinegar, and sour candies all contain acids.
3. Acids change the color of certain acid-base indicates. Two common indicators are litmus and phenolphthalein. Blue litmus turns red in the presence of an acid, while phenolphthalein turns colorless.
4. Acids react with active metals to yield hydrogen gas. Recall that an activity series is a list of metals in descending order of reactivity. Metals that are above hydrogen in the activity series will replace the hydrogen from an acid in a single-replacement reaction, as shown below:

$$\mathrm{Zn}\left(s\right)+\mathrm{H_2SO_4}\left(aq\right)\rightarrow\mathrm{ZnSO_4}\left(aq\right)+\mathrm{H_2}\left(g\right) \tag{10.1.1}$$
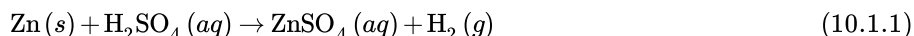
5. Acids react with bases to produce a salt compound and water. When equal moles of an acid and a base are combined, the acid is neutralized by the base. The products of this reaction are an ionic compound, which is labeled as a salt, and water.

It should not be hard for you to name several common acids (but you might find that listing bases is a little more difficult). Below is a partial list of some common acids, along with some chemical formulas:

Table 10.1.1: Common Acids and Their Uses

Chemist Name	Common Name	Uses
hydrochloric acid, HCl	muriatic acid (used in pools) and stomach acid is HCl	Used in cleaning (refining) metals, in maintenance of swimming pools, and for household cleaning.
sulfuric acid, H_2SO_4		Used in car batteries, and in the manufacture of fertilizers.
nitric acid, HNO_3		Used in the manufacture of fertilizers, explosives and in extraction of gold.
acetic acid, $HC_2H_3O_2$	vinegar	Main ingredient in vinegar.
carbonic acid, H_2CO_3	responsible for the "fizz" in carbonated drinks	As an ingredient in carbonated drinks.
citric acid, $C_6H_8O_7$		Used in food and dietary supplements. Also added as an acidulant in creams, gels, liquids, and lotions.
acetylsalicylic acid, $C_6H_4(OCOCH_3)CO_2H$	aspirin	The active ingredient in aspirin.

What exactly makes an acid an acid, and what makes a base act as a base? Take a look at the formulas given in the above table and take a guess.

Hydrochloric Acid

Hydrochloric acid is a corrosive, strong mineral acid with many industrial uses. A colorless, highly pungent solution of hydrogen chloride (HCl) in water. Hydrochloric acid is usually prepared by treating HCl with water.

$$HCl(g) + H_2O(l) \longrightarrow H_3O^+(aq) + Cl^-(aq)$$
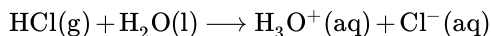
Hydrochloric acid can therefore be used to prepare chloride salts. Hydrochloric acid is a strong acid, since it is completely dissociated in water. Hydrochloric acid is the preferred acid in titration for determining the amount of bases.

Sulfuric Acid

Sulfuric acid is a highly corrosive strong mineral acid with the molecular formula H_2SO_4. Sulfuric acid is a diprotic acid and has a wide range of applications including use in domestic acidic drain cleaners,[as an electrolyte in lead-acid batteries, and in various cleaning agents. It is also a central substance in the chemical industry.

Figure 10.1.1: Drops of concentrated sulfuric acid rapidly decompose a piece of cotton towel by dehydration. (CC BY-SA 3.0; Toxic Walker).

Because the hydration of sulfuric acid is thermodynamically favorable (and is highly exothermic) and the affinity of it for water is sufficiently strong, sulfuric acid is an excellent dehydrating agent. Concentrated sulfuric acid has a very powerful dehydrating property, removing water (H_2O) from other compounds including sugar and other carbohydrates and producing carbon, heat, steam. Sulfuric acid behaves as a typical acid in its reaction with most metals by generating hydrogen gas (Equation 10.1.2).

$$M + H_2SO_4 \rightarrow M(SO_4) + H_2 \tag{10.1.2}$$

Nitric Acid

Nitric acid (HNO_3) is a highly corrosive mineral acid and is also commonly used as a strong oxidizing agent. Nitric acid is normally considered to be a strong acid at ambient temperatures. Nitric acid can be made by reacting nitrogen dioxide ($NO_2(g)$) with water.

$$3\,NO_2(g) + H_2O(l) \rightarrow 2\,HNO_3(ag) + NO(g)$$
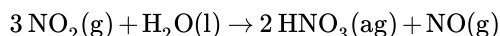
Nitric acid reacts with most metals, but the details depend on the concentration of the acid and the nature of the metal. Dilute nitric acid behaves as a typical acid in its reaction with most metals (e.g., nitric acid with magnesium, manganese or zinc will liberate H_2 gas):

$$Mg + 2\,HNO_3 \rightarrow Mg(NO_3)_2 + H_2$$

$$Mn + 2\,HNO_3 \rightarrow Mn(NO_3)_2 + H_2$$

$$Zn + 2\,HNO_3 \rightarrow Zn(NO_3)_2 + H_2$$
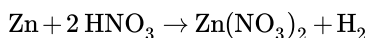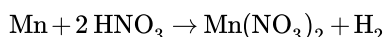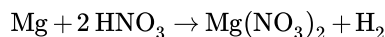
Nitric acid is a corrosive acid and a powerful oxidizing agent. The major hazard it poses is chemical burn, as it carries out acid hydrolysis with proteins (amide) and fats (ester) which consequently decomposes living tissue (Figure 10.1.2). Concentrated nitric acid stains human skin yellow due to its reaction with the keratin

Figure 10.1.2: Second degree burn caused by nitric acid. (CC BY-SA 3.0; Alcamán).

Carbonic Acid

Carbonic acid is a chemical compound with the chemical formula H_2CO_3 and is also a name sometimes given to solutions of carbon dioxide in water (carbonated water), because such solutions contain small amounts of $H_2CO_3(aq)$. Carbonic acid, which is a weak acid, forms two kinds of salts: the carbonates and the bicarbonates. In geology, carbonic acid causes limestone to dissolve, producing calcium bicarbonate—which leads to many limestone features such as stalactites and stalagmites. Carbonic acid is a polyprotic acid, specifically it is diprotic, meaning that it has two protons which may dissociate from the parent molecule.

When carbon dioxide dissolves in water, it exists in chemical equilibrium (discussed in Chapter 15), producing carbonic acid:

$$CO_2 + H_2O \rightleftharpoons H_2CO_3$$
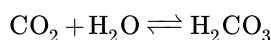
The reaction can be pushed to favor the reactants to generate $CO_2(g)$ from solution, which is key to the bubbles observed in carbonated beverages (Figure 10.1.3).

Figure 10.1.3: A glass of sparkling water. (CC BY-SA 3.0; Nevit Dilmen).

Formic Acid

Formic acid (HCO_2H) is the simplest carboxylic acid and is an important intermediate in chemical synthesis and occurs naturally, most notably in some ants. The word "formic" comes from the Latin word for ant, formica, referring to its early isolation by the distillation of ant bodies. Formic acid occurs widely in nature as its conjugate base formate.

Citric Acid

Citric acid ($C_6H_8O_7$) is a weak organic tricarboxylic acid that occurs naturally in citrus fruits. The citrate ion is an intermediate in the TCA cycle (Krebs cycle), a central metabolic pathway for animals, plants and bacteria. Because it is one of the stronger edible acids, the dominant use of citric acid is used as a flavoring and preservative in food and beverages, especially soft drinks.

Figure 10.1.4: Lemons, oranges, limes, and other citrus fruits possess high concentrations of citric acid (CC BY-SA 2.5; André Karwath).

Acetylsalicylic Acid

Acetylsalicylic acid (also known as aspirin) is a medication used to treat pain, fever, and inflammation. Aspirin, in the form of leaves from the willow tree, has been used for its health effects for at least 2,400 years.
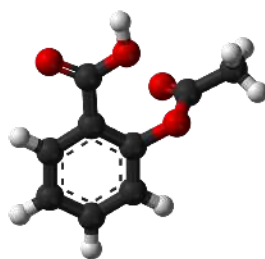
Figure 10.1.5: Ball-and-stick model of the aspirin molecule. (Public Domain; Ben Mills).

Aspirin is a white, crystalline, weakly acidic substance.

Summary

A brief summary of key aspects of several acids commonly encountered by students was given. Acids are a distinct class of compounds because of the properties of their aqueous solutions.

Contributions & Attributions

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- Peggy Lawson (Oxbow Prairie Heights School). Funded by Saskatchewan Educational Technology Consortium.

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10.2: Bases- Properties and Examples

> **❿ Learning Objectives**
>
> - Examine properties of bases.

Perhaps you have eaten too much pizza and felt very uncomfortable hours later. This feeling is due to excess stomach acid being produced. The discomfort can be dealt with by taking an antacid. The base in the antacid will react with the HCl in the stomach and neutralize it, taking care of that unpleasant feeling.

Bases

Bases have properties that mostly contrast with those of acids.

1. Aqueous solutions of bases are also electrolytes. Bases can be either strong or weak, just as acids can.
2. Bases often have a bitter taste and are found in foods less frequently than acids. Many bases, like soaps, are slippery to the touch.
3. Bases also change the color of indicators. Litmus turns blue in the presence of a base, while phenolphthalein turns pink.
4. Bases do not react with metals in the way that acids do.
5. Bases react with acids to produce a salt and water.

Figure 10.2.1: Phenolphthalein indicator in presence of base.

> **✋ Warning!**
>
> Tasting chemicals and touching them are NOT good lab practices and should be avoided—in other words—don't do this at home.

Bases are less common as foods, but they are nonetheless present in many household products. Many cleaners contain ammonia, a base. Sodium hydroxide is found in drain cleaner. **Antacids**, which combat excess stomach acid, are comprised of bases such as magnesium hydroxide or sodium hydrogen carbonate. Various common bases and corresponding uses are given in Table 10.2.2

Table 10.2.1: Common Bases and Corresponding Uses

Some Common Bases	Uses
sodium hydroxide, NaOH (lye or caustic soda)	Used in the manufacture of soaps and detergents, and as the main ingredient in oven and drain cleaners.
potassium hydroxide, KOH (lye or caustic potash)	Used in the production of liquid soaps and soft soaps. Used in alkaline batteries.
magnesium hydroxide, $Mg(OH)_2$ (milk of magnesia)	Used as an ingredient in laxatives, antacids, and deodorants. Also used in the neutralization of acidic wastewater.
calcium hydroxide, $Ca(OH)_2$ (slaked lime)	Used in the manufacture of cement and lime water. Also, added to neutralize acidic soil.
aluminum hydroxide	Used in water purification and as an ingredient in antacids.

Some Common Bases	Uses
ammonia, NH_3	Used as a building block for the synthesis of many pharmaceutical products and in many commercial cleaning products. Used in the manufacture of fertilizers.

Sodium Hydroxide

Sodium hydroxide, also known as lye and caustic soda, is an inorganic compound with formula $NaOH$. It is a white solid ionic compound consisting of sodium cations Na^+ and hydroxide anions OH^-.

Dissolution of solid sodium hydroxide in water is a highly exothermic reaction:

$$NaOH(s) \rightarrow Na^+(aq) + OH^-(aq)$$
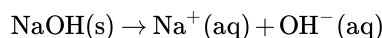
The resulting solution is usually colorless and odorless and feels slippery when it comes in contact with skin.

Figure 10.2.1: Sample of sodium hydroxide as pellets in a watch glass. (Public Domain; Walkerma.)

Potassium Hydroxide

Potassium hydroxide is an inorganic compound with the formula KOH, and is commonly called caustic potash. Along with sodium hydroxide (NaOH), this colorless solid is a prototypical strong base. It has many industrial and niche applications, most of which exploit its corrosive nature and its reactivity toward acids. Its dissolution in water is strongly exothermic.

$$KOH(s) \rightarrow K^+(aq) + OH^-(aq)$$
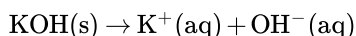
Concentrated aqueous solutions are sometimes called *potassium lyes*.

Magnesium Hydroxide

Magnesium hydroxide is the inorganic compound with the chemical formula $Mg(OH)_2$. Magnesium hydroxide is a common component of antacids, such as milk of magnesia, as well as laxatives.

Figure 10.2.1: Bottle of Antacid tablets. (CC BY 2.,5; Midnightcomm).

It is a white solid with low solubility in water. Combining a solution of many magnesium salts with basic water induces precipitation of solid $Mg(OH)_2$. However, a weak concentration of dissociated ions can be found in solution:

$$Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2\,OH^-(aq)$$
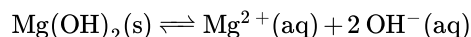
Calcium Hydroxide

Calcium hydroxide (traditionally called slaked lime) is an inorganic compound with the chemical formula $Ca(OH)_2$. It is a colorless crystal or white powder. It has many names including hydrated lime, caustic lime, builders' lime, slaked lime, cal, or pickling lime. Calcium hydroxide is used in many applications, including food preparation. Limewater is the common name for a saturated solution of calcium hydroxide.

Calcium hydroxide is relatively insoluble in water, but is large enough that its solutions are basic according to the following reaction:

$$Ca(OH)_2(s) \rightleftharpoons Ca^{2+}(aq) + 2\,OH^-(aq)$$
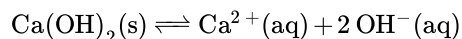
Ammonia

Ammonia is a compound of nitrogen and hydrogen with the formula NH_3 and is a colorless gas with a characteristic pungent smell. It is the active product of "smelling salts," and can quickly revive the faint of heart and light of head. Although common in nature and in wide use, ammonia is both caustic and hazardous in its concentrated form.
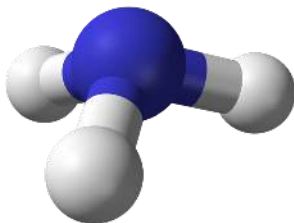
Figure 10.2.1: Ball-and-stick model of the ammonia molecule. (Public Domain; Ben Mills).

In aqueous solution, ammonia acts as a base, acquiring hydrogen ions from H_2O to yield ammonium and hydroxide ions:

$$NH_3(g) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$
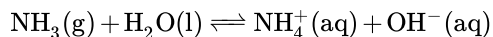
Ammonia is also a building block for the synthesis of many pharmaceutical products and is used in many commercial cleaning products.

Summary

- A brief summary of properties of bases was given.
- The properties of bases mostly contrast those of acids.
- Bases have many, varied uses.

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10.3: Molecular Definitions of Acids and Bases

> **◑ Learning Objectives**
>
> - Identify an Arrhenius acid and an Arrhenius base.
> - Identify a Brønsted-Lowry acid and a Brønsted-Lowry base.
> - Identify conjugate acid-base pairs in an acid-base reaction.

There are three major classifications of substances known as acids or bases. The theory developed by Svante Arrhenius in 1883, the Arrhenius definition, states that an acid produces H^+ in solution and a base produces OH^-. Later, two more sophisticated and general theories were proposed. These theories are the Brønsted-Lowry and Lewis definitions of acids and bases. This section will cover the Arrhenius and Brønsted-Lowry theories; the Lewis theory is discussed elsewhere.

The Arrhenius Theory of Acids and Bases

In 1884, the Swedish chemist Svante Arrhenius proposed two specific classifications of compounds, termed acids and bases. When dissolved in an aqueous solution, certain ions were released into the solution. An **Arrhenius acid** is a compound that **increases the concentration of** H^+ **ions** that are present when added to water. These H^+ ions form the hydronium ion (H_3O^+) when they combine with water molecules. This process is represented in a chemical equation by adding H_2O to the reactants side.

$$HCl(aq) \rightarrow H^+(aq) + Cl^-(aq)$$
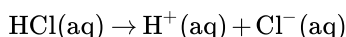
In this reaction, hydrochloric acid (HCl) dissociates completely into hydrogen (H^+) and chlorine (Cl^-) ions when dissolved in water, thereby releasing H^+ ions into solution. Formation of the hydronium ion equation:

$$HCl(aq) + H_2O(l) \rightarrow H_3O^+(aq) + Cl^-(aq)$$
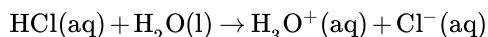
An **Arrhenius base** is a compound that **increases the concentration of** OH^- **ions** that are present when added to water. The dissociation is represented by the following equation:

$$NaOH\ (aq) \rightarrow Na^+\ (aq) + OH^-\ (aq)$$
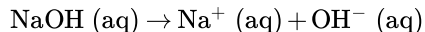
In this reaction, sodium hydroxide (NaOH) disassociates into sodium (Na^+) and hydroxide (OH^-) ions when dissolved in water, thereby releasing OH^- ions into solution.

> *Arrhenius acids are substances which produce hydrogen ions in solution and Arrhenius bases are substances which produce hydroxide ions in solution.*

> **📌 Limitations to the Arrhenius Theory**
>
> The Arrhenius theory has many more limitations than the other two theories. The theory does not explain the weak base ammonia (NH_3), which in the presence of water, releases hydroxide ions into solution, but does not contain OH- itself. The Arrhenius definition of acid and base is also limited to aqueous (i.e., water) solutions.

The Brønsted-Lowry Theory of Acids and Bases

In 1923, Danish chemist Johannes Brønsted and English chemist Thomas Lowry independently proposed new definitions for acids and bases, ones that focus on proton transfer. A **Brønsted-Lowry acid** is any species that can donate a proton (H^+) to another molecule. A **Brønsted-Lowry base** is any species that can accept a proton from another molecule. In short, **a Brønsted-Lowry acid** is a **proton donor (PD)**, while **a Brønsted-Lowry base** is a **proton acceptor (PA)**.

> *A Brønsted-Lowry acid is a proton donor, while a Brønsted-Lowry base is a proton acceptor.*

Let us use the reaction of ammonia in water to demonstrate the Brønsted-Lowry definitions of an acid and a base. Ammonia and water molecules are reactants, while the ammonium ion and the hydroxide ion are products:

$$NH_3(aq) + H_2O(\ell) \rightleftharpoons NH_4^+(aq) + OH^-(aq) \tag{10.3.1}$$
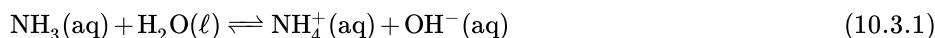
What has happened in this reaction is that the original water molecule has donated a hydrogen ion to the original ammonia molecule, which in turn has accepted the hydrogen ion. We can illustrate this as follows:

Hydrogen ion acceptor: B-L base Hydrogen ion donor: B-L acid
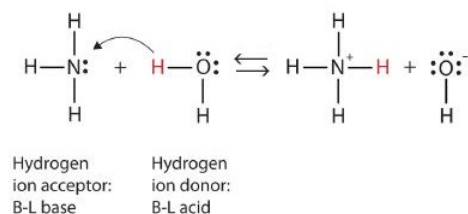
Because the water molecule donates a hydrogen ion to the ammonia, it is the Brønsted-Lowry acid, while the ammonia molecule—which accepts the hydrogen ion—is the Brønsted-Lowry base. Thus, ammonia acts as a base in both the Arrhenius sense and the Brønsted-Lowry sense.

Is an Arrhenius acid like hydrochloric acid still an acid in the Brønsted-Lowry sense? Yes, but it requires us to understand what really happens when HCl is dissolved in water. Recall that the hydrogen *atom* is a single proton surrounded by a single electron. To make the hydrogen *ion*, we remove the electron, leaving a bare proton. Do we *really* have bare protons floating around in aqueous solution? No, we do not. What really happens is that the H^+ ion attaches itself to H_2O to make H_3O^+, which is called the *hydronium ion*. For most purposes, H^+ and H_3O^+ represent the same species, but writing H_3O^+ instead of H^+ shows that we understand that there are no bare protons floating around in solution. Rather, these protons are actually attached to solvent molecules.

📌 The Hydronium Ion

A proton in aqueous solution may be surrounded by more than one water molecule, leading to formulas like $H_5O_2^+$ or $H_9O_4^+$ rather than H_3O^+. It is simpler, however, to use H_3O^+ to represent the hydronium ion.

H^+ ion   water   hydronium ion
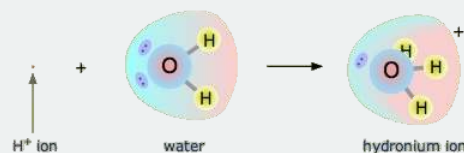
With this in mind, how do we define HCl as an acid in the Brønsted-Lowry sense? Consider what happens when HCl is dissolved in H_2O:

$$HCl(g) + H_2O(\ell) \rightarrow H_3O^+(aq) + Cl^-(aq) \tag{10.3.2}$$
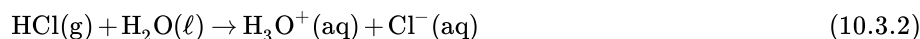
We can depict this process using Lewis electron dot diagrams:

Hydrogen ion donor: B-L acid Hydrogen ion acceptor: B-L base
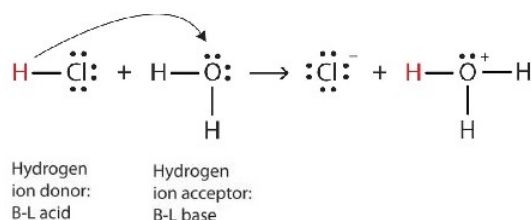
Now we see that a hydrogen ion is transferred from the HCl molecule to the H_2O molecule to make chloride ions and hydronium ions. As the hydrogen ion donor, HCl acts as a Brønsted-Lowry acid; as a hydrogen ion acceptor, H_2O is a Brønsted-Lowry base. So HCl is an acid not just in the Arrhenius sense, but also in the Brønsted-Lowry sense. Moreover, by the Brønsted-Lowry definitions, H_2O is a base in the formation of aqueous HCl. So the Brønsted-Lowry definitions of an acid and a base classify the dissolving of HCl in water as a reaction between an acid and a base—although the Arrhenius definition would not have labeled H_2O a base in this circumstance.

- A Brønsted-Lowry acid is a proton (hydrogen ion) donor.
- A Brønsted-Lowry base is a proton (hydrogen ion) acceptor.

- All Arrhenius acids and bases are Brønsted-Lowry acids and bases as well. However, not all Brønsted-Lowry acids and bases are Arrhenius acids and bases.

✔ Example 10.3.1

Aniline ($C_6H_5NH_2$) is slightly soluble in water. It has a nitrogen atom that can accept a hydrogen ion from a water molecule, just like the nitrogen atom in ammonia does. Write the chemical equation for this reaction and identify the Brønsted-Lowry acid and base.

Solution

$C_6H_5NH_2$ and H_2O are the reactants. When $C_6H_5NH_2$ accepts a proton from H_2O, it gains an extra H and a positive charge and leaves an OH^- ion behind. The reaction is as follows:

$$C_6H_5NH_2(aq) + H_2O(\ell) \rightleftharpoons C_6H_5NH_3^+(aq) + OH^-(aq)$$
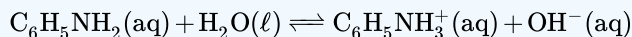
Because $C_6H_5NH_2$ accepts a proton, it is the Brønsted-Lowry base. The H_2O molecule, because it donates a proton, is the Brønsted-Lowry acid.

? Exercise 10.3.1

Identify the Brønsted-Lowry acid and the Brønsted-Lowry base in this chemical equation.

$$H_2PO_4^- + H_2O \rightleftharpoons HPO_4^{2-} + H_3O^+$$
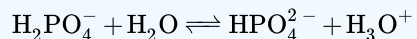
Answer

Brønsted-Lowry acid: $H_2PO_4^-$; Brønsted-Lowry base: H_2O

? Exercise 10.3.2

Which of the following compounds is a Bronsted-Lowry base?

a. HCl
b. HPO_4^{2-}
c. H_3PO_4
d. NH_4^+
e. $CH_3NH_3^+$

Answer

A Brønsted-Lowry Base is a proton acceptor, which means it will take in an H^+. This eliminates HCl, H_3PO_4, NH_4^+ and $CH_3NH_3^+$ because they are Bronsted-Lowry acids. They all give away protons. In the case of HPO_4^{2-}, consider the following equation:

$$HPO_4^{2-}(aq) + H_2O(l) \rightarrow PO_4^{3-}(aq) + H_3O^+(aq)$$
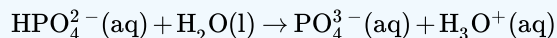
Here, it is clear that HPO_4^{2-} is the acid since it donates a proton to water to make H_3O^+ and PO_4^{3-}. Now consider the following equation:

$$HPO_4^{2-}(aq) + H_2O(l) \rightarrow H_2PO_4^- + OH^-(aq)$$
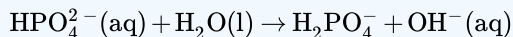
In this case, HPO_4^{2-} is the base since it accepts a proton from water to form $H_2PO_4^-$ and OH^-. Thus, HPO_4^{2-} is an acid and base together, making it amphoteric.

Since HPO_4^{2-} is the only compound from the options that can act as a base, the answer is **(b) HPO_4^{2-}.**

Conjugate Acid-Base Pair

In reality, all acid-base reactions involve the transfer of protons between acids and bases. For example, consider the acid-base reaction that takes place when ammonia is dissolved in water. A water molecule (functioning as an acid) transfers a proton to an ammonia molecule (functioning as a base), yielding the conjugate base of water, OH^-, and the conjugate acid of ammonia, NH_4^+:
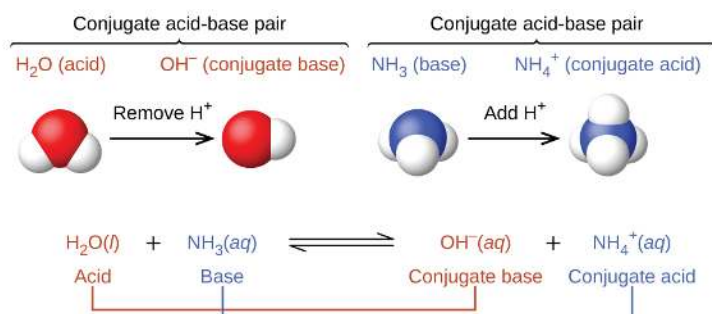
This figure has three parts in two rows. In the first row, two diagrams of acid-base pairs are shown. On the left, a space filling model of H subscript 2 O is shown with a red O atom at the center and two smaller white H atoms attached in a bent shape. Above this model is the label "H subscript 2 O (acid)" in purple. An arrow points right, which is labeled "Remove H superscript plus." To the right is another space filling model with a single red O atom to which a single smaller white H atom is attached. The label in purple above this model reads, "O H superscript negative (conjugate base)." Above both of these red and white models is an upward pointing bracket that is labeled "Conjugate acid-base pair." To the right is a space filling model with a central blue N atom to which three smaller white H atoms are attached in a triangular pyramid arrangement. A label in green above reads "N H subscript 3 (base)." An arrow labeled "Add H superscript plus" points right. To the right of the arrow is another space filling model with a blue central N atom and four smaller white H atoms in a tetrahedral arrangement. The green label above reads "N H subscript 3 superscript plus (conjugate acid)." Above both of these blue and white models is an upward pointing bracket that is labeled "Conjugate acid-base pair." The second row of the figure shows the chemical reaction, H subscript 2 O (l) is shown in purple, and is labeled below in purple as "acid," plus N H subscript 3 (a q) in green, labeled below in green as "base," followed by a double sided arrow arrow and O H superscript negative (a q) in purple, labeled in purple as "conjugate base," plus N H subscript 4 superscript plus (a q)" in green, which is labeled in green as "conjugate acid." The acid on the left side of the equation is connected to the conjugate base on the right with a purple line. Similarly, the base on the left is connected to the conjugate acid on the right side.

In the reaction of ammonia with water to give ammonium ions and hydroxide ions, ammonia acts as a base by accepting a proton from a water molecule, which in this case means that water is acting as an acid. In the reverse reaction, an ammonium ion acts as an acid by donating a proton to a hydroxide ion, and the hydroxide ion acts as a base. The conjugate acid–base pairs for this reaction are NH_4^+/NH_3 and H_2O/OH^-.
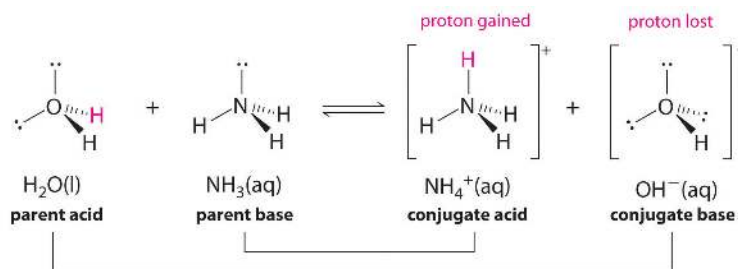
Figure 10.3.1. The pairing of parent acids and bases with conjugate acids and bases.

ACID | BASE

| negligible | OH⁻ | O²⁻ | strong |
| | HS⁻ | S²⁻ | |

(The full acid/base ladder, from top to bottom)

ACID column (relative acid strength increasing ←):
OH^- (negligible)
HS^-
H_2O
HPO_4^{2-}
HCO_3^-
NH_4^+
HCN
$H_2PO_4^-$
HSO_3^-
H_2S
H_2CO_3
$C_5H_5NH^+$
CH_3CO_2H
HF
H_3PO_4
H_2SO_3
HSO_4^- (weak)
H_3O^+
HNO_3
H_2SO_4
HCl
HBr (strong)

BASE column (Relative base strength increasing →):
O^{2-} (strong)
S^{2-}
OH^-
PO_4^{3-}
CO_3^{2-}
NH_3
CN^-
HPO_4^{2-}
SO_3^{2-}
HS^-
HCO_3^-
C_5H_5N
$CH_3CO_2^-$
F^-
$H_2PO_4^-$
HSO_3^-
SO_4^{2-} (weak)
H_2O
NO_3^-
HSO_4^-
Cl^-
Br^- (negligible)

Figure 10.3.1: The Relative Strengths of Some Common Conjugate Acid-Base Pairs. The strongest acids are at the bottom left, and the strongest bases are at the top right. The conjugate base of a strong acid is a very weak base, and, conversely, the conjugate acid of a strong base is a very weak acid.

✔ **Example 10.3.2**

Identify the conjugate acid-base pairs in this equilibrium.

$$CH_3CO_2H + H_2O \rightleftharpoons H_3O^+ + CH_3CO_2^-$$
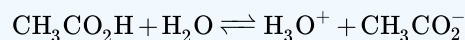
Solution

Similarly, in the reaction of acetic acid with water, acetic acid **donates** a proton to water, which acts as the base. In the reverse reaction, H_3O^+ is the acid that donates a proton to the acetate ion, which acts as the base.

Once again, we have two conjugate acid-base pairs:

- the parent acid and its conjugate base ($CH_3CO_2H/CH_3CO_2^-$) and
- the parent base and its conjugate acid (H_3O^+/H_2O).
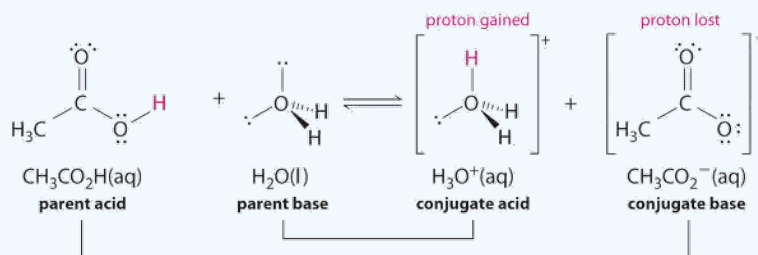
✔ **Example 10.3.3**

Identify the conjugate acid-base pairs in this equilibrium.

$$(CH_3)_3N + H_2O \rightleftharpoons (CH_3)_3NH^+ + OH^-$$
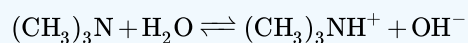
Solution

One pair is H_2O and OH^-, where H_2O has one more H^+ and is the conjugate acid, while OH^- has one less H^+ and is the conjugate base.

The other pair consists of $(CH_3)_3N$ and $(CH_3)_3NH^+$, where $(CH_3)_3NH^+$ is the conjugate acid (it has an additional proton) and $(CH_3)_3N$ is the conjugate base.

❓ **Exercise 10.3.3**

Identify the conjugate acid-base pairs in this equilibrium.

$$NH_2^- + H_2O \rightleftharpoons NH_3 + OH^-$$
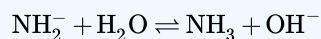
Answer

H_2O (acid) and OH^- (base); NH_2^- (base) and NH_3 (acid)

10.4: Reactions of Acids and Bases

> **Learning Objectives**
>
> - Write acid-base neutralization reactions.
> - Write reactions of acids with metals.
> - Write reactions of bases with metals.

Neutralization Reactions

The reaction that happens when an acid, such as HCl, is mixed with a base, such as NaOH:

$$HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$$
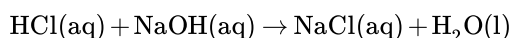
When an acid and a base are combined, water and a salt are the products. Salts are ionic compounds containing a positive ion other than H^+ and a negative ion other than the hydroxide ion, OH^-. Double displacement reactions of this type are called **neutralization reactions**. We can write an expanded version of this equation, with aqueous substances written in their longer form:

$$H^+(aq) + Cl^-(aq) + Na^+(aq) + OH^-(aq) \rightarrow Na^+(aq) + Cl^-(aq) + H_2O(l)$$
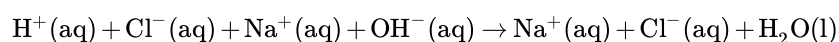
After removing the spectator ions, we get the net ionic equation:

$$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$$
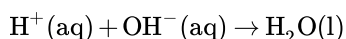
When a strong acid and a strong base are combined in the proper amounts—when $[H^+]$ equals $[OH^-]$)—a neutral solution results in which pH = 7. The acid and base have neutralized each other, and the acidic and basic properties are no longer present.

Salt solutions do not always have a pH of 7, however. Through a process known as **hydrolysis**, the ions produced when an acid and base combine may react with the water molecules to produce a solution that is slightly acidic or basic. As a general concept, if a strong acid is mixed with a weak base, the resulting solution will be slightly acidic. If a strong base is mixed with a weak acid, the solution will be slightly basic.

Video: Equimolar (~0.01 M) and equivolume solutions of HCl and NaOH are combined to make salt water. https://youtu.be/TS-I9KrUjB0

> ✔ **Example 10.4.1: Propionic Acid + Calcium Hydroxide**
>
> Calcium propionate is used to inhibit the growth of molds in foods, tobacco, and some medicines. Write a balanced chemical equation for the reaction of aqueous propionic acid ($CH_3CH_2CO_2H$) with aqueous calcium hydroxide [$Ca(OH)_2$].
>
> **Solution**
>
> Solutions to Example 14.5.1
>
> | Steps | Reaction |
> |-------|----------|
> | | |

Steps	Reaction
Write the unbalanced equation. This is a double displacement reaction, so the cations and anions swap to create the water and the salt.	$CH_3CH_2CO_2H(aq) + Ca(OH)_2(aq) \rightarrow (CH_3CH_2CO_2)_2Ca(aq) + H_2O(l)$
Balance the equation. Because there are two OH^- ions in the formula for $Ca(OH)_2$, we need two moles of propionic acid, $CH_3CH_2CO_2H$, to provide H^+ ions.	$\underline{2}CH_3CH_2CO_2H(aq) + Ca(OH)_2(aq) \rightarrow (CH_3CH_2CO_2)_2Ca(aq) + \underline{2}H_2O(l)$

? Exercise 10.4.1

Write a balanced chemical equation for the reaction of solid barium hydroxide with dilute acetic acid.

Answer

$$Ba(OH)_2(s) + 2\,CH_3CO_2H(aq) \rightarrow Ba(CH_3CO_2)_2(aq) + 2\,H_2O(l)$$
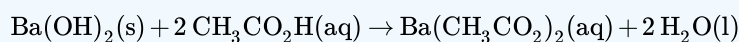
Acids and Bases React with Metals

Acids react with most metals to form a salt and hydrogen gas. As discussed previously, metals that are more active than acids can undergo a **single displacement reaction**. For example, zinc metal reacts with hydrochloric acid, producing zinc chloride and hydrogen gas.

$$Zn(s) + 2\,HCl(aq) \rightarrow ZnCl_2(aq) + H_2(g)$$
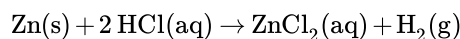
Bases also react with certain metals, like zinc or aluminum, to produce hydrogen gas. For example, sodium hydroxide reacts with zinc and water to form sodium zincate and hydrogen gas.

$$Zn(s) + 2\,NaOH(aq) + 2\,H_2O(l) \rightarrow Na_2Zn(OH)_4(aq) + H_2(g).$$
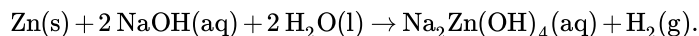
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10.5: Acid–Base Titration

🧠 Learning Objectives

- Understand the basics of acid-base titrations.
- Understand the use of indicators.
- Perform a titration calculation correctly.

The reaction of an acid with a base to make a salt and water is a common reaction in the laboratory, partly because so many compounds can act as acids or bases. Another reason that acid-base reactions are so prevalent is because they are often used to determine quantitative amounts of one or the other. Performing chemical reactions quantitatively to determine the exact amount of a reagent is called a **titration**. A titration can be performed with almost any chemical reaction for which the balanced chemical equation is known. Here, we will consider titrations that involve acid-base reactions.

During an acid-base titration, an acid with a known concentration (a **standard solution**) is slowly added to a base with an unknown concentration (or vice versa). A few drops of indicator solution are added to the base. The indicator will signal, by color change, when the base has been neutralized (when $[H^+]$ = $[OH^-]$). At that point—called the **equivalence point,** or **end point**—the titration is stopped. By knowing the volumes of acid and base used, and the concentration of the standard solution, calculations allow us to determine the concentration of the other solution.

> It is important to accurately measure volumes when doing titrations. The instrument you would use is called a burette (or buret).

Figure 10.5.1: Equipment for Titrations. A burette is a type of liquid dispensing system that can accurately indicate the volume of liquid dispensed.

For example, suppose 25.66 mL (or 0.02566 L) of 0.1078 M HCl was used to titrate an unknown sample of NaOH. What mass of NaOH was in the sample? We can calculate the number of moles of HCl reacted:

$$\text{\# mol HCl} = (0.02566 \text{ L})(0.1078 \text{ M}) = 0.002766 \text{ mol HCl}$$

We also have the balanced chemical reaction between HCl and NaOH:

$$HCl + NaOH \rightarrow NaCl + H_2O$$
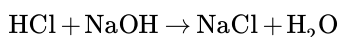
So we can construct a conversion factor to convert to number of moles of NaOH reacted:

$$0.002766 \; mol \; \cancel{HCl} \times \frac{1 \; mol \; NaOH}{1 \; mol \; \cancel{HCl}} = 0.002766 \; mol \; NaOH$$

Then we convert this amount to mass, using the molar mass of NaOH (40.00 g/mol):

$$0.002766 \; mol \; \cancel{HCl} \times \frac{40.00 \; g \; NaOH}{1 \; mol \; \cancel{HCl}} = 0.1106 \; g \; NaOH$$

This type of calculation is performed as part of a titration.

✔ Example 10.5.1: Equivalence Point

What mass of $Ca(OH)_2$ is present in a sample if it is titrated to its equivalence point with 44.02 mL of 0.0885 M HNO_3? The balanced chemical equation is as follows:

$$2\,HNO_3 + Ca(OH)_2 \rightarrow Ca(NO_3)_2 + 2\,H_2O$$
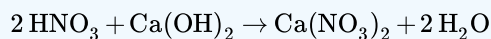
Solution

In liters, the volume is 0.04402 L. We calculate the number of moles of titrant:

moles HNO$_3$ = (0.04402 L)(0.0885 M) = 0.00390 mol HNO$_3$

Using the balanced chemical equation, we can determine the number of moles of Ca(OH)$_2$ present in the analyte:

$$0.00390 \; mol \; \cancel{HNO_3} \times \frac{1 \; mol \; Ca(OH)_2}{2 \; mol \; \cancel{HNO_3}} = 0.00195 \; mol \; Ca(OH)_2$$

Then we convert this to a mass using the molar mass of Ca(OH)$_2$:

$$0.00195 \; mol \; \cancel{Ca(OH)_2} \times \frac{74.1 \; g \; Ca(OH)_2}{mol \; \cancel{Ca(OH)_2}} = 0.144 \; g \; Ca(OH)_2$$

? Exercise 10.5.1

What mass of H$_2$C$_2$O$_4$ is present in a sample if it is titrated to its equivalence point with 18.09 mL of 0.2235 M NaOH? The balanced chemical reaction is as follows:

$$\mathrm{H_2C_2O_4 + 2\,NaOH \rightarrow Na_2C_2O_4 + 2\,H_2O}$$
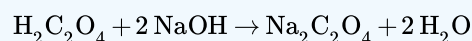
Answer

0.182 g

? Exercise 10.5.2

If 25.00 mL of HCl solution with a concentration of 0.1234 M is neutralized by 23.45 mL of NaOH, what is the concentration of the base?

Answer

0.1316 M NaOH

? Exercise 10.5.3

A 20.0 mL solution of strontium hydroxide, Sr(OH)$_2$, is placed in a flask and a drop of indicator is added. The solution turns color after 25.0 mL of a standard 0.0500 M HCl solution is added. What was the original concentration of the Sr(OH)$_2$ solution?

Answer

$3.12 \times 10^{-2} \; M$ Sr(OH)$_2$

Indicator Selection for Titrations

The indicator used depends on the type of titration performed. The indicator of choice should change color when enough of one substance (acid or base) has been added to exactly use up the other substance. Only when a strong acid and a strong base are produced will the resulting solution be neutral. The three main types of acid-base titrations, and suggested indicators, are:

The three main types of acid-base titrations, suggested indicators, and explanations

Titration between . . .	Indicator	Explanation
strong acid and strong base	any	
strong acid and weak base	methyl orange	changes color in the acidic range (3.2 - 4.4)
weak acid and strong base	phenolphthalein	changes color in the basic range (8.2 - 10.6)

Summary

A titration is the quantitative reaction of an acid and a base. Indicators are used to show that all the analyte has reacted with the titrant.

Contributions & Attributions

- Peggy Lawson (Oxbow Prairie Heights School). Funded by Saskatchewan Educational Technology Consortium.

10.6: Strong and Weak Acids and Acid Ionization Constant (K a) (Ka)

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.

$$HCl\,(g) \rightarrow H^+\,(aq) + Cl^-\,(aq) \tag{10.6.1}$$

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.

$$CH_3COOH\,(aq) \rightleftharpoons H^+\,(aq) + CH_3COO^-\,(aq) \tag{10.6.2}$$
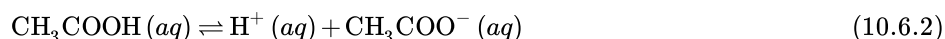
The ionization of acetic acid is incomplete, and so the equation is shown with a double arrow. The extent of ionization of weak acids varies, but is generally less than 10%. A $0.10\,M$ solution of acetic acid is only about 1.3% ionized, meaning that the equilibrium strongly favors the reactants.

Weak acids, like strong acids, ionize to yield the H^+ ion and a conjugate base. Because HCl is a strong acid, its conjugate base (Cl^-) is extremely weak. The chloride ion is incapable of accepting the 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 10.6.1: Relative Strengths of Acids and their Conjugate Bases

Acid	Conjugate Base
Strong Acids	
HCl (hydrochloric acid) (strongest)	Cl^- (chloride ion) (weakest)
H_2SO_4 (sulfuric acid)	HSO_4^- (hydrogen sulfate ion)
HNO_3 (nitric acid)	NO_3^- (nitrate ion)
Weak Acids	
H_3PO_4 (phosphoric acid)	$H_2PO_4^-$ (dihydrogen phosphate ion)
CH_3COOH (acetic acid)	CH_3COO^- (acetate ion)
H_2CO_3 (carbonic acid)	HCO_3^- (hydrogen carbonate ion)
HCN (hydrocyanic acid) (weakest)	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:

$$HA\,(aq) \rightarrow H^+\,(aq) + A^-\,(aq) \tag{10.6.3}$$

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.

$$K_a = \frac{[H^+]\,[A^-]}{[HA]} \tag{10.6.4}$$

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 10.6.2: Acid Ionization Constants at 25°C

Name of Acid	Ionization Equation	K_a	pK_a
Sulfuric acid	$H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$ $HSO_4^- \rightleftharpoons H^+ + SO_4^{2-}$	very large 1.3×10^{-2}	$pK_{a1} >>>>1$ $pK_{a2} =1.89$
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}	$pK_{a1} = 1.18$ $pK_{a2} = 4.21$
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}	$pK_{a1} = 2.12$ $pK_{a2} = 7.20$ $pK_{a3} = 12.32$
Hydrofluoric acid	$HF \rightleftharpoons H^+ + F^-$	7.1×10^{-4}	$pK_a = 3.15$
Nitrous acid	$HNO_2 \rightleftharpoons H^+ + NO_2^-$	4.5×10^{-4}	$pK_a = 3.35$
Benzoic acid	$C_6H_5COOH \rightleftharpoons H^+ + C_6H_5COO^-$	6.5×10^{-5}	$pK_a = 4.18$
Acetic acid	$CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$	1.8×10^{-5}	$pK_a = 4.74$
Carbonic acid	$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$ $HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$	4.2×10^{-7} 4.8×10^{-11}	$pK_{a1} = 6.40$ $pK_{a2} = 10.32$
Hydrocyanic acid	$HCN \rightleftharpoons H^+ + CN^-$	4.9×10^{-10}	$pK_a = 9.31$

pK$_a$ values

Because K_a values are usually very small numbers, sometimes chemists prefer to work with pK_a values, that is:

pKa = -log Ka

Table $10.6.2$ shows the pK_a values for several bases. *Notice that the stronger the acid, the higher the Ka values but the lower its pK$_a$.*

Summary

- Strong and weak acids are defined.
- The acid ionization constant (K_a) and pK_a are defined.
- The stronger the acid, the higher the Ka values but the lower its pK$_a$.

Contributors and Attributions

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10.7: Strong and Weak Bases and Base Ionization Constant (K b) (Kb)

All the complex electronics and apparatus 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 their extent of ionization. A **strong base** is a base, which 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, which 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.

$$NH_3\,(aq) + H_2O\,(l) \rightleftharpoons NH_4^+\,(aq) + OH^-\,(aq) \tag{10.7.1}$$
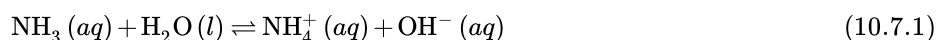
The equilibrium greatly favors the reactants and the extent of ionization of the ammonia molecule is very small.

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:

$$K_b = \frac{\left[NH_4^+\right]\left[OH^-\right]}{\left[NH_3\right]} \tag{10.7.2}$$

The numerical value of K_b is a reflection of the strength of the base. Weak bases with relatively higher K_b values are stronger than bases with relatively lower K_b values. The table below is a listing of base ionization constants for several weak bases.

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.

Table 10.7.1 : Base Ionization Constants at $25^\circ C$			
Name of Base	**Ionization Equation**	K_b	pKb
Methylamine	$CH_3NH_2 + H_2O \rightleftharpoons CH_3NH_3^+ + OH^-$	5.6×10^{-4}	3.25
Ammonia	$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$	1.8×10^{-5}	4.74
Pyridine	$C_5H_5N + H_2O \rightleftharpoons C_5H_5NH^+ + OH^-$	1.7×10^{-9}	8.77
Acetate ion	$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$	5.6×10^{-10}	9.25
Fluoride ion	$F^- + H_2O \rightleftharpoons HF + OH^-$	1.4×10^{-11}	10.85
Urea	$H_2NCONH_2 + H_2O \rightleftharpoons H_2NCONH_3^+ + OH^-$	1.5×10^{-14}	13.82

pK$_b$ values

Because Kb values are usually very small numbers, sometimes chemists prefer to work with pK$_b$ values, that is:

pK$_b$ = -log K$_b$

Table $10.7.1$ shows the pK_b values for several bases. *Notice that the stronger the base, the higher the K_b values but the lower its pK_b*.

Summary

- Strong and weak bases are defined.
- The base equilibrium constant K_b and pK_b are stated.
- The stronger the base, the higher the K_b values but the lower its pK_b.

Contributors and Attributions

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10.8: Relationship between Ka, Kb, pKa, and pKb

Learning Objectives

- To know the relationship between acid or base strength and the magnitude of K_a, K_b, pK_a, and pK_b.

The magnitude of the equilibrium constant for an ionization reaction can be used to determine the relative strengths of acids and bases. For example, the general equation for the ionization of a weak acid in water, where HA is the parent acid and A− is its conjugate base, is as follows:

$$HA_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + A^-_{(aq)} \tag{10.8.1}$$

The equilibrium constant for this dissociation is as follows:

$$K = \frac{[H_3O^+][A^-]}{[HA]} \tag{10.8.2}$$

The equilibrium constant for this reaction is the acid ionization constant K_a, also called the acid dissociation constant:

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} \tag{10.8.3}$$

Thus the numerical values of K and K_a differ by the concentration of water (55.3 M). Again, for simplicity, H_3O^+ can be written as H^+ in Equation 10.8.3. Keep in mind, though, that free H^+ does not exist in aqueous solutions and that a proton is transferred to H_2O in all acid ionization reactions to form H^3O^+. The larger the K_a, the stronger the acid and the higher the H^+ concentration at equilibrium. Like all equilibrium constants, acid–base ionization constants are actually measured in terms of the activities of H^+ or OH^-, thus making them **unitless**. The values of K_a for a number of common acids are given in Table 10.8.1.

Table 10.8.1: Values of K_a, pK_a, K_b, and pK_b for Selected Acids (HA and Their Conjugate Bases (A^-)

Acid	HA	K_a	pK_a	A^-	K_b	pK_b
hydroiodic acid	HI	2×10^9	−9.3	I^-	5.5×10^{-24}	23.26
sulfuric acid (1)*	H_2SO_4	1×10^2	−2.0	HSO_4^-	1×10^{-16}	16.0
nitric acid	HNO_3	2.3×10^1	−1.37	NO_3^-	4.3×10^{-16}	15.37
hydronium ion	H_3O^+	1.0	0.00	H_2O	1.0×10^{-14}	14.00
sulfuric acid (2)*	HSO_4^-	1.0×10^{-2}	1.99	SO_4^{2-}	9.8×10^{-13}	12.01
hydrofluoric acid	HF	6.3×10^{-4}	3.20	F^-	1.6×10^{-11}	10.80
nitrous acid	HNO_2	5.6×10^{-4}	3.25	$NO2^-$	1.8×10^{-11}	10.75
formic acid	HCO_2H	1.78×10^{-4}	3.750	HCO_2-	5.6×10^{-11}	10.25
benzoic acid	$C_6H_5CO_2H$	6.3×10^{-5}	4.20	$C_6H_5CO_2^-$	1.6×10^{-10}	9.80
acetic acid	CH_3CO_2H	1.7×10^{-5}	4.76	$CH_3CO_2^-$	5.8×10^{-10}	9.24
pyridinium ion	$C_5H_5NH^+$	5.9×10^{-6}	5.23	C_5H_5N	1.7×10^{-9}	8.77
hypochlorous acid	$HOCl$	4.0×10^{-8}	7.40	OCl^-	2.5×10^{-7}	6.60
hydrocyanic acid	HCN	6.2×10^{-10}	9.21	CN^-	1.6×10^{-5}	4.79
ammonium ion	NH_4^+	5.6×10^{-10}	9.25	NH_3	1.8×10^{-5}	4.75
water	H_2O	1.0×10^{-14}	14.00	OH^-	1.00	0.00
acetylene	C_2H_2	1×10^{-26}	26.0	HC_2^-	1×10^{12}	−12.0

*The number in parentheses indicates the ionization step referred to for a polyprotic acid.

Acid	HA	K_a	pK_a	A^-	K_b	pK_b
ammonia	NH_3	1×10^{-35}	35.0	NH_2^-	1×10^{21}	−21.0
*The number in parentheses indicates the ionization step referred to for a polyprotic acid.						

Weak bases react with water to produce the hydroxide ion, as shown in the following general equation, where B is the parent base and BH+ is its conjugate acid:

$$B_{(aq)} + H_2O_{(l)} \rightleftharpoons BH^+_{(aq)} + OH^-_{(aq)} \tag{10.8.4}$$

The equilibrium constant for this reaction is the base ionization constant (K_b), also called the base dissociation constant:

$$K_b = \frac{[BH^+][OH^-]}{[B]} \tag{10.8.5}$$

Once again, the concentration does not appear in the equilibrium constant expression.. The larger the K_b, the stronger the base and the higher the OH^- concentration at equilibrium. The values of K_b for a number of common weak bases are given in Table 10.8.2

Table 10.8.2: Values of K_b, pK_b, K_a, and pK_a for Selected Weak Bases (B) and Their Conjugate Acids (BH+)

Base	B	K_b	pK_b	BH^+	K_a	pK_a
hydroxide ion	OH^-	1.0	0.00*	H_2O	1.0×10^{-14}	14.00
phosphate ion	PO_4^{3-}	2.1×10^{-2}	1.68	HPO_4^{2-}	4.8×10^{-13}	12.32
dimethylamine	$(CH_3)_2NH$	5.4×10^{-4}	3.27	$(CH_3)_2NH_2^+$	1.9×10^{-11}	10.73
methylamine	CH_3NH_2	4.6×10^{-4}	3.34	$CH_3NH_3^+$	2.2×10^{-11}	10.66
trimethylamine	$(CH_3)_3N$	6.3×10^{-5}	4.20	$(CH_3)_3NH^+$	1.6×10^{-10}	9.80
ammonia	NH_3	1.8×10^{-5}	4.75	NH_4^+	5.6×10^{-10}	9.25
pyridine	C_5H_5N	1.7×10^{-9}	8.77	$C_5H_5NH^+$	5.9×10^{-6}	5.23
aniline	$C_6H_5NH_2$	7.4×10^{-10}	9.13	$C_6H_5NH_3^+$	1.3×10^{-5}	4.87
water	H_2O	1.0×10^{-14}	14.00	H_3O^+	1.0*	0.00
*As in Table 10.8.1.						

