# CHEM 2A: GENERAL, ORGANIC, AND BIOLOGICAL CHEMISTRY



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# Chem 2A (Ku)

## Chem 2A (Ku - PCC)

### General, Organic, and Biological Chemistry I

A custom OER textbook for Chemistry 2A at Pasadena City College

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# 1: MEASUREMENT AND PROBLEM SOLVING

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


1.1: Measurements and Significant Figures

1.1.1: Taking Measurements

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# 1.1: MEASUREMENTS AND SIGNIFICANT FIGURES

- Topic hierarchy

### 1.1.1: Taking Measurements

### 1.1.2: Expressing Numbers - Scientific Notation

1.1.2.1: Calculations Involving Scientific Notation (TO DO)

### 1.1.3: Significant Figures - Writing Numbers to Reflect Precision

### 1.1.4: Significant Figures in Calculations

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# 1.1.1: Taking Measurements

## Learning Objectives

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

A coffee maker's instructions tell you to fill the coffee pot with 4 cups of water and to use 3 scoops of coffee. When you follow these instructions, you are measuring. When you visit a doctor's office, a nurse checks your temperature, height, weight, and perhaps blood pressure (Figure 1.1.1.1); the nurse is also measuring.



Figure 1.1.1.1: Measuring Blood Pressure. A nurse or a doctor measuring a patient's blood pressure is taking a measurement. (GFDL; Pia von Lützau).

Chemists measure the properties of matter and express these measurements as quantities. A quantity is an amount of something and consists of a number and a unit. The number tells us how many (or how much), and the unit tells us what the scale of measurement is. For example, when a distance is reported as "5 kilometers," we know that the quantity has been expressed in units of kilometers and that the number of kilometers is 5. If you ask a friend how far they walk from home to school, and the friend answers "12" without specifying a unit, you do not know whether your friend walks 12 kilometers, 12 miles, 12 furlongs, or 12 yards. *Both a number and a unit must be included to express a quantity properly.*

To understand chemistry, we need a clear understanding of the units chemists work with and the rules they follow for expressing numbers. The next two sections examine the rules for expressing numbers.

## Example 1.1.1.1

Identify the number and the unit in each quantity.

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

**Solution**

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

## Key Take Away

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

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# 1.1.2: EXPRESSING NUMBERS - SCIENTIFIC NOTATION

## Learning Objectives

- Express a large number or a small number in scientific notation.
- Convert a number in scientific notation to standard conventional form.

In science, we often must deal with quantities that are extremely small or incredibly large. For example, you may have 5,000,000,000,000 red blood cells in a liter of blood, and the diameter of an iron atom is 0.000000014 inches. Numbers such as these can be cumbersome to work with, so scientists use **scientific notation**.

**Scientific notation** is a system for expressing very large or very small numbers in a compact manner. It uses the idea that such numbers can be rewritten as a simple number (called the *coefficient*) multiplied by an *exponential expression* of 10 raised to a certain exponent, or power.

## Positive and Negative Integer Exponential Expressions

Exponential expressions are a shorthand way of expressing repeated multiplication. For example,

$$5 \bullet 5 \bullet 5 \bullet 5 = 5^4$$

In this example, the 5 is known as the **base** and the superscript 4 is known as the **exponent**. In this exponential expression, the *base* (5) is multiplied by itself *exponent* (4) number of times. The value of $5^4$ is 625.

Exponential expressions can generically be written as so:

$$a^n = a \bullet a \bullet a \bullet \ldots \bullet a \quad (n \text{ factors of } a)$$

The above example utilized positive exponents. When the exponent is negative, the reciprocal of the base is multiplied *n* times instead. For example,

$$5^{-4} = \tfrac{1}{5} \bullet \tfrac{1}{5} \bullet \tfrac{1}{5} \bullet \tfrac{1}{5}$$

The final value of $5^{-4}$ is $\frac{1}{625}$ or 0.0016.

Let us look first at very large numbers. Suppose a spacecraft is 1,500,000 miles from Mars. The number 1,500,000 can be thought of as follows:

$$1.5 \times \underbrace{1{,}000{,}000}_{\underbrace{10 \times 10 \times 10 \times 10 \times 10 \times 10}_{10^6}} = 1.5 \times 10^6$$

That is, 1,500,000 is the same as 1.5 times 1 million, and 1 million is 10 × 10 × 10 × 10 × 10 × 10, or $10^6$ (which is read as "ten to the sixth power"). Therefore, 1,500,000 can be rewritten as 1.5 times $10^6$, or 1.5 × $10^6$. The distance of the spacecraft from Mars can therefore be expressed as 1.5 × $10^6$ miles.

Recall that:

- $10^0 = 1$
- $10^1 = 10$
- $10^2 = 100$
- $10^3 = 1{,}000$
- $10^4 = 10{,}000$
- and so forth

The standard convention for expressing numbers in scientific notation is to write a single *nonzero* first digit, a decimal point, and the rest of the digits, excluding any trailing zeros (see rules for significant figures in the next section for more details on what to exclude). This number is followed by a multiplication sign and then by 10 raised to the power necessary to reproduce the original number. For example, although 1,500,000 can also be written as $15. \times 10^5$ (which would be 15. × 100,000), the convention is to have only one digit before the decimal point. How do we know to what power 10 is raised? The power is the number of places you have to move the decimal point to the *left* to place it after the *first digit*, so that the number being multiplied is *between 1 and 10*:

$$1{,}500{,}000 = 1.5 \times 10^6$$

### Example 1.1.2.1: Scientific Notation

Express each number in scientific notation.

a. 67,000,000,000
b. 1,689
c. 12.6

*Answer a available at the end of this section.*

### Exercise 1.1.2.1

Express each number in scientific notation.

a. 1,492
b. 102,000,000
c. 101,325

*Answer a available at the end of this section.*

To change a number in **scientific notation** to **standard form**, we reverse the process, moving the decimal point to the right. Add zeros to the end of the number being converted, if necessary, to produce a number of the proper magnitude. Lastly, we drop the number 10 and its power.

$$1.5 \times 10^6 = 1.500000. = 1{,}500{,}000$$

### Example 1.1.2.2

Express each number in standard, or conventional notation.

a. $5.27 \times 10^4$

b. $1.0008 \times 10^6$

*Answer a available at the end of this section.*

## Exercise 1.1.2.2

Express each number in standard, or conventional notation.

a. $6.98 \times 10^8$
b. $1.005 \times 10^2$

*Answer a available at the end of this section.*

We can also use scientific notation to express numbers whose magnitudes are less than 1. For example, the quantity 0.006 centimeters can be expressed as follows:

$$6 \times \underbrace{\frac{1}{1,000}}_{\underbrace{\frac{1}{10} \times \frac{1}{10} \times \frac{1}{10}}_{10^{-3}}} = 6 \times 10^{-3}$$

That is, 0.006 centimeters is the same as 6 *divided by* one thousand, which is the same as 6 *divided* by 10 x 10 x 10 or 6 *times* $10^{-3}$ (which is read as "ten to the negative third power"). Therefore, 0.006 centimeters can be rewritten as 6 times $10^{-3}$, or $6 \times 10^{-3}$ centimeters.

Recall that:

- $10^{-1} = 1/10$
- $10^{-2} = 1/100$
- $10^{-3} = 1/1,000$
- $10^{-4} = 1/10,000$
- $10^{-5} = 1/100,000$
- and so forth

We use a negative number as the power to indicate the number of places we have to move the decimal point to the right to make it follow the first nonzero digit so that the number is between 1 and 10. This is illustrated as follows:

$$\underbrace{0.006}_{\text{3 places}} = 6 \times 10^{-3}$$

**Note:**

In writing scientific notations, the convention is to have only *one digit before the decimal point* in the coefficient.

- Numbers that are greater than one have a positive power in scientific notation. If the decimal point is moved to the left n places, the power (n) of 10 is positive. $\underbrace{1,500,000}_{\text{6 places}} = 1.5 \times 10^6$

- Numbers that are less than one have a negative power in scientific notation. If the decimal point is moved to the right n places, the power (n) of 10 is negative. $0.006 = 6 \times 10^{-3}$

**Example 1.1.2.3**

Express each number in scientific notation.

a. 0.000006567
b. −0.0004004
c. 0.000000000000123

*Answer a available at the end of this section.*

**Exercise 1.1.2.3**

Express each number in scientific notation.

a. 0.000355
b. 0.314159
c. −0.051204

*Answer a available at the end of this section.*

As with numbers with positive powers of 10, when changing from **scientific** notation to **standard or conventional** format, we reverse the process.

$$6 \times 10^{-3} = .006 = 0.006$$

**Note**

Changing a number in scientific notation to standard form:

- If the scientific notation has a positive power, the standard number is greater than one. Example: $8 \times 10^4 = 80{,}000$
- If the scientific notation has a negative power, then the standard number is less than one. Example: $8 \times 10^{-2} = 0.08$

**Example 1.1.2.4**

Change the number in scientific notation to standard form.

a. $6.22 \times 10^{-2}$
b. $9.9 \times 10^{-9}$

*Answer a available at the end of this section.*

**Exercise 1.1.2.4**

Change the number in scientific notation to standard form.

a. $9.98 \times 10^{-5}$
b. $5.109 \times 10^{-8}$

*Answer a available at the end of this section.*

Although calculators can show 8 to 10 digits in their display windows, that is not always enough when working with very large or very small numbers. For this reason, many calculators are designed to handle scientific notation. The method for entering scientific notation differs for each calculator model, so take the time to learn how to do it properly on your calculator, *asking your instructor for assistance if necessary*. If you do not learn to enter scientific notation into your calculator properly, you will not get the correct final answer when performing a calculation.

### Using a Scientific Calculator for Scientific Notation

Here is a video that walks through how to put in exponential expressions on a scientific calculator. This video goes through two different types of scientific calculators. Not every calculator will work in these exact ways but it's a good baseline for how to include those. *Regardless of which type of calculator you use, make sure you're comfortable using exponential expressions in your calculator*.

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

View this YouTube Video online

## Concept Review Exercises

1. Why it is easier to use scientific notation to express very large or very small numbers?
2. What is the relationship between how many places a decimal point moves and the power of 10 used in changing a conventional number into scientific notation?

## Answers

1. Scientific notation is more convenient than listing a large number of zeros.
2. The number of places the decimal point moves equals the power of 10. The power of 10 is positive if the decimal point moves to the left and negative if the decimal point moves to the right.

## Key Takeaway

- Large or small numbers are expressed in scientific notation, which use powers of 10.

### Answers

**Example** 1.1.2.1**: Scientific Notation**

Moving the decimal point 10 places to the left gives $6.7 \times 10^{10}$.

The decimal point is assumed to be at the end of the number, so moving it three places to the left gives $1.689 \times 10^{3}$.

In this case, we need to move the decimal point only one place to the left, which yields $1.26 \times 10^{1}$.

**Exercise** 1.1.2.1

Moving the decimal point 3 places to the left gives $1.492 \times 10^{3}$.

The decimal point is assumed to be at the end of the number, so moving it 8 places to the left gives $1.02 \times 10^{8}$.

Moving the decimal point 5 places to the left yields $1.01325 \times 10^{5}$.

**Example** 1.1.2.2

Moving the decimal four places to the right and adding zeros give 52,700.

Moving the decimal six places to the right and adding zeros give 1,000,800.

**Exercise** 1.1.2.2

Moving the decimal point eight places to the right and adding zeros give 698,000,000.

Moving the decimal point two places to the right gives 100.5

**Example** 1.1.2.3

Move the decimal point six places to the right to get $6.567 \times 10^{-6}$.

Move the decimal point four places to the right to get $-4.004 \times 10^{-4}$. The negative sign on the number itself does not affect how we apply the rules of scientific notation.

Move the decimal point 13 places to the right to get $1.23 \times 10^{-13}$.

**Exercise** 1.1.2.3

Moving the decimal point four places to the right gives $3.55 \times 10^{-4}$.

Moving the decimal point one place to the right gives $3.14159 \times 10^{-1}$.

Moving the decimal point one place to the right gives $-5.1204 \times 10^{-2}$.

**Example** 1.1.2.4

0.0622

0.0000000099

**Exercise** 1.1.2.4

0.0000998

0.00000005109

## 1.1.2.1: Calculations Involving Scientific Notation (TO DO)

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# 1.1.2.1: Calculations Involving Scientific Notation (TO DO)

## Learning Objectives

- Perform calculations with numbers in scientific notation

Outside of simply expressing numbers in a less cumbersome manner, writing numbers in scientific notation can also simplify calculations. Since we'll be mostly utilizing these numbers in multiplication and division, we'll focus on those types of calculations on this page. Before discussing these calculations, let's go ahead and review the rules for multiplying and dividing exponential expressions.

## Multiplying and Dividing Exponents

When **multiplying** exponential expressions that have the same base number *a* with exponents *x* and *y*, the final answer will be an exponential expression with the same *base* a but with the exponents added together.

$$a^x \bullet a^y = a^{x+y}$$

In this example, $5^4$ is being multiplied by $5^3$. The resulting expression is $5^7$ which has the value 78125.

$$5^4 \bullet 5^3 = 5^7 = 78125$$

When using negative exponents, remember that adding a negative number is essentially the same as subtracting. For example:

$$5^4 \bullet 5^{-3} = 5^{4+(-3)} = 5^{4-3} = 5^1 = 5$$

When **dividing** exponential expressions with the same base, the final answer will be an exponential expression with the same *base* a but with the numerator exponent subtracted by the denominator exponent. When performing division, it's imperative that you order the terms where the numerator is written first followed by the denominator.

$$a^x \div a^y = a^x / a^y = a^{x+y}$$

In this example, we are dividing $5^4$ by $5^3$ and the end result is simply $5^1$ or 5.

$$5^4 \div 5^3 = 5^{4-3} = 5^1 = 5$$

Be careful when using negative exponents. Recall that subtracting from a negative number is simply just adding the positive value of that number. Thus, when you're subtracting a negative number, this is the same as adding the two values as if they were both positive.

$$5^4 \div 5^{-3} = 5^{4-(-3)} = 5^{4+3} = 5^7 = 78125$$

Here are the steps for multiplying or dividing two numbers in scientific notation.

1. Multiply/divide the coefficients of each term together.
2. Multiply/divide the powers of 10 by adding/subtracting their exponents.
3. Convert your answer to proper scientific notation if necessary.
    - If coefficient >10, move the decimal *x* number of spaces to the left until it is one place to the right of the first non-zero number. Increase the exponent value by *x*
    - If coefficient <10, move the decimal x number of spaces to the right until it is one place to the right of the first non-zero number. Decrease the exponent value by *x*

Here is an example of multiplying two numbers written in scientific notation together.

**Example 1.1.2.1.1**

Multiply $(3.25 \times 10^{-3})(4.23 \times 10^{5})$

**Solution**

1. $(3.25)(4.23) = 13.7$ *Rounded due to significant figures*
2. $(10^{-3})(10^{5}) = 10^{-3+5} = 10^{2}$
3. $13.7 \times 10^{2}$
   - 13.7 is > 10. Move decimal *one* space to the left for 1.37. Add *one* to exponent power for $10^{3}$

Answer: **$1.37 \times 10^{3}$** *Proper way to express scientific notation is with decimal directly to the right of first non-zero.*

Now let's look at dividing two numbers in scientific notation. Note that the order in which the terms are divided does matter.

**Example 1.1.2.1.1**

Divide $(3.25 \times 10^{-3}) \div (4.23 \times 10^{5})$

**Solution**

1. $(3.25) \div (4.23) = 0.768$ *Rounded due to significant figures*
2. $(10^{-3}) \div (10^{5}) = 10^{-3-5} = 10^{-8}$
3. $0.768 \times 10^{-8}$
   - 0.768 is < 10. Move decimal *one* space to the right for 7.68. Subtract *one* from exponent power for $10^{-9}$

Answer: **$7.68 \times 10^{-9}$** *Proper way to express scientific notation is with decimal directly to the right of first non-zero.*

Now that we're familiar with the calculations. Let's go ahead and solve a problem that contains numbers where it would be very useful to express in scientific notation.

> *At its closest, the planet Neptune is 4,300,000,000 kilometers away from Earth. A group of astronauts from Earth want to make it to Neptune in 20,000 days. If they travel the same number of kilometers each day, how many kilometers will they travel each day? Convert both numbers to scientific notation before solving.*

First, convert both numbers to scientific notation.

$$4{,}300{,}000{,}000 = 4.3 \times 10^{9}$$

$$20{,}000 = 2 \times 10^{4}$$

Next, notice that the astronauts want to travel the same distance each day. You will need to divide the total distance by the number of days to find the distance they will need to travel each day.

$$(4.3 \times 10^{9}) \div (2 \times 10^{4})$$

Now, divide the decimal numbers using what you have learned about decimal division.

$$4.3 \div 2 = 2.15$$

Next, divide the powers of 10 by subtracting their exponents.

$$10^9 \div 10^4 = 10^{9-4} = 10^5$$

Now, combine the results.

$$(4.3 \times 10^9) \div (2 \times 10^4) = (4.3 \div 2) \times (10^9 \div 10^4) = 2.15 \times 10^5$$

The answer is that the astronauts will need to travel $2.15 \times 10^5$ or 215,000 kilometers per day. They will be traveling for almost 55 years!

## Concept Review Exercises

1. $(3 \times 10^4) \times (2 \times 10^3)$

2. $(5.2 \times 10^{-2}) \times (1.5 \times 10^5)$

3. $(9 \times 10^8) \div (3 \times 10^4)$

4. $(2.4 \times 10^{-6}) \div (8 \times 10^{-2})$

5. $(6.02 \times 10^{-2}) \div (1.1 \times 10^6)$

6. $(4.500 \times 10^5) \div (2.0 \times 10^3)$

7. $(9.21 \times 10^{-1}) \div (3.00 \times 10^2)$

8. $(7.300 \times 10^6) \times (2.1 \times 10^{-4}) \div (5.00 \times 10^2)$

## Answers

1. $6 \times 10^7$

2. $7.8 \times 10^3$

3. $3 \times 10^4$

4. $3.0 \times 10^{-5}$

5. $6.6 \times 10^4$

6. $2.3 \times 10^2 = 230$ (often just easier to express as a decimal)

7. $3.07 \times 10^{-3}$

8. $3.1 \times 10^0 = 3.1$

## Key Takeaways

- Multiplying and dividing numbers in scientific notation is done by multiplying/dividing the coefficients and the exponential expression separately and then rewriting back in desired format

# Attributions

- Adapted from: "Operations with Numbers in Scientific Notation" by Jen. Kershaw, M.eD and Kaityln Spong is

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# 1.1.3: Significant Figures - Writing Numbers to Reflect Precision

**Learning Objectives**

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

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

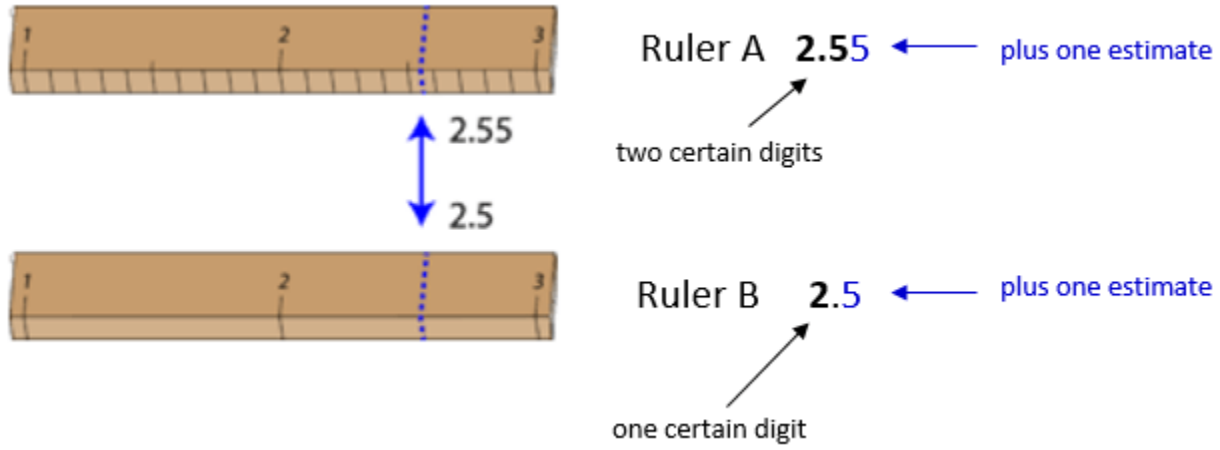



Figure 1.1.3.1: Measurement with two different rulers. Ruler A's measurement can be rounded to 2.55, with 2 certain digits, while Ruler B's measurement of 2.5 has 1 certain digit

## Measurement Uncertainty

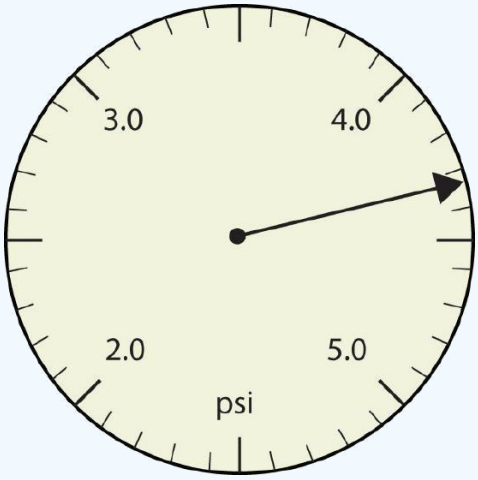
Some error or **uncertainty** always exists in any measurement. The amount of uncertainty depends both upon the skill of the measurer and upon the quality of the measuring tool. While some balances are capable of measuring masses only to the nearest $0.1\ \text{g}$, other highly sensitive balances are capable of measuring to the nearest $0.001\ \text{g}$ or even better. Many measuring tools such as rulers and graduated cylinders have small lines which need to be carefully read in order to make a measurement. Figure 1.1.3.1 shows two rulers making the same measurement of an object (indicated by the blue arrow).

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

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

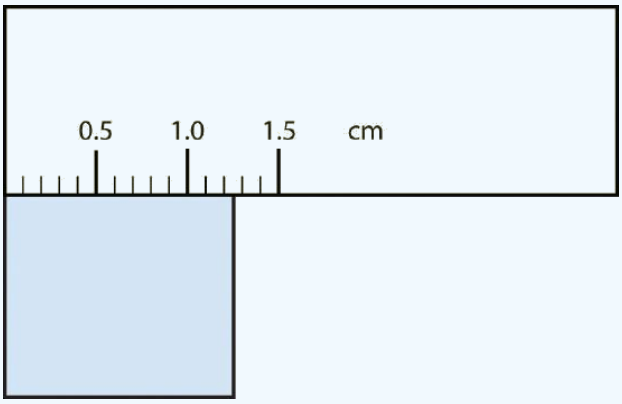
## Example 1.1.3.1: Reporting Measurements to the Proper Number of Significant Figures

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

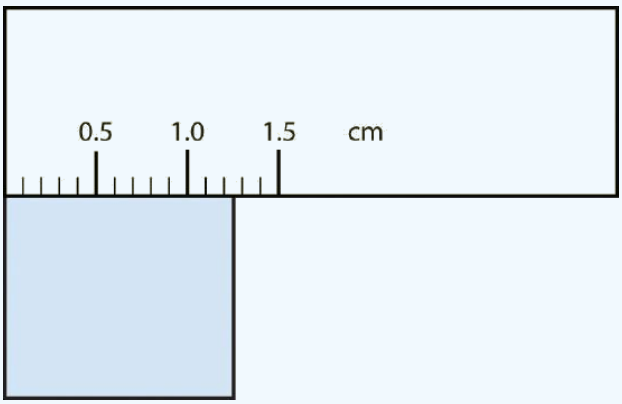
**Solutions**

*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 1.1.3.1

What would be the reported width of this rectangle?




*Answer available at the end of this section.*

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 1.1.3.1: Significant Figure Rules*

| Rule | Examples |
|---|---|
| 1. All nonzero digits in a measurement are significant. | • 237 has three significant figures.<br>• 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.<br>• 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.<br>• 0.000416 has three significant figures. |

| Rule | Examples |
|---|---|
| 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.<br>◦ $1.4 \times 10^3$ has two significant figures.<br>◦ $1.40 \times 10^3$ three significant figures.<br>◦ $1.400 \times 10^3$ 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.<br>• 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 1.1.3.2

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 |

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

### Exercise 1.1.3.2

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 available at the end of this section.*

*Answer b available at the end of this section.*

*Answer c available at the end of this section.*

*Answer d available at the end of this section.*

*Answer e available at the end of this section.*

## 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.

### YouTube Video

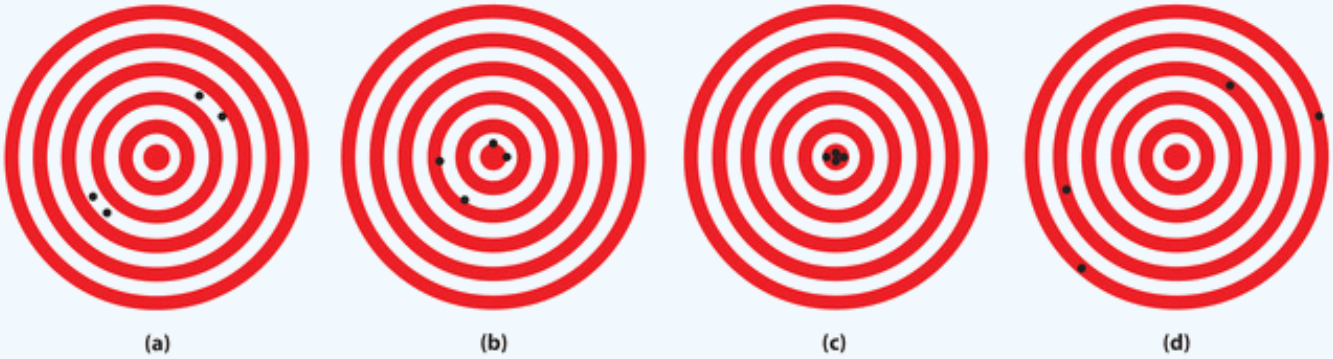
*This interactive element is not available in this format. Visit the link or scan the QR code to access it online.*

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Video 1.1.3.1: Difference between precision and accuracy.

### Example 1.1.3.3

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.

## Answers

**Exercise** 1.1.3.1
1.25 cm

**Exercise** 1.1.3.2
three significant figures

**Exercise** 1.1.3.2
four significant figures

**Exercise** 1.1.3.2
four significant figures

**Exercise** 1.1.3.2
infinite (exact number)

**Exercise** 1.1.3.2
Ambiguous, could be two, three or four significant figures.

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# 1.1.4: 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 $207.518\ \text{m}$. 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 $1.1.4.1$.

*Table $1.1.4.1$: Rounding examples*

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

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

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

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

## Multiplication and Division

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

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

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

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

**Example 1.1.4.1**

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. | $2.0856 \times 10^3$ |

b

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

## Addition and Subtraction

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

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

↑ 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 1.1.4.2

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 1.1.4.2

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: available at the end of this section.*

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.

**YouTube Video**

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Video 1.1.4.1: Significant figures in mixed operations (https://www.youtube.com/watch?v=yBntMndXQWA).

**YouTube Video**

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Video 1.1.4.2: 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 1.1.4.3**

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 =<br><br>**Perform multiplication first.**<br><br>2 (1.008 g *4 sig figs*) = **2.016 g** *4 sig figs*<br><br>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.*<br><br>**Then, perform the addition.**<br><br>**2.016 g** *thousandths place* + 15.99 g *hundredths place (least precise)* = 18.006 g<br><br>**Round the final answer.**<br><br>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<br>(rounding up) |

**b.**

| Explanation | Answer |
| --- | --- |
| 137.3 s + 2(35.45 s) =<br><br>**Perform multiplication first.**<br><br>2(35.45 s *4 sig figs*) = **70.90 s** *4 sig figs*<br><br>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.*<br><br>**Then, perform the addition.**<br><br>137.3 s *tenths place (least precise)* + **70.90 s** *hundredths place* = 208.20 s<br><br>**Round the final answer.**<br><br>Round the final answer to the tenths place based on 137.3 s. | 208.2 s |

**c.**

| Explanation | Answer |
| --- | --- |
| $\frac{118.7g}{2} - 35.5g =$<br><br>**Perform division first.**<br><br>$\frac{118.7g}{2}$ *4 sig figs* = **59.35 g** *4 sig figs*<br><br>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.*<br><br>**Perform subtraction next.**<br><br>**59.35 g** *hundredths place* – 35.5 g *tenths place (least precise)* = 23.85 g<br><br>**Round the final answer.**<br><br>Round the final answer to the tenths place based on 35.5 g. | 23.9 g (rounding up) |

### Exercise 1.1.4.3

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 available at the end of this section.*

## 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.

### Answers

**Exercise** 1.1.4.2

$0.240 = 2.40 \times 10^{-1}$
$1,437 = 1.437 \times 10^{3}$
$156 = 1.56 \times 10^{2}$
$2.14 = 2.14 \times 10^{0}$

**Exercise** 1.1.4.3

-5.62 s
110.2 cm

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# 1.2: MEASUREMENT UNITS AND DIMENSIONAL ANALYSIS



- Topic hierarchy


**1.2.1: The Basic Units of Measurement**

**1.2.2: Math Tools - Ratios, Rates, and Proportions**

**1.2.3: Problem Solving and Unit Conversions**

**1.2.4: Solving Multi-step Conversion Problems**

**1.2.5: Units Raised to a Power**

**1.2.6: Density**

**1.2.7: Dosage Calculations**



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# 1.2.1: 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).

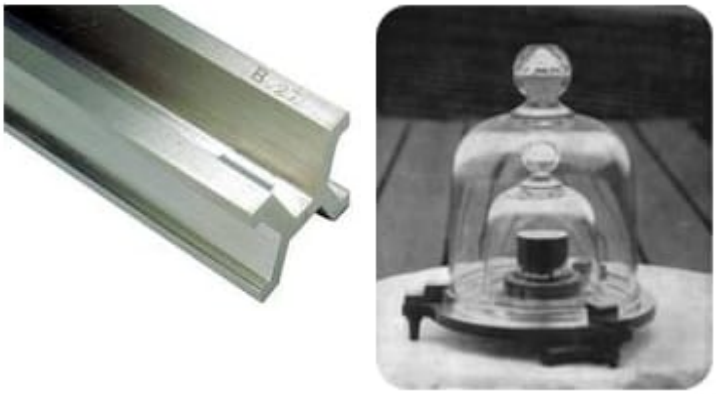


Figure 1.2.1.1: Meter standard (left) and Kilogram standard (right).

## 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 1.2.1.1.

*Table 1.2.1.1: 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.

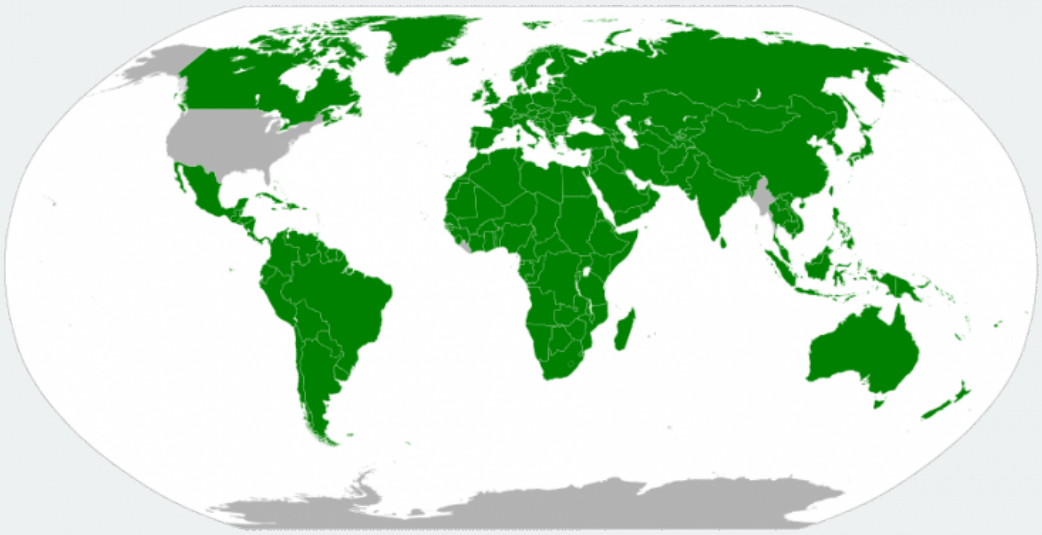


Figure 1.2.1.1: Areas of world using metric system (in green). Only a few countries are slow or resistant to adoption including the United States.

## 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 1.2.1.2 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 1.2.1.2: SI Prefixes*

| Prefix | Unit Abbreviation | Meaning | Example |
|---|---|---|---|
| giga | G | 1,000,000,000 | 1 gigameter $(\mathrm{Gm}) = 10^9\ \mathrm{m}$ |
| mega | M | 1,000,000 | 1 megameter $(\mathrm{Mm}) = 10^6\ \mathrm{m}$ |
| kilo | k | 1,000 | 1 kilometer $(\mathrm{km}) = 1,000\ \mathrm{m}$ |
| hecto | h | 100 | 1 hectometer $(\mathrm{hm}) = 100\ \mathrm{m}$ |
| deka | da | 10 | 1 dekameter $(\mathrm{dam}) = 10\ \mathrm{m}$ |
| | | **1** | 1 meter $(\mathrm{m})$ |
| deci | d | 1/10 | 1 decimeter $(\mathrm{dm}) = 0.1\ \mathrm{m}$ |
| centi | c | 1/100 | 1 centimeter $(\mathrm{cm}) = 0.01\ \mathrm{m}$ |
| milli | m | 1/1,000 | 1 millimeter $(\mathrm{mm}) = 0.001\ \mathrm{m}$ |

| Prefix | Unit Abbreviation | Meaning | Example |
|---|---|---|---|
| micro | $\mu$ | 1/1,000,000 | 1 micrometer $(\mu\text{m}) = 10^{-6}\ \text{m}$ |
| nano | n | 1/1,000,000,000 | 1 nanometer $(\text{nm}) = 10^{-9}\ \text{m}$ |
| pico | p | 1/1,000,000,000,000 | 1 picometer $(\text{pm}) = 10^{-12}\ \text{m}$ |

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

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 $6.5\ \text{kg}$, this is easier than saying it weighs $6500\ \text{g}$ or $0.65\ \text{dag}$. All three are correct, but the $\text{kg}$ 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 1.2.1.1: 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 1.2.1.1

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: available at the end of this section.*

*Answer b: available at the end of this section.*

*Answer c: available at the end of this section.*

*Answer d: available at the end of this section.*

## 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.

## Answers

**Exercise** 1.2.1.1

km

**Exercise** 1.2.1.1

mg

**Exercise** 1.2.1.1

ns

**Exercise** 1.2.1.1

cL

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# 1.2.2: Math Tools - Ratios, Rates, and Proportions

## Ratios

**Ratios** are used to compare amounts or quantities or to describe a relationship between two amounts or quantities. For example, a ratio might be used to describe the cost of a month's rent as compared to the income earned in one month. You may also use a ratio to compare the number of elephants to the total number of animals in a zoo, or the amount of calories per serving in two different brands of ice cream.

Ratios compare quantities using division. This means that you can set up a ratio between two quantities as a division expression between those same two quantities.

### Definition: Ratio

A **ratio** is a comparison of two quantities that shows how much of one quantity there is compared to another. It tells the relationship between the quantities using division.

A ratio that compares two different quantities with the same units of measurement.

Here is an example. If you have a platter containing $10$ sugar cookies and $20$ chocolate chip cookies, you can compare the cookies using a ratio.

The ratio of sugar cookies to chocolate chip cookies is:

$$\frac{\text{sugar cookies}}{\text{chocolate chip cookies}} = \frac{10}{20}$$

The ratio of chocolate chip cookies to sugar cookies is:

$$\frac{\text{chocolate chip cookies}}{\text{sugar cookies}} = \frac{20}{10}$$

You can write the ratio using words, a fraction, and also using a colon as shown below.

$$\text{Ratio of sugar cookies to chocolate chip cookies}$$

$$10 \text{ to } 20 \quad \text{or}$$
$$\frac{10}{20} \quad \text{or}$$
$$10 : 20$$
$$1 : 2 \quad \text{(Simplied form)}$$

Some people think about this ratio as: "For every $10$ sugar cookies I have, I have $20$ chocolate chip cookies."

### How to Write a Ratio?

A ratio can be written in three different ways:

- with the word "to": $3$ to $4$
- as a fraction: $\frac{3}{4}$
- with a colon: $3{:}4$

A ratio is simplified if it is equivalent to a fraction that has been simplified.

Below are two additional examples that illustrate how to compare quantities using a ratio and how to express the ratio in its simplified form.

### Example 1.2.2.1: Find Ratio

A basketball player takes $50$ jump shots during a practice. She makes $28$ of them. What is the ratio of shots made to shots taken? Simplify the ratio.

*Answer available at the end of this section.*

Often, one quantity in the ratio is greater than the second quantity. You do not have to write the ratio so that the lesser quantity comes first; the important thing is to maintain a consistent relationship.

### Your Turn 1.2.2.1: Writing Ratios

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Note that ratios can compare a *part to a part* or a *part to a whole*.

## Rates

### Definition: Rate

A **rate** is a ratio in which the units of the two quantities being compared are different.

**Rates** are a special type of ratio used to describe a relationship between different units of measure, such as speed, wages, or prices. A car can be described as traveling $60$ miles per hour; a landscaper might earn $\$35$ per lawn mowed; gas may be sold at $\$3$ per gallon.

A rate is a ratio that compares two different quantities with different units of measurement. A rate is a comparison that provides information such as dollars per hour, feet per second, miles per hour, and dollars per quart, for example. The word “per” usually indicates you are dealing with a rate. Rates can be written using words, using a colon, or as a fraction. It is essential to understand which quantities are being compared.

For example, an employer wants to rent $6$ buses to transport a group of $300$ people on a company outing. The rate to describe the relationship can be written using words, using a colon, or as a fraction, and you must include the units.

$$\begin{aligned}
&\text{six buses per 300 people}\\
&6 \text{ buses} : 300 \text{ people}\\
&\frac{6 \text{ buses}}{300 \text{ people}}\\
&\frac{1 \text{ buses}}{50 \text{ people}} \qquad \text{Divide by 6 to reduce fraction}
\end{aligned}$$

This fraction means that the rate of buses to people is $6$ to $300$ or, simplified, $1$ bus for every $50$ people.

**Example 1.2.2.2: Find Rate**

Write the rate as a simplified fraction: 8 phone lines for 36 employees.

*Answer available at the end of this section.*

**Your Turn 1.2.2.2: Find Rate**

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## Finding Unit Rates

**Definition: Unit Rate**

A **unit rate** is a rate expressed so that the denominator of the corresponding ratio is one. (Recall that the "denominator" is the bottom number of the ratio when it is expressed in fraction form.)

Think about the "miles per gallon" example above. If we hear, "this car gets 30 miles per gallon," we know that for every 30 miles driven, the car uses 1 gallon of gas. The number 1 is implicit in the way we express most rates. Even if we are given a rate that is not a unit rate, we can convert it to a unit rate using proportions, as in the example below.




Figure 1.2.2.1: The unit ratio miles per hour is often used to express speed

"Vienna Convention road sign C14-V2 (mph)" by United Nations is licensed under Public Domain

A **unit rate** compares a quantity to one unit of measure. You often see the speed at which an object is traveling in terms of its unit rate.

For example, if you wanted to describe the speed of a boy riding his bike—and you had the measurement of the distance he traveled in miles in $2$ hours—you would most likely express the speed by describing the distance traveled in *one* hour. This is a unit rate; it gives the distance traveled per one hour. The denominator of a unit rate will always be one.

Consider the example of a car that travels $300$ miles in $5$ hours. To find the unit rate, you find the number of miles traveled in ***one*** hour.

$$\begin{aligned} \frac{\text{miles}}{\text{hours}} &= \frac{300 \text{ miles}}{5 \text{ hours}} && \text{Indentify the relationship} \\ &= \frac{60 \text{ miles}}{1 \text{ hour}} && \text{Divide by } 5 \text{ to reduce fraction} \end{aligned}$$

A common way to write this unit rate is $60$ miles per hour.

### Note: Meaning of Per

The word "per." Sometimes, a slanted line / is used to mean "per." Per means division. For example, $60$ miles per hour can be written as $60$ miles/hour or $\frac{60 \text{ miles}}{1 \text{ hr}}$.

### Example 1.2.2.3: Find Unit Rate

1. A crowded subway train has $375$ passengers distributed evenly among $5$ cars. What is the unit rate of passengers per subway car?
2. Vancouver Island has a population of $734,860$, and a land mass of $32,134$ square kilometres. What is the rate of number of people per square kilometre? (This is called population density.) Round your answer to the nearest whole number.
3. Amy bought $10$ lb of oranges for $\$4.99$. What is the rate in cents per pound? Find the rate.

*Answer available at the end of this section.*

### Your Turn 1.2.2.3: Finding Unit Rates

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A **unit price** is a unit rate that expresses the price of something. The unit price always describes the price of *one* unit, so that you can easily compare prices.

You may have noticed that grocery shelves are marked with the unit price (as well as the total price) of each product. This unit price makes it easy for shoppers to compare the prices of competing brands and different package sizes.

Consider the two containers of blueberries shown below. It might be difficult to decide which is the better buy just by looking at the prices; the container on the left is cheaper, but you also get fewer blueberries. A better indicator of value is the price *per single ounce* of blueberries for each container.

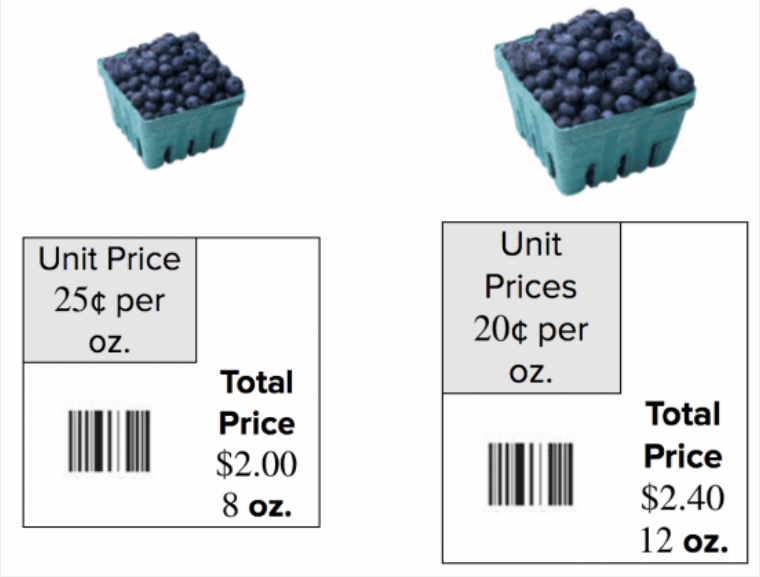



Figure 1.2.2.1: Unit Price

"Blueberry Unit Price Comparison" by The NROC Project is licensed under CC BY-NC-SA 4.0

Look at the unit prices—the container on the right is actually a better deal, since the price per ounce is *lower* than the unit price of the container on the left. You pay more money for the larger container of blueberries, but you also get more blueberries than you would with the smaller container. Put simply, the container on the right is a better value than the container on the left.

So, how do you find the unit price?

Imagine a shopper wanted to use unit prices to compare a $3$-pack of tissue for $\$4.98$ to a single box of tissue priced at $\$1.60$. Which is the better deal?

Find the unit price of the $3$-pack: $\frac{\$4.98}{3 \text{ boxes}}$

Since the price given is for $3$ boxes, divide both the numerator and the denominator by $3$ to get the price of $1$ box, the unit price. The unit price is $\$1.66$ per box.

The unit price of the $3$-pack is $\$1.66$ per box; compare this to the price of a single box at $\$1.60$. Surprisingly, the $3$-pack has a higher unit price! Purchasing the single box is the better value.

Like rates, unit prices are often described with the word “per.” Sometimes, a slanted line / is used to mean “per.” The price of the tissue might be written $\$1.60$/box, which is read "$\$1.60$ per box."

The following example shows how to use the unit price to compare two products and determine which has the lower price.

### Example 1.2.2.4: Compare Two Brand

Sami is trying to decide between two brands of crackers. Which brand has the lower unit price?

Brand A: $\$1.12$ for $8$ ounces

Brand B: $\$1.56$ for $12$ ounces

*Answer available at the end of this section.*

### Your Turn $1.2.2.4$: Rate Comparision

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### Summary: Rates and Ratio

Ratios and rates are used to compare quantities and express relationships between quantities measured in the same units of measure and in different units of measure. They both can be written as a fraction, using a colon, or using the words “to” or “per”. Since rates compare two quantities measured in different units of measurement, such as dollars per hour or sick days per year, they must include their units. A unit rate or unit price is a rate that describes the rate or price for one unit of measure.

## Proportion

### Definition: Proportion

A true **proportion** is an equation that states that two **ratios** are equal or equivalent.

If you know one ratio in a proportion, you can use that information to find values in the other equivalent ratio. Using proportions can help you solve problems such as increasing a recipe to feed a larger crowd of people, creating a design with certain consistent features, or enlarging or reducing an image to scale.

For example, imagine you want to enlarge a $5$-inch by $8$-inch photograph to fit a wood frame that you purchased. If you want the shorter edge of the enlarged photo to measure $10$ inches, how long does the photo have to be for the image to scale correctly? You can set up a proportion to determine the length of the enlarged photo.

A proportion is usually written as two equivalent fractions. For example:

$$\frac{12 \text{ inches}}{1 \text{ foot}} = \frac{36 \text{ inches}}{3 \text{ feet}}$$

Notice that the equation has a ratio on each side of the equal sign. Each ratio compares the same units, inches and feet, and the ratios are equivalent because the units are consistent, and $\frac{12}{1}$ is equivalent to $\frac{36}{3}$.

Proportions might also compare two ratios with the same units. For example, Juanita has two different-sized containers of lemonade mix. She wants to compare them. She could set up a proportion to compare the number of ounces in each container to the number of servings of lemonade that can be made from each container.

$$\frac{40 \text{ ounces}}{84 \text{ ounces}} = \frac{10 \text{ servings}}{21 \text{ servings}}$$

Since the units for each ratio are the same, you can express the proportion without the units:

$$\frac{40}{84} = \frac{10}{21}$$

When using this type of proportion, it is important that the numerators represent the same situation. In the example above, they represent 40 ounces for 10 servings. The denominators should also represent the same situation, which is ounces for servings.

Juanita could also have set up the proportion to compare the ratios of the container sizes to the number of servings of each container.

$$\frac{40 \text{ ounces}}{10 \text{ servings}} = \frac{84 \text{ ounces}}{21 \text{ servings}}$$

### Different way of Writing Proportions

Here are some proportions in different forms:

*Different Way of Writing Proportion*

| Proportion | Fraction Form | Read like this... |
|---|---|---|
| $1 : 2 = 2 : 4$ | $\frac{1}{2} = \frac{2}{4}$ | $1$ is to $2$ or $2$ is to $4$ |
| $18 : 9 = 10 : 5$ | $\frac{18}{9} = \frac{10}{5}$ | $18$ is to $9$ as $10$ is to $5$ |

## Finding an Unknown Quantity in a Proportion

Problems often give incomplete information; that is, one of the terms is missing. To solve such problems, you first identify the comparison or ratio given. It may be:

- A quantity of one thing that is mixed with a larger quantity of something else
- A scale of measurement given on a map, such as $1$ cm on the map, represents $100$ km distance on land
- Cost for a certain number of items
- Time to travel a certain distance

The problem will then give one term of the second ratio in the proportion. For example, if you have been told that $3$ heads of lettuce cost $\$1.49$, you may be asked to find the cost of $7$ heads of lettuce.

The missing term is the second cost. The proportion will be:

$$\frac{\text{number of heads of lettuce}}{\text{cost}} = \frac{\text{number of heads of lettuce}}{\text{cost}}$$

$$\frac{3}{\$1.49} = \frac{7}{?}$$

$$3 : \$1.49 = 7 :?$$

The most important thing to remember is to keep the order of comparison the same in the first and second ratios in a proportion. If the first ratio compares time to distance, then the second ratio in the proportion must compare time to distance.

$$\frac{\text{time}}{\text{distance}} = \frac{\text{time}}{\text{distance}}$$

Or it could be:

$$\frac{\text{distance}}{\text{time}} = \frac{\text{distance}}{\text{time}}$$

Once you have decided on the order of comparison, it is a simple matter to write the proportion using the numbers given in the problem. Use a letter to stand for the missing term.

How would you find a missing term?

If you know that the relationship between quantities is proportional, you can use proportions to find missing quantities. Below is an example.

### Definition: Steps to Solve Proportion

**Step 1:** Write the first ratio using the information given.
**Step 2:** Write the proportion, using a letter in place of the missing term. Be sure the **order of comparison is the same** in both the first and second ratios in your proportion.
**Step 3:** Write the proportion in the fraction form. (Try to **simplify** the ratio **before** you do all the calculations).
**Step 4:** Cross-multiply and set the cross-products equal to each other.
**Step 5:** Divide both sides of the equation by the number with the unknown term.
**Step 6:** Check by putting your answer back into the original proportion and cross-multiplying.

### Example 1.2.2.5: Solve Proportion

1. Solve proportion: $\frac{8}{10} = \frac{x}{80}$
2. Solve proportion: $\frac{n}{15} = \frac{25}{20}$

*Answer available at the end of this section.*

The numbers in a ratio often are common fractions, decimals or mixed numbers. Follow exactly the same steps that you have been using to solve whole number proportions. The calculations will use your skills with fractions.

### Your Turn 1.2.2.5: Solve Proportions

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### Example 1.2.2.6: Applying Proportion to Solve Problem

A recipe says to use $2$ teaspoons of baking powder for every $4$ cups of flour. If a recipe uses $10$ cups of flour, how much baking powder is needed?

*Answer available at the end of this section.*

## Your Turn 1.2.2.6: Applying Proportion

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Now, back to the original example. Imagine you want to enlarge a 5-inch-by-8-inch photograph to a length of 10 inches while maintaining the same width-to-length proportion. You can set up a proportion to determine the width of the enlarged photo.

$$\frac{\text{width}}{\text{length}} \text{ (First photo)} = \frac{\text{width}}{\text{length}} \text{ (Second photo)}$$

$$\frac{5}{8} = \frac{10}{n}$$

$$5 \cdot n = 8 \cdot 10$$

$$\frac{\cancel{5}\, n}{\cancel{5}} = \frac{80}{5}$$

$$n = 16$$

The length of the enlarged photograph is 16 inches.

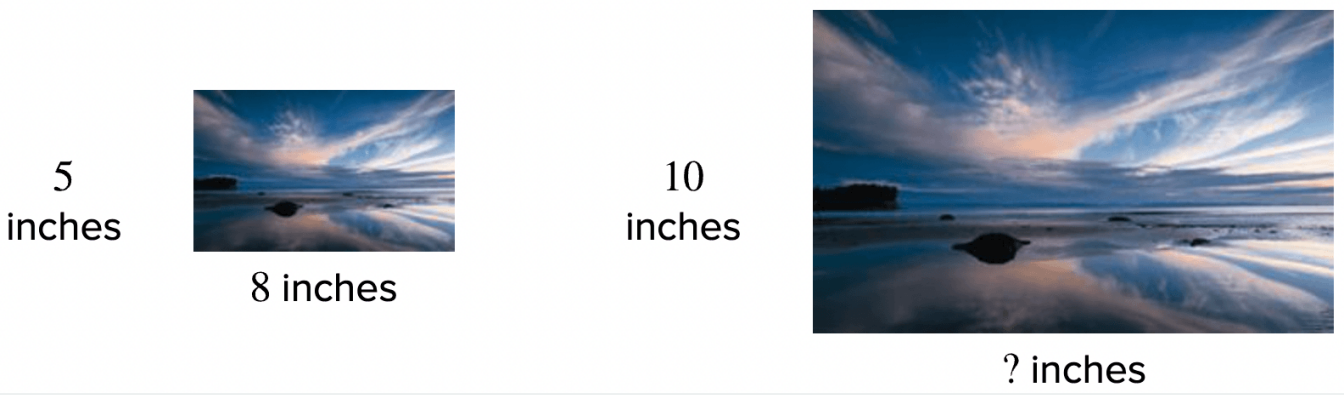



Figure 1.2.2.2 - Photograph Proportions

"Scaling a Photograph" by The NROC Project is licensed under CC BY-NC-SA 4.0

## Solving Application Problems Using Proportions

Setting up and solving a proportion is a helpful strategy for solving a variety of proportional reasoning problems. In these problems, it is always essential to determine the unknown value and then identify a proportional relationship that can be used to solve for the unknown value. Below are some examples.

## Example 1.2.2.7: Application of Proportion

Among a species of tropical birds, 30 out of every 50 birds are female. In other words, 30 birds are female and 20 birds are male. If a certain bird sanctuary has a population of 1,150 of these birds, how many of them would you expect to be female?

*Answer available at the end of this section.*

## Your Turn 1.2.2.7: Application of Proportion

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## Example 1.2.2.8: Use Proportion

A map scale indicates that $\frac{1}{2}$ inch on the map corresponds with 3 real miles. How many miles apart are two cities that are $2\frac{1}{4}$ inches apart on the map?

*Answer available at the end of this section.*

## Your Turn 1.2.2.8: Use Proportions

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## Example 1.2.2.9: Use Proportion

Your car can drive 300 miles on a tank of 15 gallons. How far can it drive on 40 gallons? How many gallons are needed to drive 50 miles?

*Answer available at the end of this section.*

## Summary: Proportion

A proportion is an equation comparing two ratios. If the ratios are equivalent, the proportion is true. If not, the proportion is false. Finding a cross product is another method for determining whether a proportion is true or false. Cross-multiplying is also helpful for finding an unknown quantity in a proportional relationship. Setting up and solving proportions is a valuable skill that can be applied to a wide range of problems.

If you wanted to power the city of Seattle using wind power, how many windmills would you need to install? Questions like these can be answered using rates and proportions.

# Notes:

World Fact Book [www.cia.gov]

World Bank Data [data.worldbank.org]

## Answers

**Example** 1.2.2.1**: Find Ratio**

$$\begin{aligned}\frac{\text{shots made}}{\text{shots taken}} &= \frac{28}{50} && \text{Unsimplified form}\\ &= \frac{14}{25} && \text{Divide by 2 to write simplified form.}\end{aligned}$$

The ratio of shots made to shots taken is $\frac{14}{25}$, 14:25, or 14 to 25.

**Example** 1.2.2.2**: Find Rate**

$$\begin{aligned}\frac{\text{phone lines}}{\text{employees}} &= \frac{8 \text{ phone lines}}{36 \text{ employees}} && \text{Indentify the relationship}\\ &= \frac{2 \text{ phone lines}}{9 \text{ employees}} && \text{Divide by 4 to reduce fraction}\end{aligned}$$

The rate of phone lines for employees can be expressed as $\frac{2 \text{ phone lines}}{9 \text{ employees}}$.

**Example** 1.2.2.3**: Find Unit Rate**

1. We need to find the passengers per subway car. Subway cars must be in the denominator.

$$\begin{aligned}\frac{\text{passengers}}{\text{subway cars}} &= \frac{375 \text{ passengers}}{5 \text{ subway cars}}\\ &= \frac{75 \text{ passengers}}{1 \text{ subway cars}} && \text{Divide by 5 to reduce fraction}\end{aligned}$$

The unit rate of the subway car is 75 riders per subway car.

2. We need to find the people per square kilometer. So the area must be in the denominator.

$$\begin{aligned}\frac{\text{population}}{\text{area}} &= \frac{734,860 \text{ population}}{32,134 \text{ area}}\\ &= \frac{23 \text{ people}}{1 \text{ area}} && \text{Divide}\end{aligned}$$

So population density is 23 people/$\text{km}^2$.

3. We need to price per pound. Therefore, the weight (in pounds) must be in the denominator.

$$\begin{aligned}\frac{4.99 \text{ dollars}}{10 \text{ lb}} &= \frac{0.499 \text{ dollar}}{1 \text{ lb}}\\ &= \$0.449 \text{ per pound}\\ &= 44.9 \text{ cent per pound}\end{aligned}$$

**Example** 1.2.2.4**: Compare Two Brand**

Brand A: Find unit Price (price per ounce)

$$\begin{aligned}\frac{\text{dollars}}{\text{ounces}} &= \frac{1.12 \text{ dollars}}{8 \text{ ounces}}\\ &= 0.14 \text{ dollar per ounce}\\ &= 14 \text{ cent per ounce}\end{aligned}$$

Brand B: Find unit Price (price per ounce)

$$\begin{aligned}\frac{\text{dollars}}{\text{ounces}} &= \frac{1.56 \text{ dollars}}{12 \text{ ounces}}\\ &= 0.13 \text{ dollar per ounce}\\ &= 13 \text{ cent per ounce}\end{aligned}$$

The unit price of Brand A crackers is 14 cents/ounce, and the unit price of Brand B is 13 cents/ounce. Brand B has a lower unit price and represents the better value.

**Example** 1.2.2.5**: Solve Proportion**

1. Given proportion

$$\frac{8}{10} = \frac{x}{80}$$

Cross multiply:

$$
\begin{aligned}
8 \times 80 &= 10 \times x \\
640 &= 10x \\
\frac{640}{10} &= \frac{10x}{10} \quad \text{Divide both side by 10} \\
\frac{\cancel{10}\, x}{\cancel{10}} &= \frac{640}{10} \\
x &= 64
\end{aligned}
$$

2. Cross multiply

$$
\begin{aligned}
20 \times n &= 15 \times 25 \\
20n &= 375 \\
\frac{\cancel{20}\, n}{\cancel{20}} &= \frac{375}{20} \qquad \text{Divide both side by 20} \\
n &= 18.75
\end{aligned}
$$

**Example** 1.2.2.6**: Applying Proportion to Solve Problem**

The missing term is the teaspoons of baking powder for $10$ cups of flour. Call this term $x$.

$$
\frac{\text{baking powder}}{\text{flour}} \ (\text{recipe}) = \frac{\text{baking powder}}{\text{flour}} \ (\text{You make})
$$

$$
\frac{2}{4} = \frac{x}{10}
$$

Cross multiply:

$$
\begin{aligned}
4 \times x &= 2 \times 10 \\
4x &= 20 \\
\frac{4x}{4} &= \frac{20}{4} \quad \text{Divide both side by 4} \\
\frac{\cancel{4}\, x}{\cancel{4}} &= \frac{20}{4} \\
x &= 5
\end{aligned}
$$

So $5$ teaspoons of baking powder are needed for $10$ cups of flour.

**Example** 1.2.2.7**: Application of Proportion**

Let $x =$ the number of female birds in the sanctuary.

Cross multiply:

$$
\begin{aligned}
\frac{30 \text{ female birds}}{50 \text{ total birds}} &= \frac{x \text{ female birds in sanctuary}}{1,150 \text{ total birds in sanctuary}} \\
\frac{30}{50} &= \frac{x}{1,150} \\
50 \times x &= 30 \times 1,150 \\
50x &= 34,500 \\
\frac{50x}{50} &= \frac{34,500}{50} \qquad \text{Divide both side by 50} \\
\frac{\cancel{50}\, x}{\cancel{50}} &= \frac{34,500}{50} \\
x &= 690
\end{aligned}
$$

You would expect $690$ birds in the sanctuary to be female.

**Example** 1.2.2.8**: Use Proportion**

We can set up a proportion by setting equal two $\frac{\text{map inches}}{\text{real miles}}$ rates, and introducing a variable, $x$, to represent the unknown quantity – the mile distance between the cities.

$$
\begin{aligned}
\frac{\text{inches}}{\text{miles}} &= \frac{\text{inches}}{\text{miles}} \\
\frac{\frac{1}{2}}{3} &= \frac{\frac{9}{4}}{x} \\
\frac{1}{2} \times x &= 3 \times \frac{9}{4} \\
\frac{1}{2}x &= \frac{27}{4} \\
\frac{\frac{1}{2}\, x}{\frac{1}{2}} &= \frac{\frac{27}{4}}{\frac{1}{2}} \\
x &= 13.5
\end{aligned}
$$

So $x = 13.5 = 13\frac{1}{2}$ miles

**Example** 1.2.2.9**: Use Proportion**

We could certainly answer this question using a proportion: $\frac{300 \text{ miles}}{15 \text{ gallons}} = \frac{x \text{ miles}}{40 \text{ gallons}}$

Cross multiply:

$$\begin{aligned} 300 \times 40 &= 15 \times x \\ 15x &= 12,000 \\ \frac{15x}{15} &= \frac{12,000}{15} \qquad \text{Divide both side by } 4 \\ \frac{\cancel{15}\, x}{\cancel{15}} &= \frac{12,000}{15} \\ x &= 800 \end{aligned}$$

So $800$ miles can be driven by $40$ gallons.

Notice if instead we were asked "how many gallons are needed to drive $50$ miles?"

Set proportion as we did before

$$\frac{300 \text{ miles}}{15 \text{ gallons}} = \frac{50 \text{ miles}}{x \text{ gallons}}$$

Cross multiply:

$$\begin{aligned} 300 \times x &= 15 \times 50 \\ 300x &= 750 \\ \frac{300x}{300} &= \frac{750}{300} \qquad \text{Divide both side by } 300 \\ \frac{\cancel{300}\, x}{\cancel{300}} &= \frac{750}{300} \\ x &= 2.5 \end{aligned}$$

So $2.5$ gallons are needed to drive $50$ miles.

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# 1.2.3: 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 $1.86 \times 10^5$ miles/sec. Either one of these can be used as a conversion factor depending on what type of calculation you are working with (Table 1.2.3.1).

*Table 1.2.3.1: 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 1.2.3.1. 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 $1\text{m}$ (both the number *and* the unit):

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

As long as we perform the same operation on both sides of the equals sign, the expression remains an equality. Look at the

right side of the equation; it now has the same quantity in the numerator (the top) as it has in the denominator (the bottom). Any fraction that has the same quantity in the numerator and the denominator has a value of 1:

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

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

## Performing Dimensional Analysis

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

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

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

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

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

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

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

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

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

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

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

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

For the answer to be meaningful, we have to *construct the conversion factor in a form that causes the original unit to cancel out*. Figure 1.2.3.1 shows a concept map for constructing a proper conversion.

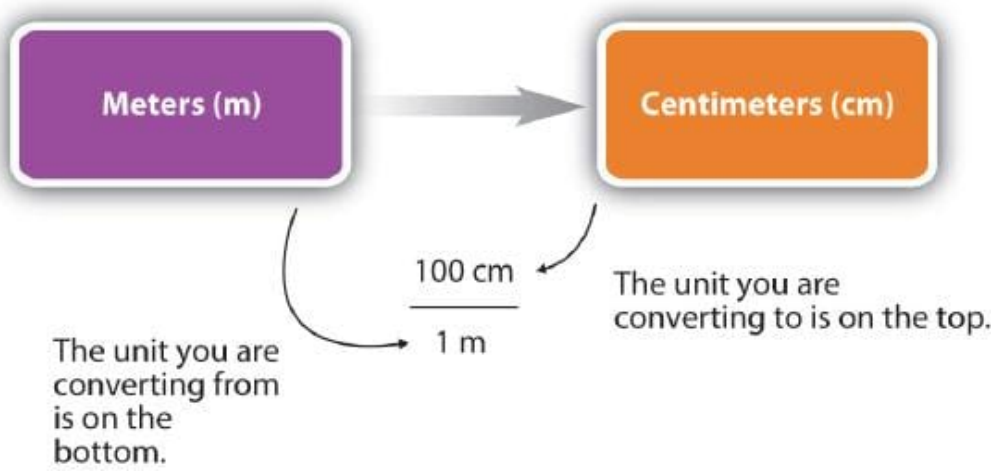



Figure 1.2.3.1: A Concept Map for Conversions. This is how you construct a conversion factor to convert from one unit to another. Converting meters to centimeters: the unit you are converting is on the bottom of the fraction, and the unit to convert to is on top

**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.

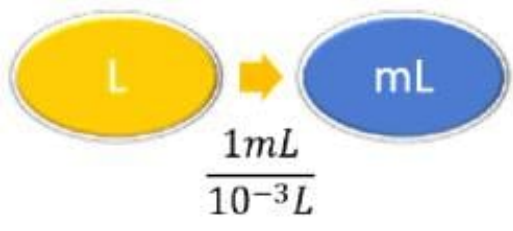
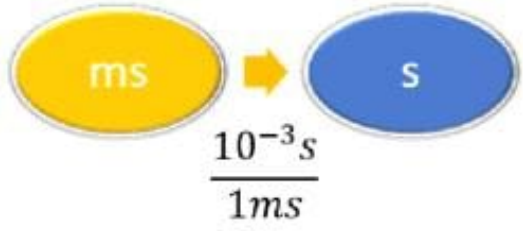
## Significant Figures in Conversions

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 1.2.3.1

*Steps for Problem Solving for Example 2.6.1 and 2.6.2*

| | **Example** 1.2.3.1 | **Example** 1.2.3.2 |
|---|---|---|
| **Steps for Problem Solving** | The average volume of blood in an adult male is 4.7 L. What is this volume in milliliters? | A hummingbird can flap its wings once in 18 ms. How many seconds are in 18 ms? |
| Identify the "given" information and what the problem is asking you to "find." | Given: 4.7 L<br>Find: mL | Given: 18 ms<br>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. |  |  |
| Cancel units and calculate. | $4.7 \cancel{L} \times \frac{1\ \text{mL}}{10^{-3}\ \cancel{L}} = 4,700\ \text{mL}$<br>or<br>$4.7 \cancel{L} \times \frac{1,000\ \text{mL}}{1\ \cancel{L}} = 4,700\ \text{mL}$<br>or<br>4.7 x $10^3$ 2SF, not ambiguous | $18\ \cancel{\text{ms}} \times \frac{10^{-3}\ \text{s}}{1\ \cancel{\text{ms}}} = 0.018\ \text{s}$<br>or<br>$18\ \cancel{\text{ms}} \times \frac{1\ \text{s}}{1,000\ \cancel{\text{ms}}} = 0.018\ \text{s}$ |
| Think about your result. | The amount in mL should be 1000 times larger than the given amount in L. | The amount in s should be 1/1000 the given amount in ms. |

## Exercise 1.2.3.1

Perform each conversion.

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

*Answer a: available at the end of this section.*

## 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.

## Answers

**Exercise** 1.2.3.1

$1.01000x10^{-4}s$

$3.208x10^{4}g$

$1.53x10^{2}cg$

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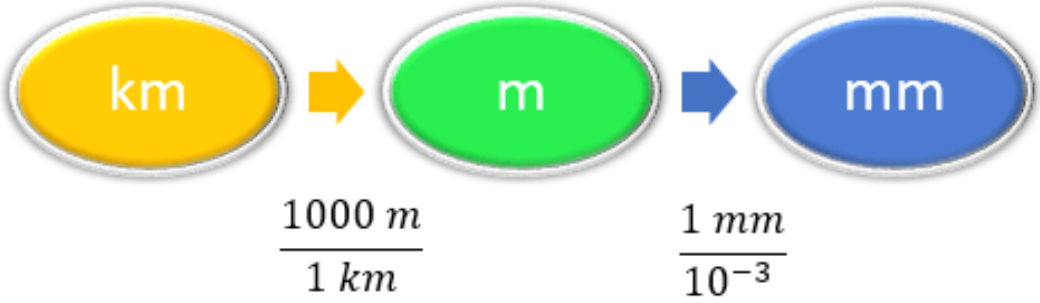
# 1.2.4: Solving Multi-step Conversion Problems

## Multiple Conversions

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

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

## Concept Map




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

## Calculation

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

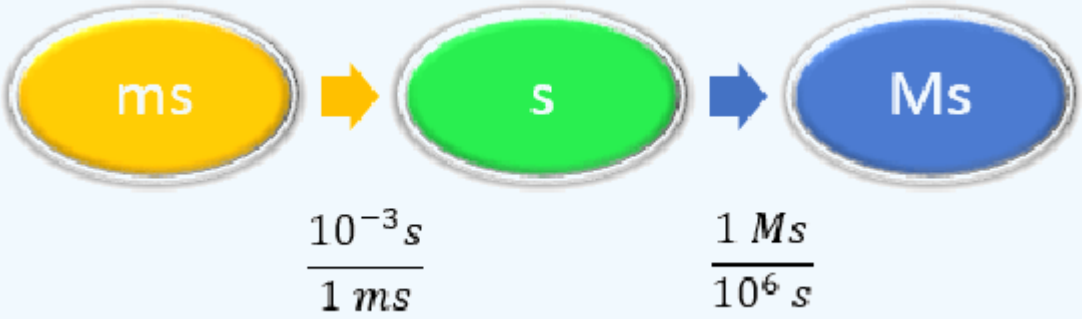
In each step, the previous unit is canceled and the next unit in the sequence is produced, each successive unit canceling out until only the unit needed in the answer is left.

### Example 1.2.4.1: 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<br><br>Find: Ms |

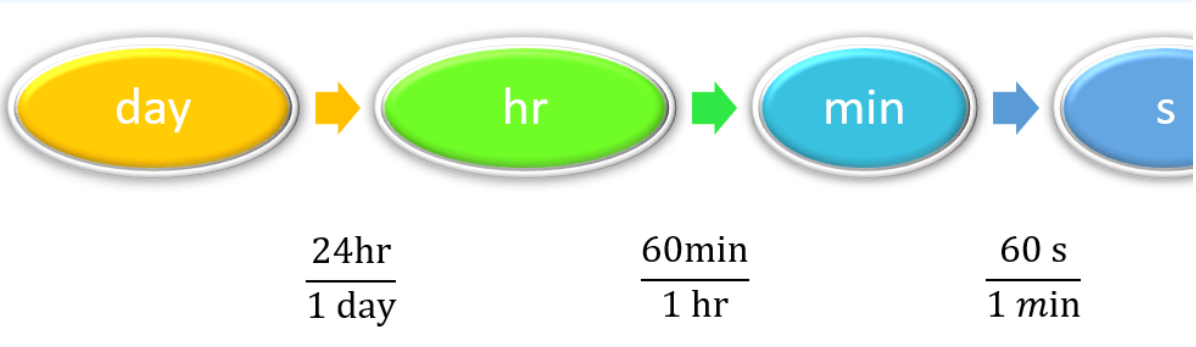
| Steps for Problem Solving | Unit Conversion |
|---|---|
| List other known quantities | $1ms = 10^{-3}s$<br>$1Ms = 10^{6}s$ |
| Prepare a concept map. |  <br>$\frac{10^{-3}s}{1\ ms}$ $\frac{1\ Ms}{10^{6}\ s}$<br>Convert milliseconds to seconds to microseconds: use conversion factors 0.001 second per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

## Example 1.2.4.2: 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<br>Find: s |

| Steps for Problem Solving | Unit Conversion |
|---|---|
| List other known quantities. | 1 day = 24 hours<br>1 hour = 60 minutes<br>1 minute = 60 seconds |
| Prepare a concept map. |  <br>$\frac{24\text{hr}}{1\text{ day}}$ $\frac{60\text{min}}{1\text{ hr}}$ $\frac{60\text{ s}}{1\ min}$<br>Convert day to hour to minute to second: use conversion factors 24 hours per day, 60 minutes per hour, and 60 seconds per |
| Calculate. | $1\text{ d} \times \frac{24\text{ hr}}{1\text{ d}} \times \frac{60\text{ min}}{1\text{ hr}} \times \frac{60\text{ s}}{1\text{ min}} = 86,400\text{ s}$ |

## Exercise 1.2.4.1

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 available at the end of this section.*

*Answer b available at the end of this section.*

*Answer c available at the end of this section.*

## Career Focus: Pharmacist

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



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

## Summary

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

### Answers

**Exercise** 1.2.4.1

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

**Exercise** 1.2.4.1

$83.75\ ft$

**Exercise** 1.2.4.1

$19\ km$

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# 1.2.5: Units Raised to a Power

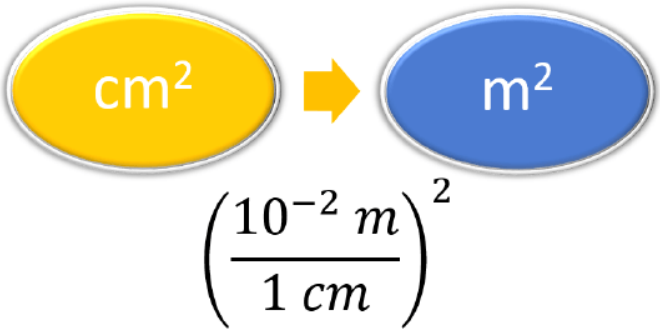
**Learning Objectives**

- 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 $1500\ \text{cm}^2$ to $\text{m}^2$, 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

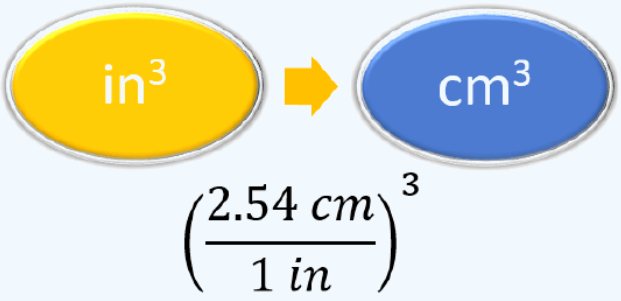
$$1500\ \cancel{\text{cm}}^2 \times \frac{1\ \text{m}^2}{10,000\ \cancel{\text{cm}^2}} = 0.15\ \text{m}^2$$

**Example 1.2.5.1: Volume of a Sphere**

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

**Solution**

*Solution for Example 2.8.1*

| Steps for Problem Solving | What is the volume of a sphere (radius 4.30 inches) in cubic cm ($cm^3$)? |
|---|---|
| Identify the "given" information and what the problem is asking you to "find." | Given: radius = 4.30 in<br>Find: $cm^3$ (volume) |
| Determine other known quantities. | Volume of a sphere: V = $\frac{4}{3} \times \pi \times r^3$<br>= $\frac{4}{3} \times 3.1416 \times (4.30in)^3$<br>= $333.04in^3$ |
| Prepare a concept map. |  <br>To convert inches cubed to centimeters cubed, use conversion factor 2.54 centimeters per 1 inch, cubed overall |
| Calculate. | $333.04 \cancel{in^3} \left(\frac{2.54cm}{1 \cancel{in}}\right)^3 = 5.46 \times 10^3 cm^3$ |
| 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 1.2.5.1

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

*Answer available at the end of this section.*

## Answers

**Exercise** 1.2.5.1

495 $km^2$

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# 1.2.6: Density

## Learning Objectives

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

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

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

or just

$$\rho = \frac{m}{V} \tag{1.2.6.1}$$

Based on this equation, it's clear that density can, and does, vary from element to element and substance to substance due to differences in the relationship of mass and volume. Pure water, for example, has a density of 0.998 g/cm$^3$ at 25° C. The average densities of some common substances are in Table 1.2.6.1. Notice that corn oil has a lower mass to volume ratio than water. This means that when added to water, corn oil will “float.”

*Table 1.2.6.1: Densities of Common Substances*

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

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

## Example 1.2.6.1: Ethyl Alcohol

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

**Solution**

This is a direct application of Equation 1.2.6.1:

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

**Exercise 1.2.6.1**

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

*Answer a available at the end of this section.*

## Density as a Conversion Factor

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

13.6 g mercury = 1 mL mercury

This relationship can be used to construct two conversion factors:

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

and

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

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

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

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

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

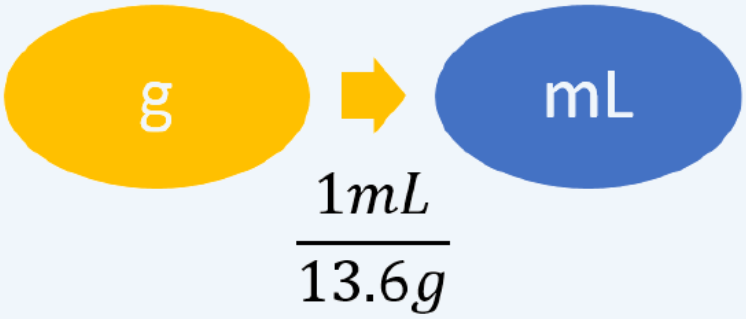
**Example 1.2.6.2: Mercury Thermometer Steps for Problem Solving**

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

**Solution**

*Solution to Example 2.9.2*

| **Steps for Problem Solving** | **Unit Conversion** |
|---|---|

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

**Exercise 1.2.6.2**

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

*Answer available at the end of this section.*

## Summary

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

### Answers

**Exercise** 1.2.6.1

$0.274\ kg/L$

$1.049\ kg/L$

**Exercise** 1.2.6.2

$77\ L$

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# 1.2.7: Dosage Calculations

**Learning Objectives**

- Calculate drug dosages using conversion factors.

## To Your Health: Dosages

A medicine can be more harmful than helpful if it is not taken in the proper dosage. A dosage (or dose) is the specific amount of a medicine that is known to be therapeutic for an ailment in a patient of a certain size. Dosages of the active ingredient in medications are usually described by units of mass, typically grams or milligrams, and generally are equated with a number of capsules or teaspoonfuls to be swallowed or injected. The amount of the active ingredient in a medicine is carefully controlled so that the proper number of pills or spoonfuls contains the proper dose.

Most drugs must be taken in just the right amount. If too little is taken, the desired effects will not occur (or will not occur fast enough for comfort); if too much is taken, there may be potential side effects that are worse than the original ailment. Some drugs are available in multiple dosages. For example, tablets of the medication levothyroxine sodium, a synthetic thyroid hormone for those suffering from decreased thyroid gland function, are available in 11 different doses, ranging from 25 micrograms (µg) to 300 µg. It is a doctor's responsibility to prescribe the correct dosage for a patient, and it is a pharmacist's responsibility to provide the patient with the correct medicine at the dosage prescribed. Thus, proper quantities—which are expressed using numbers and their associated units—are crucial for keeping us healthy.

## Effects are dose-dependent

Chemicals are the most common things for which doses are measured, but there are others, such as radiation exposure. For humans, most doses of micronutrients and medications are measured in milligrams (mg), but some are measured in micrograms because of their potency. Nonmedicinal poisons span the measurement scale; some poisons are so dangerous that a single microgram of it could be deadly, whereas other substances take much more. For example, even water is toxic when consumed in large enough quantities.

Dosage (the size of each dose) determines the strength and duration of the health benefits of nutrients, and also of the therapeutic effects of medical treatments. Dosage also determines the severity of adverse effects of treatments and toxins.

Duration of exposure, that is, the period of time over which the dose was received (all at once or gradually) also determines its effects (the body may build tolerance to gradual exposure to a drug, while a large immediate dose could be deadly).

The route by which a dose is exposed to, may affect the outcome, because some medications have different effects depending on whether they are inhaled, ingested, taken transdermally, injected, or inserted.

The dosage, route, concentration, and division over time may all be critical considerations in the administering of drugs, or in responding to exposure to a toxin. In nutrition, the route is usually a given, as nutrients are generally eaten; while dosage and the frequency of ingestion of nutrients are very important variables in preventing disease and promoting overall health.

## Calculation of dose

Calculating drug dosages for humans based on the doses used in animal studies can be based on weight (e.g., mg/kg) or surface area (e.g., $mg/m^2$) based on weight. Drug dosage calculation is required if the physician's order is different from what is available.

## Example 1.2.7.1

a. A physician ordered 100 mg of Demerol. Demerol is available as 50 mg per tablet. How many tablets should the nurse administer?
b. The doctor's order is 1.2 g of Folic Acid. Folic Acid is available as 800 mg per tablet. How many tablets should be taken?

**Solution**

a. We start with the given, 100 mg. We want to change the unit from *mg* to *tablets*. There are 50 mg in 1 tablet (Remember that *per* tablet means *one* tablet. From this relationship, we can construct the conversion factor. We use the conversion factor that will cancel out the original unit, *mg*, and introduce the unit we are converting to, which is *tablet*.

$$100 \cancel{\text{mg}} \times \frac{1 \text{ tablet}}{50 \cancel{\text{mg}}} = 2 \text{ tablets}$$

Hence, the nurse should administer 2 tablets.

b. We start with the given, 1.2 g and we want to change *grams* to number of *tablets*. First, we convert *1.2 g* to *mg* and then convert *mg to tablets*. We need a conversion factor for each step.

$$1.2 \cancel{\text{g}} \times \frac{1{,}000 \cancel{\text{mg}}}{1 \cancel{\text{g}}} \times \frac{1 \text{ tablet}}{800 \cancel{\text{mg}}} = 1.5 \text{ tablets}$$

Hence, 1.5 tablets should be taken.

## Exercise 1.2.7.1

Calculate each of the following.

a. The physician ordered 20 mg of Valium. Valium is available as 10 mg per tablet. How many tablets should the nurse administer?
b. The doctor's order is 1 g of Calcium. What is on hand is Calcium as 500 mg per tablet. How many tablets should be taken?

*Answer a available at the end of this section.*

Drug Dosage Calculation based on Body Weight. Many drugs (especially in children) are dosed according to body weight (mg/kg). These calculations are carried in 3-step conversions. The first step is to convert the body weight from *pounds (lbs)* to *kg*. The second step is to convert *kg* to *mg* (the total *mg dose* calculated based on body weight). And, finally, the *mg dose* is converted to the number of *tablets*. (as in Example 1.8.1).

## Example 1.2.7.2

a. Demerol is ordered 1.5mg/kg for a patient that is 220 lbs. Demerol is available as 50 mg per tablet. How many tablets should the nurse administer?
b. A doctor prescribes amoxicillin 30mg/kg to a child weighing 73.5 lbs. Amoxicillin is available as 500 mg tablets. How many tablets should the nurse administer?

**Solution**

a. We start with the given, 220 *lbs*. We want to change the unit from *lbs* to *kg,* and then, from *kg* to *total dose (mg)* and then *the mg dose to tablets*. The first conversion factor will cancel out the original unit, *lbs*, and introduce the unit we are converting to, which is *kg*. The second conversion factor will cancel out *kg*, and introduce the unit of the *dose* (usually *mg*) and then *mg* to *tablet*.

$$220\ \cancel{\text{lbs}} \times \frac{1\ \cancel{\text{kg}}}{2.2\ \cancel{\text{lbs}}} \times \frac{1.5\ \cancel{\text{mg}}}{1\ \cancel{\text{kg}}} \times \frac{1\ \text{tablet}}{50\ \cancel{\text{mg}}} = 3\ \text{tablets}$$

Hence, the nurse administers 3 tablets.

b. Start with the given, 73.5 *lbs*. We want to change the unit from *lbs* to *kg*, and then, from *kg* to total dose (*mg*) and then *mg* to *tablets*. The first conversion factor will cancel out the original unit, *lbs,* and convert to *kg*. The second conversion factor will cancel out *kg*, and convert to the total *mg dose* and the final conversion will cancel *mg* to introduce the final unit, *tablet*.

$$73.5\ \cancel{\text{lbs}} \times \frac{1\ \cancel{\text{kg}}}{2.2\ \cancel{\text{lbs}}} \times \frac{30\ \cancel{\text{mg}}}{1\ \cancel{\text{kg}}} \times \frac{1\ \text{tablet}}{500\ \cancel{\text{mg}}} = 2\ \text{tablets}$$

Hence, the nurse administers 2 tablets.

## Exercise 1.2.7.2

Calculate each of the following.

a. Vancomycin is ordered 15mg/kg for a patient that is 110 lbs. Vancomycin is available as 250 mg per capsule. How many capsules should the nurse administer? (ans. 3 capsules)
b. A doctor prescribes ampicillin 40mg/kg to a patient weighing 55 lbs. Ampicillin is available as 500 mg tablets. How many tablets should the nurse administer? (ans. 2 tablets)

*Answer a available at the end of this section.*

# References

1. The Use of Body Surface Area as a Criterion of Drug Dosage in Cancer Chemotherapy(opens in new window) [cancerres.aacrjournals.org] "The Use of Body Surface Area as a Criterion of Drug Dosage in Cancer Chemotherapy" D Pinkel. Cancer Research 1958

# Contributors and Attributions

- Wikipedia
- Leticia Colmenares (UH-WCC)

## Answers

**Exercise** 1.2.7.1

Start with 20 mg of Valium. For the conversion factor, we know that 10 mg Valium = 1 tablet

$$20\ \cancel{\text{mg}} \times \frac{1\ \text{tablet}}{10\ \cancel{\text{mg}}} = 2\ \text{tablets}$$

Start with 1 g (1000 mg) of Calcium. For the conversion factor, we know that 500 mg Calcium = 1 tablet

$$1000\ \cancel{\text{mg}} \times \frac{1\ \text{tablet}}{500\ \cancel{\text{mg}}} = 2\ \text{tablets}$$

**Exercise** 1.2.7.2

$$110\ \cancel{\text{lbs}} \times \frac{1\ \cancel{\text{kg}}}{2.2\ \cancel{\text{lbs}}} \times \frac{15\ \cancel{\text{mg}}}{1\ \cancel{\text{kg}}} \times \frac{1\ \text{tablet}}{250\ \cancel{\text{mg}}} = 3\ \text{tablets}$$

$$55\ \cancel{\text{lbs}} \times \frac{1\ \cancel{\text{kg}}}{2.2\ \cancel{\text{lbs}}} \times \frac{40\ \cancel{\text{mg}}}{1\ \cancel{\text{kg}}} \times \frac{1\ \text{tablet}}{500\ \cancel{\text{mg}}} = 2\ \text{tablets}$$

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# 1.E: Measurement and Problem Solving (Exercises)

2.1: Measuring Global Temperatures

2.2: Scientific Notation: Writing Large and Small Numbers

2.3: Significant Figures: Writing Numbers to Reflect Precision

1. Define *significant figures*. Why are they important?
2. Define the different types of zeros found in a number and explain whether or not they are significant.
3. How many significant figures are in each number?
    a. 140
    b. 0.009830
    c. 15,050
    d. 221,560,000
    e. $5.67 \times 10^{3}$
    f. $2.9600 \times 10^{-5}$
4. How many significant figures are in each number?
    a. 1.05
    b. 9,500
    c. 0.0004505
    d. 0.00045050
    e. $7.210 \times 10^{6}$
    f. $5.00 \times 10^{-6}$
5. Round each number to three significant figures.
    a. 34,705
    b. 34,750
    c. 34,570

2.4: Significant Figures in Calculations

2.5: The Basic Units of Measurement

2.6: Problem Solving and Unit Conversions

2.7: Solving Multi-step Conversion Problems

2.8: Units Raised to a Power

2.9: Density

2.10: Numerical Problem-Solving Strategies and the Solution Map

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# 2: ATOMS AND ELEMENTS


2.1: Chemistry - The Central Science

**2.2: What is Matter?**

2.2.1: In Your Room

2.2.2: What is Matter?

2.2.3: Classifying Matter According to Its State—Solid, Liquid, and Gas

2.2.4: Classifying Matter According to Its Composition

2.2.5: Differences in Matter- Physical and Chemical Properties

2.2.6: Changes in Matter - Physical and Chemical Changes

**2.3: What are atoms?**

2.3.1: Cutting Aluminum until you get Atoms

2.3.2: Indivisible - The Atomic Theory

2.3.3: The Nuclear Atom

2.3.4: The Properties of Protons, Neutrons, and Electrons

2.3.5: Elements- Defined by Their Number of Protons

2.3.6: Looking for Patterns - The Periodic Table

2.3.7: Ions - Losing and Gaining Electrons

2.3.8: Isotopes - When the Number of Neutrons Varies

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



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# 2.1: Chemistry - The Central Science

## Learning Objectives

- Define chemistry in relation to other sciences.
- Use physical and chemical properties, including phase, to describe matter.

Chemistry is the study of matter—what it consists of, what its properties are, and how it changes. Being able to describe the ingredients in a cake and how they change when the cake is baked is called chemistry. Matter is anything that has mass and takes up space—that is, anything that is physically real. Some things are easily identified as matter—this book, for example. Others are not so obvious. Because we move so easily through air, we sometimes forget that it, too, is matter.

Chemistry is one branch of science. Science is the process by which we learn about the natural universe by observing, testing, and then generating models that explain our observations. Because the physical universe is so vast, there are many different branches of science (Figure 2.1.1). Thus, chemistry is the study of matter, biology is the study of living things, and geology is the study of rocks and the earth. Mathematics is the language of science, and we will use it to communicate some of the ideas of chemistry.

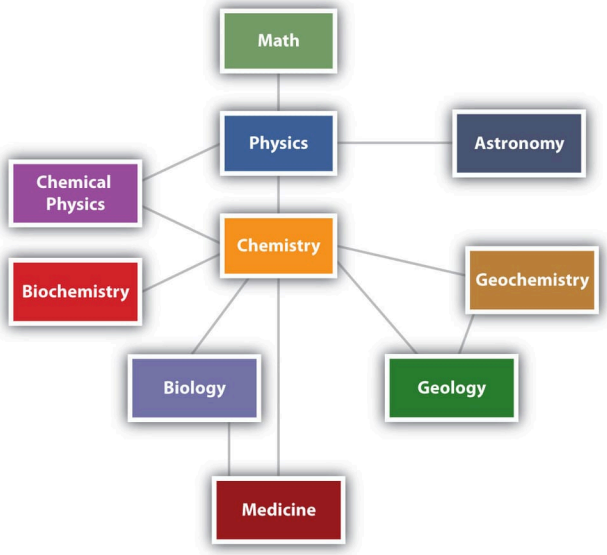



Figure 2.1.1: The Relationships between Some of the Major Branches of Science. Chemistry lies more or less in the middle, which emphasizes its importance to many branches of science. (CC BY-SA-NC; anonymous)

Although we divide science into different fields, there is much overlap among them. For example, some biologists and chemists work in both fields so much that their work is called biochemistry. Similarly, geology and chemistry overlap in the field called geochemistry. Figure 2.1.1 shows how many of the individual fields of science are related; there are many other fields of science in addition to the ones listed here.

How do scientists work? Generally, they follow a process called the **scientific method**. The scientific method is an organized procedure for learning answers to questions and making explanations for observations. The steps of the scientific method may not be as clear-cut in real life as described here, but most scientific work follows this general outline.

1. **Propose a hypothesis.** A scientist generates a testable idea, or hypothesis, to try to answer a question or explain an observation about how the natural universe works. Some people use the word *theory* in place of hypothesis, but the word hypothesis is the proper word in science. For scientific applications, the word theory is a general statement that describes a large set of observations and data. A theory represents the highest level of scientific understanding.
2. **Test the hypothesis.** A scientist evaluates the hypothesis by devising and carrying out experiments to test it. If the

hypothesis passes the test, it may be a proper answer to the question. If the hypothesis does not pass the test, it may not be a good answer.

3. **Refine the hypothesis if necessary.** Depending on the results of experiments, a scientist may want to modify the hypothesis and then test it again. Sometimes the results show the original hypothesis to be completely wrong, in which case a scientist will have to devise a new hypothesis.

Not all scientific investigations are simple enough to be separated into these three discrete steps. But these steps represent the general method by which scientists learn about our natural universe.

## Physical and Chemical Properties and Changes

The properties that chemists use to describe matter fall into two general categories. **Physical properties** are characteristics that describe matter. They include characteristics such as size, shape, color, and mass. These characteristics can be observed or measured without changing the *identity* of the matter in question. **Chemical properties** are characteristics that describe how matter changes its chemical structure or composition. An example of a chemical property is flammability—a material's ability to burn—because burning (also known as combustion) changes the chemical composition of a material. The observation of chemical properties involves a *chemical change* of the matter in question, resulting in matter with a different *identity* and different physical and chemical properties. Part of understanding matter is being able to describe it. One way chemists describe matter is to assign different kinds of properties to different categories.



Figure 2.1.1: (left) Ice Melting is a physical change. When liquid water ($H_2O$) freezes into a solid state (ice), it appears changed; However, this change is only physical as the the composition of the constituent molecules is the same: 11.19% hydrogen and 88.81% oxygen by mass. (right) Burning of wax to generate water and carbon dioxide is a chemical reaction. (CC SA-BY-3.0; Andrikkos)

We know from our experience with water that substances can change from one phase to another if the conditions are right. Typically, varying the temperature of a substance (and, less commonly, the pressure exerted on it) can cause a physical process in which a substance changes from one phase to another. Examples are summarized in Table 2.1.1.

*Table 2.1.1: Physical Changes*

| Change | Name |
|---|---|
| solid to liquid | melting, fusion |
| solid to gas | sublimation |
| liquid to gas | boiling, evaporation |
| liquid to solid | solidification, freezing |
| gas to liquid | condensation |

| Change | Name |
|---|---|
| gas to solid | deposition |

The difference between a physical reaction and a chemical reaction is **composition**. In a chemical reaction, there is a change in the composition of the substances in question; in a **physical change** there is a difference in the appearance, smell, or simple display of a sample of matter without a change in composition. Although we call them physical "reactions," no reaction is actually occurring. In order for a reaction to take place, there must be a change in the elemental composition of the substance in question. Thus, we shall simply refer to "physical reactions" as physical changes from now on.

### Example 2.1.1

Classify each of the following changes as physical or chemical:

a. condensation of steam
b. burning of gasoline
c. souring of milk
d. dissolving of sugar in water
e. melting of gold

**Solution**

The best way to determine whether a change is physical or chemical is to determine if the substance identity has changed or not.

a. Steam is water in the gas phase. When it condenses, changes from gas to liquid, it remains water. Therefore, this is a **physical** change.
b. When gasoline burns, it changes into different substances. This is a **chemical** change.
c. When milk becomes sour, several **chemical** changes have occured; proteins denature, sugars break down, and acid is produced. The milk is now made up of different substances.
d. Sugar dissolves easily into water but it still remains sugar. If the water is evaporated, the sugar will recrystalize as a solid again. Dissolving is a **physical** change, the substance does not change identity.
e. Melting solid gold into liquid gold is a **physical** change much like melting solid water (an ice cube) into liquid water is a physical change.

### Exercise 2.1.1

Classify each of the following changes as physical or chemical:

a. coal burning
b. ice melting
c. mixing chocolate syrup with milk
d. explosion of a firecracker
e. magnetizing of a screwdriver

*Answer a: available at the end of this section.*

## Key Takeaways

- Chemistry is the study of matter and how it behaves.
- The scientific method is the general process by which we learn about the natural universe.
- When a substance changes from one state to another, this is a physical change.
- If a substance undergoes a change into one or more different substances, this is a chemical change.

## Answers

**Exercise** 2.1.1

chemical
physical
physical
chemical
physical

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# 2.2: WHAT IS MATTER?

2.2.1: In Your Room
2.2.2: What is Matter?
2.2.3: Classifying Matter According to Its State—Solid, Liquid, and Gas
2.2.4: Classifying Matter According to Its Composition
2.2.5: Differences in Matter- Physical and Chemical Properties
2.2.6: Changes in Matter - Physical and Chemical Changes

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# 2.2.1: In Your Room

Matter is any substance that has mass and takes up space. Matter includes atoms and anything made up of atoms, but not other energy phenomena or waves such as light or sound. While this simple definition is easily applied, the way people view matter is often broken down into two characteristic length scales: the macroscopic and the microscopic.




Figure 2.2.1.1: A typical American university and college dormitory room in 2002 (CC BY-SA 3.0; Raul654).

The macroscopic scale is the length scale on which objects or phenomena are large enough to be visible almost practically with the naked eye, without magnifying optical instruments. Everything that one can see, touch, and handle in the dorm room of Figure 2.2.1.1 is within the macroscopic scale. To describe each of these objects, only a few macroscopic properties are required. However, each of these items can be decomposed into smaller microscopic scale properties.

The microscopic scale is the scale of objects and events smaller than those that can easily be seen by the naked eye, requiring a lens or microscope to see them clearly. All of the everyday objects that we can bump into, touch, or squeeze are ultimately composed of atoms. This ordinary atomic matter is in turn made up of interacting subatomic particles—usually a nucleus of protons and neutrons, and a cloud of orbiting electrons. Because of this, a large number of variables are needed to describe such a system which complicates the characterization.

### Matter vs. Mass

Matter should not be confused with mass, as the two are not the same in modern physics. Matter is a physical substance of which systems may be composed, while mass is not a substance, but rather a quantitative property of matter and other substances or systems.

## Contributions & Attributions

- Wikipedia

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# 2.2.2: What is Matter?

## Learning Objectives

- Define matter and explain how it is composed of building blocks known as "atoms".

We are all familiar with matter. The definition of **Matter** is anything that has mass and volume (takes up space). For most common objects that we deal with every day, it is fairly simple to demonstrate that they have mass and take up space. You might be able to imagine, however, the difficulty for people several hundred years ago to demonstrate that air had mass and volume. Air (and all other gases) are invisible to the eye, have very small masses compared to equal amounts of solids and liquids, and are quite easy to compress (change volume). Without sensitive equipment, it would have been difficult to convince people that gases are matter. Today, we can measure the mass of a small balloon when it is deflated and then blow it up, tie it off, and measure its mass again to detect the additional mass due to the air inside. The mass of air, under room conditions, that occupies a one quart jar is approximately 0.0002 pounds. This small amount of mass would have been difficult to measure in times before balances were designed to accurately measure very small masses. Later, scientists were able to compress gases into such a small volume that the gases turned into liquids, which made it clear that gases are matter.



Figure 2.2.2.1: Everything from an ant, to a truck, to the earth, and even the entire galaxy is composed of matter. Images used with permission from Wikipedia (CC_SA-BY-3.0; credit High Contrast).

Even though the universe consists of "things" as wildly different as ants and galaxies, the matter that makes up all of these "things" is composed of a very limited number of building blocks. These building blocks are known as **atoms**, and so far, scientists have discovered or created a grand total of 118 different types of atoms. Scientists have given a name to each different type of atom. A substance that is composed of only one type of atom is called an element. At this point, what should amaze you is that all forms of matter in our universe are made with only 118 different building blocks. In some ways, it's sort of like cooking a gourmet, five-course meal using only three ingredients! How is it possible? To answer that question, you have to understand the ways in which different elements are put together to form matter.

The most important method that nature uses to organize atoms into matter is the formation of **molecules**. Molecules are groups of two or more atoms that have been bonded together. There are millions of different ways to bond atoms together, which means that there are millions of different possible molecules. Each of these molecules has its own set of chemical properties, and it's these properties with which chemists are most concerned. You will learn a lot more about atoms and molecules, including how

they were discovered, in a later part of the textbook.

## Summary

All matter has mass and occupies space. All physical objects are made of matter. Matter itself is composed of tiny building blocks known as "atoms". There are only 118 different types of atoms known to man. Frequently, atoms are bonded together to form "molecules".

## Contributions & Attributions

- Wikipedia

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# 2.2.3: Classifying Matter According to Its State—Solid, Liquid, and Gas

## Learning Objectives

- To describe the solid, liquid and gas phases.

Water can take many forms. At low temperatures (below $0^\circ\text{C}$), it is a solid. When at "normal" temperatures (between $0^\circ\text{C}$ and $100^\circ\text{C}$), it is a liquid. While at temperatures above $100^\circ\text{C}$, water is a gas (steam). The state that water is in depends upon the temperature. Each state has its own unique set of physical properties. Matter typically exists in one of three states: **solid**, **liquid**, or **gas**.



Figure 2.2.3.1: Matter is usually classified into three classical states, with plasma sometimes added as a fourth state. From left to right: quartz (solid), water (liquid), nitrogen dioxide (gas).

The state that a given substance exhibits is also a physical property. Some substances exist as gases at room temperature (oxygen and carbon dioxide), while others, like water and mercury metal, exist as liquids. Most metals exist as solids at room temperature. All substances can exist in any of these three states. Figure 2.2.3.2 shows the differences among solids, liquids, and gases at the molecular level. A solid has definite volume and shape, a liquid has a definite volume but no definite shape, and a gas has neither a definite volume nor shape.

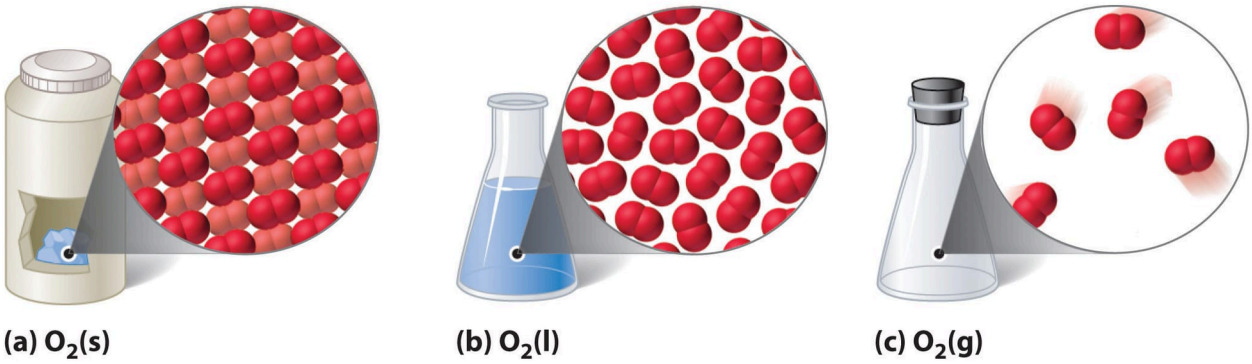
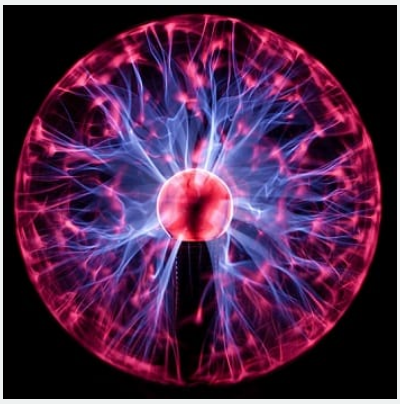



Figure 2.2.3.2: A Representation of the Solid, Liquid, and Gas States. (a) Solid $O_2$ has a fixed volume and shape, and the molecules are packed tightly together. (b) Liquid $O_2$ conforms to the shape of its container but has a fixed volume; it contains relatively densely packed molecules. (c) Gaseous $O_2$ fills its container completely—regardless of the container's size or shape—and consists of widely separated molecules.

### Plasma: A Fourth State of Matter

Technically speaking, a fourth state of matter called plasma exists, but it does not naturally occur on earth, so we will omit it from our study here.



A plasma globe operating in a darkened room. (CC BY-SA 3.0; Chocolateoak).

## Solids

In the solid state, the individual particles of a substance are in fixed positions with respect to each other because there is not enough thermal energy to overcome the intermolecular interactions between the particles. As a result, solids have a definite shape and volume. Most solids are hard, but some (like waxes) are relatively soft. Many solids composed of ions can also be quite brittle.

Solids are defined by the following characteristics:

- Definite shape (rigid)
- Definite volume
- Particles vibrate around fixed axes

If we were to cool liquid mercury to its freezing point of $-39^{\circ}\mathrm{C}$, and under the right pressure conditions, we would notice all of the liquid particles would go into the solid state. Mercury can be solidified when its temperature is brought to its freezing point. However, when returned to room temperature conditions, mercury does not exist in solid state for long, and returns back to its more common liquid form.

Solids usually have their constituent particles arranged in a regular, three-dimensional array of alternating positive and negative ions called a **crystal**. The effect of this regular arrangement of particles is sometimes visible macroscopically, as shown in Figure $2.2.3.3$. Some solids, especially those composed of large molecules, cannot easily organize their particles in such regular crystals and exist as amorphous (literally, “without form”) solids. Glass is one example of an amorphous solid.

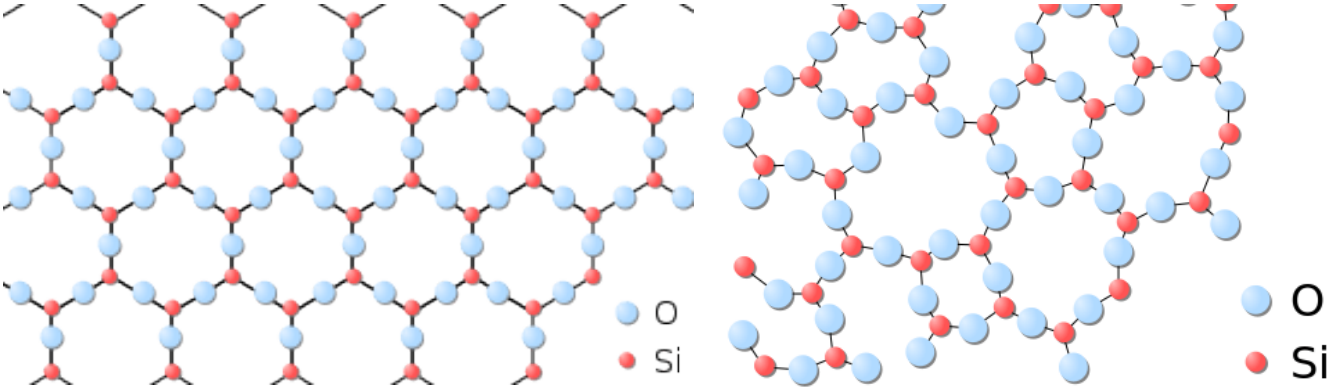



Figure 2.2.3.3: (left) The periodic crystalline lattice structure of quartz $SiO_2$ in two-dimensions. (right) The random network structure of glassy $SiO_2$ in two-dimensions. Note that, as in the crystal, each Silicon atom is bonded to 4 oxygen atoms, where the fourth oxygen atom is obscured from view in this plane. Images used with permission (public domain).

## Liquids

If the particles of a substance have enough energy to partially overcome intermolecular interactions, then the particles can move about each other while remaining in contact. This describes the liquid state. In a liquid, the particles are still in close contact, so liquids have a definite volume. However, because the particles can move about each other rather freely, a liquid has no definite shape and takes a shape dictated by its container.

Liquids have the following characteristics:

- No definite shape (takes the shape of its container).
- Has definite volume.
- Particles are free to move over each other, but are still attracted to each other.

A familiar liquid is mercury metal. Mercury is an anomaly. It is the only metal we know of that is liquid at room temperature. Mercury also has an ability to stick to itself (surface tension)—a property that all liquids exhibit. Mercury has a relatively high surface tension, which makes it very unique. Here you see mercury in its common liquid form.

YouTube Video

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

View this YouTube Video online

***Video*** 2.2.3.1*: Mercury boiling to become a gas.*

If we heat liquid mercury to its boiling point of $357^{\circ}\mathrm{C}$ under the right pressure conditions, we would notice all particles in the liquid state go into the gas state.

## Gases

If the particles of a substance have enough energy to completely overcome intermolecular interactions, then the particles can separate from each other and move about randomly in space. This describes the gas state, which we will consider in more detail elsewhere. Like liquids, gases have no definite shape, but unlike solids and liquids, gases have no definite volume either. The change from solid to liquid usually does not significantly change the volume of a substance. However, the change from a liquid to a gas significantly increases the volume of a substance, by a factor of 1,000 or more. Gases have the following characteristics:

- No definite shape (takes the shape of its container)
- No definite volume
- Particles move in random motion with little or no attraction to each other
- Highly compressible

*Table 2.2.3.1: Characteristics of the Three States of Matter*

| Characteristics | Solids | Liquids | Gases |
|---|---|---|---|
| shape | definite | indefinite | indefinite |
| volume | definite | definite | indefinite |
| relative intermolecular interaction strength | strong | moderate | weak |
| relative particle positions | in contact and fixed in place | in contact but not fixed | not in contact, random positions |

**Example 2.2.3.1**

What state or states of matter does each statement, describe?

a. This state has a definite volume, but no definite shape.
b. This state has no definite volume.
c. This state allows the individual particles to move about while remaining in contact.

**Solution**

a. This statement describes the liquid state.
b. This statement describes the gas state.
c. This statement describes the liquid state.

**Exercise 2.2.3.1**

What state or states of matter does each statement describe?

a. This state has individual particles in a fixed position with regard to each other.
b. This state has individual particles far apart from each other in space.
c. This state has a definite shape.

*Answer a: available at the end of this section.*

*Answer b: available at the end of this section.*

*Answer c: available at the end of this section.*

## Summary

- Three states of matter exist—solid, liquid, and gas.
- Solids have a definite shape and volume.
- Liquids have a definite volume, but take the shape of the container.
- Gases have no definite shape or volume.

### Answers

**Exercise** 2.2.3.1

solid

**Exercise** 2.2.3.1

gas

**Exercise** 2.2.3.1

solid

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# 2.2.4: Classifying Matter According to Its Composition

## Learning Objectives

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

One useful way of organizing our understanding of matter is to think of a hierarchy that extends down from the most general and complex to the simplest and most fundamental (Figure 2.2.4.1). Matter can be classified into two broad categories: pure substances and mixtures. A **pure substance** is a form of matter that has a constant composition (meaning that it is the same everywhere) and properties that are constant throughout the sample (meaning that there is only one set of properties such as melting point, color, boiling point, etc. throughout the matter). A material composed of two or more substances is a **mixture**. Elements and compounds are both examples of pure substances. A substance that cannot be broken down into chemically simpler components is an **element**. Aluminum, which is used in soda cans, is an element. A substance that can be broken down into chemically simpler components (because it has more than one element) is a **compound**. For example, water is a compound composed of the elements hydrogen and oxygen. Today, there are about 118 elements in the known universe. In contrast, scientists have identified tens of millions of different compounds to date.

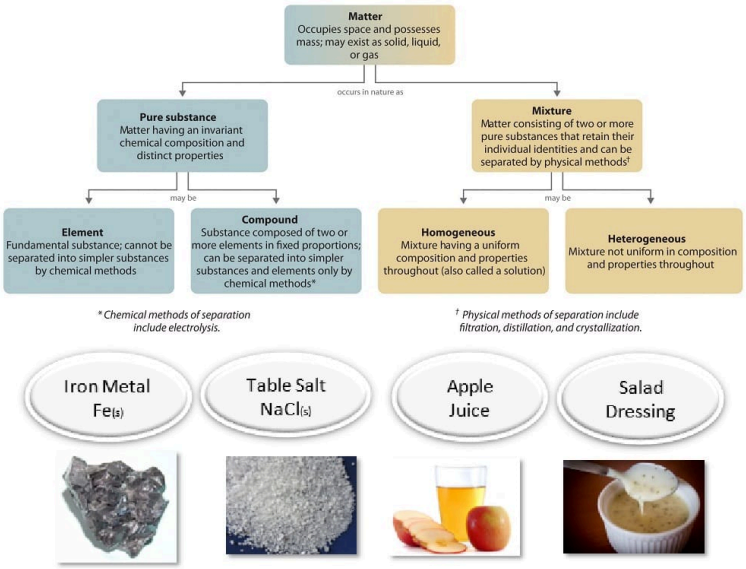



Figure 2.2.4.1: Relationships between the Types of Matter and the Methods Used to Separate Mixtures

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

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

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

of the soup.

### Phase

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

### Example 2.2.4.1

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

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

**Given**: a chemical substance

**Asked for**: its classification

**Strategy:**

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

**Solution**

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

### Exercise 2.2.4.1

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

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

*Answer a: available at the end of this section.*

**Example 2.2.4.2**

How would a chemist categorize each example of matter?

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

**Solution**

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

**Exercise 2.2.4.2**

How would a chemist categorize each example of matter?

a. coffee
b. hydrogen
c. an egg

*Answer a: available at the end of this section.*

## Summary

Matter can be classified into two broad categories: pure substances and mixtures. A pure substance is a form of matter that has a constant composition and properties that are constant throughout the sample. Mixtures are physical combinations of two or more elements and/or compounds. Mixtures can be classified as homogeneous or heterogeneous. Elements and compounds are both examples of pure substances. Compounds are substances that are made up of more than one type of atom. Elements are the simplest substances made up of only one type of atom.

## Vocabulary

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

## Contributions & Attributions

- 

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

### Answers

**Exercise** 2.2.4.1

homogeneous mixture (solution)
element
heterogeneous mixture

compound

**Exercise** 2.2.4.2

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

element

heterogeneous mixture

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# 2.2.5: Differences in Matter- Physical and Chemical Properties

**Learning Objectives**

To separate physical from chemical properties.

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

## Physical Property

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

For the elements, color does not vary much from one element to the next. The vast majority of elements are colorless, silver, or gray. Some elements do have distinctive colors: sulfur and chlorine are yellow, copper is (of course) copper-colored, and elemental bromine is red. However, density can be a very useful parameter for identifying an element. Of the materials that exist as solids at room temperature, iodine has a very low density compared to zinc, chromium, and tin. Gold has a very high density, as does platinum. Pure water, for example, has a density of 0.998 g/cm$^3$ at 25°C. The average densities of some common substances are in Table 2.2.5.1. Notice that corn oil has a lower mass to volume ratio than water. This means that when added to water, corn oil will “float.”

*Table 2.2.5.1: Densities of Common Substances*

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

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



Figure 2.2.5.1: Pencil (left) and Diamond ring (right). Both are a form of carbon, but exhibit very different physical properties.

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

## Chemical Properties

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



Figure 2.2.5.2: Heavy rust on the links of a chain near the Golden Gate Bridge in San Francisco; it was continuously exposed to moisture and salt spray, causing surface breakdown, cracking, and flaking of the metal. (CC BY-SA 3.0; Marlith).

A chemical property of iron is its capability of combining with oxygen to form iron oxide, the chemical name of rust (Figure 2.2.5.2). The more general term for rusting and other similar processes is corrosion. Other terms that are commonly used in descriptions of

chemical changes are burn, rot, explode, decompose, and ferment. Chemical properties are very useful in identifying substances. However, unlike physical properties, chemical properties can only be observed as the substance is in the process of being changed into a different substance.

*Table 2.2.5.2: Contrasting Physical and Chemical Properties*

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

### Example 2.2.5.1

Which of the following is a chemical property of iron?

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

**Solution**

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

### Exercise 2.2.5.1A

Which of the following is a physical property of matter?

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

*Answer available at the end of this section.*

### Exercise 2.2.5.1B

Which of the following is a chemical property?

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

*Answer available at the end of this section.*

## Summary

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

formation of rust is a chemical change because rust is a different kind of matter than the iron, oxygen, and water present before the rust formed.

## Answers

**Exercise** $2.2.5.1A$

c

**Exercise** $2.2.5.1B$

a

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# 2.2.6: Changes in Matter - Physical and Chemical Changes

**Learning Objectives**

- Label a change as chemical or physical.
- List evidence that can indicate a chemical change occurred.

Change is happening all around us all of the time. Just as chemists have classified elements and compounds, they have also classified types of changes. Changes are classified as either physical or chemical changes. Chemists learn a lot about the nature of matter by studying the changes that matter can undergo. Chemists make a distinction between two different types of changes that they study—physical changes and chemical changes.

## Physical Change

Physical changes are changes in which no bonds are broken or formed. This means that the same types of compounds or elements that were there at the beginning of the change are there at the end of the change. Because the ending materials are the same as the beginning materials, the properties (such as color, boiling point, etc.) will also be the same. Physical changes involve moving molecules around, but not changing them. Some types of physical changes include:

- Changes of state (changes from a solid to a liquid or a gas and vice versa).
- Separation of a mixture.
- Physical deformation (cutting, denting, stretching).
- Making solutions (special kinds of mixtures).

As an ice cube melts, its shape changes as it acquires the ability to flow. However, its composition does not change. Melting is an example of a physical change. A physical change is a change to a sample of matter in which some properties of the material change, but the identity of the matter does not. When liquid water is heated, it changes to water vapor. However, even though the physical properties have changed, the molecules are exactly the same as before. We still have each water molecule containing two hydrogen atoms and one oxygen atom covalently bonded. When you have a jar containing a mixture of pennies and nickels and you sort the mixture so that you have one pile of pennies and another pile of nickels, you have not altered the identity of the pennies or the nickels—you've merely separated them into two groups. This would be an example of a physical change. Similarly, if you have a piece of paper, you don't change it into something other than a piece of paper by ripping it up. What was paper before you started tearing is still paper when you are done. Again, this is an example of a physical change.



Figure 2.2.6.1: Ice melting is a physical change. When liquid water ($H_2O$) freezes into a solid state (ice), it appears changed; however, this change is only physical, as the composition of the constituent molecules is the same: 11.19% hydrogen and 88.81% oxygen by mass. (Public Domain; Moussa).

Physical changes can further be classified as reversible or irreversible. The melted ice cube may be refrozen, so melting is a reversible physical change. Physical changes that involve a change of state are all reversible. Other changes of state include **vaporization** (liquid to gas), **freezing** (liquid to solid), and **condensation** (gas to liquid). Dissolving is also a reversible physical change. When salt is dissolved into water, the salt is said to have entered the aqueous state. The salt may be regained by boiling off the water, leaving the salt behind.

## Chemical Change

**Chemical changes** occur when bonds are broken and/or formed between molecules or atoms. This means that one substance with a certain set of properties (such as melting point, color, taste, etc) is turned into a different substance with different properties. Chemical changes are frequently harder to reverse than physical changes.

One good example of a chemical change is burning a candle. The act of burning paper actually results in the formation of new chemicals (carbon dioxide and water) from the burning of the wax. Another example of a chemical change is what occurs when natural gas is burned in your furnace. This time, on the left there is a molecule of methane, $\mathrm{CH_4}$, and two molecules of oxygen, $\mathrm{O_2}$; on the right are two molecules of water, $\mathrm{H_2O}$, and one molecule of carbon dioxide, $\mathrm{CO_2}$. In this case, not only has the appearance changed, but the structure of the molecules has also changed. The new substances do not have the same chemical properties as the original ones. Therefore, this is a chemical change.



Figure 2.2.6.2: Burning of wax to generate water and carbon dioxide is a chemical reaction. (CC-SA-BY-3.0; Andrikkos )

We can't actually see molecules breaking and forming bonds, although that's what defines chemical changes. We have to make other observations to indicate that a chemical change has happened. Some of the evidence for chemical change will involve the energy changes that occur in chemical changes, but some evidence involves the fact that new substances with different properties are formed in a chemical change.

Observations that help to indicate chemical change include:

- Temperature changes (either the temperature increases or decreases).
- Light given off.
- Unexpected color changes (a substance with a different color is made, rather than just mixing the original colors together).
- Bubbles are formed (but the substance is not boiling—you made a substance that is a gas at the temperature of the beginning materials, instead of a liquid).
- Different smell or taste (do not taste your chemistry experiments, though!).
- A solid forms if two clear liquids are mixed (look for *floaties*—technically called a precipitate).

## Example 2.2.6.1

Label each of the following changes as a physical or chemical change. Give evidence to support your answer.

a. Boiling water.
b. A nail rusting.
c. A green solution and colorless solution are mixed. The resulting mixture is a solution with a pale green color.
d. Two colorless solutions are mixed. The resulting mixture has a yellow precipitate.

**Solution**

a. Physical: boiling and melting are physical changes. When water boils, no bonds are broken or formed. The change could be written: $\mathrm{H_2O}\,(l) \rightarrow \mathrm{H_2O}\,(g)$
b. Chemical: The dark grey nail changes color to form an orange flaky substance (the rust); this must be a chemical change. Color changes indicate chemical change. The following reaction occurs: $\mathrm{Fe} + \mathrm{O_2} \rightarrow \mathrm{Fe_2O_3}$
c. Physical: because none of the properties changed, this is a physical change. The green mixture is still green and the colorless solution is still colorless. They have just been spread together. No color *change* occurred or other evidence of chemical change.
d. Chemical: the formation of a precipitate and the color change from colorless to yellow indicate a chemical change.

**Exercise 2.2.6.1**

Label each of the following changes as a physical or chemical change.

a. A mirror is broken.
b. An iron nail corroded in moist air
c. Copper metal is melted.
d. A catalytic converter changes nitrogen dioxide to nitrogen gas and oxygen gas.

*Answer a: available at the end of this section.*

*Answer b: available at the end of this section.*

*Answer c: available at the end of this section.*

*Answer d: available at the end of this section.*

## Separating Mixtures Through Physical Changes

Homogeneous mixtures (solutions) can be separated into their component substances by physical processes that rely on differences in some physical property, such as differences in their boiling points. Two of these separation methods are distillation and crystallization. Distillation makes use of differences in volatility, a measure of how easily a substance is converted to a gas at a given temperature. A simple distillation apparatus for separating a mixture of substances, at least one of which is a liquid. The most volatile component boils first and is condensed back to a liquid in the water-cooled condenser, from which it flows into the receiving flask. If a solution of salt and water is distilled, for example, the more volatile component, pure water, collects in the receiving flask, while the salt remains in the distillation flask.

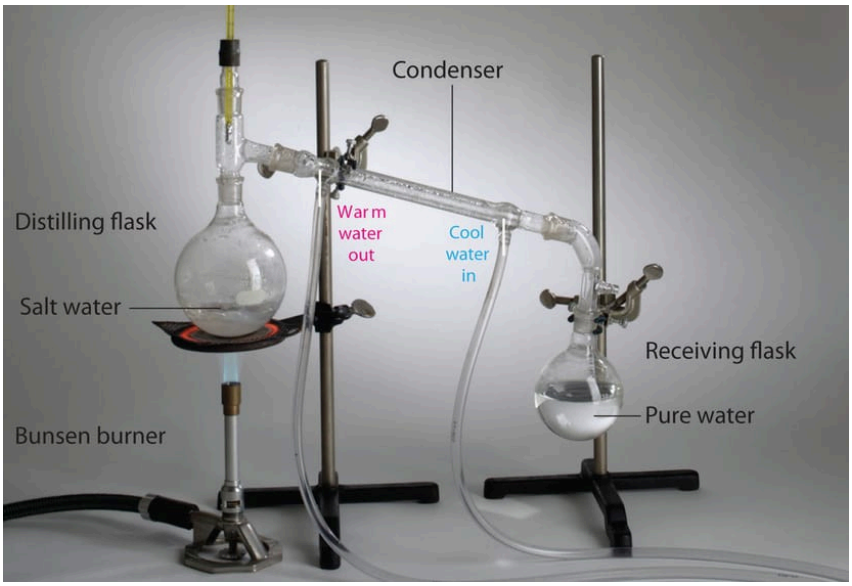



Figure 2.2.6.3**:** *The Distillation of a Solution of Table Salt in Water. The solution of salt in water is heated in the distilling flask until it boils. The resulting vapor is enriched in the more volatile component (water), which condenses to a liquid in the cold condenser and is then collected in the receiving flask.*

Parts of a distillation setup: Bunsen burner, salt water in distilling flask, condenser with cool water in and warm water out, pure water in receiving flask

Mixtures of two or more liquids with different boiling points can be separated with a more complex distillation apparatus. One example is the refining of crude petroleum into a range of useful products: aviation fuel, gasoline, kerosene, diesel fuel, and lubricating oil (in the approximate order of decreasing volatility). Another example is the distillation of alcoholic spirits such as brandy or whiskey. This relatively simple procedure caused more than a few headaches for federal authorities in the 1920s during the era of Prohibition, when illegal stills proliferated in remote regions of the United States.

Another example for using physical properties to separate mixtures is filtration (Figure 2.2.6.4). Filtration is any mechanical, physical or biological operation that separates solids from fluids (liquids or gases) by adding a medium through which only the fluid can pass. The fluid that passes through is called the filtrate. There are many different methods of filtration; all aim to attain the separation of substances. Separation is achieved by some form of interaction between the substance or objects to be removed and the filter. The substance that is to pass through the filter must be a fluid, i.e. a liquid or gas. Methods of filtration vary depending on the location of the targeted material, i.e. whether it is dissolved in the fluid phase or suspended as a solid.

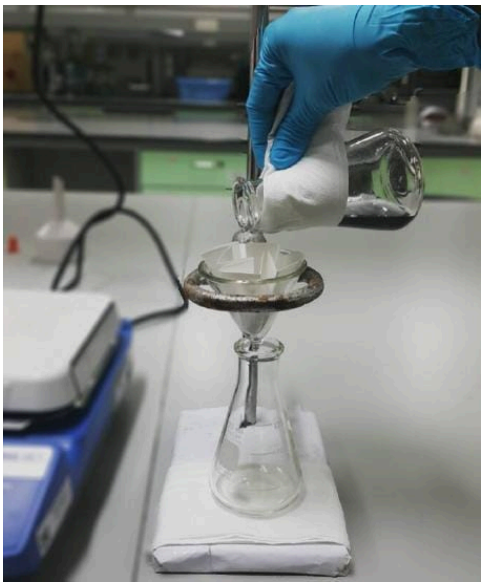


Figure 2.2.6.4: *Filtration for the separation of solids from a hot solution. (CC BY-SA 4.0; Suman6395).*

## Summary

- Chemists make a distinction between two different types of changes that they study—physical changes and chemical changes.
- Physical changes are changes that do not alter the identity of a substance.
- Chemical changes are changes that occur when one substance is turned into another substance.
- Chemical changes are frequently harder to reverse than physical changes. Observations that indicate a chemical change has occurred include color change, temperature change, light given off, formation of bubbles, formation of a precipitate, etc.

## Contributions & Attributions

- 

- Boundless (www.boundless.com)

### Answers

**Exercise** 2.2.6.1
physical change

**Exercise** 2.2.6.1
chemical change

**Exercise** 2.2.6.1
physical change

**Exercise** 2.2.6.1
chemical change

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# 2.3: WHAT ARE ATOMS?

2.3.1: Cutting Aluminum until you get Atoms
2.3.2: Indivisible - The Atomic Theory
2.3.3: The Nuclear Atom
2.3.4: The Properties of Protons, Neutrons, and Electrons
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2.3.6: Looking for Patterns - The Periodic Table
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2.3.9: Atomic Mass - The Average Mass of an Element's Atoms

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# 2.3.1: Cutting Aluminum until you get Atoms

Take some aluminum foil. Cut it in half. Now there are two smaller pieces of aluminum foil. Cut one of the pieces in half again. Cut one of those smaller pieces in half again. Continue cutting, making smaller and smaller pieces of aluminum foil. It should be obvious that the pieces are still aluminum foil; they are just becoming smaller and smaller. But how far can this exercise be taken, at least in theory? Can one continue cutting the aluminum foil into halves forever, making smaller and smaller pieces? Or is there some limit, some absolute smallest piece of aluminum foil? Thought experiments like this—and the conclusions based on them—were debated as far back as the fifth century BC by Democritus and other ancient Greek philosophers (Figure 2.3.1.1).

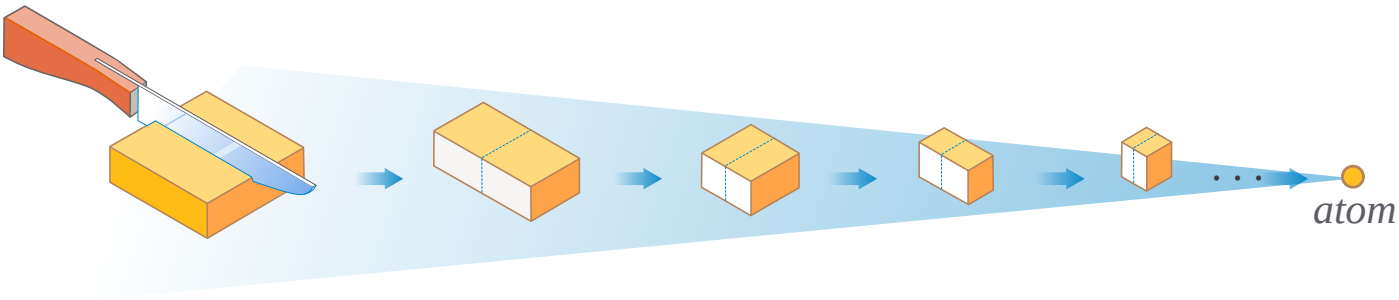



Figure 2.3.1.1: Democritus argued that matter, like an aluminum block, cannot be repeatedly cut in half perpetually. At some point, a limit is reached before the substance can no longer be called "aluminum"; this is the atomic limit. (CC BY-NC; Ümit Kaya via LibreTexts)

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

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# 2.3.2: Indivisible - The Atomic Theory

**Learning Objectives**

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

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

## Democritus and the Greek Philosophers

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



Figure 2.3.2.1: (left) Democritus by Hendrick ter Brugghen, 1628. Democritus was known as the "laughing philosopher." It was a good thing he liked to laugh, because most other philosophers were laughing at his theories. (right) British physicist and chemist John Dalton (1766-1844). Unlike the Greek philosophers, John Dalton believed in both logical thinking and experimentation.

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

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

two millennia before the theory of atomos (or "atoms," as they are known today) was fully appreciated.

### Greeks: "All Thought and No Action"

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

While it must be assumed that many more scientists, philosophers, and others studied composition of matter after Democritus, a major leap forward in our understanding of the composition of matter took place in the 1800's with the work of the British scientists John Dalton. He started teaching school at age twelve, and was primarily known as a teacher. In his twenties, he moved to the growing city of Manchester, where he was able to pursue some scientific studies. His work in several areas of science brought him a number of honors. When he died, over 40,000 people in Manchester marched at his funeral.

The modern atomic theory, proposed about 1803 by the English chemist John Dalton (Figure 2.3.2.1), is a fundamental concept that states that all elements are composed of atoms. Previously, we defined an atom as the smallest part of an element that maintains the identity of that element. Individual atoms are extremely small; even the largest atom has an approximate diameter of only $5.4 \times 10^{-10}$ m. With that size, it takes over 18 million of these atoms, lined up side by side, to equal the width of your little finger (about 1 cm).

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

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

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

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

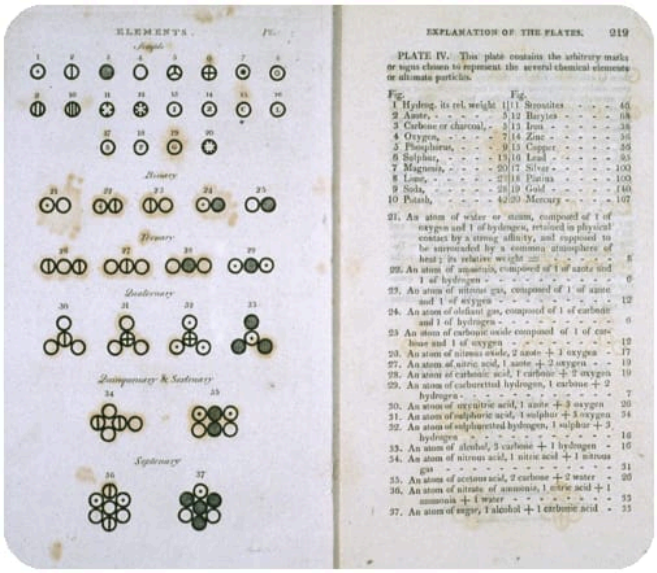


Figure 2.3.2.2: Dalton's symbols from his text "A New System of Chemical Philosophy."

The evidence for atoms is so great that few doubt their existence. In fact, individual atoms are now routinely observed with state-of-the art technologies. Moreover, they can even be used for making pretty images; or as IBM research demonstrates in Video 2.3.2.1, control of individual atoms can be use used create animations.

YouTube Video

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

View this YouTube Video online

Video 2.3.2.1: A Boy And His Atom: The World's Smallest Movie.

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

## Summary

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

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# 2.3.3: The Nuclear Atom

## Learning Objectives

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

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



Figure 2.3.3.1: J. J. Thomson (center) concluded experiments that suggested that Dalton's (left) atomic theory was not telling the entire story. Ernest Rutherford (right) later built on Thomson's work to argue for the model nuclear atom.

## Electrons and Plums

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

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

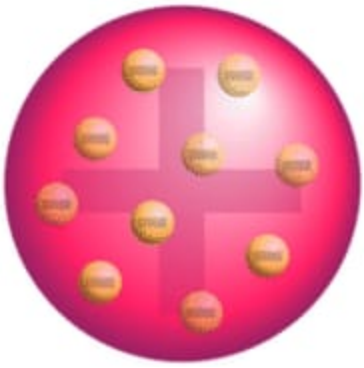


Figure 2.3.3.2: The "plum pudding" model.

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

## Atoms and Gold

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

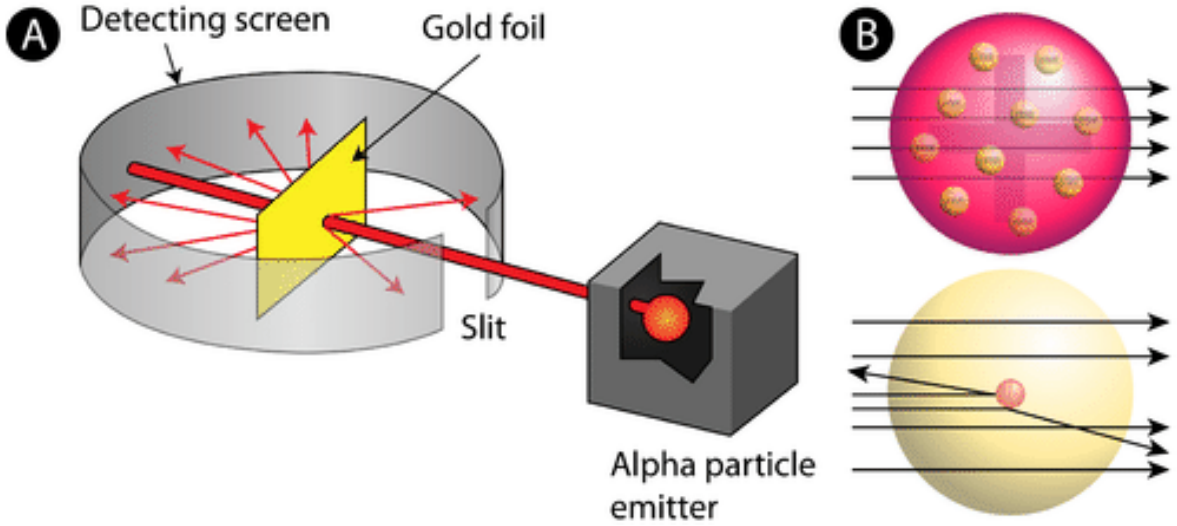



Figure 2.3.3.3: (A) The experimental setup for Rutherford's gold foil experiment: A radioactive element that emitted alpha particles was directed toward a thin sheet of gold foil that was surrounded by a screen which would allow detection of the deflected particles. (B) According to the plum pudding model (top), all of the alpha particles should have passed through the gold foil with little or no deflection. Rutherford found that a small percentage of alpha particles were deflected at large angles, which could be explained by an atom with a very small, dense, positively-charged nucleus at its center (bottom).

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

Rutherford needed to come up with an entirely new model of the atom in order to explain his results. Because the vast majority of the alpha particles had passed through the gold, he reasoned that most of the atom was empty space. In contrast, the particles

that were highly deflected must have experienced a tremendously powerful force within the atom. He concluded that all of the positive charge and the majority of the mass of the atom must be concentrated in a very small space in the atom's interior, which he called the nucleus. The **nucleus** is the tiny, dense, central core of the atom and is composed of protons and neutrons.

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

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

## Atomic Nucleus

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

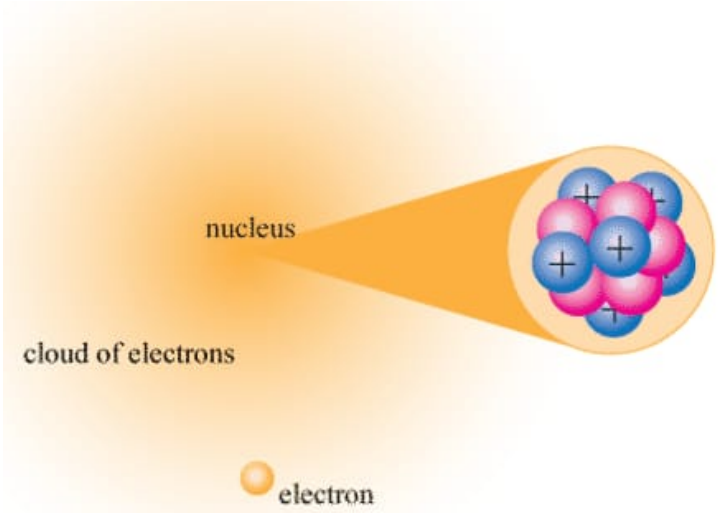



Figure 2.3.3.4: The nuclear atom.

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

### Holding it all Together

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

## Summary

- Atoms are the ultimate building blocks of all matter.

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

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# 2.3.4: The Properties of Protons, Neutrons, and Electrons

**Learning Objectives**

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

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

## Electrons

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

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




Figure 2.3.4.1: 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 $(\text{amu})$, which is about $1.67 \times 10^{-27}$ 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 $(\text{amu})$. (An atomic mass unit equals about $1.67 \times 10^{-27}$ kilograms.) A neutron also has about the same diameter as a proton, or $1.7 \times 10^{-15}$ meters.

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

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

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

*Table 2.3.4.1: Properties of Subatomic Particles*

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

Table 2.3.4.1 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 (**$\text{amu}$**)** is defined as one-twelfth of the mass of a carbon-12 atom. Atomic mass units $(\text{amu})$ are useful, because, as you can see, the mass of a proton and the mass of a neutron are almost exactly $1$ in this unit system.

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

## Summary

- Electrons are a type of subatomic particle with a negative charge.
- Protons are a type of subatomic particle with a positive charge. Protons are bound together in an atom's nucleus as a result of the strong nuclear force.
- Neutrons are a type of subatomic particle with no charge (they are neutral). Like protons, neutrons are bound into the atom's nucleus as a result of the strong nuclear force.
- Protons and neutrons have approximately the same mass, but they are both much more massive than electrons

(approximately 2,000 times as massive as an electron).
- The positive charge on a proton is equal in magnitude to the negative charge on an electron. As a result, a neutral atom must have an equal number of protons and electrons.
- The atomic mass unit (amu) is a unit of mass equal to one-twelfth the mass of a carbon-12 atom

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# 2.3.5: 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 $\mathrm{H}$ for hydrogen, $\mathrm{C}$ for carbon, or $\mathrm{He}$ for helium. However, it would more powerful if these names could be used to identify the numbers of protons and neutrons in the atoms. That's where atomic number and mass number are useful.



Figure 2.3.5.1: It is difficult to find qualities that differ between each element, and to distinguish one element from another. Each element, however, does have a unique number of protons. Sulfur has 16 protons, silicon has 14 protons, and gold has 79 protons. Images used with permission (public domain for sulfur and silicon, gold is licensed by CC-BY-SA-NC-ND; Alchemist-hp).

## Atomic Number

Scientists distinguish between different elements by counting the number of protons in the nucleus (Table 2.3.5.1). If an atom has only one proton, we know that it's a hydrogen atom. An atom with two protons is always a helium atom. If scientists count four protons in an atom, they know it's a beryllium atom. An atom with three protons is a lithium atom, an atom with five protons is a boron atom, an atom with six protons is a carbon atom . . . the list goes on.

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

*Table 2.3.5.1: Atoms of the First Six Elements*

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

Of course, since neutral atoms have to have one electron for every proton, an element's atomic number also tells you how many

electrons are in a neutral atom of that element. For example, hydrogen has an atomic number of 1. This means that an atom of hydrogen has one proton, and, if it's neutral, one electron as well. Gold, on the other hand, has an atomic number of 79, which means that an atom of gold has 79 protons, and, if it's neutral, 79 electrons as well.

**Neutral Atoms**

Atoms are neutral in electrical charge because they have the same number of negative electrons as positive protons (Table 2.3.5.1). 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 ($\text{amu}$). One atomic mass unit is the mass of a proton, or about $1.67 \times 10^{-27}$ kilograms, which is an extremely small mass. A neutron has just a tiny bit more mass than a proton, but its mass is often assumed to be one atomic mass unit as well. Because electrons have virtually no mass, just about all the mass of an atom is in its protons and neutrons. Therefore, the total number of protons and neutrons in an atom determines its mass in atomic mass units (Table 2.3.5.1).

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 ($2\ \text{amu}$ for the protons + $2\ \text{amu}$ 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 $\text{O}$ for oxygen, $\text{Zn}$ for zinc, and $\text{Fe}$ for iron. The first letter of a symbol is always capitalized. If the symbol contains two letters, the second letter is lower case. The majority of elements have symbols that are based on their English names. However, some of the elements that have been known since ancient times have maintained symbols that are based on their Latin names, as shown in Table 2.3.5.2.

*Table 2.3.5.2: Symbols and Latin Names for Elements*

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

## Summary

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

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# 2.3.6: Looking for Patterns - The Periodic Table

## Learning Objectives

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

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

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

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

The periodic table is one of the cornerstones of chemistry because it organizes all of the known elements on the basis of their chemical properties. A modern version is shown in Figure 2.3.6.1. Most periodic tables provide additional data (such as atomic mass) in a box that contains each element's symbol. The elements are listed in order of atomic number.

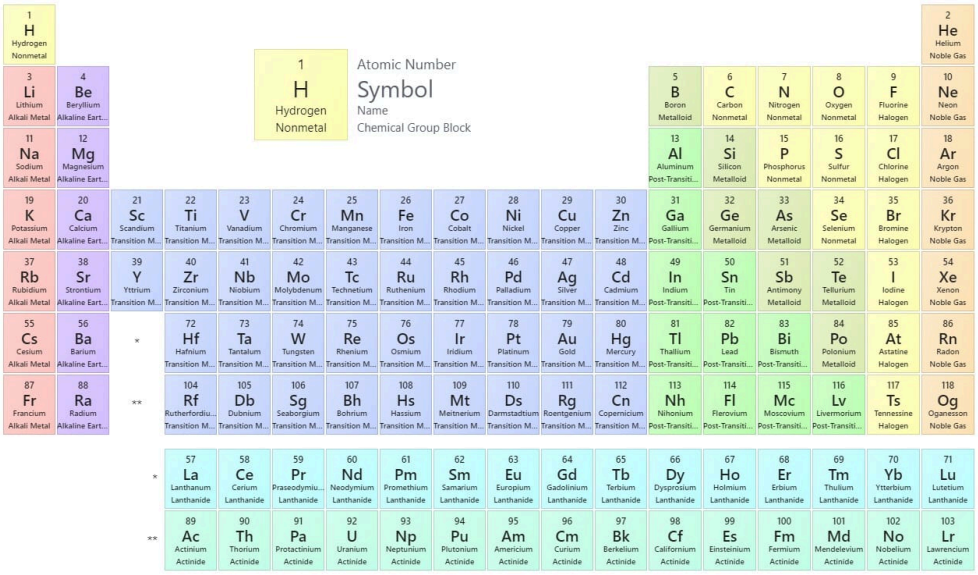



Figure 2.3.6.1: A Modern Periodic Table. A modern periodic table lists elements left to right by atomic number. An interactive Periodic table can be found Periodic Table of Elements. (Public Domain; PubChem via NIH)

## Features of the Periodic Table

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

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

### To Your Health: Radon

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

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

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

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

Certain elemental properties become apparent in a survey of the periodic table as a whole. Every element can be classified as either a metal, a nonmetal, or a metalloid (or semi metal), as shown in Figure 2.3.6.2. A **metal** is a substance that is shiny, typically (but not always) silvery in color, and an excellent conductor of electricity and heat. Metals are also malleable (they can be beaten into thin sheets) and ductile (they can be drawn into thin wires). A **nonmetal** is typically dull and a poor conductor of electricity and heat. Solid nonmetals are also very brittle. As shown in Figure 2.3.6.2, metals occupy the left three-fourths of the periodic table, while nonmetals (except for hydrogen) are clustered in the upper right-hand corner of the periodic table. The elements with properties intermediate between those of metals and nonmetals are called **metalloids** (or **semi-metals**). Elements adjacent to the bold line in the right-hand portion of the periodic table have semimetal properties.

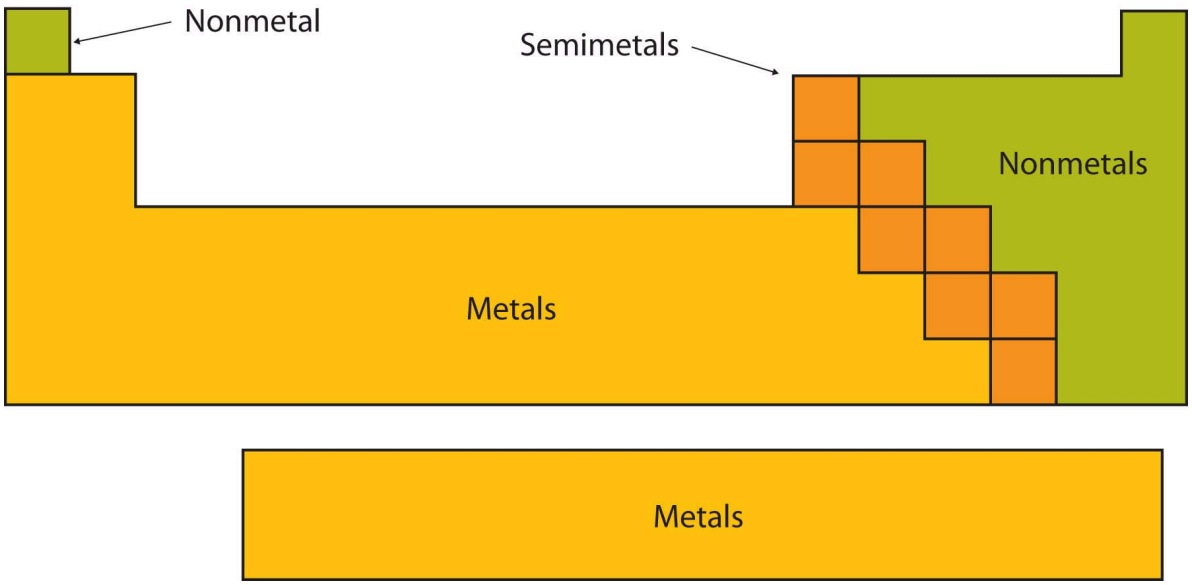



Figure 2.3.6.2: Types of Elements. Elements are either metals, nonmetals, or metalloids (or semi metals). Each group is located in a different part of the periodic table. (CC BY-NC-SA; Anonymous by request)

## Example 2.3.6.1

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

a. Se
b. Mg
c. Ge

**Solution**

a. In Figure 2.3.6.1, selenium lies above and to the right of the diagonal line marking the boundary between metals and nonmetals, so it should be a nonmetal.
b. Magnesium lies to the left of the diagonal line marking the boundary between metals and nonmetals, so it should be a metal.
c. Germanium lies within the diagonal line marking the boundary between metals and nonmetals, so it should be a metalloid.

## Exercise 2.3.6.1

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

*Answer available at the end of this section.*

Another way to categorize the elements of the periodic table is shown in Figure 2.3.6.3. The first two columns on the left and the last six columns on the right are called the main group elements. The ten-column block between these columns contains the **transition metals**. The two rows beneath the main body of the periodic table contain the **inner transition metals**. The elements in these two rows are also referred to as, respectively, the **lanthanide metals** and the **actinide metals**.

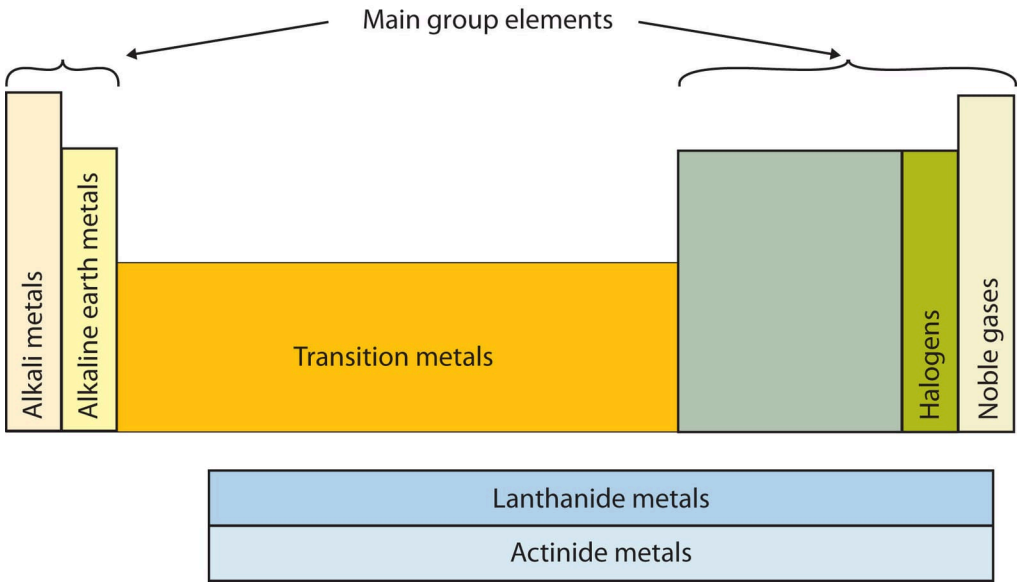



Figure 2.3.6.3: Special Names for Sections of the Periodic Table. (CC BY-NC-SA; Anonymous by request)

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.

YouTube Video

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

View this YouTube Video online

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

## Group 2: The Alkaline Earth Metals

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

## Group 17: The Halogens

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

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

## Group 18: The Noble Gases

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

Example 2.3.6.2: Groups

Provide the family or group name of each element.

a. Li
b. Ar
c. Cl

**Solution**

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

### Exercise 2.3.6.2: Groups

Provide the family or group name of each element.

a. F
b. Ca
c. Kr

*Answer a: available at the end of this section.*

### Example 2.3.6.3: Classification of Elements

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

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

**Solution**

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

### Exercise 2.3.6.3: Classification of Elements

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

a. F
b. U
c. Cu

*Answer a: available at the end of this section.*

## Summary

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

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

# References


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2. Sisler, Harry H. Electronic structure, properties, and the periodic law. New york; Reinhold publishing corporation, 1963.
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# Contributions & Attributions

## Answers

**Exercise** 2.3.6.1

Indium is a metal.

**Exercise** 2.3.6.2**: Groups**

Fluorine is a halogen (Group 17).
Calcium is a alkaline earth metal (Group 2).
Krypton is a noble gas (Group 18).

**Exercise** 2.3.6.3**: Classification of Elements**

Fluorine is a nonmetal.
Uranium is a metal (and a inner transition metal too).
Copper is a metal (and a transition metal too).


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# 2.3.7: 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.

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

The cation produced in this way, $\mathrm{Na^+}$, 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 2.3.7.1 is a graphical depiction of this process.

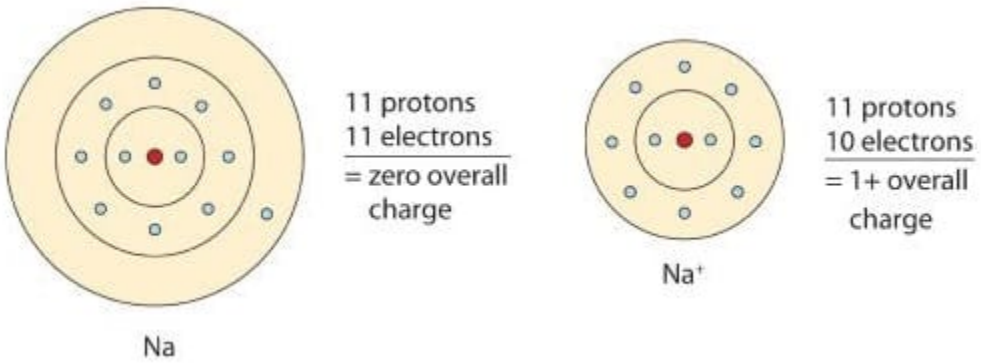



Figure 2.3.7.1: The Formation of a Sodium Ion. On the left, a sodium atom has 11 electrons. On the right, the sodium ion only has 10 electrons and a 1+ charge. Neutral sodium atom on left has 11 protons and 11 electrons. Sodium ion on right has 11 protons and 10 electrons, with a +1 overall charge.

## 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.)

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

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 2.3.7.2 is a graphical depiction of this process.

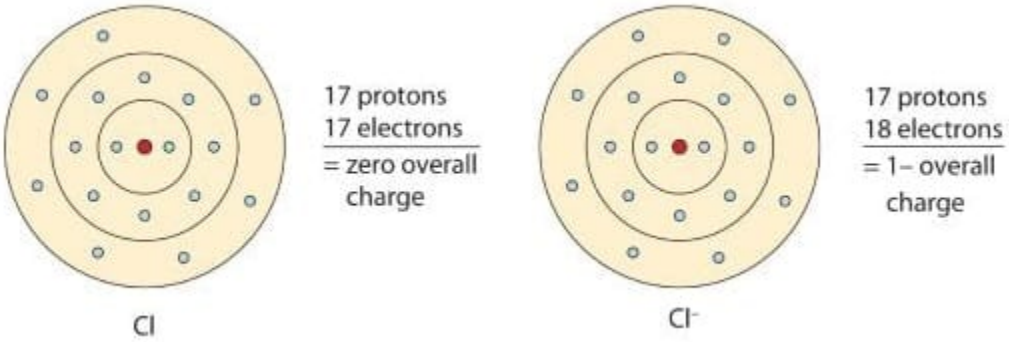



Figure 2.3.7.2: The Formation of a Chlorine Ion. On the left, the chlorine atom has 17 electrons. On the right, the chloride ion has 18 electrons and has a 1– charge. Neutral chlorine atom on left has 17 protons and 17 electrons. Sodium ion on right has 17 protons and 18 electrons, with a -1 overall 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 2.3.7.3 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 $Ba^{+2}$.

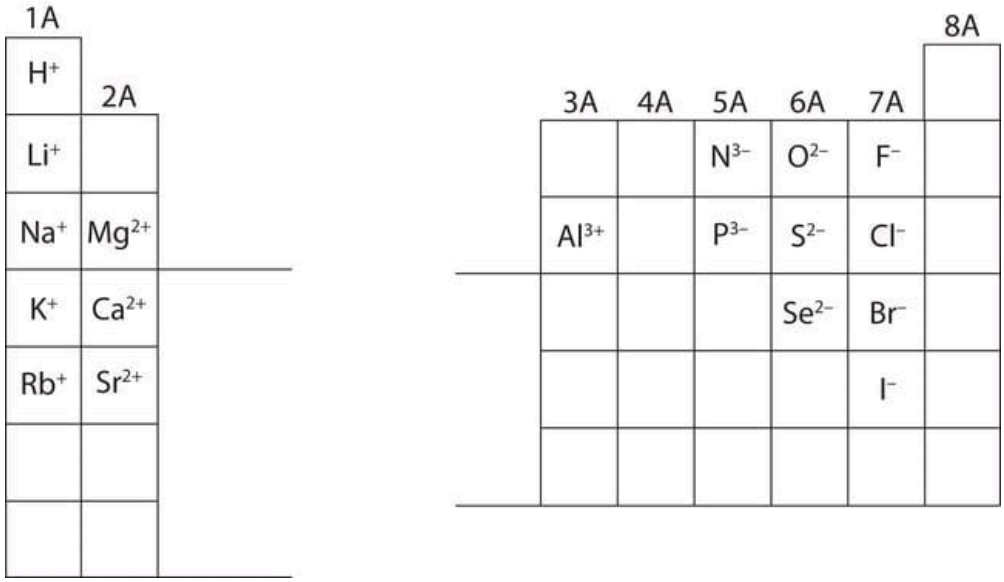



Figure 2.3.7.3: Predicting Ionic Charges. The charge that an atom acquires when it becomes an ion is related to the structure of the periodic table. Within a group (family) of elements, atoms form ions of a certain charge.

