INTRODUCTION TO CHEMISTRY & THE ENVIRONMENT



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Introduction to Chemistry & the Environment

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This text was compiled on 08/23/2026

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1: CHAPTER 1 - MEASUREMENTS IN CHEMISTRY

Making Measurements in Chemistry

Working in the field of chemistry depends on careful measurement, clear communication of quantities, and correct use of units. In this chapter, you will build the "math and measurement toolkit" that you'll use throughout your Chemistry course. We'll begin with scientific notation so you can work efficiently with very large and very small values commonly encountered in laboratory science. Next, you'll learn the International System of Units (SI), metric prefixes, and the difference between mass and weight, along with key temperature scales and common derived units such as volume, density, and energy. You will then practice how scientists report measurements using accuracy, precision, and significant figures, including scientific rounding ("rounding to the even") to avoid bias in data sets. Finally, you will apply dimensional analysis and conversion factors to solve real-world problems—such as converting medication doses and working with concentration and volume units.

By the end of this chapter, students will be able to:

1. **Use scientific notation correctly** to express, compare, and calculate with very large and very small numbers commonly used in chemistry and healthcare contexts.
2. **Identify and apply SI units and metric prefixes** to report measurements appropriately and convert between related metric units (e.g., g ↔ mg, m ↔ cm, L ↔ mL).
3. **Convert between temperature scales** (°C, K, °F) and explain why Kelvin is used for scientific calculations.
4. **Evaluate and report measurements using accuracy, precision, and significant figures**, including applying scientific rounding (round-to-even) when appropriate.
5. **Perform calculations while maintaining correct significant figures**, using the proper rules for addition/subtraction and multiplication/division.
6. **Use dimensional analysis (conversion factors) to solve applied problems**, including medication dosage conversions and IV drip-rate calculations with drop factors (gtt/mL).

How to Use This Chapter

This chapter is your "math and measurement toolbox" for Chemistry in the Health Professions. You'll use these skills in every later topic—especially when working with medication doses, lab data, concentrations, and clinical-style calculations—so it's worth moving carefully and practicing as you go.

- **Start with Section 1.1 (Scientific Notation)** and make sure you can rewrite numbers correctly *before* you try calculations. Small exponent mistakes can change an answer by a factor of 10, 100, or more.
- **In Section 1.2 (Units of Measurement), focus on units and prefixes.** As you read, keep a short list of common prefixes (kilo-, milli-, micro-) and practice moving between them.
- **As you reach Section 1.3 (Making Measurements in the Lab), slow down.** This is where you learn how scientists communicate uncertainty. Pay attention to the difference between **accuracy vs. precision** and how **significant figures** reflect instrument limits.
- **When doing problems, always write units at every step.** Unit cancellations are your built-in error-checking system. If units don't cancel the way you expect, something is set up incorrectly.
- **Don't round until the end.** Keep extra digits in intermediate steps, then apply significant-figure rules to the final answer. Use **round-to-even** only when the number you're rounding is exactly 5 (or 5 followed only by zeros).
- **Practice in short sessions.** A good approach is 15–20 minutes per section: read, do 2–3 practice problems, check your work, then move on. Revisit any section you'll use often (especially unit conversions and significant figures).

If you treat this chapter as a reference you return to during the term, it will save you time and prevent the most common calculation errors later in the course.

1.1: Chemistry and Matter

1.2: How Scientists Study Chemistry
1.3: Scientific Notation
1.4: Avogadro's Number and the Mole
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1.1: Chemistry and Matter

What is Chemistry?

Everything around us is made up of chemicals. From the color that makes a rose so red to the gasoline that fills our cars and the silicon chips that power our computers and cell phones...Chemistry is everywhere! Understanding how chemical molecules form and interact to create complex structures enables us to harness the power of chemistry and use it, just like a toolbox, to create many of the modern advances that we see today. This includes advances in medicine, communication, transportation, building infrastructure, food science and agriculture, and nearly every other technical field that you can imagine.

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. 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 1.1.1). 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.

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 1.1.1 shows how many of the individual fields of science are related.

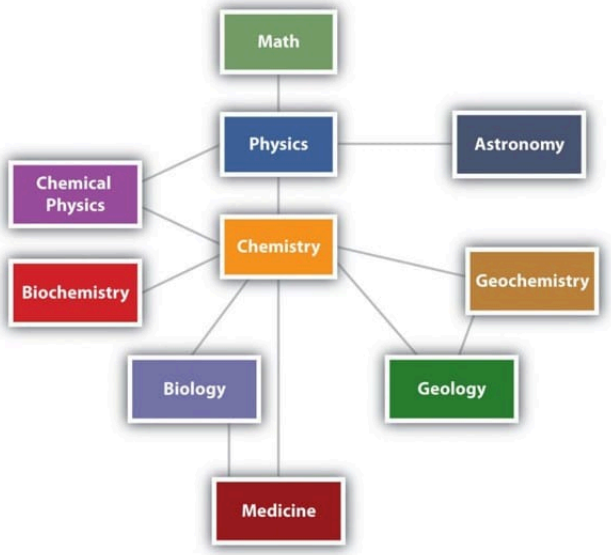


Figure 1.1.1**:The Relationships Between Some of the Major Branches of Science.** Chemistry lies more or less in the middle, which emphasizes its importance to many branches of science. Physical vs. Chemical Properties

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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. The properties that chemists use to describe matter fall into two general categories. Physical properties are characteristics that describes matter, such as boiling point, melting point and color. Physical Changes, such as melting a solid into a liquid, do not alter the chemical structure of that matter. Chemical properties are characteristics that describe how the chemical structure of matter changes during a chemical reaction. An example of a chemical property is flammability—a materials ability to burn—because burning (also known as combustion) changes the chemical composition of a material.

Elements and Compounds

Any sample of matter that has the same physical and chemical properties throughout the sample is called a substance. There are two types of 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. Water is a compound composed of the elements hydrogen and oxygen. Today, there are about 118 elements in the known universe which are organized on a fundamental chart called the Periodic Table of Elements (Fig. 1.1.2). In contrast, scientists have identified tens of millions of different compounds to date.