There is a simple relationship between the magnitude of K_a for an acid and K_b for its conjugate base. Consider, for example, the ionization of hydrocyanic acid (HCN) in water to produce an acidic solution, and the reaction of CN^- with water to produce a basic solution:

$$HCN_{(aq)} \rightleftharpoons H^+_{(aq)} + CN^-_{(aq)} \tag{10.8.6}$$

$$CN^-_{(aq)} + H_2O_{(l)} \rightleftharpoons OH^-_{(aq)} + HCN_{(aq)} \tag{10.8.7}$$
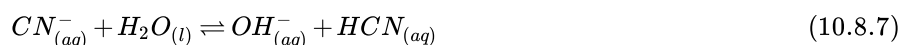
The equilibrium constant expression for the ionization of HCN is as follows:

$$K_a = \frac{[H^+][CN^-]}{[HCN]} \tag{10.8.8}$$

The corresponding expression for the reaction of cyanide with water is as follows:

$$K_b = \frac{[OH^-][HCN]}{[CN^-]} \tag{10.8.9}$$

If we add Equations 10.8.6 and 10.8.7, we obtain the following (recall that the equilibrium constant for the sum of two reactions is the product of the equilibrium constants for the individual reactions):

$$HCN_{(aq)} \rightleftharpoons H^+_{(aq)} + CN^-_{(aq)} \quad K_a = [H^+][CN^-]/[HCN] \tag{10.8.10}$$

$$CN^-_{(aq)} + H_2O_{(l)} \rightleftharpoons OH^-_{(aq)} + HCN_{(aq)} \quad K_b = [OH^-][HCN]/[CN^-] \tag{10.8.11}$$

$$H_2O_{(l)} \rightleftharpoons H^+_{(aq)} + OH^-_{(aq)} \quad K = K_a \times K_b = [H^+][OH^-] \tag{10.8.12}$$
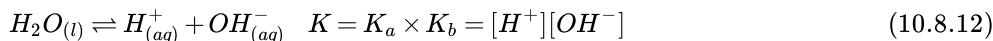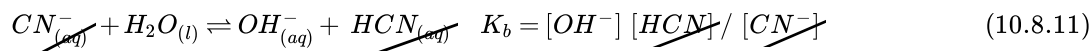
In this case, the sum of the reactions described by K_a and K_b is the equation for the autoionization of water, and the product of the two equilibrium constants is K_w:

$$K_a K_b = K_w \tag{10.8.13}$$

Thus if we know either K_a for an acid or K_b for its conjugate base, we can calculate the other equilibrium constant for any conjugate acid–base pair.

Just as with pH, pOH, and pKw, we can use negative logarithms to avoid exponential notation in writing acid and base ionization constants, by defining pK_a as follows:

$$pKa = -\log_{10} K_a \tag{10.8.14}$$

$$K_a = 10^{-pK_a} \tag{10.8.15}$$

and pK_b as

$$pK_b = -\log_{10} K_b \tag{10.8.16}$$

$$K_b = 10^{-pK_b} \tag{10.8.17}$$

Similarly, Equation 16.5.10, which expresses the relationship between K_a and K_b, can be written in logarithmic form as follows:

$$pK_a + pK_b = pK_w \tag{10.8.18}$$

At 25°C, this becomes

$$pK_a + pK_b = 14.00 \tag{10.8.19}$$

The values of pK_a and pK_b are given for several common acids and bases in Table 16.5.1 and Table 16.5.2, respectively, and a more extensive set of data is provided in Tables E1 and E2. Because of the use of negative logarithms, smaller values of pK_a correspond to larger acid ionization constants and hence stronger acids. For example, nitrous acid (HNO_2), with a pK_a of 3.25, is about a 1000 times stronger acid than hydrocyanic acid (HCN), with a pK_a of 9.21. Conversely, smaller values of pK_b correspond to larger base ionization constants and hence stronger bases.

The relative strengths of some common acids and their conjugate bases are shown graphically in Figure 16.5. The conjugate acid–base pairs are listed in order (from top to bottom) of increasing acid strength, which corresponds to decreasing values of pK_a. This order corresponds to decreasing strength of the conjugate base or increasing values of pK_b. At the bottom left of Figure 16.5.2 are the common strong acids; at the top right are the most common strong bases. **Notice the inverse relationship between the strength of the parent acid and the strength of the conjugate base. Thus the conjugate base of a strong acid is a very weak base, and the conjugate base of a very weak acid is a strong base.**

> The conjugate base of a strong acid is a weak base and vice versa.

We can use the relative strengths of acids and bases to predict the direction of an acid–base reaction by following a single rule: an acid–base equilibrium always favors the side with the weaker acid and base, as indicated by these arrows:

$$\text{stronger acid} + \text{stronger base} \rightleftharpoons \text{weaker acid} + \text{weaker base} \tag{10.8.20}$$
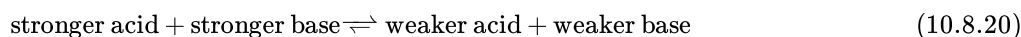
In an acid–base reaction, the proton always reacts with the stronger base.

For example, hydrochloric acid is a strong acid that ionizes essentially completely in dilute aqueous solution to produce H_3O^+ and Cl^-; only negligible amounts of HCl molecules remain undissociated. Hence the ionization equilibrium lies virtually all the way to the right, as represented by a single arrow:

$$HCl_{(aq)} + H_2O_{(l)} \rightarrow\rightarrow H_3O^+_{(aq)} + Cl^-_{(aq)} \tag{10.8.21}$$
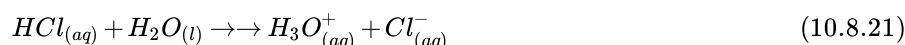
In contrast, acetic acid is a weak acid, and water is a weak base. Consequently, aqueous solutions of acetic acid contain mostly acetic acid molecules in equilibrium with a small concentration of H_3O^+ and acetate ions, and the ionization equilibrium lies far to the left, as represented by these arrows:

$$CH_3CO_2H_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + CH_3CO_2^-{}_{(aq)} \tag{10.8.22}$$
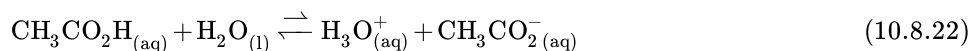
Similarly, in the reaction of ammonia with water, the hydroxide ion is a strong base, and ammonia is a weak base, whereas the ammonium ion is a stronger acid than water. Hence this equilibrium also lies to the left:

$$H_2O_{(l)} + NH_{3(aq)} \rightleftharpoons NH_4^+{}_{(aq)} + OH^-_{(aq)} \tag{10.8.23}$$
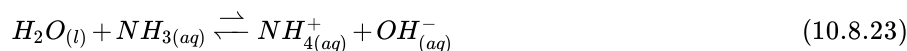
All acid–base equilibria favor the side with the weaker acid and base. Thus the proton is bound to the stronger base.

Example 10.8.1: Butyrate and Dimethylammonium Ions

a. Calculate K_b and pK_b of the butyrate ion ($CH_3CH_2CH_2CO_2^-$). The pK_a of butyric acid at 25°C is 4.83. Butyric acid is responsible for the foul smell of rancid butter.
b. Calculate K_a and pK_a of the dimethylammonium ion ($(CH_3)_2NH_2^+$). The base ionization constant K_b of dimethylamine ($(CH_3)_2NH$) is 5.4×10^{-4} at 25°C.

Given: pK_a and K_b

Asked for: corresponding K_b and pK_b, K_a and pK_a

Strategy:

The constants K_a and K_b are related as shown in Equation 16.5.10. The pK_a and pK_b for an acid and its conjugate base are related as shown in Equation 16.5.15 and Equation 16.5.16. Use the relationships pK = −log K and K = 10−pK (Equation 16.5.11 and Equation 16.5.13) to convert between K_a and pK_a or K_b and pK_b.

Solution:

We are given the pK_a for butyric acid and asked to calculate the K_b and the pK_b for its conjugate base, the butyrate ion. Because the pK_a value cited is for a temperature of 25°C, we can use Equation 16.5.16: $pK_a + pK_b$ = pKw = 14.00. Substituting the pK_a and solving for the pK_b,

$$4.83 + pK_b = 14.00 \tag{10.8.24}$$

$$pK_b = 14.00 - 4.83 = 9.17 \tag{10.8.25}$$

Because $pK_b = -\log K_b$, K_b is $10^{-9.17} = 6.8 \times 10^{-10}$.

In this case, we are given K_b for a base (dimethylamine) and asked to calculate K_a and pK_a for its conjugate acid, the dimethylammonium ion. Because the initial quantity given is K_b rather than pK_b, we can use Equation 16.5.10: $K_aK_b = K_w$. Substituting the values of K_b and K_w at 25°C and solving for K_a,

$$K_a(5.4 \times 10^{-4}) = 1.01 \times 10^{-14} \tag{10.8.26}$$

$$K_a = 1.9 \times 10^{-11} \tag{10.8.27}$$

Because pK_a = −log K_a, we have $pK_a = -\log(1.9 \times 10^{-11}) = 10.72$. We could also have converted K_b to pK_b to obtain the same answer:

$$pK_b = -\log(5.4 \times 10^{-4}) = 3.27 \tag{10.8.28}$$

$$pKa + pK_b = 14.00 \tag{10.8.29}$$

$$pK_a = 10.73 \tag{10.8.30}$$

$$K_a = 10^{-pK_a} = 10^{-10.73} = 1.9 \times 10^{-11} \tag{10.8.31}$$

If we are given any one of these four quantities for an acid or a base (K_a, pK_a, K_b, or pK_b), we can calculate the other three.

Exercise 10.8.1: Lactic Acid

Lactic acid ($CH_3CH(OH)CO_2H$) is responsible for the pungent taste and smell of sour milk; it is also thought to produce soreness in fatigued muscles. Its pK_a is 3.86 at 25°C. Calculate K_a for lactic acid and pK_b and K_b for the lactate ion.

Answer

$K_a = 1.4 \times 10^{-4}$ for lactic acid;

$pK_b = 10.14$ and $K_b = 7.2 \times 10^{-11}$ for the lactate ion

---

Summary

Two species that differ by only a proton constitute a conjugate acid–base pair. The magnitude of the equilibrium constant for an ionization reaction can be used to determine the relative strengths of acids and bases. For an aqueous solution of a weak acid, the dissociation constant is called the acid ionization constant (Ka). Similarly, the equilibrium constant for the reaction of a weak base with water is the base ionization constant (Kb). For any conjugate acid–base pair, $K_aK_b = K_w$. Smaller values of pK_a correspond to larger acid ionization constants and hence stronger acids. Conversely, smaller values of pK_b correspond to larger base ionization constants and hence stronger bases. At 25°C, $pK_a + pK_b = 14.00$. Acid–base reactions always proceed in the direction that produces the weaker acid–base pair.

Key Takeaways

- The Ka and Kb values for a conjugated acid–base pairs are related through the K_w value:

$$K_aK_b = K_w \tag{10.8.32}$$

- The conjugate base of a strong acid is a very weak base, and the conjugate base of a very weak acid is a strong base.

Key Equations

- Acid ionization constant:

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} \tag{10.8.33}$$

- Base ionization constant:

$$K_b = \frac{[BH^+][OH^-]}{[B]} \tag{10.8.34}$$

- Relationship between K_a and K_b of a conjugate acid–base pair:

$$K_aK_b = K_w \tag{10.8.35}$$

- Definition of pK_a:

$$pKa = -\log_{10} K_a$$
$$K_a = 10^{-pK_a} \tag{10.8.36}$$

- Definition of pK_b:

$$pK_b = -\log_{10} K_b$$
$$K_b = 10^{-pK_b} \tag{10.8.37}$$

- Relationship between pK_a and pK_b of a conjugate acid–base pair:

$$pK_a + pK_b = pK_w \tag{10.8.38}$$
$$pK_a + pK_b = 14.00 \text{ at } 25\,°C \tag{10.8.39}$$

Contributors and Attributions

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10.8: Relationship between Ka, Kb, pKa, and pKb is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

10.9: Calculating Ka and Kb

The pH meter was invented because Florida orange growers needed a way to test the acidity of their fruit. The first meter was invented by Arnold Beckman, who went on to form Beckman Instruments. Beckman's business was very successful, and he used much of his fortune to fund science education and research. The Beckman family donated $40 million to build the Beckman Institute at the University of Illinois.

Calculating K_a and K_b

The numerical value of K_a and K_b can be determined from an experiment. A solution of known concentration is prepared and its pH is measured with an instrument called a **pH meter**.

Figure 10.9.1: A pH meter is a laboratory device that provides quick, accurate measurements of the pH of solutions. (CC BY-NC; CK-12)

> **10.9.1** Example
>
> A $0.500\,\mathrm{M}$ solution of formic acid is prepared and its pH is measured to be 2.04. Determine the K_a for formic acid.
>
> **Solution**
>
> ***Step 1: List the known values and plan the problem.***
>
> **Known**
> - Initial $[\mathrm{HCOOH}] = 0.500\,\mathrm{M}$
> - $\mathrm{pH} = 2.04$
>
> **Unknown**
> First, the pH is used to calculate the $\left[\mathrm{H^+}\right]$ at equilibrium. An ICE table is set up in order to determine the concentrations of HCOOH and $\mathrm{HCOO^-}$ at equilibrium. All concentrations are then substituted into the K_a expression and the K_a value is calculated.
>
> ***Step 2: Solve.***
>
> $$\left[\mathrm{H^+}\right] = 10^{-\mathrm{pH}} = 10^{-2.04} = 9.12 \times 10^{-3}\,\mathrm{M}$$
>
> Since each formic acid molecule that ionizes yields one $\mathrm{H^+}$ ion and one formate ion $\left(\mathrm{HCOO^-}\right)$, the concentrations of $\mathrm{H^+}$ and $\mathrm{HCOO^-}$ are equal at equilibrium. We assume that the initial concentrations of each ion are zero, resulting in the following ICE table.
>
> | | HCOOH | H$^+$ | HCOO$^-$ |
> |-------------|-------------------------|-------------------------|-------------------------|
> | Initial | 0.500 | 0 | 0 |
> | Change | -9.12×10^{-3} | $+9.12 \times 10^{-3}$ | $+9.12 \times 10^{-3}$ |
> | Equilibrium | 0.491 | 9.12×10^{-3} | 9.12×10^{-3} |
>
> Now, substituting into the K_a expression gives:
>
> $$K_a = \frac{\left[\mathrm{H^+}\right]\left[\mathrm{HCOO^-}\right]}{[\mathrm{HCOOH}]} = \frac{\left(9.12 \times 10^{-3}\right)\left(9.12 \times 10^{-3}\right)}{0.491} = 1.7 \times 10^{-4}$$
>
> ***Step 3: Think about your result.***

> The value of K_a is consistent with that of a weak acid. Two significant figures are appropriate for the answer, since there are two digits after the decimal point in the reported pH.

Similar steps can be taken to determine the K_b of a base. For example, a $0.750\,M$ solution of the weak base ethylamine $\left(C_2H_5NH_2\right)$ has a pH of 12.31.

$$C_2H_5NH_2 + H_2O \rightleftharpoons C_2H_5NH_3^+ + OH^-$$
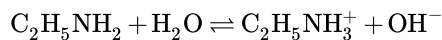
Since one of the products of the ionization reaction is the hydroxide ion, we need to first find the $\left[OH^-\right]$ at equilibrium. The pOH is $14 - 12.31 = 1.69$. The $\left[OH^-\right]$ is then found from $10^{-1.69} = 2.04 \times 10^{-2}\,M$. The ICE table is then set up as shown below.

	$C_2H_5NH_2$	$C_2H_5NH_3^+$	OH^-
Initial	0.750	0	0
Change	-2.04×10^{-2}	$+2.04 \times 10^{-2}$	$+2.04 \times 10^{-2}$
Equilibrium	0.730	2.04×10^{-2}	2.04×10^{-2}

Substituting into the K_b expression yields the K_b for ethylamine.

$$K_b = \frac{\left[C_2H_5NH_3^+\right]\left[OH^-\right]}{\left[C_2H_5NH_2\right]} = \frac{\left(2.04 \times 10^{-2}\right)\left(2.04 \times 10^{-2}\right)}{0.730} = 5.7 \times 10^{-4}$$

Summary

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- **21.14: Calculating Acid and Base Dissociation Constants** by CK-12 Foundation is licensed CK-12. Original source: https://flexbooks.ck12.org/cbook/ck-12-chemistry-flexbook-2.0/.

10.10: Water - Acid and Base in One
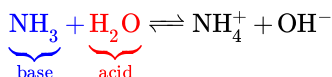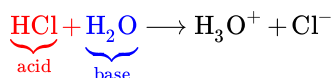
> **Learning Objectives**
>
> - Describe the autoionization of water.
> - Calculate the concentrations of H_3O^+ and OH^- in aqueous solutions, knowing the other concentration.

We have already seen that H_2O can act as an acid or a base:

$$\underbrace{NH_3}_{base} + \underbrace{H_2O}_{acid} \rightleftharpoons NH_4^+ + OH^-$$

where H_2O acts as an acid (in red).

$$\underbrace{HCl}_{acid} + \underbrace{H_2O}_{base} \longrightarrow H_3O^+ + Cl^-$$

where H_2O acts as an base (in blue).

It may not surprise you to learn, then, that within any given sample of water, some H_2O molecules are acting as acids, and other H_2O molecules are acting as bases. The chemical equation is as follows:

$$\underbrace{H_2O}_{acid} + \underbrace{H_2O}_{base} \rightleftharpoons H_3O^+ + OH^- \tag{10.10.1}$$

This occurs only to a very small degree: only about 6 in 10^8 H_2O molecules are participating in this process, which is called the **autoionization of water**.
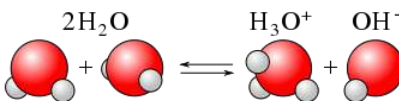

Figure 10.10.1: Autoionization of water, resulting in hydroxide and hydronium ions.

At this level, the concentration of both $H_3O^+(aq)$ and $OH^-(aq)$ in a sample of pure H_2O is about $1.0 \times 10^{-7}\ M$ (at room temperature). If we use square brackets—[ ]—around a dissolved species to imply the molar concentration of that species, we have

$$[H_3O^+] = [OH^-] = 1.0 \times 10^{-7} \tag{10.10.2}$$

for *any* sample of pure water because H_2O can act as both an acid and a base. The product of these two concentrations is 1.0×10^{-14}:

$$[H_3O^+] \times [OH^-] = (1.0 \times 10^{-7})(1.0 \times 10^{-7}) = 1.0 \times 10^{-14}$$

- For acids, the concentration of $H_3O^+(aq)$ (i.e., $[H_3O^+]$) is greater than $1.0 \times 10^{-7}\ M$.
- For bases the concentration of $OH^-(aq)$ (i.e., $[OH^-]$) is greater than $1.0 \times 10^{-7}\ M$.

However, the *product* of the two concentrations—$[H_3O^+][OH^-]$—is *always* equal to 1.0×10^{-14}, no matter whether the aqueous solution is an acid, a base, or neutral:

$$[H_3O^+][OH^-] = 1.0 \times 10^{-14}$$

This value of the product of concentrations is so important for aqueous solutions that it is called the **autoionization constant of water** and is denoted K_w:

$$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14} \tag{10.10.3}$$

This means that if you know $[H_3O^+]$ for a solution, you can calculate what $[OH^-]$) has to be for the product to equal 1.0×10^{-14}; or if you know $[OH^-]$), you can calculate $[H_3O^+]$. This also implies that as one concentration goes up, the other must go down to compensate so that their product always equals the value of K_w.

> 📌 **Warning: Temperature Matters**
>
> The degree of autoionization of water (Equation 10.10.1)—and hence the value of K_w—changes with temperature, so Equations 10.10.2- 10.10.3 are accurate only at room temperature.

> ✔ Example 10.10.1: Hydroxide Concentration
>
> What is $[OH^-]$) of an aqueous solution if $[H_3O^+]$ is $1.0 \times 10^{-4} M$?
>
> **Solution**
>
> <div align="center">Solutions to Example 14.7.1</div>
>
> | Steps for Problem Solving | |
> |---|---|
> | Identify the "given" information and what the problem is asking you to "find." | Given: $[H_3O^+] = 1.0 \times 10^{-4} M$
 Find: $[OH^-]$ = ? M |
> | List other known quantities. | none |
> | Plan the problem. | Using the expression for K_w, (Equation 10.10.3), rearrange the equation algebraically to solve for $[OH^-]$. $$[OH^-] = \frac{1.0 \times 10^{-14}}{[H_3O^+]}$$ |
> | Calculate. | Now substitute the known quantities into the equation and solve. $$[OH^-] = \frac{1.0 \times 10^{-14}}{1.0 \times 10^{-4}} = 1.0 \times 10^{-10} M$$ It is assumed that the concentration unit is molarity, so $[OH^-]$ is 1.0×10^{-10} M. |
> | Think about your result. | The concentration of the acid is high (> 1 x 10^{-7} M), so $[OH^-]$ should be low. |

> ❓ Exercise 10.10.1
>
> What is $[OH^-]$ in a 0.00032 M solution of H_2SO_4?
>
> **Hint**
>
> Assume **both** protons ionize from the molecule...although this is not the case.
>
> **Answer**
>
> $3.1 \times 10^{-11} M$

When you have a solution of a particular acid or base, you need to look at the formula of the acid or base to determine the number of H_3O^+ or OH^- ions in the formula unit because $[H_3O^+]$ or $[OH^-]$) may not be the same as the concentration of the acid or base itself.

> ✔ Example 10.10.2: Hydronium Concentration
>
> What is $[H_3O^+]$ in a 0.0044 M solution of $Ca(OH)_2$?
>
> **Solution**
>
> <div align="center">Solutions to Example 14.7.2</div>
>
> | Steps for Problem Solving | |
> |---|---|
> | | |

Steps for Problem Solving	
Identify the "given" information and what the problem is asking you to "find."	Given: $[\mathrm{Ca(OH)_2}] = 0.0044\,M$ Find: $[\mathrm{H_3O^+}] = ?\,\mathrm{M}$
List other known quantities.	We begin by determining $[\mathrm{OH^-}]$. The concentration of the solute is 0.0044 M, but because $\mathrm{Ca(OH)_2}$ is a strong base, there are two $\mathrm{OH^-}$ ions in solution for every formula unit dissolved, so the actual $[\mathrm{OH^-}]$ is two times this: $$[\mathrm{OH^-}] = 2 \times 0 \cdot 0044\ \mathrm{M} = 0 \cdot 0088\ \mathrm{M} \cdot$$
Plan the problem.	Use the expression for K_w (Equation 10.10.3) and rearrange the equation algebraically to solve for $[\mathrm{H_3O^+}]$. $$[H_3O^+] = \frac{1.0 \times 10^{-14}}{[OH^-]}$$
Calculate.	Now substitute the known quantities into the equation and solve. $$[H_3O^+] = \frac{1.0 \times 10^{-14}}{(0.0088)} = 1.1 \times 10^{-12}\,M$$ $[\mathrm{H_3O^+}]$ has decreased significantly in this basic solution.
Think about your result.	The concentration of the base is high ($> 1 \times 10^{-7}$ M) so $[\mathrm{H_3O^+}]$ should be low.

? Exercise 10.10.2

What is $[\mathrm{H_3O^+}]$ of an aqueous solution if $[\mathrm{OH^-}]$ is $1.0 \times 10^{-9}\,M$?

Answer

1.0×10^{-5} M

In any aqueous solution, the product of $[\mathrm{H_3O^+}]$ and $[\mathrm{OH^-}]$ equals 1.0×10^{-14} (at room temperature).

Contributions & Attributions

10.11: The pH and pOH Scales - Ways to Express Acidity and Basicity

🧠 Learning Objectives

- Define pH and pOH.
- Determine the pH of acidic and basic solutions.
- Determine the hydronium ion concentration and pOH from pH.

As we have seen, $[H_3O^+]$ and $[OH^-]$ values can be markedly different from one aqueous solution to another. So chemists defined a new scale that succinctly indicates the concentrations of either of these two ions.

pH is a logarithmic function of $[H_3O^+]$:

$$pH = -\log[H_3O^+] \tag{10.11.1}$$

pH is usually (but not always) between 0 and 14. Knowing the dependence of pH on $[H_3O^+]$, we can summarize as follows:

- If pH < 7, then the solution is acidic.
- If pH = 7, then the solution is neutral.
- If pH > 7, then the solution is basic.

This is known as the pH scale. The pH scale is the range of values from 0 to 14 that describes the acidity or basicity of a solution. You can use pH to make a quick determination whether a given aqueous solution is acidic, basic, or neutral. Figure 10.11.1 illustrates this relationship, along with some examples of various solutions. Because hydrogen ion concentrations are generally less than one (for example $1.3 \times 10^{-3}\ M$), the log of the number will be a negative number. To make pH even easier to work with, pH is defined as the **negative log of** $[H_3O^+]$, which will give a positive value for pH.
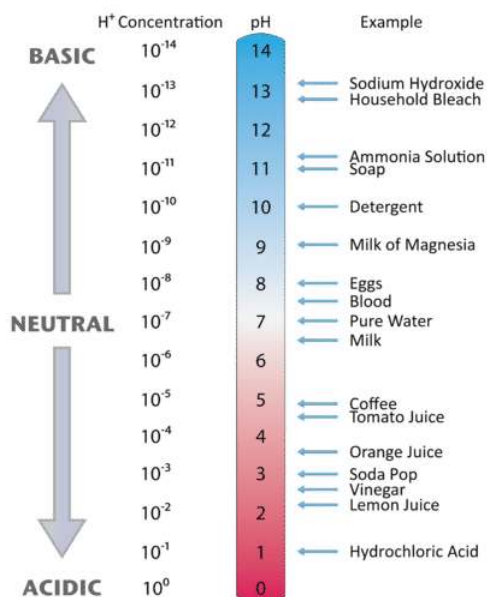

Figure 10.11.1: The pH values for several common materials.

✔ Example 10.11.1

Label each solution as acidic, basic, or neutral based only on the stated pH.

a. milk of magnesia, pH = 10.5
b. pure water, pH = 7
c. wine, pH = 3.0

Answer
a. With a pH greater than 7, milk of magnesia is basic. (Milk of magnesia is largely Mg(OH)$_2$.)
b. Pure water, with a pH of 7, is neutral.

c. With a pH of less than 7, wine is acidic.

? Exercise 10.11.1

Identify each substance as acidic, basic, or neutral based only on the stated pH.

a. human blood with $pH = 7.4$
b. household ammonia with $pH = 11.0$
c. cherries with $pH = 3.6$

Answer a

   basic

Answer b

   basic

Answer c

   acidic

Calculating pH from Hydronium Concentration

The pH of solutions can be determined by using logarithms as illustrated in the next example for stomach acid. Stomach acid is a solution of HCl with a hydronium ion concentration of 1.2×10^{-3} M, what is the pH of the solution?

$$\begin{aligned} \text{pH} &= -\log[\text{H}_3\text{O}^+] \\ &= -\log(1.2 \times 10^{-3}) \\ &= -(-2.92) = 2.92 \end{aligned}$$

📌 Logarithms

To get the **log value** on your calculator, enter the number (in this case, the hydronium ion concentration) first, then press the LOG key.

If the number is 1.0 x 10^{-5} (for [H$_3$O$^+$] = 1.0 x 10^{-5} M) you should get an answer of "-5".

If you get a different answer, or an error, try pressing the LOG key before you enter the number.

✔ Example 10.11.2: Converting Ph to Hydronium Concentration

Find the pH, given the $[H_3O^+]$ of the following:

a. 1×10^{-3} M
b. 2.5×10^{-11} M
c. 4.7×10^{-9} M

Solution

Solutions to Example 14.9.2

Steps for Problem Solving	
Identify the "given" information and what the problem is asking you to "find."	Given: a. [H$_3$O$^+$] = 1×10^{-3} M b. [H$_3$O$^+$] = 2.5×10^{-11} M c. [H$_3$O$^+$] = 4.7×10^{-9} M Find: ? pH
Plan the problem.	Need to use the expression for pH (Equation 10.11.1). pH = - log [H$_3$O$^+$]

Steps for Problem Solving	

	Now substitute the known quantity into the equation and solve.
	
	  a. pH = - log $[\underline{1} \times 10^{-3}]$ = 3.$\underline{0}$ (1 decimal places since 1 has 1 significant figure)
	
	  b. pH = - log $[\underline{2.5} \times 10^{-11}]$ = 10.$\underline{60}$ (2 decimal places since 2.5 has 2 significant figures)
	
	  c. pH = - log $[\underline{4.7} \times 10^{-9}]$ = 8.$\underline{30}$ (2 decimal places since 4.7 has 2 significant figures)
	
	The other issue that concerns us here is significant figures. Because the number(s) before the decimal point in a logarithm relate to the power on 10, the number of digits *after* the decimal point is what determines the number of significant figures in the final answer:

Calculate.	
	X.YYY ✕ Y.YY x 10^x

? Exercise 10.11.2

Find the pH, given $[H_3O^+]$ of the following:

  a. 5.8×10^{-4} M
  b. 1.0×10^{-7}

Answer a

  3.22

Answer b

  7.00

Calculating Hydronium Concentration from pH

Sometimes you need to work "backwards"—you know the pH of a solution and need to find $[H_3O^+]$, or even the concentration of the acid solution. How do you do that? To convert pH into $[H_3O^+]$ we solve Equation 10.11.1 for $[H_3O^+]$. This involves taking the antilog (or inverse log) of the negative value of pH .

$$[\mathrm{H_3O^+}] = \mathrm{antilog}(-pH)$$

or

$$[\mathrm{H_3O^+}] = 10^{-pH} \tag{10.11.2}$$

As mentioned above, different calculators work slightly differently—make sure you can do the following calculations using ***your*** calculator.

⚲ Calculator Skills

We have a solution with a pH = 8.3. What is $[H_3O^+]$?

With some calculators you will do things in the following order:

  1. Enter 8.3 as a negative number (use the key with both the +/- signs, not the subtraction key).
  2. Use your calculator's 2nd or Shift or INV (inverse) key to type in the symbol found above the LOG key. The shifted function should be 10^x.
  3. You should get the answer **5.0×10^{-9}**.

Other calculators require you to enter keys in the order they appear in the equation.

1. Use the Shift or second function to key in the 10^x function.
2. Use the +/- key to type in a negative number, then type in 8.3.
3. You should get the answer **5.0 × 10⁻⁹**.

If neither of these methods work, try rearranging the order in which you type in the keys. Don't give up—you must master your calculator!

✔ Example 10.11.3: Calculating Hydronium Concentration from pH

Find the hydronium ion concentration in a solution with a pH of 12.6. Is this solution an acid or a base? How do you know?

Solution

Solutions to Example 14.9.3

Steps for Problem Solving	
Identify the "given" information and what the problem is asking you to "find."	Given: pH = 12.6 Find: $[H_3O^+]$ = ? M
Plan the problem.	Need to use the expression for $[H_3O^+]$ (Equation 10.11.2). $[H_3O^+]$ = antilog (-pH) or $[H_3O^+] = 10^{-pH}$
Calculate.	Now substitute the known quantity into the equation and solve. $[H_3O^+]$ = antilog (12.<u>60</u>) = <u>2.5</u> x 10⁻¹³ M (2 significant figures since 4.7 has 12.60 2 decimal places) or $[H_3O^+] = 10^{-12.\underline{60}} = \underline{2.5}$ x 10⁻¹³ M (2 significant figures since 4.7 has 12.60 2 decimal places) The other issue that concerns us here is significant figures. Because the number(s) before the decimal point in a logarithm relate to the power on 10, the number of digits *after* the decimal point is what determines the number of significant figures in the final answer: X.YYY Y.YY x 10ˣ

? Exercise 10.11.3

If moist soil has a pH of 7.84, what is $[H_3O^+]$ of the soil solution?

Answer

1.5 x 10⁻⁸ M

The pOH scale

As with the hydrogen-ion concentration, the concentration of the hydroxide ion can be expressed logarithmically by the pOH. The **pOH** of a solution is the negative logarithm of the hydroxide-ion concentration.

$$\text{pOH} = -\log\left[\text{OH}^-\right]$$

The relation between the hydronium and hydroxide ion concentrations expressed as p-functions is easily derived from the K_w expression:

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] \tag{10.11.3}$$

$$-\log K_w = -\log([\text{H}_3\text{O}^+][\text{OH}^-]) = -\log[\text{H}_3\text{O}^+] + -\log[\text{OH}^-] \tag{10.11.4}$$

$$pK_w = pH + pOH \tag{10.11.5}$$

At 25 °C, the value of K_w is 1.0×10^{-14}, and so:

$$14.00 = pH + pOH \tag{10.11.6}$$

The hydronium ion molarity in pure water (or any neutral solution) is 1.0×10^{-7} M at 25 °C. The pH and pOH of a neutral solution at this temperature are therefore:

$$pH = -\log[H_3O^+] = -\log(1.0 \times 10^{-7}) = 7.00 \tag{10.11.7}$$

$$pOH = -\log[OH^-] = -\log(1.0 \times 10^{-7}) = 7.00 \tag{10.11.8}$$

And so, at this temperature, acidic solutions are those with hydronium ion molarities greater than 1.0×10^{-7} M and hydroxide ion molarities less than 1.0×10^{-7} M (corresponding to pH values less than 7.00 and pOH values greater than 7.00). Basic solutions are those with hydronium ion molarities less than 1.0×10^{-7} M and hydroxide ion molarities greater than 1.0×10^{-7} M (corresponding to pH values greater than 7.00 and pOH values less than 7.00).

✔ Example 10.11.4:

Find the pOH of a solution with a pH of 4.42.

Solution

Solutions to Example 14.9.4

Steps for Problem Solving	
Identify the "given" information and what the problem is asking you to "find."	Given: pH =4.42 Find: ? pOH
Plan the problem.	Need to use the expression pOH = 14 - pH
Calculate.	Now substitute the known quantity into the equation and solve. pOH=14−4.42=9.58
Think about your result.	The pH is that of an acidic solution, and the resulting pOH is the difference after subtracting from 14. The answer has two significant figures because the given pH has two decimal places.

? Exercise 10.11.4

The pH of a solution is 8.22. What is the pOH?

Answer
    5.78

The diagram below shows all of the interrelationships between [H3O+][H3O+], [OH−][OH−], pH, and pOH.

$$[OH^-] = \frac{1 \times 10^{-14}}{[H^+]}$$

$$[H^+] = \frac{1 \times 10^{-14}}{[OH^-]}$$

$$H^+ \qquad OH^-$$

$$[H^+] = 10^{-pH} \qquad pH = -\log[H^+] \qquad [OH^-] = 10^{-pOH} \qquad pOH = -\log[OH^-]$$

$$pOH = 14 - pH$$

$$pH \qquad pOH$$

$$pH = 14 - pOH$$
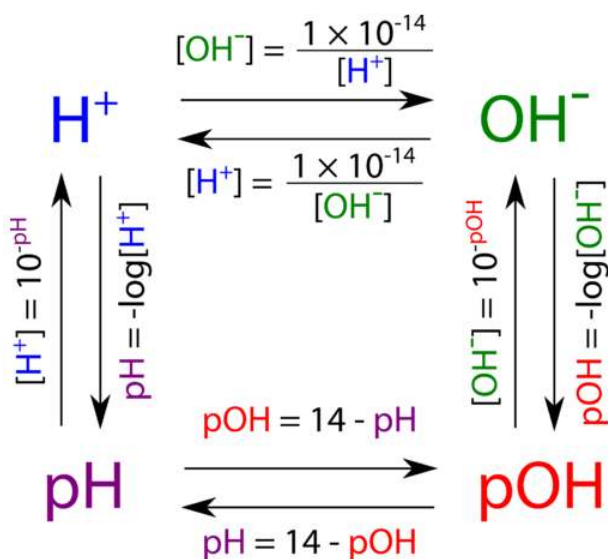
Figure 10.11.1: Relationships between hydrogen ion concentration, hydroxide ion concentration, pH and pOH.

Contributions & Attributions

- Peggy Lawson (Oxbow Prairie Heights School). Funded by Saskatchewan Educational Technology Consortium.

-
- Template:OpenStax

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10.12: Buffers are Solutions that Resist pH Change

> **◑ Learning Objective**
>
> - Define *buffer* and describe how it reacts with an acid or a base.

Weak acids are relatively common, even in the foods we eat. But we occasionally come across a strong acid or base, such as stomach acid, that has a strongly acidic pH of 1–2. By definition, strong acids and bases can produce a relatively large amount of hydrogen or hydroxide ions and, as a consequence, have marked chemical activity. In addition, very small amounts of strong acids and bases can change the pH of a solution very quickly. If 1 mL of stomach acid [which we will approximate as 0.05 M HCl(aq)] is added to the bloodstream, and if no correcting mechanism is present, the pH of the blood would go from about 7.4 to about 4.9—a pH that is not conducive to life. Fortunately, the body has a mechanism for minimizing such dramatic pH changes.

This mechanism involves a buffer, a solution that resists dramatic changes in pH. Buffers do so by being composed of certain pairs of solutes: either a weak acid plus a salt derived from that weak acid, or a weak base plus a salt of that weak base. For example, a buffer can be composed of dissolved acetic acid ($HC_2H_3O_2$, a weak acid) and sodium acetate ($NaC_2H_3O_2$, a salt derived from that acid). Another example of a buffer is a solution containing ammonia (NH_3, a weak base) and ammonium chloride (NH_4Cl, a salt derived from that base).

Let us use an acetic acid–sodium acetate buffer to demonstrate how buffers work. If a strong base—a source of $OH^-(aq)$ ions—is added to the buffer solution, those hydroxide ions will react with the acetic acid in an acid-base reaction:

$$HC_2H_3O_2(aq) + OH^-(aq) \rightarrow H_2O(\ell) + C_2H_3O_2^-(aq) \tag{10.12.1}$$
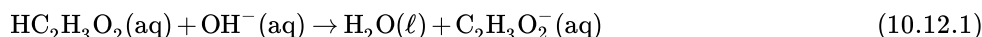
Rather than changing the pH dramatically by making the solution basic, the added hydroxide ions react to make water, and the pH does not change much.

> Many people are aware of the concept of buffers from *buffered aspirin*, which is aspirin that also has magnesium carbonate, calcium carbonate, magnesium oxide, or some other salt. The salt acts like a base, while aspirin is itself a weak acid.

If a strong acid—a source of H^+ ions—is added to the buffer solution, the H^+ ions will react with the anion from the salt. Because $HC_2H_3O_2$ is a weak acid, it is not ionized much. This means that if lots of hydrogen ions and acetate ions (from sodium acetate) are present in the same solution, they will come together to make acetic acid:

$$H^+(aq) + C_2H_3O_2^-(aq) \rightarrow HC_2H_3O_2(aq) \tag{10.12.2}$$
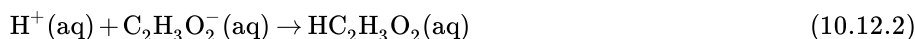
Rather than changing the pH dramatically and making the solution acidic, the added hydrogen ions react to make molecules of a weak acid. Figure 10.12.1 illustrates both actions of a buffer.
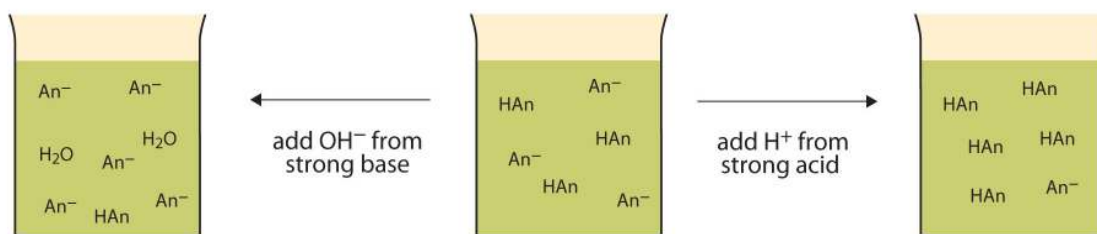
Figure 10.12.1: The Action of Buffers. Buffers can react with both strong acids (top) and strong bases (bottom) to minimize large changes in pH.

Buffers made from weak bases and salts of weak bases act similarly. For example, in a buffer containing NH_3 and NH_4Cl, ammonia molecules can react with any excess hydrogen ions introduced by strong acids:

$$NH_3(aq) + H^+(aq) \rightarrow NH_4^+(aq) \tag{10.12.3}$$

while the **ammonium ion** ($NH_4^+(aq)$) can react with any hydroxide ions introduced by strong bases:

$$NH_4^+(aq) + OH^-(aq) \rightarrow NH_3(aq) + H_2O(\ell) \tag{10.12.4}$$
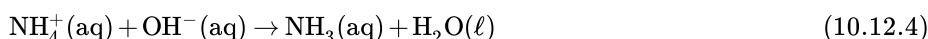
> ✔ Example 10.12.1: Making Buffer Solutions
>
> Which solute combinations can make a buffer solution? Assume that all are aqueous solutions.
>
> a. $HCHO_2$ and $NaCHO_2$
> b. HCl and $NaCl$
> c. CH_3NH_2 and CH_3NH_3Cl
> d. NH_3 and $NaOH$
>
> **Solution**
> a. Formic acid ($HCHO_2$) is a weak acid, while $NaCHO_2$ is the salt made from the anion of the weak acid—the formate ion (CHO_2^-). The combination of these two solutes would make a buffer solution.
> b. Hydrochloric acid (HCl) is a strong acid, not a weak acid, so the combination of these two solutes would not make a buffer solution.
> c. Methylamine (CH_3NH_2) is like ammonia with one of its hydrogen atoms substituted with a CH_3 (methyl) group. Because it is not on our list of strong bases, we can assume that it is a weak base. The compound CH_3NH_3Cl is a salt made from that weak base, so the combination of these two solutes would make a buffer solution.
> d. Ammonia (NH_3) is a weak base, but $NaOH$ is a strong base. The combination of these two solutes would not make a buffer solution.

> ? Exercise 10.12.1
>
> Which solute combinations can make a buffer solution? Assume that all are aqueous solutions.
>
> a. $NaHCO_3$ and $NaCl$
> b. H_3PO_4 and NaH_2PO_4
> c. NH_3 and $(NH_4)_3PO_4$
> d. $NaOH$ and $NaCl$
>
> **Answer a**
> Yes.
>
> **Answer b**
> No. Need a weak acid or base and a salt of its conjugate base or acid.
>
> **Answer c**
> Yes.
>
> **Answer d**
> No. Need a weak base or acid.

Buffers work well only for limited amounts of added strong acid or base. Once either solute is all reacted, the solution is no longer a buffer, and rapid changes in pH may occur. We say that a buffer has a certain **capacity**. Buffers that have more solute dissolved in them to start with have larger capacities, as might be expected.

Human blood has a buffering system to minimize extreme changes in pH. One buffer in blood is based on the presence of HCO_3^- and H_2CO_3 [H_2CO_3 is another way to write $CO_2(aq)$]. With this buffer present, even if some stomach acid were to find its way directly into the bloodstream, the change in the pH of blood would be minimal. Inside many of the body's cells, there is a buffering system based on phosphate ions.

> 📌 Career Focus: Blood Bank Technology Specialist
>
> At this point in this text, you should have the idea that the chemistry of blood is fairly complex. Because of this, people who work with blood must be specially trained to work with it properly.

A blood bank technology specialist is trained to perform routine and special tests on blood samples from blood banks or transfusion centers. This specialist measures the pH of blood, types it (according to the blood's ABO+/− type, Rh factors, and other typing schemes), tests it for the presence or absence of various diseases, and uses the blood to determine if a patient has any of several medical problems, such as anemia. A blood bank technology specialist may also interview and prepare donors to give blood and may actually collect the blood donation.

Blood bank technology specialists are well trained. Typically, they require a college degree with at least a year of special training in blood biology and chemistry. In the United States, training must conform to standards established by the American Association of Blood Banks.

Key Takeaway

- A buffer is a solution that resists sudden changes in pH.

Contributions & Attributions

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11: Chemical Equilibrium

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11.1: The Concept of Dynamic Equilibrium

> ◐ Learning Objectives
>
> - To understand what is meant by chemical equilibrium.

In the last chapter, we discussed the principles of chemical kinetics, which deal with the *rate of change*, or how quickly a given chemical reaction occurs. We now turn our attention to the *extent* to which a reaction occurs and how reaction conditions affect the final concentrations of reactants and products. For most of the reactions that we have discussed so far, you may have assumed that once reactants are converted to products, they are likely to remain that way. In fact, however, virtually all chemical reactions are *reversible* to some extent. That is, an opposing reaction occurs in which the products react, to a greater or lesser degree, to re-form the reactants. Eventually, the forward and reverse reaction rates become the same, and the system reaches **chemical equilibrium,** the point at which the composition of the system no longer changes with time.

Figure 11.1.1: Dinitrogen tetroxide is a powerful oxidizer that reacts spontaneously upon contact with various forms of hydrazine, which makes the pair a popular propellant combination for rockets. Nitrogen dioxide at −196 °C, 0 °C, 23 °C, 35 °C, and 50 °C. (NO$_2$) converts to the colorless dinitrogen tetroxide (N$_2$O$_4$) at low temperatures, and reverts to NO$_2$ at higher temperatures. (CC BY-SA 3.0; Eframgoldberg).

Chemical equilibrium is a dynamic process that consists of a forward reaction, in which reactants are converted to products, and a reverse reaction, in which products are converted to reactants. At equilibrium, the forward and reverse reactions proceed at equal rates. Consider, for example, a simple system that contains only one reactant and one product, the reversible dissociation of dinitrogen tetroxide (N$_2$O$_4$) to nitrogen dioxide (NO$_2$). You may recall that NO$_2$ is responsible for the brown color we associate with smog. When a sealed tube containing solid N$_2$O$_4$ (mp = −9.3°C; bp = 21.2°C) is heated from −78.4°C to 25°C, the red-brown color of NO$_2$ appears (Figure 11.1.1). The reaction can be followed visually because the product (NO$_2$) is colored, whereas the reactant (N$_2$O$_4$) is colorless:

$$\underset{colorless}{N_2O_4(g)} \underset{k_r}{\overset{k_f}{\rightleftharpoons}} \underset{red-brown}{2\,NO_2(g)} \tag{11.1.1}$$

The double arrow indicates that both the forward reaction

$$N_2O_4(g) \xrightarrow{k_f} 2\,NO_2(g) \tag{11.1.2}$$

and reverse reaction

$$2\,NO_2(g) \xrightarrow{k_r} N_2O_4(g) \tag{11.1.3}$$

occurring simultaneously (i.e, the reaction is reversible). However, this does not necessarily mean the system is equilibrium as the following chapter demonstrates.

Figure 11.1.2 shows how the composition of this system would vary as a function of time at a constant temperature. If the initial concentration of NO$_2$ were zero, then it increases as the concentration of N$_2$O$_4$ decreases. Eventually the composition of the system stops changing with time, and chemical equilibrium is achieved. Conversely, if we start with a sample that contains no N$_2$O$_4$ but an initial NO$_2$ concentration twice the initial concentration of N$_2$O$_4$ (Figure 11.1.2*a*), in accordance with the

stoichiometry of the reaction, we reach exactly the same equilibrium composition (Figure 11.1.2b). Thus equilibrium can be approached from either direction in a chemical reaction.
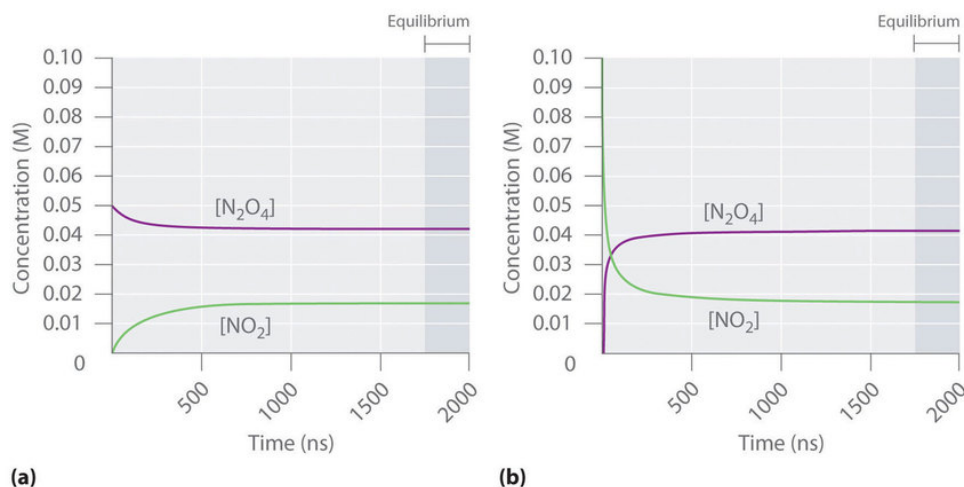

Figure 11.1.2: The Composition of N_2O_4/NO_2 Mixtures as a Function of Time at Room Temperature. (a) Initially, this idealized system contains 0.0500 M gaseous N_2O_4 and no gaseous NO_2. The concentration of N_2O_4 decreases with time as the concentration of NO_2 increases. (b) Initially, this system contains 0.1000 M NO_2 and no N_2O_4. The concentration of NO_2 decreases with time as the concentration of N_2O_4 increases. In both cases, the final concentrations of the substances are the same: [N_2O_4] = 0.0422 M and [NO_2] = 0.0156 M at equilibrium. (CC BY-SA-NC; Anonymous by request)

Figure 11.1.3 shows the forward and reverse reaction rates for a sample that initially contains pure NO_2. Because the initial concentration of N_2O_4 is zero, the forward reaction rate (dissociation of N_2O_4) is initially zero as well. In contrast, the reverse reaction rate (dimerization of NO_2) is initially very high ($2.0 \times 10^6 \ M/s$), but it decreases rapidly as the concentration of NO_2 decreases. As the concentration of N_2O_4 increases, the rate of dissociation of N_2O_4 increases—but more slowly than the dimerization of NO_2—because the reaction is only first order in N_2O_4 (rate = $k_f[N_2O_4]$, where k_f is the rate constant for the forward reaction in Equations 11.1.1 and 11.1.2). Eventually, the forward and reverse reaction rates become identical, $k_f = k_r$, and the system has reached chemical equilibrium. If the forward and reverse reactions occur at different rates, then the system is not at equilibrium.
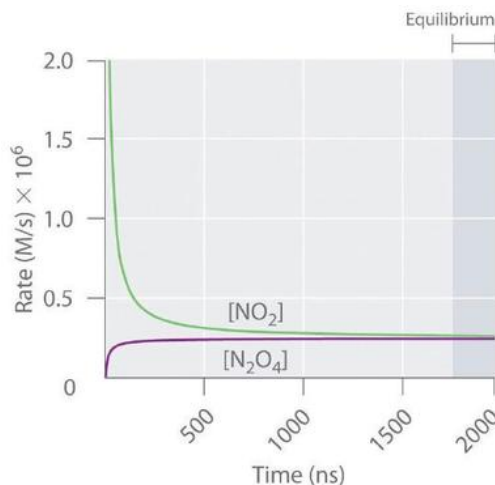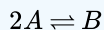

Figure 11.1.3: The Forward and Reverse Reaction Rates as a Function of Time for the $N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$ System Shown in Part (b) in Figure 11.1.2. (CC BY-SA-NC; Anonymous by request)

The rate of dimerization of NO_2 (reverse reaction) decreases rapidly with time, as expected for a second-order reaction. Because the initial concentration of N_2O_4 is zero, the rate of the dissociation reaction (forward reaction) at $t = 0$ is also zero. As the dimerization reaction proceeds, the N_2O_4 concentration increases, and its rate of dissociation also increases. Eventually the rates of the two reactions are equal: chemical equilibrium has been reached, and the concentrations of N_2O_4 and NO_2 no longer change.
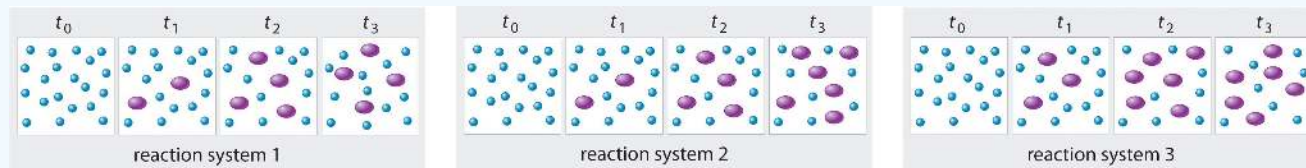
> *At equilibrium, the forward reaction rate is equal to the reverse reaction rate.*

> ✔ **Example 11.1.1**
>
> The three reaction systems (1, 2, and 3) depicted in the accompanying illustration can all be described by the equation:
>
> $$2A \rightleftharpoons B$$
>
> where the blue circles are A and the purple ovals are B. Each set of panels shows the changing composition of one of the three reaction mixtures as a function of time. Which system took the longest to reach chemical equilibrium?
>
>
>
> In reaction system 1 theree are four purple ovals at t3. In reaction system 2 there are size purple ovals at t3. In reaction system systems there are six ovals at t2 and t3.
>
> **Given**: three reaction systems
>
> **Asked for:** relative time to reach chemical equilibrium
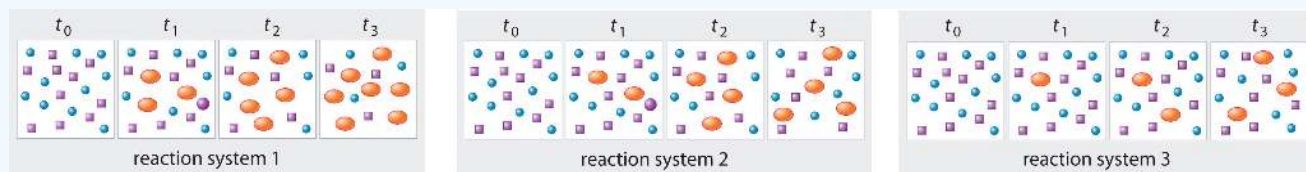>
> **Strategy**:
>
> Compare the concentrations of A and B at different times. The system whose composition takes the longest to stabilize took the longest to reach chemical equilibrium.
>
> **Solution**:
>
> In systems 1 and 3, the concentration of A decreases from t_0 through t_2 but is the same at both t_2 and t_3. Thus systems 1 and 3 are at equilibrium by t_3. In system 2, the concentrations of A and B are still changing between t_2 and t_3, so system 2 may not yet have reached equilibrium by t_3. Thus system 2 took the longest to reach chemical equilibrium.

> **? Exercise 11.1.1**
>
> In the following illustration, A is represented by blue circles, B by purple squares, and C by orange ovals; the equation for the reaction is A + B $\rightleftharpoons$ C. The sets of panels represent the compositions of three reaction mixtures as a function of time. Which, if any, of the systems shown has reached equilibrium?
>
>
>
> In reaction system 1 there are seven orange ovals at t3. In reaction system two there are four orange ovals at t3. In reaction system three there are three orange ovals at t3.
>
> **Answer**
>
> system 2

A Video Introduction to Dynamic Equilibrium: Introduction to Dynamic Equilibrium(opens in new window) [youtu.be]

Summary

At equilibrium, the forward and reverse reactions of a system proceed at equal rates. Chemical equilibrium is a dynamic process consisting of forward and reverse reactions that proceed at equal rates. At equilibrium, the composition of the system no longer changes with time. The composition of an equilibrium mixture is independent of the direction from which equilibrium is approached.