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# 2.3.8: Isotopes - When the Number of Neutrons Varies

**Learning Objectives**

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

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

## An Example: Hydrogen Isotopes

Hydrogen is an example of an element that has isotopes. Three isotopes of hydrogen are modeled in Figure 2.3.8.1. Most hydrogen atoms have just one proton, one electron, and lack a neutron. These atoms are just called hydrogen. Some hydrogen atoms have one neutron as well. These atoms are the isotope named deuterium. Other hydrogen atoms have two neutrons. These atoms are the isotope named tritium.

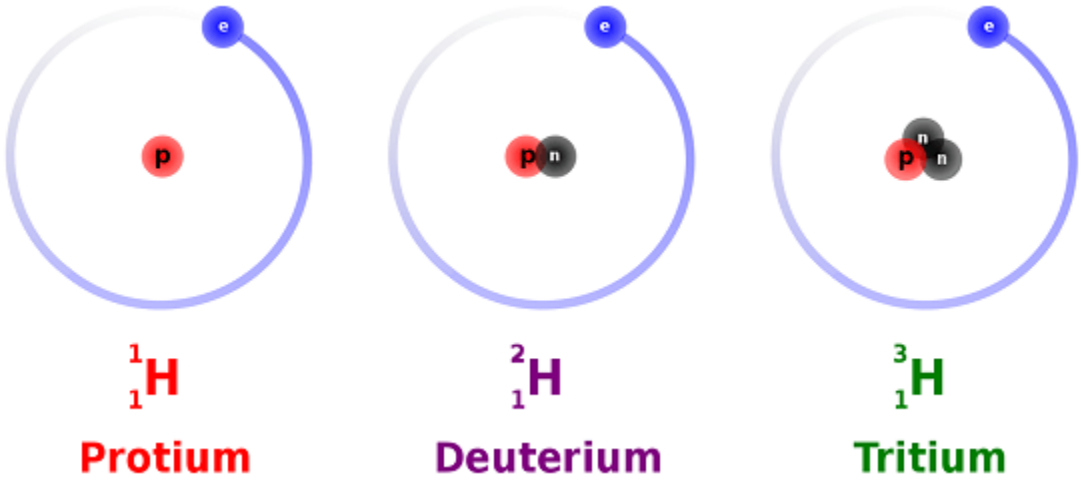



Figure 2.3.8.1: The three most stable isotopes of hydrogen: protium (A = 1), deuterium (A = 2), and tritium (A = 3). (CC SA-BY 3.0; Balajijagadesh via Wikipedia).

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

**Example 2.3.8.1: Lithium Isotopes**

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

**Solution**

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

a.

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

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

b.

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

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

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

## Stability of Isotopes

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

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

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

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

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




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

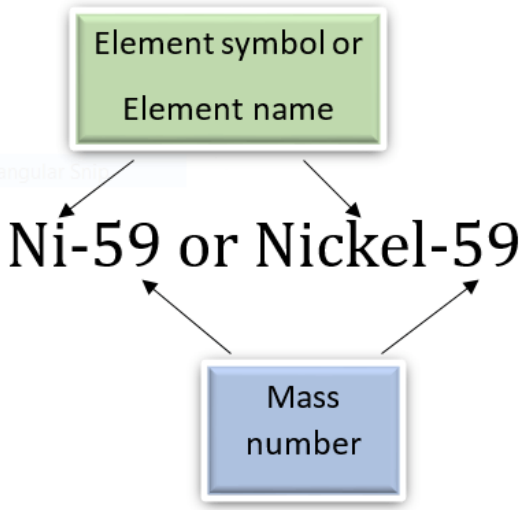
The following nuclear symbols are for a nickel nucleus with 31 neutrons and a uranium nucleus with 146 neutrons.

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

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

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

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




### Example 2.3.8.2: Potassium-40

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

**Solution**

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

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

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

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

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

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

### Example 2.3.8.3: Zinc-65

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

**Solution**

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

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

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

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

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

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

### Exercise 2.3.8.3

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

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

*Answer a: available at the end of this section.*

## 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.

## Answers

**Exercise** 2.3.8.3

27 protons, 27 electrons, 33 neutrons
11 protons, 11 electrons, 13 neutrons
20 protons, 20 electrons, 25 neutrons
38 protons, 38 electrons, 52 neutrons

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

## Learning Objectives

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

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

## Calculating Atomic Mass

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

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

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

### Example 2.3.9.1: Boron Isotopes

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

**Solution**

Boron has two isotopes. We will use the equation:

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

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

Substitute these into the equation, and we get:

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

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

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

### Example 2.3.9.2: Neon Isotopes

Neon has three naturally occurring isotopes. In a sample of neon, $90.92\%$ of the atoms are $\mathrm{Ne}$-20, which is an isotope of neon with 10 neutrons and a mass of $19.99\ \mathrm{amu}$. Another $0.3\%$ of the atoms are $\mathrm{Ne}$-21, which is an isotope of neon with 11 neutrons and a mass of $20.99\ \mathrm{amu}$. The final $8.85\%$ of the atoms are $\mathrm{Ne}$-22, which is an isotope of neon with 12 neutrons and a mass of $21.99\ \mathrm{amu}$. 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 $20.17\ \mathrm{amu}$

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 $\mathrm{B}$) is 10.8, which is what we calculated in Example 2.3.9.1, and the atomic mass of neon (symbol $\mathrm{Ne}$) is 20.8, which is what we calculated in Example 2.3.9.2. Take time to notice that not all periodic tables have the atomic number above the element's symbol and the mass number below it. If you are ever confused, remember that the atomic number should always be the smaller of the two and will be a whole number, while the atomic mass should always be the larger of the two and will be a decimal number.

### Exercise 2.3.9.1

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

*Answer available at the end of this section.*

## 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.

## Answers

**Exercise** 2.3.9.1

35.45 amu

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# 3: RADIOACTIVITY AND NUCLEAR CHEMISTRY

In today's society, the term *radioactivity* conjures up a variety of images:

- Nuclear power plants producing hydrocarbon-free energy, but with potentially deadly by-products that are difficult to store safely.
- Bombs with the capacity to use nuclear reactions that produce devastating explosions with horrible side effects on the earth as we know it, and on the surviving populations that inhabit it.
- Medical technology that utilizes nuclear chemistry to peer inside living things to detect disease, and the power to irradiate tissues to potentially cure these diseases.
- Fusion reactors that hold the promise of limitless energy with few toxic side products.

Radioactivity has a colorful history and clearly presents a variety of social and scientific dilemmas. In this chapter we will introduce the basic concepts of radioactivity, nuclear equations, and the longevity of radioisotopes using half-lives.


3.1: The Discovery of Radioactivity

3.2: Types of Radioactivity- Alpha, Beta, and Gamma Decay

3.3: Detecting Radioactivity

3.4: Half-Lives of Radioisotopes

3.5: Radiation Effects and Units

3.6: Medical uses of radioisotopes

3.7: Making radioisotopes for medical uses


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# 3.1: The Discovery of Radioactivity

**Learning Objectives**

- List the most common emissions from naturally radioactive nuclei.
- Compare the energy released per gram of matter in nuclear reactions to that in chemical reactions.
- Express the relationship between nuclear stability and the nuclei's binding energy per nucleon ratio.

No one could have known in the 1800's that the discovery of the fascinating science and art form of photography would eventually lead to the splitting of the atom. The basis of photography is the fact that visible light causes certain chemical reactions. If the chemicals are spread thinly on a surface but protected from light by a covering, no reaction occurs. When the covering is removed, however, light acting on the chemicals causes them to darken. With millions of cameras in use today, we do not think of it as a strange phenomenon—but at the time of its discovery, photography was a strange and wonderful thing.

Even stranger was the discovery by Wilhelm Roentgen—that radiation other than visible light could expose photographic film. He found that film wrapped in dark paper would react when x-rays went through the paper and struck the film.

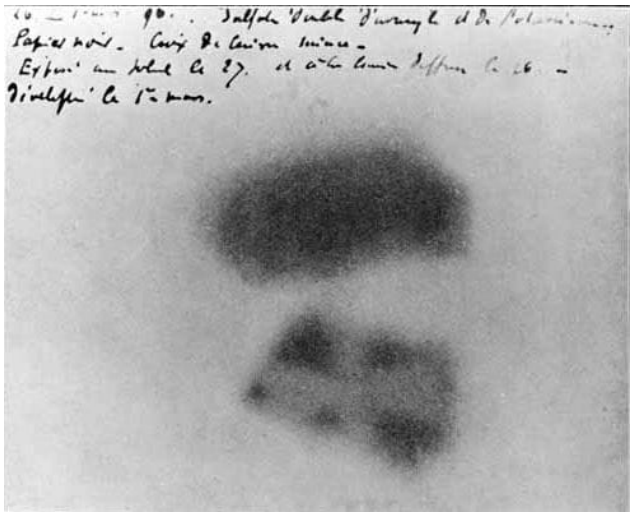


Figure 3.1.1: Image of Becquerel's photographic plate, which has been fogged by exposure to radiation from a uranium salt. The shadow of a metal Maltese Cross placed between the plate and the uranium salt is clearly visible (Public Domain).

When Henri Becquerel heard about Roentgen's discovery, he wondered if his fluorescent minerals would give the same x-rays. Becquerel placed some of his rock crystals on top of a well-covered photographic plate and sat them in the sunlight. The sunlight made the crystals glow with a bright fluorescent light, but when Becquerel developed the film he was very disappointed. He found that only one of his minerals, a uranium salt, had fogged the photographic plate. He decided to try again, and this time, to leave them out in the sun for a longer period of time. Fortunately, the weather didn't cooperate, and Becquerel had to leave the crystals and film stored in a drawer for several cloudy days. Before continuing his experiments, Becquerel decided to check one of the photographic plates to make sure the chemicals were still good. To his amazement, he found that the plate had been exposed in spots where it had been near the uranium containing rocks, and some of these rocks had not been exposed to sunlight at all. In later experiments, Becquerel confirmed that the radiation from the uranium had no connection with light or fluorescence, but the amount of radiation was directly proportional to the concentration of uranium in the rock. Becquerel had discovered **radioactivity**.

## The Curies and Radium

One of Becquerel's assistants, a young Polish scientist named Maria Sklowdowska (to become Marie Curie after she married Pierre Curie), became interested in the phenomenon of radioactivity. With her husband, she decided to find out if chemicals other than uranium were radioactive. The Austrian government was happy to send the Curies a ton of pitchblende from the mining region of Joachimstahl, because it was waste material that had to be disposed of anyway. The Curies wanted the pitchblende

because it was the residue of uranium mining. From the ton of pitchblende, the Curies separated $0.10\ \mathrm{g}$ of a previously unknown element, radium, in the form of the compound radium chloride. This radium was many times more radioactive than uranium.

By 1902, the world was aware of a new phenomenon called radioactivity and of new elements which exhibited natural radioactivity. For this work, Becquerel and the Curies shared the 1903 Nobel Prize and for subsequent work; Marie Cure received a second Nobel Prize in 1911. She is the only person ever to receive two Nobel Prizes in science.

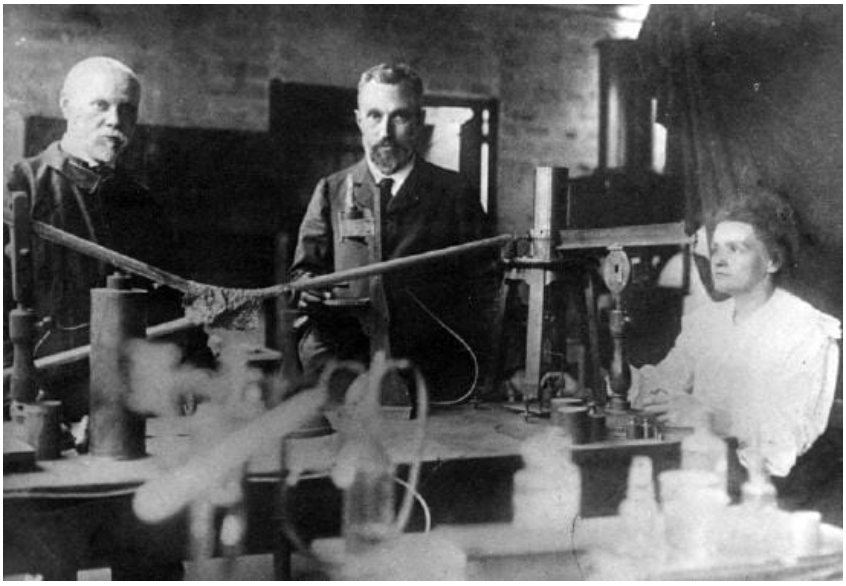


Figure 3.1.2: Marie Curie (right) and Pierre Curie (middle) with Henri Becquerel (left) shared the 1903 Nobel Prize.

Further experiments provided information about the characteristics of the penetrating emissions from radioactive substances. It was soon discovered that there were three common types of radioactive emissions. Some of the radiation could pass easily through aluminum foil while some of the radiation was stopped by the foil. Some of the radiation could even pass through foil up to a centimeter thick. The three basic types of radiation were named alpha, beta, and gamma radiation. The actual composition of the three types of radiation was still not known.

Eventually, scientists were able to demonstrate experimentally that the alpha particle, $\alpha$, was a helium nucleus (a particle containing two protons and two neutrons), a beta particle, $\beta$, was a high speed electron, and gamma rays, $\gamma$, were a very high energy form of light (even higher energy than x-rays).

## Unstable Nuclei May Disintegrate

A nucleus (with one exception, hydrogen-1) consists of some number of protons and neutrons pulled together in an extremely tiny volume. Since protons are positively charged and like charges repel, it is clear that protons cannot remain together in the nucleus unless there is a powerful force holding them there. The force which holds the nucleus together is generated by **nuclear binding energy**.

A nucleus with a large amount of binding energy per nucleon (proton or neutron) will be held together tightly and is referred to as stable. These nuclei do not break apart. When there is too little binding energy per nucleon, the nucleus will be less stable and may disintegrate (come apart). Such disintegration is referred to as **natural radioactivity**. It is also possible for scientists to smash nuclear particles together and cause nuclear reactions between normally stable nuclei. This disintegration is referred to as **artificial radioactivity**. None of the elements above #92 on the periodic table occur on earth naturally—they are all products of artificial (manmade) radioactivity.

When nuclei come apart, they come apart violently accompanied by a tremendous release of energy in the form of heat, light, and radiation. This energy comes from some of the nuclear binding energy. In nuclear changes, the energy involved comes from the nuclear binding energy. However, in chemical reactions, the energy comes from electrons moving energy levels. A typical nuclear change (such as fission) may involve millions of times more energy per atom changing compared to a chemical change (such as burning)!

## Summary

- Henri Becquerel, Marie Curie, and Pierre Curie shared the discovery of radioactivity.

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# 3.2: Types of Radioactivity- Alpha, Beta, and Gamma Decay

**Learning Objectives**

- Compare qualitatively the ionizing and penetration power of alpha particles $(\alpha)$, beta particles $(\beta)$, and gamma rays $(\gamma)$.
- Express the changes in the atomic number and mass number of a radioactive nuclei when an alpha, beta, or gamma particle is emitted.
- Write nuclear equations for alpha and beta decay reactions.

Many nuclei are radioactive; that is, they decompose by emitting particles and in doing so, become a different nucleus. In our studies up to this point, atoms of one element were unable to change into different elements. That is because in all other types of changes discussed, only the electrons were changing. In these changes, the nucleus, which contains the protons that dictate which element an atom is, is changing. All nuclei with 84 or more protons are radioactive, and elements with less than 84 protons have both stable and unstable isotopes. All of these elements can go through nuclear changes and turn into different elements.

In natural radioactive decay, three common emissions occur. When these emissions were originally observed, scientists were unable to identify them as some already known particles and so named them:

- alpha particles $(\alpha)$
- beta particles $(\beta)$
- gamma rays $(\gamma)$

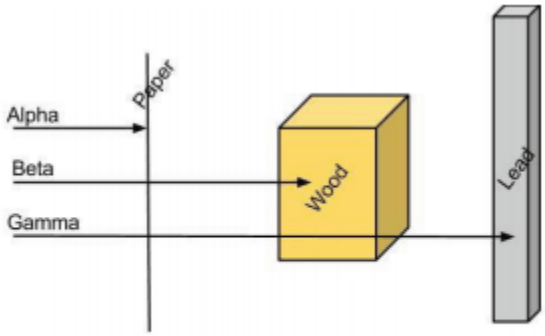
These particles were named using the first three letters of the Greek alphabet. Some later time, alpha particles were identified as helium-4 nuclei, beta particles were identified as electrons, and gamma rays as a form of electromagnetic radiation like x-rays, except much higher in energy and even more dangerous to living systems.

## The Ionizing and Penetration Power of Radiation

With all the radiation from natural and man-made sources, we should quite reasonably be concerned about how all the radiation might affect our health. The damage to living systems is done by radioactive emissions when the particles or rays strike tissue, cells, or molecules and alter them. These interactions can alter molecular structure and function; cells no longer carry out their proper function and molecules, such as DNA, no longer carry the appropriate information. Large amounts of radiation are very dangerous, even deadly. In most cases, radiation will damage a single (or very small number) of cells by breaking the cell wall or otherwise preventing a cell from reproducing.

The ability of radiation to damage molecules is analyzed in terms of what is called **ionizing power**. When a radiation particle interacts with atoms, the interaction can cause the atom to lose electrons and thus become ionized. The greater the likelihood that damage will occur by an interaction is the ionizing power of the radiation.

Much of the threat from radiation is involved with the ease or difficulty of protecting oneself from the particles. How thick of a wall do you need to hide behind to be safe? The ability of each type of radiation to pass through matter is expressed in terms of **penetration power.** The more material the radiation can pass through, the greater the penetration power and the more dangerous it is. In general, the greater mass present, the greater the ionizing power, and the lower the penetration power.



*Alpha particles can be blocked with paper. Beta particles penetrate through paper, but are blocked by wood. Gamma particles are capable of penetrating paper and wood but can be blocked by a few inches of lead.*
*CC Tracy Poulsen*

Comparing only the three common types of ionizing radiation, alpha particles have the greatest mass. Alpha particles have approximately four times the mass of a proton or neutron and approximately 8,000 times the mass of a beta particle. Because of the large mass of the alpha particle, it has the highest ionizing power and the greatest ability to damage tissue. That same large size of alpha particles, however, makes them less able to penetrate matter. They collide with

molecules very quickly when striking matter, add two electrons, and become a harmless helium atom. Alpha particles have the least penetration power and can be stopped by a thick sheet of paper or even a layer of clothes. They are also stopped by the outer layer of dead skin on people. This may seem to remove the threat from alpha particles, but it is only from external sources. In a nuclear explosion or some sort of nuclear accident, where radioactive emitters are spread around in the environment, the emitters can be inhaled or taken in with food or water and once the alpha emitter is inside you, you have no protection at all.

Beta particles are much smaller than alpha particles and therefore, have much less ionizing power (less ability to damage tissue), but their small size gives them much greater penetration power. Most resources say that beta particles can be stopped by a one-quarter inch thick sheet of aluminum. Once again, however, the greatest danger occurs when the beta emitting source gets inside of you.

Gamma rays are not particles, but a high energy form of electromagnetic radiation (like x-rays, except more powerful). Gamma rays are energy that has no mass or charge. Gamma rays have tremendous penetration power and require several inches of dense material (like lead) to shield them. Gamma rays may pass all the way through a human body without striking anything. They are considered to have the least ionizing power and the greatest penetration power.

*Table* 3.2.1 *Comparison of Penetrating Power,Ionizing Power and Shielding of Alpha and Beta Particles, and Gamma Rays.*

| Particle | Symbol | Mass | Penetrating Power | Ionizing Power | Shielding |
|---|---|---|---|---|---|
| **Alpha** | $\alpha$ | $4\text{amu}$ | Very Low | Very High | Paper Skin |
| **Beta** | $\beta$ | $1/2000\text{amu}$ | Intermediate | Intermediate | Aluminum |
| **Gamma** | $\gamma$ | 0 (energy only) | Very High | Very Low | 2 inches lead |

The safest amount of radiation to the human body is zero. It is impossible to completely avoid ionizing radiation, so the next best goal is to be exposed to as little as possible. The two best ways to minimize exposure are to limit time of exposure, and to increase distance from the source.

## Alpha Decay

The nuclear disintegration process that emits alpha particles is called alpha decay. An example of a nucleus that undergoes alpha decay is uranium-238. The alpha decay of U-238 is

$$^{238}_{92}\text{U} \rightarrow {}^{4}_{2}\text{He} + {}^{234}_{90}\text{Th} \tag{3.2.1}$$

In this nuclear change, the uranium atom $\left({}^{238}_{92}\text{U}\right)$ transmuted into an atom of thorium $\left({}^{234}_{90}\text{Th}\right)$ and, in the process, gave off an alpha particle. Look at the symbol for the alpha particle: ${}^{4}_{2}\text{He}$. Where does an alpha particle get this symbol? The bottom number in a nuclear symbol is the number of protons. That means that the alpha particle has two protons in it that were lost by the uranium atom. The two protons also have a charge of $+2$. The top number, 4, is the mass number or the total of the protons and neutrons in the particle. Because it has two protons, and a total of four protons and neutrons, alpha particles must also have two neutrons. Alpha particles always have this same composition: two protons and two neutrons.

Another alpha particle producer is thorium-230.

$$^{230}_{90}\text{Th} \rightarrow {}^{4}_{2}\text{He} + {}^{226}_{88}\text{Ra} \tag{3.2.2}$$

These types of equations are called nuclear equations and are similar to the chemical equivalent discussed through the previous chapters.

## Beta Decay

Another common decay process is beta particle emission, or beta decay. A beta particle is simply a high energy electron that is emitted from the nucleus. It may occur to you that we have a logically difficult situation here. Nuclei do not contain electrons and yet during beta decay, an electron is emitted from a nucleus. At the same time that the electron is being ejected from the nucleus, a neutron is becoming a proton. It is tempting to picture this as a neutron breaking into two pieces with the pieces being a proton and an electron. That would be convenient for simplicity, but unfortunately that is not what happens (more on this subject will be explained at the end of this section). For convenience, we will treat beta decay as a neutron splitting into a proton and an electron. The proton stays in the nucleus, increasing the atomic number of the atom by one. The electron is ejected from

the nucleus and is the particle of radiation called beta.

To insert an electron into a nuclear equation and have the numbers add up properly, an atomic number and a mass number had to be assigned to an electron. The mass number assigned to an electron is zero (0), which is reasonable since the mass number is the number of protons plus neutrons, and an electron contains no protons and no neutrons. The atomic number assigned to an electron is negative one (-1), because that allows a nuclear equation containing an electron to balance atomic numbers. Therefore, the nuclear symbol representing an electron (beta particle) is

$$ {}^{0}_{-1}\mathrm{e} \text{ or } {}^{0}_{-1}\beta $$

Thorium-234 is a nucleus that undergoes beta decay. Here is the nuclear equation for this beta decay:

$$ {}^{234}_{90}\mathrm{Th} \rightarrow {}^{0}_{-1}\mathrm{e} + {}^{234}_{91}\mathrm{Pa} \tag{3.2.3} $$

## Gamma Radiation

Frequently, gamma ray production accompanies nuclear reactions of all types. In the alpha decay of U-238, two gamma rays of different energies are emitted in addition to the alpha particle.

$$ {}^{238}_{92}\mathrm{U} \rightarrow {}^{4}_{2}\mathrm{He} + {}^{234}_{90}\mathrm{Th} + 2{}^{0}_{0}\gamma $$

Virtually all of the nuclear reactions in this chapter also emit gamma rays, but for simplicity the gamma rays are generally not shown. Nuclear reactions produce a great deal more energy than chemical reactions. Chemical reactions release the difference between the chemical bond energy of the reactants and products, and the energies released have an order of magnitude of $1 \times 10^{3}\ \mathrm{kJ/mol}$. Nuclear reactions release some of the binding energy and may convert tiny amounts of matter into energy. The energy released in a nuclear reaction has an order of magnitude of $1 \times 10^{18}\ \mathrm{kJ/mol}$. That means that nuclear changes involve almost **one million times more energy** per atom than chemical changes!

**Note**

Virtually all of the nuclear reactions in this chapter also emit gamma rays, but for simplicity the gamma rays are generally not shown.

The essential features of each reaction are shown in Figure 17.3.2

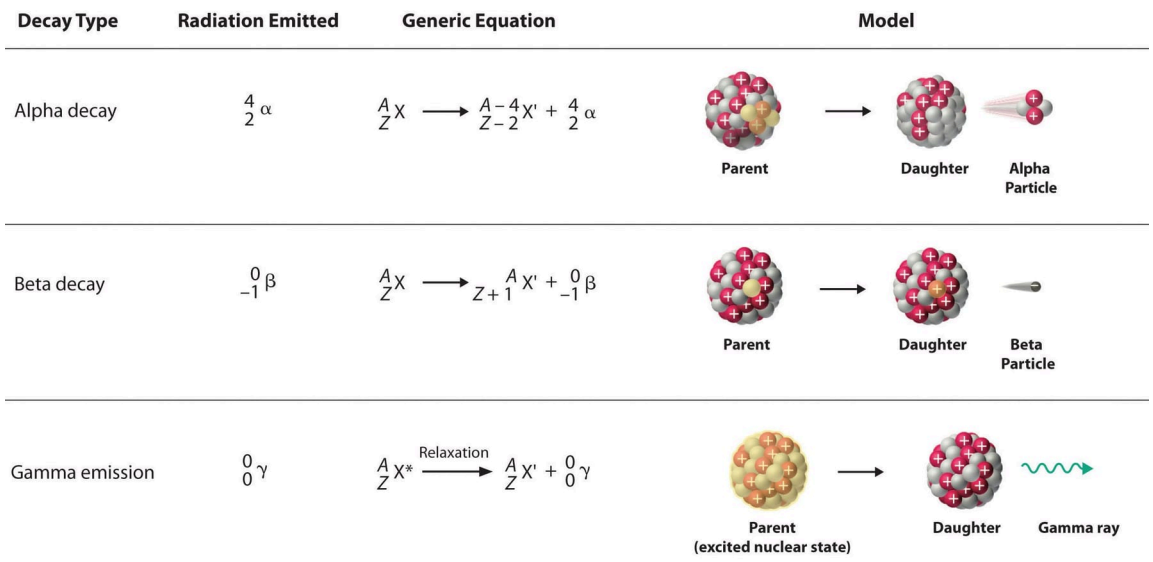



***Figure 17.3.2**: Three most common modes of nuclear decay.*

# "Nuclear Accounting"

When writing nuclear equations, there are some general rules that will help you:

- The sum of the mass numbers (top numbers) on the reactant side equal the sum of the mass numbers on the product side.
- The atomic numbers (bottom numbers) on the two sides of the reaction will also be equal.

In the alpha decay of $^{238}\mathrm{U}$ (Equation 3.2.1), both atomic and mass numbers are conserved:

- mass number: $238 = 4 + 234$
- atomic number: $92 = 2 + 90$

Confirm that this equation is correctly balanced by adding up the reactants' and products' atomic and mass numbers. Also, note that because this was an alpha reaction, one of the products is the alpha particle, $^{4}_{2}\mathrm{He}$.

Note that both the mass numbers and the atomic numbers add up properly for the beta decay of thorium-234 (Equation 3.2.3):

- mass number: $234 = 0 + 234$
- atomic number: $90 = -1 + 91$

The mass numbers of the original nucleus and the new nucleus are the same because a neutron has been lost, but a proton has been gained, and so the sum of protons plus neutrons remains the same. The atomic number in the process has been increased by one since the new nucleus has one more proton than the original nucleus. In this beta decay, a thorium-234 nucleus has one more proton than the original nucleus. In this beta decay, a thorium-234 nucleus has become a protactinium-234 nucleus. Protactinium-234 is also a beta emitter and produces uranium-234.

$$^{234}_{91}\mathrm{Pa} \rightarrow {}^{0}_{-1}\mathrm{e} + {}^{234}_{92}\mathrm{U} \tag{3.2.4}$$

Once again, the atomic number increases by one and the mass number remains the same; this confirms that the equation is correctly balanced.

## What About Balancing Charge?

Both alpha and beta particles are charged, but nuclear reactions in Equations 3.2.1, 3.2.3, and most of the other nuclear reactions above, are not balanced with respect to charge, as discussed when balancing redox reactions. When studying nuclear reactions in general, there is typically little information or concern about the chemical state of the radioactive isotopes, because the electrons from the electron cloud are not directly involved in the nuclear reaction (in contrast to chemical reactions).

So it is acceptable to **ignore** charge in balancing nuclear reactions, and concentrate on balancing mass and atomic numbers only.

## Example 3.2.1

Complete the following nuclear reaction by filling in the missing particle.

$$^{210}_{86}\mathrm{Rn} \rightarrow {}^{4}_{2}\mathrm{He} + ?$$

**Solution**

This reaction is an alpha decay. We can solve this problem one of two ways:

*Solution 1:* When an atom gives off an alpha particle, its atomic number drops by 2 and its mass number drops by 4, leaving: $^{206}_{84}\mathrm{Po}$. We know the symbol is $\mathrm{Po}$, for polonium, because this is the element with 84 protons on the periodic table.

*Solution 2:* Remember that the mass numbers on each side must total up to the same amount. The same is true of the atomic numbers.

- Mass numbers: $210 = 4 + ?$
- Atomic numbers: $86 = 2 + ?$

We are left with $^{206}_{84}\mathrm{Po}$.

**Example 3.2.2**

Write each of the following nuclear reactions.

a) Carbon-14, used in carbon dating, decays by beta emission.

b) Uranium-238 decays by alpha emission.

**Solution**

a) Beta particles have the symbol $^{0}_{-1}\mathrm{e}$. Emitting a beta particle causes the atomic number to increase by 1 and the mass number to not change. We get atomic numbers and symbols for elements using our periodic table. We are left with the following reaction:

$$^{14}_{6}\mathrm{C} \rightarrow {}^{0}_{-1}\mathrm{e} + {}^{14}_{7}\mathrm{N}$$

b) Alpha particles have the symbol $^{4}_{2}\mathrm{He}$. Emitting an alpha particle causes the atomic number to decrease by 2 and the mass number to decrease by 4. We are left with:

$$^{238}_{92}\mathrm{U} \rightarrow {}^{4}_{2}\mathrm{He} + {}^{234}_{90}\mathrm{Th}$$

## Decay Series

The decay of a radioactive nucleus is a move toward becoming stable. Often, a radioactive nucleus cannot reach a stable state through a single decay. In such cases, a series of decays will occur until a stable nucleus is formed. The decay of $\mathrm{U}$-238 is an example of this. The $\mathrm{U}$-238 decay series starts with $\mathrm{U}$-238 and goes through fourteen separate decays to finally reach a stable nucleus, $\mathrm{Pb}$-206 (Figure 17.3.3). There are similar decay series for $\mathrm{U}$-235 and $\mathrm{Th}$-232. The $\mathrm{U}$-235 series ends with $\mathrm{Pb}$-207 and the $\mathrm{Th}$-232 series ends with $\mathrm{Pb}$-208.

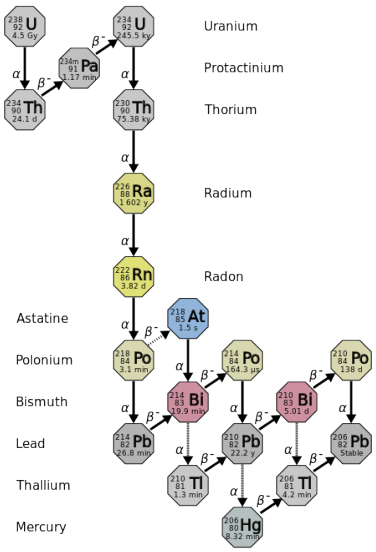



Figure 17.3.3: Uranium-238 decay chain. (CC-BY-3.0 Tosaka)

Several of the radioactive nuclei that are found in nature are present there because they are produced in one of the radioactive decay series. For example, there may have been radon on the earth at the time of its formation, but that original radon would have all decayed by this time. The radon that is present now is present because it was formed in a decay series (mostly by U-238).

## Summary

A nuclear reaction is one that changes the structure of the nucleus of an atom. The atomic numbers and mass numbers in a nuclear equation must be balanced. Protons and neutrons are made up of quarks. The two most common modes of natural radioactivity are alpha decay and beta decay. Most nuclear reactions emit energy in the form of gamma rays.

## Vocabulary

- **Alpha decay** - A common mode of radioactive decay in which a nucleus emits an alpha particle (a helium-4 nucleus).
- **Beta decay** - A common mode of radioactive decay in which a nucleus emits beta particles. The daughter nucleus will have a higher atomic number than the original nucleus.
- **Quark** - Particles that form one of the two basic constituents of matter. Various species of quarks combine in specific ways to form protons and neutrons, in each case taking exactly three quarks to make the composite particle.

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# 3.3: Detecting Radioactivity

## Learning Objectives

- Understand how the Geiger counter can be used to quantify the rate of ionization radiation.

When alpha, beta or gamma particles collide with a target, some of the energy in the particle is transferred to the target, typically resulting in the promotion of an electron to an “excited state”. In many “targets”, especially gasses, this results in *ionization*. Alpha, beta and gamma radiation are broadly referred to as **ionizing radiation**. A **Geiger counter** (or Geiger-Müller counter) takes advantage of this in order to detect these particles. In a Geiger tube, the electron produced by ionization of a captive gas travels to the anode and the change in voltage is detected by the attached circuitry. Most counters of this type are designed to emit an audible “click” in response to the change in voltage, and to also show it on a digital or analog meter. A simple schematic of a Geiger counter is shown in Figure 3.3.1.

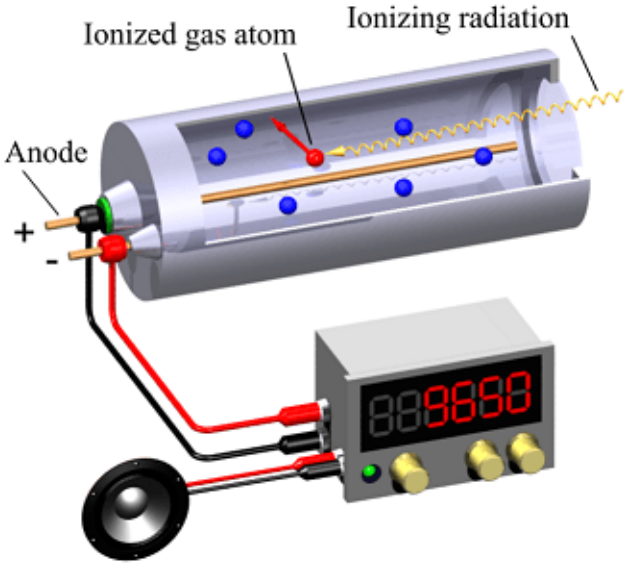



Figure 3.3.1: Schematic of a Geiger-Müller counter using an "end window" tube for low penetration radiation. A loudspeaker is also used for indication. (CC-BY-SA-3.0 Svjo-2 vai Wikipedia(opens in new window)).

Although scientists were not aware at the time of the Geiger counter's invention, all of us are subjected to a certain amount of radiation every day. This radiation is called **background radiation** and comes from a variety of natural and artificial radiation sources. Approximately 82% of background radiation comes from natural sources. These natural sources include:

1. Sources in the earth—including naturally occurring radioactive elements—which are incorporated in building materials, and also in the human body.
2. Sources from space in the form of cosmic rays.
3. Sources in the atmosphere, such as radioactive radon gas released from the earth; and radioactive atoms like carbon-14, produced in the atmosphere by bombardment from high-energy cosmic rays.

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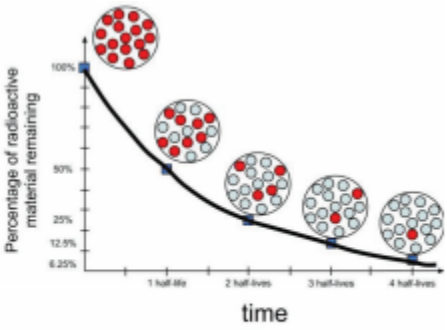
# 3.4: Half-Lives of Radioisotopes

**Learning Objectives**

- Describe what is meant by the term half-life and what factors affect half-life.
- Calculate the amount of radioactive material that will remain after an integral number of half-lives.
- Find the half-life of an isotope given graphical or other data.
- Describe how carbon-14 is used to determine the age of carbon-containing objects.

## Rate of Radioactive Decay

During natural radioactive decay, not all atoms of an element are instantaneously changed to atoms of another element. The decay process takes time and there is value in being able to express the rate at which a process occurs. A useful concept is **half-life**, which is the time required for half of the starting material to change or decay. Half-lives can be calculated from measurements on the change in mass of a nuclide and the time it takes to occur. The only thing we know is that in the time of that substance's half-life, half of the original nuclei will disintegrate. Although chemical changes are sped up or slowed down by changing factors such as temperature and concentration, these factors have no effect on half-life. Each radioactive isotope will have its own unique half-life that is independent of any of these factors.



*After one half-life, half of the radioactive atoms have decayed. After another half-life, half of the remaining atoms have changed. This pattern continues, with half of the atoms changing over each half-life time.*
*CC Tracy Poulsen*

The half-lives of many radioactive isotopes have been determined; they have been found to range from extremely long half-lives of 10 billion years, to extremely short half-lives of fractions of a second.

*Table 17.5.1: Table of Selected Half-lives*

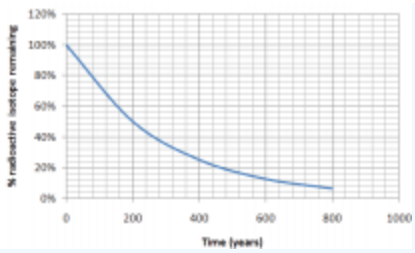
| Element | Mass Number (A) | Half-life | Element | Mass Number (A) | Half Life |
|---|---|---|---|---|---|
| Uranium | 238 | 4.5 Billion years | Californium | 251 | 800 years |
| Neptunium | 240 | 1 hour | Nobelium | 254 | 3 seconds |
| Plutonium | 243 | 5 hours | Carbon | 14 | 5730 years |
| Americium | 245 | 25 minutes | Carbon | 16 | 740 milliseconds |

The quantity of radioactive nuclei at any given time will decrease to half as much in one half-life. For example, if there are $100\ \text{g}$ of $\text{Cf}$-251 in a sample at some time, after 800 years, there will be $50\ \text{g}$ of $\text{Cf}$-251 remaining; after another 800 years (1600 years total), there will only be $25\ \text{g}$ remaining.

Remember, the half-life is the time it takes for half of your sample—no matter how much you have—to remain. Each half-life will follow the same general pattern as $\text{Cf}$-251. The only difference is the length of time it takes for half of a sample to decay.

**Example 3.4.3**

What is the half-life of an isotope that produces the following graph of decay over time?




**Solution**

We know that the half-life is the time it takes for half of a sample to change. How long did it take for half of our isotope to change? It took approximately 200 years for $100\%$ of our sample to leave only $50\%$ (half of the original amount) remaining. **The half-life is 200 years.**

*Notice that after another 200 years (400 years total), $25\%$ remains (half of $50\%$).

Look carefully at the graph in the previous example. All types of radioactive decay make a graph of the same general shape. The only difference is the scale and units of the $x$-axis, as the half-life time will be different.

## Example 3.4.2

If there are 60 grams of $\mathrm{Np}$-240 present, how much $\mathrm{Np}$-240 will remain after 4 hours? ($\mathrm{Np}$-240 has a half-life of 1 hour.)

**Solution**

We create a table based on $\mathrm{Np}$-240's half-life of 1 hour.

| Amount of Np-240 present | Amount of time passed |
|---|---|
| 60 g | 0 (this is the amount before any time has passed) |
| 30 g | 1 hour (1 half-life) |
| 15 g | 2 hours (2 half-lives) |
| 7.5 g | 3 hours |
| 3.75 g | 4 hours |

After 4 hours, only $3.75\ \mathrm{g}$ of our original $60\ \mathrm{g}$ sample would remain of the radioactive isotope $\mathrm{Np}$-240.

## Example 3.4.3

A sample of $\mathrm{Ac}$-225 originally contained 80 grams, and after 50 days only 2.55 grams of the original $\mathrm{Ac}$-225 remain. What is the half life of $\mathrm{Ac}$-225?

**Solution**

We will tackle this problem similarly to the last problem. The difference is that we are looking for the half-life time. Let's set up a similar table, though:

| Amount of Ac-225 present | Amount of time passed |
|---|---|
| 80 g | 0 |
| 40 g | 1 half-life |
| 20 g | 2 half-lives |
| 10 g | 3 half-lives |
| 5 g | 4 half-lives |
| 2.5 g | 5 half-lives |

We know that 50 days is the same as 5 half-lives. Therefore, 1 half-life is 10 days. The half-life of $\mathrm{Ac}$-225 is 10 days.

## Radioactive Dating

An ingenious application of half-life studies established a new science of determining ages of materials by half-life calculations. For geological dating, the decay of $\mathrm{U}$-238 can be used. The half-life of $\mathrm{U}$-238 is $4.5 \times 10^9$ years. The end product of the decay of $\mathrm{U}$-238 is $\mathrm{Pb}$-206. After one half-life, a 1.00 gram sample of uranium will have decayed to 0.50 grams of $\mathrm{U}$-238 and 0.43 grams of $\mathrm{Pb}$-206. By comparing the amount of $\mathrm{U}$-238 to the amount of $\mathrm{Pb}$-206 in a sample of uranium mineral, the age of the mineral can be estimated. Present day estimates for the age of the Earth's crust from this method is at 4 billion years.

Organic material (material made from things that were once living, such as paper and fabric) is radioactively dated using the long-lived nuclide of carbon, carbon-14. This method of determining the age of organic material (or once living materials) was given the name radiocarbon dating. The carbon dioxide consumed by living systems contains a certain concentration of $^{14}\mathrm{CO}_2$. When an organism dies, the acquisition of carbon-14 stops, but the decay of the $\mathrm{C}$-14 in the body continues. As time goes by, the ratio of $\mathrm{C}$-14 to $\mathrm{C}$-12 decreases at a rate determined by the half-life of $\mathrm{C}$-14. Using half-life equations, the time since the organism died can be calculated. These procedures have been used to determine the age of organic artifacts and determine, for instance, whether art works are real or fake.

## Summary and Vocabulary

The half-life of an isotope is used to describe the rate at which the isotope will decay and give off radiation. Using the half-life, it is possible to predict the amount of radioactive material that will remain after a given amount of time. $\mathrm{C}$-14 dating procedures have been used to determine the age of organic artifacts. Its half-life is approximately 5700 years.

- **Background radiation** - Radiation that comes from environmental sources including the earth's crust, the atmosphere, cosmic rays, and radioisotopes. These natural sources of radiation account for the largest amount of radiation received by most people.
- **Half-life** - The time interval required for a quantity of (radioactive) material to decay to half of its original value.

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# 3.5: Radiation Effects and Units

**Learning Objectives**

- Describe the biological impact of ionizing radiation.
- Define units for measuring radiation exposure.
- Explain the operation of common tools for detecting radioactivity.
- List common sources of radiation exposure in the US.

The increased use of radioisotopes has led to increased concerns over the effects of these materials on biological systems (such as humans). All radioactive nuclides emit high-energy particles or electromagnetic waves. When this radiation encounters living cells, it can cause heating, break chemical bonds, or ionize molecules. The most serious biological damage results when these radioactive emissions fragment or ionize molecules. For example, alpha and beta particles emitted from nuclear decay reactions possess much higher energies than ordinary chemical bond energies. When these particles strike and penetrate matter, they produce ions and molecular fragments that are extremely reactive. The damage this does to biomolecules in living organisms can cause serious malfunctions in normal cell processes, taxing the organism's repair mechanisms and possibly causing illness or even death (Figure 3.5.1).

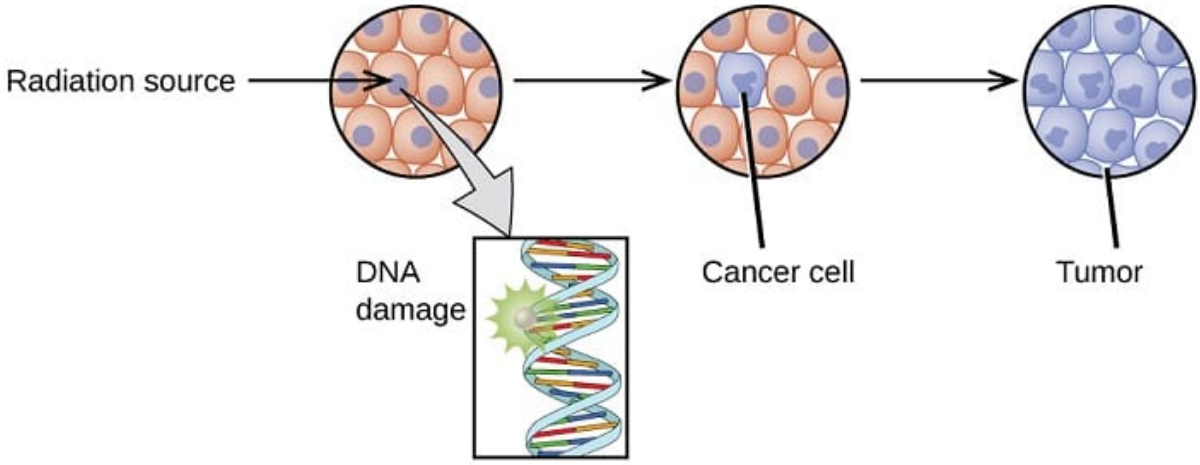



Figure 3.5.1: Radiation can harm biological systems by damaging the DNA of cells. If this damage is not properly repaired, the cells may divide in an uncontrolled manner and cause cancer.

A diagram is shown which has a white sphere followed by a right-facing arrow and a large sphere composed of many smaller white and green spheres. The single sphere has impacted the larger sphere. A right-facing arrow leads from the larger sphere to a pair of smaller spheres which are collections of the same white and green spheres. A starburst pattern lies between these two spheres and has three right-facing arrows leading from it to two white spheres and a circle full of ten smaller, peach-colored circles with purple dots in their centers. An arrow leads downward from this circle to a box that contains a helical shape with a starburst near its top left side and is labeled "D N A damage." A right-facing arrow leads from this circle to a second circle, with nine smaller, peach-colored circles with purple dots in their centers and one fully purple small circle labeled "Cancer cell." A right-facing arrow leads to a final circle, this time full of the purple cells, that is labeled "Tumor."

## Ionizing vs. Nonionizing Radiation

There is a large difference in the magnitude of the biological effects of nonionizing radiation (for example, light and microwaves) and ionizing radiation, emissions energetic enough to knock electrons out of molecules (for example, α and β particles, γ rays, X-rays, and high-energy ultraviolet radiation) (Figure 3.5.2).

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Figure 3.5.2: Lower frequency, lower-energy electromagnetic radiation is nonionizing, and higher frequency, higher-energy electromagnetic radiation is ionizing.

Energy absorbed from nonionizing radiation speeds up the movement of atoms and molecules, which is equivalent to heating the sample. Although biological systems are sensitive to heat (as we might know from touching a hot stove or spending a day at the beach in the sun), a large amount of nonionizing radiation is necessary before dangerous levels are reached. Ionizing radiation, however, may cause much more severe damage by breaking bonds or removing electrons in biological molecules, disrupting their structure and function. The damage can also be done indirectly, by first ionizing $H_2O$ (the most abundant molecule in living organisms), which forms a $H_2O^+$ ion that reacts with water, forming a hydronium ion and a hydroxyl radical:

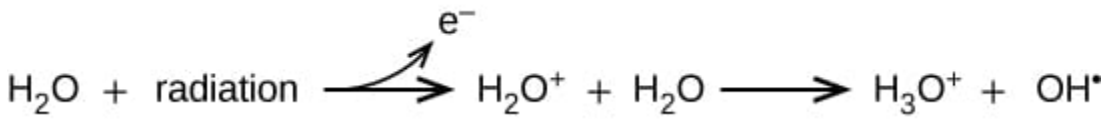



Figure 3.5.3.

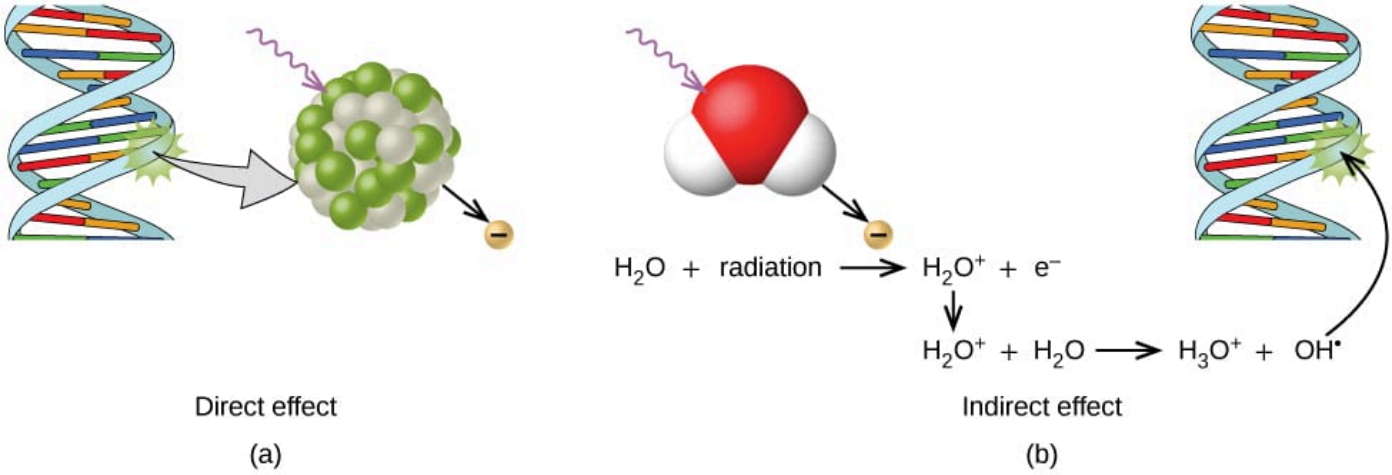



Figure 3.5.3: Ionizing radiation can (a) directly damage a biomolecule by ionizing it or breaking its bonds, or (b) create an $H_2O^+$ ion, which reacts with $H_2O$ to form a hydroxyl radical, which in turn reacts with the biomolecule, causing damage indirectly.

## Biological Effects of Exposure to Radiation

Radiation can harm either the whole body (somatic damage) or eggs and sperm (genetic damage). Its effects are more pronounced in cells that reproduce rapidly, such as the stomach lining, hair follicles, bone marrow, and embryos. This is why patients undergoing radiation therapy often feel nauseous or sick to their stomach, lose hair, have bone aches, and so on, and why particular care must be taken when undergoing radiation therapy during pregnancy.

Different types of radiation have differing abilities to pass through material (Figure 3.5.4). A very thin barrier, such as a sheet or two of paper, or the top layer of skin cells, usually stops alpha particles. Because of this, alpha particle sources are usually not dangerous if outside the body, but are quite hazardous if ingested or inhaled (see the Chemistry in Everyday Life feature on Radon Exposure). Beta particles will pass through a hand, or a thin layer of material like paper or wood, but are stopped by a thin layer of metal. Gamma radiation is very penetrating and can pass through a thick layer of most materials. Some high-energy gamma radiation is able to pass through a few feet of concrete. Certain dense, high atomic number elements (such as lead) can effectively attenuate gamma radiation with thinner material and are used for shielding. The ability of various kinds of emissions to cause ionization varies greatly, and some particles have almost no tendency to produce ionization. Alpha particles have about twice the ionizing power of fast-moving neutrons, about 10 times that of β particles, and about 20 times that of γ rays and X-rays.

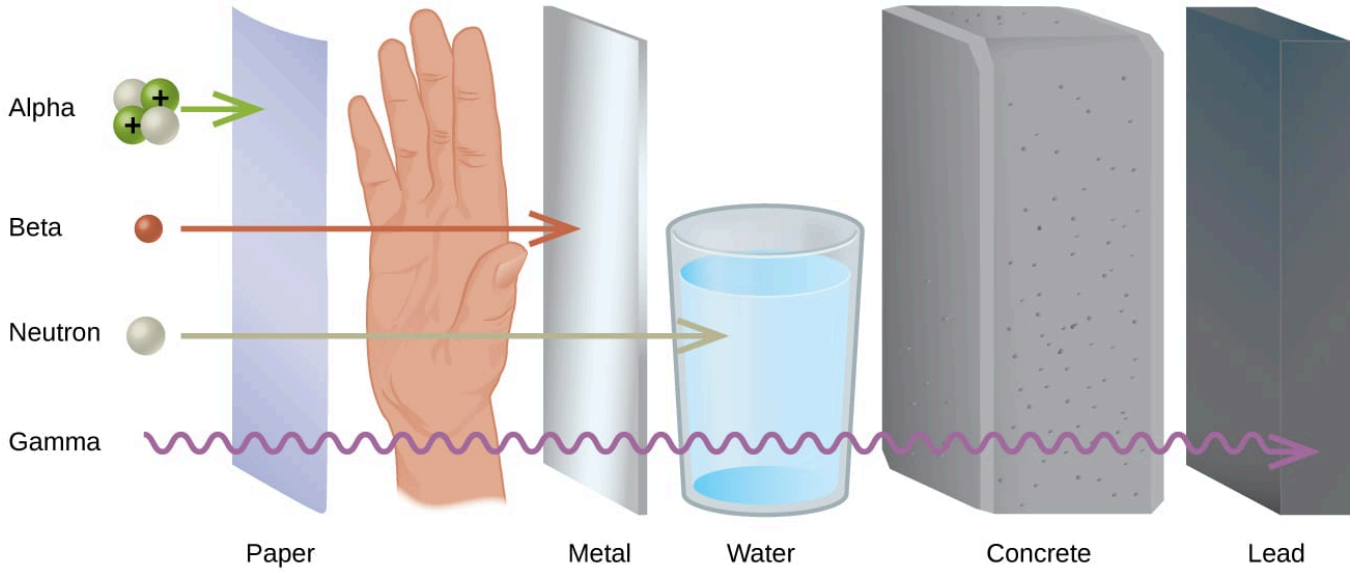



Figure 3.5.4: The ability of different types of radiation to pass through material is shown. From least to most penetrating, they are alpha < beta < neutron < gamma.

A diagram shows four particles in a vertical column on the left, followed by an upright sheet of paper, a person's hand, an upright sheet of metal, a glass of water, a thick block of concrete and an upright, thick piece of lead. The top particle listed is made up of two white spheres and two green spheres that are labeled with positive signs and is labeled "Alpha." A right-facing arrow leads from this to the paper. The second particle is a red sphere labeled "Beta" and is followed by a right-facing arrow that passes through the paper and stops at the hand. The third particle is a white sphere labeled "Neutron" and is followed by a right-facing arrow that passes through the paper, hand and metal but is stopped at the glass of water. The fourth particle is shown by a squiggly arrow and it passes through all of the substances but stops at the lead. Terms at the bottom read, from left to right, "Paper," "Metal," "Water," "Concrete" and "Lead."

For many people, one of the largest sources of exposure to radiation is from radon gas (Rn-222). Radon-222 is an α emitter with a half–life of 3.82 days. It is one of the products of the radioactive decay series of U-238, which is found in trace amounts in soil and rocks. The radon gas that is produced slowly escapes from the ground and gradually seeps into homes and other structures above. Since it is about eight times more dense than air, radon gas accumulates in basements and lower floors, and slowly diffuses throughout buildings (Figure 3.5.5).

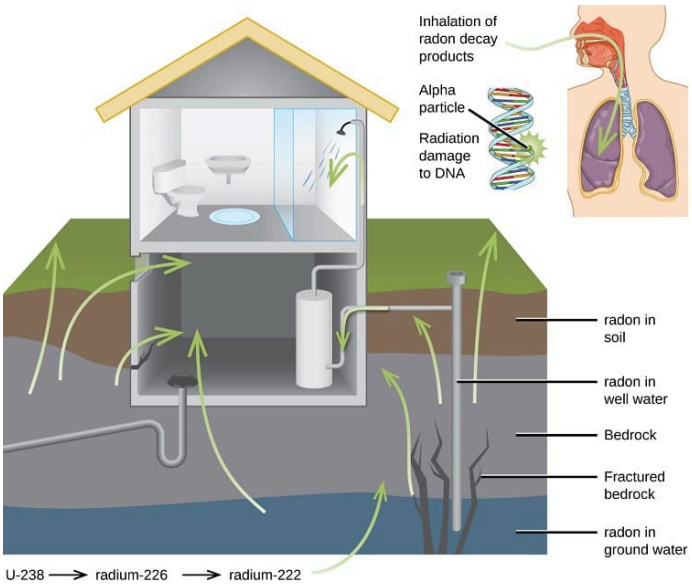



Figure 3.5.5: Radon-222 seeps into houses and other buildings from rocks that contain uranium-238, a radon emitter. The radon enters through cracks in concrete foundations and basement floors, stone or porous cinderblock foundations, and openings for water and gas pipes.

A cut-away image of the side of a house and four layers of the ground it rests on is shown, as well as a second cut-away image of a person's head and chest cavity. The house is shown with a restroom on the second floor and a basement with a water heater as the first floor. Green arrows lead from the lowest ground layer, labeled "radon in ground water," from the third ground layer, labeled "Bedrock" and "Fractured bedrock," from the second layer, labeled "radon in well water," and from the top layer, labeled "radon in soil to the inside of the basement area. In the smaller image of the torso, a green arrow is shown to enter the person's nasal passage and travel to the lungs. This is labeled "Inhalation of radon decay products." A small coiled, helical structure next to the torso is labeled "alpha particle" on one section where it has a starburst pattern and "Radiation damage to D N A" on another segment.

Radon is found in buildings across the country, with amounts dependent on location. The average concentration of radon inside houses in the US (1.25 pCi/L) is about three times the level found in outside air, and about one in six houses have radon levels high enough that remediation efforts to reduce the radon concentration are recommended. Exposure to radon increases one's risk of getting cancer (especially lung cancer), and high radon levels can be as bad for health as smoking a carton of cigarettes a day. Radon is the number one cause of lung cancer in nonsmokers and the second leading cause of lung cancer overall. Radon exposure is believed to cause over 20,000 deaths in the US per year.

## Measuring Radiation Exposure

Several different devices are used to detect and measure radiation, including Geiger counters, scintillation counters (scintillators), and radiation dosimeters (Figure 3.5.6). Probably the best-known radiation instrument, the Geiger counter (also called the Geiger-Müller counter) detects and measures radiation. Radiation causes the ionization of the gas in a Geiger-Müller tube. The rate of ionization is proportional to the amount of radiation. A scintillation counter contains a scintillator—a material that emits light (luminesces) when excited by ionizing radiation—and a sensor that converts the light into an electric signal. Radiation dosimeters also measure ionizing radiation and are often used to determine personal radiation exposure. Commonly used types are electronic, film badge, thermoluminescent, and quartz fiber dosimeters.

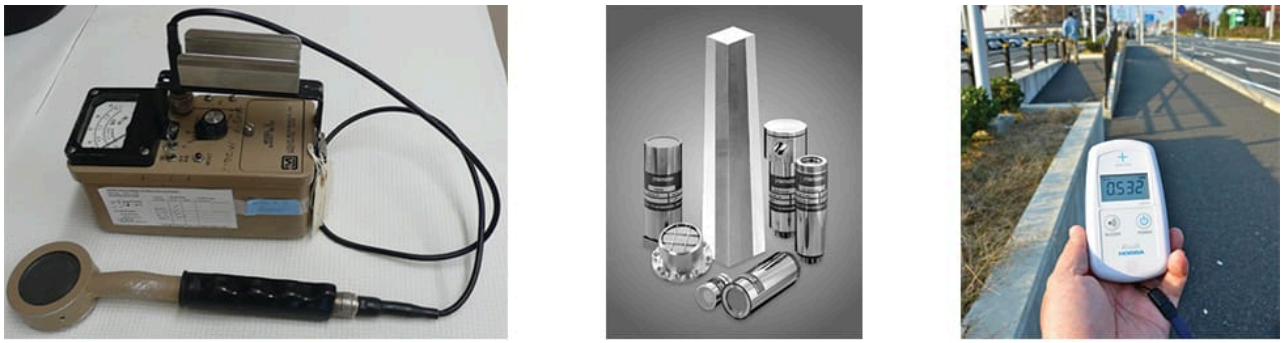



Figure 3.5.6: Devices such as (a) Geiger counters, (b) scintillators, and (c) dosimeters can be used to measure radiation. (Credit c: modification of work by "osaMu"/Wikimedia commons.)

Three photographs are shown and labeled "a," "b" and "c." Photo a shows a Geiger counter sitting on a table. It is made up of a metal box with a read-out screen and a wire leading away from the box connected to a sensor wand. Photograph b shows a collection of tall and short vertical tubes arranged in a grouping while photograph c shows a person's hand holding a small machine with a digital readout while standing on the edge of a roadway.

A variety of units are used to measure various aspects of radiation (Table 3.5.1). The SI unit for rate of radioactive decay is the becquerel (Bq), with 1 Bq = 1 disintegration per second. The curie (Ci) and millicurie (mCi) are much larger units and are frequently used in medicine (1 curie = 1 Ci = $3.7 \times 10^{10}$ disintegrations per second). The SI unit for measuring radiation dose is the gray (Gy), with 1 Gy = 1 J of energy absorbed per kilogram of tissue. In medical applications, the radiation absorbed dose (rad) is more often used (1 rad = 0.01 Gy; 1 rad results in the absorption of 0.01 J/kg of tissue). The SI unit measuring tissue damage caused by radiation is the sievert (Sv). This takes into account both the energy and the biological effects of the type of radiation involved in the radiation dose.

*Table 3.5.1: Units Used for Measuring Radiation*

| Measurement Purpose | Unit | Quantity Measured | Description |
|---|---|---|---|
| *activity of source* | becquerel (Bq) | radioactive decays or emissions | amount of sample that undergoes 1 decay/second |
| | curie (Ci) | | amount of sample that undergoes $3.7 \times 10^{10}$ decays/second |
| *absorbed dose* | gray (Gy) | energy absorbed per kg of tissue | 1 Gy = 1 J/kg tissue |
| | radiation absorbed dose (rad) | | 1 rad = 0.01 J/kg tissue |
| *biologically effective dose* | sievert (Sv) | tissue damage | Sv = RBE × Gy |
| | roentgen equivalent for man (rem) | | Rem = RBE × rad |

The roentgen equivalent for man (rem) is the unit for radiation damage that is used most frequently in medicine (1 rem = 1 Sv). Note that the tissue damage units (rem or Sv) includes the energy of the radiation dose (rad or Gy), along with a biological factor referred to as the RBE (for relative biological effectiveness), that is an approximate measure of the relative damage done by the radiation. These are related by:

$$\text{number of rems} = \text{RBE} \times \text{number of rads} \tag{3.5.1}$$

with RBE approximately 10 for α radiation, 2(+) for protons and neutrons, and 1 for β and γ radiation.

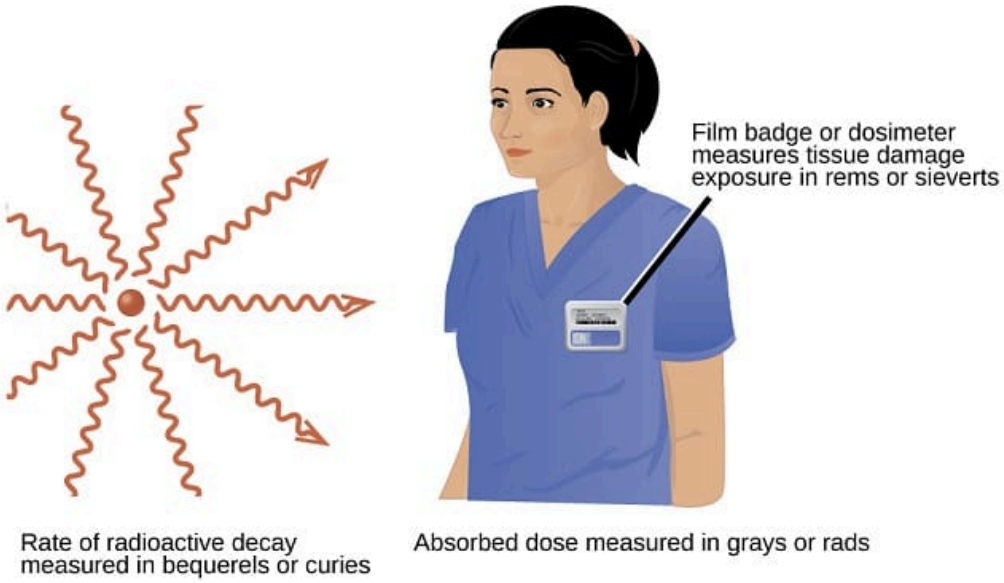



Figure 3.5.7: Different units are used to measure the rate of emission from a radioactive source, the energy that is absorbed from the source, and the amount of damage the absorbed radiation does. (CC by 4.0; OpenStax)

Two images are shown. The first, labeled “Rate of radioactive decay measured in becquerels or curies,” shows a red sphere with ten red squiggly arrows facing away from it in a 360 degree circle. The second image shows the head and torso of a woman wearing medical scrubs with a badge on her chest. The caption to the badge reads “Film badge or dosimeter measures tissue damage exposure in rems or sieverts” while a phrase under this image states “Absorbed dose measured in grays or rads.”

## Example 3.5.1: Amount of Radiation

Cobalt-60 ($t_{1/2}$ = 5.26 y) is used in cancer therapy since the $\gamma$ rays it emits can be focused in small areas where the cancer is located. A 5.00-g sample of Co-60 is available for cancer treatment.

a. What is its activity in Bq?
b. What is its activity in Ci?

**Solution**

The activity is given by:

$$\text{Activity} = \lambda N = \left(\frac{\ln 2}{t_{1/2}}\right) N = \left(\frac{\ln 2}{5.26\ \text{y}}\right) \times 5.00\ \text{g} = 0.659\ \frac{\text{g}}{\text{y}}\ \text{of}\ {}^{60}\text{Co that decay}$$

And to convert this to decays per second:

$$0.659\ \frac{\text{g}}{\text{y}} \times \frac{\text{y}}{365\ \text{day}} \times \frac{1\ \text{day}}{24\ \text{hours}} \times \frac{1\ \text{h}}{3,600\ \text{s}} \times \frac{1\ \text{mol}}{59.9\ \text{g}} \times \frac{6.02 \times 10^{23}\ \text{atoms}}{1\ \text{mol}} \times \frac{1\ \text{decay}}{1\ \text{atom}}$$

$$= 2.10 \times 10^{14}\ \frac{\text{decay}}{\text{s}}$$

(a) Since $1\ \text{Bq} = 1\ \frac{\text{decay}}{\text{s}}$, the activity in Becquerel (Bq) is:

$$2.10 \times 10^{14} \frac{\text{decay}}{\text{s}} \times \left(\frac{1\ \text{Bq}}{1\ \frac{\text{decay}}{\text{s}}}\right) = 2.10 \times 10^{14}\ \text{Bq}$$

(b) Since $1\ \text{Ci} = 3.7 \times 10^{11}\ \frac{\text{decay}}{\text{s}}$, the activity in curie (Ci) is:

$$2.10 \times 10^{14} \frac{\text{decay}}{\text{s}} \times \left(\frac{1\ \text{Ci}}{3.7 \times 10^{11}\ \frac{\text{decay}}{\text{s}}}\right) = 5.7 \times 10^{2}\ \text{Ci}$$

**Exercise 3.5.1**

Tritium is a radioactive isotope of hydrogen ($t_{1/2} = 12.32$ years) that has several uses, including self-powered lighting, in which electrons emitted in tritium radioactive decay cause phosphorus to glow. Its nucleus contains one proton and two neutrons, and the atomic mass of tritium is 3.016 amu. What is the activity of a sample containing 1.00mg of tritium (a) in Bq and (b) in Ci?

*Answer a available at the end of this section.*

## Effects of Long-term Radiation Exposure on the Human Body

The effects of radiation depend on the type, energy, and location of the radiation source, and the length of exposure. As shown in Figure 3.5.8, the average person is exposed to background radiation, including cosmic rays from the sun and radon from uranium in the ground (see the Chemistry in Everyday Life feature on Radon Exposure); radiation from medical exposure, including CAT scans, radioisotope tests, X-rays, and so on; and small amounts of radiation from other human activities, such as airplane flights (which are bombarded by increased numbers of cosmic rays in the upper atmosphere), radioactivity from consumer products, and a variety of radionuclides that enter our bodies when we breathe (for example, carbon-14) or through the food chain (for example, potassium-40, strontium-90, and iodine-131).

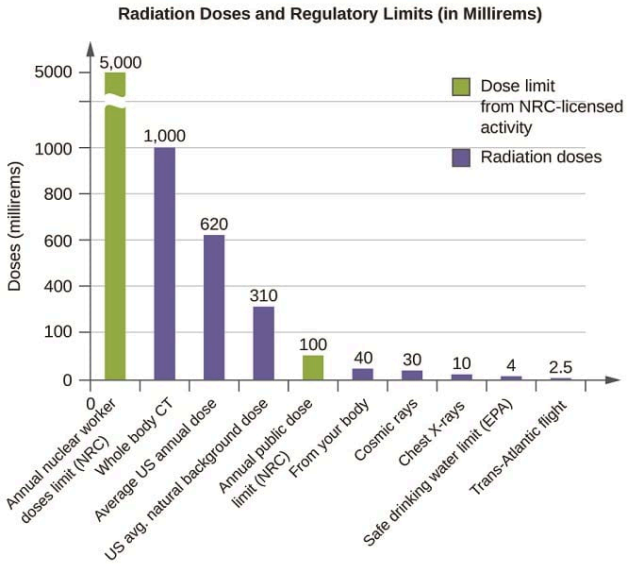



Figure 3.5.8: The total annual radiation exposure for a person in the US is about 620 mrem. The various sources and their relative amounts are shown in this bar graph. (source: U.S. Nuclear Regulatory Commission).

A bar graph titled “Radiation Doses and Regulatory Limits, open parenthesis, in Millirems, close parenthesis” is shown. The y-axis is labeled “Doses in Millirems” and has values from 0 to 5000 with a break between 1000 and 5000 to indicate a different scale to the top of the graph. The y-axis is labeled corresponding to each bar. The first bar, measured to 5000 on the y-axis, is drawn in red and is labeled “Annual Nuclear Worker Doses Limit, open parenthesis, N R C, close parenthesis.” The second bar, measured to 1000 on the y-axis, is drawn in blue and is labeled “Whole Body C T” while the third bar, measured to 620 on the y-axis, is drawn in blue and is labeled “Average U period S period Annual Dose.” The fourth bar, measured to 310 on the y-axis, is drawn in blue and is labeled “U period S period Natural Background Dose” while the fifth bar, measured to 100 on the y-axis and drawn in red reads “Annual Public Dose Limit, open parenthesis, N R C, close parenthesis.” The sixth bar, measured to 40 on the y-axis, is drawn in blue and is labeled “From Your Body” while the seventh bar, measured to 30 on the y-axis and drawn in blue reads “Cosmic rays.” The eighth bar, measured to 4 on the y-axis, is drawn in blue and is labeled “Safe Drinking Water Limit, open parenthesis, E P A, close parenthesis” while the ninth bar, measured to 2.5 on the y-axis and drawn in red reads “Trans Atlantic Flight.” A legend on the graph shows that red means “Dose Limit From N R C dash licensed activity” while blue means “Radiation Doses.”

A short-term, sudden dose of a large amount of radiation can cause a wide range of health effects, from changes in blood chemistry to death. Short-term exposure to tens of rems of radiation will likely cause very noticeable symptoms or illness; a dose of about 500 rems is estimated to have a 50% probability of causing the death of the victim within 30 days of exposure. Exposure to radioactive emissions has a cumulative effect on the body during a person’s lifetime, which is another reason why

it is important to avoid any unnecessary exposure to radiation. Health effects of short-term exposure to radiation are shown in Table 3.5.2.

*Table 3.5.2: Health Effects of Radiation*

| Exposure (rem) | Health Effect | Time to Onset (Without Treatment) |
|---|---|---|
| 5–10 | changes in blood chemistry | — |
| 50 | nausea | hours |
| 55 | fatigue | — |
| 70 | vomiting | — |
| 75 | hair loss | 2–3 weeks |
| 90 | diarrhea | — |
| 100 | hemorrhage | — |
| 400 | possible death | within 2 months |
| 1000 | destruction of intestinal lining | — |
| | internal bleeding | — |
| | death | 1–2 weeks |
| 2000 | damage to central nervous system | — |
| | loss of consciousness | minutes |
| | death | hours to days |

It is impossible to avoid some exposure to ionizing radiation. We are constantly exposed to background radiation from a variety of natural sources, including cosmic radiation, rocks, medical procedures, consumer products, and even our own atoms. We can minimize our exposure by blocking or shielding the radiation, moving farther from the source, and limiting the time of exposure.

## Summary

We are constantly exposed to radiation from a variety of naturally occurring and human-produced sources. This radiation can affect living organisms. Ionizing radiation is the most harmful because it can ionize molecules or break chemical bonds, which damages the molecule and causes malfunctions in cell processes. It can also create reactive hydroxyl radicals that damage biological molecules and disrupt physiological processes. Radiation can cause somatic or genetic damage, and is most harmful to rapidly reproducing cells. Types of radiation differ in their ability to penetrate material and damage tissue, with alpha particles the least penetrating, but potentially most damaging, and gamma rays the most penetrating.

Various devices, including Geiger counters, scintillators, and dosimeters, are used to detect and measure radiation, and monitor radiation exposure. We use several units to measure radiation: becquerels or curies for rates of radioactive decay; gray or rads for energy absorbed; and rems or sieverts for biological effects of radiation. Exposure to radiation can cause a wide range of health effects, from minor to severe, including death. We can minimize the effects of radiation by shielding with dense materials such as lead, moving away from the source of radiation, and limiting time of exposure.

## Footnotes

1. 1 Source: US Environmental Protection Agency

## Glossary

**becquerel (Bq)**
: SI unit for rate of radioactive decay; 1 Bq = 1 disintegration/s.

**curie (Ci)**
Larger unit for rate of radioactive decay frequently used in medicine; 1 Ci = $3.7 \times 10^{10}$ disintegrations/s.

**Geiger counter**
Instrument that detects and measures radiation via the ionization produced in a Geiger-Müller tube.

**gray (Gy)**
SI unit for measuring radiation dose; 1 Gy = 1 J absorbed/kg tissue.

**ionizing radiation**
Radiation that can cause a molecule to lose an electron and form an ion.

**millicurie (mCi)**
Larger unit for rate of radioactive decay frequently used in medicine; 1 Ci = $3.7 \times 10^{10}$ disintegrations/s.

**nonionizing radiation**
Radiation that speeds up the movement of atoms and molecules; it is equivalent to heating a sample, but is not energetic enough to cause the ionization of molecules.

**radiation absorbed dose (rad)**
SI unit for measuring radiation dose, frequently used in medical applications; 1 rad = 0.01 Gy.

**radiation dosimeter**
Device that measures ionizing radiation and is used to determine personal radiation exposure.

**relative biological effectiveness (RBE)**
Measure of the relative damage done by radiation.

**roentgen equivalent man (rem)**
Unit for radiation damage, frequently used in medicine; 1 rem = 1 Sv.

**scintillation counter**
Instrument that uses a scintillator—a material that emits light when excited by ionizing radiation—to detect and measure radiation.

**sievert (Sv)**
SI unit measuring tissue damage caused by radiation; takes energy and biological effects of radiation into account.

## Answers

**Exercise** 3.5.1

$3.56 \times 10^{11}\text{Bq}$

$0.962\ \text{Ci}$

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# 3.6: Medical uses of radioisotopes

The use of nuclear chemistry in medical technologies is increasing over time. The medical uses can be divided into two categories :

1. medical imaging of organs or diagnosing any malfunction and
2. therapeutic use, mainly for killing cancerous cells.

## Radioisotopes in medical imaging

**Criteria of radioisotope selection for medical imaging**

1. those that emit $\gamma$-rays, directly or indirectly, during their decay,
2. can be delivered to the organ of interest in pure form or tagged in a compound,
3. are short-lived or can be excreted from the body after use.

Table 8.6.1 lists some radioisotopes commonly used in medical imaging. A low dose of the radioisotope is administered to a patient. The $\gamma$-rays cross over the body and are recorded like X-rays. A computer finally converts the recording into a useful image. The image is compared with an image of a healthy organ to diagnose any malfunction.

*Table 8.6.1: Some of the commonly used radioisotopes in medical imaging*

| Radioisotope | Symbol | Mode of decay | Half-life | Use in medical imaging |
|---|---|---|---|---|
| Carbon-11 | $^{11}_{6}\mathrm{C}$ | $\beta^+$, g | 20.3 m | Brain scan to trace glucose |
| Fluorine-19 | $^{18}_{9}\mathrm{F}$ | $\beta^+$, g | 109m | Brain scan to trace glucose |
| Chromium-51 | $^{51}_{24}\mathrm{Cr}$ | E.C., g | 27.3 d | Diagnose albinism; image the spleen and gastrointestinal track |
| Gallium-67 | $^{67}_{31}\mathrm{Ga}$ | E.C., g | 78.3 h | Whole-body scan for tumors |
| Selenium-75 | $^{75}_{34}\mathrm{Se}$ | E.C., g | 118 d | Pancreas scan |
| Krypton-81m | $^{81m}_{36}\mathrm{Kr}$ | g | 13.3 s | Lung ventilation scan |
| Xenon-133 | $^{133}_{54}\mathrm{Xe}$ | $\beta$ | 5.24 d | Lung ventilation scan |
| Strontium-81 | $^{81}_{38}\mathrm{Sr}$ | $\beta$ | 22.2 m | Scan for bone cancer and bone diseases |
| Mercury-197 | $^{197}_{80}\mathrm{Hg}$ | E.C., g | 64.1 h | Kidney scan |
| Iron-59 | $^{59}_{26}\mathrm{Fe}$ | $\beta$, g | 44.5 d | Bone marrow function and anemias |
| Iodine-131 | $^{131}_{53}\mathrm{I}$ | $\beta$, g | 8.04 d | Diagnosis of thyroid malfunction |
| Iodine-123 | $^{123}_{53}\mathrm{I}$ | E.C., g | 13.2 h | Diagnosis of thyroid malfunction |
| Technetium-99m | $^{99m}_{43}\mathrm{Te}$ | g | 6.01 h | Brain, liver, kidney, bone scans, and diagnosis of the damaged heart muscle |
| Phosphorous-32 | $^{32}_{15}\mathrm{P}$ | $\beta$ | 14.3 d | Detect eye tumors |
| Thallium-201 | $^{201}_{81}\mathrm{Tl}$ | E.C., g | 3.05 d | Heart scan and exercise stress test |

An example of medical imaging is the thyroid gland in the neck that produces the hormone thyroxin, which controls the overall rate of metabolism in the body. Each thyroxin molecule contains four iodine atoms. Administration of radioactive $Na^{131}I$ or $Na^{123}I$ salt accumulates the iodine in the thyroid gland in a few hours. Decay of $^{131}I$ and $^{123}I$ involves $\gamma$-emission.

$$^{131}_{53}\mathrm{I} \longrightarrow {}^{131}_{54}\mathrm{Xe} + {}^{0}_{-1}\mathrm{e} + \gamma$$

$$^{123}_{53}\mathrm{I} + {}^{0}_{-1}\mathrm{e} \longrightarrow {}^{123}_{52}\mathrm{Xe} + \gamma$$

The $\gamma$-emission from the iodine localized in the thyroid gland is recorded, as shown in Fig. 8.6.1. An overactive thyroid (hyperthyroidism) cumulates more and underactive thyroid (hypothyroidism) cumulates less iodine than a healthy thyroid.

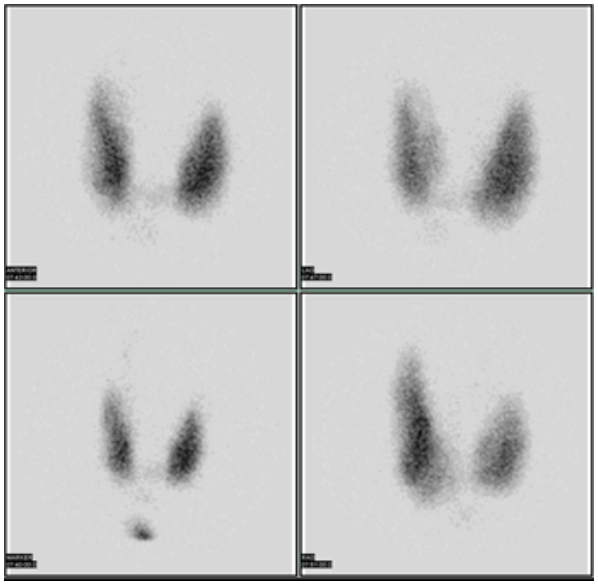


Figure 3.6.1: Thyroid scan with iodine-123 for evaluation of hyperthyroidism. Source: Myohan at en.Wikipedia / CC BY (https://creativecommons.org/licenses/by/3.0)

Another example is positron emission tomography (PET). Positron emitters like carbon-11 and fluorine-18 incorporated in a suitable compound like glucose allow following the metabolic path of the compound. For example, 18-fluorodeoxyglucose )18-FDG) is a glucose molecule in which one of the oxygen is replaced with $^{18}$F. Intravenous injection of the 18-FDG ultimately results in the cumulation of 18-FDG in the brain and other body organs where glucose is used in the metabolic process. The $^{18}$F emits a positron, which, being an anti-particle of the electron, reacts with the electron and produces two g $\gamma$-rays.

$$^{18}_{9}\mathrm{F} \longrightarrow {}^{18}_{8}\mathrm{O} + {}^{0}_{1}\mathrm{e} + \gamma$$

$${}^{0}_{1}\mathrm{e} + {}^{0}_{1}\mathrm{e} \longrightarrow 2\gamma$$

The $\gamma$-rays are used to obtain an image of the organ. The image reveals problem areas in the form of an abnormal concentration of glucose in the part of the organ. For example, Fig. 8.6.2 compares the PET image of a healthy brain versus a brain with Alzheimer's disease.

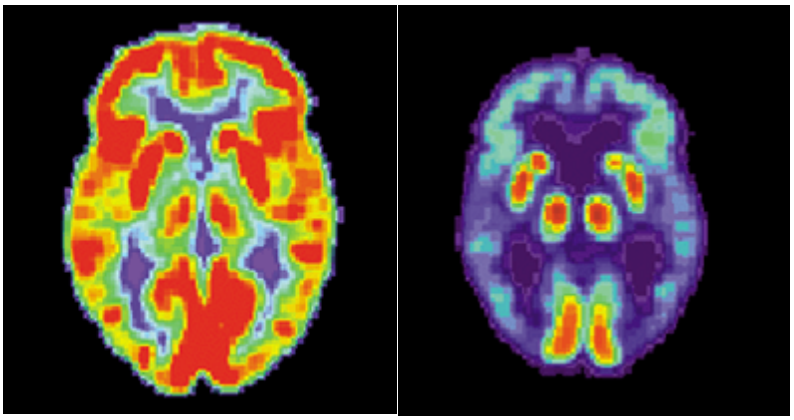


Figure 3.6.2: PET scan of brain: healthy (left) and Alzheimer's disease (right). Source: US National Institute on Aging, Alzheimer's Disease Education and Referral Center / Public domain

Since glucose metabolism happens in all organs, whole-body PET scans can be used to diagnose lung, colorectal, head and neck, and esophageal cancers as well as other diseases that involve abnormal glucose metabolism. For example, tumors have high metabolic rates; the PET scans using 18-FDG are used to detect them, as shown in Fig. 8.6.3.

File:PET-MIPS-anim.gif

Figure 3.6.3: Whole-body PET scan using $^{18}$F-FDG. The normal brain and kidneys are labeled, and radioactive urine from breakdown of the FDG is seen in the bladder. In addition, a large metastatic tumor mass from colon cancer is seen in the liver. Source: Jens Maus (http://jens-maus.de/) / Public domain

## Medical imaging without using radioisotopes

Major examples of medical imaging using external radiation sources include the following.

1. X-rays, which are external radiation source, is commonly used for medical imaging of organs and bones.
2. Computed tomography (CT) scan uses computer processing of many X-ray measurements, from different angles, to produce a cross-sectional view (virtual slices) of the organ.
3. Magnetic resonance image (MRI) is another powerful medical imaging technique that is based on the fact that hydrogen atoms splint into two two energy states when placed in a strong magnetic field. When illuminated with infrared (IR) radiation of the energy matching with the energy gap between the two groups, the hydrogen atoms are excited from the lower to higher energy state. The decay of the excited state emits the IR radiations that are recorded to obtain the image of soft tissues that contain many hydrogen atoms in the form of water molecules. Fig. 8.6.4 shows some examples.

Figure 3.6.4: Spectrum of medical imaging. Source: Martin Tornai, CC BY 4.0 <https://creativecommons.org/licenses/by/4.0>, via Wikimedia Commons

# Radiation therapy

The purpose of radiation therapy is to selective kill the diseased cells or tissues by exposing them to radiation. Higher radiation doses are required for therapy than for imaging. The radiation source can be external or internal.

## External radiation therapy

In the external irradiation, the radiation from the source, such as coba which are often used, other radiation sources are being developed, such as proton beam from the cyclotron, which have been used to kill inoperable tumors near or in the eye, skull base, or spine. Proton therapy uses a beam of proton to deliver radiation directly to the tumor.

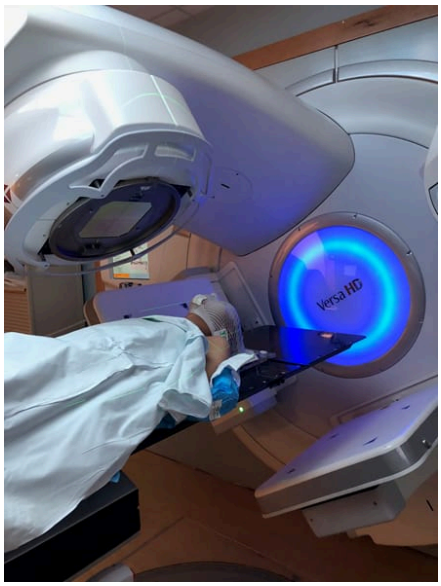



Figure 3.6.5: Radiation therapy for Hodgkin's Lymphoma in a Versa HD.. Souce: Jakembradford, CC BY-SA 4.0 <https://creativecommons.org/licenses/by-sa/4.0>, via Wikimedia Commons

## Internal radiation therapy

Internal radiation therapy is used when a short-lived radioisotope can be made to selectively concentrate in the organ or tissue of interest. For example, iodine-131 is $\beta$ and $\gamma$-emitter, is administered to a patient, is picked up by the thyroid gland, and is used to treat hyperthyroidism. Another example is actinium-225, which is an $\alpha$-emitter with a half-life of 10 days. Actinium-225 installs in a monoclonal antibody that is attached to a prostate-specific antigen and delivered selectively to treat prostate tumors.

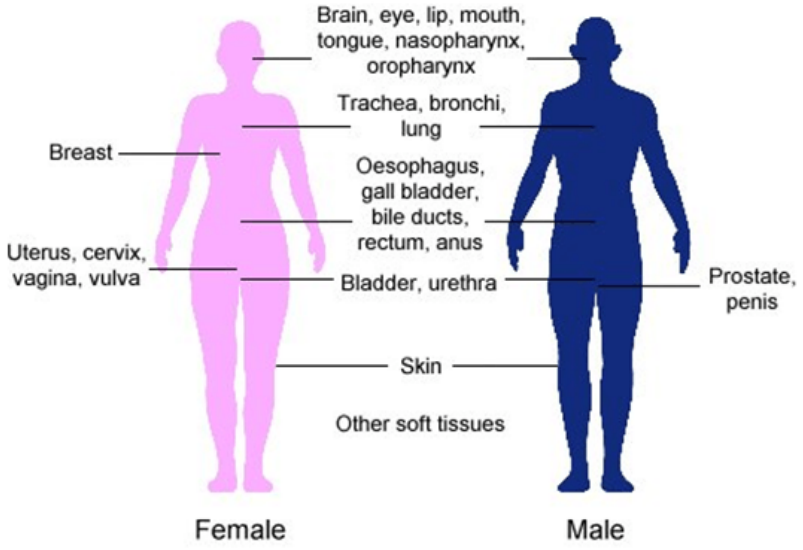



Figure 3.6.6: Body sites in which brachytherapy can be used to treat cancer. Source: Rock mc1 / CC BY-SA (https://creativecommons.org/licenses/by-sa/3.0)

## Brachytherapy

Brachytherapy or seed implantation is a form of internal radiation treatment that delivers a high dose for a short period compared to the external radiation treatment. Fig. 8.6.6 shows the sites in the body where brachytherapy can be used to treat cancer. For example, 40 or more titanium capsules, about the size of a rice grain (Fig. 8.6.7), are implanted to treat prostate cancer. The seed contains $\gamma$-emitter like iodine-125 (half-life 60 days), palladium-103 (half-life 17 days), or cesium-131 (half-life 10 days). The seed may be left in the body because, due to the short half-life, they are no more significantly radioactive after the treatment.



Figure 3.6.7: Photo of radioactive seeds. These implants are a form of radiation therapy for prostate cancer. Source: Nuclear Regulatory Commission from US / Public domain

Another option is temporary brachytherapy, e.g., iridium-192 needles that deliver higher radiation doses are inserted to treat prostate cancer and removed after 5 to 10 min. The iridium-192 wires are also used as a follow-up treatment after breast cancer

surgery to kill any residual or recurring cancer cells. The iridium-192 wires are inserted through a catheter implanted in the space from where the tumor was removed. The wires are removed after delivering the required radiation dose. The process is repeated twice a day for five days. The catheter is removed, and no radioactive material is left in the body after the treatment.

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# 3.7: Making radioisotopes for medical uses

Natural radioisotopes usually have a long half-life and are not best suited for medical applications. The medical application usually requires short-lived radioisotopes. The radioisotopes are usually produced in nuclear reactors where particles, like $\alpha$-particles, $\beta$-particles, and neutrons, are abundant. Particle accelerators, such as the one shown in Fig. 8.7.1 also accelerate and direct the nuclear particles at the targets. The high-energy nuclear particles may be absorbed by and transmute the target nuclei to radioisotopes in a nuclear reaction.

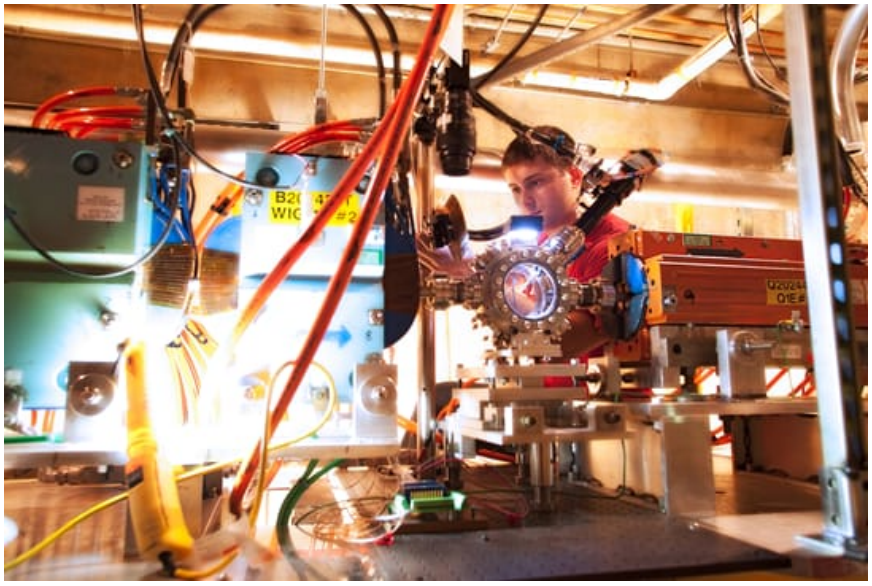


Figure 3.7.1: SLAC's particle accelerator may be two miles long, but researchers at FACET are working to develop more compact versions that could be widely used in medicine and industry -- particle accelerators are used for cancer research, processing computer chips, and even producing the shrink wrap used to keep your Thanksgiving turkey fresh. Source: ENERGY.GOV / Public domain

Radioisotopes in medical applications are usually produced by the particle bombardment method. One reaction that happens naturally by neutron bombardment from cosmic rays on nitrogen-14 is the following.

$$^{14}_{7}\mathrm{N} + ^{1}_{0}\mathrm{n} \longrightarrow ^{14}_{6}\mathrm{C} + ^{1}_{1}\mathrm{p}$$

An example of an artificial nuclear reaction initiated by $\alpha$-particle bombardment on nitrogen, observed by Rutherford that lead to the discovery of proton, is illustrated in Fig. 8.7.2.

$$^{4}_{2}\mathrm{He} + ^{14}_{7}\mathrm{N} \longrightarrow ^{17}_{8}\mathrm{O} + ^{1}_{1}\mathrm{p}$$

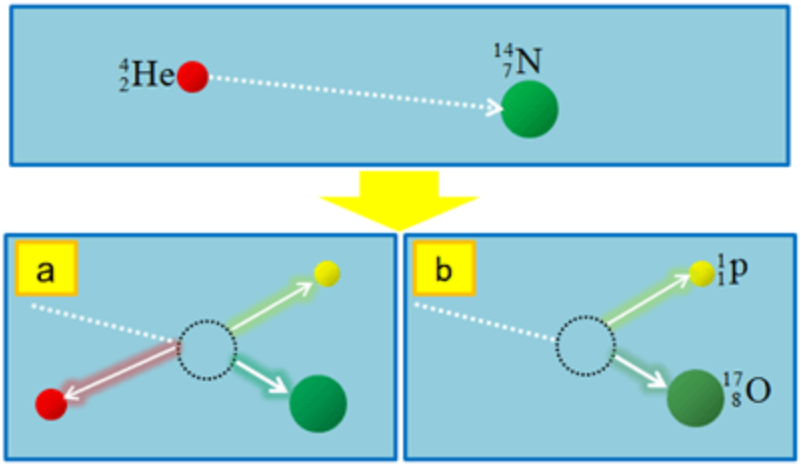



Figure 3.7.2: A nuclear reaction observed by Rutherford using a cloud chamber. When an alpha ray strikes nitrogen, reaction "a" (proton knock-off) does not occur; reaction "b" (α-p) occurs.). Source: アリオト / Public domain

Another example is the nuclear reaction initiated by $\alpha$-particles on beryllium, observed by James Chadwick, which lead to the discovery of the neutron.

$$^{4}_{2}\mathrm{He} + ^{9}_{4}\mathrm{Be} \longrightarrow ^{12}_{6}\mathrm{C} + ^{1}_{0}\mathrm{n}$$

An example of radioisotope production for medical uses is the following. Gold-198, used as a tracer in the liver, is produced by neutron bombardment on gold-197.

$$^{197}_{79}\mathrm{Au} + ^{1}_{0}\mathrm{n} \longrightarrow ^{198}_{79}\mathrm{Au}$$

Similarly, gallium-67 used in medical diagnostics is produced by proton bombardment on zinc-66.

$$^{66}_{30}\mathrm{Zn} + ^{1}_{1}\mathrm{p} \longrightarrow ^{67}_{31}\mathrm{Ga}$$

Molybdenum-99 is a radioactive isotope produced in a nuclear reactor by neutron bombardment of molybdenum-98.

$$^{98}_{42}\mathrm{Mo} + ^{1}_{0}\mathrm{n} \longrightarrow ^{99}_{42}\mathrm{Mo} + \gamma$$

Molybdenum-99 is also produced as a fission product of uranium-235. Molybdenum-99 decays to technetium-99m that has several uses in nuclear medical imaging and treatment.

$$^{99}_{42}\mathrm{Mo} \longrightarrow ^{99m}_{43}\mathrm{Tc} + ^{0}_{-1}\mathrm{e}$$

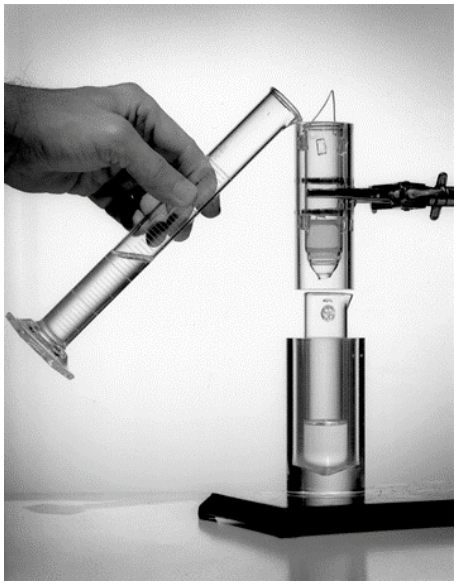


Figure 3.7.1: The first technetium-99m generator developed at Brookhaven National Laboratory, circa 1958, shown without shielding. A Tc-99m pertechnetate solution is being eluted from Mo-99 molybdate bound to a chromatographic substrate. Source: Brookhaven National Laboratory. / Public domain

Technetium-99m is short-lived (half-life 6 h), and needs to be produced in the hospital to minimize its decay during the transport. Its parent molybdenum-99 has a half-life of 66h and can be transported without significant decay during the transport. Molybdenum-99/technetium-99m generators are supplied to the hospitals in a shielded container. Fig. 8.7.3 illustrates the first Molybdenum-99/technetium-99m generator developed at Brookhaven National Laboratory. Molybdate ($MoO_4^{2}$) ion is adsorbed onto alumina adsorbent in a column. When molybdenum-99 decays to technetium-99m, the ion change to pertechnetate ($TcO_4^{-}$), which is less tightly bound to the alumina. Pouring a saline solution through the column elutes the technetium-99m as $TcO_4^{-}$ ion, which is then used for medical purposes in the hospitals.

Destruction of an inoperable tumor has also been tested by $\alpha$-emission from boron-10 upon neutron bombardment.

$$ {}^{1}_{0}\mathrm{n} + {}^{10}_{5}\mathrm{B} \longrightarrow {}^{7}_{4}\mathrm{Li} + {}^{4}_{2}\mathrm{He} $$

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# 4: THE PERIODIC TABLE AND ELECTRONIC STRUCTURE


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4.E: Electrons in Atoms and the Periodic Table (Exercises)



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# 4.1: 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 the known elements on the basis of their chemical properties. A modern version is shown in Figure 4.1.1. 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.

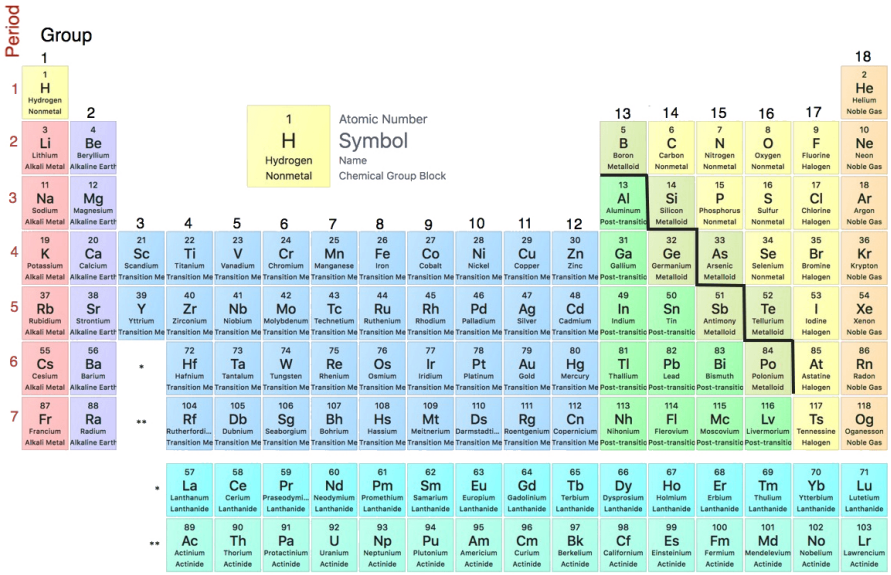



Figure 4.1.1: Modern Periodic Table. (Public Domain; PubChem modified Leticia Colmenares). An interactive Periodic table can be found here.

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).

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.

# Metals, Nonmetals, and Metalloids

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 semimetal, as shown in Figure 4.1.2. 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 4.1.2, **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 **semimetals** (or **metalloids**). Elements adjacent to the **bold zigzag** line in the right-hand portion of the periodic table have semimetal properties.

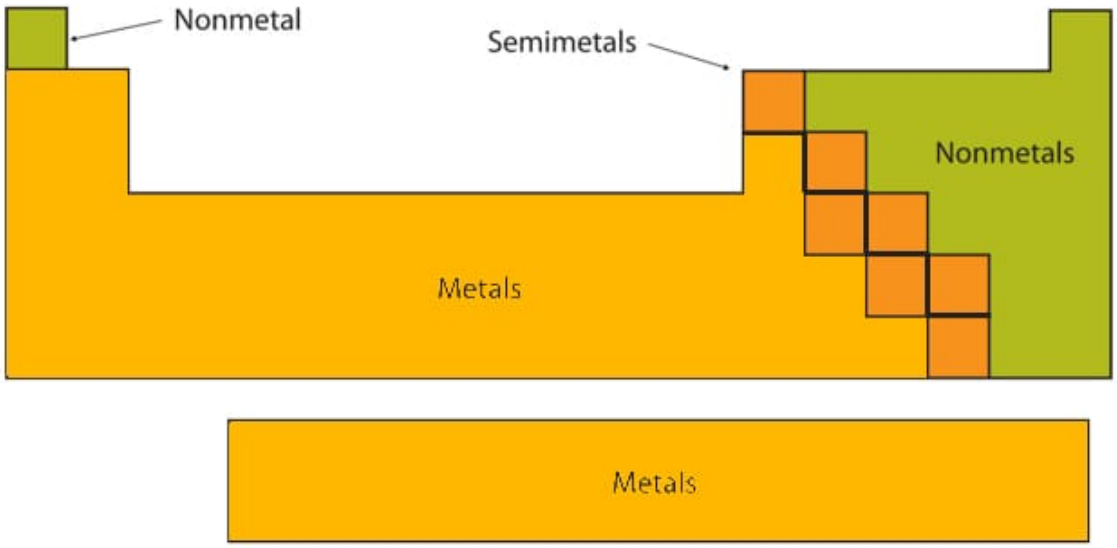



Figure 4.1.2: Types of Elements. Elements are either metals, nonmetals, or semimetals. Each group is located in a different part of the periodic table.

## Example 4.1.1

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. The atomic number of selenium is 34, which places it in period 4 and group 16. In Figure 4.1.2, selenium lies above and to the right of the diagonal line marking the boundary between metals and nonmetals, so it should be a nonmetal. Note, however, that because selenium is close to the metal-nonmetal dividing line, it would not be surprising if selenium were similar to a semimetal in some of its properties.
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 4.1.1

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

*Answer available at the end of this section.*

## Representative, Transition, and Inner-transition

Another way to categorize the elements of the periodic table is shown in Figure 4.1.3. The first two columns on the left (groups 1 and 2) and the last six columns on the right (groups 13-19) are called the **main group** or **representative** elements. The ten-column block between these columns (groups 3-12) 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.

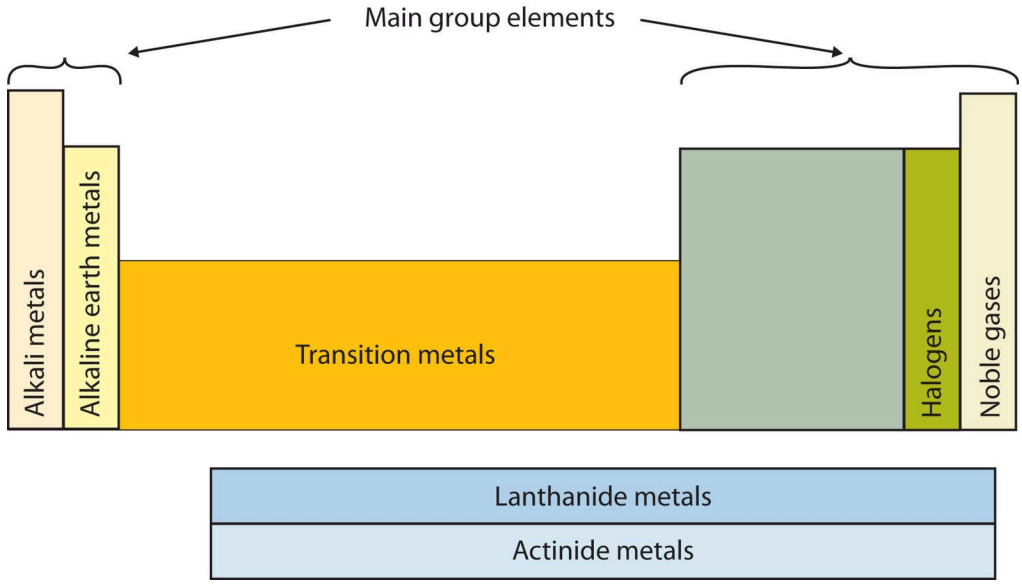



Figure 4.1.3: Special Names for Sections of the Periodic Table. Some sections of the periodic table have special names. The elements lithium, sodium, potassium, rubidium, cesium, and francium are collectively known as alkali metals.

### To Your Health: Transition Metals in the Body

Most of the elemental composition of the human body consists of main group elements. The most abundant non-main group element is iron, at 0.006 percentage by mass. Because iron has relatively massive atoms, it would appear even lower on a list organized in terms of percent by *atoms* rather than percent by mass.

Iron is a transition metal and the chemistry of iron makes it a key component in the proper functioning of red blood cells.

Red blood cells are cells that transport oxygen from the lungs to cells of the body and then transport carbon dioxide from the cells to the lungs. Without red blood cells, animal respiration as we know it would not exist. The critical part of the red blood cell is a protein called *hemoglobin*. Hemoglobin combines with oxygen and carbon dioxide, transporting these gases from one location to another in the body. Hemoglobin is a relatively large molecule, with a mass of about 65,000 u.

The crucial atom in the hemoglobin protein is iron. Each hemoglobin molecule has four iron atoms, which act as binding sites for oxygen. It is the presence of this particular transition metal in your red blood cells that allows you to use the oxygen you inhale.

Other transition metals have important functions in the body, despite being present in low amounts. Zinc is needed for the body's immune system to function properly, as well as for protein synthesis and tissue and cell growth. Copper is also needed for several proteins to function properly in the body. Manganese is needed for the body to metabolize oxygen properly. Cobalt is a necessary component of vitamin B-12, a vital nutrient. These last three metals are present in the body in very small quantities. However, even these small quantities are required for the body to function properly.

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## Answers

**Exercise** 4.1.1

metal

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# 4.2: Periodic Groups

## Learning Objectives

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

The periodic table is useful for understanding atomic properties that show **periodic trends**. Periodic trends are specific patterns that are present in the periodic table that illustrate different aspects of a certain element, including its size and its electronic properties. Major periodic trends include atomic radius, melting point, among many other properties as we will discuss. Periodic trends, arising from the arrangement of the periodic table, provide chemists with an invaluable tool to quickly predict an element's properties. These trends exist because of the similar atomic structure of the elements within their respective group families or periods, and because of the periodic nature of the elements.

One important atomic property is the **atomic radius**, which is a measure of the atomic size, usually the distance from the nucleus to the out electron shell. However, since this boundary is not well-defined, there are multiple definitions of atomic radius. Irrespective of the definition used, a clear periodic trend can be observed when atomic radius is plotted vs. atomic number (Figure 4.2.1). The radii generally decrease along each row of the table and increase down each group. The radius increases sharply between the noble gas at the end of each period and the alkali metal at the beginning of the next period. The largest atoms are found in the lower left corner of the periodic table and the smallest are found in the upper right corner

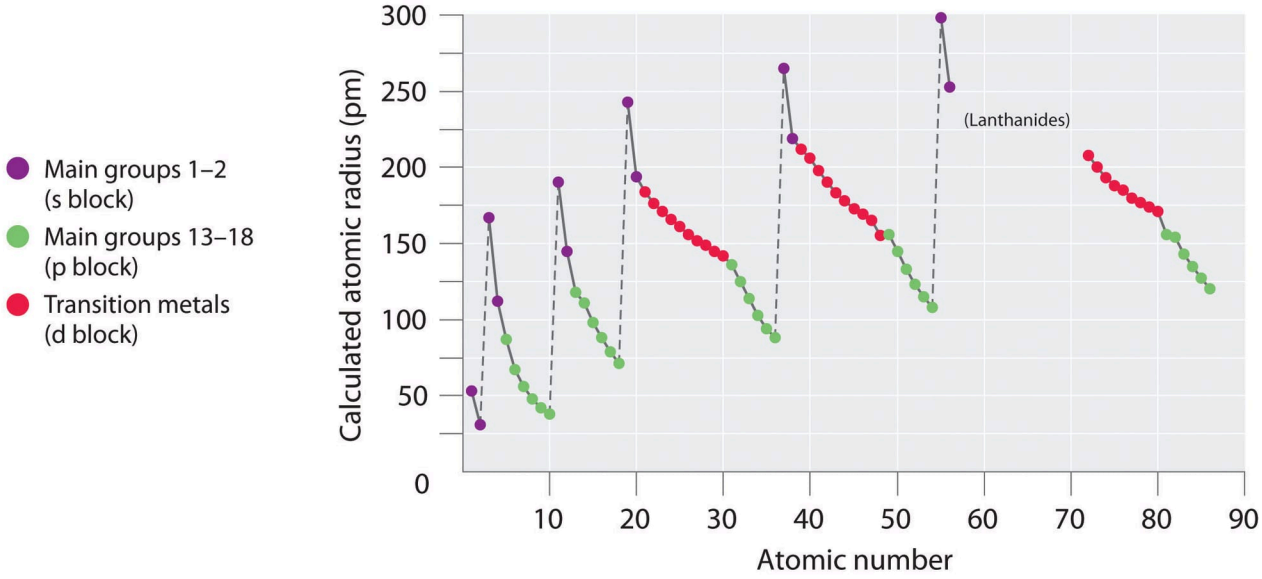



Figure 4.2.1: A Plot of Periodic Variation of Atomic Radius with Atomic Number for the First Six Rows of the Periodic Table.

The melting point is a metric of the energy required to transform the solid phase of a substance into a liquid. Generally, the stronger the bond between the atoms of an element, the more energy required to break that bond. The melting points exhibit comparable, albeit more complex, periodic trends as observed in the atomic radii (Figure 4.2.2). Key feature of these trends are:

- Metals generally possess a *high melting point*.
- Most non-metals possess *low melting points*.
- The non-metal carbon possesses *the highest melting point of all the elements*. The semi-metal boron also possesses a high melting point.

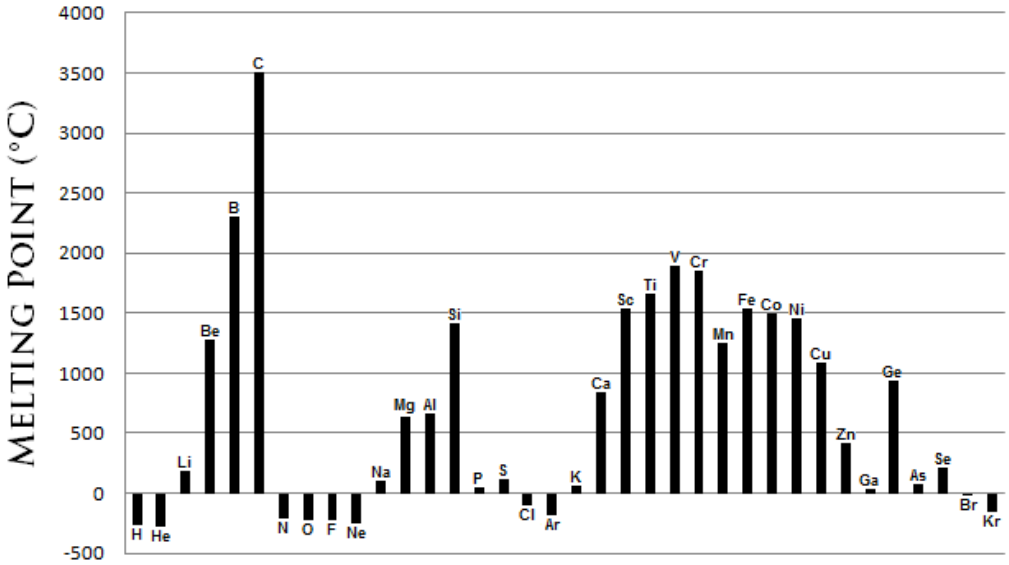



Figure 4.2.2: A plot of melting point vs. atomic number show a periodic trend.

The trends of the atomic radii and melting points (and other chemical and physical properties of the elements) can be explained by the electron shell theory of the atom discussed in the following sections.

## Element Characteristics By Group

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. For example, the elements of Group 1 are known as the alkali metals, Group 2 are the alkaline earth metals, Group 17 are the halogens, and Group 18 are the noble gases.

- **Group 1: The Alkali Metals –** lithium (Li), sodium (Na), potassium (K), rubidium (Rb), cesium (Cs), and francium (Fr) are soft, shiny, and highly reactive metals. 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. *Hydrogen is unique in that it is generally placed in Group 1, but it is not a metal.*
- **Group 2: The Alkaline Earth Metals –** beryllium (Be), magnesium (Mg), calcium (Ca), strontium (Sr), barium (Ba), and radium (Ra) are shiny, slivery-white, somewhat reactive metals. 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 –** fluorine (F), chlorine (Cl), bromine (Br), iodine (I), and astatine (At) are nonmetals. The name halogen is derived from the Greek words for "salt forming," which reflects that all the halogens react readily with metals to form compounds, such as sodium chloride and calcium chloride (used in some areas as road salt).
- **Group 18: The Noble Gases –** helium (He), neon (Ne), argon (Ar), krypton (Kr), xenon (Xe), and radon (Rn) are gases at room temperature and pressure. Because the noble gases are composed of only single atoms, they are called monatomic. 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.

### 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.

### Example 4.2.1: Groups

Provide the family/group names and period numbers (horizontal values) of each element.

a. Li
b. Ar
c. Ra

**Solution**:

a. Lithium is an alkali metal. It is located in period two.
b. Argon is a noble gas. It is located in period three.
c. Radium is an alkaline metal. It is located in period seven.

### Example 4.2.2: Classification of Elements

Provide elemental names for the following combinations:

a. The alkali metal in period three.
b. The halogen in period two
c. A metalloid in period four
d. A transition metal in period three

**Solution**:

a. Sodium
b. Fluorine
c. Germanium or Arsenic
d. There are no transition metals in period three (gotcha!)

## Key Takeaways

- The chemical elements are arranged in a chart called the periodic table.
- Some characteristics of the elements are related to their position on the periodic table.
- The number of valence electrons of an element can be determined by the group (vertical column) number in the Periodic

Table. Elements with the same number of valence electrons have similar chemical properties.

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# 4.3: Electronic Structure of Atoms

## Learning Objectives

- Describe how electrons are grouped within atoms into shells, subshells, and orbitals using quantum numbers.

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

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

In 1913, the Danish scientist Niels Bohr suggested that the electron in a hydrogen atom could not have any random energy, having *only* certain fixed values of energy that were indexed by the number $n$ (now called a **quantum number**). Bohr suggested that the energy of the electron in hydrogen was **quantized** because it was in a specific orbit; much like the steps on a staircase does not have half or quarter stairs or the keys on a piano don't have notes in between, there are no energy levels in between each orbit. Figure 4.3.1 shows a model of the hydrogen atom based on Bohr's ideas.

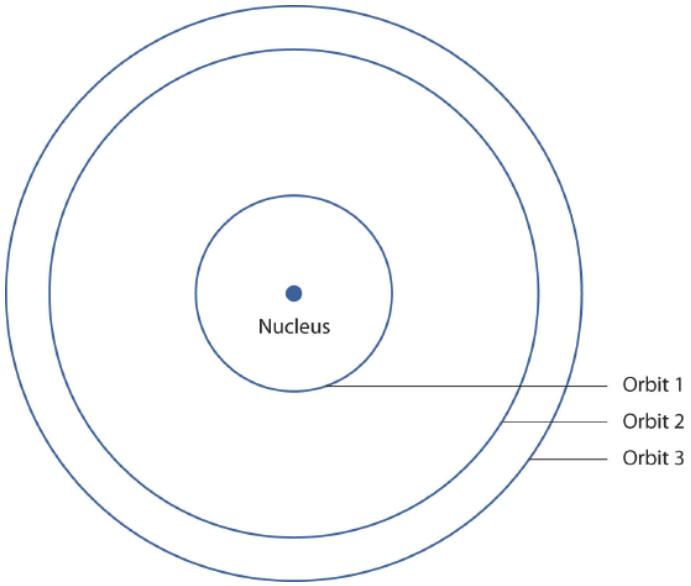



Figure 4.3.1: Bohr's Model of the Hydrogen Atom. Bohr's description of the hydrogen atom had specific orbits for the electron, which had quantized energies.

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

In the quantum-mechanical model of an atom, which is the modern and currently accepted model, the location of electrons in the atom are described by four **quantum numbers**, not just the one predicted by Bohr. Much like your home address can be used to locate you in a specific state, city, street, and house number, the first three quantum numbers identify approximately where electrons are in an atom. The fourth quantum number describes the electron and whether it is spin up or down (clockwise or

counterclockwise). The theory and mathematics behind these four quantum numbers are well beyond the scope of this textbook, however, it is useful to learn some of the basics in order to understand how atoms behave and interact with (react) with other atoms.

## Electron Arrangements: Shells, Subshells, and Orbitals

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

Shells are further divided into subsets of electrons called **subshells**, labeled by type as s, *p*, *d*, or *f*. The first shell has only one subshell, *s*. The second shell has two subshells, *s* and *p;* the third shell has three subshells, *s*, *p*, and *d,* and the fourth shell has four subshells, *s*, *p*, *d*, and *f*. Within each subshell, electrons are arranged into different numbers of **orbitals**, an s subshell is made up of one *s* orbital, a *p* subshell has two *p* orbitals, a *d* subshell, five *d* orbitals, and an *f* subshell, seven *f* orbitals. Each orbital has a different shape and orientation around the nucleus (Figure 4.3.1, however, rather than representing an orbit, as the name suggests, orbitals define a boundary for the region of space where a given electron is most likely to be found. Lastly, a single orbital can hold up to two electrons each with a different **spin**.

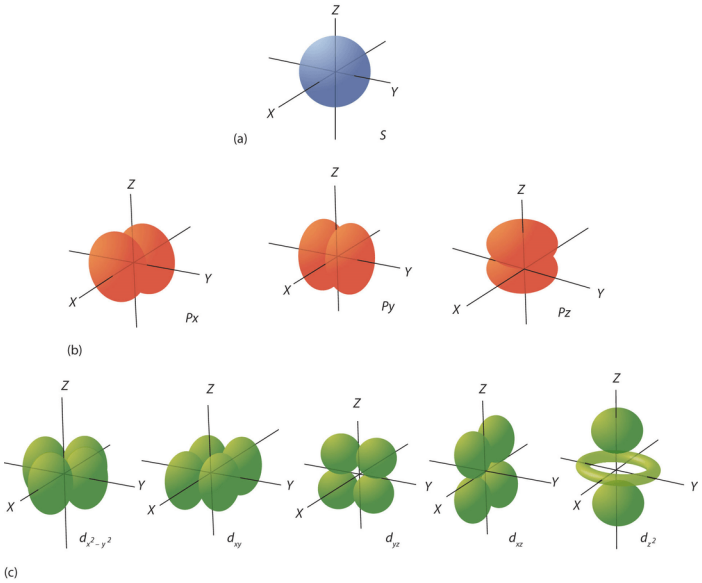



Figure 4.3.1: Electron Orbitals. (a) The lone *s* orbital in an *s* subshell is spherical in distribution. (b) The three *p* orbitals have two lobes, shaped kind of like dumbbells, each is oriented around the nucleus along a different axis. (c) The five *d* orbitals have four lobes, except for the $d_{z^2}$ orbital, which is a "dumbbell + torus" combination. They are all oriented in different directions.

It is important to note that according to quantum theory, there are specific *allowed* combinations of quantum numbers and others that are not allowed. For example, shell two can only have two subshells, *s* with one orbital and *p* with 3 orbitals, therefore, this shell can hold a maximum of eight electrons (four orbitals times two electrons each). It takes practice to learn the allowed combinations as shown in Table 4.3.1 but it is helpful to visualize the atom as a sphere with the nucleus in the center. Close to the nucleus, there is a smaller amount of space for electrons – a smaller shell. As the number of electrons increases, the shells that hold the electrons get larger and thus further away from the nucleus.

*Table 4.3.1: Shells and Subshells*

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

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

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

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# 4.4: Electron Configurations

## Learning Objectives

- Describe how electrons are arranged in an atom using electron configurations.

Previously we discussed the concept of electron *shells*, *subshells*, *orbitals*, and electron *spin*. It is the arrangement of electrons into shells and subshells that most concerns us here, so we will focus on that.

We use numbers to indicate which shell an electron is in. The first shell, closest to the nucleus and with the lowest-energy electrons, is shell 1. This first shell has only one subshell, which is labeled 1s and can hold a maximum of 2 electrons. We combine the shell and subshell labels when referring to the organization of electrons about a nucleus and use a superscript to indicate how many electrons are in a subshell. Thus, because a hydrogen atom has its single electron in the s subshell of the first shell, we use $\mathbf{1s^1}$ (spoken as “one-ess-one”) to describe the electron arrangement or distribution of electrons in hydrogen. This structure is called an **electron configuration** and is unique to hydrogen.

Helium atoms have 2 electrons. Both electrons fit into the 1s subshell because s subshells contain one s orbital which can hold up to 2 electrons; therefore, the electron configuration for helium atoms is $\mathbf{1s^2}$ (spoken as “one-ess-two”).

The 1s subshell can hold a maximum of 2 electrons, so the electron configuration for a lithium atom, which has three electrons, cannot be $1s^3$. Two of the lithium electrons can fit into the 1s subshell, but the third electron must go into the second shell and the lower energy orbital, which is the 2s orbital. Therefore, we write the electron configuration of a lithium atom as $\mathbf{1s^2 2s^1}$ (spoken as “one-ess-two two-ess-one”).

The shell diagram for a lithium atom (Figure 4.4.1). The shell closest to the nucleus (first shell) has 2 dots representing the 2 electrons in **1s**, while the outermost shell (**2s**) has 1 electron.

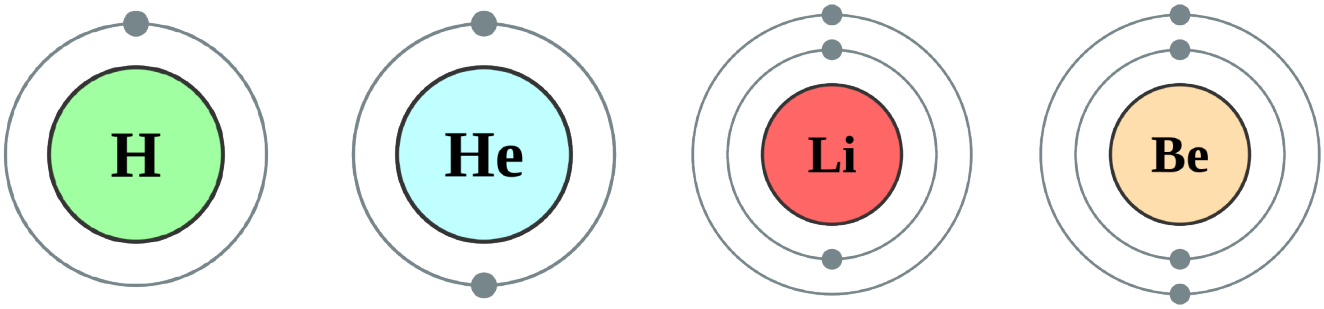



Figure 4.4.1: Shell diagrams of hydrogen (H), helium (He), lithium (Li), and Berryellium (Be) atoms. (CC BY-SA 2.0 UK; Greg Robson modified by Pumbaa via Wikipedia)

There are a set of general rules that are used to figure out the electron configuration of an atomic species: **Aufbau Principle**, **Hund's Rule** and the **Pauli-Exclusion Principle**.

- **Rule 1 (Aufbau Principle):** Electrons occupy the lowest-energy orbitals (closest to the nucleus) possible, starting with 1s, then 2s, 2*p*, and continuing on to higher energy (further away from the nucleus). Shells increase in energy in order from 1 to 2 to 3, and so on. Within these shells, an s subshell is the lowest energy followed by *p*, then *d*, then *f*.
- **Rule 2 (Hund's Rule):** When electrons occupy degenerate orbitals (i.e. same shell and subshell), they must first singly occupy (half-fill) each empty orbital in a subshell before double occupying (completely filling) them. Furthermore, the most stable configuration results when the spins are parallel (i.e. all spin up or all spin down). For example, all three *p* orbitals in a *p* subshell will have one electron before a single *p* orbital contains two electrons.
- **Rule 3 (Pauli-Exclusion Principle):** Each electron is described with a unique set of four quantum numbers (a unique address). Therefore, if two electrons occupy the same orbital, they must have different spins. This is the reason all orbitals

can hold a maximum of two electrons.

Continuing on the periodic table to the next largest atom, beryllium, with 4 electrons, the electron configuration is $1s^2 2s^2$. Now that the 2*s* subshell is filled, electrons in larger atoms, starting with boron, begin filling the 2*p* 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: $1s^2 2s^2 2p^6$

At the end of the period the element neon, has filled the 2*s*, and 2*p* subshells, which completes the second shell. Now atoms with more electrons now must begin the third shell starting with the 3*s* subshell. The first two subshells of the third shell are filled in order—for example, the electron configuration of aluminum, with 13 electrons, is $1s^2 2s^2 2p^6 3s^2 3p^1$. However, a curious thing happens after the 3*p* subshell is filled: the 4*s* subshell begins to fill before the 3*d* subshell does. In fact, the exact ordering of subshells becomes more complicated at this point (after argon, with its 18 electrons), so we will not consider the electron configurations of larger atoms.

*Table 4.4.1: Electron Configurations of the First 20 Elements*

| Atomic Number | Element Symbol | Outermost Shell | Electron Configuration | Noble Gas Configuration |
|---|---|---|---|---|
| 1 | H | 1 | $1s^1$ | $1s^1$ |
| 2 | He | 1 | $1s^2$ | $1s^2$ |
| 3 | Li | 2 | $1s^2 2s^1$ | [He] $2s^1$ |
| 4 | Be | 2 | $1s^2 2s^2$ | [He] $2s^2$ |
| 5 | B | 2 | $1s^2 2s^2 2p^1$ | [He] $2s^2 2p^1$ |
| 6 | C | 2 | $1s^2 2s^2 2p^2$ | [He] $2s^2 2p^2$ |
| 7 | N | 2 | $1s^2 2s^2 2p^3$ | [He] $2s^2 2p^3$ |
| 8 | O | 2 | $1s^2 2s^2 2p^4$ | [He] $2s^2 2p^4$ |
| 9 | F | 2 | $1s^2 2s^2 2p^5$ | [He] $2s^2 2p^5$ |
| 10 | Ne | 2 | $1s^2 2s^2 2p^6$ | [He] $2s^2 2p^6$ |
| 11 | Na | 3 | $1s^2 2s^2 2p^6 3s^1$ | [Ne] $3s^1$ |
| 12 | Mg | 3 | $1s^2 2s^2 2p^6 3s^2$ | [Ne] $3s^2$ |
| 13 | Al | 3 | $1s^2 2s^2 2p^6 3s^2 3p^1$ | [Ne] $3s^2 3p^1$ |
| 14 | Si | 3 | $1s^2 2s^2 2p^6 3s^2 3p^2$ | [Ne]$3s^2 3p^2$ |
| 15 | P | 3 | $1s^2 2s^2 2p^6 3s^2 3p^3$ | [Ne] $3s^2 3p^3$ |
| 16 | S | 3 | $1s^2 2s^2 2p^6 3s^2 3p^4$ | [Ne] $3s^2 3p^4$ |
| 17 | Cl | 3 | $1s^2 2s^2 2p^6 3s^2 3p^5$ | [Ne] $3s^2 3p^5$ |
| 18 | Ar | 3 | $1s^2 2s^2 2p^6 3s^2 3p^6$ | [Ne] $3s^2 3p^6$ |
| 19 | K | 4 | $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$ | [Ar] $4s^1$ |

| Atomic Number | Element Symbol | Outermost Shell | Electron Configuration | Noble Gas Configuration |
|---|---|---|---|---|
| 20 | Ca | 4 | $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,4s^2$ | [Ar] $4s^2$ |

## Noble Gas Configuration

The electron configuration of sodium is $1s^2 2s^2 2p^6 3s^1$ (Table $4.4.1$). The first ten electrons of the sodium atom are the inner-shell electrons and the configuration of just those ten electrons is exactly the same as the configuration of the element neon $(Z = 10)$. This provides the basis for a shorthand notation for electron configurations called the **noble gas configuration**, which atom consists of the elemental symbol of the last noble gas prior to that atom, followed by the configuration of the remaining electrons. So for sodium, we make the substitution of $[\mathrm{Ne}]$ for the $1s^2 2s^2 2p^6$ part of the configuration. Sodium's noble gas configuration becomes $[\mathrm{Ne}]\,3s^1$.

The electron filling diagram shown below in Figure $4.4.2$ is useful in remembering the order for electrons to occupy shells and subshells. Although it is much easier to use the periodic table as a guide for electron filling as you will see in the next section.

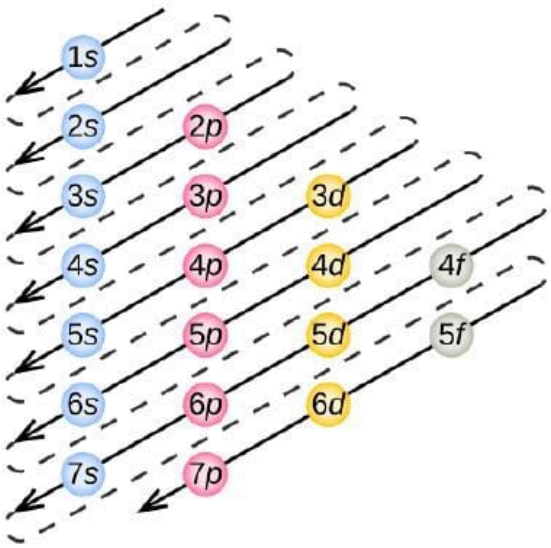



Figure $4.4.2$: The order of electron filling in an atom. Follow each arrow in order **from top to bottom**. The subshells you reach along each arrow give the ordering of filling of subshells in larger atoms.

## Example $4.4.1$: Electronic Configuration of Phosphorus Atoms

Using Figure $4.4.2$ as your guide, write the electron configuration of a neutral phosphorus atom. The atomic number of P is 15.

**Solution**

A neutral phosphorus atom has 15 electrons. Two electrons can go into the 1s subshell, 2 can go into the 2*s* subshell, and 6 can go into the 2*p* subshell. That leaves 5 electrons. Of those 5 electrons, 2 can go into the 3s subshell, and the remaining 3 electrons can go into the 3*p* subshell. Thus, the electron configuration of neutral phosphorus atoms is $1s^2 2s^2 2p^6 3s^2 3p^3$.

## Exercise $4.4.1$: Electronic Configuration of Chlorine Atoms

Using Figure $4.4.2$ as your guide, write the electron configuration of a neutral chlorine atom. The atomic number of Cl is 17.

*Answer available at the end of this section.*

# Orbital Diagrams

An **orbital diagram** is the more visual way to represent the arrangement of all the electrons in a particular atom. In an orbital diagram, the individual orbitals are shown as squares and orbitals within a sublevel are drawn next to each other horizontally. Each sublevel is labeled by its shell and sublevel. Electrons are indicated by arrows inside of the squares. 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.

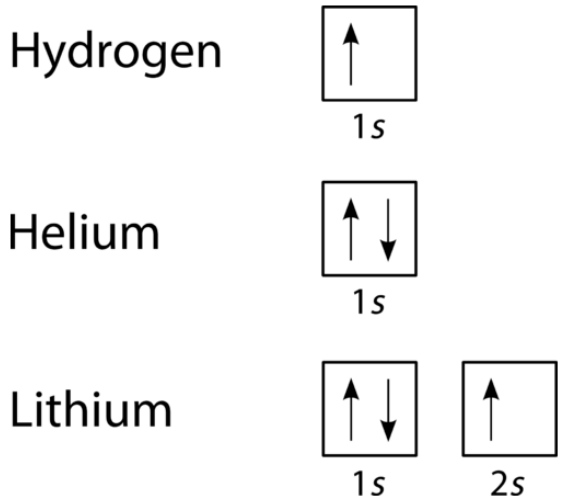



Figure 4.4.3: Orbital diagrams for hydrogen, helium, and lithium.

According to the Aufbau Principle, 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 orbital diagram for carbon is shown in Figure 4.4.10. There are two $2p$ electrons for carbon and each occupies its own $2p$ orbital (Hund's Rule).

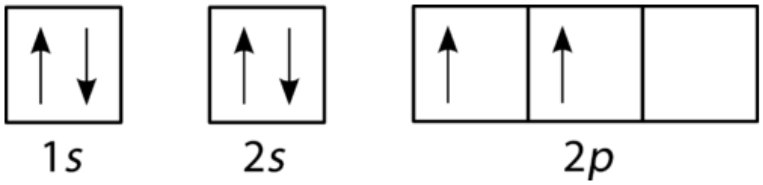



Figure 4.4.4: Orbital diagram for carbon.

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.

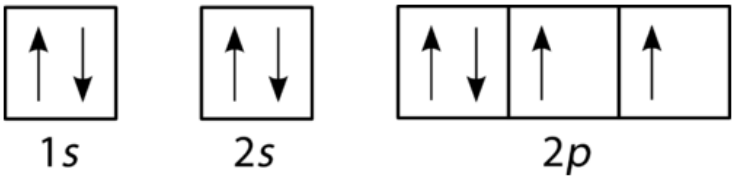



Figure 4.4.5: Orbital diagram for oxygen.

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 4.4.3: Carbon Atoms

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

**Solution**

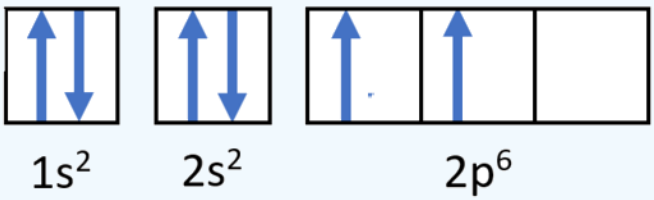
***Step 1: List the known quantities and plan the problem.***

**Known**

- Atomic number of carbon, Z=6

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

***Step 2: Construct the diagram.***




***Orbital filling diagram for carbon.***

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

***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.

## Answers

**Exercise 4.4.1: Electronic Configuration of Chlorine Atoms**

A neutral chlorine atom has 17 electrons. Two electrons can go into the 1s subshell, 2 can go into the 2*s* subshell, and 6 can go into the 2*p* subshell. That leaves 7 electrons. Of those 7 electrons, 2 can go into the 3s subshell, and the remaining 5 electrons can go into the 3*p* subshell. Thus, the electron configuration of neutral chlorine atoms is $1s^2 2s^2 2p^6 3s^2 3p^5$.

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# 4.5: Electron Configurations and the Periodic Table

## Learning Objectives

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

Remember, that the periodic table as a tool for organizing the known chemical elements(Figure 4.5.1). The elements are listed by atomic number (the number of protons in the nucleus), and elements with similar chemical properties are grouped together in columns. 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 4.5.1)

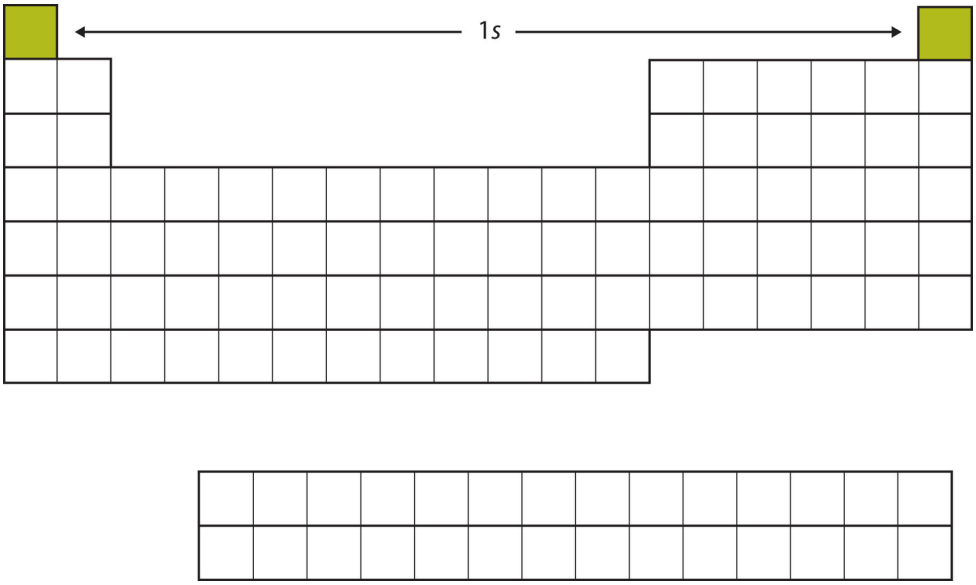



Figure 4.5.1: The 1s Subshell. H and He represent the filling of the 1s subshell.

The next two electrons, for Li and Be, would go into the 2s subshell. Figure 4.5.2 shows that these two elements are adjacent on the periodic table.

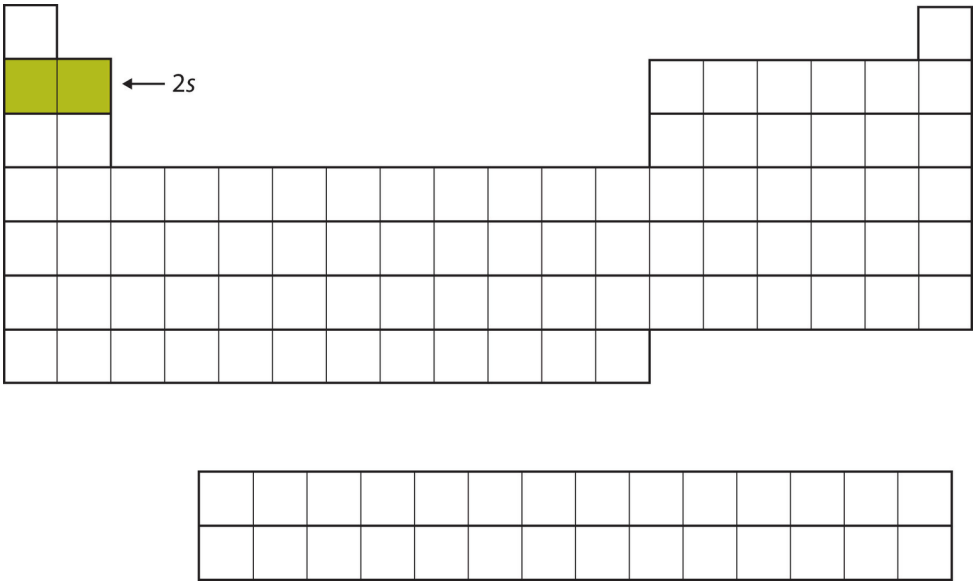



Figure 4.5.2: The 2s Subshell. In Li and Be, the 2s subshell is being filled.

For the next six elements, the 2*p* subshell is being occupied with electrons. On the right side of the periodic table, these six elements (B through Ne) are grouped together (Figure 4.5.3).

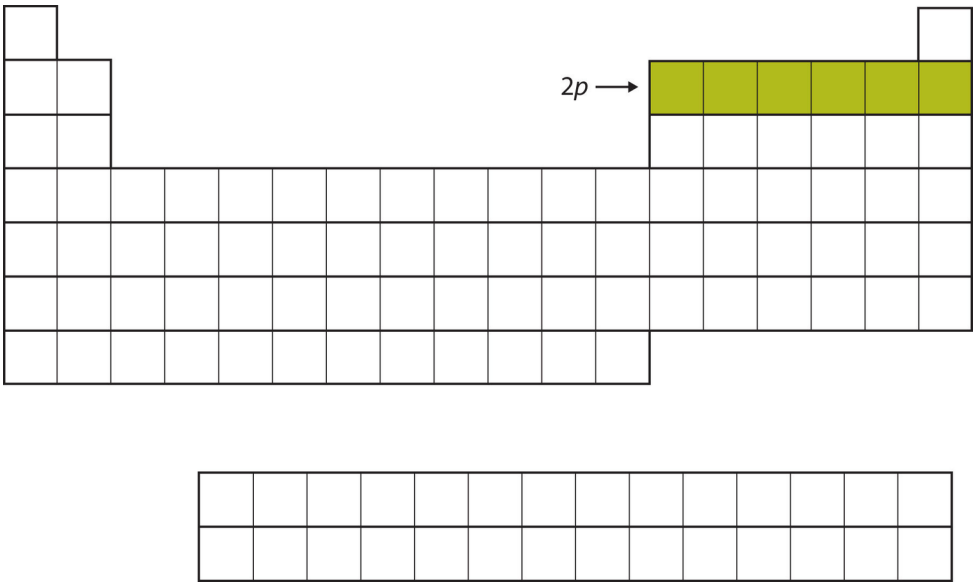



Figure 4.5.3: The 2*p* Subshell. For B through Ne, the 2*p* subshell is being occupied.

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 4.5.4).

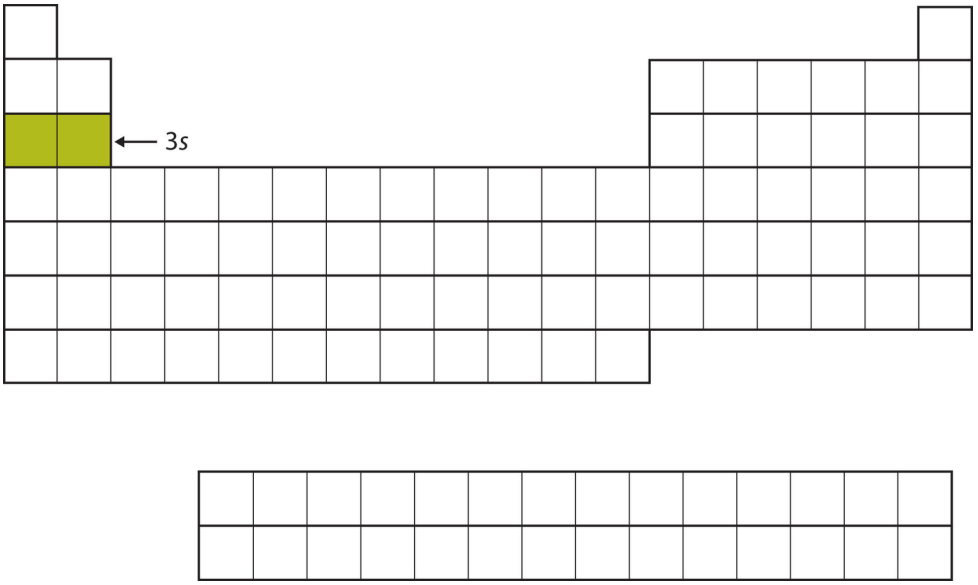



Figure 4.5.4: The 3s Subshell. Now the 3s subshell is being occupied.

Next, the 3*p* subshell is filled with the next six elements (Figure 4.5.5).

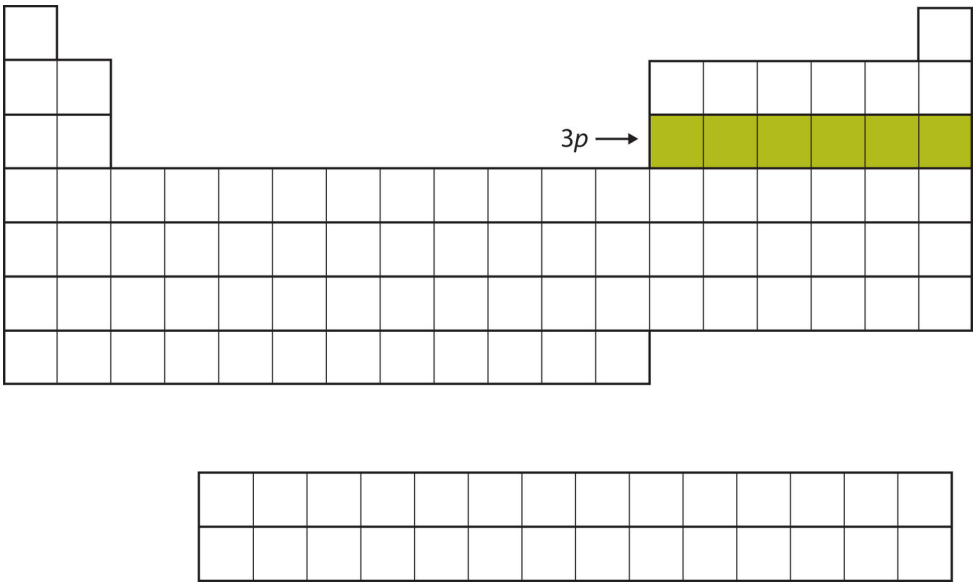



Figure 4.5.5: The 3*p* Subshell. Next, the 3*p* subshell is filled with electrons.

Instead of filling the 3*d* subshell next, electrons go into the 4*s* subshell (Figure 4.5.6).

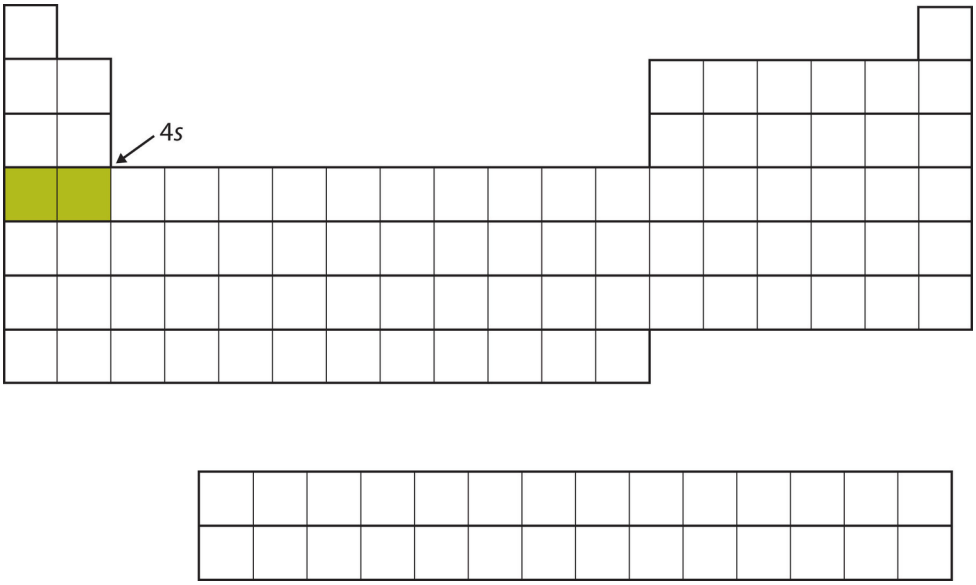



Figure 4.5.6: The 4s Subshell. The 4s subshell is filled before the 3*d* subshell. This is reflected in the structure of the periodic table.

After the 4s 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 4.5.7).

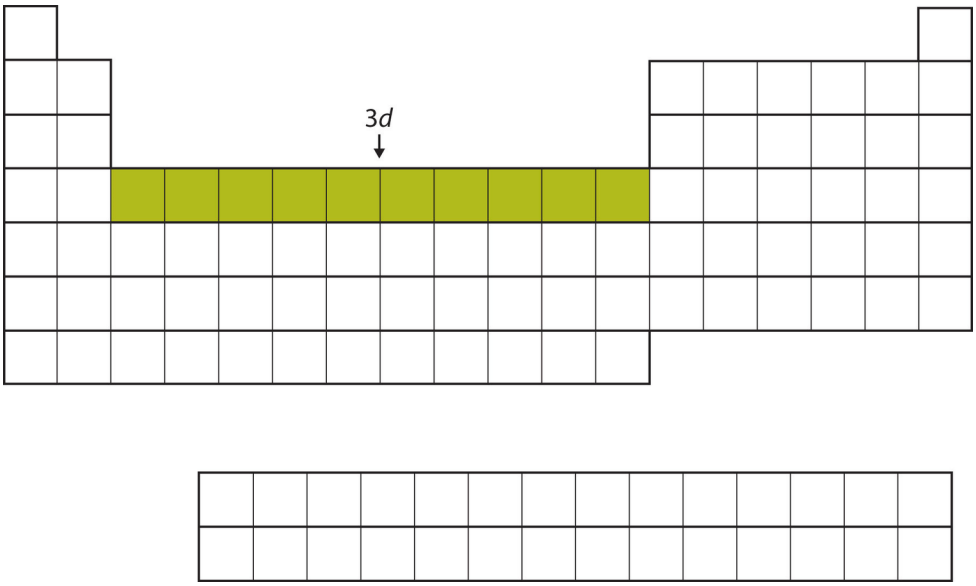



Figure 4.5.7: The 3*d* Subshell. The 3*d* subshell is filled in the middle section of the periodic table.

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

The first two columns on the left side of the periodic table are where the s subshells are being occupied. Because of this, the first two rows of the periodic table are labeled the **s block**. Similarly, the **p block** 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 4.5.8 shows the blocks of the periodic table.

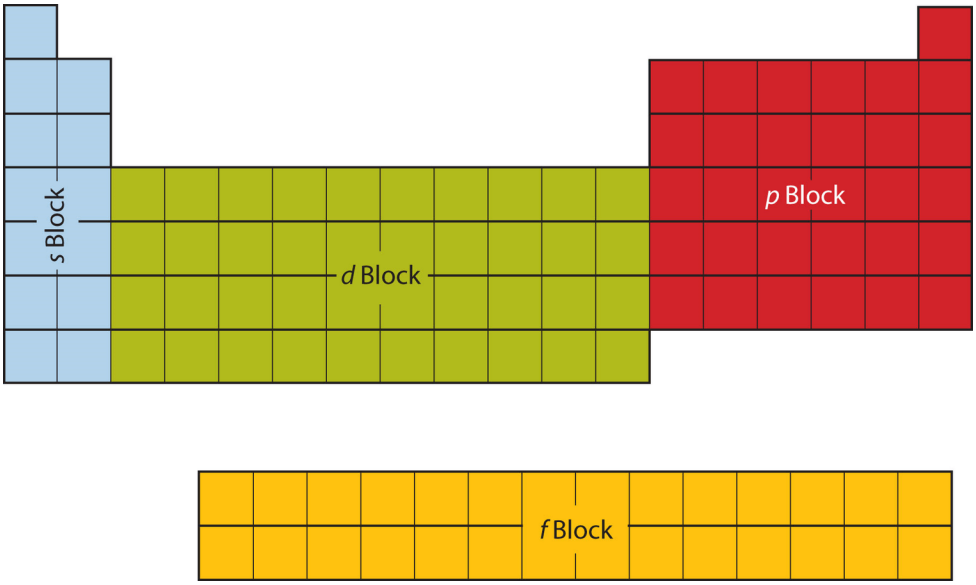



Figure 4.5.8: Blocks on the Periodic Table. The periodic table is separated into blocks depending on which subshell is being filled for the atoms that belong in that section.

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:

*Table shows first column of the periodic table and their electron configurations.*

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

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

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

Similarity of valence shell electron configuration implies that we can determine the electron configuration of an atom solely by its position on the periodic table. Consider Se, as shown in Figure 4.5.9. 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.

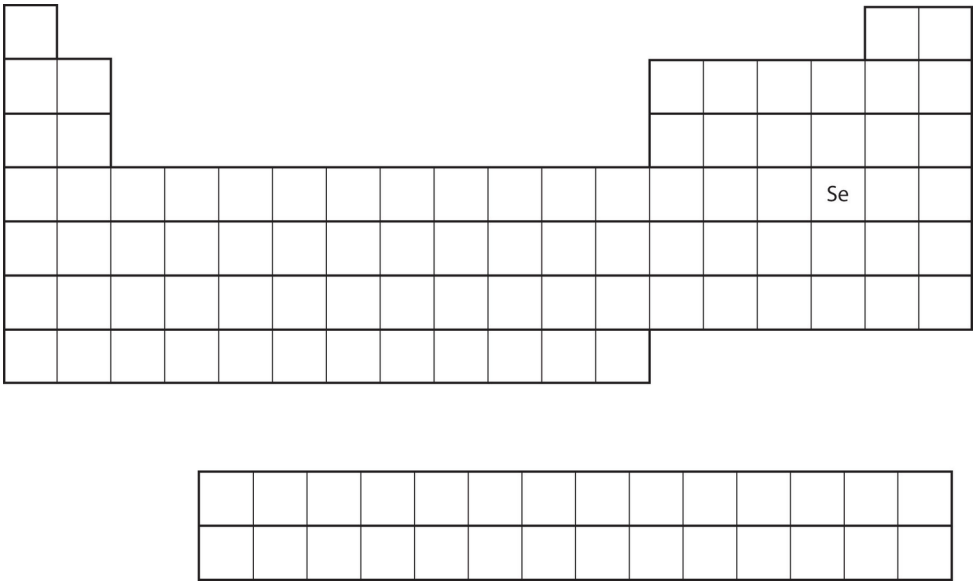



Figure 4.5.9: Selenium on the Periodic Table

## Example 4.5.1

From the element's position on the periodic table, predict the valence shell electron configuration for each atom (Figure 4.5.10).