The smallest part of an element that maintains the identity of that element is called an atom. Atoms are extremely tiny; to make a line 1 inch long, you would need 217 million iron atoms! Similarly, the smallest part of a compound that maintains the identity of that compound is called a molecule. Molecules are composed of atoms that are attached together and behave as a unit (Fig. 1.1.2). Scientists usually work with millions of atoms and molecules at a time. When a scientist is working

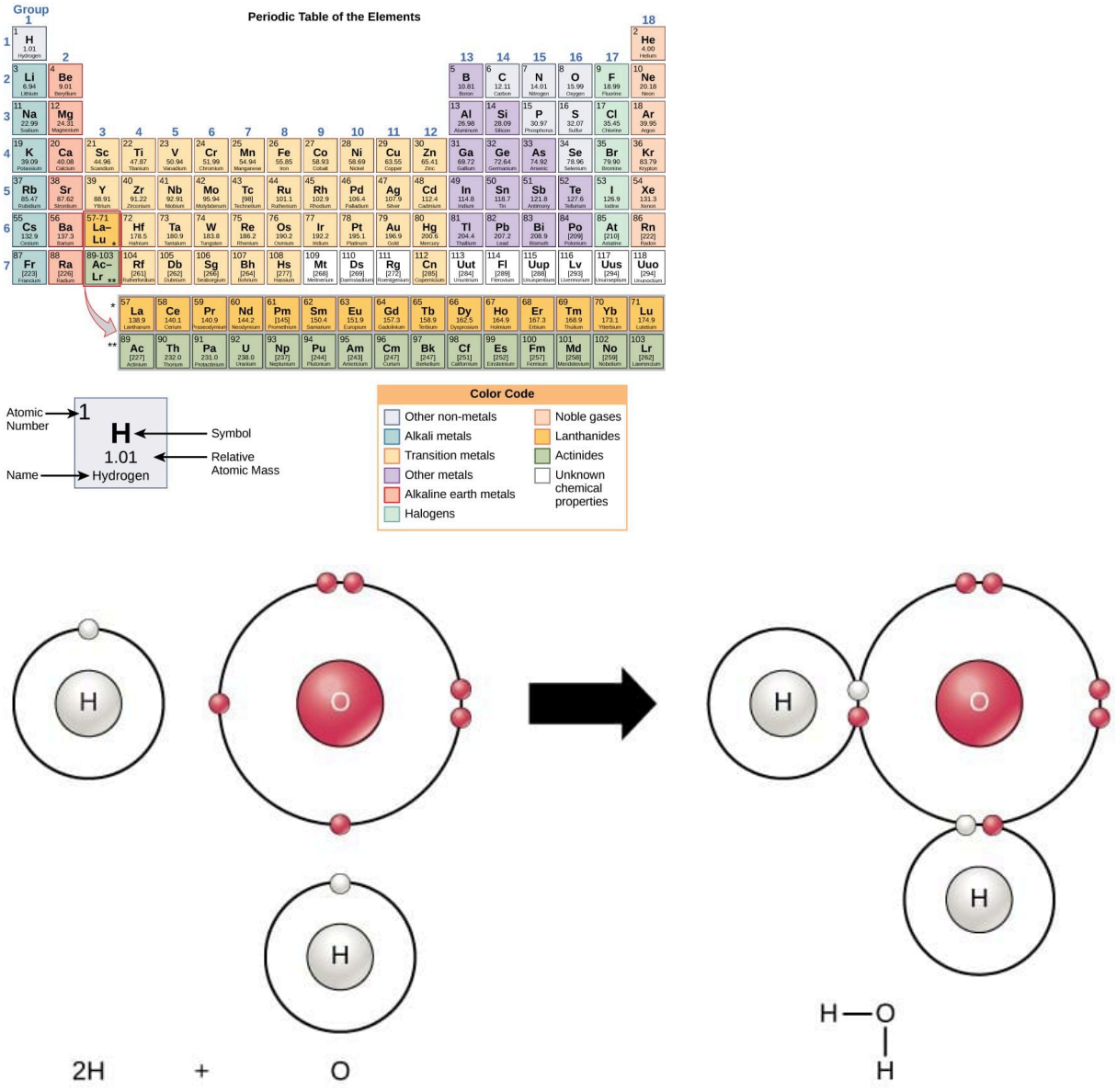


Figure 1.1.2**: (*Upper Panel)* The Periodic Table of the Elements is an organized chart that contains all of the known chemical elements. (*Lower Panel*) To the left of the arrow is shown one atom of oxygen and two atoms of hydrogen.** Each of these represent single elements. When they are combined on the righthand side, they form a single molecule of water (H_2O). Note that water is defined as a compound, because each single molecule is made up of more than one type of element, in

this case, one atom of oxygen with two atoms of hydrogen.

with large numbers of atoms or molecules at a time, the scientist is studying the macroscopic view of the universe. However, scientists can also describe chemical events on the level of individual atoms or molecules, which is referred to as the microscopic viewpoint. We will see examples of both macroscopic and microscopic viewpoints throughout this book (Figure 1.1.3).

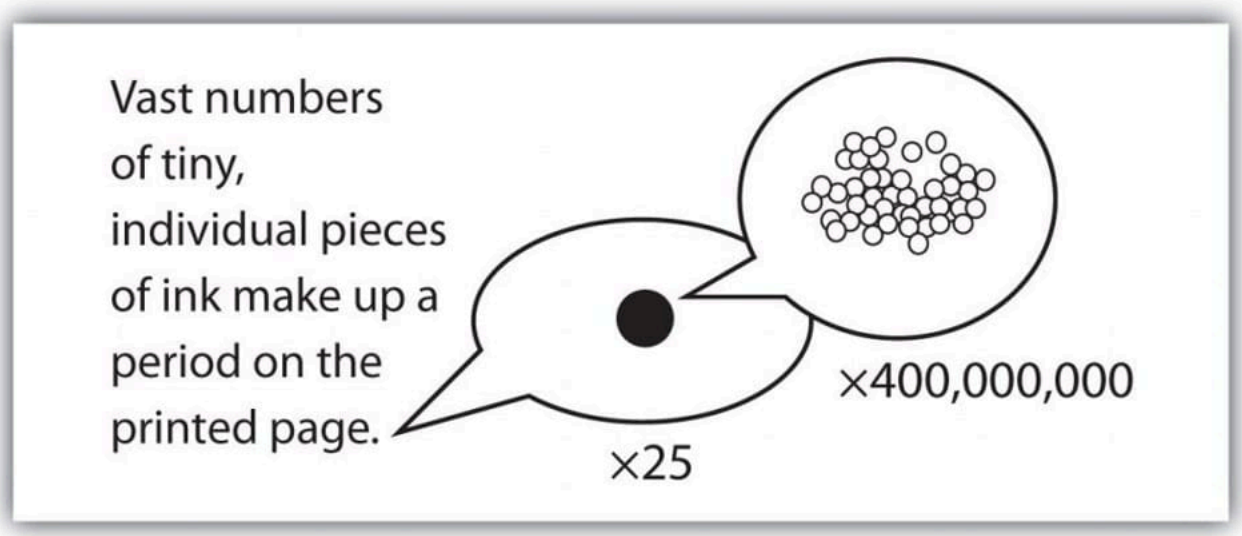


Figure 1.1.3**: How many molecules are needed for a period in a sentence?** Although we do not notice it from a macroscopic perspective, matter is composed of microscopic particles so tiny that billions of them are needed to make a speck that we can see with the naked eye. The X25 and X400,000,000 indicate the number of times the image is magnified.