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11.2: The Equilibrium Constant (K)

> **Learning Objectives**
> - To know the relationship between the equilibrium constant and the rate constants for the forward and reverse reactions.
> - To write an equilibrium constant expression for any reaction.

Because an equilibrium state is achieved when the forward reaction rate equals the reverse reaction rate, under a given set of conditions there must be a relationship between the composition of the system at equilibrium and the kinetics of a reaction (represented by rate constants). We can show this relationship using the decomposition reaction of N_2O_4 to NO_2. Both the forward and reverse reactions for this system consist of a single elementary reaction, so the reaction rates are as follows:

$$\text{forward rate} = k_f[N_2O_4]$$

and

$$\text{reverse rate} = k_r[NO_2]^2$$

At equilibrium, the forward rate equals the reverse rate (definition of equilibrium):

$$k_f[N_2O_4] = k_r[NO_2]^2 \tag{11.2.1}$$

so

$$\frac{k_f}{k_r} = \frac{[NO_2]^2}{[N_2O_4]} \tag{11.2.2}$$

The ratio of the rate constants gives us a new constant, the equilibrium constant (K), which is defined as follows:

$$K = \frac{k_f}{k_r} \tag{11.2.3}$$

Hence there is a fundamental relationship between chemical kinetics and chemical equilibrium: under a given set of conditions, the composition of the equilibrium mixture is determined by the magnitudes of the rate constants for the forward and the reverse reactions.

> *The equilibrium constant is equal to the rate constant for the forward reaction divided by the rate constant for the reverse reaction.*

A Video for Determining the Equilibrium Expression: Determining the Equilibrium Expression(opens in new window) [youtu.be]

Table 11.2.1 lists the initial and equilibrium concentrations from five different experiments using the reaction system described by Equation 11.2.1. At equilibrium the magnitude of the quantity $[NO_2]^2/[N_2O_4]$ is essentially the same for all five experiments. In fact, no matter what the initial concentrations of NO_2 and N_2O_4 are, at equilibrium the quantity $[NO_2]^2/[N_2O_4]$ will always be

$6.53 \pm 0.03 \times 10^{-3}$ at 25°C, which corresponds to the ratio of the rate constants for the forward and reverse reactions. That is, at a given temperature, the equilibrium constant for a reaction always has the same value, even though the specific concentrations of the reactants and products vary depending on their initial concentrations.

Table 11.2.1: Initial and Equilibrium Concentrations for $NO_2 : N_2O_4$ Mixtures at 25°C

	Initial Concentrations (M)		Concentrations at Equilibrium		
Experiment	$[N_2O_4]$ (M)	$[NO_2]$ (M)	$[N_2O_4]$ (M)	$[NO_2]$ (M)	$K = [NO_2]^2/[N_2O_4]$
1	0.0500	0.0000	0.0417	0.0165	6.54×10^{-3}
2	0.0000	0.1000	0.0417	0.0165	6.54×10^{-3}
3	0.0750	0.0000	0.0647	0.0206	6.56×10^{-3}
4	0.0000	0.0750	0.0304	0.0141	6.54×10^{-3}
5	0.0250	0.0750	0.0532	0.0186	6.50×10^{-3}

Developing an Equilibrium Constant Expression

In 1864, the Norwegian chemists Cato Guldberg (1836–1902) and Peter Waage (1833–1900) carefully measured the compositions of many reaction systems at equilibrium. They discovered that for any reversible reaction of the general form

$$aA + bB \rightleftharpoons cC + dD \tag{11.2.4}$$

where A and B are reactants, C and D are products, and a, b, c, and d are the stoichiometric coefficients in the balanced chemical equation for the reaction, the ratio of the product of the equilibrium concentrations of the products (raised to their coefficients in the balanced chemical equation) to the product of the equilibrium concentrations of the reactants (raised to their coefficients in the balanced chemical equation) is always a constant under a given set of conditions. This relationship is known as the law of mass action (or law of chemical equilibrium) and can be stated as follows:

$$K = \frac{[C]^c[D]^d}{[A]^a[B]^b} \tag{11.2.5}$$

where K is the equilibrium constant for the reaction. Equation 11.2.4 is called the equilibrium equation, and the right side of Equation 11.2.5 is called the equilibrium constant expression. The relationship shown in Equation 11.2.5 is true for any pair of opposing reactions regardless of the mechanism of the reaction or the number of steps in the mechanism.

The equilibrium constant can vary over a wide range of values. The values of K shown in Table 11.2.2, for example, vary by 60 orders of magnitude. Because products are in the numerator of the equilibrium constant expression and reactants are in the denominator, values of K greater than 10^3 indicate a strong tendency for reactants to form products. In this case, chemists say that equilibrium lies to the right as written, favoring the formation of products. An example is the reaction between H_2 and Cl_2 to produce HCl, which has an equilibrium constant of 1.6×10^{33} at 300 K. Because H_2 is a good reductant and Cl_2 is a good oxidant, the reaction proceeds essentially to completion. In contrast, values of K less than 10^{-3} indicate that the ratio of products to reactants at equilibrium is very small. That is, reactants do not tend to form products readily, and the equilibrium lies to the left as written, favoring the formation of reactants.

Table 11.2.2: Equilibrium Constants for Selected Reactions*

Reaction	Temperature (K)	Equilibrium Constant (K)
$S_{(s)} + O_{2(g)} \rightleftharpoons SO_{2(g)}$	300	4.4×10^{53}
$2H_{2(g)} + O_{2(g)} \rightleftharpoons 2H2O_{(g)}$	500	2.4×10^{47}
$H_{2(g)} + Cl_{2(g)} \rightleftharpoons 2HCl_{(g)}$	300	1.6×10^{33}
$H_{2(g)} + Br_{2(g)} \rightleftharpoons 2HBr_{(g)}$	300	4.1×10^{18}
$2NO_{(g)} + O_{2(g)} \rightleftharpoons 2NO_{2(g)}$	300	4.2×10^{13}

*Equilibrium constants vary with temperature. The K values shown are for systems at the indicated temperatures.

Reaction	Temperature (K)	Equilibrium Constant (K)
$3H_{2(g)} + N_{2(g)} \rightleftharpoons 2NH_{3(g)}$	300	2.7×10^8
$H_{2(g)} + D_{2(g)} \rightleftharpoons 2HD_{(g)}$	100	1.92
$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$	300	2.9×10^{-1}
$I_{2(g)} \rightleftharpoons 2I_{(g)}$	800	4.6×10^{-7}
$Br_{2(g)} \rightleftharpoons 2Br_{(g)}$	1000	4.0×10^{-7}
$Cl_{2(g)} \rightleftharpoons 2Cl_{(g)}$	1000	1.8×10^{-9}
$F_{2(g)} \rightleftharpoons 2F_{(g)}$	500	7.4×10^{-13}

*Equilibrium constants vary with temperature. The K values shown are for systems at the indicated temperatures.


📌 Effective vs. True Concentrations

You will also notice in Table 11.2.2 that equilibrium constants have no units, even though Equation 11.2.5 suggests that the units of concentration might not always cancel because the exponents may vary. **In fact, equilibrium constants are calculated using "effective concentrations," or activities, of reactants and products, which are the ratios of the measured concentrations to a standard state of 1 M.** As shown in Equation 11.2.6, the units of concentration cancel, which makes K unitless as well:

$$\frac{[A]_{measured}}{[A]_{standard\ state}} = \frac{\cancel{M}}{\cancel{M}} = \frac{\frac{mol}{\cancel{V}}}{\frac{mol}{\cancel{V}}} \tag{11.2.6}$$

Because equilibrium constants are calculated using "effective concentrations" relative to a standard state of 1 M, values of K are unitless.

Many reactions have equilibrium constants between 1000 and 0.001 ($10^3 \geq K \geq 10^{-3}$), neither very large nor very small. At equilibrium, these systems tend to contain significant amounts of both products and reactants, indicating that there is not a strong tendency to form either products from reactants or reactants from products. An example of this type of system is the reaction of gaseous hydrogen and deuterium, a component of high-stability fiber-optic light sources used in ocean studies, to form HD:

$$H_2(g) + D_2(g) \rightleftharpoons 2\,HD(g)$$
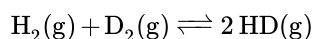
The equilibrium constant expression for this reaction is

$$K = \frac{[HD]^2}{[H_2][D_2]}$$

with K varying between 1.9 and 4 over a wide temperature range (100–1000 K). Thus an equilibrium mixture of H_2, D_2, and HD contains significant concentrations of both product and reactants.

Figure 11.2.3 summarizes the relationship between the magnitude of K and the relative concentrations of reactants and products at equilibrium for a general reaction, written as reactants $\rightleftharpoons$ products. Because there is a direct relationship between the kinetics of a reaction and the equilibrium concentrations of products and reactants (Equations 11.2.6 and 11.2.5), when $k_f \gg k_r$, K is a **large** number, and the concentration of products at equilibrium predominate. This corresponds to an essentially irreversible reaction. Conversely, when $k_f \ll k_r$, K is a very **small** number, and the reaction produces almost no products as written. Systems for which $k_f \approx k_r$ have significant concentrations of both reactants and products at equilibrium.

Magnitude of K increasing $\longrightarrow$

| Small $(K < 10^{-3})$ | Intermediate $(10^{-3} \le K \le 10^3)$ | Large $(K > 10^3)$ |

Reactants / Products

Mostly reactants | Significant amounts of reactants and products | Mostly products
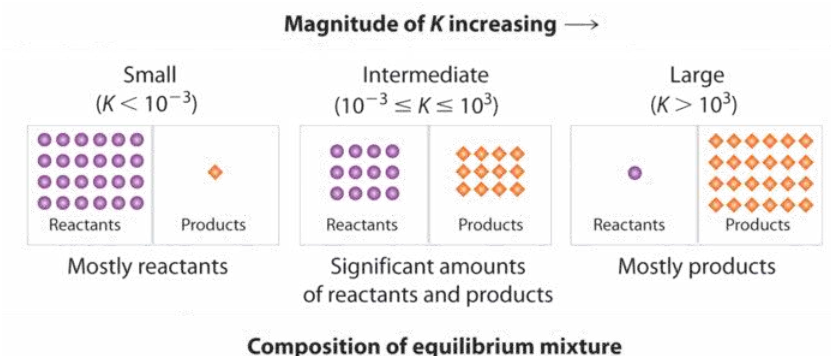
Composition of equilibrium mixture

Figure 11.2.3: The Relationship between the Composition of the Mixture at Equilibrium and the Magnitude of the Equilibrium Constant. The larger the K, the farther the reaction proceeds to the right before equilibrium is reached, and the greater the ratio of products to reactants at equilibrium.

If K is less than 0.001, it is considered small and it will be mostly reactants. If K is greater than 1000, it is considered large and it will be mostly products. If K is greater than or equal to 0.001 and less than or equal to 1000, it is considered intermediate. there will be significant amounts or reactants and products.

> *A large value of the equilibrium constant K means that products predominate at equilibrium; a small value means that reactants predominate at equilibrium.*

✔ Example 11.2.1: Equilibrium Constant Expressions

Write the equilibrium constant expression for each reaction.

- $N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$
- $CO(g) + \frac{1}{2}O_2(g) \rightleftharpoons CO_2(g)$
- $2\,CO_2(g) \rightleftharpoons 2\,CO(g) + O_2(g)$

Given: balanced chemical equations

Asked for: equilibrium constant expressions

Strategy:

Refer to Equation 11.2.5. Place the arithmetic product of the concentrations of the products (raised to their stoichiometric coefficients) in the numerator and the product of the concentrations of the reactants (raised to their stoichiometric coefficients) in the denominator.

Solution:

The only product is ammonia, which has a coefficient of 2. For the reactants, N_2 has a coefficient of 1 and H_2 has a coefficient of 3. The equilibrium constant expression is as follows:

$$\frac{[NH_3]^2}{[N_2][H_2]^3}$$

The only product is carbon dioxide, which has a coefficient of 1. The reactants are CO, with a coefficient of 1, and O_2, with a coefficient of $\frac{1}{2}$. Thus the equilibrium constant expression is as follows:

$$\frac{[CO_2]}{[CO][O_2]^{1/2}}$$

This reaction is the reverse of the reaction in part b, with all coefficients multiplied by 2 to remove the fractional coefficient for O_2. The equilibrium constant expression is therefore the inverse of the expression in part b, with all exponents multiplied by 2

$$\frac{[CO]^2[O_2]}{[CO_2]^2}$$

? Exercise 11.2.1

Write the equilibrium constant expression for each reaction.

a. $N_2O(g) \rightleftharpoons N_2(g) + \frac{1}{2}O_2(g)$
b. $2\,C_8H_{18}(g) + 25\,O_2(g) \rightleftharpoons 16\,CO_2(g) + 18\,H_2O(g)$
c. $H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g)$

Answer a

$$K = \frac{[N_2][O_2]^{1/2}}{[N_2O]}$$

Answer b

$$K = \frac{[CO_2]^{16}[H_2O]^{18}}{[C_8H_{18}]^2[O_2]^{25}}$$

Answer c

$$K = \frac{[HI]^2}{[H_2][I_2]}$$

✔ Example 11.2.2

Predict which systems at equilibrium will (a) contain essentially only products, (b) contain essentially only reactants, and (c) contain appreciable amounts of both products and reactants.

1. $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$ $K_{(700K)} = 54$
2. $2CO_{2(g)} \rightleftharpoons 2CO_{(g)} + O_{2(g)}$ $K_{(1200K)} = 3.1 \times 10^{-18}$
3. $PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$ $K_{(613K)} = 97$
4. $2O_{3(g)} \rightleftharpoons 3O_{2(g)}$ $K_{(298K)} = 5.9 \times 10^{55}$

Given: systems and values of K

Asked for: composition of systems at equilibrium

Strategy:

Use the value of the equilibrium constant to determine whether the equilibrium mixture will contain essentially only products, essentially only reactants, or significant amounts of both.

Solution:

a. Only system 4 has $K \gg 10^3$, so at equilibrium it will consist of essentially only products.
b. System 2 has $K \ll 10^{-3}$, so the reactants have little tendency to form products under the conditions specified; thus, at equilibrium the system will contain essentially only reactants.
c. Both systems 1 and 3 have equilibrium constants in the range $10^3 \geq K \geq 10^{-3}$, indicating that the equilibrium mixtures will contain appreciable amounts of both products and reactants.

? Exercise 11.2.2

Hydrogen and nitrogen react to form ammonia according to the following balanced chemical equation:

$$3\,H_2(g) + N_2(g) \rightleftharpoons 2\,NH_3(g)$$

Values of the equilibrium constant at various temperatures were reported as

- $K_{25°C} = 3.3 \times 10^8$,
- $K_{177°C} = 2.6 \times 10^3$, and
- $K_{327°C} = 4.1$.

a. At which temperature would you expect to find the highest proportion of H_2 and N_2 in the equilibrium mixture?

b. Assuming that the reaction rates are fast enough so that equilibrium is reached quickly, at what temperature would you design a commercial reactor to operate to maximize the yield of ammonia?

Answer a

327°C, where K is smallest

Answer b

25°C

Video which Discusses What Does K Tell us About a Reaction?: What Does K Tell us About a Reaction?(opens in new window) [youtu.be]

Variations in the Form of the Equilibrium Constant Expression

Because equilibrium can be approached from either direction in a chemical reaction, the equilibrium constant expression and thus the magnitude of the equilibrium constant depend on the form in which the chemical reaction is written. For example, if we write the reaction described in Equation 11.2.4 in reverse, we obtain the following:

$$cC + dD \rightleftharpoons aA + bB \tag{11.2.7}$$

The corresponding equilibrium constant K' is as follows:

$$K' = \frac{[A]^a[B]^b}{[C]^c[D]^d} \tag{11.2.8}$$

This expression is the inverse of the expression for the original equilibrium constant, so $K' = 1/K$. That is, when we write a reaction in the reverse direction, the equilibrium constant expression is inverted. For instance, the equilibrium constant for the reaction $N_2O_4 \rightleftharpoons 2\,NO_2$ is as follows:

$$K = \frac{[NO_2]^2}{[N_2O_4]} \tag{11.2.9}$$

but for the opposite reaction, $2NO_2 \rightleftharpoons N_2O_4$, the equilibrium constant K′ is given by the inverse expression:

$$K' = \frac{[N_2O_4]}{[NO_2]^2} \tag{11.2.10}$$

Consider another example, the formation of water:

$$2\,H_2(g) + O_2(g) \rightleftharpoons 2\,H_2O(g).$$
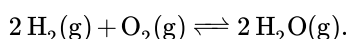
Because H_2 is a good reductant and O_2 is a good oxidant, this reaction has a very large equilibrium constant ($K = 2.4 \times 10^{47}$ at 500 K). Consequently, the equilibrium constant for the reverse reaction, the decomposition of water to form O_2 and H_2, is very

small: $K' = 1/K = 1/(2.4 \times 10^{47}) = 4.2 \times 10^{-48}$. As suggested by the very small equilibrium constant, and fortunately for life as we know it, a substantial amount of energy is indeed needed to dissociate water into H_2 and O_2.

> *The equilibrium constant for a reaction written in reverse is the inverse of the equilibrium constant for the reaction as written originally.*

Writing an equation in different but chemically equivalent forms also causes both the equilibrium constant expression and the magnitude of the equilibrium constant to be different. For example, we could write the equation for the reaction

$$2\,NO_2 \rightleftharpoons N_2O_4$$

as

$$NO_2 \rightleftharpoons \tfrac{1}{2}\,N_2O_4$$
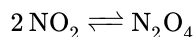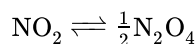
with the equilibrium constant K″ is as follows:

$$K'' = \frac{[N_2O_4]^{1/2}}{[NO_2]} \tag{11.2.11}$$

The values for K′ (Equation 11.2.10) and K″ are related as follows:

$$K'' = (K')^{1/2} = \sqrt{K'} \tag{11.2.12}$$

In general, if all the coefficients in a balanced chemical equation were subsequently multiplied by n, then the new equilibrium constant is the original equilibrium constant raised to the nth power.

A Video Discussing Relationships Involving Equilibrium Constants: Relationships Involving Equilibrium Constants(opens in new window) [youtu.be] (opens in new window)

✔ Example 11.2.3: The Haber Process

At 745 K, K is 0.118 for the following reaction:
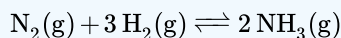
$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$$

What is the equilibrium constant for each related reaction at 745 K?

a. $2\,NH_3(g) \rightleftharpoons N_2(g) + 3\,H_2(g)$
b. $\tfrac{1}{2}N_2(g) + \tfrac{3}{2}H_2(g) \rightleftharpoons NH_3(g)$

Given: balanced equilibrium equation, K at a given temperature, and equations of related reactions

Asked for: values of K for related reactions

Strategy:

Write the equilibrium constant expression for the given reaction and for each related reaction. From these expressions, calculate K for each reaction.

Solution:

The equilibrium constant expression for the given reaction of $N_{2(g)}$ with $H_{2(g)}$ to produce $NH_{3(g)}$ at 745 K is as follows:

$$K = \frac{[NH_3]^2}{[N_2][H_2]^3} = 0.118$$

This reaction is the reverse of the one given, so its equilibrium constant expression is as follows:
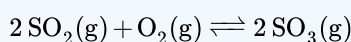
$$K' = \frac{1}{K} = \frac{[N_2][H_2]^3}{[NH_3]^2} = \frac{1}{0.118} = 8.47$$

In this reaction, the stoichiometric coefficients of the given reaction are divided by 2, so the equilibrium constant is calculated as follows:
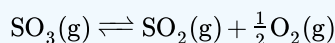
$$K'' = \frac{[NH_3]}{[N_2]^{1/2}[H_2]^{3/2}} = K^{1/2} = \sqrt{K} = \sqrt{0.118} = 0.344$$

? Exercise

At 527°C, the equilibrium constant for the reaction

$$2\,SO_2(g) + O_2(g) \rightleftharpoons 2\,SO_3(g)$$

is 7.9×10^4. Calculate the equilibrium constant for the following reaction at the same temperature:

$$SO_3(g) \rightleftharpoons SO_2(g) + \tfrac{1}{2}O_2(g)$$

Answer

3.6×10^{-3}

Equilibrium Constant Expressions for Systems that Contain Gases

For reactions that involve species in solution, the concentrations used in equilibrium calculations are usually expressed in moles/liter. For gases, however, the concentrations are usually expressed in terms of partial pressures rather than molarity, where the standard state is 1 atm of pressure. The symbol K_p is used to denote equilibrium constants calculated from partial pressures. For the general reaction $aA + bB \rightleftharpoons cC + dD$, in which all the components are gases, the equilibrium constant expression can be written as the ratio of the partial pressures of the products and reactants (each raised to its coefficient in the chemical equation):

$$K_p = \frac{(P_C)^c(P_D)^d}{(P_A)^a(P_B)^b} \tag{11.2.13}$$

Thus K_p for the decomposition of N_2O_4 (Equation 15.1) is as follows:

$$K_p = \frac{(P_{NO_2})^2}{P_{N_2O_4}} \tag{11.2.14}$$

Like K, K_p is a unitless quantity because the quantity that is actually used to calculate it is an "effective pressure," the ratio of the measured pressure to a standard state of 1 bar (approximately 1 atm), which produces a unitless quantity. The "effective pressure" is called the fugacity, just as activity is the effective concentration.

Because partial pressures are usually expressed in atmospheres or mmHg, the molar concentration of a gas and its partial pressure do not have the same numerical value. Consequently, the numerical values of K and K_p are usually different. They are, however, related by the ideal gas constant (R) and the absolute temperature (T):

$$K_p = K(RT)^{\Delta n} \tag{11.2.15}$$

where K is the equilibrium constant expressed in units of concentration and Δn is the difference between the numbers of moles of **gaseous** products and **gaseous** reactants ($n_p - n_r$). The temperature is expressed as the absolute temperature in Kelvin. According to Equation 11.2.15, $K_p = K$ only if the moles of gaseous products and gaseous reactants are the same (i.e., $\Delta n = 0$). For the decomposition of N_2O_4, there are 2 mol of gaseous product and 1 mol of gaseous reactant, so $\Delta n = 1$. Thus, for this reaction,

$$K_p = K(RT)^1 = KRT$$

✔ **Example 11.2.4: The Haber Process (again)**

The equilibrium constant for the reaction of nitrogen and hydrogen to give ammonia is 0.118 at 745 K. The balanced equilibrium equation is as follows:

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$$
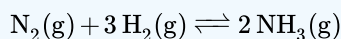
What is K_p for this reaction at the same temperature?

Given: equilibrium equation, equilibrium constant, and temperature

Asked for: K_p

Strategy:

Use the coefficients in the balanced chemical equation to calculate Δn. Then use Equation 11.2.15 to calculate K from K_p.

Solution:
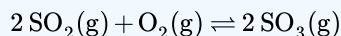
This reaction has 2 mol of gaseous product and 4 mol of gaseous reactants, so $\Delta n = (2 - 4) = -2$. We know K, and $T = 745\ K$. Thus, from Equation 11.2.12, we have the following:

$$K_p = K(RT)^{-2}$$

$$= \frac{K}{(RT)^2}$$

$$= \frac{0.118}{\{[0.08206(L \cdot atm)/(mol \cdot K)][745\ K]\}^2}$$

$$= 3.16 \times 10^{-5}$$

Because K_p is a unitless quantity, the answer is $K_p = 3.16 \times 10^{-5}$.

? **Exercise 11.2.4**

Calculate K_p for the reaction

$$2\,SO_2(g) + O_2(g) \rightleftharpoons 2\,SO_3(g)$$

at 527°C, if $K = 7.9 \times 10^4$ at this temperature.
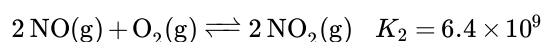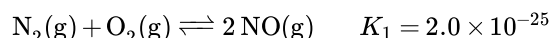
Answer

$K_p = 1.2 \times 10^3$

Video Discussing Converting Kc to Kp: Converting Kc to Kp(opens in new window) [youtu.be]
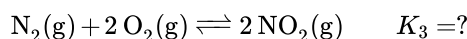
Equilibrium Constant Expressions for the Sums of Reactions

Chemists frequently need to know the equilibrium constant for a reaction that has not been previously studied. In such cases, the desired reaction can often be written as the sum of other reactions for which the equilibrium constants are known. The equilibrium constant for the unknown reaction can then be calculated from the tabulated values for the other reactions.

To illustrate this procedure, let's consider the reaction of N_2 with O_2 to give NO_2. This reaction is an important source of the NO_2 that gives urban smog its typical brown color. The reaction normally occurs in two distinct steps. In the first reaction (step 1), N_2 reacts with O_2 at the high temperatures inside an internal combustion engine to give NO. The released NO then reacts with additional O_2 to give NO_2 (step 2). The equilibrium constant for each reaction at 100°C is also given.

$$N_2(g) + O_2(g) \rightleftharpoons 2\,NO(g) \qquad K_1 = 2.0 \times 10^{-25}$$
$$2\,NO(g) + O_2(g) \rightleftharpoons 2\,NO_2(g) \quad K_2 = 6.4 \times 10^9$$

Summing reactions (step 1) and (step 2) gives the overall reaction of N_2 with O_2:

$$N_2(g) + 2\,O_2(g) \rightleftharpoons 2\,NO_2(g) \qquad K_3 =?$$

The equilibrium constant expressions for the reactions are as follows:

$$K_1 = \frac{[NO]^2}{[N_2][O_2]} \qquad K_2 = \frac{[NO_2]^2}{[NO]^2[O_2]} \qquad K_3 = \frac{[NO_2]^2}{[N_2][O_2]^2}$$

What is the relationship between K_1, K_2, and K_3, all at 100°C? The expression for K_1 has $[NO]^2$ in the numerator, the expression for K_2 has $[NO]^2$ in the denominator, and $[NO]^2$ does not appear in the expression for K_3. Multiplying K_1 by K_2 and canceling the $[NO]^2$ terms,

$$K_1 K_2 = \frac{[NO]^2}{[N_2][O_2]} \times \frac{[NO_2]^2}{[NO]^2[O_2]} = \frac{[NO_2]^2}{[N_2][O_2]^2} = K_3$$

Thus the product of the equilibrium constant expressions for K_1 and K_2 is the same as the equilibrium constant expression for K_3:
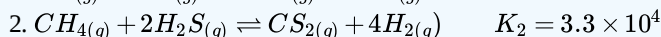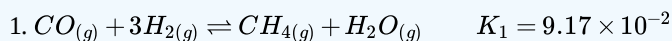
$$K_3 = K_1 K_2 = (2.0 \times 10^{-25})(6.4 \times 10^9) = 1.3 \times 10^{-15}$$

The equilibrium constant for a reaction that is the sum of two or more reactions is equal to the product of the equilibrium constants for the individual reactions. In contrast, recall that according to Hess's Law, ΔH for the sum of two or more reactions is the sum of the ΔH values for the individual reactions.
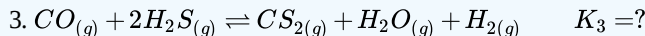
> *To determine K for a reaction that is the sum of two or more reactions, add the reactions but multiply the equilibrium constants.*

> ### ✔ Example 11.2.6
>
> The following reactions occur at 1200°C:
>
> 1. $CO_{(g)} + 3H_{2(g)} \rightleftharpoons CH_{4(g)} + H_2O_{(g)}$ $K_1 = 9.17 \times 10^{-2}$
> 2. $CH_{4(g)} + 2H_2S_{(g)} \rightleftharpoons CS_{2(g)} + 4H_{2(g)})$ $K_2 = 3.3 \times 10^4$
>
> Calculate the equilibrium constant for the following reaction at the same temperature.
>
> 3. $CO_{(g)} + 2H_2S_{(g)} \rightleftharpoons CS_{2(g)} + H_2O_{(g)} + H_{2(g)}$ $K_3 = ?$
>
> **Given**: two balanced equilibrium equations, values of K, and an equilibrium equation for the overall reaction
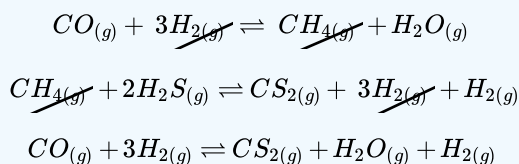>
> **Asked for**: equilibrium constant for the overall reaction
>
> **Strategy**:
>
> Arrange the equations so that their sum produces the overall equation. If an equation had to be reversed, invert the value of K for that equation. Calculate K for the overall equation by multiplying the equilibrium constants for the individual equations.
>
> **Solution**:
>
> The key to solving this problem is to recognize that reaction 3 is the sum of reactions 1 and 2:
>
> $$CO_{(g)} + 3H_{2(g)} \rightleftharpoons CH_{4(g)} + H_2O_{(g)}$$
>
> $$CH_{4(g)} + 2H_2S_{(g)} \rightleftharpoons CS_{2(g)} + 3H_{2(g)} + H_{2(g)}$$
>
> $$CO_{(g)} + 3H_{2(g)} \rightleftharpoons CS_{2(g)} + H_2O_{(g)} + H_{2(g)}$$
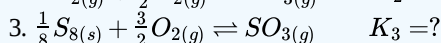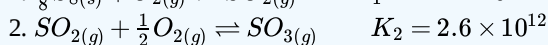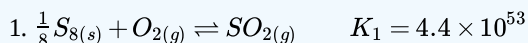>
> The values for K_1 and K_2 are given, so it is straightforward to calculate K_3:
>
> $$K_3 = K_1 K_2 = (9.17 \times 10^{-2})(3.3 \times 10^4) = 3.03 \times 10^3$$

> ### ? Exercise 11.2.6
>
> In the first of two steps in the industrial synthesis of sulfuric acid, elemental sulfur reacts with oxygen to produce sulfur dioxide. In the second step, sulfur dioxide reacts with additional oxygen to form sulfur trioxide. The reaction for each step is shown, as is the value of the corresponding equilibrium constant at 25°C. Calculate the equilibrium constant for the overall reaction at this same temperature.
>
> 1. $\frac{1}{8} S_{8(s)} + O_{2(g)} \rightleftharpoons SO_{2(g)}$ $K_1 = 4.4 \times 10^{53}$
> 2. $SO_{2(g)} + \frac{1}{2}O_{2(g)} \rightleftharpoons SO_{3(g)}$ $K_2 = 2.6 \times 10^{12}$
> 3. $\frac{1}{8} S_{8(s)} + \frac{3}{2}O_{2(g)} \rightleftharpoons SO_{3(g)}$ $K_3 = ?$
>
> **Answer**
>
> $$K_3 = 1.1 \times 10^{66}$$

Summary

The ratio of the rate constants for the forward and reverse reactions at equilibrium is the equilibrium constant (K), a unitless quantity. The composition of the equilibrium mixture is therefore determined by the magnitudes of the forward and reverse rate constants at equilibrium. Under a given set of conditions, a reaction will always have the same K. For a system at equilibrium, the law of mass action relates K to the ratio of the equilibrium concentrations of the products to the concentrations of the reactants raised to their respective powers to match the coefficients in the equilibrium equation. The ratio is called the equilibrium constant expression. When a reaction is written in the reverse direction, K and the equilibrium constant expression are inverted. For gases, the equilibrium constant expression can be written as the ratio of the partial pressures of the products to the partial pressures of the reactants, each raised to a power matching its coefficient in the chemical equation. An equilibrium constant calculated from partial pressures (K_p) is related to K by the ideal gas constant (R), the temperature (T), and the change in the number of moles of gas during the reaction. An equilibrium system that contains products and reactants in a single phase is a homogeneous equilibrium; a

system whose reactants, products, or both are in more than one phase is a heterogeneous equilibrium. When a reaction can be expressed as the sum of two or more reactions, its equilibrium constant is equal to the product of the equilibrium constants for the individual reactions.

- The law of mass action describes a system at equilibrium in terms of the concentrations of the products and the reactants.
- For a system involving one or more gases, either the molar concentrations of the gases or their partial pressures can be used.
- Definition of equilibrium constant in terms of forward and reverse rate constants:

$$K = \frac{k_f}{k_r}$$

- Equilibrium constant expression (law of mass action):

$$K = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

- Equilibrium constant expression for reactions involving gases using partial pressures:

$$K_p = \frac{(P_C)^c(P_D)^d}{(P_A)^a(P_B)^b}$$

- Relationship between K_p and K:

$$K_p = K(RT)^{\Delta n}$$

11.2: The Equilibrium Constant (K) is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

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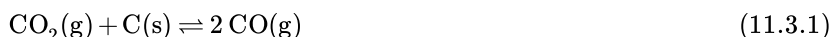# 11.3: Expressing the Equilibrium Constant in Terms of Pressure

> 🧠 **Learning Objectives**
>
> - To understand how different phases affect equilibria.

When the products and reactants of an equilibrium reaction form a single phase, whether gas or liquid, the system is a homogeneous equilibrium. In such situations, the concentrations of the reactants and products can vary over a wide range. In contrast, a system whose reactants, products, or both are in more than one phase is a heterogeneous equilibrium, such as the reaction of a gas with a solid or liquid.

As noted in the previous section, the equilibrium constant expression is actually a ratio of activities. To simplify the calculations in general chemistry courses, the activity of each substance in the reaction is often approximated using a ratio of the molarity of a substance compared to the standard state of that substance. For substances that are liquids or solids, the standard state is just the concentration of the substance within the liquid or solid. Because the molar concentrations of pure liquids and solids normally do not vary greatly with temperature, the ratio of the molarity to the standard state for substances that are liquids or solids always has a value of 1. For example, for a compound such as $CaF_2(s)$, the term going into the equilibrium expression is $[CaF_2]/[CaF_2]$ which cancels to unity. Thus, when the activities of the solids and liquids (including solvents) are incorporated into the equilibrium expression, they do not change the value.

Consider the following reaction, which is used in the final firing of some types of pottery to produce brilliant metallic glazes:

$$CO_2(g) + C(s) \rightleftharpoons 2\,CO(g) \tag{11.3.1}$$

The glaze is created when metal oxides are reduced to metals by the product, carbon monoxide. The equilibrium constant expression for this reaction is as follows:

$$K = \frac{a_{CO}^2}{a_{CO_2} a_C} = \frac{[CO]^2}{[CO_2][1]} = \frac{[CO]^2}{[CO_2]} \tag{11.3.2}$$

The equilibrium constant for this reaction can also be written in terms of the partial pressures of the gases:

$$K_p = \frac{(P_{CO})^2}{P_{CO_2}} \tag{11.3.3}$$

Incorporating all the constant values into K' or K_p allows us to focus on the substances whose concentrations change during the reaction.

Although the activities of pure liquids or solids are not written explicitly in the equilibrium constant expression, these substances must be present in the reaction mixture for chemical equilibrium to occur. Whatever the concentrations of CO and CO_2, the system described in Equation 11.3.1 will reach chemical equilibrium only if a stoichiometric amount of solid carbon or excess solid carbon has been added so that some is still present once the system has reached equilibrium. As shown in Figure 11.3.1, it does not matter whether 1 g or 100 g of solid carbon is present; in either case, the composition of the gaseous components of the system will be the same at equilibrium.
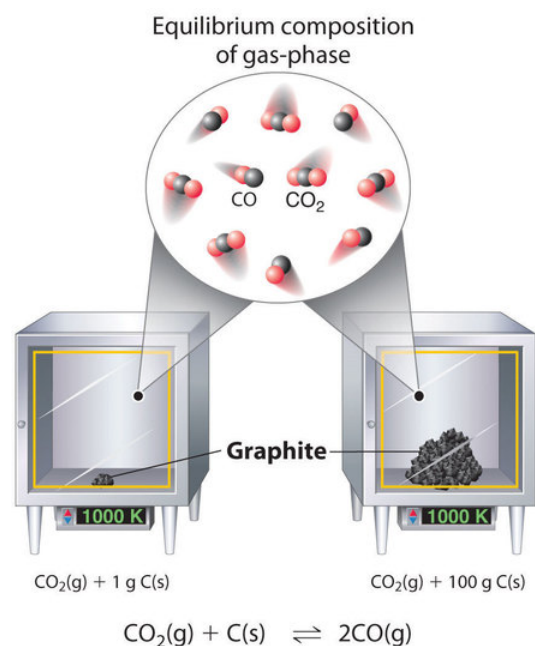
Figure 11.3.2: Effect of the Amount of Solid Present on Equilibrium in a Heterogeneous Solid–Gas System. In the system, the equilibrium composition of the gas phase at a given temperature, 1000 K in this case, is the same whether a small amount of solid carbon (left) or a large amount (right) is present.

✔ **Example 11.3.1**

Write each expression for K, incorporating all constants, and K_p for the following equilibrium reactions.

a. $PCl_3(l) + Cl_2(g) \rightleftharpoons PCl_5(s)$
b. $Fe_3O_4(s) + 4H_2(g) \rightleftharpoons 3Fe(s) + 4H_2O(g)$

Given: balanced equilibrium equations.

Asked for: expressions for K and K_p.

Strategy:

Find K by writing each equilibrium constant expression as the ratio of the concentrations of the products and reactants, each raised to its coefficient in the chemical equation. Then express K_p as the ratio of the partial pressures of the products and reactants, each also raised to its coefficient in the chemical equation.

Solution

This reaction contains a pure solid (PCl_5) and a pure liquid (PCl_3). Their activities are equal to 1, so when incorporated into the equilibrium constant expression, they do not change the value. So

$$K = \frac{1}{(1)[Cl_2]}$$

and

$$K_p = \frac{1}{(1)P_{Cl_2}}$$

This reaction contains two pure solids (Fe_3O_4 and Fe), which are each assigned a value of 1 in the equilibrium constant expressions:

$$K = \frac{(1)[H_2O]^4}{(1)[H_2]^4}$$

and

$$K_p = \frac{(1)(P_{H_2O})^4}{(1)(P_{H_2})^4}$$

For reactions carried out in solution, the solvent is assumed to be pure, and therefore is assigned an activity equal to 1 in the equilibrium constant expression. The activities of the solutes are approximated by their molarities. The result is that the equilibrium constant expressions appear to only depend upon the concentrations of the solutes.

> *The activities of pure solids, pure liquids, and solvents are defined as having a value of '1'. Often, it is said that these activities are "left out" of equilibrium constant expressions. This is an unfortunate use of words. The activities are not "left out" of equilibrium constant expressions. Rather, because they have a value of '1', they do not change the value of the equilibrium constant when they are multiplied together with the other terms. The activities of the solutes are approximated by their molarities.*

Summary

An equilibrated system that contains products and reactants in a single phase is a homogeneous equilibrium; a system whose reactants, products, or both are in more than one phase is a heterogeneous equilibrium.

Contributors and Attributions

- Anonymous
- Modified by Tom Neils (Grand Rapids Community College)

11.4: Calculating the Equilibrium Constant From Measured Equilibrium Concentrations

> **◑ Learning Objectives**
>
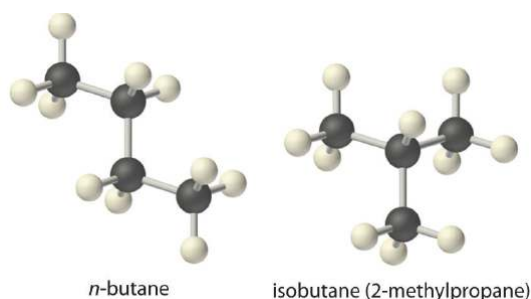> - To solve quantitative problems involving chemical equilibriums.

There are two fundamental kinds of equilibrium problems:

1. those in which we are given the concentrations of the reactants and the products at equilibrium (or, more often, information that allows us to calculate these concentrations), and we are asked to calculate the equilibrium constant for the reaction; and
2. those in which we are given the equilibrium constant and the initial concentrations of reactants, and we are asked to calculate the concentration of one or more substances at equilibrium. In this section, we describe methods for solving both kinds of problems.

Calculating an Equilibrium Constant from Equilibrium Concentrations

We saw in the exercise in Example 6 in Section 15.2 that the equilibrium constant for the decomposition of $CaCO_{3(s)}$ to $CaO_{(s)}$ and $CO_{2(g)}$ is $K = [CO_2]$. At 800°C, the concentration of CO_2 in equilibrium with solid $CaCO_3$ and CaO is 2.5×10^{-3} M. Thus K at 800°C is 2.5×10^{-3}. (Remember that equilibrium constants are unitless.)

A more complex example of this type of problem is the conversion of n-butane, an additive used to increase the volatility of gasoline, into isobutane (2-methylpropane).

n-butane   isobutane (2-methylpropane)

This reaction can be written as follows:

$$\text{n-butane}_{(g)} \rightleftharpoons \text{isobutane}_{(g)} \tag{11.4.1}$$
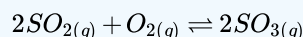
and the equilibrium constant $K = [\text{isobutane}]/[\text{n-butane}]$. At equilibrium, a mixture of n-butane and isobutane at room temperature was found to contain 0.041 M isobutane and 0.016 M n-butane. Substituting these concentrations into the equilibrium constant expression,

$$K = \frac{[isobutane]}{[n\text{-}butane]} = 0.041\ M = 2.6 \tag{11.4.2}$$

Thus the equilibrium constant for the reaction as written is 2.6.

> **✔ Example 11.4.1**
>
> The reaction between gaseous sulfur dioxide and oxygen is a key step in the industrial synthesis of sulfuric acid:
>
> $$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$$
>
> A mixture of SO_2 and O_2 was maintained at 800 K until the system reached equilibrium. The equilibrium mixture contained
>
> - 5.0×10^{-2} M SO_3,
> - 3.5×10^{-3} M O_2, and
> - 3.0×10^{-3} M SO_2.

Calculate K and K_p at this temperature.

Given: balanced equilibrium equation and composition of equilibrium mixture

Asked for: equilibrium constant

Strategy

Write the equilibrium constant expression for the reaction. Then substitute the appropriate equilibrium concentrations into this equation to obtain K.

Solution

Substituting the appropriate equilibrium concentrations into the equilibrium constant expression,

$$K = \frac{[SO_3]^2}{[SO_2]^2[O_2]} = \frac{(5.0 \times 10^{-2})^2}{(3.0 \times 10^{-3})^2(3.5 \times 10^{-3})} = 7.9 \times 10^4$$

To solve for K_p, we use the relationship derived previously

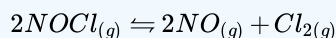$$K_p = K(RT)^{\Delta n}$$

where $\Delta n = 2 - 3 = -1$:

$$K_p = K(RT)^{\Delta n}$$

$$K_p = 7.9 \times 10^4 [(0.08206 \ L \cdot atm/mol \cdot K)(800K)]^{-1}$$

$$K_p = 1.2 \times 10^3$$

? Exercise 11.4.1

Hydrogen gas and iodine react to form hydrogen iodide via the reaction

$$2NOCl_{(g)} \rightleftharpoons 2NO_{(g)} + Cl_{2(g)}$$

A mixture of H_2 and I_2 was maintained at 740 K until the system reached equilibrium. The equilibrium mixture contained

- $1.37 \times 10^{-2} \ M \ HI$,
- $6.47 \times 10^{-3} \ M \ H_2$, and
- $5.94 \times 10^{-4} \ M \ I_2$.

Calculate K and K_p for this reaction.

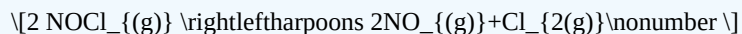**Answer**

$K = 48.8$ and $K_p = 48.8$

Chemists are not often given the concentrations of all the substances, and they are not likely to measure the equilibrium concentrations of all the relevant substances for a particular system. In such cases, we can obtain the equilibrium concentrations from the initial concentrations of the reactants and the balanced chemical equation for the reaction, as long as the equilibrium concentration of one of the substances is known. Example 11.4.2 shows one way to do this.

✔ Example 11.4.2

A 1.00 mol sample of $NOCl$ was placed in a 2.00 L reactor and heated to 227°C until the system reached equilibrium. The contents of the reactor were then analyzed and found to contain 0.056 mol of Cl_2. Calculate K at this temperature. The equation for the decomposition of $NOCl$ to NO and Cl_2 is as follows:

$$2 NOCl_{(g)} \rightleftharpoons 2NO_{(g)}+Cl_{2(g)}$$

Given: balanced equilibrium equation, amount of reactant, volume, and amount of one product at equilibrium
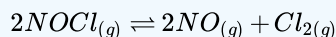
Asked for: K

Strategy:

A. Write the equilibrium constant expression for the reaction. Construct a table showing the initial concentrations, the changes in concentrations, and the final concentrations (as initial concentrations plus changes in concentrations).
B. Calculate all possible initial concentrations from the data given and insert them in the table.
C. Use the coefficients in the balanced chemical equation to obtain the changes in concentration of all other substances in the reaction. Insert those concentration changes in the table.
D. Obtain the final concentrations by summing the columns. Calculate the equilibrium constant for the reaction.

Solution

A The first step in any such problem is to balance the chemical equation for the reaction (if it is not already balanced) and use it to derive the equilibrium constant expression. In this case, the equation is already balanced, and the equilibrium constant expression is as follows:
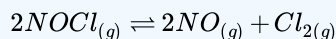
$$K = \frac{[NO]^2[Cl_2]}{[NOCl]^2}$$

To obtain the concentrations of $NOCl$, NO, and Cl_2 at equilibrium, we construct a table showing what is known and what needs to be calculated. We begin by writing the balanced chemical equation at the top of the table, followed by three lines corresponding to the initial concentrations, the changes in concentrations required to get from the initial to the final state, and the final concentrations.

$$2NOCl_{(g)} \rightleftharpoons 2NO_{(g)} + Cl_{2(g)}$$

ICE	$[NOCl]$	$[NO]$	$[Cl_2]$
Initial			
Change			
Final			

B Initially, the system contains 1.00 mol of $NOCl$ in a 2.00 L container. Thus $[NOCl]_i = 1.00 \; mol/2.00 \; L = 0.500 \; M$ The initial concentrations of NO and Cl_2 are $0 \; M$ because initially no products are present. Moreover, we are told that at equilibrium the system contains 0.056 mol of Cl_2 in a 2.00 L container, so $[Cl_2]_f = 0.056 \; mol/2.00 \; L = 0.028 \; M$ We insert these values into the following table:

$$2NOCl_{(g)} \rightleftharpoons 2NO_{(g)} + Cl_{2(g)}$$

ICE	$[NOCl]$	$[NO]$	$[Cl_2]$
Initial	0.500	0	0
Change			
Final			0.028

C We use the stoichiometric relationships given in the balanced chemical equation to find the change in the concentration of Cl_2, the substance for which initial and final concentrations are known:

$$\Delta[Cl_2] = 0.028 \; M_{(final)} - 0.00 \; M_{(initial)}] = +0.028 \; M$$
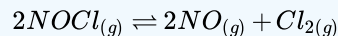
According to the coefficients in the balanced chemical equation, 2 mol of NO are produced for every 1 mol of Cl_2, so the change in the NO concentration is as follows:

$$\Delta[NO] = \left(\frac{0.028 \; mol \; Cl_2}{L}\right)\left(\frac{2 \; mol \; NO}{1 \; mol \; Cl_2}\right) = 0.056 \; M$$

Similarly, 2 mol of $NOCl$ are consumed for every 1 mol of Cl_2 produced, so the change in the $NOCl$ concentration is as follows:

$$\Delta[NOCl] = \left(\frac{0.028 \ \cancel{mol \ Cl_2}}{L}\right)\left(\frac{-2 \ mol \ NOCl}{1 \ \cancel{mol \ Cl_2}}\right) = -0.056 \ M$$

We insert these values into our table:

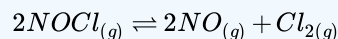$$2NOCl_{(g)} \rightleftharpoons 2NO_{(g)} + Cl_{2(g)}$$

ICE	$[NOCl]$	$[NO]$	$[Cl_2]$
Initial	0.500	0	0
Change	−0.056	+0.056	+0.028
Final			0.028

D We sum the numbers in the $[NOCl]$ and $[NO]$ columns to obtain the final concentrations of NO and $NOCl$:

$$[NO]_f = 0.000 \ M + 0.056 \ M = 0.056 \ M$$

$$[NOCl]_f = 0.500 \ M + (-0.056 \ M) = 0.444 M$$
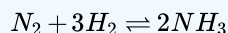
We can now complete the table:

$$2NOCl_{(g)} \rightleftharpoons 2NO_{(g)} + Cl_{2(g)}$$

ICE	\([NOCl]	$[NO]$	$[Cl_2]$
initial	0.500	0	0
change	−0.056	+0.056	+0.028
final	0.444	0.056	0.028

We can now calculate the equilibrium constant for the reaction:

$$K = \frac{[NO]^2[Cl_2]}{[NOCl]^2} = \frac{(0.056)^2(0.028)}{(0.444)^2} = 4.5 \times 10^{-4}$$

? Exercise 11.4.2

The German chemist Fritz Haber (1868–1934; Nobel Prize in Chemistry 1918) was able to synthesize ammonia (NH_3) by reacting 0.1248 M H_2 and 0.0416 M N_2 at about 500°C. At equilibrium, the mixture contained 0.00272 M NH_3. What is K for the reaction

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

at this temperature? What is K_p?

Answer
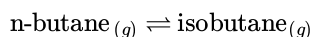
$K = 0.105$ and $K_p = 2.61 \times 10^{-5}$

A Video Disucssing Using ICE Tables to find Kc: Using ICE Tables to find Kc(opens in new window) [youtu.be]
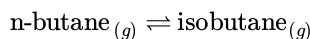
Calculating Equilibrium Concentrations from the Equilibrium Constant

To describe how to calculate equilibrium concentrations from an equilibrium constant, we first consider a system that contains only a single product and a single reactant, the conversion of n-butane to isobutane (Equation 11.4.1), for which K = 2.6 at 25°C. If we begin with a 1.00 M sample of n-butane, we can determine the concentration of n-butane and isobutane at equilibrium by constructing a table showing what is known and what needs to be calculated, just as we did in Example 11.4.2

$$\text{n-butane}_{(g)} \rightleftharpoons \text{isobutane}_{(g)}$$

ICE	[n-butane$_{(g)}$]	[isobutane$_{(g)}$]
Initial		
Change		
Final		

The initial concentrations of the reactant and product are both known: [n-butane]i = 1.00 M and [isobutane]i = 0 M. We need to calculate the equilibrium concentrations of both n-butane and isobutane. Because it is generally difficult to calculate final concentrations directly, we focus on the change in the concentrations of the substances between the initial and the final (equilibrium) conditions. If, for example, we define the change in the concentration of isobutane (Δ[isobutane]) as $+x$, then the change in the concentration of n-butane is Δ[n-butane] = $-x$. This is because the balanced chemical equation for the reaction tells us that 1 mol of n-butane is consumed for every 1 mol of isobutane produced. We can then express the final concentrations in terms of the initial concentrations and the changes they have undergone.

$$\text{n-butane}_{(g)} \rightleftharpoons \text{isobutane}_{(g)}$$

ICE	[n-butane$_{(g)}$]	[isobutane$_{(g)}$]
Initial	1.00	0
Change	$-x$	$+x$
Final	$(1.00 - x)$	$(0 + x) = x$

Substituting the expressions for the final concentrations of n-butane and isobutane from the table into the equilibrium equation,

$$K = \frac{[\text{isobutane}]}{[\text{n-butane}]} = \frac{x}{1.00 - x} = 2.6$$

Rearranging and solving for x,

$$x = 2.6(1.00 - x) = 2.6 - 2.6x$$

$$x + 2.6x = 2.6$$

$$x = 0.72$$

We obtain the final concentrations by substituting this x value into the expressions for the final concentrations of n-butane and isobutane listed in the table:

$$[\text{n-butane}]_f = (1.00 - x)M = (1.00 - 0.72)M = 0.28\ M$$

$$[\text{isobutane}]_f = (0.00 + x)M = (0.00 + 0.72)M = 0.72\ M$$

We can check the results by substituting them back into the equilibrium constant expression to see whether they give the same K that we used in the calculation:
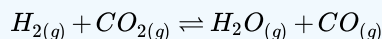
$$K = \frac{[\text{isobutane}]}{[\text{n-butane}]} = \left(\frac{0.72\ \cancel{M}}{0.28\ \cancel{M}}\right) = 2.6$$

This is the same K we were given, so we can be confident of our results.

Example 11.4.3 illustrates a common type of equilibrium problem that you are likely to encounter.