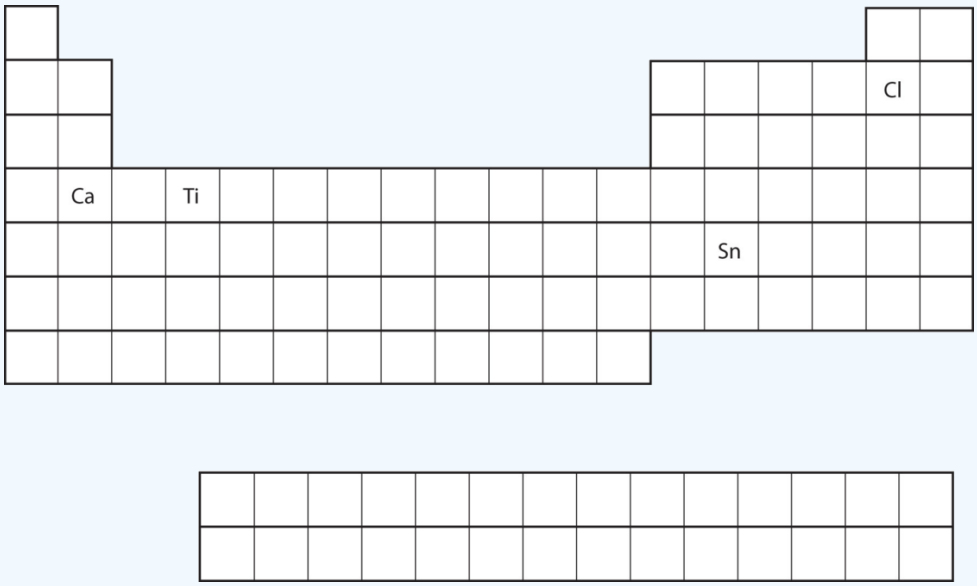



Figure 4.5.10: Various Elements on the Periodic Table

1. Ca
2. Sn

**Solution**

1. Ca is located in the second column of the s block. We would expect that its electron configuration should end with $s^2$. Calcium's electron configuration is [Ar]$4s^2$.

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

### Exercise 4.5.1

From the element's position on the periodic table, predict the valence shell electron configuration for each atom. Figure 4.5.10.

a. Ti
b. Cl

*Answer a available at the end of this section.*

### Example 4.5.2: Aluminum

Write the electron configuration of neutral aluminum atom. The atomic number of Al is 13.

**Solution**

Aluminum has 13 electrons.

*Start at Period 1 of the periodic table, Figure* 4.5.2. Place two electrons in the 1s subshell (**$1s^2$**).

*Proceed to Period 2 (left to right direction)*. Place the next two electrons in the 2s subshell (**$2s^2$**) and the next six electrons in the 2p subshell (**$2p^6$**).

*Proceed to Period 3 (left to right direction).* Place the next two electrons in the 3s subshell (**$3s^2$**) and the last one electron in the 3p subshell (**$3p^1$**).

The electron configuration of Aluminum is **$1s^2 2s^2 2p^6 3s^2 3p^1$**

### Exercise 4.5.2

Using Figure 4.5.2 as your guide, write the electron configuration of the atom that has 20 electrons

*Answer available at the end of this section.*

## 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

### Answers

**Exercise** 4.5.1

[Ar]$4s^2 3d^2$

[Ne]$3s^2 3p^5$

**Exercise** 4.5.2

*Start at Period 1 of Figure* 4.5.2. Place two electrons in the 1s subshell (**$1s^2$**).

*Proceed to Period 2 (left to right direction).* Place the next two electrons in the 2s subshell (**$2s^2$**) and the next six electrons in the 2p subshell (**$2p^6$**).

*Proceed to Period 3 (left to right direction).* Place the next two electrons in the 3s subshell (**$3s^2$**) and the next six electron in the 3p subshell (**$3p^6$**).

*Proceed to Period 4.* Place the remaining two electrons in the 4s subshell (**$4s^2$**).

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

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# 4.6: Periodic Trends

Properties of elements generally show a periodic trend that correlates with their position in the periodic table. The properties and their periodic trends are described below.

## Valence electrons

Electrons in the outermost shell are the valence electrons. Fig. 2.5.8 shows the valence electrons of the first twenty elements in red fonts.

**Periodic trend of valence electrons**

All elements in a group have the same number of valence electrons equal to the first digit of their group number. For example, 1st group of hydrogen and alkali metals has one valence electron, 2nd group of alkali metals has two valence electrons, halogens in 17th group have seven valence electrons, and noble gases in 18th group have eight valence electrons.

**Caution**

The transition metals in groups 3 to 12, and inner-transition metals, i.e., lanthanoids and actinoids -the two rows of elements placed below the periodic table, are the exception to the general trend of valence electrons described above. Valence electron configurations of transition metals and inner-transition metals are not described here; it is beyond the scope of this book.

The valence electrons mainly determine the chemical properties of the elements. The elements in the same group have similar chemical properties because they have the same valence shell electron configuration. The elements in a row show a gradual change in chemical properties because their valence shell electron configuration changes gradually along the row.

## Lewis symbols

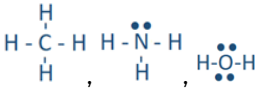
1. Lewis symbols show the valence electrons as dots around the symbol of an element. One dot represents one valence electron, e.g., $H\bullet$.
2. The dots are shown on any of the four sides of the symbol.
3. A single dot on the top, bottom, left, or right is shown four valence electrons. Then start pairing the dots beyond four valence electrons, as shown in Fig. 2.6.1 for the first twenty elements.
4. Helium is an exception that has only two valence electrons, but they are shown paired.

| Group→ Row↓ | 1 | 2 | 13 | 14 | 15 | 16 | 17 | 18 |
|---|---|---|---|---|---|---|---|---|
| 1 | H• | | | | | | | He: |
| 2 | Li• | •Be• | •B• | •C• | •N• | •O• | :F• | :Ne: |
| 3 | Na• | •Mg• | •Al• | •Si• | •P• | •S• | :Cl• | :Ar: |
| 4 | K• | •Ca• | | | | | | |

Figure 4.6.1: Lewis symbols or electron-dot symbols of the first twenty elements in the periodic table.

The electron dots in the Lewis structure are a convenient way to determine how many bonds an atom of an element can make.

> Generally, each unpaired dot can make one bond.

For example, a hydrogen atom with one unaired dot can make one bond as in H-H. A bond is represented by a line between the bonded atoms. A bond is formed by sharing unpaired valence electrons. It is called a covalent bond. Carbon, nitrogen, oxygen, and fluorine with 4, 3, 2, and 1 unpaired dot can make 4, 3, 2, and 1 bond, e.g., in the following molecules:  , , , and  .

> - Each line in these molecules represents a **bonding electron pair**, and
> - the pair of dots represent valence electrons that are not involved in bonding, called **lone pair of electrons**.

## Atomic size

Electrons exist around the nucleus in a cloud-like appearance with no clearly defined boundaries. Therefore, the atomic size generally refers to the **covalent radius** of an atom that is one-half of the distance between the nuclei covalently bonded in a homonuclear molecule, like $Cl_2$, $I_2$, $H_2$, as illustrated in Fig. 2.6.2.

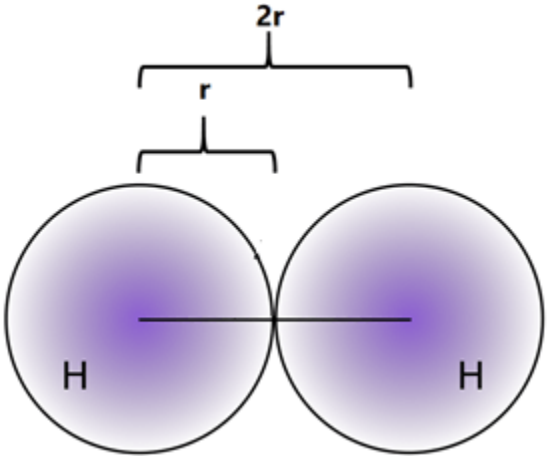



Figure 4.6.2: Diagram showing the atomic radius of $H_2$. Source: modified from CK-12 Foundation / CC BY-SA (https://creativecommons.org/licenses/by-sa/3.0)

### Periodic trend of atomic sizes

1. The atomic size generally increases from top to bottom in a group because the valence electrons add in the higher shell in each consecutive member of a group down the column.
2. The atomic size generally decreases from left to right in a row because the valence electrons are in the same shell while more protons add to the nucleus, increasing the pull on the valence electrons, as illustrated in Fig. 2.6.3.

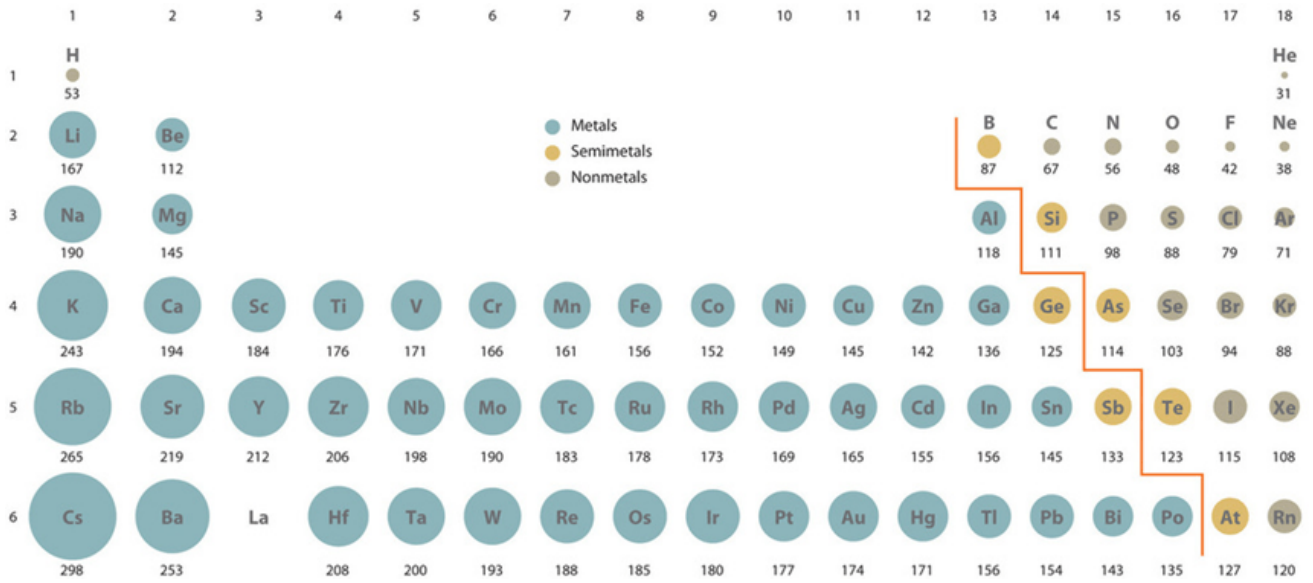



Figure 4.6.3: Illustration of the periodic trend of atomic sizes, Calculated Atomic Radii (in Picometers). Source: https://chem.libretexts.org/@api/dek...jpg?revision=1

# Ionization energy

The positively charged nucleus attracts the negatively charged electrons. Therefore removal of an electron from the atom requires energy. The ionization produces a cation with fewer electrons than the parent neutral atom, i.e., cations.

## Ionization energy

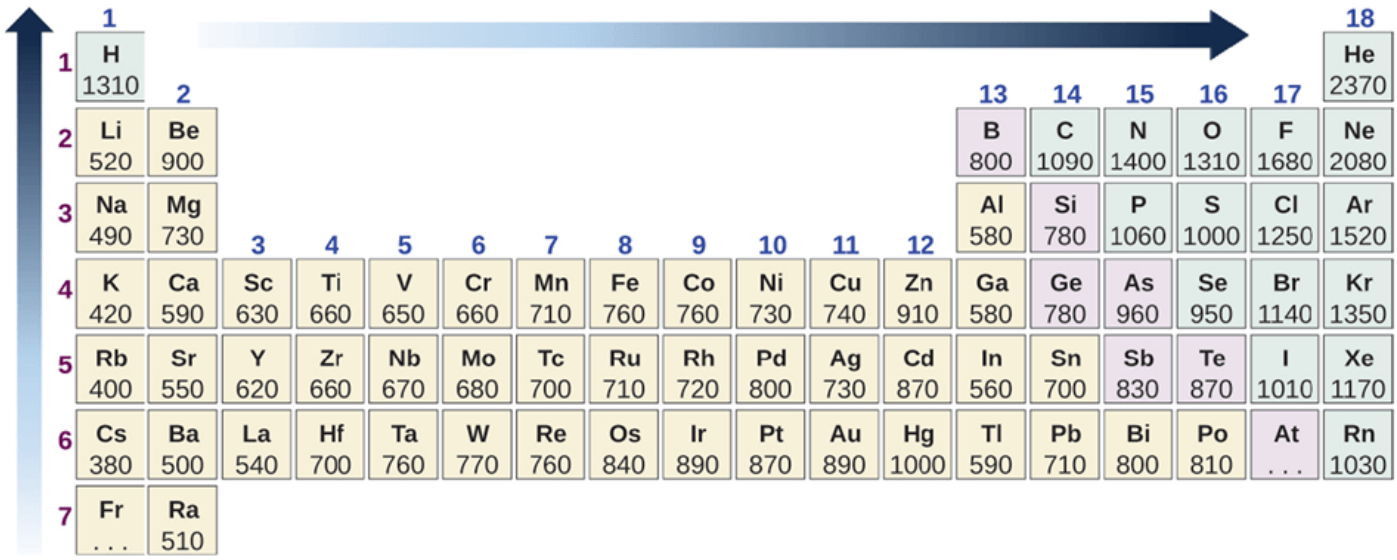
Ionization energy is the energy needed to remove an electron from a neutral atom, as in the following reaction.

$$\mathrm{Na} + \text{ ionization energy } \rightarrow \mathrm{Na}^{1+} + \mathrm{e}^{-}$$

## Periodic trend in ionization energy

1. The ionization energy generally decreases from top to bottom in a column because the valence electrons are further away and experience less pull to the nucleus down the column.
2. The ionization energy generally increases from left to right in a row because the valence electrons are in the same shell while more protons add to the nucleus, which increases the pull on the valence electrons.

Fig. 2.6.4 illustrates the periodic trend in the ionization energy.



| | 1 | | | | | | | | | | | | 13 | 14 | 15 | 16 | 17 | 18 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | H 1310 | 2 | | | | | | | | | | | | | | | | He 2370 |
| 2 | Li 520 | Be 900 | | | | | | | | | | | B 800 | C 1090 | N 1400 | O 1310 | F 1680 | Ne 2080 |
| 3 | Na 490 | Mg 730 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | Al 580 | Si 780 | P 1060 | S 1000 | Cl 1250 | Ar 1520 |
| 4 | K 420 | Ca 590 | Sc 630 | Ti 660 | V 650 | Cr 660 | Mn 710 | Fe 760 | Co 760 | Ni 730 | Cu 740 | Zn 910 | Ga 580 | Ge 780 | As 960 | Se 950 | Br 1140 | Kr 1350 |
| 5 | Rb 400 | Sr 550 | Y 620 | Zr 660 | Nb 670 | Mo 680 | Tc 700 | Ru 710 | Rh 720 | Pd 800 | Ag 730 | Cd 870 | In 560 | Sn 700 | Sb 830 | Te 870 | I 1010 | Xe 1170 |
| 6 | Cs 380 | Ba 500 | La 540 | Hf 700 | Ta 760 | W 770 | Re 760 | Os 840 | Ir 890 | Pt 870 | Au 890 | Hg 1000 | Tl 590 | Pb 710 | Bi 800 | Po 810 | At . . . | Rn 1030 |
| 7 | Fr . . . | Ra 510 | | | | | | | | | | | | | | | | |

Figure 4.6.4: The 1st ionization energy in kJ/mol. Source: Download for free at https://openstax.org/details/books/chemistry

## Electronegativity

**Definition: Electronegativity**

Electronegativity is the ability of an atom in a compound to attract the bonding electron pair to itself. Electropositivity is the opposite of electronegativity. Electronegativity is a property of an atom in a compound, i.e., a bonded atom, not a feature of an individual atom.

There are several electronegativity scales. The most commonly used is the Pauling electronegativity scale. Fig. 2.6.5 shows the electronegativities values on Pauling's electronegativity scale.




Figure 4.6.5: Periodic table of elements by Pauling scale. Source: https://en.Wikipedia.org/wiki/Electronegativity

### Periodic trend in electronegativity

1. The electronegativity generally decreases from top to bottom in a column because the atomic size increases down the column making the nucleus less effective in pulling the bonding electrons.
2. The electronegative generally increases from left to right in a row because the atomic size decrease from left to right in a row, making the nucleus more effective in pulling the bonding electron pair to itself.

## Metallic character

The metallic character relates to the ease of losing an electron in a chemical reaction. The metallic character trend is opposite to the trend of ionization energy.

### Periodic trend in metallic character

1. The metallic character generally increases from top to bottom in a column because the atomic size increases down the column, making the valence electrons less tightly held and easier to remove.
2. The metallic character generally decreases from left to right in a row because the atomic size decreases from left to right, making the valence electrons more tightly held and difficult to remove.

## Summary of the periodic trends

The ionization energy and the electronegativity generally increase from left to right in a row and from bottom to top in a column. The atomic size and the metallic character are opposite, i.e., they increase from right to left in a row and from top to bottom in a column. Fig. 2.6.6 summarizes the periodic trend in the properties of the elements.

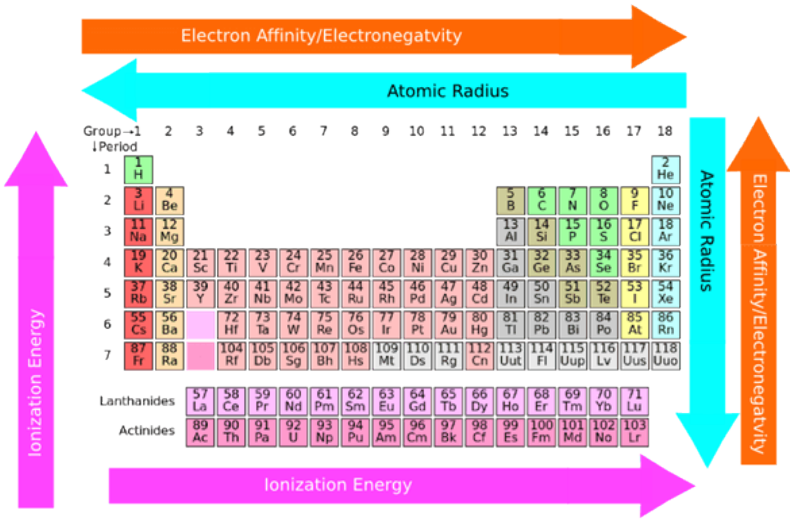



Figure 4.6.6: Summary of the periodic trend in the properties of elements. Source: https://www.hiclipart.com/free-trans...ntzga/download

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# 4.E: Electrons in Atoms and the Periodic Table (Exercises)

## 9.1: Blimps, Balloons, and Models of the Atom

## 9.2: Light: Electromagnetic Radiation

## 9.3: The Electromagnetic Spectrum

1. Choose the correct word for the following statement. Blue light has a (longer or shorter) wavelength than red light.
2. Choose the correct word for the following statement. Yellow light has a (higher or lower) frequency than blue light.
3. Choose the correct word for the following statement. Green light has a (larger or smaller) energy than red light.
4. If "light A" has a longer wavelength than "light B", then "light A" has _____ "light B".
   (a) a lower frequency than

   (b) a higher frequency than

   (c) the same frequency as

5. If "light C" has a shorter wavelength than "light D", then "light C" has _____ "light D".
   (a) a larger energy than

   (b) a smaller energy than

   (c) the same energy as

6. If "light E" has a higher frequency than "light F", then "light E" has _____ "light F".
   (a) a longer wavelength than

   (b) a shorter wavelength than

   (c) the same wavelength as

7. If "light G" has a higher frequency than "light H", then "light G" has _____ "light H".
   (a) a larger energy than

   (b) a smaller energy than

   (c) the same energy as

8. If "light J" has larger energy than "light K", then "light J" has _____ "light K".
   (a) a shorter wavelength than

   (b) a longer wavelength than

   (c) the same wavelength as

9. Which of the following statements is true?
   (a) The frequency of green light is higher than the frequency of blue light and the wavelength of green light is longer than the wavelength of blue light.

   (b) The frequency of green light is higher than the frequency of blue light and the wavelength of green light is shorter than the wavelength of blue light.

   (c) The frequency of green light is lower than the frequency of blue light and the wavelength of green light is shorter than the wavelength of blue light.

(d) The frequency of green light is lower than the frequency of blue light and the wavelength of green light is longer than the wavelength of blue light.

(e) The frequency of green light is the same as the frequency of blue light and the wavelength of green light is shorter than the wavelength of blue light.

10. As the wavelength of electromagnetic radiation increases:
    (a) its energy increases.

    (b) its frequency increases.

    (c) its speed increases.

    (d) more than one of the above statements is true.

    (e) none of the above statements is true.

11. List three examples of electromagnetic waves.
12. Why do white objects appear white?
13. Name the colors present in white light in order of increasing frequency.
14. Why do objects appear black?

## 9.4: The Bohr Model: Atoms with Orbits

1. Decide whether each of the following statements is true or false:
    (a) Niels Bohr suggested that the electrons in an atom were restricted to specific orbits and thus could only have certain energies.

    (b) Bohr's model of the atom can be used to accurately predict the emission spectrum of hydrogen.

    (c) Bohr's model of the atom can be used to accurately predict the emission spectrum of neon.

    (d) According to the Bohr model, electrons have more or less energy depending on how far around an orbit they have traveled.

2. According to the Bohr model, electrons in an atom can only have certain, allowable energies. As a result, we say that the energies of these electrons are _____.
3. The Bohr model accurately predicts the emission spectra of atoms with...
    (a) less than 1 electron.

    (b) less than 2 electrons.

    (c) less than 3 electrons.

    (d) less than 4 electrons.

4. Consider an $He^+$ atom. Like the hydrogen atom, the He+ atom only contains 1 electron, and thus can be described by the Bohr model. Fill in the blanks in the following statements.
    (a) An electron falling from the $n$ = 2 orbit of $He^+$ to the $n$ = 1 orbit of $He^+$ releases _____ energy than an electron falling from the $n$ = 3 orbit of $He^+$ to the $n$ = 1 orbit of $He^+$.

    (b) An electron falling from the $n$ = 2 orbit of $He^+$ to the $n$ = 1 orbit of $He^+$ produces light with a _____ wavelength than the light produced by an electron falling from the $n$ = 3 orbit of $He^+$ to the $n$ = 1 orbit of $He^+$.

    (c) An electron falling from the $n$ = 2 orbit of $He^+$ to the $n$ = 1 orbit of $He^+$ produces light with a _____ frequency than the light produced by an electron falling from the $n$ = 3 orbit of $He^+$ to the $n$ = 1 orbit of $He^+$.

5. According to the Bohr model, higher energy orbits are located (closer to/further from) the atomic nucleus. This makes sense since negative electrons are (attracted to/repelled from) the positive protons in the nucleus, meaning it must take energy to

move the electrons (away from/towards) the nucleus of the atom.

6. According to the Bohr model, what is the energy of an electron in the first Bohr orbit of hydrogen?
7. According to the Bohr model, what is the energy of an electron in the tenth Bohr orbit of hydrogen?
8. According to the Bohr model, what is the energy of an electron in the seventh Bohr orbit of hydrogen?
9. If an electron in a hydrogen atom has an energy of $-6.06 \times 10^{-20}$ J, which Bohr orbit is it in?
10. If an electron in a hydrogen atom has an energy of $-2.69 \times 10^{-20}$ J, which Bohr orbit is it in?
11. If an electron falls from the $5^{th}$ Bohr orbital of hydrogen to the $3^{rd}$ Bohr orbital of hydrogen, how much energy is released (you can give the energy as a positive number)?
12. If an electron falls from the $6^{th}$ Bohr orbital of hydrogen to the $3^{rd}$ Bohr orbital of hydrogen, what wavelength of light is emitted? Is this in the visible light range?

## 9.5: The Quantum-Mechanical Model: Atoms with Orbitals

## 9.6: Quantum-Mechanical Orbitals and Electron Configurations

1. Match each quantum number with the property that they describe.

   *Match each quantum number with the property that they describe.*

| (a) $n$ | i. shape |
|---|---|
| (b) $\ell$ | ii. orientation in space |
| (c) $m_l$ | iii. number of nodes |

2. A point in an electron wave where there is zero electron density is called a _____.
3. Choose the correct word in each of the following statements.

   (a) The (higher/lower) the value of $n$, the more nodes there are in the electron standing wave.

   (b) The (higher/lower) the value of $n$, the less energy the electron has.

   (c) The (more/less) energy the electron has, the more nodes there are in its electron standing wave.

4. Fill in the blank. For lower values of $n$, the electron density is typically found _____ the nucleus of the atom, while for higher values of $n$, the electron density is typically found _____the nucleus of the atom.
5. Circle all of the statements that make sense: Schrödinger discovered that certain quantities in the electron wave equation had to be integers, because when they weren't, the wave equation described waves which...

   (a) were discontinuous

   (b) were too small

   (c) were too long and narrow

   (d) were too short and fat

   (e) "doubled back" on themselves

6. What are the allowed values of $\ell$ for an electron standing wave with $n = 4$?
7. How many values of $\ell$ are possible for an electron standing wave with $n = 9$?
8. What are the allowed values of ml for an electron standing wave with $\ell = 3$?
9. How many different orientations are possible for an electron standing wave with $\ell = 4$?
10. What are the allowed values of $m_l$ for $n = 2$?
11. Fill in the blanks. When $\ell = 0$, the electron orbital is _____ and when $\ell = 1$, the electron orbital is _____ shaped.
12. The $n = 1$ s orbital has _____ nodes.
13. The $n = 2$ s orbital has _____ nodes.
14. The $n = 2$ $p$ orbital has _____ nodes.
15. The $n = 1$ $p$ orbital has _____ nodes.
16. There are ___ different $p$ orbitals.

17. What energy level (or value of $n$) has s, $p$ and $d$ orbitals, but no $f$ orbitals?
18. How many different $d$ orbital orientations are there?
19. How many $f$ orbital orientations are there?
20. How many different orbitals are there in the $n = 3$ energy level?

1. Write the electron configuration for beryllium. Beryllium has 4 electrons.
2. Write the electron configuration for silicon. Silicon has 14 electrons.
3. Write the electron configuration for nitrogen. Nitrogen has 7 electrons.
4. Write the electron configuration for chromium. Chromium has 24 electrons.
5. Write the electron configuration for silver. Silver has 47 electrons.

## 9.7: Electron Configurations and the Periodic Table

1. Use the Periodic Table to determine the energy level of the valence electrons in each of the following elements.
   (a) B

   (b) Ga

   (c) Rb

   (d) At

   (e) He

2. Fill in the blanks:
   (a) B is in the __ level block of the Periodic Table

   (b) Sr is in the __ level block of the Periodic Table

   (c) Fe is in the __ level block of the Periodic Table

   (d) Cs is in the __ level block of the Periodic Table

   (e) O is in the __ level block of the Periodic Table

3. Use the Periodic Table to determine the energy level and sublevel of the highest energy electrons in each of the following elements:
   (a) N

   (b) Ca

   (c) Rb

   (d) P

   (e) In

4. Decide whether each of the following statements is true or false.
   (a) Li has valence electrons in the $n = 1$ energy level.

   (b) Si has valence electrons in the $n = 3$ energy level.

   (c) Ga has valence electrons in the $n = 3$ energy level.

   (d) Xe has valence electrons in the $n = 5$ energy level.

   (e) P has valence electrons in the $n = 2$ energy level.

5. Match the element to the sublevel block it is found in:

*Match the element to the sublevel block it is found in:*

| (a) C | i. s sublevel block |
|---|---|
| (b) Cs | ii. *p* sublevel block |
| (c) Ce | iii. *d* sublevel block |
| (d) Cr | iv. *f* sublevel block |

6. The first row of the Periodic Table has:
   (a) 1 element

   (b) 2 elements

   (c) 3 elements

   (d) 4 elements

   (e) 5 elements

7. Use the Periodic Table to determine which of the following elements has the highest energy valence electrons.
   (a) Sr

   (b) As

   (c) H

   (d) At

   (e) Na

8. Use the Periodic Table to determine which of the following elements has the lowest energy valence electrons.
   (a) Ga

   (b) B

   (c) Cs

   (d) Bi

   (e) Cl

9. Which energy level does the first row in the *d* sublevel block correspond to?

## 9.8: The Explanatory Power of the Quantum-Mechanical Model

## 9.9: Periodic Trends: Atomic Size, Ionization Energy, and Metallic Character

1. Why is the atomic size considered to have "no definite boundary"?
2. How is atomic size measured?
   (a) using a spectrophotomer

   (b) using a tiny ruler (called a nano ruler)

   (c) indirectly

   (d) directly

3. Draw a visual representation of the atomic radii of an iodine molecule.

4. Which of the following would be smaller?
   (a) In or Ga

   (b) K or Cs

   (c) Te or Po

5. Explain in your own words why Iodine is larger than Bromine.
6. What three factors determine the trend of atomic size going down a group?
7. What groups tend to show this trend?
8. Which of the following would have the largest atomic radii?
   (a) Si

   (b) C

   (c) Sn

   (d) Pb

9. Which of the following would have the smallest atomic radius?
   (a) $2s^2$

   (b) $4s^2 4p^3$

   (c) $2s^2 2p^4$

   (d) $4s^2$

10. Arrange the following in order of increasing atomic radii: Tl, B, Ga, Al, In.
11. Arrange the following in order of increasing atomic radii: Ge, Sn, C.
12. Which of the following would be larger?
   (a) Rb or Sn

   (b) Ca or As

13. Place the following in order of increasing atomic radii: Mg, Cl, S, Na.
14. Describe the atomic size trend for the rows in the Periodic Table.
15. Draw a visual representation of the periodic table describing the trend of atomic size.
16. Which of the following would have the largest atomic radii?
   (a) Sr

   (b) Sn

   (c) Rb

   (d) In

17. Which of the following would have the smallest atomic radii?
   (a) K

   (b) Kr

   (c) Ga

   (d) Ge

18. Place the following elements in order of increasing atomic radii: In, Ca, Mg, Sb, Xe.
19. Place the following elements in order of decreasing atomic radii: Al, Ge, Sr, Bi, Cs.
20. Knowing the trend for the rows, what would you predict to be the effect on the atomic radius if an atom were to gain an electron? Use an example in your explanation.
21. Knowing the trend for the rows, what would you predict to be the effect on the atomic radius if the atom were to lose an

electron? Use an example in your explanation.

## Ionization Energy

1. Define ionization energy and show an example ionization equation.
2. Draw a visual representation of the periodic table describing the trend of ionization energy.
3. Which of the following would have the largest ionization energy?
   (a) Na

   (b) Al

   (c) H

   (d) He

4. Which of the following would have the smallest ionization energy?
   (a) K

   (b) P

   (c) S

   (d) Ca

5. Place the following elements in order of increasing ionization energy: Na, O, Ca, Ne, K.
6. Place the following elements in order of decreasing ionization energy: N, Si, S, Mg, He.
7. Using experimental data, the first ionization energy for an element was found to be 600 kJ/mol. The second ionization energy for the ion formed was found to be 1,800 kJ/mol. The third ionization energy for the ion formed was found to be 2,700 kJ/mol. The fourth ionization energy for the ion formed was found to be 11,600 kJ/mol. And finally the fifth ionization energy was found to be 15,000 kJ/mol. Write the reactions for the data represented in this question. To which group does this element belong? Explain.
8. Using electron configurations and your understanding of ionization energy, which would you predict would have higher second ionization energy: Na or Mg?
9. Comparing the first ionization energy ($IE_1$) of calcium, Ca, and magnesium, Mg, :
   (a) Ca has a higher $IE_1$ because its radius is smaller.

   (b) Mg has a higher $IE_1$ because its radius is smaller.

   (c) Ca has a higher $IE_1$ because its outer sub-shell is full.

   (d) Mg has a higher $IE_1$ because its outer sub-shell is full.

   (e) they have the same $IE_1$ because they have the same number of valence electrons.

10. Comparing the first ionization energy ($IE_1$) of beryllium, Be, and boron, B:
    (a) Be has a higher $IE_1$ because its radius is smaller.

    (b) B has a higher $IE_1$ because its radius is smaller.

    (c) Be has a higher $IE_1$ because its s sub-shell is full.

    (d) B has a higher $IE_1$ because its s sub-shell is full.

    (e) They have the same $IE_1$ because B has only one more electron than Be.

## Electron Affinity

1. Define electron affinity and show an example equation.
2. Choose the element in each pair that has the lower electron affinity:

(a) Li or N

(b) Na or Cl

(c) Ca or K

(d) Mg or F

3. Why is the electron affinity for calcium much higher than that of potassium?
4. Draw a visual representation of the periodic table describing the trend of electron affinity.
5. Which of the following would have the largest electron affinity?
   (a) Se

   (b) F

   (c) Ne

   (d) Br

6. Which of the following would have the smallest electron affinity?
   (a) Na

   (b) Ne

   (c) Al

   (d) Rb

7. Place the following elements in order of increasing electron affinity: Te, Br, S, K, Ar.
8. Place the following elements in order of decreasing electron affinity: S, Sn, Pb, F, Cs.
9. Describe the trend that would occur for electron affinities for elements in Period 3. Are there any anomalies? Explain.
10. Comparing the electron affinity (EA) of sulfur, S, and phosphorus, P:
    (a) S has a higher EA because its radius is smaller.

    (b) P has a higher EA because its radius is smaller.

    (c) S has a higher EA because its *p* sub-shell is half full.

    (d) P has a higher EA because its *p* sub-shell is half full.

    (e) they have the same EA because they are next to each other in the Periodic Table.

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# 5: IONIC BONDING AND SIMPLE IONIC COMPOUNDS

There are only 118 known chemical elements but tens of millions of known chemical compounds. Compounds can be very complex combinations of atoms, but many important compounds are fairly simple. Table salt, as we have seen, consists of only two elements: sodium and chlorine. Nevertheless, the compound has properties completely different from either elemental sodium (a chemically reactive metal) or elemental chlorine (a poisonous, green gas). We will see additional examples of such differences in this chapter as we consider how atoms combine to form compounds.


5.1: Prelude to Ionic Bonding and Simple Ionic Compounds

5.2: Two Types of Bonding

5.3: Ions

5.4: Formulas for Ionic Compounds

5.5: Ionic Nomenclature

5.6: Formula Mass

5.7: Characteristics of Ionic Compounds

5.E: Ionic Bonding and Simple Ionic Compounds (Exercises)

5.S: Ionic Bonding and Simple Ionic Compounds (Summary)


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# 5.1: Prelude to Ionic Bonding and Simple Ionic Compounds

We will see that the word salt has a specific meaning in chemistry, but to most people, this word refers to table salt. This kind of salt is used as a condiment throughout the world, but it was not always so abundant. Two thousand years ago, Roman soldiers received part of their pay as salt, which explains why the words salt and salary come from the same Latin root (salarium). Today, table salt is either mined or obtained from the evaporation of saltwater.

Table salt is sodium chloride (NaCl), which is a simple compound of two elements that are necessary for the human body to function properly. Sodium, for example, is important for nerve conduction and fluid balance. In fact, human blood is about a 0.9% sodium chloride solution, and a solution called normal saline is commonly administered intravenously in hospitals.

Although some salt in our diets is necessary to replenish the sodium and chloride ions that we excrete in urine and sweat, too much is unhealthy, and many people may be ingesting more salt than their bodies need. The RDI of sodium is 2,400 mg—the amount in about 1 teaspoon of salt—but the average intake of sodium in the United States is between 4,000 mg and 5,000 mg, partly because salt is a common additive in many prepared foods. Previously, the high ingestion of salt was thought to be associated with high blood pressure, but current research does not support this link. Even so, some doctors still recommend a low-salt diet (never a “no-salt” diet) for patients with high blood pressure, which may include using a salt substitute. Most salt substitutes use potassium instead of sodium, but some people complain that the potassium imparts a slightly bitter taste.

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# 5.2: Two Types of Bonding

## Learning Objectives

- Define the octet rule.
- Describe how ionic bonds are formed.

Atoms can join together by forming a chemical bond, which is a very strong attraction between two atoms. Chemical bonds are formed when electrons in different atoms interact with each other to make an arrangement that is more stable than when the atoms are apart.

What causes atoms to make a chemical bond with other atoms, rather than remaining as individual atoms? A clue comes by considering the noble gas elements, the rightmost column of the periodic table. These elements—helium, neon, argon, krypton, xenon, and radon—do not form compounds very easily, which suggests that they are especially stable as lone atoms. What else do the noble gas elements have in common? Except for helium, they all have eight valence electrons. Chemists have concluded that atoms are especially stable if they have eight electrons in their outermost shell. This useful rule of thumb is called the **octet rule**, and it is a key to understanding why compounds form.

> Of the noble gases, only krypton, xenon, and radon have been found to make compounds.

There are two ways for an atom that does not have an octet of valence electrons to obtain an octet in its outer shell. One way is the transfer of electrons between two atoms until all atoms have octets. Because some atoms will lose electrons and some atoms will gain electrons, there is no overall change in the number of electrons, but individual atoms acquire a nonzero electric charge. Those that lose electrons become positively charged, and those that gain electrons become negatively charged. Charged atoms are called ions. Because opposite charges attract (while like charges repel), these oppositely charged ions attract each other, forming **ionic bonds**. The resulting compounds are called **ionic compounds** and are the primary subject of this chapter.

The second way for an atom to obtain an octet of electrons is by sharing electrons with another atom. These shared electrons simultaneously occupy the outermost shell of more than one atom. The bond made by electron sharing is called a **covalent bond**.

> Despite our focus on the octet rule, we must remember that for small atoms, such as hydrogen, helium, and lithium, the first shell is, or becomes, the outermost shell and hold only two electrons. Therefore, these atoms satisfy a "**duet rule**" rather than the octet rule.

## Example 5.2.1

A sodium atom has one valence electron. Do you think it is more likely for a sodium atom to lose one electron or gain seven electrons to obtain an octet?

**Solution**

Although either event is possible, a sodium atom is more likely to lose its single valence electron. When that happens, it becomes an ion with a net positive charge. This can be illustrated as follows:

*Table explaining the solution to the example.*

| Sodium atom | | Sodium ion | |
|---|---|---|---|
| 11 protons | 11+ | 11 protons | 11+ |
| 11 electrons | 11– | 10 electrons | 10– |
| | 0 overall charge | | +1 overall charge |

**Exercise 5.2.1**

A fluorine atom has seven valence electrons. Do you think it is more likely for a fluorine atom to lose seven electrons or gain one electron to obtain an octet? Write the formula of the resulting ion.

*Answer available at the end of this section.*

## Key Takeaways

- Atoms have a tendency to have eight electrons in their valence shell.
- The attraction of oppositely charged ions is what makes ionic bonds.

## Exercises

1. What is the octet rule?

2. How are ionic bonds formed?

3. Why is an ionic compound unlikely to consist of two positively charged ions?

4. Why is an ionic compound unlikely to consist of two negatively charged ions?

5. A calcium atom has two valence electrons. Do you think it will lose two electrons or gain six electrons to obtain an octet in its outermost electron shell? Write the formula of the resulting ion.

6. An aluminum atom has three valence electrons. Do you think it will lose three electrons or gain five electrons to obtain an octet in its outermost electron shell? Write the formula of the resulting ion.

7. A selenium atom has six valence electrons. Do you think it will lose six electrons or gain two electrons to obtain an octet in its outermost electron shell? Write the formula of the resulting ion.

8. An iodine atom has seven valence electrons. Do you think it will lose seven electrons or gain one electron to obtain an octet in its outermost electron shell? Write the formula of the resulting ion.

## Answers

1. The octet rule is the concept that atoms tend to have eight electrons in their valence electron shell.

2. Ionic bonds are formed by the attraction between oppositely charged ions.

3. Positive charges repel each other, so an ionic compound is not likely between two positively charged ions.

4. Negative charges repel each other also. 5. Ca atom is more likely to lose two electrons. It will become $Ca^{2+}$ ion. 6. An Al atom is more likely to lose three electrons. It will become $Al^{3+}$ ion.

7. Selenium is more likely to gain two electrons. It will become $Se^{2-}$ ion.

8. Iodine is more likely to gain one electron. It will become $I^{-}$ ion.

## Answers

**Exercise** 5.2.1

The process that involves less number of electrons is more favorable. Fluorine would gain one electron. The formula of the resulting ion is $F^{-}$.

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# 5.3: Ions

**Learning Objectives**

- Define the two types of ions.
- Use Lewis diagrams to illustrate ion formation.

Most atoms do not have eight electrons in their valence electron shell. Some atoms have only a few electrons in their outer shell, while some atoms lack only one or two electrons to have an octet. In cases where an atom has three or fewer valence electrons, the atom may lose those valence electrons quite easily until what remains is a lower shell that contains an octet. Atoms that lose electrons acquire a positive charge as a result because they are left with fewer negatively charged electrons to balance the positive charges of the protons in the nucleus. Positively charged ions are called cations. Most metals become cations when they make ionic compounds.

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.

> The names for positive and negative ions are pronounced CAT-eye-ons (cations) and ANN-eye-ons (anions), respectively.

## Electron Transfer

We can use electron configurations to illustrate the electron transfer process between sodium atoms and chlorine atoms.

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

As demonstrated here, a sodium atom (Na) has one valence electron in the third principal energy level. It is likely to achieve an octet in its outermost shell by losing its one valence electron. The cation produced in this way, $Na^+$, is called the sodium ion to distinguish it from the element. The sodium ion, $Na^+$, has the electron configuration with an octet of electrons from the second principal energy level. It is now the same as that of the noble gas neon. The term **isoelectronic** refers to an atom and an ion of a different atom (or two different ions) that have the same electron configuration. The sodium ion is isoelectronic with the neon atom. The equation below illustrates this process.

$$\begin{array}{lcl} \mathrm{Na} & \rightarrow & \mathrm{Na^+ + e^-} \\ 1s^2\ 2s^2\ 2p^6\ 3s^1 & & 1s^2\ 2s^2\ 2p^6\ (\text{octet}) \end{array}$$

Figure $5.3.1$ is a graphical depiction of this process.

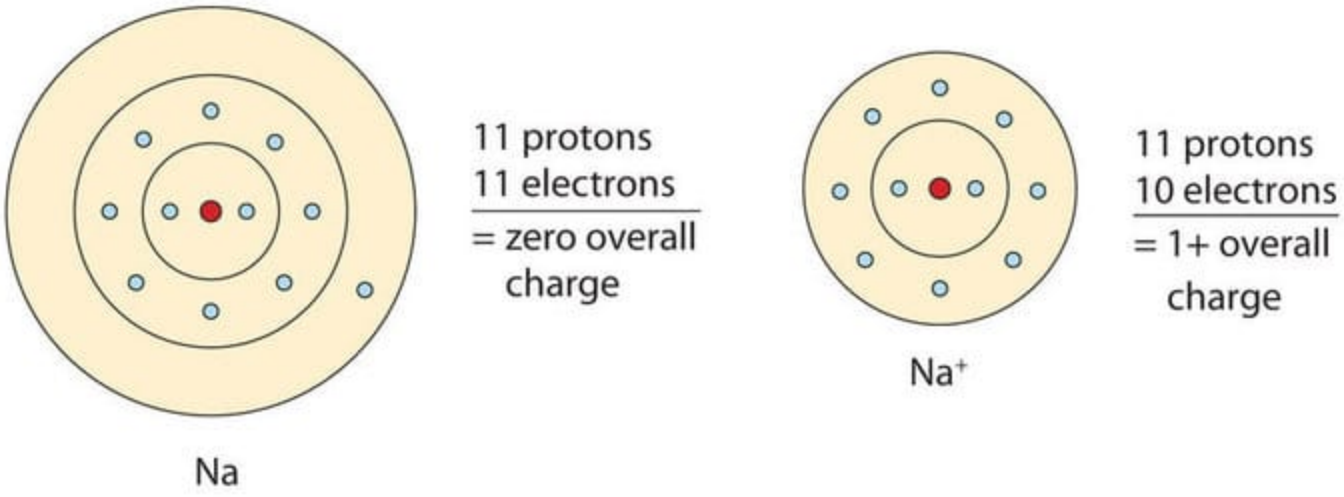



Figure 5.3.1: The Formation of a Sodium Ion. On the left, a sodium atom has 11 electrons. On the right, the sodium ion only has 10 electrons and a 1+ charge.

Now, let's consider chlorine atom, Cl: $1s^2 2s^2 2p^6 3s^2 3p^5$

Only one more electron is needed to achieve an octet in chlorine's valence shell. When a chlorine atom gains an electron, its outermost principal energy level achieves an octet. 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. This process is illustrated below. (In table salt, this electron comes from the sodium atom.)

$$\underset{1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5}{\mathrm{Cl} + \mathrm{e}^-} \rightarrow \underset{1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6 (\text{octet})}{\mathrm{Cl}^-}$$

Figure 5.3.2 is a graphical depiction of this process.

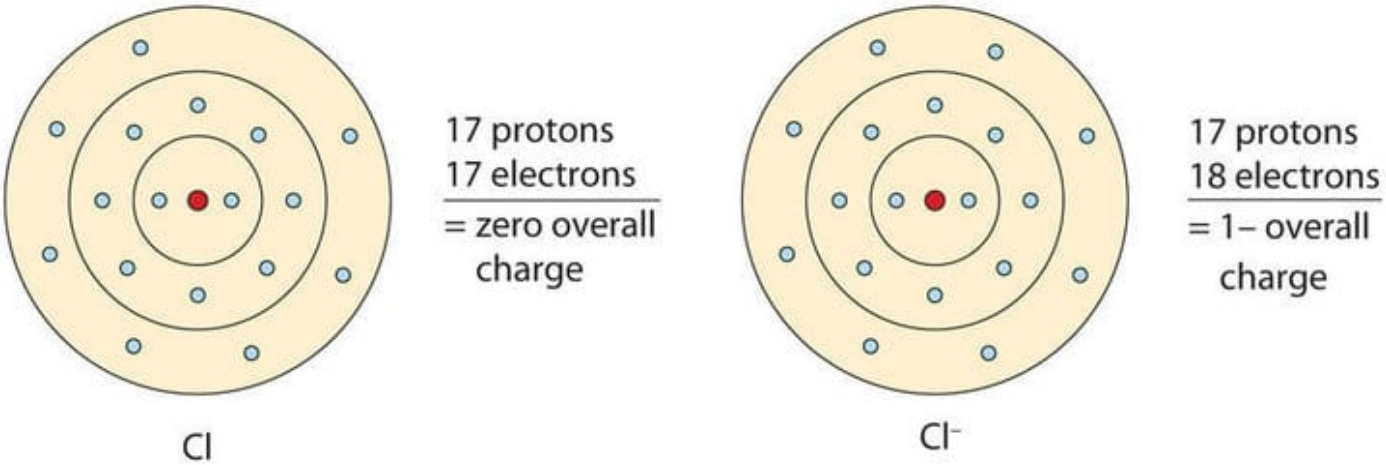



Figure 5.3.2: The Formation of a Chlorine Ion. On the left, the chlorine atom has 17 electrons. On the right, the chloride ion has 18 electrons and has a 1– charge.

With two oppositely charged ions, there is an electrostatic attraction between them because opposite charges attract. The resulting combination is the compound sodium chloride. Notice that there are no leftover electrons. The number of electrons lost by the sodium atom (one) equals the number of electrons gained by the chlorine atom (one), so the compound is electrically neutral. In macroscopic samples of sodium chloride, there are billions and billions of sodium and chloride ions, although there is

always the same number of cations and anions.

## Example 5.3.1

Write the electron configuration of aluminum atom (Z=13). How many electrons must Al lose/gain to achieve octet? Write the formula of the resulting ion and its electron configuration.

**Solution**

The electron configuration of Al atom is $1s^2 2s^2 2p^6 3s^2 3p^1$. The second shell has octet ($2s^2 2p^6$) while the valence shell has 3 electrons ($3s^2 3p^1$). Mg can achieve octet by losing the 3 valence electrons. The resulting cation is $Al^{3+}$ with electron configuration, $1s^2 2s^2 2p^6$.

## 5.3.1 Exerc

Write the electron configuration of oxygen atom (Z=8). How many electrons must O lose/gain to achieve octet? Write the formula of the resulting ion and its electron configuration.

*Answer available at the end of this section.*

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 5.3.3 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 multiply charged ion. The barium cation is written $Ba^{2+}$, not $Ba^{+2}$.

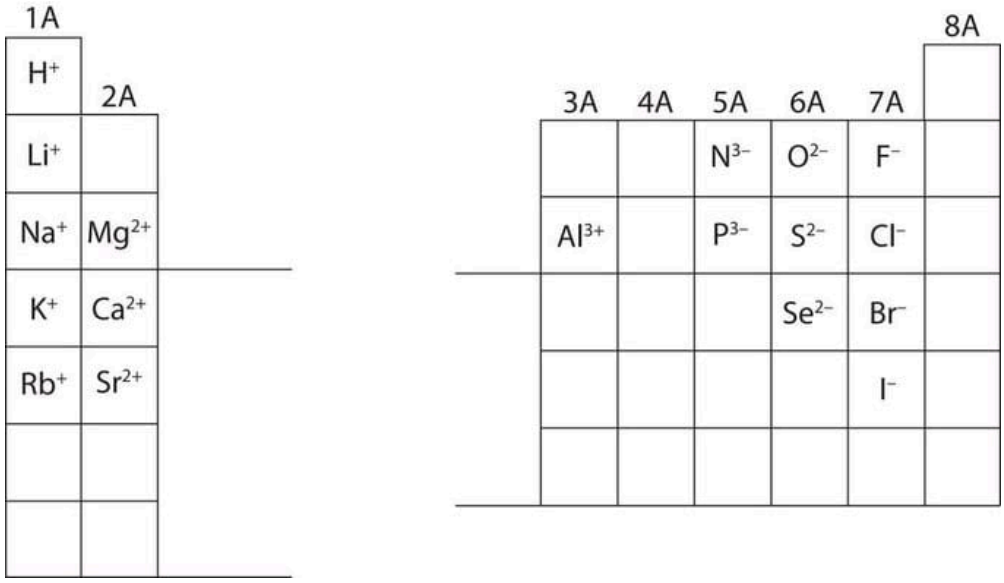



Figure 5.3.3: Predicting Ionic Charges. The charge that an atom acquires when it becomes an ion is related to the structure of the periodic table. Within a group (family) of elements, atoms form ions of a certain charge.

## Example 5.3.2

Which of these ions is *not likely* to form?

a. $Mg^{+}$
b. $K^{+}$

**Solution**

(a) Mg is in Group 2A and has two valence electrons. It achieves octet by losing two electrons to form $Mg^{2+}$ cation. Losing only one electron to form $Mg^{+}$ does not make an octet, hence, $Mg^{+}$ is not likely to form.

5.3.2 Exerc

Which of these ions is *not likely* to form?

a. $S^{3-}$
b. $N^{3-}$

*Answer available at the end of this section.*

## Lewis Diagrams

Chemists use simple diagrams to show an atom's valence electrons and how they transfer. These diagrams have two advantages over the electron shell diagrams. First, they show only valence electrons. Second, instead of having a circle around the chemical symbol to represent the electron shell, they have up to eight dots around the symbol; each dot represents a valence electron. These dots are arranged to the right and left and above and below the symbol, **with no more than two dots on a side**. For example, the representation for sodium is as follows:




and the representation for chlorine is as follows:




For the above diagrams, it does not matter what sides the dots are placed on in Lewis diagrams as long as each side has a maximum of two dots.

These diagrams are called **Lewis electron dot diagrams**, or simply Lewis diagrams, after Gilbert N. Lewis, the American chemist who introduced them. To write an element's Lewis dot symbol, place the dots representing its valence electrons, one at a time, around the element's chemical symbol. Up to four dots are placed above, below, to the left, and to the right of the symbol (in any order, as long as elements with four or fewer valence electrons have no more than one dot in each position). The next dots, for elements with more than four valence electrons, are again distributed one at a time, each paired with one of the first four. In other words, **place the dots singly on each side before pairing them**. The Lewis electron dot diagram of fluorine, for example, with seven valence electrons, is constructed as follows:

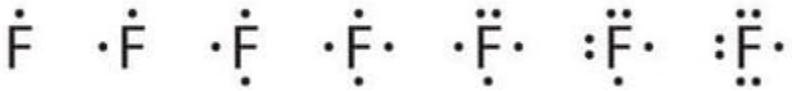


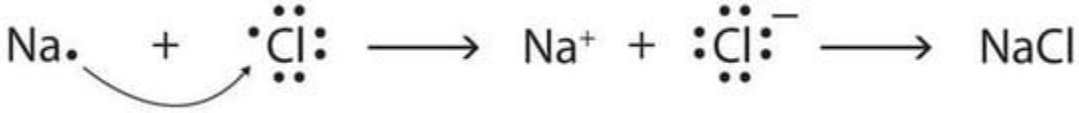

Figure 5.3.4 shows the electron configurations and Lewis diagrams of the elements lithium through neon, which is the entire second period of the periodic table. For the **main group** elements, the **number of valence electrons** is the **same as the group**

**number** listed at the top of the periodic table.




Figure 5.3.4: Lewis Electron Dot Diagrams of the Elements Lithium through Neon

The transfer of electrons can be illustrated easily with Lewis diagrams:



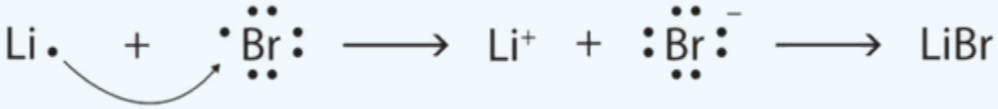

In representing the final formula, the dots are omitted.

## Example 5.3.3

Starting with lithium and bromine atoms, use Lewis diagrams to show the formation of the ionic compound LiBr.

**Solution**

From the periodic table, we see that lithium is in the same column as sodium, so it will have the same valence shell electron configuration. That means that the neutral lithium atom will have the same Lewis diagram that the sodium atom has. Similarly, bromine is in the same column as chlorine, so it will have the same Lewis diagram that chlorine has. Therefore,

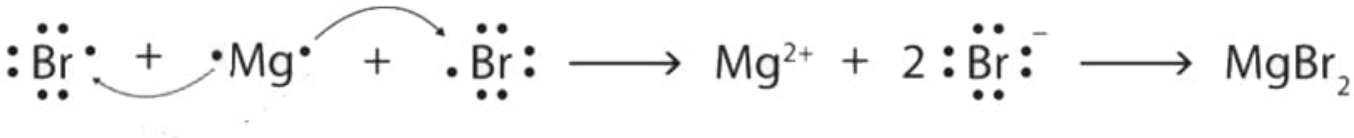



## Exercise 5.3.3

Starting with magnesium and oxygen atoms, use Lewis diagrams to show the formation of the ionic compound MgO.

*Answer available at the end of this section.*

Some ionic compounds have different numbers of cations and anions. In those cases, electron transfer occurs between more than one atom. For example, here is the formation of $MgBr_2$:




Notice that in this example there are two bromide ions (1– charge) needed for every one magnesium ion (2+ charge) in order for the overall charge of the compound to equal zero. This is called **charge balance**. The number of each type of ion is indicated in the formula by the subscript.

Most of the elements that make ionic compounds form an ion that has a characteristic charge. For example, sodium makes ionic compounds in which the sodium ion always has a 1+ charge. Chlorine makes ionic compounds in which the chloride ion always has a 1– charge. Some elements, especially transition metals, can form ions of multiple charges. Figure 5.3.5 shows the characteristic charges for some of these ions. As we saw in Figure 5.3.1, there is a pattern to the charges on many of the main group ions, but there is no simple pattern for transition metal ions (or for the larger main group elements).

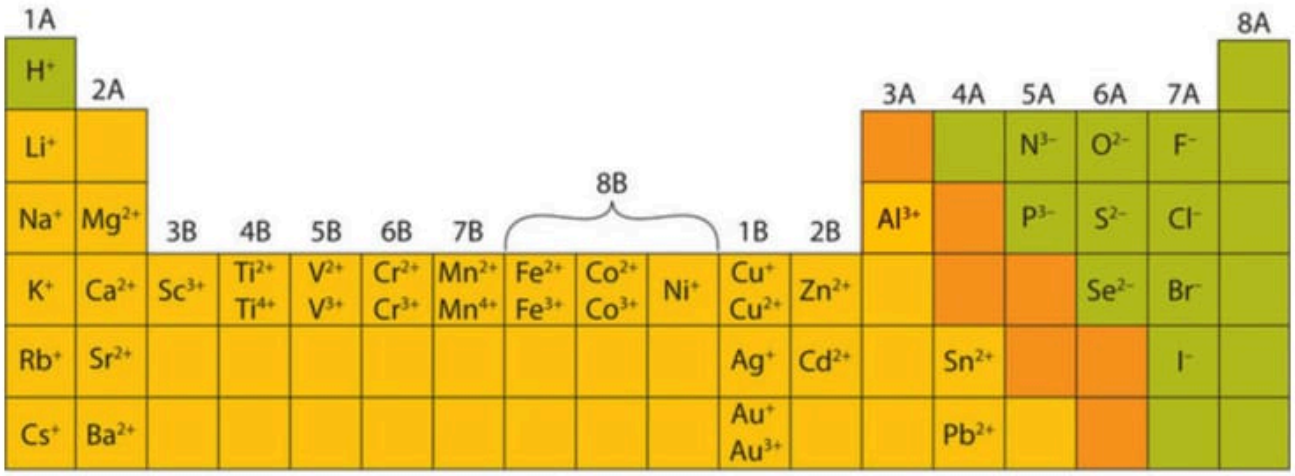



Figure 5.3.5: Charges of the Monatomic Ions. Note that some atoms commonly form ions of variable charges.

## Key Takeaways

- Ions can be positively charged or negatively charged.
- A Lewis diagram is used to show how electrons are transferred to make ions and ionic compounds.

# Exercises

1. What are the two types of ions?
2. Use Lewis diagrams to illustrate the formation of an ionic compound from a potassium atom and an iodine atom.

3. When the following atoms become ions, what charges do they acquire?

a. Li
b. S
c. Ca
d. F

4. Identify each as a cation, an anion, or neither.

a. $H^+$
b. $Cl^-$
c. $O_2$
d. $Ba^{2+}$
e. $CH_4$
f. $CS_2$

5. Identify each as a cation, an anion, or neither.

a. $NH_3$
b. $Br^-$
c. $H^-$
d. $Hg^{2+}$
e. $CCl_4$
f. $SO_3$

6. Write the electron configuration for each ion.

a. $Li^+$
b. $Mg^{2+}$
c. $F^-$
d. $S^{2-}$

7. Write the electron configuration for each ion.

a. $Na^+$
b. $Be^{2+}$
c. $Cl^-$
d. $O^{2-}$

8. Draw Lewis diagrams for the ions listed in Exercise 6. Also include Lewis diagrams for the respective neutral atoms as a comparison.

9. Draw Lewis diagrams for the ions listed in Exercise 7. Also include Lewis diagrams for the respective neutral atoms as a comparison.

10. Using Lewis diagrams, show the electron transfer for the formation of LiF.

11. Using Lewis diagrams, show the electron transfer for the formation of MgO.

12. Using Lewis diagrams, show the electron transfer for the formation of $Li_2O$.

13. Using Lewis diagrams, show the electron transfer for the formation of $CaF_2$.

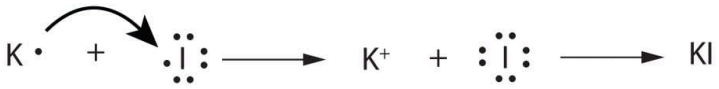
14. What characteristic charge do atoms in the first column of the periodic table have when they become ions?

15. What characteristic charge do atoms in the second column of the periodic table have when they become ions?

16. What characteristic charge do atoms in the third-to-last column of the periodic table have when they become ions?

17. What characteristic charge do atoms in the next-to-last column of the periodic table have when they become ions?

## Answers

1. Cations (positive charged) and anions (negative charged).
2. 

3. a. 1+
   b. 2–
   c. 2+
   d. 1–
4. a. cation
   b. anion
   c. neither
   d. cation
   e. neither
   f. neither
5.

a. neither
b. anion
c. anion
d. cation
e. neither
f. neither

6.

a. $1s^2$
b. $1s^2 2s^2 2p^6$
c. $1s^2 2s^2 2p^6$
d. $1s^2 2s^2 2p^6 3s^2 3p^6$

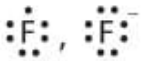
7.

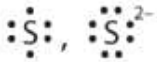
a. $1s^2 2s^2 2p^6$
b. $1s^2$
c. $1s^2 2s^2 2p^6 3s^2 3p^6$
d. $1s^2 2s^2 2p^6$

8.

a. $Li\cdot$, $Li^+$

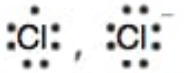
b. $\cdot Mg \cdot$, $Mg^{2+}$

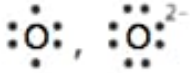
c. 

d. 

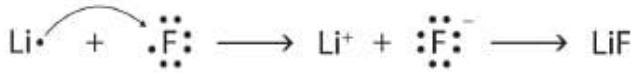
$Na\cdot$, $Na^+$

$\cdot Be \cdot$, $Be^{2+}$



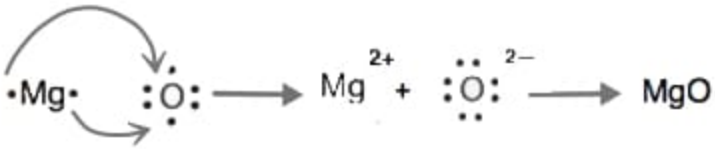


9.

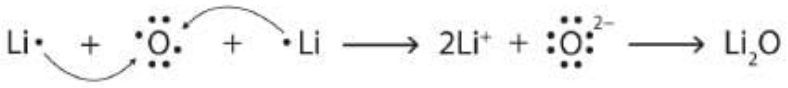


10.

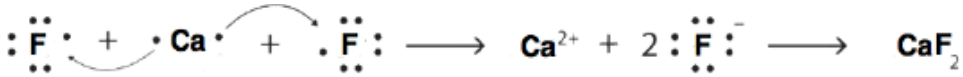
11.



12.



13.



14. 1+

15. 2+

16. 2–

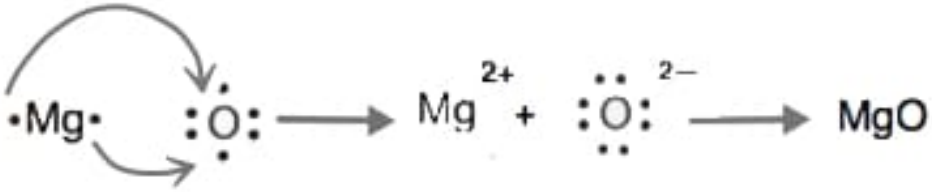
17. 1–

## Answers

The electron configuration of O atom is $1s^2 2s^2 2p^4$. The second shell has six electrons ($2s^2 2p^4$) and needs two electrons to achieve octet. Oxygen will gain 2 electrons. The resulting anion is $O^{2-}$ with electron configuration, $1s^2 2s^2 2p^6$.

(a) S is in Group 6A and has six valence electrons. It achieves octet by gaining two electrons to form $S^{2-}$ anion. Gaining three electrons to form $S^{3-}$does not make it octet, hence, $S^{3-}$ is not likely to form.

**Exercise** 5.3.3



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# 5.4: Formulas for Ionic Compounds

## Learning Objectives

- Write the chemical formula for a simple ionic compound.
- Recognize polyatomic ions in chemical formulas.

We have already encountered some chemical formulas for simple ionic compounds. A chemical formula is a concise list of the elements in a compound and the ratios of these elements. To better understand what a chemical formula means, we must consider how an ionic compound is constructed from its ions.

Ionic compounds exist as alternating positive and negative ions in regular, three-dimensional arrays called crystals (Figure $5.4.1$ ). As you can see, there are no individual $\mathrm{NaCl}$ "particles" in the array; instead, there is a continuous lattice of alternating sodium and chloride ions. However, we can use the ratio of sodium ions to chloride ions, expressed in the lowest possible whole numbers, as a way of describing the compound. In the case of sodium chloride, the ratio of sodium ions to chloride ions, expressed in lowest whole numbers, is 1:1, so we use $\mathrm{NaCl}$ (one $\mathrm{Na}$ symbol and one $\mathrm{Cl}$ symbol) to represent the compound. Thus, $\mathrm{NaCl}$ is the chemical formula for sodium chloride, which is a concise way of describing the relative number of different ions in the compound. A macroscopic sample is composed of myriads of NaCl pairs; each individual pair called a **formula unit**. Although it is convenient to think that $\mathrm{NaCl}$ crystals are composed of individual $\mathrm{NaCl}$ units, Figure $5.4.1$ shows that no single ion is exclusively associated with any other single ion. Each ion is surrounded by ions of opposite charge.

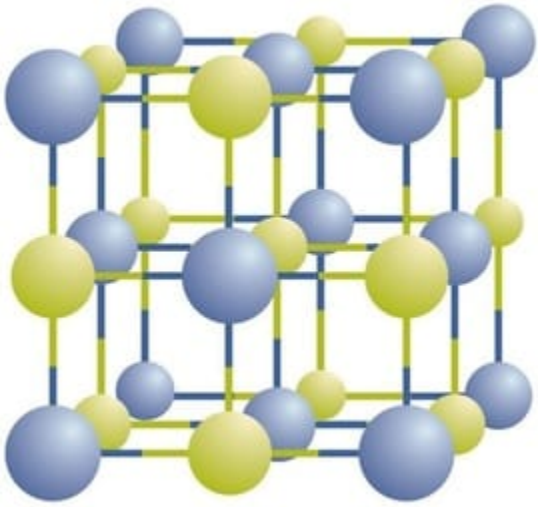


Figure $5.4.1$: A Sodium Chloride Crystal. A crystal contains a three-dimensional array of alternating positive and negative ions. The precise pattern depends on the compound. A crystal of sodium chloride, shown here, is a collection of alternating sodium and chlorine ions.

The formula for an ionic compound follows several conventions. First, the **cation** is written **before** the **anion**. Because most metals form cations and most nonmetals form anions, formulas typically list the metal first and then the nonmetal. Second, **charges** are **not written** in a formula. Remember that in an ionic compound, the component species are ions, not neutral atoms, even though the formula does not contain charges. Finally, the proper formula for an ionic compound always has ***a net zero charge,*** meaning the total positive charge must equal the total negative charge. To determine the proper formula of any combination of ions, determine how many of each ion is needed to balance the total positive and negative charges in the compound.

This rule is ultimately based on the fact that matter is, overall, electrically neutral.

> By convention, assume that there is only one atom if a subscript is not present. We do not use 1 as a subscript.

If we look at the ionic compound consisting of lithium ions and bromide ions, we see that the lithium ion has a 1+ charge and the

bromide ion has a 1– charge. Only one ion of each is needed to balance these charges. The formula for lithium bromide is $\mathrm{LiBr}$.

When an ionic compound is formed from magnesium and oxygen, the magnesium ion has a 2+ charge, and the oxygen atom has a 2– charge. Although both of these ions have higher charges than the ions in lithium bromide, they still balance each other in a one-to-one ratio. Therefore, the proper formula for this ionic compound is $\mathrm{MgO}$.

Now consider the ionic compound formed by magnesium and chlorine. A magnesium ion has a 2+ charge, while a chlorine ion has a 1– charge:

$$\mathrm{Mg^{2+}Cl^{-}}$$

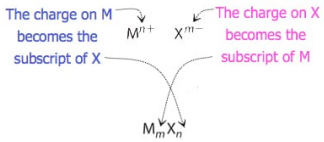
Combining one ion of each does not completely balance the positive and negative charges. The easiest way to balance these charges is to assume the presence of *two* chloride ions for each magnesium ion:

$$\mathrm{Mg^{2+}\ Cl^{-}\ Cl^{-}}$$

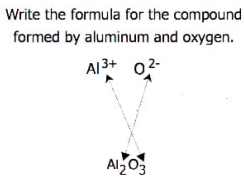
Now the positive and negative charges are balanced. We could write the chemical formula for this ionic compound as $\mathrm{MgClCl}$, but the convention is to use a numerical subscript when there is more than one ion of a given type—$\mathrm{MgCl_2}$. This chemical formula says that there are one magnesium ion and *two* chloride ions in this formula. (Do not read the "$\mathrm{Cl_2}$" part of the formula as a molecule of the diatomic elemental chlorine. Chlorine does not exist as a diatomic element in this compound. Rather, it exists as two individual chloride ions.) By convention, the **lowest whole number ratio** is used in the formulas of ionic compounds. The formula $\mathrm{Mg_2Cl_4}$ has balanced charges with the ions in a 1:2 ratio, but it is not the lowest whole number ratio.

> By convention, the lowest whole-number ratio of the ions is used in ionic formulas. There are exceptions for certain ions, such as $\mathrm{Hg_2^{2+}}$.

For compounds in which the ratio of ions is not as obvious, the subscripts in the formula can be obtained by **crossing charges**: use the absolute value of the charge on one ion as the subscript for the other ion. This method is shown schematically in Figure 3.3.2.




The image shows M with a charge of n+ and X with a charge of m-. The charge on the M becomes the subscript of X, and the charge on X becomes the subscript of M, making the final product M subscript m X subscript n.




The image asks to write the formula for the compound formed by aluminum and oxygen. It shows Al with a charge of 3+ and O with a charge of 2-. By crossing charges, the final result is Al subscript 2 O subscript 3.

Figure 5.4.2: Crossing charges. One method for obtaining subscripts in the empirical formula is by crossing charges.

When crossing charges, it is sometimes necessary to reduce the subscripts to their simplest ratio to write the empirical formula. Consider, for example, the compound formed by $Pb^{4+}$ and $O^{2-}$. Using the absolute values of the charges on the ions as subscripts gives the formula $Pb_2O_4$. This simplifies to its correct empirical formula **$PbO_2$**. The empirical formula has one $Pb^{4+}$ ion and two $O^{2-}$ ions.

## Example 5.4.1

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

a. the sodium ion and the sulfur ion

b. the aluminum ion and the fluoride ion
c. the 3+ iron ion and the oxygen ion

**Solution**

a. To obtain a valence shell octet, sodium forms an ion with a 1+ charge, while the sulfur ion has a 2– charge. Two sodium 1+ ions are needed to balance the 2– charge on the sulfur ion. Rather than writing the formula as $\mathrm{NaNaS}$, we shorten it by convention to $\mathrm{Na_2S}$.
b. The aluminum ion has a 3+ charge, while the fluoride ion formed by fluorine has a 1– charge. Three fluorine 1– ions are needed to balance the 3+ charge on the aluminum ion. This combination is written as $\mathrm{AlF_3}$.
c. Iron can form two possible ions, but the ion with a 3+ charge is specified here. The oxygen atom has a 2– charge as an ion. To balance the positive and negative charges, we look to the least common multiple—6: two iron 3+ ions will give 6+, while three 2– oxygen ions will give 6–, thereby balancing the overall positive and negative charges. Thus, the formula for this ionic compound is $\mathrm{Fe_2O_3}$. Alternatively, use the crossing charges method shown in Figure 3.3.2.

## Exercise 5.4.1

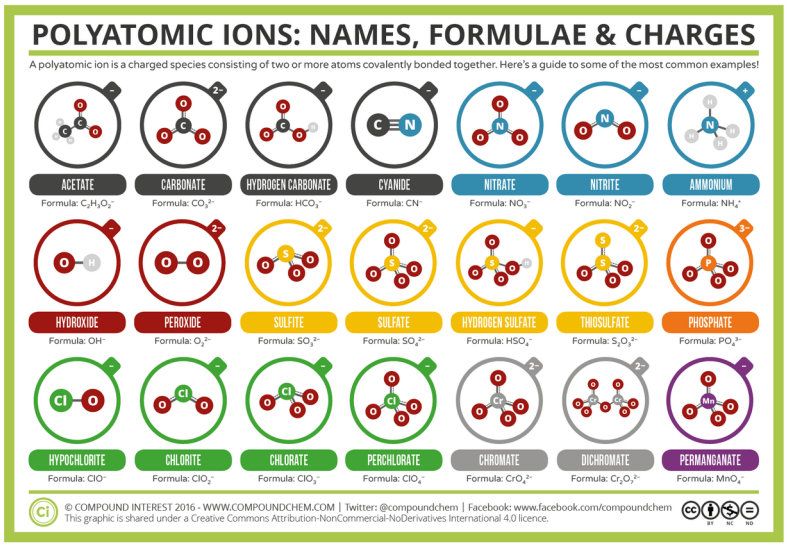
Write the chemical formula for an ionic compound composed of each pair of ions.

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: available at the end of this section.*

# Polyatomic Ions

Some ions consist of groups of atoms ***covalently*** bonded together and have an **overall electric charge**. Because these ions contain more than one atom, they are called polyatomic ions. The Lewis structures, names and formulas of some polyatomic ions are found in Table 3.3.1.




## *Some Polyatomic Ions*

Polyatomic ions have defined formulas, names, and charges that cannot be modified in any way. Table 5.4.2 lists the ion names and ion formulas of the most common polyatomic ions. For example, $\mathrm{NO_3^-}$ is the nitrate ion; it has one nitrogen atom and three

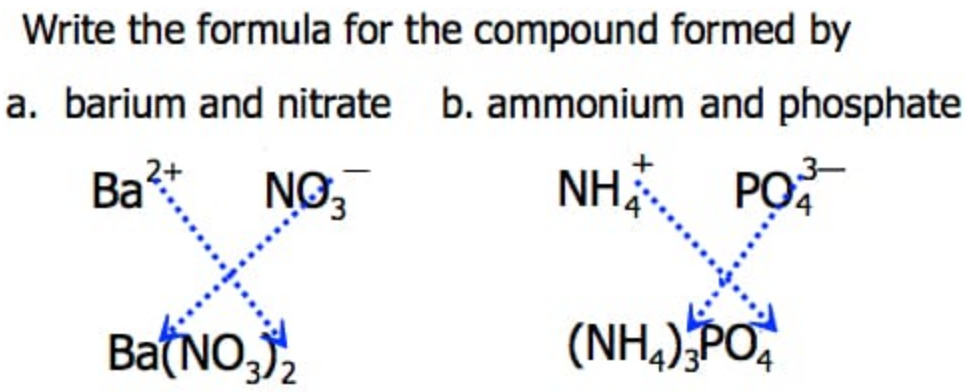
oxygen atoms and an overall 1– charge. Figure 5.4.2 lists the most common polyatomic ions.

*Table 5.4.2: Ion Names and Ion Formulas of Common Polyatomic Ions*

| Ion Name | Ion Formula |
|---|---|
| ammonium ion | $NH_4^{+1}$ |
| hydroxide ion | $OH^{-1}$ |
| cyanide ion | $CN^{-1}$ |
| carbonate ion | $CO_3^{-2}$ |
| bicarbonate or hydrogen carbonate | $HCO_3^-$ |
| acetate ion | $C_2H_3O_2^{-1}$ **or** $CH_3CO_2^{-1}$ |
| nitrate ion | $NO_3^{-1}$ |
| nitrite ion | $NO_2^{-1}$ |
| sulfate ion | $SO_4^{-2}$ |
| sulfite ion | $SO_3^{-2}$ |
| phosphate ion | $PO_4^{-3}$ |
| phosphite ion | $PO_3^{-3}$ |

Note that only one polyatomic ion in this Table, the ammonium ion ($NH_4^{+1)}$, is a cation. This polyatomic ion contains one nitrogen and four hydrogens that collectively bear a +1 charge. The remaining polyatomic ions are all negatively-charged and, therefore, are classified as anions. However, only two of these, the hydroxide ion and the cyanide ion, are named using the "-ide" suffix that is typically indicative of negatively-charged particles. The remaining polyatomic anions, which all contain oxygen, in combination with another non-metal, exist as part of a series in which the number of oxygens within the polyatomic unit can vary. As has been repeatedly emphasized in several sections of this text, no two chemical formulas should share a common chemical name. A single suffix, "-ide," is insufficient for distinguishing the names of the anions in a related polyatomic series. Therefore, "-ate" and "-ite" suffixes are employed, in order to denote that the corresponding polyatomic ions are part of a series. Additionally, these suffixes also indicate the relative number of oxygens that are contained within the polyatomic ions. Note that all of the polyatomic ions whose names end in "-ate" contain one more oxygen than those polyatomic anions whose names end in "-ite." Unfortunately, much like the common system for naming transition metals, these suffixes only indicate the *relative* number of oxygens that are contained within the polyatomic ions. For example, the nitrate ion, which is symbolized as $NO_3^{-1}$, has one more oxygen than the nitrite ion, which is symbolized as $NO_2^{-1}$. However, the sulfate ion is symbolized as $SO_4^{-2}$. While both the nitrate ion and the sulfate ion share an "-ate" suffix, the former contains three oxygens, but the latter contains four. Additionally, both the nitrate ion and the sulfite ion contain three oxygens, but these polyatomic ions do not share a common suffix. Unfortunately, the relative nature of these suffixes mandates that the ion formula/ion name combinations of the polyatomic ions must simply be memorized.

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. Two examples are shown below:




The image asks a two-part question: Write the formula for the compound formed by (a) barium and nitrate, and (b) ammonium and phosphate. For (a), Ba has a charge of 2+ and $NO_3$ has a charge of -1. By crossing charges, the formula is $Ba(NO_3)_2$. For (b), $NH_4$ has a charge of +1 and $PO_4$ has a charge of 3-, so by crossing charges the formula is $(NH_4)_3PO_4$.

### Example 5.4.2

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

a. the potassium ion and the sulfate ion
b. the calcium ion and the nitrate ion

**Solution**

a. 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 $\mathrm{K_2SO_4}$.
b. Calcium ions have a charge of 2+, while nitrate ions have a charge of 1–. We will need two nitrate ions to balance the charge on each calcium ion. The formula for nitrate must be enclosed in parentheses. Thus, we write $\mathrm{Ca(NO_3)_2}$ as the formula for this ionic compound.

### Exercise 5.4.2

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: available at the end of this section.*

## Recognizing Ionic Compounds

There are two ways to recognize ionic compounds. First, compounds between **metal and nonmetal** elements are usually **ionic**. For example, $CaBr_2$ contains a metallic element (calcium, a group 2A metal) and a nonmetallic element (bromine, a group 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 5A, and oxygen, from group 6A). It is not an ionic compound; it belongs to the category of covalent compounds discuss elsewhere. Also note that this combination of nitrogen and oxygen has no electric charge specified, so it is *not* the nitrite ion.

Second, if you recognize the formula of a **polyatomic ion** in a compound, the compound is **ionic**. For example, if you see the formula $\mathrm{Ba(NO_3)_2}$, you may recognize the "$NO_3$" part as the nitrate ion, $\mathrm{NO_3^-}$. (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, $\mathrm{Ba}$, is actually the $\mathrm{Ba^{2+}}$

ion, with the 2+ charge balancing the overall 2– charge from the two nitrate ions. Thus, this compound is also ionic.

## Example 5.4.3

Identify each compound as ionic or not ionic.

a. $\mathrm{Na_2O}$
b. $\mathrm{PCl_3}$
c. $\mathrm{NH_4Cl}$
d. $\mathrm{OF_2}$

**Solution**

a. Sodium is a metal, and oxygen is a nonmetal; therefore, $\mathrm{Na_2O}$ is expected to be ionic.
b. Both phosphorus and chlorine are nonmetals. Therefore, $\mathrm{PCl_3}$ is not ionic.
c. The $\mathrm{NH_4}$ in the formula represents the ammonium ion, $\mathrm{NH_4^+}$, which indicates that this compound is ionic.
d. Both oxygen and fluorine are nonmetals. Therefore, $\mathrm{OF_2}$ is not ionic.

## Exercise 5.4.3

Identify each compound as ionic or not ionic.

a. $\mathrm{N_2O}$
b. $\mathrm{FeCl_3}$
c. $\mathrm{(NH_4)_3PO_4}$
d. $\mathrm{SOCl_2}$

*Answer a: available at the end of this section.*

## Looking Closer: Blood and Seawater

Science has long recognized that blood and seawater have similar compositions. After all, both liquids have ionic compounds dissolved in them. The similarity may be more than mere coincidence; many scientists think that the first forms of life on Earth arose in the oceans. A closer look, however, shows that blood and seawater are quite different. A 0.9% solution of sodium chloride approximates the salt concentration found in blood. In contrast, seawater is principally a 3% sodium chloride solution, over three times the concentration in blood. Here is a comparison of the amounts of ions in blood and seawater:

*Table showing a comparison of the amounts of ions in blood and seawater.*

| Ion | Percent in Seawater | Percent in Blood |
|---|---|---|
| $\mathrm{Na^+}$ | 2.36 | 0.322 |
| $\mathrm{Cl^-}$ | 1.94 | 0.366 |
| $\mathrm{Mg^{2+}}$ | 0.13 | 0.002 |
| $\mathrm{SO_4^{2-}}$ | 0.09 | — |
| $\mathrm{K^+}$ | 0.04 | 0.016 |
| $\mathrm{Ca^{2+}}$ | 0.04 | 0.0096 |
| $\mathrm{HCO_3^-}$ | 0.002 | 0.165 |
| $\mathrm{HPO_4^{2-}}$, $\mathrm{H_2PO_4^-}$ | — | 0.01 |

Most ions are more abundant in seawater than they are in blood, with some important exceptions. There are far more hydrogen carbonate ions ($HCO_3^-$) in blood than in seawater. This difference is significant because the hydrogen carbonate ion and some related ions have a crucial role in controlling the acid-base properties of blood. The amount of hydrogen phosphate ions—$HPO_4^{2-}$ and $H_2PO_4^-$—in seawater is very low, but they are present in higher amounts in blood, where they also affect acid-base properties. Another notable difference is that blood does not have significant amounts of the sulfate ion ($SO_4^{2-}$), but this ion is present in seawater.

## Key Takeaways

- Proper chemical formulas for ionic compounds balance the total positive charge with the total negative charge.
- Groups of atoms with an overall charge, called polyatomic ions, also exist.

## EXERCISES

1. What information is contained in the formula of an ionic compound?

- Why do the chemical formulas for some ionic compounds contain subscripts, while others do not?

3. Write the chemical formula for the ionic compound formed by each pair of ions.

   a. $Mg^{2+}$ and $I^-$
   b. $Na^+$ and $O^{2-}$

4. Write the chemical formula for the ionic compound formed by each pair of ions.

   a. $Na^+$ and $Br^-$
   b. $Mg^{2+}$ and $Br^-$
   c. $Mg^{2+}$ and $S^{2-}$

5. Write the chemical formula for the ionic compound formed by each pair of ions.

   a. $K^+$ and $Cl^-$
   b. $Mg^{2+}$ and $Cl^-$
   c. $Mg^{2+}$ and $Se^{2-}$

6. Write the chemical formula for the ionic compound formed by each pair of ions.

   a. $Na^+$ and $N^{3-}$
   b. $Mg^{2+}$ and $N^{3-}$
   c. $Al^{3+}$ and $S^{2-}$

7. Write the chemical formula for the ionic compound formed by each pair of ions.

   a. $Li^+$ and $N^{3-}$
   b. $Mg^{2+}$ and $P^{3-}$
   c. $Li^+$ and $P^{3-}$

8. Write the chemical formula for the ionic compound formed by each pair of ions.

   a. $Fe^{3+}$ and $Br^-$
   b. $Fe^{2+}$ and $Br^-$
   c. $Au^{3+}$ and $S^{2-}$
   d. $Au^+$ and $S^{2-}$

9. Write the chemical formula for the ionic compound formed by each pair of ions.

a. $Cr^{3+}$ and $O^{2-}$
b. $Cr^{2+}$ and $O^{2-}$
c. $Pb^{2+}$ and $Cl^{-}$
d. $Pb^{4+}$ and $Cl^{-}$

10. Write the chemical formula for the ionic compound formed by each pair of ions.

a. $Cr^{3+}$ and $NO_3^{-}$
b. $Fe^{2+}$ and $PO_4^{3-}$
c. $Ca^{2+}$ and $CrO_4^{2-}$
d. $Al^{3+}$ and $OH^{-}$

11. Write the chemical formula for the ionic compound formed by each pair of ions.

a. $NH_4^{+}$ and $NO_3^{-}$
b. $H^{+}$ and $Cr_2O_7^{2-}$
c. $Cu^{+}$ and $CO_3^{2-}$
d. $Na^{+}$ and $HCO_3^{-}$

12. For each pair of elements, determine the charge for their ions and write the proper formula for the resulting ionic compound between them.

a. Ba and S
b. Cs and I

13. For each pair of elements, determine the charge for their ions and write the proper formula for the resulting ionic compound between them.

a. K and S
b. Sc and Br

14. Which compounds would you predict to be ionic?

a. $Li_2O$
b. $(NH_4)_2O$
c. $CO_2$
d. $FeSO_3$
e. $C_6H_6$
f. $C_2H_6O$

15. Which compounds would you predict to be ionic?

a. $Ba(OH)_2$
b. $CH_2O$
c. $NH_2CONH_2$
d. $(NH_4)_2CrO_4$
e. $C_8H_{18}$
f. $NH_3$

## Answers

1. the ratio of each kind of ion in the compound

2. Sometimes more than one ion is needed to balance the charge on the other ion in an ionic compound.

3.

a. $MgI_2$
b. $Na_2O$

4.

a. NaBr
b. $MgBr_2$
c. MgS

5.

a. KCl
b. $MgCl_2$
c. MgSe

6.

a. $Na_3N$
b. $Mg_3N_2$
c. $Al_2S_3$

7.

a. $Li_3N$
b. $Mg_3P_2$
c. $Li_3P$

8.

a. $FeBr_3$
b. $FeBr_2$
c. $Au_2S_3$
d. $Au_2S$

9.

a. $Cr_2O_3$
b. CrO
c. $PbCl_2$
d. $PbCl_4$

10.

a. $Cr(NO_3)_3$
b. $Fe_3(PO_4)_2$
c. $CaCrO_4$
d. $Al(OH)_3$

11.

a. $NH_4NO_3$
b. $H_2Cr_2O_7$
c. $Cu_2CO_3$
d. $NaHCO_3$

12.

a. $Ba^{2+}$, $S^{2-}$, BaS
b. $Cs^{+}$, $I^{-}$, CsI

13.

a. $K^{+}$, $S^{2-}$, $K_2S$
b. $Sc^{3+}$, $Br^{-}$, $ScBr_3$

14.

a. ionic
b. ionic
c. not ionic
d. ionic
e. not ionic
f. not ionic

15.

a. ionic
b. not ionic
c. not ionic
d. ionic
e. not ionic
f. not ionic

## Answers

**Exercise** 5.4.1

CaO
CuS
$Cu_2S$

**Exercise** 5.4.2

$Mg^{2+}$ and $CO_3^{2-}$ = $MgCO_3$

$Al^{3+}$ and $C_2H_3O_2^{-}$ = $Al(C_2H_3O_2)_3$

**Exercise** 5.4.3

not ionic
ionic
ionic
not ionic

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# 5.5: Ionic Nomenclature

**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 a 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. 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 5.5.1: The Common System of Cation Names*

| Element | Stem | Charge | Name |
|---|---|---|---|
| iron | ferr- | 2+ | ferrous ion |
| | | 3+ | ferric ion |
| copper | cupr- | 1+ | cuprous ion |
| | | 2+ | cupric ion |
| tin | stann- | 2+ | stannous ion |
| | | 4+ | stannic ion |
| lead | plumb- | 2+ | plumbous ion |
| | | 4+ | plumbic ion |
| chromium | chrom- | 2+ | chromous ion |
| | | 3+ | chromic ion |
| gold | aur- | 1+ | aurous ion |
| | | 3+ | 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 5.5.1 lists the elements that use the common system, along with their respective cation names.

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 5.5.2 lists the names of some common monatomic ions.

*Table 5.5.2: Some Monatomic Anions*

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

The polyatomic ions have their own characteristic names, as discussed earlier.

## Example 5.5.1

Name each ion.

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

*Answer a available at the end of this section.*

## Exercise 5.5.1

Name each ion.

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

*Answer a available at the end of this section.*

## Example 5.5.2

Write the formula for each ion.

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

*Answer a available at the end of this section.*

**Exercise 5.5.2**

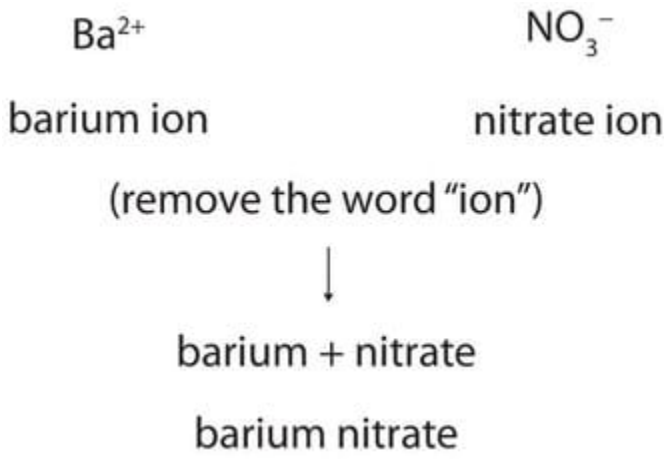
Write the formula for each ion.

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

*Answer a available at the end of this section.*

## Naming Compounds

Now that we know how to name ions, we are ready to name ionic compounds. We do so by placing the name of the cation first, followed by the name of the anion, and dropping the word *ion* from both parts. For example, what is the name of the compound whose formula is $\mathrm{Ba(NO_3)_2}$?




The compound's name does not indicate that there are two nitrate ions for every barium ion. You must determine the relative numbers of ions by balancing the positive and negative charges.

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 $\mathrm{FeCl_2}$ and $\mathrm{FeCl_3}$. In the first compound, the iron ion has a 2+ charge because there are two $\mathrm{Cl^-}$ 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 $\mathrm{Cl^-}$ 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. If we were to use the stems and suffixes of the common system, the names would be ferrous chloride and ferric chloride, respectively.

**Example 5.5.3**

Name each ionic compound, using both Stock and common systems if necessary.

a. $Ca_3(PO_4)_2$
b. $(NH_4)_2Cr_2O_7$
c. KCl
d. CuCl
e. $SnF_2$

*Answer a available at the end of this section.*

## Exercise 5.5.3

Name each ionic compound, using both Stock and common systems if necessary.

a. $ZnBr_2$
b. $Fe(NO_3)_3$
c. $Al_2O_3$
d. $CuF_2$
e. AgF

*Answer a available at the end of this section.*

Figure 5.5.1 is a synopsis of how to name simple ionic compounds.

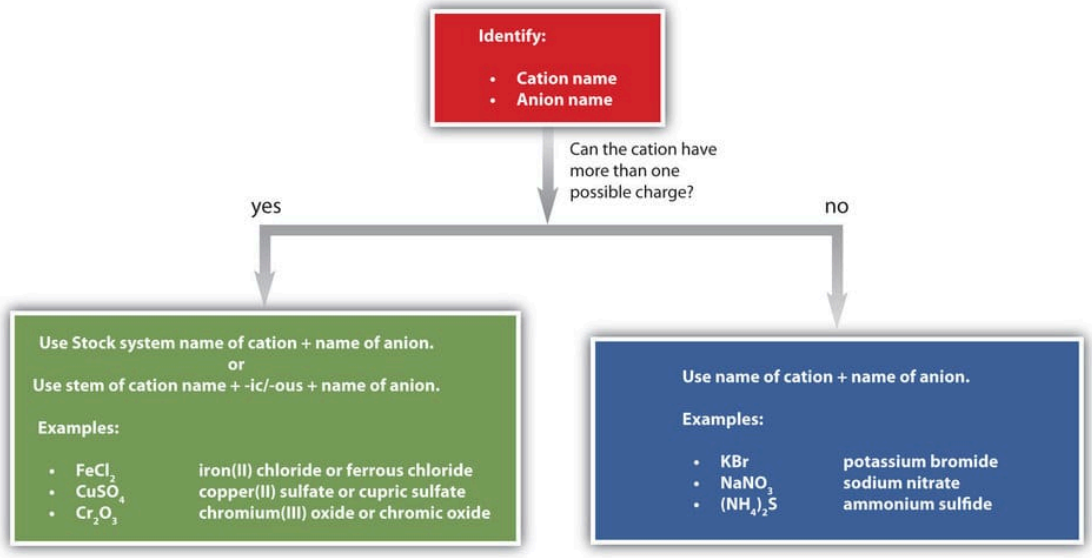



Figure 5.5.1: A Guide to Naming Simple Ionic Compounds. Follow these steps to name a simple ionic compound.

Identify the cation name and the anion name. If the cation can have more than one possible charge, either use the Stock system name of the cation and name of the anion, or use the stem of the cation name and -ic/-ous and the name of the anion. Examples of this would be $FeCl_2$, which is iron(II) chloride of ferrous chloride, $CuSO_4$, which is copper(II) sulfate or cupric sulfate, and $Cr_2O_3$, which is chromium(III) oxide or chromic oxide. If the cation can not have more than one possible charge, use the name of the cation and the name of the anion. Examples of this would be KBr, which is potassium bromide, $NaNO_3$, which is sodium nitrate, and $(NH_4)_2S$, which is ammonium sulfide.

# KEY TAKEAWAY

- Each ionic compound has its own unique name that comes from the names of the ions.

# EXERCISES

1. Briefly describe the process for naming an ionic compound.

- In what order do the names of ions appear in the names of ionic compounds?

3. Which ionic compounds can be named using two different systems? Give an example.

4. Name each ion.

a. $Ra^{2+}$
b. $P^{3-}$
c. $H_2PO_4^-$
d. $Sn^{4+}$

5. Name each ion.

a. $Cs^+$
b. $As^{3-}$
c. $HSO_4^-$
d. $Sn^{2+}$

6. Name the ionic compound formed by each pair of ions.

a. $Na^+$ and $Br^-$
b. $Mg^{2+}$ and $Br^-$
c. $Mg^{2+}$ and $S^{2-}$

7. Name the ionic compound formed by each pair of ions.

a. $K^+$ and $Cl^-$
b. $Mg^{2+}$ and $Cl^-$
c. $Mg^{2+}$ and $Se^{2-}$

8. Name the ionic compound formed by each pair of ions.

a. $Na^+$ and $N^{3-}$
b. $Mg^{2+}$ and $N^{3-}$
c. $Al^{3+}$ and $S^{2-}$

9. Name the ionic compound formed by each pair of ions.

a. $Li^+$ and $N^{3-}$
b. $Mg^{2+}$ and $P^{3-}$
c. $Li^+$ and $P^{3-}$

10. Name the ionic compound formed by each pair of ions. Use both the Stock and common systems, where appropriate.

a. $Fe^{3+}$ and $Br^-$
b. $Fe^{2+}$ and $Br^-$
c. $Au^{3+}$ and $S^{2-}$
d. $Au^+$ and $S^{2-}$

11. Name the ionic compound formed by each pair of ions. Use both the Stock and common systems, where appropriate.

    a. $Cr^{3+}$ and $O^{2-}$
    b. $Cr^{2+}$ and $O^{2-}$
    c. $Pb^{2+}$ and $Cl^{-}$
    d. $Pb^{4+}$ and $Cl^{-}$

12. Name the ionic compound formed by each pair of ions. Use both the Stock and common systems, where appropriate.

    a. $Cr^{3+}$ and $NO_3^{-}$
    b. $Fe^{2+}$ and $PO_4^{3-}$
    c. $Ca^{2+}$ and $CrO_4^{2-}$
    d. $Al^{3+}$ and $OH^{-}$

13. Name the ionic compound formed by each pair of ions. Use both the Stock and common systems, where appropriate.

    a. $NH_4^{+}$ and $NO_3^{-}$
    b. $K^{+}$ and $Cr_2O_7^{2-}$
    c. $Cu^{+}$ and $CO_3^{2-}$
    d. $Na^{+}$ and $HCO_3^{-}$

14. Give two names for each compound.

    a. $Al(HSO_4)_3$
    b. $Mg(HSO_4)_2$

15. Give two names for each compound.

    a. $Co(HCO_3)_2$
    b. $LiHCO_3$

## AnswerS

1. Name the cation and then the anion but don't use numerical prefixes.
2. the cation name followed by the anion name
3. Ionic compounds in which the cation can have more than one possible charge have two naming systems. $FeCl_3$ is either iron(III) chloride or ferric chloride (answers will vary).

4.

    a. the radium ion
    b. the phosphide ion
    c. the dihydrogen phosphate ion
    d. the tin(IV) ion or the stannic ion

5.

    a. the cesium ion
    b. the arsenide ion
    c. the hydrogen sulfate ion
    d. the tin(II) ion or the stannous ion

6.

    a. sodium bromide

b. magnesium bromide
c. magnesium sulfide

7.

a. potassium chloride
b. magnesium chloride
c. magnesium selenide

8.

a. sodium nitride
b. magnesium nitride
c. aluminum sulfide

9.

a. lithium nitride
b. magnesium phosphide
c. lithium phosphide

10.

a. iron(III) bromide or ferric bromide
b. iron(II) bromide or ferrous bromide
c. gold(III) sulfide or auric sulfide
d. gold(I) sulfide or aurous sulfide

11.

a. chromium(III) oxide or chromic oxide
b. chromium(II) oxide or chromous oxide
c. lead(II) chloride or plumbous chloride
d. lead(IV) chloride or plumbic chloride

12.

a. chromium(III) nitrate or chromic nitrate
b. iron(II) phosphate or ferrous phosphate
c. calcium chromate
d. aluminum hydroxide

13.

a. ammonium nitrate
b. potassium dichromate
c. copper(I) carbonate or cuprous carbonate
d. sodium hydrogen carbonate or sodium bicarbonate

14.

a. aluminum hydrogen sulfate or aluminum bisulfate
b. magnesium hydrogen sulfate or magnesium bisulfate

15.

a. cobalt hydrogen carbonate or cobalt bicarbonate
b. lithium hydrogen carbonate or lithium bicarbonate

## Answers

**Example** 5.5.1

the calcium ion
the sulfide ion (from Table 5.5.2 )
the sulfite ion
the ammonium ion
the copper(I) ion or the cuprous ion (copper can form cations with either a 1+ or 2+ charge, so we have to specify which charge this ion has

**Exercise** 5.5.1

the iron (II) or ferrous ion
the iron (III) or ferric ion
the sulfate ion
the barium ion
the bicarbonate ion or hydrogen carbonate ion

**Example** 5.5.2

$Br^-$
$PO_4^{3-}$
$Cu^{2+}$
$Mg^{2+}$

**Exercise** 5.5.2

$F^-$
$CO_3^{2-}$
$Fe^{2+}$
$K^+$

**Example** 5.5.3

calcium phosphate
ammonium dichromate (the prefix *di-* is part of the name of the anion)
potassium chloride
copper(I) chloride or cuprous chloride
tin(II) fluoride or stannous fluoride

**Exercise** 5.5.3

zinc bromide
iron (III) nitrate or ferric nitrate
aluminum oxide
copper (II) fluoride or cupric fluoride
silver fluoride

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# 5.6: Formula Mass

## Learning Objectives

- To determine the formula mass of an ionic compound.

One skill needed in 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:

*Table shows how to calculate the formula mass of sodium chloride by using their atomic masses.*

| | |
|---|---|
| **Na:** | 22.99 amu |
| **Cl:** | + 35.45 amu |
| **Total:** | 58.44 amu |

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:

*Table shows how to find the formula mass of calcium fluoride by using their atomic masses.*

| | | |
|---|---|---|
| **Ca:** | 1 × 40.08 | 40.08 amu |
| **F:** | 2 × 19.00 = | + 38.00 amu |
| **Total:** | | 78.08 amu |

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:

*Table shows how to find the formula mass of potassium nitrate by using their atomic masses.*

| | | |
|---|---|---|
| **K:** | 1 × 39.10 | 39.10 amu |
| **N:** | 1 × 14.01 | + 14.01 amu |
| **O:** | 3 × 16.00 = | + 48.00 amu |
| **Total:** | | 101.11 amu |

The formula mass of $KNO_3$ is 101.11 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 the parentheses by the subscript outside 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:

*Table shows how to find the formula mass of $Ca(NO_3)_2$ by using their atomic masses.*

| | | |
|---|---|---|
| **Ca:** | 1 × 40.08 | 40.08 amu |
| **N:** | 2 × 14.01 = | + 28.02 amu |
| **O:** | 6 × 16.00 = | + 96.00 amu |
| **Total:** | | 164.10 amu |

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.

The Periodic Table is found in this link: Periodic Table of Elements with Atomic Mass [pubchem.ncbi.nlm.nih.gov]

## Example 5.6.1

Use the atomic masses (**rounded to two decimal places**) from the **Periodic Table** to determine the formula mass for each ionic compound.

a. $FeCl_3$
b. $(NH_4)_3PO_4$

**Solution**

a.

*Table shows how to find the formula mass of $FeCl_3$ by using their atomic masses.*

| | | |
|---|---|---|
| **Fe:** | | 55.84 amu |
| **Cl:** | 3 × 35.45 = | + 106.35 amu |
| **Total:** | | 162.19 amu |

The formula mass of $FeCl_3$ is 162.19 amu.

a. 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:

*Table shows how to find the formula mass of $(NH_4)_3PO_4$ by using their atomic masses.*

| | | |
|---|---|---|
| **N:** | 3 × 14.01 = | 42.03 amu |
| **H:** | 12 × 1.01 = | + 12.12 amu |
| **P:** | | + 30.97 amu |
| **O:** | 4 × 16.00 = | + 64.00 amu |
| **Total:** | | 149.12 amu |

The formula mass for $(NH_4)_3PO_4$ is 149.12 amu.

## Exercise 5.6.1

Use the atomic masses (**rounded to two decimal places**) from the **Periodic Table** 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: available at the end of this section.*

## To Your Health: Hydrates

Some ionic compounds have water ($H_2O$) incorporated within their formula unit. These compounds, called *hydrate*s, 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.



*Magnesium sulfate heptahydrate. (Public Domain; Chemicalinterest).*

Hydrates have various uses in the health industry. Calcium sulfate hemihydrate ($CaSO_4 \cdot ½H_2O$), 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. The accompanying table lists some useful hydrates.

*Table 5.6.1: Names and Formulas of Some Widely Used Hydrates*

| Formula | Name | Uses |
|---|---|---|
| $AlCl_3$•$6H_2O$ | aluminum chloride hexahydrate | antiperspirant |
| $CaSO_4$•$½H_2O$ | calcium sulfate hemihydrate (plaster of Paris) | casts (for broken bones and castings) |
| $CaSO_4$•$2H_2O$ | calcium sulfate dihydrate (gypsum) | drywall component |
| $CoCl_2$•$6H_2O$ | cobalt(II) chloride hexahydrate | drying agent, humidity indicator |
| $CuSO_4$•$5H_2O$ | copper(II) sulfate pentahydrate | fungicide, algicide, herbicide |
| $MgSO_4$•$7H_2O$ | magnesium sulfate heptahydrate (Epsom salts) | laxative, bathing salt |

| Formula | Name | Uses |
|---|---|---|
| $Na_2CO_3•10H_2O$ | sodium carbonate decahydrate (washing soda) | laundry additive/cleaneKEY TAKEAWAY |

## KEY TAKEAWAY

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

## EXERCISES

1. What is the relationship between atomic mass and formula mass?

2. How are subscripts used to determine a formula mass when more than one polyatomic ion is present in a chemical formula?

3. What is the formula mass for the ionic compound formed by each pair of ions?

   a. $Na^+$ and $Br^-$
   b. $Mg^{2+}$ and $Br^-$
   c. $Mg^{2+}$ and $S^{2-}$

4. What is the formula mass for the ionic compound formed by each pair of ions?

   a. $K^+$ and $Cl^-$
   b. $Mg^{2+}$ and $Cl^-$
   c. $Mg^{2+}$ and $Se^{2-}$

5. What is the formula mass for the ionic compound formed by each pair of ions?

   a. $Na^+$ and $N^{3-}$
   b. $Mg^{2+}$ and $N^{3-}$
   c. $Al^{3+}$ and $S^{2-}$

6. What is the formula mass for the ionic compound formed by each pair of ions?

   a. $Li^+$ and $N^{3-}$
   b. $Mg^{2+}$ and $P^{3-}$
   c. $Li^+$ and $P^{3-}$

7. What is the formula mass for each compound?

   a. $FeBr_3$
   b. $FeBr_2$
   c. $Au_2S_3$
   d. $Au_2S$

8. What is the formula mass for each compound?

   a. $Cr_2O_3$
   b. $CrO$
   c. $PbCl_2$
   d. $PbCl_4$

9. What is the formula mass for each compound?

a. $Cr(NO_3)_3$
b. $Fe_3(PO_4)_2$
c. $CaCrO_4$
d. $Al(OH)_3$

10. What is the formula mass for each compound?

a. $NH_4NO_3$
b. $K_2Cr_2O_7$
c. $Cu_2CO_3$
d. $NaHCO_3$

11. What is the formula mass for each compound?

a. $Al(HSO_4)_3$
b. $Mg(HSO_4)_2$

12. What is the formula mass for each compound?

a. $Co(HCO_3)_2$
b. $LiHCO_3$

## Answers

1. The formula mass is the sum of the atomic masses of the atoms in the formula.
2. The subscript is distributed throughout the parentheses to determine the total number of atoms in the formula.

3.

a. 102.89 amu
b. 184.11 amu
c. 56.38 amu

4.

a. 74.55 amu
b. 95.21 amu
c. 103.28 amu

5.

a. 82.98 amu
b. 100.95 amu
c. 150.17 amu

6.

a. 35.01 amu
b. 134.87 amu
c. 51.79 amu

7.

a. 295.55 amu
b. 215.65 amu
c. 490.15 amu
d. 426.01 amu

8.

a. 152.00 amu
b. 68.00 amu
c. 278.10 amu
d. 349.00 amu

9.

a. 238.03 amu
b. 357.49 amu
c. 156.08 amu
d. 78.01 amu

10.

a. 80.06 amu
b. 294.20 amu
c. 187.11 amu
d. 84.01 amu

11.

a. 318.22 amu
b. 218.47 amu

12.

a. 180.97 amu
b. 67.96 amu

## Answers

**Exercise** 5.6.1

47.87 + 2 (16.00) = 79.87 amu
107.87 + 79.90 = 187.77 amu
196.97 + 3(14.01) + 9(16.00) = 383.00 amu
3(55.84) + 2(30.97) + 8(16.00) = 357.46 amu

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# 5.7: Characteristics of Ionic Compounds

**Learning Objectives**

- To describe the physical properties of ionic compounds.

The figure below shows just a few examples of the color and brilliance of naturally occurring ionic crystals. The regular and orderly arrangement of ions in the crystal lattice is responsible for the various shapes of these crystals, while transition metal ions give rise to the colors.

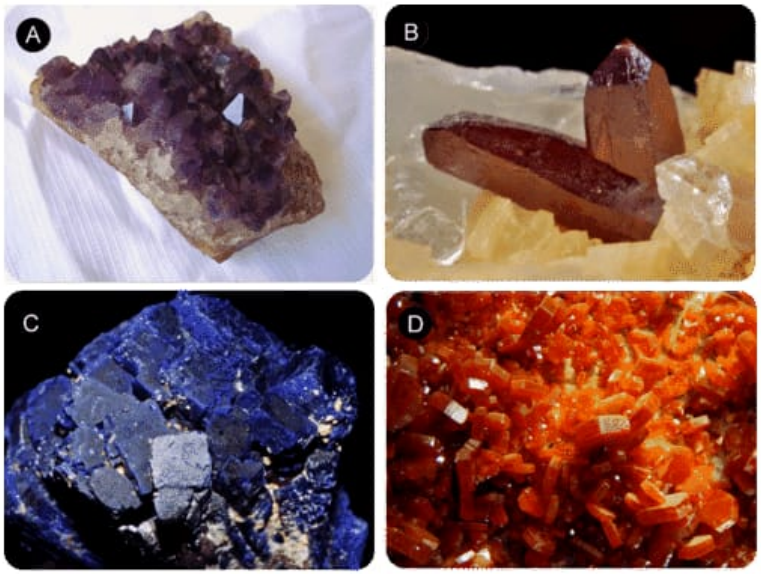



Figure 3.6.1: *In nature, the ordered arrangement of ionic solids gives rise to beautiful crystals. (A) Amethyst - a form of quartz, $SiO_2$, whose purple color comes from iron ions. (B) Cinnabar - the primary ore of mercury is mercury (II) sulfide, HgS (C) Azurite - a copper mineral, $Cu_3(CO_3)_2(OH)_2$. (D) Vanadinite - the primary ore of vanadium, $Pb_3(VO_4)_3Cl$.*

## Physical Properties of Ionic Compounds

### Melting Points

Because of the many simultaneous attractions between cations and anions that occur, ionic crystal lattices are very strong. The process of melting an ionic compound requires the addition of large amounts of energy in order to break all of the ionic bonds in the crystal. For example, sodium chloride has a melting temperature of about $800^{o}$C. As a comparison, the molecular compound water melts at 0 °C.

### Shattering

Ionic compounds are generally hard, but **brittle.** Why? It takes a large amount of mechanical force, such as striking a crystal with a hammer, to force one layer of ions to shift relative to its neighbor. However, when that happens, it brings ions of the same charge next to each other (see below). The repulsive forces between like-charged ions cause the crystal to shatter. When an ionic crystal breaks, it tends to do so along smooth planes because of the regular arrangement of the ions.

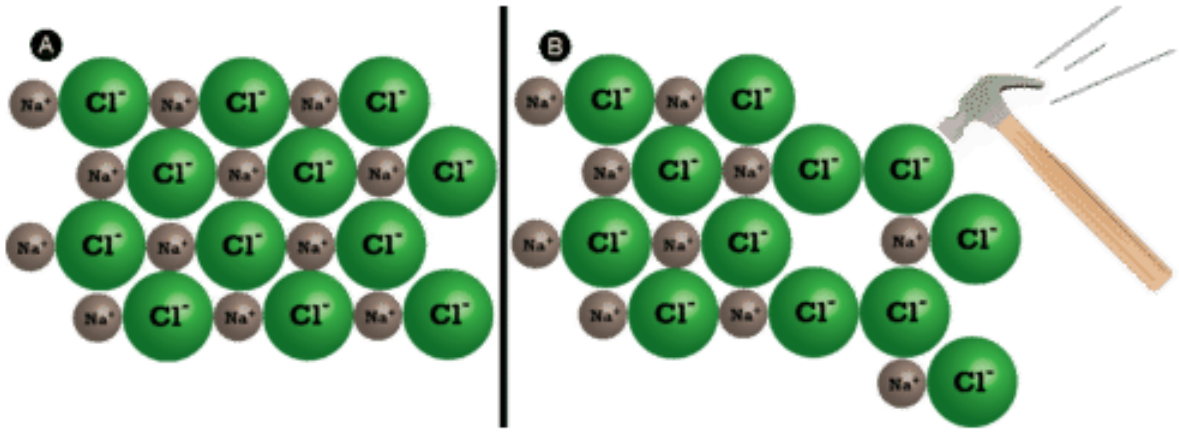



Figure 3.6.2: *(A) The sodium chloride crystal is shown in two dimensions. (B) When struck by a hammer, the negatively-charged chloride ions are forced near each other and the repulsive force causes the crystal to shatter.*

## Conductivity

Another characteristic property of ionic compounds is their **electrical conductivity**. The figure below shows three experiments in which two electrodes that are connected to a light bulb are placed in beakers containing three different substances.

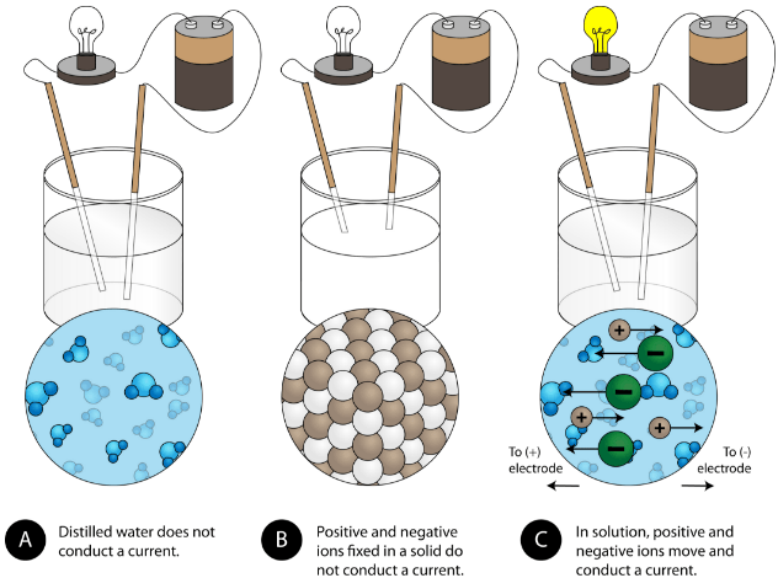



Figure 3.6.3: *(A) Distilled water does not conduct electricity. (B) A solid ionic compound also does not conduct. (C) A water solution of an ionic compound conducts electricity well.*

In the first beaker, distilled water does not conduct a current because water is a molecular compound. In the second beaker, solid sodium chloride also does not conduct a current. Despite being ionic and thus composed of charged particles, the solid crystal lattice does not allow the ions to move between the electrodes. Mobile charged particles are required for the circuit to be complete and the light bulb to light up. In the third beaker, the NaCl has been dissolved into the distilled water. Now the crystal lattice has been broken apart and the individual positive and negative ions can move. Cations move to one electrode, while anions move to the other, allowing electricity to flow (see figure below). Melting an ionic compound also frees the ions to conduct a current. Ionic compounds conduct an electric current when melted or dissolved in water. The dissolution of ionic compounds in water will be discussed in Section 9.3.

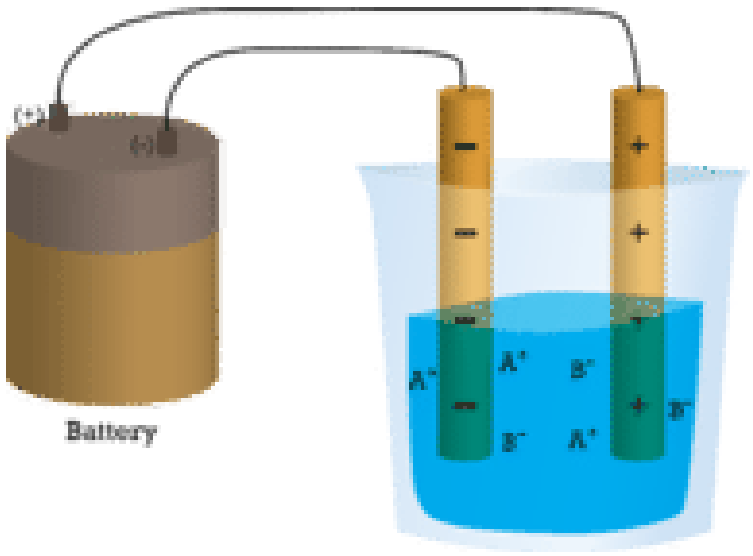



Figure 3.6.4: *In an ionic solution, the $A^+$ ions migrate toward the negative electrode, while the $B^-$ ions migrate toward the positive electrode.*

**Example 5.7.1**

Write the dissociation equation of solid NaCl in water.

**Solution**

$NaCl(s) \rightarrow Na^+(aq) + Cl^-(aq)$

**5.7.1 Exerc**

Write the dissociation equation of solid $NH_4NO_3$ in water.

*Answer available at the end of this section.*

## Key Takeaways

- Ionic compounds have high melting points.
- Ionic compounds are hard and brittle.
- Ionic compounds dissociate into ions when dissolved in water.
- Solutions of ionic compounds and melted ionic compounds conduct electricity, but solid materials do not.
- An ionic compound can be identified by its chemical formula: metal + nonmetal or polyatomic ions.

## Contributors and Attributions

- CK-12 Foundation by Sharon Bewick, Richard Parsons, Therese Forsythe, Shonna Robinson, and Jean Dupon.

## Exercises

1. Explain how the bonding in an ionic solid explains some of the properties of these solids.

2. Which type(s) of solid conduct(s) electricity in their liquid state but not in their solid state?

3. Based on chemical formula, identify which of the following is an ionic solid?

a. Hg

b. $PH_3$

c. $Ba(NO_3)_2$

## Answers

$NH_4NO_3(s) \rightarrow NH_4^+(aq) + NO_3^-(aq)$

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# 5.E: Ionic Bonding and Simple Ionic Compounds (Exercises)

## Additional Exercises

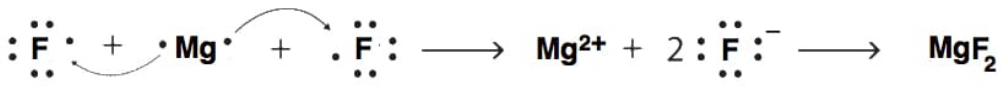
1. What number shell is the valence electron shell of a sodium atom? What number shell is the valence shell of a sodium ion? Explain the difference.
2. What number shell is the valence electron shell of a bromine atom? What number shell is the valence shell of a bromide ion? Explain the difference between these answers and the answers to Exercise 1.
3. What is the electron configuration of each ion?
    1. $K^+$
    2. $Mg^{2+}$
    3. $F^-$
    4. $S^{2-}$
4. What is the electron configuration of each ion?
    1. $Li^+$
    2. $Ca^{2+}$
    3. $Cl^-$
    4. $O^{2-}$
5. 1. If a sodium atom were to lose two electrons, what would be the electron configuration of the resulting cation?
    2. Considering that electron shells are typically separated by large amounts of energy, use your answer to Exercise 5a to suggest why sodium atoms do not form a 2+ cation.
6. 1. If a chlorine atom were to gain two electrons, what would be the electron configuration of the resulting anion?
    2. Considering that electron shells are typically separated by large amounts of energy, use your answer to Exercise 6a to suggest why chlorine atoms do not form a 2– anion.
7. Use Lewis diagrams and arrows to show the electron transfer that occurs during the formation of an ionic compound among Mg atoms and F atoms. (Hint: how many atoms of each will you need?)
8. Use Lewis diagrams and arrows to show the electron transfer that occurs during the formation of an ionic compound among K atoms and O atoms. (Hint: how many atoms of each will you need?)
9. Mercury forms two possible cations—$Hg^{2+}$ and $Hg_2^{2+}$, the second of which is actually a two-atom cation with a 2+ charge.
    1. Using common names, give the probable names of these ions.
    2. What are the chemical formulas of the ionic compounds these ions make with the oxide ion, $O^{2-}$?
10. The uranyl ion ($UO_2^{2+}$) is a common water-soluble form of uranium. What is the chemical formula of the ionic compound uranyl nitrate? What is the chemical formula of the ionic compound uranyl phosphate?
11. The formal chemical name of the mineral *strengite* is iron(III) phosphate dihydrate. What is the chemical formula of strengite? What is the formula mass of strengite?
12. What is the formula mass of $MgSO_4{\cdot}7H_2O$?
13. What is the formula mass of $CaSO_4{\cdot}½H_2O$?
14. What mass does 20 formula units of NaCl have?
15. What mass does 75 formula units of $K_2SO_4$ have?
16. If an atomic mass unit equals $1.66 \times 10^{-24}$ g, what is the mass in grams of one formula unit of NaCl?
17. If an atomic mass unit equals $1.66 \times 10^{-24}$ g, what is the mass in grams of $5.00 \times 10^{22}$ formula units of NaOH?
18. If an atomic mass unit equals $1.66 \times 10^{-24}$ g, what is the mass in grams of $3.96 \times 10^{23}$ formula units of $(NH_4)_2SO_4$?
19. Both tin and lead acquire 2+ or 4+ charges when they become ions. Use the periodic table to explain why this should not surprise you.
20. Which ion would you expect to be larger in size—$In^{3+}$ or $Tl^{3+}$? Explain.
21. Which ion would you expect to be smaller in size—$I^-$ or $Br^-$? Explain.
22. Which ion with a 2+ charge has the following electron configuration? $1s^2 2s^2 2p^6$
23. Which ion with a 3– charge has the following electron configuration? $1s^2 2s^2 2p^6$

# Answers

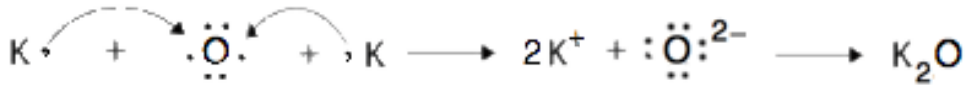
1. For sodium, the valence shell is the third shell; for the sodium ion, the valence shell is the second shell because it has lost all its third shell electrons.
2. The valence shell for both bromine atom and bromide ion is n=4. This is because the valence shell of bromine atom can accommodate one more electron.
3. 1. $1s^2 2s^2 2p^6 3s^2 3p^6$
   2. $1s^2 2s^2 2p^6$
   3. $1s^2 2s^2 2p^6$
   4. $1s^2 2s^2 2p^6 3s^2 3p^6$
4. 1. $1s^2$
   2. $1s^2 2s^2 2p^6 3s^2 3p^6$
   3. $1s^2 2s^2 2p^6 3s^2 3p^6$
   4. $1s^2 2s^2 2p^6$
5. 1. $1s^2 2s^2 2p^5$
   2. It probably requires too much energy to form.
6. 1. $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$

2. Gaining the second electron would probably require too much energy.

7.




8.




9. 1. mercuric and mercurous, respectively

2. HgO and $Hg_2O$, respectively

10. uranyl nitrate $UO_2(NO_3)_2$ and uranyl phosphate $(UO_2)_3(PO4)_2$

11. $FePO_4 \cdot 2H_2O$; 186.86 u

12. 246.51 u

13. 145.16 u

14. 1,169 u

15. 13,070 u

16. $9.701 \times 10^{-23}$ g

17. 3.32 g

18. 86.9 g

19. Both tin and lead have two *p* electrons and two *s* electrons in their valence shells.

20. $Tl^{3+}$ is larger because it is found lower on the periodic table

21. $Br^{-}$ because it is higher up on the periodic table

22. $Mg^{2+}$

23. $N^{3-}$

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# 5.S: Ionic Bonding and Simple Ionic Compounds (Summary)

*To ensure that you understand the material in this chapter, you should review the meanings of the following bold terms and ask yourself how they relate to the topics in the chapter.*

Atoms combine into compounds by forming **chemical bonds**. A survey of stable atoms and molecules leads to the **octet rule**, which says that stable atoms tend to have eight electrons in their outermost, or valence, shell. One way atoms obtain eight electrons in the valence shell is for some atoms to lose electrons while other atoms gain them. When this happens, the atoms take on an electrical charge. Charged atoms are called **ions**. Ions having opposite charges attract each other. This attraction is called **ionic bonding**, and the compounds formed are called **ionic compounds**.

Positively charged ions are called **cations**, while negatively charged ions are called **anions**. The formation of both cations and anions can be illustrated using electron configurations. Because elements in a column of the periodic table have the same valence shell electron configuration, atoms in the same column of the periodic table tend to form ions having the same charge. **Electron dot diagrams**, or **Lewis diagrams**, can also be used to illustrate the formation of cations and anions.

Ionic compounds are represented in writing by a **chemical formula**, which gives the lowest ratio of cations and anions present in the compound. In a formula, the symbol of the cation is written first, followed by the symbol of the anion. **Formula unit** is considered the basic unit of an ionic compound because ionic compounds do not exist as discrete units. Instead, they exist as **crystals**, three-dimensional arrays of ions, with cations surrounded by anions and anions surrounded by cations. Chemical formulas for ionic compounds are determined by balancing the positive charge from the cation(s) with the negative charge from the anion(s). A subscript to the right of the ion indicates that more than one of that ion is present in the chemical formula.

Some ions are groups of atoms bonded together and having an overall electrical charge. These are called **polyatomic ions**. Writing formulas with polyatomic ions follows the same rules as with monatomic ions, except that when more than one polyatomic ion is present in a chemical formula, the polyatomic ion is enclosed in parentheses and the subscript is outside the right parenthesis. Ionic compounds typically form between metals and nonmetals or between polyatomic ions.

Names of ionic compounds are derived from the names of the ions, with the name of the cation coming first, followed by the name of the anion. If an element can form cations of different charges, there are two alternate systems for indicating the compound's name. In the **Stock system**, a roman numeral in parentheses indicates the charge on the cation. An example is the name for $FeCl_2$, which is iron(II) chloride. In the common system, the suffixes *-ous* and *-ic* are used to stand for the lower and higher possible charge of the cation, respectively. These suffixes are attached to a stem representing the element (which frequently comes from the Latin form of the element name). An example is the common name for $FeCl_2$, which is ferrous chloride.

The **formula mass** of an ionic compound is the sum of the masses of each individual atom in the formula. Care must be taken when calculating formula masses for formulas containing multiple polyatomic ions because the subscript outside the parentheses refers to all the atoms in the polyatomic ion.

Ionic compounds are hard, brittle and have very high melting points. When in solution, the ions separate and form **electrolyte** solutions.

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# 6: MOLECULAR COMPOUNDS AND STRUCTURES

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.


## 6.1: Bonding and Lewis Structures

6.1.1: Representing Valence Electrons with Dots

6.1.2: Lewis Structures of Ionic Compounds- Electrons Transferred

6.1.3: Covalent Bonds - Electrons Shared

6.1.4: Covalent Compounds - Formulas and Names

6.1.5: Naming Acids

6.1.6: Writing Lewis Structures for Covalent Compounds

## 6.2: Structures of Organic Molecules

6.2.1: Carbon - The Chemical Basis for Life

6.2.2: Hydrocarbons- Compounds Containing Only Carbon and Hydrocarbon

6.2.3: Bond-Line Formulas

## 6.3: Molecular Shape and Polarity

6.3.1: Predicting the Shapes of Molecules

6.3.2: Electronegativity and Polarity - Why Oil and Water Do not Mix



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# 6.1: BONDING AND LEWIS STRUCTURES

6.1.1: Representing Valence Electrons with Dots
6.1.2: Lewis Structures of Ionic Compounds- Electrons Transferred
6.1.3: Covalent Bonds - Electrons Shared
6.1.4: Covalent Compounds - Formulas and Names
6.1.5: Naming Acids
6.1.6: Writing Lewis Structures for Covalent Compounds

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# 6.1.1: Representing Valence Electrons with Dots

## Learning Objective

- Draw a Lewis electron dot diagram for an atom or a monatomic ion.

In almost all cases, chemical bonds are formed by interactions of valence electrons in atoms. To facilitate our understanding of how valence electrons interact, a simple way of representing those valence electrons would be useful.

A **Lewis electron dot diagram** (or electron dot diagram, or a Lewis diagram, or a Lewis structure) is a representation of the valence electrons of an atom that uses dots around the symbol of the element. The number of dots equals the number of valence electrons in the atom. These dots are arranged to the right and left and above and below the symbol, with no more than two dots on a side. (The order in which the positions are used does not matter.) For example, the Lewis electron dot diagram for hydrogen is simply

$$\mathbf{H}\cdot$$

Because the side is not important, the Lewis electron dot diagram could also be drawn as follows:

$$\dot{\mathbf{H}} \quad or \quad \cdot\mathbf{H} \quad or \quad \underset{\cdot}{\mathbf{H}}$$

The electron dot diagram for helium, with two valence electrons, is as follows:

$$\mathbf{He}\!:$$

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 2*s* shell, so its electron dot diagram is like that of helium:

$$\mathbf{Be}\!:$$

The next atom is boron. Its valence electron shell is $2s^2 2p^1$, so it has three valence electrons. The third electron will go on another side of the symbol:

$$\dot{\mathbf{B}}\!:$$

Again, it does not matter on which sides of the symbol the electron dots are positioned.

For carbon, there are four valence electrons, two in the 2*s* subshell and two in the 2*p* subshell. As usual, we will draw two dots together on one side, to represent the 2*s* electrons. However, conventionally, we draw the dots for the two *p* electrons on different sides. As such, the electron dot diagram for carbon is as follows:

$$\cdot\dot{\mathbf{C}}\!:$$

With N, which has three *p* electrons, we put a single dot on each of the three remaining sides:

$$\cdot\underset{\cdot}{\dot{\mathbf{N}}}\!:$$

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.



Fluorine and neon have seven and eight dots, respectively:





With the next element, sodium, the process starts over with a single electron because sodium has a single electron in its highest-numbered shell, the $n = 3$ shell. By going through the periodic table, we see that the Lewis electron dot diagrams of atoms will never have more than eight dots around the atomic symbol.

### Example 6.1.1.1: Lewis Dot Diagrams

What is the Lewis electron dot diagram for each element?

a. aluminum
b. selenium

**Solution**

a. The valence electron configuration for aluminum is $3s^2 3p^1$. So it would have three dots around the symbol for aluminum, two of them paired to represent the 3s electrons:



2. The valence electron configuration for selenium is $4s^2 4p^4$. In the highest-numbered shell, the $n = 4$ shell, there are six electrons. Its electron dot diagram is as follows:



### Exercise 6.1.1.1

What is the Lewis electron dot diagram for each element?

a. phosphorus
b. argon

*Answer a available at the end of this section.*

## 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.

## Answers

**Exercise** 6.1.1.1





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# 6.1.2: Lewis Structures of Ionic Compounds- Electrons Transferred

## Learning Objectives

- State the octet rule.
- Define *ionic bond*.
- Draw Lewis structures for ionic compounds.

In previous sections, 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:

$$\mathbf{Na}\cdot \qquad \cdot\ddot{\underset{\cdot\,\cdot}{\mathbf{Cl}}}\mathbf{:}$$

$$[Ne]\,3s^1 \qquad [Ne]\,3s^2 3p^5$$

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:

$$\mathbf{Na}\cdot \rightsquigarrow \cdot\ddot{\underset{\cdot\,\cdot}{\mathbf{Cl}}}\mathbf{:}$$

resulting in two ions—the $Na^+$ ion and the $Cl^-$ ion:

$$\mathbf{Na}^+ \qquad :\ddot{\underset{\cdot\,\cdot}{\mathbf{Cl}}}\mathbf{:}^-$$

$$[Ne] \qquad [Ne]\,3s^2 3p^6$$

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:

$$\mathbf{Na}^+ + :\ddot{\underset{\cdot\,\cdot}{\mathbf{Cl}}}\mathbf{:}^- \rightarrow Na^+Cl^- \;\; or \;\; NaCl$$

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:

$$\mathrm{Mg}^{2+} + \left[:\ddot{\mathrm{O}}:\right]^{2-} \qquad Mg^{2+}O^{2-} \; or \; MgO$$

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:

$$\mathrm{Na}\cdot \rightharpoonup \cdot\ddot{\mathrm{O}}:$$

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:



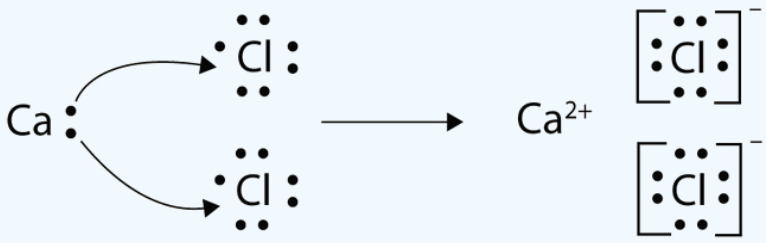

These three ions attract each other to give an overall neutral-charged ionic compound, which we write as $Na_2O$. The need for the number of electrons lost being equal to the number of electrons gained explains why ionic compounds have the ratio of cations to anions that they do. This is required by the law of conservation of matter as well.

### Example 6.1.2.1: Synthesis of Calcium Chloride from Elements

With arrows, illustrate the transfer of electrons to form calcium chloride from $Ca$ atoms and $Cl$ atoms.

**Solution**

A $Ca$ atom has two valence electrons, while a $Cl$ atom has seven electrons. A $Cl$ atom needs only one more to complete its octet, while $Ca$ atoms have two electrons to lose. Thus we need two $Cl$ atoms to accept the two electrons from one $Ca$ atom. The transfer process looks as follows:




The oppositely charged ions attract each other to make $CaCl_2$.

**Exercise** 6.1.2.1

With arrows, illustrate the transfer of electrons to form potassium sulfide from $K$ atoms and $S$ atoms.

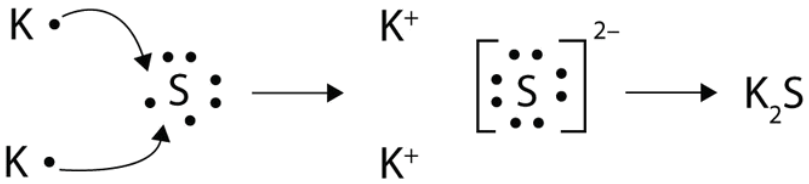
*Answer available at the end of this section.*

## 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.

### Answers

**Exercise** 6.1.2.1




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# 6.1.3: Covalent Bonds - 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**.

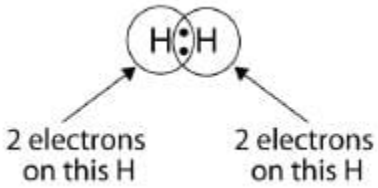
Let us illustrate a covalent bond by using H atoms, with the understanding that H atoms need only two electrons to fill the 1s subshell. Each H atom starts with a single electron in its valence shell:

$$\mathbf{H}\cdot \quad \cdot\mathbf{H}$$

The two H atoms can share their electrons:

$$\mathbf{H:H}$$

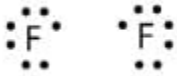
We can use circles to show that each H atom has two electrons around the nucleus, completely filling each atom's valence shell:




Because each H atom has a filled valence shell, this bond is stable, and we have made a diatomic hydrogen molecule. (This explains why hydrogen is one of the diatomic elements.) For simplicity's sake, it is not unusual to represent the covalent bond with a dash, instead of with two dots:

H–H

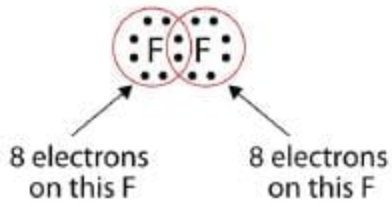
Because two atoms are sharing one pair of electrons, this covalent bond is called a **single bond**. As another example, consider fluorine. F atoms have seven electrons in their valence shell:



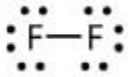

These two atoms can do the same thing that the H atoms did; they share their unpaired electrons to make a covalent bond.




Note that each F atom has a complete octet around it now:




We can also write this using a dash to represent the shared electron pair:

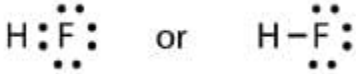



There are two different types of electrons in the fluorine diatomic molecule. The **bonding electron pair** makes the covalent bond. Each F atom has three other pairs of electrons that do not participate in the bonding; they are called **lone pair electrons**. Each F atom has one bonding pair and three lone pairs of electrons.

Covalent bonds can be made between different elements as well. One example is HF. Each atom starts out with an odd number of electrons in its valence shell:




The two atoms can share their unpaired electrons to make a covalent bond:




We note that the H atom has a full valence shell with two electrons, while the F atom has a complete octet of electrons.

**Example 6.1.3.1:**

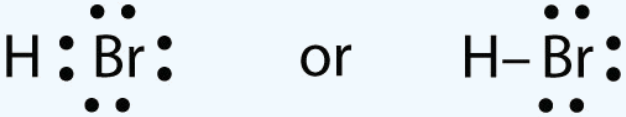
Use Lewis electron dot diagrams to illustrate the covalent bond formation in HBr.

**Solution**

HBr is very similar to HF, except that it has Br instead of F. The atoms are as follows:




The two atoms can share their unpaired electron:



**Exercise 6.1.3.1**

Use Lewis electron dot diagrams to illustrate the covalent bond formation in $Cl_2$.

*Answer available at the end of this section.*

When working with covalent structures, it sometimes looks like you have leftover electrons. You apply the rules you learned so far, and there are still some electrons that remain unattached. You can't just leave them there. So where do you put them?

## Multiple Covalent Bonds

Some molecules are not able to satisfy the octet rule by making only single covalent bonds between the atoms. Consider the compound ethene, which has a molecular formula of $C_2H_4$. The carbon atoms are bonded together, with each carbon also bonded to two hydrogen atoms.

$$\text{two C atoms } = 2 \times 4 = 8 \text{ valence electrons}$$

$$\text{four H atoms } = 4 \times 1 = 4 \text{ valence electrons}$$

$$\text{total of 12 valence electrons in the molecule}$$

If the Lewis electron dot structure was drawn with a single bond between the carbon atoms and with the octet rule followed, it would look like this:

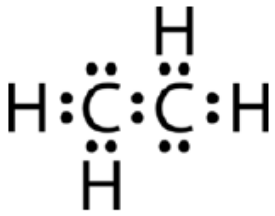


Figure 6.1.3.1: Incorrect dot structure of ethene. (CK12 License)

This Lewis structure is incorrect because it contains a total of 14 electrons. However, the Lewis structure can be changed by eliminating the lone pairs on the carbon atoms and having to share two pairs instead of only one pair.

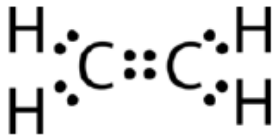


Figure 6.1.3.2: Correct dot structure for ethene. (CK12 License)

A **double covalent bond** is a covalent bond formed by atoms that share two pairs of electrons. The double covalent bond that occurs between the two carbon atoms in ethane can also be represented by a structural formula and with a molecular model as shown in the figure below.

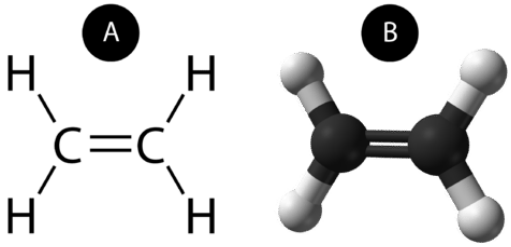



Figure 6.1.3.3: (A) The structural model for $C_2H_4$ consists of a double covalent bond between the two carbon atoms and single bonds to the hydrogen atoms. (B) Molecular model of $C_2H_4$.

A **triple covalent bond** is a covalent bond formed by atoms that share three pairs of electrons. The element nitrogen is a gas that composes the majority of Earth's atmosphere. A nitrogen atom has five valence electrons, which can be shown as one pair and three single electrons. When combining with another nitrogen atom to form a diatomic molecule, the three single electrons on each atom combine to form three shared pairs of electrons.

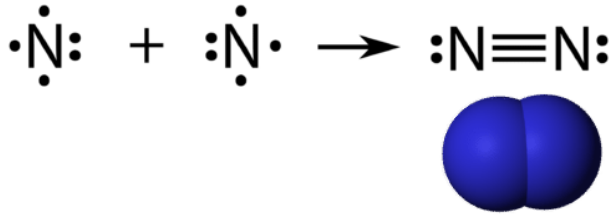


Figure 6.1.3.4: Triple bond in $N_2$.

Each nitrogen atom follows the octet rule with one lone pair of electrons, and six electrons that are shared between the atoms.

## Summary

- Covalent bonds are formed when atoms share electrons.
- Lewis electron dot diagrams can be drawn to illustrate covalent bond formation.
- Double bonds or triple bonds between atoms may be necessary to properly illustrate the bonding in some molecules.

## Contributions & Attributions

- 

- Anonymous by request

### Answers

**Exercise** 6.1.3.1



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# 6.1.4: Covalent Compounds - Formulas and Names

**Learning Objectives**

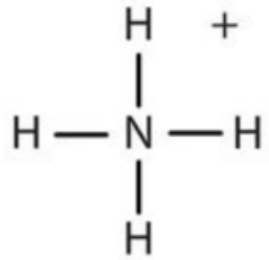
- Identify covalent and ionic compounds.
- Determine the chemical formula of a simple covalent compound from its name.
- Determine the name of a simple covalent compound from its chemical formula.

## COVALENT AND IONIC COMPOUNDS

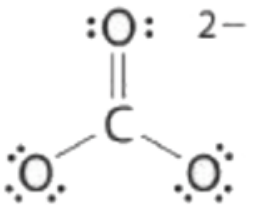
What elements make covalent bonds? Covalent bonds form when two or more nonmetals combine. For example, both hydrogen and oxygen are nonmetals, and when they combine to make water, they do so by forming covalent bonds. Compounds that are composed of only non-metals or semi-metals with non-metals will display covalent bonding and will be classified as molecular compounds.

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). Nitrogen monoxide (NO) will be a covalently bound molecule (two non-metals), silicon dioxide ($SiO_2$) will be a covalently bound molecule (a semi-metal and a non-metal) and $MgCl_2$ will be ionic (a metal and a non-metal).

A polyatomic ion is an ion composed of two or more atoms that have a charge as a group (poly = many). The ammonium ion (see figure below) consists of one nitrogen atom and four hydrogen atoms. Together, they comprise a single ion with a 1+ charge and a formula of $NH_4^+$. The carbonate ion (see figure below) consists of one carbon atom and three oxygen atoms and carries an overall charge of 2–. The formula of the carbonate ion is $CO_3^{2-}$.



ammonium ion



carbonate ion

The atoms of a polyatomic ion are tightly bonded together and so the entire ion behaves as a single unit. Several examples are found in Table 3.3.1. Nonmetal atoms in polyatomic ions are joined by covalent bonds, but the ion as a whole participates in ionic bonding. For example, ammonium chloride ($NH_4Cl$) has ionic bonding between a polyatomic ion, $\mathrm{NH_4^+}$, and $\mathrm{Cl^-}$ ions, but within the ammonium ion ($NH_4^+$), the nitrogen and hydrogen atoms are connected by covalent bonds (shown above).

Both ionic and covalent bonding are also found in calcium carbonate. Calcium carbonate ($CaCO_3$) has ionic bonding between calcium ion $\mathrm{Ca^{2+}}$ and a polyatomic ion, $\mathrm{CO_3^{2-}}$, but within the carbonate ion ($CO_3^{2-}$), the carbon and oxygen atoms are connected by covalent bonds (shown above).

## Characteristics of Covalent (Molecular) Compounds

Compounds that contain covalent bonds (also called molecular compounds) exhibit different physical properties than ionic compounds. Because the attraction between molecules, which are electrically neutral, is weaker than that between electrically charged ions, covalent compounds generally have much lower melting and boiling points than ionic compounds (discussed in

Section 3.6). For example, water (molecular compound) boils at 100 °C while sodium chloride (ionic compound) boils at 1413 °C. In fact, many covalent compounds are liquids or gases at room temperature, and, in their solid states, they are typically much softer than ionic solids. Furthermore, whereas ionic compounds are good conductors of electricity when dissolved in water, most covalent compounds, being electrically neutral, are poor conductors of electricity in any state. The attraction between molecules (called intermolecular forces) will be discussed in more detail in Section 8.1

**Example 6.1.4.1**

Is each compound formed from ionic bonds, covalent bonds, or both?

a. $Na_2O$
b. $Na_3PO_4$
c. $N_2O_4$

*Answer a available at the end of this section.*

**Exercise 6.1.4.1**

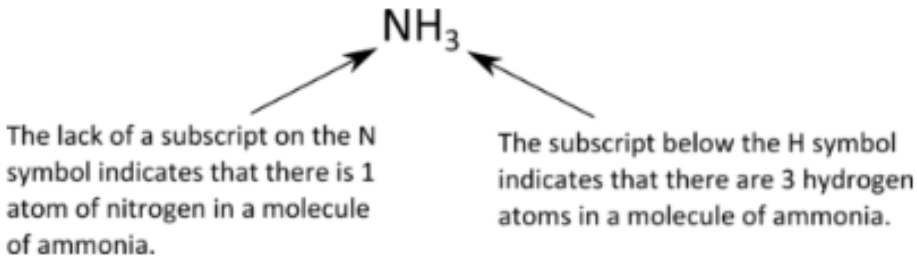
Is each compound are formed from ionic bonds, covalent bonds, or both?

a. $Ba(OH)_2$
b. $F_2$
c. $PCl_3$

*Answer a: available at the end of this section.*

## MOLECULAR FORMULAS

The chemical formulas for covalent compounds are referred to as **molecular formulas** because these compounds exist as separate, discrete molecules. Typically, a molecular formula begins with the nonmetal that is closest to the lower left corner of the periodic table, except that hydrogen is almost never written first ($H_2O$ is the prominent exception). Then the other nonmetal symbols are listed. Numerical subscripts are used if there is more than one of a particular atom. For example, we have already seen $CH_4$, the molecular formula for methane. Below is the molecular formula of ammonia, $NH_3$.




$NH_3$. An arrow points to the N and says, "The lack of a subscript on the N symbol indicates that there is 1 atom of nitrogen in a molecule of ammonia". An arrow points to H and says, "The subscript below the H symbol indicates that there are 3 hydrogen atoms in a molecule of ammonia".

## NAMING COVALENT COMPOUNDS

Naming *binary* (two-element) covalent 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 6.1.4.1 lists these numerical prefixes. Normally, no prefix is added to the first element's name if there is only one atom of the first element in a molecule. If the second element is oxygen, the trailing vowel is usually omitted from the end of a polysyllabic prefix but not a

monosyllabic one (that is, we would say “monoxide” rather than “monooxide” and “trioxide” rather than “troxide”).

*Table* 6.1.4.1*: Numerical Prefixes for Naming Binary Covalent Compounds*

| Number of Atoms in Compound | Prefix on the Name of the Element |
|---|---|
| 1 | mono-* |
| 2 | di- |
| 3 | tri- |
| 4 | tetra- |
| 5 | penta- |
| 6 | hexa- |
| 7 | hepta- |
| 8 | octa- |
| 9 | nona- |
| 10 | deca- |
| ***This prefix is not used for the first element’s name.** | |

Let us practice by naming the compound whose molecular formula is $CCl_4$. The name begins with the name of the first element—carbon. The second element, chlor*ine*, becomes chlor*ide*, and we attach the correct numerical prefix (“tetra-”) to indicate that the molecule contains four chlorine atoms. Putting these pieces together gives the name *carbon tetrachloride* for this compound.

## Example 6.1.4.2

Write the molecular formula for each compound.

a. chlorine trifluoride
b. phosphorus pentachloride
c. sulfur dioxide
d. dinitrogen pentoxide

**Solution**

If there is no numerical prefix on the first element’s name, we can assume that there is only one atom of that element in a molecule.

a. $ClF_3$
b. $PCl_5$
c. $SO_2$
d. $N_2O_5$ (The *di-* prefix on nitrogen indicates that two nitrogen atoms are present.)

## Exercise 6.1.4.2

Write the molecular formula for each compound.

a. nitrogen dioxide
b. dioxygen difluoride
c. sulfur hexafluoride
d. selenium monoxide

*Answer a: available at the end of this section.*

Because it is so unreactive, sulfur hexafluoride is used as a spark suppressant in electrical devices such as transformers.

### Example 6.1.4.3

Write the name for each compound.

a. $BrF_5$
b. $S_2F_2$
c. CO

**Solution**

a. bromine pentafluoride
b. disulfur difluoride
c. carbon monoxide

### Exercise 6.1.4.3

Write the name for each compound.

a. $CF_4$
b. $SeCl_2$
c. $SO_3$

*Answer a: available at the end of this section.*

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

Methane is the simplest organic compound. Organic compounds are compounds with carbon atoms and are named by a separate nomenclature system that we will introduce in in a separate section.

## Key Takeaways

- The chemical formula of a simple covalent compound can be determined from its name.
- The name of a simple covalent compound can be determined from its chemical formula.

---

### Answers

**Example** 6.1.4.1

The elements in $Na_2O$ are a metal and a nonmetal, which form ionic bonds.

Because sodium is a metal and we recognize the formula for the phosphate ion, we know that this compound is ionic. However, within the polyatomic phosphate ion, the atoms are held together by covalent bonds, so this compound contains both ionic and covalent bonds.

The elements in $N_2O_4|$ are both nonmetals, rather than a metal and a nonmetal. Therefore, the atoms form covalent bonds.

**Exercise** 6.1.4.1

both

covalent

covalent

**Exercise** 6.1.4.2

a. $NO_2$

$O_2F_2$

$SF_6$

SeO

**Exercise** 6.1.4.3

carbon tetrafluoride

selenium dichloride

sulfur trioxide

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# 6.1.5: 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 $(\mathrm{H^+})$ when dissolved in water.




Figure $6.1.5.1$: (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 $\mathrm{NaCl}$. However, when these molecules are dissolved in water, the chemical bond between the hydrogen atom and the rest of the molecule breaks, leaving a positively-charged hydrogen ion and an anion. This can be symbolized in a chemical equation:

$$\mathrm{HCl \rightarrow H^+ + Cl^-}$$

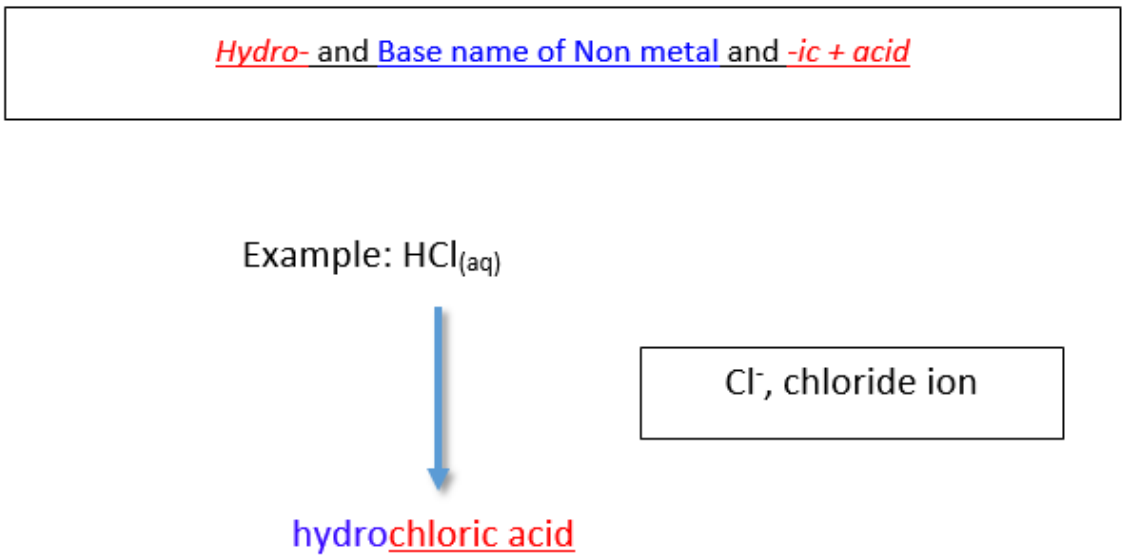
Since acids produce $\mathrm{H^+}$ cations upon dissolving in water, the $\mathrm{H}$ of an acid is written first in the formula of an inorganic acid. The remainder of the acid (other than the $\mathrm{H}$) is the anion after the acid dissolves. Organic acids are also an important class of compounds,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

## Naming Acids

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

### Naming Binary acids (in aqueous form)

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



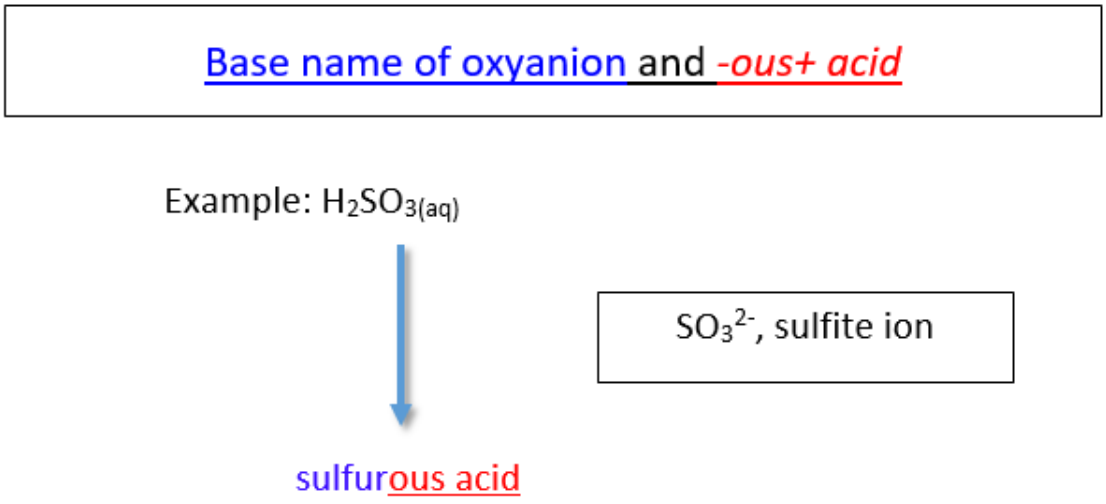

Formula for naming acids: Hydro- and Base name of nonmetal and -ic + acid. Example: HCl is hydrochloric acid.

## Naming Oxyacids

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

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

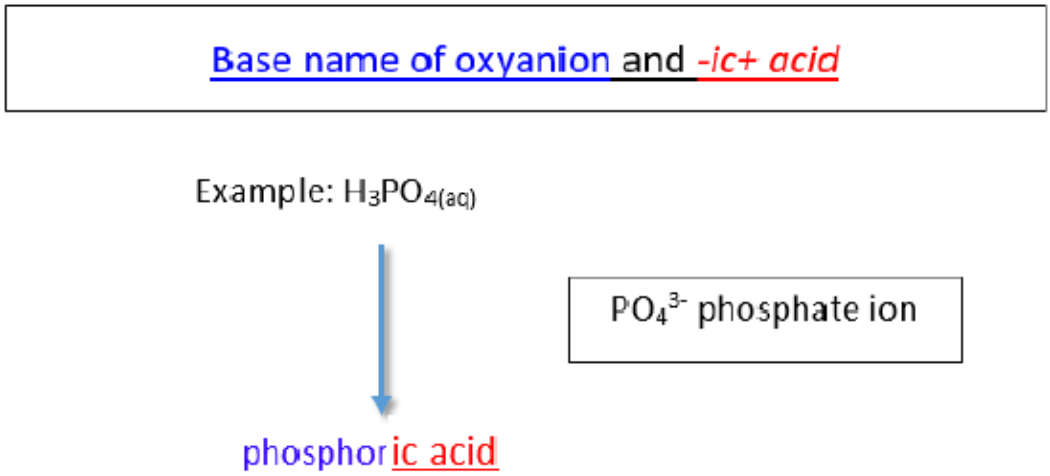
The name of the acid is the root of the anion followed by the suffix ***-ous***. There is no prefix.