Mixtures

A material composed of two or more substances is a mixture. In a mixture, the individual substances maintain their chemical identities. Many mixtures are obvious combinations of two or more substances, such as a mixture of sand and water. Such mixtures are called heterogeneous mixtures. In some mixtures, the components are so intimately combined that they act like a single substance even though they are not. Mixtures with a consistent composition throughout are called homogeneous mixtures Homogeneous mixtures that are mixed so thoroughly that neither component can be observed independently of the other are called solutions. Sugar dissolved in water is an example of a solution. A metal alloy, such as steel, is an example of a solid solution. Air, a mixture of mainly nitrogen and oxygen, is a gaseous solution.

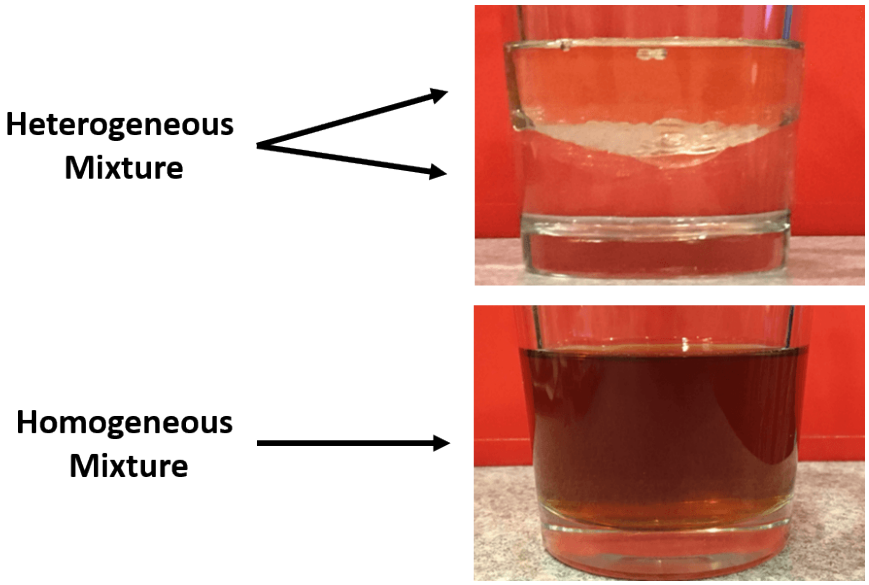


Figure 1.1.4: Heterogeneous vs. Homogeneous Mixtures. A mixture contains more than one substance. In the upper panel you see an example of a heterogeneous mixture of oil and water. The mixture is heterogeneous because you can visibly see two different components in the mixture. In the lower panel, you see an example of a homogeneous mixture, coffee. It is homogeneous because you cannot distinguish the many different components that make up a cup of coffee (water; caffeine; coffee alkaloids and tannins). It looks the same throughout. If the mixture is homogeneous and is also see through or clear, it is called a solution. In our example, the coffee is a solution; however, a concentrated espresso may be very opaque and would only be homogeneous mixture, not a solution.

States of Matter

Another way to classify matter is to describe it as a solid, a liquid, or a gas, which was done in the examples of solutions, above. These three descriptions, each implying that the matter has certain physical properties, represent the three phases of matter. A solid has a definite shape and a definite volume. Liquids have a definite volume but not a definite shape; they take the shape of their containers. Gases have neither a definite shape nor a definite volume, and they expand to fill their containers. We encounter matter in each phase every day. In fact, we regularly encounter water in all three phases: ice (solid), water (liquid), and steam (gas).

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 phase change or a physical process in which a substance goes from one phase to another (Figure 1.1.5). Phase changes have particular names depending on what phases are involved, as summarized in Table 1.1A.

Table 1.1A: Phase 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
Gas to Solid	Deposition



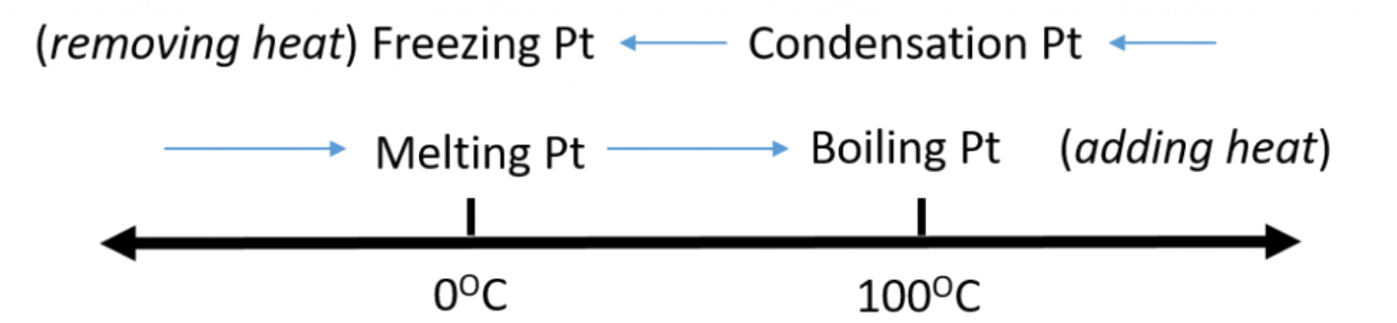


Figure 1.1.5**: Analyzing Phase Changes.** (*Upper panel*) A photo of boiling water demonstrates the phase change of water from the liquid to the gaseous phase. Note that phase changes are a physical property of a molecule. The water is still chemically the same (H_2O) in the solid, liquid, or gaseous state. (*Lower panel*) Change in temperature can cause phase changes . Above is the temperature scale for the phase changes of water. If you add heat to solid ice, water will melt at 0^oC and boil at 100^oC. If you remove heat from gaseous water, it will condense into the liquid state at 100^oC and freeze at 0^oC.

In summary, Figure 1.1.6 “The Classification of Matter” illustrates the relationships between the different ways matter can be classified.