> ✔ **Example 11.4.3: The water–gas shift reaction**
>
> The water–gas shift reaction is important in several chemical processes, such as the production of H_2 for fuel cells. This reaction can be written as follows:
>
> $$H_{2(g)} + CO_{2(g)} \rightleftharpoons H_2O_{(g)} + CO_{(g)}$$
>
> $K = 0.106$ at 700 K. If a mixture of gases that initially contains 0.0150 M H_2 and 0.0150 M CO_2 is allowed to equilibrate at 700 K, what are the final concentrations of all substances present?
>
> **Given**: balanced equilibrium equation, K, and initial concentrations
>
> Asked for: final concentrations
>
> **Strategy**:
>
> A. Construct a table showing what is known and what needs to be calculated. Define x as the change in the concentration of one substance. Then use the reaction stoichiometry to express the changes in the concentrations of the other substances in terms of x. From the values in the table, calculate the final concentrations.
> B. Write the equilibrium equation for the reaction. Substitute appropriate values from the ICE table to obtain x.
> C. Calculate the final concentrations of all species present. Check your answers by substituting these values into the equilibrium constant expression to obtain K.
>
> **Solution**
>
> A The initial concentrations of the reactants are $[H_2]_i = [CO_2]_i = 0.0150\ M$. Just as before, we will focus on the change in the concentrations of the various substances between the initial and final states. If we define the change in the concentration of H_2O as x, then $\Delta[H_2O] = +x$. We can use the stoichiometry of the reaction to express the changes in the concentrations of the other substances in terms of x. For example, 1 mol of CO is produced for every 1 mol of H_2O, so the change in the CO concentration can be expressed as $\Delta[CO] = +x$. Similarly, for every 1 mol of H_2O produced, 1 mol each of H_2 and CO_2 are consumed, so the change in the concentration of the reactants is $\Delta[H_2] = \Delta[CO_2] = -x$. We enter the values in the following table and calculate the final concentrations.
>
> $$H_{2(g)} + CO_{2(g)} \rightleftharpoons H_2O_{(g)} + CO_{(g)}$$
>
> | ICE | $[H_2]$ | $[CO_2]$ | $[H_2O]$ | $[CO]$ |
> |---|---|---|---|---|
> | **Initial** | 0.0150 | 0.0150 | 0 | 0 |
> | **Change** | $-x$ | $-x$ | $+x$ | $+x$ |
> | **Final** | $(0.0150 - x)$ | $(0.0150 - x)$ | x | x |

B We can now use the equilibrium equation and the given K to solve for x:

$$K = \frac{[H_2O][CO]}{[H_2][CO_2]} = \frac{(x)(x)}{(0.0150-x)(0.0150-x)} = \frac{x^2}{(0.0150-x)^2} = 0.106$$

We could solve this equation with the quadratic formula, but it is far easier to solve for x by recognizing that the left side of the equation is a perfect square; that is,

$$\frac{x^2}{(0.0150-x)^2} = \left(\frac{x}{0.0150-x}\right)^2 = 0.106$$

Taking the square root of the middle and right terms,

$$\frac{x}{(0.0150-x)} = (0.106)^{1/2} = 0.326$$

$$x = (0.326)(0.0150) - 0.326x$$

$$1.326x = 0.00489$$

$$x = 0.00369 = 3.69 \times 10^{-3}$$

C The final concentrations of all species in the reaction mixture are as follows:

- $[H_2]_f = [H_2]_i + \Delta[H_2] = (0.0150 - 0.00369)\ M = 0.0113\ M$
- $[CO_2]_f = [CO_2]_i + \Delta[CO_2] = (0.0150 - 0.00369)\ M = 0.0113\ M$
- $[H_2O]_f = [H_2O]_i + \Delta[H_2O] = (0 + 0.00369)\ M = 0.00369\ M$
- $[CO]_f = [CO]_i + \Delta[CO] = (0 + 0.00369)\ M = 0.00369\ M$

We can check our work by inserting the calculated values back into the equilibrium constant expression:

$$K = \frac{[H_2O][CO]}{[H_2][CO_2]} = \frac{(0.00369)^2}{(0.0113)^2} = 0.107$$

To two significant figures, this K is the same as the value given in the problem, so our answer is confirmed.

? Exercise 11.4.3

Hydrogen gas reacts with iodine vapor to give hydrogen iodide according to the following chemical equation:

$$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$$
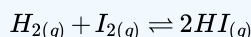
$K = 54$ at 425°C. If 0.172 M H_2 and I_2 are injected into a reactor and maintained at 425°C until the system equilibrates, what is the final concentration of each substance in the reaction mixture?

Answer

- $[HI]_f = 0.270\ M$
- $[H_2]_f = [I_2]_f = 0.037\ M$

In Example 11.4.3, the initial concentrations of the reactants were the same, which gave us an equation that was a perfect square and simplified our calculations. Often, however, the initial concentrations of the reactants are not the same, and/or one or more of the products may be present when the reaction starts. Under these conditions, there is usually no way to simplify the problem, and we must determine the equilibrium concentrations with other means. Such a case is described in Example 11.4.4.

✔ Example 11.4.4

In the water–gas shift reaction shown in Example 11.4.3, a sample containing 0.632 M CO2 and 0.570 M H_2 is allowed to equilibrate at 700 K. At this temperature, $K = 0.106$. What is the composition of the reaction mixture at equilibrium?

Given: balanced equilibrium equation, concentrations of reactants, and K

Asked for: composition of reaction mixture at equilibrium

Strategy:

A. Write the equilibrium equation. Construct a table showing the initial concentrations of all substances in the mixture. Complete the table showing the changes in the concentrations (\(x) and the final concentrations.
B. Write the equilibrium constant expression for the reaction. Substitute the known K value and the final concentrations to solve for x.
C. Calculate the final concentration of each substance in the reaction mixture. Check your answers by substituting these values into the equilibrium constant expression to obtain K.

Solution

A $[CO_2]_i = 0.632$ M and $[H_2]_i = 0.570$ M. Again, x is defined as the change in the concentration of H_2O: $\Delta[H_2O] = +x$. Because 1 mol of CO is produced for every 1 mol of H_2O, the change in the concentration of CO is the same as the change in the concentration of H2O, so Δ[CO] = +x. Similarly, because 1 mol each of H_2 and CO_2 are consumed for every 1 mol of H_2O produced, $\Delta[H_2] = \Delta[CO_2] = -x$. The final concentrations are the sums of the initial concentrations and the changes in concentrations at equilibrium.

$$H_{2(g)} + CO_{2(g)} \rightleftharpoons H_2O_{(g)} + CO_{(g)}$$

ICE	$H_{2(g)}$	$CO_{2(g)}$	$H_2O_{(g)}$	$CO_{(g)}$
Initial	0.570	0.632	0	0
Change	$-x$	$-x$	$+x$	$+x$
Final	$(0.570 - x)$	$(0.632 - x)$	x	x

B We can now use the equilibrium equation and the known K value to solve for x:

$$K = \frac{[H_2O][CO]}{[H_2][CO_2]} = \frac{x^2}{(0.570 - x)(0.632 - x)} = 0.106$$

In contrast to Example 11.4.3, however, there is no obvious way to simplify this expression. Thus we must expand the expression and multiply both sides by the denominator:

$$x^2 = 0.106(0.360 - 1.202x + x^2)$$

Collecting terms on one side of the equation,

$$0.894x^2 + 0.127x - 0.0382 = 0$$

This equation can be solved using the quadratic formula:

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{-0.127 \pm \sqrt{(0.127)^2 - 4(0.894)(-0.0382)}}{2(0.894)}$$

$$x = 0.148 \text{ and } -0.290$$

Only the answer with the positive value has any physical significance, so $\Delta[H_2O] = \Delta[CO] = +0.148M$, and $\Delta[H_2] = \Delta[CO_2] = -0.148$ M.

C The final concentrations of all species in the reaction mixture are as follows:

- $[H_2]_f [= [H_2]_i + \Delta[H_2] = 0.570$ $M - 0.148$ $M = 0.422M$
- $[CO_2]_f = [CO_2]_i + \Delta[CO_2] = 0.632$ $M - 0.148$ $M = 0.484M$
- $[H_2O]_f = [H_2O]_i + \Delta[H_2O] = 0$ $M + 0.148$ $M = 0.148$ M
- $[CO]_f = [CO]_i + \Delta[CO] = 0M + 0.148$ $M = 0.148M$

We can check our work by substituting these values into the equilibrium constant expression:

$$K = \frac{[H_2O][CO]}{[H_2][CO_2]} = \frac{(0.148)^2}{(0.422)(0.484)} = 0.107$$

Because K is essentially the same as the value given in the problem, our calculations are confirmed.

? Exercise 11.4.4

The exercise in Example 11.4.1 showed the reaction of hydrogen and iodine vapor to form hydrogen iodide, for which $K = 54$ at 425°C. If a sample containing 0.200 M H_2 and 0.0450 M I_2 is allowed to equilibrate at 425°C, what is the final concentration of each substance in the reaction mixture?

Answer
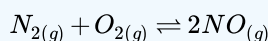
- $[H_I]_f = 0.0882 \ M$
- $[H_2]_f = 0.156 \ M$
- $[I_2]_f = 9.2 \times 10^{-4} M$

In many situations it is not necessary to solve a quadratic (or higher-order) equation. Most of these cases involve reactions for which the equilibrium constant is either very small ($K \le 10^{-3}$) or very large ($K \ge 10^3$), which means that the change in the concentration (defined as x) is essentially negligible compared with the initial concentration of a substance. Knowing this simplifies the calculations dramatically, as illustrated in Example 11.4.5.

✔ Example 11.4.5

Atmospheric nitrogen and oxygen react to form nitric oxide:

$$N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$$

with $K_p = 2.0 \times 10^{-31}$ at 25°C.

What is the partial pressure of NO in equilibrium with N_2 and O_2 in the atmosphere (at 1 atm, $P_{N_2} = 0.78 \ atm$ and $P_{O_2} = 0.21 \ atm$?

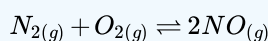**Given**: balanced equilibrium equation and values of K_p, P_{O_2}, and P_{N_2}

Asked for: partial pressure of NO

Strategy:

A. Construct a table and enter the initial partial pressures, the changes in the partial pressures that occur during the course of the reaction, and the final partial pressures of all substances.
B. Write the equilibrium equation for the reaction. Then substitute values from the table to solve for the change in concentration (\(x).
C. Calculate the partial pressure of NO. Check your answer by substituting values into the equilibrium equation and solving for K.

Solution

A Because we are given Kp and partial pressures are reported in atmospheres, we will use partial pressures. The initial partial pressure of O_2 is 0.21 atm and that of N_2 is 0.78 atm. If we define the change in the partial pressure of NO as $2x$, then the change in the partial pressure of O_2 and of N_2 is $-x$ because 1 mol each of N_2 and of O_2 is consumed for every 2 mol of NO produced. Each substance has a final partial pressure equal to the sum of the initial pressure and the change in that pressure at equilibrium.

$$N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$$

ICE	P_{N_2}	P_{O_2}	P_{NO}
Initial	0.78	0.21	0
Change	$-x$	$-x$	$+2x$

ICE	P_{N_2}	P_{O_2}	P_{NO}
Final	$(0.78 - x)$	$(0.21 - x)$	$2x$

B Substituting these values into the equation for the equilibrium constant,

$$K_p = \frac{(P_{NO})^2}{(P_{N_2})(P_{O_2})} = \frac{(2x)^2}{(0.78 - x)(0.21 - x)} = 2.0 \times 10^{-31}$$

In principle, we could multiply out the terms in the denominator, rearrange, and solve the resulting quadratic equation. In practice, it is far easier to recognize that an equilibrium constant of this magnitude means that the extent of the reaction will be very small; therefore, the x value will be negligible compared with the initial concentrations. If this assumption is correct, then to two significant figures, $(0.78 - x) = 0.78$ and $(0.21 - x) = 0.21$. Substituting these expressions into our original equation,

$$\frac{(2x)^2}{(0.78)(0.21)} = 2.0 \times 10^{-31}$$

$$\frac{4x^2}{0.16} = 2.0 \times 10^{-31}$$

$$x^2 = \frac{0.33 \times 10^{-31}}{4}$$

$$x = 9.1 \times 10^{-17}$$

C Substituting this value of x into our expressions for the final partial pressures of the substances,

- $P_{NO} = 2x \; atm = 1.8 \times 10^{-16} \; atm$
- $P_{N_2} = (0.78 - x) \; atm = 0.78 \; atm$
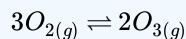- $P_{O_2} = (0.21 - x) \; atm = 0.21 \; atm$

From these calculations, we see that our initial assumption regarding x was correct: given two significant figures, 2.0×10^{-16} is certainly negligible compared with 0.78 and 0.21. When can we make such an assumption? As a general rule, if x is less than about 5% of the total, or $10^{-3} > K > 10^3$, then the assumption is justified. Otherwise, we must use the quadratic formula or some other approach. The results we have obtained agree with the general observation that toxic NO, an ingredient of smog, does not form from atmospheric concentrations of N_2 and O_2 to a substantial degree at 25°C. We can verify our results by substituting them into the original equilibrium equation:

$$K_p = \frac{(P_{NO})^2}{(P_{N_2})(P_{O_2})} = \frac{(1.8 \times 10^{-16})^2}{(0.78)(0.21)} = 2.0 \times 10^{-31}$$

The final K_p agrees with the value given at the beginning of this example.

? Exercise 11.4.5

Under certain conditions, oxygen will react to form ozone, as shown in the following equation:

$$3O_{2(g)} \rightleftharpoons 2O_{3(g)}$$

with $K_p = 2.5 \times 10^{-59}$ at 25°C. What ozone partial pressure is in equilibrium with oxygen in the atmosphere ($P_{O_2} = 0.21 \; atm$)?
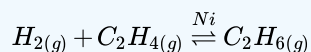
Answer

$4.8 \times 10^{-31} \; atm$

Another type of problem that can be simplified by assuming that changes in concentration are negligible is one in which the equilibrium constant is very large ($K \geq 10^3$). A large equilibrium constant implies that the reactants are converted almost entirely to products, so we can assume that the reaction proceeds 100% to completion. When we solve this type of problem, we view the

system as equilibrating from the products side of the reaction rather than the reactants side. This approach is illustrated in Example 11.4.6.

The chemical equation for the reaction of hydrogen with ethylene (C_2H_4) to give ethane (C_2H_6) is as follows:

$$H_{2(g)} + C_2H_{4(g)} \overset{Ni}{\rightleftharpoons} C_2H_{6(g)}$$

with $K = 9.6 \times 10^{18}$ at 25°C. If a mixture of 0.200 M H_2 and 0.155 M C_2H_4 is maintained at 25°C in the presence of a powdered nickel catalyst, what is the equilibrium concentration of each substance in the mixture?

Given: balanced chemical equation, K, and initial concentrations of reactants

Asked for: equilibrium concentrations

Strategy:

A. Construct a table showing initial concentrations, concentrations that would be present if the reaction were to go to completion, changes in concentrations, and final concentrations.
B. Write the equilibrium constant expression for the reaction. Then substitute values from the table into the expression to solve for x (the change in concentration).
C. Calculate the equilibrium concentrations. Check your answers by substituting these values into the equilibrium equation.

Solution:

A From the magnitude of the equilibrium constant, we see that the reaction goes essentially to completion. Because the initial concentration of ethylene (0.155 M) is less than the concentration of hydrogen (0.200 M), ethylene is the limiting reactant; that is, no more than 0.155 M ethane can be formed from 0.155 M ethylene. If the reaction were to go to completion, the concentration of ethane would be 0.155 M and the concentration of ethylene would be 0 M. Because the concentration of hydrogen is greater than what is needed for complete reaction, the concentration of unreacted hydrogen in the reaction mixture would be 0.200 M − 0.155 M = 0.045 M. The equilibrium constant for the forward reaction is very large, so the equilibrium constant for the reverse reaction must be very small. The problem then is identical to that in Example 11.4.5. If we define $-x$ as the change in the ethane concentration for the reverse reaction, then the change in the ethylene and hydrogen concentrations is $+x$. The final equilibrium concentrations are the sums of the concentrations for the forward and reverse reactions.

$$H_{2(g)} + C_2H_{4(g)} \overset{Ni}{\rightleftharpoons} C_2H_{6(g)}$$

IACE	$[\boldsymbol{H_{2(g)}}]$	$[\boldsymbol{C_2H_{4(g)}}]$	$[\boldsymbol{C_2H_{6(g)}}]$
Initial	0.200	0.155	0
Assuming 100% reaction	0.045	0	0.155
Change	$+x$	$+x$	$-x$
Final	$(0.045 + x)$	$(0 + x)$	$(0.155 - x)$

B Substituting values into the equilibrium constant expression,

$$K = \frac{[C_2H_6]}{[H_2][C_2H_4]} = \frac{0.155 - x}{(0.045 + x)x} = 9.6 \times 10^{18}$$

Once again, the magnitude of the equilibrium constant tells us that the equilibrium will lie far to the right as written, so the reverse reaction is negligible. Thus x is likely to be very small compared with either 0.155 M or 0.045 M, and the equation can be simplified ($(0.045 + x) = 0.045$ and $(0.155 - x) = 0.155$) as follows:

$$K = \frac{0.155}{0.045x} = 9.6 \times 10^{18}$$

$$x = 3.6 \times 10^{-19}$$

C The small x value indicates that our assumption concerning the reverse reaction is correct, and we can therefore calculate the final concentrations by evaluating the expressions from the last line of the table:

- $[C_2H_6]_f = (0.155 - x)\ M = 0.155\ M$
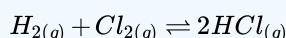- $[C_2H_4]_f = x\ M = 3.6 \times 10^{-19} M$
- $[H_2]_f = (0.045 + x)\ M = 0.045\ M$

We can verify our calculations by substituting the final concentrations into the equilibrium constant expression:

$$K = \frac{[C_2H_6]}{[H_2][C_2H_4]} = \frac{0.155}{(0.045)(3.6 \times 10^{-19})} = 9.6 \times 10^{18}$$

This K value agrees with our initial value at the beginning of the example.

? Exercise 11.4.6

Hydrogen reacts with chlorine gas to form hydrogen chloride:

$$H_{2(g)} + Cl_{2(g)} \rightleftharpoons 2HCl_{(g)}$$

with $K_p = 4.0 \times 10^{31}$ at 47°C. If a mixture of 0.257 M H_2 and 0.392 M Cl_2 is allowed to equilibrate at 47°C, what is the equilibrium composition of the mixture?

Answer

$[H_2]_f = 4.8 \times 10^{-32}\ M\ [Cl_2]_f = 0.135\ M\ [HCl]_f = 0.514\ M$

A Video Discussing Using ICE Tables to find Eq. Concentrations & Kc: Using ICE Tables to find Eq. Concentrations & Kc(opens in new window) [youtu.be]

Summary

Various methods can be used to solve the two fundamental types of equilibrium problems: (1) those in which we calculate the concentrations of reactants and products at equilibrium and (2) those in which we use the equilibrium constant and the initial concentrations of reactants to determine the composition of the equilibrium mixture. When an equilibrium constant is calculated from equilibrium concentrations, molar concentrations or partial pressures are substituted into the equilibrium constant expression for the reaction. Equilibrium constants can be used to calculate the equilibrium concentrations of reactants and products by using the quantities or concentrations of the reactants, the stoichiometry of the balanced chemical equation for the reaction, and a tabular format to obtain the final concentrations of all species at equilibrium.

11.5: Heterogenous Equilibria - Reactions Involving Solids and Liquids

> **♦ Learning Objectives**
> - To understand how different phases affect equilibria.

When the products and reactants of an equilibrium reaction form a single phase, whether gas or liquid, the system is a homogeneous equilibrium. In such situations, the concentrations of the reactants and products can vary over a wide range. In contrast, a system whose reactants, products, or both are in more than one phase is a heterogeneous equilibrium, such as the reaction of a gas with a solid or liquid.

As noted in the previous section, the equilibrium constant expression is actually a ratio of activities. To simplify the calculations in general chemistry courses, the activity of each substance in the reaction is often approximated using a ratio of the molarity of a substance compared to the standard state of that substance. For substances that are liquids or solids, the standard state is just the concentration of the substance within the liquid or solid. Because the molar concentrations of pure liquids and solids normally do not vary greatly with temperature, the ratio of the molarity to the standard state for substances that are liquids or solids always has a value of 1. For example, for a compound such as $CaF_2(s)$, the term going into the equilibrium expression is $[CaF_2]/[CaF_2]$ which cancels to unity. Thus, when the activities of the solids and liquids (including solvents) are incorporated into the equilibrium expression, they do not change the value.

Consider the following reaction, which is used in the final firing of some types of pottery to produce brilliant metallic glazes:

$$CO_2(g) + C(s) \rightleftharpoons 2\,CO(g) \tag{11.5.1}$$

The glaze is created when metal oxides are reduced to metals by the product, carbon monoxide. The equilibrium constant expression for this reaction is as follows:

$$K = \frac{a_{CO}^2}{a_{CO_2}a_C} = \frac{[CO]^2}{[CO_2][1]} = \frac{[CO]^2}{[CO_2]} \tag{11.5.2}$$

The equilibrium constant for this reaction can also be written in terms of the partial pressures of the gases:

$$K_p = \frac{(P_{CO})^2}{P_{CO_2}} \tag{11.5.3}$$

Incorporating all the constant values into K' or K_p allows us to focus on the substances whose concentrations change during the reaction.

Although the activities of pure liquids or solids are not written explicitly in the equilibrium constant expression, these substances must be present in the reaction mixture for chemical equilibrium to occur. Whatever the concentrations of CO and CO_2, the system described in Equation 11.5.1 will reach chemical equilibrium only if a stoichiometric amount of solid carbon or excess solid carbon has been added so that some is still present once the system has reached equilibrium. As shown in Figure 11.5.1, it does not matter whether 1 g or 100 g of solid carbon is present; in either case, the composition of the gaseous components of the system will be the same at equilibrium.
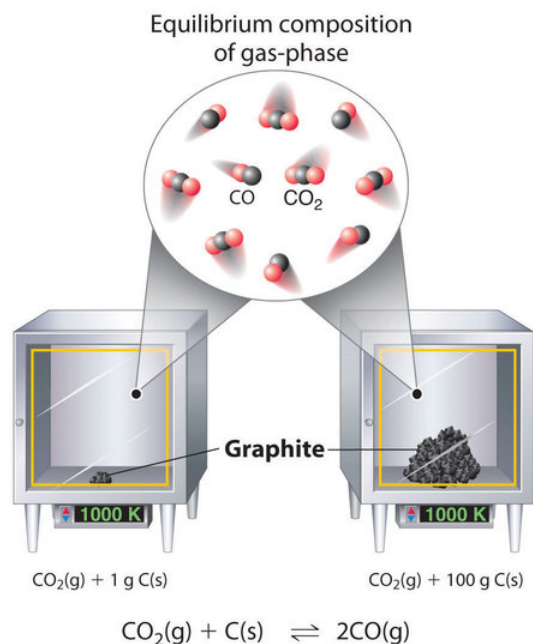
Figure 11.5.2: Effect of the Amount of Solid Present on Equilibrium in a Heterogeneous Solid–Gas System. In the system, the equilibrium composition of the gas phase at a given temperature, 1000 K in this case, is the same whether a small amount of solid carbon (left) or a large amount (right) is present.

✔ Example 11.5.1

Write each expression for K, incorporating all constants, and K_p for the following equilibrium reactions.

a. $PCl_3(l) + Cl_2(g) \rightleftharpoons PCl_5(s)$
b. $Fe_3O_4(s) + 4\,H_2(g) \rightleftharpoons 3\,Fe(s) + 4\,H_2O(g)$

Given: balanced equilibrium equations.

Asked for: expressions for K and K_p.

Strategy:

Find K by writing each equilibrium constant expression as the ratio of the concentrations of the products and reactants, each raised to its coefficient in the chemical equation. Then express K_p as the ratio of the partial pressures of the products and reactants, each also raised to its coefficient in the chemical equation.

Solution

This reaction contains a pure solid (PCl_5) and a pure liquid (PCl_3). Their activities are equal to 1, so when incorporated into the equilibrium constant expression, they do not change the value. So

$$K = \frac{1}{(1)[Cl_2]}$$

and

$$K_p = \frac{1}{(1)P_{Cl_2}}$$

This reaction contains two pure solids (Fe_3O_4 and Fe), which are each assigned a value of 1 in the equilibrium constant expressions:
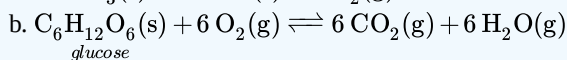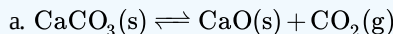
$$K = \frac{(1)[H_2O]^4}{(1)[H_2]^4}$$

and

$$K_p = \frac{(1)(P_{H_2O})^4}{(1)(P_{H_2})^4}$$

Write the expressions for K and K_p for the following reactions.

a. $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

b. $C_6H_{12}O_6(s) + 6\,O_2(g) \rightleftharpoons 6\,CO_2(g) + 6\,H_2O(g)$
   glucose

Answer a

$K = [CO_2]$ and $K_p = P_{CO_2}$

Answer b

$K = \dfrac{[CO_2]^6[H_2O]^6}{[O_2]^6}$ and $K_p = \dfrac{(P_{CO_2})^6(P_{H_2O})^6}{(P_{O_2})^6}$

For reactions carried out in solution, the solvent is assumed to be pure, and therefore is assigned an activity equal to 1 in the equilibrium constant expression. The activities of the solutes are approximated by their molarities. The result is that the equilibrium constant expressions appear to only depend upon the concentrations of the solutes.

> *The activities of pure solids, pure liquids, and solvents are defined as having a value of '1'. Often, it is said that these activities are "left out" of equilibrium constant expressions. This is an unfortunate use of words. The activities are not "left out" of equilibrium constant expressions. Rather, because they have a value of '1', they do not change the value of the equilibrium constant when they are multiplied together with the other terms. The activities of the solutes are approximated by their molarities.*

Summary

An equilibrated system that contains products and reactants in a single phase is a homogeneous equilibrium; a system whose reactants, products, or both are in more than one phase is a heterogeneous equilibrium.

Contributors and Attributions

- Anonymous
- Modified by Tom Neils (Grand Rapids Community College)

# 11.6: The Reaction Quotient- Predicting the Direction of Change

> **◐ Learning Objectives**
>
> - To predict in which direction a reaction will proceed.

We previously saw that knowing the magnitude of the equilibrium constant under a given set of conditions allows chemists to predict the extent of a reaction. Often, however, chemists must decide whether a system has reached equilibrium or if the composition of the mixture will continue to change with time. In this section, we describe how to quantitatively analyze the composition of a reaction mixture to make this determination.

The Reaction Quotient

To determine whether a system has reached equilibrium, chemists use a Quantity called the reaction Quotient (Q). The expression for the reaction Quotient has precisely the same form as the equilibrium constant expression, except that Q may be derived from a set of values measured at any time during the reaction of any mixture of the reactants and the products, regardless of whether the system is at equilibrium. Therefore, for the following general reaction:

$$aA + bB \rightleftharpoons cC + dD$$
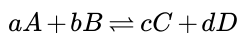
the reaction quotient is defined as follows:

$$Q = \frac{[C]^c [D]^d}{[A]^a [B]^b} \tag{11.6.1}$$

To understand how information is obtained using a reaction Quotient, consider the dissociation of dinitrogen tetroxide to nitrogen dioxide,

$$N_2O_4(g) \rightleftharpoons 2\,NO_2(g)$$
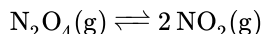
for which $K = 4.65 \times 10^{-3}$ at 298 K. We can write Q for this reaction as follows:

$$Q = \frac{[NO_2]^2}{[N_2O_4]} \tag{11.6.2}$$

The following table lists data from three experiments in which samples of the reaction mixture were obtained and analyzed at equivalent time intervals, and the corresponding values of Q were calculated for each. Each experiment begins with different proportions of product and reactant:

Table 11.6.1: Equilibrium Experiment data

Experiment	$[NO_2]\ (M)$	$[N_2O_4]\ (M)$	$Q = \dfrac{[NO_2]^2}{[N_2O_4]}$
1	0	0.0400	$\dfrac{0^2}{0.0400} = 0$
2	0.0600	0	$\dfrac{(0.0600)^2}{0} = \text{undefined}$
3	0.0200	0.0600	$\dfrac{(0.0200)^2}{0.0600} = 6.67 \times 10^{-3}$

As these calculations demonstrate, Q can have any numerical value between 0 and infinity (undefined); that is, Q can be greater than, less than, or equal to K.

Comparing the magnitudes of Q and K enables us to determine whether a reaction mixture is already at equilibrium and, if it is not, predict how its composition will change with time to reach equilibrium (i.e., whether the reaction will proceed to the right or to the left as written). All you need to remember is that the composition of a system not at equilibrium will change in a way that makes Q approach K:

- If $Q = K$, for example, then the system is already at equilibrium, and **no further change** in the composition of the system will occur unless the conditions are changed.
- If $Q < K$, then the ratio of the concentrations of products to the concentrations of reactants is less than the ratio at equilibrium. Therefore, the reaction will proceed to the **right** as written, forming products at the expense of reactants.
- If $Q > K$, then the ratio of the concentrations of products to the concentrations of reactants is greater than at equilibrium, so the reaction will proceed to the **left** as written, forming reactants at the expense of products.

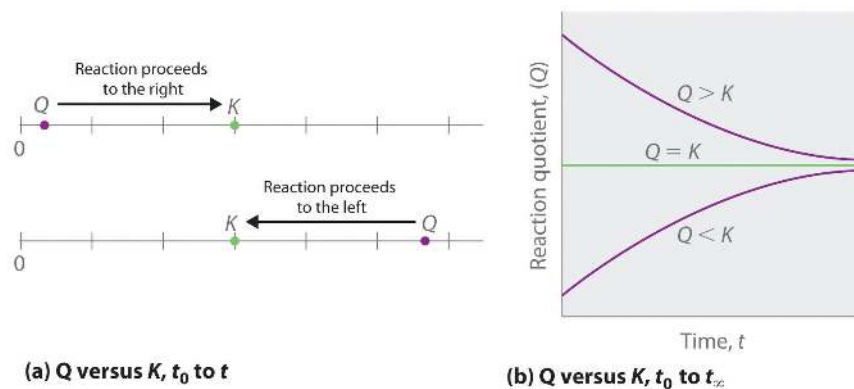These points are illustrated graphically in Figure 11.6.1.

(a) Q versus K, t_0 to t

(b) Q versus K, t_0 to t_∞

Figure 11.6.1: Two Different Ways of Illustrating How the Composition of a System Will Change Depending on the Relative Values of Q and K.(a) Both Q and K are plotted as points along a number line: the system will always react in the way that causes Q to approach K. (b) The change in the composition of a system with time is illustrated for systems with initial values of $Q > K$, $Q < K$, and $Q = K$.

One way is used two number lines. The second way is to use a graph of reaction quotient against time.

> If $Q < K$, the reaction will proceed to the right as written. If $Q > K$, the reaction will proceed to the left as written. If $Q = K$, then the system is at equilibrium.

A Video Discussing Using the Reaction Quotient (Q): Using the Reaction Quotient (Q) (opens in new window) [youtu.be]

✔ Example 11.6.1

At elevated temperatures, methane (CH_4) reacts with water to produce hydrogen and carbon monoxide in what is known as a steam-reforming reaction:

$$\text{CH}_4(g) + \text{H}_2\text{O}(g) \rightleftharpoons \text{CO}(g) + 3\,\text{H}_2(g)$$
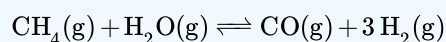
$K = 2.4 \times 10^{-4}$ at 900 K. Huge amounts of hydrogen are produced from natural gas in this way and are then used for the industrial synthesis of ammonia. If 1.2×10^{-2} mol of CH_4, 8.0×10^{-3} mol of H_2O, 1.6×10^{-2} mol of CO, and 6.0×10^{-3} mol of H_2 are placed in a 2.0 L steel reactor and heated to 900 K, will the reaction be at equilibrium or will it proceed to the right to produce CO and H_2 or to the left to form CH_4 and H_2O?

Given: balanced chemical equation, K, amounts of reactants and products, and volume

Asked for: direction of reaction

Strategy:

 A. Calculate the molar concentrations of the reactants and the products.
 B. Use Equation 11.6.1 to determine Q. Compare Q and K to determine in which direction the reaction will proceed.

Solution:

A We must first find the initial concentrations of the substances present. For example, we have $1.2 \times 10^{-2} \, mol$ of CH_4 in a 2.0 L container, so

$$[CH_4] = \frac{1.2 \times 10^{-2} \text{ mol}}{2.0 \text{ L}} = 6.0 \times 10^{-3} \, M$$

We can calculate the other concentrations in a similar way:

- $[H_2O] = 4.0 \times 10^{-3} \, M$,
- $[CO] = 8.0 \times 10^{-3} \, M$, and
- $[H_2] = 3.0 \times 10^{-3} \, M$.

**B** We now compute Q and compare it with K:

$$Q = \frac{[CO][H_2]^3}{[CH_4][H_2O]}$$

$$= \frac{(8.0 \times 10^{-3})(3.0 \times 10^{-3})^3}{(6.0 \times 10^{-3})(4.0 \times 10^{-3})}$$

$$= 9.0 \times 10^{-6}$$

Because $K = 2.4 \times 10^{-4}$, we see that $Q < K$. Thus the ratio of the concentrations of products to the concentrations of reactants is less than the ratio for an equilibrium mixture. The reaction will therefore proceed to the right as written, forming H_2 and CO at the expense of H_2O and CH_4.

? Exercise 11.6.2

In the water–gas shift reaction introduced in Example 11.6.1, carbon monoxide produced by steam-reforming reaction of methane reacts with steam at elevated temperatures to produce more hydrogen:

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$
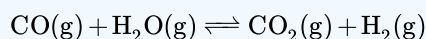
$K = 0.64$ at 900 K. If 0.010 mol of both CO and H_2O, 0.0080 mol of CO_2, and 0.012 mol of H_2 are injected into a 4.0 L reactor and heated to 900 K, will the reaction proceed to the left or to the right as written?

Answer

   $Q = 0.96$. Since (Q > K), so the reaction will proceed to the left, and CO and H_2O will form.

Predicting the Direction of a Reaction with a Graph

By graphing a few equilibrium concentrations for a system at a given temperature and pressure, we can readily see the range of reactant and product concentrations that correspond to equilibrium conditions, for which $Q = K$. Such a graph allows us to predict what will happen to a reaction when conditions change so that Q no longer equals K, such as when a reactant concentration or a product concentration is increased or decreased.

Reaction 1

Lead carbonate decomposes to lead oxide and carbon dioxide according to the following equation:

$$PbCO_3(s) \rightleftharpoons PbO(s) + CO_2(g) \tag{11.6.3}$$
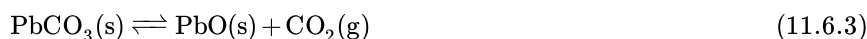
Because $PbCO_3$ and PbO are solids, the equilibrium constant is simply

$$K = [CO_2].$$

At a given temperature, therefore, any system that contains solid $PbCO_3$ and solid PbO will have exactly the same concentration of CO_2 at equilibrium, regardless of the ratio or the amounts of the solids present. This situation is represented in Figure 11.6.3, which shows a plot of $[CO_2]$ versus the amount of $PbCO_3$ added. Initially, the added $PbCO_3$ decomposes completely to CO_2 because the amount of $PbCO_3$ is not sufficient to give a CO_2 concentration equal to K. Thus the left portion of the graph represents a system that is not at equilibrium because it contains only $CO_2(g)$ and $PbO(s)$. In contrast, when just enough $PbCO_3$ has been added to give $[CO_2] = K$, the system has reached equilibrium, and adding more $PbCO_3$ has no effect on the CO_2 concentration: the graph is a horizontal line.

Thus any CO_2 concentration that is not on the horizontal line represents a nonequilibrium state, and the system will adjust its composition to achieve equilibrium, provided enough $PbCO_3$ and PbO are present. For example, the point labeled **A** in Figure 11.6.2 lies above the horizontal line, so it corresponds to a $[CO_2]$ that is greater than the equilibrium concentration of CO_2 (i.e., $Q > K$). To reach equilibrium, the system must decrease $[CO_2]$, which it can do only by reacting CO_2 with solid PbO to form solid $PbCO_3$. Thus the reaction in Equation 11.6.3 will proceed to the left as written, until $[CO_2] = K$. Conversely, the point labeled **B** in Figure 11.6.2 lies below the horizontal line, so it corresponds to a $[CO_2]$ that is less than the equilibrium concentration of CO_2 (i.e., $Q < K$). To reach equilibrium, the system must increase $[CO_2]$, which it can do only by decomposing solid $PbCO_3$ to form CO_2 and solid PbO. The reaction in Equation 11.6.3 will therefore proceed to the right as written, until $[CO_2] = K$.
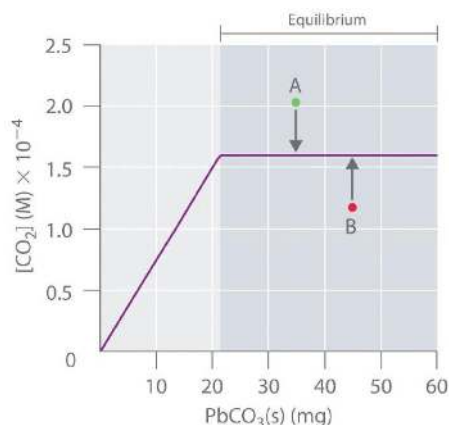

Figure 11.6.2: The Concentration of Gaseous CO_2 in a Closed System at Equilibrium as a Function of the Amount of Solid $PbCO_3$ Added. Initially the concentration of CO2(g) increases linearly with the amount of solid $PbCO_3$ added, as $PbCO_3$ decomposes to $CO_2(g)$ and solid PbO. Once the CO_2 concentration reaches the value that corresponds to the equilibrium concentration, however, adding more solid $PbCO_3$ has no effect on $[CO_2]$, as long as the temperature remains constant.

Reaction 2

In contrast, the reduction of cadmium oxide by hydrogen gives metallic cadmium and water vapor:

$$CdO(s) + H_2(g) \rightleftharpoons Cd(s) + H_2O(g) \tag{11.6.4}$$

and the equilibrium constant is

$$K = \frac{[H_2O]}{[H_2]}.$$

If $[H_2O]$ is doubled at equilibrium, then $[H_2]$ must also be doubled for the system to remain at equilibrium. A plot of $[H_2O]$ versus $[H_2]$ at equilibrium is a straight line with a slope of K (Figure 11.6.3). Again, only those pairs of concentrations of H_2O and H_2 that lie on the line correspond to equilibrium states. Any point representing a pair of concentrations that does not lie on the line corresponds to a nonequilibrium state. In such cases, the reaction in Equation 11.6.4 will proceed in whichever direction causes the composition of the system to move toward the equilibrium line. For example, point **A** in Figure 11.6.3 lies below the line, indicating that the $[H_2O]/[H_2]$ ratio is less than the ratio of an equilibrium mixture (i.e., $Q < K$). Thus the reaction in Equation 11.6.4 will proceed to the right as written, consuming H_2 and producing H_2O, which causes the concentration ratio to move up and to the left toward the equilibrium line. Conversely, point **B** in Figure 11.6.3 lies above the line, indicating that the $[H_2O]/[H_2]$

ratio is greater than the ratio of an equilibrium mixture ($Q > K$). Thus the reaction in Equation 11.6.4 will proceed to the left as written, consuming H_2O and producing H_2, which causes the concentration ratio to move down and to the right toward the equilibrium line.
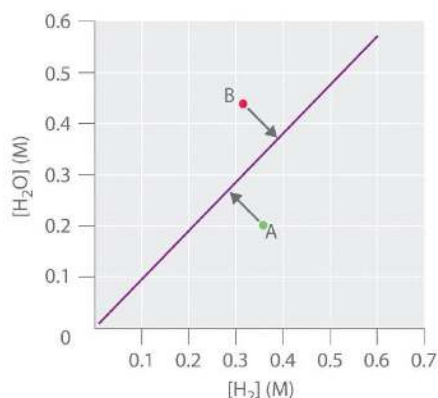

Figure 11.6.3: The Concentration of Water Vapor versus the Concentration of Hydrogen for the $CdO_{(s)} + H_{2(g)} \rightleftharpoons Cd_{(s)} + H_2O_{(g)}$ System at Equilibrium. For any equilibrium concentration of $H_2O_{(g)}$, there is only one equilibrium concentration of $H_{2(g)}$. Because the magnitudes of the two concentrations are directly proportional, a large $[H_2O]$ at equilibrium requires a large $[H_2]$ and vice versa. In this case, the slope of the line is equal to K.

Reaction 3

In another example, solid ammonium iodide dissociates to gaseous ammonia and hydrogen iodide at elevated temperatures:

$$NH_4I(s) \rightleftharpoons NH_3(g) + HI(g) \tag{11.6.5}$$

For this system, K is equal to the product of the concentrations of the two products:

$$K = [NH_3][HI].$$

If we double the concentration of NH_3, the concentration of HI must decrease by approximately a factor of 2 to maintain equilibrium, as shown in Figure 11.6.4 As a result, for a given concentration of either HI or NH_3, only a single equilibrium composition that contains equal concentrations of both NH_3 and HI is possible, for which

$$[NH_3] = [HI] = \sqrt{K}.$$

Any point that lies below and to the left of the equilibrium curve (such as point **A** in Figure 11.6.4) corresponds to $Q < K$, and the reaction in Equation 11.6.5 will therefore proceed to the right as written, causing the composition of the system to move toward the equilibrium line. Conversely, any point that lies above and to the right of the equilibrium curve (such as point **B** in Figure 11.6.5) corresponds to $Q > K$, and the reaction in Equation 11.6.5 will therefore proceed to the left as written, again causing the composition of the system to move toward the equilibrium line. By graphing equilibrium concentrations for a given system at a given temperature and pressure, we can predict the direction of reaction of that mixture when the system is not at equilibrium.
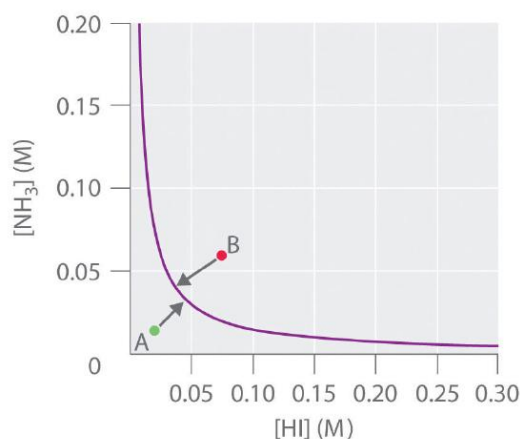
Figure 11.6.4: The Concentration of $NH_{3(g)}$ versus the Concentration of $HI_{(g)}$ for system in Reaction 11.6.5 at Equilibrium. Only one equilibrium concentration of $NH_3(g)$ is possible for any given equilibrium concentration of $HI(g)$. In this case, the two are inversely proportional. Thus a large $[HI]$ at equilibrium requires a small $[NH_3]$ at equilibrium and vice versa.

Summary

The reaction Quotient (Q) is used to determine whether a system is at equilibrium and if it is not, to predict the direction of reaction. The reaction Quotient (Q or Q_p) has the same form as the equilibrium constant expression, but it is derived from concentrations obtained at any time. When a reaction system is at equilibrium, $Q = K$. Graphs derived by plotting a few equilibrium concentrations for a system at a given temperature and pressure can be used to predict the direction in which a reaction will proceed. Points that do not lie on the line or curve represent nonequilibrium states, and the system will adjust, if it can, to achieve equilibrium.

11.6: The Reaction Quotient- Predicting the Direction of Change is shared under a not declared license and was authored, remixed, and/or curated by LibreTexts.

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11.7: Finding Equilibrium Concentrations

> **◀◗ Learning Objectives**
>
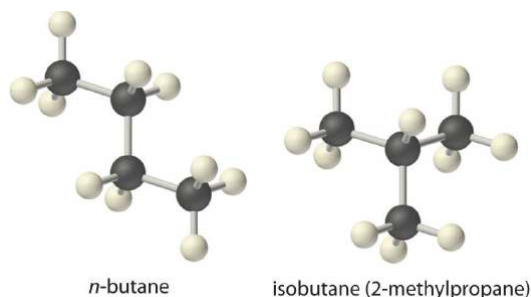> - To solve quantitative problems involving chemical equilibriums.

There are two fundamental kinds of equilibrium problems:

1. those in which we are given the concentrations of the reactants and the products at equilibrium (or, more often, information that allows us to calculate these concentrations), and we are asked to calculate the equilibrium constant for the reaction; and
2. those in which we are given the equilibrium constant and the initial concentrations of reactants, and we are asked to calculate the concentration of one or more substances at equilibrium. In this section, we describe methods for solving both kinds of problems.

Calculating an Equilibrium Constant from Equilibrium Concentrations

We saw in the exercise in Example 6 in Section 15.2 that the equilibrium constant for the decomposition of $CaCO_{3(s)}$ to $CaO_{(s)}$ and $CO_{2(g)}$ is $K = [CO_2]$. At 800°C, the concentration of CO_2 in equilibrium with solid $CaCO_3$ and CaO is $2.5 \times 10^{-3}\ M$. Thus K at 800°C is 2.5×10^{-3}. (Remember that equilibrium constants are unitless.)

A more complex example of this type of problem is the conversion of n-butane, an additive used to increase the volatility of gasoline, into isobutane (2-methylpropane).

n-butane   isobutane (2-methylpropane)

This reaction can be written as follows:

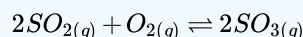$$\text{n-butane}_{(g)} \rightleftharpoons \text{isobutane}_{(g)} \tag{11.7.1}$$

and the equilibrium constant $K = [\text{isobutane}]/[\text{n-butane}]$. At equilibrium, a mixture of n-butane and isobutane at room temperature was found to contain 0.041 M isobutane and 0.016 M n-butane. Substituting these concentrations into the equilibrium constant expression,

$$K = \frac{[isobutane]}{[n\text{-}butane]} = 0.041\ M = 2.6 \tag{11.7.2}$$

Thus the equilibrium constant for the reaction as written is 2.6.

> **✔ Example 11.7.1**
>
> The reaction between gaseous sulfur dioxide and oxygen is a key step in the industrial synthesis of sulfuric acid:
>
> $$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$$
>
> A mixture of SO_2 and O_2 was maintained at 800 K until the system reached equilibrium. The equilibrium mixture contained
>
> - $5.0 \times 10^{-2}\ M\ SO_3$,
> - $3.5 \times 10^{-3}\ M\ O_2$, and
> - $3.0 \times 10^{-3}\ M\ SO_2$.
>
> Calculate K and K_p at this temperature.

Given: balanced equilibrium equation and composition of equilibrium mixture

Asked for: equilibrium constant

Strategy

Write the equilibrium constant expression for the reaction. Then substitute the appropriate equilibrium concentrations into this equation to obtain K.

Solution

Substituting the appropriate equilibrium concentrations into the equilibrium constant expression,

$$K = \frac{[SO_3]^2}{[SO_2]^2[O_2]} = \frac{(5.0 \times 10^{-2})^2}{(3.0 \times 10^{-3})^2(3.5 \times 10^{-3})} = 7.9 \times 10^4$$

To solve for K_p, we use the relationship derived previously

$$K_p = K(RT)^{\Delta n}$$

where $\Delta n = 2 - 3 = -1$:

$$K_p = K(RT)^{\Delta n}$$

$$K_p = 7.9 \times 10^4 [(0.08206 \ L \cdot atm/mol \cdot K)(800K)]^{-1}$$

$$K_p = 1.2 \times 10^3$$

? Exercise 11.7.1

Hydrogen gas and iodine react to form hydrogen iodide via the reaction

$$2NOCl_{(g)} \leftrightharpoons 2NO_{(g)} + Cl_{2(g)}$$

A mixture of H_2 and I_2 was maintained at 740 K until the system reached equilibrium. The equilibrium mixture contained

- $1.37 \times 10^{-2} \ M \ HI$,
- $6.47 \times 10^{-3} \ M \ H_2$, and
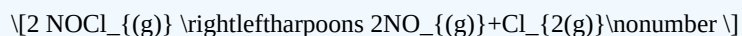- $5.94 \times 10^{-4} \ M \ I_2$.

Calculate K and K_p for this reaction.

Answer

$K = 48.8$ and $K_p = 48.8$

Chemists are not often given the concentrations of all the substances, and they are not likely to measure the equilibrium concentrations of all the relevant substances for a particular system. In such cases, we can obtain the equilibrium concentrations from the initial concentrations of the reactants and the balanced chemical equation for the reaction, as long as the equilibrium concentration of one of the substances is known. Example $11.7.2$ shows one way to do this.

✔ Example 11.7.2

A 1.00 mol sample of $NOCl$ was placed in a 2.00 L reactor and heated to 227°C until the system reached equilibrium. The contents of the reactor were then analyzed and found to contain 0.056 mol of Cl_2. Calculate K at this temperature. The equation for the decomposition of $NOCl$ to NO and Cl_2 is as follows:

$$2 NOCl_{(g)} \rightleftharpoons 2NO_{(g)} + Cl_{2(g)}$$

Given: balanced equilibrium equation, amount of reactant, volume, and amount of one product at equilibrium
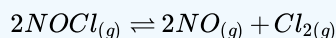
Asked for: K

Strategy:

A. Write the equilibrium constant expression for the reaction. Construct a table showing the initial concentrations, the changes in concentrations, and the final concentrations (as initial concentrations plus changes in concentrations).
B. Calculate all possible initial concentrations from the data given and insert them in the table.
C. Use the coefficients in the balanced chemical equation to obtain the changes in concentration of all other substances in the reaction. Insert those concentration changes in the table.
D. Obtain the final concentrations by summing the columns. Calculate the equilibrium constant for the reaction.

Solution

A The first step in any such problem is to balance the chemical equation for the reaction (if it is not already balanced) and use it to derive the equilibrium constant expression. In this case, the equation is already balanced, and the equilibrium constant expression is as follows:

$$K = \frac{[NO]^2[Cl_2]}{[NOCl]^2}$$

To obtain the concentrations of $NOCl$, NO, and Cl_2 at equilibrium, we construct a table showing what is known and what needs to be calculated. We begin by writing the balanced chemical equation at the top of the table, followed by three lines corresponding to the initial concentrations, the changes in concentrations required to get from the initial to the final state, and the final concentrations.

$$2NOCl_{(g)} \rightleftharpoons 2NO_{(g)} + Cl_{2(g)}$$

ICE	$[NOCl]$	$[NO]$	$[Cl_2]$
Initial			
Change			
Final			

B Initially, the system contains 1.00 mol of $NOCl$ in a 2.00 L container. Thus $[NOCl]_i = 1.00\ mol/2.00\ L = 0.500\ M$ The initial concentrations of NO and Cl_2 are $0\ M$ because initially no products are present. Moreover, we are told that at equilibrium the system contains 0.056 mol of Cl_2 in a 2.00 L container, so $[Cl_2]_f = 0.056\ mol/2.00\ L = 0.028\ M$ We insert these values into the following table:

$$2NOCl_{(g)} \rightleftharpoons 2NO_{(g)} + Cl_{2(g)}$$

ICE	$[NOCl]$	$[NO]$	$[Cl_2]$
Initial	0.500	0	0
Change			
Final			0.028

C We use the stoichiometric relationships given in the balanced chemical equation to find the change in the concentration of Cl_2, the substance for which initial and final concentrations are known:

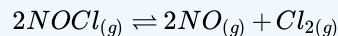$$\Delta[Cl_2] = 0.028\ M_{(final)} - 0.00\ M_{(initial)}] = +0.028\ M$$

According to the coefficients in the balanced chemical equation, 2 mol of NO are produced for every 1 mol of Cl_2, so the change in the NO concentration is as follows:

$$\Delta[NO] = \left(\frac{0.028\ mol\ Cl_2}{L} \right) \left(\frac{2\ mol\ NO}{1\ mol\ Cl_2} \right) = 0.056\ M$$

Similarly, 2 mol of $NOCl$ are consumed for every 1 mol of Cl_2 produced, so the change in the $NOCl$ concentration is as follows:

$$\Delta[NOCl] = \left(\frac{0.028 \ mol \ Cl_2}{L} \right) \left(\frac{-2 \ mol \ NOCl}{1 \ mol \ Cl_2} \right) = -0.056 \ M$$

We insert these values into our table:

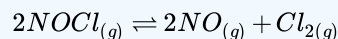$$2NOCl_{(g)} \rightleftharpoons 2NO_{(g)} + Cl_{2(g)}$$

ICE	[NOCl]	[NO]	$[Cl_2]$
Initial	0.500	0	0
Change	−0.056	+0.056	+0.028
Final			0.028

D We sum the numbers in the $[NOCl]$ and $[NO]$ columns to obtain the final concentrations of NO and $NOCl$:

$$[NO]_f = 0.000 \ M + 0.056 \ M = 0.056 \ M$$

$$[NOCl]_f = 0.500 \ M + (-0.056 \ M) = 0.444M$$

We can now complete the table:

$$2NOCl_{(g)} \rightleftharpoons 2NO_{(g)} + Cl_{2(g)}$$

ICE	\([NOCl]	[NO]	$[Cl_2]$
initial	0.500	0	0
change	−0.056	+0.056	+0.028
final	0.444	0.056	0.028

We can now calculate the equilibrium constant for the reaction:

$$K = \frac{[NO]^2[Cl_2]}{[NOCl]^2} = \frac{(0.056)^2(0.028)}{(0.444)^2} = 4.5 \times 10^{-4}$$

? Exercise 11.7.2

The German chemist Fritz Haber (1868–1934; Nobel Prize in Chemistry 1918) was able to synthesize ammonia (NH_3) by reacting 0.1248 M H_2 and 0.0416 M N_2 at about 500°C. At equilibrium, the mixture contained 0.00272 M NH_3. What is K for the reaction

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

at this temperature? What is K_p?

Answer

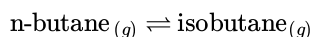$K = 0.105$ and $K_p = 2.61 \times 10^{-5}$

A Video Disucssing Using ICE Tables to find Kc: Using ICE Tables to find Kc(opens in new window) [youtu.be]
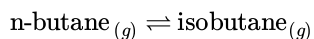
Calculating Equilibrium Concentrations from the Equilibrium Constant

To describe how to calculate equilibrium concentrations from an equilibrium constant, we first consider a system that contains only a single product and a single reactant, the conversion of n-butane to isobutane (Equation 11.7.1), for which K = 2.6 at 25°C. If we begin with a 1.00 M sample of n-butane, we can determine the concentration of n-butane and isobutane at equilibrium by constructing a table showing what is known and what needs to be calculated, just as we did in Example 11.7.2

$$\text{n-butane}_{(g)} \rightleftharpoons \text{isobutane}_{(g)}$$

ICE	$[\text{n-butane}_{(g)}]$	$[\text{isobutane}_{(g)}]$
Initial		
Change		
Final		

The initial concentrations of the reactant and product are both known: [n-butane]i = 1.00 M and [isobutane]i = 0 M. We need to calculate the equilibrium concentrations of both n-butane and isobutane. Because it is generally difficult to calculate final concentrations directly, we focus on the change in the concentrations of the substances between the initial and the final (equilibrium) conditions. If, for example, we define the change in the concentration of isobutane (Δ[isobutane]) as $+x$, then the change in the concentration of n-butane is Δ[n-butane] = $-x$. This is because the balanced chemical equation for the reaction tells us that 1 mol of n-butane is consumed for every 1 mol of isobutane produced. We can then express the final concentrations in terms of the initial concentrations and the changes they have undergone.

$$\text{n-butane}_{(g)} \rightleftharpoons \text{isobutane}_{(g)}$$

ICE	$[\text{n-butane}_{(g)}]$	$[\text{isobutane}_{(g)}]$
Initial	1.00	0
Change	$-x$	$+x$
Final	$(1.00 - x)$	$(0 + x) = x$

Substituting the expressions for the final concentrations of n-butane and isobutane from the table into the equilibrium equation,

$$K = \frac{[\text{isobutane}]}{[\text{n-butane}]} = \frac{x}{1.00 - x} = 2.6$$

Rearranging and solving for x,

$$x = 2.6(1.00 - x) = 2.6 - 2.6x$$

$$x + 2.6x = 2.6$$

$$x = 0.72$$

We obtain the final concentrations by substituting this x value into the expressions for the final concentrations of n-butane and isobutane listed in the table:

$$[\text{n-butane}]_f = (1.00 - x)M = (1.00 - 0.72)M = 0.28 \ M$$

$$[\text{isobutane}]_f = (0.00 + x)M = (0.00 + 0.72)M = 0.72 \ M$$

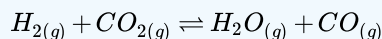We can check the results by substituting them back into the equilibrium constant expression to see whether they give the same K that we used in the calculation:

$$K = \frac{[\text{isobutane}]}{[\text{n-butane}]} = \left(\frac{0.72 \ \cancel{M}}{0.28 \ \cancel{M}} \right) = 2.6$$

This is the same K we were given, so we can be confident of our results.