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

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

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



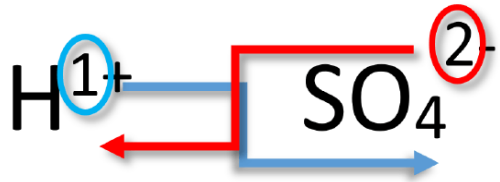

Formula for naming oxyanions with -ate ending: Base name of oxyanion and -ic + acid. Example: H3PO4 is phosphoric acid.

**Note**

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

## Writing Formulas for Acids

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




H2SO4: H has +1 charge and SO4 has -2 charge, so there must be 2 H+ and 1 SO4 for the charges to balance out.

Formula: $H_2SO_4$

***Figure*** $6.1.5.2$***:*** *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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# 6.1.6: 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 6.1.6.1: Water

Write the Lewis Structure for $H_2O$.

**Solution**

*Solutions to Example 10.4.1*

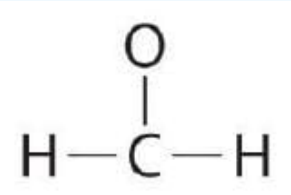
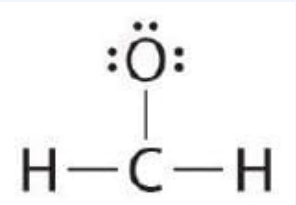
| Steps for Writing Lewis Structures | Example 6.1.6.1 |
|---|---|
| 1. Determine the total number of valence electrons in the molecule or ion. | Each H atom (group 1) has 1 valence electron, and the O atom (group 16) has 6 valence electrons, for a total of 8 valence electrons. |
| 2. Arrange the atoms to show specific connections. | **H O H**<br><br>Because H atoms are almost always terminal, the arrangement within the molecule must be HOH. |
| 3. Place a bonding pair of electrons between each pair of adjacent atoms to give a single bond.<br><br>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<br><br>**H -O- H**<br><br>with 4 electrons left over.<br><br>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:<br><br>  |
| 6. If the central atom has fewer electrons than an octet, use lone pairs from terminal atoms to form multiple (double or triple) bonds to the central atom to achieve an octet. | Not necessary. |
| 7. Final check. | The Lewis structure gives oxygen an octet and each hydrogen 2 electrons. |

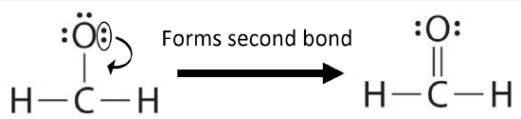
## Example 6.1.6.2

Write the Lewis structure for the $CH_2O$ molecule

**Solution**

*Solutions to Example 10.4.2*

| Steps for Writing Lewis Structures | Example 6.1.6.2 |
|---|---|
| 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] = 12 valence electrons. |
| 2. Arrange the atoms to show specific connections. |  <br><br>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:<br>  <br><br>6 electrons are used, and 6 are left over. |
| 4. Beginning with the terminal atoms, add enough electrons to each atom to give each atom an octet (two for hydrogen). | Adding all 6 remaining electrons to oxygen (as three lone pairs) gives the following:<br>  <br><br>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.<br>There are no electrons left to place on the central atom. |

| Steps for Writing Lewis Structures | Example 6.1.6.2 |
|---|---|
| 6. If the central atom has fewer electrons than an octet, use lone pairs from terminal atoms to form multiple (double or triple) bonds to the central atom to achieve an octet. | To give carbon an octet of electrons, we use one of the lone pairs of electrons on oxygen to form a carbon–oxygen double bond:   |
| 7. Final check | 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 6.1.6.1**

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 CO2 available at the end of this section.*

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.

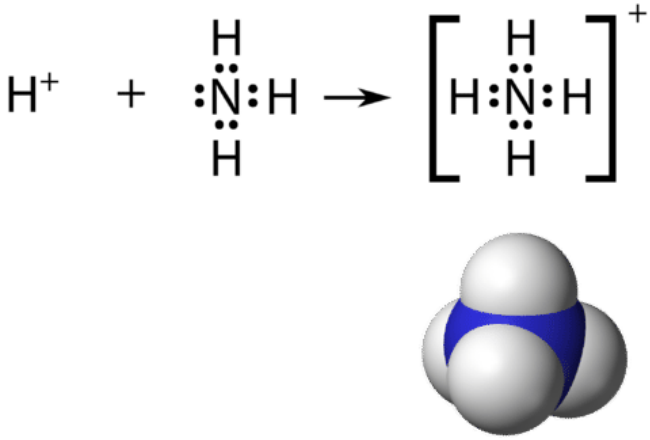


Figure 6.1.6.3: The ammonium ion. (CK12 License)

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:

$$1 \text{ N atom } = 5 \text{ valence electrons}$$

$$4 \text{ H atoms } = 4 \times 1 = 4 \text{ valence electrons}$$

subtract 1 electron for the $1+$ charge of the ion

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 6.1.6.2**

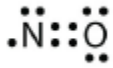
Draw the Lewis electron dot structure for the sulfate ion.

*Answer (CK12 License) available at the end of this section.*

## Exceptions to the Octet Rule (BC Campus)

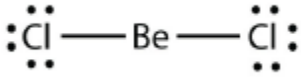
As important and useful as the octet rule is in chemical bonding, there are some well-known violations. This does not mean that the octet rule is useless—quite the contrary. As with many rules, there are exceptions, or violations.

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:

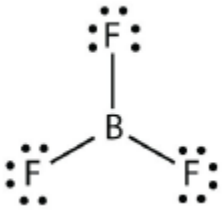



Although the O atom has an octet of electrons, the N atom has only seven electrons in its valence shell. Although NO is a stable compound, it is very chemically reactive, as are most other odd-electron compounds.

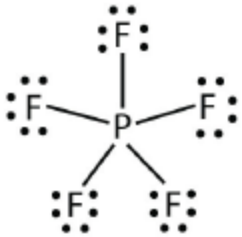
Electron-deficient molecules represent the second violation to the octet rule. These stable compounds have less than eight electrons around an atom in the molecule. The most common examples are the covalent compounds of beryllium and boron. For example, beryllium can form two covalent bonds, resulting in only four electrons in its valence shell:




Boron commonly makes only three covalent bonds, resulting in only six valence electrons around the B atom. A well-known example is $BF_3$:




The third violation to the octet rule is found in those compounds with more than eight electrons assigned to their valence shell. These are called expanded valence shell molecules. Such compounds are 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 6.1.6.3: Octet Violations

Identify each violation to the octet rule by drawing a Lewis electron dot diagram.

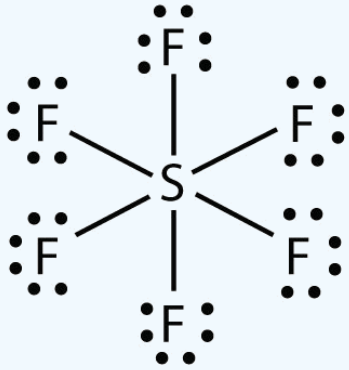
a. ClO
b. $SF_6$

**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 6.1.6.3: Xenon Difluoride

Identify the violation to the octet rule in $XeF_2$ by drawing a Lewis electron dot diagram.

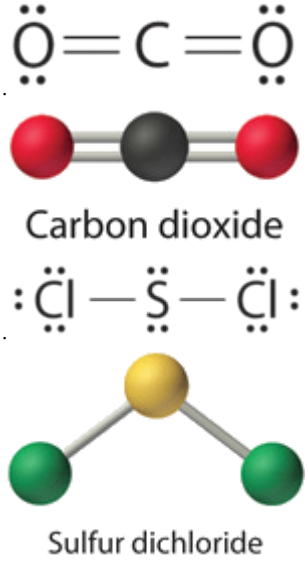
*Answer available at the end of this section.*

## Summary

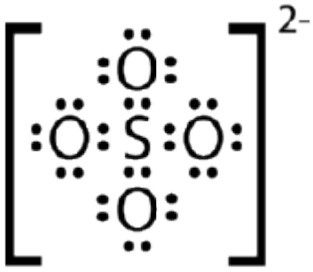
Lewis dot symbols provide a simple rationalization of why elements form compounds with the observed stoichiometries. A plot of the overall energy of a covalent bond as a function of internuclear distance is identical to a plot of an ionic pair because both result from attractive and repulsive forces 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.

## Answers

**Exercise** 6.1.6.1




**Exercise** 6.1.6.2



**Exercise** 6.1.6.3**: Xenon Difluoride**



The Xe atom has an expanded valence shell with more than eight electrons around it.

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# 6.2: STRUCTURES OF ORGANIC MOLECULES

A fundamental understanding of organic chemistry is crucial for understanding how biological macromolecules are formed. In this section, we introduce the topic of organic chemistry and learn about the different ways we can draw organic molecules.

## Vitalism

Vitalism was a popular philosophical doctrine that posits that living organisms are fundamentally different from non-living entities because they are governed by a "vital force" or "life principle" that cannot be explained solely by physical or chemical processes. This vital force is thought to imbue living beings with qualities such as growth, reproduction, and metabolism, which are not present in inanimate matter.

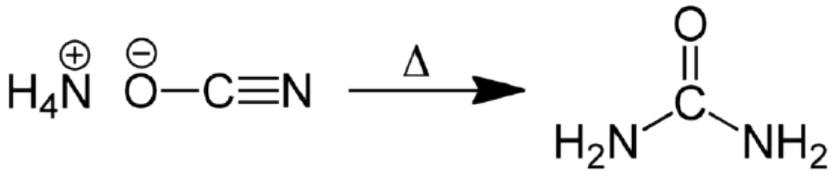
Historically, vitalism was a dominant theory in biology and medicine. Proponents believed that the processes of life could not be understood through the laws of physics and chemistry alone. However, with the advancement of molecular biology, biochemistry, and genetics in the 19th and 20th centuries, vitalism has largely been discredited in the scientific community. Modern science explains the functions and behaviors of living organisms through biochemical and physical principles without invoking a separate vital force. Nonetheless, vitalism has influenced various holistic and alternative medicine practices, where it remains a philosophical underpinning.

## Organic vs. Inorganic

The term "organic" in organic chemistry originally derives from the notion that these compounds were fundamentally related to life, or "organisms." In the early days of chemistry, substances were broadly classified into two categories: inorganic and organic. Inorganic substances were those found in the mineral world, while organic substances were associated with living organisms, including plants and animals.

The belief in vitalism posited that organic compounds could **only** be synthesized by living organisms through a "vital force," reinforced the idea that organic compounds were inherently linked to life processes. Compounds such as urea, sugars, fats, and proteins, which were derived from living organisms, were classified as organic. This classification implied that such substances were fundamentally different from inorganic compounds found in the non-living environment.

The synthesis of urea played a crucial role in disproving vitalism by demonstrating that organic compounds, which were thought to be producible only by living organisms due to a "vital force," could be synthesized from inorganic materials in a laboratory setting. In 1828, the German chemist Friedrich Wöhler accidentally synthesized urea, an organic compound found in urine, from ammonium cyanate, an inorganic substance. Wöhler's experiment showed that organic molecules could be created from inorganic precursors without any "vital force."




Wöhler's synthesis of urea bridged the gap between organic and inorganic chemistry. It provided concrete evidence that the same chemical principles applied to both living and non-living matter. The success of Wöhler's experiment challenged the vitalist notion that a special life force was necessary for the formation of organic compounds. It demonstrated that life processes could be explained by the same physical and chemical laws that govern non-living processes. This discovery paved the way for the development of organic chemistry as a robust scientific discipline. It encouraged further research into the chemical processes of life, leading to a better understanding of biochemistry and molecular biology.

Over time, as the understanding of chemistry advanced, the definition of organic chemistry shifted. Today, organic chemistry is defined as the study of carbon-containing compounds, regardless of their origin. This includes not only compounds derived from living organisms but also synthetic compounds made in laboratories.

6.2.1: Carbon - The Chemical Basis for Life
6.2.2: Hydrocarbons- Compounds Containing Only Carbon and Hydrocarbon
6.2.3: Bond-Line Formulas

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# 6.2.1: Carbon - The Chemical Basis for Life

**Learning Objectives**

- Explain the properties of carbon that allow it to serve as a building block for biomolecules

Carbon is the fourth most abundant element in the universe and is the building block of life on earth. On earth, carbon circulates through the land, ocean, and atmosphere, creating what is known as the Carbon Cycle. This global carbon cycle can be divided further into two separate cycles: the geological carbon cycles takes place over millions of years, whereas the biological or physical carbon cycle takes place from days to thousands of years. In a nonliving environment, carbon can exist as carbon dioxide ($CO_2$), carbonate rocks, coal, petroleum, natural gas, and dead organic matter. Plants and algae convert carbon dioxide to organic matter through the process of photosynthesis, the energy of light.



Figure 6.2.1.1: Carbon is present in all life: All living things contain carbon in some form, and carbon is the primary component of macromolecules, including proteins, lipids, nucleic acids, and carbohydrates. Carbon exists in many forms in this leaf, including in the cellulose to form the leaf's structure and in chlorophyll, the pigment which makes the leaf green.

## Carbon is Important to Life

In its metabolism of food and respiration, an animal consumes glucose ($C_6H_{12}O_6$), which combines with oxygen ($O_2$) to produce carbon dioxide ($CO_2$), water ($H_2O$), and energy, which is given off as heat. The animal has no need for the carbon dioxide and releases it into the atmosphere. A plant, on the other hand, uses the opposite reaction of an animal through photosynthesis. It intakes carbon dioxide, water, and energy from sunlight to make its own glucose and oxygen gas. The glucose is used for chemical energy, which the plant metabolizes in a similar way to an animal. The plant then emits the remaining oxygen into the environment.

Cells are made of many complex molecules called macromolecules, which include proteins, nucleic acids (RNA and DNA), carbohydrates, and lipids. The macromolecules are a subset of organic molecules (any carbon-containing liquid, solid, or gas) that are especially important for life. The fundamental component for all of these macromolecules is carbon. The carbon atom has unique properties that allow it to form covalent bonds to as many as four different atoms, making this versatile element ideal to serve as the basic structural component, or "backbone," of the macromolecules.

## Structure of Carbon

Individual carbon atoms have an incomplete outermost electron shell. With an atomic number of 6 (six electrons and six protons),

the first two electrons fill the inner shell, leaving four in the second shell. Therefore, carbon atoms can form four covalent bonds with other atoms to satisfy the octet rule. The methane molecule provides an example: it has the chemical formula $CH_4$. Each of its four hydrogen atoms forms a single covalent bond with the carbon atom by sharing a pair of electrons. This results in a filled outermost shell.

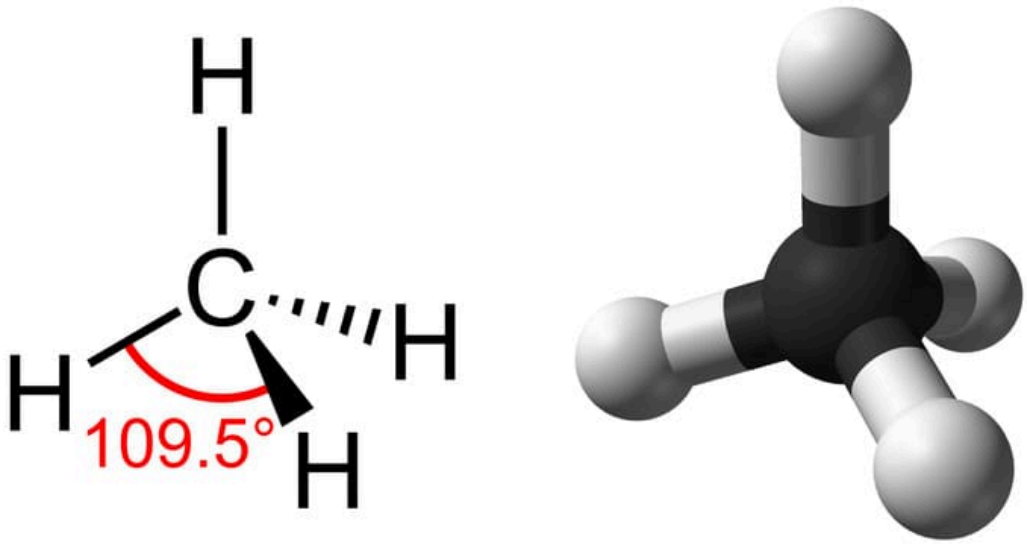



Figure 6.2.1.1: Structure of Methane: Methane has a tetrahedral geometry, with each of the four hydrogen atoms spaced 109.5° apart.

## Key Points

- All living things contain carbon in some form.
- Carbon is the primary component of macromolecules, including proteins, lipids, nucleic acids, and carbohydrates.
- Carbon's molecular structure allows it to bond in many different ways and with many different elements.
- The carbon cycle shows how carbon moves through the living and non-living parts of the environment.

## Key Terms

- **octet rule**: A rule stating that atoms lose, gain, or share electrons in order to have a full valence shell of 8 electrons (has some exceptions).
- **carbon cycle**: the physical cycle of carbon through the earth's biosphere, geosphere, hydrosphere, and atmosphere; includes such processes as photosynthesis, decomposition, respiration and carbonification
- **macromolecule**: a very large molecule, especially used in reference to large biological polymers (e.g., nucleic acids and proteins)

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# 6.2.2: Hydrocarbons- Compounds Containing Only Carbon and Hydrocarbon

## Learning Objectives

- Identify alkanes, alkenes, alkynes, and aromatic compounds.
- Draw structural formulas for organic compounds and identify compounds from structural formulas

The simplest organic compounds are those composed of only two elements: carbon and hydrogen. These compounds are called **hydrocarbons**. Hydrocarbons themselves are separated into two types: aliphatic hydrocarbons and aromatic hydrocarbons.

**Aliphatic hydrocarbons** are hydrocarbons based on chains of C atoms. There are three types of aliphatic hydrocarbons. **Alkanes** are aliphatic hydrocarbons with only single covalent bonds. **Alkenes** are hydrocarbons that contain at least one C–C double bond, and **Alkynes** are hydrocarbons that contain a C–C triple bond. Occasionally, we find an aliphatic hydrocarbon with a ring of C atoms; these hydrocarbons are called *cycloalkane*s (or *cycloalkene*s or *cycloalkyne*s).

**Aromatic hydrocarbons** have a special six-carbon ring called a *benzene* ring. Electrons in the benzene ring have special energetic properties that give benzene physical and chemical properties that are markedly different from alkanes. Originally, the term *aromatic* was used to describe this class of compounds because they were particularly fragrant. However, in modern chemistry the term *aromatic* denotes the presence of a six-membered ring that imparts different and unique properties to a molecule.

The simplest alkanes have their C atoms bonded in a straight chain; these are called *normal* alkanes. They are named according to the number of C atoms in the chain. The smallest alkane is methane:

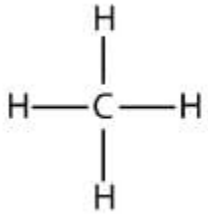



Figure 6.2.2.1 - Three-Dimensional Representation of Methane.

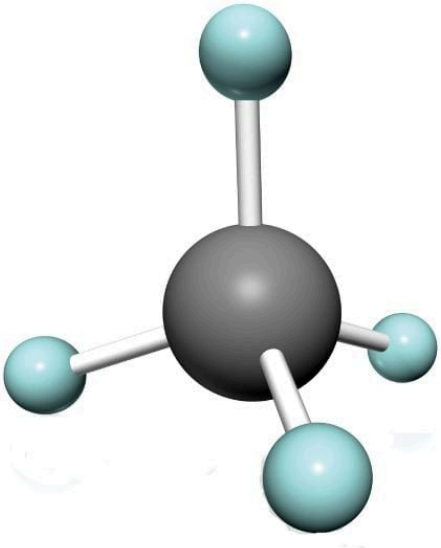
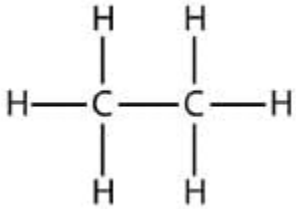
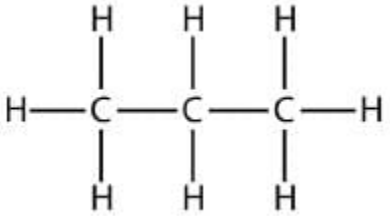


Figure 6.2.2.1 Three-Dimensional Representation of Methane © Thinkstock. The methane molecule is three dimensional, with the H atoms in the positions of the four corners of a tetrahedron.

The next-largest alkane has two C atoms that are covalently bonded to each other. For each C atom to make four covalent bonds, each C atom must be bonded to three H atoms. The resulting molecule, whose formula is $C_2H_6$, is ethane:



Propane has a backbone of three C atoms surrounded by H atoms. You should be able to verify that the molecular formula for propane is $C_3H_8$:



The diagrams representing alkanes are called **structural formulas** because they show the structure of the molecule. As molecules get larger, structural formulas become more and more complex. One way around this is to use a **condensed structural formula**, which lists the formula of each C atom in the backbone of the molecule. For example, the condensed structural formula for ethane is $CH_3CH_3$, while for propane it is $CH_3CH_2CH_3$. Table 6.2.2.1 - The First 10 Alkanes, gives the molecular formulas, the condensed structural formulas, and the names of the first 10 alkanes.

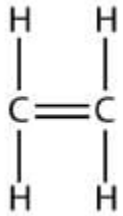
*Table 6.2.2.1 The First 10 Alkanes*

| Molecular Formula | Condensed Structural Formula | Name |
|---|---|---|
| $CH_4$ | $CH_4$ | methane |
| $C_2H_6$ | $CH_3CH_3$ | ethane |

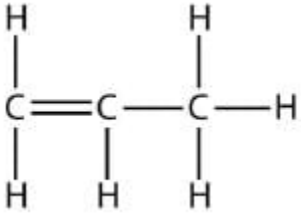
| Molecular Formula | Condensed Structural Formula | Name |
|---|---|---|
| $C_3H_8$ | $CH_3CH_2CH_3$ | propane |
| $C_4H_{10}$ | $CH_3CH_2CH_2CH_3$ | butane |
| $C_5H_{12}$ | $CH_3CH_2CH_2CH_2CH_3$ | pentane |
| $C_6H_{14}$ | $CH_3(CH_2)_4CH_3$ | hexane |
| $C_7H_{16}$ | $CH_3(CH_2)_5CH_3$ | heptane |
| $C_8H_{18}$ | $CH_3(CH_2)_6CH_3$ | octane |
| $C_9H_{20}$ | $CH_3(CH_2)_7CH_3$ | nonane |
| $C_{10}H_{22}$ | $CH_3(CH_2)_8CH_3$ | decane |

Because alkanes have the maximum number of H atoms possible according to the rules of covalent bonds, alkanes are also referred to as **saturated hydrocarbons**.

Alkenes have a C–C double bond. Because they have less than the maximum number of H atoms possible, they are **unsaturated hydrocarbons**. The smallest alkene—ethene—has two C atoms and is also known by its common name ethylene:

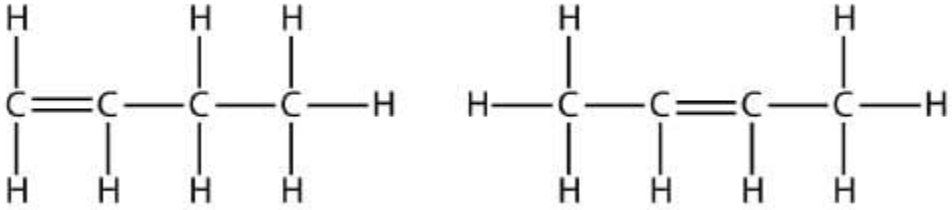


The next largest alkene—propene—has three C atoms with a C–C double bond between two of the C atoms. It is also known as propylene:



What do you notice about the names of alkanes and alkenes? The names of alkenes are the same as their corresponding alkanes except that the ending is *-ene*, rather than *-ane*. Using a stem to indicate the number of C atoms in a molecule and an ending to represent the type of organic compound is common in organic chemistry, as we shall see.

With the introduction of the next alkene, butene, we begin to see a major issue with organic molecules: choices. With four C atoms, the C–C double bond can go between the first and second C atoms or between the second and third C atoms:



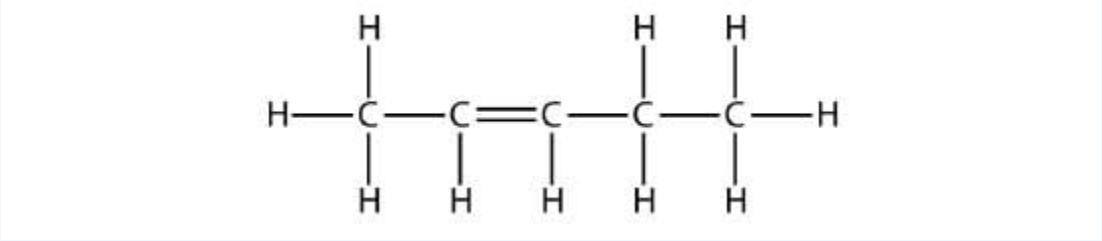
2 structural formulas for butene, with the first butene having the double bond on the first and second carbon from the left and the latter having its double bond on the second and third carbon from the left.

(A double bond between the third and fourth C atoms is the same as having it between the first and second C atoms, only flipped over.) The rules of naming in organic chemistry require that these two substances have different names. The first molecule is named *1-butene*, while the second molecule is named *2-butene*. The number at the beginning of the name indicates where the double bond originates. The lowest possible number is used to number a feature in a molecule; hence, calling the second molecule 3-butene would be incorrect. Numbers are common parts of organic chemical names because they indicate which C atom in a chain contains a distinguishing feature.

The compounds 1-butene and 2-butene have different physical and chemical properties, even though they have the same molecular formula—$C_4H_8$. Different molecules with the same molecular formula are called **isomers**. Isomers are common in organic chemistry and contribute to its complexity.

## Example 6.2.2.1

Based on the names for the butene molecules, propose a name for this molecule.



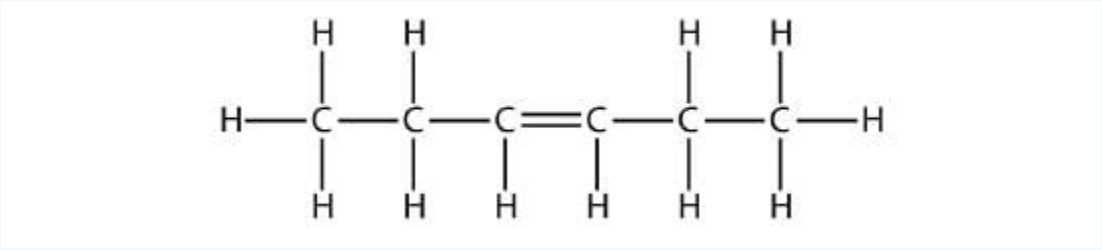
A structural formula of a five carbon molecule with a double bond on the third and fourth carbon from the left. There are ten hydrogen atoms in total.

**Solution**

With five C atoms, we will use the *pent-* stem, and with a C–C double bond, this is an alkene, so this molecule is a pentene. In numbering the C atoms, we use the number *2* because it is the lower possible label. So this molecule is named 2-pentene.

## Exercise 6.2.2.1

Based on the names for the butene molecules, propose a name for this molecule.



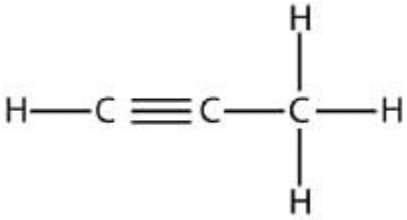
A structural formula of a six carbon molecule with a double bond on the third and fourth carbon from the left. There are twelve hydrogen atoms in total.

*Answer available at the end of this section.*

Alkynes, with a C–C triple bond, are named similarly to alkenes except their names end in *-yne*. The smallest alkyne is ethyne, which is also known as acetylene:

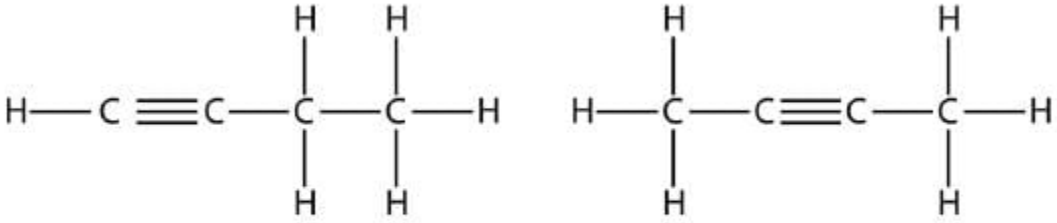


Propyne has the structure



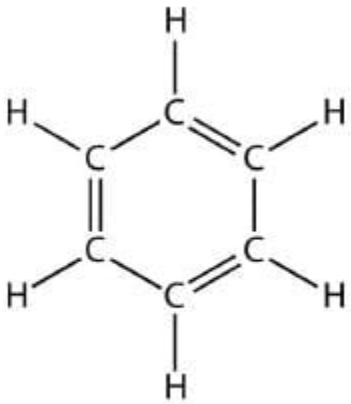
Structural formula showing three carbon molecules with a triple bond present between the first and second carbon atom. The appropriate number of hydrogen atoms is attached to each carbon atom.

With butyne, we need to start numbering the position of the triple bond, just as we did with alkenes:




Two structural formula of butyne. One butyne has a triple bond between the first and second carbon atom, while two butyne has the triple bond between the second and third carbon atom.

Aromatic compounds contain the benzene unit. Benzene itself is composed of six C atoms in a ring, with alternating single and double C–C bonds:



The six carbons are arranged in a hexagon pattern with one hydrogen atom emerging outwards from each carbon atom. The presence of a double bond is alternated between every other carbon atom.

The alternating single and double C–C bonds give the benzene ring a special stability, and it does not react like an alkene as

might be suspected. Benzene has the molecular formula $C_6H_6$; in larger aromatic compounds, a different atom replaces one or more of the H atoms.

As fundamental as hydrocarbons are to organic chemistry, their properties and chemical reactions are rather mundane. Most hydrocarbons are nonpolar because of the close electronegativities of the C and H atoms. As such, they dissolve only sparingly in $H_2O$ and other polar solvents. Small hydrocarbons, such as methane and ethane, are gases at room temperature, while larger hydrocarbons, such as hexane and octane, are liquids. Even larger hydrocarbons are solids at room temperature and have a soft, waxy consistency. In contrast to the mundane nature of hydrocarbon chemistry, adding different types of atoms and structures (known as *functional groups*, more on that later) changes many of the physical and chemical properties of the molecule.

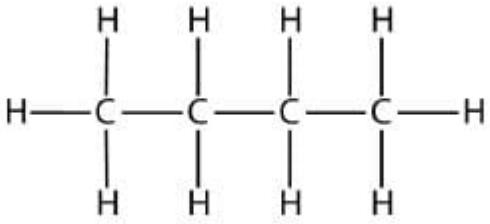
## Key Takeaways

- The simplest organic compounds are hydrocarbons and are composed of carbon and hydrogen.
- Organic molecules are often represented as skeletal formulas for convenience
- The physical and chemical properties of hydrocarbons are rather mundane but the inclusion of functional groups makes organic molecules much more interesting

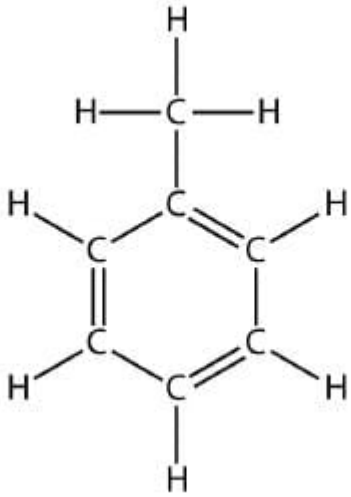
### Exercise 6.2.2.2

1. Define *hydrocarbon*. What are the two general types of hydrocarbons?
2. What are the three different types of aliphatic hydrocarbons? How are they defined?
3. Indicate whether each molecule is an aliphatic or an aromatic hydrocarbon; if aliphatic, identify the molecule as an alkane, an alkene, or an alkyne.

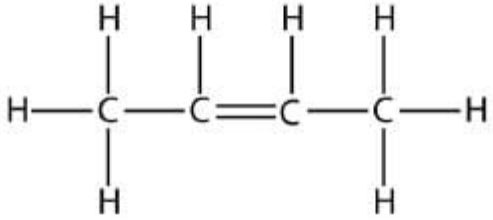
a.



b.

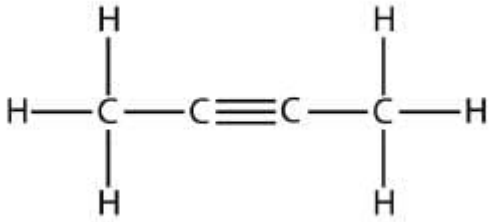


c.

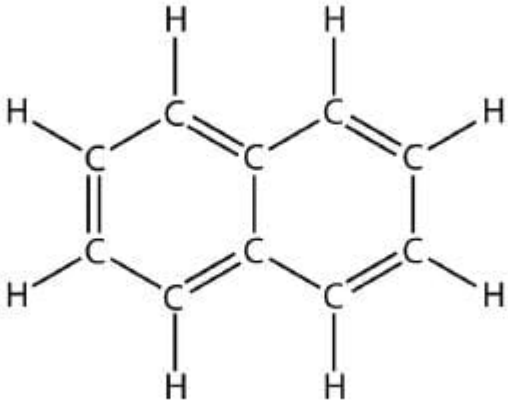


4. Indicate whether each molecule is an aliphatic or an aromatic hydrocarbon; if aliphatic, identify the molecule as an alkane, an alkene, or an alkyne.

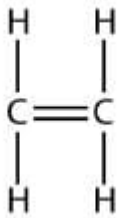
a.



b.

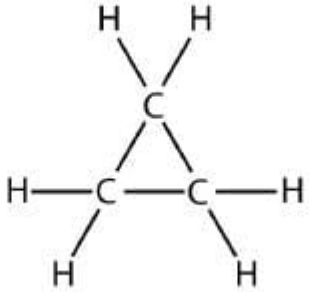


c.

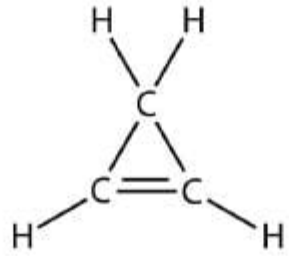


5. Indicate whether each molecule is an aliphatic or an aromatic hydrocarbon; if aliphatic, identify the molecule as an alkane, an alkene, or an alkyne.

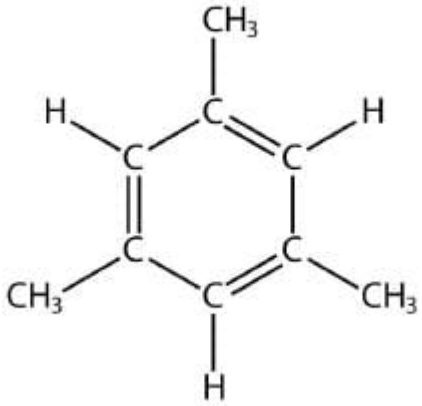
a.



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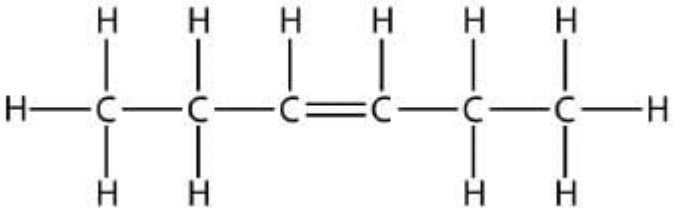


c.

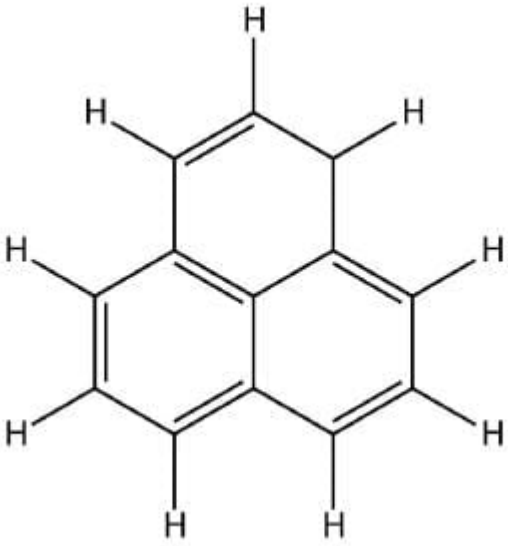


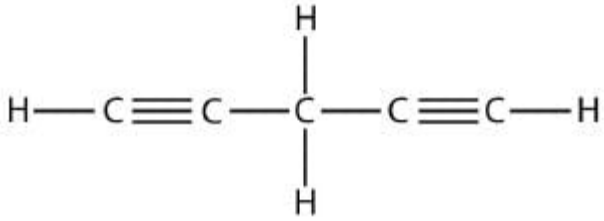
6. Indicate whether each molecule is an aliphatic or an aromatic hydrocarbon; if aliphatic, identify the molecule as an alkane, an alkene, or an alkyne.

a.



b.

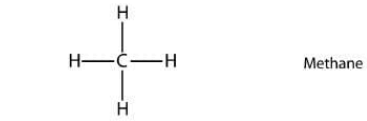


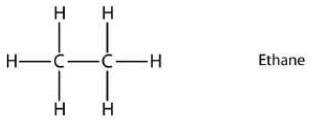
c. 

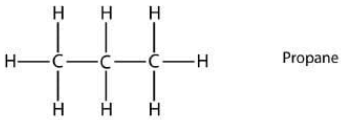
7. Name and draw the structural formulas for the four smallest alkanes.
8. Name and draw the structural formulas for the four smallest alkenes.
9. What does the term *aromatic* imply about an organic molecule?
10. What does the term *normal* imply when used for alkanes?
11. Explain why the name *1-propene* is incorrect. What is the proper name for this molecule?
12. Explain why the name *3-butene* is incorrect. What is the proper name for this molecule?
13. Name and draw the structural formula of each isomer of pentene.
14. Name and draw the structural formula of each isomer of hexyne.

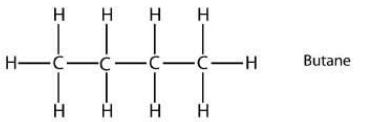
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## Answers

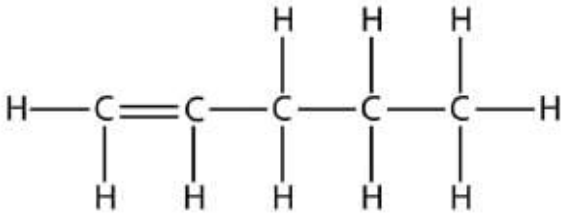
1. an organic compound composed of only carbon and hydrogen; aliphatic hydrocarbons and aromatic hydrocarbons
2. 
3. a. aliphatic; alkane
   b. aromatic
   c. aliphatic; alkene
4. 
5. a. aliphatic; alkane
   b. aliphatic; alkene
   c. aromatic
6. 
7. 



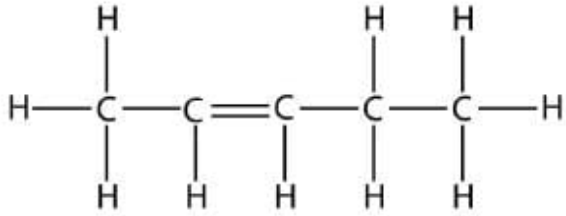




8. 
9. Aromatic means that the molecule has a benzene ring.
10. 
11. The 1 is not necessary. The name of the compound is simply *propene*.
12. 



1-Pentene



2-Pentene

13.

14.

## Answers

**Exercise** 6.2.2.1

3-hexene

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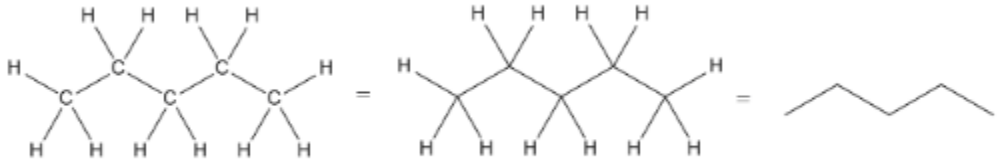
- 16.2: Hydrocarbons by Anonymous is licensed CC BY-NC-SA 3.0. Original source: https://2012books.lardbucket.org/books/beginning-chemistry.

# 6.2.3: Bond-Line Formulas

## *Bond-Line Formulas*

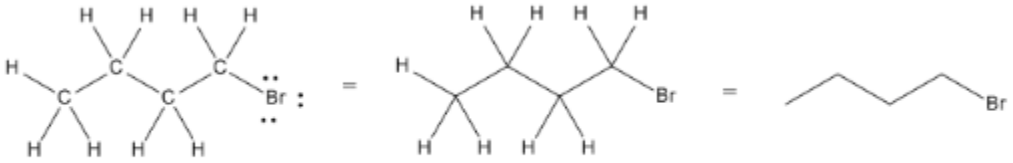
Lewis structures can tell us a lot about how atoms come together to make molecules. They can also be cumbersome, especially if we are dealing with very large molecules. Drawing a line instead of a pair of dots for bonding pairs of electrons makes it easier to draw structures. There are other abbreviations that are helpful in some situations.

Because organic chemistry is based on the compounds of carbon, we would have to draw the letter C over and over again unless we had a shortcut. In line structures, we drop the label "C" for the carbon atoms. Anytime there is a joint between two bonds (drawn as a vertex in a zig-zag line), the atom attached to that bond is assumed to be a carbon unless written otherwise.



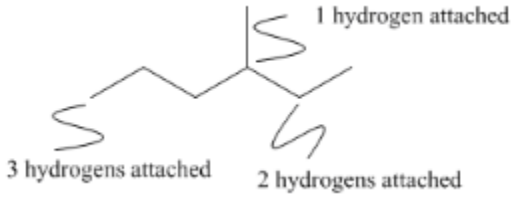
pentane

The atom at the end of a zig-zag line would also be a carbon, unless it is explicitly written as another atom.



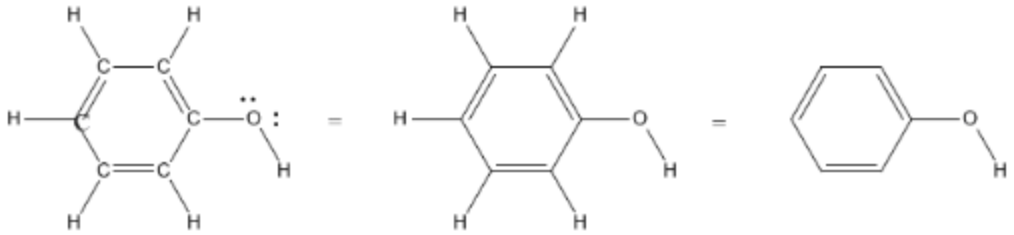
1-bromobutane

Taken even further, we will omit the hydrogens from our structures, since the compounds of carbon almost always contain hydrogen as well. Since we know carbon has a valence of four, we always know how many hydrogen atoms are attached to each carbon in order to reach that valence. A carbon with two bonds drawn in must have two hydrogens on it. A carbon with only one bond drawn to it must have three hydrogens.




Breakdown of a skeletal structure. Three hydrogens are attached to a terminal carbon. Two hydrogens are attached to a carbon surrounded by two other carbons. One hydrogen is attached to a carbon with bonds to three other carbons.

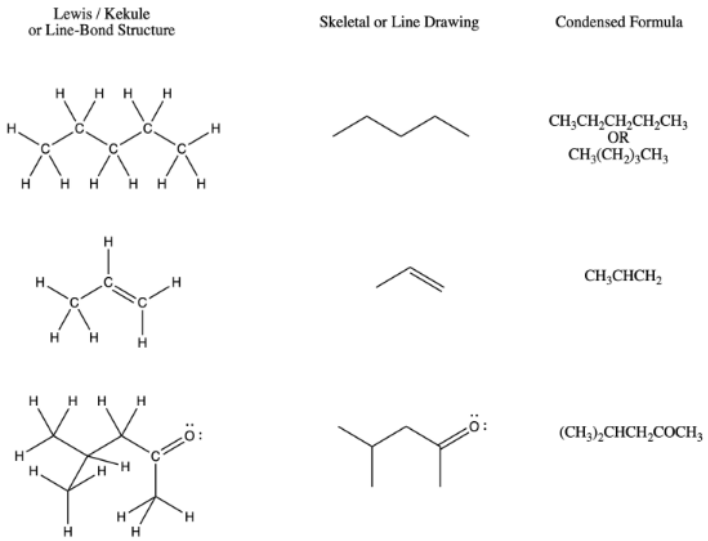
Note that the hydrogens are not normally omitted if they are attached to heteroatoms (atoms other than carbon, such as oxygen or nitrogen).



phenol

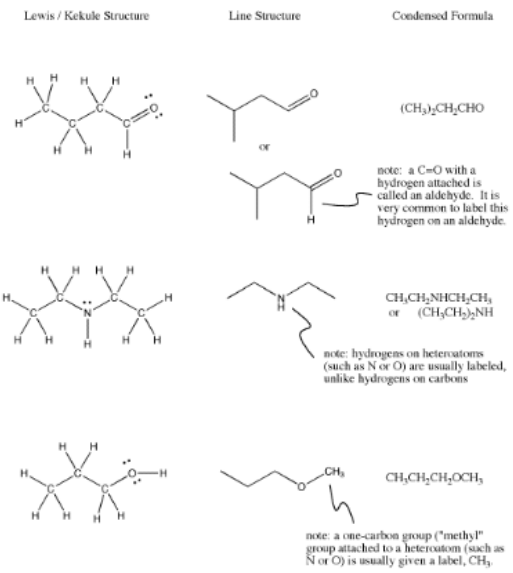
You will also note that lone pairs are frequently left out when we use line structures, so you will have to add them back in to think about Lewis structures. Adding the lone pairs back to the heteroatoms in line structures is a good habit to get into, because later in the course we will be very concerned with keeping track of where all the electrons are.

Below is a summary, showing the relationship between Lewis structures, line structures and condensed formulae for a few different compounds.




Lewis structures, skeletal structures, and condensed formulas for pentane, propene, and 4-methyl-2-pentanone.

Remember, in phenol, the hydrogen attached to oxygen was labeled in the line structure. Sometimes there are exceptions in line structures, in which atoms that you might not think about labeling usually do get labels. The most common exceptions are shown below.




Lewis structures, line structures, and condensed formulas of 3-methylbutanal, diethyl amine, and 1-methoxypropane.

## Exercise 6.2.3.1

Translate the following condensed formulae into line drawings.

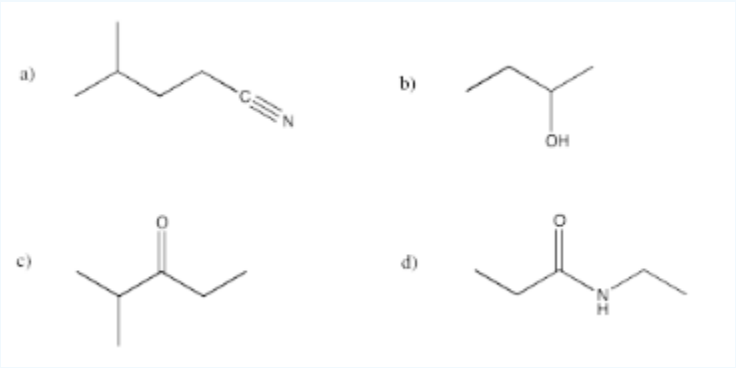
a) $CH_3CH_2NHCH_2CH_3$ b) $CH_3CHFCH_2CH_2CH_2Cl$

c) $CH_2CHOCH_2CH_3$ d) $CH_3CHClCH_2SCH_2CH_3$

*Answer available at the end of this section.*

## Exercise 6.2.3.2

Translate the following structures into condensed formula.

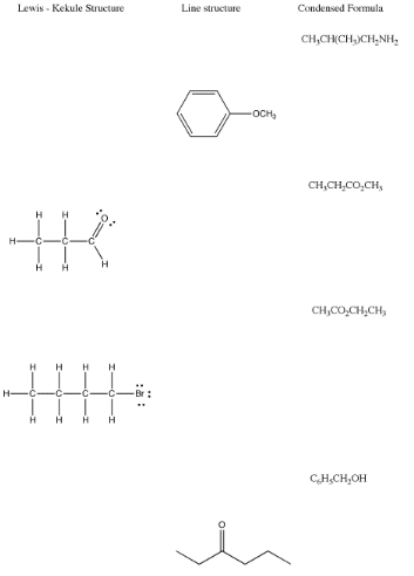



*Answer available at the end of this section.*

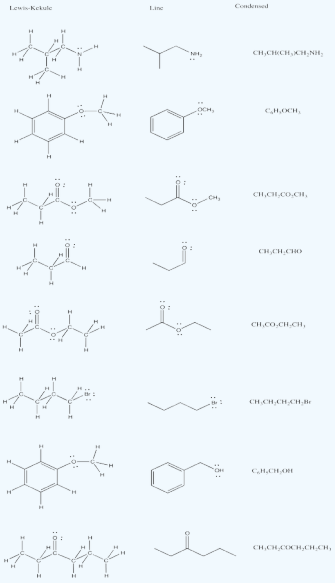
Answer a(CH3)2CHCH2CH2CNAnswer bCH3CH2CH(OH)CH3Answer c(CH3)2CHCOCH2CH3Answer dCH3CH2CONHCH2CH3

## Exercise 6.2.3.3

Try filling in the missing line drawing, Lewis / Kekule structures or condensed formulae in each line of the table below.



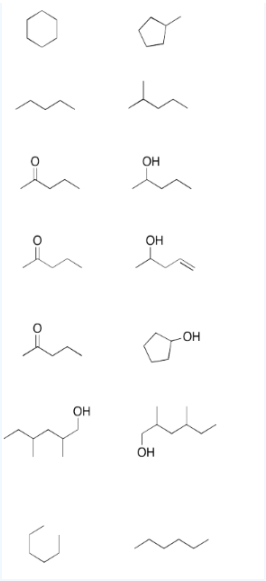

*Answer available at the end of this section.*



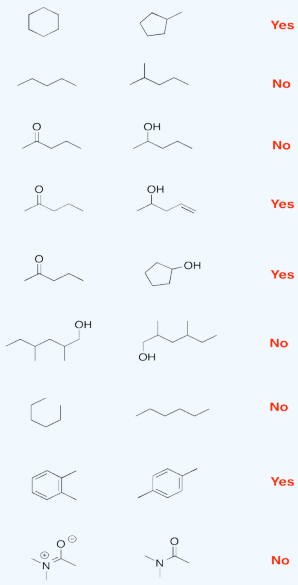
Answer

## Exercise 6.2.3.4

Look at the following pairs of compounds. Are the compounds constitutional isomers? (Hint: You may need to add in all hydrogens)



*Answer available at the end of this section.*

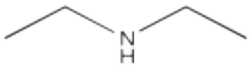



Answer

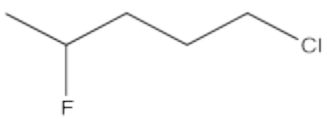
## Answers

**Exercise** 6.2.3.1

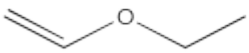
a)



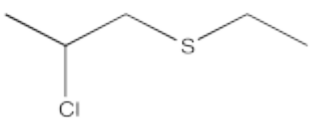

b)




c)




d)



**Exercise** 6.2.3.2

**Exercise** 6.2.3.3

**Exercise** 6.2.3.4

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# 6.3: MOLECULAR SHAPE AND POLARITY

In this section, we will delve deeper into some properties that arise from our understanding of bonding and drawing Lewis structures.



-  Topic hierarchy 

### 6.3.1: Predicting the Shapes of Molecules

### 6.3.2: Electronegativity and Polarity - Why Oil and Water Do not Mix

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# 6.3.1: Predicting the Shapes of Molecules

**Learning Objective**

- Determine the shape of simple molecules.

Molecules have shapes. There is an abundance of experimental evidence to that effect—from their physical properties to their chemical reactivity. Small molecules—molecules with a single central atom—have shapes that can be easily predicted. The basic idea in molecular shapes is called **valence shell electron pair repulsion (VSEPR).** VSEPR says that electron pairs, being composed of negatively charged particles, repel each other to get as far away from one another as possible. VSEPR makes a distinction between *electron group geometry*, which expresses how electron groups (bonds and nonbonding electron pairs) are arranged, and *molecular geometry*, which expresses how the atoms in a molecule are arranged. However, the two geometries are related.

There are two types of **electron groups**: any type of bond—single, double, or triple—and lone electron pairs. When applying VSEPR to simple molecules, the first thing to do is to count the number of electron groups around the central atom. Remember that a multiple bond counts as only *one* electron group.

Any molecule with only two atoms is linear. A molecule whose central atom contains only two electron groups orients those two groups as far apart from each other as possible—180° apart. When the two electron groups are 180° apart, the atoms attached to those electron groups are also 180° apart, so the overall molecular shape is linear. Examples include $BeH_2$ and $CO_2$:




Figure 6.3.1.1: Beryllium hydride and carbon dioxide bonding.

The two molecules, shown in the figure below in a "ball and stick" model.

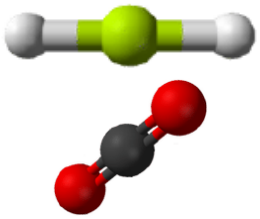


Figure 6.3.1.2: Beryllium hydride and carbon dioxide models. (CK12 Licence)

A molecule with three electron groups orients the three groups as far apart as possible. They adopt the positions of an equilateral triangle—120° apart and in a plane. The shape of such molecules is *trigonal planar*. An example is $BF_3$:

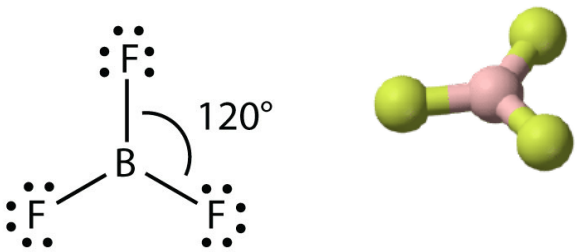



Figure 6.3.1.3: Boron trifluoride bonding. (CK12 Licence)

Some substances have a trigonal planar electron group distribution but have atoms bonded to only two of the three electron groups. An example is $GeF_2$:

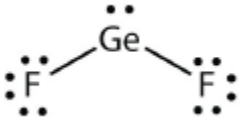



Figure 6.3.1.4: Germanium difluoride bonding.

From an electron group geometry perspective, $GeF_2$ has a trigonal planar shape, but its real shape is dictated by the positions of the atoms. This shape is called *bent* or *angular*.

A molecule with four electron groups about the central atom orients the four groups in the direction of a tetrahedron, as shown in Figure 6.3.1.1 Tetrahedral Geometry. If there are four atoms attached to these electron groups, then the molecular shape is also *tetrahedral*. Methane ($CH_4$) is an example.

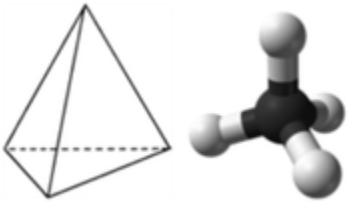


Figure 6.3.1.5: Tetrahedral structure of methane. (CK12 Licence)

This diagram of $CH_4$ illustrates the standard convention of displaying a three-dimensional molecule on a two-dimensional surface. The straight lines are in the plane of the page, the solid wedged line is coming out of the plane toward the reader, and the dashed wedged line is going out of the plane away from the reader.

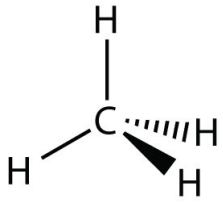



Figure 6.3.1.6: Methane bonding. (CK12 Licence)

$NH_3$ is an example of a molecule whose central atom has four electron groups, but only three of them are bonded to surrounding atoms.

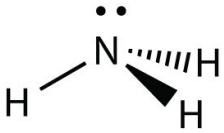



Figure 6.3.1.7: Ammonia bonding. (CK12 Licence)

Although the electron groups are oriented in the shape of a tetrahedron, from a molecular geometry perspective, the shape of $NH_3$ is *trigonal pyramidal*.

$H_2O$ is an example of a molecule whose central atom has four electron groups, but only two of them are bonded to surrounding atoms.




Figure 6.3.1.8: Water bonding.

Although the electron groups are oriented in the shape of a tetrahedron, the shape of the molecule is *bent* or *angular*. A molecule with four electron groups about the central atom, but only one electron group bonded to another atom, is linear because there are only two atoms in the molecule.

Double or triple bonds count as a single electron group. The Lewis electron dot diagram of formaldehyde ($CH_2O$) is shown in Figure 6.3.1.9.

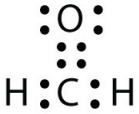



Figure 6.3.1.9: Lewis Electron Dot Diagram of Formaldehyde.

The central C atom has three electron groups around it because the double bond counts as one electron group. The three electron groups repel each other to adopt a trigonal planar shape.

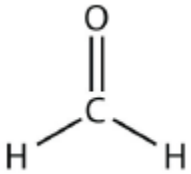



Figure 6.3.1.10: Formaldehyde bonding.

(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 6.3.1.1 summarizes the shapes of molecules based on the number of electron groups and surrounding atoms.

*Table 6.3.1.1: 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 6.3.1.1**

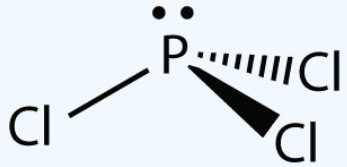
What is the approximate shape of each molecule?

a. PCl3
b. NOF

**Solution**

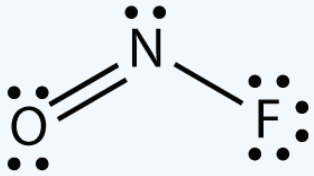
The first step is to draw the Lewis structure of the molecule.

For $\mathrm{PCl_3}$, 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 $\mathrm{NOF}$ is as follows:




The N atom has three electron groups on it, two of which are bonded to other atoms. The molecular shape is bent.

### Exercise 6.3.1.1

What is the approximate molecular shape of $\mathrm{CH_2Cl_2}$?

*Answer available at the end of this section.*

### Exercise 6.3.1.2

Ethylene $(\mathrm{C_2H_4})$ 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 available at the end of this section.*

*Answer available at the end of this section.*

## Summary

The approximate shape of a molecule can be predicted from the number of electron groups and the number of surrounding atoms.

## Answers

**Exercise** 6.3.1.1

Tetrahedral

**Exercise** 6.3.1.2

**Exercise** 6.3.1.2

Trigonal planar about both central C atoms.

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# 6.3.2: Electronegativity and Polarity - Why Oil and Water Do not 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 6.3.2.1.

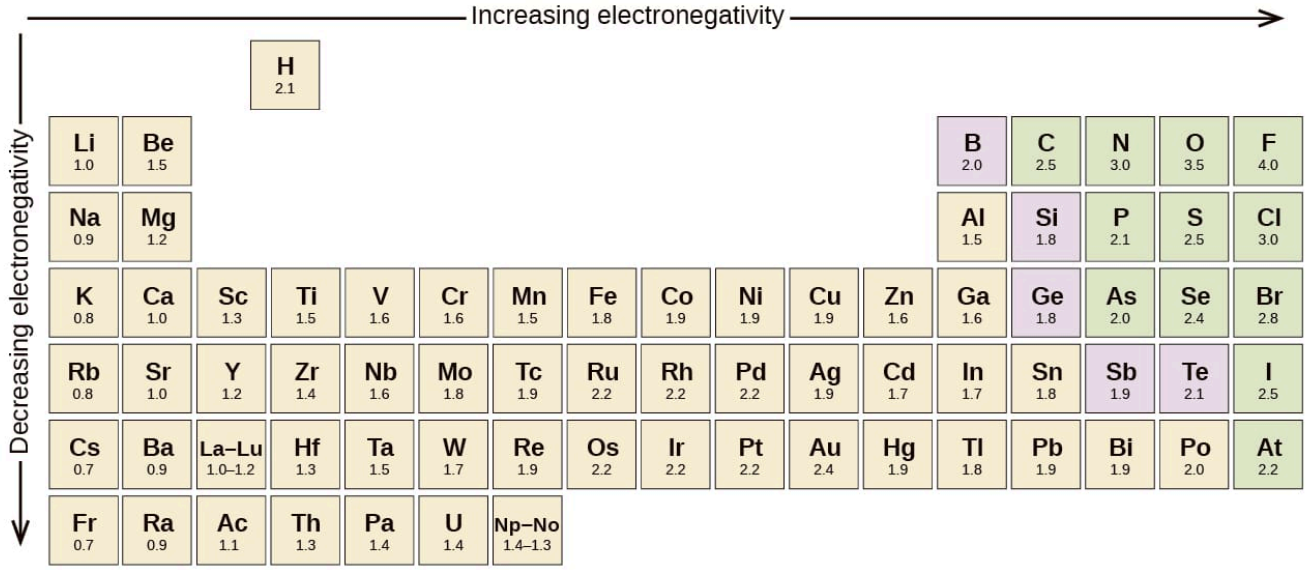



Figure 6.3.2.1: Electronegativities of the Elements. Electronegativities are used to determine the polarity of covalent bonds.

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 |

| Electronegativity Difference | Bond Type |
|---|---|
| >2.0 | likely ionic |

## Nonpolar Covalent Bonds

A bond in which the electronegativity difference is less than 1.9 is considered to be mostly covalent in character. However, at this point we need to distinguish between two general types of covalent bonds. A **nonpolar covalent bond** is a covalent bond in which the bonding electrons are shared equally between the two atoms. In a nonpolar covalent bond, the distribution of electrical charge is balanced between the two atoms.

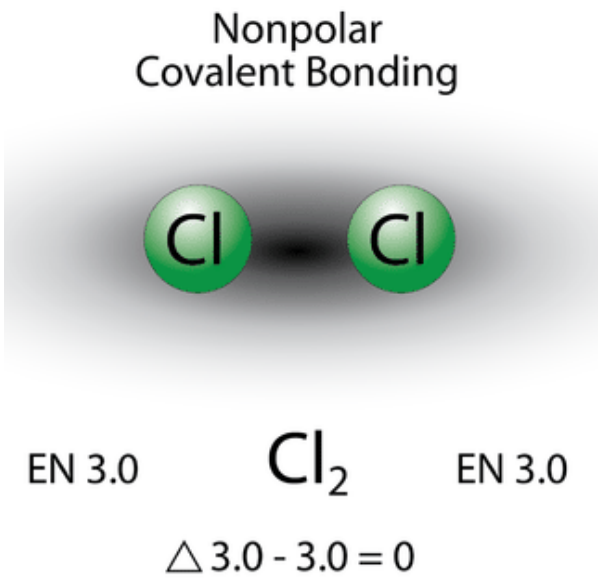



Figure 6.3.2.2: A nonpolar covalent bond is one in which the distribution of electron density between the two atoms is equal.

The two chlorine atoms share the pair of electrons in the single covalent bond equally, and the electron density surrounding the $\mathrm{Cl_2}$ molecule is symmetrical. Also note that molecules in which the electronegativity difference is very small (<0.5) are also considered nonpolar covalent. An example would be a bond between chlorine and bromine ($\Delta \mathrm{EN} = 3.0 - 2.8 = 0.2$).

## Polar Covalent Bonds

A bond in which the electronegativity difference between the atoms is between 0.5 and 2.0 is called a polar covalent bond. A **polar covalent bond** is a covalent bond in which the atoms have an unequal attraction for electrons and so the sharing is unequal. In a polar covalent bond, sometimes simply called a polar bond, the distribution of electrons around the molecule is no longer symmetrical.

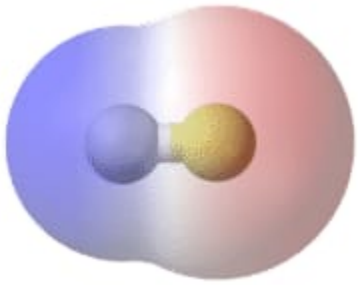


Figure 6.3.2.3: In the polar covalent bond of $\mathrm{HF}$, the electron density is unevenly distributed. There is a higher density (red) near the fluorine atom, and a lower density (blue) near the hydrogen atom.

An easy way to illustrate the uneven electron distribution in a polar covalent bond is to use the Greek letter delta ($\delta$).

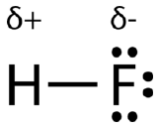



Figure 6.3.2.4: Use of $\delta$ to indicate partial charge.

The atom with the greater electronegativity acquires a partial negative charge, while the atom with the lesser electronegativity acquires a partial positive charge. The delta symbol is used to indicate that the quantity of charge is less than one. A crossed arrow can also be used to indicate the direction of greater electron density.

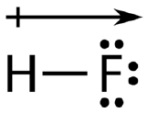



Figure 6.3.2.5: Use of crossed arrow to indicate polarity.

**YouTube Video**

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

View this YouTube Video online

*Electronegativity differences in bonding using Pauling scale. Differences in electronegativity classify bonds as covalent, polar covalent, or ionic.*

## Example 6.3.2.1: Bond Polarity

What is the polarity of each bond?

a. C–H
b. O–H

**Solution**

Using Figure 6.3.2.1, we can calculate the difference of the electronegativities of the atoms involved in the bond.

a. For the C–H bond, the difference in the electronegativities is 2.5 – 2.1 = 0.4. Thus we predict that this bond will be nonpolar covalent.
b. For the O–H bond, the difference in electronegativities is 3.5 – 2.1 = 1.4, so we predict that this bond will be polar covalent.

## Exercise 6.3.2.1

What is the polarity of each bond?

a. Rb–F
b. P–Cl

*Answer a available at the end of this section.*

# 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 $\mathrm{HF}$, is a polar molecule. The two electrically charged regions on either end of the molecule are called poles, similar to a magnet having a north and a south pole. A molecule with two poles is called a **dipole** (see figure below). Hydrogen fluoride is a dipole.




Figure $6.3.2.6$: A dipole is any molecule with a positive end and a negative end, resulting from unequal distribution of electron density throughout the molecule.

For molecules with more than two atoms, the molecular geometry must also be taken into account when determining if the molecule is polar or nonpolar. The figure below shows a comparison between carbon dioxide and water. Carbon dioxide $(\mathrm{CO_2})$ is a linear molecule. The oxygen atoms are more electronegative than the carbon atom, so there are two individual dipoles pointing outward from the $\mathrm{C}$ atom to each $\mathrm{O}$ atom. However, since the dipoles are of equal strength and are oriented this way, they cancel out and the overall molecular polarity of $\mathrm{CO_2}$ is zero.

Water is a bent molecule because of the two lone pairs on the central oxygen atom. The individual dipoles point from the $\mathrm{H}$ atoms toward the $\mathrm{O}$ atom. Because of the shape, the dipoles do not cancel each other out and the water molecule is polar. In the figure below, the net dipole is shown in blue and points upward.

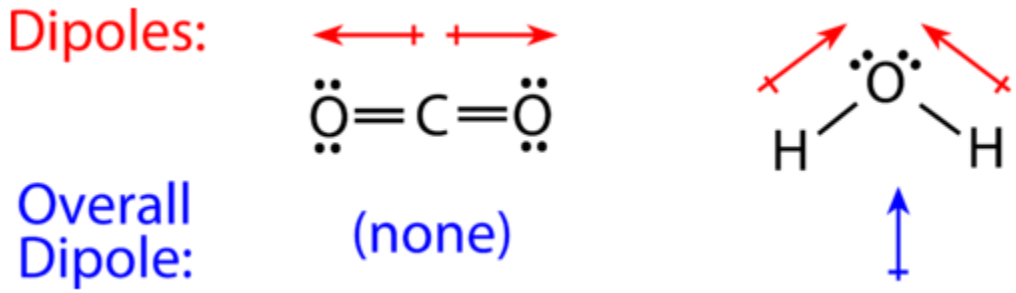



Figure $6.3.2.7$: The molecular geometry of a molecule affects its polarity. Each CO bond has a dipole moment, but they point in opposite directions so that the net CO2 molecule is nonpolar. In contrast, water is polar because the OH bond moments do not cancel out.

Some other molecules are shown in the figure below. Notice that a tetrahedral molecule such as $\mathrm{CH_4}$ is nonpolar. However, if one of the peripheral $\mathrm{H}$ atoms is replaced with another atom that has a different electronegativity, the molecule becomes polar. A trigonal planar molecule $(\mathrm{BF_3})$ may be nonpolar if all three peripheral atoms are the same, but a trigonal pyramidal molecule $(\mathrm{NH_3})$ is polar.

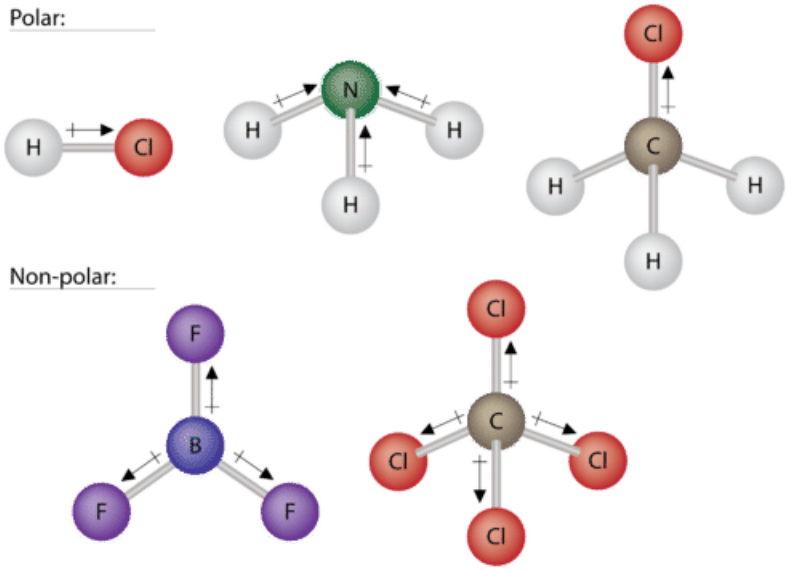



Figure 6.3.2.8: Some examples of polar and nonpolar molecules based on molecular geometry.

**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 6.3.2.14). 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.

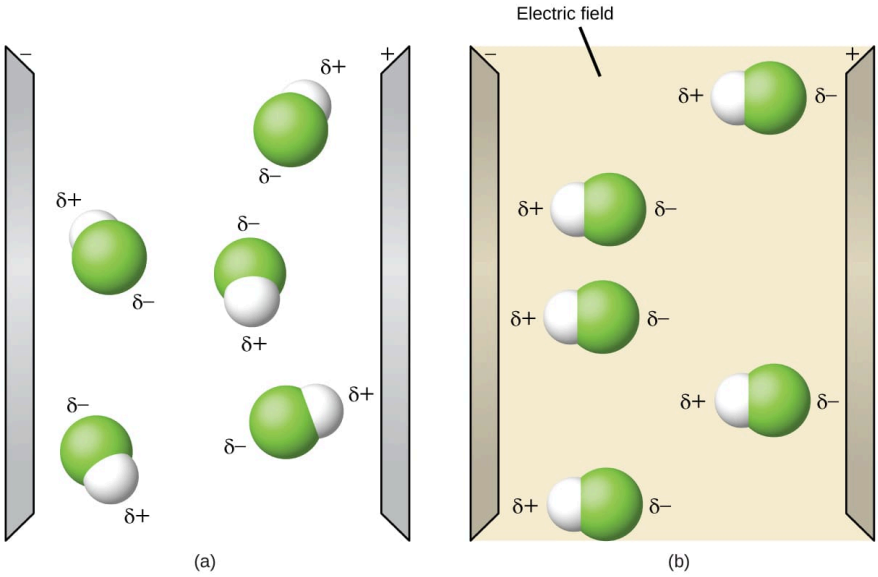


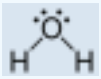

Figure 6.3.2.9: (a) Molecules are always randomly distributed in the liquid state in the absence of an electric field. (b) When an electric field is applied, polar molecules like HF will align to the dipoles with the field direction. (OpenStax CC-BY-SA);

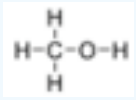
While molecules can be described as "polar covalent" or "ionic", it must be noted that this is often a relative term, with one molecule simply being *more polar* or *less polar* than another. However, the following properties are typical of such molecules. Polar molecules tend to:

- 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 6.3.2.2:

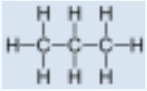
Label each of the following as polar or nonpolar.

a. Water, $H_2O$: 

b. Methanol, $CH_3OH$: 

c. Hydrogen Cyanide, HCN: 

d. Oxygen, $O_2$: 

e. Propane, $C_3H_8$: 

**Solution**

a. Water is polar. Any molecule with lone pairs of electrons around the central atom is polar.
b. Methanol is polar. This is not a symmetric molecule. The $-\mathrm{OH}$ side is different from the other 3 $-\mathrm{H}$ sides.
c. Hydrogen cyanide is polar. The molecule is not symmetric. The nitrogen and hydrogen have different electronegativities, creating an uneven pull on the electrons.
d. Oxygen is nonpolar. The molecule is symmetric. The two oxygen atoms pull on the electrons by exactly the same amount.

e. Propane is nonpolar, because it is symmetric, with $\mathrm{H}$ atoms bonded to every side around the central atoms and no unshared pairs of electrons.

### Exercise 6.3.2.2

Label each of the following as polar or nonpolar.

a. $\mathrm{SO_3}$
b. $\mathrm{NH_3}$

*Answer a available at the end of this section.*

*Answer b available at the end of this section.*

## Contributions & Attributions

- StackExchange (thomij).

### Answers

**Exercise** 6.3.2.1
likely ionic
polar covalent

**Exercise** 6.3.2.2
nonpolar

**Exercise** 6.3.2.2
polar

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# 7: INTERMOLECULAR FORCES AND FUNCTIONAL GROUPS

Why is water a liquid at room temperature while carbon dioxide is a gas? Why do some substances dissolve well in water while others do not? Why are deoxyribose nucleic acid (DNA) molecules so well adapted to serve as genetic material?

All of these questions are all partially answered by the types of intermolecular forces that exist between particles of these substances. In this chapter, we will develop an understanding of how the strength of intermolecular forces affect the boiling/melting point of substances and learn about how the inclusion of certain elements can affect the overall intermolecular forces particles can exhibit. Understanding this key concept is fundamental to explaining why biomolecules function the way that they do...but we'll save that for later. For now, let's dive into intermolecular forces!

*Title Image:* Hydrogen bonds observed between particles of water (image credit below)

"Liquid water hydrogen bond" by Thomas Splettstoesser (www.scistyle.com) is licensed under CC BY-SA 3.0.

**7.1: Changes of State and Intermolecular Forces**

7.1.1: States of Matter and Their Changes

7.1.2: Temperature - Random Motion of Molecules and Atoms

7.1.3: Heating and Cooling Curves

7.1.4: Temperature Changes - Heat Capacity

7.1.5: Energy and Heat Capacity Calculations

7.1.6: Intermolecular Forces

7.2: Functional Groups and Intermolecular Forces

7.2.1: Organic Compounds with Functional Groups

**7.2.2: Functional Groups w/ Oxygen and Sulfur**

7.2.2.1: Physical Properties of Alcohols

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7.2.2.4: Physical Properties of Esters

7.2.2.5: Organic Sulfur Compounds

**7.2.3: Functional Groups w/ Nitrogen**

7.2.3.1: Physical Properties of Amines

7.2.3.2: Physical Properties of Amides

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# 7.1: CHANGES OF STATE AND INTERMOLECULAR FORCES


7.1.1: States of Matter and Their Changes

7.1.2: Temperature - Random Motion of Molecules and Atoms

7.1.3: Heating and Cooling Curves

7.1.4: Temperature Changes - Heat Capacity

7.1.5: Energy and Heat Capacity Calculations

7.1.6: Intermolecular Forces



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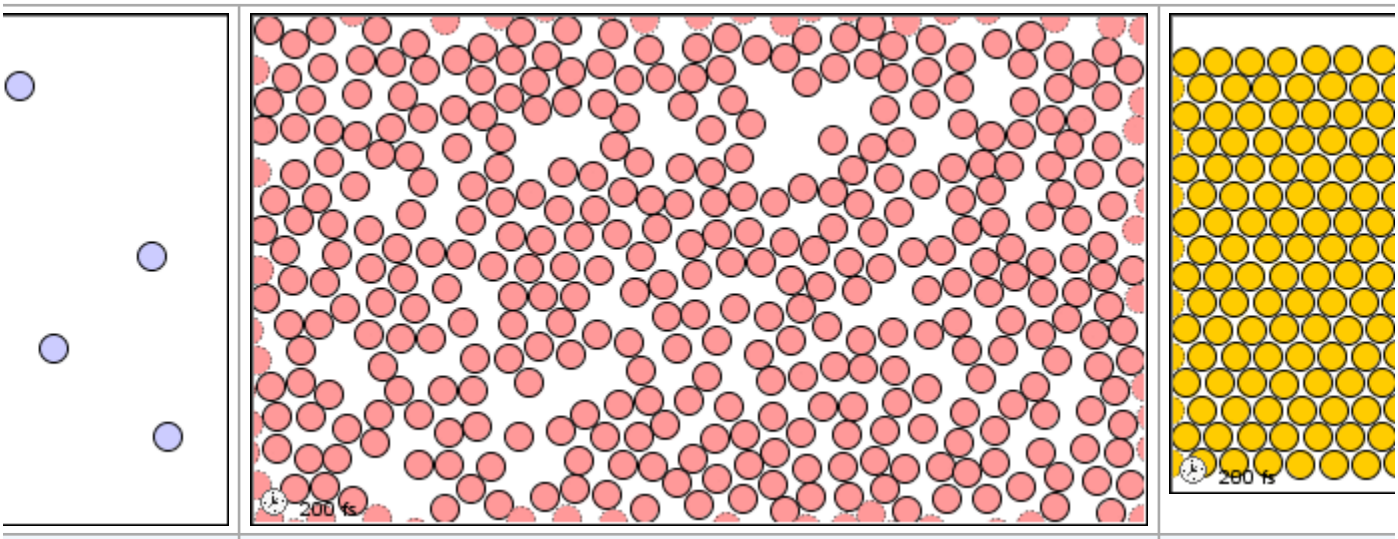
# 7.1.1: States of Matter and Their Changes

## Learning Objectives

- Review the states of matter and their properties
- Describe how change in temperature will affect the state of matter.

Previously, you were introduced to the three states, also called phases, of matter; solid, liquid, and gas. A phase is a certain form of matter that includes a specific set of physical properties. That is, the atoms, the molecules, or the ions that make up the phase do so in a consistent manner throughout the phase. Science recognizes three stable phases: the ***solid*** *phase*, in which individual particles can be thought of as in contact and held in place; the ***liquid*** *phase*, in which individual particles are in contact but moving with respect to each other; and the ***gas*** *phase*, in which individual particles are separated from each other by relatively large distances (see Figure 7.1.1.1).

The *state* of a substance depends on the balance between the *kinetic energy* of the individual particles (molecules or atoms) and the attractive forces between molecules, called *intermolecular forces*. The kinetic energy keeps the molecules apart and moving around, and is a function of the temperature of the substance. The intermolecular forces draw the particles together. A discussed previously, gasses are very sensitive to temperatures and pressure. However, these also affect liquids and solids too. Heating and cooling can change the *kinetic energy* of the particles in a substance, and so, we can change the physical state of a substance by heating or cooling it. Increasing the pressure on a substance forces the molecules closer together, which *increases* the strength of intermolecular forces.




*(b) as a liquid*

Figure 7.1.1.1: Molecular level picture of gases, liquids and solids.

We take advantage of changes between the gas, liquid, and solid states to cool a drink with ice cubes (solid to liquid), cool our bodies by perspiration (liquid to gas), and cool food inside a refrigerator (gas to liquid and vice versa). We use dry ice, which is solid $CO_2$, as a refrigerant (solid to gas), and we make artificial snow for skiing and snowboarding by transforming a liquid to a solid. In this section, we examine what happens when any of the three forms of matter is converted to either of the other two. These **changes of state** are often called phase changes. The six most common phase changes are shown in Figure 7.1.1.2.

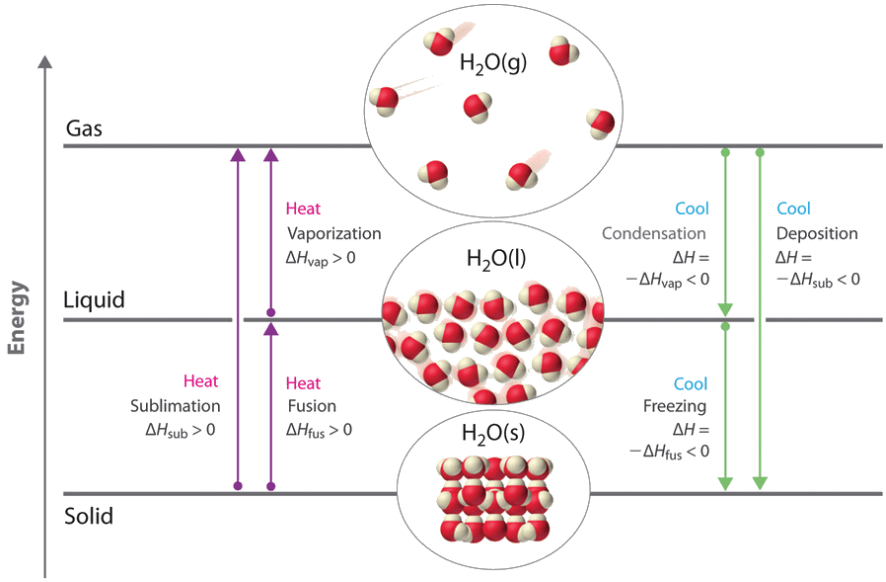



Figure 7.1.1.2: Enthalpy changes that accompany phase transitions are indicated by purple and green arrows. (CC BY-SA-NC; anoymous)

## Energy Changes That Accompany Phase Changes

Phase changes are *always* accompanied by a change in the enthalpy, $\Delta H$, of a system. For example, converting a liquid, in which the molecules are close together, to a gas, in which the molecules are, on average, far apart, requires an input of energy (heat) to give the molecules enough kinetic energy to allow them to overcome the intermolecular attractive forces. The stronger the attractive forces, the more energy is needed to overcome them. Solids, which are highly ordered, have the strongest intermolecular interactions, whereas gases, which are very disordered, have the weakest. Thus any transition from a more ordered to a less ordered state (solid to liquid, liquid to gas, or solid to gas) requires an input of energy; the $\Delta H$ is positive (endothermic). Conversely, any transition from a less ordered to a more ordered state (liquid to solid, gas to liquid, or gas to solid) releases energy; the $\Delta H$ is negative (exothermic). The energy change associated with each common phase change is shown in Figure 7.1.1.2.

> $\Delta H$ is positive for any transition from a more ordered to a less ordered state and negative for a transition from a less ordered to a more ordered state.

Previously, we defined the enthalpy changes associated with various chemical and physical processes. The molar **enthalpy of fusion** ($\Delta H_{fus}$), is the energy required to convert a solid to a liquid, a process known as fusion (or melting). As noted above, the process of melting requires energy and therefore, the ($\Delta H_{fus}$) is positive. The reverse process of freezing would release energy making the ($\Delta H_{fus}$) negative. The molar **enthalpy of vaporization** ($\Delta H_{vap}$), is the energy required to convert a liquid to a gas, known as vaporization. Melting points, enthalpies of fusion, boiling points, and enthalpies of vaporization for selected compounds are listed in Table 7.1.1.1.

*Table 7.1.1.1: Melting and Boiling Points and Enthalpies of Fusion and Vaporization for Selected Substances. Values given under 1 atm. of external pressure.*

| Substance | Melting Point (°C) | $\Delta H_{fus}$ (kJ/mol) | Boiling Point (°C) | $\Delta H_{vap}$ (kJ/mol) |
|---|---|---|---|---|
| $N_2$ | −210.0 | 0.71 | −195.8 | 5.6 |
| HCl | −114.2 | 2.00 | −85.1 | 16.2 |
| $Br_2$ | −7.2 | 10.6 | 58.8 | 30.0 |
| $CCl_4$ | −22.6 | 2.56 | 76.8 | 29.8 |
| $CH_3CH_2OH$ (ethanol) | −114.1 | 4.93 | 78.3 | 38.6 |
| $CH_3(CH_2)_4CH_3$ (*n*-hexane) | −95.4 | 13.1 | 68.7 | 28.9 |
| $H_2O$ | 0 | 6.01 | 100 | 40.7 |

| Substance | Melting Point (°C) | $\Delta H_{fus}$ (kJ/mol) | Boiling Point (°C) | $\Delta H_{vap}$ (kJ/mol) |
|---|---|---|---|---|
| Na | 97.8 | 2.6 | 883 | 97.4 |
| NaF | 996 | 33.4 | 1704 | 176.1 |

The substances with the highest melting points usually have the highest enthalpies of fusion; they tend to be ionic compounds that are held together by very strong electrostatic interactions. Substances with high boiling points are those with strong intermolecular interactions that must be overcome to convert a liquid to a gas, resulting in high enthalpies of vaporization. The enthalpy of vaporization of a given substance is much greater than its enthalpy of fusion because it takes more energy to completely separate molecules (conversion from a liquid to a gas) than to enable them only to move past one another freely (conversion from a solid to a liquid).

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# 7.1.2: Temperature - Random Motion of Molecules and Atoms

## Learning Objectives

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

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



Figure 7.1.2.1: The glowing charcoal on the left represents high kinetic energy, while the snow and ice on the right are of much lower kinetic energy.

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



Figure 7.1.2.2: Daniel Gabriel Fahrenheit (left), Anders Celsius (center), and Lord Kelvin (right).

## The Fahrenheit Scale

The first thermometers were glass and contained alcohol, which expanded and contracted as the temperature changed. The German scientist, Daniel Gabriel Fahrenheit used mercury in the tube, an idea put forth by Ismael Boulliau. The Fahrenheit scale

was first developed in 1724 and tinkered with for some time after that. The main problem with this scale is the arbitrary definitions of temperature. The freezing point of water was defined as $32^{\circ}\mathrm{F}$ and the boiling point as $212^{\circ}\mathrm{F}$. The Fahrenheit scale is typically not used for scientific purposes.

## The Celsius Scale

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

## The Kelvin Scale

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

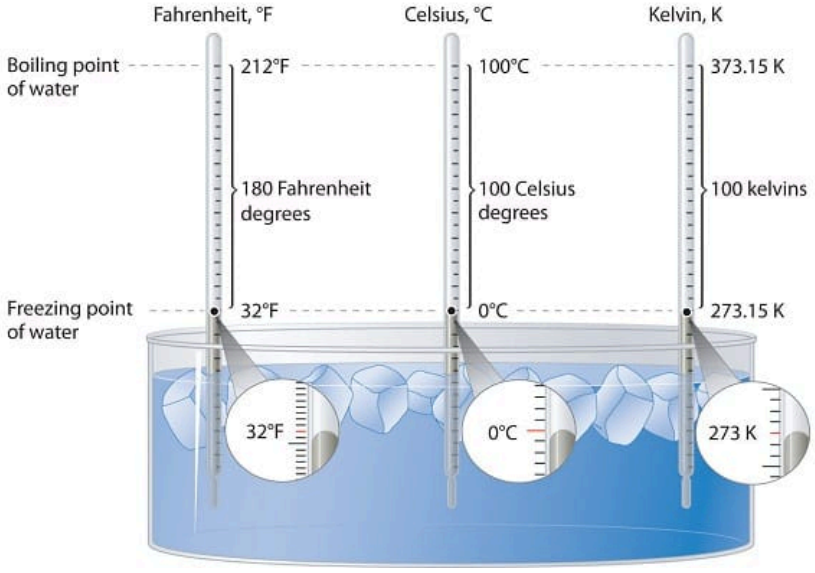



Figure 7.1.2.1: A Comparison of the Fahrenheit, Celsius, and Kelvin Temperature Scales. Because the difference between the freezing point of water and the boiling point of water is 100° on both the Celsius and Kelvin scales, the size of a degree Celsius (°C) and a kelvin (K) are precisely the same. In contrast, both a degree Celsius and a kelvin are 9/5 the size of a degree Fahrenheit (°F). (CC BY-SA-NC 3.0; anonymous)

## Converting Between Scales

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

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

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

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

is as follows:

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

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

### Example 7.1.2.1: Temperature Conversions

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

**Solution**

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

$$°C = \frac{(103.5°F - 32)}{1.8} \tag{7.1.2.1}$$

$$= 39.7\,°C \tag{7.1.2.2}$$

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

$$K = 39.7\,°C + 273.15 \tag{7.1.2.3}$$

$$= 312.9\,K \tag{7.1.2.4}$$

### Exercise 7.1.2.1

Convert each temperature to °C and °F.

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

*Answer (a) available at the end of this section.*

*Answer (b) available at the end of this section.*

*Answer (c) available at the end of this section.*

## Summary

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

## Contributions & Attributions

### Answers

**Exercise** 7.1.2.1
5527 K, 9980 °F

**Exercise** 7.1.2.1
2807 K, 5084 °F

**Exercise** 7.1.2.1
-195.79 K, -320.42 °F

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# 7.1.3: Heating and Cooling Curves

During the lifetime of Mark Twain (real name: Samuel Langhorne Clemens, 1835-1910), the steamboat was a major means of transportation on the rivers and lakes of the United States. Twain himself was a steamboat pilot on the Mississippi River for a period of time, and took his pen name from the measurement of water depth (twelve feet, which was a safe depth for the boats). The boats got their power from steam—liquid water converted to a gas at high temperatures. The steam would push the pistons of the engine, causing the paddle wheels to turn and propel the boat.

## Heating Curves

Imagine that you have a block of ice that is at a temperature of $-30^{\circ}\mathrm{C}$, well below its **melting** point. The ice is in a closed container. As heat is steadily added to the ice block, the water molecules will begin to vibrate faster and faster as they absorb kinetic energy. Eventually, when the ice has warmed to $0^{\circ}\mathrm{C}$, the added energy will start to break apart the hydrogen bonding that keeps the water molecules in place when it is in the **solid** form. As the ice melts, its temperature does not rise. All of the energy that is being put into the ice goes into the melting process and not into any increase in temperature. During the melting process, the two states—solid and **liquid**—are in equilibrium with one another. If the system was isolated at that point and no energy was allowed to enter or leave, the ice-water mixture at $0^{\circ}\mathrm{C}$ would remain. Temperature is always constant during a change of state.

Continued heating of the water after the ice has completely melted will now increase the kinetic energy of the liquid molecules and the temperature will rise. Assuming that the atmospheric pressure is standard, the temperature will rise steadily until it reaches $100^{\circ}\mathrm{C}$. At this point, the added energy from the heat will cause the liquid to begin to vaporize. As with the previous state change, the temperature will remain at $100^{\circ}\mathrm{C}$ while the water molecules are going from the liquid to the **gas** or vapor state. Once all the liquid has completely boiled away, continued heating of the steam (since the container is closed) will increase its temperature above $100^{\circ}\mathrm{C}$.

The experiment described above can be summarized in a graph called a heating curve (figure below).

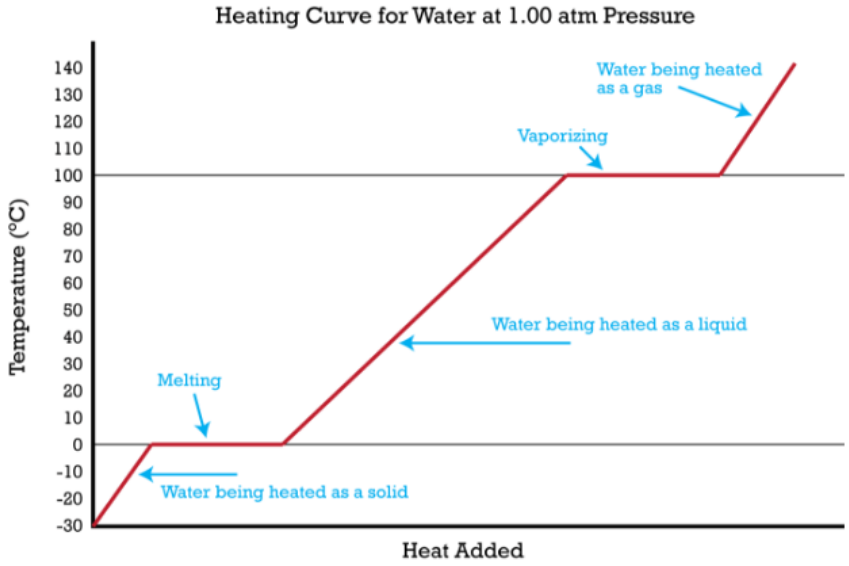



Figure 7.1.3.1: In the heating curve of water, the temperature is shown as heat is continually added. Changes of state occur during plateaus, because the temperature is constant.

The change of state behavior of all substances can be represented with a heating curve of this type. The melting and boiling points of the substance can be determined by the horizontal lines or plateaus on the curve. Other substances have melting and boiling points that are different from those of water. An exception to this blueprint heating curve is for a substance such as carbon dioxide, which sublimes rather than melts at standard pressure. The heating curve for carbon dioxide would have only one plateau, at the **sublimation** temperature of $\mathrm{CO_2}$.

The entire experiment could be run in reverse. Steam above $100^{\circ}\mathrm{C}$ could be steadily cooled down to $100^{\circ}\mathrm{C}$, at which point it would condense to liquid water. The water could then be cooled to $0^{\circ}\mathrm{C}$, at which point continued cooling would freeze the water to ice. The ice could then be cooled to a point below $0^{\circ}\mathrm{C}$. This could be diagrammed in a cooling curve that would be the reverse of the heating curve.

## Summary of State Changes

All of the changes of state that occur between solid, liquid, and gas are summarized in the diagram in the figure below. **Freezing** is the opposite of melting, and both represent the equilibrium between the solid and liquid states. **Evaporation** occurs when a liquid turns to a gas. **Condensation** is the opposite of vaporization, and both represent the equilibrium between the liquid and gas states. **Deposition** is the opposite of sublimation, and both represent the equilibrium between the solid and gas states.

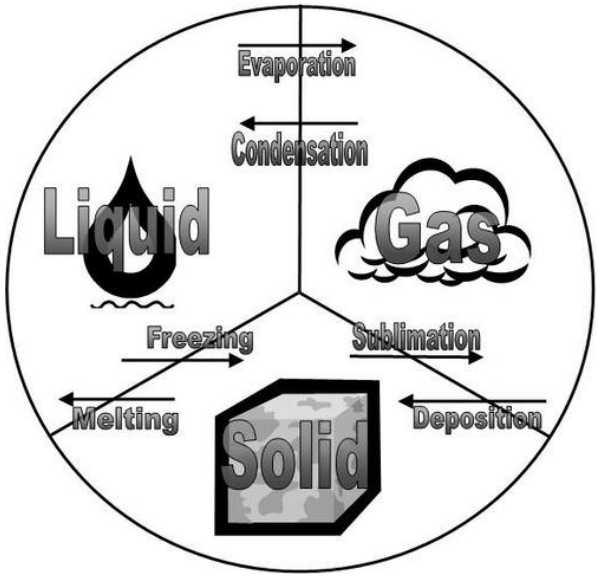



Figure 7.1.3.2: Solid, liquid, and gas states with the terms for each change of state that occurs between them.

## Summary

- A change of state can be brought about by putting heat into a system or removing it from the system.
- The temperature of a system will not change as long as the substance is undergoing a change from solid to liquid to gas, as well as the reverse.
- Freezing is the opposite of melting.
- Evaporation occurs when a liquid turns to a gas.
- Condensation is the opposite of vaporization.
- Deposition is the opposite of sublimation.

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# 7.1.4: Temperature Changes - Heat Capacity

If a swimming pool and wading pool, both full of water at the same temperature, were subjected to the same input of heat energy, the wading pool would certainly rise in temperature more quickly than the swimming pool. The heat capacity of an object depends on both its mass and its chemical composition. Because of its much larger mass, the swimming pool of water has a larger heat capacity than the wading pool.

## Heat Capacity and Specific Heat

Different substances respond to heat in different ways. If a metal chair sits in the bright sun on a hot day, it may become quite hot to the touch. An equal mass of water in the same sun will not become nearly as hot. We would say that water has a high **heat capacity** (the amount of heat required to raise the temperature of an object by $1^{\circ}\mathrm{C}$). Water is very resistant to changes in temperature, while metals in general are not. The **specific heat** of a substance is the amount of energy required to raise the temperature of 1 gram of the substance by $1^{\circ}\mathrm{C}$. The symbol for specific heat is $c_p$, with the $p$ subscript referring to the fact that specific heats are measured at constant pressure. The units for specific heat can either be joules per gram per degree $(\mathrm{J/g^{\circ}C})$ or calories per gram per degree $(\mathrm{cal/g^{\circ}C})$ (Table 7.1.4.1). This text will use $\mathrm{J/g^{\circ}C}$ for specific heat.

$$\text{specific heat} = \frac{\text{heat}}{\text{mass} \times \mathrm{cal/g^{\circ}C}}$$

Notice that water has a very high specific heat compared to most other substances.

*Table 7.1.4.1: Specific Heat Capacities*

| Substance | Specific Heat Capacity at 25°C in J/g °C | Substance | Specific Heat Capacity at 25°C in J/g °C |
|---|---|---|---|
| $H_2$ gas | 14.267 | steam @ 100°C | 2.010 |
| He gas | 5.300 | vegetable oil | 2.000 |
| $H_2O\,(l)$ | 4.184 | sodium | 1.23 |
| lithium | 3.56 | air | 1.020 |
| ethyl alcohol | 2.460 | magnesium | 1.020 |
| ethylene glycol | 2.200 | aluminum | 0.900 |
| ice @ 0°C | 2.010 | concrete | 0.880 |
| steam @ 100°C | 2.010 | glass | 0.840 |

Water is commonly used as a coolant for machinery because it is able to absorb large quantities of heat (see table above). Coastal climates are much more moderate than inland climates because of the presence of the ocean. Water in lakes or oceans absorbs heat from the air on hot days and releases it back into the air on cool days.



Figure 7.1.4.1: This power plant in West Virginia, like many others, is located next to a large lake so that the water from the lake can be used as a coolant. Cool water from the lake is pumped into the plant, while warmer water is pumped out of the plant and back into the lake.

## Summary

- Heat capacity is the amount of heat required to raise the temperature of an object by $1^{\circ}\mathrm{C}$).
- The specific heat of a substance is the amount of energy required to raise the temperature of 1 gram of the substance by $1^{\circ}\mathrm{C}$.

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# 7.1.5: Energy and Heat Capacity Calculations

## Learning Objectives

- To relate heat transfer to temperature change.

Heat is a familiar manifestation of transferring energy. When we touch a hot object, energy flows from the hot object into our fingers, and we perceive that incoming energy as the object being “hot.” Conversely, when we hold an ice cube in our palms, energy flows from our hand into the ice cube, and we perceive that loss of energy as “cold.” In both cases, the temperature of the object is different from the temperature of our hand, so we can conclude that differences in temperatures are the ultimate cause of heat transfer.

The specific heat of a substance can be used to calculate the temperature change that a given substance will undergo when it is either heated or cooled. The equation that relates heat $(q)$ to specific heat $(c_p)$, mass $(m)$, and temperature change $(\Delta T)$ is shown below.

$$q = c_p \times m \times \Delta T$$

The heat that is either absorbed or released is measured in joules. The mass is measured in grams. The change in temperature is given by $\Delta T = T_f - T_i$, where $T_f$ is the final temperature and $T_i$ is the initial temperature.

Every substance has a characteristic specific heat, which is reported in units of cal/g•°C or cal/g•K, depending on the units used to express Δ*T*. The specific heat of a substance is the amount of energy that must be transferred to or from 1 g of that substance to change its temperature by 1°. Table $7.1.5.1$ lists the specific heats for various materials.

*Table* $7.1.5.1$*: Specific Heats of Some Common Substances*

| Substance | Specific Heat $(\mathrm{J/g^{\circ}C})$ |
|---|---|
| Water (l) | 4.18 |
| Water (s) | 2.06 |
| Water (g) | 1.87 |
| Ammonia (g) | 2.09 |
| Ethanol (l) | 2.44 |
| Aluminum (s) | 0.897 |
| Carbon, graphite (s) | 0.709 |
| Copper (s) | 0.385 |
| Gold (s) | 0.129 |
| Iron (s) | 0.449 |
| Lead (s) | 0.129 |
| Mercury (l) | 0.140 |
| Silver (s) | 0.233 |

The *direction* of heat flow is not shown in heat = *mc*Δ*T*. If energy goes into an object, the total energy of the object increases, and the values of heat Δ*T* are positive. If energy is coming out of an object, the total energy of the object decreases, and the values of heat and Δ*T* are negative.

## Example 7.1.5.1

A $15.0\ \text{g}$ piece of cadmium metal absorbs $134\ \text{J}$ of heat while rising from $24.0^\circ\text{C}$ to $62.7^\circ\text{C}$. Calculate the specific heat of cadmium.

**Solution**

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

**Known**

- Heat $= q = 134\ \text{J}$
- Mass $= m = 15.0\ \text{g}$
- $\Delta T = 62.7^\circ\text{C} - 24.0^\circ\text{C} = 38.7^\circ\text{C}$

**Unknown**

- $c_p$ of cadmium $=?\ \text{J/g}^\circ\text{C}$

The specific heat equation can be rearranged to solve for the specific heat.

***Step 2: Solve.***

$$c_p = \frac{q}{m \times \Delta T} = \frac{134\ \text{J}}{15.0\ \text{g} \times 38.7^\circ\text{C}} = 0.231\ \text{J/g}^\circ\text{C}$$

***Step 3: Think about your result.***

The specific heat of cadmium, a metal, is fairly close to the specific heats of other metals. The result has three significant figures.

Since most specific heats are known (Table $7.1.5.1$), they can be used to determine the final temperature attained by a substance when it is either heated or cooled. Suppose that a $60.0\ \text{g}$ of water at $23.52^\circ\text{C}$ was cooled by the removal of $813\ \text{J}$ of heat. The change in temperature can be calculated using the specific heat equation:

$$\Delta T = \frac{q}{c_p \times m} = \frac{813\ \text{J}}{4.18\ \text{J/g}^\circ\text{C} \times 60.0\ \text{g}} = 3.24^\circ\text{C}$$

Since the water was being cooled, the temperature decreases. The final temperature is:

$$T_f = 23.52^\circ\text{C} - 3.24^\circ\text{C} = 20.28^\circ\text{C}$$

## Example 7.1.5.2

What quantity of heat is transferred when a 150.0 g block of iron metal is heated from 25.0°C to 73.3°C? What is the direction of heat flow?

**Solution**

We can use heat = $mc\Delta T$ to determine the amount of heat, but first we need to determine $\Delta T$. Because the final temperature of the iron is 73.3°C and the initial temperature is 25.0°C, $\Delta T$ is as follows:

$$\Delta T = T_{\text{final}} - T_{\text{initial}} = 73.3^\circ\text{C} - 25.0^\circ\text{C} = 48.3^\circ\text{C}$$

The mass is given as 150.0 g, and Table 7.3 gives the specific heat of iron as 0.108 cal/g•°C. Substitute the known values into heat = $mc\Delta T$ and solve for amount of heat:

$$\text{heat} = (150.0\ \text{g})\left(0.108\ \frac{\text{cal}}{\text{g} \cdot {}^\circ\text{C}}\right)(48.3^\circ\text{C}) = 782\ \text{cal}$$

Note how the gram and °C units cancel algebraically, leaving only the calorie unit, which is a unit of heat. Because the temperature of the iron increases, energy (as heat) must be flowing *into* the metal.

### Exercise 7.1.5.1

What quantity of heat is transferred when a 295.5 g block of aluminum metal is cooled from 128.0°C to 22.5°C? What is the direction of heat flow?

*Answer available at the end of this section.*

### Example 7.1.5.2

A 10.3 g sample of a reddish-brown metal gave off 71.7 cal of heat as its temperature decreased from 97.5°C to 22.0°C. What is the specific heat of the metal? Can you identify the metal from the data in Table 7.1.5.1?

**Solution**

The question gives us the heat, the final and initial temperatures, and the mass of the sample. The value of $\Delta T$ is as follows:

$$\Delta T = T_{\text{final}} - T_{\text{initial}} = 22.0°\text{C} - 97.5°\text{C} = -75.5°\text{C}$$

If the sample gives off 71.7 cal, it loses energy (as heat), so the value of heat is written as a negative number, –71.7 cal. Substitute the known values into heat = $mc\Delta T$ and solve for $c$:

$$-71.7 \text{ cal} = (10.3 \text{ g})(c)(-75.5°\text{C})$$

$$c = \frac{-71.7 \text{ cal}}{(10.3 \text{ g})(-75.5^{\circ}\text{C})}$$

$$c = 0.0923 \text{ cal/g•°C}$$

This value for specific heat is very close to that given for copper in Table 7.3.

### Exercise 7.1.5.2

A 10.7 g crystal of sodium chloride (NaCl) has an initial temperature of 37.0°C. What is the final temperature of the crystal if 147 cal of heat were supplied to it?

*Answer available at the end of this section.*

*Answer available at the end of this section.*

## Summary

Specific heat calculations are illustrated.

## Answers

**Exercise** 7.1.5.1

Heat leaves the aluminum block.

**Exercise** 7.1.5.2

**Exercise** 7.1.5.2

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# 7.1.6: Intermolecular Forces

**Learning Objective**

- Identify the different types of intermolecular forces.
- Relate the physical properties of a substance to the strength of attractive forces.

Why does a substance exist as a solid, liquid, or a gas at specific temperatures? Why do some substances evaporate quickly or melt more easily? These questions can be answered by considering the balance between the energy of the particles and **intermolecular forces** (or intermolecular interactions) between the particles. If the forces between particles are strong enough, the substance is a liquid or, if stronger, a solid. If the forces between particles are weak and sufficient energy is present, the particles separate from each other, so the gas phase is the preferred phase. The energy of the particles is mostly determined by temperature, so temperature is the main variable that determines what phase is stable at any given point.

There are three types of intermolecular forces: *London Dispersion, dipole-dipole, and hydrogen bonding*, collectively termed van der Waals forces, that will be introduced below.

## London Dispersion Forces

There are forces between all molecules that are caused by electrons being in different places in a molecule at any one time, which sets up a temporary separation of charge (a temporary dipole moment) that disappears almost as soon as it appears. These very weak intermolecular interactions are called **dispersion forces** (or **London dispersion forces**, named for the physicist Fritz London, who first described this force in the early 1900s).

Dispersion forces that develop between atoms in different molecules can attract the two molecules to each other. The forces are relatively weak, however, and become significant only when the molecules are very close. **Larger and heavier atoms and molecules** exhibit **stronger dispersion forces** than do smaller and lighter atoms and molecules. $F_2$ and $Cl_2$ are gases at room temperature (reflecting weaker attractive forces); $Br_2$ is a liquid, and $I_2$ is a solid (reflecting stronger attractive forces). Trends in observed melting and boiling points for the halogens clearly demonstrate this effect, as seen in Table 7.1.6.1.

*Table 7.1.6.1:* ***Melting and Boiling Points of the Halogens***

| Halogen | Molar Mass | Atomic Radius | Melting Point | Boiling Point |
|---|---|---|---|---|
| fluorine, $F_2$ | 38 g/mol | 72 pm | 53 K | 85 K |
| chlorine, $Cl_2$ | 71 g/mol | 99 pm | 172 K | 238 K |
| bromine, $Br_2$ | 160 g/mol | 114 pm | 266 K | 332 K |
| iodine, $I_2$ | 254 g/mol | 133 pm | 387 K | 457 K |
| astatine, $At_2$ | 420 g/mol | 150 pm | 575 K | 610 K |

The increase in melting and boiling points with increasing atomic/molecular size may be rationalized by considering how the strength of dispersion forces is affected by the electronic structure of the atoms or molecules in the substance. In a larger atom, the valence electrons are, on average, farther from the nuclei than in a smaller atom. Thus, they are less tightly held and can more easily form the temporary dipoles that produce the attraction. The measure of how easy or difficult it is for another electrostatic charge (for example, a nearby ion or polar molecule) to distort a molecule's charge distribution (its electron cloud) is known as **polarizability**. A molecule that has a charge cloud that is easily distorted is said to be very polarizable and will have large

dispersion forces; one with a charge cloud that is difficult to distort is not very polarizable and will have small dispersion forces.

### Example 7.1.6.1

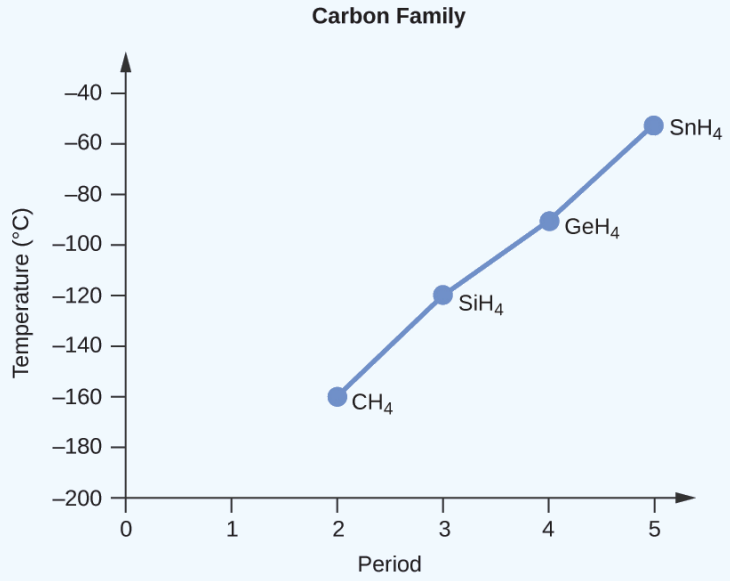
Order the following compounds of a group 14 element and hydrogen from lowest to highest boiling point: $CH_4$, $SiH_4$, $GeH_4$, and $SnH_4$. Explain your reasoning.

**Solution**

Applying the skills acquired in the chapter on chemical bonding and molecular geometry, all of these compounds are predicted to be nonpolar, so they may experience only dispersion forces: the smaller the molecule, the less polarizable and the weaker the dispersion forces; the larger the molecule, the larger the dispersion forces. The molar masses of $CH_4$, $SiH_4$, $GeH_4$, and $SnH_4$ are approximately 16 g/mol, 32 g/mol, 77 g/mol, and 123 g/mol, respectively. Therefore, $CH_4$ is expected to have the lowest boiling point and $SnH_4$ the highest boiling point. The ordering from lowest to highest boiling point is expected to be

$CH_4 < SiH_4 < GeH_4 < SnH_4$

A graph of the actual boiling points of these compounds versus the period of the group 14 elements shows this prediction to be correct:




### Exercise 7.1.6.1

Order the following hydrocarbons from lowest to highest boiling point: $C_2H_6$, $C_3H_8$, and $C_4H_{10}$.

*Answer available at the end of this section.*

*Answer available at the end of this section.*

## Dipole-Dipole Intermolecular Forces

Recall that a polar molecule will have a net unequal distribution of electrons in its covalent bonds resulting in a partial positive charge on one side of the molecule and a partial negative charge on the other side of the molecule—a separation of charge called a ***dipole***. The electrostatic attraction between oppositely charged ends of polar molecules are called **dipole-dipole interactions**, (as illustrated in Figure 7.1.6.1). Dipole-dipole attractions are between permanent dipoles and are therefore generally *stronger*

than dispersion forces, which are between temporary dipoles. Thus, a polar molecule such as $CH_2Cl_2$ has a significantly higher boiling point (313 K, or 40°C) than a nonpolar molecule like $CF_4$ (145 K, or –128°C), even though it has a lower molar mass (85 g/mol vs. 88 g/mol).

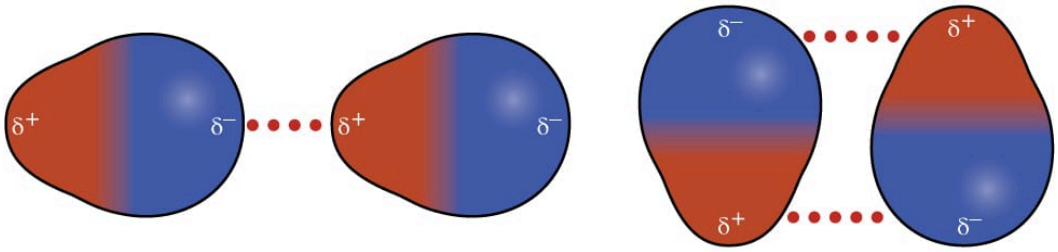



Figure 7.1.6.1: This image illustrates a dipole-dipole interaction, two arrangements of polar molecules that allow an attraction between the partial negative end of one molecule and the partial positive end of another.

**Example 7.1.6.2**

Predict which will have the higher boiling point: $N_2$ or CO. Explain your reasoning.

**Solution**

CO and $N_2$ are both diatomic molecules with masses of about 28 amu, so they experience similar London dispersion forces. Because CO is a polar molecule, it experiences dipole-dipole attractions. Because $N_2$ is nonpolar, its molecules cannot exhibit dipole-dipole attractions. The dipole-dipole attractions between CO molecules are comparably stronger than the dispersion forces between nonpolar $N_2$ molecules, so CO is expected to have the higher boiling point.

**Exercise 7.1.6.2**

Predict which will have the higher boiling point: $\mathrm{ICl}$ or $\mathrm{Br_2}$. Explain your reasoning.

*Answer available at the end of this section.*

## Hydrogen Bonds

An unusually strong form of dipole-dipole interaction is called **hydrogen bonding**. Hydrogen bonding is found in molecules with an H atom bonded to an N atom, an O atom, or an F atom. Such covalent bonds are very polar, and the dipole-dipole interaction between these bonds in two or more molecules is strong enough to create a new category of intermolecular force. Hydrogen bonding is the reason water has unusual properties. For such a small molecule (its molar mass is only 18 g/mol), $H_2O$ has relatively high melting and boiling points. Its boiling point is 373 K (100°C), while the boiling point of a similar molecule, $H_2S$, is 233 K (–60°C). This is because $H_2O$ molecules experience hydrogen bonding, while $H_2S$ molecules do not. This strong attraction between $H_2O$ molecules requires additional energy to separate the molecules in the condensed phase, so its boiling point is higher than would be expected. Hydrogen bonding is also responsible for water's ability as a solvent, its high heat capacity, and its ability to expand when freezing; the molecules line up in such a way that there is extra space between the molecules, increasing its volume in the solid state (Figure 7.1.6.2).

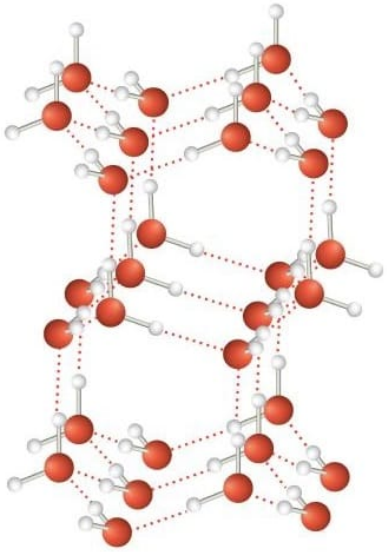


Figure 7.1.6.2: Hydrogen Bonding. When water solidifies, hydrogen bonding between the molecules forces the molecules to line up in a way that creates empty space between the molecules, increasing the overall volume of the solid. This is why ice is less dense than liquid water.

Despite use of the word "bond," keep in mind that hydrogen bonds are *intermolecular* attractive forces, not *intramolecular* attractive forces (covalent bonds). Hydrogen bonds are much weaker than covalent bonds, but are generally much stronger than other dipole-dipole attractions and dispersion forces.

## Hydrogen Bonding and DNA

Deoxyribonucleic acid (DNA) is found in every living organism and contains the genetic information that determines the organism's characteristics, provides the blueprint for making the proteins necessary for life, and serves as a template to pass this information on to the organism's offspring. A DNA molecule consists of two (anti-)parallel chains of repeating nucleotides, which form its well-known double helical structure, as shown in Figure 7.1.6.3.

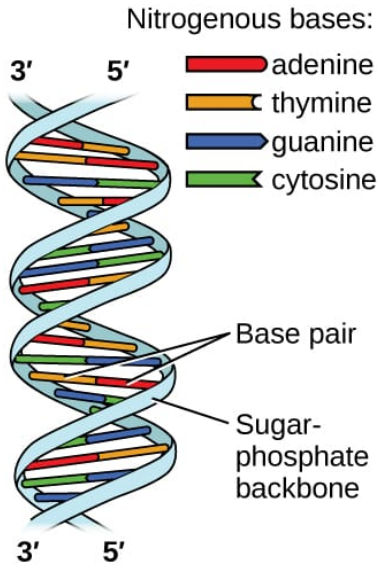



Figure 7.1.6.3: Two separate DNA molecules form a double-stranded helix in which the molecules are held together via hydrogen bonding. (credit: modification of work by Jerome Walker, Dennis Myts)

Each nucleotide contains a (deoxyribose) sugar bound to a phosphate group on one side, and one of four nitrogenous bases on the other. Two of the bases, cytosine (C) and thymine (T), are single-ringed structures known as pyrimidines. The other two, adenine (A) and guanine (G), are double-ringed structures called purines. These bases form complementary base pairs consisting

of one purine and one pyrimidine, with adenine pairing with thymine, and cytosine with guanine. Each base pair is held together by hydrogen bonding. A and T share two hydrogen bonds, C and G share three, and both pairings have a similar shape and structure Figure 7.1.6.4

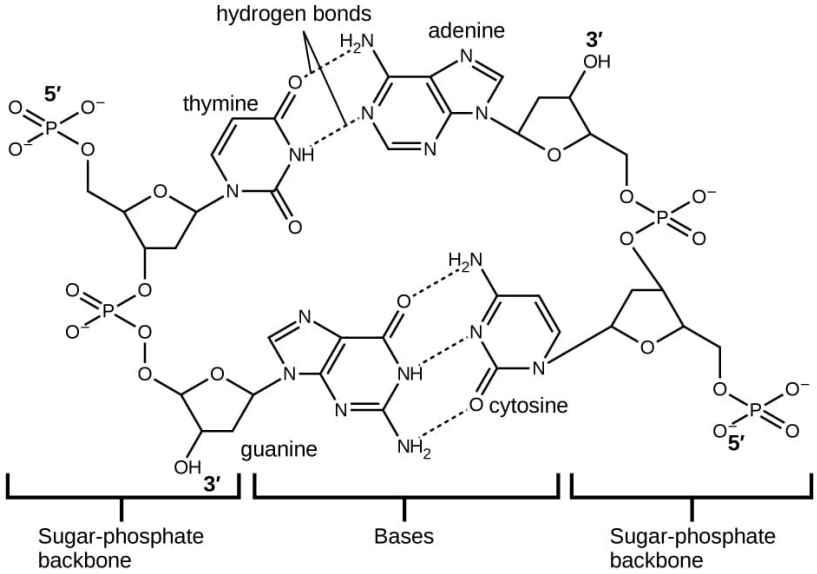



Figure 7.1.6.4: The geometries of the base molecules result in maximum hydrogen bonding between adenine and thymine (AT) and between guanine and cytosine (GC), so-called “complementary base pairs.”

The cumulative effect of millions of hydrogen bonds effectively holds the two strands of DNA together. Importantly, the two strands of DNA can relatively easily “unzip” down the middle since hydrogen bonds are relatively weak compared to the covalent bonds that hold the atoms of the individual DNA molecules together. This allows both strands to function as a template for replication.

## Applications: Geckos and Intermolecular Forces

Geckos have an amazing ability to adhere to most surfaces. They can quickly run up smooth walls and across ceilings that have no toe-holds, and they do this without having suction cups or a sticky substance on their toes. And while a gecko can lift its feet easily as it walks along a surface, if you attempt to pick it up, it sticks to the surface. How are geckos (as well as spiders and some other insects) able to do this? Although this phenomenon has been investigated for hundreds of years, scientists only recently uncovered the details of the process that allows geckos’ feet to behave this way.

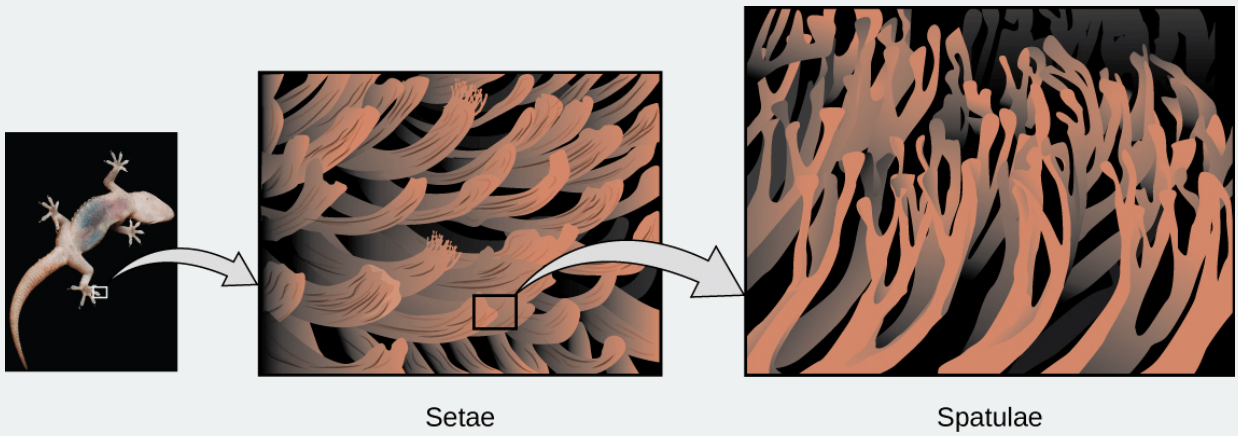



Figure 7.1.6.12: *Geckos’ toes contain large numbers of tiny hairs (setae), which branch into many triangular tips (spatulae). Geckos adhere to surfaces because of van der Waals attractions between the surface and a gecko’s millions of spatulae. By changing how the spatulae contact the surface, geckos can turn their stickiness “on” and “off.” (credit photo: modification of work by “JC*+A!”/Flickr)*

Geckos' toes are covered with hundreds of thousands of tiny hairs known as *setae*, with each seta, in turn, branching into hundreds of tiny, flat, triangular tips called *spatulae*. The huge numbers of spatulae on its setae provide a gecko, shown in Figure 8.1.12, with a large total surface area for sticking to a surface. In 2000, Kellar Autumn, who leads a multi-institutional gecko research team, found that geckos adhered equally well to both polar silicon dioxide and nonpolar gallium arsenide. This proved that geckos stick to surfaces because of dispersion forces—weak intermolecular attractions arising from temporary, synchronized charge distributions between adjacent molecules. Although dispersion forces are very weak, the total attraction over millions of spatulae is large enough to support many times the gecko's weight.

In 2014, two scientists developed a model to explain how geckos can rapidly transition from "sticky" to "non-sticky." Alex Greaney and Congcong Hu at Oregon State University described how geckos can achieve this by changing the angle between their spatulae and the surface. Geckos' feet, which are normally nonsticky, become sticky when a small shear force is applied. By curling and uncurling their toes, geckos can alternate between sticking and unsticking from a surface, and thus easily move across it. Further investigations may eventually lead to the development of better adhesives and other applications.

## Boiling Points and Bonding Types

In order for a substance to enter the gas phase, its particles must completely overcome the intermolecular forces holding them together. Therefore, a comparison of boiling points is essentially equivalent to comparing the strengths of the attractive intermolecular forces exhibited by the individual molecules. For small molecular compounds, London dispersion forces are the weakest intermolecular forces. Dipole-dipole forces are somewhat stronger, and hydrogen bonding is a particularly strong form of dipole-dipole interaction. However, when the mass of a nonpolar molecule is sufficiently large, its dispersion forces can be stronger than the dipole-dipole forces in a lighter polar molecule. Thus, nonpolar $Cl_2$ has a higher boiling point than polar HCl.

*Table 7.1.6.3: Intermolecular Forces and Boiling Points*

| Substance | Strongest Intermolecular Force | Boiling Point (°C) |
|---|---|---|
| $H_2$ | dispersion | -253 |
| Ne | dispersion | -246 |
| $O_2$ | dispersion | -183 |
| $Cl_2$ | dispersion | -34 |
| HCl | dipole-dipole | -85 |
| HBr | dipole-dipole | -66 |
| $H_2S$ | dipole-dipole | -61 |
| $NH_3$ | hydrogen bonding | -33 |
| HF | hydrogen bonding | 20 |
| $H_2O$ | hydrogen bonding | 100 |

### Example 7.1.6.3

Consider the compounds dimethylether ($CH_3OCH_3$), ethanol ($CH_3CH_2OH$), and propane ($CH_3CH_2CH_3$). Their boiling points, not necessarily in order, are −42.1 °C, −24.8 °C, and 78.4 °C. Match each compound with its boiling point. Explain your reasoning.

**Solution**

The shapes of $CH_3OCH_3$, $CH_3CH_2OH$, and $CH_3CH_2CH_3$ are similar, as are their molar masses (46 g/mol, 46 g/mol, and 44 g/mol, respectively), so they will exhibit similar dispersion forces. Since $CH_3CH_2CH_3$ is nonpolar, it may exhibit *only* dispersion forces. Because $CH_3OCH_3$ is polar, it will also experience dipole-dipole attractions. Finally, $CH_3CH_2OH$ has an –OH group,

and so it will experience the uniquely strong dipole-dipole attraction known as hydrogen bonding. So the ordering in terms of strength of IMFs, and thus boiling points, is $CH_3CH_2CH_3 < CH_3OCH_3 < CH_3CH_2OH$. The boiling point of propane is –42.1 °C, the boiling point of dimethylether is –24.8 °C, and the boiling point of ethanol is 78.5 °C.

### Exercise 7.1.6.3

Ethane ($CH_3CH_3$) has a melting point of –183 °C and a boiling point of –89 °C. Predict the melting and boiling points for methylamine ($CH_3NH_2$). Explain your reasoning.

*Answer available at the end of this section.*

### Example 7.1.6.4: Intermolecular Forces

What intermolecular forces besides dispersion forces, if any, exist in each substance? Are any of these substances solids at room temperature?

a. potassium chloride (KCl)
b. ethanol ($C_2H_5OH$)
c. bromine ($Br_2$)

**Solution**

a. Potassium chloride is composed of ions, so the intermolecular interaction in potassium chloride is ionic forces. Because ionic interactions are strong, it might be expected that potassium chloride is a solid at room temperature.
b. Ethanol has a hydrogen atom attached to an oxygen atom, so it would experience hydrogen bonding. If the hydrogen bonding is strong enough, ethanol might be a solid at room temperature, but it is difficult to know for certain. (Ethanol is actually a liquid at room temperature.)
c. Elemental bromine has two bromine atoms covalently bonded to each other. Because the atoms on either side of the covalent bond are the same, the electrons in the covalent bond are shared equally, and the bond is a nonpolar covalent bond. Thus, diatomic bromine does not have any intermolecular forces other than dispersion forces. It is unlikely to be a solid at room temperature unless the dispersion forces are strong enough. Bromine is a liquid at room temperature.

### Exercise 7.1.6.4

What intermolecular forces besides dispersion forces, if any, exist in each substance? Are any of these substances solids at room temperature?

a. methylamine ($CH_3NH_2$)
b. calcium sulfate ($CaSO_4$)
c. carbon monoxide (CO)

*Answer available at the end of this section.*

## Concept Review Exercise

1. What types of intermolecular interactions can exist in compounds?

2. What is the difference between covalent network and covalent molecular compounds?

## Answer

1. ionic bonding, network covalent, dispersion forces, dipole-dipole interactions, and hydrogen bonding.

2. Covalent network compounds contain atoms that are covalently bonded to other individual atoms in a giant 3-dimensional network. Covalent molecular compounds contain individual molecules that are attracted to one another through dispersion, dipole-dipole or hydrogen bonding.

## Key Takeaways

- A phase is a form of matter that has the same physical properties throughout.
- Molecules interact with each other through various forces: dipole-dipole interactions, hydrogen bonding, and dispersion forces.
- Dipole-dipole attractions result from the electrostatic attraction of the partial negative end of one dipolar molecule for the partial positive end of another.
- Hydrogen bonds are a special type of dipole-dipole attraction that results when hydrogen is bonded to one of the three most electronegative elements: F, O, or N.
- The temporary dipole that results from the motion of the electrons in an atom can induce a dipole in an adjacent atom and give rise to the London dispersion force. London forces increase with increasing molecular size.

## Exercises

1. List the three common phases in the order you are likely to find them—from lowest temperature to highest temperature.

2. List the three common phases in the order they exist from lowest energy to highest energy.

3. List these intermolecular interactions from weakest to strongest: London forces, hydrogen bonding, and ionic interactions.

4. List these intermolecular interactions from weakest to strongest: covalent network bonding, dipole-dipole interactions, and dispersion forces.

5. What type of intermolecular interaction is predominate in each substance?

    a. water ($H_2O$)
    b. sodium sulfate ($Na_2SO_4$)
    c. decane ($C_{10}H_{22}$)

6. What type of intermolecular interaction is predominate in each substance?

    a. diamond (C, crystal)
    b. helium (He)
    c. ammonia ($NH_3$)

7. Explain how a molecule like carbon dioxide ($CO_2$) can have polar covalent bonds but be nonpolar overall.

8. Sulfur dioxide ($SO_2$) has a formula similar to that of carbon dioxide (see Exercise 7) but is a polar molecule overall. What can you conclude about the shape of the $SO_2$ molecule?

9. What are some of the physical properties of substances that experience covalent network bonding?

10. What are some of the physical properties of substances that experience only dispersion forces?

## Answers

1. solid, liquid, and gas

2. solid, liquid, and gas

3. London forces, hydrogen bonding, and ionic interactions

4. dispersion, dipole-dipole, network covalent

5. a. hydrogen bonding
   b. ionic interactions
   c. dispersion forces

6. a. network covalent
b. dispersion
c. hydrogen bonding

7. The two covalent bonds are oriented in such a way that their dipoles cancel out.

8. $SO_2$ is not a linear molecule. It has a bent or V-shape.

9. very hard, high melting point

10. very soft, very low melting point

## Answers

**Exercise** 7.1.6.1

**Exercise** 7.1.6.1

All of these compounds are nonpolar and only have London dispersion forces: the larger the molecule, the larger the dispersion forces and the higher the boiling point. The ordering from lowest to highest boiling point is therefore

$$C_2H_6 < C_3H_8 < C_4H_{10}.$$

**Exercise** 7.1.6.2

ICl. ICl and $Br_2$ have similar masses (~160 amu) and therefore experience similar London dispersion forces. ICl is polar and thus also exhibits dipole-dipole attractions; $Br_2$ is nonpolar and does not. The relatively stronger dipole-dipole attractions require more energy to overcome, so ICl will have the higher boiling point.

**Exercise** 7.1.6.3

The melting point and boiling point for methylamine are predicted to be significantly greater than those of ethane. $CH_3CH_3$ and $CH_3NH_2$ are similar in size and mass, but methylamine possesses an –NH group and therefore may exhibit hydrogen bonding. This greatly increases its IMFs, and therefore its melting and boiling points. It is difficult to predict values, but the known values are a melting point of –93 °C and a boiling point of –6 °C.

**Exercise** 7.1.6.4

a. dipole-dipole, hydrogen bonding

b. ionic forces (solid at room temperature)

c. dipole-dipole

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# 7.2: FUNCTIONAL GROUPS AND INTERMOLECULAR FORCES


### 7.2.1: Organic Compounds with Functional Groups

### 7.2.2: Functional Groups w/ Oxygen and Sulfur

7.2.2.1: Physical Properties of Alcohols

7.2.2.2: Properties of Aldehydes and Ketones

7.2.2.3: Physical Properties of Carboxylic Acids

7.2.2.4: Physical Properties of Esters

7.2.2.5: Organic Sulfur Compounds

### 7.2.3: Functional Groups w/ Nitrogen

7.2.3.1: Physical Properties of Amines

7.2.3.2: Physical Properties of Amides



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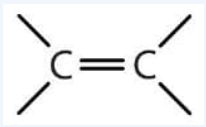
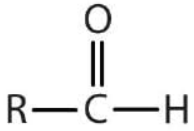
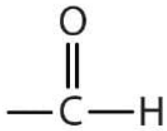
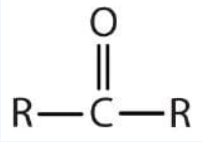
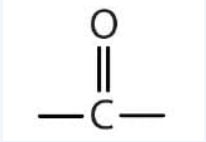
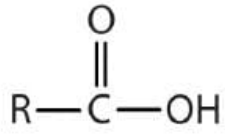
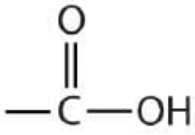
# 7.2.1: Organic Compounds with Functional Groups

**Learning Objectives**

- to describe functional groups and explain why they are useful in the study of organic chemistry.

Previously, we considered several kinds of hydrocarbons. Now we examine some of the many organic compounds that contain functional groups. We first introduced the idea of the functional group, a specific structural arrangement of atoms or bonds that imparts a characteristic chemical reactivity to the molecule. If you understand the behavior of a particular functional group, you will know a great deal about the general properties of that class of compounds. In this chapter, we make a brief yet systematic study of some of organic compound families. Each family is based on a common, simple functional group that contains an oxygen atom or a nitrogen atom. Some common functional groups are listed in Table 7.2.1.1.

*Table 7.2.1.1: Selected Organic Functional Groups*

| Name of Family | General Formula | Functional Group | Suffix* |
|---|---|---|---|
| alkane | RH | none | *-ane* |
| alkene | $R_2C{=}CR_2$ |  | *-ene* |
| alkyne | RC≡CR | –C≡C– | *-yne* |
| alcohol | ROH | –OH | *-ol* |
| thiol | RSH | –SH | *-thiol* |
| ether | ROR | –O– | ether |
| aldehyde |  |  | *-al* |
| ketone |  |  | *-one* |
| carboxylic acid |  |  | *-oic acid* |

***Ethers do not have a suffix in their common name; all ethers end with the word *ether*.**

## Summary

The functional group, a structural arrangement of atoms and/or bonds, is largely responsible for the properties of organic compound families.

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# 7.2.2: FUNCTIONAL GROUPS W/ OXYGEN AND SULFUR


7.2.2.1: Physical Properties of Alcohols

7.2.2.2: Properties of Aldehydes and Ketones

7.2.2.3: Physical Properties of Carboxylic Acids

7.2.2.4: Physical Properties of Esters

7.2.2.5: Organic Sulfur Compounds



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# 7.2.2.1: Physical Properties of Alcohols

## 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 7.2.2.1.1).

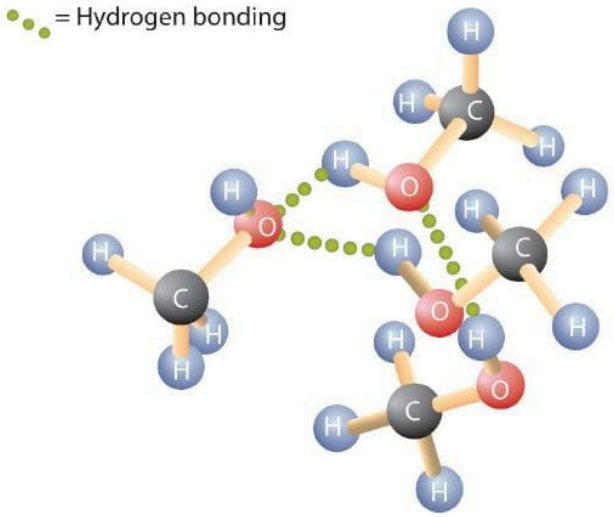



Figure 7.2.2.1.1: Intermolecular Hydrogen Bonding in Methanol. The OH groups of alcohol molecules make hydrogen bonding possible.

Recall that physical properties are determined to a large extent by the type of intermolecular forces. Table 7.2.2.1.1 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 7.2.2.1.1: Comparison of Boiling Points and Molar Masses*

| Formula | Name | Molar Mass | Boiling Point (°C) |
|---|---|---|---|
| $CH_4$ | methane | 16 | –164 |
| HOH | water | 18 | 100 |
| $C_2H_6$ | ethane | 30 | –89 |
| $CH_3OH$ | methanol | 32 | 65 |

| Formula | Name | Molar Mass | Boiling Point (°C) |
|---|---|---|---|
| $C_3H_8$ | 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 7.2.2.1.2). 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.

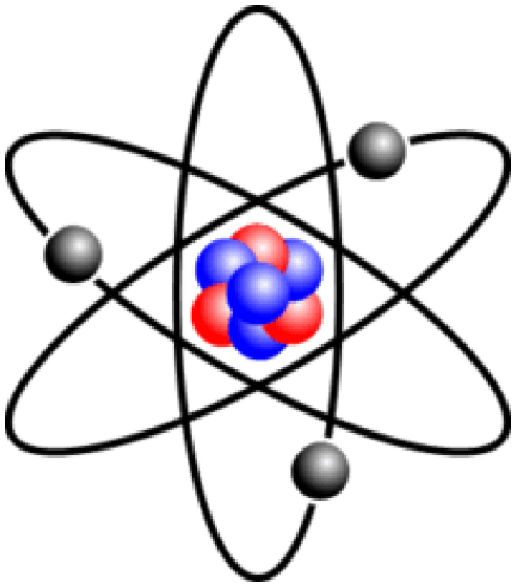


Figure 7.2.2.1.2: Hydrogen Bonding between Methanol Molecules and Water Molecules. Hydrogen bonding between the OH of methanol and water molecules accounts for the solubility of methanol in water.

## 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.

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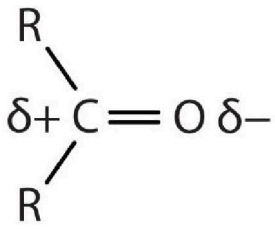
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# 7.2.2.2: Properties of Aldehydes and Ketones

## Learning Objectives

- Explain why the boiling points of aldehydes and ketones are higher than those of ethers and alkanes of similar molar masses but lower than those of comparable alcohols.
- Compare the solubilities in water of aldehydes and ketones of four or fewer carbon atoms with the solubilities of comparable alkanes and alcohols.
- Name the typical reactions take place with aldehydes and ketones.
- Describe some of the uses of common aldehydes and ketones.

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:




In aldehydes and ketones, this charge separation leads to dipole-dipole interactions that are great enough to significantly affect the boiling points. Table 7.2.2.2.1 shows that the polar single bonds in ethers have little such effect, whereas hydrogen bonding between alcohol molecules is even stronger.

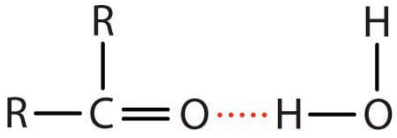
*Table 7.2.2.2.1: Boiling Points of Compounds Having Similar Molar Masses but Different Types of Intermolecular Forces*

| 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.

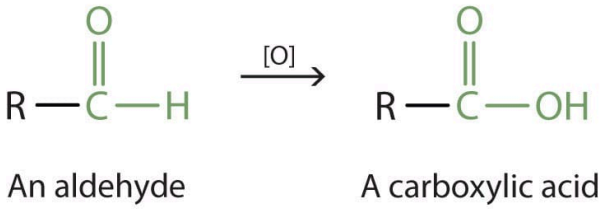
The oxygen atom of the carbonyl group engages in hydrogen bonding with a water molecule.

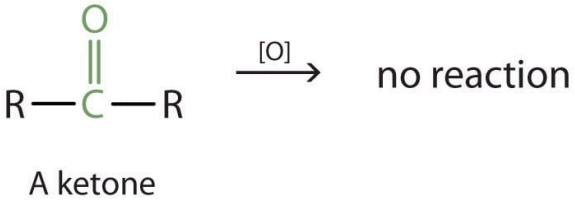


The solubility of aldehydes is therefore about the same as that of alcohols and ethers. Formaldehyde, acetaldehyde, and acetone are soluble in water. As the carbon chain increases in length, solubility in water decreases. The borderline of solubility occurs at about four carbon atoms per oxygen atom. 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.




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 7.2.2.2.1). Ordinary ketones do not react with Tollens' reagent.



Figure 7.2.2.2.1: 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 7.2.2.2.2).

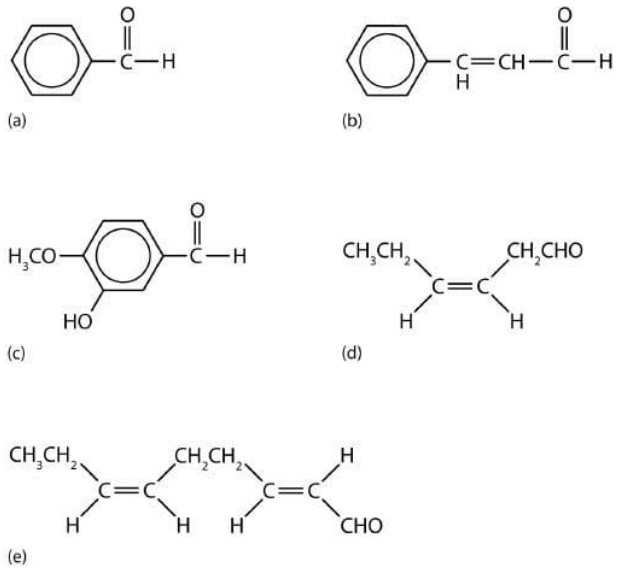


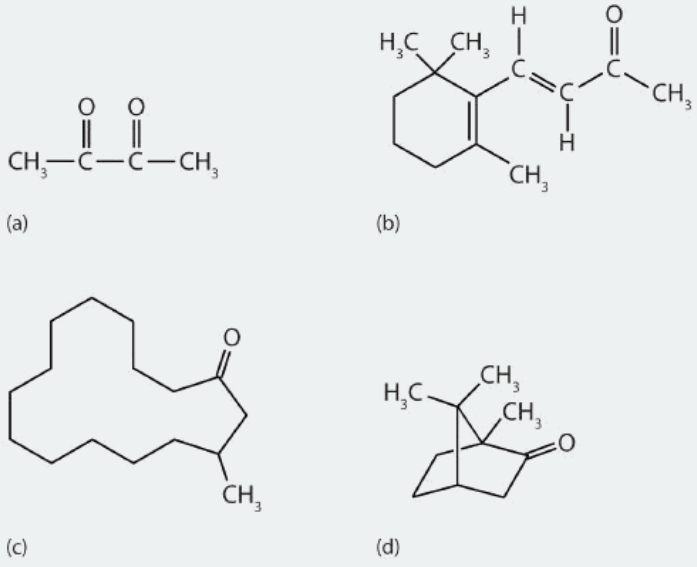

Figure 7.2.2.2.2 Some Interesting Aldehydes. (a) Benzaldehyde is an oil found in almonds; (b) cinnamaldehyde is oil of cinnamon; (c) vanillin gives vanilla its flavor; (d) *cis*-3-hexenal provides an herbal odor; and (e) *trans*-2-*cis*-6-nonadienal gives a cucumber odor.

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.

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# 7.2.2.3: Physical Properties of Carboxylic Acids

## Learning Objectives

- Compare the boiling points of carboxylic acids with alcohols of similar molar mass.
- Compare the solubilities of carboxylic acids in water with the solubilities of comparable alkanes and alcohols in water.

Many carboxylic acids are colorless liquids with disagreeable odors. The carboxylic acids with 5 to 10 carbon atoms all have "goaty" odors (explaining the odor of Limburger cheese). These acids are also produced by the action of skin bacteria on human sebum (skin oils), which accounts for the odor of poorly ventilated locker rooms. The acids with more than 10 carbon atoms are waxlike solids, and their odor diminishes with increasing molar mass and resultant decreasing volatility.

Carboxylic acids exhibit strong hydrogen bonding between molecules. They therefore have high boiling points compared to other substances of comparable molar mass.

The carboxyl group readily engages in hydrogen bonding with water molecules (Figure 7.2.2.3.1). The acids with one to four carbon atoms are completely miscible with water. Solubility decreases as the carbon chain length increases because dipole forces become less important and dispersion forces become more predominant. Hexanoic acid [$CH_3(CH_2)_4COOH$] is barely soluble in water (about 1.0 g/100 g of water). Palmitic acid [$CH_3(CH_2)_{14}COOH$], with its large nonpolar hydrocarbon component, is essentially insoluble in water. The carboxylic acids generally are soluble in such organic solvents as ethanol, toluene, and diethyl ether.

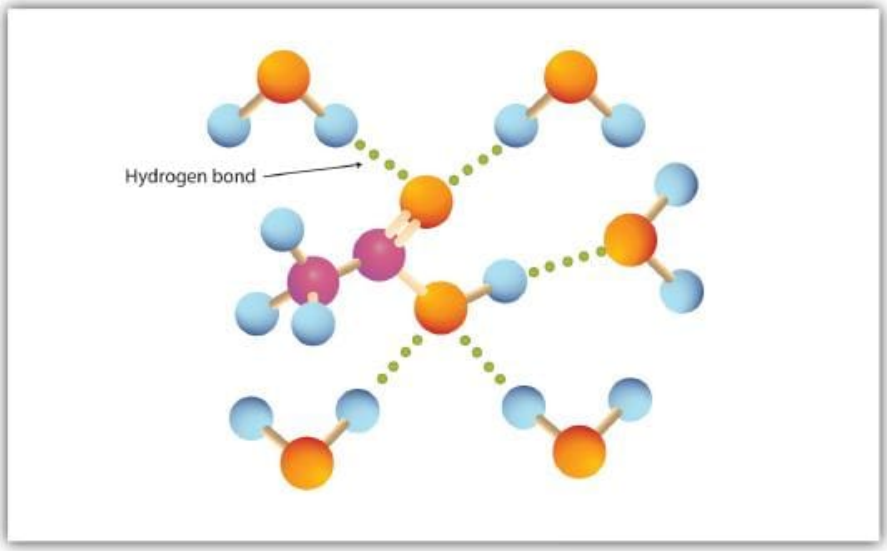



Figure 7.2.2.3.1: Hydrogen Bonding between an Acetic Acid Molecule and Water Molecules. Carboxylic acids of low molar mass are quite soluble in water.

Table 15.4.1 lists some physical properties for selected carboxylic acids. The first six are homologs. Notice that the boiling points increase with increasing molar mass, but the melting points show no regular pattern.

*Table 7.2.2.3.1: Physical Constants of Carboxylic Acids*

| Condensed Structural Formula | Name of Acid | Melting Point (°C) | Boiling Point (°C) | Solubility (g/100 g of Water) |
|---|---|---|---|---|
| HCOOH | formic acid | 8 | 100 | miscible |
| $CH_3COOH$ | acetic acid | 17 | 118 | miscible |
| $CH_3CH_2COOH$ | propionic acid | –22 | 141 | miscible |

| Condensed Structural Formula | Name of Acid | Melting Point (°C) | Boiling Point (°C) | Solubility (g/100 g of Water) |
|---|---|---|---|---|
| $CH_3(CH_2)_2COOH$ | butyric acid | –5 | 163 | miscible |
| $CH_3(CH_2)_3COOH$ | valeric acid | –35 | 187 | 5 |
| $CH_3(CH_2)_4COOH$ | caproic acid | –3 | 205 | 1.1 |
| $C_6H_5COOH$ | benzoic acid | 122 | 249 | 0.29 |

## Key Takeaways

- Carboxylic acids have high boiling points compared to other substances of comparable molar mass. Boiling points increase with molar mass.
- Carboxylic acids having one to four carbon atoms are completely miscible with water. Solubility decreases with molar mass.

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# 7.2.2.4: Physical Properties of Esters

## Learning Objectives

- Compare the boiling points of esters with alcohols of similar molar mass.
- Compare the solubilities of esters in water with the solubilities of comparable alkanes and alcohols in water.

Ester molecules are polar but have no hydrogen atom attached directly to an oxygen atom. They are therefore incapable of engaging in intermolecular hydrogen bonding with one another and thus have considerably lower boiling points than their isomeric carboxylic acids counterparts. Because ester molecules can engage in hydrogen bonding with water molecules, however, esters of low molar mass are somewhat soluble in water. Borderline solubility occurs in those molecules that have three to five carbon atoms. Table 7.2.2.4.1 lists the physical properties of some common esters.

Esters are common solvents. Ethyl acetate is used to extract organic solutes from aqueous solutions—for example, to remove caffeine from coffee. It also is used to remove nail polish and paint. Cellulose nitrate is dissolved in ethyl acetate and butyl acetate to form lacquers. The solvent evaporates as the lacquer "dries," leaving a thin film on the surface. High boiling esters are used as softeners (plasticizers) for brittle plastics.

*Table 7.2.2.4.1: Physical Properties of Some Esters*

| Condensed Structural Formula | Name | Molar Mass | Melting Point (°C) | Boiling Point (°C) | Aroma |
|---|---|---|---|---|---|
| $HCOOCH_3$ | methyl formate | 60 | −99 | 32 | |
| $HCOOCH_2CH_3$ | ethyl formate | 74 | −80 | 54 | rum |
| $CH_3COOCH_3$ | methyl acetate | 74 | −98 | 57 | |
| $CH_3COOCH_2CH_3$ | ethyl acetate | 88 | −84 | 77 | |
| $CH_3CH_2CH_2COOCH_3$ | methyl butyrate | 102 | −85 | 102 | apple |
| $CH_3CH_2CH_2COOCH_2CH_3$ | ethyl butyrate | 116 | −101 | 121 | pineapple |
| $CH_3COO(CH_2)_4CH_3$ | pentyl acetate | 130 | −71 | 148 | pear |
| $CH_3COOCH_2CH_2CH(CH_3)_2$ | isopentyl acetate | 130 | −79 | 142 | banana |
| $CH_3COOCH_2C_6H_5$ | benzyl acetate | 150 | −51 | 215 | jasmine |
| $CH_3CH_2CH_2COO(CH_2)_4CH_3$ | pentyl butyrate | 158 | −73 | 185 | apricot |
| $CH_3COO(CH_2)_7CH_3$ | octyl acetate | 172 | −39 | 210 | orange |

## Summary

Esters have polar bonds but do not engage in hydrogen bonding and are therefore intermediate in boiling points between the nonpolar alkanes and the alcohols, which engage in hydrogen bonding. Ester molecules can engage in hydrogen bonding with water, so esters of low molar mass are therefore somewhat soluble in water.

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# 7.2.2.5: Organic Sulfur Compounds

## Learning Objectives

- Identify thiols (mercaptans) by the presence of an SH group.
- The mild oxidation of thiols gives disulfides.

Because sulfur is in the same group (6A) of the periodic table as oxygen, the two elements have some similar properties. We might expect sulfur to form organic compounds related to those of oxygen, and indeed it does. Thiols (also called mercaptans), which are sulfur analogs of alcohols, have the general formula RSH. Methanethiol (also called methyl mercaptan), has the formula $CH_3SH$. Ethanethiol (ethyl mercaptan) is the most common odorant for liquid propane (LP) gas.

The mild oxidation of thiols gives compounds called **disulfides**.

$$2\mathrm{RSH} \xrightarrow{[O]} \mathrm{RSSR}$$

The amino acids cysteine [$HSCH_2CH(NH_2)COOH$] and methionine [$CH_3SCH_2CH_2CH(NH_2)COOH$] contain sulfur atoms, as do all proteins that contain these amino acids. Disulfide linkages (–S–S–) between protein chains are extremely important in protein structure.

Thioethers, which are sulfur analogs of ethers, have the form general formula RSR′. An example is dimethylsulfide ($CH_3SCH_3$), which is responsible for the sometimes unpleasant odor of cooking cabbage and related vegetables. Note that methionine has a thioether functional group.

## Career Focus: Paramedic

Paramedics are highly trained experts at providing emergency medical treatment. Their critical duties often include rescue work and emergency medical procedures in a wide variety of settings, sometimes under extremely harsh and difficult conditions. Like other science-based professions, their work requires knowledge, ingenuity, and complex thinking, as well as a great deal of technical skill. The recommended courses for preparation in this field include anatomy, physiology, medical terminology, and—not surprisingly—chemistry. An understanding of basic principles of organic chemistry, for example, is useful when paramedics have to deal with such traumas as burns from fuel (hydrocarbons) or solvent (alcohols, ethers, esters, and so on) fires and alcohol and drug overdoses.

To become a paramedic requires 2–4 y of training and usually includes a stint as an emergency medical technician (EMT). An EMT provides basic care, can administer certain medications and treatments, such as oxygen for respiratory problems and epinephrine (adrenalin) for allergic reactions, and has some knowledge of common medical conditions. A paramedic, in contrast, must have extensive knowledge of common medical problems and be trained to administer a wide variety of emergency drugs.

Paramedics usually work under the direction of a medical doctor with a title such as “medical director.” Some paramedics are employed by fire departments and may work from a fire engine that carries medical equipment as well as fire-fighting gear. Some work from hospital-sponsored ambulances and continue to care for their patients after reaching the hospital emergency room. Still other paramedics work for a government department responsible for emergency health care in a specific geographical area. Finally, some work for private companies that contract to provide service for a government body.

An experienced paramedic has a broad range of employment options, including training for mountain or ocean rescue, working with police department special weapons and tactics (SWAT) teams, or working in isolated settings such as on oil rigs. With their expertise at treating and stabilizing patients before quickly moving them to a hospital, paramedics often provide the first critical steps in saving an endangered life. The following quotation, inscribed on the Arlington National Cemetery headstone of Army Lieutenant R. Adams Cowley, who is often called the “father” of shock trauma medicine, serves as the motto for many paramedic units: “Next to creating a life the finest thing a man can do is save one.” —Abraham Lincoln

## Summary

Thiols, thioethers, and disulfides are common in biological compounds.

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# 7.2.3: FUNCTIONAL GROUPS W/ NITROGEN


### 7.2.3.1: Physical Properties of Amines

### 7.2.3.2: Physical Properties of Amides


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# 7.2.3.1: Physical Properties of Amines

## Learning Objectives

- Explain why the boiling points of primary and secondary amines are higher than those of alkanes or ethers of similar molar mass but are lower than those of alcohols.
- Compare the boiling points of tertiary amines with alcohols, alkanes, and ethers of similar molar mass.
- Compare the solubilities in water of amines of five or fewer carbon atoms with the solubilities of comparable alkanes and alcohols in water.

Primary and secondary amines have hydrogen atoms bonded to an nitrogen atom and are therefore capable of hydrogen bonding (part (a) of Figure 7.2.3.1.1), although not as strongly as alcohol molecules (which have hydrogen atoms bonded to an oxygen atom, which is more electronegative than nitrogen). These amines boil at higher temperatures than alkanes but at lower temperatures than alcohols of comparable molar mass. For example, compare the boiling point of methylamine ($CH_3NH_2$; –6°C) with those of ethane ($CH_3CH_3$; –89°C) and methanol ($CH_3OH$; 65°C). Tertiary amines have no hydrogen atom bonded to the nitrogen atom and so cannot participate in intermolecular hydrogen bonding. They have boiling points comparable to those of ethers (Table 7.2.3.1.1 ).