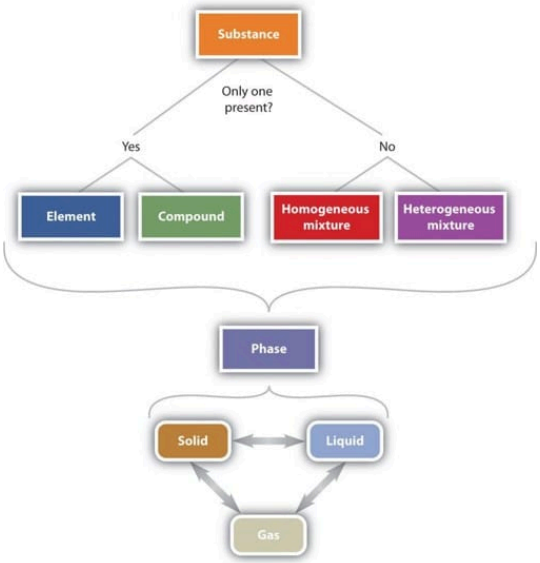


Figure 1.1.6**: The Classification of Matter.** Matter can be classified in a variety of ways depending on its properties

Reactions in Chemistry

Atoms can react chemically with one another to form new compounds and arrangements. When chemical reactions are written, they share some conventional features: (1) The reactants are written on the left hand side of the equation, (2) The products are written on the right hand side of the equation, (3) The reactants and products are separated by an arrow that shows the direction of the reaction, note that some reactions are reversible and are denoted by a double-headed arrow, (4) Conditions that are required for the reaction, such as heat or a *catalyst* (an agent that speeds up the chemical reaction without being used up in the process) are typically indicated above the arrow of the reaction, and (5) the reactants and products can be fully written out, or they can be represented by their chemical structures or by their chemical abbreviations (which you will learn how to formulate in the following chapters).

Reactions are written out with the quantities of the reactants and products in mind as well. During a chemical reaction, matter can never be destroyed. Thus, the atoms that are present on the left hand side of the equation must also be on the right hand side of the equation. They can be rearranged or in different forms, but they must be present. This is known as the ***law of conservation of matter***. To conform to this law, reactions are always written with the minimal amount of reactants required to make the minimal amount of products. An example of a chemical reaction is given below in Figure 1.1.7.

To represent the amounts of atoms present within a chemical reactions, numbers are present as either coefficients or subscripts within the equation. When the number is represented as a subscript, this indicates how many atoms of that element are required to make up a single molecule of the compound. In Figure 1.1.7, the chemical formula for carbon dioxide is given as CO_2 The number 2 subscript next to the oxygen atom indicates that there are two atoms of oxygen within a single molecule of carbon dioxide. When there is no subscript present, this means that there is only one atom present. Thus, for one molecule of carbon dioxide, CO_2, there is one atom of carbon and two atoms of oxygen. The coefficients in front of each substance, indicates how many molecules are required for a single reaction. In Figure 1.1.7, one molecule of methane reacts with 2 molecules of oxygen to yield one molecule of carbon dioxide and two molecules of water.

Since molecules are so small, it is impossible to ever measure out a single molecule when conducting an experiment in a laboratory. Thus, chemists will work with mole quantities of chemicals. The coefficients within chemical equations are also equivalent to mole quantities of each substance. Thus, the equation in Figure 1.1.7 can also be read as, one mole of methane reacts with 2 moles of oxygen to yield one mole of carbon dioxide and two moles of water. The mole will be defined in greater detail in section 1.4.

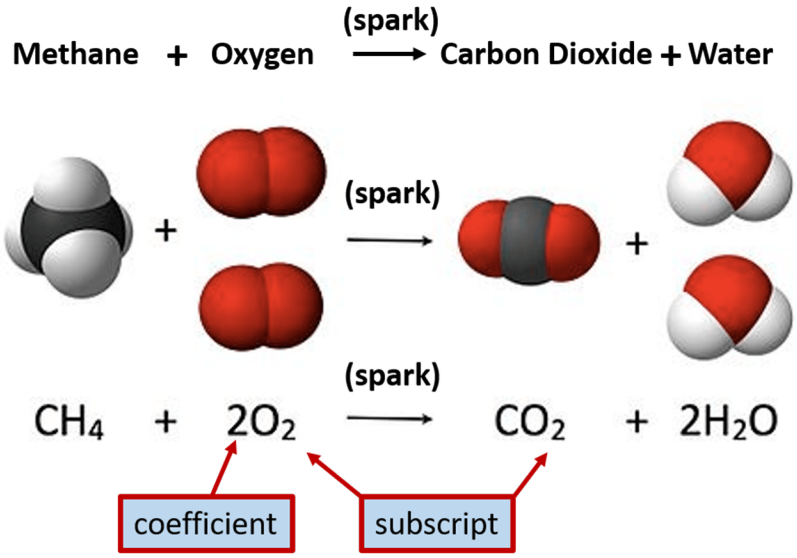


Figure 1.1.7**: Representations of Chemical Reactions.** In the example above the compound methane reacts with oxygen to form the products, carbon dioxide and water. Methane is also known as natural gas and is commonly burned to release usable energy. Subscripts present in the equation represent how many atoms of that element are involved with a chemical bond. If there is no number listed, the number one is implied. (ie in the carbon dioxide (CO_2) molecule denoted above, there is one atom of carbon (C) bonded with two atoms of oxygen (O) to form one molecule of carbon dioxide.) Note that to begin the burning process, a spark is needed to get the reaction started. This spark is noted over the arrow, as it is not a reactant or a product of the reaction. This figure is adapted from *Jynto and Jynto (2013)*(opens in new window).

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1.2: How Scientists Study Chemistry

The Scientific Method

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. To find the answer to a question (for example, "Why do birds fly toward Earth's equator during the cold months?"), a scientist goes through the following steps, which are also illustrated in Figure 1.2.1.

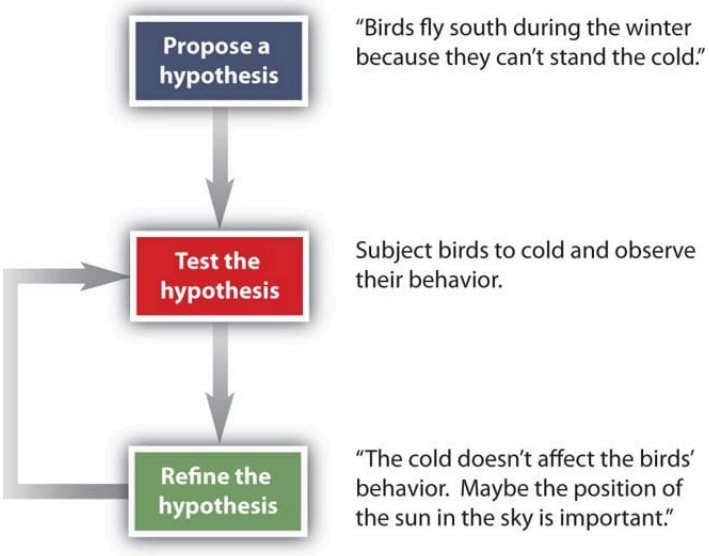


Figure 1.2.1**:The General Steps of the Scientific Method**. The steps may not be as clear-cut in real life as described here, but most scientific work follows this general outline.

Propose a hypothesis. A scientist generates a testable idea, or hypothesis, to try to answer a question or explain 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, and is built from a wide array of factual knowledge or data.