Example 11.7.3 illustrates a common type of equilibrium problem that you are likely to encounter.

> **✔ Example 11.7.3: The water–gas shift reaction**
>
> The water–gas shift reaction is important in several chemical processes, such as the production of H₂ for fuel cells. This reaction can be written as follows:
>
> $$H_{2(g)} + CO_{2(g)} \rightleftharpoons H_2O_{(g)} + CO_{(g)}$$
>
> $K = 0.106$ at 700 K. If a mixture of gases that initially contains 0.0150 M H_2 and 0.0150 M CO_2 is allowed to equilibrate at 700 K, what are the final concentrations of all substances present?
>
> **Given**: balanced equilibrium equation, K, and initial concentrations
>
> Asked for: final concentrations
>
> **Strategy**:
>
> A. Construct a table showing what is known and what needs to be calculated. Define x as the change in the concentration of one substance. Then use the reaction stoichiometry to express the changes in the concentrations of the other substances in terms of x. From the values in the table, calculate the final concentrations.
> B. Write the equilibrium equation for the reaction. Substitute appropriate values from the ICE table to obtain x.
> C. Calculate the final concentrations of all species present. Check your answers by substituting these values into the equilibrium constant expression to obtain K.
>
> **Solution**
> A The initial concentrations of the reactants are $[H_2]_i = [CO_2]_i = 0.0150 \ M$. Just as before, we will focus on the change in the concentrations of the various substances between the initial and final states. If we define the change in the concentration of H_2O as x, then $\Delta[H_2O] = +x$. We can use the stoichiometry of the reaction to express the changes in the concentrations of the other substances in terms of x. For example, 1 mol of CO is produced for every 1 mol of H_2O, so the change in the CO concentration can be expressed as $\Delta[CO] = +x$. Similarly, for every 1 mol of H_2O produced, 1 mol each of H_2 and CO_2 are consumed, so the change in the concentration of the reactants is $\Delta[H_2] = \Delta[CO_2] = -x$. We enter the values in the following table and calculate the final concentrations.
>
> $$H_{2(g)} + CO_{2(g)} \rightleftharpoons H_2O_{(g)} + CO_{(g)}$$
>
> | ICE | $[H_2]$ | $[CO_2]$ | $[H_2O]$ | $[CO]$ |
> |---|---|---|---|---|
> | **Initial** | 0.0150 | 0.0150 | 0 | 0 |
> | **Change** | $-x$ | $-x$ | $+x$ | $+x$ |
> | **Final** | $(0.0150 - x)$ | $(0.0150 - x)$ | x | x |

B We can now use the equilibrium equation and the given K to solve for x:

$$K = \frac{[H_2O][CO]}{[H_2][CO_2]} = \frac{(x)(x)}{(0.0150 - x)(0.0150 - x)} = \frac{x^2}{(0.0150 - x)^2} = 0.106$$

We could solve this equation with the quadratic formula, but it is far easier to solve for x by recognizing that the left side of the equation is a perfect square; that is,

$$\frac{x^2}{(0.0150 - x)^2} = \left(\frac{x}{0.0150 - x}\right)^2 = 0.106$$

Taking the square root of the middle and right terms,

$$\frac{x}{(0.0150 - x)} = (0.106)^{1/2} = 0.326$$

$$x = (0.326)(0.0150) - 0.326x$$

$$1.326x = 0.00489$$

$$x = 0.00369 = 3.69 \times 10^{-3}$$

C The final concentrations of all species in the reaction mixture are as follows:

- $[H_2]_f = [H_2]_i + \Delta[H_2] = (0.0150 - 0.00369)\ M = 0.0113\ M$
- $[CO_2]_f = [CO_2]_i + \Delta[CO_2] = (0.0150 - 0.00369)\ M = 0.0113\ M$
- $[H_2O]_f = [H_2O]_i + \Delta[H_2O] = (0 + 0.00369)\ M = 0.00369\ M$
- $[CO]_f = [CO]_i + \Delta[CO] = (0 + 0.00369)\ M = 0.00369\ M$

We can check our work by inserting the calculated values back into the equilibrium constant expression:

$$K = \frac{[H_2O][CO]}{[H_2][CO_2]} = \frac{(0.00369)^2}{(0.0113)^2} = 0.107$$

To two significant figures, this K is the same as the value given in the problem, so our answer is confirmed.

? Exercise 11.7.3

Hydrogen gas reacts with iodine vapor to give hydrogen iodide according to the following chemical equation:

$$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$$
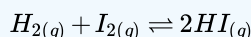
$K = 54$ at 425°C. If 0.172 M H_2 and I_2 are injected into a reactor and maintained at 425°C until the system equilibrates, what is the final concentration of each substance in the reaction mixture?

Answer

- $[HI]_f = 0.270\ M$
- $[H_2]_f = [I_2]_f = 0.037\ M$

In Example 11.7.3, the initial concentrations of the reactants were the same, which gave us an equation that was a perfect square and simplified our calculations. Often, however, the initial concentrations of the reactants are not the same, and/or one or more of the products may be present when the reaction starts. Under these conditions, there is usually no way to simplify the problem, and we must determine the equilibrium concentrations with other means. Such a case is described in Example 11.7.4.

✔ Example 11.7.4

In the water–gas shift reaction shown in Example 11.7.3, a sample containing 0.632 M CO2 and 0.570 M H_2 is allowed to equilibrate at 700 K. At this temperature, $K = 0.106$. What is the composition of the reaction mixture at equilibrium?

**Given**: balanced equilibrium equation, concentrations of reactants, and K

Asked for: composition of reaction mixture at equilibrium

Strategy:

A. Write the equilibrium equation. Construct a table showing the initial concentrations of all substances in the mixture. Complete the table showing the changes in the concentrations (\(x) and the final concentrations.
B. Write the equilibrium constant expression for the reaction. Substitute the known K value and the final concentrations to solve for x.
C. Calculate the final concentration of each substance in the reaction mixture. Check your answers by substituting these values into the equilibrium constant expression to obtain K.

Solution

A $[CO_2]_i = 0.632\ M$ and $[H_2]_i = 0.570\ M$. Again, x is defined as the change in the concentration of H_2O: $\Delta[H_2O] = +x$. Because 1 mol of CO is produced for every 1 mol of H_2O, the change in the concentration of CO is the same as the change in the concentration of H2O, so $\Delta[CO] = +x$. Similarly, because 1 mol each of H_2 and CO_2 are consumed for every 1 mol of H_2O produced, $\Delta[H_2] = \Delta[CO_2] = -x$. The final concentrations are the sums of the initial concentrations and the changes in concentrations at equilibrium.
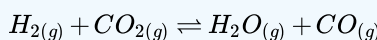
$$H_{2(g)} + CO_{2(g)} \rightleftharpoons H_2O_{(g)} + CO_{(g)}$$

ICE	$H_{2(g)}$	$CO_{2(g)}$	$H_2O_{(g)}$	$CO_{(g)}$
Initial	0.570	0.632	0	0
Change	$-x$	$-x$	$+x$	$+x$
Final	$(0.570 - x)$	$(0.632 - x)$	x	x

B We can now use the equilibrium equation and the known K value to solve for x:

$$K = \frac{[H_2O][CO]}{[H_2][CO_2]} = \frac{x^2}{(0.570 - x)(0.632 - x)} = 0.106$$

In contrast to Example 11.7.3, however, there is no obvious way to simplify this expression. Thus we must expand the expression and multiply both sides by the denominator:

$$x^2 = 0.106(0.360 - 1.202x + x^2)$$

Collecting terms on one side of the equation,

$$0.894x^2 + 0.127x - 0.0382 = 0$$

This equation can be solved using the quadratic formula:

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{-0.127 \pm \sqrt{(0.127)^2 - 4(0.894)(-0.0382)}}{2(0.894)}$$

$$x = 0.148 \text{ and } -0.290$$

Only the answer with the positive value has any physical significance, so $\Delta[H_2O] = \Delta[CO] = +0.148M$, and $\Delta[H_2] = \Delta[CO_2] = -0.148\ M$.

C The final concentrations of all species in the reaction mixture are as follows:

- $[H_2]_f [= [H_2]_i + \Delta[H_2] = 0.570\ M - 0.148\ M = 0.422M$
- $[CO_2]_f = [CO_2]_i + \Delta[CO_2] = 0.632\ M - 0.148\ M = 0.484M$
- $[H_2O]_f = [H_2O]_i + \Delta[H_2O] = 0\ M + 0.148\ M = 0.148\ M$
- $[CO]_f = [CO]_i + \Delta[CO] = 0M + 0.148\ M = 0.148M$

We can check our work by substituting these values into the equilibrium constant expression:

$$K = \frac{[H_2O][CO]}{[H_2][CO_2]} = \frac{(0.148)^2}{(0.422)(0.484)} = 0.107$$

Because K is essentially the same as the value given in the problem, our calculations are confirmed.

? Exercise 11.7.4

The exercise in Example 11.7.1 showed the reaction of hydrogen and iodine vapor to form hydrogen iodide, for which $K = 54$ at 425°C. If a sample containing 0.200 M H_2 and 0.0450 M I_2 is allowed to equilibrate at 425°C, what is the final concentration of each substance in the reaction mixture?

Answer

- $[H_I]_f = 0.0882 \ M$
- $[H_2]_f = 0.156 \ M$
- $[I_2]_f = 9.2 \times 10^{-4} M$

In many situations it is not necessary to solve a quadratic (or higher-order) equation. Most of these cases involve reactions for which the equilibrium constant is either very small ($K \leq 10^{-3}$) or very large ($K \geq 10^{3}$), which means that the change in the concentration (defined as x) is essentially negligible compared with the initial concentration of a substance. Knowing this simplifies the calculations dramatically, as illustrated in Example 11.7.5.

✔ Example 11.7.5

Atmospheric nitrogen and oxygen react to form nitric oxide:

$$N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$$

with $K_p = 2.0 \times 10^{-31}$ at 25°C.

What is the partial pressure of NO in equilibrium with N_2 and O_2 in the atmosphere (at 1 atm, $P_{N_2} = 0.78 \ atm$ and $P_{O_2} = 0.21 \ atm$?

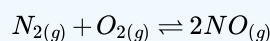**Given**: balanced equilibrium equation and values of K_p, P_{O_2}, and P_{N_2}

Asked for: partial pressure of NO

Strategy:

A. Construct a table and enter the initial partial pressures, the changes in the partial pressures that occur during the course of the reaction, and the final partial pressures of all substances.
B. Write the equilibrium equation for the reaction. Then substitute values from the table to solve for the change in concentration (\(x).
C. Calculate the partial pressure of NO. Check your answer by substituting values into the equilibrium equation and solving for K.

Solution

A Because we are given Kp and partial pressures are reported in atmospheres, we will use partial pressures. The initial partial pressure of O_2 is 0.21 atm and that of N_2 is 0.78 atm. If we define the change in the partial pressure of NO as $2x$, then the change in the partial pressure of O_2 and of N_2 is $-x$ because 1 mol each of N_2 and of O_2 is consumed for every 2 mol of NO produced. Each substance has a final partial pressure equal to the sum of the initial pressure and the change in that pressure at equilibrium.

$$N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$$

ICE	P_{N_2}	P_{O_2}	P_{NO}
Initial	0.78	0.21	0
Change	$-x$	$-x$	$+2x$

ICE	P_{N_2}	P_{O_2}	P_{NO}
Final	$(0.78 - x)$	$(0.21 - x)$	$2x$

B Substituting these values into the equation for the equilibrium constant,

$$K_p = \frac{(P_{NO})^2}{(P_{N_2})(P_{O_2})} = \frac{(2x)^2}{(0.78 - x)(0.21 - x)} = 2.0 \times 10^{-31}$$

In principle, we could multiply out the terms in the denominator, rearrange, and solve the resulting quadratic equation. In practice, it is far easier to recognize that an equilibrium constant of this magnitude means that the extent of the reaction will be very small; therefore, the x value will be negligible compared with the initial concentrations. If this assumption is correct, then to two significant figures, $(0.78 - x) = 0.78$ and $(0.21 - x) = 0.21$. Substituting these expressions into our original equation,

$$\frac{(2x)^2}{(0.78)(0.21)} = 2.0 \times 10^{-31}$$

$$\frac{4x^2}{0.16} = 2.0 \times 10^{-31}$$

$$x^2 = \frac{0.33 \times 10^{-31}}{4}$$

$$x^= 9.1 \times 10^{-17}$$

C Substituting this value of x into our expressions for the final partial pressures of the substances,

- $P_{NO} = 2x \; atm = 1.8 \times 10^{-16} \; atm$
- $P_{N_2} = (0.78 - x) \; atm = 0.78 \; atm$
- $P_{O_2} = (0.21 - x) \; atm = 0.21 \; atm$

From these calculations, we see that our initial assumption regarding x was correct: given two significant figures, 2.0×10^{-16} is certainly negligible compared with 0.78 and 0.21. When can we make such an assumption? As a general rule, if x is less than about 5% of the total, or $10^{-3} > K > 10^3$, then the assumption is justified. Otherwise, we must use the quadratic formula or some other approach. The results we have obtained agree with the general observation that toxic NO, an ingredient of smog, does not form from atmospheric concentrations of N_2 and O_2 to a substantial degree at 25°C. We can verify our results by substituting them into the original equilibrium equation:

$$K_p = \frac{(P_{NO})^2}{(P_{N_2})(P_{O_2})} = \frac{(1.8 \times 10^{-16})^2}{(0.78)(0.21)} = 2.0 \times 10^{-31}$$

The final K_p agrees with the value given at the beginning of this example.

? Exercise 11.7.5

Under certain conditions, oxygen will react to form ozone, as shown in the following equation:

$$3O_{2(g)} \rightleftharpoons 2O_{3(g)}$$

with $K_p = 2.5 \times 10^{-59}$ at 25°C. What ozone partial pressure is in equilibrium with oxygen in the atmosphere ($P_{O_2} = 0.21 \; atm$)?
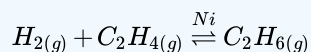
Answer

$4.8 \times 10^{-31} \; atm$

Another type of problem that can be simplified by assuming that changes in concentration are negligible is one in which the equilibrium constant is very large ($K \geq 10^3$). A large equilibrium constant implies that the reactants are converted almost entirely to products, so we can assume that the reaction proceeds 100% to completion. When we solve this type of problem, we view the

system as equilibrating from the products side of the reaction rather than the reactants side. This approach is illustrated in Example 11.7.6.

The chemical equation for the reaction of hydrogen with ethylene (C_2H_4) to give ethane (C_2H_6) is as follows:

$$H_{2(g)} + C_2H_{4(g)} \overset{Ni}{\rightleftharpoons} C_2H_{6(g)}$$

with $K = 9.6 \times 10^{18}$ at 25°C. If a mixture of 0.200 M H_2 and 0.155 M C_2H_4 is maintained at 25°C in the presence of a powdered nickel catalyst, what is the equilibrium concentration of each substance in the mixture?

Given: balanced chemical equation, K, and initial concentrations of reactants

Asked for: equilibrium concentrations

Strategy:

A. Construct a table showing initial concentrations, concentrations that would be present if the reaction were to go to completion, changes in concentrations, and final concentrations.
B. Write the equilibrium constant expression for the reaction. Then substitute values from the table into the expression to solve for x (the change in concentration).
C. Calculate the equilibrium concentrations. Check your answers by substituting these values into the equilibrium equation.

Solution:

A From the magnitude of the equilibrium constant, we see that the reaction goes essentially to completion. Because the initial concentration of ethylene (0.155 M) is less than the concentration of hydrogen (0.200 M), ethylene is the limiting reactant; that is, no more than 0.155 M ethane can be formed from 0.155 M ethylene. If the reaction were to go to completion, the concentration of ethane would be 0.155 M and the concentration of ethylene would be 0 M. Because the concentration of hydrogen is greater than what is needed for complete reaction, the concentration of unreacted hydrogen in the reaction mixture would be 0.200 M − 0.155 M = 0.045 M. The equilibrium constant for the forward reaction is very large, so the equilibrium constant for the reverse reaction must be very small. The problem then is identical to that in Example 11.7.5. If we define $-x$ as the change in the ethane concentration for the reverse reaction, then the change in the ethylene and hydrogen concentrations is $+x$. The final equilibrium concentrations are the sums of the concentrations for the forward and reverse reactions.

$$H_{2(g)} + C_2H_{4(g)} \overset{Ni}{\rightleftharpoons} C_2H_{6(g)}$$

IACE	$[\boldsymbol{H_{2(g)}}]$	$[\boldsymbol{C_2H_{4(g)}}]$	$[\boldsymbol{C_2H_{6(g)}}]$
Initial	0.200	0.155	0
Assuming 100% reaction	0.045	0	0.155
Change	$+x$	$+x$	$-x$
Final	$(0.045 + x)$	$(0 + x)$	$(0.155 - x)$

B Substituting values into the equilibrium constant expression,

$$K = \frac{[C_2H_6]}{[H_2][C_2H_4]} = \frac{0.155 - x}{(0.045 + x)x} = 9.6 \times 10^{18}$$

Once again, the magnitude of the equilibrium constant tells us that the equilibrium will lie far to the right as written, so the reverse reaction is negligible. Thus x is likely to be very small compared with either 0.155 M or 0.045 M, and the equation can be simplified ($(0.045 + x) = 0.045$ and $(0.155 - x) = 0.155$) as follows:

$$K = \frac{0.155}{0.045x} = 9.6 \times 10^{18}$$

$$x = 3.6 \times 10^{-19}$$

C The small x value indicates that our assumption concerning the reverse reaction is correct, and we can therefore calculate the final concentrations by evaluating the expressions from the last line of the table:

- $[C_2H_6]_f = (0.155 - x)\ M = 0.155\ M$
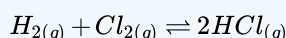- $[C_2H_4]_f = x\ M = 3.6 \times 10^{-19} M$
- $[H_2]_f = (0.045 + x)\ M = 0.045\ M$

We can verify our calculations by substituting the final concentrations into the equilibrium constant expression:

$$K = \frac{[C_2H_6]}{[H_2][C_2H_4]} = \frac{0.155}{(0.045)(3.6 \times 10^{-19})} = 9.6 \times 10^{18}$$

This K value agrees with our initial value at the beginning of the example.

? Exercise 11.7.6

Hydrogen reacts with chlorine gas to form hydrogen chloride:

$$H_{2(g)} + Cl_{2(g)} \rightleftharpoons 2HCl_{(g)}$$

with $K_p = 4.0 \times 10^{31}$ at 47°C. If a mixture of 0.257 M H_2 and 0.392 M Cl_2 is allowed to equilibrate at 47°C, what is the equilibrium composition of the mixture?

Answer

$[H_2]_f = 4.8 \times 10^{-32}\ M\ \ [Cl_2]_f = 0.135\ M\ [HCl]_f = 0.514\ M$

A Video Discussing Using ICE Tables to find Eq. Concentrations & Kc: Using ICE Tables to find Eq. Concentrations & Kc(opens in new window) [youtu.be]

Summary

Various methods can be used to solve the two fundamental types of equilibrium problems: (1) those in which we calculate the concentrations of reactants and products at equilibrium and (2) those in which we use the equilibrium constant and the initial concentrations of reactants to determine the composition of the equilibrium mixture. When an equilibrium constant is calculated from equilibrium concentrations, molar concentrations or partial pressures are substituted into the equilibrium constant expression for the reaction. Equilibrium constants can be used to calculate the equilibrium concentrations of reactants and products by using the quantities or concentrations of the reactants, the stoichiometry of the balanced chemical equation for the reaction, and a tabular format to obtain the final concentrations of all species at equilibrium.

11.8: Le Châtelier's Principle- How a System at Equilibrium Responds to Disturbances

◑ Learning Objectives

- Describe the ways in which an equilibrium system can be stressed
- Predict the response of a stressed equilibrium using Le Chatelier's principle

As we saw in the previous section, reactions proceed in both directions (reactants go to products and products go to reactants). We can tell a reaction is at equilibrium if the reaction quotient (Q) is equal to the equilibrium constant (K). We next address what happens when a system at equilibrium is disturbed so that Q is no longer equal to K. If a system at equilibrium is subjected to a perturbance or stress (such as a change in concentration) the position of equilibrium changes. Since this stress affects the concentrations of the reactants and the products, the value of Q will no longer equal the value of K. To re-establish equilibrium, the system will either shift toward the products (if ($Q \leq K$) or the reactants (if ($Q \geq K$) until Q returns to the same value as K. This process is described by Le Chatelier's principle.

✏ Le Chatelier's principle

When a chemical system at equilibrium is disturbed, it returns to equilibrium by counteracting the disturbance. As described in the previous paragraph, the disturbance causes a change in Q; the reaction will shift to re-establish $Q = K$.

Predicting the Direction of a Reversible Reaction

Le Chatelier's principle can be used to predict changes in equilibrium concentrations when a system that is at equilibrium is subjected to a stress. However, if we have a mixture of reactants and products that have not yet reached equilibrium, the changes necessary to reach equilibrium may not be so obvious. In such a case, we can compare the values of Q and K for the system to predict the changes.

> *A chemical system at equilibrium can be **temporarily** shifted out of equilibrium by adding or removing one or more of the reactants or products. The concentrations of both reactants and products then undergo additional changes to return the system to equilibrium.*

The stress on the system in Figure 11.8.1 is the reduction of the equilibrium concentration of SCN^- (lowering the concentration of one of the reactants would cause Q to be larger than K). As a consequence, Le Chatelier's principle leads us to predict that the concentration of $Fe(SCN)^{2+}$ should decrease, increasing the concentration of SCN^- part way back to its original concentration, and increasing the concentration of Fe^{3+} above its initial equilibrium concentration.
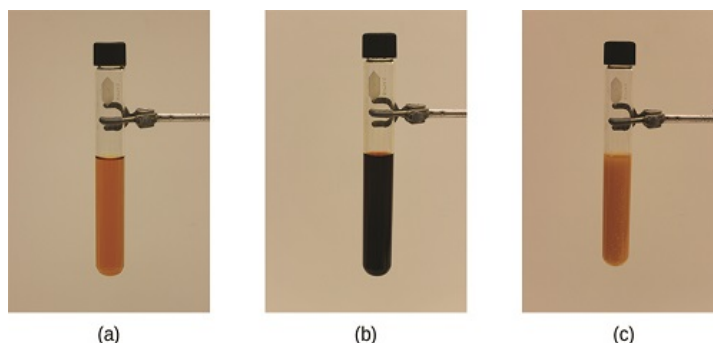

Figure 11.8.1: (a) The test tube contains 0.1 M Fe^{3+}. (b) Thiocyanate ion has been added to solution in (a), forming the red $Fe(SCN)^{2+}$ ion. $Fe^{3+}(aq) + SCN^-(aq) \rightleftharpoons Fe(SCN)^{2+}(aq)$. (c) Silver nitrate has been added to the solution in (b), precipitating some of the SCN$^-$ as the white solid AgSCN. $Ag^+(aq) + SCN^-(aq) \rightleftharpoons AgSCN(s)$. The decrease in the SCN$^-$ concentration shifts the first equilibrium in the solution to the left, decreasing the concentration (and lightening color) of the $Fe(SCN)^{2+}$. (credit: modification of work by Mark Ott).

The effect of a change in concentration on a system at equilibrium is illustrated further by the equilibrium of this chemical reaction:

$$H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g) \tag{11.8.1}$$

$$K_c = 50.0 \text{ at } 400\,^{\circ}C \tag{11.8.2}$$

The numeric values for this example have been determined experimentally. A mixture of gases at 400 °C with $[H_2] = [I_2] = 0.221\ M$ and $[HI] = 1.563\ M$ is at equilibrium; for this mixture, $Q_c = K_c = 50.0$. If H_2 is introduced into the system so quickly that its concentration doubles before it begins to react (new $[H_2] = 0.442\ M$), the reaction will shift so that a new equilibrium is reached, at which

- $[H_2] = 0.374\ M$,
- $[I_2] = 0.153\ M$, and
- $[HI] = 1.692\ M$.

This gives:

$$
\begin{aligned}
Q_c &= \frac{[HI]^2}{[H_2][I_2]} \\[2mm]
&= \frac{(1.692)^2}{(0.374)(0.153)} \\[2mm]
&= 50.0 = K_c
\end{aligned}
$$

We have stressed this system by introducing additional H_2. The stress is relieved when the reaction shifts to the right, using up some (but not all) of the excess H_2, reducing the amount of uncombined I_2, and forming additional HI. **Le Chatelier's Principle (Changing Concentrations):** Le Chatelier's Principle (Changing Concentrations)(opens in new window) [youtu.be]

A Video Discussing Le Chatelier's Principle (Changing Concentrations): Le Chatelier's Principle (Changing Concentrations)(opens in new window) [youtu.be] (opens in new window)

Effect of Change in Pressure on Equilibrium

Sometimes we can change the position of equilibrium by changing the pressure of a system. However, changes in pressure have a measurable effect only in systems in which gases are involved, and then only when the chemical reaction produces a change in the total number of gas molecules in the system. An easy way to recognize such a system is to look for different numbers of moles of gas on the reactant and product sides of the equilibrium. While evaluating pressure (as well as related factors like volume), it is important to remember that equilibrium constants are defined with regard to concentration (for K_c) or partial pressure (for K_P). Some changes to total pressure, like adding an inert gas that is not part of the equilibrium, will change the total pressure but not the partial pressures of the gases in the equilibrium constant expression. Thus, addition of a gas not involved in the equilibrium will not perturb the equilibrium.

As we increase the pressure of a gaseous system at equilibrium, either by decreasing the volume of the system or by adding more of one of the components of the equilibrium mixture, we introduce a stress by increasing the partial pressures of one or more of the

components. In accordance with Le Chatelier's principle, a shift in the equilibrium that reduces the total number of molecules per unit of volume will be favored because this relieves the stress. The reverse reaction would be favored by a decrease in pressure.

Consider what happens when we increase the pressure on a system in which NO, O_2, and NO_2 are at equilibrium:

$$2\,NO(g) + O_2(g) \rightleftharpoons 2\,NO_2(g) \tag{11.8.3}$$

The formation of additional amounts of NO_2 decreases the total number of molecules in the system because each time two molecules of NO_2 form, a total of three molecules of NO and O_2 are consumed. This reduces the total pressure exerted by the system and reduces, but does not completely relieve, the stress of the increased pressure. On the other hand, a decrease in the pressure on the system favors decomposition of NO_2 into NO and O_2, which tends to restore the pressure.

Now consider this reaction:

$$N_2(g) + O_2(g) \rightleftharpoons 2\,NO(g) \tag{11.8.4}$$
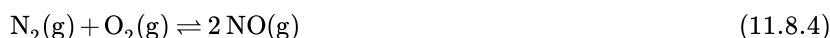
Because there is no change in the total number of molecules in the system during reaction, a change in pressure does not favor either formation or decomposition of gaseous nitrogen monoxide.

Le Chatelier's Principle (Changes in Pressure or Volume):

Le Chatelier's Principle (Changes in Pressure or Volume)(opens in new window) [youtu.be]

Effect of Change in Temperature on Equilibrium

Changing concentration or pressure perturbs an equilibrium because the reaction quotient is shifted away from the equilibrium value. Changing the temperature of a system at equilibrium has a different effect: A change in temperature actually changes the value of the equilibrium constant. However, we can qualitatively predict the effect of the temperature change by treating it as a stress on the system and applying Le Chatelier's principle.

When hydrogen reacts with gaseous iodine, heat is evolved.

$$H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g) \quad \Delta H = -9.4 \text{ kJ (exothermic)} \tag{11.8.5}$$
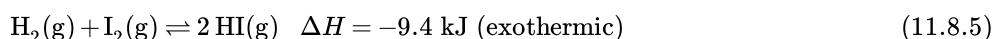
Because this reaction is exothermic, we can write it with heat as a product.

$$H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g) + heat \tag{11.8.6}$$

Increasing the temperature of the reaction increases the internal energy of the system. Thus, increasing the temperature has the effect of increasing the amount of one of the products of this reaction. The reaction shifts to the left to relieve the stress, and there is an increase in the concentration of H_2 and I_2 and a reduction in the concentration of HI. Lowering the temperature of this system reduces the amount of energy present, favors the production of heat, and favors the formation of hydrogen iodide.

When we change the temperature of a system at equilibrium, the equilibrium constant for the reaction changes. Lowering the temperature in the HI system increases the equilibrium constant: At the new equilibrium the concentration of HI has increased and the concentrations of H_2 and I_2 decreased. Raising the temperature decreases the value of the equilibrium constant, from 67.5 at 357 °C to 50.0 at 400 °C.

Temperature affects the equilibrium between NO_2 and N_2O_4 in this reaction

$$N_2O_4(g) \rightleftharpoons 2\,NO_2(g) \quad \Delta H = 57.20 \text{ kJ} \tag{11.8.7}$$

The positive ΔH value tells us that the reaction is endothermic and could be written

$$\text{heat} + N_2O_4(g) \rightleftharpoons 2\,NO_2(g) \tag{11.8.8}$$

At higher temperatures, the gas mixture has a deep brown color, indicative of a significant amount of brown NO_2 molecules. If, however, we put a stress on the system by cooling the mixture (withdrawing energy), the equilibrium shifts to the left to supply some of the energy lost by cooling. The concentration of colorless N_2O_4 increases, and the concentration of brown NO_2 decreases, causing the brown color to fade.

The overview of how different disturbances affect the reaction equilibrium properties is tabulated in Table 11.8.1.

Table 11.8.1: Effects of Disturbances of Equilibrium and K

Disturbance	Observed Change as Equilibrium is Restored	Direction of Shift	Effect on K
reactant added	added reactant is partially consumed	toward products	none
product added	added product is partially consumed	toward reactants	none
decrease in volume/increase in gas pressure	pressure decreases	toward side with fewer moles of gas	none
increase in volume/decrease in gas pressure	pressure increases	toward side with more moles of gas	none
temperature increase	heat is absorbed	toward products for endothermic, toward reactants for exothermic	changes
temperature decrease	heat is given off	toward reactants for endothermic, toward products for exothermic	changes

---

✔ Example 11.8.1

Write an equilibrium constant expression for each reaction and use this expression to predict what will happen to the concentration of the substance in bold when the indicated change is made if the system is to maintain equilibrium.

a. $2HgO_{(s)} \rightleftharpoons 2Hg_{(l)} + \mathbf{O_2}_{(g)}$: the amount of HgO is doubled.
b. $NH_4HS_{(s)} \rightleftharpoons \mathbf{NH_3}_{(g)} + H_2S_{(g)}$: the concentration of H_2S is tripled.
c. $\mathbf{n\text{-}butane}_{(g)} \rightleftharpoons isobutane_{(g)}$: the concentration of isobutane is halved.

Given: equilibrium systems and changes

Asked for: equilibrium constant expressions and effects of changes

Strategy:

Write the equilibrium constant expression, remembering that pure liquids and solids do not appear in the expression. From this expression, predict the change that must occur to maintain equilibrium when the indicated changes are made.

Solution:

Because $HgO_{(s)}$ and $Hg_{(l)}$ are pure substances, they do not appear in the equilibrium constant expression. Thus, for this reaction, $K = [O_2]$. The equilibrium concentration of O_2 is a constant and does not depend on the amount of HgO present. Hence adding more HgO will not affect the equilibrium concentration of O_2, so no compensatory change is necessary.

NH_4HS does not appear in the equilibrium constant expression because it is a solid. Thus $K = [NH_3][H_2S]$, which means that the concentrations of the products are inversely proportional. If adding H_2S triples the H_2S concentration, for example, then the NH_3 concentration must decrease by about a factor of 3 for the system to remain at equilibrium so that the product of the concentrations equals K.

For this reaction, $K = \frac{[isobutane]}{[\text{n-butane}]}$, so halving the concentration of isobutane means that the n-butane concentration must also decrease by about half if the system is to maintain equilibrium.

? Exercise 11.8.1

Write an equilibrium constant expression for each reaction. What must happen to the concentration of the substance in bold when the indicated change occurs if the system is to maintain equilibrium?

a. $HBr(g) + NaH(s) \rightleftharpoons NaBr(s) + \mathbf{H_2(g)}$: the concentration of HBr is decreased by a factor of 3.
b. $6\,Li(s) + \mathbf{N_2(g)} \rightleftharpoons 2\,Li_3N(s)$: the amount of Li is tripled.
c. $\mathbf{SO_2(g)} + Cl_2(g) \rightleftharpoons SO_2Cl_2(l)$: the concentration of Cl_2 is doubled.

Answer a

$K = \dfrac{[H_2]}{[HBr]}$; $[H_2]$ must decrease by about a factor of 3.

Answer b

$K = \dfrac{1}{[N_2]}$; solid lithium does not appear in the equilibrium constant expression, so no compensatory change is necessary.

Answer c

$K = \dfrac{1}{[SO_2][Cl_2]}$; $[SO_2]$ must decrease by about half.

Le Chatelier's Principle (Changes in Temperature):

Le Chatelier's Principle (Changes in Temperature)(opens in new window) [youtu.be]

Catalysts Do Not Affect Equilibrium

As we learned during our study of kinetics, a catalyst can speed up the rate of a reaction. Though this increase in reaction rate may cause a system to reach equilibrium more quickly (by speeding up the forward and reverse reactions), a catalyst has no effect on the value of an equilibrium constant nor on equilibrium concentrations. The interplay of changes in concentration or pressure, temperature, and the lack of an influence of a catalyst on a chemical equilibrium is illustrated in the industrial synthesis of ammonia from nitrogen and hydrogen according to the equation

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g) \tag{11.8.9}$$

A large quantity of ammonia is manufactured by this reaction. Each year, ammonia is among the top 10 chemicals, by mass, manufactured in the world. About 2 billion pounds are manufactured in the United States each year. Ammonia plays a vital role in our global economy. It is used in the production of fertilizers and is, itself, an important fertilizer for the growth of corn, cotton, and other crops. Large quantities of ammonia are converted to nitric acid, which plays an important role in the production of fertilizers, explosives, plastics, dyes, and fibers, and is also used in the steel industry.

> ### 📌 Fritz Haber
>
> Haber was born in Breslau, Prussia (presently Wroclaw, Poland) in December 1868. He went on to study chemistry and, while at the University of Karlsruhe, he developed what would later be known as the Haber process: the catalytic formation of ammonia from hydrogen and atmospheric nitrogen under high temperatures and pressures. For this work, Haber was awarded the 1918 Nobel Prize in Chemistry for synthesis of ammonia from its elements (Equation 11.8.9). The Haber process was a boon to agriculture, as it allowed the production of fertilizers to no longer be dependent on mined feed stocks such as sodium nitrate.
>
>
>
> Figure 11.8.1: The work of Nobel Prize recipient Fritz Haber revolutionized agricultural practices in the early 20th century. His work also affected wartime strategies, adding chemical weapons to the artillery.
>
> Currently, the annual production of synthetic nitrogen fertilizers exceeds 100 million tons and synthetic fertilizer production has increased the number of humans that arable land can support from 1.9 persons per hectare in 1908 to 4.3 in 2008. The availability of nitrogen is a strong limiting factor to the growth of plants. Despite accounting for 78% of air, diatomic nitrogen (N_2) is nutritionally unavailable to a majority of plants due the tremendous stability of the nitrogen-nitrogen triple bond. Therefore, the nitrogen must be converted to a more bioavailable form (this conversion is called nitrogen fixation). Legumes achieve this conversion at ambient temperature by exploiting bacteria equipped with suitable enzymes.
>
> In addition to his work in ammonia production, Haber is also remembered by history as one of the fathers of chemical warfare. During World War I, he played a major role in the development of poisonous gases used for trench warfare. Regarding his role in these developments, Haber said, "During peace time a scientist belongs to the World, but during war time he belongs to his country."[1] Haber defended the use of gas warfare against accusations that it was inhumane, saying that death was death, by whatever means it was inflicted. He stands as an example of the ethical dilemmas that face scientists in times of war and the double-edged nature of the sword of science.
>
> Like Haber, the products made from ammonia can be multifaceted. In addition to their value for agriculture, nitrogen compounds can also be used to achieve destructive ends. Ammonium nitrate has also been used in explosives, including improvised explosive devices. Ammonium nitrate was one of the components of the bomb used in the attack on the Alfred P. Murrah Federal Building in downtown Oklahoma City on April 19, 1995.

Summary

Systems at equilibrium can be disturbed by changes to temperature, concentration, and, in some cases, volume and pressure; volume and pressure changes will disturb equilibrium if the number of moles of gas is different on the reactant and product sides of the reaction. The system's response to these disturbances is described by Le Chatelier's principle: The system will respond in a way that counteracts the disturbance. Not all changes to the system result in a disturbance of the equilibrium. Adding a catalyst affects the rates of the reactions but does not alter the equilibrium, and changing pressure or volume will not significantly disturb systems with no gases or with equal numbers of moles of gas on the reactant and product side.

Footnotes

1. 1 Herrlich, P. "The Responsibility of the Scientist: What Can History Teach Us About How Scientists Should Handle Research That Has the Potential to Create Harm?" *EMBO Reports* 14 (2013): 759–764.

Glossary

Le Chatelier's principle

when a chemical system at equilibrium is disturbed, it returns to equilibrium by counteracting the disturbance

position of equilibrium

concentrations or partial pressures of components of a reaction at equilibrium (commonly used to describe conditions before a disturbance)

stress

change to a reaction's conditions that may cause a shift in the equilibrium

Contributors and Attributions

CHAPTER OVERVIEW

12: Oxidation and Reduction

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12.1: Oxidation States - Electron Bookkeeping

Redox reactions are all about electrons being transferred from one substance to another, so it is useful to have a system for keeping track of what gains and what loses electrons, and how many electrons are involved. The record-keeping system for redox reactions is called **Oxidation Numbers.** You may also remember something called **electronegativity** from earlier chemistry classes.

> 📌 Electronegativity
>
> The ability of a bonded atom to attract shared electrons toward itself.

When two atoms of different elements are bonded together by a covalent bond (sharing electrons), the electrons are generally not shared equally between the two atoms due to differences in their electronegativities. Think of this as a tug-of-war for electrons. Sometimes both atoms pull with equal strength on shared electrons; other times there is clearly a stronger player that will pull the electrons closer to itself.

Consider the bond between a hydrogen atom (with one valence electron) and an oxygen atom (with its six valence electrons):

$$\text{H}\cdot \quad + \quad \cdot\ddot{\text{O}}\cdot \quad = \quad \text{H}\,:\!\ddot{\text{O}}\cdot$$
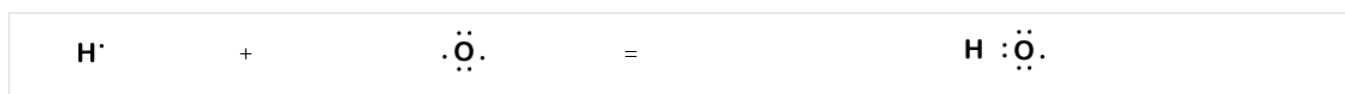
Because oxygen has a higher electronegativity than hydrogen, the shared electrons are closer to the oxygen atom than to the hydrogen atom. This is not the total transfer of electrons that would create an ion, but partial charges do form. The hydrogen end of the bond is partially positive (+1) because it has partially lost one electron, and the oxygen end of the H–O is partially negative (-1) because it has partially gained the one electron from hydrogen:

$$\overset{\delta^+}{\text{H}}\;\;\;\overset{\delta^-}{:\!\ddot{\text{O}}\cdot}$$
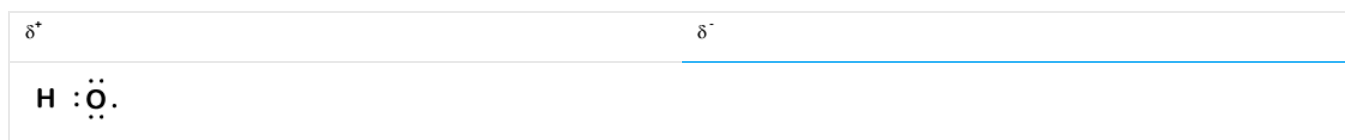
Our molecule is incomplete, however, because there is a lone electron around oxygen. Let's add one more hydrogen to complete our water molecule:

$$\overset{\delta^+}{\text{H}}\;\;\overset{\delta^-\;\;\delta^-}{:\!\ddot{\text{O}}\!:}\;\;\overset{\delta^+}{\text{H}}$$
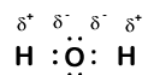
We see that each of the two hydrogens has "lost" one electron to oxygen. Oxygen has "gained" two electrons—one from each hydrogen. Again, these are not true ions, but it is useful to think of them in the same way.

Charges given to atoms in a molecule in this way are called **oxidation numbers**. We can use oxidation numbers to keep track of where electrons are in a molecule, and how they move during a reaction. In our water example, hydrogen is assigned an oxidation number of +1 because each individual hydrogen has "lost" one electron. Oxygen has an oxidation number of +2 because the single oxygen atom has "gained" a total of two electrons, one from each hydrogen.

Here is another molecule involving hydrogen and oxygen—hydrogen peroxide, H_2O_2:

$$\overset{\delta^+}{\text{H}}\;\;\overset{\delta^-}{:\!\ddot{\text{O}}\!:}\;\;\overset{\delta^-}{\ddot{\text{O}}\!:}\;\;\overset{\delta^+}{\text{H}}$$
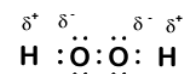
In hydrogen peroxide, each hydrogen still has an oxidation number of +1 because each hydrogen "gives up" a single electron to oxygen. Oxygen, however, now has an oxidation number of -1 because each oxygen gains just one electron from its neighboring hydrogen. The electrons between the two identical oxygen atoms are shared equally, so there is no partial charge resulting from that bond.

> 📌 **Oxidation Number**
>
> A positive or negative number assigned to an atom in a molecule or ion that reflects a partial gain or loss of electrons.

Knowing the oxidation number of each individual element in a molecule will be a key step in our understanding of redox reactions. Fortunately it will not usually involve drawing electron dot diagrams. Instead, there are a series of rules that we can use to determine oxidation numbers. Here are the main rules:

		Element	Oxidation Number
1.	The oxidation number of a pure element (by itself, and not an ion) is zero.	Na	0
		H_2	0
		O_2	0
		P_4	0

		Ionic Compound	Ions	Charge	Oxidation Number
2.	The oxidation number of a monatomic ion (by itself or as part of an ionic compound) is equal to its charge. Alkali metals—elements in the first column of the periodic table—will always have an oxidation number of +1; Alkaline earth metals (column 2) are almost always +2.	NaCl	Na^+	+1	+1
			Cl^-	-1	-1
		Mg_3N_2	Mg^{+2}	+2	+2
			N^{-3}	-3	-3

		Compound	Element	Oxidation Number
3.	The oxidation number of hydrogen is almost always +1 when it is in a compound.	HCl	H	+1
			Cl	-1
		H_2S	H	+1
			S	-2

Element	Oxidation Number
Na	0
H_2	0
O_2	0
P_4	0

1. The oxidation number of a pure element (by itself, and not an ion) is zero.

4. The oxidation number of oxygen is almost always -2 when it is in a compound.
The exceptions:
- Peroxides, such as hydrogen peroxide. In peroxides, oxygen has an oxidation number of -1.
- When oxygen is combined with fluorine, its oxidation number is +2.

Compound	Element	Oxidation Number
MgO magnesium oxide	Mg	+2
	O	-2
Na_2O sodium oxide	Na	+1
	O	-2
Na_2O_2 sodium peroxide	Na	+1
	O	-1

5. The sum of the oxidation numbers in a compound is zero.
To determine the oxidation number of Mn in Mn_2O_7, we must work backwards:
- We know each oxygen is -2 (Rule 4).
- 7 oxygen gives a total of:
-2 × 7 atoms = -14 total
Since the sum of oxidation numbers must be zero, the total oxidation number of Mn must be +14 to cancel out oxygen's -14, but since there are 2 Mn atoms, each **individual atom** will have an oxidation number of +7:

$$\frac{+14 \text{ total}}{2 \text{ Mn atoms}} = +7$$

Compound	Element	Oxidation Number	Number of Atoms	Total
Mg_3N_2	Mg	+2	3	+6
	N	-3	2	-6
			SUM	0
Mn_2O_7	Mn	+7	2	+14
	O	-2	7	-14
			SUM	**0**
Cl_2O_3	Cl	+3	2	+6
	O	-2	3	-6
			SUM	**0**

	Element	Oxidation Number
1.	The oxidation number of a pure element (by itself, and not an ion) is zero.	

Element	Oxidation Number
Na	0
H_2	0
O_2	0
P_4	0

6.

The sum of the oxidation numbers in a polyatomic ion is equal to the charge on that ion.

Again, work backwards to determine the oxidation number of any non-oxygen or non-hydrogen atom.

To determine the oxidation number of Cr in $Cr_2O_7^{2-}$:

- Oxygen will be -2 (Rule 4), for a total of:

$-2 \times 7 = -14$

- Since the sum of the oxidation numbers will be -2 (the charge on the entire ion), the total for all Cr must be +12 because:

+12 + (-14) = -2

- Since there are two Cr, each Cr will have an oxidation number of +6.

= +7

$$\frac{+12}{2} = +6$$

Compound	Element	Oxidation Number	Number of Atoms	Total
NO_3^-	N	+5	1	+5
	O	-2	3	-6
			SUM	-1
$Cr_2O_7^{2-}$	Cr	+6	2	+12
	O	-2	7	-14
			SUM	**-2**
SO_4^{2-}	S	+6	1	+6
	O	-2	4	-8
			SUM	**-2**

It is important to note that oxidation number always refers to *each individual atom* in the compound, not to the total for that element.

For example, in H_2O, the total positive "charge" for both hydrogen atoms will be +2 (which balances with the -2 from oxygen), but *each hydrogen* has an oxidation number of +1.

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12.2: Oxidation and Reduction- Some Definitions

"Redox" is short for "oxidation and reduction", two complimentary types of chemical reactions. The term **oxidation** originally referred to substances combining with oxygen, as happens when an iron bar rusts or a campfire log burns. We often refer to these two examples as corrosion and combustion. **Reduction** originally referred to the process of converting metal ores to pure metals, a process that is accompanied by a reduction in the mass of the ore.

These two terms have broader meanings now. In all oxidation-reduction reactions, an exchange of electrons occurs—one substance loses electrons while another gains them. That is the key to understanding redox reactions. We'll define these terms below.

Figure 12.2.1: *Reaction of copper wire in a silver nitrate solution.*

A simple demonstration of a redox reaction involves placing a solid piece of copper wire in a silver nitrate solution. Within minutes, the wire begins to look fuzzy or furry as small silver crystals begin to form on the wire. Meanwhile, the originally clear silver nitrate solution begins to take on a pale bluish tint. Furthermore, if the crystals are shaken off of the wire, we see that the wire partially disintegrated.

The overall equation for our demonstration describes the events:

$$Cu(s) + 2\,AgNO_3(aq) \rightarrow Cu(NO_3)_2(aq) + 2\,Ag(s)$$
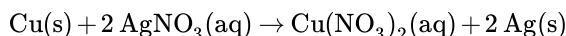
Remember that when we have aqueous solutions of ionic compounds, the ions are really present as separate ions, not as bonded particles. So we can write an expanded equation:

$$Cu(s) + 2\,Ag^+(aq) + 2\,NO_3^-(aq) \rightarrow Cu^{2+}(aq) + 2\,NO_3^-(aq) + 2\,Ag(s)$$
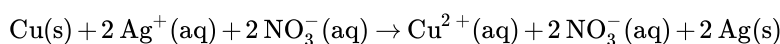
Finally we remove spectator ions from the equation. Remember that spectator ions are ions that undergo no change during a reaction. Notice the nitrate ions, NO_3^-, they start as aqueous ions and end up exactly the same.

Removing the spectator ions gives us our **net ionic equation:**

$$Cu(s) + 2\,Ag^+(aq) \rightarrow Cu^{2+}(aq) + 2\,Ag(s)$$
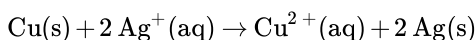
We can now see a bit more clearly what changes are occurring with this reaction.

Oxidation of Copper Metal to Make Copper Ions

Copper began as a neutral atom with no charge, but changed into an ion with a charge of +2. An atom becomes a positive ion by losing electrons:

$$Cu(s) \rightarrow Cu^{2+}(aq) + 2\,e^- \tag{12.2.1}$$

Notice that copper began as a solid, but is converted into aqueous ions—this is why the copper wire disintegrates. We say that copper was **oxidized** because it has lost electrons (i.e., electrons appear on the product side of the Equation 12.2.1).

Reduction of Silver Ions to Make Silver Metal

Silver was converted from an ion with a charge of +1, Ag+, to a neutral atom, Ag. The only way an ion can undergo this change is to gain an electron:

$$Ag^+ (aq) + e^- \rightarrow Ag(s) \qquad\qquad (12.2.2)$$

Notice that solid silver is formed—this is what causes the fuzzy appearance to begin appearing on the wire—solid silver crystals. Silver has gained electrons, it has been reduced (i.e., electrons appear on the reactant side of Equation 12.2.2).

The electrons that silver gained had to come from somewhere—they came from copper. Conversely, a substance such as copper can only lose electrons if there is something else that will take them up, the silver ions. **One cannot occur without the other**. This exchange of electrons is what defines an **oxidation-reduction reaction**.

> 📌 Definition: Oxidation
>
> Oxidation is the **loss** of electrons.

> 📌 Definition: Reduction
>
> Reduction is the **gain** of electrons.

You will be learning several new terms in this chapter and it is important that you learn them very quickly. You may find it useful to have some tricks to help you remember these terms, including the LEO/GER.

> 📌 LEO the Lion Says GER
>
> - LEO: Loss of Electrons is Oxidation.
> - GER: Gain of Electrons is Reduction.
>
>

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12.3: Balancing Oxidation-Reduction Equations

> ### ◖◗ Learning Objectives
>
> - To identify oxidation–reduction reactions in solution.

We described the defining characteristics of oxidation–reduction, or redox, reactions. Most of the reactions we considered there were relatively simple, and balancing them was straightforward. When oxidation–reduction reactions occur in aqueous solution, however, the equations are more complex and can be more difficult to balance by inspection. Because a balanced chemical equation is the most important prerequisite for solving any stoichiometry problem, we need a method for balancing oxidation–reduction reactions in aqueous solution that is generally applicable. One such method uses *oxidation states*, and a second is referred to as the *half-reaction* method.

Balancing Redox Equations Using Oxidation States

To balance a redox equation using the oxidation state method, we conceptually separate the overall reaction into two parts: an oxidation—in which the atoms of one element lose electrons—and a reduction—in which the atoms of one element gain electrons. Consider, for example, the reaction of Cr^{2+}(aq) with manganese dioxide (MnO_2) in the presence of dilute acid. Equation 12.3.1 is the net ionic equation for this reaction before balancing; the oxidation state of each element in each species has been assigned using the procedure described previously (in red above each element):

$$\overset{+2}{Cr^{2+}}(aq) + \overset{+4}{Mn}\overset{-2}{O_2}(aq) + \overset{+1}{H^+}(aq) \rightarrow \overset{+3}{Cr^{3+}}(aq) + \overset{+2}{Mn^{2+}}(aq) + \overset{+1}{H_2}\overset{-2}{O}(l) \tag{12.3.1}$$
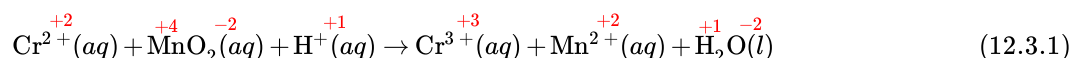
Notice that chromium is oxidized from the +2 to the +3 oxidation state, while manganese is reduced from the +4 to the +2 oxidation state. We can write an equation for this reaction that shows only the atoms that are oxidized and reduced (ignoring the oxygen and hydrogen atoms):

$$Cr^{2+} + Mn^{4+} \longrightarrow Cr^{3+} + Mn^{2+} \tag{12.3.2}$$

The oxidation can be written as

$$\underbrace{Cr^{2+} \longrightarrow Cr^{3+} + e^-}_{\text{oxidation with 1 electron lost}} \tag{12.3.3}$$

and the reduction as

$$\underbrace{Mn^{4+} + 2\,e^- \rightarrow Mn^{2+}}_{\text{reduction with 2 electrons gained}} \tag{12.3.4}$$

For the overall chemical equation to be balanced, the number of electrons lost by the reductant must equal the number gained by the oxidant. We must therefore multiply the oxidation and the reduction equations by appropriate coefficients to give us the same number of electrons in both. In this example, we must multiply the oxidation (Equation 12.3.3) by 2 to give

$$2\,Cr^{2+} \longrightarrow 2\,Cr^{3+} + 2\,e^- \tag{12.3.5}$$

The number of electrons lost in the oxidation now equals the number of electrons gained in the reduction (Equation 12.3.4):

$$2\,Cr^{2+} \rightarrow 2\,Cr^{3+} + 2\,e^-$$

$$Mn^{4+} + 2\,e^- \rightarrow Mn^{2+}$$
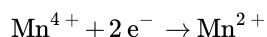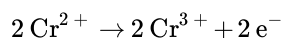
We then add the equations for the oxidation and the reduction and cancel the electrons on both sides of the equation, using the actual chemical forms of the reactants and products:

$$2\,Cr^{2+} \rightarrow 2\,Cr^{3+} + 2\,\cancel{e^-}$$

$$Mn^{4+} + 2\,\cancel{e^-} \rightarrow Mn^{2+}$$
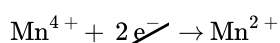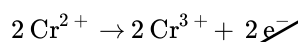
to result in the balanced redox reaction (metals only)

$$\mathrm{Mn^{4\,+} + 2\,Cr^{2\,+} \rightarrow 2\,Cr^{3\,+} + Mn^{2\,+}} \tag{12.3.6}$$

now we can add the non-redox active atoms back into the equation (ignoring water and hydronium for now)

$$\mathrm{MnO_2(aq) + 2\,Cr^{2\,+}(aq) \longrightarrow 2\,Cr^{3\,+}(aq) + Mn^{2\,+}(aq)} \tag{12.3.7}$$
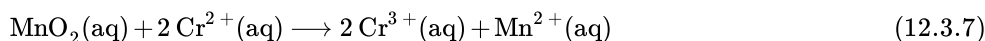
> *In a balanced redox reaction, the number of electrons lost by the reductant equals the number of electrons gained by the oxidant.*

Although the electrons cancel and the metal atoms are balanced, the total charge on the left side of Equation 12.3.7 (+4) does not equal the charge on the right side (+8). Because the reaction is carried out in the presence of aqueous acid, we can add $\mathrm{H^+}$ as necessary to either side of the equation to balance the charge. By the same token, if the reaction were carried out in the presence of aqueous base, we could balance the charge by adding $\mathrm{OH^-}$ as necessary to either side of the equation to balance the charges.