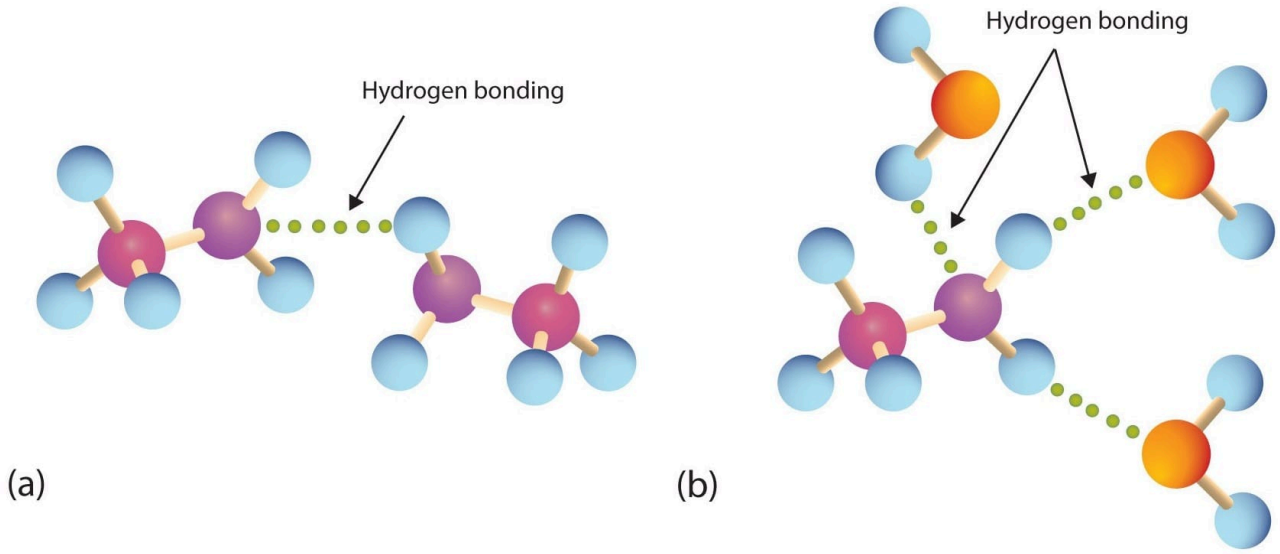



Figure 7.2.3.1.1: Hydrogen Bonding. (a) Amine molecules are associated through hydrogen bonding. (b) An amine molecule can form a hydrogen bond with water molecules.

*Table 7.2.3.1.1: Physical Properties of Some Amines and Comparable Oxygen-Containing Compounds*

| Name | Condensed Structural Formula | Class | Molar Mass | Boiling Point (°C) | Solubility at 25°C (g/100 g Water) |
|---|---|---|---|---|---|
| butylamine | $CH_3CH_2CH_2CH_2NH_2$ | 1° | 73 | 78 | miscible |
| diethylamine | $(CH_3CH_2)_2NH$ | 2° | 73 | 55 | miscible |
| butyl alcohol | $CH_3CH_2CH_2CH_2OH$ | — | 74 | 118 | 8 |
| dipropylamine | $(CH_3CH_2CH_2)_2NH$ | 2° | 101 | 111 | 4 |
| triethylamine | $(CH_3CH_2)_3N$ | 3° | 101 | 90 | 14 |
| dipropyl ether | $(CH_3CH_2CH_2)_2O$ | — | 102 | 91 | 0.25 |

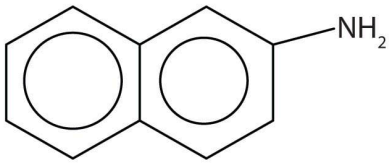
All three classes of amines can engage in hydrogen bonding with water (Figure $7.2.3.1.1b$). Amines of low molar mass are quite soluble in water; the borderline of solubility in water is at five or six carbon atoms.

### To Your Health: Amines in Death and Life

Amines have “interesting” odors. The simple ones smell very much like ammonia. Higher aliphatic amines smell like decaying fish. Or perhaps we should put it the other way around: Decaying fish give off odorous amines. The stench of rotting fish is due in part to two diamines: putrescine and cadaverine. They arise from the decarboxylation of ornithine and lysine, respectively, amino acids that are found in animal cells.

$$HOCH_2CH_2OH$$

Aromatic amines generally are quite toxic. They are readily absorbed through the skin, and workers must exercise caution when handling these compounds. Several aromatic amines, including β-naphthylamine, are potent carcinogens.




## Key Takeaways

- Primary and secondary amines have higher boiling points than those of alkanes or ethers of similar molar mass because they can engage in intermolecular hydrogen bonding. Their boiling points are lower than those of alcohols because alcohol molecules have hydrogen atoms bonded to an oxygen atom, which is more electronegative.
- The boiling points of tertiary amines, which cannot engage in hydrogen bonding because they have no hydrogen atom on the nitrogen atom, are comparable to those of alkanes and ethers of similar molar mass.
- Because all three classes of amines can engage in hydrogen bonding with water, amines of low molar mass are quite soluble in water.

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# 7.2.3.2: Physical Properties of Amides

## Learning Objectives

- Compare the boiling points of amides with alcohols of similar molar mass.
- Compare the solubilities in water of amides of five or fewer carbon atoms with the solubilities of comparable alkanes and alcohols in water.

With the exception of formamide ($HCONH_2$), which is a liquid, all simple amides are solids (Table 7.2.3.2.1). The lower members of the series are soluble in water, with borderline solubility occurring in those that have five or six carbon atoms. Like the esters, solutions of amides in water usually are neutral—neither acidic nor basic.

*Table 7.2.3.2.1: Physical Constants of Some Unsubstituted Amides*

| Condensed Structural Formula | Name | Melting Point (°C) | Boiling Point (°C) | Solubility in Water |
|---|---|---|---|---|
| $HCONH_2$ | formamide | 2 | 193 | soluble |
| $CH_3CONH_2$ | acetamide | 82 | 222 | soluble |
| $CH_3CH_2CONH_2$ | propionamide | 81 | 213 | soluble |
| $CH_3CH_2CH_2CONH_2$ | butyramide | 115 | 216 | soluble |
| $C_6H_5CONH_2$ | benzamide | 132 | 290 | slightly soluble |

The amides generally have high boiling points and melting points. These characteristics and their solubility in water result from the polar nature of the amide group and hydrogen bonding (Figure 7.2.3.2.1). (Similar hydrogen bonding plays a critical role in determining the structure and properties of proteins, deoxyribonucleic acid [DNA], ribonucleic acid [RNA], and other giant molecules so important to life processes.

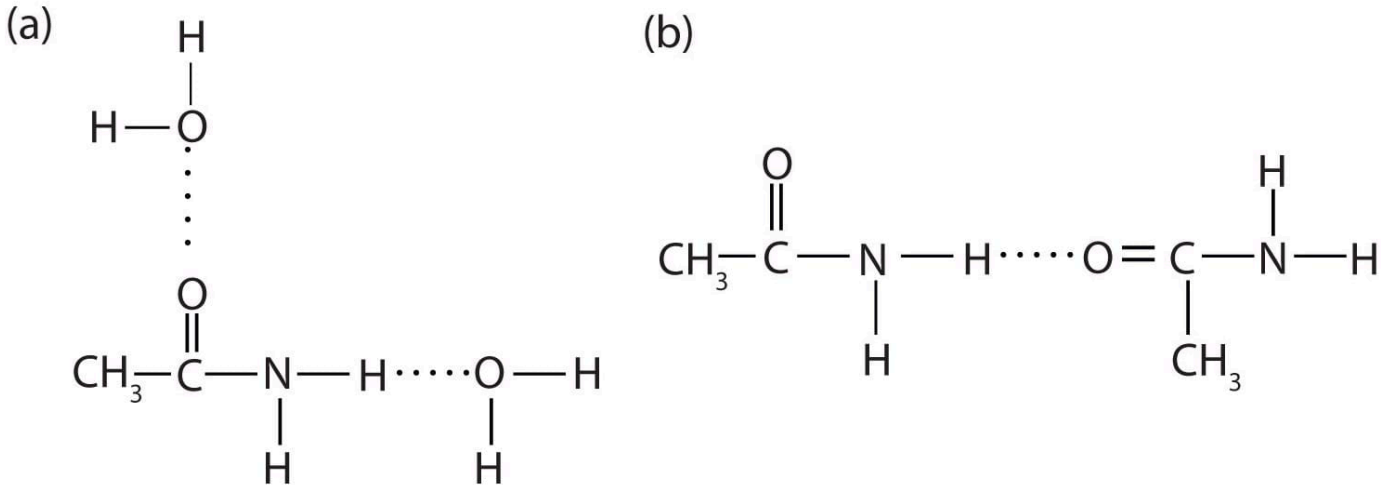



Figure 7.2.3.2.1: Hydrogen Bonding in Amides. Amide molecules can engage in hydrogen bonding with water molecules (a). Those amides with a hydrogen atom on the nitrogen atom can also engage in hydrogen bonding (b). Both hydrogen bonding networks extend in all directions.

## Key Takeaways

- Most amides are solids at room temperature; the boiling points of amides are much higher than those of alcohols of similar molar mass.
- Amides of five or fewer carbon atoms are soluble in water?.

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# 8: CHEMICAL REACTIONS AND EQUATIONS


8.1: Evidence of a Chemical Reaction

**8.2: Balanced Chemical Equations**

8.2.1: The Chemical Equation

8.2.2: How to Write Balanced Chemical Equations

**8.3: Types of Reactions**

8.3.1: Classifying Chemical Reactions

8.3.2: Acid–Base and Gas Evolution Reactions

8.3.3: Oxidation–Reduction Reactions

8.3.4: The Activity Series- Predicting Spontaneous Redox Reactions



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# 8.1: Evidence of a Chemical Reaction

## Learning Objectives

- Identify the evidence for chemical reactions.

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.

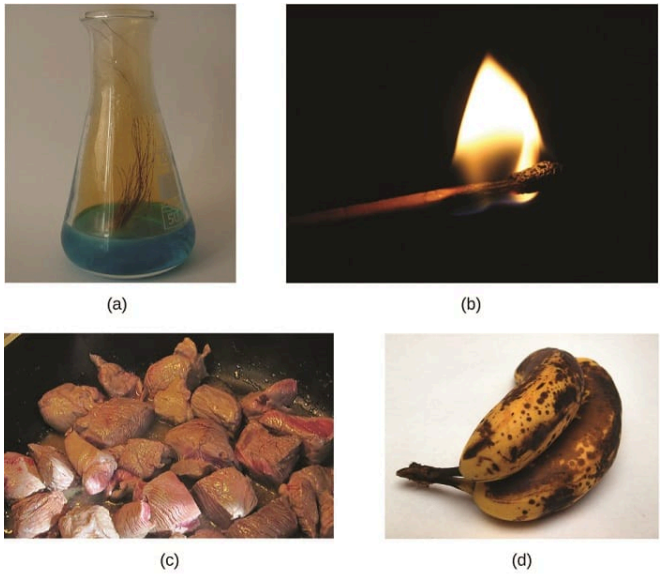



Figure 8.1.1: (a) Copper and nitric acid undergo a chemical change to form copper nitrate and brown, gaseous nitrogen dioxide. (b) During the combustion of a match, cellulose in the match and oxygen from the air undergo a chemical change to form carbon dioxide and water vapor. (c) Cooking red meat causes a number of chemical changes, including the oxidation of iron in myoglobin that results in the familiar red-to-brown color change. (d) A banana turning brown is a chemical change as new, darker (and less tasty) substances form. (Credit b: modification of work by Jeff Turner; credit c: modification of work by Gloria Cabada-Leman; credit d: modification of work by Roberto Verzo.)

To identify a chemical reaction, we look for a **chemical change**. A chemical change always produces one or more types of matter that differ from the matter present before the change. The formation of rust is a chemical change because rust is a different kind of matter than the iron, oxygen, and water present before the rust formed. The explosion of nitroglycerin is a chemical change because the gases produced are very different kinds of matter from the original substance. Other examples of chemical changes include: reactions that are performed in a lab (such as copper reacting with nitric acid), all forms of combustion (burning), and food being cooked, digested, or rotting (Figure 8.1.1).

## YouTube Video

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

View this YouTube Video online

***Video*** 8.1.1***:*** *Evidence of a Chemical Reaction*

## Example 8.1.1: Evidence of a Chemical Reaction

Which of the following is a chemical reaction?

a. Freezing liquid mercury.
b. Adding yellow to blue to make green.
c. Cutting a piece of paper into two pieces.
d. Dropping a sliced orange into a vat of sodium dydroxide.
e. Filling a balloon with natural air.

**Solution**

A, B, C, & E involve only physical changes. A sliced orange has acid (citric acid) that can react with sodium hydroxide, so the answer is D.

## Exercise 8.1.1

Which of the following is a chemical reaction?

a. Painting a wall blue.
b. A bicycle rusting.
c. Ice cream melting.
d. Scratching a key across a desk.
e. Making a sand castle.

*Answer available at the end of this section.*

## Example 8.1.2: Evidence of a Chemical Reaction

Which of the following is not a chemical reaction?

a. Shattering glass with a baseball.
b. Corroding metal.
c. Fireworks exploding.
d. Lighting a match.
e. Baking a cake.

**Solution**

Shattering glass with a baseball results in glass broken into many pieces but no chemical change happens, so the answer is A.

## Exercise 8.1.2

Which of the following is NOT a chemical reaction?

a. Frying an egg.
b. Slicing carrots.
c. A Macbook falling out of a window.
d. Creating ATP in the human body.
e. Dropping a fizzy tablet into a glass of water.

*Answer available at the end of this section.*

## Summary

Chemical reactions can be identified via a wide range of different observable factors including change in color, energy change (temperature change or light produced), gas production, formation of precipitate and change in properties.

## Answers

**Exercise** 8.1.1

B

**Exercise** 8.1.2

B and C

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# 8.2: BALANCED CHEMICAL EQUATIONS



- Topic hierarchy


### 8.2.1: The Chemical Equation

### 8.2.2: How to Write Balanced Chemical Equations


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# 8.2.1: The Chemical Equation

**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, $\mathrm{SO_2} + \mathrm{O_2}$, are reactants and sulfur trioxide, $\mathrm{SO_3}$, is the product.

$$\underbrace{2\,\mathrm{SO_2\,(g)} + \mathrm{O_2\,(g)}}_{\text{Reactants}} \rightarrow \underbrace{2\,\mathrm{SO_3\,(g)}}_{\text{Products}}$$

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 $8.2.1.1$ shows a listing of symbols used in chemical equations.

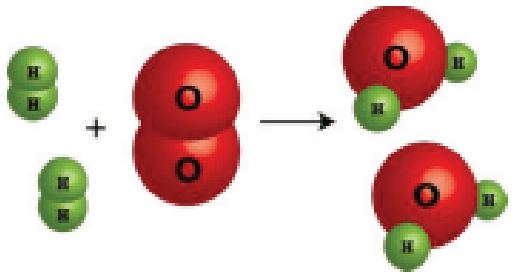
*Table $8.2.1.1$: Symbols Used in Chemical Equations*

| 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 |
|---|---|---|---|
| $\xrightarrow{\text{Pt}}$ | 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.

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

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:

$$\text{Ca}(\text{NO}_3)_2\,(aq) + 2\text{NaOH}\,(aq) \rightarrow \text{Ca}(\text{OH})_2\,(s) + 2\text{NaNO}_3\,(aq)$$

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:

$$\text{Cu}\,(s) + \text{AgNO}_3\,(aq) \rightarrow \text{Cu}(\text{NO}_3)_2\,(aq) + \text{Ag}\,(s)$$

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* 8.2.1.1*: 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 8.2.1.1

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

a. $\mathrm{HCl}\,(aq) + \mathrm{NaOH}\,(aq) \rightarrow \mathrm{NaCl}\,(aq) + \mathrm{H_2O}\,(l)$
b. Gaseous propane, $\mathrm{C_3H_8}$, 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 ($\mathrm{C_3H_8}$) and oxygen ($\mathrm{O_2}$)

Product: carbon dioxide ($\mathrm{CO_2}$) and water ($\mathrm{H_2O}$)

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

c. Reactants: hydrogen fluoride and potassium carbonate

Products: potassium fluoride, water, and carbon dioxide

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

## Exercise 8.2.1.1

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. $\mathrm{HCl}\,(aq) + \mathrm{LiOH}\,(aq) \rightarrow \mathrm{LiCl}\,(aq) + \mathrm{H_2O}\,(l)$
c. Copper metal is heated with oxygen gas to produce solid copper(II) oxide.

*Answer a available at the end of this section.*

# 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.

## Answers

**Exercise** 8.2.1.1

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

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.

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

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# 8.2.2: 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.

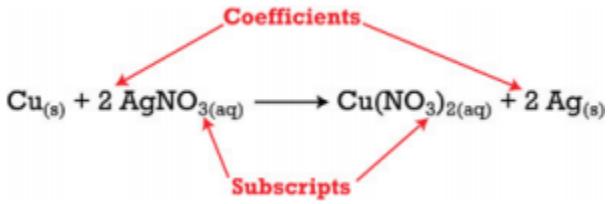
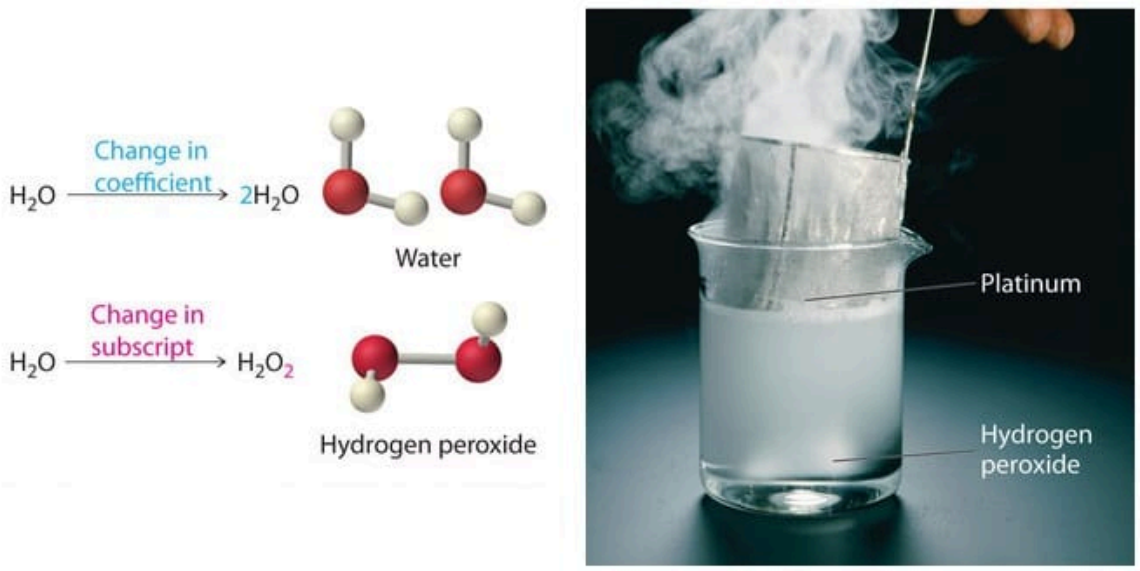



Figure 8.2.2.1: Balancing Equations. You cannot change subscripts in a chemical formula to balance a chemical equation; you can change only the coefficients. Changing subscripts changes the ratios of atoms in the molecule and the resulting chemical properties. For example, water ($H_2O$) and hydrogen 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 8.2.2.1.




Original molecule $\mathrm{H_2O}$: if the coefficient 2 is added in front, that makes 2 water molecules; but if the subscript 2 is added to make $\mathrm{H_2O_2}$, 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 8.2.2.1: Combustion of Heptane

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

$$\mathrm{C_7H_{16}\,(l) + O_2\,(g) \longrightarrow CO_2\,(g) + H_2O\,(g)}$$

**Solution**

*Solutions to Example* 8.2.2.1

| 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 assum that the final balanced chemical equation contains 1 molecule or formula unit of this substance. |

| Steps | Example |
|---|---|
| 2. **Adjust the coefficients.** | a. Because one molecule of n-heptane contains 7 carbon atoms, we need 7 $CO_2$ molecules, each of which cont carbon atom, on the right side:<br>$$C_7H_{16}(l) + O_2(g) \longrightarrow \underline{7}CO_2(g) + H_2O(g)$$<br>• 7 carbon atoms on both reactant and product sides<br>b. Because one molecule of n-heptane contains 16 hydrogen atoms, we need 8 $H_2O$ molecules, each of which hydrogen atoms, on the right side:<br>$$C_7H_{16}(l) + O_2(g) \longrightarrow 7\,CO_2(g) + \underline{8}H_2O(g)$$<br>• 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 atoms on the left. We can balance the oxygen atoms by adjusting the coefficient in front of the least complex s $O_2$, on the reactant side:<br>$$C_7H_{16}(l) + \underline{11}O_2(g) \longrightarrow 7\,CO_2(g) + 8\,H_2O(g)$$<br>• 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 ato oxygen atoms on each side. Always check to be sure that a chemical equation is balanced. |

## Example 8.2.2.2: 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 assum that the final balanced chemical equation contains 1 molecule or formula unit of this substance. |

| Steps | Example |
|---|---|
| 2. **Adjust the coefficients.** | a. The first element that appears only once in the reactants is carbon: 8 carbon atoms in isooctane means tha must be 8 $CO_2$ molecules in the products:<br>$$C_8H_{18}(l) + O_2(g) \longrightarrow \underline{8}CO_2(g) + H_2O(g)$$<br>• 8 carbon atoms on both reactant and product sides<br>b. 18 hydrogen atoms in isooctane means that there must be 9 $H_2O$ molecules in the products:<br>$$C_8H_{18}(l) + O_2(g) \longrightarrow 8\,CO_2(g) + \underline{9}H_2O(g)$$<br>• 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 atoms on the left. We can balance the least complex substance, $O_2$, but because there are 2 oxygen atoms per molecule, we must use a fractional coefficient ($\frac{25}{2}$) to balance the oxygen atoms:<br>$$C_8H_{18}(l) + \underline{\frac{25}{2}}O_2\ (g) \longrightarrow 8\,CO_2(g) + 9\,H_2O(g)$$<br>• 25 oxygen atoms on both reactant and product sides<br>The equation is now balanced, but we usually write equations with whole number coefficients. We can eliminat fractional coefficient by multiplying all coefficients on both sides of the chemical equation by **2**:<br>$$\underline{2}C_8H_{18}(l) + \underline{25}O_2(g) \longrightarrow \underline{16}CO_2(g) + \underline{18}H_2O(g)$$ |
| 5. **Check your work.** | The balanced chemical equation has 16 carbon atoms, 36 hydrogen atoms, and 50 oxygen atoms on each sid<br>Balancing equations requires some practice on your part as well as some common sense. If you find yourself u large coefficients or if you have spent several minutes without success, go back and make sure that you have v formulas of the reactants and products correctly. |

## Example 8.2.2.3: 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.<br>$\mathrm{Pb(NO_3)_2\,(aq) + NaCl\,(aq) \longrightarrow NaNO_3\,(aq) + PbCl_2\,(s)}$ |
| 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 Na to balance the chloride ions.<br>$\mathrm{Pb(NO_3)_2\,(aq) + \underline{2}NaCl\,(aq) \longrightarrow NaNO_3\,(aq) + PbCl_2\,(s)}$<br>• 1 Pb atom on both reactant and product sides<br>• 2 Na atoms on reactant side, 1 Na atom on product side<br>• 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:<br>$\mathrm{Pb(NO_3)_2\,(aq) + 2\,NaCl\,(aq) \longrightarrow \underline{2}NaNO_3\,(aq) + PbCl_2\,(s)}$<br>• 1 Pb atom on both reactant and product sides<br>• 2 Na atoms on both reactant and product sides<br>• 2 Cl atoms on both reactant and product sides<br>• 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.** | $\mathrm{Pb(NO_3)_2\,(aq) + 2\,NaCl\,(aq) \longrightarrow 2\,NaNO_3\,(aq) + PbCl_2\,(s)}$<br>• 1 Pb atom on both reactant and product sides<br>• 2 Na atoms on both reactant and product sides<br>• 2 Cl atoms on both reactant and product sides<br>• 2 $NO_3^-$ atoms on both reactant and product sides |

## Exercise 8.2.2.1

Is each chemical equation balanced?

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

*Answer a available at the end of this section.*

*Answer b available at the end of this section.*

*Answer c available at the end of this section.*

**Exercise 8.2.2.2**

Balance the following chemical equations.

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

*Answer a available at the end of this section.*

*Answer b available at the end of this section.*

*Answer c available at the end of this section.*

## 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.

### Answers

**Exercise** 8.2.2.1
yes

**Exercise** 8.2.2.1
no

**Exercise** 8.2.2.1
yes

**Exercise** 8.2.2.2
$N_2$ (g) + $2O_2$ (g) → $2NO_2$ (g)

**Exercise** 8.2.2.2
$3Pb(NO_3)_2$(aq) + $2FeCl_3$(aq) → $2Fe(NO_3)_3$(aq) + $3PbCl_2$(s)

**Exercise** 8.2.2.2
$2C_6H_{14}$(l) + $19O_2$(g)→ $12CO_2$(g) + $14H_2O$(g)

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# 8.3: TYPES OF REACTIONS



- Topic hierarchy


8.3.1: Classifying Chemical Reactions

8.3.2: Acid–Base and Gas Evolution Reactions

8.3.3: Oxidation–Reduction Reactions

8.3.4: The Activity Series- Predicting Spontaneous Redox Reactions



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# 8.3.1: Classifying Chemical Reactions

**Learning Objectives**

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

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

Most chemical reactions can be classified into one or more of five basic types: acid–base reactions, exchange reactions, condensation reactions (and the reverse, cleavage reactions), and oxidation–reduction reactions. The general forms of these five kinds of reactions are summarized in Table 8.3.1.1, along with examples of each. It is important to note, however, that many reactions can be assigned to more than one classification, as you will see in our discussion.

*Table 8.3.1.1: Basic Types of Chemical Reactions*

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

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

## Combination Reactions

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

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

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

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

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

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

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

Sulfur reacts with oxygen to form sulfur dioxide:

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

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

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

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

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

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

## Example 8.3.1.1: Combustion of Solid Potassium

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

**Solution**

*Solutions to Example 7.10.1*

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

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

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

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

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

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

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

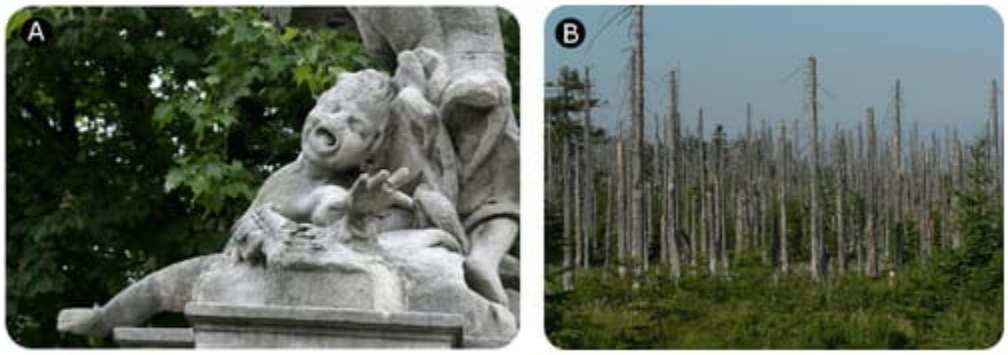



Figure 8.3.1.1: Acid rain has severe consequences on both natural and manmade objects. Acid rain degrades marble statues like the one on the left (A). The trees in the forest on the right (B) have been killed by acid rain.

**Exercise 8.3.1.1**

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

*Answer a: available at the end of this section.*

## Decomposition Reactions

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

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

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

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

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

**YouTube Video**

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

View this YouTube Video online

***Video*** $8.3.1.2$***:*** *Mercury (II) oxide is a red solid. When it is heated, it decomposes into mercury metal and oxygen gas.*

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

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

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

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

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

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

## Example $8.3.1.2$: Electrolysis of Water

When an electric current is passed through pure water, it decomposes into its elements. Write a balanced equation for the decomposition of water.

**Solution**

*Solutions to Example 7.10.2*

| Steps | Example Solution |
|---|---|
| Plan the problem. | Water is a binary compound composed of hydrogen and oxygen. The hydrogen and oxygen gases produced in the rea are both diatomic molecules. |
| Solve. | The skeleton (unbalanced) equation: $$\mathrm{H_2O}\,(l) \overset{\text{elec}}{\rightarrow} \mathrm{H_2}\,(g) + \mathrm{O_2}\,(g)$$ Note the abbreviation "elec" above the arrow to indicate the passage of an electric current to initiate the reaction. E the equation. $$2\mathrm{H_2O}\,(l) \overset{\text{elec}}{\rightarrow} 2\mathrm{H_2}\,(g) + \mathrm{O_2}\,(g)$$ |
| Think about your result. | The products are elements and the equation is balanced. |

## Exercise $8.3.1.2$

Write the chemical equation for the decomposition of:

a. $\mathrm{Al_2O_3}$
b. $\mathrm{Ag_2S}$

*Answer a available at the end of this section.*

# Single Replacement Reactions

A third type of reaction is the single replacement reaction, in which one element replaces a similar element in a compound. The general form of a single-replacement (also called single-displacement) reaction is:

$$\mathrm{A} + \mathrm{BC} \rightarrow \mathrm{AC} + \mathrm{B}$$

In this general reaction, element $\mathrm{A}$ is a metal and replaces element $\mathrm{B}$, also a metal, in the compound. When the element that is doing the replacing is a nonmetal, it must replace another nonmetal in a compound, and the general equation becomes:

$$\mathrm{Y} + \mathrm{XZ} \rightarrow \mathrm{XY} + \mathrm{Z}$$

where $\mathrm{Y}$ is a nonmetal and replaces the nonmetal $\mathrm{Z}$ in the compound with $\mathrm{X}$.

## Metal Replacement

Magnesium is a more reactive metal than copper. When a strip of magnesium metal is placed in an aqueous solution of copper (II) nitrate, it replaces the copper. The products of the reaction are aqueous magnesium nitrate and solid copper metal.

$$\mathrm{Mg}\,(s) + \mathrm{Cu(NO_3)_2}\,(aq) \rightarrow \mathrm{Mg(NO_3)_2}\,(aq) + \mathrm{Cu}\,(s)$$

This subcategory of single-replacement reactions is called a metal replacement reaction because it is a metal that is being replaced (copper).

## Hydrogen Replacement

Many metals react easily with acids and when they do so, one of the products of the reaction is hydrogen gas. Zinc reacts with hydrochloric acid to produce aqueous zinc chloride and hydrogen (figure below).

$$\mathrm{Zn}\,(s) + 2\mathrm{HCl}\,(aq) \rightarrow \mathrm{ZnCl_2}\,(aq) + \mathrm{H_2}\,(g)$$

In a hydrogen replacement reaction, the hydrogen in the acid is replaced by an active metal. Some metals are so reactive that they are capable of replacing the hydrogen in water. The products of such a reaction are the metal hydroxide and hydrogen gas. All Group 1 metals undergo this type of reaction. Sodium reacts vigorously with water to produce aqueous sodium hydroxide and hydrogen (see figure below).

$$2\mathrm{Na}\,(s) + 2\mathrm{H_2O}\,(l) \rightarrow 2\mathrm{NaOH}\,(aq) + \mathrm{H_2}\,(g)$$



Figure 8.3.1.2: (First image) Zinc metal reacts with hydrochloric acid to give off hydrogen gas in a single-displacement reaction. (Second image) Sodium metal reacts vigorously with water, giving off hydrogen gas. A large piece of sodium will often generate so much heat that the hydrogen will ignite.

## Halogen Replacement

The element chlorine reacts with an aqueous solution of sodium bromide to produce aqueous sodium chloride and elemental bromine:

$$\mathrm{Cl_2}\,(g) + 2\mathrm{NaBr}\,(aq) \rightarrow 2\mathrm{NaCl}\,(aq) + \mathrm{Br_2}\,(l)$$

The reactivity of the halogen group (group 17) decreases from top to bottom within the group. Fluorine is the most reactive halogen, while iodine is the least. Since chlorine is above bromine, it is more reactive than bromine and can replace it in a halogen replacement reaction.

### Example 8.3.1.3

What are the products of the reaction between solid aluminum ($\mathrm{Al}$) and iron (III) oxide ($\mathrm{Fe_2O_3}$)?

**Solution**

*Solutions to Example 7.10.3*

| Steps | Example Solution |
|---|---|
| Plan the problem. | To predict the products, we need to know that aluminum will replace iron and form aluminum oxide (the metal will rep the metal ion in the compound). Aluminum has a charge of $+3$ and oxygen has a charge of $-2$. The compound formed between aluminum and oxygen, therefore, will be $\mathrm{Al_2O_3}$. Since iron is replaced in the compound by aluminum, the iror now be the single element in the products. |
| Solve. | The unbalanced equation will be: $$\mathrm{Al + Fe_2O_3 \rightarrow Al_2O_3 + Fe}$$ and the balanced equation will be: $$\mathrm{2Al + Fe_2O_3 \rightarrow Al_2O_3 + 2Fe}$$ |
| Think about your result. | This is a single replacement reaction, and when balanced the coefficients accurately reflect that the iron and aluminu the same charge in this reaction. |

### Exercise 8.3.1.3

a. Write the chemical equation for the single replacement reaction between zinc solid and lead (II) nitrate solution to produce zinc nitrate solution and solid lead. (Note that zinc forms ions with a $+2$ charge.)
b. Predict the products for the following reaction: $\mathrm{Fe + CuSO_4}$. (In this reaction, assume iron forms ions with a $+2$ charge.)

*Answer a available at the end of this section.*

# Double Replacement Reactions

A **double-replacement reaction** is a reaction in which the positive and negative ions of two ionic compounds exchange places to form two new compounds. The general form of a double-replacement (also called double-displacement) reaction is:

$$\mathrm{AB + CD \rightarrow AD + BC}$$

In this reaction, $\mathrm{A}$ and $\mathrm{C}$ are positively-charged cations, while $\mathrm{B}$ and $\mathrm{D}$ are negatively-charged anions. Double-replacement reactions generally occur between substances in aqueous solution. In order for a reaction to occur, one of the products is usually

a solid precipitate, a gas, or a molecular compound such as water.

## Formation of a Precipitate

A precipitate forms in a double-replacement reaction when the cations from one of the reactants combine with the anions from the other reactant to form an insoluble ionic compound. When aqueous solutions of potassium iodide and lead (II) nitrate are mixed, the following reaction occurs:

$$2\mathrm{KI}\,(aq) + \mathrm{Pb(NO_3)_2}\,(aq) \rightarrow 2\mathrm{KNO_3}\,(aq) + \mathrm{PbI_2}\,(s) \tag{8.3.1.1}$$

There are very strong attractive forces that occur between $\mathrm{Pb^{2+}}$ and $\mathrm{I^-}$ ions and the result is a brilliant yellow precipitate (Figure 8.3.1.3). The other product of the reaction, potassium nitrate, remains soluble.



Figure 8.3.1.3: Lead (II) iodide precipitates when potassium iodide is mixed with lead (II) nitrate (Equation 8.3.1.1). (CC BY-SA 3.0; PRHaney).

## Formation of a Gas

Some double-replacement reactions produce a gaseous product which then bubbles out of the solution and escapes into the air. When solutions of sodium sulfide and hydrochloric acid are mixed, the products of the reaction are aqueous sodium chloride and hydrogen sulfide gas:

$$\mathrm{Na_2S}\,(aq) + 2\mathrm{HCl}\,(aq) \rightarrow 2\mathrm{NaCl}\,(aq) + \mathrm{H_2S}\,(g)$$

## Formation of a Molecular Compound

Another kind of double-replacement reaction is one that produces a molecular compound as one of its products. Many examples in this category are reactions that produce water. When aqueous hydrochloric acid is reacted with aqueous sodium hydroxide, the products are aqueous sodium chloride and water:

$$\mathrm{HCl}\,(aq) + \mathrm{NaOH}\,(aq) \rightarrow \mathrm{NaCl}\,(aq) + \mathrm{H_2O}\,(l)$$

**Example 8.3.1.4**

Write a complete and balanced chemical equation for the double-replacement reaction $\mathrm{NaCN}\,(aq) + \mathrm{HBr}\,(aq) \rightarrow$ (hydrogen cyanide gas is formed).

**Solution**

*Solutions to Example 7.10.4*

| Steps | Example Solution |
|---|---|
| Plan the problem. | The production of a gas drives the reaction. |
| Solve. | The cations of both reactants are $+1$ charged ions, while the anions are $-1$ charged ions. After exchanging partner balanced equation is: $$\mathrm{NaCN}\,(aq) + \mathrm{HBr}\,(aq) \rightarrow \mathrm{NaBr}\,(aq) + \mathrm{HCN}\,(g)$$ |
| Think about your result. | This is a double replacement reaction. All formulas are correct and the equation is balanced. |

## Exercise 8.3.1.4

Write a complete and balanced chemical equation for the double-replacement reaction $(\mathrm{NH_4})_2\mathrm{SO_4}\,(aq) + \mathrm{Ba(NO_3)_2}\,(aq) \rightarrow$ (a precipitate of barium sulfate forms).

*Answer a: available at the end of this section.*

Occasionally, a reaction will produce both a gas and a molecular compound. The reaction of a sodium carbonate solution with hydrochloric acid produces aqueous sodium chloride, carbon dioxide gas, and water:

$$\mathrm{Na_2CO_3}\,(aq) + 2\mathrm{HCl}\,(aq) \rightarrow 2\ \mathrm{NaCl}\,(aq) + \mathrm{CO_2}\,(g) + \mathrm{H_2O}\,(l)$$

## Answers

**Exercise** 8.3.1.1

$2\mathrm{Ag} + \mathrm{Br_2} \rightarrow 2\mathrm{AgBr}$

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

**Exercise** 8.3.1.2

$2\mathrm{Al_2O_3} \rightarrow 4\mathrm{Al} + 3\mathrm{O_2}$

$\mathrm{Ag_2S} \rightarrow 2\mathrm{Ag} + \mathrm{S}$

**Exercise** 8.3.1.3

$\mathrm{Zn} + \mathrm{Pb(NO_3)_2} \rightarrow \mathrm{Pb} + \mathrm{Zn(NO_3)_2}$

$\mathrm{Fe} + \mathrm{CuSO_4} \rightarrow \mathrm{Cu} + \mathrm{FeSO_4}$

**Exercise** 8.3.1.4

$$(\mathrm{NH_4})_2\mathrm{SO_4}\,(aq) + \mathrm{Ba(NO_3)_2}\,(aq) \rightarrow 2\mathrm{NH_4NO_3}\,(aq) + \mathrm{BaSO_4}\,(s)$$

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# 8.3.2: Acid–Base and Gas Evolution Reactions

## Learning Objectives

- Identify when a reaction will evolve a gas.

## Neutralization Reactions

Acids and bases react chemically with each other to form *salts*. A salt is a general chemical term for any ionic compound formed from an acid and a base. In reactions where the acid is a hydrogen-ion-containing compound and the base is a hydroxide-ion-containing compound, water is also a product. The general reaction is as follows:

$$\text{acid} + \text{base} \rightarrow \text{water} + \text{salt}$$

The reaction of acid and base to make water and a salt is called **neutralization**. Like any chemical equation, a neutralization chemical equation must be properly balanced. For example, the neutralization reaction between sodium hydroxide and hydrochloric acid is as follows:

$$\mathrm{NaOH\,(aq) + HCl\,(aq) \rightarrow NaCl\,(aq) + H_2O\ (\ell)} \tag{8.3.2.1}$$

with coefficients all understood to be one. The neutralization reaction between sodium hydroxide and sulfuric acid is as follows:

$$\mathrm{2\,NaOH\,(aq) + H_2SO_4\,(aq) \rightarrow Na_2SO_4\,(aq) + 2\,H_2O\ (\ell)} \tag{8.3.2.2}$$

### Example 8.3.2.1: Neutralizing Nitric Acid

Nitric acid ($HNO_3(aq)$) can be neutralized by calcium hydroxide ($Ca(OH)_2(aq)$). Write a balanced chemical equation for the reaction between these two compounds and identify the salt that it produces.

**Solution**

*Solutions to Example 7.8.1*

| Steps | Explanation | Equation |
|---|---|---|
| Write the unbalanced equation. | This is a double displacement reaction, so the cations and anions swap to create new products. | $Ca(OH)_2(aq) + HNO_3(aq) \rightarrow Ca(NO_3)_2(aq) + H_2O(\ell)$ |
| Balance the equation. | Because there are two $OH^-$ ions in the formula for $Ca(OH)_2$, we need two moles of $HNO_3$ to provide $H^+$ ions | $Ca(OH)_2(aq) + \underline{2}HNO_3(aq) \rightarrow Ca(NO_3)_2(aq) + \underline{2}H_2O(\ell)$ |
| Additional step: identify the salt. | | The salt formed is calcium nitrate. |

### Exercise 8.3.2.1

Hydrocyanic acid ($\mathrm{HCN\,(aq)}$) can be neutralized by potassium hydroxide ($\mathrm{KOH\,(aq)}$). Write a balanced chemical equation for the reaction between these two compounds and identify the salt that it produces.

**Answer**

\[\ce{KOH (aq) + HCN(aq) → KCN (aq) + H2O(ℓ)} \nonumber \]

# Gas Evolving Reactions

A gas evolution reaction is a chemical process that produces a gas, such as oxygen or carbon dioxide. In the following examples, an acid reacts with a carbonate, producing salt, carbon dioxide, and water, respectively. For example, nitric acid reacts with sodium carbonate to form sodium nitrate, carbon dioxide, and water (Table 8.3.2.1):

$$2\,HNO_3(aq) + Na_2CO_3(aq) \longrightarrow 2\,NaNO_3(aq) + CO_2(g) + H_2O(l)$$

Sulfuric acid reacts with calcium carbonate to form calcium sulfate, carbon dioxide, and water:

$$H_2SO_4\,(aq) + CaCO_3\,(aq) \longrightarrow CaSO_4\,(aq) + CO_2(g) + H_2O\,(l)$$

Hydrochloric acid reacts with calcium carbonate to form calcium chloride, carbon dioxide, and water:

$$2\,HCl\,(aq) + CaCO_3\,(aq) \longrightarrow CaCl_2\,(aq) + CO_2\,(g) + H_2O\,(l)$$

Figure 8.3.2.1 demonstrates this type of reaction:

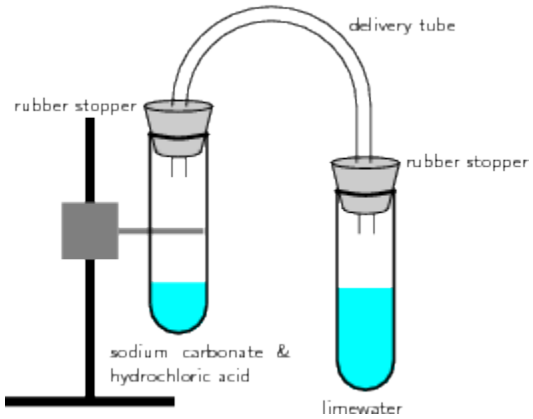



Figure 8.3.2.1: Reaction of acids with carbonates. In this reaction setup, lime water (water + calcium hydroxide) is poured into one of the test tubes and sealed with a stopper. A small amount of hydrochloric acid is carefully poured into the remaining test tube. A small amount of sodium carbonate is added to the acid, and the tube is sealed with a rubber stopper. The two tubes are connected. As a result of the acid-carbonate reaction, carbon dioxide is produced and the lime water turns milky.

In this reaction setup, lime water, a dilute calcium hydroxide ($Ca(OH)_2$) solution, is poured into one of the test tubes and sealed with a stopper. A small amount of hydrochloric acid is carefully poured into the remaining test tube. A small amount of sodium carbonate is added to the acid, and the tube is sealed with a rubber stopper. The two tubes are connected. As a result of the acid-carbonate reaction, carbon dioxide is produced and the lime water turns milky.

*Table 8.3.2.1: Types of Compounds That Undergo Gas-Evolution Reactions*

| Reactant Type | Intermediate Product | Gas Evolved | Example |
|---|---|---|---|
| sulfide | none | $H_2S$ | $2\,HCl\,(aq) + K_2S \rightarrow H_2S\,(g) + 2\,KCl\,(aq)$ |
| carbonates and bicarbonates | $H_2CO_3$ | $CO_2$ | $2\,HCl\,(aq) + K_2CO_2 \rightarrow H_2O\,(l) + CO_2\,(g) + 2\,KCl\,(aq)$ |
| sulfites and bisulfites | $H_2SO_3$ | $SO_2$ | $2\,HCl\,(aq) + K_2SO_2 \rightarrow H_2O\,(l) + SO_2\,(g) + 2\,KCl\,(aq)$ |
| ammonia | $NH_4OH$ | $NH_3$ | \(\ce{NH4Cl(aq) + KOH \rightarrow H2O (l) + NH3(g) + 2KCl (aq)}\) |

The gas-evolving experiment lime water is illustrated in the following video:

YouTube Video

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

View this YouTube Video online

***Video*** 8.3.2.1***:*** *Carbon Dioxide ($CO_2$) & Limewater (Chemical Reaction). As the reaction proceeds, the limewater on the turns from clear to milky; this is due to the $CO_2(g)$ reacting with the aqueous calcium hydroxide to form calcium carbonate, which is only slightly soluble in water.*

When this experiment is repeated with nitric or sulfuric acid instead of $HCl$, it yields the same results: the clear limewater turns milky, indicating the production of carbon dioxide. Another method to chemically generate gas is the oxidation of metals in acidic solutions. This reaction will yield a metal salt and hydrogen gas.

$$2\,\mathrm{HCl\,(aq)} + \mathrm{Zn\,(s)} \rightarrow \mathrm{ZnCl_2\,(aq)} + \mathrm{H_2\,(g)}$$

Here, hydrochloric acid oxidizes zinc to produce an aqueous metal salt and hydrogen gas bubbles. Recall that oxidation refers to a loss of electrons, and reduction refers to the gain of electrons. In the above redox reaction, neutral zinc is oxidized to $Zn^{2+}$, and the acid, $H^+$, is reduced to $H_2(g)$. The oxidation of metals by strong acids is another common example of a gas evolution reaction.

## Contributors & Affiliations

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# 8.3.3: Oxidation–Reduction Reactions

**Learning Objectives**

- Define *oxidation* and *reduction*.
- Assign oxidation numbers to atoms in simple compounds.
- Recognize a reaction as an oxidation-reduction reaction.

In the course of a chemical reaction between a metal and a nonmetal, electrons are transferred from the metal atoms to the nonmetal atoms. For example, when zinc metal is mixed with sulfur and heated, the compound zinc sulfide is produced. Two valence electrons from each zinc atom are transferred to each sulfur atom.

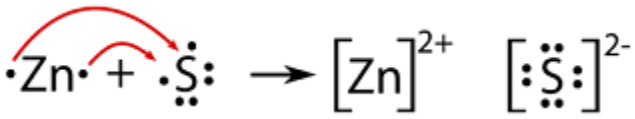


Figure 8.3.3.1: Reaction between zinc and sulfur.

Since the zinc is losing electrons in the reaction, it is being oxidized. The sulfur is gaining electrons and is thus being reduced. An **oxidation-reduction reaction** is a reaction that involves the full or partial transfer of electrons from one reactant to another. **Oxidation** is the full or partial loss of electrons or the gain of oxygen. **Reduction** is the full or partial gain of electrons or the loss of oxygen. A **redox reaction** is another term for an oxidation-reduction reaction.

Each of these processes can be shown in a separate equation called a half-reaction. A **half-reaction** is an equation that shows either the oxidation or the reduction reaction that occurs during a redox reaction.

$$\underbrace{\mathrm{Zn} \longrightarrow \mathrm{Zn_2^{2+}} + \mathrm{e^-}}_{\text{Oxidation}} \tag{8.3.3.1}$$

$$\underbrace{\mathrm{S^+} \ 2\,\mathrm{e^-} \longrightarrow \mathrm{S^{2-}}}_{\text{Reduction}} \tag{8.3.3.2}$$

It is important to remember that the two half-reactions occur simultaneously. The resulting ions that are formed are then attracted to one another in an ionic bond.

Another example of an oxidation-reduction reaction involving electron transfer is the well-known combination of metallic sodium and chlorine gas to form sodium chloride:

$$2\,\mathrm{Na^+Cl_2} \longrightarrow 2\,\mathrm{NaCl} \tag{8.3.3.3}$$

The half reactions are as follows:

$$\underbrace{2\,\mathrm{Na} \longrightarrow 2\,\mathrm{Na^+} + 2\,\mathrm{e^-}}_{\text{Oxidation}} \tag{8.3.3.4}$$

$$\underbrace{\mathrm{Cl_2} + 2\,\mathrm{e^-} \longrightarrow 2\,\mathrm{Cl^-}}_{\text{Reduction}} \tag{8.3.3.5}$$

We will concern ourselves with the balancing of these equations at another time.

## Oxidation Numbers

Redox reactions require that we keep track of the electrons assigned to each atom in a chemical reaction. How do we do that? We use **oxidation numbers** to keep track of electrons in atoms. Oxidation numbers are assigned to atoms based on four rules. Oxidation numbers are not necessarily equal to the charge on the atom (although sometimes they can be); we must keep the concepts of charge and oxidation numbers separate.

## Assigning Oxidation Numbers

The rules for assigning oxidation numbers to atoms are as follows:

**1. Atoms in their elemental state are assigned an oxidation number of 0.**

*In $H_2$, both H atoms have an oxidation number of 0.*

**2. Atoms in monatomic (i.e., one-atom) ions are assigned an oxidation number equal to their charge. Oxidation numbers are usually written with the sign first, then the magnitude, to differentiate them from charges.**

*In $MgCl_2$, magnesium has an oxidation number of +2, while chlorine has an oxidation number of –1.*

**3. In compounds, fluorine is assigned a –1 oxidation number; oxygen is usually assigned a –2 oxidation number (except in peroxide compounds [where it is –1] and in binary compounds with fluorine [where it is positive]); and hydrogen is usually assigned a +1 oxidation number [except when it exists as the hydride ion ($H^-$), in which case rule 2 prevails].**

*In $H_2O$, the H atoms each have an oxidation number of +1, while the O atom has an oxidation number of –2, even though hydrogen and oxygen do not exist as ions in this compound (rule 3). By contrast, by rule 3, each H atom in hydrogen peroxide ($H_2O_2$) has an oxidation number of +1, while each O atom has an oxidation number of –1.*

**4. In compounds, all other atoms are assigned an oxidation number so that the sum of the oxidation numbers on all the atoms in the species equals the charge on the species (which is zero if the species is neutral).**

*In $SO_2$, each O atom has an oxidation number of –2; for the sum of the oxidation numbers to equal the charge on the species (which is zero), the S atom is assigned an oxidation number of +4. Does this mean that the sulfur atom has a 4+ charge on it? No, it means only that the S atom is assigned a +4 oxidation number by our rules of apportioning electrons among the atoms in a compound.*

## Example 8.3.3.1: Assigning Oxidation States

Assign oxidation numbers to the atoms in each substance.

a. $Cl_2$
b. $GeO_2$
c. $Ca(NO_3)_2$

**Solution**

a. $Cl_2$ is the elemental form of chlorine. Rule 1 states that each atom has an oxidation number of 0.
b. By rule 3, oxygen is normally assigned an oxidation number of –2. For the sum of the oxidation numbers to equal the charge on the species (zero), the Ge atom is assigned an oxidation number of +4.
c. $Ca(NO_3)_2$ can be separated into two parts: the $Ca^{2+}$ ion and the $NO_3^-$ ion. Considering these separately, the $Ca^{2+}$ ion has an oxidation number of +2 by rule 2. Now consider the $NO_3^-$ ion. Oxygen is assigned an oxidation number of –2, and there are three of them. According to rule 4, the sum of the oxidation numbers on all atoms must equal the charge on the species, so we have the simple algebraic equation

$$x + 3(-2) = -1$$

where *x* is the oxidation number of the N atom and the –1 represents the charge on the species. Evaluating for *x*,

$$x + (-6) = -1x = +5$$

Thus the oxidation number on the N atom in the $NO_3^-$ ion is +5.

## Exercise 8.3.3.1: Assigning Oxidation States

Assign oxidation numbers to the atoms in the following:

a. $H_3PO_4$
b. MgO

*Answer a available at the end of this section.*

*Answer b available at the end of this section.*

All redox reactions occur with a simultaneous change in the oxidation numbers of some atoms. At least two elements must change their oxidation numbers. When an oxidation number of an atom is increased in the course of a redox reaction, that atom is being *oxidized*. When an oxidation number of an atom is decreased in the course of a redox reaction, that atom is being *reduced*. Thus oxidation and reduction can also be defined in terms of increasing or decreasing oxidation numbers, respectively.

## Example 8.3.3.2: Formation of Sodium Bromide

Identify what is being oxidized and reduced in the following redox reaction.

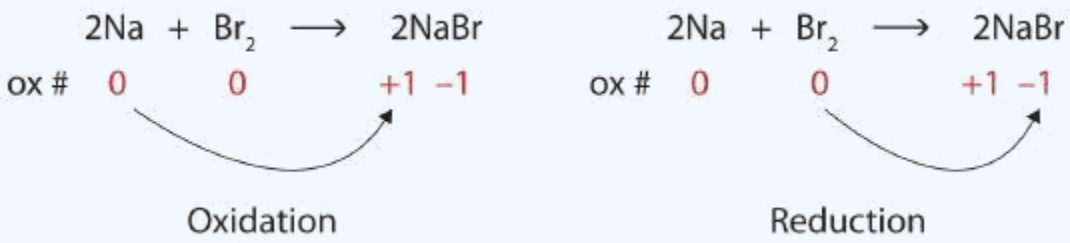
$$2\,\mathrm{Na} + \mathrm{Br_2} \longrightarrow 2\,\mathrm{NaBr}$$

**Solution**

Both reactants are the elemental forms of their atoms, so the Na and Br atoms have oxidation numbers of 0. In the ionic product, the $Na^+$ ions have an oxidation number of +1, while the $Br^-$ ions have an oxidation number of –1.

$$\overset{0}{2Na} + \overset{0}{Br_2} \rightarrow \overset{+1-1}{2NaBr}$$

Sodium is increasing its oxidation number from 0 to +1, so it is being oxidized; bromine is decreasing its oxidation number from 0 to –1, so it is being reduced:




Equation of sodium and bromine reacting, labeled with sodium's oxidation number change from 0 to +1 and bromine's oxidation number change from 0 to -1

Because oxidation numbers are changing, this is a redox reaction. The total number of electrons being lost by sodium (two, one lost from each Na atom) is gained by bromine (two, one gained for each Br atom).

## Exercise 8.3.3.2: Oxidation of Carbon

Identify what is being oxidized and reduced in this redox reaction.

$$C + O_2 \rightarrow CO_2$$

*Answer available at the end of this section.*

*Answer available at the end of this section.*

Oxidation reactions can become quite complex, as attested by the following redox reaction:

$$6H^+(aq) + 2\underset{+7}{MnO_4^-}(aq) + 5\underset{-1}{H_2O_2}(l) \rightarrow 2\underset{+2}{Mn^{2+}}(aq) + 5\underset{0}{O_2}(g) + 8H_2O(l)$$

To demonstrate that this is a redox reaction, the oxidation numbers of the species being oxidized and reduced are listed; can you determine what is being oxidized and what is being reduced? This is also an example of a net ionic reaction; spectator ions that do not change oxidation numbers are not displayed in the equation. Eventually, we will need to learn techniques for writing correct (i.e., balanced) redox reactions.

## Combustion Reactions

A **combustion reaction** is a reaction in which a substance reacts with oxygen gas, releasing energy in the form of light and heat. Combustion reactions must involve $\mathrm{O_2}$ as one reactant. The combustion of hydrogen gas produces water vapor.

$$\mathrm{2H_2\,(g) + O_2\,(g) \rightarrow 2H_2O\,(g)} \tag{8.3.3.6}$$

Notice that this reaction also qualifies as a combination reaction.

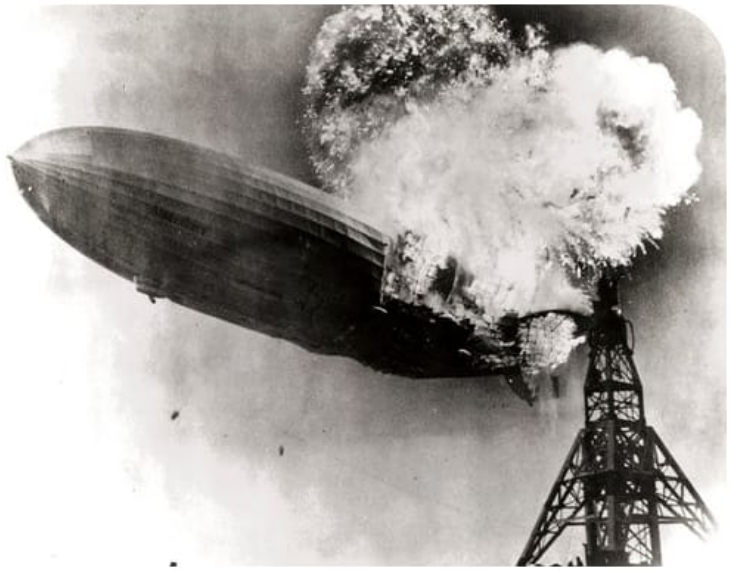


Figure 8.3.3.2: Explosion of the Hindenberg.

The *Hindenberg* was a hydrogen-filled airship that suffered an accident upon its attempted landing in New Jersey in 1937. The hydrogen immediately combusted in a huge fireball, destroying the airship and killing 36 people. The chemical reaction was a simple one: hydrogen combining with oxygen to produce water (Equation 8.3.3.6).

Many combustion reactions occur with a hydrocarbon, a compound made up solely of carbon and hydrogen. The products of the combustion of hydrocarbons are carbon dioxide and water. Many hydrocarbons are used as fuel because their combustion releases very large amounts of heat energy. Propane $(\mathrm{C_3H_8})$ is a gaseous hydrocarbon that is commonly used as the fuel source in gas grills.

$$\mathrm{C_3H_8\,(g) + 5O_2\,(g) \rightarrow 3CO_2\,(g) + 4H_2O\,(g)}$$

### Example 8.3.3.3: Combustion of Ethanol

Ethanol can be used as a fuel source in an alcohol lamp. The formula for ethanol is $\mathrm{C_2H_5OH}$. Write the balanced equation for the combustion of ethanol.

**Solution**

*Solutions to Example 7.9.3*

| Steps | Example Solution |
|---|---|
| Write the unbalanced reaction. | $\mathrm{C_2H_5OH\,(l) + O_2\,(g) \rightarrow CO_2\,(g) + H_2O\,(g)}$<br>Ethanol and atmospheric oxygen are the reactants. As with a hydrocarbon, the products of the combustion of an alcohol are carbon dioxide and water. |
| Balance the equation. | $\mathrm{C_2H_5OH\,(l) + 3O_2\,(g) \rightarrow 2CO_2\,(g) + 3H_2O\,(g)}$ |
| Think about your result. | Combustion reactions must have oxygen as a reactant. Note that the water produced is in the gas state, rather than the liquid state, because of the high temperatures that accompany a combustion reaction. |

### Exercise 8.3.3.3: Combustion of Hexane

Write the balanced equation for the combustion of hexane, $C_6H_{14}$

*Answer available at the end of this section.*

## Contributors & Affiliations

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## Answers

**Exercise 8.3.3.1: Assigning Oxidation States**

H: +1; O: −2; P: +5

**Exercise 8.3.3.1: Assigning Oxidation States**

Mg: +2, O: −2

**Exercise 8.3.3.2: Oxidation of Carbon**

C is being oxidized from 0 to +4; O is being reduced from 0 to −2

**Exercise 8.3.3.2: Oxidation of Carbon**

**Exercise 8.3.3.3: Combustion of Hexane**

$$\mathrm{2\,C_6H_{14}\,(\ell) + 19\,O_2\,(g) \longrightarrow 12\,CO_2\,(g) + 14\,H_2O(\ell)}$$

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# 8.3.4: The Activity Series- Predicting Spontaneous Redox Reactions

**Learning Objectives**

- Use the activity series to predict if a reaction will occur.

We see below two metals that can be exposed to water. The picture on the left is of sodium, which has a violent reaction when it comes in contact with water. The picture on the right is of silver, a metal so unreactive with water that it can be made into drinking vessels. Both metals have a single $s$ electron in their outer shell, so you would predict a similar reactivity from each. However, we have a tool that allows us to make better predictions about how certain elements will react with others.



Figure 8.3.4.1: On the left, sodium reacts with water. On the right, silver in the form of cups does not react with water.

## The Activity Series

Single-replacement reactions only occur when the element that is doing the replacing is more reactive than the element that is being replaced. Therefore, it is useful to have a list of elements in order of their relative reactivity. The **activity series** is a list of elements in decreasing order of their reactivity. Since metals replace other metals, while nonmetals replace other nonmetals, they each have a separate activity series. The table 8.3.4.1 below is an activity series of most common metals, and the table 8.3.4.2 is an activity series of the halogens.

*Table 8.3.4.1: Activity Series of Metal Elements*

| Elements, from most to least reactive | Reaction Occurring |
|---|---|
| Li<br>K<br>Ba<br>Sr<br>Ca<br>Na | React with cold water, replacing hydrogen. |

| Elements, from most to least reactive | Reaction Occurring |
|---|---|
| Mg<br>Al<br>Zn<br>Cr<br>Fe<br>Cd | React with steam, but not cold water, replacing hydrogen. |
| Co<br>Ni<br>Sn<br>Pb | Do not react with water. React with acids, replacing hydrogen. |
| $H_2$ | |
| Cu<br>Hg<br>Ag<br>Pt<br>Au | Unreactive with water or acids. |

*Table 8.3.4.2: Activity Series of Nonmetal elements*

| Elements, from most to least reactive |
|---|
| $F_2$ |
| $Cl_2$ |
| $Br_2$ |
| $I_2$ |

For a single-replacement reaction, a given element is capable of replacing an element that is below it in the activity series. This can be used to predict if a reaction will occur. Suppose that small pieces of the metal nickel were placed into two separate aqueous solutions: one of iron (III) nitrate and one of lead (II) nitrate. Looking at the activity series, we see that nickel is below iron, but above lead. Therefore, the nickel metal will be capable of replacing the lead in a reaction, but will not be capable of replacing iron.

$$\mathrm{Ni}\,(s) + \mathrm{Pb(NO_3)_2}\,(aq) \rightarrow \mathrm{Ni(NO_3)_2}\,(aq) + \mathrm{Pb}\,(s)$$

$$\mathrm{Ni}\,(s) + \mathrm{Fe(NO_3)_3}\,(aq) \rightarrow \mathrm{NR\ (no\ reaction)}$$

In the descriptions that accompany the activity series of metals, a given metal is also capable of undergoing the reactions described below that section. For example, lithium will react with cold water, replacing hydrogen. It will also react with steam and

with acids, since that requires a lower degree of reactivity.

## Examples 8.3.4.1

Use the activity series to predict if the following reactions will occur. If not, write NR. If the reaction does occur, write the products of the reaction and balance the equation.

a. $\mathrm{Al}\,(s) + \mathrm{Zn(NO_3)_2}\,(aq) \rightarrow$
b. $\mathrm{Ag}\,(s) + \mathrm{HCl}\,(aq) \rightarrow$

**Solution**

*Solutions to Example 7.11.1*

| Steps | **Example** 8.3.4.1$A$<br>$\mathrm{Al}\,(s) + \mathrm{Zn(NO_3)_2}\,(aq) \rightarrow$ | **Example** 8.3.4.1$B$<br>$\mathrm{Ag}\,(s) + \mathrm{HCl}\,(aq) \rightarrow$ |
|---|---|---|
| *Plan the problem.* | Compare the placements of aluminum and zinc on the activity series (Table 8.3.4.1) | Compare the placements of silver and hydrogen (Table 8.3.4.1) |
| *Solve.* | Since aluminum is above zinc, it is capable of replacing it and a reaction will occur. The products of the reaction will be aqueous aluminum nitrate and solid zinc. Take care to write the correct formulas for the products before balancing the equation. Aluminum adopts a $+3$ charge in an ionic compound, so the formula for aluminum nitrate is $\mathrm{Al(NO_3)_3}$. The balanced equation is:<br>$2\mathrm{Al}\,(s) + 3\mathrm{Zn(NO_3)_2}\,(aq) \rightarrow 2\mathrm{Al(NO_3)_3}\,(aq) + 3\mathrm{Zn}\,(s)$ | Since silver is below hydrogen, it is not capable of replacing hydrogen in a reaction with an acid.<br>$\mathrm{Ag}\,(s) + \mathrm{HCl}\,(aq) \rightarrow \mathrm{NR}$ |

## Exercise 8.3.4.1

Use the activity series to predict the products, if any, of each equation.

a. $\mathrm{FeCl_2} + \mathrm{Zn} \longrightarrow$
b. $\mathrm{HNO_3} + \mathrm{Au} \longrightarrow$

*Answer a available at the end of this section.*

*Answer b available at the end of this section.*

# Summary

- Metals and halogens are ranked according to their ability to displace other metals or halogens below them in the activity series.

## Answers

**Exercise** 8.3.4.1

The products are $\mathrm{ZnCl_2}$ + Fe.

**Exercise** 8.3.4.1

No reaction.

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# 9: QUANTITIES IN CHEMICAL REACTIONS

So far, we have talked about chemical reactions in terms of individual atoms and molecules. Although this works, most of the reactions occurring around us involve much larger amounts of chemicals. Even a tiny sample of a substance will contain millions, billions, or a hundred billion billions of atoms and molecules. How do we compare amounts of substances to each other, in chemical terms, when it is so difficult to count to a hundred billion billion? Actually, there are ways to do this, which we will explore in this chapter. In doing so, we will increase our understanding of stoichiometry, which is the study of the numerical relationships between the reactants and the products in a balanced chemical reaction.


9.1: Climate Change - Too Much Carbon Dioxide

**9.2: The Mole Concept**

9.2.1: Counting Nails by the Pound

9.2.2: Counting Atoms by the Gram

9.2.3: Counting Molecules by the Gram

9.2.4: Chemical Formulas as Conversion Factors

**9.3: Stoichiometry**

9.3.1: Stoichiometry

9.3.2: Making Pancakes- Relationships Between Ingredients

9.3.3: Making Molecules- Mole-to-Mole Conversions

9.3.4: Making Molecules- Mass-to-Mass Conversions

9.3.5: Limiting Reactant and Theoretical Yield

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

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



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# 9.1: Climate Change - Too Much Carbon Dioxide

Carbon dioxide ($CO_2$) is an important heat-trapping (greenhouse) gas, which is released through human activities such as deforestation and burning fossil fuels, as well as natural processes such as respiration and volcanic eruptions. Figure $9.1.1$ shows $CO_2$ levels during the last three glacial cycles, as reconstructed from ice cores.

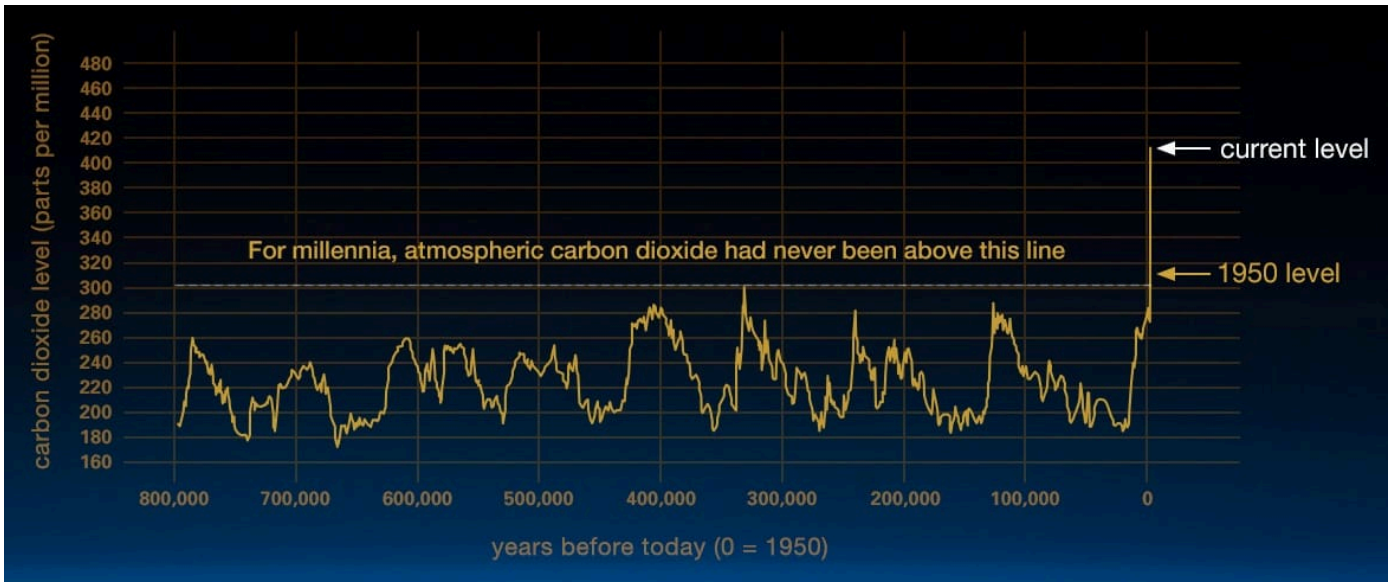



Figure $9.1.1$: This graph, based on the comparison of atmospheric samples contained in ice cores and more recent direct measurements, provides evidence that atmospheric CO2 has increased since the Industrial Revolution. (Luthi, D., et al. 2008; Etheridge, D.M., et al. 2010; Vostok ice core data/J.R.R. Petit et al.; NOAA Mauna Loa CO2 record. NASA.) Line graph of carbon dioxide levels from 800 thousand before up until present day; current carbon dioxide level is higher than all historical levels.

Carbon dioxide ($CO_2$) is the primary greenhouse gas emitted through human activities. In 2015, $CO_2$ accounted for about 82.2% of all U.S. greenhouse gas emissions from human activities. Carbon dioxide is naturally present in the atmosphere as part of the Earth's carbon cycle (the natural circulation of carbon among the atmosphere, oceans, soil, plants, and animals). Human activities are altering the carbon cycle, both by adding more $CO_2$ to the atmosphere and by influencing the ability of natural sinks, like forests, to remove $CO_2$ from the atmosphere. While $CO_2$ emissions come from a variety of natural sources, human-related emissions are responsible for the increase that has occurred in the atmosphere since the industrial revolution.

The main human activity that emits $CO_2$ is the combustion of fossil fuels (coal, natural gas, and oil) for energy and transportation, although certain industrial processes and land-use changes also emit $CO_2$. As an example of how $CO_2$ can be generated, consider the combustion of octane, a component of gasoline:

$$2\,C_8H_{18}\,(l) + 21\,O_2\,(g) \rightarrow 16\,CO_2\,(g) + 18\,H_2O\,(g) \tag{9.1.1}$$

The balanced reaction in Equation $9.1.1$ demonstrates that for every two molecules of octane that are burned, 16 molecules of $CO_2$ are generated.

## Contributions & Attributions

- Earth Science Communications Team at NASA's Jet Propulsion Laboratory, California Institute of Technology
- EPA

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# 9.2: THE MOLE CONCEPT



- Topic hierarchy


9.2.1: Counting Nails by the Pound

9.2.2: Counting Atoms by the Gram

9.2.3: Counting Molecules by the Gram

9.2.4: Chemical Formulas as Conversion Factors


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# 9.2.1: Counting Nails by the Pound

## Counting by Weighing and Avogadro's number

The size of molecule is so small that it is physically difficult, if not impossible, to directly count out molecules (Figure 9.2.1.1). However, we can count them indirectly by using a common trick of "counting by weighing".

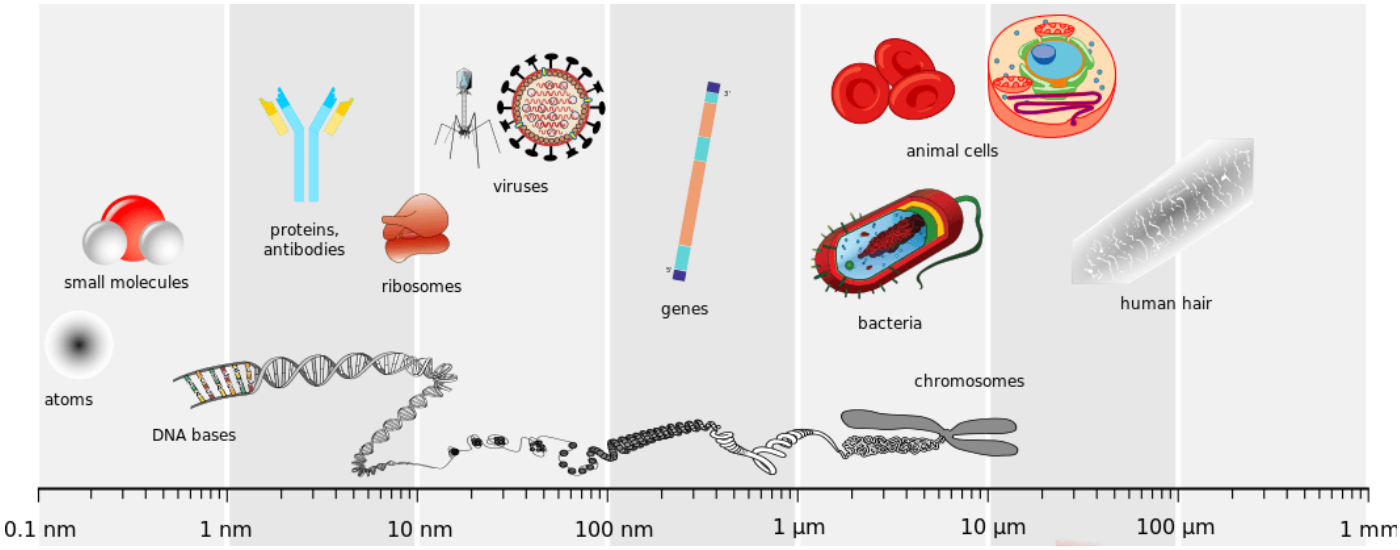



Figure 9.2.1.1: A comparison of the scales of various biological and technological objects. (CC BY-SA 3.0; Wikipedia)

Consider the example of counting nails in a big box at a hardware store. You need to estimate the number of nails in a box. The weight of an empty box is $213\ g$ and the weight of the box plus a bunch of big nails is $1340\ g$. Assume that we know that the weight of one big nail is 0.450 g. Hopefully it's not necessary to tear open the package and count the nails. We agree that

$$\text{mass of big nails} = 1340\,g - 213\,g = 1227\,g$$

Therefore

$$\text{Number of big nails in box} = \frac{1227\,g}{0.450\,g/\text{big nail}} = 2,726.6\,\text{big nails} = 2,730\,\text{big nails}. \tag{9.2.1.1}$$

You have just counted the number of big nails in the box by weighing them (rather than by counting them individually).



Figure 9.2.1.2: Galvanized nails. Individually counting nails in a box would would require significant effort. Alternatively, we can count them by weighing. (Public Domain; Wikipedia).

Now consider if the box of nails weighed the same, but the box were filled with small nails with an individual mass of $0.23\ g/\text{small nail}$ instead? You would do the same math, but use a different denominator in Equation 9.2.1.1:

$$\text{Number of small nails in box} = \frac{1227\,g}{0.230\,g/\text{small nail}} = 5,334.7\,\text{small nails} = 5,335\,\text{small nails}. \tag{9.2.1.2}$$

The individual mass is the conversion factor used in the calculation and changes, based on the nature of the nail (big or small). Let's ask a different question: how many *dozens* of nails are there in the same box of small nails described above?

If we know the information from Equation 9.2.1.2, we can just use the conversion of how many nails are in a dozen:

$$\frac{5,335\,\text{small nails}}{12\,\text{small nails/dozen}} = 444.6\,\text{dozen small nails} \tag{9.2.1.3}$$

If we want to get this value from weighing, we use the "dozen mass" instead of individual mass:

$$12 \times 0.23g = 2.76\,g/\text{dozen small nails}. \tag{9.2.1.4}$$

So following Equation 9.2.1.2, we get:

$$\text{Number of dozens of small nails} = \frac{1227\,g}{2.76\,g/\text{dozen small nails}} = 444.6\,\text{dozen small nails} \tag{9.2.1.5}$$

and this is the same result as Equation 9.2.1.3. These calculations demonstrate the difference between individual mass (i.e., per individual) and collective mass (e.g., per dozen or per gross). The collective mass of most importance to chemistry is *molar mass* (i.e., mass per mole or mass per $6.022 \times 10^{23}$).

## Avogadro's Number

Avogadro's number is an accident of nature. It is the number of particles that delivers a mole of a substance. Avogadro's number = $6.022 \times 10^{23}$. The reason why the value is an accident of nature is that the mole is tied to the gram mass unit. The gram is a convenient mass unit because it matches human sizes. If we were a thousand times greater in size (like Paul Bunyan) we would find it handy to use kilogram amounts. This means the kilogram mole would be convenient. The number of particles handled in a kilogram mole is 1000 times greater. The kilo Avogadro number for the count of particles in a kilomole is $6.022 \times 10^{26}$.

If humans were tiny creatures (like Lilliputians) only 1/1000 our present size, milligrams would be more convenient. This means the milligram mole would be more useful. The number of particles handled in a milligram mole (millimole) would be 1/1000 times smaller. The milli Avogadro number for the count of particles in a millimole is $6.022 \times 10^{20}$.

What do you think would happen to Avogadro's number if the American system was used and amounts were measured in pound moles? Remember 1 pound = 454 grams. Avogadro's number would be larger by a factor of 454. A pound mole of hydrogen would weigh 1 pound, which is 454 grams. A gram mole of hydrogen weighs 1 gram and contains $6.022 \times 10^{23}$ H atoms.

## Molar Mass for Elements

You are able to read the periodic table and determine the average atomic mass for an element like carbon. The average mass is 12.01 amu. This mass is a ridiculously tiny number of grams. It is too small to handle normally. The molar mass of carbon is defined as the mass in grams that is numerically equal to the average atomic weight. This means

$$1 g/mole carbon = 12.01\, g\, carbon$$

this is commonly written

$$1\, mol\, carbon = 12.01\, grams\, carbon.$$

This is the mass of carbon that contains $6.022 \times 10^{23}$ carbon atoms.

- Avogadro's number is $6.022 \times 10^{23}$ particles.

This same process gives us the molar mass of any element. For example:

- $1\ mol\ neon = 20.18\ g\ neon\ Ne$
- $1\ mol\ sodium = 22.99\ g\ sodium\ Na$

## Molar Mass for Compounds

### Example 9.2.1.1: Molar Mass of Water

The formulas for compounds are familiar to you. You know the formula for water is $H_2O$. It should be reasonable that the weight of a formula unit can be calculated by adding up the weights for the atoms in the formula.

**Solution**

The formula weight for water

weight from hydrogen + weight from oxygen

The formula weight for water

2 H atoms x 1.008 amu + 1 O atom x 16.00 amu = 18.016 amu

The molar mass for water

18.016 grams water or 18 grams to the nearest gram

### Example 9.2.1.2: Molar Mass of Methane

The formula for methane, the major component in natural gas, is $CH_4$.

**Solution**

The formula weight for methane

weight from hydrogen + weight from carbon

The formula weight for methane

4 H atoms x 1.008 amu + 1 C atom x 12.01 amu = 16.04 amu

The molar mass for methane

16.04 grams per mole of methane

## Example 9.2.1.3: Molar Mass of Ethyl Chloride

What is its molar mass for ethyl chloride $\mathrm{CH_3CH_2Cl}$?

**Solution**

The *formula weight*

weight from hydrogen + weight from carbon + weight from chlorine

The formula weight

5 H atoms x 1.008 amu + 2 C atom x 12.01 amu + 35.5 amu = 64.5 amu

The molar mass for ethyl chloride

64.5 grams per mole of ethyl chloride

## Example 9.2.1.4: Molar Mass of Sulfur Dioxide

What is the molar mass for sulfur dioxide, $\mathrm{SO_2\,(g)}$, a gas used in bleaching and disinfection processes?

**Solution**

Look up the atomic weight for each of the elements in the formula.

- 1 sulfur atom = 32.07 amu
- 1 oxygen atom = 16.00 amu

Count the atoms of each element in the formula unit.

- one sulfur atom
- two oxygen atoms

The formula weight

weight from sulfur + weight from oxygen

The formula weight

1 sulfur atom x (32. 07 amu ) + 2 oxygen atoms x (16.00 amu)

The formula weight

$SO_2$ = 32. 07 amu + 32.00 amu = 64.07 amu = 64 amu $SO_2$

The molar mass for $SO_2$ is

64.07 grams of $SO_2$; 1 mol $SO_2$ = 64 grams per mole of $SO_2$

## Exercise 9.2.1.1

What is the formula weight and molar mass for alum, $KAl(SO_4)_2 \cdot 12\,H_2O$ ?

*Answer available at the end of this section.*

## Answers

**Exercise** 9.2.1.1

1. Check the periodic table for the atomic masses for each atom in the formula.
2. Count the number of each type of atom in the formula.
3. Multiply the number of atoms by the atomic mass for each element.
4. Add up the masses for all of the elements.

*Table* 9.2.1.1*: Masses of each element in alum,* $KAl(SO_4)_2 \cdot 12\,H_2O$

| element | average atomic mass | number of atoms in formula | rounded to nearest one unit for simplicity |
|---|---|---|---|
| potassium k | 39.1 amu | 1 | 39. amu |
| aluminum | 26.98 amu | 1 | 27. amu |
| sulfur | 32.07 amu | 2 | 64. amu |
| oxygen | 16.00 amu | 8 + 12 = 20 | 320. amu |
| hydrogen | 1.008 amu | 2 x 12 = 24 | 24. amu |

Molar mass is 474 grams (add up the amu of each element to find the total of 474 amu). This is a mass in grams that is numerically (474) the same as the formula weight.

1 mole alum $KAl(SO_4)_2 \cdot 12\,H_2O$ = 474 grams alum $KAl(SO_4)_2 \cdot 12\,H_2O$

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# 9.2.2: 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 $6.02 \times 10^{23}$ particles and the name of this group is the **mole** (the abbreviation for ***mole*** is $\mathrm{mol}$). One mole of any object is $6.02 \times 10^{23}$ 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 9.2.2.1: Moles of Carbon

The element carbon exists in two primary forms: graphite and diamond. How many moles of carbon atoms is $4.72 \times 10^{24}$ atoms of carbon?

**Solution**

*Solutions to Example 6.3.1*

| Steps for Problem Solving | The element carbon exists in two primary forms: graphite and diamond. How many moles of carbon atom $\times 10^{24}$ atoms of carbon? |
|---|---|
| Identify the "given" information and what the problem is asking you to "find." | Given: $4.72 \times 10^{24}$ C atoms<br>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. | # C atoms → mol C<br>$\frac{1\ mol\ C}{6.022\ \times 10^{23} C\ atoms}$ |
| Cancel units and calculate. | $4.72 \times 10^{24}\ \cancel{\text{C atoms}} \times \frac{1\ \text{mol C}}{6.02 \times 10^{23}\ \cancel{\text{C atoms}}} = 7.84\ \text{mol C}$ |
| 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 gr 1 mole. Since Avogadro's number is a measured quantity with three significant figures, the result of the calcula 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 $6.022 \times 10^{23}$ atoms of that particular element. The units for molar mass are grams per mole or g/mol. $1.00\ \text{mol}$ of carbon-12 atoms has a mass of $12.0\ \text{g}$ and contains $6.022 \times 10^{23}$ atoms. 1.00 mole of any element has a mass numerically equal to its atomic mass in grams and contains $6.022 \times 10^{23}$ 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 $\text{g/mol}$.

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.

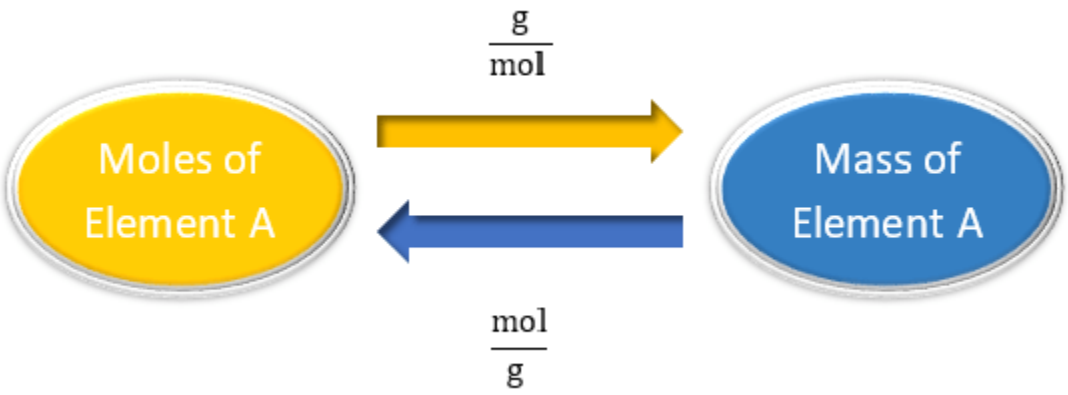



Figure 9.2.2.1: A Simple Flowchart for Converting Between Mass and Moles of an Element.
Flowchart: to convert moles of Element A to mass of Element A, use g/mol, and to convert vice versa, use mol/g.

## Example 9.2.2.2: Chromium

Chromium metal is used for decorative electroplating of car bumpers and other surfaces. Find the mass of 0.560 moles of chromium.

**Solution**

*Solutions to Example 6.3.2*

| Steps for Problem Solving | Chromium metal is used for decorative electroplating of car bumpers and other surfaces. Find the mass moles of chromium. |
|---|---|
| Identify the "given" information and what the problem is asking you to "find." | Given: 0.560 mol Cr<br>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<br>$\frac{52.00g\ Cr}{1\ mol\ Cr}$ |
| Cancel units and calculate. | $0.560\ \cancel{\text{mol Cr}} \times \frac{52.00\ \text{g Cr}}{1\ \cancel{\text{mol Cr}}} = 29.1\ \text{g Cr}$ |

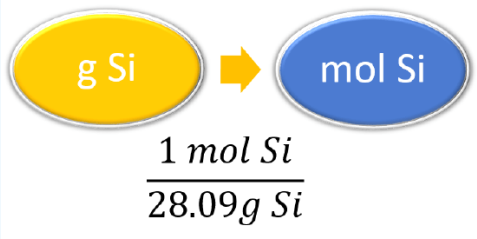
| Steps for Problem Solving | Chromium metal is used for decorative electroplating of car bumpers and other surfaces. Find the mass moles of chromium. |
|---|---|
| Think about your result. | Since the desired amount was slightly more than one half of a mole, the mass should be slightly more than one h molar mass. The answer has three significant figures because of the $0.560\ \text{mol}$ |

## Example 9.2.2.3: Silicon

How many moles are in 107.6g of Si?

**Solution**

*Solutions to Example 6.3.3*

| 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<br>Find: mol Si |
| List other known quantities. | 1 mol Si = 28.09g Si |
| Prepare a concept map and use the proper conversion factor. |  |
| Cancel units and calculate. | $107.6\ \cancel{\text{g Si}} \times \frac{1\ \text{mol Si}}{28.09\ \cancel{\text{g Si}}} = 3.83\ \text{mol Si}$ |
| Think about your result. | Since 1 mol of Si is 28.09g, 107.6 should be about 4 moles. |

## Exercise 9.2.2.1

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: available at the end of this section.*

*Answer b: available at the end of this section.*

## Summary

- A mole is defined as exactly 6.02214076×10$^{23}$ 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

### Answers

**Exercise** 9.2.2.1

3.706 mol Al

**Exercise** 9.2.2.1

59.5 g Ag

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# 9.2.3: 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 $9.2.3.1$.

**Example $9.2.3.1$: Ethanol**

Calculate the molecular mass of ethanol, whose condensed structural formula is $\mathrm{CH_3CH_2OH}$. Among its many uses, ethanol is a fuel for internal combustion engines

**Solution**

*Solutions to Example 6.4.1*

| **Steps for Problem Solving** | **Calculate the molecular mass of ethanol, whose condensed structural formula is $\mathrm{CH_3CH_2OH}$** |
|---|---|
| Identify the "given"information and what the problem is asking you to "find." | Given: Ethanol molecule ($CH_3CH_2OH$)<br>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:<br>• $CH_3CH_2OH$ (which illustrates the presence of an ethyl group<br>• $CH_3CH_2$–, and an –OH group)<br>• $C_2H_5OH$, and $C_2H_6O$;<br>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<br>1 H atom = 1.0079 amu<br>1 O atom = 15.9994 amu |

| Steps for Problem Solving | Calculate the molecular mass of ethanol, whose condensed structural formula is $CH_3CH_2OH$ |
|---|---|
| Add the masses together to obtain the molecular mass. | 2C: (2 atoms)(12.011amu/atom) = 24.022 amu<br><br>6H: (6 atoms)(1.0079amu/atom) = 6.0474amu<br><br>+1O: (1 atoms)(15.9994amu/atom) =15.9994amu<br><br>$C_2H_6O$ : molecular mass of ethanol = 46.069amu |

## Exercise 9.2.3.1: 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:

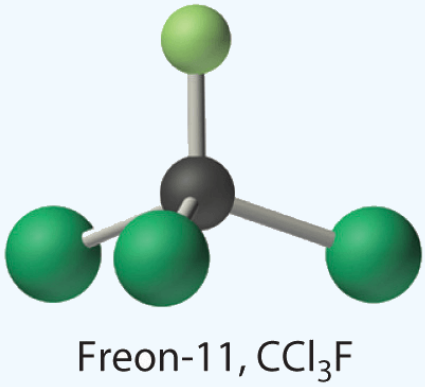



Figure 9.2.3.1: Molecular structure of freon-11, $CCl_3F$.

*Answer available at the end of this section.*

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 9.2.3.2: 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<br>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.<br>• 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<br>1 P atom = 30.973761 amu<br>1 O atom = 15.9994 amu |
| Add together the masses to give the formula mass. | 3Ca: (3 atoms) (40.078 amu/atom)=120.234amu<br>2P: (2 atoms) (30.973761amu/atom)=61.947522amu<br>+ 8O: (8 atoms)(15.9994amu/atom)=127.9952amu<br>Formula mass of $Ca_3(PO_4)_2$=310.177amu |

## Exercise 9.2.3.2: 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 9.2.3.2: $Si_3N_4$ bearing parts. (Public Domain; David W. Richerson and Douglas W. Freitag; Oak Ridge National Laboratory).

*Answer available at the end of this section.*

# 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 $6.022 \times 10^{23}$ 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 $6.022 \times 10^{23}$ carbon atoms—is therefore 12.011 g/mol:

*Table 9.2.3.1: 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 9.2.3.3.

## Example 9.2.3.3: Calcium Chloride

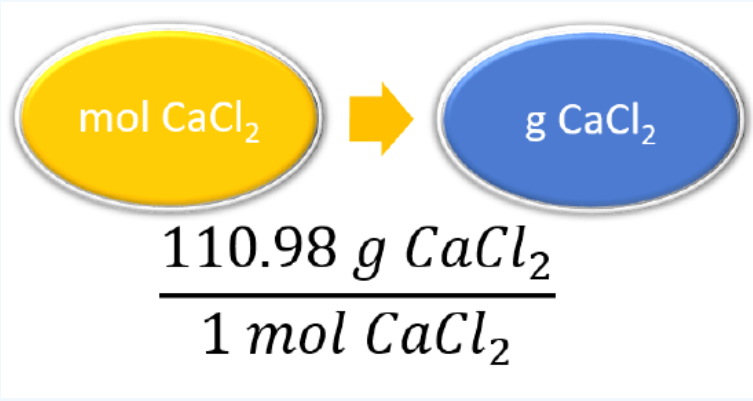
Calculate the mass of 3.00 moles of calcium chloride ($CaCl_2$).




Figure 9.2.3.3: 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 $\mathrm{CaCl_2}$<br>Find: g $\mathrm{CaCl_2}$ |
| List other known quantities. | 1 mol $\mathrm{CaCl_2}$ = 110.98 g $\mathrm{CaCl_2}$ |
| Prepare a concept map and use the proper conversion factor. |  |
| Cancel units and calculate. | $3.00\ \cancel{\text{mol CaCl}_2} \times \frac{110.98\ \text{g CaCl}_2}{1\ \cancel{\text{mol CaCl}_2}} = 333\ \text{g CaCl}_2$ |
| Think about your result. | |

## Exercise 9.2.3.3: Calcium Oxide

What is the mass of $7.50\ \text{mol}$ of (calcium oxide) $\mathrm{CaO}$?

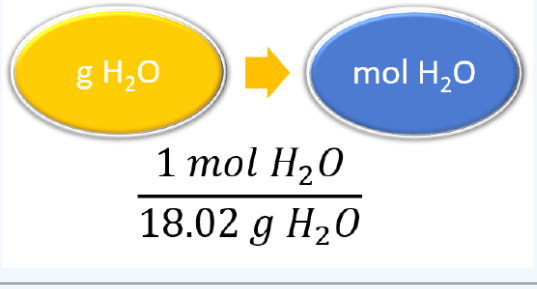
*Answer available at the end of this section.*

## Example 9.2.3.4: 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 $\mathrm{H_2O}$<br>Find: mol $\mathrm{H_2O}$ |
| List other known quantities. | $1\ \text{mol}\ \mathrm{H_2O} = 18.02\ \text{g}$ H2O |
| Prepare a concept map and use the proper conversion factor. |  |

| Steps for Problem Solving | How many moles are present in 108 grams of water? |
|---|---|
| Cancel units and calculate. | $108 \ \cancel{\text{g H}_2\text{O}} \times \frac{1 \text{ mol H}_2\text{O}}{18.02 \ \cancel{\text{g H}_2\text{O}}} = 5.99 \text{ mol H}_2\text{O}$ |
| Think about your result. | |

### Exercise 9.2.3.4: Nitrogen Gas

What is the mass of $7.50 \text{ mol}$ of Nitrogen gas $\text{N}_2$?

*Answer available at the end of this section.*

## 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 9.2.3.1 and Example 9.2.3.5.

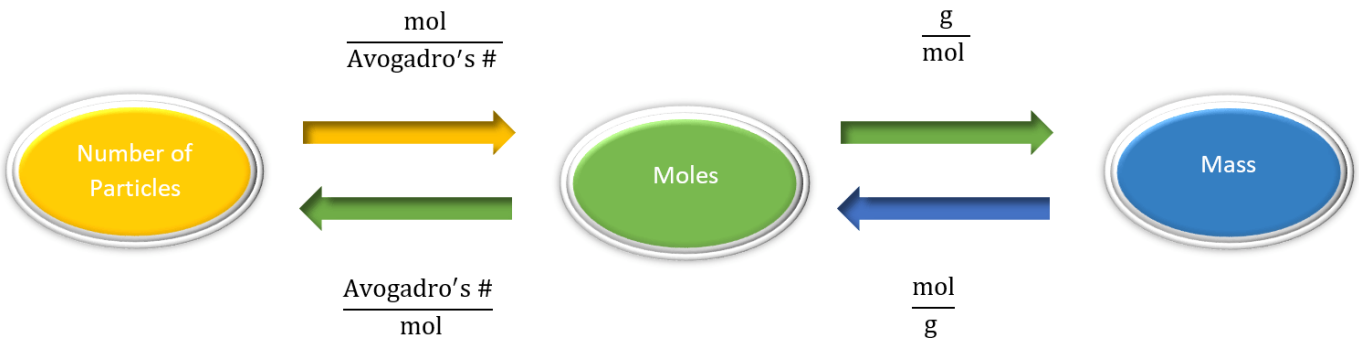


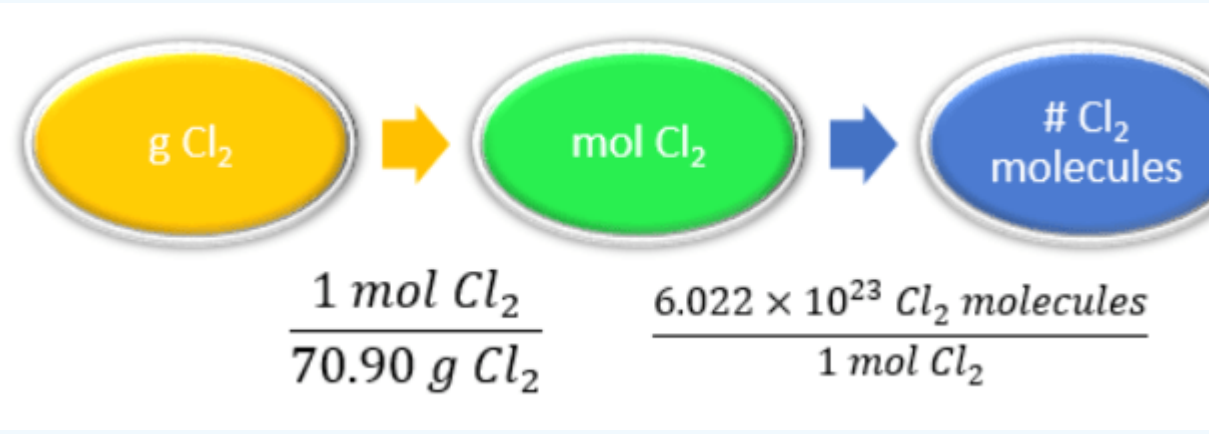

Figure 9.2.3.4: Conversion from number of particles to mass, or from mass to number of particles, requires two steps. To convert from number of particles to moles, use mol/Avogrado's #, an d to convert from moles to mass, use g/mol.

### Example 9.2.3.5: Chlorine

How many molecules is $20.0 \text{ g}$ of chlorine gas, $\text{Cl}_2$?

**Solution**

*Solutions to Example 6.4.5*

| **Steps for Problem Solving** | **How many molecules is $20.0\ \text{g}$ of chlorine gas, $Cl_2$?** |
|---|---|
| Identify the "given" information and what the problem is asking you to "find." | Given: 20.0 g $Cl_2$<br>Find: # $Cl_2$ molecules |
| List other known quantities. | • 1 mol $Cl_2$ = 70.90 g $Cl_2$,<br>• 1mol $Cl_2$ = $6.022 \times 10^{23}$ $Cl_2$ molecules |
| Prepare a concept map and use the proper conversion factor. |  <br>The conversion factors are 1 mole $Cl_2$ over 70.90 grams $Cl_2$, and $6.022 \times 10^{2}3$ $Cl_2$ molecules over 1 mole $Cl_2$. |
| Cancel units and calculate. | $20.0\ \cancel{\text{g Cl}_2} \times \frac{1\ \cancel{\text{mol Cl}_2}}{70.90\ \cancel{\text{g Cl}_2}} \times \frac{6.02 \times 10^{23}\ \text{molecules Cl}_2}{1\ \cancel{\text{mol Cl}_2}} = 1.70 \times 10^{23}\ \text{molecules Cl}_2$ |
| 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 of Avogadro's number. |

### Exercise 9.2.3.5: Calcium Chloride

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

*Answer available at the end of this section.*

## 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.

## Answers

**Exercise** 9.2.3.1**: Freon**

137.37 amu

**Exercise** 9.2.3.2**: Silicon Nitride**

140.29 amu

**Exercise** 9.2.3.3**: Calcium Oxide**

420.60 g

**Exercise** 9.2.3.4**: Nitrogen Gas**

210 g

**Exercise** 9.2.3.5**: Calcium Chloride**

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

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# 9.2.4: Chemical Formulas as Conversion Factors

## Learning Objectives

- Use chemical formulas as conversion factors.

Figure 9.2.4.1 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.

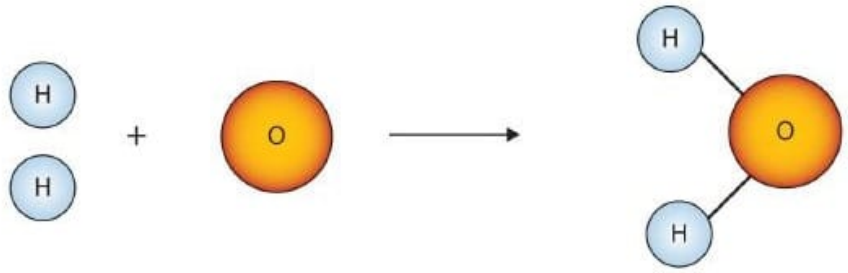



Figure 9.2.4.1 Water Molecules. The ratio of hydrogen atoms to oxygen atoms used to make water molecules is always 2:1, no matter how many water molecules are being made.

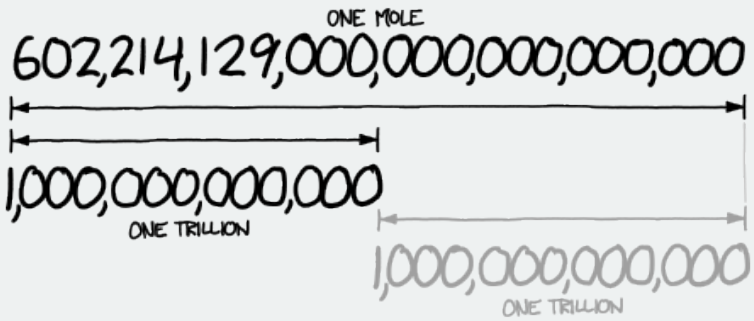
Using formulas to indicate how many atoms of each element we have in a substance, we can relate the number of moles of molecules to the number of moles of atoms. For example, in 1 mol of water ($H_2O$) we can construct the relationships given in (Table 9.2.4.1).

*Table 9.2.4.1: Molecular Relationships for Water*

| 1 Molecule of $H_2O$ Has | 1 Mol of $H_2O$ Has | Molecular Relationships |
|---|---|---|
| 2 H atoms | 2 mol of H atoms | $\frac{2\text{ mol H atoms}}{1\text{ mol }H_2O\text{ molecules}}$ or $\frac{1\text{ mol }H_2O\text{ molecules}}{2\text{ mol H atoms}}$ |
| 1 O atom | 1 mol of O atoms | $\frac{1\text{ mol O atoms}}{1\text{ mol }H_2O\text{ molecules}}$ or $\frac{1\text{ mol }H_2O\text{ molecules}}{1\text{ mol O atoms}}$ |

## The Mole is big

A mole represents a very large number! The number 602,214,129,000,000,000,000,000 looks about twice as long as a trillion, which means it's about a trillion trillion.



(CC BY-SA NC; what if? [what-if.xkcd.com]).

A trillion trillion kilograms is how much a planet weighs. If 1 mol of quarters were stacked in a column, it could stretch back and forth between Earth and the sun *6.8 billion* times.

*Table 9.2.4.2: Molecular and Mass Relationships for Ethanol*

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

The following example illustrates how we can use the relationships in Table 9.2.4.2 as conversion factors.

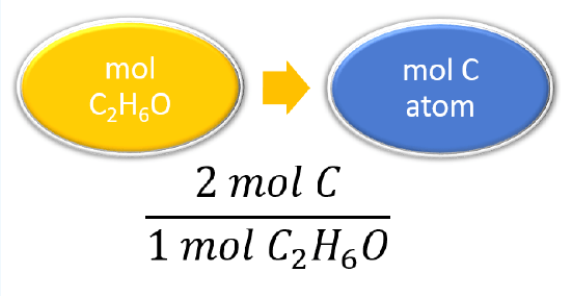
## Example 9.2.4.1: Ethanol

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 $C_2H_6O$<br>Find: mol C atoms |
| List other known quantities. | 1 mol $C_2H_6O$ = 2 mol C |

| 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? |
|---|---|
| Prepare a concept map and use the proper conversion factor. |  $\frac{2\ mol\ C}{1\ mol\ C_2H_6O}$ |
| Cancel units and calculate. | Note how the unit *mol $C_2H_6O$ molecules* cancels algebraically. $2.5\ \cancel{\text{mol } C_2H_6O \text{ molecules}} \times \frac{2\ \text{mol C atoms}}{1\ \cancel{\text{mol } C_2H_6O \text{ molecules}}} = 5.0\ \text{mol C atoms}$ |
| Think about your result. | There are twice as many C atoms in one $C_2H_6O$ molecule, so the final amount should be double. |

## Exercise 9.2.4.1

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 available at the end of this section.*

*Answer available at the end of this section.*

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

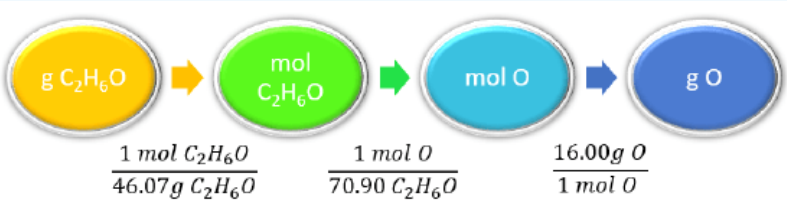
## Example 9.2.4.2: Oxygen Mass

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 $C_2H_6O$<br>Find: g O |
| List other known quantities. | 1 mol O = 16.0g O<br>1 mol $C_2H_6O$ = 1 mol O<br>1 mol $C_2H_6O$ = 46.07g $C_2H_6O$ |

| Steps for Problem Solving | Determine the mass of Oxygen in 75.0g of $C_2H_6O$ |
|---|---|
| Prepare a concept map and use the proper conversion factor. |  The conversion factors are 1 mol C2H6O over 46.07 g C2H6O, 1 mol O over 1 mol C2H6O, and 16.00 g O over 1 mole O. |
| Cancel units and calculate. | $75.0\ \cancel{\text{g C}_2\text{H}_6\text{O}} \times \frac{1\ \cancel{\text{mol C}_2\text{H}_6\text{O}}}{46.07\ \cancel{\text{g C}_2\text{H}_6\text{O}}} \times \frac{1\ \cancel{\text{mol O}}}{1\ \cancel{\text{mol C}_2\text{H}_6\text{O}}} \times \frac{16.00\ \text{g O}}{1\ \cancel{\text{mol O}}} = 26.0\ \text{g O}$ |
| Think about your result. | |

## Exercise 9.2.4.2

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: available at the end of this section.*

*Answer b: available at the end of this section.*

# 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.

## Answers

**Exercise** 9.2.4.1

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

**Exercise** 9.2.4.1

**Exercise** 9.2.4.2

9.647 x $10^{24}$ $C_4H_{10}$ molecules and 3.859 x $10^{25}$ C atoms

**Exercise** 9.2.4.2

5.16 mol Na atoms, 2.58 mol S atoms, and 10.3 mol O atoms

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# 9.3: STOICHIOMETRY



- Topic hierarchy


9.3.1: Stoichiometry

9.3.2: Making Pancakes- Relationships Between Ingredients

9.3.3: Making Molecules- Mole-to-Mole Conversions

9.3.4: Making Molecules- Mass-to-Mass Conversions

9.3.5: Limiting Reactant and Theoretical Yield

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

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



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# 9.3.1: Stoichiometry

**Learning Objectives**

- Explain the meaning of the term "stoichiometry".
- Determine the relative amounts of each substance in chemical equations.

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.

$$2\mathrm{CuSO_4} + 4\mathrm{KI} \rightarrow 2\mathrm{CuI} + 2\mathrm{K_2SO_4} + \mathrm{I_2}$$

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 ($\mathrm{CuSO_4}$) we have, we need to have 4 units of potassium iodide ($\mathrm{KI}$). 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 ($\mathrm{NH_3}$) from nitrogen and hydrogen gases is an important industrial reaction called the Haber process, after German chemist Fritz Haber.

$$\mathrm{N_2}\,(g) + 3\mathrm{H_2}\,(g) \rightarrow 2\mathrm{NH_3}\,(g)$$

The balanced equation can be analyzed in several ways, as shown in the figure below.

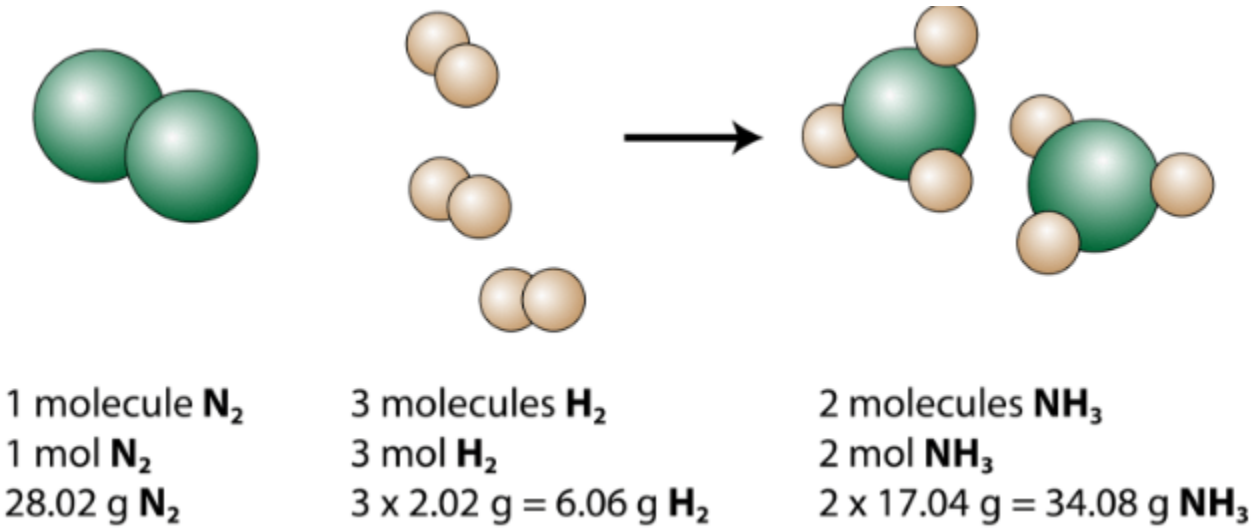



Figure 9.3.1.1: This representation of the production of ammonia from nitrogen and hydrogen show several ways to interpret the quantitative information of a chemical reaction.

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. $1\ \text{mol}$ of nitrogen has a mass of $28.02\ \text{g}$, while $3\ \text{mol}$ of hydrogen has a mass of $6.06\ \text{g}$, and $2\ \text{mol}$ of ammonia has a mass of $34.08\ \text{g}$.

$$28.02\ \text{g}\ \text{N}_2 + 6.06\ \text{g}\ \text{H}_2 \rightarrow 34.08\ \text{g}\ \text{NH}_3$$

Mass and the number of atoms must be conserved in any chemical reaction. The number of molecules is not necessarily conserved.

### Example 9.3.1.1

The equation for the combustion of ethane ($\text{C}_2\text{H}_6$) is

$$2_2\text{CH}_6 + 7\text{O}_2 \rightarrow 4\text{CO}_2 + 6\text{H}_2\text{O}$$

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 $\text{C}_2\text{H}_6$ plus seven molecules of $\text{O}_2$ yields four molecules of $\text{CO}_2$ plus six molecules of $\text{H}_2\text{O}$.
b. Two moles of $\text{C}_2\text{H}_6$ plus seven moles of $\text{O}_2$ yields four moles of $\text{CO}_2$ plus six moles of $\text{H}_2\text{O}$.

### Exercise 9.3.1.1

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

$$\text{KBrO}_3 + 6\text{KI} + 6\text{HBr} \rightarrow 7\text{KBr} + 3\text{H}_2\text{O}$$

*Answer available at the end of this section.*

## 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.

## Answers

**Exercise** 9.3.1.1

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

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# 9.3.2: Making Pancakes- Relationships Between Ingredients

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# 9.3.3: Making Molecules- Mole-to-Mole Conversions

## /;Learning Objectives

- Use a balanced chemical equation to determine molar relationships between substances.

Previously, you learned to balance chemical equations by comparing the numbers of each type of atom in the reactants and products. The coefficients in front of the chemical formulas represent the numbers of molecules or formula units (depending on the type of substance). As follows, we will extend the meaning of the coefficients in a chemical equation.

Consider the simple chemical equation:

$$2H_2 + O_2 \rightarrow 2H_2O$$

The convention for writing balanced chemical equations is to use the lowest whole-number ratio for the coefficients. However, the equation is balanced as long as the coefficients are in a 2:1:2 ratio. For example, this equation is also balanced if we write it as

$$4H_2 + 2O_2 \rightarrow 4H_2O$$

The ratio of the coefficients is 4:2:4, which reduces to 2:1:2. The equation is also balanced if we were to write it as

$$22H_2 + 11O_2 \rightarrow 22H_2O$$

because 22:11:22 also reduces to 2:1:2.

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

$$12.044 \times 10^{23}\ \mathrm{H_2} + 6.022 \times 10^{23}\ \mathrm{O_2} \rightarrow 12.044 \times 10^{23}\ \mathrm{H_2O}$$

These coefficients also have the ratio 2:1:2 (check it and see), so this equation is balanced. But $6.022 \times 10^{23}$ is 1 mol, while $12.044 \times 10^{23}$ is 2 mol (and the number is written that way to make this more obvious), so we can simplify this version of the equation by writing it as

$$2\ mol\ \mathrm{H_2} + 1\ mol\ \mathrm{O_2} \rightarrow 2\ mol\ \mathrm{H_2O}$$

We can leave out the word *mol* and not write the 1 coefficient (as is our habit), so the final form of the equation, still balanced, is

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

Now we interpret the coefficients as referring to molar amounts, not individual molecules. The lesson? *Balanced chemical equations are balanced not only at the molecular level, but also in terms of molar amounts of reactants and products*. Thus, we can read this reaction as “two moles of hydrogen react with one mole of oxygen to produce two moles of water.”

By the same token, the ratios we constructed to describe a molecular reaction can also be constructed in terms of moles rather than molecules. For the reaction in which hydrogen and oxygen combine to make water, for example, we can construct the following ratios:

$$\frac{2\ \mathrm{mol\ H_2}}{1\ \mathrm{mol\ O_2}} \text{ or } \frac{1\ \mathrm{mol\ O_2}}{2\ \mathrm{mol\ H_2}}$$

$$\frac{2\ \mathrm{mol\ H_2O}}{1\ \mathrm{mol\ O_2}} \text{ or } \frac{1\ \mathrm{mol\ O_2}}{2\ \mathrm{mol\ H_2O}}$$

$$\frac{2\ \mathrm{mol\ H_2}}{2\ \mathrm{mol\ H_2O}} \text{ or } \frac{2\ \mathrm{mol\ H_2O}}{2\ \mathrm{mol\ H_2}}$$

We can use these ratios to determine what amount of a substance, in moles, will react with or produce a given number of moles

of a different substance. The study of the numerical relationships between the reactants and the products in balanced chemical reactions is called *stoichiometry*.

## Example 9.3.3.1

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

**Solution**

*Solutions to Example 8.3.1*

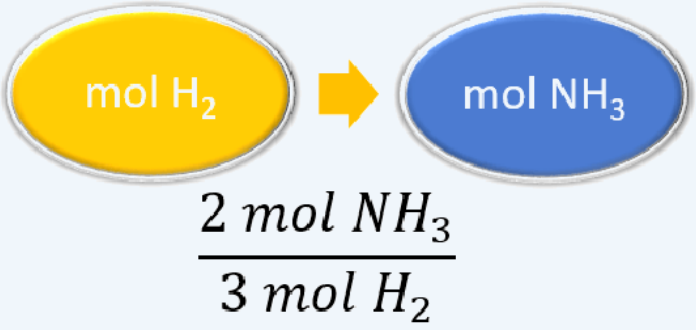
| Steps for Problem Solving | How many moles of oxygen react with hydrogen to produce 27.6 mol of $H_2O$? |
|---|---|
| Find a balanced equation that describes the reaction. | Unbalanced: $H_2 + O_2 \rightarrow H_2O$<br>Balanced: $\underline{\mathbf{2}}H_2 + O_2 \rightarrow \underline{\mathbf{2}}H_2O$ |
| Identify the "given" information and what the problem is asking you to "find." | Given: moles $H_2O$ Find: moles oxygen |
| List other known quantities. | 1 mol $O_2$ = 2 mol $H_2O$ |
| Prepare a concept map and use the proper conversion factor. |  $\frac{1\ mol\ O_2}{2\ mol\ H_2O}$ |
| Cancel units and calculate. | $\cancel{27.6\ mol\ H_2O} \times \frac{1\ mol\ O_2}{\cancel{2\ mol\ H_2O}} = 13.8\ mol\ O_2$<br>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 9.3.3.2

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: $N_2 + H_2 \rightarrow NH_3$<br>Balanced: $N_2 + \mathbf{3}H_2 \rightarrow \mathbf{2}NH_3$ |
| Identify the "given" information and what the problem is asking you to "find." | Given: $\mathrm{H_2} = 4.20\ \mathrm{mol}$<br>Find: $\mathrm{mol}$ of $\mathrm{NH_3}$ |
| List other known quantities. | 3 mol $H_2$ = 2 mol $NH_3$ |
| Prepare a concept map and use the proper conversion factor. |  <br>$\frac{2\ mol\ NH_3}{3\ mol\ H_2}$ |
| Cancel units and calculate. | $\cancel{4.20\ mol\ H_2} \times \frac{2\ \mathrm{mol}\ NH_3}{\cancel{3\ mol\ H_2}} = 2.80\ \mathrm{mol}\ NH_3$<br>The reaction of $4.20\ \mathrm{mol}$ of hydrogen with excess nitrogen produces $2.80\ \mathrm{mol}$ of ammonia. |
| Think about your result. | The result corresponds to the 3:2 ratio of hydrogen to ammonia from the balanced equation. |

## Exercise 9.3.3.3

a. Given the following balanced chemical equation:

$$\mathrm{C_5H_{12} + 8\,O_2 \longrightarrow 5\,CO_2 + 6\,H_2O}$$

, How many moles of $\mathrm{H_2O}$ can be formed if 0.0652 mol of $\mathrm{C_5H_{12}}$ were to react?

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

$$\mathrm{NH_3 + O_2 \longrightarrow N_2 + H_2O}$$

*Answer a available at the end of this section.*

## Summary

- The balanced chemical reaction can be used to determine molar relationships between substances.

## Answers

**Exercise** 9.3.3.3

0.391 mol $H_2O$

$4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O$; 2.48 mol $H_2O$

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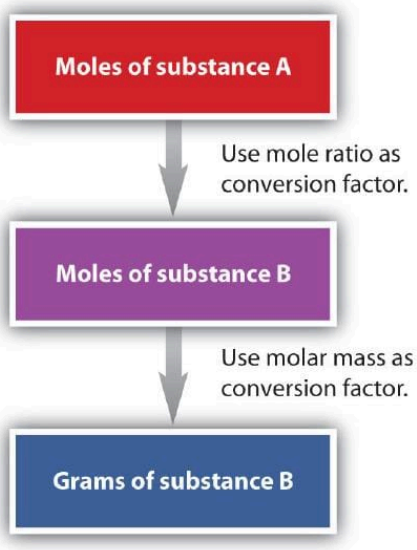
# 9.3.4: Making Molecules- Mass-to-Mass Conversions

**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

$$\mathrm{Fe_2O_3 + 3\,SO_3 \ \rightarrow Fe_2(SO_4)_3} \tag{9.3.4.1}$$

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:

$$3.59 \ \cancel{\mathrm{mol\ Fe_2O_3}} \times \left( \frac{3\ \mathrm{mol\ SO_3}}{1\ \cancel{\mathrm{mol\ Fe_2O_3}}} \right) = 10.77\ \mathrm{mol\ SO_3} \tag{9.3.4.2}$$

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:

$$10.77 \cancel{\text{ mol SO}_3} \times \left( \frac{80.06 \text{ g SO}_3}{1 \cancel{\text{ mol SO}_3}} \right) = 862 \text{ g SO}_3 \tag{9.3.4.3}$$

Our final answer is expressed to three significant figures. Thus, in a two-step process, we find that 862 g of $SO_3$ will react with 3.59 mol of $Fe_2O_3$. 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:

$$3.59 \cancel{\ mol\ Fe_2O_3} \times \underbrace{\left( \frac{3 \cancel{\ mol\ SO_3}}{1 \cancel{\ mol\ Fe_2O_3}} \right)}_{\text{converts to moles of } SO_3} \times \underbrace{\left( \frac{80.06\ g\ SO_3}{1 \cancel{\ mol\ SO_3}} \right)}_{\text{converts to grams of } SO_3} = 862\ g\ SO_3$$

We get exactly the same answer when combining all math steps together.

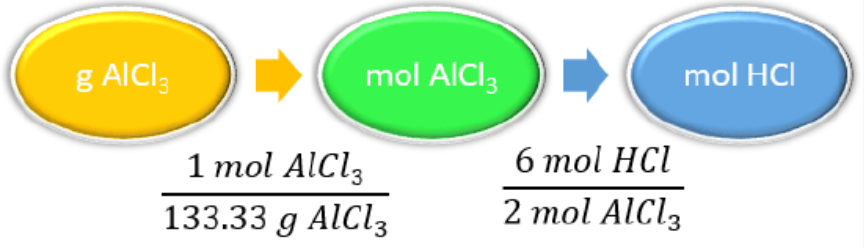
## Example 9.3.4.1: Generation of Aluminum Oxide

How many moles of $HCl$ will be produced when 249 g of $AlCl_3$ are reacted according to this chemical equation?

$$2\,AlCl_3 + 3\,H_2O(\ell) \longrightarrow Al_2O_3 + 6\,HCl\,(g)$$

**Solution**

*Solutions to Example 8.5.1*

| Steps for Problem Solving | Example 9.3.4.1 |
|---|---|
| Identify the "given" information and what the problem is asking you to "find." | Given: 249 g AlCl3<br>Find: moles HCl |
| List other known quantities. | 1 mol AlCl3 = 133.33 g AlCl3<br>6 mol of HCl to 2 mol $AlCl_3$ |
| Prepare a concept map and use the proper conversion factor. |  <br>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. | $249 \cancel{\ g\ AlCl_3} \times \frac{1 \cancel{\ mol\ AlCl_3}}{133.33 \cancel{\ g\ AlCl_3}} \times \frac{6\ mol\ HCl}{2 \cancel{\ mol\ AlCl_3}} = 5.60\ mol\ HCl$ |
| 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 9.3.4.1: Generation of Aluminum Oxide

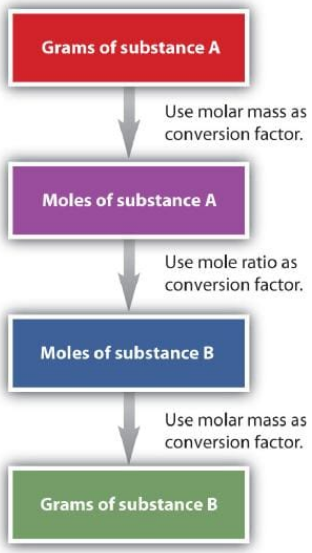
How many moles of $Al_2O_3$ will be produced when 23.9 g of $H_2O$ are reacted according to this chemical equation?

$$2\,AlCl_3 + 3\,H_2O(\ell) \longrightarrow Al_2O_3 + 6\,HCl\,(g)$$

*Answer available at the end of this section.*

## 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:




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 9.3.4.2: Decomposition of Ammonium Nitrate

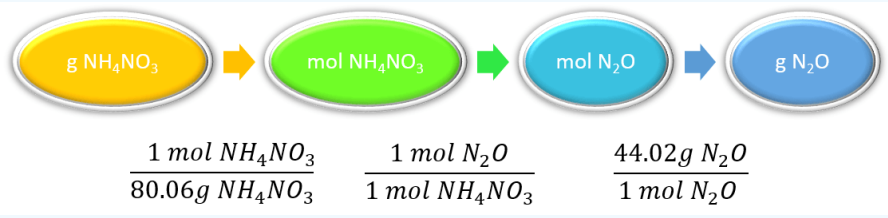
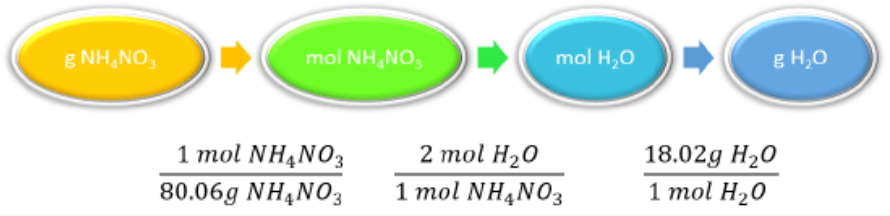
Ammonium nitrate decomposes to dinitrogen monoxide and water according to the following equation.

$$NH_4NO_3\,(s) \rightarrow N_2O\,(g) + 2H_2O\,(l)$$

In a certain experiment, $45.7\ \text{g}$ of ammonium nitrate is decomposed. Find the mass of each of the products formed.

*Solutions to Example 8.5.2*

| Steps for Problem Solving | Example 9.3.4.2 |
|---|---|
| Identify the "given" information and what the problem is asking you to "find." | Given: $45.7\ \text{g}\ NH_4NO_3$<br>Find:<br>Mass $N_2O = ?\ \text{g}$<br>Mass $H_2O = ?\ \text{g}$ |

| Steps for Problem Solving | Example 9.3.4.2 |
|---|---|
| List other known quantities. | 1 mol $NH_4NO_3 = 80.06$ g<br>1 mol $N_2O = 44.02$ g<br>1 mol $H_2O = 18.02$ g<br>1 mol $NH_4NO_3$ to 1 mol $N_2O$ to 2 mol $H_2O$ |
| Prepare two concept maps and use the proper conversion factor. |  <br>$\frac{1\ mol\ NH_4NO_3}{80.06g\ NH_4NO_3}$ $\frac{1\ mol\ N_2O}{1\ mol\ NH_4NO_3}$ $\frac{44.02g\ N_2O}{1\ mol\ N_2O}$<br>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<br>  <br>$\frac{1\ mol\ NH_4NO_3}{80.06g\ NH_4NO_3}$ $\frac{2\ mol\ H_2O}{1\ mol\ NH_4NO_3}$ $\frac{18.02g\ H_2O}{1\ mol\ H_2O}$<br>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. | $45.7\ \text{g}\ NH_4NO_3 \times \frac{1\ \text{mol}\ NH_4NO_3}{80.06\ \text{g}\ NH_4NO_3} \times \frac{1\ \text{mol}\ N_2O}{1\ \text{mol}\ NH_4NO_3} \times \frac{44.02\ \text{g}\ N_2O}{1\ \text{mol}\ N_2O} = 25.1\ \text{g}\ N_2O$<br>$45.7\ \text{g}\ NH_4NO_3 \times \frac{1\ \text{mol}\ NH_4NO_3}{80.06\ \text{g}\ NH_4NO_3} \times \frac{2\ \text{mol}\ H_2O}{1\ \text{mol}\ NH_4NO_3} \times \frac{18.02\ \text{g}\ H_2O}{1\ \text{mol}\ H_2O} = 20.6\ \text{g}\ H_2O$ |
| 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 9.3.4.2: Carbon Tetrachloride

Methane can react with elemental chlorine to make carbon tetrachloride ($CCl_4$). The balanced chemical equation is as follows:

$$CH_4\,(g) + 4\,Cl_2\,(g) \longrightarrow CCl_2\,(l) + 4\,HCl\,(l)$$

How many grams of $HCl$ are produced by the reaction of 100.0 g of $CH_4$?

*Answer available at the end of this section.*

## 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.

## Answers

**Exercise** 9.3.4.1**: Generation of Aluminum Oxide**

0.442 mol $Al_2O_3$

**Exercise** 9.3.4.2**: Carbon Tetrachloride**

908.7g HCl

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# 9.3.5: 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:

$$1\,\text{box mix} + 2\,\text{eggs} \rightarrow 1\,\text{batch brownies} \tag{9.3.5.1}$$

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

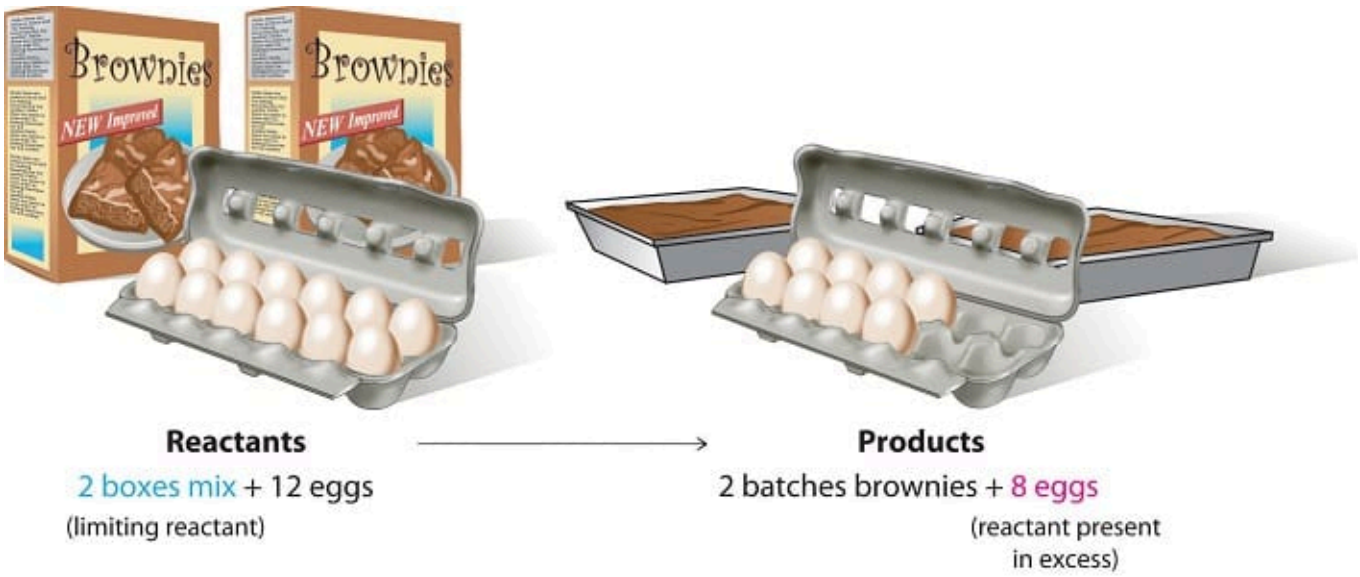



Figure 9.3.5.1: The Concept of a Limiting Reactant in the Preparation of Brownies. For a chemist, the **balanced** chemical equation is the recipe that must be followed.

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:

$$\mathrm{H_2} + \mathrm{Cl_2}(g) \rightarrow 2\,\mathrm{HCl}(g)$$

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:

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

Complete reaction of the provided chlorine would produce:

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

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 9.3.5.2).

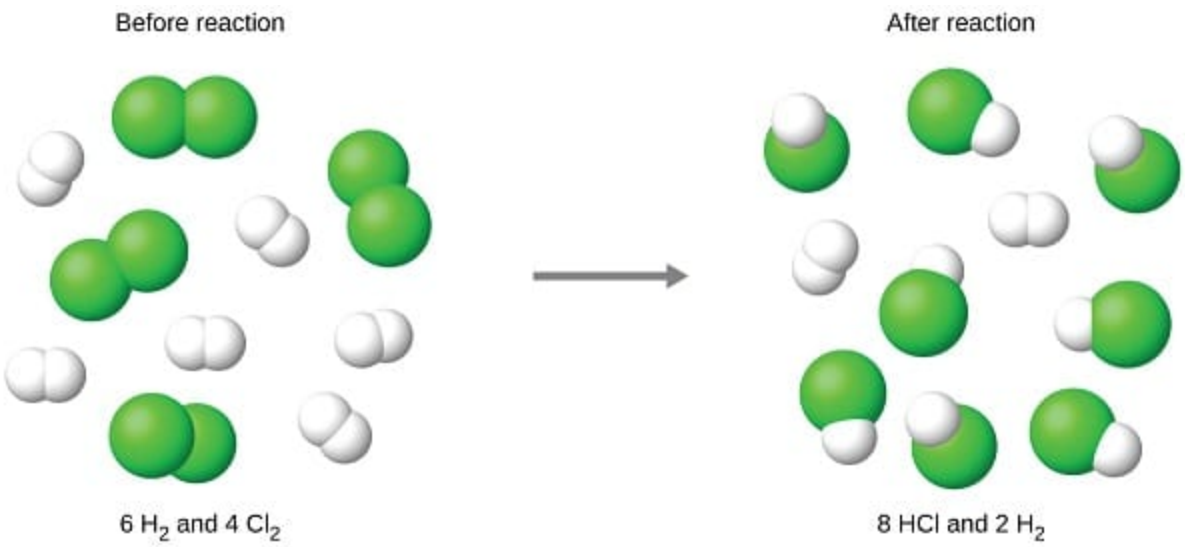



Figure 9.3.5.2: When $H_2$ and $Cl_2$ are combined in nonstoichiometric amounts, one of these reactants will limit the amount of HCl that can be produced. This illustration shows a reaction in which hydrogen is present in excess and chlorine is the limiting reactant. The figure shows a space-filling 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 9.3.5.1: 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.***

$$76.4 \text{ g } C_2H_3Br_3 \times \frac{1 \text{ mol } C_2H_3Br_3}{266.72 \text{ g } C_2H_3B_3} = 0.286 \text{ mol } C_2H_3Br_3$$

$$49.1 \text{ g } O_2 \times \frac{1 \text{ mol } O_2}{32.00 \text{ g } O_2} = 1.53 \text{ mol } O_2$$

***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,

$$1.53 \text{ mol } O_2 \times \frac{4 \text{ mol } C_2H_3Br_3}{11 \text{ mol } O_2} = 0.556 \text{ mol } C_2H_3Br_3 \text{ are required.}$$

**Because 0.556 moles of $C_2H_3Br_3$ required > 0.286 moles of $C_2H_3Br_3$ available, $C_2H_3Br_3$ is the limiting reactant.**

Using Approach 2:

**Step 1: *Balance the chemical equation.***

The equation is already balanced with the relationship

$$4 \text{ mol } C_2H_3Br_3 \text{ to } 11 \text{ mol } O_2 \text{ to } 6 \text{ mol } H_2O \text{ to } 6 \text{ mol } Br_2$$

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

$$76.4 \text{ g } C_2H_3Br_3 \times \frac{1 \text{ mol } C_2H_3Br_3}{266.72 \text{ g } C_2H_3Br_3} \times \frac{8 \text{ mol } CO_2}{4 \text{ mol } C_2H_3Br_3} \times \frac{44.01 \text{ g } CO_2}{1 \text{ mol } CO_2} = 25.2 \text{ g } CO_2$$

$$49.1 \text{ g } O_2 \times \frac{1 \text{ mol } O_2}{32.00 \text{ g } O_2} \times \frac{8 \text{ mol } CO_2}{11 \text{ mol } O_2} \times \frac{44.01 \text{ g } CO_2}{1 \text{ mol } CO_2} = 49.1 \text{ g } CO_2$$

***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 9.3.5.2: Identifying the Limiting Reactant and the Mass of Excess Reactant

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

**Solution**

Following Approach 1:

***Step 1: Balance the chemical equation.***

$$\underline{\mathbf{2}}\ \mathrm{Mg\ (s)} + \mathrm{O_2\ (g)} \rightarrow \underline{\mathbf{2}}\ \mathrm{MgO\ (s)}$$

The balanced equation provides the relationship of 2 mol Mg to 1 mol $O_2$ to 2 mol MgO

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

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

$$10.0\ \cancel{\mathrm{g\ O_2}} \times \frac{1\ \cancel{\mathrm{mol\ O_2}}}{32.00\ \cancel{\mathrm{g\ O_2}}} \times \frac{2\ \cancel{\mathrm{mol\ MgO}}}{1\ \cancel{\mathrm{mol\ O_2}}} \times \frac{40.31\ \mathrm{g\ MgO}}{1\ \cancel{\mathrm{mol\ MgO}}} = 25.2\ \mathrm{g\ MgO}$$

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

Mg produces less MgO than does $O_2$ (3.98 g MgO vs. 25.2 g MgO), therefore Mg is the limiting reactant in this reaction.

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

$O_2$ produces more amount of MgO than Mg (25.2g MgO vs. 3.98 MgO), therefore $O_2$ is the excess reactant in this reaction.

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

Mass of excess reactant calculated using the limiting reactant:

$$2.40\ \cancel{\mathrm{g\ Mg}} \times \frac{1\ \cancel{\mathrm{mol\ Mg}}}{24.31\ \cancel{\mathrm{g\ Mg}}} \times \frac{1\ \cancel{\mathrm{mol\ O_2}}}{2\ \cancel{\mathrm{mol\ Mg}}} \times \frac{32.00\ \mathrm{g\ O_2}}{1\ \cancel{\mathrm{mol\ O_2}}} = 1.58\ \mathrm{g\ O_2}$$

**OR**

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

$$3.98\ \cancel{\mathrm{g\ MgO}} \times \frac{1\ \cancel{\mathrm{mol\ MgO}}}{40.31\ \cancel{\mathrm{g\ MgO}}} \times \frac{1\ \cancel{\mathrm{mol\ O_2}}}{2\ \cancel{\mathrm{mol\ MgO}}} \times \frac{32.0\ \mathrm{g\ O_2}}{1\ \cancel{\mathrm{mol\ O_2}}} = 1.58\ \mathrm{g\ O_2}$$

Mass of total excess reactant given – mass of excess reactant consumed in the reaction:

10.0g $O_2$ - (available) 1.58g $O_2$ (used) = 8.42g $O_2$ (excess)

**Therefore, $O_2$ is in excess.**

## Example 9.3.5.3: Limiting Reactant

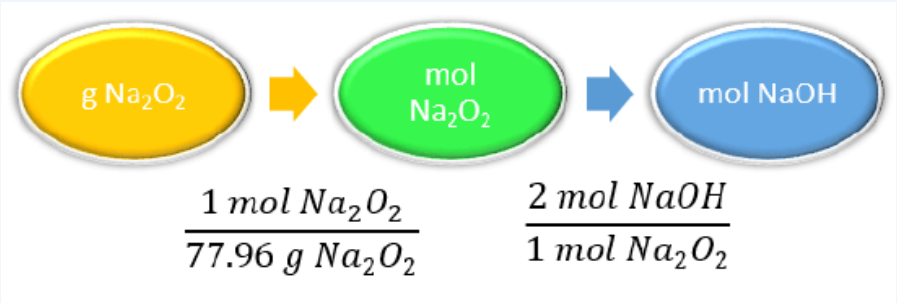
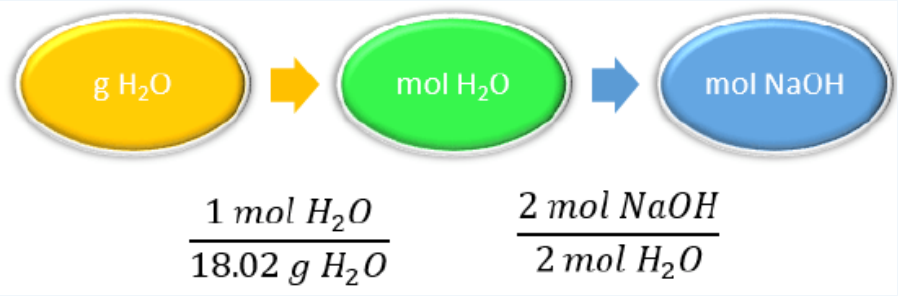
What is the limiting reactant if 78.0 grams of $Na_2O_2$ were reacted with 29.4 grams of $H_2O$? The unbalanced chemical equation is

$$Na_2O_2\,(s) + H_2O\,(l) \longrightarrow NaOH\,(aq) + H_2O_2\,(l)$$

**Solution**

*Solutions to Example 8.4.3*

| **Steps for Problem Solving- The Product Method** | **Example 9.3.5.1** |
|---|---|
| Identify the "given" information and what the problem is asking you to "find." | Given: 78.0 grams of $Na_2O_2$<br><br>29.4 g $H_2O$<br><br>Find: limiting reactant |
| List other known quantities. | 1 mol $Na_2O_2$= 77.96 g/mol<br>1 mol $H_2O$ = 18.02 g/mol<br><br>Since the amount of product in grams is not required, only the molar mass of the reactants is needed. |
| Balance the equation. | $Na_2O_2$ (s) + **2**$H_2O$ (l) → **2**NaOH (aq) + $H_2O_2$ (l)<br><br>The balanced equation provides the relationship of 1 mol $Na_2O_2$ to 2 mol $H_2O$ 2mol NaOH to 1 mol $H_2O_2$ |

| Steps for Problem Solving- The Product Method | Example 9.3.5.1 |
|---|---|
| Prepare a concept map and use the proper conversion factor. |  <br>  <br>Because the question only asks for the limiting reactant, we can perform two **mass-mole** calculations and de which amount is less. |
| Cancel units and calculate. | $78.0\ \text{g}\ \text{Na}_2\text{O}_2 \times \frac{1\ \text{mol}\ \text{Na}_2\text{O}_2}{77.96\ \text{g}\ \text{Na}_2\text{O}_2} \times \frac{2\ \text{mol NaOH}}{1\ \text{mol}\ \text{Na}_2\text{O}_2} \times \frac{40\ \text{g NaOH}}{1\ \text{mol NaOH}} = 2.00\ \text{mol NaOH}$<br>$29.4\ \text{g}\ \text{H}_2\text{O} \times \frac{1\ \text{mol}\ \text{H}_2\text{O}}{18.02\ \text{g}\ \text{H}_2\text{O}} \times \frac{2\ \text{mol NaOH}}{2\ \text{mol}\ \text{Na}_2\text{O}_2} \times \frac{40\ \text{g NaOH}}{1\ \text{mol NaOH}} = 1.63\ \text{mol NaOH}$<br>Therefore, $H_2O$ is the *limiting reactant*. |

Think about your result.

## Example 9.3.5.4: Limiting Reactant and Mass of Excess Reactant

A 5.00 g quantity of $\text{Rb}$ is combined with 3.44 g of $\text{MgCl}_2$ according to this chemical reaction:

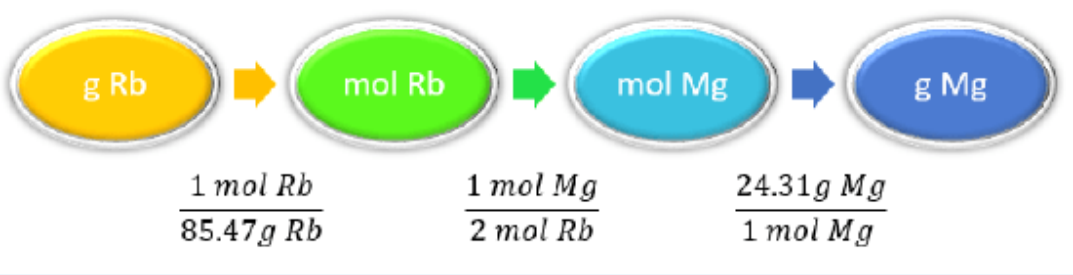
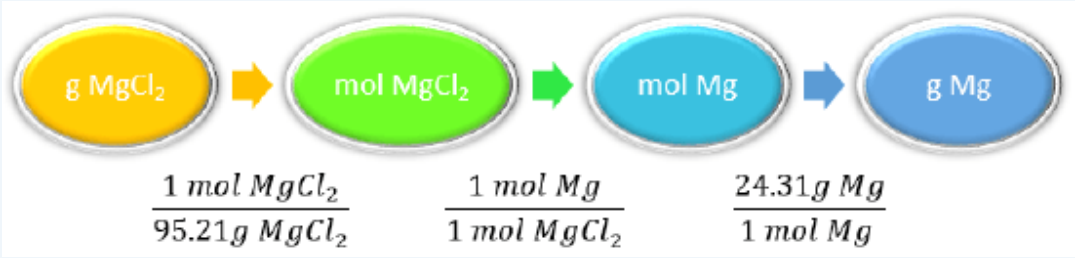
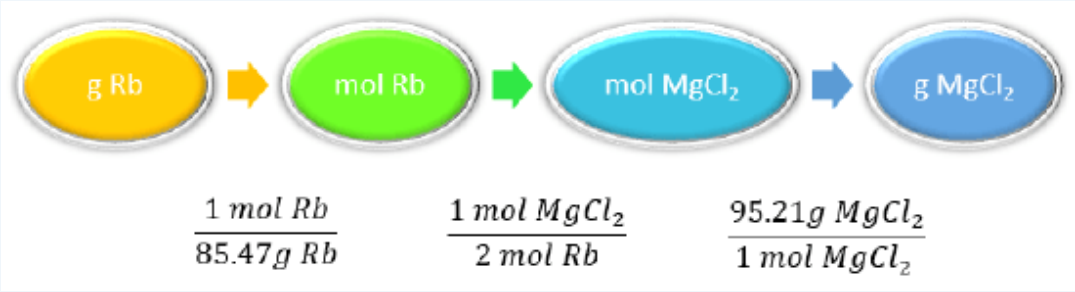
$$2Rb(s) + MgCl_2(s) \rightarrow Mg(s) + 2RbCl(s)$$

What mass of $\text{Mg}$ 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 9.3.5.2 |
|---|---|
| **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:<br>$$2Rb(s) + MgCl_2(s) \rightarrow Mg(s) + 2RbCl(s)$$<br>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<br>Find: mass of Mg formed, mass of remaining reactant |
| List other known quantities. | • molar mass: Rb = 85.47 g/mol<br>• molar mass: $MgCl_2$ = 95.21 g/mol<br>• molar mass: Mg = 24.31 g/mol |

| Steps for Problem Solving- The Product Method | Example 9.3.5.2 |
|---|---|
| Prepare concept maps and use the proper conversion factor. | Find mass Mg formed based on mass of Rb<br>  <br>Find mass of Mg formed based on mass of $MgCl_2$<br>  <br>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<br>Use limiting reactant to determine amount of excess reactant consumed<br>  <br>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 9.3.5.2 |
|---|---|
| Cancel units and calculate. | Because the question asks what mass of magnesium is formed, we can perform two mass-mass calculations an determine which amount is less.<br>$$5.00\ \cancel{g\ Rb} \times \frac{1\ \cancel{mol\ Rb}}{85.47\ \cancel{g\ Rb}} \times \frac{1\ \cancel{mol\ Mg}}{2\ \cancel{mol\ Rb}} \times \frac{24.31\ g\ Mg}{1\ \cancel{mol\ Mg}} = 0.711\ g\ Mg$$<br>$$3.44\ \cancel{g\ MgCl_2} \times \frac{1\ \cancel{mol\ MgCl_2}}{95.21\ \cancel{g\ MgCl_2}} \times \frac{1\ \cancel{mol\ Mg}}{1\ \cancel{mol\ MgCl_2}} \times \frac{24.31\ g\ Mg}{1\ \cancel{mol\ Mg}} = 0.878\ g\ Mg$$<br>The 0.711 g of Mg is the lesser quantity, so the associated reactant—5.00 g of Rb—is the limiting reactant. To de how much of the other reactant is left, we have to do one more mass-mass calculation to determine what mass reacted with the 5.00 g of Rb, and then subtract the amount reacted from the original amount.<br>$$5.00\ \cancel{g\ Rb} \times \frac{1\ \cancel{mol\ Rb}}{85.47\ \cancel{g\ Rb}} \times \frac{1\ \cancel{mol\ MgCl_2}}{2\ \cancel{mol\ Rb}} \times \frac{95.21\ g\ MgCl_2}{1\ \cancel{mol\ MgCl_2}} = 2.78\ g\ MgCl_2\ \ reacted$$<br>Because we started with 3.44 g of $MgCl_2$, we have<br>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 diffe masses and coefficients. |

## Exercise 9.3.5.1

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

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

*Answer available at the end of this section.*

## Answers

**Exercise** 9.3.5.1

H2S is the limiting reagent; 1.5 g of MgO are left over.

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# 9.3.6: 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 $9.3.6.1$ illustrates the steps for determining percent yield.

### Example $9.3.6.1$: Decomposition of Potassium Chlorate

Potassium chlorate decomposes upon slight heating in the presence of a catalyst, according to the reaction below:

$$2\text{KClO}_3\,(s) \rightarrow 2\text{KCl}\,(s) + 3\text{O}_2\,(g)$$

In a certain experiment, $40.0\ \text{g}\ \text{KClO}_3$ is heated until it completely decomposes. The experiment is performed and the oxygen gas is collected and its mass is found to be $14.9\ \text{g}$.

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 $\mathrm{KClO_3} = 40.0\ \mathrm{g}$

Mass of $O_2$ collected = 14.9g

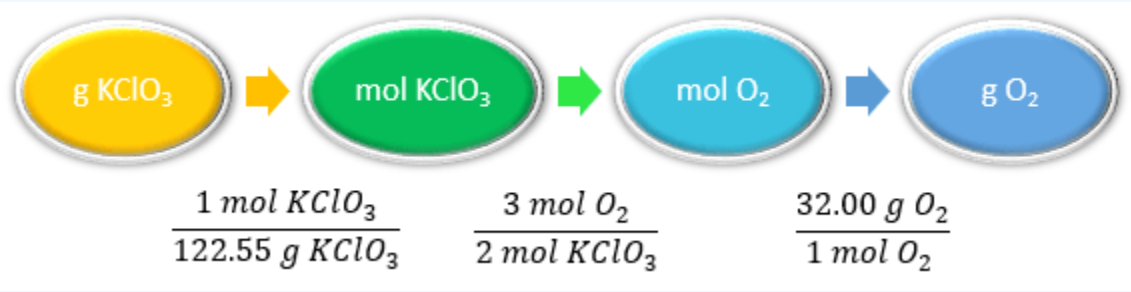
Find: Theoretical yield, g $O_2$

***Step 2: List other known quantities and plan the problem.***

1 mol $KClO_3$ = 122.55 g/mol

1 mol $O_2$ = 32.00 g/mol

**Step 3: Apply stoichiometry to convert from the mass of a reactant to the mass of a product:**




***Step 4: Solve.***

$$40.0\ \cancel{\mathrm{g\ KClO_3}} \times \frac{1\ \cancel{\mathrm{mol\ KClO_3}}}{122.55\ \cancel{\mathrm{g\ KClO_3}}} \times \frac{3\ \cancel{\mathrm{mol\ O_2}}}{2\ \cancel{\mathrm{mol\ KClO_3}}} \times \frac{32.00\ \mathrm{g\ O_2}}{1\ \cancel{\mathrm{mol\ O_2}}} = 15.7\ \mathrm{g\ O_2}$$

The theoretical yield of $O_2$ is $15.7\ \mathrm{g}$, 15.67 g unrounded.

***Step 5: Think about your result.***

The mass of oxygen gas must be less than the $40.0\ \mathrm{g}$ 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 =15.67 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.***

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

***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 $9.3.6.2$: 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:

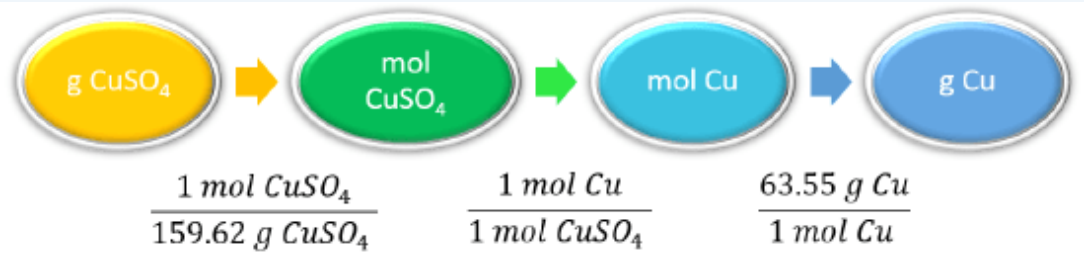
$$\text{CuSO}_4(aq) + \text{Zn}(s) \rightarrow \text{Cu}(s) + \text{ZnSO}_4(aq)$$

What is the percent yield?

**Solution**

*Solutions to Example 8.6.2*

| Steps for Problem Solving-The Product Method | Example $9.3.6.1$ |
|---|---|
| Identify the "given" information and what the problem is asking you to "find." | Given: 1.274 g CuSO4<br>Actual yield = 0.392 g Cu<br>Find: Percent yield |
| List other known quantities. | 1 mol CuSO4= 159.62 g/mol<br>1 mol Cu = 63.55 g/mol<br>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.<br>The balanced equation provides the relationship of 1 mol CuSO4 to 1 mol Zn to 1 mol Cu to 1 mol ZnSO4. |

| Steps for Problem Solving-The Product Method | Example 9.3.6.1 |
|---|---|
| Prepare a concept map and use the proper conversion factor. |  $\frac{1\ mol\ CuSO_4}{159.62\ g\ CuSO_4}$ $\frac{1\ mol\ Cu}{1\ mol\ CuSO_4}$ $\frac{63.55\ g\ Cu}{1\ mol\ Cu}$ <br> The provided information identifies copper sulfate as the limiting reactant, and so the theoretical yield (g Cu) is found by performing **mass-mass** calculation based on the initial amount of $CuSO_4$. |
| Cancel units and calculate. | Double subscripts: use braces to clarify <br> Using this theoretical yield and the provided value for actual yield, the percent yield is calculated to be: $$\begin{aligned}\text{percent yield} &= \left(\frac{\text{actual yield}}{\text{theoretical yield}}\right) \times 100 \\ &= \left(\frac{0.392\,g\,\text{Cu}}{0.5072\,g\,\text{Cu}}\right) \times 100 \\ &= 77.3\%\end{aligned}$$ |
| Think about your result. | Since the actual yield is slightly less than the theoretical yield, the percent yield is just under $100\%$. |

## Exercise 9.3.6.1

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?

$$\text{CCl}_4 + 2\,\text{HF} \rightarrow \text{CF}_2\text{Cl}_2 + 2\,\text{HCl}$$

*Answer available at the end of this section.*

## 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.

### Answers

**Exercise** 9.3.6.1

48.3%

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# 9.3.7: 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.