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.

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.

Exercise 1.2.1

1. Define Science and Chemistry.

2. Define the Scientific Method

Answer available at the end of this section.

Answers

Exercise 1.2.1

1. Science is the process by which we learn about the natural univers by observing, testing and then generating models that explain our observations. Chemistry is the study of matter and how it behaves.
2. The Scientific Method is the general process by which we learn about the natural universe.

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1.3: Scientific Notation

The study of chemistry can involve numbers that are very large. It can also involve numbers that are very small. Writing out such numbers and using them in their long form is problematic, because we would spend far too much time writing zeroes, and we would probably make a lot of mistakes! There is a solution to this problem. It is called scientific notation.

Scientific notation allows us to express very large and very small numbers using powers of 10.

Recall that:

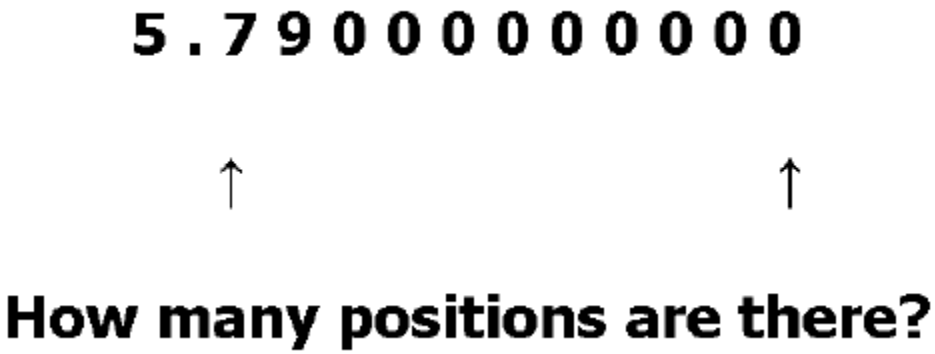
Table 1.3A Defining Factors of Ten - Exponents and Standard Numbers With Large Numbers

Factors of Ten		
$10^0 = 1$	$10^1 = 10$	$10^2 = 100$
$10^3 = 1000$	$10^4 = 10000$	$10^5 = 100000$

As you can see, the power to which 10 is raised is equal to the number of zeroes that follow the 1. This will be helpful for determining which exponent to use when we express numbers using scientific notation.

Let us take a very large number: **579, 000, 000, 000** and express it using scientific notation. First, we find the coefficient, which is a number between 1 and 10 that will be multiplied by 10 raised to some power. **Our coefficient is: 5.79.** This number will be multiplied by 10 that is raised to some power. Now let us figure out what power that is.

We can do this by counting the number of positions that stand between the end of the original number and the new position of the decimal point in our coefficient.



We can see that there are 11 positions between our decimal and the end of the original number. This means that our coefficient, 5.79, will be multiplied by 10 raised to the 11th power. Our number expressed in scientific notation is: **5.79×10^{11}.** But what about very small numbers?

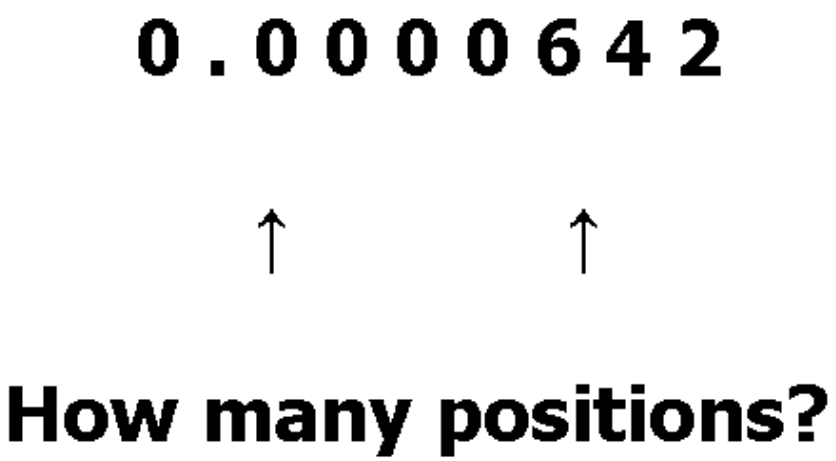
You may recall that:

Table 1.3B Defining Factors of Ten - Exponents and Standard Numbers With Very Small Numbers

Factors of Ten		
$10^{-1} = 0.1$	$10^{-2} = 0.01$	$10^{-3} = 0.001$
$10^{-4} = 0.0001$	$10^{-5} = 0.00001$	$10^{-6} = 0.000001$

The number of spaces to the right of the decimal point for our 1 is equal to the number in the exponent that is behind the negative sign. This is useful to keep in mind when we express very small numbers in scientific notation.

Here is a very small number: **0.0000642.** Let us express this number using scientific notation. **Our coefficient will be 6.42.** This number will be multiplied by 10 raised to some power, which will be negative. Let us figure out the correct power. We can figure this out by counting how many positions stand between the decimal point in our coefficient and the decimal point in our original number.



There are 5 positions between our new decimal point and the decimal point in the original number, so our coefficient will be multiplied by 10 raised to the negative 5th power.

Our number written in scientific notation is: **6.42×10^{-5}.** You can use these methods to express any large or small number using scientific notation.

Here is a short video tutorial to get your started: Scientific Notation Video (opens in new window)

Practice Problems:

1. Express each large number using scientific notation:

a) 2,300,000

b) 45,000

c) 976,000,000,000,000

d) 1,120

2. Express each small number using scientific notation:

a) 0.0012

b) 0.00000326

c) 0.057

d) 0.00000088

3. Fill in the missing exponent

a) 324,000 = 3.24 x $10^{?}$

b) 9,100,000 = 9.1 x $10^{?}$

c) 0.000038 = 3.8 x $10^{?}$

d) 0.0046 = 4.6 x $10^{?}$

Solutions

1. a) 2.3 x 10^{6} b) 4.5 x 10^{4} c) 9.76 x 10^{14} d) 1.12 x 10^{3}

2. a) 1.2 x 10^{-3} b) 3.26 x 10^{-6} c) 5.7 x 10^{-2} d) 8.8 x 10^{-7}

3. a) 5 b) 6 c) -5 d) -3

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1.4: Avogadro's Number and the Mole

Why Do Chemists Use the Mole?

Atoms and molecules are incredibly small. A single drop of water contains more water molecules than there are drops of water in all of Earth's oceans! Because individual atoms and molecules are far too numerous to count directly, chemists use a special counting unit called the **mole**.

A mole is simply a large counting unit, much like a dozen.

Table 1.4A: Common Counting Units in Science

Counting Unit	Number of Objects
Pair	2
Dozen	12
Gross	144
Mole	**6.022×10^{23}**

One mole always contains exactly **6.022×10^{23} representative particles**. This number is called **Avogadro's number** in honor of the Italian scientist Amedeo Avogadro.