In this case, adding four $\mathrm{H^+}$ ions to the left side of Equation 12.3.7 to give

$$\mathrm{MnO_2(s) + 2\,Cr^{2\,+}(aq) + 4\,H^+(aq) \longrightarrow 2\,Cr^{3\,+}(aq) + Mn^{2\,+}(aq)} \tag{12.3.8}$$
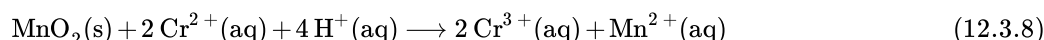
Although the charges are now balanced in Equation 12.3.8, we have two oxygen atoms on the left side of the equation and none on the right. We can balance the oxygen atoms without affecting the overall charge balance by adding $\mathrm{H_2O}$ as necessary to either side of the equation. Here, we need to add two $\mathrm{H_2O}$ molecules to the right side of Equation 12.3.8:

$$\mathrm{MnO_2(s) + 2\,Cr^{2\,+}(aq) + 4\,H^+(aq) \longrightarrow 2\,Cr^{3\,+}(aq) + Mn^{2\,+}(aq) + 2\,H_2O(l)} \tag{12.3.9}$$
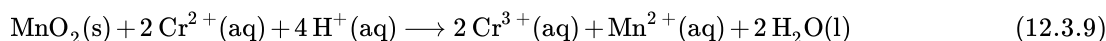
Although we did not explicitly balance the hydrogen atoms, we can see by inspection that the overall chemical equation is now balanced with respect to all atoms and charge. All that remains is to check to make sure that we have not made a mistake. This procedure for balancing reactions is summarized below and illustrated in Example 12.3.1 below.

📌 **Procedure for Balancing Oxidation–Reduction Reactions by the Oxidation State Method**

1. Write the unbalanced chemical equation for the reaction, showing the reactants and the products.
2. Assign oxidation states to all atoms in the reactants and the products and determine which atoms change oxidation state.
3. Write separate equations for oxidation and reduction, showing (a) the atom(s) that is (are) oxidized and reduced and (b) the number of electrons accepted or donated by each.
4. Multiply the oxidation and reduction equations by appropriate coefficients so that both contain the same number of electrons.
5. Write the oxidation and reduction equations showing the actual chemical forms of the reactants and the products, adjusting the coefficients as necessary to give the numbers of atoms in step 4.
6. Add the two equations and cancel the electrons.
7. Balance the charge by adding $\mathrm{H^+}$ or $\mathrm{OH^-}$ ions as necessary for reactions in acidic or basic solution, respectively.
8. Balance the oxygen atoms by adding $\mathrm{H_2O}$ molecules to one side of the equation.
9. Check to make sure that the equation is balanced in both atoms and total charges.

✔ **Example 12.3.1: Balancing in Acid Solutions**

Arsenic acid ($\mathrm{H_3AsO_4}$) is a highly poisonous substance that was once used as a pesticide. The reaction of elemental zinc with arsenic acid in acidic solution yields arsine ($\mathrm{AsH_3}$, a highly toxic and unstable gas) and $\mathrm{Zn^{2\,+}(aq)}$. Balance the equation for this reaction using oxidation states:

$$\mathrm{H_3AsO_4(aq) + Zn(s) \longrightarrow AsH_3(g) + Zn^{2\,+}(aq)}$$
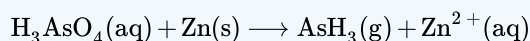
**Given:** reactants and products in acidic solution

Asked for: balanced chemical equation using oxidation states

Strategy:

Follow the procedure given above for balancing a redox equation using oxidation states. When you are done, be certain to check that the equation is balanced.

Solution:

1. *Write a chemical equation showing the reactants and the products.* Because we are given this information, we can skip this step.

2. *Assign oxidation states and determine which atoms change oxidation state.* The oxidation state of arsenic in arsenic acid is +5, and the oxidation state of arsenic in arsine is −3. Conversely, the oxidation state of zinc in elemental zinc is 0, and the oxidation state of zinc in $Zn^{2+}(aq)$ is +2:

$$H_3 \overset{+5}{As} O_4(aq) + \overset{0}{Zn}(s) \rightarrow \overset{-3}{As}H_3(g) + \overset{+2}{Zn}^{2+}(aq)$$
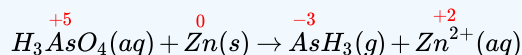
3. *Write separate equations for oxidation and reduction.* The arsenic atom in H_3AsO_4 is reduced from the +5 to the −3 oxidation state, which requires the addition of eight electrons:

$$\underbrace{\overset{+5}{As} + 8e^- \rightarrow \overset{-3}{As}}_{\text{Reduction with gain of 8 electrons}}$$
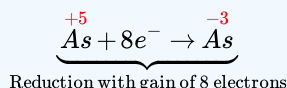
Each zinc atom in elemental zinc is oxidized from 0 to +2, which requires the loss of two electrons per zinc atom:
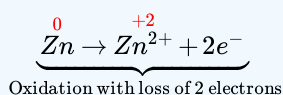
$$\underbrace{\overset{0}{Zn} \rightarrow \overset{+2}{Zn}^{2+} + 2e^-}_{\text{Oxidation with loss of 2 electrons}}$$

4. *Multiply the oxidation and reduction equations by appropriate coefficients so that both contain the same number of electrons.* The reduction equation has eight electrons, and the oxidation equation has two electrons, so we need to multiply the oxidation equation by 4 to obtain
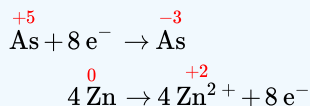
$$\overset{+5}{As} + 8\,e^- \rightarrow \overset{-3}{As}$$
$$4\,\overset{0}{Zn} \rightarrow 4\,\overset{+2}{Zn}^{2+} + 8\,e^-$$

5. *Write the oxidation and reduction equations showing the actual chemical forms of the reactants and the products, adjusting coefficients as necessary to give the numbers of atoms shown in step 4.* Inserting the actual chemical forms of arsenic and zinc and adjusting the coefficients gives

   ○ Reduction:

   $$H_3AsO_4(aq) + 8\,e^- \rightarrow AsH_3(g)$$

   ○ Oxidation:

   $$4\,Zn(s) \longrightarrow 4\,Zn^{2+}(aq) + 8\,e^-$$
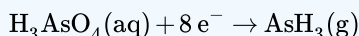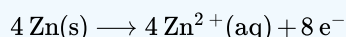
6. *Add the two equations and cancel the electrons.* The sum of the two equations in step 5 is

$$H_3AsO_4(aq) + 4\,Zn(s) + 8\,\cancel{e^-} \rightarrow AsH_3(g) + 4\,Zn^{2+}(aq) + 8\,\cancel{e^-}$$
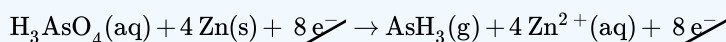
which then yields after canceling electrons
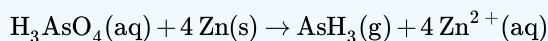
$$H_3AsO_4(aq) + 4\,Zn(s) \rightarrow AsH_3(g) + 4\,Zn^{2+}(aq)$$

7. *Balance the charge by adding* H^+ *or* OH^- *ions as necessary for reactions in acidic or basic solution, respectively.* Because the reaction is carried out in acidic solution, we can add H^+ ions to whichever side of the equation requires them to balance the charge. The overall charge on the left side is zero, and the total charge on the right side is 4 × (+2) = +8. Adding eight H^+ ions to the left side gives a charge of +8 on both sides of the equation:

$$H_3AsO_4(aq) + 4\,Zn(s) + 8\,H^+(aq) \rightarrow AsH_3(g) + 4\,Zn^{2+}(aq)$$
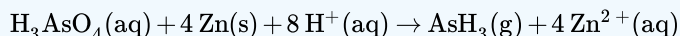
8. *Balance the oxygen atoms by adding* H_2O *molecules to one side of the equation.* There are 4 O atoms on the left side of the equation. Adding 4 H_2O molecules to the right side balances the O atoms:

$$H_3AsO_4(aq) + 4\,Zn(s) + 8\,H^+(aq) \rightarrow AsH_3(g) + 4\,Zn^{2+}(aq) + 4\,H_2O(l)$$
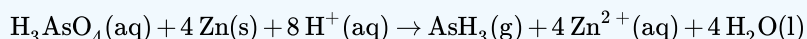
Although we have not explicitly balanced H atoms, each side of the equation has 11 H atoms.

9. *Check to make sure that the equation is balanced in both atoms and total charges.* To guard against careless errors, it is important to check that both the total number of atoms of each element and the total charges are the same on both sides of the equation:
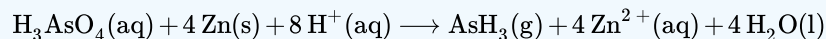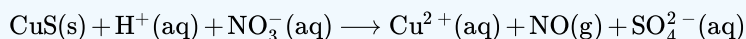
- Atoms:

$$1\,As + 4\,Zn + 4\,O + 11\,H \overset{\checkmark}{=} 1\,As + 4\,Zn + 4\,O + 11\,H$$
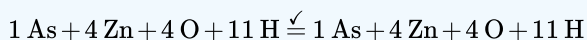
- Charge:

$$8(+1) \overset{\checkmark}{=} 4(+2)$$

The balanced chemical equation (both for charge and for atoms) for this reaction is therefore:

$$H_3AsO_4(aq) + 4\,Zn(s) + 8\,H^+(aq) \longrightarrow AsH_3(g) + 4\,Zn^{2+}(aq) + 4\,H_2O(l)$$

? Exercise 12.3.1: Oxidizing Copper

Copper commonly occurs as the sulfide mineral CuS. The first step in extracting copper from CuS is to dissolve the mineral in nitric acid, which oxidizes the sulfide to sulfate and reduces nitric acid to NO. Balance the equation for this reaction using oxidation states:

$$CuS(s) + H^+(aq) + NO_3^-(aq) \longrightarrow Cu^{2+}(aq) + NO(g) + SO_4^{2-}(aq)$$

Answer

$$3\,CuS(s) + 8\,H^+(aq) + 8\,NO_3^-(aq) \rightarrow 3\,Cu^{2+}(aq) + 8\,NO(g) + 3\,SO_4^{2-}(aq) + 4\,H_2O(l)$$
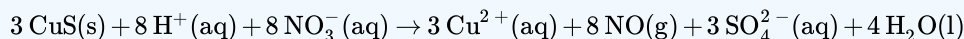
Reactions in basic solutions are balanced in exactly the same manner. To make sure you understand the procedure, consider Example 12.3.2

✔ Example 12.3.2: Balancing in Basic Solution

The commercial solid drain cleaner, Drano, contains a mixture of sodium hydroxide and powdered aluminum. The sodium hydroxide dissolves in standing water to form a strongly basic solution, capable of slowly dissolving organic substances, such as hair, that may be clogging the drain. The aluminum dissolves in the strongly basic solution to produce bubbles of hydrogen gas that agitate the solution to help break up the clogs. The reaction is as follows:

$$Al(s) + H_2O(l) \rightarrow [Al(OH)_4]^-(aq) + H_2(g)$$
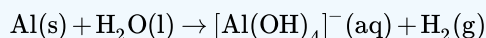
Balance this equation using oxidation states.

Given: reactants and products in a basic solution

Asked for: balanced chemical equation

Strategy:

Follow the procedure given above for balancing a redox reaction using oxidation states. When you are done, be certain to check that the equation is balanced.

Solution:

We will apply the same procedure used in Example 12.3.1, but in a more abbreviated form.

1. The equation for the reaction is given, so we can skip this step.
2. The oxidation state of aluminum changes from 0 in metallic Al to +3 in $[Al(OH)_4]^-$. The oxidation state of hydrogen changes from +1 in H_2O to 0 in H_2. Aluminum is oxidized, while hydrogen is reduced:
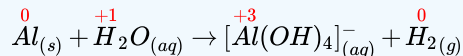
$$\overset{0}{Al}_{(s)} + \overset{+1}{H}_2O_{(aq)} \rightarrow [\overset{+3}{Al}(OH)_4]^-_{(aq)} + \overset{0}{H}_{2(g)}$$

3. Write separate equations for oxidation and reduction.

  - Reduction:

$$\overset{+1}{H} + e^- \rightarrow \overset{0}{H} \; (in \; H_2)$$

  - Oxidation:

$$\overset{0}{Al} \rightarrow \overset{+3}{Al} + 3e^-$$
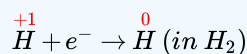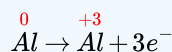
4. Multiply the reduction equation by 3 to obtain an equation with the same number of electrons as the oxidation equation:
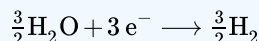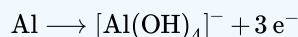
  - Reduction:

$$3\,\mathrm{H}^+ + 3\,\mathrm{e}^- \longrightarrow 3\,\mathrm{H}^0 \; (in \; \mathrm{H}_2)$$

  - Oxidation:

$$\mathrm{Al}^0 \longrightarrow \mathrm{Al}^{3+} + 3\,\mathrm{e}^-$$
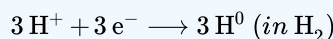
5. Insert the actual chemical forms of the reactants and products, adjusting the coefficients as necessary to obtain the correct numbers of atoms as in step 4. Because a molecule of $\mathrm{H}_2\mathrm{O}$ contains two protons, in this case, $3\,\mathrm{H}^+$ corresponds to $\frac{3}{2}\mathrm{H}_2\mathrm{O}$. Similarly, each molecule of hydrogen gas contains two H atoms, so $3\,\mathrm{H}$ corresponds to $\frac{3}{2}\mathrm{H}_2$.

  - Reduction:

$$\tfrac{3}{2}\mathrm{H}_2\mathrm{O} + 3\,\mathrm{e}^- \longrightarrow \tfrac{3}{2}\mathrm{H}_2$$

  - Oxidation:

$$\mathrm{Al} \longrightarrow [\mathrm{Al(OH)}_4]^- + 3\,\mathrm{e}^-$$

6. Adding the equations and canceling the electrons gives

$$\mathrm{Al} + \tfrac{3}{2}\mathrm{H}_2\mathrm{O} + \cancel{3\,\mathrm{e}^-} \longrightarrow [\mathrm{Al(OH)}_4]^- + \tfrac{3}{2}\mathrm{H}_2 + \cancel{3\,\mathrm{e}^-}$$

$$\mathrm{Al} + \tfrac{3}{2}\mathrm{H}_2\mathrm{O} \longrightarrow [\mathrm{Al(OH)}_4]^- + \tfrac{3}{2}\mathrm{H}_2$$
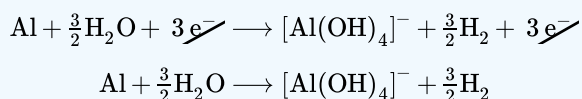
To remove the fractional coefficients, multiply both sides of the equation by 2:

$$2\,\mathrm{Al} + 3\,\mathrm{H}_2\mathrm{O} \rightarrow 2\,[\mathrm{Al(OH)}_4]^- + 3\,\mathrm{H}_2$$
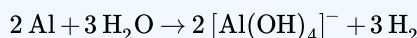
7. The right side of the equation has a total charge of −2, whereas the left side has a total charge of 0. Because the reaction is carried out in basic solution, we can balance the charge by adding two OH^- ions to the left side:

$$2\,\mathrm{Al} + 2\,\mathrm{OH}^- + 3\,\mathrm{H}_2\mathrm{O} \longrightarrow 2\,[\mathrm{Al(OH)}_4]^- + 3\,\mathrm{H}_2$$
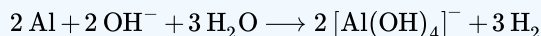
8. The left side of the equation contains five O atoms, and the right side contains eight O atoms. We can balance the O atoms by adding three $\mathrm{H}_2\mathrm{O}$ molecules to the left side:

$$2\,\mathrm{Al} + 2\,\mathrm{OH}^- + 6\,\mathrm{H}_2\mathrm{O} \longrightarrow 2\,[\mathrm{Al(OH)}_4]^- + 3\,\mathrm{H}_2$$
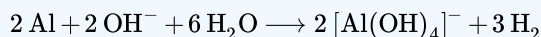
9. Be sure the equation is balanced:

  1. Atoms:

$$2\,\mathrm{Al} + 8\,\mathrm{O} + 14\,\mathrm{H} \overset{\checkmark}{=} 2\,\mathrm{Al} + 8\,\mathrm{O} + 14\,\mathrm{H}$$

  2. Charge:

$$(2)(0) + (2)(-1) + (6)(0) \overset{\checkmark}{=} (2)(-1) + (3)(0)$$

The balanced chemical equation is therefore

$$2\,\mathrm{Al(s)} + 2\,\mathrm{OH}^-(\mathrm{aq}) + 6\,\mathrm{H}_2\mathrm{O(l)} \rightarrow 2\,[\mathrm{Al(OH)}_4]^-(\mathrm{aq}) + 3\,\mathrm{H}_2(\mathrm{g})$$
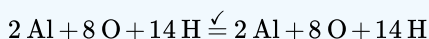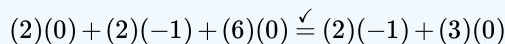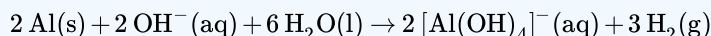
Thus 3 mol of H_2 gas are produced for every 2 mol of Al consumed.

> **? Exercise 12.3.2: Reducing Manganese in permanganate**
>
> The permanganate ion reacts with nitrite ion in basic solution to produce manganese (IV) oxide and nitrate ion. Write a balanced chemical equation for the reaction.
>
> **Answer**
>
> $$2\,MnO_4^-\,(aq) + 3\,NO_2^-\,(aq) + H_2O(l) \longrightarrow 2\,MnO_2(s) + 3\,NO_3^-\,(aq) + 2\,OH^-\,(aq)$$
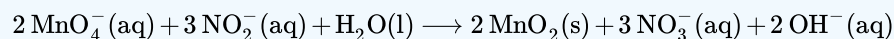
As suggested in Examples 12.3.1 and 12.3.2, a wide variety of redox reactions are possible in aqueous solutions. The identity of the products obtained from a given set of reactants often depends on both the ratio of oxidant to reductant and whether the reaction is carried out in acidic or basic solution, which is one reason it can be difficult to predict the outcome of a reaction. Because oxidation–reduction reactions in solution are so common and so important, however, chemists have developed two general guidelines for predicting whether a redox reaction will occur and the identity of the products:

1. Compounds of elements in high oxidation states (such as ClO_4^-, NO_3^-, MnO_4^-, $Cr_2O_7^{2-}$, and UF_6) tend to act as *oxidants* and *become reduced* in chemical reactions.
2. Compounds of elements in low oxidation states (such as CH_4, NH_3, H_2S, and HI) tend to act as *reductants* and *become oxidized* in chemical reactions.

When an aqueous solution of a compound that contains an element in a high oxidation state is mixed with an aqueous solution of a compound that contains an element in a low oxidation state, an oxidation–reduction reaction is likely to occur.

> *Species in high oxidation states act as oxidants, whereas species in low oxidation states act as reductants.*
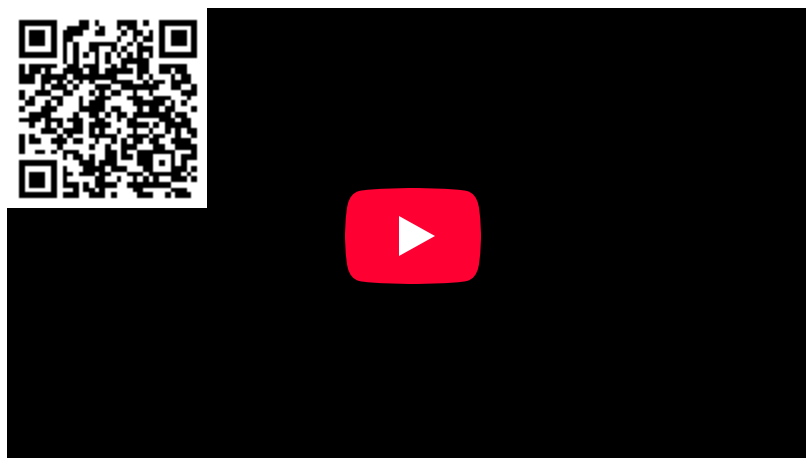
Balancing a Redox Reaction in Acidic Conditions: Balancing a Redox Reaction in Acidic Conditions (opens in new window) [youtu.be]

Summary

Oxidation–reduction reactions are balanced by separating the overall chemical equation into an oxidation equation and a reduction equation. In oxidation–reduction reactions, electrons are transferred from one substance or atom to another. We can balance oxidation–reduction reactions in solution using the oxidation state method, in which the overall reaction is separated into an oxidation equation and a reduction equation.

Contributors and Attributions

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12.4: Voltaic (or Galvanic) Cells- Generating Electricity from Spontaneous Chemical Reactions

> 🧠 **Learning Objectives**
>
> - To understand the basics of voltaic cells
> - To connect voltage from a voltaic cell to underlying redox chemistry

In any electrochemical process, electrons flow from one chemical substance to another, driven by an oxidation–reduction (redox) reaction. A redox reaction occurs when electrons are transferred from a substance that is oxidized to one that is being reduced. The **reductant** is the substance that loses electrons and is oxidized in the process; the **oxidant** is the species that gains electrons and is reduced in the process. The associated potential energy is determined by the potential difference between the valence electrons in atoms of different elements.

Because it is impossible to have a reduction without an oxidation and vice versa, a redox reaction can be described as two **half-reactions**, one representing the oxidation process and one the reduction process. For the reaction of zinc with bromine, the overall chemical reaction is as follows:

$$Zn(s) + Br_2(aq) \rightarrow Zn^{2+}(aq) + 2\,Br^-(aq)$$
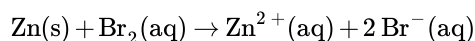
The half-reactions are as follows:

reduction half-reaction:

$$Br_2(aq) + 2\,e^- \rightarrow 2\,Br^-(aq)$$

oxidation half-reaction:

$$Zn(s) \rightarrow Zn^{2+}(aq) + 2\,e^-$$
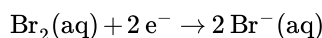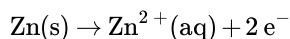
Each half-reaction is written to show what is actually occurring in the system; Zn is the *reductant* in this reaction (it loses electrons), and Br_2 is the *oxidant* (it gains electrons). Adding the two half-reactions gives the overall chemical reaction (Equation 12.4.1). A redox reaction is balanced when the number of electrons lost by the reductant equals the number of electrons gained by the oxidant. Like any balanced chemical equation, the overall process is electrically neutral; that is, the net charge is the same on both sides of the equation.

> *In any redox reaction, the number of electrons lost by the oxidation reaction(s) equals the number of electrons gained by the reduction reaction(s).*

In most of our discussions of chemical reactions, we have assumed that the reactants are in intimate physical contact with one another. Acid–base reactions, for example, are usually carried out with the acid and the base dispersed in a single phase, such as a liquid solution. With redox reactions, however, it is possible to physically separate the oxidation and reduction half-reactions in space, as long as there is a complete circuit, including an external electrical connection, such as a wire, between the two half-reactions. As the reaction progresses, the electrons flow from the reductant to the oxidant over this electrical connection, producing an electric current that can be used to do work. An apparatus that is used to generate electricity from a spontaneous redox reaction or, conversely, that uses electricity to drive a nonspontaneous redox reaction is called an **electrochemical cell**.

There are two types of electrochemical cells: galvanic cells and electrolytic cells. Galvanic cells are named for the Italian physicist and physician Luigi Galvani (1737–1798), who observed that dissected frog leg muscles twitched when a small electric shock was applied, demonstrating the electrical nature of nerve impulses. A **galvanic (voltaic) cell** uses the energy released during a spontaneous redox reaction ($\Delta G < 0$) to generate electricity. This type of electrochemical cell is often called a voltaic cell after its inventor, the Italian physicist Alessandro Volta (1745–1827). In contrast, an **electrolytic cell** consumes electrical energy from an external source, using it to cause a nonspontaneous redox reaction to occur ($\Delta G > 0$). Both types contain two **electrodes**, which are solid metals connected to an external circuit that provides an electrical connection between the two parts of the system (Figure 12.4.1). The oxidation half-reaction occurs at one electrode (the **anode**), and the reduction half-reaction occurs at the other (the **cathode**). When the circuit is closed, electrons flow from the anode to the cathode. The electrodes are also connected by an

electrolyte, an ionic substance or solution that allows ions to transfer between the electrode compartments, thereby maintaining the system's electrical neutrality. In this section, we focus on reactions that occur in galvanic cells.
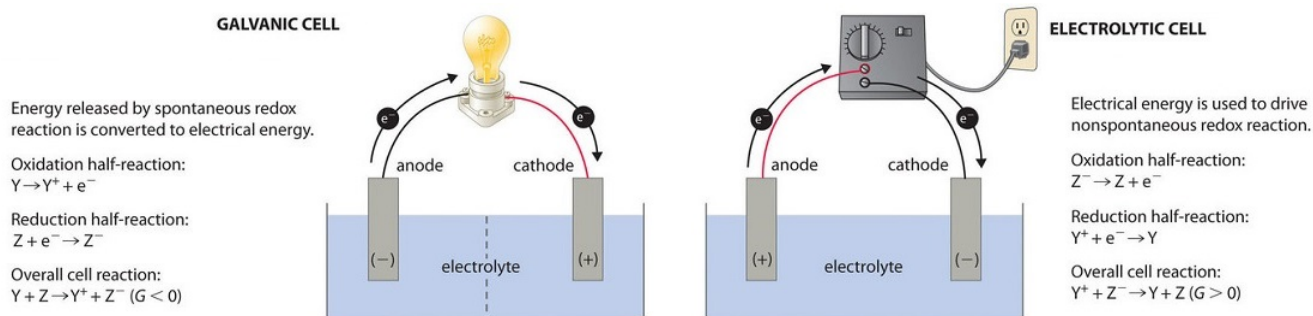

Figure 12.4.1: Electrochemical Cells. A galvanic cell (left) transforms the energy released by a spontaneous redox reaction into electrical energy that can be used to perform work. The oxidative and reductive half-reactions usually occur in separate compartments that are connected by an external electrical circuit; in addition, a second connection that allows ions to flow between the compartments (shown here as a vertical dashed line to represent a porous barrier) is necessary to maintain electrical neutrality. The potential difference between the electrodes (voltage) causes electrons to flow from the reductant to the oxidant through the external circuit, generating an electric current. In an electrolytic cell (right), an external source of electrical energy is used to generate a potential difference between the electrodes that forces electrons to flow, driving a nonspontaneous redox reaction; only a single compartment is employed in most applications. In both kinds of electrochemical cells, the anode is the electrode at which the oxidation half-reaction occurs, and the cathode is the electrode at which the reduction half-reaction occurs.

Voltaic (Galvanic) Cells

To illustrate the basic principles of a galvanic cell, let's consider the reaction of metallic zinc with cupric ion (Cu^{2+}) to give copper metal and Zn^{2+} ion. The balanced chemical equation is as follows:

$$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s) \tag{12.4.1}$$
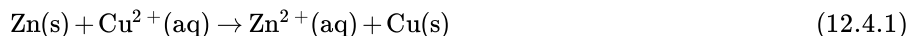
We can cause this reaction to occur by inserting a zinc rod into an aqueous solution of copper(II) sulfate. As the reaction proceeds, the zinc rod dissolves, and a mass of metallic copper forms. These changes occur spontaneously, but all the energy released is in the form of heat rather than in a form that can be used to do work.

Figure 12.4.2: The Reaction of Metallic Zinc with Aqueous Copper(II) Ions in a Single Compartment. When a zinc rod is inserted into a beaker that contains an aqueous solution of copper(II) sulfate, a spontaneous redox reaction occurs: the zinc electrode dissolves to give $Zn^{2+}(aq)$ ions, while $Cu^{2+}(aq)$ ions are simultaneously reduced to metallic copper. The reaction occurs so rapidly that the copper is deposited as very fine particles that appear black, rather than the usual reddish color of copper. (youtu.be/2gPRK0HmYu4)

This same reaction can be carried out using the galvanic cell illustrated in Figure $12.4.3a$. To assemble the cell, a copper strip is inserted into a beaker that contains a 1 M solution of Cu^{2+} ions, and a zinc strip is inserted into a different beaker that contains a 1 M solution of Zn^{2+} ions. The two metal strips, which serve as electrodes, are connected by a wire, and the compartments are connected by a **salt bridge**, a U-shaped tube inserted into both solutions that contains a concentrated liquid or gelled electrolyte. The ions in the salt bridge are selected so that they do not interfere with the electrochemical reaction by being oxidized or reduced

themselves or by forming a precipitate or complex; commonly used cations and anions are Na^+ or K^+ and NO_3^- or SO_4^{2-}, respectively. (The ions in the salt bridge do not have to be the same as those in the redox couple in either compartment.) When the circuit is closed, a spontaneous reaction occurs: zinc metal is oxidized to Zn^{2+} ions at the zinc electrode (the anode), and Cu^{2+} ions are reduced to Cu metal at the copper electrode (the cathode). As the reaction progresses, the zinc strip dissolves, and the concentration of Zn^{2+} ions in the solution increases; simultaneously, the copper strip gains mass, and the concentration of Cu^{2+} ions in the solution decreases (Figure 12.4.3b). Thus we have carried out the same reaction as we did using a single beaker, but this time the oxidative and reductive half-reactions are physically separated from each other. The electrons that are released at the anode flow through the wire, producing an electric current. Galvanic cells therefore transform chemical energy into electrical energy that can then be used to do work.
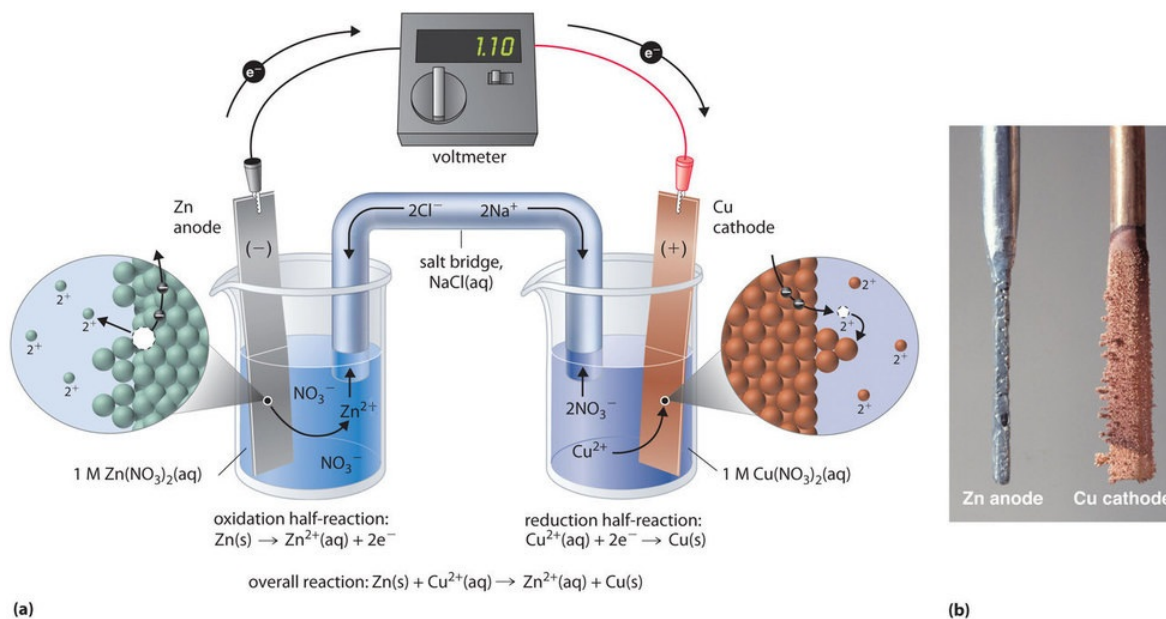
Figure 12.4.3: The Reaction of Metallic Zinc with Aqueous Copper(II) Ions in a Galvanic Cell. (a) A galvanic cell can be constructed by inserting a copper strip into a beaker that contains an aqueous 1 M solution of Cu^{2+} ions and a zinc strip into a different beaker that contains an aqueous 1 M solution of Zn^{2+} ions. The two metal strips are connected by a wire that allows electricity to flow, and the beakers are connected by a salt bridge. When the switch is closed to complete the circuit, the zinc electrode (the anode) is spontaneously oxidized to Zn^{2+} ions in the left compartment, while Cu^{2+} ions are simultaneously reduced to copper metal at the copper electrode (the cathode). (b) As the reaction progresses, the Zn anode loses mass as it dissolves to give Zn^{2+}(aq) ions, while the Cu cathode gains mass as Cu^{2+}(aq) ions are reduced to copper metal that is deposited on the cathode. (CC BY-SA-NC; anonymous)

The electrolyte in the salt bridge serves two purposes: it completes the circuit by carrying electrical charge and maintains electrical neutrality in both solutions by allowing ions to migrate between them. The identity of the salt in a salt bridge is unimportant, as long as the component ions do not react or undergo a redox reaction under the operating conditions of the cell. Without such a connection, the total positive charge in the Zn^{2+} solution would increase as the zinc metal dissolves, and the total positive charge in the Cu^{2+} solution would decrease. The salt bridge allows charges to be neutralized by a flow of anions into the Zn^{2+} solution and a flow of cations into the Cu^{2+} solution. In the absence of a salt bridge or some other similar connection, the reaction would rapidly cease because electrical neutrality could not be maintained.

A voltmeter can be used to measure the difference in electrical potential between the two compartments. Opening the switch that connects the wires to the anode and the cathode prevents a current from flowing, so no chemical reaction occurs. With the switch closed, however, the external circuit is closed, and an electric current can flow from the anode to the cathode. The **potential** (E_{cell}) of the cell, measured in volts, is the difference in electrical potential between the two half-reactions and is related to the energy needed to move a charged particle in an electric field. In the cell we have described, the voltmeter indicates a potential of 1.10 V (Figure 12.4.3a). Because electrons from the oxidation half-reaction are released at the anode, the anode in a galvanic cell is negatively charged. The cathode, which attracts electrons, is positively charged.

Not all electrodes undergo a chemical transformation during a redox reaction. The electrode can be made from an inert, highly conducting metal such as platinum to prevent it from reacting during a redox process, where it does not appear in the overall electrochemical reaction. This phenomenon is illustrated in Example 12.4.1.

*A galvanic (voltaic) cell converts the energy released by a **spontaneous** chemical reaction to electrical energy. An electrolytic cell consumes electrical energy from an external source to drive a **nonspontaneous** chemical reaction.*

✔ Example 12.4.1

A chemist has constructed a galvanic cell consisting of two beakers. One beaker contains a strip of tin immersed in aqueous sulfuric acid, and the other contains a platinum electrode immersed in aqueous nitric acid. The two solutions are connected by a salt bridge, and the electrodes are connected by a wire. Current begins to flow, and bubbles of a gas appear at the platinum electrode. The spontaneous redox reaction that occurs is described by the following balanced chemical equation:
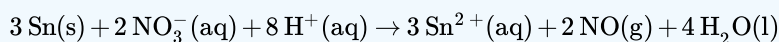
$$3\,\text{Sn(s)} + 2\,\text{NO}_3^-\,(\text{aq}) + 8\,\text{H}^+\,(\text{aq}) \rightarrow 3\,\text{Sn}^{2+}\,(\text{aq}) + 2\,\text{NO(g)} + 4\,\text{H}_2\text{O(l)}$$

For this galvanic cell,

a. write the half-reaction that occurs at each electrode.
b. indicate which electrode is the cathode and which is the anode.
c. indicate which electrode is the positive electrode and which is the negative electrode.

Given: galvanic cell and redox reaction

Asked for: half-reactions, identity of anode and cathode, and electrode assignment as positive or negative

Strategy:
A. Identify the oxidation half-reaction and the reduction half-reaction. Then identify the anode and cathode from the half-reaction that occurs at each electrode.
B. From the direction of electron flow, assign each electrode as either positive or negative.

Solution

A In the reduction half-reaction, nitrate is reduced to nitric oxide. (The nitric oxide would then react with oxygen in the air to form NO_2, with its characteristic red-brown color.) In the oxidation half-reaction, metallic tin is oxidized. The half-reactions corresponding to the actual reactions that occur in the system are as follows:

reduction:

$$\text{NO}_3^-\,(\text{aq}) + 4\,\text{H}^+\,(\text{aq}) + 3\,\text{e}^- \rightarrow \text{NO(g)} + 2\,\text{H}_2\text{O(l)}$$

oxidation:

$$\text{Sn(s)} \rightarrow \text{Sn}^{2+}\,(\text{aq}) + 2\,\text{e}^-$$
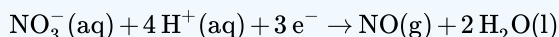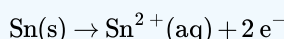
Thus nitrate is reduced to NO, while the tin electrode is oxidized to Sn^{2+}.

Because the reduction reaction occurs at the Pt electrode, it is the cathode. Conversely, the oxidation reaction occurs at the tin electrode, so it is the anode.

B Electrons flow from the tin electrode through the wire to the platinum electrode, where they transfer to nitrate. The electric circuit is completed by the salt bridge, which permits the diffusion of cations toward the cathode and anions toward the anode. Because electrons flow from the tin electrode, it must be electrically negative. In contrast, electrons flow toward the Pt electrode, so that electrode must be electrically positive.

❓ Exercise 12.4.1

Consider a simple galvanic cell consisting of two beakers connected by a salt bridge. One beaker contains a solution of MnO_4^- in dilute sulfuric acid and has a Pt electrode. The other beaker contains a solution of Sn^{2+} in dilute sulfuric acid, also with a Pt electrode. When the two electrodes are connected by a wire, current flows and a spontaneous reaction occurs that is described by the following balanced chemical equation:
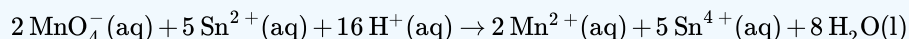
$$2\,\text{MnO}_4^-\,(\text{aq}) + 5\,\text{Sn}^{2+}\,(\text{aq}) + 16\,\text{H}^+\,(\text{aq}) \rightarrow 2\,\text{Mn}^{2+}\,(\text{aq}) + 5\,\text{Sn}^{4+}\,(\text{aq}) + 8\,\text{H}_2\text{O(l)}$$

For this galvanic cell,

   a. write the half-reaction that occurs at each electrode.
   b. indicate which electrode is the cathode and which is the anode.
   c. indicate which electrode is positive and which is negative.

Answer a

$$\text{MnO}_4^-\,(\text{aq}) + 8\,\text{H}^+(\text{aq}) + 5\,\text{e}^- \;\rightarrow \text{Mn}^{2+}(\text{aq}) + 4\,\text{H}_2\text{O}(\text{l})$$

$$\text{Sn}^{2+}(\text{aq}) \rightarrow \text{Sn}^{4+}(\text{aq}) + 2\,\text{e}^-$$
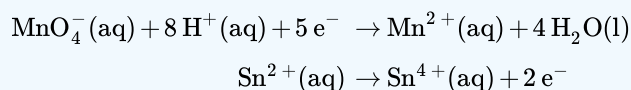
Answer b

The Pt electrode in the permanganate solution is the cathode; the one in the tin solution is the anode.

Answer c

The cathode (electrode in beaker that contains the permanganate solution) is positive, and the anode (electrode in beaker that contains the tin solution) is negative.

Electrochemical Cells: Electrochemical Cells(opens in new window) [youtu.be]

Constructing Cell Diagrams (Cell Notation)

Because it is somewhat cumbersome to describe any given galvanic cell in words, a more convenient notation has been developed. In this line notation, called a cell diagram, the identity of the electrodes and the chemical contents of the compartments are indicated by their chemical formulas, with the anode written on the far left and the cathode on the far right. Phase boundaries are shown by single vertical lines, and the salt bridge, which has two phase boundaries, by a double vertical line. Thus the cell diagram for the Zn/Cu cell shown in Figure $12.4.3a$ is written as follows:
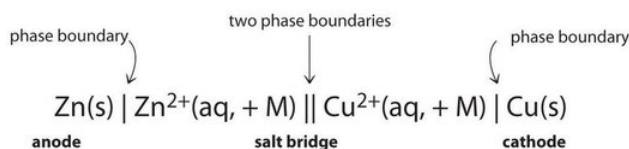
Figure 12.4.4: A cell diagram includes solution concentrations when they are provided. The + M term is meant to indicate the applicable concentration of the species. If the species is a gas, then you substitute the pressure instead.

At the anode is solid zinc. after the phase boundary is aq Zinc two plus and plus M. After the two phase boundary is aq copper two plus and plus M. At the cathode is solid copper.

Galvanic cells can have arrangements other than the examples we have seen so far. For example, the voltage produced by a redox reaction can be measured more accurately using two electrodes immersed in a single beaker containing an electrolyte that completes the circuit. This arrangement reduces errors caused by resistance to the flow of charge at a boundary, called the **junction potential**. One example of this type of galvanic cell is as follows:

$$\text{Pt(s)} \,|\, \text{H}_2(\text{g}) |\text{HCl(aq, 1 M)} \,|\, \text{AgCl(s)} \, \text{Ag(s)}$$
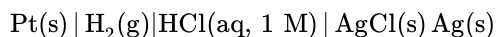
This cell diagram does not include a double vertical line representing a salt bridge because there is no salt bridge providing a junction between two dissimilar solutions. Moreover, solution concentrations have not been specified, so they are not included in the cell diagram. The half-reactions and the overall reaction for this cell are as follows:

cathode reaction:

$$\text{AgCl(s)} + \text{e}^- \rightarrow \text{Ag(s)} + \text{Cl}^-(\text{aq})$$

anode reaction:

$$\tfrac{1}{2}\text{H}_2(\text{g}) \longrightarrow \text{H}^+(\text{aq}) + \text{e}^-$$

overall:

$$\text{AgCl(s)} + \tfrac{1}{2}\text{H}_2(\text{g}) \longrightarrow \text{Ag(s)} + \text{Cl}^- + \text{H}^+(\text{aq})$$
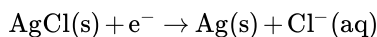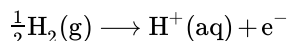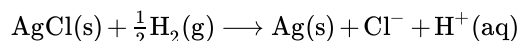
A single-compartment galvanic cell will initially exhibit the same voltage as a galvanic cell constructed using separate compartments, but it will discharge rapidly because of the direct reaction of the reactant at the anode with the oxidized member of the cathodic redox couple. Consequently, cells of this type are not particularly useful for producing electricity.

✔ **Example 12.4.2**

Draw a cell diagram for the galvanic cell described in Example 12.4.1. The balanced chemical reaction is as follows:

$$3\,\text{Sn(s)} + 2\,\text{NO}_3^-(\text{aq}) + 8\,\text{H}^+(\text{aq}) \rightarrow 3\,\text{Sn}^{2+}(\text{aq}) + 2\,\text{NO(g)} + 4\,\text{H}_2\text{O(l)}$$
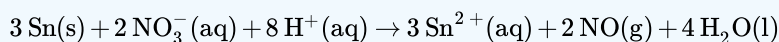
Given: galvanic cell and redox reaction

Asked for: cell diagram

Strategy:
Using the symbols described, write the cell diagram beginning with the oxidation half-reaction on the left.

Solution
The anode is the tin strip, and the cathode is the Pt electrode. Beginning on the left with the anode, we indicate the phase boundary between the electrode and the tin solution by a vertical bar. The anode compartment is thus $\text{Sn(s)} \,|\, \text{Sn}^{2+}(\text{aq})$. We could include $\text{H}_2\text{SO}_4(\text{aq})$ with the contents of the anode compartment, but the sulfate ion (as HSO_4^-) does not participate in the overall reaction, so it does not need to be specifically indicated. The cathode compartment contains aqueous nitric acid, which does participate in the overall reaction, together with the product of the reaction (NO) and the Pt electrode. These are written as $\text{HNO}_3(\text{aq}) \,|\, \text{NO(g)} \,|\, \text{Pt(s)}$, with single vertical bars indicating the phase boundaries. Combining the two compartments and using a double vertical bar to indicate the salt bridge,

$$\text{Sn(s)} \,|\, \text{Sn}^{2+}(\text{aq}) \,||\, \text{HNO}_3(\text{aq}) \,|\, \text{NO(g)} \,|\, \text{Pt(s)}$$

The solution concentrations were not specified, so they are not included in this cell diagram.

? **Exercise 12.4.2**

Draw the cell diagram for the following reaction, assuming the concentration of Ag^+ and Mg^{2+} are each 1 M:

$$\text{Mg(s)} + 2\,\text{Ag}^+(\text{aq}) \rightarrow \text{Mg}^{2+}(\text{aq}) + 2\,\text{Ag(s)}$$

Answer

$$\text{Mg(s)} \,|\, \text{Mg}^{2+}(\text{aq, 1 M)} \,||\, \text{Ag}^+(\text{aq, 1 M)} \,|\, \text{Ag(s)}$$
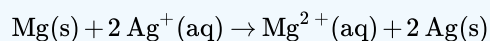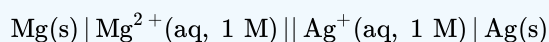
Cell Diagrams: Cell Diagrams(opens in new window) [youtu.be]

Summary

A galvanic (voltaic) cell uses the energy released during a spontaneous redox reaction to generate electricity, whereas an electrolytic cell consumes electrical energy from an external source to force a reaction to occur. Electrochemistry is the study of the relationship between electricity and chemical reactions. The oxidation–reduction reaction that occurs during an electrochemical process consists of two half-reactions, one representing the oxidation process and one the reduction process. The sum of the half-reactions gives the overall chemical reaction. The overall redox reaction is balanced when the number of electrons lost by the reductant equals the number of electrons gained by the oxidant. An electric current is produced from the flow of electrons from the reductant to the oxidant. An electrochemical cell can either generate electricity from a spontaneous redox reaction or consume electricity to drive a nonspontaneous reaction. In a galvanic (voltaic) cell, the energy from a spontaneous reaction generates electricity, whereas in an electrolytic cell, electrical energy is consumed to drive a nonspontaneous redox reaction. Both types of cells use two electrodes that provide an electrical connection between systems that are separated in space. The oxidative half-reaction occurs at the anode, and the reductive half-reaction occurs at the cathode. A salt bridge connects the separated solutions, allowing ions to migrate to either solution to ensure the system's electrical neutrality. A voltmeter is a device that measures the flow of electric current between two half-reactions. The potential of a cell, measured in volts, is the energy needed to move a charged particle in an electric field. An electrochemical cell can be described using line notation called a cell diagram, in which vertical lines indicate phase boundaries and the location of the salt bridge. Resistance to the flow of charge at a boundary is called the junction potential.

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12.5: Standard Reduction Potentials

> **◑ Learning Objectives**
>
> - To use redox potentials to predict whether a reaction is spontaneous.
> - To balance redox reactions using half-reactions.

In a galvanic cell, current is produced when electrons flow externally through the circuit from the anode to the cathode because of a difference in potential energy between the two electrodes in the electrochemical cell. In the Zn/Cu system, the valence electrons in zinc have a substantially higher potential energy than the valence electrons in copper because of shielding of the s electrons of zinc by the electrons in filled d orbitals. Hence electrons flow spontaneously from zinc to copper(II) ions, forming zinc(II) ions and metallic copper. Just like water flowing spontaneously downhill, which can be made to do work by forcing a waterwheel, the flow of electrons from a higher potential energy to a lower one can also be harnessed to perform work.
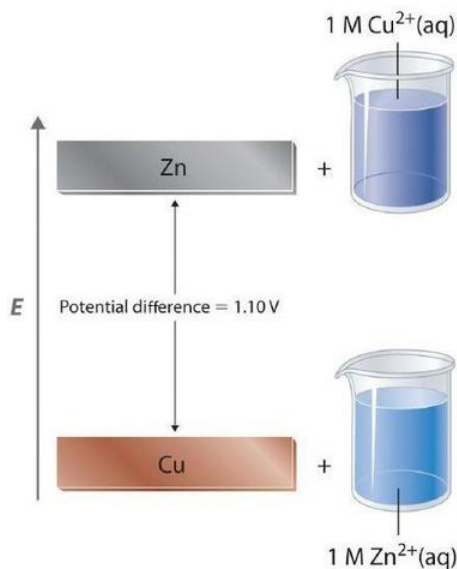
Figure 12.5.1: Potential Energy Difference in the Zn/Cu System. The potential energy of a system consisting of metallic Zn and aqueous Cu^{2+} ions is greater than the potential energy of a system consisting of metallic Cu and aqueous Zn^{2+} ions. Much of this potential energy difference is because the valence electrons of metallic Zn are higher in energy than the valence electrons of metallic Cu. Because the Zn(s) + Cu^{2+}(aq) system is higher in energy by 1.10 V than the Cu(s) + Zn^{2+}(aq) system, energy is released when electrons are transferred from Zn to Cu^{2+} to form Cu and Zn^{2+}.

Because the potential energy of valence electrons differs greatly from one substance to another, the voltage of a galvanic cell depends partly on the identity of the reacting substances. If we construct a galvanic cell similar to the one in part (a) in Figure 12.5.1 but instead of copper use a strip of cobalt metal and 1 M Co^{2+} in the cathode compartment, the measured voltage is not 1.10 V but 0.51 V. Thus we can conclude that the difference in potential energy between the valence electrons of cobalt and zinc is less than the difference between the valence electrons of copper and zinc by 0.59 V.

The measured potential of a cell also depends strongly on the concentrations of the reacting species and the temperature of the system. To develop a scale of relative potentials that will allow us to predict the direction of an electrochemical reaction and the magnitude of the driving force for the reaction, the potentials for oxidations and reductions of different substances must be measured under comparable conditions. To do this, chemists use the **standard cell potential** (E°cell), defined as the potential of a cell measured under standard conditions—that is, with all species in their standard states (1 M for solutions, concentrated solutions of salts (about 1 M) generally do not exhibit ideal behavior, and the actual standard state corresponds to an activity of 1 rather than a concentration of 1 M. Corrections for non ideal behavior are important for precise quantitative work but not for the more qualitative approach that we are taking here. 1 atm for gases, pure solids or pure liquids for other substances) and at a fixed temperature, usually 25°C.

> *Measured redox potentials depend on the potential energy of valence electrons, the concentrations of the species in the reaction, and the temperature of the system.*

Measuring Standard Electrode Potentials

It is physically impossible to measure the potential of a single electrode: only the difference between the potentials of two electrodes can be measured (this is analogous to measuring **absolute enthalpies** or **free energies**; recall that only differences in enthalpy and free energy can be measured.) We can, however, compare the standard cell potentials for two different galvanic cells that have one kind of electrode in common. This allows us to measure the potential difference between two dissimilar electrodes. For example, the measured standard cell potential (E°) for the Zn/Cu system is 1.10 V, whereas E° for the corresponding Zn/Co system is 0.51 V. This implies that the potential difference between the Co and Cu electrodes is 1.10 V − 0.51 V = 0.59 V. In fact, that is exactly the potential measured under standard conditions if a cell is constructed with the following cell diagram:

$$Co_{(s)} \mid Co^{2+}(aq, 1M) \parallel Cu^{2+}(aq, 1M) \mid Cu(s) \qquad E^{\circ} = 0.59 \ V \tag{12.5.1}$$
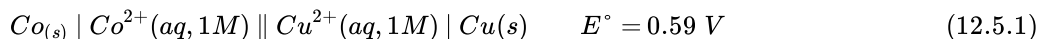
This cell diagram corresponds to the oxidation of a cobalt anode and the reduction of Cu^{2+} in solution at the copper cathode.

All tabulated values of standard electrode potentials by convention are listed for a reaction written as a reduction, not as an oxidation, to be able to compare standard potentials for different substances (Table P1). The standard cell potential (E°$_{cell}$) is therefore the difference between the tabulated reduction potentials of the two half-reactions, not their sum:

$$E^{\circ}_{cell} = E^{\circ}_{cathode} - E^{\circ}_{anode} \tag{12.5.2}$$

In contrast, recall that half-reactions are written to show the reduction and oxidation reactions that actually occur in the cell, so the overall cell reaction is written as the sum of the two half-reactions. According to Equation 12.5.2, when we know the standard potential for any single half-reaction, we can obtain the value of the standard potential of many other half-reactions by measuring the standard potential of the corresponding cell.
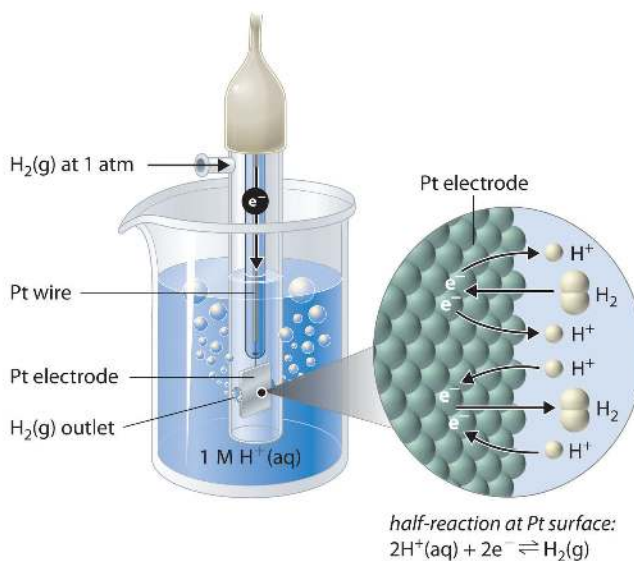
Figure 12.5.2: The Standard Hydrogen Electrode. The SHE consists of platinum wire that is connected to a Pt surface in contact with an aqueous solution containing 1 M H^+ in equilibrium with H_2 gas at a pressure of 1 atm. In the molecular view, the Pt surface catalyzes the oxidation of hydrogen molecules to protons or the reduction of protons to hydrogen gas. (Water is omitted for clarity.) The standard potential of the SHE is arbitrarily assigned a value of 0 V.