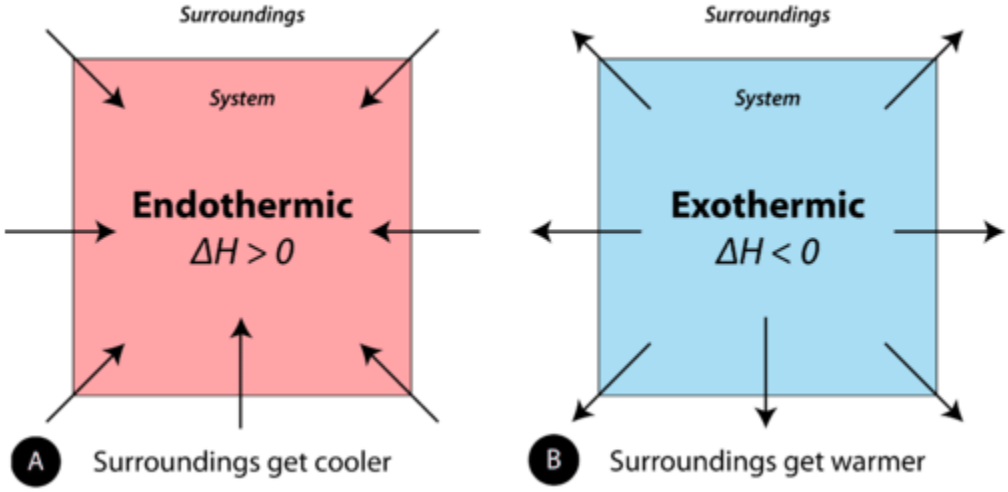



Figure 9.3.7.1: (A) Endothermic reaction. (B) Exothermic reaction.

## 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 $\Delta H$. 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:

$$\text{CH}_4\,(g) + 2\text{O}_2\,(g) \rightarrow \text{CO}_2\,(g) + 2\text{H}_2\text{O}\,(l) + 890.4\,\text{kJ}$$

The equation tells us that $1\ \text{mol}$ of methane combines with $2\ \text{mol}$ of oxygen to produce $1\ \text{mol}$ of carbon dioxide and $2\ \text{mol}$ of water. In the process, $890.4\ \text{kJ}$ 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 $9.3.7.2$.

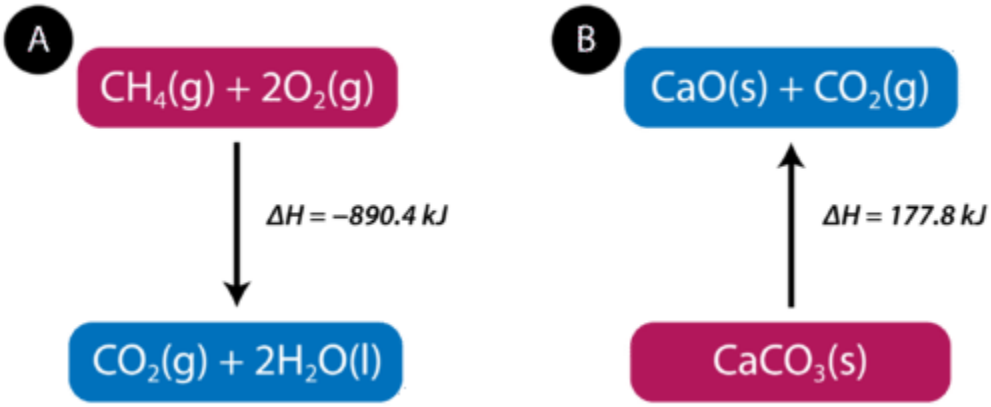



Figure $9.3.7.2$: (A) As reactants are converted to products in an exothermic reaction, enthalpy is released into the surroundings. The enthalpy change of the reaction is negative. (B) As reactants are converted to products in an endothermic reaction, enthalpy is absorbed from the surroundings. The enthalpy 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 $-890.4\ \text{kJ}$. The thermochemical reaction can also be written in this way:

$$\text{CH}_4\,(g) + 2\text{O}_2\,(g) \rightarrow \text{CO}_2\,(g) + 2\text{H}_2\text{O}\,(l) \quad \Delta H = -890.4\,\text{kJ}$$

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 $\Delta H$ depends on those states.

Endothermic reactions absorb energy from the surroundings as the reaction occurs. When $1\ \text{mol}$ of calcium carbonate decomposes into $1\ \text{mol}$ of calcium oxide and $1\ \text{mol}$ of carbon dioxide, $177.8\ \text{kJ}$ of heat is absorbed. The process is shown visually in Figure $9.3.7.2B$. The thermochemical reaction is shown below.

$$\text{CaCO}_3\,(s) + 177.8\,\text{kJ} \rightarrow \text{CaO}\,(s) + \text{CO}_2\,(g)$$

Because the heat is absorbed by the system, the $177.8\ \text{kJ}$ is written as a reactant. The heat of reaction is positive for an endothermic reaction.

$$\text{CaCO}_3\,(s) \rightarrow \text{CaO}\,(s) + \text{CO}_2\,(g) \quad \Delta H = 177.8\,\text{kJ}$$

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 $\Delta H$ changes. For example, we can write an equation for the reaction of calcium oxide with carbon dioxide to form calcium carbonate.

$$\mathrm{CaO}\,(s) + \mathrm{CO_2}\,(g) \rightarrow \mathrm{CaCO_3}\,(s) + 177.8\ \mathrm{kJ}$$

The reaction is exothermic and thus the sign of the enthalpy change is negative.

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

## 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 $1\ \mathrm{mol}$ of methane released $890.4\ \mathrm{kJ}$, the reaction of $2\ \mathrm{mol}$ of methane would release $2 \times 890.4\ \mathrm{kJ} = 1781\ \mathrm{kJ}$. The reaction of $0.5\ \mathrm{mol}$ of methane would release $\frac{890,4\ \mathrm{kJ}}{2} = 445.2\ \mathrm{kJ}$. As with other stoichiometry problems, the moles of a reactant or product can be linked to mass or volume.

### Example 9.3.7.1

Sulfur dioxide gas reacts with oxygen to form sulfur trioxide in an exothermic reaction, according to the following thermochemical equation.

$$2\mathrm{SO_2}\,(g) + \mathrm{O_2}\,(g) \rightarrow 2\mathrm{SO_3}\,(g) + 198\ \mathrm{kJ}$$

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

**Unknown**

- $\Delta H = ?\ \mathrm{kJ}$

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

***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 $1\ \mathrm{mol}$. Since $198\ \mathrm{kJ}$ is released for every $2\ \mathrm{mol}$ of $\mathrm{SO_2}$ that reacts, the heat released when about $1\ \mathrm{mol}$ reacts is one half of 198. The $89.6\ \mathrm{kJ}$ is slightly less than half of 198. The sign of $\Delta H$ is negative because the reaction is exothermic.

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# 10: REACTION RATES AND EQUILIBRIUM

In previous science classes, you may have learned that one way to distinguish chemical changes from physical changes is that physical changes—such as the melting and freezing of water—are reversible, but that chemical changes are not. In this chapter, we will see that this simple answer is not necessarily what it seems.


## 10.1: Equilibrium

10.1.1: The Idea of Dynamic Chemical Equilibrium

10.1.2: The Equilibrium Constant - A Measure of How Far a Reaction Goes

10.1.3: Calculating and Using Equilibrium Constants

## 10.2: Le Chatelier's Principle

10.2.1: Disturbing a Reaction at Equilibrium- Le Châtelier's Principle

10.2.2: The Effect of a Concentration Change on Equilibrium

10.2.3: The Effect of a Volume Change on Equilibrium

10.2.4: The Effect of Temperature Changes on Equilibrium

10.2.5: The Solubility-Product Constant

10.2.6: The Path of a Reaction and the Effect of a Catalyst

## 10.3: Kinetics and Collision Theory

10.3.1: Chemical Reaction Rate

10.3.2: Collision Theory

10.3.3: Activation Energy

10.3.4: Potential Energy Diagrams

10.3.5: Activated Complex

10.3.6: Factors Affecting Reaction Rate

10.3.7: Catalysts



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# 10.1: EQUILIBRIUM



- Topic hierarchy


10.1.1: The Idea of Dynamic Chemical Equilibrium

10.1.2: The Equilibrium Constant - A Measure of How Far a Reaction Goes

10.1.3: Calculating and Using Equilibrium Constants



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# 10.1.1: The Idea of Dynamic Chemical Equilibrium


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**Learning Objectives**

- Describe the three possibilities that exist when reactants come together.
- Describe what is occurring in a system at equilibrium.

Think for a minute about sitting down to a table to eat dinner. There are three possibilities that could happen when you eat dinner. You could (1) finish your entire dinner, (2) you could not want any of it and leave it all on your plate, or (3) you could eat some of it and leave some of it. Reactions have the same possibilities. Reactions do not always proceed all the way from start to finish. You may have reactions that (1) go to completion so that at the end, the reaction vessel contains all products and only products. Some reactions (2) may not start at all, so at the end the reaction vessel contains all reactants and only reactants. And some reactions (3) may start but not go to completion, that is, the reaction might start but not go completely to products. In this last case, the reaction vessel would contain some reactants and some products. In this section, we are going to take a closer look at the third type of reaction.

## Reversible Reactions and Equilibrium

Consider the hypothetical reaction:

$$\mathrm{A} + \mathrm{B} \rightarrow \mathrm{C} + \mathrm{D}.$$

If we looked at this reaction using what we have learned, this reaction will keep going, forming $\mathrm{C}$ and $\mathrm{D}$ until $\mathrm{A}$ and $\mathrm{B}$ run out. This is what we call an "irreversible reaction" or a "reaction that goes to completion".

Some reactions, however, are **reversible**, meaning the reaction can go backwards in which products react to form reactants, so that: $\mathrm{A} + \mathrm{B} \leftarrow \mathrm{C} + \mathrm{D}$. The direction of the arrow shows that $\mathrm{C}$ and $\mathrm{D}$ are reacting to form $\mathrm{A}$ and $\mathrm{B}$. What if the two reactions, the forward reaction and the reverse reaction, were occurring at the same time? What would this look like? If you could peer into the reaction, you would be able to find $\mathrm{A}$, $\mathrm{B}$, $\mathrm{C}$, and $\mathrm{D}$ particles. $\mathrm{A}$ and $\mathrm{B}$ would react to form $\mathrm{C}$ and $\mathrm{D}$ at the same time that $\mathrm{C}$ and $\mathrm{D}$ are reacting to form $\mathrm{A}$ and $\mathrm{B}$.

If the forward and reverse reactions are happening at the same rate, the reaction is said to be at **equilibrium** or **dynamic equilibrium**. At this point, the concentrations of $\mathrm{A}$, $\mathrm{B}$, $\mathrm{C}$, and $\mathrm{D}$ are not changing (or, are constant) and we would see no difference in our reaction container, but reactions are still occurring in both directions. It is important to point out that having constant amounts of reactants and products does NOT mean that the concentration of the reactants is equal to the concentration of the products. It means they are not changing. These reactions appear to have stopped before one of the reactants has run out.

Chemists use a double-headed arrow, $\rightleftharpoons$, to show that a reaction is at equilibrium. We would write the example reaction as:

$$\mathrm{A} + \mathrm{B} \rightleftharpoons \mathrm{C} + \mathrm{D}.$$

The arrow indicates that both directions of the reaction are happening.

Another way to think about reversible and irreversible reactions is to compare them to two types of games of tag. Reversible reactions are in many ways like a traditional game of tag: the "it" person can become "not it" and somebody who is "not it" is tagged and becomes "it". In this way, it is a reversible change. It is also like a reaction at equilibrium, because overall no change is occurring. There is always a constant number of "it" people and "not it" people in the game. Also, having constant numbers of "it" and "not it" people in our game does not mean that the number of "it" people (reactants) is equal to the number of "not it" people (products). Furthermore, this is similar to equilibrium in that this game never truly ends (unless everybody gets tired of playing). The game could go on forever. We could write this as the following reversible reaction:

$$\text{"It"} \rightleftharpoons \text{"Not it"}$$

**Irreversible reactions** (those that only go in one direction from reactants to products and cannot reach a state of equilibrium) are more like a game of sharks and minnows. In sharks and minnows, almost everybody starts out as a minnow. Once tagged, they become a shark. However, the difference here is that once you are a shark you are always a shark; there is no way to go back to becoming a minnow. The game continues until everybody has been tagged and becomes a shark. This is similar to irreversible

reactions in that the reactants turn into products, but can't change back. Furthermore, the reaction will proceed until the reactants have been used up and there are not any more left. We could write the reaction as:

$$\text{Minnow} \rightarrow \text{Shark}$$

Here's another example of a reversible reaction—dissolving salt in a beaker of water, described by the following reaction:

$$\text{NaCl}\,(\text{s}) \;\leftrightarrow \text{NaCl}\,(\text{aq})$$

If you keep adding more and more solid salt, eventually you'll reach the point where no more salt dissolves, and the excess sits at the bottom of the beaker. At this point we have a saturated solution. Has the dissolving reaction stopped? It would appear so, but that's not the case (wouldn't that be too easy?).

What happens in our saturated solution, which has reached the point of **equilibrium**, is that both the forward

$$\text{NaCl}\,(\text{s}) \;\rightarrow \text{NaCl}\,(\text{aq})$$

and reverse

$$\text{NaCl}\,(\text{aq}) \;\rightarrow \text{NaCl}\,(\text{s})$$

reactions are still going on, but at the same ***rate***. This in effect cancels out any observable, or measurable, changes in our system. At the same rate that solid NaCl produces aqueous NaCl (dissolved salt), the dissolved salt is re-crystallizing to form more solid NaCl.

- **Equilibrium** is the state at which the rate of the forward reaction equals the rate of the reverse reaction.
- At the point of equilibrium, no more measurable or observable changes in the system can be noted.

It is important for you to understand that equilibrium means the ***rates*** of the forward and reverse reactions are equal; it does ***not*** mean that there are equal amounts of reactants and products present at equilibrium.

For example, the following reaction was allowed to come to the point of equilibrium, and concentrations of all reaction participants were measured at that time:

$$\text{H}_2\,(\text{g}) + \text{I}_2\,(\text{g}) \;\leftrightarrow 2\,\text{HI}\,(\text{g})$$

**At equilibrium:**

$$[\text{H}_2] = 0.022\ \text{M}$$

$$[\text{I}_2] = 0.022\ \text{M}$$

$$[\text{HI}] = 0.156\ \text{M}$$

For this particular reversible reaction, there is more HI at equilibrium (0.156 M) than there is of $\text{H}_2$ and $\text{I}_2$ (both at 0.022M). We say that the product side of the reaction is favored.

> Equilibrium does not mean equal amounts at equilibrium!

Here is an example to help you understand how equilibrium works: imagine yourself on a escalator that is going down. You start at the top (reactants) and end up at the bottom (products). But when you are partway down, you start walking up the escalator as it continues going down. If you match your rate of walking up to the same rate that the escalator is going down, you make no progress and appear to be at a standstill. To an observer it would look as if you and the escalator had come to a stop, when actually both upward and downward movements continue.

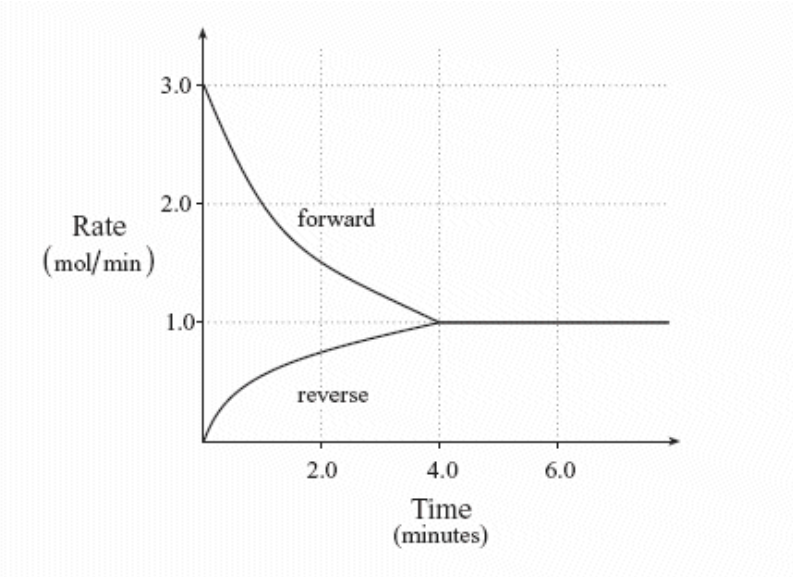
Equilibrium is **dynamic**—both forward and reverse reactions continue, even though the reaction appears to have stopped. And this equilibrium does not need to occur right in the middle of two floors—you could be near the bottom, near the top, or anywhere in between when you carry out your reverse process.

In order for a reversible reaction to reach the point of equilibrium, the reaction must be carried out in a closed system—no additional reactants can be added or products removed. If, in our last example, the product HI was removed as it formed, the reaction would never reach the point of equilibrium; instead, $H_2$ and $I_2$ would continue to react to produce HI until one or both of the reactants was used up.

If reactants are constantly being added, and products removed as they form, the system would appear to be at equilibrium because to an outside observer it would appear that the reaction has stopped—but that would not be the case. This situation—with new material constantly being added as products are removed—is called a **steady state system**. A factory with an assembly line is a steady state system—new raw materials are constantly being added; finished products are removed. A campfire with wood being added to the fire is another steady state system. Be careful not to confuse steady state with equilibrium.

How do the rates of the forward and reverse reactions change as the reaction heads towards equilibrium (before it reaches equilibrium)?

If we start our above reaction with $H_2$ and $I_2$, and with no HI, the two gases will react at a certain rate. But remember that the rate of a reaction slows down over time, as the reactants get used up (and lower their concentrations). Eventually, however, the amount of the product HI increases, and it will begin producing $H_2$ and $I_2$. Thus the rate of the reverse reaction starts out slowly (there is no HI present), but will speed up as the concentration of HI increases. Eventually both rates will level off (not always to the same level as shown by this example, however):




Chemists have found that there is a mathematical relationship that exists between the concentration of the reactants and products, once equilibrium has been reached, that is independent of the initial concentration of the participants. For any general reaction,

$$a\,\mathrm{A} + b\,\mathrm{B} \rightleftharpoons c\,\mathrm{D} + d\,\mathrm{D} \tag{10.1.1.1}$$

an equilibrium constant expression can be written as:

$$\mathrm{K_{eq}} = \frac{[\mathrm{C}]^{\mathrm{c}} \times [\mathrm{D}]^{\mathrm{d}}}{[\mathrm{A}]^{\mathrm{a}} \times [\mathrm{B}]^{\mathrm{b}}} \tag{10.1.1.2}$$

This mathematical relationship exists for all equilibrium systems, and produces a constant ratio called the ***equilibrium constant, $K_{eq}$*** .

## Law of Mass-Action

Equation 10.1.1.2 is sometimes called the Law of Mass-Action.

This relationship will be very important to us for the next few units, so it is important that you understand how to set this relationship up and what it tells us about an equilibrium system.

The products of the reaction (C and D) are placed in the numerator, and their concentrations are raised to the power of the coefficients from the balanced equation. The reactants (A and B) are placed in the denominator, with their concentrations raised to the power of *their* coefficients.

## Example 10.1.1.1

For the reaction between hydrogen and iodine gas to produce hydrogen iodide:

$$\mathrm{H_2\,(g) + I_2\,(g) \;\rightleftharpoons\; 2\,HI\,(g)} \tag{10.1.1.3}$$

the equilibrium constant expression will be:

$$\mathrm{K_{eq} = \frac{[HI]^2}{[H_2] \times [I_2]}} \tag{10.1.1.4}$$

Using the example we examined in our last section, equilibrium concentrations for each substance were measured at equilibrium and found to be:

| **At equilibrium:** |
|---|
| $\mathrm{[H_2] = 0.022\ M}$ |
| $\mathrm{[I_2] = 0.022\ M}$ |
| $\mathrm{[HI] = 0.156\ M}$ |

We substitute these values into our equilibrium expression and solve for $K_{eq}$:

$$\mathrm{K_{eq} = \frac{[HI]^2}{[H_2] \times [I_2]} = \frac{(0.156)^2}{(0.022)(0.022)} = 50.3}$$

The value of $K_{eq}$, which has no units, is a constant for any particular reaction, and its value does not change unless the temperature of the system is changed. It does not depend on the initial concentrations used to reach the point of equilibrium.

For example, the following data were obtained for equilibrium concentrations of $H_2$, $I_2$ and HI, and the value of $K_{eq}$ was calculated for each trial:

| **Trial** |
|---|
| $[HI]$ |
| $[\ H_2]$ |
| $[\ I_2]$ |
| $K_{eq}$ |
| 1 |
| 0.156 |
| 0.0220 |
| 0.0220 |
| 50.3 |
| 2 |
| 0.750 |
| 0.106 |
| 0.106 |
| 50.1 |
| 3 |

1.00
0.820
0.0242
50.4
4
1.00
0.0242
0.820
50.4
5
1.56
0.220
0.220
50.3

Aside from accounting for slight experimental variation between trials, the value for $K_{eq}$ is the same despite differences in equilibrium concentrations for the individual participants.

There is one other important point to make at this time.

$K_{eq}$ relates the concentrations of products to reactants at equilibrium.

For aqueous solutions, concentration is often measured as mol · $L^{-1}$. For gases, concentration is often measured as partial pressure.

The concentrations of both aqueous solutions and gases change during the progress of a reaction. For reactions involving a solid or a liquid, while the ***amounts*** of the solid or liquid will change during a reaction, their ***concentrations*** (much like their densities) will ***not*** change during the reaction. Instead, their values will remain constant. Because they are constant, their values **are not included in the equilibrium constant expression**.

**Example 10.1.1.2**

For example, consider the reaction showing the formation of solid calcium carbonate from solid calcium oxide and carbon dioxide gas:

$$\mathrm{CaO\,(s) + CO_2\,(g)} \leftrightarrow \mathrm{CaCO_3\,(s)}$$

The equilibrium constant for this reaction is (before modification):

$$\mathrm{K_{eq}} = \frac{[\mathrm{CaCO_3}]}{[\mathrm{CaO}] \times [\mathrm{CO_2}]}$$

But we remove those participants whose state is either a solid or a liquid, which leaves us with the following equilibrium constant expression:

$$\mathrm{K_{eq}} = \frac{1}{[\mathrm{CO_2}]}$$

## Summary

- There are a few possible ways a reaction can go: it can go to completion ($\mathrm{reactants} \rightarrow \mathrm{products}$), and it can occur but not go to completion. Instead, it will reach chemical equilibrium ($\mathrm{reactants} \rightleftharpoons \mathrm{products}$).
- Chemical equilibrium occurs when the number of particles becoming products is equal to the number of particles becoming reactants.
- A dynamic equilibrium is a state where the rate of the forward reaction is equal to the rate of the reverse reaction.

## Vocabulary

- **Equilibrium** - A state that occurs when the rate of the forward reaction is equal to the rate of the reverse reaction.

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# 10.1.2: The Equilibrium Constant - A Measure of How Far a Reaction Goes

**Learning Objectives**

- Write equilibrium constant expressions.
- Use equilibrium constant expressions to solve for unknown concentrations.
- Use known concentrations to solve for the equilibrium constants.
- Explain what the value of $K$ means in terms of relative concentrations of reactants and products.

In the previous section, you learned about reactions that can reach a state of equilibrium, in which the concentration of reactants and products aren't changing. If these amounts are changing, we should be able to make a relationship between the amount of product and reactant when a reaction reaches equilibrium.

## The Equilibrium Constant

Equilibrium reactions are those that do not go to completion, but are in a state where the reactants are reacting to yield products and the products are reacting to produce reactants. In a reaction at equilibrium, the equilibrium concentrations of all reactants and products can be measured. The **equilibrium constant ($K$)** is a mathematical relationship that shows how the concentrations of the products vary with the concentration of the reactants. Sometimes, subscripts are added to the equilibrium constant symbol $K$, such as $K_{\text{eq}}$, $K_{\text{c}}$, $K_{\text{p}}$, $K_{\text{a}}$, $K_{\text{b}}$, and $K_{\text{sp}}$. These are all equilibrium constants and are subscripted to indicate special types of equilibrium reactions.

There are some rules about writing equilibrium constant expressions that need to be learned:

1. Concentrations of products are multiplied on the top of the expression. Concentrations of reactants are multiplied together on the bottom.
2. Coefficients in the equation become exponents in the equilibrium constant expression.
3. Solids, liquids, and solvents are assigned a value of 1, so their concentrations do not affect the value of K.

**Example 10.1.2.1**

Write the equilibrium constant expression for:

$$\text{CO}\,(g) + 3\text{H}_2\,(g) \rightleftharpoons \text{CH}_4\,(g) + \text{H}_2\text{O}\,(g)$$

**Solution**

$$K = \frac{[\text{CH}_4]\,[\text{H}_2\text{O}]}{[\text{CO}]\,[\text{H}_2]^3}$$

*Note that the coefficients become exponents. Also, note that the concentrations of products in the numerator are *multiplied*. The same is true of the reactants in the denominator.

**Example 10.1.2.2**

Write the equilibrium constant expression for:

$$2\text{TiCl}_3\,(s) + 2\text{HCl}\,(g) \rightleftharpoons 2\text{TiCl}_4\,(s) + \text{H}_2\,(g)$$

**Solution**

$$K = \frac{[\mathrm{H_2}]}{[\mathrm{HCl}]^2}$$

*Note that the solids have a value of 1, and multiplying or dividing by 1 does not change the value of K.

**Example 10.1.2.2**

Write the equilibrium constant expression for:

$$\mathrm{P_4}\,(s) + 6\mathrm{Cl_2}\,(g) \rightleftharpoons 4\mathrm{PCl_3}\,(s)$$

**Solution**

$$K = \frac{1}{[\mathrm{Cl_2}]^6}$$

*Note that the only product is a solid, which is defined to have a value of 1. That leaves just 1 on top in the numerator.

**Example 10.1.2.3**

Write the equilibrium constant expression for:

$$\mathrm{H_2O}\,(l) \rightleftharpoons \mathrm{H^+}\,(aq) + \mathrm{OH^-}\,(aq)$$

**Solution**

$$K = [\mathrm{H^+}]\,[\mathrm{OH^-}]$$

*Note that the water is the solvent, and thus has a value of 1. Dividing by 1 does not change the value of K.

## Equilibrium Constant Expressions

The equilibrium constant value is the ratio of the concentrations of the products over the reactants. This means that we can use the value of $K$ to predict whether there are more products or reactants at equilibrium for a given reaction. What can the value of $K_{eq}$ tell us about a reaction?

- **If $K_{eq}$ is very large**, the concentration of the products is much greater than the concentration of the reactants. The reaction essentially "goes to completion"; all, or most of, the reactants are used up to form the products.
- **If $K_{eq}$ is very small**, the concentration of the reactants is much greater than the concentration of the products. The reaction does not occur to any great extent—most of the reactants remain unchanged, and there are few products produced.
- **When $K_{eq}$ is not very large or very small** (close to a value of 1) then roughly equal amounts of reactants and products are present at equilibrium.

Here are some examples to consider:

| Reaction | Chemical Equations | Equilibrium Constant |
|---|---|---|
| the decomposition of ozone, $\mathrm{O_3}$ | $2\,\mathrm{O_3}\,(\mathrm{g}) \rightleftharpoons 3\,\mathrm{O_2}\,(\mathrm{g})$ | $\mathrm{K_{eq}} = 2.0 \times 10^{57}$ |
| | $K_{eq}$ is very large, indicating that mostly $\mathrm{O_2}$ is present in an equilibrium system, with very little $\mathrm{O_3}$. | |
| production of nitrogen monoxide | $\mathrm{N_2}\,(\mathrm{g}) + \mathrm{O_2}\,(\mathrm{g}) \rightleftharpoons 2\,\mathrm{NO}\,(\mathrm{g})$ | $\mathrm{K_{eq}} = 1.0 \times 10^{-25}$ |
| | Very little $\mathrm{NO}$ is produced by this reaction; $\mathrm{N_2}$ and $\mathrm{O_2}$ do not react readily to produce $\mathrm{NO}$ (this is lucky for us—otherwise we would have little oxygen to breath in our atmosphere!). | |

| Reaction | Chemical Equations | Equilibrium Constant |
|---|---|---|
| reaction of carbon monoxide and water | $\mathrm{CO\,(g) + H_2O\,(g) \rightleftharpoons CO_2\,(g) + H_2\,(g)}$ | $\mathrm{K_{eq} = 5.09\ (at\ 700\ K)}$ |
| | The concentrations of the reactants are very close to the concentrations of the products at equilibrium. | |

If the equilibrium constant is 1 or nearly 1, it indicates that the molarities of the reactants and products are about the same. If the equilibrium constant value is a large number, like 100, or a very large number, like $1 \times 10^{15}$, it indicates that the products (numerator) are a great deal larger than the reactants. This means that at equilibrium, the great majority of the material is in the form of products and it is said that the "products are strongly favored". If the equilibrium constant is small, like 0.10, or very small, like $1 \times 10^{-12}$, it indicates that the reactants are much larger than the products and the reactants are strongly favored. With large $K$ values, most of the material at equilibrium is in the form of products and with small $K$ values, most of the material at equilibrium is in the form of the reactants.

The equilibrium constant expression is an equation that we can use to solve for $K$ or for the concentration of a reactant or product.

## Example 10.1.2.4

Determine the value of $K$ for the reaction

$$\mathrm{SO_2\,(g) + NO_2\,(g) \rightleftharpoons SO_3\,(g) + NO\,(g)}$$

when the equilibrium concentrations are: $\mathrm{[SO_2] = 1.20\ M}$, $\mathrm{[NO_2] = 0.60\ M}$, $\mathrm{[NO] = 1.6\ M}$, and $\mathrm{[SO_3] = 2.2\ M}$.

**Solution**

Step 1: Write the equilibrium constant expression:

$$K = \frac{\mathrm{[SO_3]\,[NO]}}{\mathrm{[SO_2]\,[NO_2]}}$$

Step 2: Substitute in given values and solve:

$$K = \frac{(2.2)\,(1.6)}{(1.20)\,(0.60)} = 4.9$$

## Example 10.1.2.5

Consider the following reaction:

$$\mathrm{CO\,(g) + H_2O\,(g) \rightleftharpoons H_2\,(g) + CO_2\,(g)}$$

with $K = 1.34$. If the $\mathrm{[H_2O] = 0.100\ M}$, $\mathrm{[H_2] = 0.100\ M}$, and $\mathrm{[CO_2] = 0.100\ M}$ at equilibrium, what is the equilibrium concentration of $\mathrm{CO}$?

**Solution**

Step 1: Write the equilibrium constant expression:

$$K = \frac{\mathrm{[H_2]\,[CO_2]}}{\mathrm{[CO]\,[H_2O]}}$$

Step 2: Substitute in given values and solve:

$$1.34 = \frac{(0.100)\,(0.100)}{\mathrm{[CO]}\,(0.100)}$$

Solving for $[\mathrm{CO}]$, we get: $[\mathrm{CO}] = 0.0746\ \mathrm{M}$

## Summary

- The equilibrium constant expression is a mathematical relationship that shows how the concentrations of the products vary with the concentration of the reactants.
- If the value of $K$ is greater than 1, the products in the reaction are favored. If the value of $K$ is less than 1, the reactants in the reaction are favored. If $K$ is equal to 1, neither reactants nor products are favored.

## Vocabulary

- **Equilibrium constant** $(K)$ - A mathematical ratio that shows the concentrations of the products divided by the concentrations of the reactants.

## Contributions & Attributions

- 

- Modified by Tom Neils (Grand Rapids Community College)

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# 10.1.3: Calculating and Using Equilibrium Constants

## 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:

$$\mathrm{CO_2\,(g) + C\,(s)} \rightleftharpoons \mathrm{2\,CO\,(g)} \tag{10.1.3.1}$$

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:

$$K = \frac{a_{\mathrm{CO}}^2}{a_{\mathrm{CO_2}} a_C} = \frac{[\mathrm{CO}]^2}{[\mathrm{CO_2}][1]} = \frac{[\mathrm{CO}]^2}{[\mathrm{CO_2}]} \tag{10.1.3.2}$$

The equilibrium constant for this reaction can also be written in terms of the partial pressures of the gases:

$$K_p = \frac{(P_{CO})^2}{P_{CO_2}} \tag{10.1.3.3}$$

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 $\mathrm{CO}$ and $\mathrm{CO_2}$, the system described in Equation 10.1.3.1 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 10.1.3.1, 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.

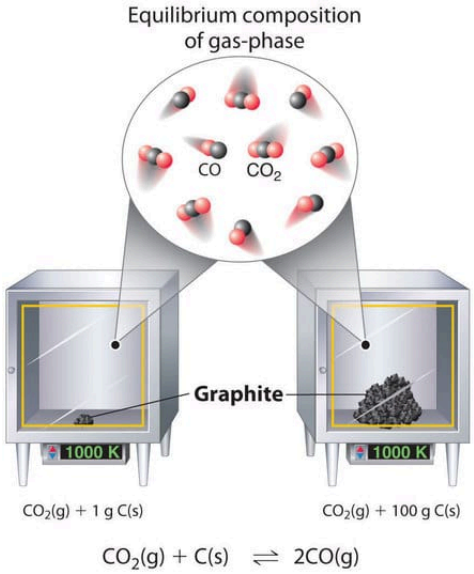



Figure 10.1.3.2: Effect of the Amount of Solid Present on Equilibrium in a Heterogeneous Solid–Gas System. In the system, the equilibrium composition of the gas phase at a given temperature, 1000 K in this case, is the same whether a small amount of solid carbon (left) or a large amount (right) is present.

## Example 10.1.3.1

Write each expression for $K$, incorporating all constants, and $K_p$ for the following equilibrium reactions.

a. $\mathrm{PCl_3\,(l) + Cl_2\,(g) \rightleftharpoons PCl_5\,(s)}$
b. $\mathrm{Fe_3O_4\,(s) + 4\,H_2\,(g) \rightleftharpoons 3\,Fe\,(s) + 4\,H_2O\,(g)}$

**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

$$K_p = \frac{(1)(P_{H_2O})^4}{(1)(P_{H_2})^4}$$

**Exercise** 10.1.3.1

Write the expressions for $K$ and $K_p$ for the following reactions.

a. $\mathrm{CaCO_3\,(s) \rightleftharpoons CaO\,(s) + CO_2\,(g)}$
b. $\underset{glucose}{\mathrm{C_6H_{12}O_6\,(s)}} + \mathrm{6\,O_2\,(g) \rightleftharpoons 6\,CO_2\,(g) + 6\,H_2O\,(g)}$

*Answer a available at the end of this section.*

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)

### Answers

**Exercise** 10.1.3.1

$K = [\mathrm{CO_2}]$ and $K_p = P_{\mathrm{CO_2}}$

$K = \frac{[CO_2]^6[H_2O]^6}{[O_2]^6}$ and $K_p = \frac{(P_{CO_2})^6(P_{H_2O})^6}{(P_{O_2})^6}$

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# 10.2: LE CHATELIER'S PRINCIPLE



- Topic hierarchy


10.2.1: Disturbing a Reaction at Equilibrium- Le Châtelier's Principle

10.2.2: The Effect of a Concentration Change on Equilibrium

10.2.3: The Effect of a Volume Change on Equilibrium

10.2.4: The Effect of Temperature Changes on Equilibrium

10.2.5: The Solubility-Product Constant

10.2.6: The Path of a Reaction and the Effect of a Catalyst



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# 10.2.1: Disturbing a Reaction at Equilibrium- Le Châtelier's Principle

**Learning Objectives**

- State Le Chatelier's Principle.
- Describe the effect of concentration on an equilibrium system.
- Describe the effect of temperature as a stress on an equilibrium system.

When a reaction has reached equilibrium with a given set of conditions, if the conditions are not changed, the reaction will remain at equilibrium forever. The forward and reverse reactions continue at the same equal and opposite rates and the macroscopic properties remain constant.

It is possible, however, to disturb that equilibrium by changing conditions. For example, you could increase the concentration of one of the products, or decrease the concentration of one of the reactants, or change the temperature. When a change of this type is made within a reaction at equilibrium, the reaction is no longer in equilibrium. When you alter something in a reaction at equilibrium, chemists say that you put **stress** on the equilibrium. When this occurs, the reaction will no longer be in equilibrium and the reaction itself will begin changing the concentrations of reactants and products until the reaction comes to a new position of equilibrium. How a reaction will change when a stress is applied can be explained and predicted. That is the topic of this section.

## Le Chatelier's Principle

Think back to our escalator example, with you walking up a downward moving escalator. With the rate of the moving stairs and your walking evenly matched, you appear to be at a standstill. But what happens if the escalator begins moving just a little faster? If you want to maintain the same position you had, at some specific point between the bottom and the top of the stairs, you'll also need to make some adjustments. Chemical systems at equilibrium tend to make these adjustments as well.

In the late 1800's, a chemist by the name of Henry-Louis Le Chatelier was studying stresses that were applied to chemical equilibria. He formulated a principle from this research and, of course, the principle is called Le Chatelier's Principle. **Le Chatelier's Principle** states that when a stress is applied to a system at equilibrium, the equilibrium will shift in a direction to partially counteract the stress and once again reach equilibrium. Le Chatelier's principle is not an explanation of what happens on the molecular level to cause the equilibrium shift, it is simply a quick way to determine which way the reaction will run in response to a stress applied to the system at equilibrium.

**Le Chatelier's Principle**

If a system at **equilibrium** is subjected to an external stress, the equilibrium will shift to **minimize** the effects of that stress.

Equilibrium is all about rates—the rate of the forward reaction is equal to the rate of the reverse reaction. External stresses are factors that will cause the rate of either the forward or reverse reaction to change, throwing the system out of balance. Le Chatelier's Principle allows us to predict how this will affect our system.

In our unit on Kinetics we examined factors that influenced reaction rates. Recall these factors:

1. concentration
2. pressure and volume
3. temperature
4. catalysts

We will see how changing these factors affects a system at equilibrium.

# Effect of Concentration Changes on a System at Equilibrium

For instance, if a stress is applied by increasing the concentration of a reactant, the reaction will adjust in such a way that the reactants and products can get back to equilibrium. In the case of too much reactant, the reaction will use up some of the reactant to make more product. It is said in this scenario that the reaction "shifts to the products" or "shifts to the right". If the concentration of a product is increased, there is an opposite effect. The reaction will use up some of the product to make more reactant. The reaction "shifts to the reactants" or "shifts to the left".

What if some reactant or product is removed? If a stress is applied by lowering a reactant concentration, the reaction will try to replace some of the missing reactant. It uses up some of the product to make more reactant, and the reaction "shifts to the reactants". If a stress is applied by reducing the concentration of a product, the equilibrium position will shift toward the products.

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# 10.2.2: The Effect of a Concentration Change on Equilibrium

Consider the following system under equilibrium:

$$\underbrace{\mathrm{Fe^{3+}\,(aq)}}_{\text{colorless}} + \underbrace{\mathrm{SCN^{-}\,(aq)}}_{\text{colorless}} \rightleftharpoons \underbrace{\mathrm{FeSCN^{2+}\,(aq)}}_{\text{red}}$$

If more $Fe^{3+}$ is added to the reaction, what will happen?

According to Le Chatelier's Principle, the system will react to minimize the stress. Since $Fe^{3+}$ is on the reactant side of this reaction, the rate of the forward reaction will increase in order to "use up" the additional reactant. This will cause the equilibrium to **shift to the right**, producing more $FeSCN^{2+}$. For this particular reaction, we will be able to see that this has happened, as the solution will become a darker red color.

There are a few different ways to state what happens here when more $Fe^{3+}$ is added, all of which have the same meaning:

- equilibrium shifts to the right
- equilibrium shifts to the product side
- the forward reaction is favored

What changes does this cause in the concentrations of the reaction participants?

*Changes within reaction participants*

| $\mathrm{Fe^{3+}}$ | **Since this is what was added to cause the stress, the concentration of $\mathrm{Fe^{3+}}$ will increase. (A shorthand way to indicate this: $[\mathrm{Fe}]^{3+}\ \uparrow$ (Reminder: the square brackets represent "concentration")** |
|---|---|
| $\mathrm{SCN^{-}\,(aq)}$ | Equilibrium will shift to the right, which will use up the reactants. The concentration of $\mathrm{SCN^{-}\,(aq)}$ will decrease $[\mathrm{SCN}]^{-}\ \downarrow$ as the rate of the forward reaction increases. |
| $\mathrm{FeSCN^{2+}}$ | When the forward reaction rate increases, more products are produced, and the concentration of $\mathrm{FeSCN^{2+}}$ will increase. $[\mathrm{FeSCN}]^{2+}\uparrow$ |

How about the value of $K_{eq}$? Notice that the concentration of some reaction participants have increased, while others have decreased. Once equilibrium has re-established itself, the value of $K_{eq}$ will be unchanged.

> The value of $K_{eq}$ does not change when changes in concentration cause a shift in equilibrium.

What if more $FeSCN^{2+}$ is added?

Again, equilibrium will shift to use up the added substance. In this case, equilibrium will shift to favor the *reverse* reaction, since the reverse reaction will use up the additional $FeSCN^{2+}$.

- equilibrium shifts to the left
- equilibrium shifts to the reactant side
- the reverse reaction is favored

How do the concentrations of reaction participants change?

*Change of concentrations of reaction participants when adding substance*

| $\mathrm{Fe^{3+}}$ | $[\mathrm{Fe}]^{3+}\ \uparrow$ **as the reverse reaction is favored** |
|---|---|
| $\mathrm{SCN^{-}\,(aq)}$ | $[\mathrm{SCN}]^{-}\ \uparrow$ as the reverse reaction is favored |
| $\mathrm{FeSCN^{2+}}$ | $[\mathrm{FeSCN}]^{2+}\uparrow$ because this is the substance that was added |

Concentration can also be changed by **removing** a substance from the reaction. This is often accomplished by adding another

substance that reacts (in a side reaction) with something already in the reaction.

Let's remove $SCN^-$ from the system (perhaps by adding some $Pb^{2+}$ ions—the lead(II) ions will form a precipitate with $SCN^-$, removing them from the solution). What will happen now? Equilibrium will shift to **replace** $SCN^-$—the reverse reaction will be favored because that is the direction that produces more $SCN^-$.

- equilibrium shifts to the left
- equilibrium shifts to the reactant side
- the reverse reaction is favored

How do the concentrations of reaction participants change?

*Change of concentrations of reaction participants when removing a substance*

| $Fe^{3+}$ | $[Fe]^{3+}$ ↑ **as the reverse reaction is favored** |
|---|---|
| $SCN^-$ | $[SCN]^-$ ↑ as the reverse reaction is favored<br>(but also ↓ because it was removed) |
| $FeSCN^{2+}$ | $[FeSCN]^{2+}$ ↑ because this is the substance that was added |

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# 10.2.3: The Effect of a Volume Change on Equilibrium

Changing the pressure or volume of a container enclosing an equilibrium system will only affect the reaction if gases are present.

You may remember from earlier chemistry classes that equal volumes of gases contain an equal number of particles and, under standard conditions of temperature and pressure (STP), one mole of gas occupies a volume of 22.4 L. This is known as the molar volume of gases. So, two moles of any gas will occupy a volume of 44.8 L and one-half mole would occupy 11.2 L.

How does changing pressure and volume affect equilibrium systems?

- If you increase the pressure of a system at equilibrium (typically by reducing the volume of the container), the stress will best be reduced by reaction that favors the side with the ***fewest*** moles of gas, since fewer moles will occupy the smallest volume.
- Conversely, if you decrease the pressure (by increasing the volume of the container), equilibrium will shift to favor the side with the ***most*** moles of gas, since more moles will occupy a greater volume.
- If both sides of the equation have the same number of moles of gas, then there will be no change in the position of equilibrium.

When considering the effect of changing volume or pressure on equilibrium systems, be sure to only count the number of moles of **gases** on each side of the equation. Solids, liquids, and aqueous solutions will not be affected by changing pressure and volume.

## Example 10.2.3.1

Predict the effect on equilibrium when the pressure is increased for the following reaction:

$$\mathrm{N_2O_4\,(g)} \rightleftharpoons 2\,\mathrm{NO_2\,(g)}$$

**Solution**

The reactant side of the equation has 1 mole of a gas; the product side has 2 moles. Increasing the pressure favors the side with the fewest moles of gas, so the equilibrium will shift to the left (the reverse reaction will be favored).

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# 10.2.4: The Effect of Temperature Changes on Equilibrium

## Learning Objectives

- Explain how temperature changes affect a system at equilibrium.

When temperature is the stress that affects a system at equilibrium, there are two important consequences:

- an increase in temperature will favor that reaction direction that ***absorbs*** heat (i.e. the endothermic reaction)
- the value of $K_{eq}$ will change

Consider the following equilibrium system:

$$\mathrm{N_2O_4\,(g)} \leftrightarrow 2\,\mathrm{NO_2\,(g)}$$

with $\Delta \mathrm{H^\circ} = 58.0\ k\,\mathrm{J}$

We see by the sign of ΔH° that the forward reaction is endothermic. Heat is absorbed (required as a reactant) when the reaction proceeds as

$$\mathrm{N_2O_4\,(g)} \rightarrow 2\,\mathrm{NO_2\,(g)}$$

By adding more heat, equilibrium will shift to use up the additional heat, thus favoring this forward direction.

Why will $K_{eq}$ change, when it did not change when concentration, pressure, and volume were the applied stresses?

When temperature changes cause an equilibrium to shift, one entire side of the reaction equation is favored over the other side. Mathematically, this will alter the value of $K_{eq}$ as follows:

$$\mathrm{K_{eq}} = \frac{[products]}{[reactants]}$$

*\[\ce{K_{eq} \] forward and reverse reactions*

| **if the forward reaction is favored** | **more products are produced; fewer reactants** | **$K_{eq}$ will increase** |
|---|---|---|
| if the reverse reaction is favored | fewer products; more reactants | $K_{eq}$ will decrease |

So in our example given above, increasing the temperature will favor the forward direction. The value of $K_{eq}$ will increase. **Removing heat (making the system colder) will favor the exothermic reaction**—the exothermic reaction ***releases heat*** to the surroundings, thus "replacing" the heat that has been removed.

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# 10.2.5: The Solubility-Product Constant

## Learning Objectives

- Understand the basic concept of solution-solid equilibria.

We will now return to an important mathematical relationship that we first learned about in our unit on Equilibrium, the equilibrium constant expression. Recall that for any general reaction:

$$aA + bB \rightleftharpoons cD + dD$$

an equilibrium constant expression can be defined as:

$$K_{eq} = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

Since saturated solutions are equilibrium systems, we can apply this mathematical relationship to solutions. We will refer to our equilibrium constant as $K_{sp}$, where "sp" stands for "solubility product"

For our silver sulfate saturated solution,

$$Ag_2SO_{4(s)} \rightleftharpoons 2Ag^+_{(aq)} + SO^{2-}_{4(aq)}$$

we can write a solubility product constant expression as

$$K_{sp} = \frac{[Ag^+_{(aq)}]^2[SO^{2-}_{4(aq)}]}{[Ag_2SO_{4(s)}]}$$

However, remember from our earlier introduction to the equilibrium constant expression that the concentrations of solids and liquids are ***NOT*** included in the expression because while their *amounts* will change during a reaction, their *concentrations* will remain constant. Therefore, we will write our solubility product constant expression for our saturated silver sulfate solution as:

$$K_{sp} = [Ag^+]^2[SO^{2-}_4]$$

Please note that it is **VERY IMPORTANT** to include the ion charges when writing this equation.

## Example 10.2.5.1

Write the expression for the solubility product constant, $K_{sp}$, for $Ca_3(PO_4)_2$.

**Solution**

Step 1: Begin by writing the balanced equation for the reaction. Remember that polyatomic ions remain together as a unit and do not break apart into separate elements.

$$Ca_3(PO_4)_{2(s)} \rightleftharpoons 3Ca^{2+}_{(aq)} + 2PO^{3-}_{4(aq)}$$

Step 2: Write the expression for $K_{sp}$:

$$K_{sp} = [Ca^{2+}]^3[PO^{3-}_4]^2$$

Solubility Product Tables that give $K_{sp}$ values for various ionic compounds are available. Because temperature affects solubility, values are given for specific temperatures (usually 25°C). Recall what we learned about $K_{eq}$:

- If $K_{eq}$ is very large, the concentration of the products must be much greater than the concentration of the reactants. The reaction essentially "goes to completion", which means that all—or most of—the reactants are used up to form the products.
- If $K_{eq}$ is very small, the concentration of the reactants is much greater than the concentration of the products. The reaction does not occur to any great extent—most of the reactants remain unchanged, and there are few products produced.
- When $K_{eq}$ is not very large or very small, then roughly equal amounts of reactants and products are present at equilibrium.

$K_{sp}$, which again is just a special case of $K_{eq}$, provides us with the same useful information:

A low value of $K_{sp}$ indicates a substance that has a low solubility (it is generally insoluble); for ionic compounds this means that there will be few ions in solution.

- Iron(II) sulfide, FeS, is an example of a low $K_{sp}$ : $K_{sp} = 4 \times 10^{-19}$. In a saturated solution of FeS there would be few $Fe^{2+}$ or $S^{2-}$ ions.

A large value of $K_{sp}$ indicates a soluble substance; for ionic compounds it tells us that there will be many ions in solution.

- An example of a relatively large $K_{sp}$ would be for lead(II) chloride, $PbCl_2$ which has a $K_{sp}$ of $1.8 \times 10^{-4}$. A saturated solution of $PbCl_2$ would have a relatively high concentration of $Pb^{2+}$ and $Cl^-$ ions.

There are several types of problems we can solve:

## Example 10.2.5.1: Calculating $K_{sp}$ of a Saturated Solution

The concentration of a saturated solution of $BaSO_4$ is $3.90 \times 10^{-5}$M. Calculate $K_{sp}$ for barium sulfate at 25°C.

**Solution**

Always begin problems involving $K_{sp}$ by writing a balanced equation:

$BaSO_{4\,(s)} \rightleftharpoons Ba^{2+}_{(aq)} + SO_4^{2-}{}_{(aq)}$

Next, write the $K_{sp}$ expression:

$$K_{sp} = [Ba^{2+}][SO_4^{2-}]$$

The question provides us with the concentration of the solution, $BaSO_4$ . We need to find the concentration of the individual ***ions*** for our equation.

Recall from Section 2.5: since 1 mole of $BaSO_4$ produces 1 mole of $Ba^{2+}$ and also 1 mole of $SO_4^{2-}$, then...

- $[BaSO_4] = 3.90 \times 10^{-5}$M
- $[Ba^{2+}] = 3.90 \times 10^{-5}$M
- $[SO_4^{2-}] = 3.90 \times 10^{-5}$M

Substitute values into the $K_{sp}$ expression and solve for the unknown:

$$K_{sp} = [Ba^{2+}][SO_4^{2-}]$$

$$= (3.90 \times 10^{-5})(3.90 \times 10^{-5})$$

$$= 1.52 \times 10^{-9}$$

## Example 10.2.5.3: Calculating Ion Concentrations When $K_{sp}$ is Known

The $K_{sp}$ for $MgCO_3$ at 25°C is $2.0 \times 10^{-8}$. What are the ion concentrations in a saturated solution at this temperature?

**Solution**

As always, begin with a balanced equation:

$MgCO_{3(s)} \rightleftharpoons Mg^{2+}_{(aq)} + CO_3^{2-}{}_{(aq)}$

Write the $K_{sp}$ expression:

$$K_{sp} = [Mg^{2+}][CO_3^{2-}]$$

For this example, we are given the value for $K_{sp}$ and need to find the ion concentrations.

We will let our unknown ion concentrations equal ***x***.

**The balanced equation tells us that both $Mg^{2+}$ and $CO_3^{2-}$ will have the same concentration.**

Substitute values into the equation and solve for the unknown:

$$K_{sp} = [Mg^{2+}][CO_3^{2-}]$$

$$x^2 = 2.0 \times 10^{-8}$$

$$x = \sqrt{(2.0 \times 10^{-8})}$$

find the square root of $2.0 \times 10^{-8}$:

$$= 1.4\times 10^{-4}\text{M}$$

$$x = [Mg^{2+}]$$

$$= 1.4\times 10^{-4}\text{M}$$

AND $x = [CO_3^{2-}]$

# Answer

$= 1.4\times 10^{-4}\text{M}$

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# 10.2.6: The Path of a Reaction and the Effect of a Catalyst

The addition of a catalyst to an equilibrium system is a final stress factor. We consider how adding a catalyst affects the following:

$$\mathrm{N_2\,(g) + O_2\,(g)} \rightleftharpoons \mathrm{2\,NO\,(g)}$$

Adding a catalyst to this, or any other equilibrium system, will ***not*** affect the position of an equilibrium. A catalyst speeds up both the forward and the reverse reactions, so there is no uneven change in reaction rates. Generally, a catalyst will help a reaction to reach the point of equilibrium *sooner*, but it will not affect the equilibrium otherwise.

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# 10.3: KINETICS AND COLLISION THEORY



- Topic hierarchy


10.3.1: Chemical Reaction Rate

10.3.2: Collision Theory

10.3.3: Activation Energy

10.3.4: Potential Energy Diagrams

10.3.5: Activated Complex

10.3.6: Factors Affecting Reaction Rate

10.3.7: Catalysts



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# 10.3.1: Chemical Reaction Rate

Drag racing is a sport that involves two cars starting from a dead stop, and driving as fast as they can down a quarter-mile strip. At the end of the strip are timers that determine both elapsed time (how long it took for the cars to cover the quarter mile) and top speed (how fast they were going as they went through the timer chute). Both pieces of data are important. One car may accelerate faster and get ahead that way, while the other car may be slower off the line, but can get up to a higher top speed at the end of the run.

## Chemical Reaction Rate

Chemical reactions vary widely in terms of the speed with which they occur. Some reactions occur very quickly. If a lit match is brought in contact with lighter fluid or another flammable liquid, it erupts into flames instantly and burns fast. Other reactions occur very slowly. A container of milk in the refrigerator will be good to drink for weeks before it begins to turn sour. Millions of years were required for dead plants under Earth's surface to accumulate and eventually turn into fossil fuels such as coal and oil.

Chemists need to be concerned with the rates at which chemical reactions occur. Rate is another word for speed. If a sprinter takes $11.0\ \text{s}$ to run a $100\ \text{m}$ dash, his rate is given by the distance traveled divided by the time.

$$\text{speed} = \frac{\text{distance}}{\text{time}} = \frac{100\ \text{m}}{11.0\ \text{s}} = 9.09\ \text{m/s}$$

The sprinter's average running rate for the race is $9.09\ \text{m/s}$. We say that it is his average rate because he did not run at that speed for the entire race. At the very beginning of the race, while coming from a standstill, his rate must be slower until he is able to get up to his top speed. His top speed must then be greater than $9.09\ \text{m/s}$ so that, taken over the entire race, the average ends up at $9.09\ \text{m/s}$.



Figure 10.3.1.1: Runner. (CC BY-NC; CK-12)

Chemical reactions can't be measured in units of meters per second, as that would not make any sense. A **reaction rate** is the change in concentration of a reactant or product with time. Suppose that a simple reaction were to take place in which a $1.00\ \text{M}$ aqueous solution of substance $\text{A}$ was converted to substance $\text{B}$.

$$\text{A}\,(aq) \rightarrow \text{B}\,(aq)$$

Suppose that after 20.0 seconds, the concentration of $\text{A}$ had dropped from $1.00\ \text{M}$ to $0.72\ \text{M}$ as $\text{A}$ was slowly being converted to $\text{B}$. We can express the rate of this reaction as the change in concentration of $\text{A}$ divided by time.

$$\text{rate} = -\frac{\Delta\,[\text{A}]}{\Delta t} = -\frac{[\text{A}]_{\text{final}} - [\text{A}]_{\text{initial}}}{\Delta t}$$

A bracket around a symbol or formula means the concentration in molarity of that substance. The change in concentration of $\text{A}$ is its final concentration minus its initial concentration. Because the concentration of $\text{A}$ is decreasing over time, the negative sign is used. Thus, the rate for the reaction is positive and the units are molarity per second or $\text{M/s}$.

$$\text{rate} = -\frac{0.72\ \text{M} - 1.00\ \text{M}}{20.0\ \text{s}} = -\frac{-0.28\ \text{M}}{20.0\ \text{s}} = 0.014\ \text{M/s}$$

The molarity of $\text{A}$ decreases by an average rate of $0.014\ \text{M}$ every second. In summary, the rate of a chemical reaction is measured by the change in concentration over time for a reactant or product. The unit of measurement for a reaction rate is molarity per second $(\text{M/s})$.

## Summary

- Chemists need to be concerned with the rates at which chemical reactions occur.
- The reaction rate indicates how fast the reaction proceeds.

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# 10.3.2: Collision Theory

Car damage can be very expensive, especially if the driver who did the damage does not have car insurance. Many people have had the experience of backing up while parallel parking and hearing that "bump". Fortunately, cars are often not going fast enough to do any damage. Every once in a while, though, there is a rearrangement of the body parts of a car when it is hit with sufficient speed; then things need to be fixed.

## Collision Theory

The behavior of the atoms, molecules, or ions that comprise the reactants is responsible for the rates of a given chemical reaction. **Collision theory** is a set of principles that states that the reacting particles can form products when they collide with one another, provided those collisions have enough kinetic energy and the correct orientation. Particles that lack the necessary kinetic energy may collide, but the particles will simply bounce off one another unchanged. The figure below illustrates the difference. In the first collision, the particles bounce off one another, and no rearrangement of atoms has occurred. The second collision occurs with greater kinetic energy, and so the bond between the two red atoms breaks. One red atom bonds with the other molecule as one product, while the single red atom is the other product. The first collision is called an **ineffective collision**, while the second collision is called an **effective collision**.

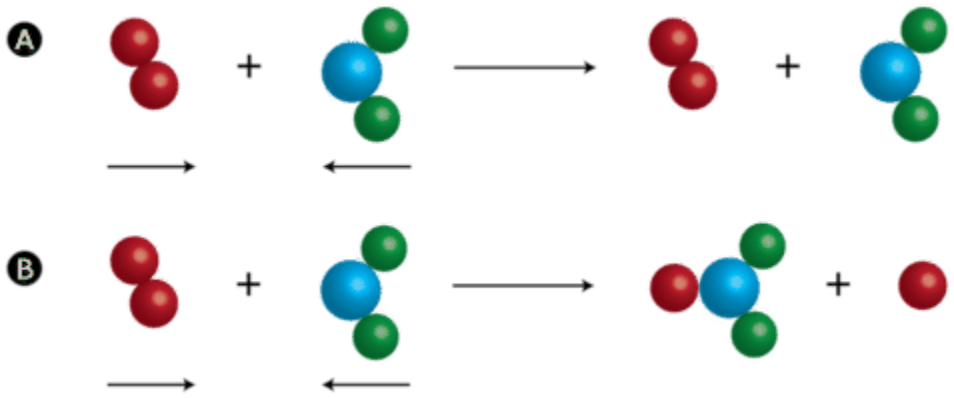



Figure 10.3.2.1: An ineffective collision (A) is one that does not result in product formation. An effective collision (B) is one in which chemical bonds are broken and a product is formed. (CC BY-NC; CK-12)

## Summary

- Collision theory explains how materials can collide and become new materials.
- Effective collisions result in product formation.
- Ineffective collisions do not result in product formation.

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# 10.3.3: Activation Energy

The sight of fireworks cascading across the night sky is a hallmark of special occasions. These materials, invented hundreds of years ago, can be dangerous if not handled properly. The chemicals do not react until the fuse burns down and heat is applied to the system. Then, the rocket is launched and explodes high in the sky.

## Activation Energy



Figure 10.3.3.1: Calcium metal stored in an argon atmosphere. (CC BY-NC; CK-12)

Why do some chemical reactions occur readily while others require input of heat in order to take place? If we mix metallic sodium with water, a reaction occurs immediately, releasing a great deal of heat (enough to ignite the hydrogen gas that is formed). Group II metals, such as calcium, react at a much slower rate. Unlike the extremely vigorous reaction with sodium, the reaction with calcium is slow enough that we can trap the hydrogen gas released.

Supplying reactant particles with energy causes the bonds between the atoms to vibrate with a greater frequency. This increase in vibrational energy makes a chemical bond more likely to break, and a chemical reaction more likely to occur, when those particles collide with other particles. The **activation energy** for a reaction is the minimum energy that colliding particles must have in order to undergo a reaction. Some reactions occur readily at room temperature because the reacting particles already have the requisite activation energy at that temperature. Other reactions only occur when heated because the particles do not have enough energy unless an external source of heat provides the particles with more kinetic energy.

## Summary

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# 10.3.4: Potential Energy Diagrams

Sisyphus was a mythological being who was a very evil king. As a punishment for his misdoings, he was supposed to roll a large stone up to the top of a long hill. A spell had been placed on the stone so that it would roll back down before reaching the top, never to complete the task. Sisyphus was condemned to an eternity of trying to get to the top of the hill, but never succeeding.

## Potential Energy Diagrams

The energy changes that occur during a chemical reaction can be shown in a diagram called a potential energy diagram, or sometimes called a reaction progress curve. A **potential energy diagram** shows the change in potential energy of a system as reactants are converted into products. The figure below shows basic potential energy diagrams for an endothermic (A) and an exothermic (B) reaction. Recall that the enthalpy change $(\Delta H)$ is positive for an endothermic reaction and negative for an exothermic reaction. This can be seen in the potential energy diagrams. The total potential energy of the system increases for the endothermic reaction as the system absorbs energy from the surroundings. The total potential energy of the system decreases for the exothermic reaction as the system releases energy to the surroundings.

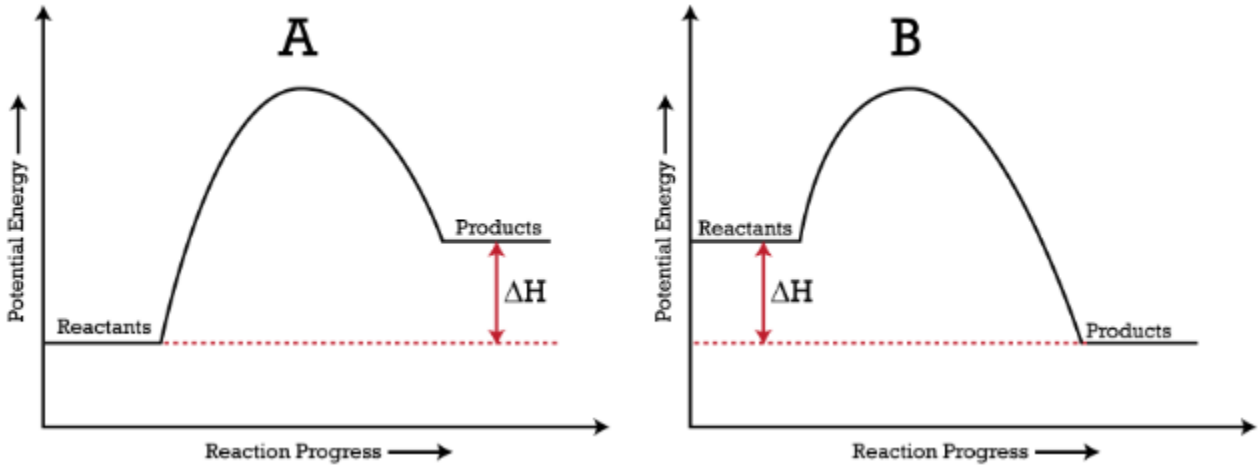



Figure 10.3.4.1: A potential energy diagram shows the total potential energy of a reacting system as the reaction proceeds. (A) In an endothermic reaction, the energy of the products is greater than the energy of the reactants and $\Delta H$ is positive. (B) In an exothermic reaction, the energy of the products is lower than the energy of the reactants and $\Delta H$ is negative. (CC BY-NC; CK-12)

The activation energy for a reaction is illustrated in the potential energy diagram by the height of the hill between the reactants and the products. For this reason, the activation energy of a reaction is sometimes referred to as the activation energy barrier. Reacting particles must have enough energy so that when they collide, they can overcome that barrier (see figure below).

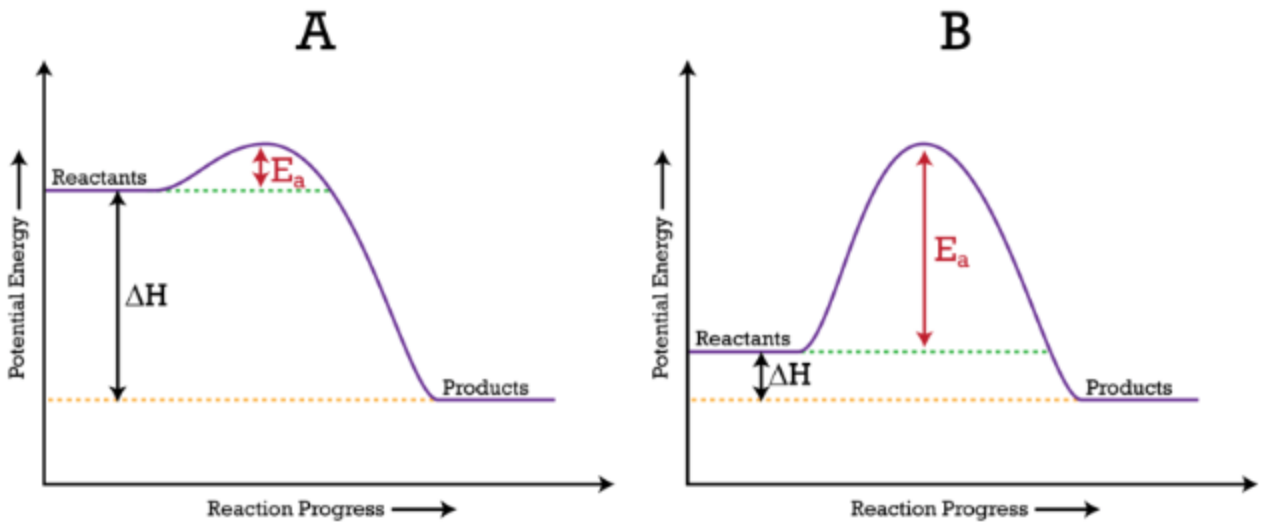



Figure 10.3.4.2: The activation energy $(E_a)$ of a reaction is the barrier that must be overcome for the reactants to be able to become products. (A) The activation energy is low, meaning that the reaction is likely to be fast. (B) The activation energy is high, meaning that the reaction is likely to be slow. (CC BY-NC; CK-12)

## Summary

- A potential energy diagram shows the change in potential energy of a system as reactants are converted into products.
- Potential energy diagrams for endothermic and exothermic reactions are described.
- Diagrams of activation energy and reaction progress are given.

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# 10.3.5: Activated Complex

Velcro is a synthetic material that allows fabric (among other things) to stick together. Another, more unusual, use for Velcro is the sport of "Velcro-jumping". The participant wears clothing made of Velcro and jumps at a Velcro-covered wall. Sometimes the collision with the wall will result in the person sticking to the wall. Other times, the person simply bounces off the wall and does not connect.

## Activated Complex

Reactant particles sometimes collide with one another and remain unchanged by the collision. Other times, the collision leads to the formation of products. The state of the particles that is in between the reactants and products is called the activated complex. An **activated complex** is an unstable arrangement of atoms that exists momentarily at the peak of the activation energy barrier. Because of its high energy, the activated complex exists for an extremely short period of time (about $10^{-13}$ s). There is equal likelihood that the activated complex either reforms the original reactants or goes on to form products. The figure below shows the formation of a possible activated complex between colliding hydrogen and oxygen molecules. Because of their unstable nature and brief existence, very little is known about the exact structures of many activated complexes.

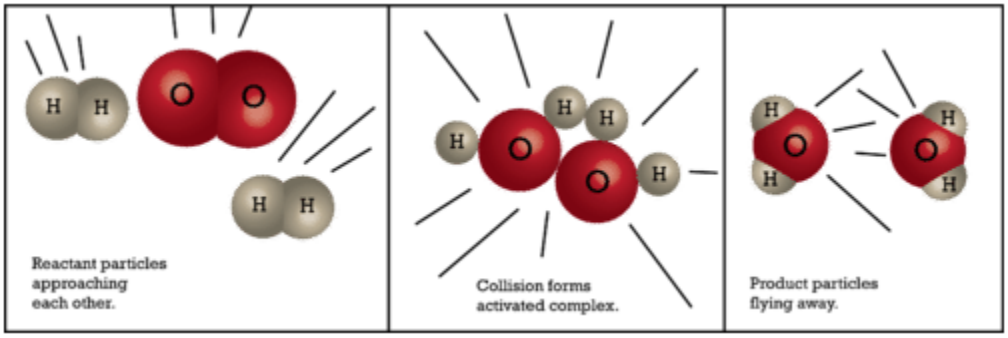



Figure 10.3.5.1: An activated complex is a short-lived state in which the colliding particles are at the peak of the potential energy curve. (CC BY-NC; CK-12)

## Summary

- An activated complex is an unstable arrangement of atoms that exists momentarily at the peak of the activation energy barrier.
- The role of the activated complex in reactions is described.

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# 10.3.6: Factors Affecting Reaction Rate

Driving on a crowded freeway can be stressful. Lots of cars, drivers who aren't paying attention, people who speed or who drive too slow—the chances of a collision are rather high. A lot of cars in a particular amount of space means a high car concentration and many opportunities for unwanted connections with other cars.

## Factors Affecting Reaction Rates

According to their nature, some reactions occur very quickly, while others are very slow. However, certain changes in the reacting conditions can have an effect on the rate of a given chemical reaction. Collision theory can be utilized to explain these rate effects.

### Concentration

An increase in the concentration of one or more reacting substances results in an increase in the rate of reaction. When more particles are present in a given amount of space, a greater number of collisions will naturally occur between those particles. Since the rate of a reaction is dependent on the number of collisions occurring between reactants, the rate increases as the concentration increases.

### Pressure

When the pressure of a gas is increased, its particles are forced closer together, decreasing the amount of empty space between the particles. Therefore, an increase in the pressure of a gas is also an increase in the concentration of the gas. For gaseous reactions, an increase in pressure increases the rate of reaction due to a greater number of collisions between reacting particles.

### Surface Area

A large log placed in a fire will burn relatively slowly. If the same mass of wood were added to the fire in the form of small twigs, the twigs would burn much more quickly. This is because the twigs provide a greater surface area than the log does. An increase in the surface area of a reactant increases the rate of a reaction. Surface area is larger when a given amount of a solid is present as smaller particles. A powdered reactant has a greater surface area than the same reactant as a solid chunk. In order to increase the surface area of a substance, it may be ground into smaller particles or dissolved into a liquid. In solution, the dissolved particles are separated from each other and will react more quickly with other reactants.

### Temperature

Raising the temperature of a chemical reaction usually results in a higher rate of reaction. When the reactant particles are heated, they move faster and faster. This results in a greater frequency of collisions. A more important effect of the temperature increase is that the collisions occur with a greater force, and are thus more likely to surmount the activation energy barrier and go on to form products. Increasing the temperature of a reaction increases the number of effective collisions between reacting particles, so the reaction rate increases.

## Summary

- Factors that affect (and generally increase) reaction rate are:
  - Concentration of reactants
  - Pressure (in the case of a gas)
  - Surface area
  - Temperature

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# 10.3.7: Catalysts

Gasoline-powered vehicles emit various harmful materials. Nitrogen oxides are formed when atmospheric nitrogen reacts with oxygen at the high temperatures found in a car engine. Carbon monoxide is a by-product of the incomplete combustion of hydrocarbons. Evaporated and unused fuel releases volatile hydrocarbons into the atmosphere to help form smog. The presence of a catalytic converter in the exhaust system of the car causes these materials to react and be changed into less harmful products.

## Catalysts

Sometimes a particular substance added to a chemical reaction will cause that reaction to undergo a dramatic increase in rate. Hydrogen peroxide is used as a disinfectant for scrapes and cuts, and is found in many medicine cabinets as a $3\%$ aqueous solution. Hydrogen peroxide naturally decomposes to produce water and oxygen gas, but the reaction is very slow. A bottle of hydrogen peroxide will last for several years before it needs to be replaced. However, the addition of just a small amount of manganese (IV) oxide to hydrogen peroxide will cause it to decompose completely in just a matter of minutes. A **catalyst** is a substance that increases the rate of a chemical reaction by lowering the activation energy without being used up in the reaction. After the reaction occurs, a catalyst returns to its original state; so catalysts can be used over and over again. Because it is neither a reactant nor a product, a catalyst is shown in a chemical equation by being written above the yield arrow.

$$\mathrm{H_2O_2}\,(aq) \overset{\mathrm{MnO_2}}{\rightarrow} 2\mathrm{H_2O}\,(l) + \mathrm{O_2}\,(g)$$

A catalyst works by changing the specific way in which the reaction occurs, called its mechanism. The important outcome from the use of a catalyst is that the overall activation energy of the reaction is lowered (see figure below). With a lower activation energy barrier, a greater percentage of reactant molecules are able to have effective collisions, and the reaction rate increases.

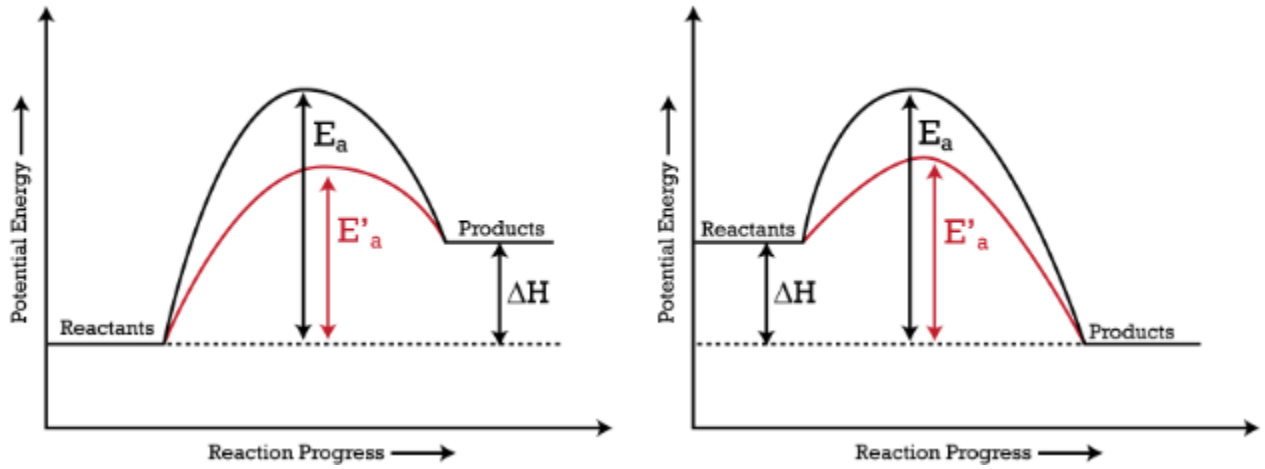



Figure $10.3.7.1$: The addition of a catalyst to a reaction lowers the activation energy, increasing the rate of the reaction. The activation energy of the uncatalyzed reaction is shown by $E_a$, while the catalyzed reaction is shown by $E'_a$. The heat of reaction $(\Delta H)$ is unchanged by the presence of the catalyst. (CC BY-NC; CK-12)

Catalysts are an extremely important part of many chemical reactions. Enzymes in your body acts as nature's catalysts, allowing important biochemical reactions to occur at reasonable rates. Chemical companies constantly search for new and better catalysts to make reactions go faster and thus make the company more profitable.

## Summary

- A catalyst is a substance that increases the rate of a chemical reaction by lowering the activation energy without being used up in the reaction.
- Catalysts are an important part of many chemical reactions.

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# 11: GASES

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


11.1: Extra-Long Straws

11.2: Kinetic Molecular Theory- A Model for Gases

11.3: Pressure - The Result of Constant Molecular Collisions

11.4: Boyle's Law - Pressure and Volume

11.5: Charles's Law- Volume and Temperature

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

11.7: Avogadro's Law- Volume and Moles

11.8: The Ideal Gas Law- Pressure, Volume, Temperature, and Moles

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

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



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# 11.1: Extra-Long Straws

A drinking straw is a tube for transferring a beverage from its container to the mouth of the drinker and is typically a thin tube of plastic (such as polypropylene and polystyrene) or other material. Many people believe that when they drink a liquid they are sucking the liquid up, however the liquid is really being pushed up. A straw works because when you suck the air out of the straw, it creates a vacuum. This causes a decrease in air pressure on the inside of the straw. Since the atmospheric pressure is greater on the outside of the straw, liquid is forced into and up the straw and into your mouth (Figure 11.1.1).

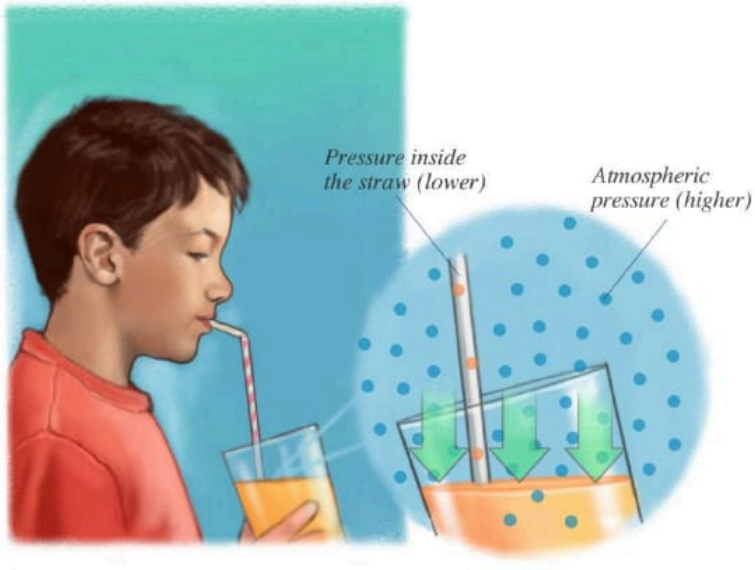



Figure 11.1.1: As you suck the air out of the straw, it creates a low pressure zone inside of it. With a low pressure zone, there is nothing pushing down on the juice, so it moves upward easily. (CC BY-NC 4.0; Ümit Kaya)

## How Long of a Straw is Possible?

With the straw just sitting in the glass, the pressure on the surface of the tea is the same all over, including on the little bit of surface inside the straw. When you suck the air out of the straw, you decrease the pressure inside the straw, allowing the higher pressure on the rest of the surface to push the tea up the straw and into your mouth. Because it is really the atmosphere that is doing the pushing, the atmospheric pressure limits how high water will go up a straw.

If you formed a perfect vacuum within the straw, the pressure outside of the straw at sea level would be enough to push water to a total height of about 10.3 m. A 10.3-m column of water exerts the same pressure—101,325 $N/m^2$ or 14.7 $lb/in^2$ (psi)—as do the gas molecules in our atmosphere. At sea level, the air pressure is enough to support a column of water about thirty feet high. This means that even if you could suck all the air out of a forty-foot straw, the water would not rise more than thirty feet.

## Contributions & Attributions

- Lisa Peck's Conceptual Physics Class

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# 11.2: 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 11.2.1 shows a representation of how we mentally picture the gas phase.

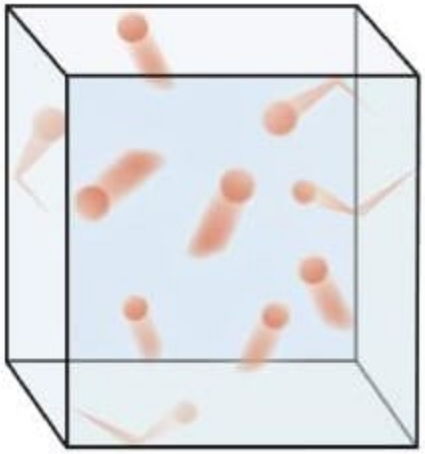


Figure 11.2.1: The Kinetic Theory of Gases. The kinetic theory of gases describes this state of matter as composed of tiny particles in constant motion with a lot of distance between the particles.

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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# 11.3: 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.

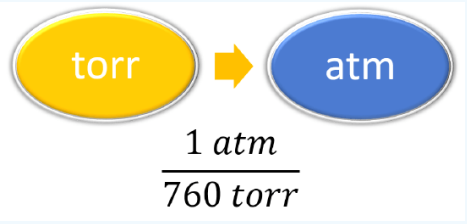
## Example 11.3.1: Pressure Conversion

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<br>Find: ? atm |
| List other known quantities. | 1 atm = 760 torr |

| Steps for Problem Solving | Unit Conversion |
|---|---|
| Prepare a concept map. |   |
| Cancel units and calculate. | $595\ \cancel{torr} \times \frac{1\ atm}{760\ \cancel{torr}} = 0.783\ atm$ |
| Think about your result. | 595 torr is less than 760 torr so the final answer should be less than 1 atm. |

## Exercise 11.3.1

How many atmospheres are there in 1,022 torr?

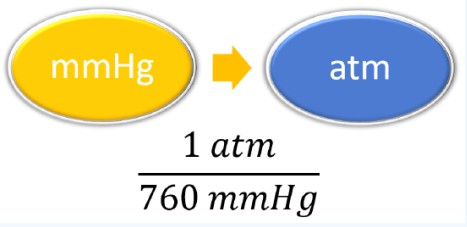
*Answer available at the end of this section.*

## Example 11.3.2: Mars

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

**Solution**

*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<br>Find: ? atm |
| List other known quantities. | 1 atm = 760 mmHg |
| Prepare a concept map. |   |
| Cancel units and calculate. | $6.01\ \cancel{mmHg} \times \frac{1\ atm}{760\ \cancel{mmHg}} = 0.00791\ atm = 7.91 \times 10^{-3} atm$ |

| Steps for Problem Solving | Unit Conversion |
| --- | --- |
| Think about your result. | 6.01 is a very small number relative to 760 mmHg, just like the value in atmospheres. |

**Exercise 11.3.2**

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

*Answer available at the end of this section.*

## Summary

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

### Answers

**Exercise** 11.3.1

1.345 atm

**Exercise** 11.3.2

652 torr

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# 11.4: 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

$$P_1V_1 = \text{constant} = P_2V_2$$

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

$$P_1V_1 = P_2V_2 \text{ at constant n and T}$$

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 11.4.1 shows two representations of how Boyle's Law works.

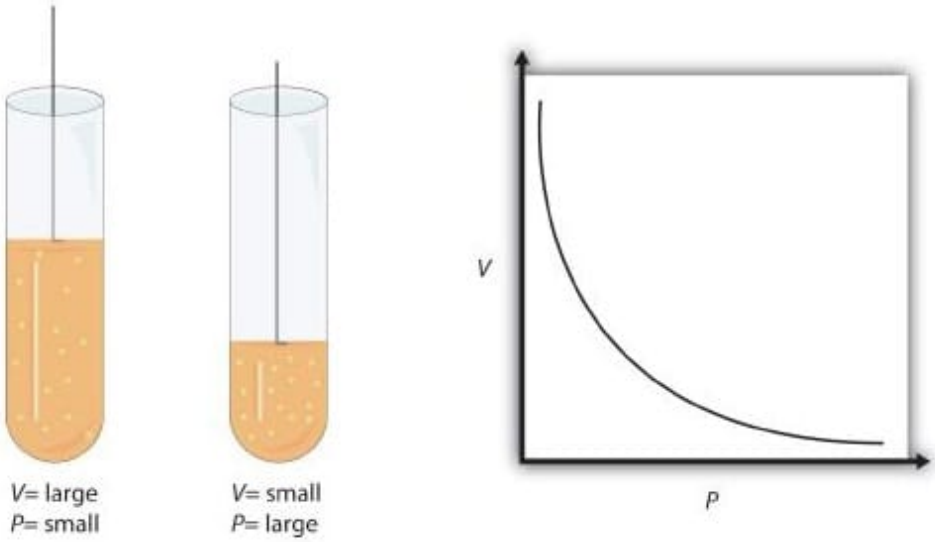



Figure 11.4.1: Boyle's Law. A piston having a certain pressure and volume (left piston) will have half the volume when its pressure is twice as much (right piston). One can also plot *P* versus *V* for a given amount of gas at a certain temperature; such a plot will look like the graph on the right.

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 11.4.1

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<br>$P_2$ = 1.93 atm<br>Find: $V_2$ = ? L |
| List other known quantities. | none |
| Plan the problem. | First, rearrange the equation algebraically to solve for $V_2$.<br>$$V_2 = \frac{P_1 \times V_1}{P_2}$$ |
| Cancel units and calculate. | Now substitute the known quantities into the equation and solve.<br>$$V_2 = \frac{2.44 \cancel{\text{ atm}} \times 4.01 \text{ L}}{1.93 \cancel{\text{ atm}}} = 5.07 \text{ L}$$ |
| Think about your result. | We know that pressure and volume are inversely related; as one decreases, the other increases. Pressure is decreas 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 answ sense based on Boyle's Law. |

## Exercise 11.4.1

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

*Answer available at the end of this section.*

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 11.4.2:

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<br><br>$V_2$ = 0.633 L<br><br>Find: $P_2$ = ? torr |
| List other known quantities. | 1 L = 1000 mL to have the same units for volume. |
| Plan the problem. | 1. Perform the conversion of the second volume unit from L to mL.<br><br>2. Rearrange the equation algebraically to solve for $P_2$.<br><br>$$P_2 = \frac{P_1 \times V_1}{V_2}$$ |
| Cancel units and calculate. | 1.<br><br>$$0.663 \cancel{L} \times \frac{1000\,ml}{1\,\cancel{L}} = 663\,ml$$<br><br>2. Substitute the known quantities into the equation and solve.<br><br>$$P_2 = \frac{722\text{ torr} \times 88.8\,\cancel{\text{mL}}}{663\,\cancel{\text{mL}}} = 96.7\text{ torr}$$ |
| Think about your result. | When the volume increased, the pressure decreased, which is as expected for Boyle's Law. |

## Exercise 11.4.2

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

*Answer available at the end of this section.*

## 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.

## Answers

**Exercise** 11.4.1

124 mL

**Exercise** 11.4.2

119 mL

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# 11.5: 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.

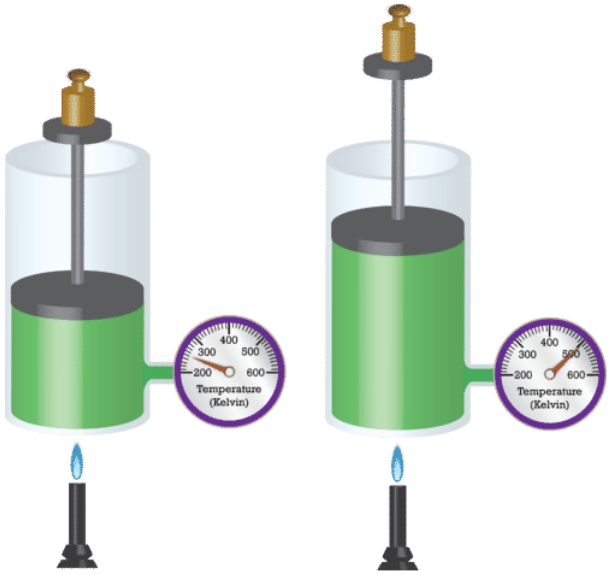



Figure 11.5.1: As a container of confined gas is heated, its molecules increase in kinetic energy and push the movable piston outward, resulting in an increase in volume.

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 11.5.1: Temperature-Volume Data*

| **Temperature** $(\mathrm{K})$ | **Volume** $(\mathrm{mL})$ | $\frac{V}{T} = k \left(\frac{\mathrm{mL}}{\mathrm{K}}\right)$ |
|---|---|---|
| 50 | 20 | 0.40 |
| 100 | 40 | 0.40 |

| Temperature $(\mathrm{K})$ | Volume $(\mathrm{mL})$ | $\frac{V}{T} = k\left(\frac{\mathrm{mL}}{\mathrm{K}}\right)$ |
|---|---|---|
| 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.

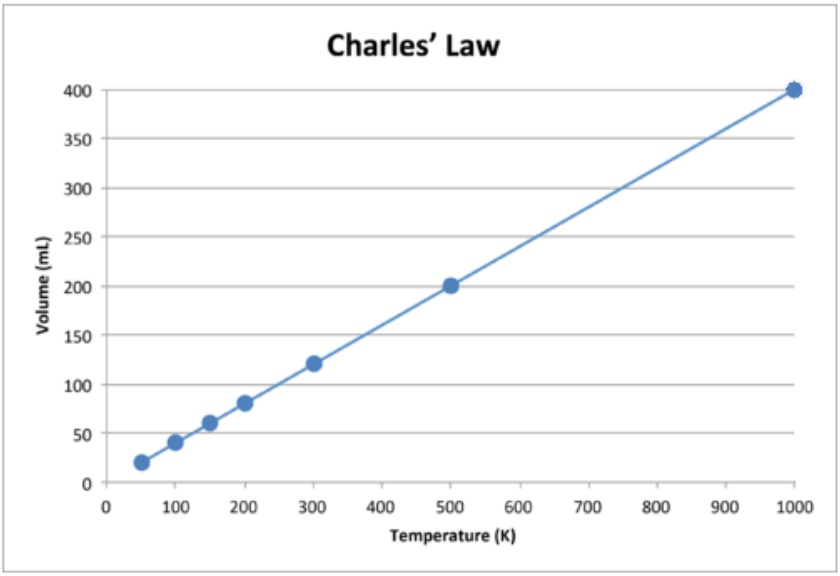



Figure $11.5.2$:The volume of a gas increases as the Kelvin temperature increases.

Notice that the line goes exactly toward the origin, meaning that as the absolute temperature of the gas approaches zero, its volume approaches zero. However, when a gas is brought to extremely cold temperatures, its molecules would eventually condense into the liquid state before reaching absolute zero. The temperature at which this change into the liquid state occurs varies for different gases.

Charles's Law can also be used to compare changing conditions for a gas. Now we use $V_1$ and $T_1$ to stand for the initial volume and temperature of a gas, while $V_2$ and $T_2$ stand for the final volume and temperature. The mathematical relationship of Charles's Law becomes:

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

This equation can be used to calculate any one of the four quantities if the other three are known. The direct relationship will only hold if the temperatures are expressed in Kelvin. Temperatures in Celsius will not work. Recall the relationship that $\mathrm{K} = {}^{\circ}\mathrm{C} + 273$.

## Example $11.5.1$:

A balloon is filled to a volume of $2.20\ \mathrm{L}$ at a temperature of $22^{\circ}\mathrm{C}$. The balloon is then heated to a temperature of $71^{\circ}\mathrm{C}$. Find the new volume of the balloon.

**Solution**

*Solutions to Example 11.5.1*

| Steps for Problem Solving | |
|---|---|
| Identify the "given" information and what the problem is asking you to "find." | Given:<br>$V_1 = 2.20\ \text{L}$ and<br>$T_1 = 22^\circ\text{C} = 295\ \text{K}$<br>$T_2 = 71^\circ\text{C} = 344\ \text{K}$<br>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 $V_2$.<br>$$V_2 = \frac{V_1 \times T_2}{T_1}$$ |
| Cancel units and calculate. | Now substitute the known quantities into the equation and solve.<br>$$V_2 = \frac{2.20\ \text{L} \times 344\ \cancel{\text{K}}}{295\ \cancel{\text{K}}} = 2.57\ \text{L}$$ |
| Think about your result. | The volume increases as the temperature increases. The result has three significant figures. |

## Exercise 11.5.1

If $V_1$ = 3.77 L and $T_1$ = 255 K, what is $V_2$ if $T_2$ = 123 K?

*Answer available at the end of this section.*

## Example 11.5.2:

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:<br><br>Given:$T_1$ = -27°C and $V_1$ = 34.8 L<br><br>$V_2$ = 25.0 L<br><br>Find: $T_2$ = ? K |
| List other known quantities. | K = -27°C + 273 |
| Plan the problem. | 1. Convert the initial temperature to Kelvin<br><br>2. Rearrange the equation algebraically to solve for $T_2$.<br><br>$$T_2 = \frac{V_2 \times T_1}{V_1}$$ |
| Cancel units and calculate. | 1. –67°C + 273 = 206 K<br><br>2. Substitute the known quantities into the equation and solve.<br><br>$$T_2 = \frac{25.0 \cancel{\text{L}} \times 206 \text{ K}}{34.8 \cancel{\text{L}}} = 148 \text{ K}$$ |
| Think about your result. | This is also equal to –125°C. As temperature decreases, volume decreases—which it does in this example. |

## Exercise 11.5.2

If $V_1$ = 623 mL, $T_1$ = 255°C, and $V_2$ = 277 mL, what is $T_2$?

*Answer available at the end of this section.*

# Summary

- Charles's Law relates the volume and temperature of a gas at constant pressure and amount.

## Answers

**Exercise** 11.5.1

1.82 L

**Exercise** 11.5.2

235 K, or –38°C

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# 11.6: 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

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \; at \; constant \; n$$

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 11.6.1:

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:<br><br>$V_1$ = 8.33 L, $P_1$ = 1.82 atm, and $T_1$ = 286 K<br><br>V2 = 5.72 L and $T_2$ = 355 K<br><br>Find: *P*2 = ? atm |
| List other known quantities. | none |
| Plan the problem. | First, rearrange the equation algebraically to solve for $V_2$.<br><br>$$P_2 = \frac{P_1V_1T_2}{T_1V_2}$$ |

| Steps for Problem Solving | |
|---|---|
| Calculate. | Now substitute the known quantities into the equation and solve.<br>$$P_2 = \frac{(1.82\,atm)(8.33\,\cancel{L})(355\,\cancel{K})}{(286\,\cancel{K})(5.72\,\cancel{L})} = 3.22atm$$ |
| Think about your result. | Ultimately, the pressure increased, which would have been difficult to predict because two properties of the gas we changing. |

### Exercise 11.6.1

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 available at the end of this section.*

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.

### Answers

**Exercise** 11.6.1

105 mL

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# 11.7: 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 11.7.1

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:<br>$V_1 = 1.90\ \text{L}$<br>$n_1 = 0.0920\ \text{mol}$<br>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 o helium.<br>$n_2 = 0.0920 + 0.0210 = 0.1130\ \text{mol}$ |

| Steps for Problem Solving | |
|---|---|
| Plan the problem. | First, rearrange the equation algebraically to solve for $V_2$.<br>$$V_2 = \frac{V_1 \times n_2}{n_1}$$ |
| Calculate. | Now substitute the known quantities into the equation and solve.<br>$$V_2 = \frac{1.90\ \text{L} \times 0.1130\ \cancel{\text{mol}}}{0.0920\ \cancel{\text{mol}}} = 2.33\ \text{L}$$ |
| Think about your result. | Since a relatively small amount of additional helium was added to the balloon, its volume increases slightly. |

**Exercise 11.7.1**

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 available at the end of this section.*

## Summary

- Calculations for relationships between volume and number of moles of a gas can be performed using Avogadro's Law.

### Answers

**Exercise** 11.7.1

0.350 L

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# 11.8: 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 $\frac{(P \times V)}{(T \times n)}$ 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: $\mathrm{kPa}$, $\mathrm{atm}$, or $\mathrm{mm\ Hg}$. Therefore, $R$ can have three different values.

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

$$\begin{aligned} R &= \frac{PV}{nT} \\ &= \frac{101.325\,\mathrm{kPa} \times 22.414\,\mathrm{L}}{1.000\,\mathrm{mol} \times 273.15\,\mathrm{K}} \\ &= 8.314\,\mathrm{kPa \cdot L/K \cdot mol} \end{aligned}$$

This is the value of $R$ that is to be used in the ideal gas equation when the pressure is given in $\mathrm{kPa}$. 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* 11.8.1*: 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 | $8.314\ \text{J/K} \cdot \text{mol}$ |
| atm | L | mol | K | $0.08206\ \text{L} \cdot \text{atm/K} \cdot \text{mol}$ |
| mm Hg | L | mol | K | $62.36\ \text{L} \cdot \text{mm Hg/K} \cdot \text{mol}$ |

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 $(\text{J})$.

## Example 11.8.1 Oxygen Gas

What volume is occupied by $3.76\ \text{g}$ of oxygen gas at a pressure of $88.4\ \text{kPa}$ and a temperature of $19^{\circ}\text{C}$? 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:<br>• $P = 88.4\ \text{kPa}$<br>• $T = 19^{\circ}\text{C} = 292\ \text{K}$<br>Mass $\text{O}_2 = 3.76\ \text{g}$<br>Find: *V* = ? L |
| List other known quantities. | $\text{O}_2 = 32.00\ \text{g/mol}$<br>$R = 8.314\ \text{J/K} \cdot \text{mol}$ |
| Plan the problem. | 1. First, determine the number of moles of $\text{O}_2$ from the given mass and the molar mass.<br>2. Then, rearrange the equation algebraically to solve for V<br>$$V = \frac{nRT}{P}$$ |

| Steps for Problem Solving | |
|---|---|
| Calculate. | 1. $$3.76 \cancel{g} \times \frac{1 \text{ mol } O_2}{32.00 \cancel{g} \text{ } O_2} = 0.1175 \text{ mol } O_2$$ 2. Now substitute the known quantities into the equation and solve. $$V = \frac{nRT}{P} = \frac{0.1175 \cancel{\text{mol}} \times 8.314 \text{ J}/\cancel{\text{K}} \cdot \cancel{\text{mol}} \times 292 \cancel{\text{K}}}{88.4 \cancel{\text{kPa}}} = 3.23 \text{ L } O_2$$ |
| 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 v $(22.4 \text{ L/mol})$ since the pressure and temperature are reasonably close to standard. The result has three significant 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 lite |

## Example 11.8.2: 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:<br>n = 4.22 mol<br>P = 1.21 atm<br>T = 34°C<br>Find: *V* = ? L |
| List other known quantities. | none |
| Plan the problem. | 1. The first step is to convert temperature to Kelvin.<br>2. Then, rearrange the equation algebraically to solve for V $$V = \frac{nRT}{P}$$ |

| Steps for Problem Solving | |
|---|---|
| Calculate. | 1. 34 + 273 = 307 K<br><br>2. Now substitute the known quantities into the equation and solve.<br><br>$$V = \frac{(4.22\ \cancel{mol})(0.08205\frac{L.\cancel{atm}}{\cancel{mol}.K})(307\ \cancel{K})}{1.21\ \cancel{atm}}$$<br>$$= 87.9\ L$$ |
| Think about your result. | The number of moles of Ar is large so the expected volume should also be large. |

### Exercise 11.8.1

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 available at the end of this section.*

### Exercise 11.8.2

For a 0.00554 mol sample of $H_2$, $P$ = 23.44 torr and $T$ = 557 K. What is its volume?

*Answer available at the end of this section.*

## Summary

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

### Answers

**Exercise** 11.8.1

3.94 L

**Exercise** 11.8.2

8.21 L

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# 11.9: 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 $2700\ \text{mm Hg}$. 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 $460^{\circ}\text{C}$.

## 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 $1.00\ \text{atm}$, then the pressure of just the nitrogen in the air is $0.78\ \text{atm}$. The pressure of the oxygen in the air is $0.21\ \text{atm}$.

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

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

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

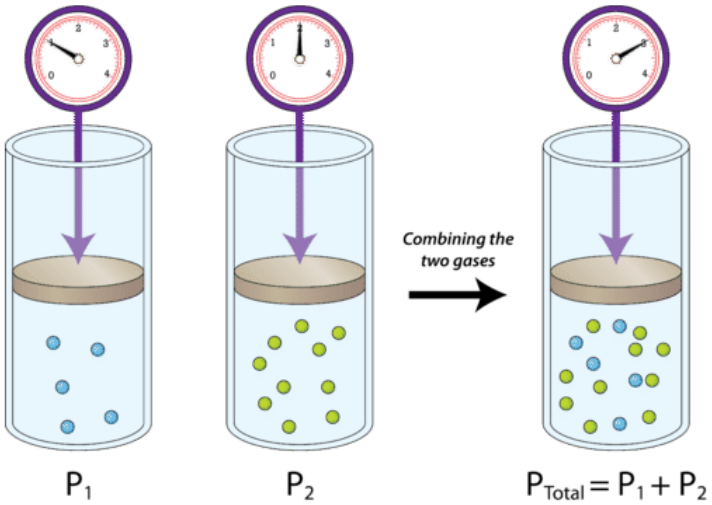



Figure 11.9.1: Dalton's Law states that the pressure of a gas mixture is equal to the partial pressures of the combining gases.

## 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 11.9.2 ). 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 11.9.2: 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* 11.9.1*: Vapor Pressure of Water* $(\text{mm Hg})$ *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 $20^\circ\text{C}$ 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 $\text{kPa}$ to $\text{mm Hg}$ in order to match units with the table. The sum of the pressures of the hydrogen and the water vapor is equal to the atmospheric pressure. The pressure of the hydrogen is found by subtraction. Then, the volume of the gas at STP can be calculated by using the combined gas law.

***Step 2: Solve.***

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

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

$$\begin{aligned} V_2 &= \frac{P_1 \times V_1 \times T_2}{P_2 \times T_1} \\ &= \frac{722.2\ \text{mm Hg} \times 2.58\ \text{L} \times 273\ \text{K}}{760\ \text{mm Hg} \times 293\ \text{K}} \\ &= 2.28\ \text{L H}_2 \end{aligned}$$

***Step 3: Think about your result.***

If the hydrogen gas were to be collected at STP and without the presence of the water vapor, its volume would be $2.28\ \text{L}$. 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.

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# 11.10: 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 11.10.1: 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 11.10.1**

The gas in an aerosol can is under a pressure of $3.00\ \text{atm}$ at a temperature of $25^\circ\text{C}$. It is dangerous to dispose of an aerosol can by incineration. What would the pressure in the aerosol can be at a temperature of $845^\circ\text{C}$?

**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:<br><br>$P_1 = 3.00\ \text{atm}$<br><br>$T_1 = 25^\circ\text{C} = 298\ \text{K}$<br><br>$T_2 = 845^\circ\text{C} = 1118\ \text{K}$<br><br>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 $P_2$.<br><br>$$P_2 = \frac{P_1 \times T_2}{T_1}$$ |
| Calculate. | Now substitute the known quantities into the equation and solve.<br><br>$$P_2 = \frac{3.00\ \text{atm} \times 1118\ \cancel{\text{K}}}{298\ \cancel{\text{K}}} = 11.3\ \text{atm}$$ |
| Think about your result. | The pressure increases dramatically due to a large increase in temperature. |

## Summary

- Pressure and temperature at constant volume are directly proportional.

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# 12: AQUEOUS SOLUTIONS AND CONCENTRATION

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 the last chapter will be of particular importance again. Quantitative measurements of solutions are another key component of this chapter. Solutions can involve all physical states—gases dissolved in gases (the air around us), solids dissolved in solids (metal alloys), and liquids dissolved in solids (amalgams—liquid mercury dissolved in another metal such as silver, tin or copper). This chapter is almost exclusively concerned with aqueous solutions, substances dissolved in water.


12.1: Tragedy in Cameroon

**12.2: Formation of Solutions**

12.2.1: Solutions - Homogeneous Mixtures

12.2.2: Dissolving Process

12.2.3: Liquid-Liquid Solutions

**12.3: Aqueous Solutions**

12.3.1: Structure of Water

12.3.2: Solute and Solvent

12.3.3: Aqueous Solutions and Solubility - Compounds Dissolved in Water

12.3.4: Precipitation Reactions

12.3.5: Writing Chemical Equations for Reactions in Solution- Molecular, Complete Ionic, and Net Ionic Equations

12.3.6: Solutions of Gases in Water

**12.4: Concentrations and Dilution**

12.4.1: Concentration of solutions

12.4.2: Concentrations as Conversion Factors

12.4.3: Solution Stoichiometry

12.5: Osmosis and Hypotonic/Hypertonic Solutions



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# 12.1: Tragedy in Cameroon

Lake Nyos is a deep crater lake in the Northwest region of Cameroon, high on the flank of an inactive volcano in the Oku volcanic plain along the Cameroon line of volcanic activity. A volcanic dam impounds the lake waters. A pocket of magma lies beneath the lake and leaks carbon dioxide ($CO_2$) into the water, changing it into carbonic acid. Nyos is one of only three known exploding lakes to be saturated with carbon dioxide in this way.

In 1986, more than 1700 people in Cameroon were killed when a cloud of gas, almost certainly carbon dioxide, bubbled from Lake Nyos (Figure 12.1.1), a deep lake in a volcanic crater. It is believed that the lake underwent a turnover due to gradual heating from below the lake, and the warmer, less-dense water saturated with carbon dioxide reached the surface. Consequently, tremendous quantities of dissolved $CO_2$ were released, and the colorless gas, which is denser than air, flowed down the valley below the lake and suffocated humans and animals living in the valley.




Figure 12.1.1: Two photos are shown. The first is an aerial view of a lake surrounded by green hills. The second shows a large body of water with a fountain sending liquid up into the air several yards or meters above the surface of the water. (a) It is believed that the 1986 disaster, that killed more than 1700 people near Lake Nyos in Cameroon, resulted when a large volume of carbon dioxide gas was released from the lake. (b) A $CO_2$ vent has since been installed to help outgas the lake in a slow, controlled fashion and prevent a similar catastrophe from happening in the future. (Credit a: modification of work by Jack Lockwood; credit b: modification of work by Bill Evans.)

Following the Lake Nyos tragedy, scientists investigated other African lakes to see if a similar phenomenon could happen elsewhere. Lake Kivu in Democratic Republic of Congo, 2,000 times larger than Lake Nyos, was also found to be supersaturated, and geologists found evidence for out-gassing events around the lake about every one thousand years.

## Contributions & Attributions

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# 12.2: FORMATION OF SOLUTIONS



- 


12.2.1: Solutions - Homogeneous Mixtures

12.2.2: Dissolving Process

12.2.3: Liquid-Liquid Solutions



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# 12.2.1: Solutions - Homogeneous Mixtures

## Learning Objectives

- Learn terminology involving solutions.
- Explain the significance of the statement "like dissolves like."
- Explain why certain substances dissolve in other substances.

The major component of a solution is called the **solvent.** The minor component of a solution is called the **solute**. By major and minor we mean whichever component has the greater or lesser presence by mass or by moles. Sometimes this becomes confusing, especially with substances with very different molar masses. However, here we will confine the discussion to solutions for which the major component and the minor component are obvious.



Figure 12.2.1.1: Making a saline water solution by dissolving table salt (NaCl) in water. The salt is the solute and the water the solvent. (CC-BY-SA 3.0; Chris 73).

Solutions exist for every possible phase of the solute and the solvent. Salt water, for example, is a solution of solid $\mathrm{NaCl}$ in liquid water, while air is a solution of a gaseous solute ($\mathrm{O_2}$) in a gaseous solvent ($\mathrm{N_2}$). In all cases, however, the overall phase of the solution is the same phase as the solvent. Table 12.2.1.1 lists some common types of solutions, with examples of each.

*Table 12.2.1.1: Types of Solutions*

| Solvent Phase | Solute Phase | Example |
|---|---|---|
| gas | gas | air |
| liquid | gas | carbonated beverages |
| liquid | liquid | ethanol ($\mathrm{C_2H_5OH}$) in $\mathrm{H_2O}$ (alcoholic beverages) |
| liquid | solid | salt water |
| solid | gas | $\mathrm{H_2}$ gas absorbed by Pd metal |
| solid | liquid | Hg(ℓ) in dental fillings |
| solid | solid | steel alloys |

### Example 12.2.1.1: Sugar and Water

A solution is made by dissolving 1.00 g of sucrose ($C_{12}H_{22}O_{11}$) in 100.0 g of liquid water. Identify the solvent and solute in the resulting solution.

**Solution**

Either by mass or by moles, the obvious minor component is **sucrose**, so it is **the solute**. **Water**—the majority component—is **the solvent**. The fact that the resulting solution is the same phase as water also suggests that water is the solvent.

### Exercise 12.2.1.1

A solution is made by dissolving 3.33 g of $HCl(g)$ in 40.0 g of liquid methyl alcohol ($CH_3OH$). Identify the solvent and solute in the resulting solution.

*Answer available at the end of this section.*

## Like Dissolves Like

A simple way to predict which compounds will dissolve in other compounds is the phrase "like dissolves like". What this means is that polar compounds dissolve polar compounds, nonpolar compounds dissolve nonpolar compounds, but polar and nonpolar do not dissolve in each other.

Even some nonpolar substances dissolve in water but only to a limited degree. Have you ever wondered why fish are able to breathe? Oxygen gas, a nonpolar molecule, does dissolve in water—it is this oxygen that the fish take in through their gills. The reason we can enjoy carbonated sodas is also due to a nonpolar compound that dissolves in water. Pepsi-cola and all the other sodas have carbon dioxide gas, $CO_2$, a nonpolar compound, dissolved in a sugar-water solution. In this case, to keep as much gas in solution as possible, the sodas are kept under pressure.

This general trend of "like dissolves like" is summarized in the following table:

*Table 12.2.1.2: Summary of Solubilities*

| Solute (Polarity of Compound) | Solvent (Polarity of Compound) | Dominant Intermolecular Force | Is Solution Formed? |
|---|---|---|---|
| Polar | Polar | Dipole-Dipole Force and/or Hydrogen Bond | yes |
| Non-polar | Non-polar | Dispersion Force | yes |
| Polar | Non-polar | | no |
| Non-polar | Polar | | no |
| Ionic | Polar | Ion-Dipole | yes |
| Ionic | Non-polar | | no |

Note that every time charged particles (ionic compounds or polar substances) are mixed, a solution is formed. When particles with no charges (nonpolar compounds) are mixed, they will form a solution. However, if substances with charges are mixed with other substances without charges, a solution does not form. When an ionic compound is considered "insoluble", it doesn't necessarily mean the compound is completely untouched by water. All ionic compounds dissolve to some extent. An insoluble compound just doesn't dissolve in any noticeable or appreciable amount.

***What is it that makes a solute soluble in some solvents but not others?***

The answer is intermolecular interactions. The intermolecular interactions include London dispersion forces, dipole-dipole

interactions, and hydrogen bonding (as described in Chapter 10). From experimental studies, it has been determined that if molecules of a solute experience the same intermolecular forces that the solvent does, the solute will likely dissolve in that solvent. So, NaCl—a very polar substance because it is composed of ions—dissolves in water, which is very polar, but not in oil, which is generally nonpolar. Nonpolar wax dissolves in nonpolar hexane, but not in polar water.



Figure 12.2.1.2: Water (clear liquid) and oil (yellow) do not form liquid solutions. (CC BY-SA 1.0 Generic; Victor Blacus)

## Example 12.2.1.2: Polar and Nonpolar Solvents

Would $\mathrm{I_2}$ be more soluble in $\mathrm{CCl_4}$ or $\mathrm{H_2O}$? Explain your answer.

**Solution**

$\mathrm{I_2}$ is nonpolar. Of the two solvents, $\mathrm{CCl_4}$ is nonpolar and $\mathrm{H_2O}$ is polar, so $\mathrm{I_2}$ would be expected to be more soluble in $\mathrm{CCl_4}$.

## Exercise 12.2.1.2

Would $\mathrm{C_3H_7OH}$ be more soluble in $\mathrm{CCl_4}$ or $\mathrm{H_2O}$? Explain your answer.

*Answer available at the end of this section.*

## Example 12.2.1.3

Water is considered a polar solvent. Which substances should dissolve in water?

a. methanol ($\mathrm{CH_3OH}$)
b. sodium sulfate (\ce{Na2SO4}\))
c. octane ($\mathrm{C_8H_{18}}$)

**Solution**

Because water is polar, substances that are polar or ionic will dissolve in it.

a. Because of the OH group in methanol, we expect its molecules to be polar. Thus, we expect it to be soluble in water. As both water and methanol are liquids, the word *miscible* can be used in place of *soluble*.
b. Sodium sulfate is an ionic compound, so we expect it to be soluble in water.

c. Like other hydrocarbons, octane is nonpolar, so we expect that it would not be soluble in water.

### Exercise 12.2.1.3: Toluene

Toluene ($C_6H_5CH_3$) is widely used in industry as a nonpolar solvent. Which substances should dissolve in toluene?

a. water ($H_2O$)
b. sodium sulfate ($Na_2SO_4$)
c. octane ($C_8H_{18}$)

*Answer available at the end of this section.*

## Summary

- Solutions are composed of a solvent (major component) and a solute (minor component).
- "Like dissolves like" is a useful rule for deciding if a solute will be soluble in a solvent.

## Answers

**Exercise** 12.2.1.1
solute: $HCl(g)$
solvent: $CH_3OH$

**Exercise** 12.2.1.2
$H_2O$, because both experience hydrogen bonding.

**Exercise** 12.2.1.3**: Toluene**
Octane ($C_8H_{18}$) will dissolve. It is also non-polar.

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# 12.2.2: Dissolving Process

Many people start their day with a cup of coffee (others drink coffee all day long). The coffee typically consumed is a type of solution—sometimes a very complex one. The coffee itself has been brewed so that material from the coffee bean will dissolve in hot water. Some people add sugar, while others add milk or cream. In some areas of the country, lattés are popular; one or more special flavors might be added along with the milk. Whatever the situation, the end result is an enjoyable solution to drink.

## The Process of Dissolution

Water typically dissolves many ionic compounds and polar molecules. Nonpolar molecules such as those found in grease or oil do not dissolve in water. We will first examine the process that occurs when an ionic compound such as table salt (sodium chloride) dissolves in water.

Water molecules move about continuously due to their kinetic energy. When a crystal of sodium chloride is placed into water, the water's molecules collide with the crystal lattice. Recall that the crystal lattice is composed of alternating positive and negative ions. Water is attracted to the sodium chloride crystal because water is polar and has both a positive and a negative end. The positively charged sodium ions in the crystal attract the oxygen end of the water molecules because they are partially negative. The negatively charged chloride ions in the crystal attract the hydrogen end of the water molecules because they are partially positive. The action of the polar water molecules takes the crystal lattice apart (see image below).

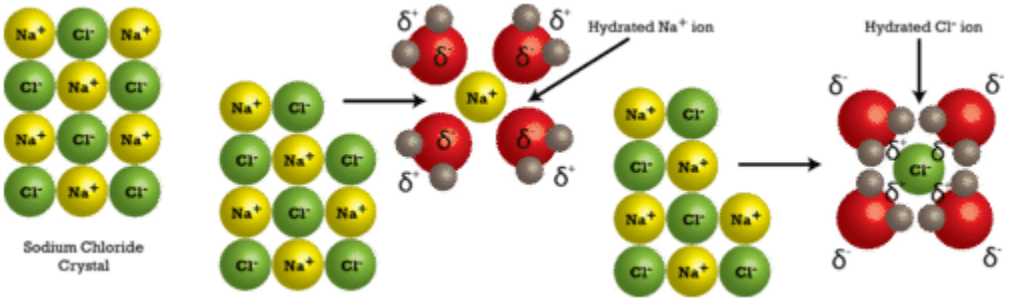



Figure 12.2.2.1: The dissolving of sodium chloride in water.

After coming apart from the crystal, the individual ions are then surrounded by solvent particles in a process called **solvation**. Note that the individual $\mathrm{Na^+}$ ions are surrounded by water molecules with the oxygen atom oriented near the positive ion. Likewise, the chloride ions are surrounded by water molecules with the opposite orientation. **Hydration** is the process of solute particles being surrounded by water molecules arranged in a specific manner. Hydration helps to stabilize aqueous solutions by preventing the positive and negative ions from coming back together and forming a precipitate.

Table sugar is sucrose $(\mathrm{C_{12}H_{22}O_{11}})$, and is an example of a molecular compound. Solid sugar consists of individual sugar molecules held together by intermolecular attractive forces. When water dissolves sugar, it separates the individual sugar molecules by disrupting the attractive forces, but does not break the covalent bonds between the carbon, hydrogen, and oxygen atoms. Dissolved sugar molecules are also hydrated, but without as distinct an orientation to the water molecules as in the case of the ions. The sugar molecules contain many $-\mathrm{OH}$ groups that can form hydrogen bonds with the water molecules, helping to form the sucrose solution.

## Summary

- Motion of water molecules helps break up interactions between solid ions or molecules.
- Solvation involves surrounding ions with solvent particles.
- Ionic solute molecules are hydrated (surrounded by water molecules in a specific orientation).

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# 12.2.3: Liquid-Liquid Solutions

In 2010, a major oil spill occurred when an explosion on a drilling rig in the Gulf of Mexico released millions of gallons of crude oil into the Gulf. Oil is primarily a mixture of hydrocarbons (organic compounds composed of only carbon and hydrogen atoms). Because of its composition, oil does not dissolve in water. As a result, much of the Gulf of Mexico was contaminated, as was a great deal of shoreline in the affected area.

## Liquid-Liquid Solutions

Nonpolar compounds do not dissolve in water. The attractive forces that operate between the particles in a nonpolar compound are weak dispersion forces. However, the nonpolar molecules are more attracted to themselves than they are to the **polar** water molecules. When a nonpolar liquid such as oil is mixed with water, two separate layers form because the liquids will not dissolve into each other (figure below). When another polar liquid such as ethanol is mixed with water, they completely blend and dissolve into one another. Liquids that dissolve in one another in all proportions are said to be **miscible**. Liquids that do not dissolve in one another are deemed **immiscible**. The general rule for deciding if one substance is capable of dissolving another is "like dissolves like". A nonpolar solid such as iodine will dissolve in nonpolar lighter fluid, but will not dissolve in polar water.



Figure 12.2.3.1: Water and oil form separate layers when they are mixed because the nonpolar oil will not dissolve into the polar water. The oil forms the top layer because it is less dense than the water.

For molecular compounds, the major factor that contributes to the material dissolving in water is the ability to form hydrogen bonds with the water solvent. Small compounds such as methanol, ethanol, acetic acid, and acetone have polar groups that can interact with the polar H of water. However, as the nonpolar portion of the molecule gets larger, solubility with water drops off. The nonpolar portion of the molecule increasingly repels the water and eventually overrides the interaction of the polar component with water.

## Summary

- Liquids that dissolve in one another in all proportions are miscible; liquids that do not dissolve in one another are immiscible.
- The general rule for deciding if one substance is capable of dissolving another is "like dissolves like".
- Nonpolar molecules are usually insoluble in water.
- A non-ionized molecule must be relatively polar to interact with water molecules.

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# 12.3: AQUEOUS SOLUTIONS

- Topic hierarchy


12.3.1: Structure of Water

12.3.2: Solute and Solvent

12.3.3: Aqueous Solutions and Solubility - Compounds Dissolved in Water

12.3.4: Precipitation Reactions

12.3.5: Writing Chemical Equations for Reactions in Solution- Molecular, Complete Ionic, and Net Ionic Equations

12.3.6: Solutions of Gases in Water


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# 12.3.1: Structure of Water

In his well-known poem "The Rime of the Ancient Mariner", Samuel Coleridge wrote "water, water everywhere, nor any drop to drink." Coleridge was talking about being out on the ocean, but not having any water because he had killed an albatross (apparently bringing bad luck to everyone on the ship). About $75\%$ of the Earth's surface is water. The major constituent of the human body (over $60\%$) is water. This simple molecule plays important roles in all kinds of processes.

## Structure of Water

Water is a simple molecule consisting of one oxygen atom bonded to two different hydrogen atoms. Because of the higher **electronegativity** of the oxygen atom, the bonds are polar covalent (**polar bonds**). The oxygen atom attracts the shared electrons of the covalent bonds to a significantly greater extent than the hydrogen atoms. As a result, the oxygen atom acquires a partial negative charge $(\delta-)$, while the hydrogen atoms each acquire a partial positive charge $(\delta+)$. The molecule adopts a bent structure because of the two lone pairs of electrons on the oxygen atom. The $\mathrm{H-O-H}$ bond angle is about $105^{\circ}$, slightly smaller than the ideal $109.5^{\circ}$ of an $sp^3$ hybridized atomic orbital.

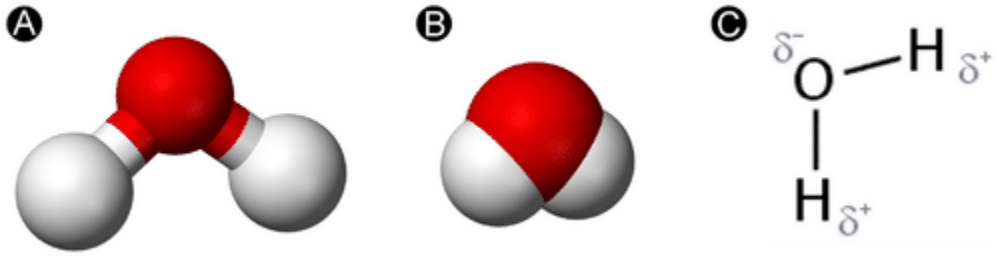



Figure $12.3.1.1$: The water molecule, visualized three different ways: ball-and-stick model, space-filling model, and structural formula with partial charges.

The bent shape of the water molecule is critical because the polar $\mathrm{O-H}$ bonds do not cancel one another and the molecule as a whole is polar. The figure below illustrates the net polarity of the water molecule. The oxygen is the negative end of the molecule, while the area between the hydrogen atoms is the positive end of the molecule.

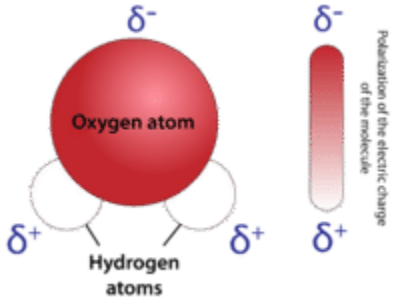



Figure $12.3.1.2$: Water is a polar molecule, as greater electron density is found around the more electronegative oxygen atom.

Polar molecules attract one another by dipole-dipole forces, as the positive end of one molecule is attracted to the negative end of the nearby molecule. In the case of water, the highly polar $\mathrm{O-H}$ bonds results in very little electron density around the hydrogen atoms. Each hydrogen atom is strongly attracted to the lone-pair electrons on an adjacent oxygen atom. These are called hydrogen bonds and are stronger than conventional dipole-dipole forces.

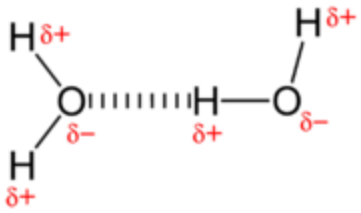



Figure 12.3.1.3: A hydrogen bond is the attraction between a lone pair of electrons on the oxygen atom of one molecule and the electron-deficient hydrogen atom of a nearby molecule.

Because each oxygen atom has two lone pairs, it can make hydrogen bonds to the hydrogen atoms of two separate other molecules. The figure below shows the result—an approximately tetrahedral geometry around each oxygen atom, consisting of two covalent bonds and two hydrogen bonds.

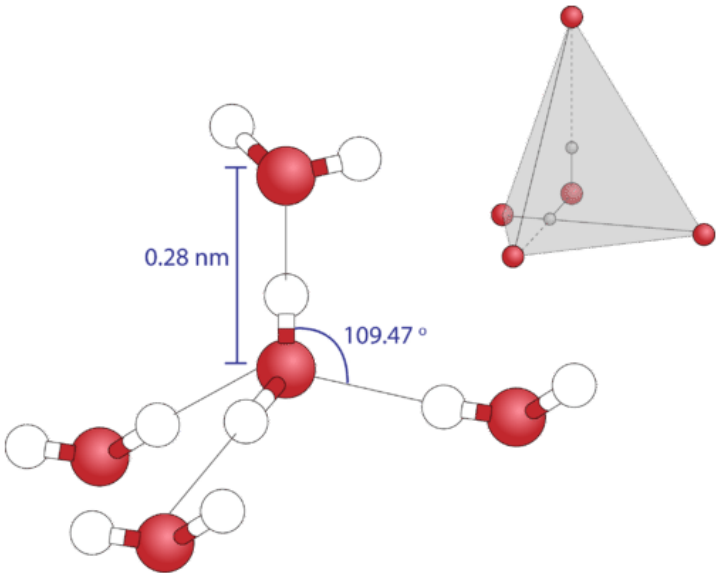



Figure 12.3.1.4: As a result of two covalent bonds and two hydrogen bonds, the geometry around each oxygen atom is approximately tetrahedral.

## Summary

- Water is a molecular compound consisting of polar molecules that have a bent shape.
- The oxygen atom acquires a partial negative charge, while the hydrogen atom acquires a partial positive charge.

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# 12.3.2: Solute and Solvent

In the winter, the temperature often gets well below the freezing point of water. This condition can create problems in car radiators. If the water freezes, water hoses will break, the engine block can crack, and significant damage can be done to the car.

## Solute and Solvent

When one substance dissolves into another, a **solution** is formed. A solution is a homogeneous mixture consisting of a **solute** dissolved into a **solvent**. The solute is the substance that is being dissolved, while the solvent is the dissolving medium. Solutions can be formed with many different types and forms of solutes and solvents.

We know of many types of solutions. Check out a few examples in the table below.

*Table* 12.3.2.1*: Types of Solutions*

| Type | Solvent | Solute | Example |
|---|---|---|---|
| gas/gas | nitrogen | oxygen | air |
| gas/liquid | water | carbon dioxide | soda pop |
| liquid/liquid | water | ethylene glycol | antifreeze |
| solid/liquid | water | salts | seawater |

This section's focus is on solutions where the solvent is water. An aqueous solution is water that contains one or more dissolved substances. The dissolved substances in an aqueous solution many be solids, gases, or other liquids. Some examples are listed in the table above. Other examples include vinegar (acetic acid in water), alcoholic beverages (ethanol in water), and liquid cough medicines (various drugs in water).



Figure 12.3.2.1: Typical solution: clear and stable.

In order to be a true solution, a mixture must be stable. When sugar is fully dissolved into water, it can stand for an indefinite amount of time and the sugar will not settle out of the solution. Further, if the sugar-water solution is passed through a filter, it will be unchanged. The dissolved sugar particles will pass through the filter along with the water. This is because the dissolved particles in a solution are very small, usually less than $1 \text{ nm}$ in diameter. Solute particles can be atoms, ions, or molecules, depending on the type of substance that has been dissolved.

## Summary

- A solution is a homogeneous mixture of a solute in a solvent.
- A solute is the material present in the smaller amount in the solution.
- A solvent is the material present in the larger amount in the solution.

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# 12.3.3: 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 12.3.3.1).

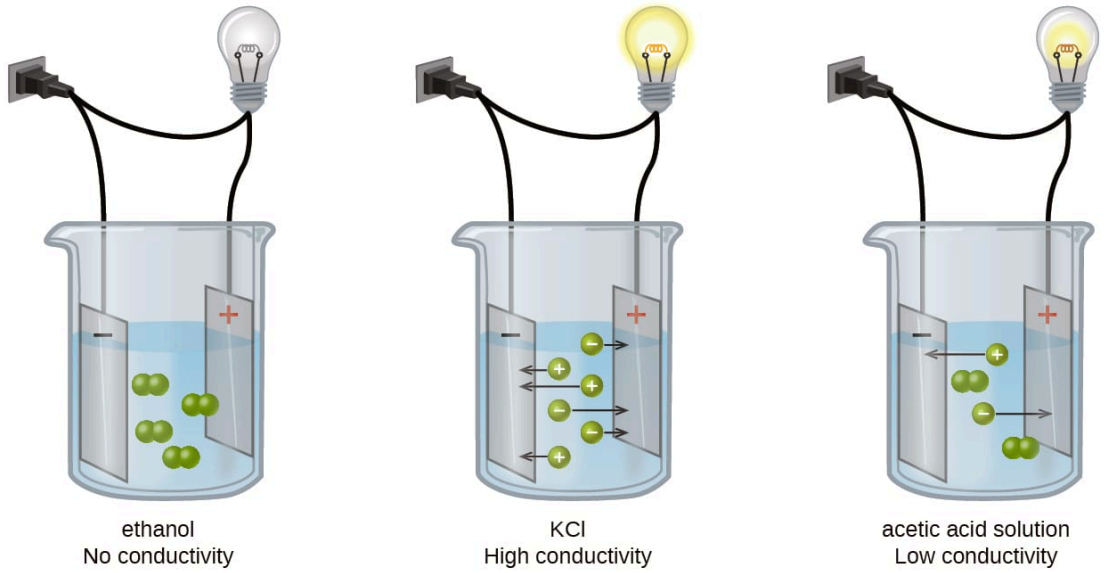



Figure 12.3.3.1: Solutions of nonelectrolytes, such as ethanol, do not contain dissolved ions and cannot conduct electricity. Solutions of electrolytes contain ions that permit the passage of electricity. The conductivity of an electrolyte solution is related to the strength of the electrolyte. This 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 12.3.3.2. The electrostatic attraction between an ion and a molecule with a dipole is called an ion-dipole attraction. These attractions play an important role in the dissolution of ionic compounds in water.

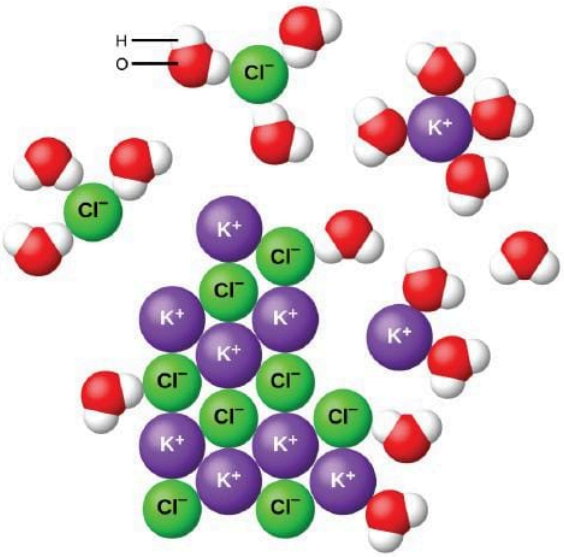



Figure 12.3.3.2: As potassium chloride (KCl) dissolves in water, the ions are hydrated. The polar water molecules are attracted by the charges on the $K^+$ and $Cl^-$ ions. Water molecules in front of and behind the ions are not shown. The diagram shows eight purple spheres labeled K superscript plus 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 12.3.3.2 shows. The reduction of the electrostatic attraction permits the independent motion of each hydrated ion in a dilute solution, resulting in an increase in the disorder of the system, as the ions change from their fixed and ordered positions in the crystal to mobile and much more disordered states in solution. This increased disorder is responsible for the dissolution of many ionic compounds, including KCl, which dissolve with absorption of heat.

In other cases, the electrostatic attractions between the ions in a crystal are so large, or the ion-dipole attractive forces between the ions and water molecules are so weak, that the increase in disorder cannot compensate for the energy required to separate the ions, and the crystal is insoluble. Such is the case for compounds such as calcium carbonate (limestone), calcium phosphate (the inorganic component of bone), and iron oxide (rust).

# Solubility Rules

Some combinations of aqueous reactants result in the formation of a solid precipitate as a product. However, some combinations will not produce such a product. If solutions of sodium nitrate and ammonium chloride are mixed, no reaction occurs. One could write a molecular equation showing a double-replacement reaction, but both products, sodium chloride and ammonium nitrate,

are soluble and would remain in the solution as ions. Every ion is a spectator ion and there is no net ionic equation at all. It is useful to be able to predict when a precipitate will occur in a reaction. To do so, you can use a set of guidelines called the **solubility rules** (Tables 12.3.3.1 and 12.3.3.2).

*Table 12.3.3.1: 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 12.3.3.2: Solubility Rules for Sparingly Soluble Substances*

| Sparingly Soluble in Water | Important Exceptions (Soluble) |
|---|---|
| All carbonates and phosphates | Group IA and $NH_4^+$ salts |
| All hydroxides | Group IA and $NH_4^+$ salts; $Ba^{2+}$, $Sr^{2+}$, $Ca^{2+}$ sparingly soluble |
| All sulfides | Group IA, IIA and $NH_4^+$ salts; MgS, CaS, BaS sparingly soluble |
| All oxalates | Group IA and $NH_4^+$ salts |
| Special note: The following electrolytes are of only moderate solubility in water: $CH_3COOAg$, $Ag_2SO_4$, $KClO_4$. They will precipitate only if rather concentrated solutions are used. | |

As an example on how to use the solubility rules, predict if a precipitate will form when solutions of cesium bromide and lead (II) nitrate are mixed.

$$\mathrm{Cs^+}\,(aq) + \mathrm{Br^-}\,(aq) + \blacksquare\,(aq) + 2\mathrm{NO_3^-}\,(aq) \rightarrow ?$$

The potential precipitates from a double-replacement reaction are cesium nitrate and lead (II) bromide. According to the solubility rules table, cesium nitrate is soluble because all compounds containing the nitrate ion, as well as all compounds containing the alkali metal ions, are soluble. Most compounds containing the bromide ion are soluble, but lead (II) is an exception. Therefore, the cesium and nitrate ions are spectator ions and the lead (II) bromide is a precipitate. The balanced net ionic reaction is:

$$\blacksquare\,(aq) + 2\mathrm{Br^-}\,(aq) \rightarrow \mathrm{PbBr_2}\,(s)$$

## Example 12.3.3.1: Solubility

Classify each compound as soluble or insoluble

a. Zn(NO3)2
b. PbBr2
c. Sr3(PO4)2

**Solution**

a. All nitrates are soluble in water, so Zn(NO3)2 is soluble.
b. All bromides are soluble in water, except those combined with $Pb^{2+}$, so PbBr2 is insoluble.
c. All phosphates are insoluble, so Sr3(PO4)2 is insoluble.

### Exercise 12.3.3.1: Solubility

Classify each compound as soluble or insoluble.

a. $Mg(OH)_2$
b. KBr
c. $Pb(NO_3)_2$

*Answer a available at the end of this section.*

*Answer b available at the end of this section.*

*Answer c available at the end of this section.*

## Summary

Substances that dissolve in water to yield ions are called electrolytes. Nonelectrolytes are substances that do not produce ions when dissolved in water. Solubility rules allow prediction of what products will be insoluble in water.

## Contributions & Attributions


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### Answers

**Exercise 12.3.3.1: Solubility**
insoluble

**Exercise 12.3.3.1: Solubility**
soluble

**Exercise 12.3.3.1: Solubility**
soluble

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# 12.3.4: Precipitation Reactions

## Learning Objectives

- To identify a precipitation reaction and predict solubility.

A precipitation reaction is a reaction that yields an insoluble product—a precipitate—when two solutions are mixed. When a colorless solution of silver nitrate is mixed with a yellow-orange solution of potassium dichromate, a reddish precipitate of silver dichromate is produced.

$$\mathrm{AgNO_3\,(aq) + K_2Cr_2O_7\,(aq)\ \rightarrow Ag_2Cr_2O_7\,(s) + KNO_3\,(aq)} \tag{12.3.4.1}$$

This unbalanced equation has the general form of an exchange reaction:

$$\mathrm{AC + BD\ \rightarrow \underset{insoluble}{AD} + BC} \tag{12.3.4.2}$$

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.

## YouTube Video

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

View this YouTube Video online

Video: Mixing potassium dichromate and silver nitrate together to initiate a precipitation reaction (Equation 12.3.4.1).

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 12.3.4.1), none of these species reacts with any of the others. When these solutions are mixed, the only effect is to dilute each solution with the other.

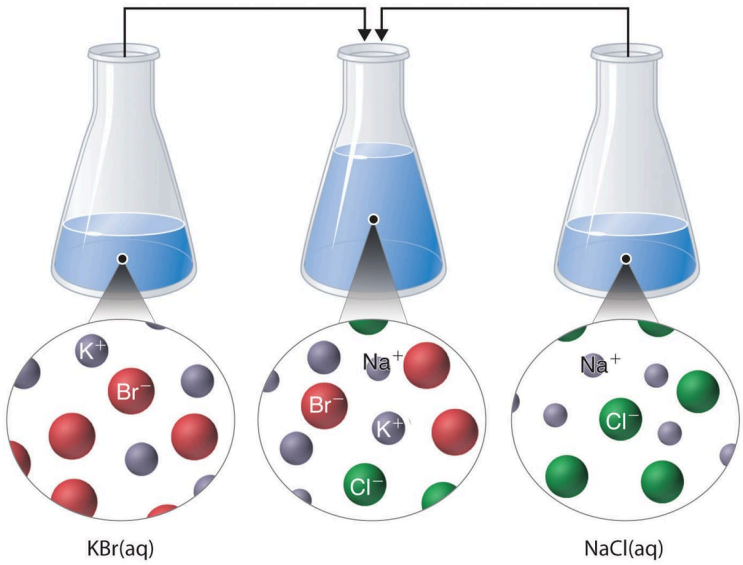


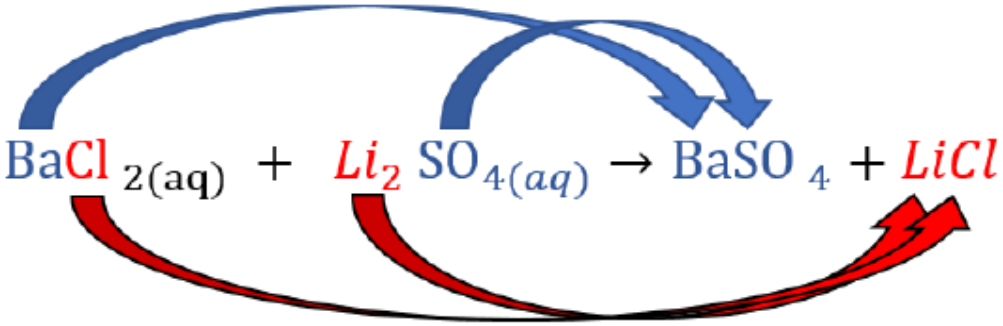

Figure 12.3.4.1: The Effect of Mixing Aqueous $\mathrm{KBr}$ and $\mathrm{NaCl}$ Solutions. Because no net reaction occurs, the only effect is to dilute each solution with the other. (Water molecules are omitted from molecular views of the solutions for clarity.)

## Predicting Precipitation Reactions

A precipitation reaction occurs when a solid precipitate forms after mixing two strong electrolyte solutions. As stated previously, if none of the species in the solution reacts then no net reaction occurred.

Predict what will happen when aqueous solutions of barium chloride and lithium sulfate are mixed.

**Change the partners of the anions and cations on the reactant side to form new compounds (products):**




Chemical equation of the reactants barium chloride and lithium sulfate forming the products barium sulfate and lithium chloride.

Because barium chloride and lithium sulfate are strong electrolytes, each dissociates completely in water to give a solution that contains the constituent anions and cations. Mixing the two solutions *initially* gives an aqueous solution that contains $\mathrm{Ba^{2+}}$, $\mathrm{Cl^-}$, $\mathrm{Li^+}$, and $\mathrm{SO_4{}^{2-}}$ ions. The only possible exchange reaction is to form $\mathrm{LiCl}$ and $\mathrm{BaSO_4}$.

## Correct the formulas of the products based on the charges of the ions.

No need to correct the formula as both compounds already have their charges balanced.

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

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

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

Table 7.5.1 from the previous section shows that $\mathrm{LiCl}$ is soluble in water, but $\mathrm{BaSO_4}$ 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, $\mathrm{BaSO_4}$ 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 $\mathrm{BaSO_4}$ particles in water.



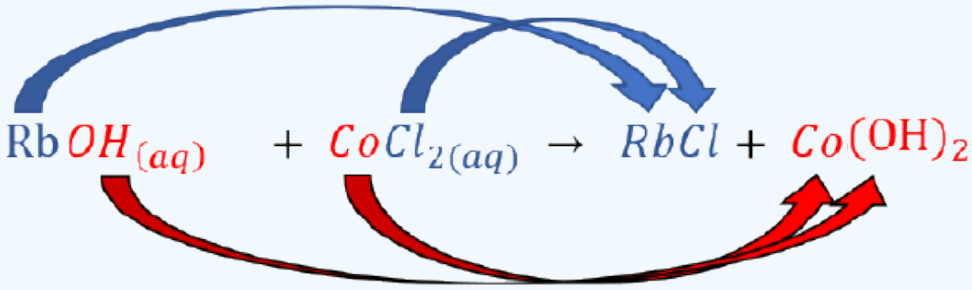
Figure 12.3.4.2: An x-ray of the digestive organs of a patient who has swallowed a "barium milkshake." A barium milkshake is a suspension of very fine $BaSO_4$ particles in water; the high atomic mass of barium makes it opaque to x-rays. (Public Domain; Glitzy queen00 via Wikipedia).

### Example 12.3.4.1

Predict what will happen if aqueous solutions of rubidium hydroxide and cobalt(II) chloride are mixed.

**Solution**

*Solutions to Example 7.6.1*

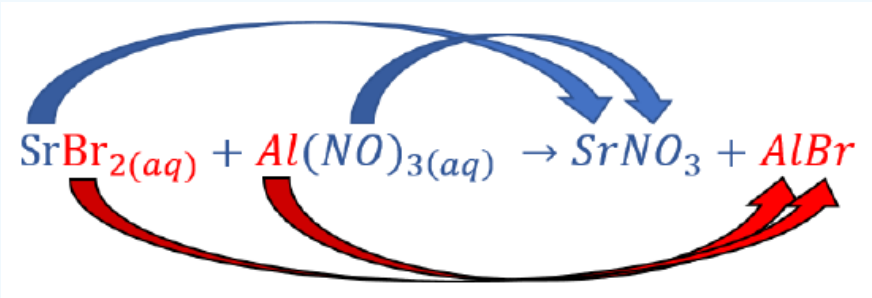
| Steps | Example |
|---|---|
| Change the partners of the anions and cations on the reactant side to form new compounds (products). |  Chemical equation of the reactants rubidium hydroxide and cobalt(II) chloride forming the products rubidium chloride and cobalt hydroxide. |
| Correct the formulas of the products based on the charges of the ions. | $\mathrm{RbOH\,(aq) + CoCl_2\,(aq) \rightarrow RbCl + Co(OH)_2}$ |
| Refer to the solubility rules table to determine insoluble products which will therefore form a precipitate. | $\mathrm{RbOH\,(aq) + CoCl_2\,(aq) \rightarrow RbCl\,(aq) + Co(OH)_2\,(s)}$ |
| Balance the equation. | Coefficients already balanced. $\mathrm{RbOH\,(aq) + CoCl_2\,(aq) \rightarrow RbCl\,(aq) + Co(OH)_2\,(s)}$ |

## Example 12.3.4.2

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

**Solution**

*Solutions for Example 7.6.2*

| Steps | Example |
|---|---|
| Change the partners of the anions and cations on the reactant side to form new compounds (products). |  Chemical equation of the reactants strontium bromide and aluminum nitrate forming the products strontium nitrate and aluminum bromide. |
| Correct the formulas of the products based on the charges of the ions. | $\mathrm{SrBr_2\,(aq) + Al(NO_3)_3\,(aq) \rightarrow Sr(NO_3)_2 + AlBr_3}$ |

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

### Exercise 12.3.4.2

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 available at the end of this section.*

*Answer b available at the end of this section.*

*Answer c available at the end of this section.*

*Answer d available at the end of this section.*

## 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

- Modified by Joshua Halpern (Howard University)

### Answers

**Exercise** 12.3.4.2
$Fe(OH)_2$ precipitate is formed.

**Exercise** 12.3.4.2
$Hg_3(PO_4)_2$ precipitate is formed.

**Exercise** 12.3.4.2
No Reaction.

**Exercise** 12.3.4.2
$CaCO_3$ is precipitate formed.

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# 12.3.5: Writing Chemical Equations for Reactions in Solution- Molecular, Complete Ionic, and Net Ionic Equations

A typical precipitation reaction occurs when an aqueous solution of barium chloride is mixed with one containing sodium sulfate. The **complete chemical equation** can be written to describe what happens, and such an equation is useful in making chemical calculations.

$$\underbrace{\mathrm{BaCl_2\,(aq) + Na_2SO_4\,(aq) \longrightarrow BaSO_4\,(s) + 2\,NaCl\,(aq)}}_{\text{Complete Chemical Equation}} \tag{12.3.5.1}$$

However, Equation 12.3.5.1 does not really represent the microscopic particles (that is, the ions) present in the solution. Below is the complete ionic equation:

$$\underbrace{\mathrm{Ba^{2+}\,(aq) + \overbrace{2Cl^-(aq)}^{\text{spectator}} + \overbrace{2Na^+(aq)}^{\text{spectator}} + {SO_4}^{2-}\,(aq) \longrightarrow BaSO_4\,(s) + \overbrace{2Na^+(aq)}^{\text{spectator}} + \overbrace{Cl^-(aq)}^{\text{spectator}}}}_{\text{Complete Ionic Equation}} \tag{12.3.5}$$

Equation 12.3.5.2 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 12.3.5.2. These ions are called **spectator ions** because they do not participate in the reaction. When we want to emphasize the independent behavior of ions, a **net ionic equation** is written, omitting the spectator ions. For precipitation of $\mathrm{BaSO_4}$ the net ionic equation is

$$\underbrace{\mathrm{Ba^{2+}\,(aq) + {SO_4}^{2-}\,(aq) \longrightarrow BaSO_4\,(s)}}_{\text{Net Ionic Equation}} \tag{12.3.5.3}$$

## Example 12.3.5.1

a. When a solution of $\mathrm{AgNO_3}$ is added to a solution of $\mathrm{CaCl_2}$, insoluble $\mathrm{AgCl}$ 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 12.3.5.1$a$ | Example 12.3.5.1$b$ |
|---|---|---|
| Complete Chemical Equation | $\mathrm{2\,AgNO_3\,(aq) + CaCl_2\,(aq) \longrightarrow\ 2\,AgCl\,(s) + Ca(NO_3)_2\,(aq)}$<br>The proper states and formulas of all products are written and the chemical equation is balanced. | $\mathrm{Na_2SO_4\,(aq) + 2\,NH_4I\,(aq) \longrightarrow 2\,NaI\,(aq) + (NH_4)_2SO_4\,(aq)}$<br>Both products are aqueous so there is no net ionic equation that can be written. |
| Complete Ionic Equation | $\mathrm{2\,Ag^+\,(aq) + 2\,{NO_3}^-\,(aq) + Ca^{2+}\,(aq) + 2\,Cl^-\,(aq) \longrightarrow 2\,AgCl\,(s) + Ca^{2+}\,(aq) + 2\,{NO_3}^-\,(aq)}$<br>AgCl is a solid so it does not break up into ions in solution. | |

| Equation Type | Example 12.3.5.1$a$ | Example 12.3.5.1$b$ |
|---|---|---|
| Net Ionic Equation | $Ag^+(aq) + Cl^-(aq) \longrightarrow AgCl(s)$<br>All spectator ions are removed.<br>The chemical equation is written using the lowest common coefficients. | $NaI$ and $(NH_4)_2SO_4$ are both soluble.<br>No net ionic equation.<br>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 12.3.5.1: 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 12.3.5.1). 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 12.3.5.1

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 available at the end of this section.*

*Answer b available at the end of this section.*

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.

### Answers

**Exercise** 12.3.5.1

$$\mathrm{Sr^{2+}(aq) + CO_3{}^{2-}(aq) \longrightarrow SrCO_3(s)}$$

**Exercise** 12.3.5.1

$$\mathrm{Ba^{2+}(aq) + SO_4{}^{2-}(aq) \longrightarrow Ba(SO_4)(s)}$$

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# 12.3.6: Solutions of Gases in Water

## Learning Objectives

- Explain how temperature and pressure affect the solubility of gases.

In an earlier module of this chapter, the effect of intermolecular attractive forces on solution formation was discussed. The chemical structures of the solute and solvent dictate the types of forces possible and, consequently, are important factors in determining solubility. For example, under similar conditions, the water solubility of oxygen is approximately three times greater than that of helium, but 100 times less than the solubility of chloromethane, $CHCl_3$. Considering the role of the solvent's chemical structure, note that the solubility of oxygen in the liquid hydrocarbon hexane, $C_6H_{14}$, is approximately 20 times greater than it is in water.

Other factors also affect the solubility of a given substance in a given solvent. Temperature is one such factor, with gas solubility typically decreasing as temperature increases (Figure 12.3.6.1). This is one of the major impacts resulting from the thermal pollution of natural bodies of water.

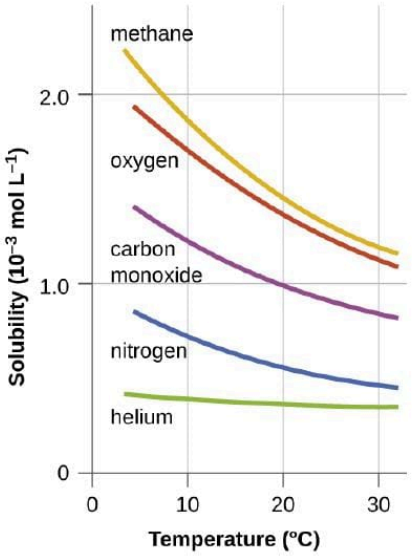



Figure 12.3.6.1: The solubilities of these gases in water decrease as the temperature increases. All solubilities were measured with a constant pressure of 101.3 kPa (1 atm) of gas above the solutions.

When the temperature of a river, lake, or stream is raised abnormally high, usually due to the discharge of hot water from some industrial process, the solubility of oxygen in the water is decreased. Decreased levels of dissolved oxygen may have serious consequences for the health of the water's ecosystems and, in severe cases, can result in large-scale fish kills (Figure 12.3.6.2).




Figure 12.3.6.2: (a) The small bubbles of air in this glass of chilled water formed when the water warmed to room temperature and the solubility of its dissolved air decreased. (b) The decreased solubility of oxygen in natural waters subjected to thermal pollution can result in large-scale fish kills. (Credit a: modification of work by Liz West; credit b: modification of work by U.S. Fish and Wildlife Service.)

The solubility of a gaseous solute is also affected by the partial pressure of solute in the gas to which the solution is exposed. Gas solubility increases as the pressure of the gas increases. Carbonated beverages provide a nice illustration of this relationship. The carbonation process involves exposing the beverage to a relatively high pressure of carbon dioxide gas and then sealing the beverage container, thus saturating the beverage with $CO_2$ at this pressure. When the beverage container is opened, a familiar hiss is heard as the carbon dioxide gas pressure is released, and some of the dissolved carbon dioxide is typically seen leaving solution in the form of small bubbles (Figure 12.3.6.3). At this point, the beverage is *supersaturated* with carbon dioxide and, with time, the dissolved carbon dioxide concentration will decrease to its equilibrium value and the beverage will become "flat."

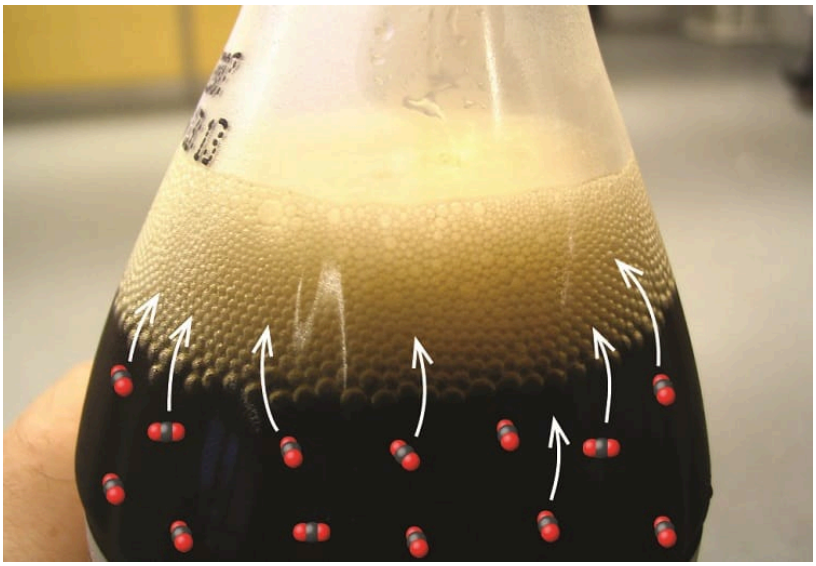


Figure 12.3.6.3: Opening the bottle of carbonated beverage reduces the pressure of the gaseous carbon dioxide above the beverage. The solubility of $CO_2$ is thus lowered, and some dissolved carbon dioxide may be seen leaving the solution as small gas bubbles. A dark brown liquid is shown in a clear, colorless container. A thick layer of beige bubbles appear at the surface of the liquid. In the liquid, thirteen small clusters of single black spheres with two red spheres attached to the left and right are shown. Red spheres represent oxygen atoms and black represent carbon atoms. Seven white arrows point upward in the container from these clusters to the bubble layer at the top of the liquid. (Credit: modification of work by Derrick Coetzee.)

"Fizz"

The dissolution in a liquid, also known as fizz, usually involves carbon dioxide under high pressure. When the pressure is reduced, the carbon dioxide is released from the solution as small bubbles, which causes the solution to become effervescent, or fizzy. A common example is the dissolving of carbon dioxide in water, resulting in carbonated water.

Carbon dioxide is weakly soluble in water, therefore it separates into a gas when the pressure is released. This process is generally represented by the following reaction, where a pressurized dilute solution of carbonic acid in water releases gaseous carbon dioxide at decompression:

$$\mathrm{H_2CO_3\,(aq) \longrightarrow H_2O\,(l) + CO_2\,(g)}$$

In simple terms, it is the result of the chemical reaction occurring in the liquid which produces a gaseous product.

For many gaseous solutes, the relation between solubility, $C_g$, and partial pressure, $P_g$, is a proportional one:

$$C_\mathrm{g} = kP_\mathrm{g}$$

where *k* is a proportionality constant that depends on the identities of the gaseous solute and solvent, and on the solution temperature. This is a mathematical statement of Henry's law: *The quantity of an ideal gas that dissolves in a definite volume of liquid is directly proportional to the pressure of the gas.*

## Example 12.3.6.1: Application of Henry's Law

At 20 °C, the concentration of dissolved oxygen in water exposed to gaseous oxygen at a partial pressure of 101.3 kPa (760 torr) is $1.38 \times 10^{-3}$ mol $L^{-1}$. Use Henry's law to determine the solubility of oxygen when its partial pressure is 20.7 kPa (155 torr), the approximate pressure of oxygen in earth's atmosphere.

**Solution**

According to Henry's law, for an ideal solution the solubility, $C_g$, of a gas ($1.38 \times 10^{-3}$ mol $L^{-1}$, in this case) is directly proportional to the pressure, $P_g$, of the undissolved gas above the solution (101.3 kPa, or 760 torr, in this case). Because we know both $C_g$ and $P_g$, we can rearrange this expression to solve for *k*.

$$\begin{aligned} C_\mathrm{g} &= kP_\mathrm{g} \\ k &= \frac{C_\mathrm{g}}{P_\mathrm{g}} \\ &= \frac{1.38 \times 10^{-3}\ \mathrm{mol\ L^{-1}}}{101.3\ \mathrm{kPa}} \\ &= 1.36 \times 10^{-5}\ \mathrm{mol\ L^{-1}\ kPa^{-1}} \\ &\quad (1.82 \times 10^{-6}\ \mathrm{mol\ L^{-1}\ torr^{-1}}) \end{aligned}$$

Now we can use *k* to find the solubility at the lower pressure.

$$C_\mathrm{g} = kP_\mathrm{g}$$

$$\begin{gathered} 1.36 \times 10^{-5}\ \mathrm{mol\ L^{-1}\ kPa^{-1}} \times 20.7\ \mathrm{kPa} \\ (\mathrm{or}\ 1.82 \times 10^{-6}\ \mathrm{mol\ L^{-1}\ torr^{-1}} \times 155\ \mathrm{torr}) \\ = 2.82 \times 10^{-4}\ \mathrm{mol\ L^{-1}} \end{gathered}$$

Note that various units may be used to express the quantities involved in these sorts of computations. Any combination of units that yield to the constraints of dimensional analysis are acceptable.