The representative particles depend on the substance being measured. Always write the correct representative particle in your final answer.

Table 1.4B: Types of Particles Commonly Represented by Moles

Substance	Representative Particle
Copper	Atoms
Oxygen gas (O_2)	Molecules
Sodium Chloride (NaCl)	Formula Unit
Calcium Ions (Ca^{2+})	Ions

Using Dimensional Analysis

Since the mole is simply another unit, we can use the same dimensional analysis techniques introduced earlier in this chapter. Notice that the units cancel just as they do in any dimensional analysis problem.

Example 1.4.1

Convert 2.00 mol of carbon atoms into atoms.

Solution

$$2.00\ mol\ C\ x\ \frac{6.022\ x\ 10^{23} atoms\ of\ C}{1\ mol\ C} = 1.20\ x\ 10^{24}\ atoms\ of\ C$$

Example 1.4.2

Convert 3.01 × 10^{23} molecules of oxygen (O_2) into moles.

Solution

$$3.01\ x\ 10^{23}\ molecules\ of\ O_2\ x\ \frac{1\ mol\ O_2}{6.022\ x\ 10^{23}\ molecule\ O_2} = 0.500\ mol\ O_2$$

Example 1.4.1

How many formula units are present in 0.250 mol of sodium chloride?

Solution

$$0.250\ mol\ NaCl\ x\ \frac{6.022\ x\ 10^{23}\ formula\ units\ NaCl}{1\ mol\ NaCl} = 1.51\ x\ 10^{23}\ formula\ units\ NaCl$$

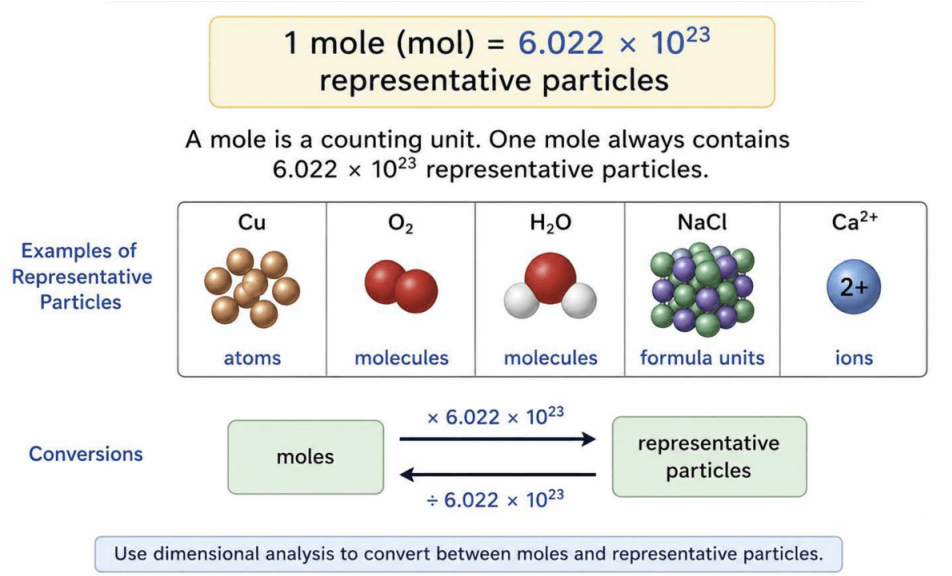


Figure 1.4.1 **Avogadro's Number and the Mole.** One mole is a counting unit equal to **6.022 × 10^{23} representative particles**, known as **Avogadro's number**. Depending on the substance, the representative particles may be atoms, molecules, formula units, or ions. Dimensional analysis can be used to convert between moles and representative particles. The figure states that one mole equals 6.022 × 10^{23} representative particles and explains that a mole is a counting unit. Examples of representative particles include copper atoms, oxygen molecules (O_2), water molecules (H_2O), sodium chloride formula units (NaCl), and calcium ions (Ca^{2+}). A conversion diagram shows that multiplying by 6.022 × 10^{23} converts moles to representative particles, while dividing by 6.022 × 10^{23} converts representative particles to moles. A note at the bottom reminds students to use dimensional analysis for these conversions.

Looking Ahead

In this chapter, the mole is used only as a **counting unit**.

In later chapters, you will learn how to use the mole to:

- convert between mass and moles using molar mass,
- interpret balanced chemical equations using mole ratios,
- predict the amounts of products formed in chemical reactions,
- calculate solution concentrations (molarity).

The mole will become one of the most important tools you use throughout chemistry.

Key Takeaways

After completing this section, you should be able to:

- Define Avogadro's number.
- Explain why chemists use the mole.
- Identify the representative particle for a substance.
- Convert between representative particles and moles using dimensional analysis.
- Express answers using the correct units and significant figures.

Practice Problems

1. Convert **4.50 mol Cu atoms** into atoms.
2. Convert **1.20 × 10^{24} molecules of CO_2** into moles.
3. How many **formula units** are present in **0.800 mol $CaCl_2$**?
4. Convert **6.022 × 10^{23} molecules of H_2O** into moles.
5. Convert **3.50 mol Na^+ ions** into ions.
6. Convert **9.03 × 10^{22} formula units of NaCl** into moles.

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1.5: Units of Measurement

International System of Units and the Metric System

The International System of Units, abbreviated SI from the French Système International D'unités, is the main system of measurement units used in science. Since the 1960s, the International System of Units has been internationally agreed upon as the standard metric system. The SI base units are based on physical standards. The definitions of the SI base units have been and continue to be modified and new base units added as advancements in science are made. Each SI base unit except the kilogram is described by stable properties of the universe.

There are seven base units, which are listed in Table 1.5A. Chemistry primarily uses five of the base units: the mole for amount, the kilogram for mass, the meter for length, the second for time, and the kelvin for temperature. The degree Celsius (^{o}C) is also commonly used for temperature. The numerical relationship between Temperature in Kelvins and Temperature in degrees Celsius is as follows:

$$T_{\mathrm{K}} = T_{^{\circ}\mathrm{C}} + 273.15 \tag{1.5.1}$$

where T_K is degrees Kelvin, and T^{o}_{C} is degrees Celcius

Table 1.5A: Scientific Measurement Base Units

Property	Unit	Abbreviation
Length	**Meter**	**m**
Mass	**Kilogram**	**kg**
Time	**Seconds**	**s**
Amount	**Mole**	**mol**
Temperature	**Kelvin**	**K**
Electric Current	**Ampere**	**amp**
Luminous Intensity	**Candella**	**cd**



Figure1.5.1**: The Kilogram.** The standard for the kilogram is a platinum-iridium cylinder kept in a special vault in France. Source: wikimedia (opens in new window)

The size of each base unit is defined by international convention. For example, the kilogram is defined as the quantity of mass of a special metal cylinder kept in a vault in France (*Figure 1.5.1*). The other base units have similar definitions. The sizes of the base units are not always convenient for all measurements. For example, a meter is a rather large unit for describing the width of something as narrow as human hair. Instead of reporting the diameter of hair as 0.00012 m or even 1.2×10^{-4} m, SI also provides a series of prefixes that can be attached to the units, creating units that are larger or smaller by powers of 10, known as the metric system.