Although it is impossible to measure the potential of any electrode directly, we can choose a reference electrode whose potential is defined as 0 V under standard conditions. The **standard hydrogen electrode (SHE)** is universally used for this purpose and is assigned a standard potential of 0 V. It consists of a strip of platinum wire in contact with an aqueous solution containing 1 M H^+. The $[H^+]$ in solution is in equilibrium with H_2 gas at a pressure of 1 atm at the Pt-solution interface (Figure 12.5.2). Protons are reduced or hydrogen molecules are oxidized at the Pt surface according to the following equation:

$$2H^+_{(aq)} + 2e^- \rightleftharpoons H_{2(g)} \tag{12.5.3}$$

One especially attractive feature of the SHE is that the Pt metal electrode is not consumed during the reaction.
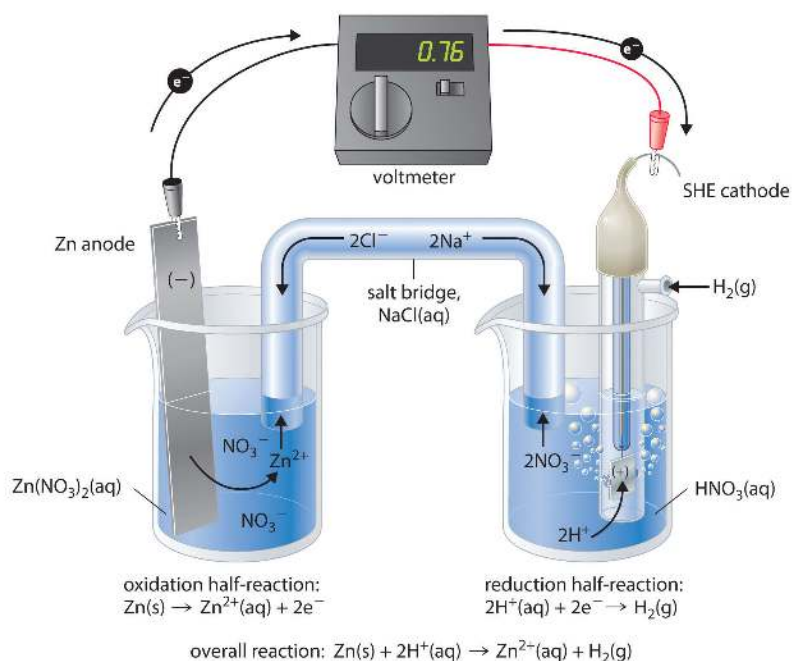
Figure 12.5.3: Determining a Standard Electrode Potential Using a Standard Hydrogen Electrode. The voltmeter shows that the standard cell potential of a galvanic cell consisting of a SHE and a Zn/Zn²⁺ couple is $E°_{cell}$ = 0.76 V. Because the zinc electrode in this cell dissolves spontaneously to form Zn²⁺(aq) ions while H⁺(aq) ions are reduced to H₂ at the platinum surface, the standard electrode potential of the Zn²⁺/Zn couple is −0.76 V.

Figure 12.5.3 shows a galvanic cell that consists of a SHE in one beaker and a Zn strip in another beaker containing a solution of Zn²⁺ ions. When the circuit is closed, the voltmeter indicates a potential of 0.76 V. The zinc electrode begins to dissolve to form Zn²⁺, and H⁺ ions are reduced to H₂ in the other compartment. Thus the hydrogen electrode is the cathode, and the zinc electrode is the anode. The diagram for this galvanic cell is as follows:

$$Zn_{(s)} \mid Zn^{2+}_{(aq)} \parallel H^+(aq, 1M) \mid H_2(g, 1atm) \mid Pt_{(s)} \tag{12.5.4}$$
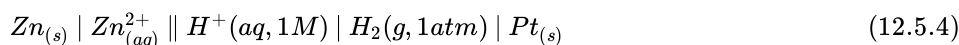
The half-reactions that actually occur in the cell and their corresponding electrode potentials are as follows:

- cathode:
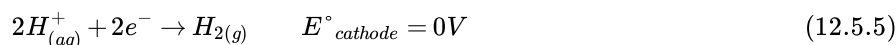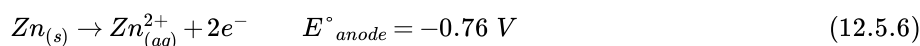
$$2H^+_{(aq)} + 2e^- \rightarrow H_{2(g)} \qquad E°_{cathode} = 0V \tag{12.5.5}$$

- anode:

$$Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^- \qquad E°_{anode} = -0.76\ V \tag{12.5.6}$$

- overall:

$$Zn_{(s)} + 2H^+_{(aq)} \rightarrow Zn^{2+}_{(aq)} + H_{2(g)} \tag{12.5.7}$$

We then use Equation 12.5.2 to calculate the cell potential

$$E°_{cell} = E°_{cathode} - E°_{anode}$$
$$= 0.76\ V$$

Although the reaction at the anode is an oxidation, by convention its tabulated E° value is reported as a reduction potential. The potential of a half-reaction measured against the SHE under standard conditions is called the **standard electrode potential** for that half-reaction. In this example, the standard reduction potential for Zn²⁺(aq) + 2e⁻ → Zn(s) is −0.76 V, which means that the standard electrode potential for the reaction that occurs at the anode, the oxidation of Zn to Zn²⁺, often called the Zn/Zn²⁺ redox couple, or the Zn/Zn²⁺ couple, is −(−0.76 V) = 0.76 V. We must therefore subtract E°₍anode₎ from E°₍cathode₎ to obtain

$$E°_{cell} : 0\ V - (-0.76\ V) = 0.76\ V$$

Because electrical potential is the energy needed to move a charged particle in an electric field, standard electrode potentials for half-reactions are intensive properties and do not depend on the amount of substance involved. Consequently, E° values are independent of the stoichiometric coefficients for the half-reaction, and, most important, the coefficients used to produce a balanced overall reaction do not affect the value of the cell potential.

> *E° values do NOT depend on the stoichiometric coefficients for a half-reaction, because it is an intensive property.*

The Standard Hydrogen Electrode (SHE): The Standard Hydrogen Electrode (SHE)(opens in new window) [youtu.be]

Standard Electrode Potentials

To measure the potential of the Cu/Cu^{2+} couple, we can construct a galvanic cell analogous to the one shown in Figure $12.5.3$ but containing a Cu/Cu^{2+} couple in the sample compartment instead of Zn/Zn^{2+}. When we close the circuit this time, the measured potential for the cell is negative (−0.34 V) rather than positive. The negative value of $E°_{cell}$ indicates that the direction of spontaneous electron flow is the opposite of that for the Zn/Zn^{2+} couple. Hence the reactions that occur spontaneously, indicated by a positive $E°_{cell}$, are the reduction of Cu^{2+} to Cu at the copper electrode. The copper electrode gains mass as the reaction proceeds, and H$_2$ is oxidized to H$^+$ at the platinum electrode. In this cell, the copper strip is the cathode, and the hydrogen electrode is the anode. The cell diagram therefore is written with the SHE on the left and the Cu^{2+}/Cu couple on the right:

$$Pt_{(s)} \mid H_2(g, 1atm) \mid H^+(aq, 1\ M) \parallel Cu^{2+}(aq, 1M) \mid Cu_{(s)} \tag{12.5.8}$$
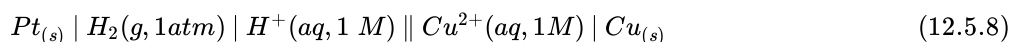
The half-cell reactions and potentials of the spontaneous reaction are as follows:

- Cathode:
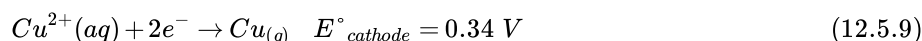
$$Cu^{2+}(aq) + 2e^- \rightarrow Cu_{(g)} \quad E°_{cathode} = 0.34\ V \tag{12.5.9}$$

- Anode:

$$H_{2(g)} \rightarrow 2H^+_{(aq)} + 2e^- \quad E°_{anode} = 0\ V \tag{12.5.10}$$

- Overall:

$$H_{2(g)} + Cu^{2+}_{(aq)} \rightarrow 2H^+_{(aq)} + Cu_{(s)} \tag{12.5.11}$$

We then use Equation $12.5.2$ to calculate the cell potential

$$E°_{cell} = E°_{cathode} - E°_{anode}$$
$$= 0.34\ V$$

Thus the standard electrode potential for the Cu^{2+}/Cu couple is 0.34 V.

Balancing Redox Reactions Using the Half-Reaction Method

In Section 4.4, we described a method for balancing redox reactions using oxidation numbers. Oxidation numbers were assigned to each atom in a redox reaction to identify any changes in the oxidation states. Here we present an alternative approach to balancing redox reactions, the half-reaction method, in which the overall redox reaction is divided into an oxidation half-reaction and a reduction half-reaction, each balanced for mass and charge. This method more closely reflects the events that take place in an electrochemical cell, where the two half-reactions may be physically separated from each other.

We can illustrate how to balance a redox reaction using half-reactions with the reaction that occurs when Drano, a commercial solid drain cleaner, is poured into a clogged drain. Drano contains a mixture of sodium hydroxide and powdered aluminum, which in solution reacts to produce hydrogen gas:

$$Al_{(s)} + OH^-_{(aq)} \rightarrow Al(OH)^-_{4(aq)} + H_{2(g)} \tag{12.5.12}$$

In this reaction, $Al_{(s)}$ is oxidized to Al^{3+}, and H^+ in water is reduced to H_2 gas, which bubbles through the solution, agitating it and breaking up the clogs.

The overall redox reaction is composed of a reduction half-reaction and an oxidation half-reaction. From the standard electrode potentials listed Table P1, we find the corresponding half-reactions that describe the reduction of H^+ ions in water to H_2 and the oxidation of Al to Al^{3+} in basic solution:

- reduction:

$$2H_2O_{(l)} + 2e^- \rightarrow 2OH^-_{(aq)} + H_{2(g)} \tag{12.5.13}$$

- oxidation:

$$Al_{(s)} + 4OH^-_{(aq)} \rightarrow Al(OH)^-_{4(aq)} + 3e^- \tag{12.5.14}$$

The half-reactions chosen must exactly reflect the reaction conditions, such as the basic conditions shown here. Moreover, the physical states of the reactants and the products must be identical to those given in the overall reaction, whether gaseous, liquid, solid, or in solution.

In Equation 12.5.13, two H^+ ions gain one electron each in the reduction; in Equation 12.5.14, the aluminum atom loses three electrons in the oxidation. The charges are balanced by multiplying the reduction half-reaction (Equation 12.5.13) by 3 and the oxidation half-reaction (Equation 12.5.14) by 2 to give the same number of electrons in both half-reactions:

- reduction:

$$6H_2O_{(l)} + 6e^- \rightarrow 6OH^-_{(aq)} + 3H_{2(g)} \tag{12.5.15}$$

- oxidation:

$$2Al_{(s)} + 8OH^-_{(aq)} \rightarrow 2Al(OH)^-_{4(aq)} + 6e^- \tag{12.5.16}$$

Adding the two half-reactions,

$$6H_2O_{(l)} + 2Al_{(s)} + 8OH^-_{(aq)} \rightarrow 2Al(OH)^-4(aq) + 3H_{2(g)} + 6OH^-_{(aq)} \tag{12.5.17}$$
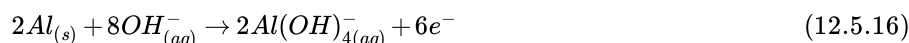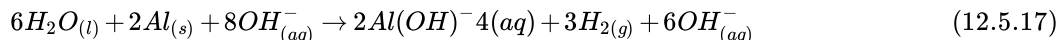
Simplifying by canceling substances that appear on both sides of the equation,

$$6H_2O_{(l)} + 2Al_{(s)} + 2OH^-_{(aq)} \rightarrow 2Al(OH)^-_{4(aq)} + 3H_{2(g)} \tag{12.5.18}$$
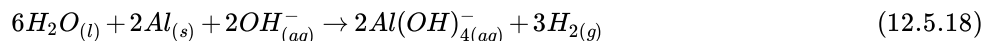
We have a −2 charge on the left side of the equation and a −2 charge on the right side. Thus the charges are balanced, but we must also check that atoms are balanced:

$$2Al + 8O + 14H = 2Al + 8O + 14H \tag{12.5.19}$$

The atoms also balance, so Equation 12.5.18 is a balanced chemical equation for the redox reaction depicted in Equation 12.5.12

> *The half-reaction method requires that half-reactions exactly reflect reaction conditions, and the physical states of the reactants and the products must be identical to those in the overall reaction.*

We can also balance a redox reaction by first balancing the atoms in each half-reaction and then balancing the charges. With this alternative method, we do not need to use the half-reactions listed in Table P1, but instead focus on the atoms whose oxidation states change, as illustrated in the following steps:

Step 1: Write the reduction half-reaction and the oxidation half-reaction.

For the reaction shown in Equation 12.5.12, hydrogen is reduced from H^+ in OH^- to H_2, and aluminum is oxidized from $Al°$ to Al^{3+}:

- reduction:

$$OH^-_{(aq)} \rightarrow H_{2(g)} \tag{12.5.20}$$

- oxidation:

$$Al_{(s)} \rightarrow Al(OH)^-_{4(aq)} \tag{12.5.21}$$

Step 2: Balance the atoms by balancing elements other than O and H. Then balance O atoms by adding H_2O and balance H atoms by adding H^+.

Elements other than O and H in the previous two equations are balanced as written, so we proceed with balancing the O atoms. We can do this by adding water to the appropriate side of each half-reaction:

- reduction:

$$OH^-_{(aq)} \rightarrow H_{2(g)} + H_2O_{(l)} \tag{12.5.22}$$

- oxidation:

$$Al_{(s)} + 4H_2O_{(l)} \rightarrow Al(OH)^-_{4(aq)} \tag{12.5.23}$$

Balancing H atoms by adding H^+, we obtain the following:

- reduction:

$$OH^-_{(aq)} + 3H^+_{(aq)} \rightarrow H_{2(g)} + H_2O_{(l)} \tag{12.5.24}$$

- oxidation:

$$Al_{(s)} + 4H_2O_{(l)} \rightarrow Al(OH)^-_{4(aq)} + 4H^+_{(aq)} \tag{12.5.25}$$
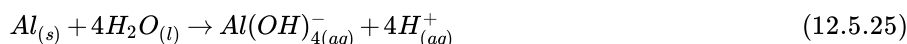
We have now balanced the atoms in each half-reaction, but the charges are not balanced.

Step 3: Balance the charges in each half-reaction by adding electrons.

Two electrons are gained in the reduction of H^+ ions to H_2, and three electrons are lost during the oxidation of $Al°$ to Al^{3+}:

- reduction:

$$OH^-_{(aq)} + 3H^+_{(aq)} + 2e^- \rightarrow H_{2(g)} + H_2O_{(l)} \tag{12.5.26}$$

- oxidation:

$$Al_{(s)} + 4H_2O_{(l)} \rightarrow Al(OH)^-_{4(aq)} + 4H^+_{(aq)} + 3e^- \tag{12.5.27}$$
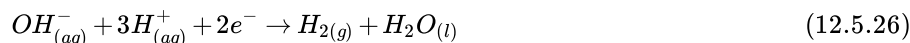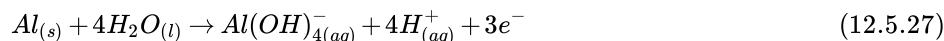
Step 4: Multiply the reductive and oxidative half-reactions by appropriate integers to obtain the same number of electrons in both half-reactions.

In this case, we multiply Equation 12.5.26 (the reductive half-reaction) by 3 and Equation 12.5.27 (the oxidative half-reaction) by 2 to obtain the same number of electrons in both half-reactions:

- reduction:

$$3OH^-_{(aq)} + 9H^+_{(aq)} + 6e^- \rightarrow 3H_{2(g)} + 3H_2O_{(l)} \tag{12.5.28}$$

- oxidation:

$$2Al_{(s)} + 8H_2O_{(l)} \rightarrow 2Al(OH)^-_{4(aq)} + 8H^+_{(aq)} + 6e^- \tag{12.5.29}$$
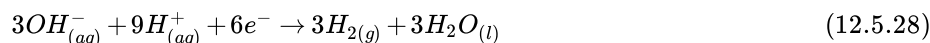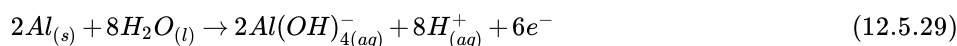
Step 5: Add the two half-reactions and cancel substances that appear on both sides of the equation.

Adding and, in this case, canceling $8H^+$, $3H_2O$, and $6e^-$,

$$2Al_{(s)} + 5H_2O_{(l)} + 3OH^-_{(aq)} + H^+_{(aq)} \rightarrow 2Al(OH)^-_{4(aq)} + 3H_{2(g)} \tag{12.5.30}$$
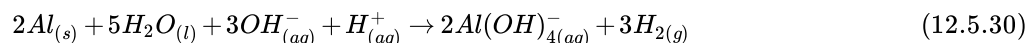
We have three OH^- and one H^+ on the left side. Neutralizing the H^+ gives us a total of $5H_2O + H_2O = 6H_2O$ and leaves $2OH^-$ on the left side:

$$2Al_{(s)} + 6H_2O_{(l)} + 2OH^-_{(aq)} \rightarrow 2Al(OH)^-_{4(aq)} + 3H_{2(g)} \tag{12.5.31}$$
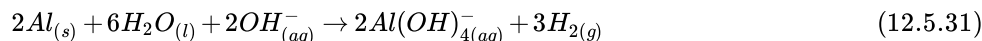
Step 6: Check to make sure that all atoms and charges are balanced.

Equation 12.5.31 is identical to Equation 12.5.18 obtained using the first method, so the charges and numbers of atoms on each side of the equation balance.

> ✔ **Example 12.5.1**
>
> In acidic solution, the redox reaction of dichromate ion ($Cr_2O_7^{2-}$) and iodide (I^-) can be monitored visually. The yellow dichromate solution reacts with the colorless iodide solution to produce a solution that is deep amber due to the presence of a green $Cr^{3+}(aq)$ complex and brown $I_2(aq)$ ions (Figure 12.5.4):
>
> $$Cr_2O_7^{2-}(aq) + I^-(aq) \longrightarrow Cr^{3+}(aq) + I_2(aq)$$
>
> Balance this equation using half-reactions.
>
> **Given:** redox reaction and Table P1
>
> **Asked for:** balanced chemical equation using half-reactions
>
> **Strategy:**
> Follow the steps to balance the redox reaction using the half-reaction method.
>
> **Solution**
> From the standard electrode potentials listed in Table P1, we find the half-reactions corresponding to the overall reaction:
>
> - reduction:
>
> $$Cr_2O_7^{2-}(aq) + 14\,H^+(aq) + 6\,e^- \longrightarrow 2\,Cr^{3+}(aq) + 7\,H_2O(l)$$
>
> - oxidation:
>
> $$2\,I^-(aq) \longrightarrow I_2(aq) + 2\,e^-$$
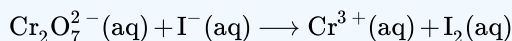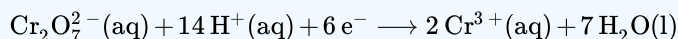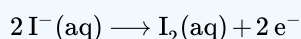
Balancing the number of electrons by multiplying the oxidation reaction by 3,

- oxidation:

$$6\,I^-(aq) \longrightarrow 3\,I_2(aq) + 6\,e^-$$
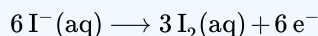
Adding the two half-reactions and canceling electrons,

$$Cr_2O_7^{2-}(aq) + 14\,H^+(aq) + 6\,I^-(aq) \longrightarrow 2\,Cr^{3+}(aq) + 7\,H_2O(l) + 3\,I_2(aq)$$
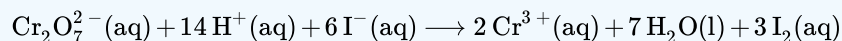
We must now check to make sure the charges and atoms on each side of the equation balance:

$$(-2) + 14 + (-6) = +6$$

$$+6 \overset{\checkmark}{=} +6$$

and atoms

$$2\,Cr + 7\,O + 14\,H + 6\,I \overset{\checkmark}{=} 2\,Cr + 7\,O + 14\,H + 6\,I$$
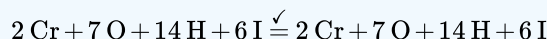
Both the charges and atoms balance, so our equation is balanced.

We can also use the alternative procedure, which does not require the half-reactions listed in Table P1.

Step 1: Chromium is reduced from Cr^{6+} in $Cr_2O_7^{2-}$ to Cr^{3+}, and I^- ions are oxidized to I_2. Dividing the reaction into two half-reactions,

- reduction:

$$Cr_2O_{7(aq)}^{2-} \to Cr_{(aq)}^{3+}$$

- oxidation:

$$I_{(aq)}^- \to I_{2(aq)}$$
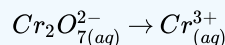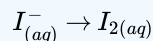
Step 2: Balancing the atoms other than oxygen and hydrogen,

- reduction:

$$Cr_2O_{7(aq)}^{2-} \to 2Cr_{(aq)}^{3+}$$

- oxidation:

$$2I_{(aq)}^- \to I_{2(aq)}$$
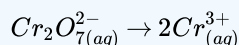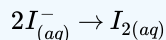
We now balance the O atoms by adding H_2O—in this case, to the right side of the reduction half-reaction. Because the oxidation half-reaction does not contain oxygen, it can be ignored in this step.

- reduction:

$$Cr_2O_{7(aq)}^{2-} \to 2Cr_{(aq)}^{3+} + 7H_2O_{(l)}$$
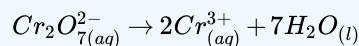
Next we balance the H atoms by adding H^+ to the left side of the reduction half-reaction. Again, we can ignore the oxidation half-reaction.

- reduction:

$$Cr_2O_{7(aq)}^{2-} + 14H_{(aq)}^+ \to 2Cr_{(aq)}^{3+} + 7H_2O_{(l)}$$
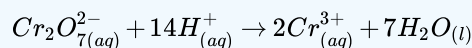
Step 3: We must now add electrons to balance the charges. The reduction half-reaction ($2Cr^{+6}$ to $2Cr^{+3}$) has a +12 charge on the left and a +6 charge on the right, so six electrons are needed to balance the charge. The oxidation half-reaction ($2I^-$ to I_2) has a −2 charge on the left side and a 0 charge on the right, so it needs two electrons to balance the charge:

- reduction: $Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \to 2Cr^{3+}(aq) + 7H_2O(l)$
- oxidation: $2I^-(aq) \to I_2(aq) + 2e^-$

Step 4: To have the same number of electrons in both half-reactions, we must multiply the oxidation half-reaction by 3:

- oxidation: $6\text{I}^-(\text{aq}) \rightarrow 3\text{I}_2(\text{s}) + 6\text{e}^-$

Step 5: Adding the two half-reactions and canceling substances that appear in both reactions,

$$\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 14\,\text{H}^+(\text{aq}) + 6\,\text{I}^-(\text{aq}) \rightarrow 2\,\text{Cr}^{3+}(\text{aq}) + 7\,\text{H}_2\text{O}(\text{l}) + 3\,\text{I}_2(\text{aq})$$
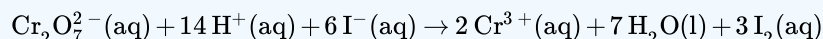
Step 6: This is the same equation we obtained using the first method. Thus the charges and atoms on each side of the equation balance.

? Exercise 12.5.1

Copper is found as the mineral covellite (CuS). The first step in extracting the copper is to dissolve the mineral in nitric acid (HNO_3), which oxidizes sulfide to sulfate and reduces nitric acid to NO:

$$\text{CuS}(\text{s}) + \text{HNO}_3(\text{aq}) \rightarrow \text{NO}(\text{g}) + \text{CuSO}_4(\text{aq})$$
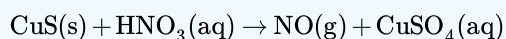
Balance this equation using the half-reaction method.
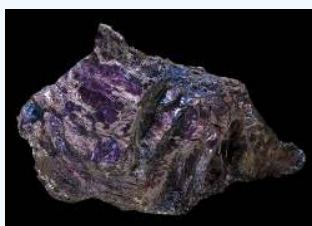
Covellite (also known as covelline) is a rare copper sulfide mineral with an indigo blue color that is ubiquitous in copper ores. (CC SA-BY 3.0;'Didier Descouens).

Answer

$$3\,\text{CuS}(\text{s}) + 8\,\text{HNO}_3(\text{aq}) \longrightarrow 8\,\text{NO}(\text{g}) + 3\,\text{CuSO}_4(\text{aq}) + 4\,\text{H}_2\text{O}(\text{l})$$

Calculating Standard Cell Potentials

The standard cell potential for a redox reaction ($E°_{cell}$) is a measure of the tendency of reactants in their standard states to form products in their standard states; consequently, it is a measure of the driving force for the reaction, which earlier we called voltage. We can use the two standard electrode potentials we found earlier to calculate the standard potential for the Zn/Cu cell represented by the following cell diagram:

$$Zn(s) \mid Zn^{2+}(aq, 1M) \parallel Cu^{2+}(aq, 1M) \mid Cu_{(s)} \tag{12.5.32}$$

We know the values of $E°_{anode}$ for the reduction of Zn^{2+} and $E°_{cathode}$ for the reduction of Cu^{2+}, so we can calculate $E°_{cell}$:

- cathode:

$$Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)} \qquad E°_{cathode} = 0.34\ V \tag{12.5.33}$$

- anode:

$$Zn_{(s)} \rightarrow Zn^{2+}(aq, 1M) + 2e^- \qquad E°_{anode} = -0.76\ V \tag{12.5.34}$$

- overall:

$$Zn_{(s)} + Cu^{2+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + Cu_{(s)} \tag{12.5.35}$$

$$E°_{cell} = E°_{cathode} - E°_{anode} = 1.10\ V$$
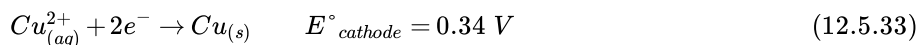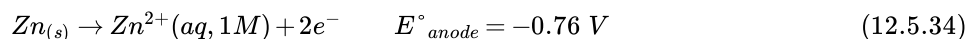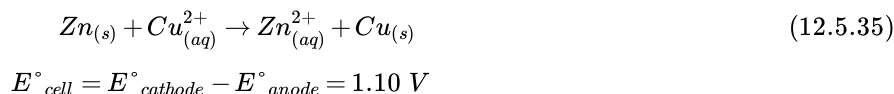
This is the same value that is observed experimentally. If the value of $E°_{cell}$ is positive, the reaction will occur spontaneously as written. If the value of $E°_{cell}$ is negative, then the reaction is not spontaneous, and it will not occur as written under standard conditions; it will, however, proceed spontaneously in the opposite direction. As we shall see in Section 20.9, this does not mean

that the reaction cannot be made to occur at all under standard conditions. With a sufficient input of electrical energy, virtually any reaction can be forced to occur. Example 12.5.2 and its corresponding exercise illustrate how we can use measured cell potentials to calculate standard potentials for redox couples.

> *A positive $E°_{cell}$ means that the reaction will occur spontaneously as written. A negative $E°_{cell}$ means that the reaction will proceed spontaneously in the opposite direction.*

✔ Example 12.5.2

A galvanic cell with a measured standard cell potential of 0.27 V is constructed using two beakers connected by a salt bridge. One beaker contains a strip of gallium metal immersed in a 1 M solution of $GaCl_3$, and the other contains a piece of nickel immersed in a 1 M solution of $NiCl_2$. The half-reactions that occur when the compartments are connected are as follows:

$$\text{cathode: } Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$$

$$\text{anode: } Ga(s) \rightarrow Ga^{3+}(aq) + 3e^-$$
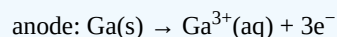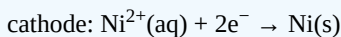
If the potential for the oxidation of Ga to Ga^{3+} is 0.55 V under standard conditions, what is the potential for the oxidation of Ni to Ni^{2+}?

Given: galvanic cell, half-reactions, standard cell potential, and potential for the oxidation half-reaction under standard conditions

Asked for: standard electrode potential of reaction occurring at the cathode

Strategy:
A. Write the equation for the half-reaction that occurs at the anode along with the value of the standard electrode potential for the half-reaction.
B. Use Equation 12.5.2 to calculate the standard electrode potential for the half-reaction that occurs at the cathode. Then reverse the sign to obtain the potential for the corresponding oxidation half-reaction under standard conditions.

Solution
A We have been given the potential for the oxidation of Ga to Ga^{3+} under standard conditions, but to report the standard electrode potential, we must reverse the sign. For the reduction reaction $Ga^{3+}(aq) + 3e^- \rightarrow Ga(s)$, E°$_{anode}$ = −0.55 V.

B Using the value given for $E°_{cell}$ and the calculated value of E°$_{anode}$, we can calculate the standard potential for the reduction of Ni^{2+} to Ni from Equation 12.5.2:

$$E°_{cell} = E°_{cathode} - E°_{anode}$$

$$0.27\,V = E°°_{cathhode} - (-0.55\,V)$$

$$E°_{cathode} = -0.28\,V$$

This is the standard electrode potential for the reaction $Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$. Because we are asked for the potential for the oxidation of Ni to Ni^{2+} under standard conditions, we must reverse the sign of E°$_{cathode}$. Thus E° = −(−0.28 V) = 0.28 V for the oxidation. With three electrons consumed in the reduction and two produced in the oxidation, the overall reaction is not balanced. Recall, however, that standard potentials are independent of stoichiometry.

? Exercise 12.5.2

A galvanic cell is constructed with one compartment that contains a mercury electrode immersed in a 1 M aqueous solution of mercuric acetate $Hg(CH_3CO_2)_2$ and one compartment that contains a strip of magnesium immersed in a 1 M aqueous solution of $MgCl_2$. When the compartments are connected, a potential of 3.22 V is measured and the following half-reactions occur:

- cathode: $Hg^{2+}(aq) + 2\,e^- \rightarrow Hg(l)$
- anode: $Mg(s) \rightarrow Mg^{2+}(aq) + 2\,e^-$

If the potential for the oxidation of Mg to Mg^{2+} is 2.37 V under standard conditions, what is the standard electrode potential for the reaction that occurs at the cathode?

> **Answer**
>
> 0.85 V

Reference Electrodes and Measuring Concentrations

When using a galvanic cell to measure the concentration of a substance, we are generally interested in the potential of only one of the electrodes of the cell, the so-called **indicator electrode**, whose potential is related to the concentration of the substance being measured. To ensure that any change in the measured potential of the cell is due to only the substance being analyzed, the potential of the other electrode, the **reference electrode**, must be constant. You are already familiar with one example of a reference electrode: the SHE. The potential of a reference electrode must be unaffected by the properties of the solution, and if possible, it should be physically isolated from the solution of interest. To measure the potential of a solution, we select a reference electrode and an appropriate indicator electrode. Whether reduction or oxidation of the substance being analyzed occurs depends on the potential of the half-reaction for the substance of interest (the sample) and the potential of the reference electrode.

> *The potential of any reference electrode should not be affected by the properties of the solution to be analyzed, and it should also be physically isolated.*

There are many possible choices of reference electrode other than the SHE. The SHE requires a constant flow of highly flammable hydrogen gas, which makes it inconvenient to use. Consequently, two other electrodes are commonly chosen as reference electrodes. One is the **silver–silver chloride electrode**, which consists of a silver wire coated with a very thin layer of AgCl that is dipped into a chloride ion solution with a fixed concentration. The cell diagram and reduction half-reaction are as follows:

$$Cl^-_{(aq)} \mid AgCl_{(s)} \mid Ag_{(s)} \tag{12.5.36}$$

$$AgCl_{(s)} + e^- \rightarrow Ag_{(s)} + Cl^-_{(aq)}$$
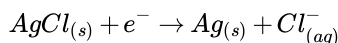
If a saturated solution of KCl is used as the chloride solution, the potential of the silver–silver chloride electrode is 0.197 V versus the SHE. That is, 0.197 V must be subtracted from the measured value to obtain the standard electrode potential measured against the SHE.

A second common reference electrode is the **saturated calomel electrode (SCE)**, which has the same general form as the silver–silver chloride electrode. The SCE consists of a platinum wire inserted into a moist paste of liquid mercury (Hg₂Cl₂; called calomel in the old chemical literature) and KCl. This interior cell is surrounded by an aqueous KCl solution, which acts as a salt bridge between the interior cell and the exterior solution (part (a) in Figure 12.5.5. Although it sounds and looks complex, this cell is actually easy to prepare and maintain, and its potential is highly reproducible. The SCE cell diagram and corresponding half-reaction are as follows:

$$Pt_{(s)} \mid Hg_2Cl_{2(s)} \mid KCl_{(aq,sat)} \tag{12.5.37}$$

$$Hg_2Cl_{2(s)} + 2e^- \rightarrow 2Hg_{(l)} + 2Cl^-(aq) \tag{12.5.38}$$
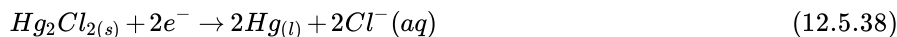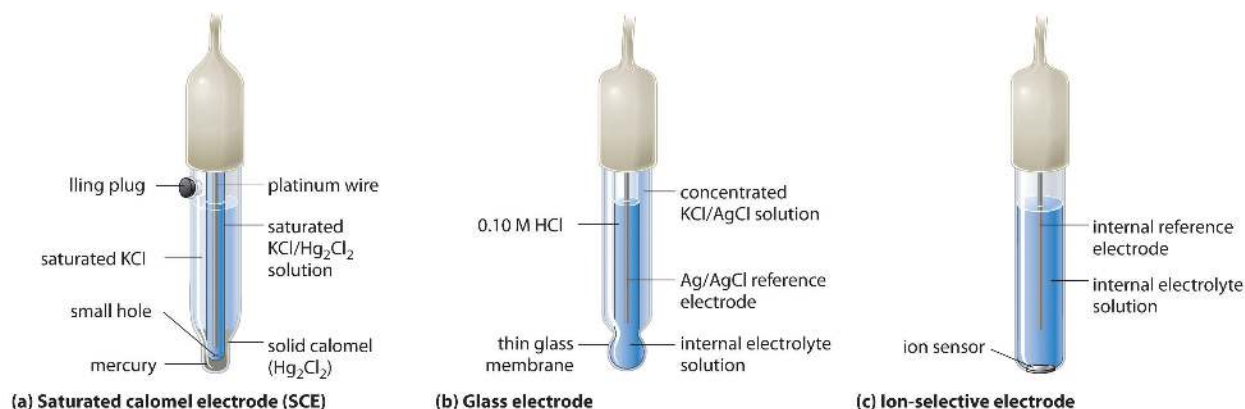
Figure 12.5.5: Three Common Types of Electrodes. (a) The SCE is a reference electrode that consists of a platinum wire inserted into a moist paste of liquid mercury (calomel; Hg_2Cl_2) and KCl. The interior cell is surrounded by an aqueous KCl solution, which acts as a salt bridge between the interior cell and the exterior solution. (b) In a glass electrode, an internal Ag/AgCl electrode is immersed in a 1 M HCl solution that is separated from the sample solution by a very thin glass membrane. The potential of the electrode depends on the H^+ ion concentration of the sample. (c) The potential of an ion-selective electrode depends on the concentration of only a single ionic species in solution. (CC BY-SA-NC; anonymous)

At 25°C, the potential of the SCE is 0.2415 V versus the SHE, which means that 0.2415 V must be subtracted from the potential versus an SCE to obtain the standard electrode potential.

One of the most common uses of electrochemistry is to measure the H^+ ion concentration of a solution. A **glass electrode** is generally used for this purpose, in which an internal Ag/AgCl electrode is immersed in a 0.10 M HCl solution that is separated from the solution by a very thin glass membrane (part (b) in Figure 12.5.5. The glass membrane absorbs protons, which affects the measured potential. The extent of the adsorption on the inner side is fixed because $[H^+]$ is fixed inside the electrode, but the adsorption of protons on the outer surface depends on the pH of the solution. The potential of the glass electrode depends on $[H^+]$ as follows (recall that pH = $-\log[H^+]$):

$$E_{glass} = E' + (0.0591\ V \times \log[H^+]) = E' - 0.0591\ V \times pH \tag{12.5.39}$$

The voltage E′ is a constant that depends on the exact construction of the electrode. Although it can be measured, in practice, a glass electrode is calibrated; that is, it is inserted into a solution of known pH, and the display on the pH meter is adjusted to the known value. Once the electrode is properly calibrated, it can be placed in a solution and used to determine an unknown pH.

Ion-selective electrodes are used to measure the concentration of a particular species in solution; they are designed so that their potential depends on only the concentration of the desired species (part (c) in Figure 12.5.5). These electrodes usually contain an internal reference electrode that is connected by a solution of an electrolyte to a crystalline inorganic material or a membrane, which acts as the sensor. For example, one type of ion-selective electrode uses a single crystal of Eu-doped LaF_3 as the inorganic material. When fluoride ions in solution diffuse to the surface of the solid, the potential of the electrode changes, resulting in a so-called fluoride electrode. Similar electrodes are used to measure the concentrations of other species in solution. Some of the species whose concentrations can be determined in aqueous solution using ion-selective electrodes and similar devices are listed in Table 12.5.1.

Table 12.5.1: Some Species Whose Aqueous Concentrations Can Be Measured Using Electrochemical Methods

Species	Type of Sample
H^+	laboratory samples, blood, soil, and ground and surface water
NH_3/NH_4^+	wastewater and runoff water
K^+	blood, wine, and soil
CO_2/HCO_3^-	blood and groundwater
F^-	groundwater, drinking water, and soil
Br^-	grains and plant extracts
I^-	milk and pharmaceuticals

Species	Type of Sample
NO_3^-	groundwater, drinking water, soil, and fertilizer

Summary

Redox reactions can be balanced using the half-reaction method. The standard cell potential is a measure of the driving force for the reaction. \(E°_{cell} = E°_{cathode} − E°_{anode} \nonumber \] The flow of electrons in an electrochemical cell depends on the identity of the reacting substances, the difference in the potential energy of their valence electrons, and their concentrations. The potential of the cell under standard conditions (1 M for solutions, 1 atm for gases, pure solids or liquids for other substances) and at a fixed temperature (25°C) is called the standard cell potential ($E°_{cell}$). Only the difference between the potentials of two electrodes can be measured. By convention, all tabulated values of standard electrode potentials are listed as standard reduction potentials. The overall cell potential is the reduction potential of the reductive half-reaction minus the reduction potential of the oxidative half-reaction ($E°_{cell} = E°_{cathode} − E°_{anode}$). The potential of the standard hydrogen electrode (SHE) is defined as 0 V under standard conditions. The potential of a half-reaction measured against the SHE under standard conditions is called its standard electrode potential. The standard cell potential is a measure of the driving force for a given redox reaction. All E° values are independent of the stoichiometric coefficients for the half-reaction. Redox reactions can be balanced using the half-reaction method, in which the overall redox reaction is divided into an oxidation half-reaction and a reduction half-reaction, each balanced for mass and charge. The half-reactions selected from tabulated lists must exactly reflect reaction conditions. In an alternative method, the atoms in each half-reaction are balanced, and then the charges are balanced. Whenever a half-reaction is reversed, the sign of E° corresponding to that reaction must also be reversed. If $E°_{cell}$ is positive, the reaction will occur spontaneously under standard conditions. If $E°_{cell}$ is negative, then the reaction is not spontaneous under standard conditions, although it will proceed spontaneously in the opposite direction. The potential of an indicator electrode is related to the concentration of the substance being measured, whereas the potential of the reference electrode is held constant. Whether reduction or oxidation occurs depends on the potential of the sample versus the potential of the reference electrode. In addition to the SHE, other reference electrodes are the silver–silver chloride electrode; the saturated calomel electrode (SCE); the glass electrode, which is commonly used to measure pH; and ion-selective electrodes, which depend on the concentration of a single ionic species in solution. Differences in potential between the SHE and other reference electrodes must be included when calculating values for E°.

12.6: Batteries- Using Chemistry to Generate Electricity

Because galvanic cells can be self-contained and portable, they can be used as batteries and fuel cells. A **battery (storage cell)** is a galvanic cell (or a series of galvanic cells) that contains all the reactants needed to produce electricity. In contrast, a **fuel cell** is a galvanic cell that requires a constant external supply of one or more reactants to generate electricity. In this section, we describe the chemistry behind some of the more common types of batteries and fuel cells.

Batteries

There are two basic kinds of batteries: disposable, or primary, batteries, in which the electrode reactions are effectively irreversible and which cannot be recharged; and rechargeable, or secondary, batteries, which form an insoluble product that adheres to the electrodes. These batteries can be recharged by applying an electrical potential in the reverse direction. The recharging process temporarily converts a rechargeable battery from a galvanic cell to an electrolytic cell.

Batteries are cleverly engineered devices that are based on the same fundamental laws as galvanic cells. The major difference between batteries and the galvanic cells we have previously described is that commercial batteries use solids or pastes rather than solutions as reactants to maximize the electrical output per unit mass. The use of highly concentrated or solid reactants has another beneficial effect: the concentrations of the reactants and the products do not change greatly as the battery is discharged; consequently, the output voltage remains remarkably constant during the discharge process. This behavior is in contrast to that of the Zn/Cu cell, whose output decreases logarithmically as the reaction proceeds (Figure 12.6.1). When a battery consists of more than one galvanic cell, the cells are usually connected in series—that is, with the positive (+) terminal of one cell connected to the negative (−) terminal of the next, and so forth. The overall voltage of the battery is therefore the sum of the voltages of the individual cells.
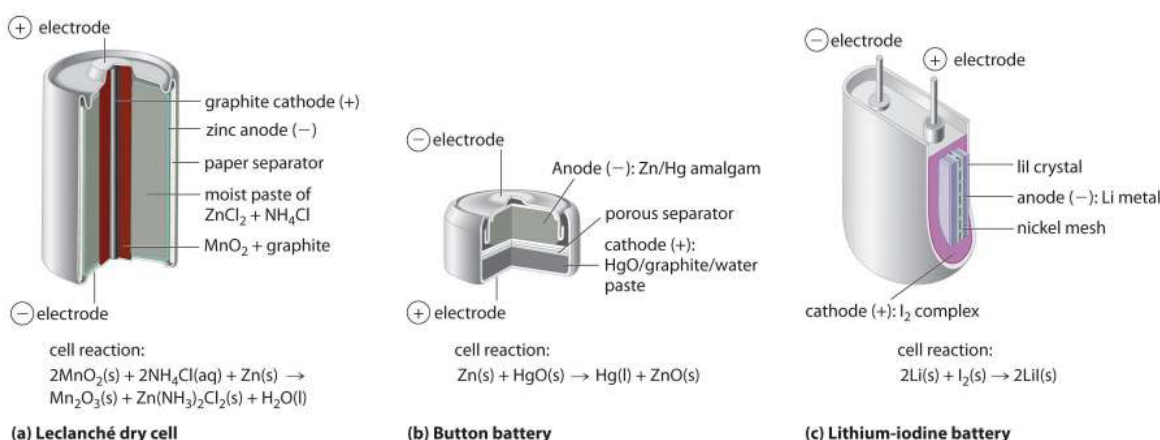
Figure 12.6.1: Three Kinds of Primary (Nonrechargeable) Batteries. (a) A Leclanché dry cell is actually a "wet cell," in which the electrolyte is an acidic water-based paste containing MnO_2, NH_4Cl, $ZnCl_2$, graphite, and starch. Though inexpensive to manufacture, the cell is not very efficient in producing electrical energy and has a limited shelf life. (b) In a button battery, the anode is a zinc–mercury amalgam, and the cathode can be either HgO (shown here) or Ag_2O as the oxidant. Button batteries are reliable and have a high output-to-mass ratio, which allows them to be used in applications such as calculators and watches, where their small size is crucial. (c) A lithium–iodine battery consists of two cells separated by a metallic nickel mesh that collects charge from the anodes. The anode is lithium metal, and the cathode is a solid complex of I_2. The electrolyte is a layer of solid LiI that allows Li^+ ions to diffuse from the cathode to the anode. Although this type of battery produces only a relatively small current, it is highly reliable and long-lived.

> The major difference between batteries and the galvanic cells is that commercial typically batteries use solids or pastes rather than solutions as reactants to maximize the electrical output per unit mass. An obvious exception is the standard car battery which used solution phase chemistry.

Leclanché Dry Cell

The dry cell, by far the most common type of battery, is used in flashlights, electronic devices such as the Walkman and Game Boy, and many other devices. Although the dry cell was patented in 1866 by the French chemist Georges Leclanché and more than 5 billion such cells are sold every year, the details of its electrode chemistry are still not completely understood. In spite of its name, the **Leclanché dry cell** is actually a "wet cell": the electrolyte is an acidic water-based paste containing MnO_2, NH_4Cl, $ZnCl_2$, graphite, and starch (part (a) in Figure 12.6.1). The half-reactions at the anode and the cathode can be summarized as follows:

- cathode (reduction):

$$2\,\mathrm{MnO_2(s)} + 2\,\mathrm{NH_4^+(aq)} + 2\,e^- \longrightarrow \mathrm{Mn_2O_3(s)} + 2\,\mathrm{NH_3(aq)} + \mathrm{H_2O(l)}$$

- anode (oxidation):

$$\mathrm{Zn(s)} \longrightarrow \mathrm{Zn^{2+}(aq)} + 2\,e^-$$
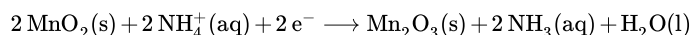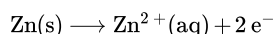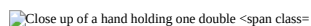
The Zn^{2+} ions formed by the oxidation of $Zn(s)$ at the anode react with NH_3 formed at the cathode and Cl^- ions present in solution, so the overall cell reaction is as follows:

- overall reaction:

$$2\,MnO_2(s) + 2\,NH_4Cl(aq) + Zn(s) \longrightarrow Mn_2O_3(s) + Zn(NH_3)_2Cl_2(s) + H_2O(l) \tag{12.6.1}$$
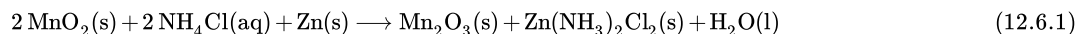
The dry cell produces about 1.55 V and is inexpensive to manufacture. It is not, however, very efficient in producing electrical energy because only the relatively small fraction of the MnO_2 that is near the cathode is actually reduced and only a small fraction of the zinc cathode is actually consumed as the cell discharges. In addition, dry cells have a limited shelf life because the Zn anode reacts spontaneously with NH_4Cl in the electrolyte, causing the case to corrode and allowing the contents to leak out.

Source: Photo courtesy of Mitchclanky2008, www.flickr.com/photos/25597837@N05/2422765479/.

The **alkaline battery** is essentially a Leclanché cell adapted to operate under alkaline, or basic, conditions. The half-reactions that occur in an alkaline battery are as follows:

- cathode (reduction)

$$2\,MnO_2(s) + H_2O(l) + 2\,e^- \longrightarrow Mn_2O_3(s) + 2\,OH^-(aq)$$

- anode (oxidation):

$$Zn(s) + 2\,OH^-(aq) \longrightarrow ZnO(s) + H_2O(l) + 2\,e^-$$

- overall reaction:

$$Zn(s) + 2\,MnO_2(s) \longrightarrow ZnO(s) + Mn_2O_3(s)$$
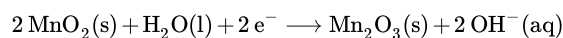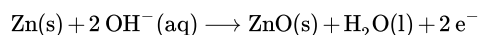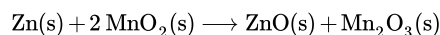
This battery also produces about 1.5 V, but it has a longer shelf life and more constant output voltage as the cell is discharged than the Leclanché dry cell. Although the alkaline battery is more expensive to produce than the Leclanché dry cell, the improved performance makes this battery more cost-effective.

Button Batteries

Although some of the small button batteries used to power watches, calculators, and cameras are miniature alkaline cells, most are based on a completely different chemistry. In these "button" batteries, the anode is a zinc–mercury amalgam rather than pure zinc, and the cathode uses either HgO or Ag_2O as the oxidant rather than MnO_2 in Figure 12.6.1b).

Button batteries. (Gerhard H Wrodnigg via Wikipedia)

The cathode, anode and overall reactions and cell output for these two types of button batteries are as follows (two half-reactions occur at the anode, but the overall oxidation half-reaction is shown):

- cathode (mercury battery):

$$HgO(s) + H_2O(l) + 2\,e^- \longrightarrow Hg(l) + 2\,OH^-(aq)$$
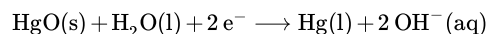
- Anode (mercury battery):

$$Zn + 2\,OH^- \longrightarrow ZnO + H_2O + 2\,e^-$$
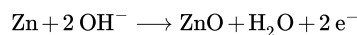
- overall reaction (mercury battery):

$$Zn(s) + 2\,HgO(s) \longrightarrow 2\,Hg(l) + ZnO(s)$$
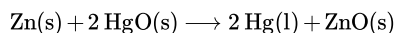
with $E_{cell} = 1.35\,V$.

- cathode reaction (silver battery):

$$Ag_2O(s) + H_2O(l) + 2\,e^- \longrightarrow 2\,Ag(s) + 2\,OH^-(aq)$$
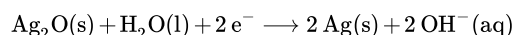
- anode (silver battery):

$$Zn + 2\,OH^- \longrightarrow ZnO + H_2O + 2\,e^-$$
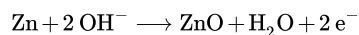
- Overall reaction (silver battery):

$$Zn(s) + 2\,Ag_2O(s) \longrightarrow 2\,Ag(s) + ZnO(s)$$

with $E_{cell} = 1.6\,V$.

The major advantages of the mercury and silver cells are their reliability and their high output-to-mass ratio. These factors make them ideal for applications where small size is crucial, as in cameras and hearing aids. The disadvantages are the expense and the environmental problems caused by the disposal of heavy metals, such as Hg and Ag.

Lithium–Iodine Battery

None of the batteries described above is actually "dry." They all contain small amounts of liquid water, which adds significant mass and causes potential corrosion problems. Consequently, substantial effort has been expended to develop water-free batteries. One of the few commercially successful water-free batteries is the **lithium–iodine battery**. The anode is lithium metal, and the cathode is a solid complex of I_2. Separating them is a layer of solid LiI, which acts as the electrolyte by allowing the diffusion of Li^+ ions. The electrode reactions are as follows:

- cathode (reduction):

$$I_{2(s)} + 2e^- \rightarrow 2I^-{}_{(LiI)} \tag{12.6.2}$$

- anode (oxidation):

$$2Li_{(s)} \rightarrow 2Li^+_{(LiI)} + 2e^- \tag{12.6.3}$$

- overall:

$$2Li_{(s)} + I_{2(s)} \rightarrow 2LiI_{(s)} \tag{12.6.4}$$

with $E_{cell} = 3.5\,V$
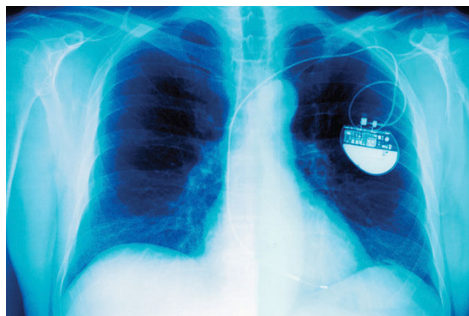
Cardiac pacemaker: An x-ray of a patient showing the location and size of a pacemaker powered by a lithium–iodine battery.

As shown in part (c) in Figure $12.6.1$, a typical lithium–iodine battery consists of two cells separated by a nickel metal mesh that collects charge from the anode. Because of the high internal resistance caused by the solid electrolyte, only a low current can be drawn. Nonetheless, such batteries have proven to be long-lived (up to 10 yr) and reliable. They are therefore used in applications where frequent replacement is difficult or undesirable, such as in cardiac pacemakers and other medical implants and in computers for memory protection. These batteries are also used in security transmitters and smoke alarms. Other batteries based on lithium anodes and solid electrolytes are under development, using TiS_2, for example, for the cathode.

Dry cells, button batteries, and lithium–iodine batteries are disposable and cannot be recharged once they are discharged. Rechargeable batteries, in contrast, offer significant economic and environmental advantages because they can be recharged and discharged numerous times. As a result, manufacturing and disposal costs drop dramatically for a given number of hours of battery usage. Two common rechargeable batteries are the nickel–cadmium battery and the lead–acid battery, which we describe next.

Nickel–Cadmium (NiCad) Battery

The **nickel–cadmium**, or NiCad, battery is used in small electrical appliances and devices like drills, portable vacuum cleaners, and AM/FM digital tuners. It is a water-based cell with a cadmium anode and a highly oxidized nickel cathode that is usually described as the nickel(III) oxo-hydroxide, NiO(OH). As shown in Figure $12.6.2$, the design maximizes the surface area of the electrodes and minimizes the distance between them, which decreases internal resistance and makes a rather high discharge current possible.

cell reaction:
Cd(s) + 2NiO(OH)(s) + 2H$_2$O(l) →
Cd(OH)$_2$(s) + 2Ni(OH)$_2$(s)
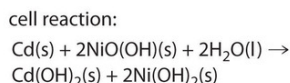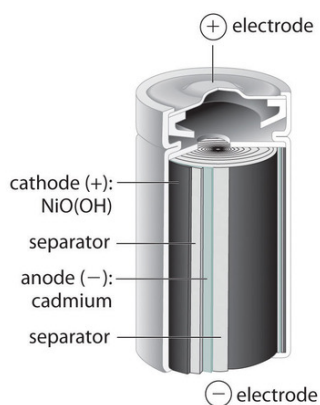
Figure 12.6.2: The Nickel–Cadmium (NiCad) Battery, a Rechargeable Battery. NiCad batteries contain a cadmium anode and a highly oxidized nickel cathode. This design maximizes the surface area of the electrodes and minimizes the distance between them, which gives the battery both a high discharge current and a high capacity.