## Exercise 12.3.6.1

A 100.0 mL sample of water at 0 °C to an atmosphere containing a gaseous solute at 20.26 kPa (152 torr) resulted in the dissolution of $1.45 \times 10^{-3}$ g of the solute. Use Henry's law to determine the solubility of this gaseous solute when its pressure is 101.3 kPa (760 torr).

*Answer available at the end of this section.*

## Case Study: Decompression Sickness ("The Bends")

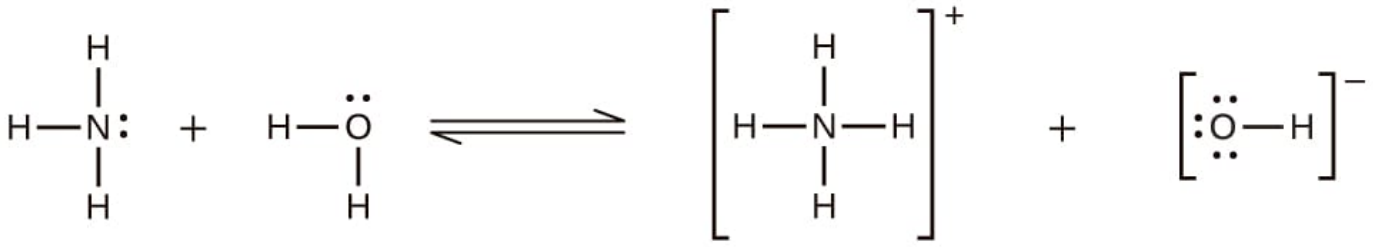
Decompression sickness (DCS), or "the bends," is an effect of the increased pressure of the air inhaled by scuba divers when swimming underwater at considerable depths. In addition to the pressure exerted by the atmosphere, divers are subjected to additional pressure due to the water above them, experiencing an increase of approximately 1 atm for each 10 m of depth. Therefore, the air inhaled by a diver while submerged contains gases at the corresponding higher ambient pressure, and the concentrations of the gases dissolved in the diver's blood are proportionally higher per Henry's law.

As the diver ascends to the surface of the water, the ambient pressure decreases and the dissolved gases becomes less soluble. If the ascent is too rapid, the gases escaping from the diver's blood may form bubbles that can cause a variety of symptoms ranging from rashes and joint pain to paralysis and death. To avoid DCS, divers must ascend from depths at relatively slow speeds (10 or 20 m/min) or otherwise make several decompression stops, pausing for several minutes at given depths during the ascent. When these preventative measures are unsuccessful, divers with DCS are often provided hyperbaric oxygen therapy in pressurized vessels called decompression (or recompression) chambers (Figure 12.3.6.4).




Figure 12.3.6.4: (a) US Navy divers undergo training in a recompression chamber. (b) Divers receive hyperbaric oxygen therapy. Two photos are shown. The first shows two people seated in a steel chamber on benches that run length of the chamber on each side. The chamber has a couple of small circular windows and an open hatch-type door. One of the two people is giving a thumbs up gesture. The second image provides a view through a small, circular window. Inside the two people can be seen with masks over their mouths and noses. The people appear to be reading.

Deviations from Henry's law are observed when a chemical reaction takes place between the gaseous solute and the solvent. Thus, for example, the solubility of ammonia in water does not increase as rapidly with increasing pressure as predicted by the law because ammonia, being a base, reacts to some extent with water to form ammonium ions and hydroxide ions.



This reaction diagram shows three H atoms bonded to an N atom above, below, and two the left of the N. A single pair of dots is present on the right side of the N. This is followed by a plus, then two H atoms bonded to an O atom to the left and below the O. Two pairs of dots are present on the O, one above and the other to the right of the O. A double arrow, with a top arrow pointing right and a bottom arrow pointing left follows. To the right of the double arrow, four H atoms are shown bonded to a central N atom. These 5 atoms are enclosed in brackets with a superscript plus outside. A plus follows, then an O atom linked by a bond to an H atom on its right. The O atom has pairs of dots above, to the left, and below the atom. The linked O and H are enclosed in brackets with superscript minus outside.

Gases can form supersaturated solutions. If a solution of a gas in a liquid is prepared either at low temperature or under pressure (or both), then as the solution warms or as the gas pressure is reduced, the solution may become supersaturated.

## Contributions & Attributions

- Wikipedia
- 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).

### Answers

**Exercise** 12.3.6.1

$7.25 \times 10^{-3}$ g

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# 12.4: CONCENTRATIONS AND DILUTION



- Topic hierarchy


12.4.1: Concentration of solutions

12.4.2: Concentrations as Conversion Factors

12.4.3: Solution Stoichiometry


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# 12.4.1: Concentration of solutions

The concentration of a solution tells the amount of solute dissolved in a given amount of solution.

## Making a solution of know concentration

A measured amount of solute is dissolved in enough solvent to make the desired volume of the solution, as illustrated in Fig. 5.4.1. The concentration of the solution can be expressed in different ways using mass, volume, or mole units, as explained in the following.

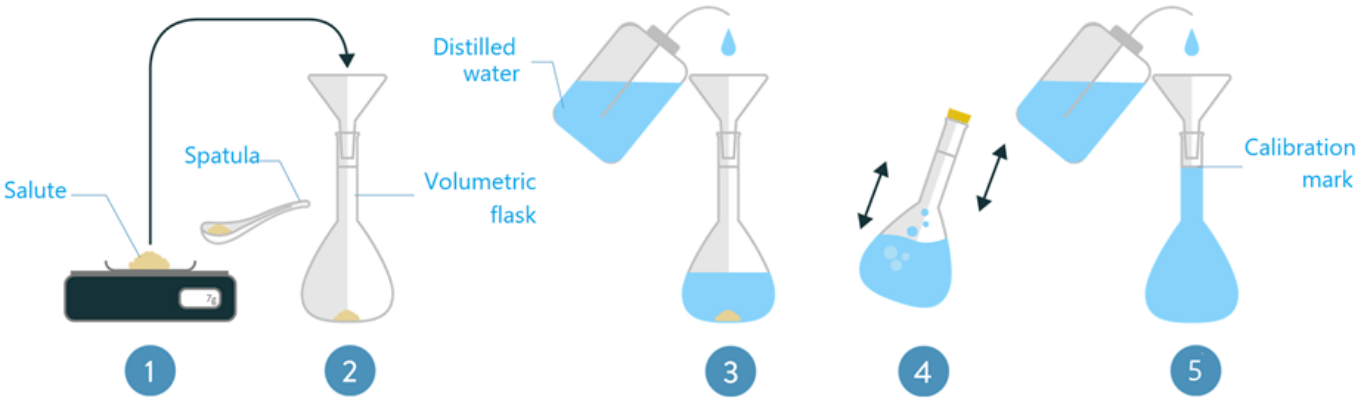



Figure 12.4.1.1: Making an aqueous solution: 1) measure the mass of the solute on an analytical balance, 2) pour the solute into a volumetric flask of know volume, 3) add distilled water (or solvent) to more than half fill the flask, 4) stopper the flask and shake it to dissolve the solute, 5) add more water to fill the flask to the calibration mark –measure from the lowest point of the water meniscus, 6) stopper the flask and shake again to make a homogeneous solution. Source: modified from https://www.hiclipart.com/free-trans...cvcrq/download

## Concentration in percent (%)

### What is percent (%)

Percentage (%) is a number or ratio that represent a fraction of 100.

For example, 5% means 5:100, where 5 is the part, and 100 is the total. The percentage is calculated as a hundred times of part by total, i.e.,

$$\text{Percentage } (\%) = \frac{\text{part}}{\text{Total}} \times 100.$$

### Example 12.4.1.1

A 50.0 g NaCl is dissolved in water to make a 500 g solution. What is the percentage of NaCl in the solution?

**Solution**

Given part = 50.0 g NaCl, and total = 500 g solution. Desired: %NaCl in the solution?

Formula: $\text{Percentage } (\%) = \frac{\text{part}}{\text{Total}} \times 100.$

Calculations: $\text{Percentage } (\%) = \frac{50.0 cancel\ g}{500 cancel\ g} \times 100 = 10.0\ \%\text{NaCl}$

The units cancel in the fraction calculation part, and a % sign is added to the answer to tell that it is a fraction out of a hundred.

## Mass percent (m/m)% concentration

The mass percent concentration expresses the mass units of solute in a hundred mass units of the solution.

$$\text{Mass}(\%) = \frac{\text{mass of solute } (g)}{\text{mass of solute } (g) + \text{ mass of solvent } (g)} \times 100 = \frac{\text{mass of solute } (g)}{\text{mass of solution } (g)} \times 100$$

Note that the total is solute and solvent added together, i.e., solution.

### Example 12.4.1.2

What is the mass % of NaOH in a solution prepared by dissolving 10.0 g NaOH in 100 g water?

**Solution**

Given solute = 10.0 g, and solvent = 100 g, Desired: Mass% NaOH?

Formula: $\text{Mass } (\%) = \frac{\text{mass of solute } (g)}{\text{mass of solute } (g) + \text{ mass of solvent } (g)} \times 100$

Calculations: $\text{Mass } (\%) = \frac{10.0 \text{ gNaOH}}{(10.0 \text{ g} + 100 \text{ g}) \text{ solution}} \times 100 = 9.09\%\text{NaOH}$

Note that the mass% concentration and its reciprocal are two conversion factor: $\frac{\text{given } g \text{ solute}}{100 g \text{ solution}}$ and $\frac{100 g \text{ solution}}{\text{given g solute}}$

### Example 12.4.1.3

Neosporin antibiotic is a 3.5% m/m neomycin solution. How many grams of neomycin are in 50 g of ointment?

**Solution**

Given: $3.5\% \text{ neomycin } = \frac{3.5 \text{ g neomycin}}{100 \text{ g solution}}$, and Solution amount = 50 g, Desired: ? g neomycin

Calculations:

$$50 \cancel{\text{ g solution}} \times \frac{3.5 \text{ g neomycin}}{100 \cancel{\text{ g solution}}} = 1.8 \text{ g neomycin.}$$

## Volume percent (v/v)% concentration

The volume percent concentration expresses the volume units of solute in a hundred volume units of the solution.

The mathematical form of the v/v % is:

$$\text{Volume } (\%) = \frac{\text{volume of solute (mL)}}{\text{volume of solution (mL)}} \times 100$$

Fig. 5.4.2 shows the volume percent concentration ranges of different classes of fragrances.

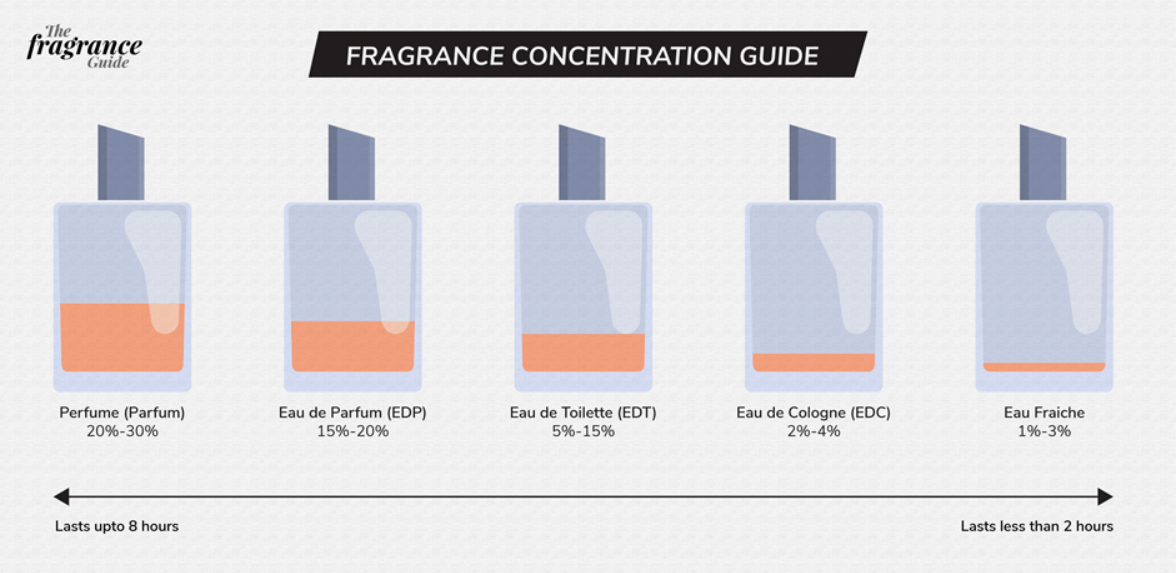



Figure 12.4.1.2: This info-graphic explains the differences between Parfums, Perfumes, Eau de Perfume, Eau de Parfum, Eau de Toilette, and Cologne. It also gives an approximate idea of how the concentration of Parfum oils vary as we move to lighter scents. Source: Nicole Smith / CC BY-SA (https://creativecommons.org/licenses/by-sa/4.0)

## Example 12.4.1.4

What is the volume % of rose extract in a solution prepared by dissolving 14.0 mL rose extract in a solvent to make 200 mL of solution?

**Solution**

Given: Solute = 14.0 g, and solution = 200 g, Desired: Volume% rose solution?

Formula:

$$\text{Volume } (\%) = \frac{\text{volume of solute } (mL)}{\text{volume of solution } (mL)} \times 100$$

Calculations:

$$\text{Volume } (\%) = \frac{14 \text{ mL rose extract}}{200 \text{ mL solution}} \times 100 = 7.0\% \text{ rose solution}$$

The two conversion factors for v/v % concentration are:

$$\frac{\text{given mL solute}}{100 \text{ mL solution}} \quad \text{, and} \quad \frac{100 \text{ mL solution}}{\text{given mL solute}}$$

## Example 12.4.1.5

What is the volume of bromine ($Br_2$) in 250 mL of 4.8% v/v of $Br_2$ solution in carbon tetrachloride?

**Solution**

Given: Concentration 4.8% v/v bromine $= \frac{4.8\ mL \text{ bromine}}{100\ mL \text{ solution}}$, volume of solution = 250 mL, Desired: Volume of solute, i.e., ? mL bromine.

Calculations:

$$250 \text{ mL solution} \times \frac{4.8 \text{ mL bromine}}{100 \text{ mL solution.}} = 12 \text{ mL bromine.}$$

## Mass/volume percent (m/v)% concentration

The mass/volume percent concentration expresses the mass units of solute in a hundred volume units of solution.

Mathematical form of m/v % is:

$$\text{Mass/volume } (\%) = \frac{\text{mass of solute } (g)}{\text{volume of solution } (mL)} \times 100$$

### Example 12.4.1.6

What is the mass/volume % of glucose solution prepared by dissolving 50 g glucose in enough water to make 1000 mL of solution?

**Solution**

Given: Solute = 50.0 g, and Solution = 1000 mL, Desired: Mass/volume % glucose solution?

Formula:

$$\text{Mass/volume } (\%) = \frac{\text{mass of solute } (g)}{\text{volume of solution } (mL)} \times 100$$

Calculations:

$$\frac{\text{Mass}}{\text{volume}}(\%) = \frac{50 \text{ g glucose}}{1000 \text{ mL solution}} \times 100 = 5.0\% \text{ glucose solution by } \frac{\text{m}}{\text{v}}.$$

The two conversion factors from ms/v % concentration are:

$$\frac{\text{given } g \text{ solute}}{100 \text{ mL solution}} \quad \text{and} \quad \frac{100 \text{ mL solution}}{\text{given g solute}}$$

### Example 12.4.1.7

How many grams of clindamycin antibiotics are in a 45 mL capsule of the 1.0% (m/v) clindamycin?

**Solution**

Given: % m/v concentration: 1.08 % m/v clindamycin $= \frac{1.0 \text{ g clindamycin}}{100 \text{ mL solution}}$, and volume of solution = 45 mL, Desired: ? g clindamycin?

Calculations:

$$45 \text{ mL solution} \times \frac{1.0 \text{ g clindamycin}}{100 \text{ mL solution}} = 4.5 \text{ g clindamycin.}$$

## Parts per million (ppm) and parts per billion (ppb) concentration

Parts per million (ppm) is a number or ratio expressed as a fraction of a million ($10^6$).

For example, 2 ppm means $\frac{2}{1{,}000{,}000}$ or 2:1,000,000, where 2 is the part, and 1,000,000 is the total. The concentration in ppm is

calculated as a million times of part by total, i.e.:

$$\text{Concentration in ppm } = \frac{part}{\text{Total}} \times 10^6$$

Parts per billion (ppb) is a number or ratio expressed as a fraction of billion ($10^9$).

That is:

$$\text{Concentration in ppb } = \frac{\text{part}}{\text{Total}} \times 10^9$$

Like percentage concentration, the ppm and ppb can be mass/mass (m/m), volume/volume (v/v) or mass/volume (m/v).

## Example 12.4.1.8

EPA's action limit for copper is 1.3 mg/L in drinking water. What is this limit in ppm of copper m/v in the drinking water?

**Solution**

Given: 1.3 mg copper in 1L solution, Desired: ? ppm m/v of Copper in water

Formula: $\text{Concentration in ppm } = \frac{\text{solute( g)}}{\text{solution( mL)}} \times 10^6$

Calculations: First, convert the given units of mass and volume into the corresponding units that the formula takes, then plug the values in the formula and calculate.

$$\text{Solute } = 1.3 \text{ mg} \times \frac{1 \text{ g}}{1000 \text{ mg}} = 0.0013 \text{ g}$$

$$\text{Solution } = 1 \text{ L} \times \frac{1000 \text{ mL}}{1 \text{ L}} = 1000 \text{ mL}$$

$$\text{Concentration in ppm } = \frac{0.0013 \text{ g}}{1000 \text{ mL}} \times 10^6 = 1.3 \text{ ppm copper } v/\text{m}$$

## Example 12.4.1.9

EPA's action limit for lead is 0.015 mg/L in drinking water. What is this limit in ppb of lead m/v in the drinking water?

**Solution**

Given: 0.015 mg in 1L solution, Desired: ? ppb m/v of Lead in water

Formula: $\text{Concentration in ppb } = \frac{\text{solute}(g)}{\text{solution}(\text{mL})} \times 10^9$

Calculations: First, convert the given units of mass and volume into the corresponding units that the formula takes, then plug the values in the formula and calculate.

$$\text{Solute } = 0.015 \text{ mg} \times \frac{1 \text{ g}}{1000 \text{ mg}} = 0.000015 \text{ g}$$

$$\text{Solution } = 1 \text{ L} \times \frac{1000 \text{ mL}}{1 \text{ L}} = 1000 \text{ mL}$$

$$\text{Concentration in ppb } = \frac{0.000015 \text{ g}}{1000 \text{ mL}} \times 10^9 = 15 \text{ ppb lead v/m}$$

# Molarity

Molarity (M) expresses the moles of solute in a liter of solution.

The most common solution concentration unit used in chemistry is molarity (M):

$$\text{Molarity } (M) = \frac{n \text{ (moles of solute )}}{V \text{ (Litters of solution )}}$$

## Example 12.4.1.10

What is the molarity (M) of a solution prepared by dissolving 50.0 g NaOH in enough water to make 250 mL solution?

**Solution**

Given: Solute = 50.0 g NaOH, Volume of solution = 250 mL, Desired: ? M NaOH solution?

Formula: $\text{Molarity } (M) = \frac{n \text{ (moles of solute )}}{V \text{ (Litters of solution )}}$

Calculations: First, convert the given units of mass and volume into the corresponding units that the formula takes, then plug the values in the formula and calculate.

$$\text{Solute } = 50.0 \text{ g NaOH} \times \frac{1 \text{ mol NaOH}}{40.00 \text{ g NaOH}} = 1.25 \text{ mol NaOH}$$

$$\text{Solution } = 250 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}} = 0.250 \text{ L}$$

$$\text{Molarity } (M) = \frac{1.25 \text{ mol NaOH}}{0.250 \text{ L solution}} = 5.00 \text{ M NaOH}$$

The two conversion factor from molarity are the following:

$$\frac{n \text{ (moles of solute)}}{V \text{ (Litters of solution)}} \quad \text{and} \quad \frac{V \text{ (Litters of solution)}}{n \text{ (moles of solute )}}$$

## Example 12.4.1.11

How many litters of 0.211 M HCl solution are needed to provide 0.400 mol of HCl?

**Solution**

Given: amount of solute = 0.400 mol HCl, Concentration of solute = 0.211M = $\frac{0.211 \text{ mol HCl}}{1L \text{ solution}}$

Calculations:

$$\text{Liters of solution needed } = 0.400 \text{ mol HCl} \times \frac{1 \text{ L soluton}}{0.211 \text{ mol HCl}} = 1.90 \text{ L solution}$$

## Example 12.4.1.12

A 2.50 L of 1.12 M NaOH solution contains how many moles of NaOH?

**Solution**

Given: Volume of solution = 2.50 L solution, concentration of solution = $1.12\ \text{M NaOH} = \frac{1.12\ \text{mol NaOH}}{1\ \text{L solution}}$, Desired: ? moles of NaOH?

Calculations:

$$\text{Moles of NaOH in the solution} = 2.50\ \text{L solution} \times \frac{1.12\ \text{mol NaOH}}{1\ \text{L solution}} = 2.80\ \text{mol NaOH}$$

## Dilution of solutions

Dilution of a solution is the addition of a solvent to decrease the solute concentration of the solute in the solution.

The product of concentration (C) and volume (V) is the amount of solute, i.e.,

$$\text{Amount of solute} = C \text{ in } \frac{\text{amount of solute}}{\text{volume of solution}} \times V \text{ in volume of solution.}$$

The amount of solute does not change by adding solvent. Therefore, the product of concentration and volume, i.e., CV, which is the amount of solute, is a constant, i.e.,

$$C_1V_1 = C_2V_2 = \text{amount of solute}$$

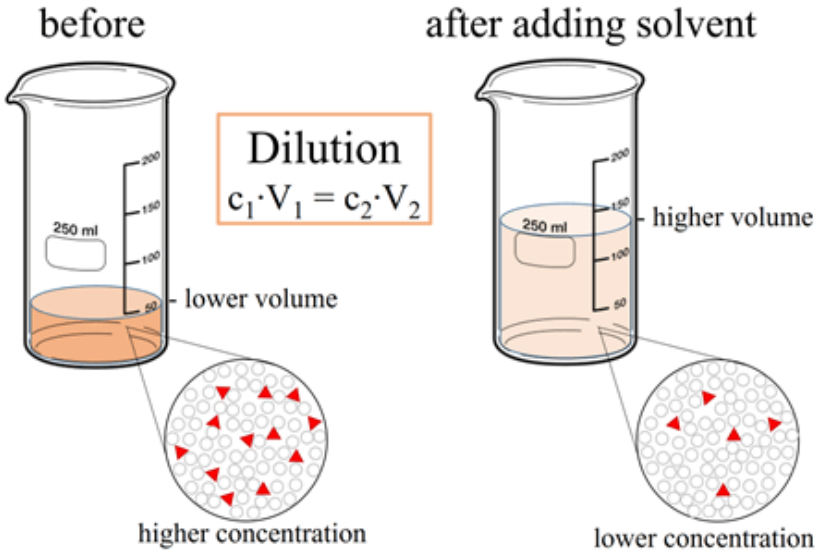



Figure 12.4.1.3: This image illustrates that when more solvent is mixed with the solution, the amount of solute remains the same, but its concentration decreases. Source: Theislikerice / CC BY-SA (https://creativecommons.org/licenses/by-sa/4.0)

Fig. 5.4.3 shows that if the initial concentration is $C_1$, the initial volume is $V_1$, and after dilution, the final concentration is $C_2$, the final volume is $V_2$, then $C_1V_1 = C_2V_2$ = amount of solute that is constant. If three of the four variables in this equation are known, the missing one can be calculated, as explained in the following example.

**Caution**

Keep in mind that the concentrations and volumes should be in the same units on both sides of the equation: $C_1V_1 = C_2V_2$. If they are not in the same units, convert them to the same units before plunging them in the formula.

**Example 12.4.1.13**

how much volume of 11.3 M HCl is needed to prepare 250 mL of 2.00 M HCl?

**Solution**

Given: $C_1$ = 11.3 M HCl, $C_2$ = 2.00 M HCl, $V_2$ = 250 mL solution, Desired $V_1$ = ?

Formula: $C_1V_1 = C_2V_2$, rearrange it to isolate the desired parameter: $V_1 = \frac{C_2V_2}{C_1}$

Calculations:

$$V_1 = \frac{C_2V_2}{C_1} = \frac{2.00 \text{ M HCl} \times 250 \text{ mL solution}}{11.3 \text{ M HCl}} = 44.2 \text{ mL solution}$$

**Example 12.4.1.14**

what is the molarity of the NaOH solution prepared by diluting 100 mL of 0.521 M NaOH solution to 500 mL?

**Solution**

Given $C_1$ = 0.521 M NaOH, $V_1$ = 100 mL solution, $V_2$ = 500 mL solution, Desired: Concentration of the final solution $C_2$ = ? M NaOH

Formula: $C_1V_1 = C_2V_2$, rearrange to isolate the desired parameter: $C_2 = \frac{C_1V_1}{V_2}$

Calculations:

$$C_2 = \frac{C_1V_1}{V_2} = \frac{0.521 \text{ M NaOH} \times 100 \text{ mL NaOH}}{500 \text{ mL NaOH}} = 0.104 \text{ M NaOH}$$

**Example 12.4.1.15**

Dopamine is administered intravenously to a patient to increase blood pressure. How many milliliters (mL) of a 4.0% (m/v) dopamine solution is needed to prepare 250 mL of a 0.030% m/v) solution?

**Solution**

Given: $C_1$ = 4.0% (m/v), $C_2$ = 0.030% (m/v), $V_2$ = 250 mL solution, Desired $V_1$= ?

Formula: $C_1V_1 = C_2V_2$, rearrange to isolate the desired parameter: $V_1 = \frac{C_2V_2}{C_1}$

Calculations:

$$V_1 = \frac{C_2V_2}{C_1} = \frac{0.030\% \times 250 \text{ mL solution}}{4.0\%} = 5.0 \text{ mL of solution}$$

## Logarithmic dilution

> Take a unit volume of a given solution and add enough solvent to increase the volume of the solution 10 times for a logarithmic diluiton.

A logarithmic dilution is ten times dilution, i.e., proven by the following formula:

$$C_2 = \frac{C_1V_1}{V_2} = \frac{1 \text{ mL} \times C_1}{10 \text{ mL}} = 0.1 \times C_1$$

Repeating the above step with the diluted solution results in 10x10 = 100-time dilution, and repeating third-time results in 10x10x10 = 1000-time dilution. This dilution of 10 times in each step is called logarithmic dilution. Fig. 5.4.4 shows that five steps of logarithmic dilution on a 10% initial solution results in a concentration of 10 ppm in the final solution.

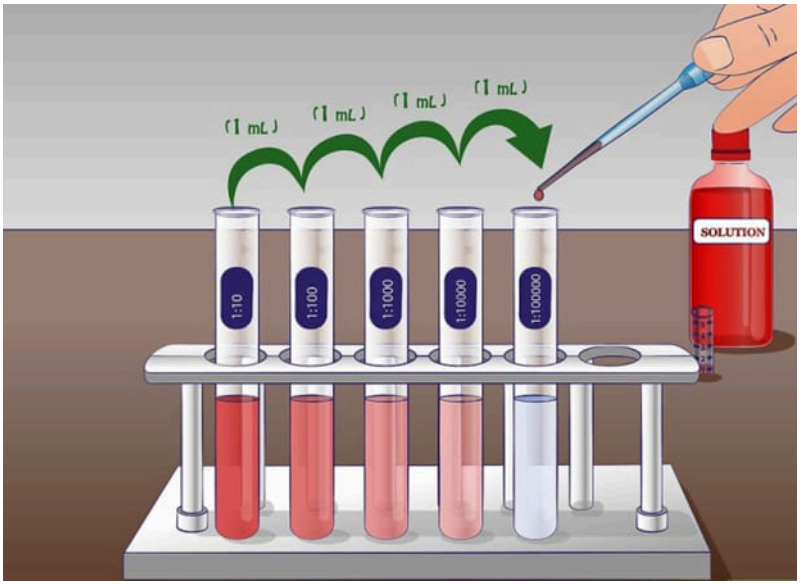



Figure 12.4.1.4: Logarithmic dilution: five steps of logarithmic dilution on a 10% initial solution results in a concentration of 10 ppm of the final solution. Source: Grasso Luigi / CC BY-SA (https://creativecommons.org/licenses/by-sa/4.0)

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# 12.4.2: Concentrations as Conversion Factors

## Learning Objective

- Apply concentration units as conversion factors.

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

A simple example of using a concentration unit as a conversion factor is one in which we use the definition of the concentration unit and rearrange; we can do the calculation again as a unit conversion, rather than as a definition. For example, suppose we ask how many moles of solute are present in 0.108 L of a 0.887 M NaCl solution. Because 0.887 M means 0.887 mol/L, we can use this second expression for the concentration as a conversion factor:

$$0.108 \cancel{L\,NaCl} \times \frac{0.887\,mol\,NaCl}{\cancel{L\,NaCl}} = 0.0958\,mol\,NaCl$$

(There is an understood 1 in the denominator of the conversion factor.) If we used the definition approach, we get the same answer, but now we are using conversion factor skills. Like any other conversion factor that relates two different types of units, the reciprocal of the concentration can be also used as a conversion factor.

## Example 12.4.2.1

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

**Solution**

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

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

## Exercise 12.4.2.1

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

*Answer: available at the end of this section.*

Of course, once quantities in moles are available, another conversion can give the mass of the substance, using molar mass as a conversion factor.

## Example 12.4.2.2

What mass of solute is present in 0.765 L of 1.93 M NaOH?

**Solution**

This is a two-step conversion, first using concentration as a conversion factor to determine the number of moles and then the molar mass of NaOH (40.0 g/mol) to convert to mass:

$$0.765 \cancel{L} \times \frac{1.93 \cancel{mol\ NaOH}}{\cancel{L\ solution}} \times \frac{40.0 g\ NaOH}{1 \cancel{mol\ NaOH}} = 59.1\ g\ NaOH$$

### Exercise 12.4.2.2

What mass of solute is present in 1.08 L of 0.0578 M $H_2SO_4$?

*Answer available at the end of this section.*

More complex stoichiometry problems using balanced chemical reactions can also use concentrations as conversion factors. For example, suppose the following equation represents a chemical reaction:

$$2\,AgNO_3\,(aq) + CaCl_2\,(aq) \longrightarrow 2\,AgCl\,(s) + Ca(NO_3)_2\,(aq)$$

If we wanted to know what volume of 0.555 M $CaCl_2$ would react with 1.25 mol of $AgNO_3$, we first use the balanced chemical equation to determine the number of moles of $CaCl_2$ that would react and then use concentration to convert to liters of solution:

$$1.25 \cancel{mol\ AgNO_3} \times \frac{1 \cancel{mol\ CaCl_2}}{2 \cancel{mol\ AgNO_3}} \times \frac{1L\ solution}{0.555 \cancel{mol\ CaCl_2}} = 1.13\ L\ CaCl_2$$

This can be extended by starting with the mass of one reactant, instead of moles of a reactant.

### Example 12.4.2.3

What volume of 0.0995 M $Al(NO_3)_3$ will react with 3.66 g of Ag according to the following chemical equation?

$$3\,Ag\,(s) + Al(NO_3)_3\,(aq) \longrightarrow 3\,AgNO_3 + Al\,(s)$$

**Solution**

Here, we first must convert the mass of Ag to moles before using the balanced chemical equation and then the definition of molarity as a conversion factor:

$$3.66 \cancel{g\ Ag} \times \frac{1 \cancel{mol\ Ag}}{107.97 \cancel{g\ Ag}} \times \frac{1 \cancel{mol\ Al(NO_3)_3}}{3 \cancel{mol\ Ag}} \times \frac{1L\ solution}{0.0995 \cancel{mol\ Al(NO_3)_3}} = 0.114\ L$$

The strikeouts show how the units cancel.

### Exercise 12.4.2.3

What volume of 0.512 M NaOH will react with 17.9 g of $H_2C_2O_4(s)$ according to the following chemical equation?

$$H_2C_2O_4\,(s) + 2\,NaOH\,(aq) \longrightarrow Na_2C_2O_4\,(aq) + 2\,H_2O(\ell)$$

*Answer: available at the end of this section.*

We can extend our skills even further by recognizing that we can relate quantities of one solution to quantities of another solution. Knowing the volume and concentration of a solution containing one reactant, we can determine how much of another solution of another reactant will be needed using the balanced chemical equation.

## Example 12.4.2.4

A student takes a precisely measured sample, called an *aliquot*, of 10.00 mL of a solution of FeCl3. The student carefully adds 0.1074 M Na2C2O4 until all the $Fe^{3+}$(aq) has precipitated as Fe2(C2O4)3(s). Using a precisely measured tube called a burette, the student finds that 9.04 mL of the Na2C2O4 solution was added to completely precipitate the $Fe^{3+}$(aq). What was the concentration of the FeCl3 in the original solution? (A precisely measured experiment like this, which is meant to determine the amount of a substance in a sample, is called a *titration*.) The balanced chemical equation is as follows:

$$2\,\mathrm{FeCl_3\,(aq)} + 3\,\mathrm{Na_2C_2O_4\,(aq)} \longrightarrow \mathrm{Fe_2(C_2O_4)_3\,(s)} + 6\,\mathrm{NaCl\,(aq)}$$

**Solution**

First we need to determine the number of moles of Na2C2O4 that reacted. We will convert the volume to liters and then use the concentration of the solution as a conversion factor:

$$9.04\,\cancel{mL} \times \frac{1\,\cancel{L}}{1000\,\cancel{mL}} \times \frac{0.1074 mol\,Na_2C_2O_4}{\cancel{L}} = 0.000971\,mol\,Na_2C_2O_4$$

Now we will use the balanced chemical equation to determine the number of moles of $Fe^{3+}$(aq) that were present in the initial aliquot:

$$0.000971\,\cancel{mol\,Na_2C_2O_4} \times \frac{2 mol\,FeCl_3}{3\,\cancel{mol\,Na_2C_2O_4}} = 0.000647 mol\,FeCl_3$$

Then we determine the concentration of FeCl3 in the original solution. Converting 10.00 mL into liters (0.01000 L), we use the definition of molarity directly:

$$M = \frac{mol}{L} = \frac{0.000647 mol\,FeCl_3}{0.01000 L} = 0.0647 M\,FeCl_3$$

## Exercise 12.4.2.4

A student titrates 25.00 mL of H3PO4 with 0.0987 M KOH. She uses 54.06 mL to complete the chemical reaction. What is the concentration of H3PO4?

$$\mathrm{H_3PO_4\,(aq)} + 3\,\mathrm{KOH\,(aq)} \longrightarrow \mathrm{K_3PO_4\,(aq)} + 3\,\mathrm{H_2O}$$

*Answer: available at the end of this section.*

We have used molarity exclusively as the concentration of interest, but that will not always be the case. The next example shows a different concentration unit being used.

## Example 12.4.2.5

H2O2 is used to determine the amount of Mn according to this balanced chemical equation:

$$2\,\mathrm{MnO_4^-\,(aq)} + 5\,\mathrm{H_2O_2\,(aq)} + 6\,\mathrm{H^+\,(aq)} \longrightarrow 2\,\mathrm{Mn_2^+\,(aq)} + 5\,\mathrm{O_2\,(g)} + 8\,\mathrm{H_2O(\ell)}$$

What mass of 3.00% m/m H2O2 solution is needed to react with 0.355 mol of $MnO_4^-$(aq)?

**Solution**

Because we are given an initial amount in moles, all we need to do is use the balanced chemical equation to determine the number of moles of $H_2O_2$ and then convert to find the mass of $H_2O_2$. Knowing that the $H_2O_2$ solution is 3.00% by mass, we can determine the mass of solution needed:

$$0.355 \cancel{mol\ MnO_4^-} \times \frac{5\ \cancel{mol\ H_2O_2}}{2\ \cancel{mol MnO_4^-}} \times \frac{34.02\ \cancel{g\ H_2O_2}}{\cancel{mol\ H_2O_2}} \times \frac{100g\ solution}{3\ \cancel{g\ H_2O_2}} = 1006g\ sol$$

The first conversion factor comes from the balanced chemical equation, the second conversion factor is the molar mass of $H_2O_2$, and the third conversion factor comes from the definition of percentage concentration by mass.

### Exercise 12.4.2.5

Use the balanced chemical reaction for $MnO_4^-$ and $H_2O_2$ to determine what mass of $O_2$ is produced if 258 g of 3.00% m/m $H_2O_2$ is reacted with $MnO_4^-$.

*Answer available at the end of this section.*

## Summary

Know how to apply concentration units as conversion factors.

## Answers

**Exercise** 12.4.2.1
1.74 L

**Exercise** 12.4.2.2
6.12 g

**Exercise** 12.4.2.3
0.777 L

**Exercise** 12.4.2.4
0.0711 M



Figure 12.4.2.1 Titration © Thinkstock. When a student performs a titration, a measured amount of one solution is added to another reactant.

**Exercise** 12.4.2.5
7.28 g

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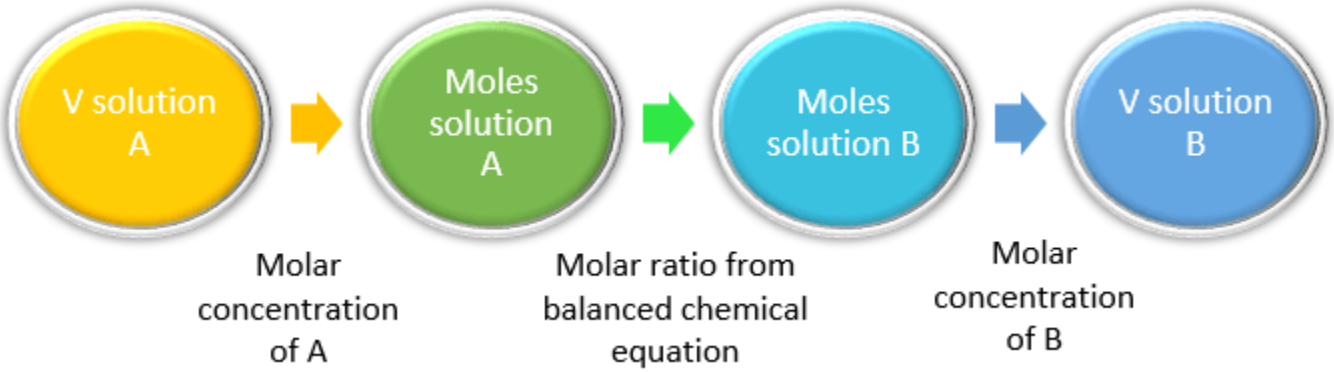
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# 12.4.3: Solution Stoichiometry

## 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.

$$\mathrm{Pb(NO_3)_2\,(aq) + 2\,NaCl\,(aq) \longrightarrow PbCl_2\,(s) + 2\,NaNO_3\,(aq)} \tag{12.4.3.1}$$

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

The molar concentration can also be expressed as the following:

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

and

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

First, we must examine the reaction stoichiometry in the balanced reaction (Equation 12.4.3.1). In this reaction, one mole of $\mathrm{Pb(NO_3)_2}$ reacts with two moles of $\mathrm{NaCl}$ to give one mole of $\mathrm{PbCl_2}$ precipitate. Thus, the concept map utilizing the stoichiometric ratios is:



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

$$0.123\ L\ \text{NaCl solution} \times \frac{1.00\ mol\ \text{NaCl}}{1\ L\ \text{NaCl solution}} \times \frac{1\ mol\ \text{Pb(NO}_3)_2}{2\ mol\ \text{NaCl}} \times \frac{1\ L\ \text{Pb(NO}_3)_2\ \text{solution}}{1.5\ mol\ \text{Pb(NO}_3)_2} = 0.041\ \text{Pb(NO}_3)_2\ L\ \text{solution}$$

This volume makes intuitive sense for two reasons: (1) the number of moles of $\text{Pb(NO}_3)_2$ required is half of the number of moles of $\text{NaCl}$, based off of the stoichiometry in the balanced reaction (Equation 12.4.3.1); (2) the concentration of $\text{Pb(NO}_3)_2$ solution is 50% greater than the $\text{NaCl}$ solution, so less volume is needed.

## Example 12.4.3.1

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 $\text{Ba}^{2+}$ in the solution?

**Solution**

*Solutions to Example 13.8.1*

| Steps for Problem Solving | Example 12.4.3.1 |
|---|---|
| Identify the "given" information and what the problem is asking you to "find." | Given: 275 mL $BaCl_2$<br>0.250 M $\text{BaCl}_2$ or $\frac{0.250\ mol BaCl_2}{1\ L\ BaCl_2\ solution}$<br>0.500 M $\text{Na}_2\text{SO}_4$ or $\frac{0.500\ mol Na_2SO_4}{1\ L\ Na_2SO_4\ solution}$<br>Find: Volume $\text{Na}_2\text{SO}_4$ solution. |
| Set up and balance the chemical equation. | $\text{Na}_2\text{SO}_4\,(\text{aq}) + \text{BaCl}_2\,(\text{aq}) \longrightarrow \text{BaSO}_4\,(\text{s}) + \underline{2}\text{NaCl}\,(\text{aq})$<br>An insoluble product is formed after the reaction. |
| List other known quantities. | 1 mol of $Na_2SO_4$ to 1 mol $BaCl_2$<br>1000 mL = 1 L |
| Prepare a concept map and use the proper conversion factor. | mL $BaCl_2$ solution → L $BaCl_2$ solution → mol $BaCl_2$ solution → mol $Na_2SO_4$ solution<br>$\frac{1\ L}{1000\ mL}$ $\frac{0.250\ mol\ BaCl_2}{1\ L\ BaCl_2 solution}$ $\frac{1\ mol\ Na_2SO_4}{1\ mol\ BaCl_2}$ $\frac{1\ L\ Na_2SO_4\ solution}{0.500\ mol}$ |

| Steps for Problem Solving | Example 12.4.3.1 |
|---|---|
| Cancel units and calculate. | $275\ \cancel{mL\ BaCl_2\ solution} \times \frac{1\ \cancel{L}}{1000\ \cancel{mL}} \times \frac{0.250\ \cancel{mol\ BaCl_2}}{1\ \cancel{L\ BaCl_2\ solution}} \times \frac{1\ \cancel{mol\ Na_2SO}}{1\ \cancel{mol\ BaCl}} \times \frac{1\ L\ Na_2SO_4\ solution}{0.500\ \cancel{molNa_2SO_4}}$ = 0.1375 L sodium sulfate |
| Think about your result. | The lesser amount (almost half) of sodium sulfate is to be expected as it is more concentrated than barium chloride. Also, the units are correct. |

**Exercise 12.4.3.1**

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

*Answer available at the end of this section.*

## Answers

**Exercise** 12.4.3.1

0.250 L LiOH solution

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# 12.5: Osmosis and Hypotonic/Hypertonic Solutions

Semipermeable membranes surround living cells and organelles in the cells. The semipermeable membranes allow water and small molecules but do not allow the passage of large molecules and ions.

> Osmosis is the passage of water and small molecules across a semipermeable membrane with a net flow from a less concentrated solution to a more concentrated solution.

Osmosis helps in the absorption, retention, and flow of water, nutrients, and other molecules required in the biological systems. Fig. 5.5.1 illustrates the process of osmosis.

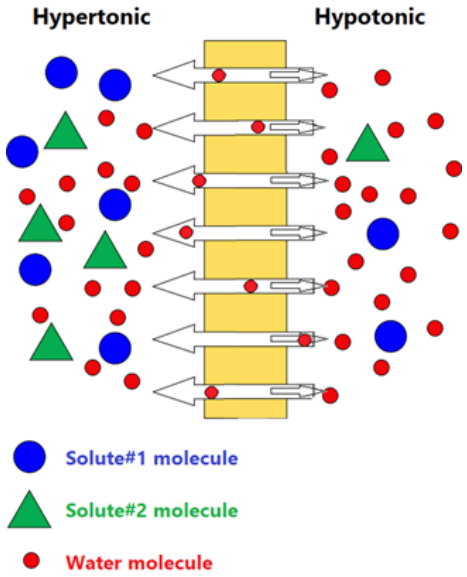



Figure 12.5.1: Illustration of osmosis. Osmosis is the passage of water and small molecules through a semipermeable membrane with a net flow from low solute concentration to high solute concentration. The larger molecules and ions cannot pass the semipermeable membrane.

## Osmotic pressure

Osmosis causes net water flow from the less concentrated to the more concentrated solution across the semipermeable membrane. Consequently, the water level rises in the less concentrated solution compartment, as illustrated in Fig. 5.5.2. The difference in the height of water increases and applies pressure, pumping water back to the more concentrated side until the flow of water is equal on the two sides.

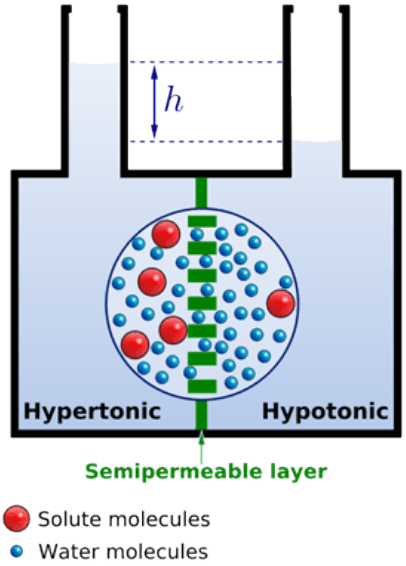



Figure 12.5.2: Osmotic pressure is the pressure, due to the difference in the height of water in this example, that prevents the excess flow of water from less concentrated to more concentrated solution side across the semipermeable membrane that separates the two solutions. Source: WYassineMrabetTalk✉ This W3C-unspecified vector image was created with Inkscape. / CC BY-SA (https://creativecommons.org/licenses/by-sa/3.0)

The pressure that prevents additional water flow to the more concentrated solution side of the semipermeable membrane is called osmotic pressure.

The osmotic pressure is proportional to the overall concentration of the solute particles. For example, 0.1 molar NaCl has osmotic pressure about twice that of 0.1 molar glucose because each mole of glucose adds one mole of solute particles, while each mole of NaCl produces two moles of particles, i.e., one-mole $Na^+$ and one-mole $Cl^-$ ions in the solution.

## Reverse Osmosis

Reverse osmosis is the net flow of water to the less concentrated or pure water across the semipermeable membrane by applying external pressure more than the osmotic pressure on the more concentrated solution side.

Reverse osmosis is the net flow of water to the less concentrated or pure water across the semipermeable membrane by applying external pressure more than the osmotic pressure. Note that solvent flow in reverse osmosis driven by external pressure is the opposite of regular osmosis. Reverse osmosis is used to produce drinking water from seawater sources, as illustrated in Fig. 5.5.3.

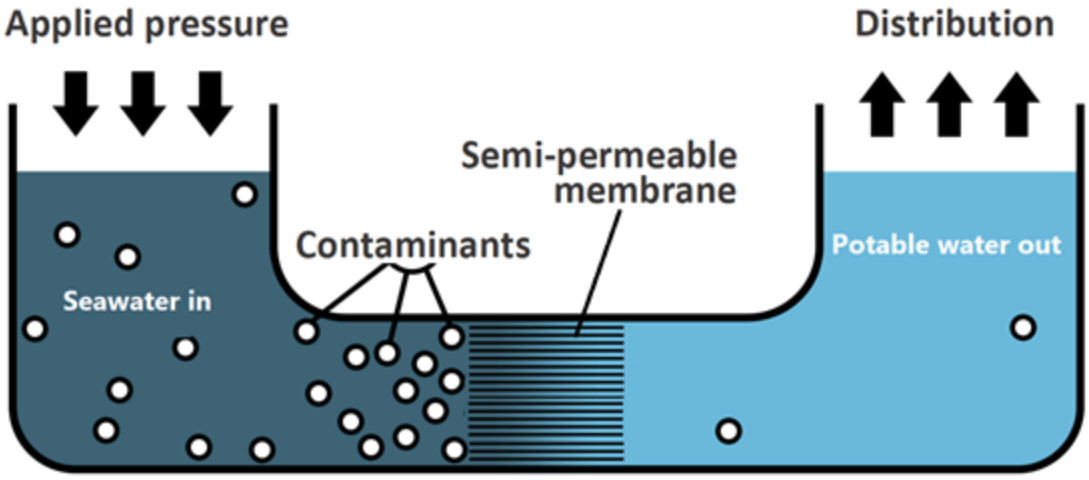



Figure 12.5.3: Illustration of reverse osmosis –used to produce drinking water from a seawater source. Source: Colby Fisher / CC BY-SA (https://creativecommons.org/licenses/by-sa/3.0)

## Isotonic, hypertonic, and hypotonic solutions

Cell membranes are semipermeable membranes that separate intracellular and extracellular fluids. The concentration difference across the membrane and the resulting osmotic pressure plays an essential role in cell functions. Intravenous solutions injected into patients must have the same osmotic pressure as the body fluids.

Solutions with the same solute particle concentration and osmotic pressure are called **isotonic**. If the two solutions across a semipermeable membrane do not have the same solute particle concentration, the solution with higher solute particle concentration and higher osmotic pressure is **hypertonic**, and the other has lower solute particle concentration and lower osmotic pressure is **hypotonic**.

Remember that hyper- means more and hypo-means less, concerning solute particle concentration in the case of osmosis.

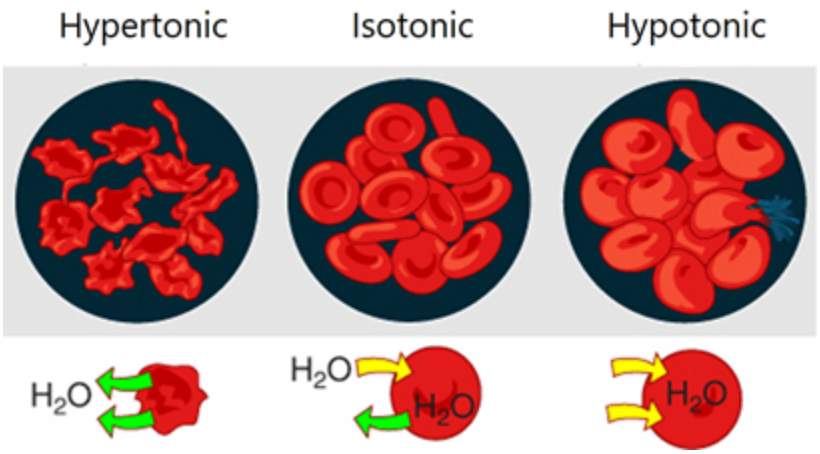



Figure 12.5.4: A hypertonic solution has a solute concentration higher than another solution. An isotonic solution has a solute concentration equal to another solution. A hypotonic solution has a solute concentration lower than another solution. Source: OpenStax / CC BY (https://creativecommons.org/licenses/by/3.0)

Cells placed in an external solution may retain their size, shrink, or swell depending on the relative osmotic pressure of fluid inside and outside of the cell, as illustrated in Fig. 5.5.4. For example, red blood cells placed in an isotonic solution retain their size because the flow of water into and out of the cell is the same.

- Typical isotonic solutions are 0.9% m/v NaCl solution in water or 5% m/v glucose solution in water.

- Red blood cells placed in a hypertonic solution shrink in size due to more flow of water out than into the cell –a process called **crenation**.
- Red blood cells placed in a hypotonic solution swell and burst due to more water flow into than out of the cells –a process called **hemolysis**.

A similar situation happens in plant cells that are placed in different environments concerning osmotic pressure, as illustrated In Fig. 5.5.5.

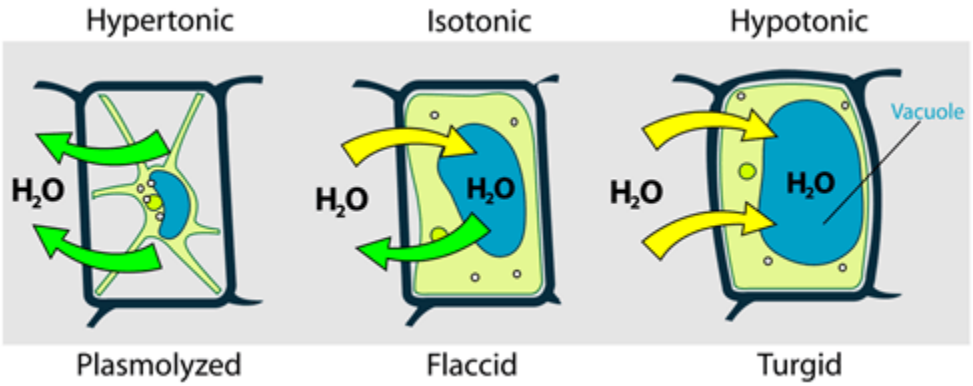



Figure 12.5.5: Plant cells under different environments concerning osmotic pressure. source: LadyofHats / Public domain

## Dialysis

Dialysis separates colloids from water, dissolved ions, and molecules of small dimention

Dialysis is similar to osmosis with the difference that in dialysis water, small molecules and ions can pass through a dialyzing membrane leaving behind collide particles like proteins and starch molecules, as illustrated in Fig. 5.5.6.

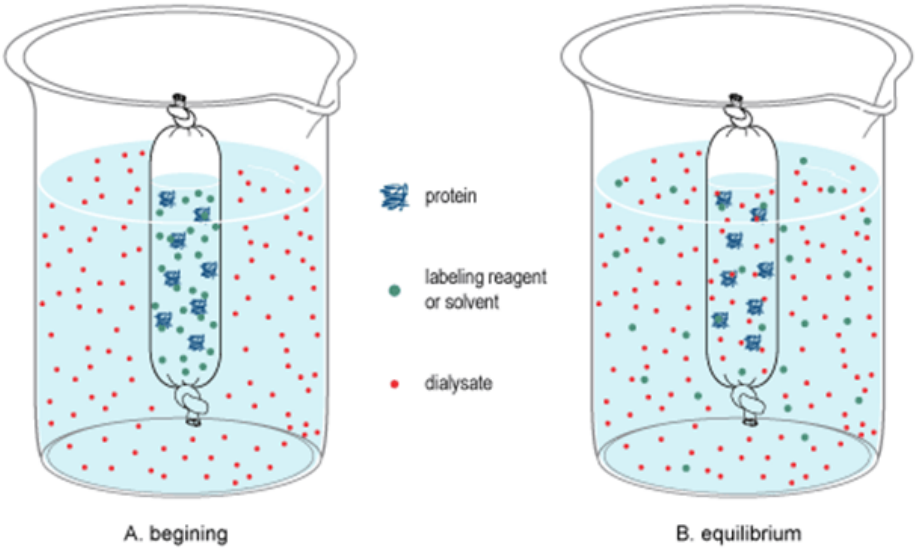



Figure 12.5.6: Dialysis separates colloidal particles like protein and starch from water, small molecules, and ions. Source: Potcherboy at English Wikipedia / CC BY (https://creativecommons.org/licenses/by/3.0)

### Role of dialysis in the human body

Kidneys filter the blood by dialysis process. There are over a million tubular structures, called nephrons, in the kidney surrounded by dialyzing membranes. The nephrons filter the water, small molecules like glucose, amino acids, urea, and ions from the blood.

Useful products and most of the water reabsorb later on, but urea and other waste products excrete through urine, as illustrated in Fig. 5.5.7.

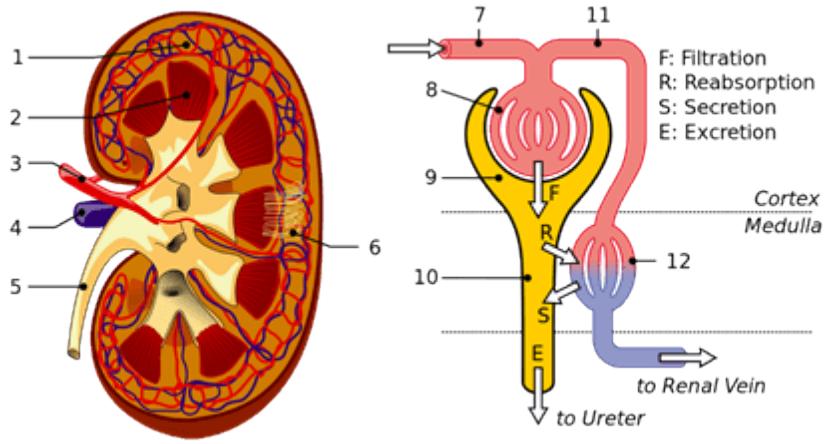



Figure 12.5.7: Schematics of dialysis for blood cleaning through kidney and nephron. 1: Renal cortex. 2: Medulla. 3: Renal artery. 4: Renal vein. 5: Ureter. 6: Nephrons. 7: Afferent arteriole. 8: Glomerulus. 9: Bowman's capsule. 10: Tubuli and loop of Henle. 11: Efferent arteriole. 12: Peritubular capillaries. Source: File:Physiology_of_Nephron.svg: Madhero88File:KidneyStructures_PioM.svg: Piotr Michał Jaworski; PioM EN DE PLderivative work: Daniel Sachse (Antares42) / CC BY-SA (https://creativecommons.org/licenses/by-sa/3.0)

## Hemodialysis

Hemodialysis is used to extract urea and other waste products from the blood when a person's kidney fails to remove them, as illustrated in Fig. 5.5.8. A hemodialysis system is a kind of artificial kidney in which the blood flows through long cellophane tubes placed in an isotonic solution containing NaCl, KCl, $NaHCO_3$, and glucose. Cellophane is a dialyzing membrane that does not let proteins, other large molecules, and blood pass through it, but urea excretes.

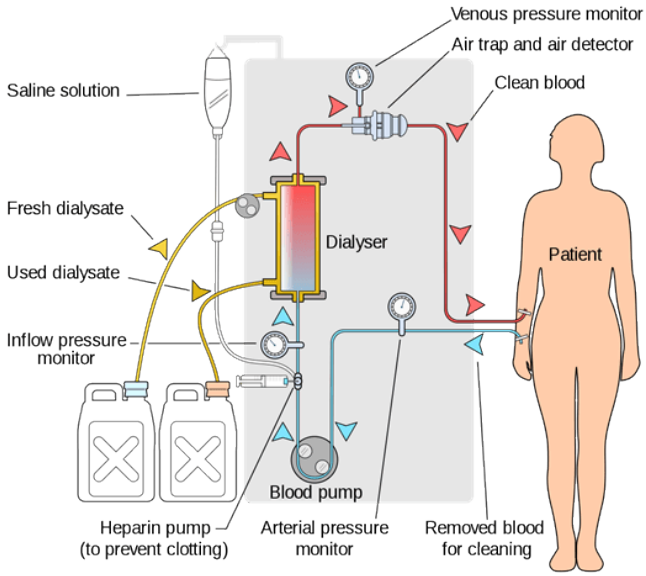



Figure 12.5.8: Simplified hemodialysis circuit. Source: GYassineMrabetTalk✉ This W3C-unspecified vector image was created with Inkscape. / CC BY (https://creativecommons.org/licenses/by/3.0)

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# 13: ACIDS AND BASES

Acids and bases are common substances found in many every day items, from fruit juices and soft drinks to soap. In this chapter, we will examine the properties of acids and bases, and learn about the chemical nature of these important compounds. We will cover pH, and how to calculate the pH of a solution.


## 13.1: Definitions and Properties of Acids/Bases

13.1.1: Acids and Bases Definitions

13.1.2: Reactions of Acids and Bases

13.1.3: Acid and Base Strength

13.1.4: Acid Dissociation Constants

## 13.2: Measuring Acidity

13.2.1: Water as Both an Acid and a Base

13.2.2: Measuring Acidity in Aqueous Solutions- The pH Scale

13.2.3: Working with pH

## 13.3: Maintaining pH Using Buffer Solutions

13.3.1: Biological Buffers



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# 13.1: DEFINITIONS AND PROPERTIES OF ACIDS/BASES



- Topic hierarchy


13.1.1: Acids and Bases Definitions

13.1.2: Reactions of Acids and Bases

13.1.3: Acid and Base Strength

13.1.4: Acid Dissociation Constants



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# 13.1.1: Acids and Bases Definitions

**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 hydrogen ions, $H^+$, in solution and a base produces hydroxide ions, $OH^-$. 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; Lewis theory is discussed elsewhere.

## The Arrhenius Theory of Acids and Bases

In 1884, the Swedish chemist Svante Arrhenius proposed two specific classifications of compounds, termed acids and bases. When dissolved in an aqueous solution, certain ions were released into the solution. An **Arrhenius acid** is a compound that *increases the concentration* of $H^+$ ions that are present when added to water. These $H^+$ ions form the **hydronium ion** ($H_3O^+$) when they combine with water molecules. This process is represented in a chemical equation by adding $H_2O$ to the reactants side.

$$\mathrm{HCl\,(aq)} \rightarrow \mathrm{H^+\,(aq) + Cl^-\,(aq)} \tag{13.1.1.1}$$

In this reaction, hydrochloric acid ($HCl$) dissociates completely into hydrogen ($H^+$) and chloride (\Cl^{-}\) ions when dissolved in water, thereby releasing $H^+$ ions into solution. Formation of the hydronium ion equation:

$$\mathrm{HCl\,(aq) + H_2O(\ell) \rightarrow H_3O^+\,(aq) + Cl^-\,(aq)} \tag{13.1.1.2}$$

An **Arrhenius base** is a compound that *increases the concentration* of $OH^-$ ions that are present when added to water. The dissociation is represented by the following equation:

$$\mathrm{NaOH\,(aq) \rightarrow Na^+\,(aq) + OH^-\,(aq)} \tag{13.1.1.3}$$

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

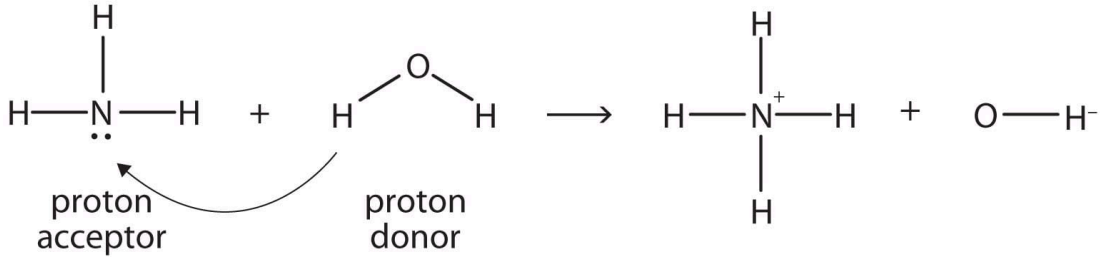
In 1923, Danish chemist Johannes Brønsted and English chemist Thomas Lowry independently proposed new definitions for acids and bases, ones that focus on proton transfer. A **Brønsted-Lowry acid** is any species that can donate a proton ($H^+$) to another molecule. A **Brønsted-Lowry base** is any species that can accept a proton from another molecule. In short, a Brønsted-Lowry acid is a proton donor, while a Brønsted-Lowry base is a proton acceptor.

A Brønsted-Lowry acid is a proton donor, while a Brønsted-Lowry base is a proton acceptor.

Let us use the reaction of ammonia in water to demonstrate the Brønsted-Lowry definitions of an acid and a base. Ammonia and water molecules are reactants, while the ammonium ion and the hydroxide ion are products:

$$\mathrm{NH_3\,(aq) + H_2O(\ell) \rightleftharpoons NH_4^+\,(aq) + OH^-\,(aq)} \tag{13.1.1.4}$$

What has happened in this reaction is that the original water molecule has donated a hydrogen ion to the original ammonia molecule, which in turn has accepted the hydrogen ion. We can illustrate this as follows:



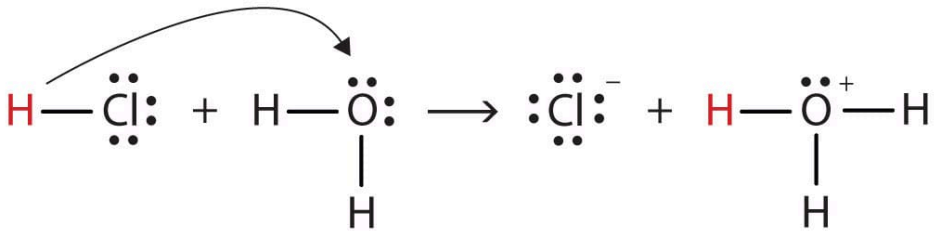

Because the water molecule *donates* a hydrogen ion to the ammonia, it is the Brønsted-Lowry acid, while the ammonia molecule—which *accepts* the hydrogen ion—is the Brønsted-Lowry base. Thus, ammonia acts as a base in both the Arrhenius sense and the Brønsted-Lowry sense.

Is an Arrhenius acid like hydrochloric acid still an acid in the Brønsted-Lowry sense? Yes, but it requires us to understand what really happens when HCl is dissolved in water. Recall that the hydrogen *atom* is a single proton surrounded by a single electron. To make the hydrogen ion, we remove the electron, leaving a bare proton. Do we really have bare protons floating around in aqueous solution? No, we do not. What really happens is that the $H^+$ ion attaches itself to $H_2O$ to make $H_3O^+$, which is called the *hydronium ion*. For most purposes, $H^+$ and $H_3O^+$ represent the same species, but writing $H_3O^+$ instead of $H^+$ shows that we understand that there are no bare protons floating around in solution. Rather, these protons are actually attached to solvent molecules.

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 $H_2O$:

$$\mathrm{HCl\,(g) + H_2O(\ell)\ \rightarrow H_3O^+\,(aq)\ Cl^-\,(aq) + H_3O^+\,(aq)} \tag{13.1.1.5}$$

We can depict this process using Lewis electron dot diagrams:



Now we see that a hydrogen ion is transferred from the HCl molecule to the $H_2O$ molecule to make chloride ions and hydronium ions. As the hydrogen ion donor, HCl acts as a Brønsted-Lowry acid; the 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.

**Note: Acid and Base Definitions**

- 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 13.1.1.1**

Aniline ($C_6H_5NH_2$) is slightly soluble in water. It has a nitrogen atom that can accept a hydrogen ion from a water molecule, just like the nitrogen atom in ammonia does. Write the chemical equation for this reaction and identify the Brønsted-Lowry acid and base.

**Solution**

$C_6H_5NH_2$ and $H_2O$ are the reactants. When $C_6H_5NH_2$ accepts a proton from $H_2O$, it gains an extra H and a positive charge and leaves an $OH^-$ ion behind. The reaction is as follows:

$$\mathrm{C_6H_5NH_2\,(aq) + H_2O(\ell) \rightleftharpoons C_6H_5NH_3{}^+\,(aq) + OH^-\,(aq)}$$

Because $C_6H_5NH_2$ accepts a proton, it is the Brønsted-Lowry base. The $H_2O$ molecule, because it donates a proton, is the Brønsted-Lowry acid.

**Exercise 13.1.1.1**

Identify the Brønsted-Lowry acid and the Brønsted-Lowry base in this chemical equation.

$$\mathrm{H_2PO_4{}^- + H_2O \rightleftharpoons HPO_4{}^{2-} + H_3O^+} \tag{13.1.1.6}$$

*Answer available at the end of this section.*

**Exercise 13.1.1.2**

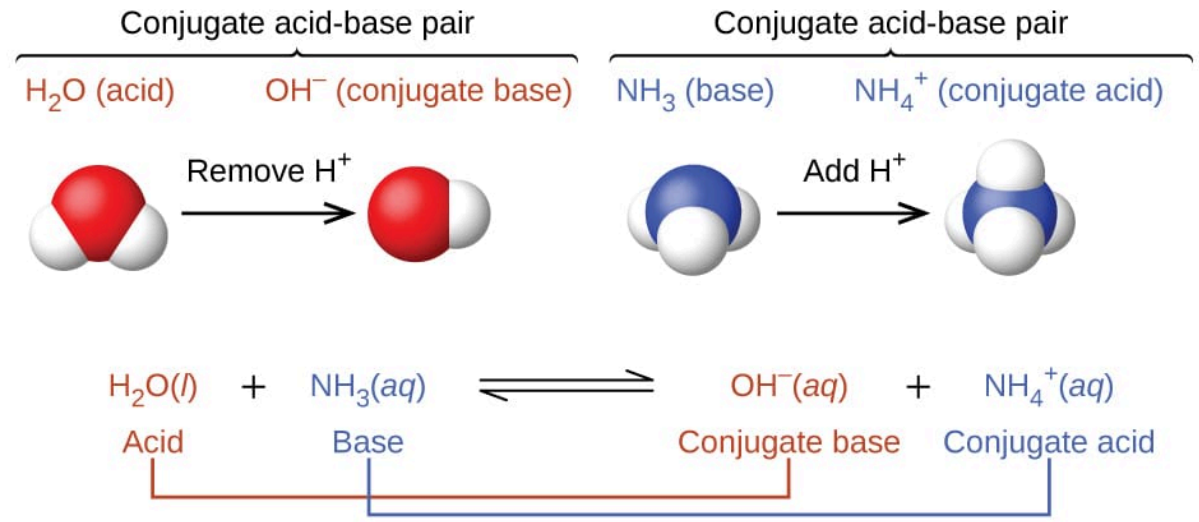
Which of the following compounds is a Bronsted-Lowry base?

a. HCl
b. $HPO_4^{2-}$
c. $H_3PO_4$
d. $NH_4^+$
e. $CH_3NH_3^+$

*Answer available at the end of this section.*

## 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, $\mathrm{OH^-}$, and the conjugate acid of ammonia, $\mathrm{NH_4{}^+}$ :




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 $H_2O/OH^-$.

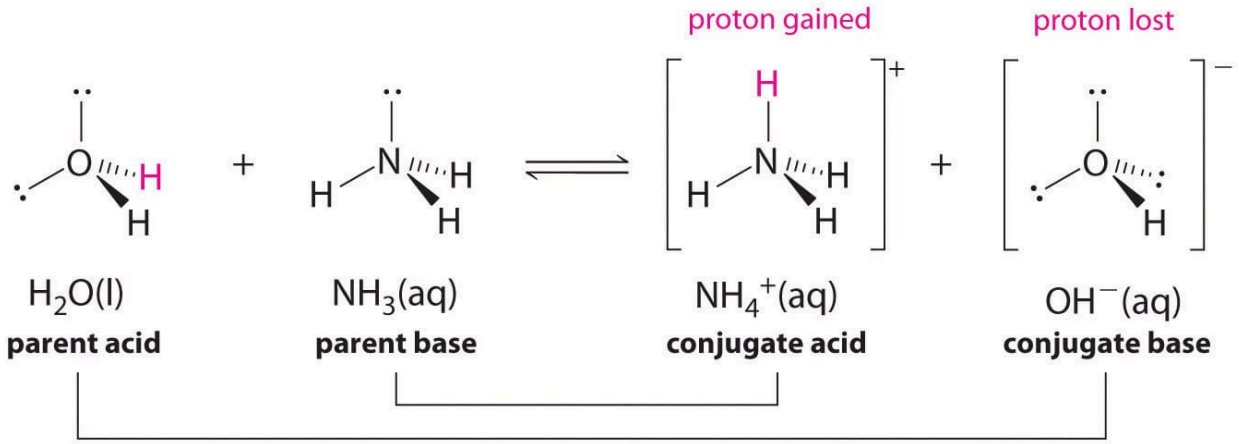



Figure 13.1.1.1. The pairing of parent acids and bases with conjugate acids and bases.

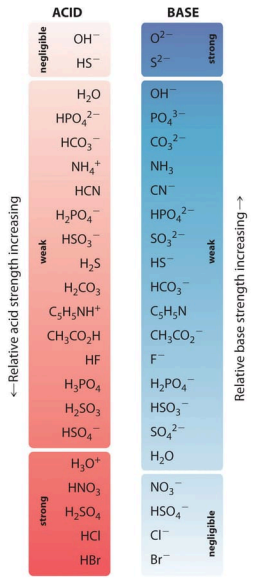



Figure 13.1.1.2: The Relative Strengths of Some Common Conjugate Acid-Base Pairs. The strongest acids are at the bottom left, and the strongest bases are at the top right. The conjugate base of a strong acid is a very weak base, and, conversely, the conjugate acid of a strong base is a very weak acid.

## Example 13.1.1.2

Identify the conjugate acid-base pairs in this equilibrium.

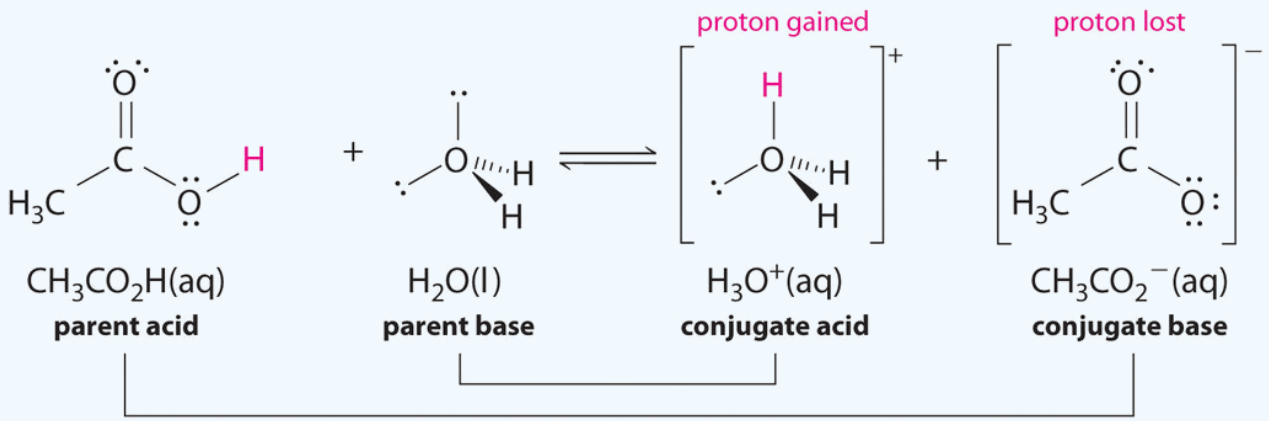
$$\mathrm{CH_3CO_2H + H_2O \rightleftharpoons H_3O^+ + CH_3CO_2^-}$$

**Solution**

Similarly, in the reaction of acetic acid with water, acetic acid **donates** a proton to water, which acts as the base. In the reverse reaction, $H_3O^+$ is the acid that donates a proton to the acetate ion, which acts as the base.

Once again, we have two conjugate acid-base pairs:

- the parent acid and its conjugate base ($CH_3CO_2H/CH_3CO_2^-$) and
- the parent base and its conjugate acid ($H_3O^+/H_2O$).




## Example 13.1.1.3

Identify the conjugate acid-base pairs in this equilibrium.

$$(CH_3)_3N + H_2O \rightleftharpoons (CH_3)_3NH^+ + OH^-$$

**Solution**

One pair is H2O and $OH^-$, where H2O 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 (CH3)3N and $(CH_3)_3NH^+$, where $(CH_3)_3NH^+$ is the conjugate acid (it has an additional proton) and (CH3)3N is the conjugate base.

## Exercise 13.1.1.3

Identify the conjugate acid-base pairs in this equilibrium.

$$\mathrm{NH_2^- + H_2O \rightleftharpoons NH_3 + OH^-}$$

*Answer available at the end of this section.*

# Contributions & Attributions

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## Answers

**Exercise** 13.1.1.1

Brønsted-Lowry acid: $H_2PO_4^-$; Brønsted-Lowry base: H2O

**Exercise** 13.1.1.2

A Brønsted-Lowry Base is a proton acceptor, which means it will take in an $H^+$. This eliminates $\mathrm{HCl}$, $\mathrm{H_3PO_4}$, $\mathrm{NH_4^+}$ and $\mathrm{CH_3NH_3^+}$ because they are Bronsted-Lowry acids. They all give away protons. In the case of $\mathrm{HPO_4^{2-}}$, consider the following equation:

$$\mathrm{HPO_4^{2-}(aq) + H_2O(l) \rightarrow PO_4^{3-}(aq) + H_3O^+(aq)}$$

Here, it is clear that $HPO_4^{2-}$ is the acid since it donates a proton to water to make $H_3O^+$ and $PO_4^{3-}$. Now consider the following equation:

$$\mathrm{HPO_4^{2-}(aq) + H_2O(l) \rightarrow H_2PO_4^- + OH^-(aq)}$$

In this case, $HPO_4^{2-}$ is the base since it accepts a proton from water to form $H_2PO_4^-$ and $OH^-$. Thus, $HPO_4^{2-}$ is an acid and base together, making it amphoteric. Since $HPO_4^{2-}$ is the only compound from the options that can act as a base, the answer is **(b) $HPO_4^{2-}$.**

**Exercise** 13.1.1.3

$H_2O$ (acid) and $OH^-$ (base); $NH_2^-$ (base) and $NH_3$ (acid)

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# 13.1.2: Reactions of Acids and Bases

**Learning Objectives**

- Write acid-base neutralization reactions.
- Write reactions of acids with metals.
- Write reactions of bases with metals.

## Neutralization Reactions

The reaction that happens when an acid, such as $\mathrm{HCl}$, is mixed with a base, such as $\mathrm{NaOH}$:

$$\mathrm{HCl\,(aq) + NaOH\,(aq) \longrightarrow NaCl\,(aq) + H_2O\,(l)}$$

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 $\mathrm{H^+}$ and a negative ion other than the hydroxide ion, $\mathrm{OH^-}$. Double displacement reactions of this type are called **neutralization reactions**. We can write an expanded version of this equation, with aqueous substances written in their longer form:

$$\mathrm{H^+\,(aq) + Cl^-\,(aq) + Na^+\,(aq) + OH^-\,(aq) \longrightarrow Na^+\,(aq) + Cl^-\,(aq) + H_2O\,(l)}$$

After removing the spectator ions, we get the net ionic equation:

$$\mathrm{H^+\,(aq) + OH^-\,(aq) \longrightarrow H_2O\,(l)}$$

When a strong acid and a strong base are combined in the proper amounts—when $[\mathrm{H^+}]$ equals $[\mathrm{OH^-}]$\)—a neutral solution results in which pH = 7. The acid and base have neutralized each other, and the acidic and basic properties are no longer present.

Salt solutions do not always have a pH of 7, however. Through a process known as **hydrolysis**, the ions produced when an acid and base combine may react with the water molecules to produce a solution that is slightly acidic or basic. As a general concept, if a strong acid is mixed with a weak base, the resulting solution will be slightly acidic. If a strong base is mixed with a weak acid, the solution will be slightly basic.

**YouTube Video**

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

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Video: Equimolar (~0.01 M) and equivolume solutions of $\mathrm{HCl}$ and $\mathrm{NaOH}$ are combined to make salt water. https://youtu.be/TS-I9KrUjB0

**Example 13.1.2.1: Propionic Acid + Calcium Hydroxide**

Calcium propionate is used to inhibit the growth of molds in foods, tobacco, and some medicines. Write a balanced chemical equation for the reaction of aqueous propionic acid ($CH_3CH_2CO_2H$) with aqueous calcium hydroxide [$Ca(OH)_2$].

**Solution**

*Solutions to Example 14.5.1*

| Steps | Reaction |
|---|---|
| *Write the unbalanced equation.*<br><br>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.*<br><br>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 13.1.2.1**

Write a balanced chemical equation for the reaction of solid barium hydroxide with dilute acetic acid.

*Answer available at the end of this section.*

## Acids and Bases React with Metals

Acids react with most metals to form a salt and hydrogen gas. As discussed previously, metals that are more active than acids can undergo a **single displacement reaction**. For example, zinc metal reacts with hydrochloric acid, producing zinc chloride and hydrogen gas.

$$\mathrm{Zn\,(s) + 2\,HCl\,(aq) \longrightarrow ZnCl_2\,(aq) + H_2\,(g)}$$

Bases also react with certain metals, like zinc or aluminum, to produce hydrogen gas. For example, sodium hydroxide reacts with zinc and water to form sodium zincate and hydrogen gas.

$$\mathrm{Zn\,(s) + 2\,NaOH\,(aq) + 2\,H_2O\,(l) \longrightarrow Na_2Zn(OH)_4\,(aq) + H_2\,(g).}$$

### Answers

**Exercise** 13.1.2.1

$$\mathrm{Ba(OH)_2\,(s) + 2\,CH_3CO_2H\ (aq) \longrightarrow Ba(CH_3CO_2)_2\,(aq) + 2\,H_2O\,(l)}$$

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# 13.1.3: Acid and Base Strength

**Learning Objectives**

- Define a strong and a weak acid and base.
- Recognize an acid or a base as strong or weak.

## Strong and Weak Acids

Except for their names and formulas, so far we have treated all acids as equals, especially in a chemical reaction. However, acids can be very different in a very important way. Consider $\mathrm{HCl(aq)}$. When $\mathrm{HCl}$ is dissolved in $\mathrm{H_2O}$, it completely **dissociates** (separates) into $H^+$(aq) and $Cl^-$(aq) ions; all the HCl molecules become ions:

$$\mathrm{HCl} \xrightarrow{100\,\%} \mathrm{H^+(aq) + Cl^-(aq)} \tag{13.1.3.1}$$

Any acid that dissociates 100% into ions is called a **strong acid**. If it does not dissociate 100%, it is a **weak acid**. $HC_2H_3O_2$ is an example of a weak acid:

$$HC_2H_3O_2 \xrightarrow{\sim 5\%} H^+(aq) + C_2H_3O_2^-(aq) \tag{13.1.3.2}$$

Because this reaction does not go 100% to completion, it is more appropriate to write it as **a reversible reaction**:

$$HC_2H_3O_2 \rightleftharpoons H^+(aq) + C_2H_3O_2^-(aq) \tag{13.1.3.3}$$

As it turns out, there are very few strong acids, which are given in Table 13.1.3.1. If an acid is not listed here, it is a weak acid. It may be 1% ionized or 99% ionized, but it is still classified as a weak acid.

Any acid that dissociates 100% into ions is called a strong acid. If it does not dissociate 100%, it is a weak acid.

*Figure 13.1.3.1: Some of the common strong acids and bases are listed here.*

| Strong Acids | | Strong Bases | |
|---|---|---|---|
| $\mathrm{HClO_4}$ | perchloric acid | $\mathrm{LiOH}$ | lithium hydroxide |
| $\mathrm{HCl}$ | hydrochloric acid | $\mathrm{NaOH}$ | sodium hydroxide |
| $\mathrm{HBr}$ | hydrobromic acid | $\mathrm{KOH}$ | potassium hydroxide |
| $\mathrm{HI}$ | hydroiodic acid | $\mathrm{Ca(OH)_2}$ | calcium hydroxide |
| $\mathrm{HNO_3}$ | nitric acid | $\mathrm{Sr(OH)_2}$ | strontium hydroxide |
| $\mathrm{H_2SO_4}$ | sulfuric acid | $\mathrm{Ba(OH)_2}$ | barium hydroxide |

## Strong and Weak Bases

The issue is similar with bases: a **strong base** is a base that is 100% ionized in solution. If it is less than 100% ionized in solution, it is a **weak base**. There are very few strong bases (Table 13.1.3.1); any base not listed is a weak base. All strong bases are $OH^-$ compounds. So a base based on some other mechanism, such as $NH_3$ (which does not contain $OH^-$ ions as part of its

formula), will be a weak base.

### Example 13.1.3.1: Identifying Strong and Weak Acids and Bases

Identify each acid or base as strong or weak.

a. HCl
b. $Mg(OH)_2$
c. $C_5H_5N$

**Solution**

a. Because HCl is listed in Table 13.1.3.1, it is a strong acid.
b. Because $Mg(OH)_2$ is listed in Table 13.1.3.1, it is a strong base.
c. The nitrogen in $C_5H_5N$ would act as a proton acceptor and therefore can be considered a base, but because it does not contain an OH compound, it cannot be considered a strong base; it is a weak base.

### Exercise 13.1.3.1

Identify each acid or base as strong or weak.

a. $\mathrm{RbOH}$
b. $\mathrm{HNO_2}$

*Answer available at the end of this section.*

### Example 13.1.3.2: Characterizing Base Ionization

Write the balanced chemical equation for the dissociation of $Ca(OH)_2$ and indicate whether it proceeds 100% to products or not.

**Solution**

This is an ionic compound of $Ca^{2+}$ ions and $OH^-$ ions. When an ionic compound dissolves, it separates into its constituent ions:

$$\mathrm{Ca(OH)_2 \longrightarrow Ca^{2+}\,(aq) + 2\,OH^-\,(aq)}$$

Because $Ca(OH)_2$ is listed in Table 13.1.3.1, this reaction proceeds 100% to products.

### Exercise 13.1.3.2

Write the balanced chemical equation for the dissociation of hydrazoic acid ($HN_3$) and indicate whether it proceeds 100% to products or not.

*Answer a available at the end of this section.*

### Looking Closer: Household Acids and Bases

Many household products are acids or bases. For example, the owner of a swimming pool may use muriatic acid to clean the pool. Muriatic acid is another name for hydrochloric acid [$\mathrm{HCl\,(aq)}$]. Vinegar has already been mentioned as a dilute solution of acetic acid [$\mathrm{HC_2H_3O_2\,(aq)}$]. In a medicine chest, one may find a bottle of vitamin C tablets; the chemical name of vitamin C is ascorbic acid ($\mathrm{HC_6H_7O_6}$).

One of the more familiar household bases is ammonia ($\mathrm{NH_3}$), which is found in numerous cleaning products. As we mentioned previously, ammonia is a base because it increases the hydroxide ion concentration by reacting with water:

$$\mathrm{NH_3\,(aq) + H_2O(\ell) \rightarrow NH_4^+\,(aq) + OH^-\,(aq)} \tag{13.1.3.4}$$

Many soaps are also slightly basic because they contain compounds that act as Brønsted-Lowry bases, accepting protons from water and forming excess hydroxide ions. This is one reason that soap solutions are slippery.




Figure 13.1.3.1: (left) Bottles of alkaline drain cleaners containing sodium hydroxide can dissolve greases and hair. (right) Chemical burns caused by sodium hydroxide solution photographed 44 hours after exposure. Figures used with permission from Wikipedia.

Perhaps the most dangerous household chemical is the lye-based drain cleaner. Lye is a common name for sodium hydroxide, although it is also used as a synonym for potassium hydroxide. Lye is an extremely caustic chemical that can react with grease, hair, food particles, and other substances that may build up and form a clog in a pipe. Unfortunately, lye can also attack tissues and other substances in our bodies. Thus, when we use lye-based drain cleaners, we must be very careful not to touch any of the solid drain cleaner or spill the water it was poured into. Safer, nonlye drain cleaners use peroxide compounds to react on the materials in the clog and clear the drain.

## Chemical Equilibrium in Weak Acids and Bases

Ionization of weak acids or bases are reversible reactions, which means the forward and reverse reactions occur and eventually reach equilbrium. For example, the ionization of the weak acid $\mathrm{HC_2H_3O_2\,(aq)}$ is as follows:

$$\mathrm{HC_2H_3O_2\,(aq) + H_2O(\ell) \rightarrow H_3O^+\,(aq) + C_2H_3O_2^-\,(aq)} \tag{13.1.3.5}$$

The reverse process also begins to occur:

$$\mathrm{H_3O^+\,(aq) + C_2H_3O_2^-\,(aq) \rightarrow HC_2H_3O_2\,(aq) + H_2O(\ell)} \tag{13.1.3.6}$$

Eventually, there is a balance between the two opposing processes, and no additional change occurs. The chemical reaction is better represented at this point with a double arrow:

$$\mathrm{HC_2H_3O_2\,(aq) + H_2O(\ell) \rightleftharpoons H_3O^+\,(aq) + C_2H_3O_2^-\,(aq)} \tag{13.1.3.7}$$

The $\rightleftharpoons$ implies that both the forward and reverse reactions are occurring, and their effects cancel each other out. A process at this point is considered to be at **chemical equilibrium** (or equilibrium). It is important to note that the processes do not stop. They balance out each other so that there is no further net change; that is, chemical equilibrium is a *dynamic equilibrium*.

### Example 13.1.3.3: Partial Ionization

Write the equilibrium chemical equation for the partial ionization of each weak acid or base.

a. $HNO_2(aq)$
b. $C_5H_5N(aq)$

**Solution**

a. $HNO_2(aq) + H_2O(\ell) \rightleftharpoons NO_2^-(aq) + H_3O^+(aq)$
b. $C_5H_5N(aq) + H_2O(\ell) \rightleftharpoons C_5H_5NH^+(aq) + OH^-(aq)$

### Exercise 13.1.3.3

Write the equilibrium chemical equation for the partial ionization of each weak acid or base.

a. $HF_{(aq)}$
b. $AgOH_{(aq)}$
c. $CH_3NH_2(aq)$

*Answer available at the end of this section.*

## Strengths of Conjugate Acid and Base Pairs

The extent to which an acid, $\mathrm{HA}$, donates protons to water molecules depends on the strength of the conjugate base, $\mathrm{A^-}$, of the acid. If $\mathrm{A^-}$ is a strong base, any protons that are donated to water molecules are recaptured by $\mathrm{A^-}$. Thus there is relatively little $\mathrm{A^-}$ and $\mathrm{H_3O^+}$ in solution, and the acid, $\mathrm{HA}$, is weak. If $\mathrm{A^-}$ is a weak base, water binds the protons more strongly, and the solution contains primarily $\mathrm{A^-}$ and $\mathrm{H_3O^+}$—the acid is strong. Strong acids form very weak conjugate bases, and weak acids form stronger conjugate bases (Figure 13.1.3.2).

The first six acids in Figure 13.1.3.2 are the most common strong acids. These acids are completely dissociated in aqueous solution. The conjugate bases of these acids are weaker bases than water. When one of these acids dissolves in water, their protons are completely transferred to water, the stronger base.

Those acids that lie between the hydronium ion and water in Figure 13.1.3.2 form conjugate bases that can compete with water for possession of a proton. Both hydronium ions and non-ionized acid molecules are present in equilibrium in a solution of one of these acids. Compounds that are weaker acids than water (those found below water in the column of acids) in Figure 13.1.3.2 exhibit no observable acidic behavior when dissolved in water. Their conjugate bases are stronger than the hydroxide ion, and if any conjugate base were formed, it would react with water to re-form the acid.

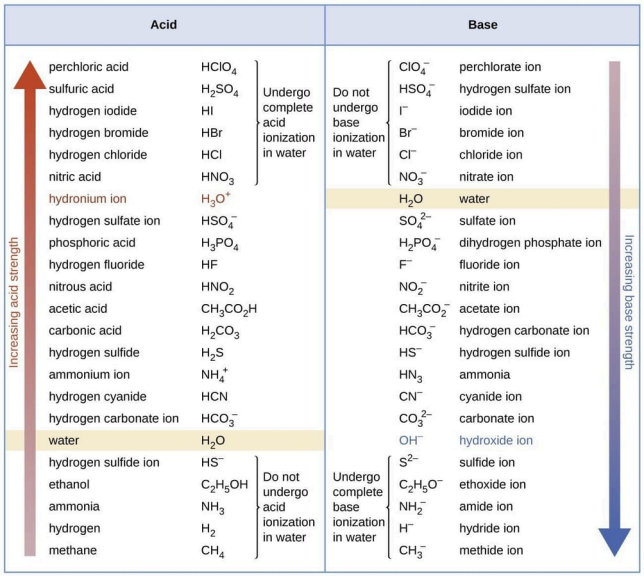



Figure 13.1.3.2: The chart shows the relative strengths of conjugate acid-base pairs.

The extent to which a base forms hydroxide ion in aqueous solution depends on the strength of the base relative to that of the hydroxide ion, as shown in the last column in Figure 13.1.3.2. A strong base, such as one of those lying below hydroxide ion, accepts protons from water to yield 100% of the conjugate acid and hydroxide ion. Those bases lying between water and hydroxide ion accept protons from water, but a mixture of the hydroxide ion and the base results. Bases that are weaker than water (those that lie above water in the column of bases) show no observable basic behavior in aqueous solution.

# Key Takeaways

- Strong acids and bases are 100% ionized in aqueous solution.
- Weak acids and bases are less than 100% ionized in aqueous solution.

## Answers

**Exercise** 13.1.3.1

a. strong base
b. weak acid

**Exercise** 13.1.3.2

The reaction is as follows:

$$\mathrm{HN_3} \longrightarrow \mathrm{H^+(aq) + N_3^-(aq)}$$

It does not proceed 100% to products because hydrazoic acid is not a strong acid.

**Exercise** 13.1.3.3

a. $HF(aq) + H_2O(\ell) \diamond F^-(aq) + H_3O^+(aq)$

b. $AgOH(aq) \diamond Ag^+(aq) + OH^-(aq)$

c. $CH_3NH_2(aq) + H_2O(\ell) \diamond CH_3NH_3^+(aq) + OH^-(aq)$

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# 13.1.4: Acid Dissociation Constants

## Learning Objectives

- Write the acid dissociation constant ($K_a$) expression.
- Determine the relative strength of an acid using the ($K_a$) value.

The ionization for a general weak acid, $\mathrm{HA}$, can be written as follows:

$$\mathrm{HA}\,(aq) \rightleftharpoons \mathrm{H^+}\,(aq) + \mathrm{A^-}\,(aq)$$

Because the acid is weak, an equilibrium expression can be written. An **acid ionization constant** $(K_\mathrm{a})$ is the *equilibrium constant* for the ionization of an acid.

$$K_\mathrm{a} = \frac{[\mathrm{H^+}]\,[\mathrm{A^-}]}{[\mathrm{HA}]}$$

The acid ionization represents the fraction of the original acid that has been *ionized* in solution. Therefore, the numerical value of $K_\mathrm{a}$ is a reflection of the strength of the acid. Weak acids with relatively higher $K_\mathrm{a}$ values are stronger than acids with relatively lower $K_\mathrm{a}$ values. Because strong acids are essentially $100\%$ ionized, the concentration of the acid in the denominator is nearly zero and the $K_\mathrm{a}$ value approaches infinity. For this reason, $K_\mathrm{a}$ 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* 13.1.4.1*: Acid Ionization Constants at* $25^\circ\mathrm{C}$

| Name of Acid | Ionization Equation | $K_\mathrm{a}$ |
|---|---|---|
| Sulfuric acid | $\mathrm{H_2SO_4} \rightleftharpoons \mathrm{H^+} + \mathrm{HSO_4^-}$<br>$\mathrm{HSO_4} \rightleftharpoons \mathrm{H^+} + \mathrm{SO_4^{2-}}$ | very large<br>$1.3 \times 10^{-2}$ |
| Hydrofluoric acid | $\mathrm{HF} \rightleftharpoons \mathrm{H^+} + \mathrm{F^-}$ | $7.1 \times 10^{-4}$ |
| Nitrous acid | $\mathrm{HNO_2} \rightleftharpoons \mathrm{H^+} + \mathrm{NO_2^-}$ | $4.5 \times 10^{-4}$ |
| Benzoic acid | $\mathrm{C_6H_5COOH} \rightleftharpoons \mathrm{H^+} + \mathrm{C_6H_5COO^-}$ | $6.5 \times 10^{-5}$ |
| Acetic acid | $\mathrm{CH_3COOH} \rightleftharpoons \mathrm{H^+} + \mathrm{CH_3COO^-}$ | $1.8 \times 10^{-5}$ |
| Carbonic acid | $\mathrm{H_2CO_3} \rightleftharpoons \mathrm{H^+} + \mathrm{HCO_3^-}$<br>$\mathrm{HCO_3^-} \rightleftharpoons \mathrm{H^+} + \mathrm{CO_3^{2-}}$ | $4.2 \times 10^{-7}$<br>$4.8 \times 10^{-11}$ |

Hydrofluoric acid $HF_{(aq)}$ reacts directly with glass (very few chemicals react with glass). Hydrofluoric acid is used in glass etching.

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# 13.2: MEASURING ACIDITY



- Topic hierarchy


13.2.1: Water as Both an Acid and a Base

13.2.2: Measuring Acidity in Aqueous Solutions- The pH Scale

13.2.3: Working with pH



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# 13.2.1: Water as Both an Acid and a Base

## Learning Objectives

- To write chemical equations for water acting as an acid and as a base.
- Define and use the ion product constant for water, $K_w$, to calculate concentrations of $\mathrm{H_3O^+}$ and $\mathrm{OH^-}$ in aqueous solutions.

Water ($H_2O$) is an interesting compound in many respects. Here, we will consider its ability to behave as an acid or a base.

In some circumstances, a water molecule will accept a proton and thus act as a **Brønsted-Lowry base**. We saw an example in the dissolving of HCl in $H_2O$:

$$HCl + H_2O(\ell) \rightarrow H_3O^+(aq) + Cl^-(aq) \tag{13.2.1.1}$$

In other circumstances, a water molecule can donate a proton and thus act as a **Brønsted-Lowry acid**. For example, in the presence of the amide ion, a water molecule donates a proton, making ammonia as a product:

$$H_2O(\ell) + NH_2^-(aq) \rightarrow OH^-(aq) + NH_3(aq) \tag{13.2.1.2}$$

In this case, $NH_2^-$ is a Brønsted-Lowry base (the proton acceptor).

So, depending on the circumstances, $H_2O$ can act as either a Brønsted-Lowry acid or a Brønsted-Lowry base. Water is not the only substance that can react as an acid in some cases or a base in others, but it is certainly the most common example—and the most important one. A substance that can either donate or accept a proton, depending on the circumstances, is called an **amphiprotic** compound.

A water molecule can act as an acid or a base even in a sample of pure water. About 6 in every 100 million (6 in $10^8$) water molecules undergo the following reaction:

$$H_2O(\ell) + H_2O(\ell) \rightarrow H_3O^+(aq) + OH^-(aq) \tag{13.2.1.3}$$

This process is called the **autoionization of water** (Figure 13.2.1.1) and occurs in every sample of water, whether it is pure or part of a solution. Autoionization occurs to some extent in any amphiprotic liquid. (For comparison, liquid ammonia undergoes autoionization as well, but only about 1 molecule in a million billion (1 in $10^{15}$) reacts with another ammonia molecule.)

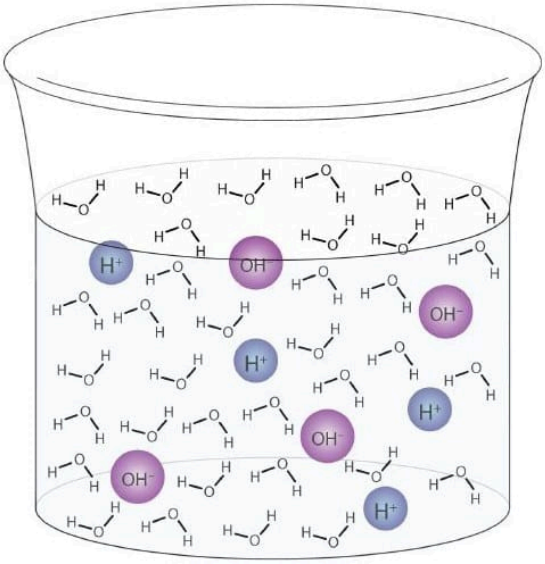



Figure 13.2.1.1 Autoionization. A small fraction of water molecules—approximately 6 in 100 million—ionize spontaneously into hydronium ions and hydroxide ions. This picture necessarily overrepresents the amount of autoionization that really occurs in pure water.

## Example 13.2.1.1

Identify water as either a Brønsted-Lowry acid or a Brønsted-Lowry base.

1. $H_2O(\ell) + NO_2^-(aq) \rightarrow HNO_2(aq) + OH^-(aq)$
2. $HC_2H_3O_2(aq) + H_2O(\ell) \rightarrow H_3O^+(aq) + C_2H_3O_2^-(aq)$

**Solution**

1. In this reaction, the water molecule donates a proton to the $NO_2^-$ ion, making $OH^-(aq)$. As the proton donor, $H_2O$ acts as a Brønsted-Lowry acid.
2. In this reaction, the water molecule accepts a proton from $HC_2H_3O_2$, becoming $H_3O^+(aq)$. As the proton acceptor, $H_2O$ is a Brønsted-Lowry base.

## Exercise 13.2.1.2

Identify water as either a Brønsted-Lowry acid or a Brønsted-Lowry base.

1. $HCOOH(aq) + H_2O(\ell) \rightarrow H_3O^+(aq) + HCOO^-(aq)$
2. $H_2O(\ell) + PO_4^{3-}(aq) \rightarrow OH^-(aq) + HPO_4^{2-}(aq)$

*Answer available at the end of this section.*

# Dissociation of Water

As we have already seen, $H_2O$ can act as an acid or a base. Within any given sample of water, some $H_2O$ molecules are acting as acids, and other $H_2O$ molecules are acting as bases. The chemical equation is as follows:

$$\underbrace{H_2O}_{\text{acid}} + \underbrace{H_2O}_{\text{base}} \rightleftharpoons H_3O^+ + OH^- \tag{13.2.1.4}$$

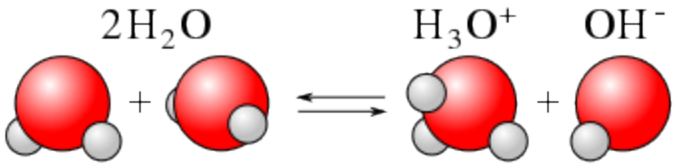



Figure 13.2.1.2: Autoionization of water, giving hydroxide and hydronium ions.

Similar to a weak acid, the autoionization of water is an equilibrium process, and is more properly written as follows:

$$\mathrm{H_2O}(\ell) + \mathrm{H_2O}(\ell) \rightleftharpoons \mathrm{H_3O^+\,(aq)} + \mathrm{OH^-\,(aq)} \tag{13.2.1.5}$$

We often use the simplified form of the reaction:

$$\mathrm{H_2O\,(l)} \rightleftharpoons \mathrm{H^+\,(aq)} + \mathrm{OH^-\,(aq)}$$

The equilibrium constant for the autoionization of water is referred to as the ion-product for water and is given the symbol $K_w$.

$$K_w = [\mathrm{H^+}][\mathrm{OH^-}]$$

The **ion-product constant for water ($K_w$)** is the mathematical product of the concentration of hydrogen ions and hydroxide ions. Note that $H_2O$ is not included in the ion-product expression because it is a pure liquid. The value of $K_w$ is very small, in accordance with a reaction that favors the reactants. At 25°C, the experimentally determined value of $K_w$ in pure water is $1.0\times10^{-14}$.

$$K_w = [\mathrm{H^+}][\mathrm{OH^-}] = 1.0 \times 10^{-14}$$

In a sample of pure water, the concentrations of hydrogen and hydroxide ions are equal to one another. Pure water or any other aqueous solution in which this ratio holds is said to be *neutral*. To find the molarity of each ion, the square root of $K_w$ is taken.

$$[\mathrm{H^+}] = [\mathrm{OH^-}] = 1.0\times10^{-7}$$

The product of these two concentrations is $1.0\times10^{-14}$

$$[\mathrm{H^+}]\times[\mathrm{OH^-}] = (1.0 \times 10^{-7})(1.0 \times 10^{-7}) = 1.0 \times 10^{-14}$$

- For acids, the concentration of $H^+$ or $[H^+]$ is greater than $1.0\times10^{-7}$ M
- For bases, the concentration of $OH^-$ or $[OH^-]$ is greater than $1.0\times10^{-7}$ M.

Aqueous HCl is an example of acidic solution. Hydrogen chloride (HCl) ionizes to produce $H^+$ and $Cl^-$ ions upon dissolving in water. This increases the concentration of $H^+$ ions in the solution. According to Le Chatelier's principle, the equilibrium represented by

$$\mathrm{H_2O\,(l)} \rightleftharpoons \mathrm{H^+\,(aq)} + \mathrm{OH^-\,(aq)}$$

$$\mathrm{HCl\,(g)} \longrightarrow \mathrm{H^+\,(aq)} + \mathrm{Cl^-\,(aq)}$$

is **f**orced to the left, towards the reactant. As a result, the concentration of the hydroxide ion decreases.

Now, consider KOH (aq), a **basic solution**. Solid potassium hydroxide (KOH) dissociates in water to yield potassium ions and hydroxide ions.

$$\mathrm{KOH(s)} \rightarrow \mathrm{K^+(aq)} + \mathrm{OH^-(aq)}$$

The increase in concentration of the $OH^-$ ions will cause a decrease in the concentration of the $H^+$ ions.

No matter whether the aqueous solution is an acid, a base, or neutral:and the ion-product of $[H^+][OH^-]$ remains constant.

- For acidic solutions, [$H^+$] is greater than [$OH^-$].
- For basic solutions, [OH–] is greater than [$H^+$].
- For neutral solutions, [$H_3O^+$] = [OH–] = 1.0×10$^{-7}$M

This means that if you know $[H^+]$ for a solution, you can calculate what $[OH^-]$) has to be for the product to equal $1.0 \times 10^{-14}$, or if you know $[OH^-]$), you can calculate $[H^+]$. 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 $K_w$.

$$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14} \tag{13.2.1.6}$$

## Example 13.2.1.2

Hydrochloric acid (HCl) is a strong acid, meaning it is 100% ionized in solution. What is the [$H^+$] and the [$OH^-$] in a solution of 2.0×10$^{-3}$ M HCl?

**Solution**

*Step 1: List the known values and plan the problem.*

Known

- [HCl] = 2.0×10$^{-3}$ M
- Kw = 1.0×10$^{-14}$

Unknown

- [$H^+$]=?M
- [$OH^-$]=?M

Because HCl is 100% ionized, the concentration of H+ ions in solution will be equal to the original concentration of HCl. Each HCl molecule that was originally present ionizes into one H+ ion and one Cl– ion. The concentration of OH– can then be determined from the [H+] and Kw.

*Step 2: Solve.*

$$[H^+]=2.0\times10^{-3}\ M$$

$$Kw = [H^+][OH^-] = 1.0\times10^{-14}$$

$$[OH^-] = Kw/[H^+] = 1.0\times10^{-14}/2.0\times10^{-3} = 5.0\times10^{-12}\ M$$

*Step 3: Think about your result.*

The [$H^+$] is much higher than the [$OH^-$] because the solution is acidic. As with other equilibrium constants, the unit for Kw is customarily omitted.

## Exercise 13.2.1.2

Sodium hydroxide (NaOH) is a strong base. What is the [$H^+$] and the [$OH^-$] in a 0.001 M NaOH solution at 25 °C?

*Answer available at the end of this section.*

## Concept Review Exercises

1. Explain how water can act as an acid.
2. Explain how water can act as a base.

## Answers

1. Under the right conditions, $H_2O$ can donate a proton, making it a Brønsted-Lowry acid.
2. Under the right conditions, $H_2O$ can accept a proton, making it a Brønsted-Lowry base.

## Key Takeaway

- Water molecules can act as both an acid and a base, depending on the conditions.

## Exercises

1. Is $H_2O(\ell)$ acting as an acid or a base?

   $H_2O(\ell) + NH_4^+(aq) \rightarrow H_3O^+(aq) + NH_3(aq)$

2. Is $H_2O(\ell)$ acting as an acid or a base?

   $CH_3^-(aq) + H_2O(\ell) \rightarrow CH_4(aq) + OH^-(aq)$

3. In the aqueous solutions of some salts, one of the ions from the salt can react with water molecules. In some $C_2H_3O_2^-$ solutions, the following reaction can occur:

   $C_2H_3O_2^-(aq) + H_2O(\ell) \rightarrow HC_2H_3O_2(aq) + OH^-(aq)$

   Is $H_2O$ acting as an acid or a base in this reaction?

4. In the aqueous solutions of some salts, one of the ions from the salt can react with water molecules. In some $NH_4^+$ solutions, the following reaction can occur:

   $NH_4^+(aq) + H_2O \rightarrow NH_3(aq) + H_3O^+(aq)$

   Is $H_2O$ acting as an acid or a base in this reaction?

5. Why is pure water considered neutral?

## Answers

1. base
2. acid

3. acid
4. base

5. When water ionizes, equal amounts of $H^+$ (acid) and $OH^-$ (base) are formed, so the solution is neither acidic nor basic: $H_2O(\ell) \rightarrow H^+(aq) + OH^-(aq)$

[SIDE NOTE: It is rare to truly have pure water. Water exposed to air will usually be slightly acidic because dissolved carbon dioxide gas, or carbonic acid, decreases the pH slightly below 7. Alternatively, dissolved minerals, like calcium carbonate

(limestone), can make water slightly basic.]

## Answers

**Exercise** 13.2.1.2

1. $H_2O$ acts as the proton acceptor (Brønsted-Lowry base)
2. $H_2O$ acts as the proton donor (Brønsted-Lowry acid)

**Exercise** 13.2.1.2

$[OH^-]$ = 0.001M or 1 x $10^{-3}$M; $[H^+]$=1×$10^{-11}$M.

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# 13.2.2: Measuring Acidity in Aqueous Solutions- The pH Scale

**Learning Objectives**

- Define the pH scale and use it to describe acids and bases.
- Calculate the pH of a solution from $[H_3O^+]$ and $[OH^-]$.

Knowing the amount of acid and base in solutions is extremely important for a wide variety of applications ranging from brewing beer or wine to studying the effects of ocean acidification to health and medicine. Scientists are good at calculating and measuring the concentration of hydronium in a solution, however, there is a more convenient way to make comparisons between solutions – *the pH scale*.

## The pH Scale

One qualitative measure of the strength of an acid or a base solution is the pH scale, which is based on the concentration of the hydronium (or hydrogen) ion in aqueous solution.

$$pH = -\log[H^+]$$

or

$$pH = -\log[H_3O^+]$$

Figure 13.2.2.1 illustrates this relationship, along with some examples of various solutions. Because hydrogen ion concentrations are generally less than one (for example $1.3 \times 10^{-3}\ M$), the log of the number will be a negative number. To make pH even easier to work with, pH is defined as the *negative* log of $[H_3O^+]$, which will give a positive value for pH.

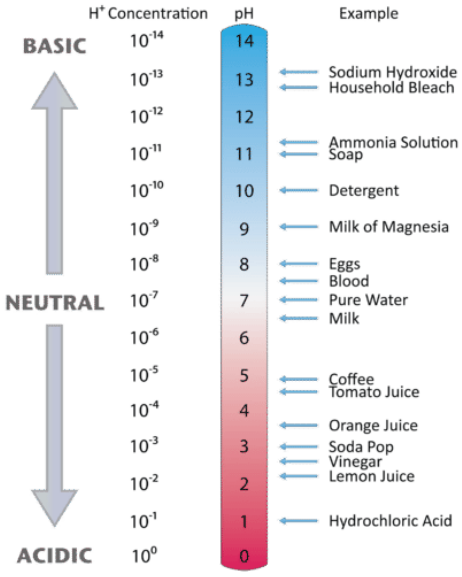



Figure 13.2.2.1: The relationship between [H+] and $pH$ *values for several common materials.*

A neutral (neither acidic nor basic) solution has a pH of 7. A pH below 7 means that a solution is acidic, with lower values of pH corresponding to increasingly acidic solutions. A pH greater than 7 indicates a basic solution, with higher values of pH corresponding to increasingly basic solutions. Thus, given the pH of several solutions, you can state which ones are acidic, which ones are basic, and which are more acidic or basic than others. These are summarized in Table \({13{.}2{.}2{.}\eatSpaces{1}

\endSpaces}.

Table 13.2.2.1: Acidic, Basic and Neutral pH Values

| Classification | Relative Ion Concentrations | pH at 25 °C |
|---|---|---|
| acidic | $[H^+] > [OH^-]$ | pH < 7 |
| neutral | $[H^+] = [OH^-]$ | pH = 7 |
| basic | $[H^+] < [OH^-]$ | pH > 7 |

## Example 13.2.2.1

Find the pH, given the $[H^+]$ of the following:

a. $1 \times 10^{-3}$ M
b. $2.5 \times 10^{-11}$ M
c. $4.7 \times 10^{-9}$ M

**Solution**

$pH = - \log [H_3O^+]$

Substitute the known quantity into the equation and solve. Use a scientific calculator for b and c.

a. $pH = - \log [1 \times 10^{-3}] = 3.0$ (1 decimal place since 1 has 1 significant figure)
b. $pH = - \log [2.5 \times 10^{-11}] = 10.60$ (2 decimal places since 2.5 has 2 significant figures)
c. $pH = - \log [4.7 \times 10^{-9}] = 8.33$ (2 decimal places since 4.7 has 2 significant figures)

Note on significant figures:

Because the number(s) before the decimal point in the pH value relate to the power on 10, the number of digits *after* the decimal point (underlined) is what determines the number of significant figures in the final answer.

## Exercise 13.2.2.1

Find the pH, given $[H^+]$ of the following:

a. $5.8 \times 10^{-4}$ M
b. $1.0 \times 10^{-7}$ M

*Answer available at the end of this section.*

Figure 13.2.2.2 lists the pH of several common solutions. The most *acid*ic among the listed solutions is 1 M HCl with the lowest pH value (0.0): battery acid is the next most acidic solution with a pH value of 0.3. The most *basic* is 1M NaOH solution with the highest pH value of 14.0. Notice that some biological fluids (stomach acid and urine) are nowhere near neutral. You may also notice that many food products are slightly acidic. They are acidic because they contain solutions of weak acids. If the acid components of these foods were strong acids, the food would likely be inedible.

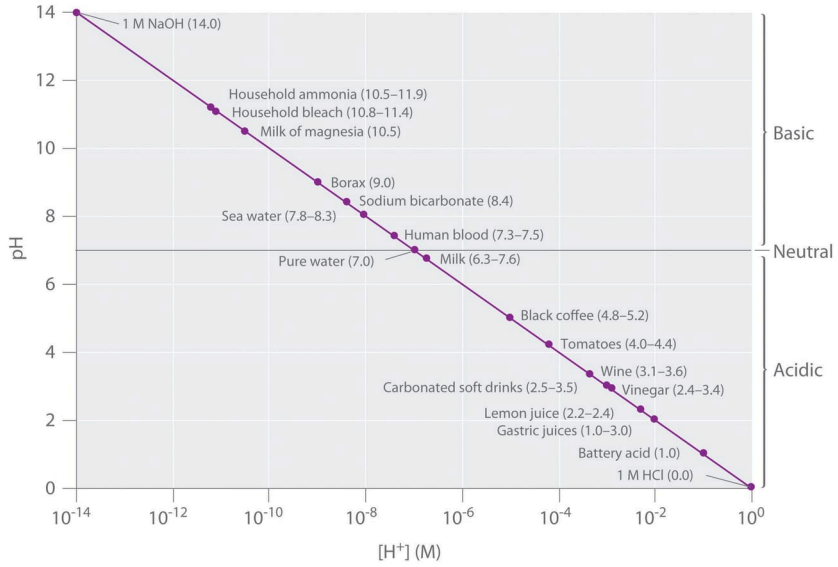



Figure 13.2.2.2: A Plot of pH versus [$H^+$] for Some Common Aqueous Solutions. Although many substances exist in a range of pH values (indicated in parentheses), they are plotted using typical values.

## Example 13.2.2.2

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

**Solution**

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 13.2.2.2

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 available at the end of this section.*

# Measuring pH

Tools have been developed that make the measurement of pH simple and convenient. For example, pH paper (Figure 13.2.2.3 )consists of strips of paper impregnated with one or more **acid-base indicators**, which are intensely colored organic molecules whose colors change dramatically depending on the pH of the solution. Placing a drop of a solution on a strip of pH paper and comparing its color with standards give the solution's approximate pH. A more accurate tool, the pH meter, uses a glass electrode, a device whose voltage depends on the $H^+$ ion concentration (Figure 13.2.2.3).

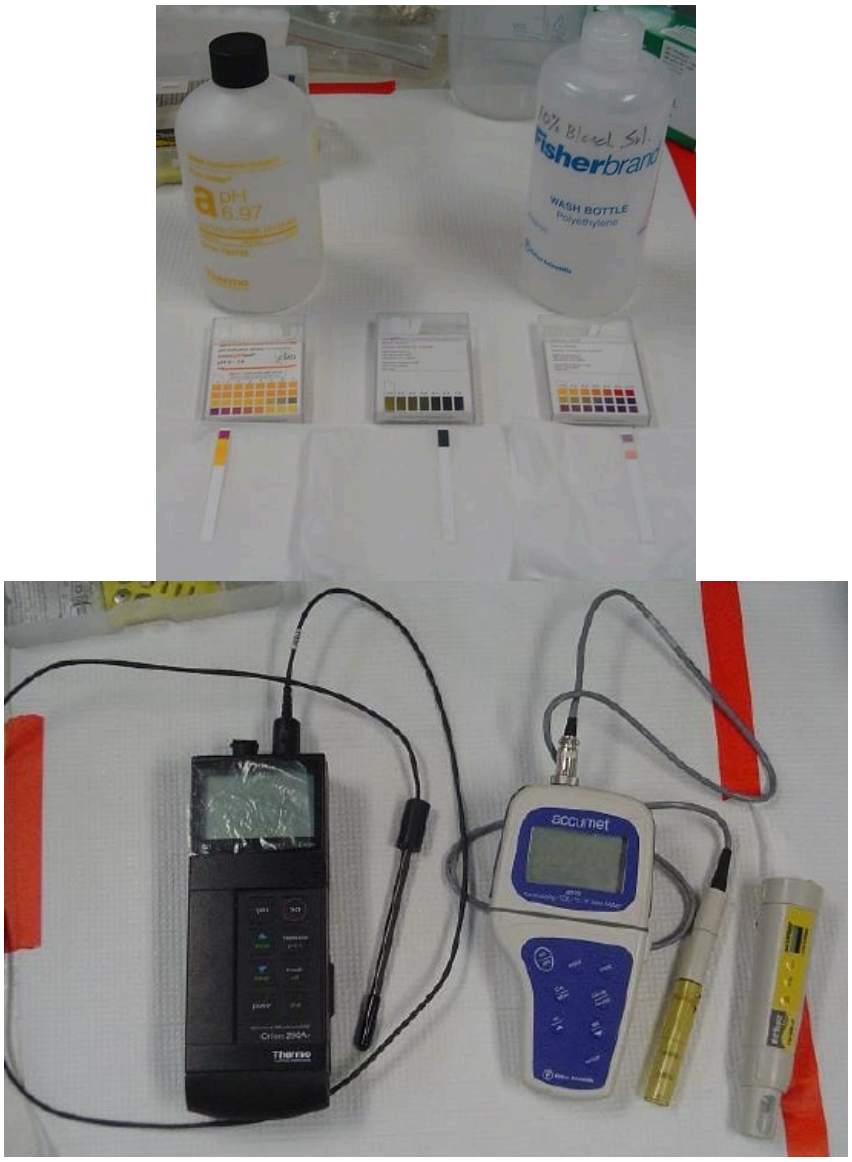



Figure 13.2.2.3: Ways to measure pH. (left) These pH strips can measure pH in a series of ranges by putting sample on a strip and comparing its color change with colors on the box that correspond to a certain pH. The strip on the left measures pH 0-7 and shows results of a strong acid sample; the center strip is pH range 5-10 and shows results of a 6.97 buffer solution sample; the strip on the right measures a broad range (pH 1-14) and shows results of a 10% bleach water solution sample. This image can be enlarged by clicking on it. (right) These three meters and probes can measure pH (left) and electrical conductivity (center and right). Photos by Monica Bruckner (courtesy of the Science Education Resource Center (SERC) at Carleton College).

## Acid Rain

Normal rainwater has a pH between 5 and 6 due to the presence of dissolved $CO_2$ which forms carbonic acid:

$$\mathrm{H_2O\,(l) + CO_2\,(g) \longrightarrow H_2CO_3\,(aq)} \tag{13.2.2.1}$$

$$\mathrm{H_2CO_3\,(aq) \rightleftharpoons H^+\,(aq) + HCO_3{}^-\,(aq)} \tag{13.2.2.2}$$

Acid rain is rainwater that has a pH of less than 5, due to a variety of nonmetal oxides, including $CO_2$, $SO_2$, $SO_3$, NO, and $NO_2$ being dissolved in the water and reacting with it to form not only carbonic acid, but sulfuric acid and nitric acid. The formation and subsequent ionization of sulfuric acid are shown here:

$$\mathrm{H_2O\,(l) + SO_3\,(g) \longrightarrow H_2SO_4\,(aq)} \tag{13.2.2.3}$$

$$H_2SO_4\,(aq) \longrightarrow H^+\,(aq) + HSO_4{}^-\,(aq) \qquad (13.2.2.4)$$

Carbon dioxide is naturally present in the atmosphere because we and most other organisms produce it as a waste product of metabolism. Carbon dioxide is also formed when fires release carbon stored in vegetation or when we burn wood or fossil fuels. Sulfur trioxide in the atmosphere is naturally produced by volcanic activity, but it also stems from burning fossil fuels, which have traces of sulfur, and from the process of "roasting" ores of metal sulfides in metal-refining processes. Oxides of nitrogen are formed in internal combustion engines where the high temperatures make it possible for the nitrogen and oxygen in air to chemically combine.

Acid rain is a particular problem in industrial areas where the products of combustion and smelting are released into the air without being stripped of sulfur and nitrogen oxides. In North America and Europe until the 1980s, it was responsible for the destruction of forests and freshwater lakes, when the acidity of the rain actually killed trees, damaged soil, and made lakes uninhabitable for all but the most acid-tolerant species. Acid rain also corrodes statuary and building facades that are made of marble and limestone (Figure 13.2.2.4). Regulations limiting the amount of sulfur and nitrogen oxides that can be released into the atmosphere by industry and automobiles have reduced the severity of acid damage to both natural and manmade environments in North America and Europe. It is now a growing problem in industrial areas of China and India.

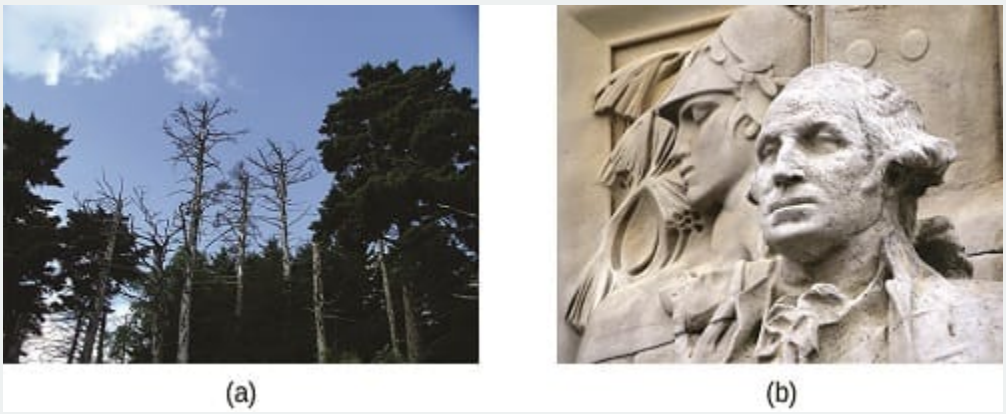



Figure 13.2.2.4: (a) Acid rain makes trees more susceptible to drought and insect infestation, and depletes nutrients in the soil. (b) It also is corrodes statues that are carved from marble or limestone. (credit a: modification of work by Chris M Morris; credit b: modification of work by "Eden, Janine and Jim"/Flickr)

## Answers

**Exercise** 13.2.2.1

a. 3.24

b. 7.00

**Exercise** 13.2.2.2

a. slightly basic

b. basic

c. acidic

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# 13.2.3: Working with pH

## Learning Objectives

- Calculate pH from $[H_3O^+]$ and $[H_3O^+]$ from pH.

## Calculating pH from Hydronium Concentration

The pH of solutions can be determined by using logarithms as illustrated in the next example for stomach acid. Stomach acid is a solution of $HCl$ with a hydronium ion concentration of $1.2 \times 10^{-3}\ M$, what is the $pH$ of the solution?

$$\begin{aligned} \text{pH} &= -\log[\text{H}_3\text{O}^+] \\ &= -\log(1.2 \times 10^{-3}) \\ &= -(-2.92) = 2.92 \end{aligned}$$

### 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 $[H_3O^+]$ = 1.0 x $10^{-5}$ M) you should get an answer of "-5".

If you get a different answer, or an error, try pressing the LOG key before you enter the number.

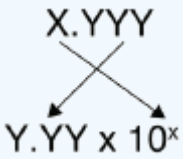
### Example 13.2.3.2: Converting Ph to Hydronium Concentration

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**

| Steps for Problem Solving | |
|---|---|
| Identify the "given" information and what the problem is asking you to "find." | Given:<br><br>a. $[H_3O^+]$ =1 × $10^{-3}$ M<br>b. $[H_3O^+]$ =2.5 ×$10^{-11}$ M<br>c. $[H_3O^+]$ = 4.7 ×$10^{-9}$ M<br><br>Find: ? pH |

| Steps for Problem Solving | |
|---|---|
| Plan the problem. | Need to use the expression for pH (Equation ???).<br>$pH = - \log [H_3O^+]$ |
| Calculate. | Now substitute the known quantity into the equation and solve.<br>a. $pH = - \log [1 \times 10^{-3}] = 3.0$ (1 decimal places since 1 has 1 significant figure)<br>b. $pH = - \log [2.5 \times 10^{-11}] = 10.60$ (2 decimal places since 2.5 has 2 significant figures)<br>c. $pH = - \log [4.7 \times 10^{-9}] = 8.30$ (2 decimal places since 4.7 has 2 significant figures)<br>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:<br>  |

**Exercise 13.2.3.2**

Find the pH, given $[H_3O^+]$ of the following:

a. $5.8 \times 10^{-4}$ M
b. $1.0 \times 10^{-7}$

*Answer a available at the end of this section.*

*Answer b available at the end of this section.*

## 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 ??? for $[H_3O^+]$. This involves taking the antilog (or inverse log) of the negative value of pH .

$$[\mathrm{H_3O^+}] = \mathrm{antilog}(-pH) \tag{13.2.3.1}$$

or

$$[\mathrm{H_3O^+}] = 10^{-pH} \tag{13.2.3.2}$$

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 $\mathbf{5.0 \times 10^{-9}}$.

**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 $\mathbf{5.0 \times 10^{-9}}$.

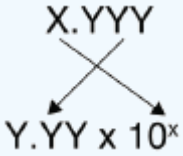
If neither of these methods work, try rearranging the order in which you type in the keys. Don't give up—you must master your calculator!

## Example 13.2.3.3: 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**

| Steps for Problem Solving | |
|---|---|
| Identify the "given" information and what the problem is asking you to "find." | Given: pH = 12.6<br><br>Find: $[H_3O^+]$ = ? M |
| Plan the problem. | Need to use the expression for $[H_3O^+]$ (Equation 13.2.3.2).<br><br>$[H_3O^+]$ = antilog (-pH) or $[H_3O^+] = 10^{-pH}$ |

| Steps for Problem Solving | |
|---|---|
| Calculate. | Now substitute the known quantity into the equation and solve.<br><br>$[H_3O^+]$ = antilog (12.60) = 2.5 x $10^{-13}$ M (2 significant figures since 4.7 has 12.60 2 decimal places)<br><br>or<br><br>$[H_3O^+] = 10^{-12.60} = 2.5 \times 10^{-13}$ M (2 significant figures since 4.7 has 12.60 2 decimal places)<br><br>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:<br><br>  |

## Exercise 13.2.3.3

If moist soil has a pH of 7.84, what is $[H_3O^+]$ of the soil solution?

*Answer available at the end of this section.*

## Answers

**Exercise** 13.2.3.2

3.22

**Exercise** 13.2.3.2

7.00

**Exercise** 13.2.3.3

1.5 x $10^{-8}$ M

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# 13.3: MAINTAINING PH USING BUFFER SOLUTIONS

## Learning Objectives

- Describe the composition and function of acid–base buffers
- Calculate the pH of a buffer before and after the addition of added acid or base

A mixture of a weak acid and its conjugate base (or a mixture of a weak base and its conjugate acid) is called a buffer solution, or a buffer. Buffer solutions resist a change in pH when small amounts of a strong acid or a strong base are added (Figure 13.3.1). A solution of acetic acid ($CH_3COOH$ and sodium acetate $CH_3COONa$) is an example of a buffer that consists of a weak acid and its salt. An example of a buffer that consists of a weak base and its salt is a solution of ammonia ($NH_3\,(aq)$) and ammonium chloride ($NH_4Cl\,(aq)$).

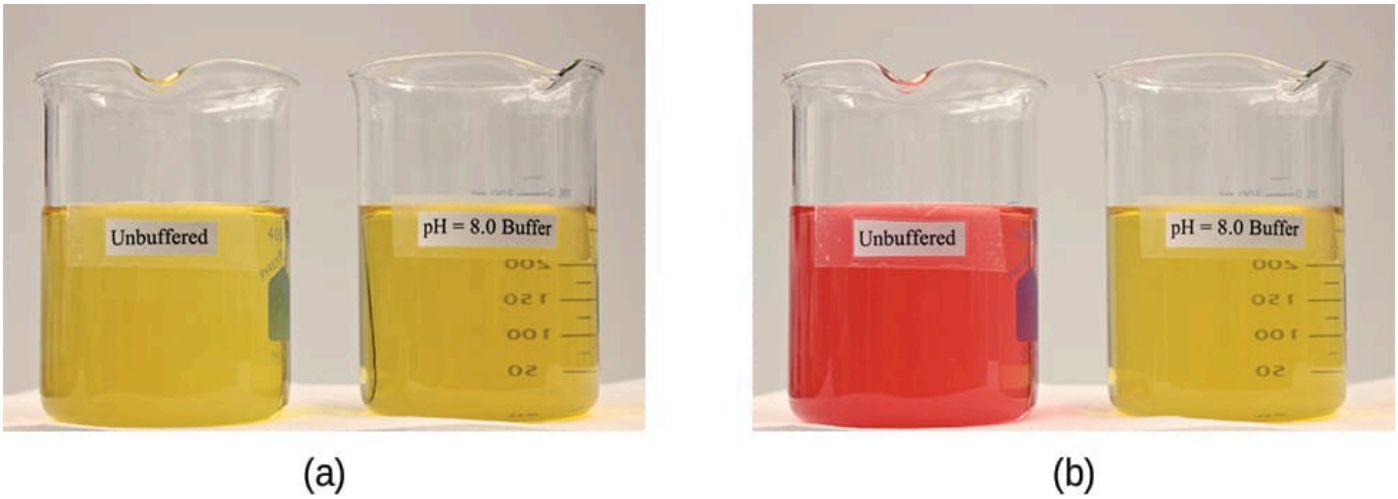



Figure 13.3.1: (a) The unbuffered solution on the left and the buffered solution on the right have the same pH (pH 8); they are basic, showing the yellow color of the indicator methyl orange at this pH. (b) After the addition of 1 mL of a 0.01-M HCl solution, the buffered solution has not detectably changed its pH but the unbuffered solution has become acidic, as indicated by the change in color of the methyl orange, which turns red at a pH of about 4. (credit: modification of work by Mark Ott)

## How Buffers Work

A mixture of acetic acid and sodium acetate is acidic because the $K_a$ of acetic acid is greater than the $K_b$ of its conjugate base acetate. It is a buffer because it contains both the weak acid and its salt. Hence, it acts to keep the hydronium ion concentration (and the pH) almost constant by the addition of either a small amount of a strong acid or a strong base. If we add a base such as sodium hydroxide, the hydroxide ions react with the few hydronium ions present. Then more of the acetic acid reacts with water, restoring the hydronium ion concentration almost to its original value:

$$CH_3CO_2H(aq) + H_2O(l) \longrightarrow H_3O^+(aq) + CH_3CO_2{}^-(aq)$$

The pH changes very little. If we add an acid such as hydrochloric acid, most of the hydronium ions from the hydrochloric acid combine with acetate ions, forming acetic acid molecules:

$$H_3O^+(aq) + CH_3CO_2{}^-(aq) \longrightarrow CH_3CO_2H(aq) + H_2O(l)$$

Thus, there is very little increase in the concentration of the hydronium ion, and the pH remains practically unchanged (Figure 13.3.2).

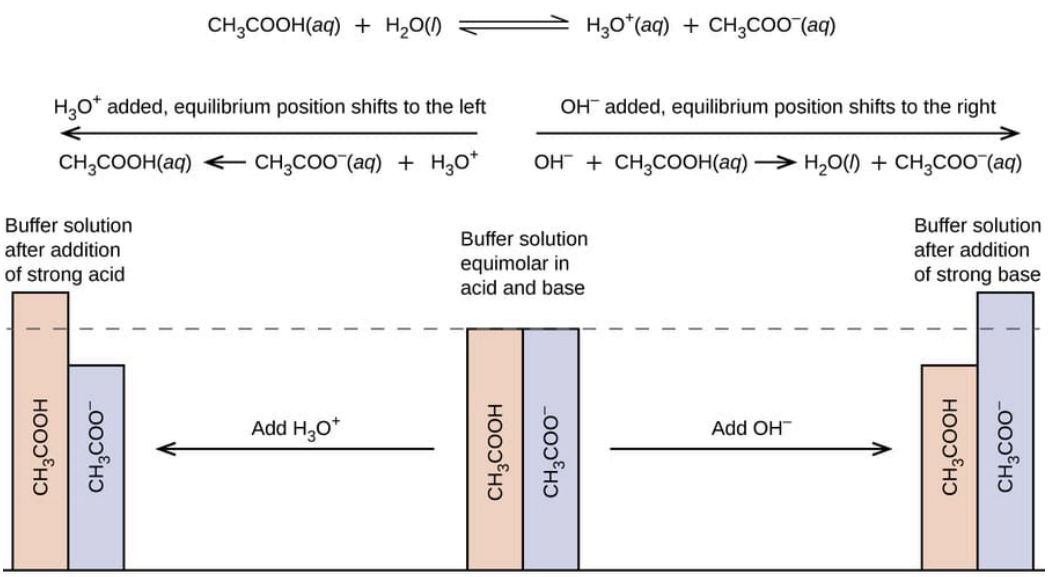



Figure 13.3.2: This diagram shows the buffer action of these reactions.

A mixture of ammonia and ammonium chloride is basic because the $K_b$ for ammonia is greater than the $K_a$ for the ammonium ion. It is a buffer because it also contains the salt of the weak base. If we add a base (hydroxide ions), ammonium ions in the buffer react with the hydroxide ions to form ammonia and water and reduce the hydroxide ion concentration almost to its original value:

$$\mathrm{NH_4^+}(aq) + \mathrm{OH^-}(aq) \longrightarrow \mathrm{NH_3}(aq) + \mathrm{H_2O}(l)$$

If we add an acid (hydronium ions), ammonia molecules in the buffer mixture react with the hydronium ions to form ammonium ions and reduce the hydronium ion concentration almost to its original value:

$$\mathrm{H_3O^+}(aq) + \mathrm{NH_3}(aq) \longrightarrow \mathrm{NH_4^+}(aq) + \mathrm{H_2O}(l)$$

The three parts of the following example illustrate the change in pH that accompanies the addition of base to a buffered solution of a weak acid and to an unbuffered solution of a strong acid.

## Example 13.3.1: pH Changes in Buffered and Unbuffered Solutions

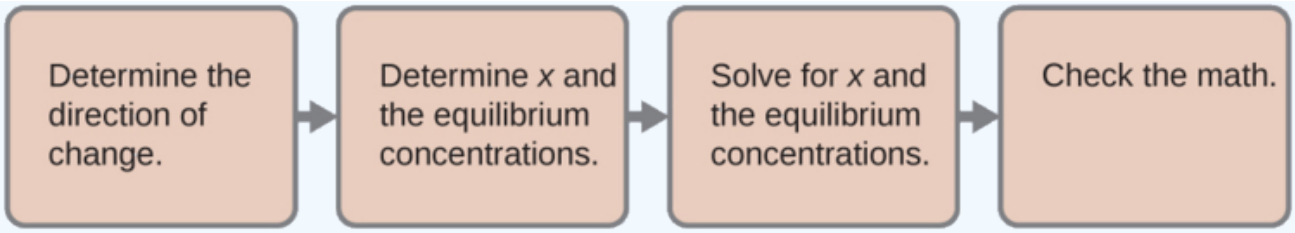
Acetate buffers are used in biochemical studies of enzymes and other chemical components of cells to prevent pH changes that might change the biochemical activity of these compounds.

a. Calculate the pH of an acetate buffer that is a mixture with 0.10 *M* acetic acid and 0.10 *M* sodium acetate.
b. Calculate the pH after 1.0 mL of 0.10 *M* NaOH is added to 100 mL of this buffer, giving a solution with a volume of 101 mL.

**Solution**

a. Calculate the pH of an acetate buffer that is a mixture with 0.10 *M* acetic acid and 0.10 *M* sodium acetate.

   To determine the pH of the buffer solution we use a typical equilibrium calculation (as illustrated in earlier Examples):




1. *Determine the direction of change*. The equilibrium in a mixture of $H_3O^+$, $CH_3CO_2^-$, and $CH_3CO_2H$ is:

$$CH_3CO_2H(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3CO_2^-(aq)$$

The equilibrium constant for $CH_3CO_2H$ is not given, so we look it up in Table E1: $K_a = 1.8 \times 10^{-5}$. With $[CH_3CO_2H] = [CH_3CO_2^-] = 0.10\ M$ and $[H_3O^+] = \sim 0\ M$, the reaction shifts to the right to form $H_3O^+$.

2. *Determine* x *and equilibrium concentrations*. A table of changes and concentrations follows:

| | $[CH_3CO_2H]$ + $[H_2O]$ $\rightleftharpoons$ | $H_3O^+$ + | $[CH_3CO_2^-]$ |
|---|---|---|---|
| **Initial concentration (*M*)** | 0.10 | ~0 | 0.10 |
| **Change (*M*)** | $-x$ | $x$ | $x$ |
| **Equilibrium constant (*M*)** | $0.10 - x$ | $x$ | $0.10 + x$ |

- *Solve for x and the equilibrium concentrations*. We find:

$$x = 1.8 \times 10^{-5}\ M$$

- and

$$[H_3O^+] = 0 + x = 1.8 \times 10^{-5}\ M$$

Thus:

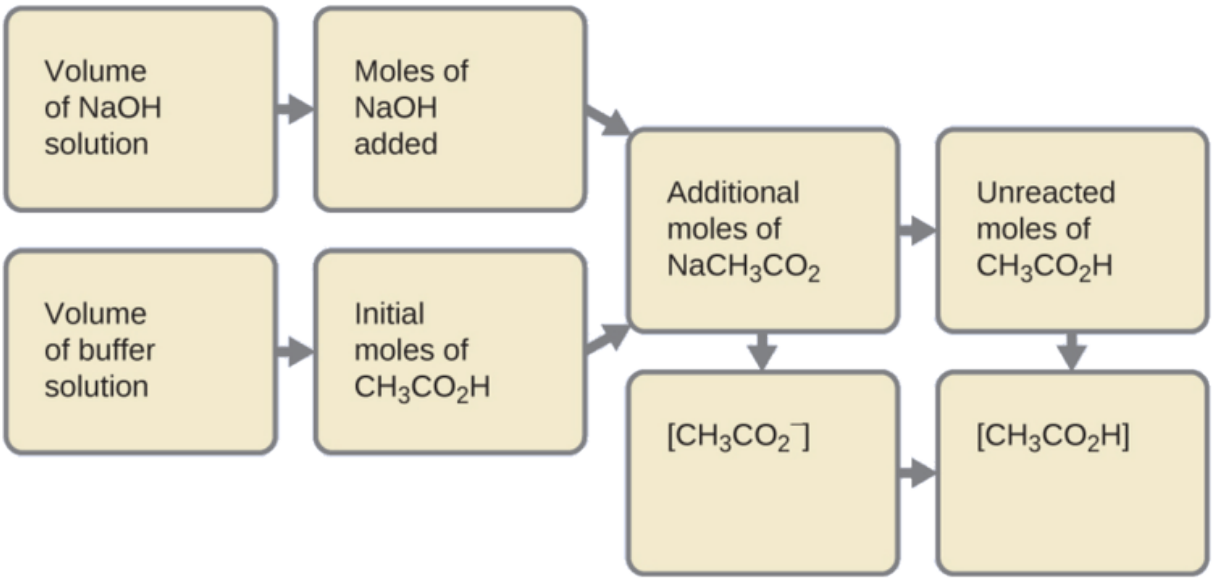
$$pH = -\log[H_3O^+] = -\log(1.8 \times 10^{-5})$$

$$= 4.74$$

4. *Check the work*. If we calculate all calculated equilibrium concentrations, we find that the equilibrium value of the reaction coefficient, $Q = K_a$.

(b) Calculate the pH after 1.0 mL of 0.10 *M* NaOH is added to 100 mL of this buffer, giving a solution with a volume of 101 mL.

First, we calculate the concentrations of an intermediate mixture resulting from the complete reaction between the acid in the buffer and the added base. Then we determine the concentrations of the mixture at the new equilibrium:




1. *Determine the moles of NaOH.* One milliliter (0.0010 L) of 0.10 *M* NaOH contains:

$$0.0010 \cancel{L} \times \left( \frac{0.10 \text{ mol NaOH}}{1 \cancel{L}} \right) = 1.0 \times 10^{-4} \text{ mol NaOH}$$

2. *Determine the moles of $CH_2CO_2H$.* Before reaction, 0.100 L of the buffer solution contains:

$$0.100 \cancel{L} \times \left( \frac{0.100 \text{ mol } CH_3CO_2H}{1 \cancel{L}} \right) = 1.00 \times 10^{-2} \text{ mol } CH_3CO_2H$$

3. *Solve for the amount of $NaCH_3CO_2$ produced.* The $1.0 \times 10^{-4}$ mol of NaOH neutralizes $1.0 \times 10^{-4}$ mol of $CH_3CO_2H$, leaving:

$$(1.0 \times 10^{-2}) - (0.01 \times 10^{-2}) = 0.99 \times 10^{-2} \text{ mol } CH_3CO_2H$$

and producing $1.0 \times 10^{-4}$ mol of $NaCH_3CO_2$. This makes a total of:

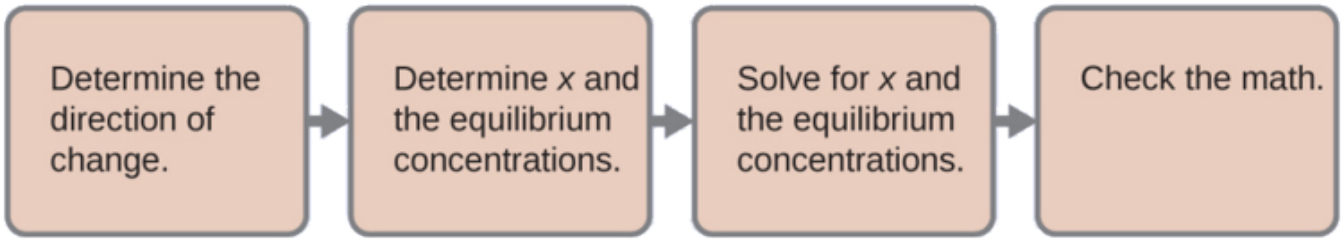
[\mathrm{(1.0×10^{−2})+(0.01×10^{−2})=1.01×10^{−2}\:mol\:NaCH_3CO_2} \nonumber \]

4. *Find the molarity of the products.* After reaction, $CH_3CO_2H$ and $NaCH_3CO_2$ are contained in 101 mL of the intermediate solution, so:

$$[CH_3CO_2H] = \frac{9.9 \times 10^{-3} \text{ mol}}{0.101 \text{ L}} = 0.098 \, M$$

$$[NaCH_3CO_2] = \frac{1.01 \times 10^{-2} \text{ mol}}{0.101 \text{ L}} = 0.100 \, M$$

Now we calculate the pH after the intermediate solution, which is 0.098 *M* in $CH_3CO_2H$ and 0.100 *M* in $NaCH_3CO_2$, comes to equilibrium. The calculation is very similar to that in part (a) of this example:




*This series of calculations gives a pH = 4.75. Thus the addition of the base barely changes the pH of the solution.*

(c) For comparison, calculate the pH after 1.0 mL of 0.10 *M* NaOH is added to 100 mL of a solution of an unbuffered solution with a pH of 4.74 (a $1.8 \times 10^{-5}$-*M* solution of HCl). The volume of the final solution is 101 mL.

**Solution**

This $1.8 \times 10^{-5}$-*M* solution of HCl has the same hydronium ion concentration as the 0.10-*M* solution of acetic acid-sodium acetate buffer described in part (a) of this example. The solution contains:

$$0.100\ \text{L} \times \left(\frac{1.8 \times 10^{-5}\ \text{mol HCl}}{1\ \text{L}}\right) = 1.8 \times 10^{-6}\ \text{mol HCl}$$

As shown in part (b), 1 mL of 0.10 *M* NaOH contains $1.0 \times 10^{-4}$ mol of NaOH. When the NaOH and HCl solutions are mixed, the HCl is the limiting reagent in the reaction. All of the HCl reacts, and the amount of NaOH that remains is:

$$(1.0 \times 10^{-4}) - (1.8 \times 10^{-6}) = 9.8 \times 10^{-5}\ \ M$$

The concentration of NaOH is:

$$\frac{9.8 \times 10^{-5}\ M\ \text{NaOH}}{0.101\ \text{L}} = 9.7 \times 10^{-4}\ \ M$$

The pOH of this solution is:

$$\text{pOH} = -\log[\text{OH}^-] = -\log(9.7 \times 10^{-4}) = 3.01$$

The pH is:

$$\text{pH} = 14.00 - \text{pOH} = 10.99$$

The pH changes from 4.74 to 10.99 in this unbuffered solution. This compares to the change of 4.74 to 4.75 that occurred when the same amount of NaOH was added to the buffered solution described in part (b).

**Exercise 13.3.1**

Show that adding 1.0 mL of 0.10 *M* HCl changes the pH of 100 mL of a $1.8 \times 10^{-5}$ *M* HCl solution from 4.74 to 3.00.

*Answer available at the end of this section.*

## Buffer Capacity

Buffer solutions do not have an unlimited capacity to keep the pH relatively constant (Figure 13.3.3). If we add so much base to a buffer that the weak acid is exhausted, no more buffering action toward the base is possible. On the other hand, if we add an excess of acid, the weak base would be exhausted, and no more buffering action toward any additional acid would be possible. In fact, we do not even need to exhaust all of the acid or base in a buffer to overwhelm it; its buffering action will diminish rapidly as a given component nears depletion.




Figure 13.3.3: The indicator color (methyl orange) shows that a small amount of acid added to a buffered solution of pH 8 (beaker on the left) has little affect on the buffered system (middle beaker). However, a large amount of acid exhausts the buffering capacity of the solution and the pH changes dramatically (beaker on the right). (credit: modification of work by Mark Ott)

The buffer capacity is the amount of acid or base that can be added to a given volume of a buffer solution before the pH changes significantly, usually by one unit. Buffer capacity depends on the amounts of the weak acid and its conjugate base that are in a buffer mixture. For example, 1 L of a solution that is 1.0 *M* in acetic acid and 1.0 *M* in sodium acetate has a greater buffer capacity than 1 L of a solution that is 0.10 *M* in acetic acid and 0.10 *M* in sodium acetate even though both solutions have the same pH. The first solution has more buffer capacity because it contains more acetic acid and acetate ion.

## Selection of Suitable Buffer Mixtures

There are two useful rules of thumb for selecting buffer mixtures:

1. A good buffer mixture should have about equal concentrations of both of its components. A buffer solution has generally lost its usefulness when one component of the buffer pair is less than about 10% of the other. Figure 13.3.4 shows an acetic acid-acetate ion buffer as base is added. The initial pH is 4.74. A change of 1 pH unit occurs when the acetic acid concentration is reduced to 11% of the acetate ion concentration.

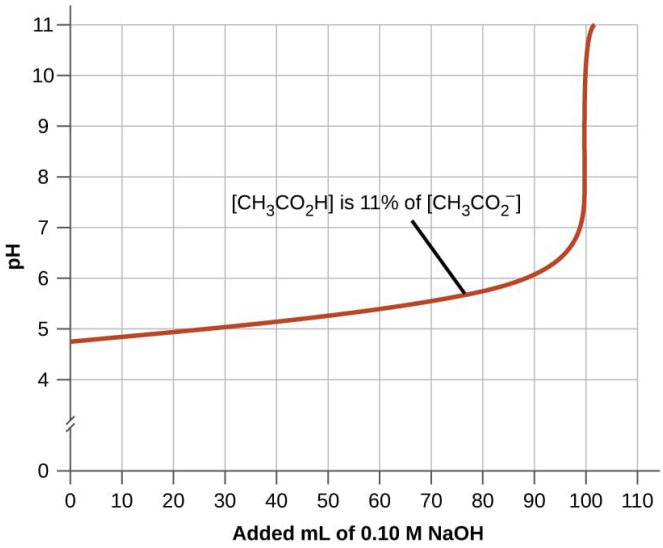



Figure 13.3.4: The graph, an illustration of buffering action, shows change of pH as an increasing amount of a 0.10-M NaOH solution is added to 100 mL of a buffer solution in which, initially, $[CH_3CO_2H] = 0.10\ M$ and $[CH_3CO_2{}^-] = 0.10\ M$.

2. Weak acids and their salts are better as buffers for pHs less than 7; weak bases and their salts are better as buffers for pHs greater than 7.

Blood is an important example of a buffered solution, with the principal acid and ion responsible for the buffering action being carbonic acid, $H_2CO_3$, and the bicarbonate ion, $HCO_3{}^-$. When an excess of hydrogen ion enters the blood stream, it is

removed primarily by the reaction:

$$H_3O^+(aq) + HCO_3^-(aq) \longrightarrow H_2CO_3(aq) + H_2O(l)$$

When an excess of the hydroxide ion is present, it is removed by the reaction:

$$OH^-(aq) + H_2CO_3(aq) \longrightarrow HCO_3^-(aq) + H_2O(l)$$

The pH of human blood thus remains very near 7.35, that is, slightly basic. Variations are usually less than 0.1 of a pH unit. A change of 0.4 of a pH unit is likely to be fatal.

## The Henderson-Hasselbalch Approximation

The ionization-constant expression for a solution of a weak acid can be written as:

$$K_a = \frac{[H3O+][A-]}{[HA]}$$

Rearranging to solve for $[H_3O^+]$, we get:

$$[H_3O^+] = K_a \times \frac{[HA]}{[A-]}$$

Taking the negative logarithm of both sides of this equation, we arrive at:

$$-\log[H_3O^+] = -\log K_a - \log\frac{[HA]}{[A^-]}$$

which can be written as

$$pH = pK_a + \log\frac{[A^-]}{[HA]}$$

where $pK_a$ is the negative of the common logarithm of the ionization constant of the weak acid ($pK_a = -\log K_a$). This equation relates the pH, the ionization constant of a weak acid, and the concentrations of the weak acid and its salt in a buffered solution. Scientists often use this expression, called the Henderson-Hasselbalch approximation, to calculate the pH of buffer solutions. It is important to note that the "*x* is small" assumption must be valid to use this equation.

### Lawrence Joseph Henderson and Karl Albert Hasselbalch

Lawrence Joseph Henderson (1878–1942) was an American physician, biochemist and physiologist, to name only a few of his many pursuits. He obtained a medical degree from Harvard and then spent 2 years studying in Strasbourg, then a part of Germany, before returning to take a lecturer position at Harvard. He eventually became a professor at Harvard and worked there his entire life. He discovered that the acid-base balance in human blood is regulated by a buffer system formed by the dissolved carbon dioxide in blood. He wrote an equation in 1908 to describe the carbonic acid-carbonate buffer system in blood. Henderson was broadly knowledgeable; in addition to his important research on the physiology of blood, he also wrote on the adaptations of organisms and their fit with their environments, on sociology and on university education. He also founded the Fatigue Laboratory, at the Harvard Business School, which examined human physiology with specific focus on work in industry, exercise, and nutrition.

In 1916, Karl Albert Hasselbalch (1874–1962), a Danish physician and chemist, shared authorship in a paper with Christian Bohr in 1904 that described the Bohr effect, which showed that the ability of hemoglobin in the blood to bind with oxygen was inversely related to the acidity of the blood and the concentration of carbon dioxide. The pH scale was introduced in 1909 by another Dane, Sørensen, and in 1912, Hasselbalch published measurements of the pH of blood. In 1916, Hasselbalch expressed Henderson's equation in logarithmic terms, consistent with the logarithmic scale of pH, and thus the Henderson-Hasselbalch equation was born.

### Medicine: The Buffer System in Blood

The normal pH of human blood is about 7.4. The carbonate buffer system in the blood uses the following equilibrium reaction:

$$\mathrm{CO_2}(g) + 2\,\mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_2CO_3}(aq) \rightleftharpoons \mathrm{HCO_3}^-(aq) + \mathrm{H_3O}^+(aq)$$

The concentration of carbonic acid, $H_2CO_3$ is approximately 0.0012 *M*, and the concentration of the hydrogen carbonate ion, $\mathrm{HCO_3}^-$, is around 0.024 *M*. Using the Henderson-Hasselbalch equation and the p$K_a$ of carbonic acid at body temperature, we can calculate the pH of blood:

$$\mathrm{pH} = \mathrm{p}K_\mathrm{a} + \log\frac{[\mathrm{base}]}{[\mathrm{acid}]} = 6.1 + \log\frac{0.024}{0.0012} = 7.4$$

The fact that the $H_2CO_3$ concentration is significantly lower than that of the $\mathrm{HCO_3}^-$ ion may seem unusual, but this imbalance is due to the fact that most of the by-products of our metabolism that enter our bloodstream are acidic. Therefore, there must be a larger proportion of base than acid, so that the capacity of the buffer will not be exceeded.

Lactic acid is produced in our muscles when we exercise. As the lactic acid enters the bloodstream, it is neutralized by the $\mathrm{HCO_3}^-$ ion, producing $H_2CO_3$. An enzyme then accelerates the breakdown of the excess carbonic acid to carbon dioxide and water, which can be eliminated by breathing. In fact, in addition to the regulating effects of the carbonate buffering system on the pH of blood, the body uses breathing to regulate blood pH. If the pH of the blood decreases too far, an increase in breathing removes $CO_2$ from the blood through the lungs driving the equilibrium reaction such that $[H_3O^+]$ is lowered. If the blood is too alkaline, a lower breath rate increases $CO_2$ concentration in the blood, driving the equilibrium reaction the other way, increasing $[H^+]$ and restoring an appropriate pH.

## Summary

A solution containing a mixture of an acid and its conjugate base, or of a base and its conjugate acid, is called a buffer solution. Unlike in the case of an acid, base, or salt solution, the hydronium ion concentration of a buffer solution does not change greatly when a small amount of acid or base is added to the buffer solution. The base (or acid) in the buffer reacts with the added acid (or base).