Common prefixes and their multiplicative factors are listed in *Table 1.5B: Examples of Metric Conversions Using the Gram as the base Unit*. (Perhaps you have already noticed that the base unit kilogram is a combination of a prefix, kilo- meaning 1,000 ×, and a unit of mass, the gram.) Some prefixes create a multiple of the original unit: 1 kilogram equals 1,000 grams (or 1 kg = 1,000 g), and 1 megameter equals 1,000,000 meters (or 1 Mm = 1,000,000 m). Other prefixes create a fraction of the original unit. Thus, 1 centimeter equals 1/100 of a meter, 1 millimeter equals 1/1,000 of a meter, 1 microgram equals 1/1,000,000 of a gram, and so forth.

Table 1.5B provides an example of the correct conversions using the gram as the base unit. In addition, the larger unit, tera- is also included.

Table 1.5B Example of Metric Conversions Using the Gram as the Base Unit

Prefix	Abbr.	example using g as base unit	conversion nearest neighbor
tera-	T	1,000,000,000,000 g = 1 Tg	1,000 Gg = 1 Tg
giga-	G	1,000,000,000 g = 1 Gg	1,000 Mg = 1 Gg
mega-	M	1,000,000 g = 1 Mg	1,000 kg = 1 Mg

Prefix	Abbr.	example using g as base unit	conversion nearest neighbor
kilo-	k	1,000 g = 1 kg	100 Dg = 1 kg
deca-	D	10 g = 1 Dg	
Base Unit		base unit	
deci-	d	10 dg = 1 g	
centi-	c	100 cg = 1 g	10 cg = 1 dg
milli-	m	1,000 mg = 1 g	10 mg = 1 cg
micro-	m	1,000,000 mg = 1 g	1,000 mg = 1 mg
nano-	n	1,000,000,000 ng = 1 g	1,000 ng = 1 mg
pico-	p	1,000,000,000,000 pg = 1 g	1,000 pg = 1 ng
femto-	f	1,000,000,000,000,000 = 1 g	1,000 fg = 1 pg

Mass

The basic unit of mass in the International System of Units is the kilogram. A kilogram is equal to 1000 grams. A gram is a relatively small amount of mass and so larger masses are often expressed in kilograms. When very tiny amounts of matter are measured, we often use milligrams which are equal to 0.001 gram. There are numerous larger, smaller, and intermediate mass units that may also be appropriate. At the end of the 18th century, a kilogram was the mass of a liter of water. In 1889, a new international prototype of the kilogram was made of a platinum-iridium alloy. The kilogram is equal to the mass of this international prototype, which is held in Paris, France.

Mass and weight are not the same thing. Although we often use the terms mass and weight interchangeably, each one has a specific definition and usage. The mass of an object is a measure of the amount of matter in it. The mass (amount of matter) of an object remains the same regardless of where the object is placed. For example, moving a brick to the moon does not cause any matter in it to disappear or be removed.

The weight of an object is determined by the force that gravitation exerts upon the object. The weight is equal to the mass of the object times the local acceleration of gravity. Thus, on the Earth, weight is determined by the force of attraction between the object and the Earth. Since the force of gravity is not the same at every point on the Earth's surface, the weight of an object is not constant. The gravitational pull on the object varies depending on where the object is with respect to the Earth or other gravity-producing object. For example, a man who weighs 180 pounds on Earth would weigh only 45 pounds if he were in a

stationary position, 4,000 miles above the Earth's surface. This same man would weigh only 30 pounds on the moon because the moon's gravity is only one-sixth that of Earth. The mass of this man, however, would be the same in each situation. For scientific experiments, it is important to measure the mass of a substance rather than the weight to retain consistency in the results regardless of where you are performing the experiment.

Length

The SI unit of length is the meter. In 1889, the definition of the meter was a bar of platinum-iridium alloy stored under conditions specified by the International Bureau of Standards. In 1960, this definition of the standard meter was replaced by a definition based on a wavelength of krypton-86 radiation. In 1983, that definition was replaced by the following: the meter is the length of the path traveled by light in a vacuum during a time interval of a second.

Temperature

When used in a scientific context, the words heat and temperature do NOT mean the same thing. Temperature represents the average kinetic energy of the particles that make up a material. Increasing the temperature of a material increases its thermal energy. Thermal energy is the sum of the kinetic and potential energy in the particles that make up a material. Objects do not "contain" heat; rather they contain thermal energy. Heat is the movement of thermal energy from a warmer object to a cooler object. When thermal energy moves from one object to another, the temperature of both objects change.

A thermometer is a device that measures temperature. The name is made up of "thermo" which means heat and "meter" which means to measure. The temperature of a substance is directly proportional to the average kinetic energy it contains. In order for the average kinetic energy and temperature of a substance to be directly proportional, it is necessary that when the temperature is zero, the average kinetic energy must also be zero. It was necessary for use in calculations in science for a third temperature scale in which zero degrees corresponds with zero kinetic energy, that is, the point where molecules cease to move. This temperature scale was designed by Lord Kelvin. Lord Kelvin stated that there is no upper limit of how hot things can get, but there is a limit as to how cold things can get. In 1848, William Lord Kelvin developed the idea of absolute zero, which is the temperature at which molecules stop moving and therefore, have zero kinetic energy. This is known as the Kelvin temperature scale.

The Celsius scale is based on the freezing point and boiling point of water. Thus, 0°C is the freezing point of water, whereas 100°C is the boiling point of water. Most of us are familiar with temperatures that are below the freezing point of water. It should be apparent that even though the air temperature may be -5°C, the molecules of air are still moving (i.e. 0°C is not absolute zero). Substances like oxygen gas and nitrogen gas have already melted and boiled to vapor at temperatures below -150°C.