The electrode reactions during the discharge of a $NiCad$ battery are as follows:

- cathode (reduction):

$$2NiO(OH)_{(s)} + 2H_2O_{(l)} + 2e^- \rightarrow 2Ni(OH)_{2(s)} + 2OH^-_{(aq)} \tag{12.6.5}$$

- anode (oxidation):

$$Cd_{(s)} + 2OH^-_{(aq)} \rightarrow Cd(OH)_{2(s)} + 2e^- \tag{12.6.6}$$

- overall:

$$Cd_{(s)} + 2NiO(OH)_{(s)} + 2H_2O_{(l)} \rightarrow Cd(OH)_{2(s)} + 2Ni(OH)_{2(s)} \tag{12.6.7}$$
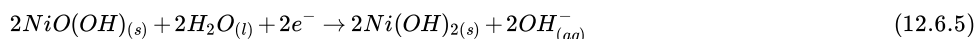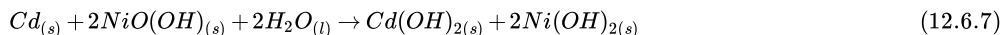
$$E_{cell} = 1.4V$$

Because the products of the discharge half-reactions are solids that adhere to the electrodes [Cd(OH)$_2$ and 2Ni(OH)$_2$], the overall reaction is readily reversed when the cell is recharged. Although NiCad cells are lightweight, rechargeable, and high capacity, they have certain disadvantages. For example, they tend to lose capacity quickly if not allowed to discharge fully before recharging, they do not store well for long periods when fully charged, and they present significant environmental and disposal problems because of the toxicity of cadmium.

A variation on the NiCad battery is the nickel–metal hydride battery (NiMH) used in hybrid automobiles, wireless communication devices, and mobile computing. The overall chemical equation for this type of battery is as follows:

\[NiO(OH)_{(s)} + MH \rightarrow Ni(OH)_{2(s)} + M_{(s)} \label{Eq16} \]

The NiMH battery has a 30%–40% improvement in capacity over the NiCad battery; it is more environmentally friendly so storage, transportation, and disposal are not subject to environmental control; and it is not as sensitive to recharging memory. It is, however, subject to a 50% greater self-discharge rate, a limited service life, and higher maintenance, and it is more expensive than the NiCad battery.

> Directive 2006/66/EC of the European Union prohibits the placing on the market of portable batteries that contain more than 0.002% of cadmium by weight. The aim of this directive was to improve "the environmental performance of batteries and accumulators"

Lead–Acid (Lead Storage) Battery

The **lead–acid battery** is used to provide the starting power in virtually every automobile and marine engine on the market. Marine and car batteries typically consist of multiple cells connected in series. The total voltage generated by the battery is the potential per cell (E°$_{cell}$) times the number of cells.

cell reaction:
Pb(s) + PbO$_2$(s) + 2HSO$_4^-$(aq) + 2H$^+$(aq) →
2PbSO$_4$(s) + 2H$_2$O(l)
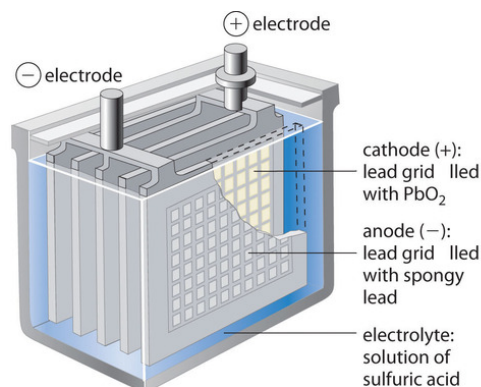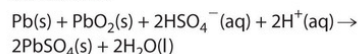
Figure 12.6.3: One Cell of a Lead–Acid Battery. The anodes in each cell of a rechargeable battery are plates or grids of lead containing spongy lead metal, while the cathodes are similar grids containing powdered lead dioxide (PbO$_2$). The electrolyte is an aqueous solution of sulfuric acid. The value of E° for such a cell is about 2 V. Connecting three such cells in series produces a 6 V battery, whereas a typical 12 V car battery contains six cells in series. When treated properly, this type of high-capacity battery can be discharged and recharged many times over.

As shown in Figure 12.6.3, the anode of each cell in a lead storage battery is a plate or grid of spongy lead metal, and the cathode is a similar grid containing powdered lead dioxide (PbO_2). The electrolyte is usually an approximately 37% solution (by mass) of sulfuric acid in water, with a density of 1.28 g/mL (about 4.5 M H_2SO_4). Because the redox active species are solids, there is no need to separate the electrodes. The electrode reactions in each cell during discharge are as follows:

- cathode (reduction):

$$PbO_{2(s)} + HSO^-_{4(aq)} + 3H^+_{(aq)} + 2e^- \rightarrow PbSO_{4(s)} + 2H_2O_{(l)} \label{Eq17}$$
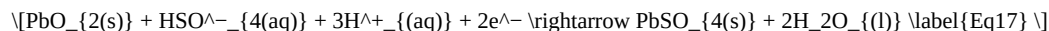
with $E°_{cathode} = 1.685\ V$

- anode (oxidation):

$$Pb_{(s)} + HSO^-_{4(aq)} \rightarrow PbSO_{4(s)} + H^+_{(aq)} + 2e^- \tag{12.6.8}$$

with $E°_{anode} = -0.356\ V$

- overall:

$$Pb_{(s)} + PbO_{2(s)} + 2HSO^-_{4(aq)} + 2H^+_{(aq)} \rightarrow 2PbSO_{4(s)} + 2H_2O_{(l)} \tag{12.6.9}$$
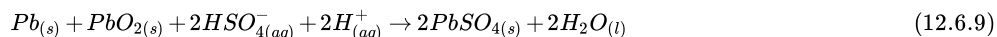
and $E°_{cell} = 2.041\ V$

As the cell is discharged, a powder of $PbSO_4$ forms on the electrodes. Moreover, sulfuric acid is consumed and water is produced, decreasing the density of the electrolyte and providing a convenient way of monitoring the status of a battery by simply measuring the density of the electrolyte. This is often done with the use of a hydrometer.

A hydrometer can be used to test the specific gravity of each cell as a measure of its state of charge (www.youtube.com/watch?v=SRcOqfL6GqQ).

When an external voltage in excess of 2.04 V per cell is applied to a lead–acid battery, the electrode reactions reverse, and $PbSO_4$ is converted back to metallic lead and PbO_2. If the battery is recharged too vigorously, however, electrolysis of water can occur:

$$2H_2O_{(l)} \rightarrow 2H_{2(g)} + O_{2(g)} \tag{12.6.10}$$

This results in the evolution of potentially explosive hydrogen gas. The gas bubbles formed in this way can dislodge some of the $PbSO_4$ or PbO_2 particles from the grids, allowing them to fall to the bottom of the cell, where they can build up and cause an internal short circuit. Thus the recharging process must be carefully monitored to optimize the life of the battery. With proper care, however, a lead–acid battery can be discharged and recharged thousands of times. In automobiles, the alternator supplies the electric current that causes the discharge reaction to reverse.

Fuel Cells

A fuel cell is a galvanic cell that requires a constant external supply of reactants because the products of the reaction are continuously removed. Unlike a battery, it does not store chemical or electrical energy; a fuel cell allows electrical energy to be extracted directly from a chemical reaction. In principle, this should be a more efficient process than, for example, burning the fuel to drive an internal combustion engine that turns a generator, which is typically less than 40% efficient, and in fact, the efficiency of a fuel cell is generally between 40% and 60%. Unfortunately, significant cost and reliability problems have hindered the wide-scale adoption of fuel cells. In practice, their use has been restricted to applications in which mass may be a significant cost factor, such as US manned space vehicles.
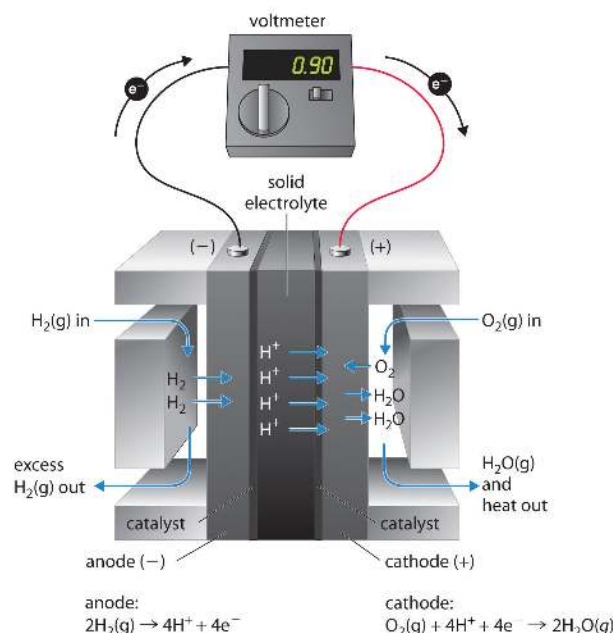
Figure 12.6.4: A Hydrogen Fuel Cell Produces Electrical Energy Directly from a Chemical Reaction. Hydrogen is oxidized to protons at the anode, and the electrons are transferred through an external circuit to the cathode, where oxygen is reduced and combines with H^+ to form water. A solid electrolyte allows the protons to diffuse from the anode to the cathode. Although fuel cells are an essentially pollution-free means of obtaining electrical energy, their expense and technological complexity have thus far limited their applications.

These space vehicles use a hydrogen/oxygen fuel cell that requires a continuous input of H₂(g) and O₂(g), as illustrated in Figure 12.6.4 The electrode reactions are as follows:

- cathode (reduction):

$$O_{2(g)} + 4H^+ + 4e^- \rightarrow 2H_2O_{(g)} \tag{12.6.11}$$

- anode (oxidation):

$$2H_{2(g)} \rightarrow 4H^+ + 4e^- \tag{12.6.12}$$

- overall:

$$2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(g)} \tag{12.6.13}$$

The overall reaction represents an essentially pollution-free conversion of hydrogen and oxygen to water, which in space vehicles is then collected and used. Although this type of fuel cell should produce 1.23 V under standard conditions, in practice the device achieves only about 0.9 V. One of the major barriers to achieving greater efficiency is the fact that the four-electron reduction of $O_2(g)$ at the cathode is intrinsically rather slow, which limits current that can be achieved. All major automobile manufacturers have major research programs involving fuel cells: one of the most important goals is the development of a better catalyst for the reduction of $O_2(g)$.

Summary

Commercial batteries are galvanic cells that use solids or pastes as reactants to maximize the electrical output per unit mass. A battery is a contained unit that produces electricity, whereas a fuel cell is a galvanic cell that requires a constant external supply of one or more reactants to generate electricity. One type of battery is the Leclanché dry cell, which contains an electrolyte in an acidic water-based paste. This battery is called an alkaline battery when adapted to operate under alkaline conditions. Button batteries have a high output-to-mass ratio; lithium–iodine batteries consist of a solid electrolyte; the nickel–cadmium (NiCad) battery is rechargeable; and the lead–acid battery, which is also rechargeable, does not require the electrodes to be in separate compartments. A fuel cell requires an external supply of reactants as the products of the reaction are continuously removed. In a fuel cell, energy is not stored; electrical energy is provided by a chemical reaction.

12.7: Electrolysis- Driving Non-spontaneous Chemical Reactions with Electricity

> **Learning Objectives**
>
> - To understand electrolysis and describe it quantitatively.

In this chapter, we have described various galvanic cells in which a spontaneous chemical reaction is used to generate electrical energy. In an electrolytic cell, however, the opposite process, called **electrolysis**, occurs: an external voltage is applied to drive a nonspontaneous reaction. In this section, we look at how electrolytic cells are constructed and explore some of their many commercial applications.

Electrolytic Cells

If we construct an electrochemical cell in which one electrode is copper metal immersed in a 1 M Cu^{2+} solution and the other electrode is cadmium metal immersed in a $1\ M\ Cd^{2+}$ solution and then close the circuit, the potential difference between the two compartments will be 0.74 V. The cadmium electrode will begin to dissolve (Cd is oxidized to Cd^{2+}) and is the anode, while metallic copper will be deposited on the copper electrode (Cu^{2+} is reduced to Cu), which is the cathode (Figure 12.7.1a).
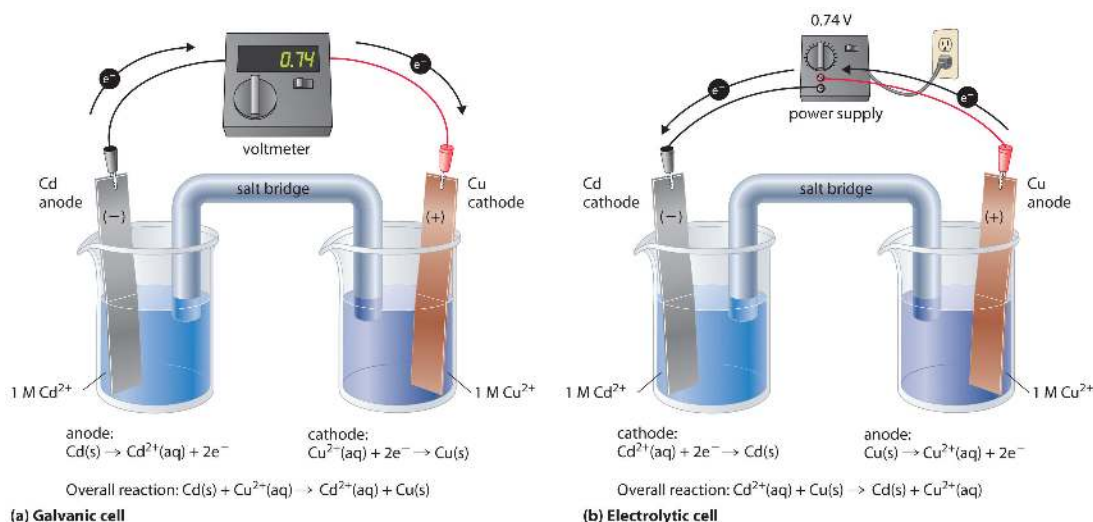
Figure 12.7.1: An Applied Voltage Can Reverse the Flow of Electrons in a Galvanic Cd/Cu Cell. (a) When compartments that contain a Cd electrode immersed in 1 M Cd^{2+}(aq) and a Cu electrode immersed in 1 M Cu^{2+}(aq) are connected to create a galvanic cell, Cd(s) is spontaneously oxidized to Cd^{2+}(aq) at the anode, and Cu^{2+}(aq) is spontaneously reduced to Cu(s) at the cathode. The potential of the galvanic cell is 0.74 V. (b) Applying an external potential greater than 0.74 V in the reverse direction forces electrons to flow from the Cu electrode [which is now the anode, at which metallic Cu(s) is oxidized to Cu^{2+}(aq)] and into the Cd electrode [which is now the cathode, at which Cd^{2+}(aq) is reduced to Cd(s)]. The anode in an electrolytic cell is positive because electrons are flowing from it, whereas the cathode is negative because electrons are flowing into it. (CC BY-SA-NC; anonymous)

The overall reaction is as follows:

$$Cd(s) + Cu^{2+}(aq) \rightarrow Cd^{2+}(aq) + Cu(s)$$
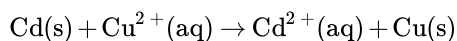
with $E°_{cell} = 0.74\ V$

This reaction is thermodynamically spontaneous as written ($\Delta G^o < 0$):

$$\Delta G° = -nFE°_{cell}$$
$$= -(2\ \text{mol e}^-)[96,485\ \text{J/(V·mol)}](0.74\ \text{V})$$
$$= -140\ \text{kJ (per mole Cd)}$$

In this direction, the system is acting as a galvanic cell.

> *In an electrolytic cell, an external voltage is applied to drive a nonspontaneous reaction.*

The reverse reaction, the reduction of Cd^{2+} by Cu, is thermodynamically nonspontaneous and will occur only with an input of 140 kJ. We can force the reaction to proceed in the reverse direction by applying an electrical potential greater than 0.74 V from an external power supply. The applied voltage forces electrons through the circuit in the reverse direction, converting a galvanic cell to an electrolytic cell. Thus the copper electrode is now the anode (Cu is oxidized), and the cadmium electrode is now the cathode (Cd^{2+} is reduced) (Figure 12.7.1b). The signs of the cathode and the anode have switched to reflect the flow of electrons in the circuit. The half-reactions that occur at the cathode and the anode are as follows:

- half-reaction at the cathode:

$$Cd^{2\,+}(aq) + 2\,e^{-} \rightarrow Cd(s) \tag{12.7.1}$$
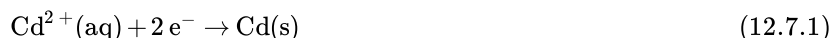
with $E^{\circ}_{cathode} = -0.40\,V$

- half-reaction at the anode:

$$Cu(s) \rightarrow Cu^{2\,+}(aq) + 2\,e^{-} \tag{12.7.2}$$

with $E^{\circ}_{anode} = 0.34\,V$

- Overall Reaction:

$$Cd^{2\,+}(aq) + Cu(s) \rightarrow Cd(s) + Cu^{2\,+}(aq) \tag{12.7.3}$$
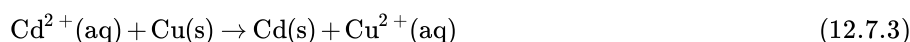
with $E^{\circ}_{cell} = -0.74\,V$

Because $E^{\circ}_{cell} < 0$, the overall reaction—the reduction of Cd^{2+} by Cu—clearly **cannot** occur spontaneously and proceeds only when sufficient electrical energy is applied. The differences between galvanic and electrolytic cells are summarized in Table 12.7.1.

Table 12.7.1: Comparison of Galvanic and Electrolytic Cells

Property	Galvanic Cell	Electrolytic Cell
ΔG	< 0	> 0
E_{cell}	> 0	< 0
Electrode Process		
anode	oxidation	oxidation
cathode	reduction	reduction
Sign of Electrode		
anode	−	+
cathode	+	−

Electrolytic Reactions

At sufficiently high temperatures, ionic solids melt to form liquids that conduct electricity extremely well due to the high concentrations of ions. If two inert electrodes are inserted into molten $NaCl$, for example, and an electrical potential is applied, Cl^{-} is oxidized at the anode, and Na^{+} is reduced at the cathode. The overall reaction is as follows:

$$2\,NaCl(l) \rightarrow 2\,Na(l) + Cl_2(g) \tag{12.7.4}$$

This is the reverse of the formation of $NaCl$ from its elements. The product of the reduction reaction is liquid sodium because the melting point of sodium metal is 97.8°C, well below that of $NaCl$ (801°C). Approximately 20,000 tons of sodium metal are produced commercially in the United States each year by the electrolysis of molten $NaCl$ in a Downs cell (Figure 12.7.2). In this specialized cell, $CaCl_2$ (melting point = 772°C) is first added to the $NaCl$ to lower the melting point of the mixture to about 600°C, thereby lowering operating costs.
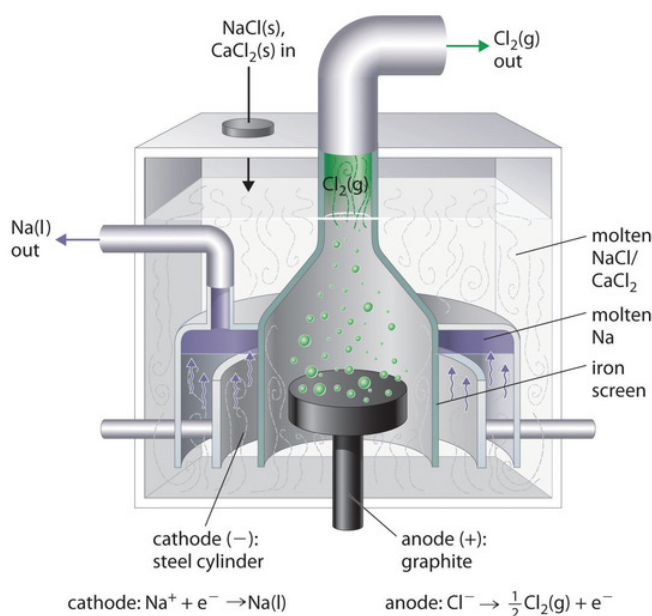
Figure 12.7.2: A Downs Cell for the Electrolysis of Molten NaCl. The electrolysis of a molten mixture of NaCl and $CaCl_2$ results in the formation of elemental sodium and chlorine gas. Because sodium is a liquid under these conditions and liquid sodium is less dense than molten sodium chloride, the sodium floats to the top of the melt and is collected in concentric capped iron cylinders surrounding the cathode. Gaseous chlorine collects in the inverted cone over the anode. An iron screen separating the cathode and anode compartments ensures that the molten sodium and gaseous chlorine do not come into contact. (CC BY-SA-NC; anonymous)

Similarly, in the Hall–Heroult process used to produce aluminum commercially, a molten mixture of about 5% aluminum oxide (Al_2O_3; melting point = 2054°C) and 95% cryolite (Na_3AlF_6; melting point = 1012°C) is electrolyzed at about 1000°C, producing molten aluminum at the cathode and CO_2 gas at the carbon anode. The overall reaction is as follows:

$$2\,Al_2O_3(l) + 3\,C(s) \longrightarrow 4\,Al(l) + 3\,CO_2(g) \tag{12.7.5}$$
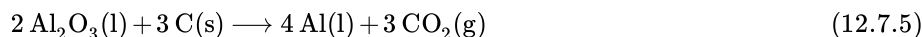
Oxide ions react with oxidized carbon at the anode, producing $CO_2(g)$.

There are two important points to make about these two commercial processes and about the electrolysis of molten salts in general.

1. The electrode potentials for molten salts are likely to be very different from the standard cell potentials listed in Table P2, which are compiled for the reduction of the hydrated ions in aqueous solutions under standard conditions.
2. Using a mixed salt system means there is a possibility of competition between different electrolytic reactions. When a mixture of NaCl and $CaCl_2$ is electrolyzed, Cl^- is oxidized because it is the only anion present, but either Na^+ or Ca^{2+} can be reduced. Conversely, in the Hall–Heroult process, only one cation is present that can be reduced (Al^{3+}), but there are three species that can be oxidized: C, O^{2-}, and F^-.

In the Hall–Heroult process, C is oxidized instead of O^{2-} or F^- because oxygen and fluorine are more electronegative than carbon, which means that C is a weaker oxidant than either O_2 or F_2. Similarly, in the Downs cell, we might expect electrolysis of a NaCl/$CaCl_2$ mixture to produce calcium rather than sodium because Na is slightly less electronegative than Ca (χ = 0.93 versus 1.00, respectively), making Na easier to oxidize and, conversely, Na^+ more difficult to reduce. In fact, the reduction of Na^+ to Na is the observed reaction. In cases where the electronegativities of two species are similar, other factors, such as the formation of complex ions, become important and may determine the outcome.

> ✔ Example 12.7.1
>
> If a molten mixture of $MgCl_2$ and KBr is electrolyzed, what products will form at the cathode and the anode, respectively?
>
> **Given:** identity of salts
>
> **Asked for:** electrolysis products
>
> **Strategy:**

A. List all the possible reduction and oxidation products. Based on the electronegativity values shown in Figure 7.5, determine which species will be reduced and which species will be oxidized.
B. Identify the products that will form at each electrode.

Solution

A The possible reduction products are Mg and K, and the possible oxidation products are Cl_2 and Br_2. Because Mg is more electronegative than K (χ = 1.31 versus 0.82), it is likely that Mg will be reduced rather than K. Because Cl is more electronegative than Br (3.16 versus 2.96), Cl_2 is a stronger oxidant than Br_2.

B Electrolysis will therefore produce Br_2 at the anode and Mg at the cathode.

? Exercise 12.7.1

Predict the products if a molten mixture of $AlBr_3$ and LiF is electrolyzed.

Answer

Br_2 and Al

Electrolysis can also be used to drive the thermodynamically nonspontaneous decomposition of water into its constituent elements: H_2 and O_2. However, because pure water is a very poor electrical conductor, a small amount of an ionic solute (such as H_2SO_4 or Na_2SO_4) must first be added to increase its electrical conductivity. Inserting inert electrodes into the solution and applying a voltage between them will result in the rapid evolution of bubbles of H_2 and O_2 (Figure 12.7.3).
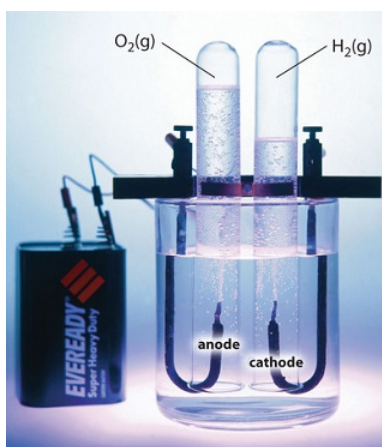
Figure 12.7.3: The Electrolysis of Water. Applying an external potential of about 1.7–1.9 V to two inert electrodes immersed in an aqueous solution of an electrolyte such as H_2SO_4 or Na_2SO_4 drives the thermodynamically nonspontaneous decomposition of water into H_2 at the cathode and O_2 at the anode. (CC BY-SA-NC; anonymous)

The reactions that occur are as follows:

- cathode:

$$2H^+_{(aq)} + 2e^- \rightarrow H_{2(g)} \qquad E^\circ_{cathode} = 0V \qquad (12.7.6)$$

- anode:

$$2H_2O_{(l)} \rightarrow O_{2(g)} + 4H^+_{(aq)} + 4e^- \qquad E^\circ_{anode} = 1.23\ V \qquad (12.7.7)$$

- overall:

$$2H_2O_{(l)} \rightarrow O_{2(g)} + 2H_{2(g)} \qquad E^\circ_{cell} = -1.23\ V \qquad (12.7.8)$$
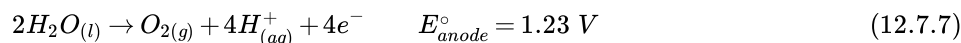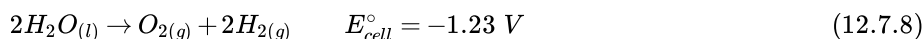
For a system that contains an electrolyte such as Na_2SO_4, which has a negligible effect on the ionization equilibrium of liquid water, the pH of the solution will be 7.00 and $[H^+] = [OH^-] = 1.0 \times 10^{-7}$. Assuming that $P_{O_2} = P_{H_2} = 1$ atm, we can use the standard potentials to calculate E for the overall reaction:

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \left(\frac{0.0591\ \text{V}}{n}\right) \log(P_{O_2} P^2_{H_2}) \qquad (12.7.9)$$

$$= -1.23\ \text{V} - \left(\frac{0.0591\ \text{V}}{4}\right) \log(1) = -1.23\ \text{V} \qquad (12.7.10)$$

Thus E_{cell} is −1.23 V, which is the value of E°_{cell} if the reaction is carried out in the presence of 1 M H^+ rather than at pH 7.0.

In practice, a voltage about 0.4–0.6 V greater than the calculated value is needed to electrolyze water. This added voltage, called an **overvoltage**, represents the additional driving force required to overcome barriers such as the large activation energy for the formation of a gas at a metal surface. Overvoltages are needed in all electrolytic processes, which explain why, for example, approximately 14 V must be applied to recharge the 12 V battery in your car.

In general, any metal that does not react readily with water to produce hydrogen can be produced by the electrolytic reduction of an aqueous solution that contains the metal cation. The p-block metals and most of the transition metals are in this category, but metals in high oxidation states, which form oxoanions, cannot be reduced to the metal by simple electrolysis. Active metals, such as aluminum and those of groups 1 and 2, react so readily with water that they can be prepared only by the electrolysis of molten salts. Similarly, any nonmetallic element that does not readily oxidize water to O_2 can be prepared by the electrolytic oxidation of an aqueous solution that contains an appropriate anion. In practice, among the nonmetals, only F_2 cannot be prepared using this method. Oxoanions of nonmetals in their highest oxidation states, such as NO_3^-, SO_4^{2-}, PO_4^{3-}, are usually difficult to reduce electrochemically and usually behave like spectator ions that remain in solution during electrolysis.

> *In general, any metal that does not react readily with water to produce hydrogen can be produced by the electrolytic reduction of an aqueous solution that contains the metal cation.*

Electroplating

In a process called **electroplating**, a layer of a second metal is deposited on the metal electrode that acts as the cathode during electrolysis. Electroplating is used to enhance the appearance of metal objects and protect them from corrosion. Examples of electroplating include the chromium layer found on many bathroom fixtures or (in earlier days) on the bumpers and hubcaps of cars, as well as the thin layer of precious metal that coats silver-plated dinnerware or jewelry. In all cases, the basic concept is the same. A schematic view of an apparatus for electroplating silverware and a photograph of a commercial electroplating cell are shown in Figure 12.7.4.
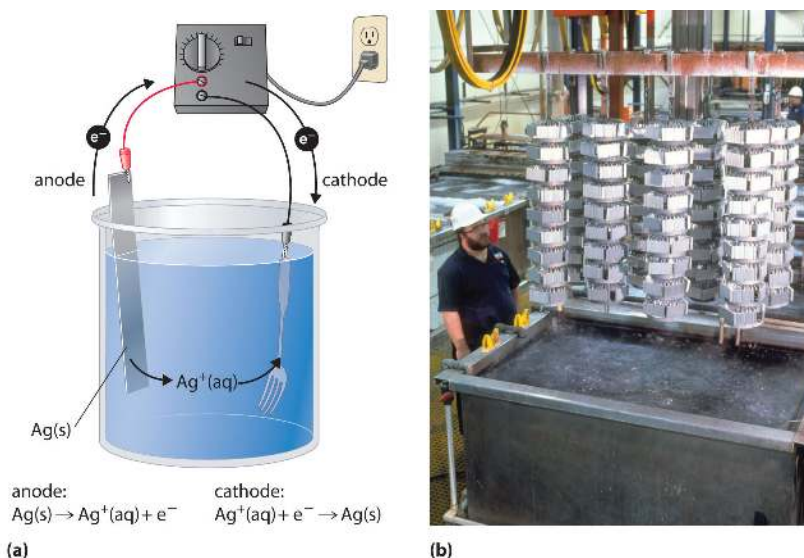
Figure 12.7.3: Electroplating. (a) Electroplating uses an electrolytic cell in which the object to be plated, such as a fork, is immersed in a solution of the metal to be deposited. The object being plated acts as the cathode, on which the desired metal is deposited in a thin layer, while the anode usually consists of the metal that is being deposited (in this case, silver) that maintains the solution concentration as it dissolves. (b) In this commercial electroplating apparatus, a large number of objects can be plated simultaneously by lowering the rack into the Ag^+ solution and applying the correct potential. (CC BY-SA-NC; anonymous)

The half-reactions in electroplating a fork, for example, with silver are as follows:

- cathode (fork):

$$\mathrm{Ag^+(aq)+e^- \longrightarrow Ag(s)} \qquad E°_{cathode}=0.80V$$

- anode (silver bar):

$$\mathrm{Ag(s) \longrightarrow Ag^+(aq)+e^-} \qquad E°_{anode}=0.80V$$
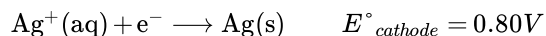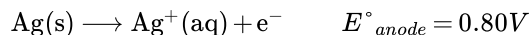
The overall reaction is the transfer of silver metal from one electrode (a silver bar acting as the anode) to another (a fork acting as the cathode). Because $E^o_{cell}=0\,V$, it takes only a small applied voltage to drive the electroplating process. In practice, various other substances may be added to the plating solution to control its electrical conductivity and regulate the concentration of free metal ions, thus ensuring a smooth, even coating.

Quantitative Considerations

If we know the stoichiometry of an electrolysis reaction, the amount of current passed, and the length of time, we can calculate the amount of material consumed or produced in a reaction. Conversely, we can use stoichiometry to determine the combination of current and time needed to produce a given amount of material.

The quantity of material that is oxidized or reduced at an electrode during an electrochemical reaction is determined by the stoichiometry of the reaction and the amount of charge that is transferred. For example, in the reaction

$$\mathrm{Ag^+(aq)+e^- \to Ag(s)}$$
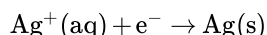
1 mol of electrons reduces 1 mol of $\mathrm{Ag^+}$ to Ag metal. In contrast, in the reaction

$$\mathrm{Cu^{2+}(aq)+2\,e^- \to Cu(s)}$$
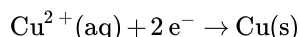
1 mol of electrons reduces only 0.5 mol of $\mathrm{Cu^{2+}}$ to Cu metal. Recall that the charge on 1 mol of electrons is 1 faraday (1 F), which is equal to 96,485 C. We can therefore calculate the number of moles of electrons transferred when a known current is passed through a cell for a given period of time. The total charge (q in coulombs) transferred is the product of the current (I in amperes) and the time (t, in seconds):

$$q = I \times t \tag{12.7.11}$$

The stoichiometry of the reaction and the total charge transferred enable us to calculate the amount of product formed during an electrolysis reaction or the amount of metal deposited in an electroplating process.

For example, if a current of 0.60 A passes through an aqueous solution of $\mathrm{CuSO_4}$ for 6.0 min, the total number of coulombs of charge that passes through the cell is as follows:

$$q = (0.60\ \mathrm{A})(6.0\ \mathrm{min})(60\ \mathrm{s/min})$$
$$= 220\ \mathrm{A \cdot s}$$
$$= 220\ \mathrm{C}$$

The number of moles of electrons transferred to $\mathrm{Cu^{2+}}$ is therefore

$$\mathrm{moles\ e^-} = \frac{220\ \mathrm{C}}{96{,}485\ \mathrm{C/mol}}$$
$$= 2.3 \times 10^{-3}\ \mathrm{mol\ e^-}$$

Because two electrons are required to reduce a single $\mathrm{Cu^{2+}}$ ion, the total number of moles of Cu produced is half the number of moles of electrons transferred, or 1.2×10^{-3} mol. This corresponds to 76 mg of Cu. In commercial electrorefining processes, much higher currents (greater than or equal to 50,000 A) are used, corresponding to approximately 0.5 F/s, and reaction times are on the order of 3–4 weeks.

✔ **Example 12.7.2**

A silver-plated spoon typically contains about 2.00 g of Ag. If 12.0 h are required to achieve the desired thickness of the Ag coating, what is the average current per spoon that must flow during the electroplating process, assuming an efficiency of 100%?

Given: mass of metal, time, and efficiency

Asked for: current required

Strategy:
  A. Calculate the number of moles of metal corresponding to the given mass transferred.
  B. Write the reaction and determine the number of moles of electrons required for the electroplating process.
  C. Use the definition of the faraday to calculate the number of coulombs required. Then convert coulombs to current in amperes.

Solution

A We must first determine the number of moles of Ag corresponding to 2.00 g of Ag:

$$\text{moles Ag} = \frac{2.00 \text{ g}}{107.868 \text{ g/mol}} = 1.85 \times 10^{-2} \text{ mol Ag}$$

B The reduction reaction is $Ag^+(aq) + e^- \rightarrow Ag(s)$, so 1 mol of electrons produces 1 mol of silver.

C Using the definition of the faraday,

$$\text{coulombs} = (1.85 \times 10^{-2}\text{mol e}^-)(96{,}485 \text{ C/mol e}^-) = 1.78 \times 10^3 \text{ C / mole}$$

The current in amperes needed to deliver this amount of charge in 12.0 h is therefore

$$\text{amperes} = \frac{1.78 \times 10^3 \text{ C}}{(12.0 \text{ h})(60 \text{ min/h})(60 \text{ s/min})}$$
$$= 4.12 \times 10^{-2} \text{ C/s} = 4.12 \times 10^{-2} \text{ A}$$

Because the electroplating process is usually much less than 100% efficient (typical values are closer to 30%), the actual current necessary is greater than 0.1 A.

? **Exercise 12.7.2**

A typical aluminum soft-drink can weighs about 29 g. How much time is needed to produce this amount of Al(s) in the Hall–Heroult process, using a current of 15 A to reduce a molten Al_2O_3/Na_3AlF_6 mixture?

Answer

   5.8 h

Electroplating: Electroplating(opens in new window) [youtu.be]

Summary

In electrolysis, an external voltage is applied to drive a **nonspontaneous** reaction. The quantity of material oxidized or reduced can be calculated from the stoichiometry of the reaction and the amount of charge transferred. Relationship of charge, current and time:

$$q = I \times t$$

In electrolysis, an external voltage is applied to drive a nonspontaneous reaction. Electrolysis can also be used to produce H_2 and O_2 from water. In practice, an additional voltage, called an overvoltage, must be applied to overcome factors such as a large activation energy and a junction potential. Electroplating is the process by which a second metal is deposited on a metal surface, thereby enhancing an object's appearance or providing protection from corrosion. The amount of material consumed or produced in a reaction can be calculated from the stoichiometry of an electrolysis reaction, the amount of current passed, and the duration of the electrolytic reaction.

12.8: Corrosion- Undesirable Redox Reactions

> **◀▶ Learning Objectives**
>
> - To understand the process of corrosion.

Corrosion is a galvanic process by which metals deteriorate through oxidation—usually but not always to their oxides. For example, when exposed to air, iron rusts, silver tarnishes, and copper and brass acquire a bluish-green surface called a patina. Of the various metals subject to corrosion, iron is by far the most important commercially. An estimated $100 billion per year is spent in the United States alone to replace iron-containing objects destroyed by corrosion. Consequently, the development of methods for protecting metal surfaces from corrosion constitutes a very active area of industrial research. In this section, we describe some of the chemical and electrochemical processes responsible for corrosion. We also examine the chemical basis for some common methods for preventing corrosion and treating corroded metals.

Corrosion is a REDOX process.

Under ambient conditions, the oxidation of most metals is thermodynamically spontaneous, with the notable exception of gold and platinum. Hence it is actually somewhat surprising that any metals are useful at all in Earth's moist, oxygen-rich atmosphere. Some metals, however, are resistant to corrosion for kinetic reasons. For example, aluminum in soft-drink cans and airplanes is protected by a thin coating of metal oxide that forms on the surface of the metal and acts as an impenetrable barrier that prevents further destruction. Aluminum cans also have a thin plastic layer to prevent reaction of the oxide with acid in the soft drink. Chromium, magnesium, and nickel also form protective oxide films. Stainless steels are remarkably resistant to corrosion because they usually contain a significant proportion of chromium, nickel, or both.

In contrast to these metals, when iron corrodes, it forms a red-brown hydrated metal oxide ($Fe_2O_3 \cdot xH_2O$), commonly known as rust, that does not provide a tight protective film (Figure 12.8.1). Instead, the rust continually flakes off to expose a fresh metal surface vulnerable to reaction with oxygen and water. Because both oxygen and water are required for rust to form, an iron nail immersed in deoxygenated water will not rust—even over a period of several weeks. Similarly, a nail immersed in an organic solvent such as kerosene or mineral oil will not rust because of the absence of water even if the solvent is saturated with oxygen.
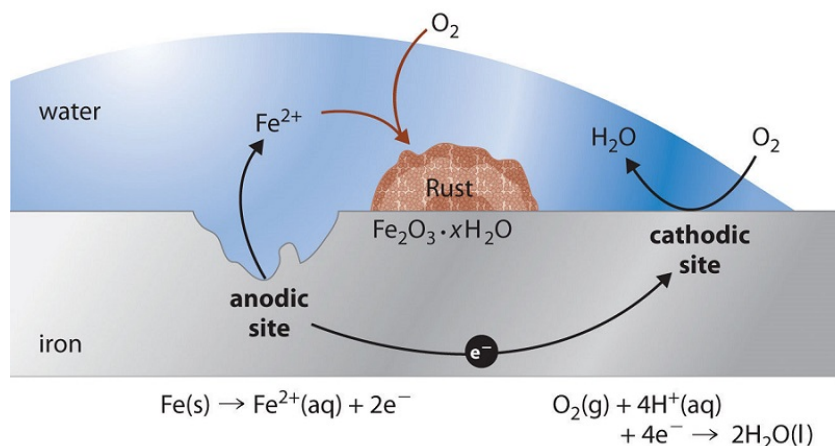
Figure 12.8.1: Rust, the Result of Corrosion of Metallic Iron. Iron is oxidized to Fe^{2+}(aq) at an anodic site on the surface of the iron, which is often an impurity or a lattice defect. Oxygen is reduced to water at a different site on the surface of the iron, which acts as the cathode. Electrons are transferred from the anode to the cathode through the electrically conductive metal. Water is a solvent for the Fe^{2+} that is produced initially and acts as a salt bridge. Rust (Fe_2O_3•xH$_2$O) is formed by the subsequent oxidation of Fe^{2+} by atmospheric oxygen. (CC BY-NC-SA; anonymous)

In the corrosion process, iron metal acts as the anode in a galvanic cell and is oxidized to Fe^{2+}; oxygen is reduced to water at the cathode. The relevant reactions are as follows:

- at cathode:

$$O_2(g) + 4\,H^+(aq) + 4\,e^- \longrightarrow 2\,H_2O(l)$$

with $E^o_{SRP} = 1.23\ V$.

- at anode:

$$Fe(s) \longrightarrow Fe^{2+}(aq) + 2\,e^-$$

with $E^o_{SRP} = -0.45\ V$.

- overall:

$$2\,Fe(s) + O_2(g) + 4\,H^+(aq) \longrightarrow 2\,Fe^{2+}(aq) + 2\,H_2O(l) \tag{12.8.1}$$
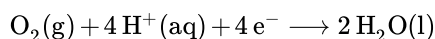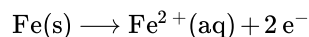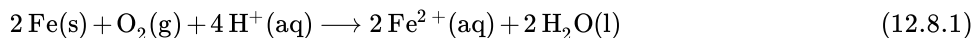
with $E^o_{cell} = 1.68\ V$.

The Fe^{2+} ions produced in the initial reaction are then oxidized by atmospheric oxygen to produce the insoluble hydrated oxide containing Fe^{3+}, as represented in the following equation:

$$4\,Fe^{2+}(aq) + O_2(g) + (2 + 4\,x)H_2O \rightarrow 2\,Fe_2O_3 \cdot xH_2O + 4\,H^+(aq) \tag{12.8.2}$$
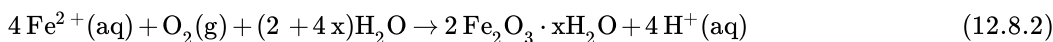
The sign and magnitude of E^o_{cell} for the corrosion process (Equation 12.8.1) indicate that there is a strong driving force for the oxidation of iron by O_2 under standard conditions (1 M H^+). Under neutral conditions, the driving force is somewhat less but still appreciable (E = 1.25 V at pH 7.0). Normally, the reaction of atmospheric CO_2 with water to form H^+ and HCO_3^- provides a low enough pH to enhance the reaction rate, as does acid rain. Automobile manufacturers spend a great deal of time and money developing paints that adhere tightly to the car's metal surface to prevent oxygenated water, acid, and salt from coming into contact with the underlying metal. Unfortunately, even the best paint is subject to scratching or denting, and the electrochemical nature of the corrosion process means that two scratches relatively remote from each other can operate together as anode and cathode, leading to sudden mechanical failure (Figure 12.8.2).
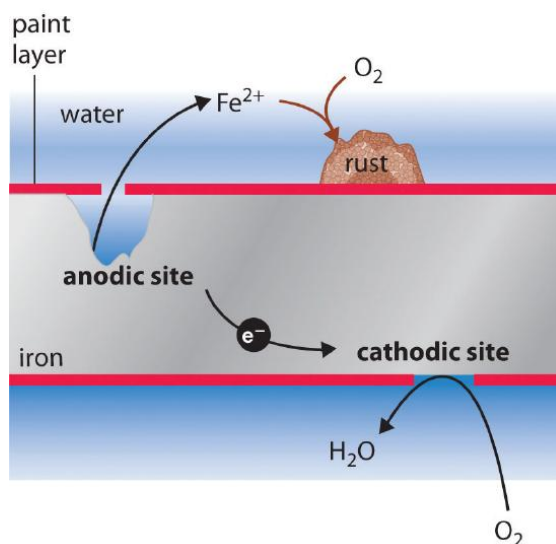
Figure 12.8.2: Small Scratches in a Protective Paint Coating Can Lead to the Rapid Corrosion of Iron. Holes in a protective coating allow oxygen to be reduced at the surface with the greater exposure to air (the cathode), while metallic iron is oxidized to $Fe^{2+}(aq)$ at the less exposed site (the anode). Rust is formed when $Fe^{2+}(aq)$ diffuses to a location where it can react with atmospheric oxygen, which is often remote from the anode. The electrochemical interaction between cathodic and anodic sites can cause a large pit to form under a painted surface, eventually resulting in sudden failure with little visible warning that corrosion has occurred.

Prophylactic Protection

One of the most common techniques used to prevent the corrosion of iron is applying a protective coating of another metal that is more difficult to oxidize. Faucets and some external parts of automobiles, for example, are often coated with a thin layer of chromium using an electrolytic process. With the increased use of polymeric materials in cars, however, the use of chrome-plated steel has diminished in recent years. Similarly, the "tin cans" that hold soups and other foods are actually consist of steel container that is coated with a thin layer of tin. While neither chromium nor tin metals are intrinsically resistant to corrosion, they both form protective oxide coatings that hinder access of oxygen and water to the underlying steel (iron alloy).
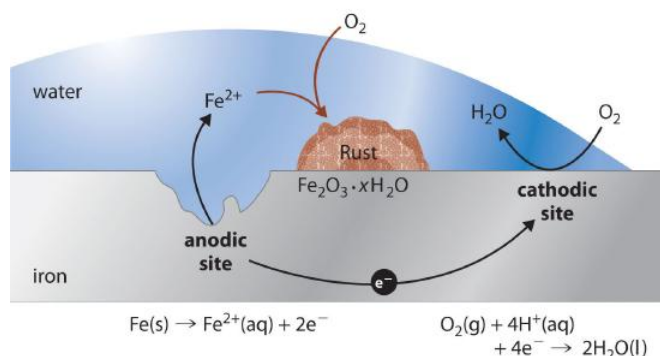
Figure 12.8.3: Galvanic Corrosion. If iron is in contact with a more corrosion-resistant metal such as tin, copper, or lead, the other metal can act as a large cathode that greatly increases the rate of reduction of oxygen. Because the reduction of oxygen is coupled to the oxidation of iron, this can result in a dramatic increase in the rate at which iron is oxidized at the anode. Galvanic corrosion is likely to occur whenever two dissimilar metals are connected directly, allowing electrons to be transferred from one to the other.

As with a protective paint, scratching a protective metal coating will allow corrosion to occur. In this case, however, the presence of the second metal can actually increase the rate of corrosion. The values of the standard electrode potentials for Sn^{2+} (E° = −0.14 V) and Fe^{2+} (E° = −0.45 V) in Table P2 show that Fe is more easily oxidized than Sn. As a result, the more corrosion-resistant metal (in this case, tin) accelerates the corrosion of iron by acting as the cathode and providing a large surface area for the reduction of oxygen (Figure 12.8.3). This process is seen in some older homes where copper and iron pipes have been directly connected to each other. The less easily oxidized copper acts as the cathode, causing iron to dissolve rapidly near the connection and occasionally resulting in a catastrophic plumbing failure.

Cathodic Protection

One way to avoid these problems is to use a more easily oxidized metal to protect iron from corrosion. In this approach, called cathodic protection, a more reactive metal such as Zn (E° = −0.76 V for $Zn^{2+} + 2e^- \longrightarrow Zn$) becomes the anode, and iron becomes the cathode. This prevents oxidation of the iron and protects the iron object from corrosion. The reactions that occur under these conditions are as follows:

$$\underbrace{O_{2(g)} + 4e^- + 4H^+_{(aq)} \rightarrow 2H_2O_{(l)}}_{\text{reduction at cathode}} \qquad (12.8.3)$$

$$\underbrace{Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^-}_{\text{oxidation at anode}} \qquad (12.8.4)$$

$$\underbrace{2Zn_{(s)} + O_{2(g)} + 4H^+_{(aq)} \rightarrow 2Zn^{2+}_{(aq)} + 2H_2O_{(l)}}_{\text{overall}} \qquad (12.8.5)$$
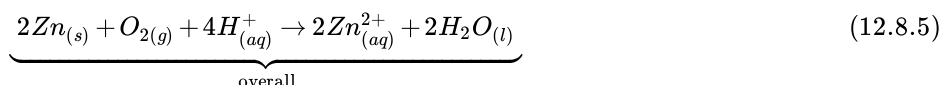
The more reactive metal reacts with oxygen and will eventually dissolve, "sacrificing" itself to protect the iron object. Cathodic protection is the principle underlying galvanized steel, which is steel protected by a thin layer of zinc. Galvanized steel is used in objects ranging from nails to garbage cans.

Crystalline surface of a hot-dip galvanized steel surface. This served both as prophylactic protection (protecting the underlying steel from the oxygen in the air) and cathodic protection (once exposed, the zinc will oxidize before the underlying steel).

In a similar strategy, **sacrificial electrodes** using magnesium, for example, are used to protect underground tanks or pipes (Figure 12.8.4). Replacing the sacrificial electrodes is more cost-effective than replacing the iron objects they are protecting.
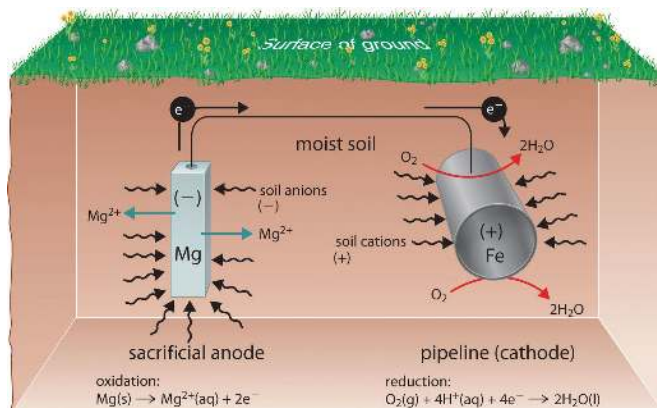
Figure 12.8.4: The Use of a Sacrificial Electrode to Protect Against Corrosion. Connecting a magnesium rod to an underground steel pipeline protects the pipeline from corrosion. Because magnesium (E° = −2.37 V) is much more easily oxidized than iron (E° = −0.45 V), the Mg rod acts as the anode in a galvanic cell. The pipeline is therefore forced to act as the cathode at which oxygen is reduced. The soil between the anode and the cathode acts as a salt bridge that completes the electrical circuit and maintains electrical neutrality. As Mg(s) is oxidized to Mg^{2+} at the anode, anions in the soil, such as nitrate, diffuse toward the anode to neutralize the positive charge. Simultaneously, cations in the soil, such as H^+ or NH_4^+, diffuse toward the cathode, where they replenish the protons that are consumed as oxygen is reduced. A similar strategy uses many miles of somewhat less reactive zinc wire to protect the Alaska oil pipeline.

✔ Example 12.8.1

Suppose an old wooden sailboat, held together with iron screws, has a bronze propeller (recall that bronze is an alloy of copper containing about 7%–10% tin).

 a. If the boat is immersed in seawater, what corrosion reaction will occur? What is $E^{o\,\circ}{}_{cell}$?
 b. How could you prevent this corrosion from occurring?

Given: identity of metals

Asked for: corrosion reaction, $E^{o\,\circ}{}_{cell}$, and preventive measures

Strategy:
 A. Write the reactions that occur at the anode and the cathode. From these, write the overall cell reaction and calculate $E^{o\,\circ}{}_{cell}$.
 B. Based on the relative redox activity of various substances, suggest possible preventive measures.

Solution
 a. **A** According to Table P2, both copper and tin are less active metals than iron (i.e., they have higher positive values of $E^{o\,\circ}{}_{cell}$ than iron). Thus if tin or copper is brought into electrical contact by seawater with iron in the presence of oxygen, corrosion will occur. We therefore anticipate that the bronze propeller will act as the cathode at which O_2 is reduced, and the iron screws will act as anodes at which iron dissolves:

cathode:	$O_2(s) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$	$E^\circ_{cathode} = 1.23\ \text{V}$
anode:	$Fe(s) \rightarrow Fe^{2+} + 2e^-$	$E^\circ_{anode} = -0.45\ \text{V}$
overall:	$2Fe(s) + O_2(g) + 4H^+(aq) \rightarrow 2Fe^{2+}(aq) + 2H_2O(l)$	$E^\circ_{overall} = 1.68\ \text{V}$
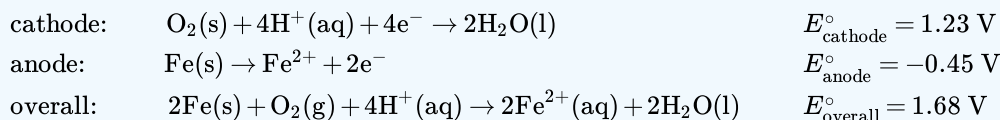
Over time, the iron screws will dissolve, and the boat will fall apart.

 b. **B** Possible ways to prevent corrosion, in order of decreasing cost and inconvenience, are as follows: disassembling the boat and rebuilding it with bronze screws; removing the boat from the water and storing it in a dry place; or attaching an inexpensive piece of zinc metal to the propeller shaft to act as a sacrificial electrode and replacing it once or twice a year. Because zinc is a more active metal than iron, it will act as the sacrificial anode in the electrochemical cell and dissolve (Equation 12.8.5).

Zinc sacrificial anode (rounded object screwed to underside of hull) used to prevent corrosion on the screw in a boat via cathodic protection. Image by Rémi Kaupp and used with permission.

? Exercise 12.8.1

Suppose the water pipes leading into your house are made of lead, while the rest of the plumbing in your house is iron. To eliminate the possibility of lead poisoning, you call a plumber to replace the lead pipes. He quotes you a very low price if he can use up his existing supply of copper pipe to do the job.

a. Do you accept his proposal?
b. What else should you have the plumber do while at your home?

Answer a

Not unless you plan to sell the house very soon because the Cu/Fe pipe joints will lead to rapid corrosion.

Answer b

Any existing Pb/Fe joints should be examined carefully for corrosion of the iron pipes due to the $Pb–Fe$ junction; the less active Pb will have served as the cathode for the reduction of O_2, promoting oxidation of the more active Fe nearby.

Summary

Corrosion is a galvanic process that can be prevented using cathodic protection. The deterioration of metals through oxidation is a galvanic process called corrosion. Protective coatings consist of a second metal that is more difficult to oxidize than the metal being protected. Alternatively, a more easily oxidized metal can be applied to a metal surface, thus providing cathodic protection of the surface. A thin layer of zinc protects galvanized steel. Sacrificial electrodes can also be attached to an object to protect it.

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