## Key Equations

- p$K_a$ = –log $K_a$
- p$K_b$ = –log $K_b$
- $\mathrm{pH} = \mathrm{p}K_\mathrm{a} + \log\frac{[\mathrm{A}^-]}{[\mathrm{HA}]}$

## Glossary

**buffer capacity**
: amount of an acid or base that can be added to a volume of a buffer solution before its pH changes significantly (usually by one pH unit)

**buffer**
: mixture of a weak acid or a weak base and the salt of its conjugate; the pH of a buffer resists change when small amounts of acid or base are added

**Henderson-Hasselbalch equation**
: equation used to calculate the pH of buffer solutions

## Answers

**Exercise** 13.3.1

Initial pH of $1.8 \times 10^{-5}$ *M* HCl; pH = $-\log[H_3O^+] = -\log[1.8 \times 10^{-5}] = 4.74$

Moles of $H_3O^+$ added by addition of 1.0 mL of 0.10 *M* HCl: 0.10 moles/L × 0.0010 L = $1.0 \times 10^{-4}$ moles; final pH after addition of 1.0 mL of 0.10 *M* HCl:

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log\left(\frac{\text{total moles H}_3\text{O}^+}{\text{total volume}}\right) = -\log\left(\frac{1.0 \times 10^{-4}\ \text{mol} + 1.8 \times 10^{-6}\ \text{mol}}{101\ \text{mL}\left(\frac{1\ \text{L}}{1000\ \text{mL}}\right)}\right) = 3.00$$

## 13.3.1: Biological Buffers

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# 13.3.1: Biological Buffers

Learning Objectives

- Identify and understand the buffer systems in the body

## Buffer Systems in the Body

The buffer systems in the human body are extremely efficient, and different systems work at different rates. It takes only seconds for the chemical buffers in the blood to make adjustments to pH. The respiratory tract can adjust the blood pH upward in minutes by exhaling $CO_2$ from the body. The renal system can also adjust blood pH through the excretion of hydrogen ions ($H^+$) and the conservation of bicarbonate, but this process takes hours to days to have an effect.

The buffer systems functioning in blood plasma include plasma proteins, phosphate, and bicarbonate and carbonic acid buffers. The kidneys help control acid-base balance by excreting hydrogen ions and generating bicarbonate that helps maintain blood plasma pH within a normal range. Protein buffer systems work predominantly inside cells.

### Phosphate Buffer

Phosphates are found in the blood in two forms: sodium dihydrogen phosphate ($Na_2H_2PO_4^-$), which is a weak acid, and sodium monohydrogen phosphate ($Na_2HPO_4^{2-}$), which is a weak base. When $Na_2HPO_4^{2-}$ comes into contact with a strong acid, such as HCl, the base picks up a second hydrogen ion to form the weak acid $Na_2H_2PO_4^-$ and sodium chloride, NaCl. When $Na_2HPO_4^{2-}$ (the weak acid) comes into contact with a strong base, such as sodium hydroxide (NaOH), the weak acid reverts back to the weak base and produces water. Acids and bases are still present, but they hold onto the ions.

$$HCl + Na_2HPO_4 \rightarrow NaH_2PO_4 + NaCl$$

$$\text{(strong acid)} + \text{(weak base)} \rightarrow \text{(weak acid)} + \text{(salt)}$$

$$NaOH + NaH_2PO_4 \rightarrow Na_2HPO_4 + H_2O$$

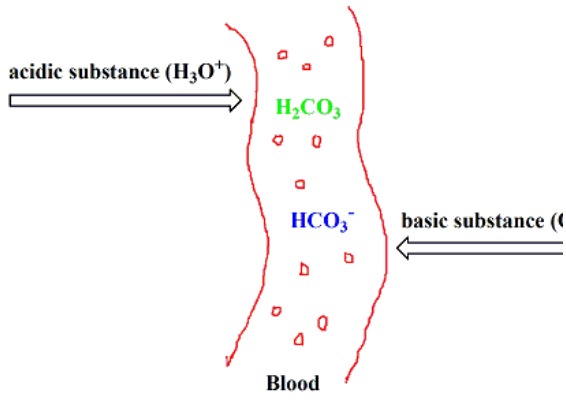
$$\text{(strong base)} + \text{(weak acid)} \rightarrow \text{(weak base)} + \text{(water)}$$

### Bicarbonate-Carbonic Acid Buffer

Maintaining a constant blood pH is critical for the proper functioning of our body. The buffer that maintains the pH of human blood involves a carbonic acid ($H_2CO_3$) - bicarbonate ion ($HCO_3^-$)

$H_2CO_3 + H_2O \rightleftharpoons HCO_3^- + H_3O^+$

weak acid — conjugate base



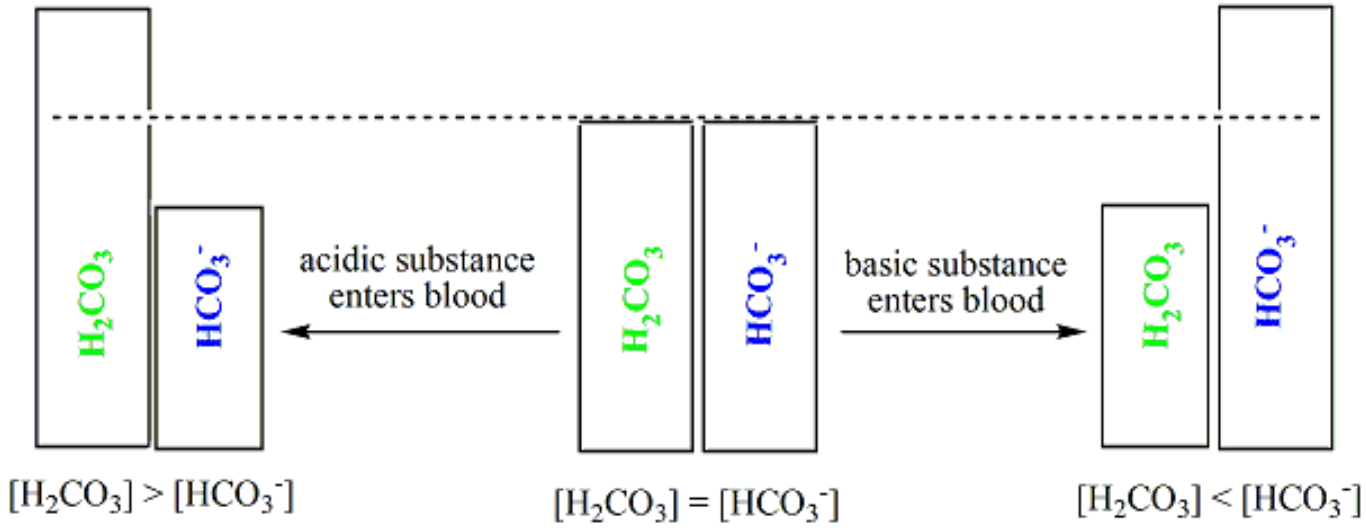

When any acidic substance enters the bloodstream, the bicarbonate ions neutralize the hydronium ions forming carbonic acid and water. Carbonic acid is already a component of the buffering system of blood. Thus hydronium ions are removed, preventing the pH of blood from becoming acidic.

$$HCO_3^- + H_3O^+ \longrightarrow H_2CO_3 + H_2O$$

On the other hand, when a basic substance enters the bloodstream, carbonic acid reacts with the hydroxide ions producing bicarbonate ions and water. Bicarbonate ions are already a component of the buffer. In this manner, the hydroxide ions are removed from blood, preventing the pH of blood from becoming basic.

$$H_2CO_3 + OH^- \longrightarrow HCO_3^- + H_2O$$

As depicted below, in the process of neutralizing hydronium ions or hydroxide ions, the relative concentrations of carbonic acid ($H_2CO_3$) and bicarbonate ions ($HCO_3^-$) fluctuate in the bloodstream. But this slight change in the concentrations of the two components of the buffering system doesn't have any adverse effect; the critical thing is that this buffering mechanism prevents the blood from becoming acidic or basic, which can be detrimental.




*The pH of blood is maintained at ~ 7.4 by the carbonic acid–bicarbonate ion buffering system.*

# Disorders of Acid-Base Balance

## Respiratory Acidosis: Primary Carbonic Acid/$CO_2$ Excess

**Respiratory acidosis** occurs when the blood is overly acidic due to an excess of carbonic acid, resulting from too much $CO_2$ in the blood. Respiratory acidosis can result from anything that interferes with respiration, such as pneumonia, emphysema, or congestive heart failure.

## Respiratory Alkalosis: Primary Carbonic Acid/$CO_2$ Deficiency

**Respiratory alkalosis** occurs when the blood is overly alkaline due to a deficiency in carbonic acid and $CO_2$ levels in the blood. This condition usually occurs when too much $CO_2$ is exhaled from the lungs, as occurs in hyperventilation, which is breathing that is deeper or more frequent than normal. An elevated respiratory rate leading to hyperventilation can be due to extreme emotional upset or fear, fever, infections, hypoxia, or abnormally high levels of catecholamines, such as epinephrine and norepinephrine. Surprisingly, aspirin overdose—salicylate toxicity—can result in respiratory alkalosis as the body tries to compensate for initial acidosis.

## Respiratory Compensation

Respiratory compensation for metabolic acidosis increases the respiratory rate to drive off $CO_2$ and readjust the bicarbonate to carbonic acid ratio to the 20:1 level. This adjustment can occur within minutes. Respiratory compensation for metabolic alkalosis is not as adept as its compensation for acidosis. The normal response of the respiratory system to elevated pH is to increase the amount of $CO_2$ in the blood by decreasing the respiratory rate to conserve $CO_2$. There is a limit to the decrease in respiration, however, that the body can tolerate. Hence, the respiratory route is less efficient at compensating for metabolic alkalosis than for acidosis.

## Key Takeaway

# Contributors and Attributions

*1.* Phosphate buffer: *The source content can be found at* https://pressbooks.bccampus.ca/dcbiol12031209/chapter/26-4-acid-base-balance/. *Page content has been edited and updated to conform to the style and standards of the LibreTexts platform.*

2. Bicarbonate-Carbonic Acid Buffer: *The source content can be found at https://www.khanacademy.org/test-prep/mcat/chemical-processes/acid-base-equilibria/a/chemistry-of-buffers-and-buffers-in-blood. Page content has been edited and updated to conform to the style and standards of the LibreTexts platform.*

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# 14: BIOMOLECULES- BUILDING BLOCKS OF LIFE


**14.1: Synthesis of Biomolecules**

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# 14.1: SYNTHESIS OF BIOMOLECULES

14.1.1: Types of Biological Macromolecules
14.1.2: Dehydration Synthesis
14.1.3: Hydrolysis

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# 14.1.1: Types of Biological Macromolecules

## Learning Objectives

- Identify the four major classes of biological macromolecules

Nutrients are the molecules that living organisms require for survival and growth but that animals and plants cannot synthesize themselves. Animals obtain nutrients by consuming food, while plants pull nutrients from soil.



Figure 14.1.1.1: Sources of biological macromolecules: Foods such as bread, fruit, and cheese are rich sources of biological macromolecules.

Many critical nutrients are biological macromolecules. The term “macromolecule” was first coined in the 1920s by Nobel laureate Hermann Staudinger. Staudinger was the first to propose that many large biological molecules are built by covalently linking smaller biological molecules together.

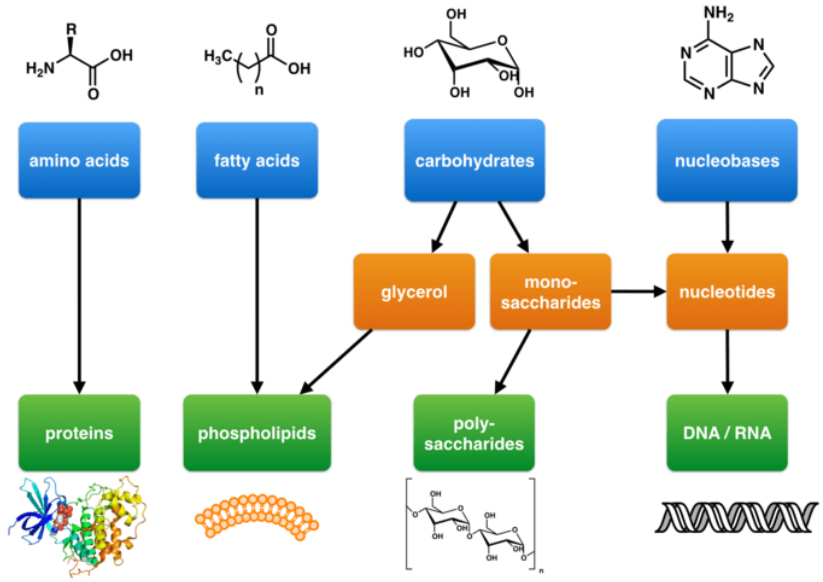
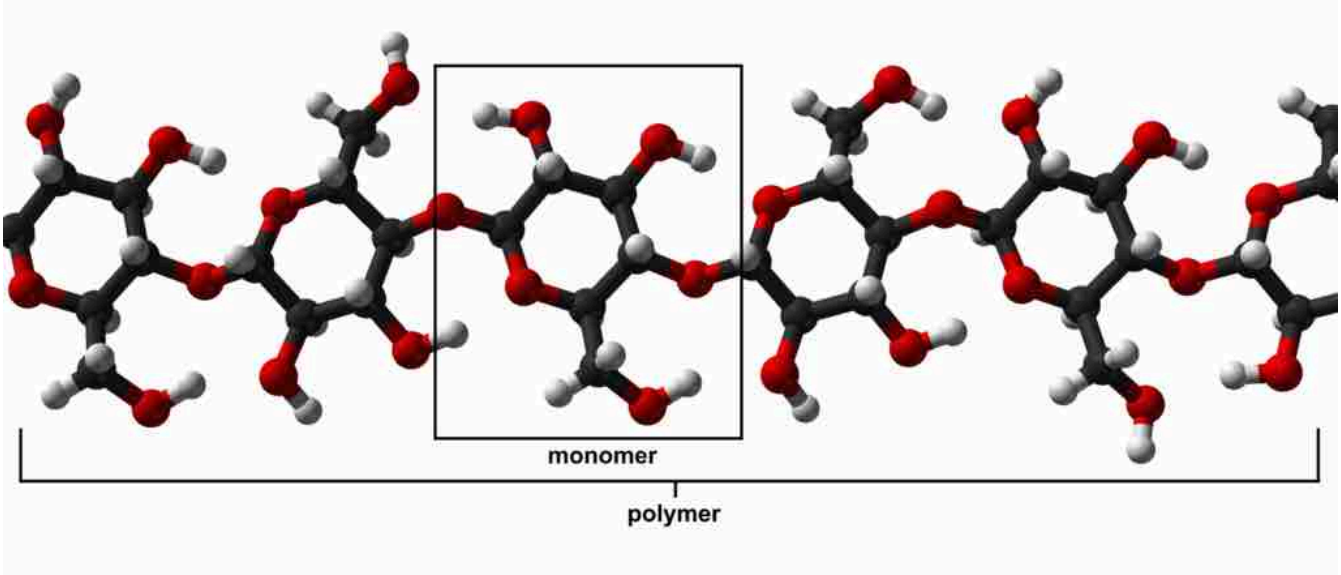



Figure 14.1.1.2: Living organisms are made up of chemical building blocks: All organisms are composed of a variety of these biological macromolecules.

# Monomers and Polymers

Biological macromolecules play a critical role in cell structure and function. Most (but not all) biological macromolecules are polymers, which are any molecules constructed by linking together many smaller molecules, called monomers. Typically all the monomers in a polymer tend to be the same, or at least very similar to each other, linked over and over again to build up the larger macromolecule. These simple monomers can be linked in many different combinations to produce complex biological polymers, just as a few types of Lego blocks can build anything from a house to a car.




Monomers and polymers: Many small monomer subunits combine to form this carbohydrate polymer.

Examples of these monomers and polymers can be found in the sugar you might put in your coffee or tea. Regular table sugar is the disaccharide sucrose (a polymer), which is composed of the monosaccharides fructose and glucose (which are monomers). If we were to string many carbohydrate monomers together we could make a polysaccharide like starch. The prefixes “mono-” (one), “di-” (two),and “poly-” (many) will tell you how many of the monomers have been joined together in a molecule.

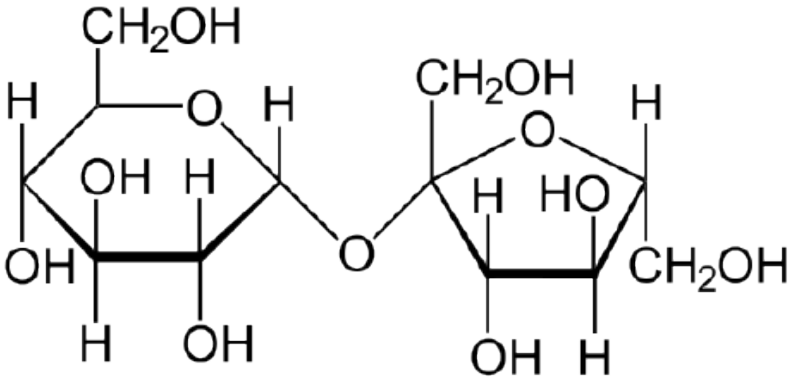



Figure 14.1.1.3: The molecule sucrose (common table sugar): The carbohydrate monosaccharides (fructose and glucose) are joined to make the disaccharide sucrose.

Biological macromolecules all contain carbon in ring or chain form, which means they are classified as organic molecules. They usually also contain hydrogen and oxygen, as well as nitrogen and additional minor elements.

# Four Classes of Biological Macromolecules

There are four major classes of biological macromolecules:

1. carbohydrates
2. lipids
3. proteins
4. nucleic acids

Each of these types of macromolecules performs a wide array of important functions within the cell; a cell cannot perform its role within the body without many different types of these crucial molecules. In combination, these biological macromolecules make up the majority of a cell's dry mass. (Water molecules make up the majority of a cell's total mass.) All the molecules both inside and outside of cells are situated in a water-based (i.e., aqueous) environment, and all the reactions of biological systems are occurring in that same environment.

**Interactive: Monomers and Polymers**

Carbohydrates, proteins, and nucleic acids are built from small molecular units that are connected to each other by strong covalent bonds. The small molecular units are called monomers (mono means one, or single), and they are linked together into long chains called polymers (poly means many, or multiple). Each different type of macromolecule, except lipids, is built from a different set of monomers that resemble each other in composition and size. Lipids are not polymers, because they are not built from monomers (units with similar composition).

## Key Points

- Biological macromolecules are important cellular components and perform a wide array of functions necessary for the survival and growth of living organisms.
- The four major classes of biological macromolecules are carbohydrates, lipids, proteins, and nucleic acids.

## Key Terms

- **polymer**: A relatively large molecule consisting of a chain or network of many identical or similar monomers chemically bonded to each other.
- **monomer**: A relatively small molecule that can form covalent bonds with other molecules of this type to form a polymer.

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# 14.1.2: Dehydration Synthesis

**Learning Objectives**

- Explain dehydration (or condensation) reactions

## Dehydration Synthesis

Most macromolecules are made from single subunits, or building blocks, called monomers. The monomers combine with each other via covalent bonds to form larger molecules known as polymers. In doing so, monomers release water molecules as byproducts. This type of reaction is known as dehydration synthesis, which means “to put together while losing water. ” It is also considered to be a condensation reaction since two molecules are condensed into one larger molecule with the loss of a smaller molecule (the water.)

In a dehydration synthesis reaction between two un-ionized monomers, such as monosaccharide sugars, the hydrogen of one monomer combines with the hydroxyl group of another monomer, releasing a molecule of water in the process. The removal of a hydrogen from one monomer and the removal of a hydroxyl group from the other monomer allows the monomers to share electrons and form a covalent bond. Thus, the monomers that are joined together are being *dehydrated* to allow for *synthesis* of a larger molecule.

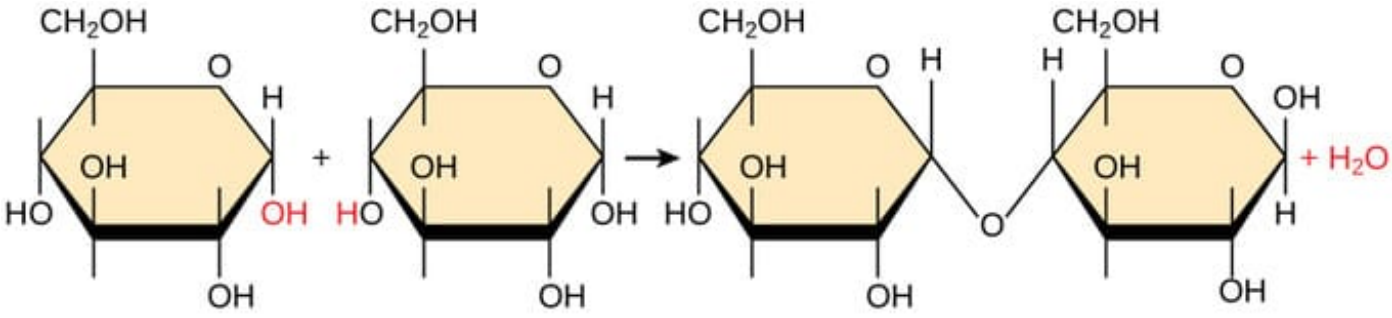



Figure 14.1.2.1: A dehydration synthesis reaction involving un-ionized moners..: In the dehydration synthesis reaction between two molecules of glucose, a hydroxyl group from the first glucose is combined with a hydrogen from the second glucose, creating a covalent bond that links the two monomeric sugars (monosaccharides) together to form the dissacharide maltose. In the process, a water molecule is formed.

When the monomers are ionized, such as is the case with amino acids in an aqueous environment like cytoplasm, two hydrogens from the positively-charged end of one monomer are combined with an oxygen from the negatively-charged end of another monomer, again forming water, which is released as a side-product, and again joining the two monomers with a covalent bond.

image Figure 14.1.2.1: A dehydration synthesis reaction involving ionized monomers.: In the dehydration synthesis reaction between two amino acids, with are ionized in aqueous environments like the cell, an oxygen from the first amino acid is combined with two hydrogens from the second amino acid, creating a covalent bond that links the two monomers together to form a dipeptide. In the process a water molecule is formed.

As additional monomers join via multiple dehydration synthesis reactions, the chain of repeating monomers begins to form a polymer. Different types of monomers can combine in many configurations, giving rise to a diverse group of macromolecules. Three of the four major classes of biological macromolecules (complex carbohydrates, nucleic acids, and proteins), are composed of monomers that join together via dehydration synthesis reactions. Complex carbohydrates are formed from monosaccharides, nucleic acids are formed from mononucleotides, and proteins are formed from amino acids.

There is great diversity in the manner by which monomers can combine to form polymers. For example, glucose monomers are the constituents of starch, glycogen, and cellulose. These three are polysaccharides, classified as carbohydrates, that have formed as a result of multiple dehydration synthesis reactions between glucose monomers. However, the manner by which

glucose monomers join together, specifically locations of the covalent bonds between connected monomers and the orientation (stereochemistry) of the covalent bonds, results in these three different polysaccharides with varying properties and functions. In nucleic acids and proteins, the location and stereochemistry of the covalent linkages connecting the monomers do not vary from molecule to molecule, but instead the multiple kinds of monomers (five different monomers in nucleic acids, A, G, C, T, and U mononucleotides; 21 different amino acids monomers in proteins) are combined in a huge variety of sequences. Each protein or nucleic acid with a different sequence is a different molecule with different properties.

## Key Points

- During dehydration synthesis, either the hydrogen of one monomer combines with the hydroxyl group of another monomer releasing a molecule of water, or two hydrogens from one monomer combine with one oxygen from the other monomer releasing a molecule of water.
- The monomers that are joined via dehydration synthesis reactions share electrons and form covalent bonds with each other.
- As additional monomers join via multiple dehydration synthesis reactions, this chain of repeating monomers begins to form a polymer.
- Complex carbohydrates, nucleic acids, and proteins are all examples of polymers that are formed by dehydration synthesis.
- Monomers like glucose can join together in different ways and produce a variety of polymers. Monomers like mononucleotides and amino acids join together in different sequences to produce a variety of polymers.

## Key Terms

- **covalent bond**: A type of chemical bond where two atoms are connected to each other by the sharing of two or more electrons.
- **monomer**: A relatively small molecule which can be covalently bonded to other monomers to form a polymer.

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# 14.1.3: Hydrolysis

## Learning Objectives

- Explain hydrolysis reactions

Polymers are broken down into monomers in a process known as hydrolysis, which means “to split water,” a reaction in which a water molecule is used during the breakdown. During these reactions, the polymer is broken into two components. If the components are un-ionized, one part gains a hydrogen atom (H-) and the other gains a hydroxyl group (OH–) from a split water molecule. This is what happens when monosaccharides are released from complex carbohydrates via hydrolysis.

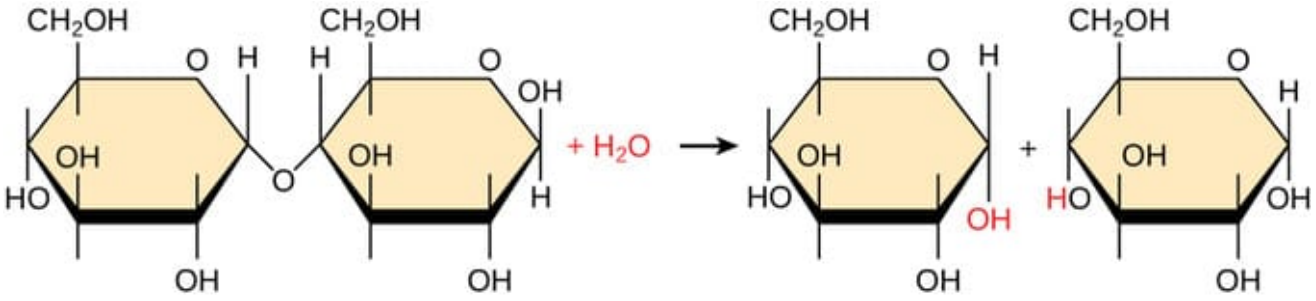



Figure 14.1.3.1: Hydrolysis reaction generating un-ionized products.: In the hydrolysis reaction shown here, the disaccharide maltose is broken down to form two glucose monomers with the addition of a water molecule. One glucose gets a hydroxyl group at the site of the former covalent bond, the other glucose gets a hydrogen atom. This is the reverse of the dehydration synthesis reaction joining these two monomers.

If the components are ionized after the split, one part gains two hydrogen atoms and a positive charge, the other part gains an oxygen atom and a negative charge. This is what happens when amino acids are released from protein chains via hydrolysis.

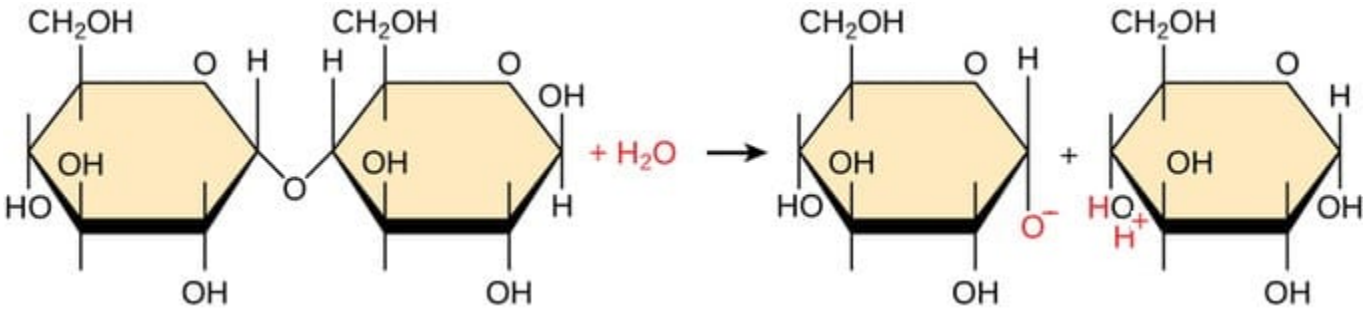



Figure 14.1.3.1: Hydrolysis reaction generating ionized products.: In the hydrolysis reaction shown here, the dipeptide is broken down to form two ionized amino acids with the addition of a water molecule. One amino acid gets an oxygen atom and a negative charge, the other amino acid gets two hydrogen atoms and a positive charge. This is the reverse of the dehydration synthesis reaction joining these two monomers.

These reactions are in contrast to dehydration synthesis (also known as condensation) reactions. In dehydration synthesis reactions, a water molecule is formed as a result of generating a covalent bond between two monomeric components in a larger polymer. In hydrolysis reactions, a water molecule is consumed as a result of breaking the covalent bond holding together two components of a polymer.

Dehydration and hydrolysis reactions are chemical reactions that are catalyzed, or “sped up,” by specific enzymes; dehydration reactions involve the formation of new bonds, requiring energy, while hydrolysis reactions break bonds and release energy.

In our bodies, food is first hydrolyzed, or broken down, into smaller molecules by catalytic enzymes in the digestive tract. This allows for easy absorption of nutrients by cells in the intestine. Each macromolecule is broken down by a specific enzyme. For

instance, carbohydrates are broken down by amylase, sucrase, lactase, or maltase. Proteins are broken down by the enzymes trypsin, pepsin, peptidase and others. Lipids are broken down by lipases. Once the smaller metabolites that result from these hydrolytic enzymezes are absorbed by cells in the body, they are further broken down by other enzymes. The breakdown of these macromolecules is an overall energy-releasing process and provides energy for cellular activities.

### Exercise 14.1.3.1

1. What are biological macromolecules? Name the four major classes.
2. Biological macromolecules are organic. What does that mean?
3. What are monomers? What are polymer?
4. Explain the process “dehydration synthesis.” Is there another name for this process? Explain.
5. Explain Figure 1 in your own words.
6. Give an example of how condensation can form different carbohydrates.
7. Explain the process of Hydrolysis.
8. Explain Figure 2 in your own words.
9. What role do enzymes play in hydrolysis and condensation? Explain.
10. In our bodies, food is hydrolyzed, or broken down into smaller molecules. Explain why.
11. The breakdown of macromolecules provides...
12. Create a comparison chart to indicate the enzymes that break down carbohydrates, proteins, and lipids.

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## Key Points

- Hydrolysis reactions use water to breakdown polymers into monomers and is the opposite of dehydration synthesis, which forms water when synthesizing a polymer from monomers.
- Hydrolysis reactions break bonds and release energy.
- Biological macromolecules are ingested and hydrolyzed in the digestive tract to form smaller molecules that can be absorbed by cells and then further broken down to release energy.

## Key Terms

- **enzyme**: a globular protein that catalyses a biological chemical reaction
- **hydrolysis**: A chemical process of decomposition involving the splitting of a bond by the addition of water.

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# 14.2: CARBOHYDRATES - ENERGY STORAGE AND STRUCTURE MOLECULES

14.2.1: Carbohydrate Molecules
14.2.2: Importance of Carbohydrates

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# 14.2.1: Carbohydrate Molecules

**Learning Objectives**

- Describe the structure of mono-, di-, and poly-saccharides

Carbohydrates can be represented by the stoichiometric formula $(CH_2O)_n$, where n is the number of carbons in the molecule. Therefore, the ratio of carbon to hydrogen to oxygen is 1:2:1 in carbohydrate molecules. The origin of the term "carbohydrate" is based on its components: carbon ("carbo") and water ("hydrate"). Carbohydrates are classified into three subtypes: monosaccharides, disaccharides, and polysaccharides.

## Monosaccharides

Monosaccharides (mono- = "one"; sacchar- = "sweet") are simple sugars. In monosaccharides, the number of carbons usually ranges from three to seven. If the sugar has an aldehyde group (the functional group with the structure R-CHO), it is known as an aldose, and if it has a ketone group (the functional group with the structure RC(=O)R'), it is known as a ketose. Depending on the number of carbons in the sugar, they also may be known as trioses (three carbons), pentoses (five carbons), and or hexoses (six carbons). Monosaccharides can exist as a linear chain or as ring-shaped molecules; in aqueous solutions they are usually found in ring forms.

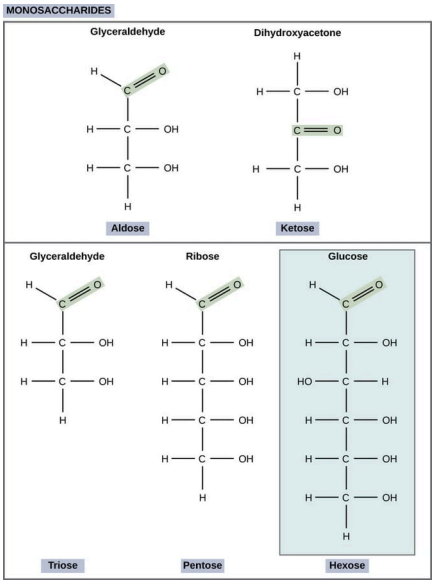



Figure 14.2.1.1: Monosaccharides: Monosaccharides are classified based on the position of their carbonyl group and the number of carbons in the backbone. Aldoses have a carbonyl group (indicated in green) at the end of the carbon chain, and ketoses have a carbonyl group in the middle of the carbon chain. Trioses, pentoses, and hexoses have three, five, and six carbon backbones, respectively.

## Common Monosaccharides

Glucose ($C_6H_{12}O_6$) is a common monosaccharide and an important source of energy. During cellular respiration, energy is released from glucose and that energy is used to help make adenosine triphosphate (ATP). Plants synthesize glucose using carbon dioxide and water, and glucose, in turn, is used for energy requirements for the plant.

Galactose (a milk sugar) and fructose (found in fruit) are other common monosaccharides. Although glucose, galactose, and fructose all have the same chemical formula ($C_6H_{12}O_6$), they differ structurally and stereochemically. This makes them different molecules despite sharing the same atoms in the same proportions, and they are all isomers of one another, or isomeric

monosaccharides. Glucose and galactose are aldoses, and fructose is a ketose.

## Disaccharides

Disaccharides (di- = “two”) form when two monosaccharides undergo a dehydration reaction (also known as a condensation reaction or dehydration synthesis). During this process, the hydroxyl group of one monosaccharide combines with the hydrogen of another monosaccharide, releasing a molecule of water and forming a covalent bond. A covalent bond formed between a carbohydrate molecule and another molecule (in this case, between two monosaccharides) is known as a glycosidic bond. Glycosidic bonds (also called glycosidic linkages) can be of the alpha or the beta type.

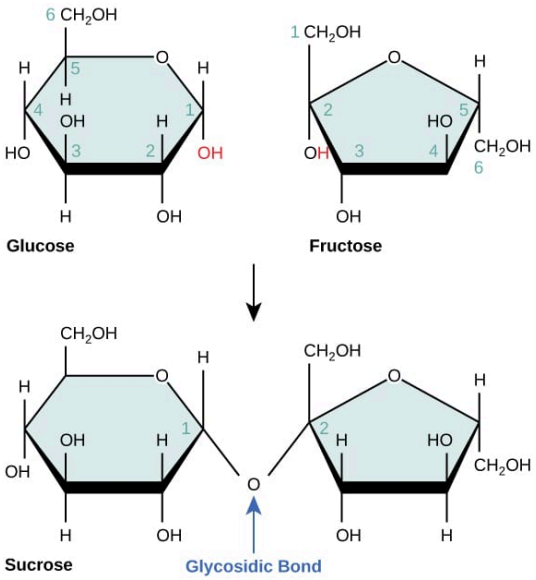



Figure 14.2.1.1: Disaccharides: Sucrose is formed when a monomer of glucose and a monomer of fructose are joined in a dehydration reaction to form a glycosidic bond. In the process, a water molecule is lost. By convention, the carbon atoms in a monosaccharide are numbered from the terminal carbon closest to the carbonyl group. In sucrose, a glycosidic linkage is formed between carbon 1 in glucose and carbon 2 in fructose.

## Common Disaccharides

Common disaccharides include lactose, maltose, and sucrose. Lactose is a disaccharide consisting of the monomers glucose and galactose. It is found naturally in milk. Maltose, or malt sugar, is a disaccharide formed by a dehydration reaction between two glucose molecules. The most common disaccharide is sucrose, or table sugar, which is composed of the monomers glucose and fructose.

## Polysaccharides

A long chain of monosaccharides linked by glycosidic bonds is known as a polysaccharide (poly- = “many”). The chain may be branched or unbranched, and it may contain different types of monosaccharides. Starch, glycogen, cellulose, and chitin are primary examples of polysaccharides.

Plants are able to synthesize glucose, and the excess glucose is stored as starch in different plant parts, including roots and seeds. Starch is the stored form of sugars in plants and is made up of glucose monomers that are joined by α1-4 or 1-6 glycosidic bonds. The starch in the seeds provides food for the embryo as it germinates while the starch that is consumed by humans is broken down by enzymes into smaller molecules, such as maltose and glucose. The cells can then absorb the glucose.

## Common Polysaccharides

Glycogen is the storage form of glucose in humans and other vertebrates. It is made up of monomers of glucose. Glycogen is the animal equivalent of starch and is a highly branched molecule usually stored in liver and muscle cells. Whenever blood glucose

levels decrease, glycogen is broken down to release glucose in a process known as glycogenolysis.

Cellulose is the most abundant natural biopolymer. The cell wall of plants is mostly made of cellulose and provides structural support to the cell. Cellulose is made up of glucose monomers that are linked by β 1-4 glycosidic bonds. Every other glucose monomer in cellulose is flipped over, and the monomers are packed tightly as extended long chains. This gives cellulose its rigidity and high tensile strength—which is so important to plant cells.

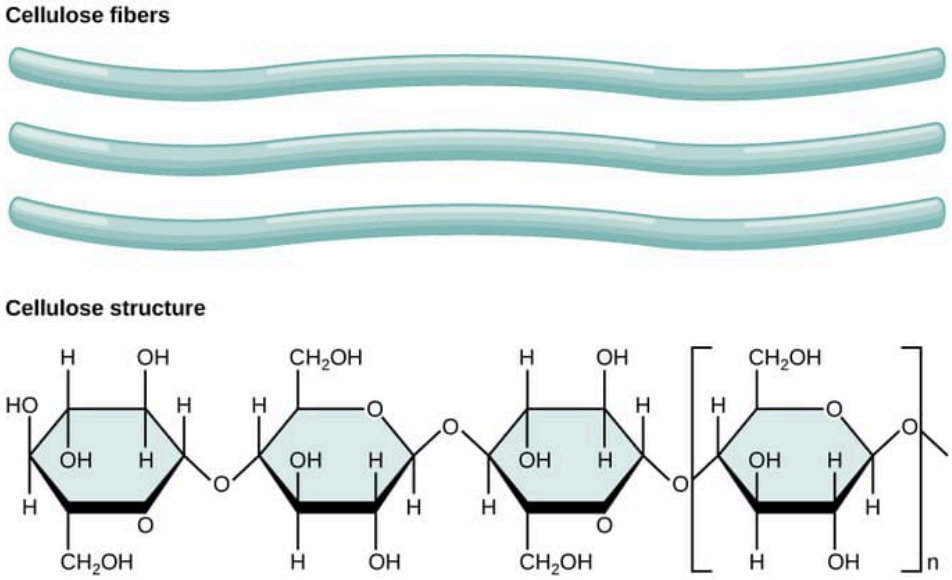



Figure 14.2.1.1: Polysaccharides: In cellulose, glucose monomers are linked in unbranched chains by β 1-4 glycosidic linkages. Because of the way the glucose subunits are joined, every glucose monomer is flipped relative to the next one resulting in a linear, fibrous structure.

## Carbohydrate Function

Carbohydrates serve various functions in different animals. Arthropods have an outer skeleton, the exoskeleton, which protects their internal body parts. This exoskeleton is made of chitin, which is a polysaccharide-containing nitrogen. It is made of repeating units of N-acetyl-β-d-glucosamine, a modified sugar. Chitin is also a major component of fungal cell walls.

## Key Points

- Monosaccharides are simple sugars made up of three to seven carbons, and they can exist as a linear chain or as ring-shaped molecules.
- Glucose, galactose, and fructose are monosaccharide isomers, which means they all have the same chemical formula but differ structurally and chemically.
- Disaccharides form when two monosaccharides undergo a dehydration reaction (a condensation reaction); they are held together by a covalent bond.
- Sucrose (table sugar) is the most common disaccharide, which is composed of the monomers glucose and fructose.
- A polysaccharide is a long chain of monosaccharides linked by glycosidic bonds; the chain may be branched or unbranched and can contain many types of monosaccharides.

## Key Terms

- **isomer**: Any of two or more compounds with the same molecular formula but with different structure.
- **dehydration reaction**: A chemical reaction in which two molecules are covalently linked in a reaction that generates H2O as a second product.
- **biopolymer**: Any macromolecule of a living organism that is formed from the polymerization of smaller entities; a polymer that occurs in a living organism or results from life.

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# 14.2.2: Importance of Carbohydrates

**Learning Objectives**

- Describe the benefits provided to organisms by carbohydrates

## Benefits of Carbohydrates

Biological macromolecules are large molecules that are necessary for life and are built from smaller organic molecules. One major class of biological macromolecules are carbohydrates, which are further divided into three subtypes: monosaccharides, disaccharides, and polysaccharides. Carbohydrates are, in fact, an essential part of our diet; grains, fruits, and vegetables are all natural sources of carbohydrates. Importantly, carbohydrates provide energy to the body, particularly through glucose, a simple sugar that is a component of starch and an ingredient in many basic foods.

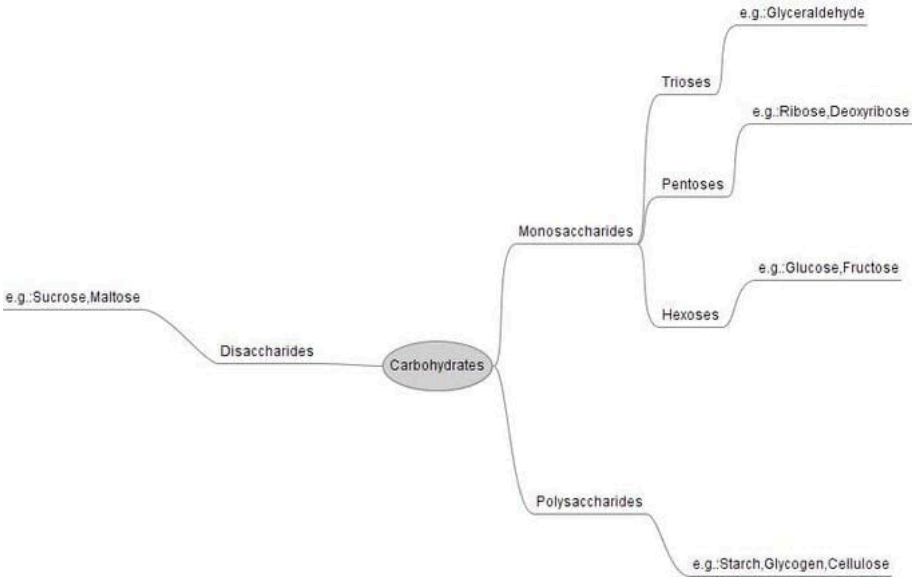



Figure 14.2.2.1: Carbohydrates: Carbohydrates are biological macromolecules that are further divided into three subtypes: monosaccharides, disaccharides, and polysaccharides. Like all macromolecules, carbohydrates are necessary for life and are built from smaller organic molecules.

## Carbohydrates in Nutrition

Carbohydrates have been a controversial topic within the diet world. People trying to lose weight often avoid carbs, and some diets completely forbid carbohydrate consumption, claiming that a low-carb diet helps people to lose weight faster. However, carbohydrates have been an important part of the human diet for thousands of years; artifacts from ancient civilizations show the presence of wheat, rice, and corn in our ancestors' storage areas.

Carbohydrates should be supplemented with proteins, vitamins, and fats to be parts of a well-balanced diet. Calorie-wise, a gram of carbohydrate provides 4.3 Kcal. In comparison, fats provide 9 Kcal/g, a less desirable ratio. Carbohydrates contain soluble and insoluble elements; the insoluble part is known as fiber, which is mostly cellulose. Fiber has many uses; it promotes regular bowel movement by adding bulk, and it regulates the rate of consumption of blood glucose. Fiber also helps to remove excess cholesterol from the body. Fiber binds and attaches to the cholesterol in the small intestine and prevents the cholesterol particles from entering the bloodstream. Then cholesterol exits the body via the feces. Fiber-rich diets also have a protective role in reducing the occurrence of colon cancer. In addition, a meal containing whole grains and vegetables gives a feeling of fullness. As an immediate source of energy, glucose is broken down during the process of cellular respiration, which produces adenosine triphosphate (ATP), the energy currency of the cell. Without the consumption of carbohydrates, the availability of "instant energy" would be reduced. Eliminating carbohydrates from the diet is not the best way to lose weight. A low-calorie diet that is rich in

whole grains, fruits, vegetables, and lean meat, together with plenty of exercise and plenty of water, is the more sensible way to lose weight.

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## Key Points

- Carbohydrates provide energy to the body, particularly through glucose, a simple sugar that is found in many basic foods.
- Carbohydrates contain soluble and insoluble elements; the insoluble part is known as fiber, which promotes regular bowel movement, regulates the rate of consumption of blood glucose, and also helps to remove excess cholesterol from the body.
- As an immediate source of energy, glucose is broken down during the process of cellular respiration, which produces ATP, the energy currency of the cell.
- Since carbohydrates are an important part of the human nutrition, eliminating them from the diet is not the best way to lose weight.

## Key Terms

- **carbohydrate**: A sugar, starch, or cellulose that is a food source of energy for an animal or plant; a saccharide.
- **glucose**: a simple monosaccharide (sugar) with a molecular formula of C6H12O6; it is a principal source of energy for cellular metabolism
- **ATP**: A nucleotide that occurs in muscle tissue, and is used as a source of energy in cellular reactions, and in the synthesis of nucleic acids. ATP is the abbreviation for adenosine triphosphate.

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# 14.3: LIPIDS - HYDROPHOBIC MOLECULES



- Topic hierarchy


14.3.1: Lipid Molecules

14.3.2: Phospholipids

14.3.3: Steroids



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# 14.3.1: Lipid Molecules

**Learning Objectives**

- Differentiate between saturated and unsaturated fatty acids

## Glycerol and Fatty Acids

A fat molecule consists of two main components: glycerol and fatty acids. Glycerol is an alcohol with three carbons, five hydrogens, and three hydroxyl (OH) groups. Fatty acids have a long chain of hydrocarbons with a carboxyl group attached and may have 4-36 carbons; however, most of them have 12-18. In a fat molecule, the fatty acids are attached to each of the three carbons of the glycerol molecule with an ester bond through the oxygen atom. During the ester bond formation, three molecules are released. Since fats consist of three fatty acids and a glycerol, they are also called triacylglycerols or triglycerides.

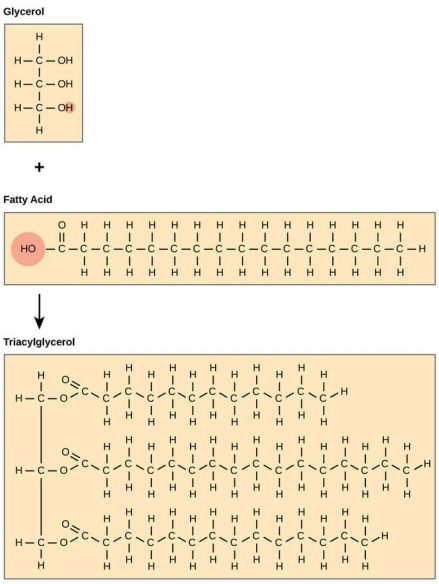



Figure 14.3.1.1: Triacylglycerols: Triacylglycerol is formed by the joining of three fatty acids to a glycerol backbone in a dehydration reaction. Three molecules of water are released in the process.

## Saturated vs. Unsaturated Fatty Acids

Fatty acids may be saturated or unsaturated. In a fatty acid chain, if there are only single bonds between neighboring carbons in the hydrocarbon chain, the fatty acid is said to be saturated. Saturated fatty acids are saturated with hydrogen since single bonds increase the number of hydrogens on each carbon. Stearic acid and palmitic acid, which are commonly found in meat, are examples of saturated fats.

When the hydrocarbon chain contains a double bond, the fatty acid is said to be unsaturated. Oleic acid is an example of an unsaturated fatty acid. Most unsaturated fats are liquid at room temperature and are called oils. If there is only one double bond in the molecule, then it is known as a monounsaturated fat; e.g. olive oil. If there is more than one double bond, then it is known as a polyunsaturated fat; e.g. canola oil. Unsaturated fats help to lower blood cholesterol levels whereas saturated fats contribute to plaque formation in the arteries.

Unsaturated fats or oils are usually of plant origin and contain cis unsaturated fatty acids. Cis and trans indicate the configuration of the molecule around the double bond. If hydrogens are present in the same plane, it is referred to as a cis fat; if the hydrogen atoms are on two different planes, it is referred to as a trans fat. The cis double bond causes a bend or a “kink” that prevents the fatty acids from packing tightly, keeping them liquid at room temperature.

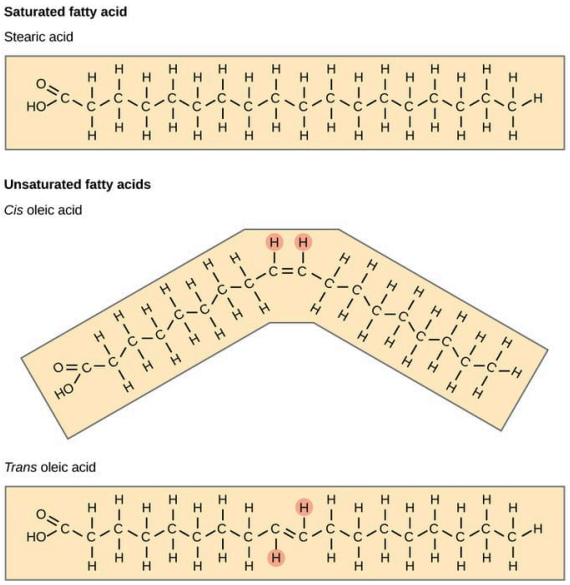


Figure 14.3.1.1: Fatty Acids: Saturated fatty acids have hydrocarbon chains connected by single bonds only. Unsaturated fatty acids have one or more double bonds. Each double bond may be in a cis or trans configuration. In the cis configuration, both hydrogens are on the same side of the hydrocarbon chain. In the trans configuration, the hydrogens are on opposite sides. A cis double bond causes a kink in the chain.

## Trans Fats

In the food industry, oils are artificially hydrogenated to make them semi-solid and of a consistency desirable for many processed food products. During this hydrogenation process, gas is bubbled through oils to solidify them, and the double bonds of the cis-conformation in the hydrocarbon chain may be converted to double bonds in the trans-conformation.

Margarine, some types of peanut butter, and shortening are examples of artificially-hydrogenated trans fats. Recent studies have shown that an increase in trans fats in the human diet may lead to an increase in levels of low-density lipoproteins (LDL), or “bad” cholesterol, which in turn may lead to plaque deposition in the arteries, resulting in heart disease. Many fast food restaurants have recently banned the use of trans fats, and food labels are required to display the trans fat content.

## Essential Fatty Acids

Essential fatty acids are fatty acids required for biological processes, but not synthesized by the human body. Consequently, they have to be supplemented through ingestion via the diet and are nutritionally very important. Omega-3 fatty acid, or alpha-linoleic acid (ALA), falls into this category and is one of only two fatty acids known to be essential for humans (the other being omega-6 fatty acid, or linoleic acid). These polyunsaturated fatty acids are called omega-3 because the third carbon from the end of the hydrocarbon chain is connected to its neighboring carbon by a double bond. Salmon, trout, and tuna are good sources of omega-3 fatty acids.

Research indicates that omega-3 fatty acids reduce the risk of sudden death from heart attacks, reduce triglycerides in the blood, lower blood pressure, and prevent thrombosis by inhibiting blood clotting. They also reduce inflammation and may help reduce the risk of some cancers in animals.

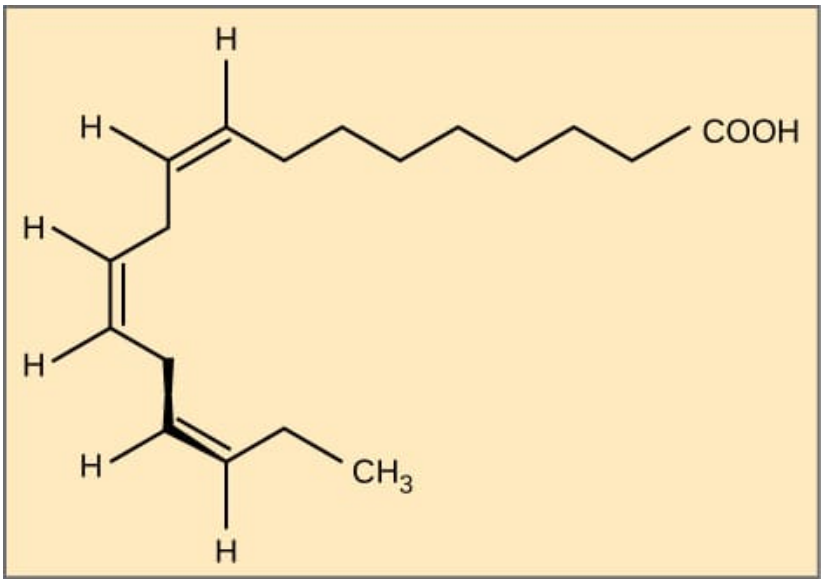



Figure 14.3.1.1: Omega Fatty Acids: Alpha-linolenic acid is an example of an omega-3 fatty acid. It has three cis double bonds and, as a result, a curved shape. For clarity, the carbons are not shown. Each singly bonded carbon has two hydrogens associated with it, also not shown.

Fats have important functions, and many vitamins are fat soluble. Fats serve as a long-term storage form of fatty acids and act as a source of energy. They also provide insulation for the body.

## Key Points

- Fats provide energy, insulation, and storage of fatty acids for many organisms.
- Fats may be saturated (having single bonds) or unsaturated (having double bonds).
- Unsaturated fats may be cis (hydrogens in same plane) or trans (hydrogens in two different planes).
- Olive oil, a monounsaturated fat, has a single double bond whereas canola oil, a polyunsaturated fat, has more than one double bond.
- Omega-3 fatty acid and omega-6 fatty acid are essential for human biological processes, but they must be ingested in the diet because they cannot be synthesized.

## Key Terms

- **hydrogenation**: The chemical reaction of hydrogen with another substance, especially with an unsaturated organic compound, and usually under the influence of temperature, pressure and catalysts.
- **ester**: Compound most often formed by the condensation of an alcohol and an acid, by removing water. It contains the functional group carbon-oxygen double bond joined via carbon to another oxygen atom.
- **carboxyl**: A univalent functional group consisting of a carbonyl and a hydroxyl functional group (-CO.OH); characteristic of carboxylic acids.

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# 14.3.2: Phospholipids

**Learning Objectives**

- Describe phospholipids and their role in cells

## Defining Characteristics of Phospholipids

Phospholipids are major components of the plasma membrane, the outermost layer of animal cells. Like fats, they are composed of fatty acid chains attached to a glycerol backbone. Unlike triglycerides, which have three fatty acids, phospholipids have two fatty acids that help form a diacylglycerol. The third carbon of the glycerol backbone is also occupied by a modified phosphate group. However, just a phosphate group attached to a diacylglycerol does not qualify as a phospholipid. This would be considered a phosphatidate (diacylglycerol 3-phosphate), the precursor to phospholipids. To qualify as a phospholipid, the phosphate group should be modified by an alcohol. Phosphatidylcholine and phosphatidylserine are examples of two important phospholipids that are found in plasma membranes.

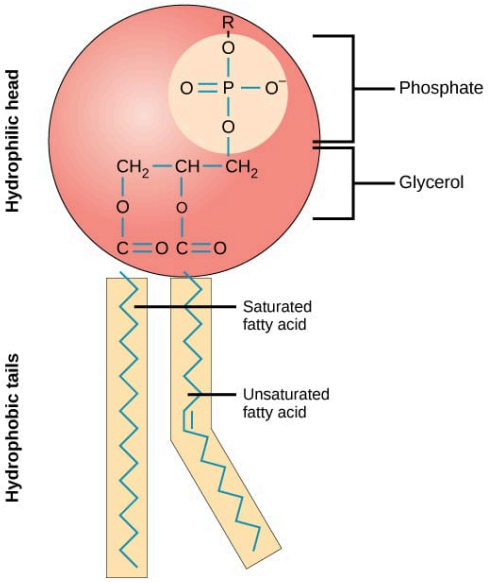



Figure 14.3.2.1: Phospholipid Molecule: A phospholipid is a molecule with two fatty acids and a modified phosphate group attached to a glycerol backbone. The phosphate may be modified by the addition of charged or polar chemical groups. Two chemical groups that may modify the phosphate, choline and serine, are shown here. Both choline and serine attach to the phosphate group at the position labeled R via the hydroxyl group indicated in green.

## Structure of a Phospholipid Molecule

A phospholipid is an amphipathic molecule which means it has both a hydrophobic and a hydrophilic component. A single phospholipid molecule has a phosphate group on one end, called the “head,” and two side-by-side chains of fatty acids that make up the lipid “tails. ” The phosphate group is negatively charged, making the head polar and hydrophilic, or “water loving.” The phosphate heads are thus attracted to the water molecules in their environment.

The lipid tails, on the other hand, are uncharged, nonpolar, and hydrophobic, or “water fearing.” A hydrophobic molecule repels and is repelled by water. Some lipid tails consist of saturated fatty acids and some contain unsaturated fatty acids. This combination adds to the fluidity of the tails that are constantly in motion.

# Phospholipids and Biological Membranes

The cell membrane consists of two adjacent layers of phospholipids, which form a bilayer. The fatty acid tails of phospholipids face inside, away from water, whereas the phosphate heads face the outward aqueous side. Since the heads face outward, one layer is exposed to the interior of the cell and one layer is exposed to the exterior. As the phosphate groups are polar and hydrophilic, they are attracted to water in the intracellular fluid.

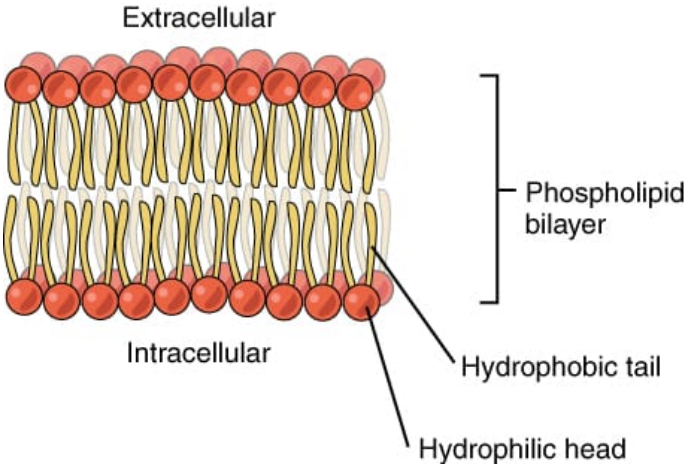



Figure 14.3.2.1: Phospholipid Bilayer: The phospholipid bilayer consists of two adjacent sheets of phospholipids, arranged tail to tail. The hydrophobic tails associate with one another, forming the interior of the membrane. The polar heads contact the fluid inside and outside of the cell.

Because of the phospholipds' chemical and physical characteristics, the lipid bilayer acts as a semipermeable membrane; only lipophilic solutes can easily pass the phospholipd bilayer. As a result, there are two distinct aqueous compartments on each side of the membrane. This separation is essential for many biological functions, including cell communication and metabolism.

# Membrane Fluidity

A cell's plasma membrane contain proteins and other lipids (such as cholesterol) within the phospholipid bilayer. Biological membranes remain fluid because of the unsaturated hydrophobic tails, which prevent phospholipid molecules from packing together and forming a solid.

If a drop of phospholipids is placed in water, the phospholipids spontaneously form a structure known as a micelle, with their hydrophilic heads oriented toward the water. Micelles are lipid molecules that arrange themselves in a spherical form in aqueous solution. The formation of a micelle is a response to the amphipathic nature of fatty acids, meaning that they contain both hydrophilic and hydrophobic regions.

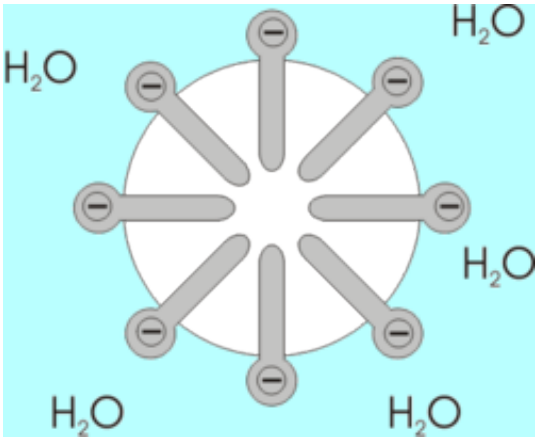



Figure 14.3.2.1: Micelles: An example of micelles in water.

## Key Points

- Phospholipids consist of a glycerol molecule, two fatty acids, and a phosphate group that is modified by an alcohol.
- The phosphate group is the negatively-charged polar head, which is hydrophilic.
- The fatty acid chains are the uncharged, nonpolar tails, which are hydrophobic.
- Since the tails are hydrophobic, they face the inside, away from the water and meet in the inner region of the membrane.
- Since the heads are hydrophilic, they face outward and are attracted to the intracellular and extracellular fluid.
- If phospholipids are placed in water, they form into micelles, which are lipid molecules that arrange themselves in a spherical form in aqueous solutions.

## Key Terms

- **micelle**: Lipid molecules that arrange themselves in a spherical form in aqueous solutions.
- **amphipathic**: Describing a molecule, such as a detergent, which has both hydrophobic and hydrophilic groups.

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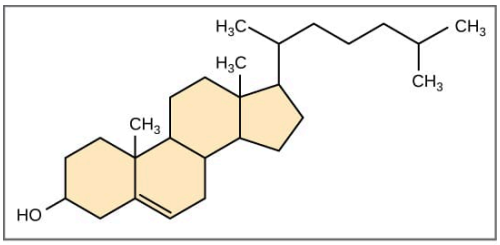
# 14.3.3: Steroids

**Learning Objectives**

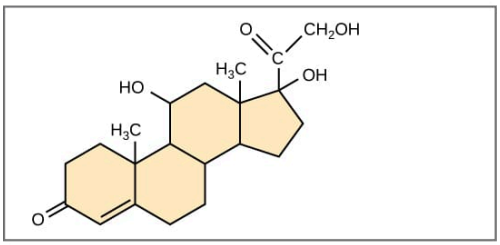
- Describe some functions of steroids

## Structure of Steroid Molecules

Unlike phospholipids and fats, steroids have a fused ring structure. Although they do not resemble the other lipids, they are grouped with them because they are also hydrophobic and insoluble in water. All steroids have four linked carbon rings, and many of them, like cholesterol, have a short tail. Many steroids also have the –OH functional group, and these steroids are classified as alcohols called sterols.




**Cholesterol**




**Cortisol**

Figure 14.3.3.1: Steroid Structures: Steroids, such as cholesterol and cortisol, are composed of four fused hydrocarbon rings.

## Cholesterol

Cholesterol is the most common steroid and is mainly synthesized in the liver; it is the precursor to vitamin D. Cholesterol is also a precursor to many important steroid hormones like estrogen, testosterone, and progesterone, which are secreted by the gonads and endocrine glands. Therefore, steroids play very important roles in the body's reproductive system. Cholesterol also plays a role in synthesizing the steroid hormones aldosterone, which is used for osmoregulation, and cortisol, which plays a role in metabolism.

Cholesterol is also the precursor to bile salts, which help in the emulsification of fats and their absorption by cells. It is a component of the plasma membrane of animal cells and the phospholipid bilayer. Being the outermost structure in animal cells, the plasma membrane is responsible for the transport of materials and cellular recognition; and it is involved in cell-to-cell communication. Thus, steroids also play an important role in the structure and function of membranes.

It has also been discovered that steroids can be active in the brain where they affect the nervous system, These neurosteroids alter electrical activity in the brain. They can either activate or tone down receptors that communicate messages from neurotransmitters. Since these neurosteroids can tone down receptors and decrease brain activity, steroids are often used in anesthetic medicines.

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## Key Points

- Steroids are lipids because they are hydrophobic and insoluble in water, but they do not resemble lipids since they have a structure composed of four fused rings.
- Cholesterol is the most common steroid and is the precursor to vitamin D, testosterone, estrogen, progesterone, aldosterone, cortisol, and bile salts.
- Cholesterol is a component of the phospholipid bilayer and plays a role in the structure and function of membranes.
- Steroids are found in the brain and alter electrical activity in the brain.
- Because they can tone down receptors that communicate messages from neurotransmitters, steroids are often used in anesthetic medicines.

## Key Terms

- **neurotransmitter**: any substance, such as acetylcholine or dopamine, responsible for sending nerve signals across a synapse between two neurons
- **osmoregulation**: the homeostatic regulation of osmotic pressure in the body in order to maintain a constant water content
- **hormone**: any substance produced by one tissue and conveyed by the bloodstream to another to affect physiological activity

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# 14.4: PROTEINS - MOLECULES WITH DIVERSE STRUCTURES



- Topic hierarchy


14.4.1: Types and Functions of Proteins

14.4.2: Amino Acids

14.4.3: Proteins



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# 14.4.1: Types and Functions of Proteins

**Learning Objectives**

- Differentiate among the types and functions of proteins

## Types and Functions of Proteins

Proteins perform essential functions throughout the systems of the human body. These long chains of amino acids are critically important for:

- catalyzing chemical reactions
- synthesizing and repairing DNA
- transporting materials across the cell
- receiving and sending chemical signals
- responding to stimuli
- providing structural support

Proteins (a polymer) are macromolecules composed of amino acid subunits (the monomers ). These amino acids are covalently attached to one another to form long linear chains called polypeptides, which then fold into a specific three-dimensional shape. Sometimes these folded polypeptide chains are functional by themselves. Other times they combine with additional polypeptide chains to form the final protein structure. Sometimes non-polypeptide groups are also required in the final protein. For instance, the blood protein hemogobin is made up of four polypeptide chains, each of which also contains a heme molecule, which is ring structure with an iron atom in its center.

Proteins have different shapes and molecular weights, depending on the amino acid sequence. For example, hemoglobin is a globular protein, which means it folds into a compact globe-like structure, but collagen, found in our skin, is a fibrous protein, which means it folds into a long extended fiber-like chain. You probably look similar to your family members because you share similar proteins, but you look different from strangers because the proteins in your eyes, hair, and the rest of your body are different.

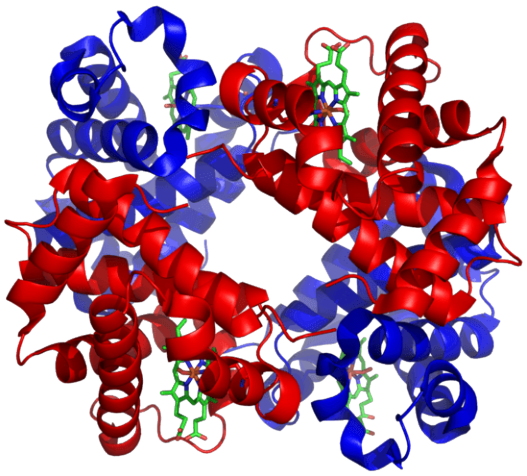


Figure 14.4.1.1: Human Hemoglobin: Structure of human hemoglobin. The proteins' α and β subunits are in red and blue, and the iron-containing heme groups in green. From the protein data base.

Because form determines function, any slight change to a protein's shape may cause the protein to become dysfunctional. Small changes in the amino acid sequence of a protein can cause devastating genetic diseases such as Huntington's disease or sickle

cell anemia.

## Enzymes

Enzymes are proteins that catalyze biochemical reactions, which otherwise would not take place. These enzymes are essential for chemical processes like digestion and cellular metabolism. Without enzymes, most physiological processes would proceed so slowly (or not at all) that life could not exist.

Because form determines function, each enzyme is specific to its substrates. The substrates are the reactants that undergo the chemical reaction catalyzed by the enzyme. The location where substrates bind to or interact with the enzyme is known as the active site, because that is the site where the chemistry occurs. When the substrate binds to its active site at the enzyme, the enzyme may help in its breakdown, rearrangement, or synthesis. By placing the substrate into a specific shape and microenvironment in the active site, the enzyme encourages the chemical reaction to occur. There are two basic classes of enzymes:

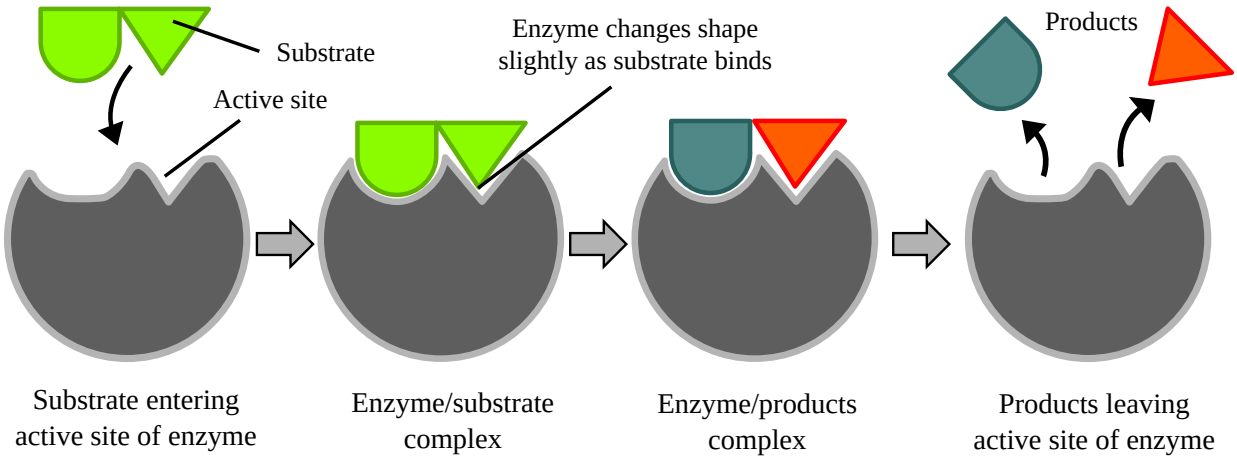



Figure 14.4.1.1: Enzyme reaction: A catabolic enzyme reaction showing the substrate matching the exact shape of the active site.

- Catabolic enzymes: enzymes that break down their substrate
- Anabolic enzymes: enzymes that build more complex molecules from their substrates

Enzymes are essential for digestion: the process of breaking larger food molecules down into subunits small enough to diffuse through a cell membrane and to be used by the cell. These enzymes include amylase, which catalyzes the digestion carbohydrates in the mouth and small intestine; pepsin, which catalyzes the digestion of proteins in the stomach; lipase, which catalyzes reactions need to emulsify fats in the small intestine; and trypsin, which catalyzes the further digestion of proteins in the small intestine.

Enzymes are also essential for biosynthesis: the process of making new, complex molecules from the smaller subunits that are provided to or generated by the cell. These biosynthetic enzymes include DNA Polymerase, which catalyzes the synthesis of new strands of the genetic material before cell division; fatty acid synthetase, which the synthesis of new fatty acids for fat or membrane lipid formation; and components of the ribosome, which catalyzes the formation of new polypeptides from amino acid monomers.

## Hormones

Some proteins function as chemical-signaling molecules called hormones. These proteins are secreted by endocrine cells that act to control or regulate specific physiological processes, which include growth, development, metabolism, and reproduction. For example, insulin is a protein hormone that helps to regulate blood glucose levels. Other proteins act as receptors to detect the concentrations of chemicals and send signals to respond. Some types of hormones, such as estrogen and testosterone, are lipid steroids, not proteins.

# Other Protein Functions

Proteins perform essential functions throughout the systems of the human body. In the respiratory system, hemoglobin (composed of four protein subunits) transports oxygen for use in cellular metabolism. Additional proteins in the blood plasma and lymph carry nutrients and metabolic waste products throughout the body. The proteins actin and tubulin form cellular structures, while keratin forms the structural support for the dead cells that become fingernails and hair. Antibodies, also called immunoglobins, help recognize and destroy foreign pathogens in the immune system. Actin and myosin allow muscles to contract, while albumin nourishes the early development of an embryo or a seedling.

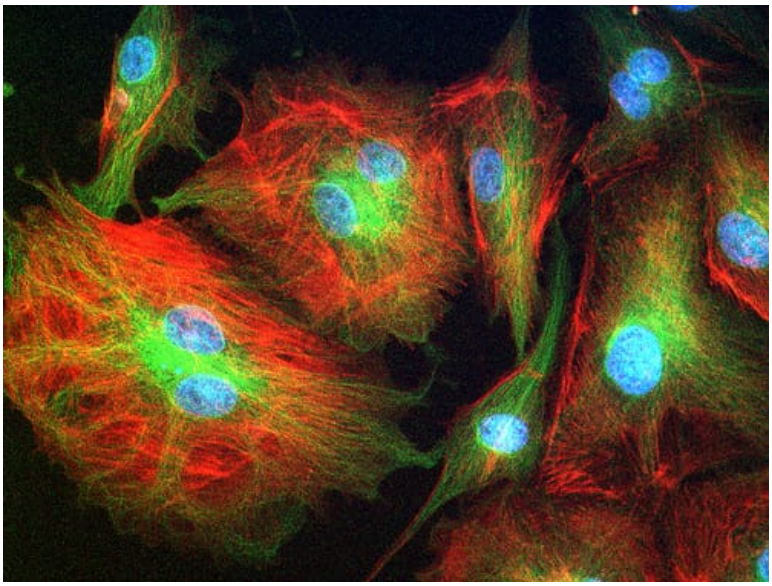


Figure 14.4.1.1: Tubulin: The structural protein tubulin stained red in mouse cells.

## Key Points

- Proteins are essential for the main physiological processes of life and perform functions in every system of the human body.
- A protein's shape determines its function.
- Proteins are composed of amino acid subunits that form polypeptide chains.
- Enzymes catalyze biochemical reactions by speeding up chemical reactions, and can either break down their substrate or build larger molecules from their substrate.
- The shape of an enzyme's active site matches the shape of the substrate.
- Hormones are a type of protein used for cell signaling and communication.

## Key Terms

- **amino acid**: Any of 20 naturally occurring α-amino acids (having the amino, and carboxylic acid groups on the same carbon atom), and a variety of side chains, that combine, via peptide bonds, to form proteins.
- **polypeptide**: Any polymer of (same or different) amino acids joined via peptide bonds.
- **catalyze**: To accelerate a process.

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# 14.4.2: Amino Acids

**Learning Objectives**

- Describe the structure of an amino acid and the features that confer its specific properties

## Structure of an Amino Acid

Amino acids are the monomers that make up proteins. Each amino acid has the same fundamental structure, which consists of a central carbon atom, also known as the alpha (α) carbon, bonded to an amino group ($NH_2$), a carboxyl group (COOH), and to a hydrogen atom. In the aqueous environment of the cell, the both the amino group and the carboxyl group are ionized under physiological conditions, and so have the structures $-NH_3^+$ and $-COO^-$, respectively. Every amino acid also has another atom or group of atoms bonded to the central atom known as the R group. This R group, or side chain, gives each amino acid proteins specific characteristics, including size, polarity, and pH.

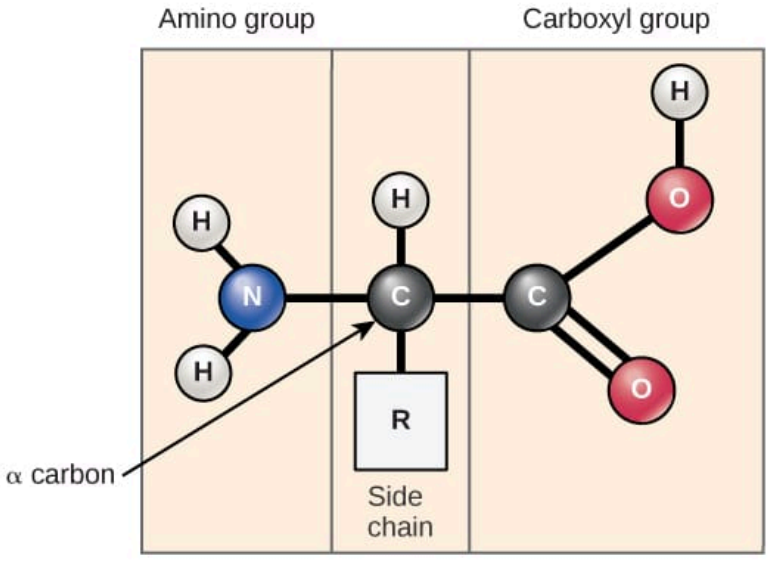



Figure 14.4.2.1: Amino acid structure: Amino acids have a central asymmetric carbon to which an amino group, a carboxyl group, a hydrogen atom, and a side chain (R group) are attached. This amino acid is unionized, but if it were placed in water at pH 7, its amino group would pick up another hydrogen and a positive charge, and the hydroxyl in its carboxyl group would lose and a hydrogen and gain a negative charge.

## Types of Amino Acids

The name “amino acid” is derived from the amino group and carboxyl-acid-group in their basic structure. There are 21 amino acids present in proteins, each with a specific R group or side chain. Ten of these are considered essential amino acids in humans because the human body cannot produce them and they must be obtained from the diet. All organisms have different essential amino acids based on their physiology.

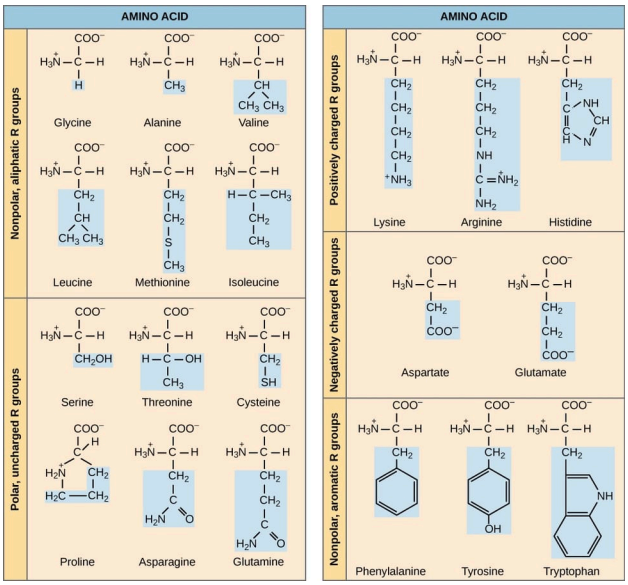



Figure 14.4.2.1: Types of amino acids: There are 21 common amino acids commonly found in proteins, each with a different R group (variant group) that determines its chemical nature. The 21st amino acid, not shown here, is selenocysteine, with an R group of -$CH_2$-SeH.

## Characteristics of Amino Acids

Which categories of amino acid would you expect to find on the surface of a soluble protein, and which would you expect to find in the interior? What distribution of amino acids would you expect to find in a protein embedded in a lipid bilayer?

The chemical composition of the side chain determines the characteristics of the amino acid. Amino acids such as valine, methionine, and alanine are nonpolar (hydrophobic), while amino acids such as serine, threonine, and cysteine are polar (hydrophilic). The side chains of lysine and arginine are positively charged so these amino acids are also known as basic (high pH) amino acids. Proline is an exception to the standard structure of an amino acid because its R group is linked to the amino group, forming a ring-like structure.

Amino acids are represented by a single upper case letter or a three-letter abbreviation. For example, valine is known by the letter V or the three-letter symbol val.

## Peptide Bonds

The sequence and the number of amino acids ultimately determine the protein's shape, size, and function. Each amino acid is attached to another amino acid by a covalent bond, known as a peptide bond. When two amino acids are covalently attached by a peptide bond, the carboxyl group of one amino acid and the amino group of the incoming amino acid combine and release a molecule of water. Any reaction that combines two monomers in a reaction that generates $H_2O$ as one of the products is known as a dehydration reaction, so peptide bond formation is an example of a dehydration reaction.

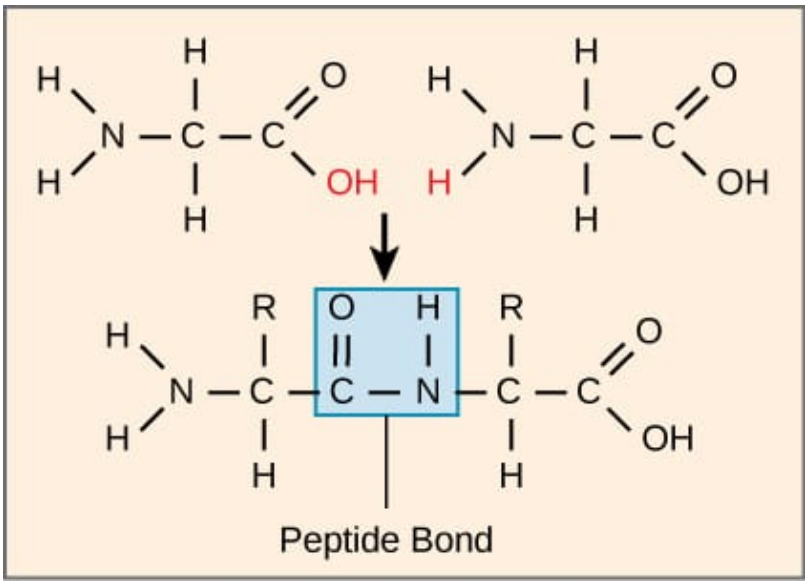



Figure 14.4.2.1: Peptide bond formation: Peptide bond formation is a dehydration synthesis reaction. The carboxyl group of one amino acid is linked to the amino group of the incoming amino acid. In the process, a molecule of water is released.

## Polypeptide Chains

The resulting chain of amino acids is called a polypeptide chain. Each polypeptide has a free amino group at one end. This end is called the N terminal, or the amino terminal, and the other end has a free carboxyl group, also known as the C or carboxyl terminal. When reading or reporting the amino acid sequence of a protein or polypeptide, the convention is to use the N-to-C direction. That is, the first amino acid in the sequence is assumed to the be one at the N terminal and the last amino acid is assumed to be the one at the C terminal.

Although the terms polypeptide and protein are sometimes used interchangeably, a polypeptide is technically any polymer of amino acids, whereas the term protein is used for a polypeptide or polypeptides that have folded properly, combined with any additional components needed for proper functioning, and is now functional.

## Key Points

- Each amino acid contains a central C atom, an amino group (NH2), a carboxyl group (COOH), and a specific R group.
- The R group determines the characteristics (size, polarity, and pH) for each type of amino acid.
- Peptide bonds form between the carboxyl group of one amino acid and the amino group of another through dehydration synthesis.
- A chain of amino acids is a polypeptide.

## Key Terms

- **amino acid**: Any of 20 naturally occurring α-amino acids (having the amino, and carboxylic acid groups on the same carbon atom), and a variety of side chains, that combine, via peptide bonds, to form proteins.
- **R group**: The R group is a side chain specific to each amino acid that confers particular chemical properties to that amino acid.
- **polypeptide**: Any polymer of (same or different) amino acids joined via peptide bonds.

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# 14.4.3: Proteins

## Learning Objectives

- Describe the four levels of protein structure.
- Identify the types of attractive interactions that hold proteins in their most stable three-dimensional structure.
- Explain what happens when proteins are denatured.
- Identify how a protein can be denatured.

Each of the thousands of naturally occurring proteins has its own characteristic amino acid composition and sequence that result in a unique three-dimensional shape. Since the 1950s, scientists have determined the amino acid sequences and three-dimensional conformation of numerous proteins and thus obtained important clues on how each protein performs its specific function in the body.

Proteins are compounds of high molar mass consisting largely or entirely of chains of amino acids. Because of their great complexity, protein molecules cannot be classified on the basis of specific structural similarities, as carbohydrates and lipids are categorized. The two major structural classifications of proteins are based on far more general qualities: whether the protein is (1) fiberlike and insoluble or (2) globular and soluble. Some proteins, such as those that compose hair, skin, muscles, and connective tissue, are fiberlike. These fibrous proteins are insoluble in water and usually serve structural, connective, and protective functions. Examples of fibrous proteins are keratins, collagens, myosins, and elastins. Hair and the outer layer of skin are composed of keratin. Connective tissues contain collagen. Myosins are muscle proteins and are capable of contraction and extension. Elastins are found in ligaments and the elastic tissue of artery walls.

Globular proteins, the other major class, are soluble in aqueous media. In these proteins, the chains are folded so that the molecule as a whole is roughly spherical. Familiar examples include egg albumin from egg whites and serum albumin in blood. Serum albumin plays a major role in transporting fatty acids and maintaining a proper balance of osmotic pressures in the body. Hemoglobin and myoglobin, which are important for binding oxygen, are also globular proteins.

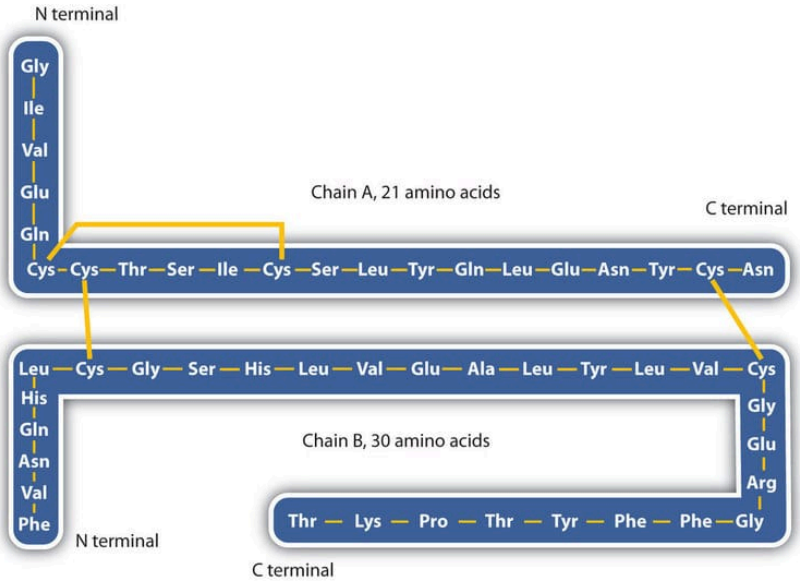



Figure 14.4.3.1: Primary Structure of Human Insulin. Human insulin, whose amino acid sequence is shown here, is a hormone that is required for the proper metabolism of glucose.

## Levels of Protein Structure

The structure of proteins is generally described as having four organizational levels. The first of these is the primary structure, which is the number and sequence of amino acids in a protein's polypeptide chain or chains, beginning with the free amino group

and maintained by the peptide bonds connecting each amino acid to the next. The primary structure of insulin, composed of 51 amino acids, is shown in Figure 14.4.3.1.

A protein molecule is not a random tangle of polypeptide chains. Instead, the chains are arranged in unique but specific conformations. The term secondary structure refers to the fixed arrangement of the polypeptide backbone. On the basis of X ray studies, Linus Pauling and Robert Corey postulated that certain proteins or portions of proteins twist into a spiral or a helix. This helix is stabilized by *intrachain* hydrogen bonding between the carbonyl oxygen atom of one amino acid and the amide hydrogen atom four amino acids up the chain (located on the next turn of the helix) and is known as a right-handed α-helix. X ray data indicate that this helix makes one turn for every 3.6 amino acids, and the side chains of these amino acids project outward from the coiled backbone (Figure 14.4.3.2). The α-keratins, found in hair and wool, are exclusively α-helical in conformation. Some proteins, such as gamma globulin, chymotrypsin, and cytochrome c, have little or no helical structure. Others, such as hemoglobin and myoglobin, are helical in certain regions but not in others.

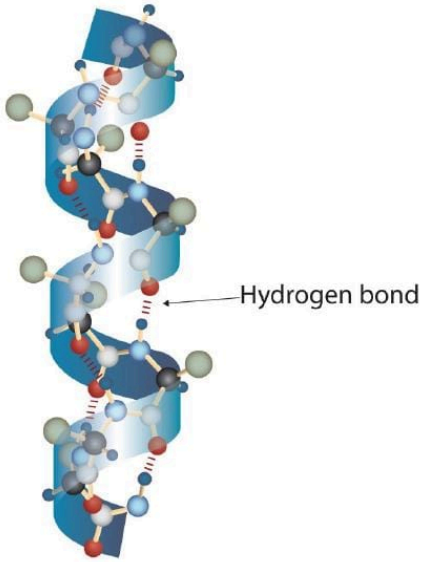



Figure 14.4.3.2 A Ball-and-Stick Model of an α-Helix. This ball-and-stick model shows the intrachain hydrogen bonding between carbonyl oxygen atoms and amide hydrogen atoms. Each turn of the helix spans 3.6 amino acids. Note that the side chains (represented as green spheres) point out from the helix.

Another common type of secondary structure, called the *β-pleated sheet conformation*, is a sheetlike arrangement in which two or more extended polypeptide chains (or separate regions on the same chain) are aligned side by side. The aligned segments can run either parallel or antiparallel—that is, the N-terminals can face in the same direction on adjacent chains or in different directions—and are connected by *interchain* hydrogen bonding (Figure 14.4.3.3). The β-pleated sheet is particularly important in structural proteins, such as silk fibroin. It is also seen in portions of many enzymes, such as carboxypeptidase A and lysozyme.

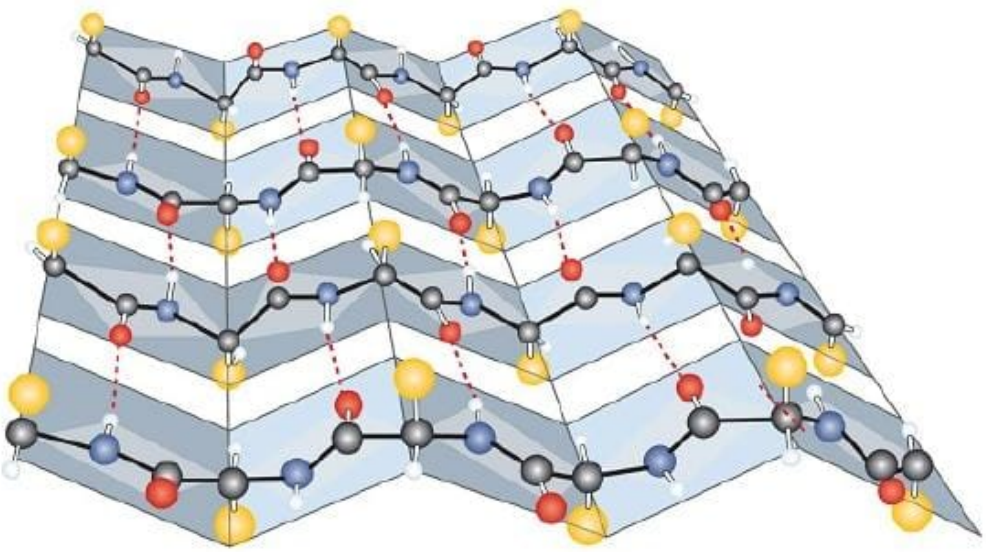


Figure 14.4.3.3: A Ball-and-Stick Model of the β-Pleated Sheet Structure in Proteins. The side chains extend above or below the sheet and alternate along the chain. The protein chains are held together by interchain hydrogen bonding.

Tertiary structure refers to the unique three-dimensional shape of the protein as a whole, which results from the folding and bending of the protein backbone. The tertiary structure is intimately tied to the proper biochemical functioning of the protein. Figure 14.4.3.4 shows a depiction of the three-dimensional structure of insulin.

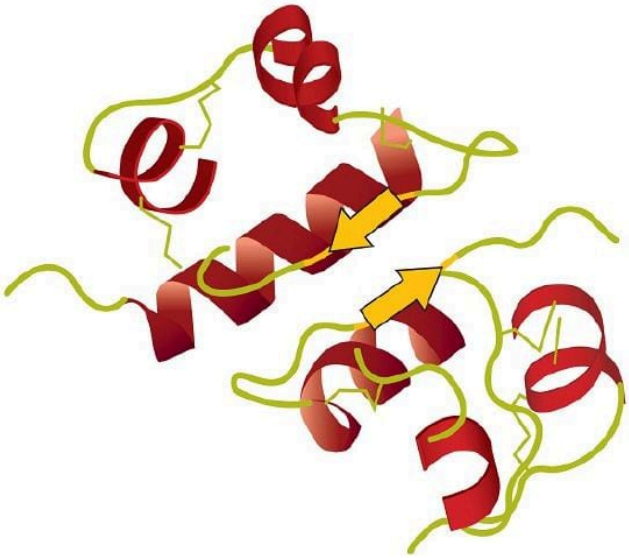
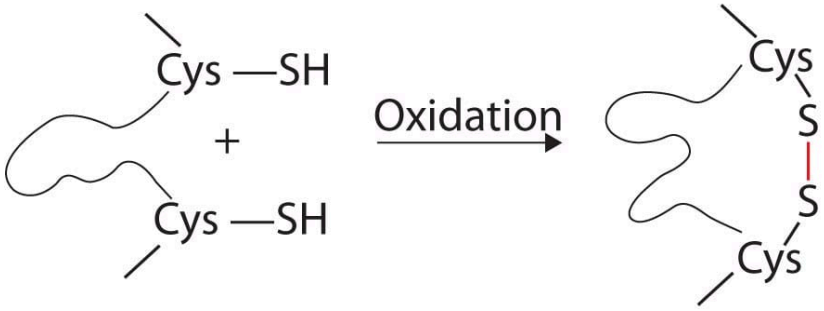


Figure 14.4.3.4: A Ribbon Model of the Three-Dimensional Structure of Insulin. The spiral regions represent sections of the polypeptide chain that have an α-helical structure, while the broad arrows represent β-pleated sheet structures.

Four major types of attractive interactions determine the shape and stability of the tertiary structure of proteins. You studied several of them previously.

1. Ionic bonding. Ionic bonds result from electrostatic attractions between positively and negatively charged side chains of amino acids. For example, the mutual attraction between an aspartic acid carboxylate ion and a lysine ammonium ion helps to maintain a particular folded area of a protein (part (a) of Figure 14.4.3.5).
2. Hydrogen bonding. Hydrogen bonding forms between a highly electronegative oxygen atom or a nitrogen atom and a hydrogen atom attached to another oxygen atom or a nitrogen atom, such as those found in polar amino acid side chains. Hydrogen bonding (as well as ionic attractions) is extremely important in both the intra- and intermolecular interactions of proteins (part (b) of Figure 14.4.3.5).
3. Disulfide linkages. Two cysteine amino acid units may be brought close together as the protein molecule folds. Subsequent

oxidation and linkage of the sulfur atoms in the highly reactive sulfhydryl (SH) groups leads to the formation of cystine (part (c) of Figure 14.4.3.5). Intrachain disulfide linkages are found in many proteins, including insulin (yellow bars in Figure 14.4.3.1 ) and have a strong stabilizing effect on the tertiary structure.




4. Dispersion forces. Dispersion forces arise when a normally nonpolar atom becomes momentarily polar due to an uneven distribution of electrons, leading to an instantaneous dipole that induces a shift of electrons in a neighboring nonpolar atom. Dispersion forces are weak but can be important when other types of interactions are either missing or minimal (part (d) of Figure 14.4.3.5). This is the case with fibroin, the major protein in silk, in which a high proportion of amino acids in the protein have nonpolar side chains. The term *hydrophobic interaction* is often misused as a synonym for dispersion forces. Hydrophobic interactions arise because water molecules engage in hydrogen bonding with other water molecules (or groups in proteins capable of hydrogen bonding). Because nonpolar groups cannot engage in hydrogen bonding, the protein folds in such a way that these groups are buried in the interior part of the protein structure, minimizing their contact with water.

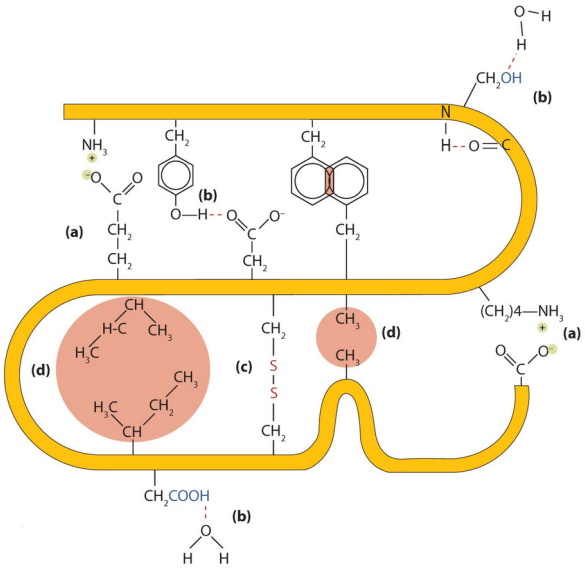



Figure 14.4.3.5: Tertiary Protein Structure Interactions. Four interactions stabilize the tertiary structure of a protein: (a) ionic bonding, (b) hydrogen bonding, (c) disulfide linkages, and (d) dispersion forces.

When a protein contains more than one polypeptide chain, each chain is called a *subunit*. The arrangement of multiple subunits represents a fourth level of structure, the quaternary structure of a protein. Hemoglobin, with four polypeptide chains or subunits, is the most frequently cited example of a protein having quaternary structure (Figure 14.4.3.6). The quaternary structure of a protein is produced and stabilized by the same kinds of interactions that produce and maintain the tertiary structure. A schematic representation of the four levels of protein structure is in Figure 14.4.3.7.



Figure 14.4.3.6 The Quaternary Structure of Hemoglobin. Hemoglobin is a protein that transports oxygen throughout the body.

Source: Image from the RCSB PDB (www.pdb.org(opens in new window)) of PDB ID 1I3D (R.D. Kidd, H.M. Baker, A.J. Mathews, T. Brittain, E.N. Baker (2001) Oligomerization and ligand binding in a homotetrameric hemoglobin: two high-resolution crystal structures of hemoglobin Bart's (gamma(4)), a marker for alpha-thalassemia. Protein Sci. 1739–1749).

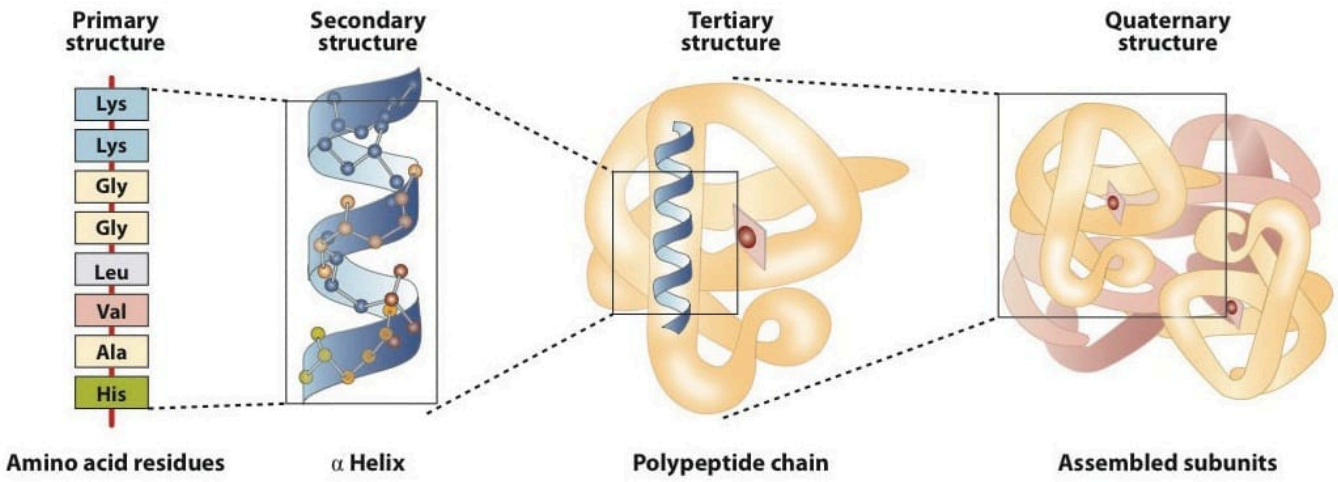



Figure 14.4.3.7: Levels of Structure in Proteins

The *primary structure* consists of the specific amino acid sequence. The resulting peptide chain can twist into an α-helix, which is one type of *secondary structure*. This helical segment is incorporated into the *tertiary structure* of the folded polypeptide chain. The single polypeptide chain is a subunit that constitutes the *quaternary structure* of a protein, such as hemoglobin that has four polypeptide chains.

## Denaturation of Proteins

The highly organized structures of proteins are truly masterworks of chemical architecture. But highly organized structures tend to have a certain delicacy, and this is true of proteins. Denaturation is the term used for any change in the three-dimensional structure of a protein that renders it incapable of performing its assigned function. A denatured protein cannot do its job. (Sometimes denaturation is equated with the precipitation or coagulation of a protein; our definition is a bit broader.) A wide variety of reagents and conditions, such as heat, organic compounds, pH changes, and heavy metal ions can cause protein denaturation (Figure 14.4.3.1).

*Figure* 14.4.3.1*: Protein Denaturation Methods*

| Method | Effect on Protein Structure |
|---|---|
| Heat above 50°C or ultraviolet (UV) radiation | Heat or UV radiation supplies kinetic energy to protein molecules, causing their atoms to vibrate more rapidly and disrupting relatively weak hydrogen bonding and dispersion forces. |
| Use of organic compounds, such as ethyl alcohol | These compounds are capable of engaging in intermolecular hydrogen bonding with protein molecules, disrupting intramolecular hydrogen bonding within the protein. |
| Salts of heavy metal ions, such as mercury, silver, and lead | These ions form strong bonds with the carboxylate anions of the acidic amino acids or SH groups of cysteine, disrupting ionic bonds and disulfide linkages. |
| Alkaloid reagents, such as tannic acid (used in tanning leather) | These reagents combine with positively charged amino groups in proteins to disrupt ionic bonds. |

Anyone who has fried an egg has observed denaturation. The clear egg white turns opaque as the albumin denatures and coagulates. No one has yet reversed that process. However, given the proper circumstances and enough time, a protein that has unfolded under sufficiently gentle conditions can refold and may again exhibit biological activity (Figure 14.4.3.8). Such evidence suggests that, at least for these proteins, the primary structure determines the secondary and tertiary structure. A given sequence of amino acids seems to adopt its particular three-dimensional arrangement naturally if conditions are right.

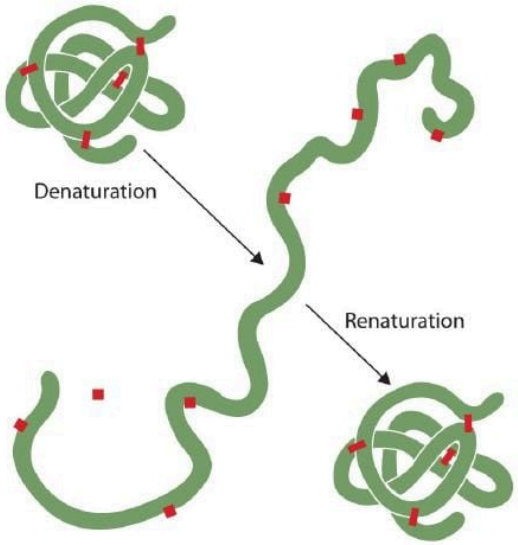



Figure 14.4.3.8: Denaturation and Renaturation of a Protein. The denaturation (unfolding) and renaturation (refolding) of a protein is depicted. The red boxes represent stabilizing interactions, such as disulfide linkages, hydrogen bonding, and/or ionic bonds.

The primary structures of proteins are quite sturdy. In general, fairly vigorous conditions are needed to hydrolyze peptide bonds. At the secondary through quaternary levels, however, proteins are quite vulnerable to attack, though they vary in their vulnerability to denaturation. The delicately folded globular proteins are much easier to denature than are the tough, fibrous proteins of hair and skin.

## Summary

Proteins can be divided into two categories: fibrous, which tend to be insoluble in water, and globular, which are more soluble in water. A protein may have up to four levels of structure. The primary structure consists of the specific amino acid sequence. The resulting peptide chain can form an α-helix or β-pleated sheet (or local structures not as easily categorized), which is known as secondary structure. These segments of secondary structure are incorporated into the tertiary structure of the folded polypeptide chain. The quaternary structure describes the arrangements of subunits in a protein that contains more than one subunit. Four major types of attractive interactions determine the shape and stability of the folded protein: ionic bonding, hydrogen bonding, disulfide linkages, and dispersion forces. A wide variety of reagents and conditions can cause a protein to unfold or denature.

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# 14.5: NUCLEIC ACIDS - INFORMATION MOLECULES

- Topic hierarchy


**14.5.1: Prelude to Nucleic Acids**

**14.5.2: Nucleotides**

**14.5.3: Nucleic Acid Structure**

**14.5.4: Replication and Expression of Genetic Information**

**14.5.5: Protein Synthesis and the Genetic Code**



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# 14.5.1: Prelude to Nucleic Acids

Following the initial isolation of insulin in 1921, diabetic patients could be treated with insulin obtained from the pancreases of cattle and pigs. Unfortunately, some patients developed an allergic reaction to this insulin because its amino acid sequence was not identical to that of human insulin. In the 1970s, an intense research effort began that eventually led to the production of genetically engineered human insulin—the first genetically engineered product to be approved for medical use. To accomplish this feat, researchers first had to determine how insulin is made in the body and then find a way of causing the same process to occur in nonhuman organisms, such as bacteria or yeast cells. Many aspects of these discoveries are presented in this chapter on nucleic acids.




Figure 14.5.1.1: A vial of insulin. It has been given a trade name, Actrapid, by the manufacturer. (Public Domain; Mr Hyde).

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# 14.5.2: Nucleotides

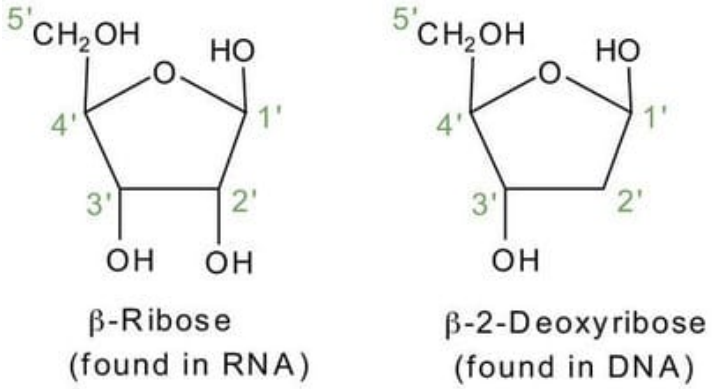
## Learning Objectives

- To identify the different molecules that combine to form nucleotides.

The repeating, or monomer, units that are linked together to form nucleic acids are known as nucleotides. The deoxyribonucleic acid (DNA) of a typical mammalian cell contains about $3 \times 10^9$ nucleotides. Nucleotides can be further broken down to phosphoric acid ($H_3PO_4$), a pentose sugar (a sugar with five carbon atoms), and a nitrogenous base (a base containing nitrogen atoms).

$$\text{nucleic acids} \xrightarrow[\text{down into}]{\text{can be broken}} \text{nucleotides} \xrightarrow[\text{down into}]{\text{can be broken}} H_3PO_4 + \text{nitrogen base} + \text{pentose sugar}$$

If the pentose sugar is ribose, the nucleotide is more specifically referred to as a *ribonucleotide*, and the resulting nucleic acid is ribonucleic acid (RNA). If the sugar is 2-deoxyribose, the nucleotide is a *deoxyribonucleotide*, and the nucleic acid is DNA.




The nitrogenous bases found in nucleotides are classified as pyrimidines or purines. Pyrimidines are heterocyclic amines with two nitrogen atoms in a six-member ring and include uracil, thymine, and cytosine. Purines are heterocyclic amines consisting of a pyrimidine ring fused to a five-member ring with two nitrogen atoms. Adenine and guanine are the major purines found in nucleic acids (Figure 14.5.2.1).

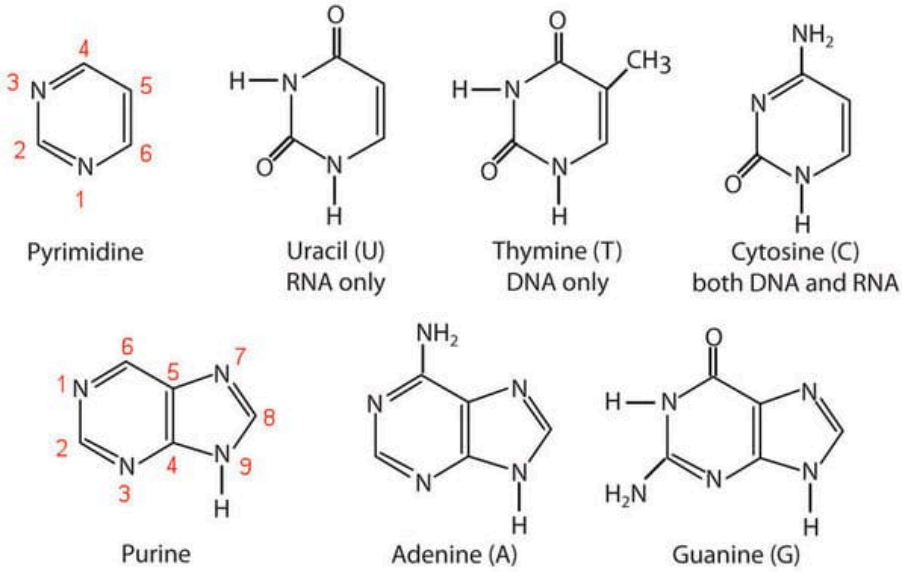



Figure 14.5.2.1: The Nitrogenous Bases Found in DNA and RNA

The formation of a bond between C1′ of the pentose sugar and N1 of the pyrimidine base or N9 of the purine base joins the pentose sugar to the nitrogenous base. In the formation of this bond, a molecule of water is removed. Table 14.5.2.1 summarizes the similarities and differences in the composition of nucleotides in DNA and RNA.

> The numbering convention is that primed numbers designate the atoms of the pentose ring, and unprimed numbers designate the atoms of the purine or pyrimidine ring.

*Table 14.5.2.1: Composition of Nucleotides in DNA and RNA*

| Composition | DNA | RNA |
|---|---|---|
| purine bases | adenine and guanine | adenine and guanine |
| pyrimidine bases | cytosine and thymine | cytosine and uracil |
| pentose sugar | 2-deoxyribose | ribose |
| inorganic acid | phosphoric acid ($H_3PO_4$) | $H_3PO_4$ |

The names and structures of the major ribonucleotides and one of the deoxyribonucleotides are given in Figure 14.5.2.2.

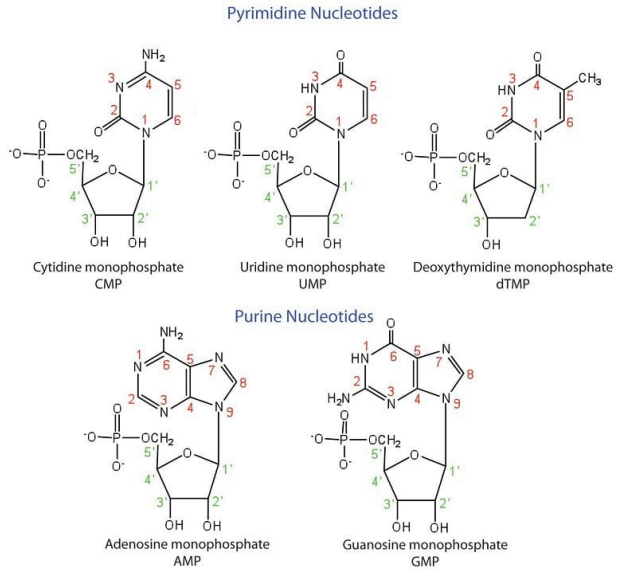



Figure 14.5.2.2: The Pyrimidine and Purine Nucleotides

Apart from being the monomer units of DNA and RNA, the nucleotides and some of their derivatives have other functions as well. Adenosine diphosphate (ADP) and adenosine triphosphate (ATP), shown in Figure 14.5.2.3, have a role in cell metabolism. Moreover, a number of coenzymes, including flavin adenine dinucleotide (FAD), nicotinamide adenine dinucleotide ($NAD^+$), and coenzyme A, contain adenine nucleotides as structural components.

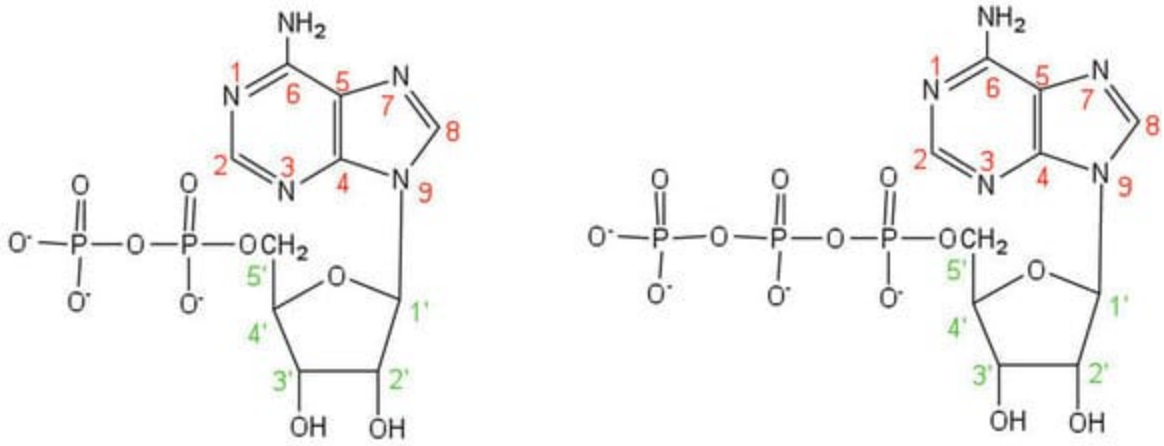



Figure 14.5.2.3: Structures of Two Important Adenine-Containing Nucleotides

## Summary

Nucleotides are composed of phosphoric acid, a pentose sugar (ribose or deoxyribose), and a nitrogen-containing base (adenine, cytosine, guanine, thymine, or uracil). Ribonucleotides contain ribose, while deoxyribonucleotides contain deoxyribose.

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# 14.5.3: Nucleic Acid Structure

Skills to Develop

- Identify the two types of nucleic acids and the function of each type.
- Describe how nucleotides are linked together to form nucleic acids.
- Describe the secondary structure of DNA and the importance of complementary base pairing.

Nucleic acids are large polymers formed by linking nucleotides together and are found in every cell. Deoxyribonucleic acid (DNA) is the nucleic acid that stores genetic information. If all the DNA in a typical mammalian cell were stretched out end to end, it would extend more than 2 m. Ribonucleic acid (RNA) is the nucleic acid responsible for using the genetic information encoded in DNA to produce the thousands of proteins found in living organisms.

## Primary Structure of Nucleic Acids

Nucleotides are joined together through the phosphate group of one nucleotide connecting in an ester linkage to the OH group on the third carbon atom of the sugar unit of a second nucleotide. This unit joins to a third nucleotide, and the process is repeated to produce a long nucleic acid chain (Figure 14.5.3.1). The backbone of the chain consists of alternating phosphate and sugar units (2-deoxyribose in DNA and ribose in RNA). The purine and pyrimidine bases branch off this backbone.

> Each phosphate group has one acidic hydrogen atom that is ionized at physiological pH. This is why these compounds are known as nucleic acids.

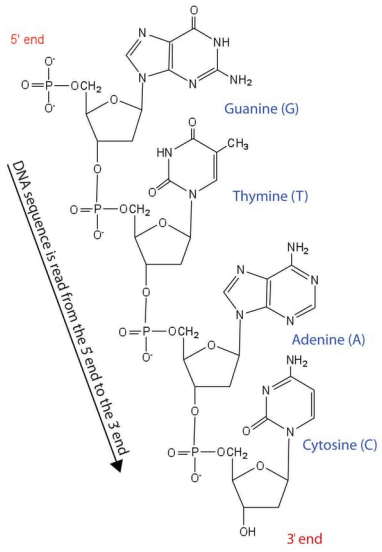



***Figure*** 14.5.3.1 *Structure of a Segment of DNA. A similar segment of RNA would have OH groups on each C2′, and uracil would replace thymine.*

Like proteins, nucleic acids have a primary structure that is defined as the sequence of their nucleotides. Unlike proteins, which have 20 different kinds of amino acids, there are only 4 different kinds of nucleotides in nucleic acids. For amino acid sequences in proteins, the convention is to write the amino acids in order starting with the N-terminal amino acid. In writing nucleotide sequences for nucleic acids, the convention is to write the nucleotides (usually using the one-letter abbreviations for the bases, shown in Figure 14.5.3.1) starting with the nucleotide having a free phosphate group, which is known as the 5′ end, and indicate the nucleotides in order. For DNA, a lowercase *d* is often written in front of the sequence to indicate that the monomers are deoxyribonucleotides. The final nucleotide has a free OH group on the 3′ carbon atom and is called the *3′ end*. The sequence of nucleotides in the DNA segment shown in Figure 14.5.3.1 would be written 5′-dG-dT-dA-dC-3′, which is often further abbreviated

to dGTAC or just GTAC.

## Secondary Structure of DNA

The three-dimensional structure of DNA was the subject of an intensive research effort in the late 1940s to early 1950s. Initial work revealed that the polymer had a regular repeating structure. In 1950, Erwin Chargaff of Columbia University showed that the molar amount of adenine (A) in DNA was always equal to that of thymine (T). Similarly, he showed that the molar amount of guanine (G) was the same as that of cytosine (C). Chargaff drew no conclusions from his work, but others soon did.

At Cambridge University in 1953, James D. Watson and Francis Crick announced that they had a model for the secondary structure of DNA. Using the information from Chargaff's experiments (as well as other experiments) and data from the X ray studies of Rosalind Franklin (which involved sophisticated chemistry, physics, and mathematics), Watson and Crick worked with models that were not unlike a child's construction set and finally concluded that DNA is composed of two nucleic acid chains running antiparallel to one another—that is, side-by-side with the 5′ end of one chain next to the 3′ end of the other. Moreover, as their model showed, the two chains are twisted to form a double helix—a structure that can be compared to a spiral staircase, with the phosphate and sugar groups (the backbone of the nucleic acid polymer) representing the outside edges of the staircase. The purine and pyrimidine bases face the inside of the helix, with guanine always opposite cytosine and adenine always opposite thymine. These specific base pairs, referred to as complementary bases, are the steps, or treads, in our staircase analogy (Figure 14.5.3.2).

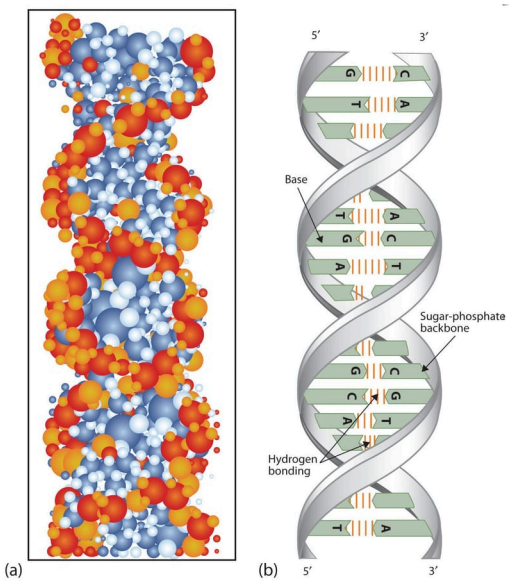



***Figure*** 14.5.3.2 *DNA Double Helix. (a) This represents a computer-generated model of the DNA double helix. (b) This represents a schematic representation of the double helix, showing the complementary bases.*

The structure proposed by Watson and Crick provided clues to the mechanisms by which cells are able to divide into two identical, functioning daughter cells; how genetic data are passed to new generations; and even how proteins are built to required specifications. All these abilities depend on the pairing of complementary bases. Figure 14.5.3.3 shows the two sets of base pairs and illustrates two things. First, a pyrimidine is paired with a purine in each case, so that the long dimensions of both pairs are identical (1.08 nm).

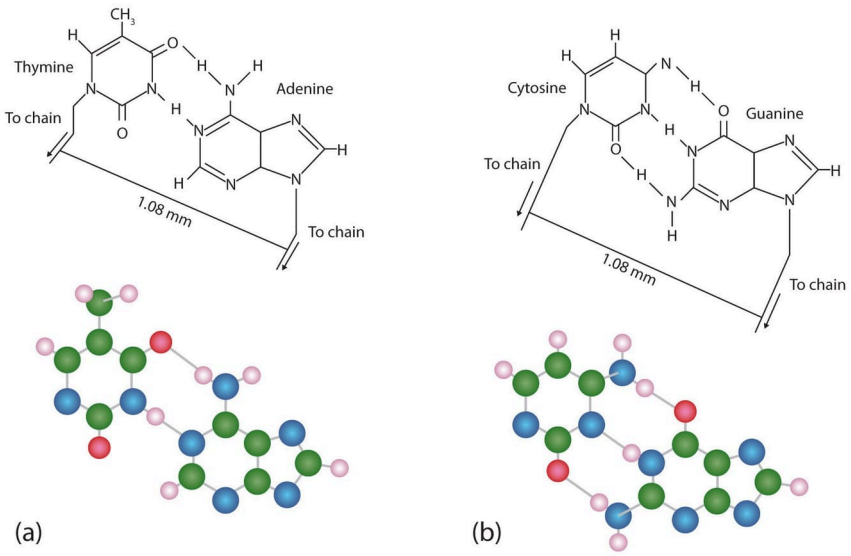



***Figure*** 14.5.3.3 *Complementary Base Pairing. Complementary bases engage in hydrogen bonding with one another: (a) thymine and adenine; (b) cytosine and guanine.*

If two pyrimidines were paired or two purines were paired, the two pyrimidines would take up less space than a purine and a pyrimidine, and the two purines would take up more space, as illustrated in Figure 14.5.3.4. If these pairings were ever to occur, the structure of DNA would be like a staircase made with stairs of different widths. For the two strands of the double helix to fit neatly, a pyrimidine must always be paired with a purine. The second thing you should notice in Figure 14.5.3.3 is that the correct pairing enables formation of three instances of hydrogen bonding between guanine and cytosine and two between adenine and thymine. The additive contribution of this hydrogen bonding imparts great stability to the DNA double helix.

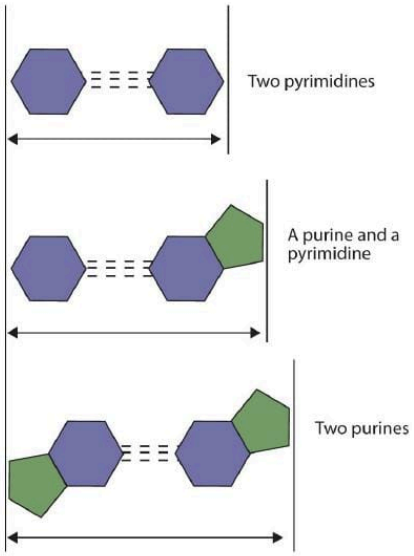



***Figure*** 14.5.3.4 *Difference in Widths of Possible Base Pairs*

## Summary

- DNA is the nucleic acid that stores genetic information. RNA is the nucleic acid responsible for using the genetic information in DNA to produce proteins.
- Nucleotides are joined together to form nucleic acids through the phosphate group of one nucleotide connecting in an ester linkage to the OH group on the third carbon atom of the sugar unit of a second nucleotide.

- Nucleic acid sequences are written starting with the nucleotide having a free phosphate group (the 5′ end).
- Two DNA strands link together in an antiparallel direction and are twisted to form a double helix. The nitrogenous bases face the inside of the helix. Guanine is always opposite cytosine, and adenine is always opposite thymine.

## Concept Review Exercises

1. a. Name the two kinds of nucleic acids.
   b. Which type of nucleic acid stores genetic information in the cell?

2. What are complementary bases?

3. Why is it structurally important that a purine base always pair with a pyrimidine base in the DNA double helix?

## Answers

1. a. deoxyribonucleic acid (DNA) and ribonucleic acid (RNA)
   b. DNA

2. the specific base pairings in the DNA double helix in which guanine is paired with cytosine and adenine is paired with thymine

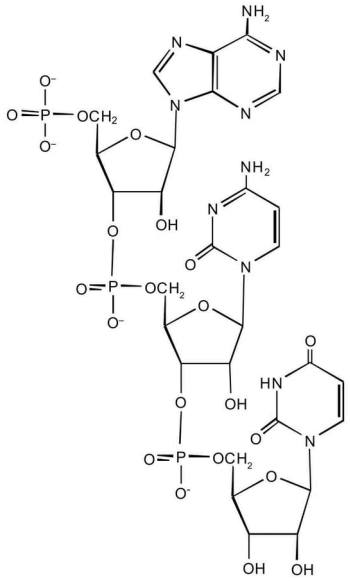
3. The width of the DNA double helix is kept at a constant width, rather than narrowing (if two pyrimidines were across from each other) or widening (if two purines were across from each other).

## Exercises

1. For this short RNA segment,

   a. identify the 5′ end and the 3′ end of the molecule.
   b. circle the atoms that comprise the backbone of the nucleic acid chain.

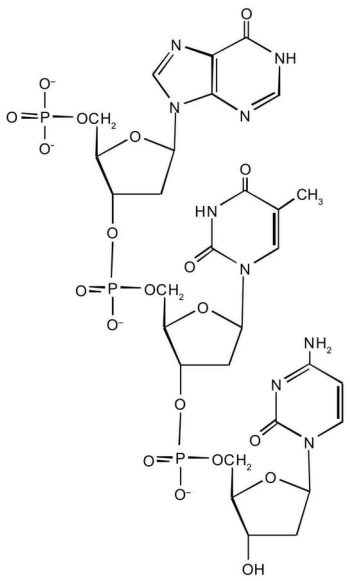
   c. write the nucleotide sequence of this RNA segment.



2. For this short DNA segment,

   a. identify the 5′ end and the 3′ end of the molecule.
   b. circle the atoms that comprise the backbone of the nucleic acid chain.

   c. write the nucleotide sequence of this DNA segment.



3. Which nitrogenous base in DNA pairs with each nitrogenous base?

    a. cytosine
    b. adenine
    c. guanine
    d. thymine

4. Which nitrogenous base in RNA pairs with each nitrogenous base?

    a. cytosine
    b. adenine
    c. guanine
    d. thymine

5. How many hydrogen bonds can form between the two strands in the short DNA segment shown below?

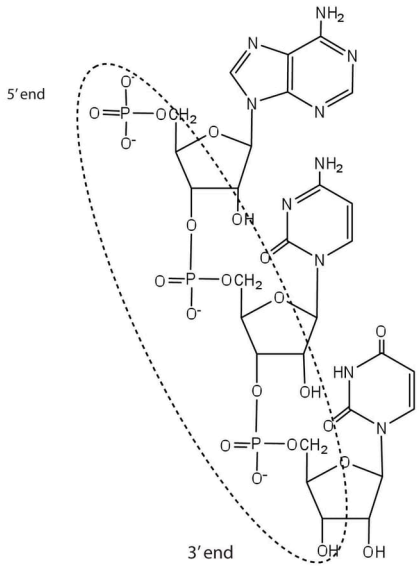
    5′ ATGCGACTA 3′ 3′ TACGCTGAT 5′

6. How many hydrogen bonds can form between the two strands in the short DNA segment shown below?

    5′ CGATGAGCC 3′ 3′ GCTACTCGG 5′

# Answers

1.




c. ACU

3. a. guanine
   b. thymine
   c. cytosine
   d. adenine

5. 22 (2 between each AT base pair and 3 between each GC base pair)

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# 14.5.4: Replication and Expression of Genetic Information

**Learning Objectives**

- Describe how a new copy of DNA is synthesized.
- Describe how RNA is synthesized from DNA.
- Identify the different types of RNA and the function of each type of RNA.

We previously stated that deoxyribonucleic acid (DNA) stores genetic information, while ribonucleic acid (RNA) is responsible for transmitting or expressing genetic information by directing the synthesis of thousands of proteins found in living organisms. But how do the nucleic acids perform these functions? Three processes are required: (1) *replication*, in which new copies of DNA are made; (2) *transcription*, in which a segment of DNA is used to produce RNA; and (3) *translation*, in which the information in RNA is translated into a protein sequence.

## Replication

New cells are continuously forming in the body through the process of cell division. For this to happen, the DNA in a dividing cell must be copied in a process known as replication. The complementary base pairing of the double helix provides a ready model for how genetic replication occurs. If the two chains of the double helix are pulled apart, disrupting the hydrogen bonding between base pairs, each chain can act as a *template*, or pattern, for the synthesis of a new complementary DNA chain.

The nucleus contains all the necessary enzymes, proteins, and nucleotides required for this synthesis. A short segment of DNA is "unzipped," so that the two strands in the segment are separated to serve as templates for new DNA. DNA polymerase, an enzyme, recognizes each base in a template strand and matches it to the complementary base in a free nucleotide. The enzyme then catalyzes the formation of an ester bond between the 5′ phosphate group of the nucleotide and the 3′ OH end of the new, growing DNA chain. In this way, each strand of the original DNA molecule is used to produce a duplicate of its former partner (Figure 14.5.4.1). Whatever information was encoded in the original DNA double helix is now contained in each replicate helix. When the cell divides, each daughter cell gets one of these replicates and thus all of the information that was originally possessed by the parent cell.

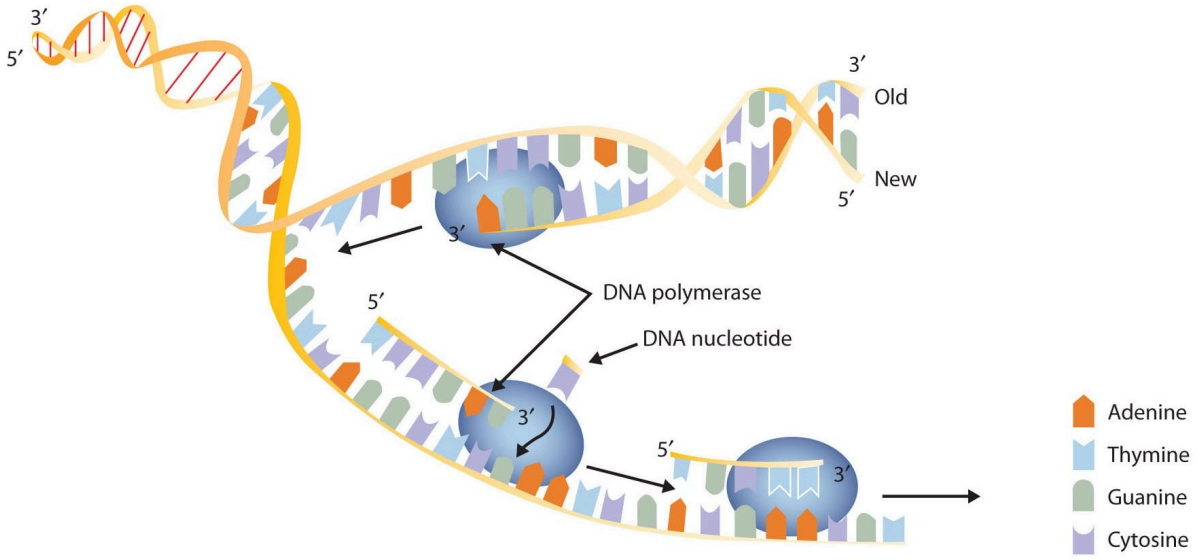



Figure 14.5.4.1: A Schematic Diagram of DNA Replication. DNA replication occurs by the sequential unzipping of segments of the double helix. Each new nucleotide is brought into position by DNA polymerase and is added to the growing strand by the formation of a phosphate ester bond. Thus, two double helixes form from one, and each consists of one old strand and one new strand, an outcome called *semiconservative replications*. (This representation is simplified; many more proteins are involved in replication.)

**Example 14.5.4.1**

A segment of one strand from a DNA molecule has the sequence 5′-TCCATGAGTTGA-3′. What is the sequence of nucleotides in the opposite, or complementary, DNA chain?

**Solution**

Knowing that the two strands are antiparallel and that T base pairs with A, while C base pairs with G, the sequence of the complementary strand will be 3′-AGGTACTCAACT-5′ (can also be written as TCAACTCATGGA).

**Exercise 14.5.4.1**

A segment of one strand from a DNA molecule has the sequence 5′-CCAGTGAATTGCCTAT-3′. What is the sequence of nucleotides in the opposite, or complementary, DNA chain?

What do we mean when we say information is encoded in the DNA molecule? An organism's DNA can be compared to a book containing directions for assembling a model airplane or for knitting a sweater. Letters of the alphabet are arranged into words, and these words direct the individual to perform certain operations with specific materials. If all the directions are followed correctly, a model airplane or sweater is produced.

In DNA, the particular sequences of nucleotides along the chains encode the directions for building an organism. Just as *saw* means one thing in English and *was* means another, the sequence of bases CGT means one thing, and TGC means something different. Although there are only four letters—the four nucleotides—in the genetic code of DNA, their sequencing along the DNA strands can vary so widely that information storage is essentially unlimited.

## Transcription

For the hereditary information in DNA to be useful, it must be "expressed," that is, used to direct the growth and functioning of an organism. The first step in the processes that constitute DNA expression is the synthesis of RNA, by a template mechanism that is in many ways analogous to DNA replication. Because the RNA that is synthesized is a complementary copy of information contained in DNA, RNA synthesis is referred to as transcription. There are three key differences between replication and transcription:

1. RNA molecules are much shorter than DNA molecules; only a portion of one DNA strand is copied or transcribed to make an RNA molecule.
2. RNA is built from ribonucleotides rather than deoxyribonucleotides.
3. The newly synthesized RNA strand does not remain associated with the DNA sequence it was transcribed from.

The DNA sequence that is transcribed to make RNA is called the *template strand*, while the complementary sequence on the other DNA strand is called the *coding* or *informational strand*. To initiate RNA synthesis, the two DNA strands unwind at specific sites along the DNA molecule. Ribonucleotides are attracted to the uncoiling region of the DNA molecule, beginning at the 3′ end of the template strand, according to the rules of base pairing. Thymine in DNA calls for adenine in RNA, cytosine specifies guanine, guanine calls for cytosine, and adenine requires uracil. RNA polymerase—an enzyme—binds the complementary ribonucleotide and catalyzes the formation of the ester linkage between ribonucleotides, a reaction very similar to that catalyzed by DNA polymerase (Figure 14.5.4.2). Synthesis of the RNA strand takes place in the 5′ to 3′ direction, antiparallel to the template strand. Only a short segment of the RNA molecule is hydrogen-bonded to the template strand at any time during transcription. When transcription is completed, the RNA is released, and the DNA helix reforms. The nucleotide sequence of the RNA strand formed during transcription is identical to that of the corresponding coding strand of the DNA, except that U replaces T.

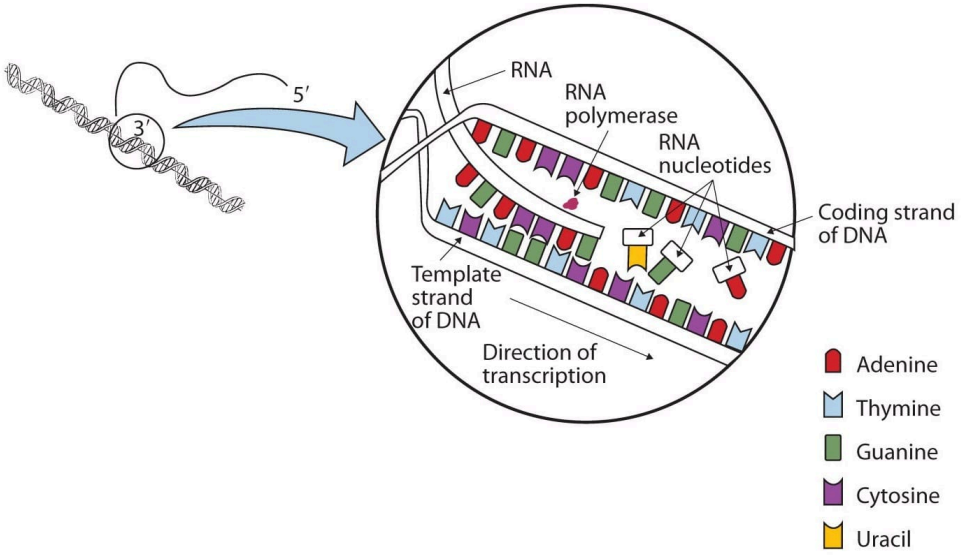



Figure 14.5.4.2: A Schematic Diagram of RNA Transcription from a DNA Template. The representation of RNA polymerase is proportionately much smaller than the actual molecule, which encompasses about 50 nucleotides at a time.

## Example 14.5.4.2

A portion of the template strand of a gene has the sequence 5′-TCCATGAGTTGA-3′. What is the sequence of nucleotides in the RNA that is formed from this template?

**Solution**

Four things must be remembered in answering this question: (1) the DNA strand and the RNA strand being synthesized are antiparallel; (2) RNA is synthesized in a 5′ to 3′ direction, so transcription begins at the 3′ end of the template strand; (3) ribonucleotides are used in place of deoxyribonucleotides; and (4) thymine (T) base pairs with adenine (A), A base pairs with uracil (U; in RNA), and cytosine (C) base pairs with guanine (G). The sequence is determined to be 3′-AGGUACUCAACU-5′ (can also be written as 5′-UCAACUCAUGGA-3′).

## Exercise 14.5.4.2

A portion of the template strand of a gene has the sequence 5′-CCAGTGAATTGCCTAT-3′. What is the sequence of nucleotides in the RNA that is formed from this template?

Three types of RNA are formed during transcription: *messenger RNA* (mRNA), *ribosomal RNA* (rRNA), and *transfer RNA* (tRNA). These three types of RNA differ in function, size, and percentage of the total cell RNA (Table 14.5.4.1). mRNA makes up only a small percent of the total amount of RNA within the cell, primarily because each molecule of mRNA exists for a relatively short time; it is continuously being degraded and resynthesized. The molecular dimensions of the mRNA molecule vary according to the amount of genetic information a given molecule contains. After transcription, which takes place in the nucleus, the mRNA passes into the cytoplasm, carrying the genetic message from DNA to the ribosomes, the sites of protein synthesis. Elsewhere, we shall see how mRNA directly determines the sequence of amino acids during protein synthesis.

*Table 14.5.4.1: Properties of Cellular RNA in Escherichia coli*

| Type | Function | Approximate Number of Nucleotides | Percentage of Total Cell RNA |
|---|---|---|---|
| mRNA | codes for proteins | 100–6,000 | ~3 |

| Type | Function | Approximate Number of Nucleotides | Percentage of Total Cell RNA |
|---|---|---|---|
| rRNA | component of ribosomes | 120–2900 | 83 |
| tRNA | adapter molecule that brings the amino acid to the ribosome | 75–90 | 14 |

Ribosomes are cellular substructures where proteins are synthesized. They contain about 65% rRNA and 35% protein, held together by numerous noncovalent interactions, such as hydrogen bonding, in an overall structure consisting of two globular particles of unequal size.

Molecules of tRNA, which bring amino acids (one at a time) to the ribosomes for the construction of proteins, differ from one another in the kinds of amino acid each is specifically designed to carry. A set of three nucleotides, known as a codon, on the mRNA determines which kind of tRNA will add its amino acid to the growing chain. Each of the 20 amino acids found in proteins has at least one corresponding kind of tRNA, and most amino acids have more than one.

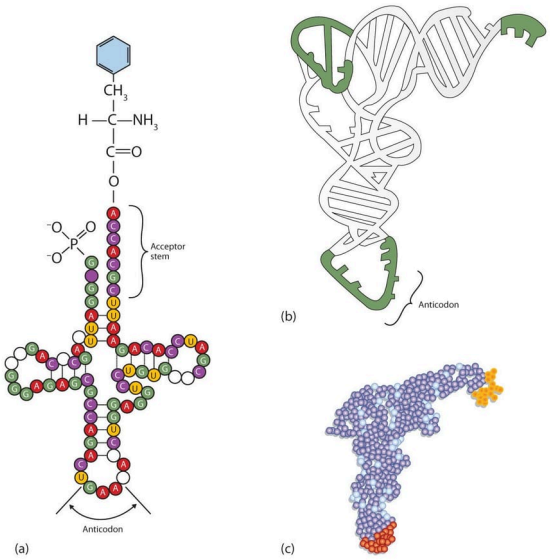



Figure 14.5.4.3: Transfer RNA. (a) In the two-dimensional structure of a yeast tRNA molecule for phenylalanine, the amino acid binds to the acceptor stem located at the 3′ end of the tRNA primary sequence. (The nucleotides that are not specifically identified here are slightly altered analogs of the four common ribonucleotides A, U, C, and G.) (b) In the three-dimensional structure of yeast phenylalanine tRNA, note that the anticodon loop is at the bottom and the acceptor stem is at the top right. (c) This shows a space-filling model of the tRNA.

The two-dimensional structure of a tRNA molecule has three distinctive loops, reminiscent of a cloverleaf (Figure 14.5.4.3). On one loop is a sequence of three nucleotides that varies for each kind of tRNA. This triplet, called the anticodon, is complementary to and pairs with the codon on the mRNA. At the opposite end of the molecule is the acceptor stem, where the amino acid is attached.

## Summary

- In DNA replication, each strand of the original DNA serves as a template for the synthesis of a complementary strand.
- DNA polymerase is the primary enzyme needed for replication.
- In transcription, a segment of DNA serves as a template for the synthesis of an RNA sequence.
- RNA polymerase is the primary enzyme needed for transcription.
- Three types of RNA are formed during transcription: mRNA, rRNA, and tRNA.

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# 14.5.5: Protein Synthesis and the Genetic Code

## Learning Objectives

- describe the characteristics of the genetic code.
- describe how a protein is synthesized from mRNA.

One of the definitions of a gene is as follows: a segment of deoxyribonucleic acid (DNA) carrying the code for a specific polypeptide. Each molecule of messenger RNA (mRNA) is a transcribed copy of a gene that is used by a cell for synthesizing a polypeptide chain. If a protein contains two or more different polypeptide chains, each chain is coded by a different gene. We turn now to the question of how the sequence of nucleotides in a molecule of ribonucleic acid (RNA) is translated into an amino acid sequence.

How can a molecule containing just 4 different nucleotides specify the sequence of the 20 amino acids that occur in proteins? If each nucleotide coded for 1 amino acid, then obviously the nucleic acids could code for only 4 amino acids. What if amino acids were coded for by groups of 2 nucleotides? There are $4^2$, or 16, different combinations of 2 nucleotides (AA, AU, AC, AG, UU, and so on). Such a code is more extensive but still not adequate to code for 20 amino acids. However, if the nucleotides are arranged in groups of 3, the number of different possible combinations is $4^3$, or 64. Here we have a code that is extensive enough to direct the synthesis of the primary structure of a protein molecule.

## YouTube Video

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

View this YouTube Video online

***Video**: NDSU Virtual Cell Animations project animation "Translation". For more information, see VCell, NDSU(opens in new window) [vcell.ndsu.nodak.edu]*

The genetic code can therefore be described as the identification of each group of three nucleotides and its particular amino acid. The sequence of these triplet groups in the mRNA dictates the sequence of the amino acids in the protein. Each individual three-nucleotide coding unit, as we have seen, is called a *codon*.

Protein synthesis is accomplished by orderly interactions between mRNA and the other ribonucleic acids (transfer RNA [tRNA] and ribosomal RNA [rRNA]), the ribosome, and more than 100 enzymes. The mRNA formed in the nucleus during transcription is transported across the nuclear membrane into the cytoplasm to the ribosomes—carrying with it the genetic instructions. The process in which the information encoded in the mRNA is used to direct the sequencing of amino acids and thus ultimately to synthesize a protein is referred to as translation.

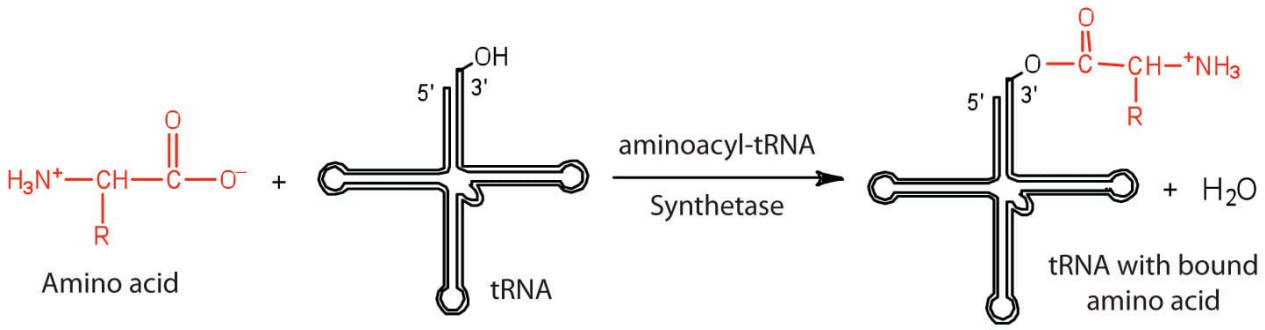



Figure 14.5.5.1: Binding of an Amino Acid to Its tRNA

Before an amino acid can be incorporated into a polypeptide chain, it must be attached to its unique tRNA. This crucial process requires an enzyme known as aminoacyl-tRNA synthetase (Figure 14.5.5.1). There is a specific aminoacyl-tRNA synthetase for each amino acid. This high degree of specificity is vital to the incorporation of the correct amino acid into a protein. After the amino acid molecule has been bound to its tRNA carrier, protein synthesis can take place. Figure 14.5.5.2 depicts a schematic stepwise representation of this all-important process.

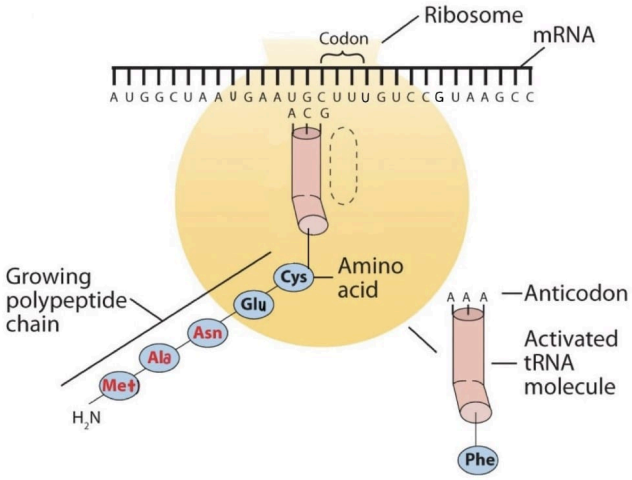



Figure 14.5.5.2a: The Elongation Steps in Protein Synthesis - Protein synthesis is already in progress at the ribosome. The growing polypeptide chain is attached to the tRNA that brought in the previous amino acid (in this illustration, cys.)

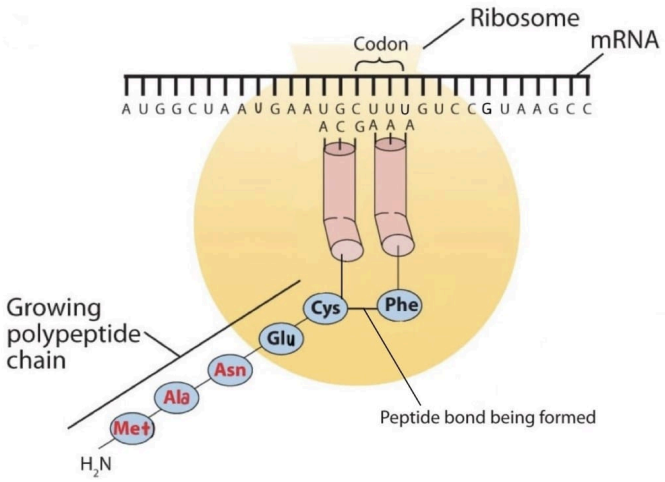



Figure 14.5.5.2*b*: The Elongation Steps in Protein Synthesis - An activated tRNA, which has the anticodon AAA, binds to the ribosome next to the previous bound tRNA and interacts with the mRNA molecule though basepairing of the codon and anticodon. The amino acid Phe is being incorporated into the polypeptide chain by the formation of a peptide linkage between the carboxyl group of Cys and the amino acid group of the Phe. This reaction is catalyzed by the enzyme peptidyl transferase, a component of the ribosome.

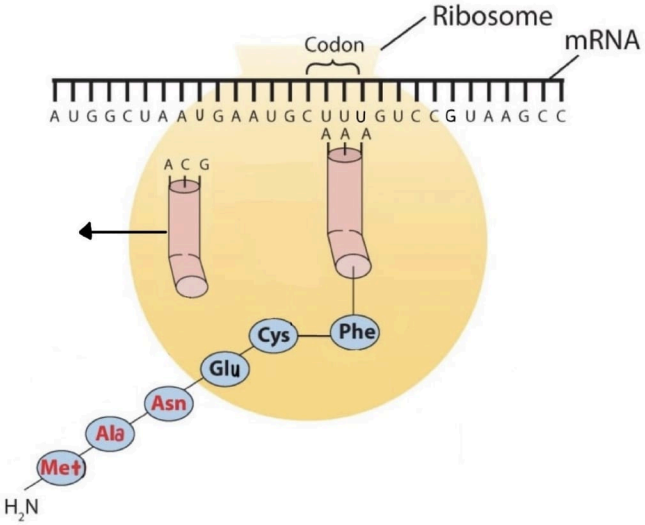



Figure 14.5.5.2*c*: The Elongation Steps in Protein Synthesis - The Cys-Phe linkage is now complete, and the growing polypeptide chain remains attached to the tRNA for Phe.

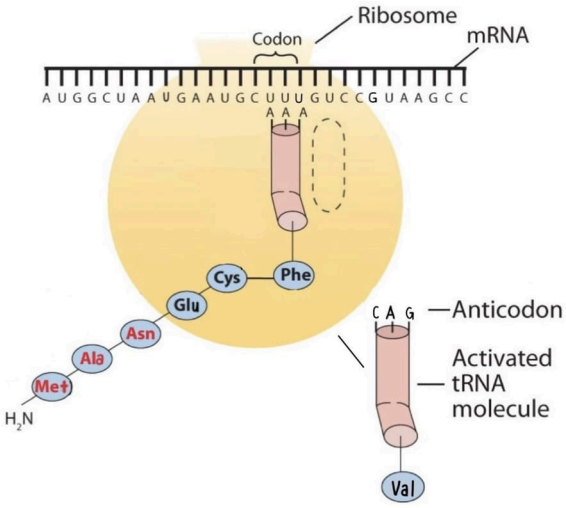



Figure 14.5.5.2*d*: The Elongation Steps in Protein Synthesis - The ribosome moves to the right along the mRNA strand. This shift brings the next codon, GUC, into its correct position on the surface of the ribosome. Note that an activated tRNA molecule, containing the next amino acid to be attached to the chain is moving to the ribosome. Steps (b)-(d) will be repeated until the ribosome reaches a stop codon.

Early experimenters were faced with the task of determining which of the 64 possible codons stood for each of the 20 amino acids. The cracking of the genetic code was the joint accomplishment of several well-known geneticists—notably Har Khorana, Marshall Nirenberg, Philip Leder, and Severo Ochoa—from 1961 to 1964. The genetic dictionary they compiled, summarized in Figure 14.5.5.3, shows that 61 codons code for amino acids, and 3 codons serve as signals for the termination of polypeptide synthesis (much like the period at the end of a sentence). Notice that only methionine (AUG) and tryptophan (UGG) have single codons. All other amino acids have two or more codons.

| First base | Second base: U | Second base: C | Second base: A | Second base: G | Third base |
|---|---|---|---|---|---|
| U | Phe | Ser | Tyr | Cys | U |
| | Phe | Ser | Tyr | Cys | C |
| | Leu | Ser | Stop | Stop | A |
| | Leu | Ser | Stop | Trp | G |
| C | Leu | Pro | His | Arg | U |
| | Leu | Pro | His | Arg | C |
| | Leu | Pro | Gln | Arg | A |
| | Leu | Pro | Gln | Arg | G |
| A | Ile | Thr | Asn | Ser | U |
| | Ile | Thr | Asn | Ser | C |
| | Ile | Thr | Lys | Arg | A |
| | Met | Thr | Lys | Arg | G |
| G | Val | Ala | Asp | Gly | U |
| | Val | Ala | Asp | Gly | C |
| | Val | Ala | Glu | Gly | A |
| | Val | Ala | Glu | Gly | G |

Figure 14.5.5.3: The Genetic Code

## Example 14.5.5.1: Using the Genetic Code

A portion of an mRNA molecule has the sequence 5′-AUGCCACGAGUUGAC-3′. What amino acid sequence does this code for?

**Solution**

Use Figure 14.5.5.3 to determine what amino acid each set of three nucleotides (codon) codes for. Remember that the sequence is read starting from the 5′ end and that a protein is synthesized starting with the N-terminal amino acid. The sequence 5′-AUGCCACGAGUUGAC-3′ codes for met-pro-arg-val-asp.

**Exercise 14.5.5.4**

A portion of an RNA molecule has the sequence 5′-AUGCUGAAUUGCGUAGGA-3′. What amino acid sequence does this code for?

Further experimentation threw much light on the nature of the genetic code, as follows:

1. The code is virtually universal; animal, plant, and bacterial cells use the same codons to specify each amino acid (with a few exceptions).
2. The code is “degenerate”; in all but two cases (methionine and tryptophan), more than one triplet codes for a given amino acid.
3. The first two bases of each codon are most significant; the third base often varies. This suggests that a change in the third base by a mutation may still permit the correct incorporation of a given amino acid into a protein. The third base is sometimes called the “wobble” base.
4. The code is continuous and nonoverlapping; there are *no* nucleotides between codons, and adjacent codons do not overlap.
5. The three termination codons are read by special proteins called release factors, which signal the end of the translation process.
6. The codon AUG codes for methionine and is also the initiation codon. Thus methionine is the first amino acid in each newly synthesized polypeptide. This first amino acid is usually removed enzymatically before the polypeptide chain is completed; the vast majority of polypeptides do not begin with methionine.

## Summary

In translation, the information in mRNA directs the order of amino acids in protein synthesis. A set of three nucleotides (codon) codes for a specific amino acid.

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# GLOSSARY

## S

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