The Fahrenheit scale is also defined by the freezing point and boiling points of water. However, the scale is different from that of the Kelvin and Celsius scales. In the Fahrenheit scale, the freezing point of water is 32°F and the boiling point of water is 212°F. To convert between the Fahrenheit scale and the Celsius scale , the following conversions can be used:

$$T_{^\circ\mathrm{C}} = (T_{^\circ\mathrm{F}} - 32) \times \frac{5}{9} \qquad \text{or} \qquad T_{^\circ\mathrm{F}} = T_{^\circ\mathrm{C}} \times \frac{9}{5} + 32 \tag{1.5.2}$$

Where T_F is Temperature in degrees Fahrenheit, and $T°_C$ is Temperature in degrees Celcius

The Kelvin temperature scale has its zero at absolute zero (determined to be -273.15°C), and uses the same degree scale as the Celsius scale. Therefore, the mathematical relationship between the Celsius scale and the Kelvin scale is

$$T_{\mathrm{K}} = T_{^\circ\mathrm{C}} + 273.15 \tag{1.5.3}$$

where T_k is Temperature in degrees Kelvin, and $T°_C$ is Temperature in degrees Celcius. In the case of the Kelvin scale, the degree sign is not used. Temperatures are expressed simply as 450 K, and are always positive.

Time

The SI unit for time is the second. The second was originally defined as a tiny fraction of the time required for the Earth to orbit the Sun. It has since been redefined several times. The definition of a second (established in 1967 and reaffirmed in 1997) is: the duration of 9,192,631,770 periods of the radiation corresponding to the transition between the two hyperfine levels of the ground state of the cesium-133 atom.

Amount

Chemists use the term mole to represent a large number of atoms or molecules. Just as a dozen implies 12 things, a mole (mol) represents 6.022×10^{23} things. The number 6.022×10^{23}, called Avogadro's number after the 19th-century chemist Amedeo Avogadro, is the number we use in chemistry to represent macroscopic amounts of atoms and molecules. Thus, if we have 6.022×10^{23} Oxygen atoms, we say we have 1 mol of Oxygen atoms. If we have 2 mol of Na atoms, we have $2 \times (6.022 \times 10^{23})$ Na atoms, or 1.2044×10^{24} Na atoms. Similarly, if we have 0.5 mol of benzene (C_6H_6) molecules, we have $0.5 \times (6.022 \times 10^{23})$ C_6H_6 molecules, or 3.011×10^{23} C_6H_6 molecules.

Derived SI Units

Derived units are combinations of SI base units. Units can be multiplied and divided, just as numbers can be multiplied and divided. For example, the area of a square having a side of 2 cm is 2 cm × 2 cm, or 4 cm^2 (read as "four centimeters squared" or "four square centimeters"). Notice that we have squared a length unit, the centimeter, to get a derived unit for area, the square centimeter.

Table 1.5C: Common Metric to English Conversions

Conversions
1 m = 39.36 in = 3.28 ft = 1.09 yd
1 in = 2.54 cm
1 km = 0.62 mi
1 kg = 2.20 lb
1 lb = 454 g
1 L = 1.06 qt = 0.26 gal

Volume

Volume is an important quantity that uses a derived unit. Volume is the amount of space that a given substance occupies and is defined geometrically as length × width × height. Each distance can be expressed using the meter unit, so volume has the derived unit m × m × m, or m^3 (read as “meters cubed” or “cubic meters”). A cubic meter is a rather large volume, so scientists typically express volumes in terms of 1/1,000 of a cubic meter. This unit has its own name—the liter (L). A liter is a little larger than 1 US quart in volume. (Table 1.6) gives approximate equivalents for some of the units used in chemistry.) As shown in Figure 1.10 “The Liter”, a liter is also 1,000 cm^3. By definition, there are 1,000 mL in 1 L, so 1 milliliter and 1 cubic centimeter represent the same volume.

$$1\,\text{mL} = 1\,\text{cm}^3 \tag{1.5.4}$$

diagram of a cubic centimeter

Figure1.5.2**: Volume and the Liter.** A liter is defined as a cube that is 10 cm (1/10th of a meter) on a side. A milliliter, 1/1000th of a liter, is equal to 1 cubic centimeter (1 cm^3).

Energy

Energy, another important quantity in chemistry, is the ability to perform work. Moving a box of books from one side of a room to the other side, for example, requires energy. It has a derived unit of kg·m^2/s^2. (The dot between the kg and m^2 units implies the units are multiplied together and then the whole term is divided by s^2.) Because this combination is cumbersome, this collection of units is redefined as a joule (J), which is the SI unit of energy. Thus, 1 J = 1 kg·m^2/s^2. An older unit of energy, the calorie (cal), is also widely used. There are:

$$4.184\ \text{J} = 1\ \text{cal} \tag{1.5.5}$$

Note that this differs from our common use of the big ‘Calorie’or ‘Cal’ listed on food packages in the United States. The big ‘Cal’ is actually a kilocalorie or kcal (Fig 1.10) Note that all chemical processes or reactions occur with a simultaneous change in energy and that energy can be stored in chemical bonds. We can think of this in terms of our food molecules. The chemical bonds in proteins, carbohydrates, and fats store a large amount of energy that our bodies can harvest and convert into usable forms of energy to power brain function, muscle contraction, and build new bone, muscle, and other tissues. This energy can be calculated with proteins yielding 4 Cal/g (4 kcal/g), carbohydrates yielding 4 Cal/g (4 kcal/g), and fats yielding 9 Cal/g (9 kcal/g).

image of a label on packaged food

Figure1.5.3**: The Difference between kilocalories in Scientific and Common Use**. Calories represented on food packaging actually refer to kilocalories in scientific terms.

Thus, we can calculate the amount of energy that we are receiving from each food source. For example, in the food label presented in Figure 1.10, there is 4.5 g of fat present. We can calculate how many Calories are generated from this fat using our conversion factor of 9 Cal/g for fat.

$$(4.5\ \text{g fat})\left(\frac{9\ \text{Cal}}{1\ \text{g fat}}\right) = 40.5\ \text{Cal} \tag{1.5.6}$$

This matches what the manufacturer indicates on the label (40 Cal coming from fat). Note that the manufacturer is rounding down to the evens in this case. This is the scientific way of rounding and is discussed in more detail below in section 1.5.

Density

Density is defined as the mass of an object divided by its volume; it describes the amount of matter contained in a given amount of space. Density (ρ) is calculated using the following equation:

$$\rho = \frac{m}{V} \tag{1.5.7}$$

where:

table: **ρ** = density, **m** = mass, and **V** = volume

Thus, the units of density are the units of mass divided by the units of volume: g/cm^3 or g/mL (for solids and liquids, respectively), g/L (for gases), kg/m^3, and so forth. For example, the density of water is about 1.00 g/mL, while the density of mercury is 13.6 g/mL. Mercury is over 13 times as dense as water, meaning that it contains over 13 times the amount of matter in the same amount of space. The density of air at room temperature is about 1.3 g/L.

Drop Units

Within a hospital setting, medications are often delivered by intravenous fluids (IV). This means that dosages are often calculated by using the number of drops delivered per mL of solution over time. The abbreviation ***gtt*** is used to denote drop and comes from the Latin word for drop which is *gutta*. The *drop factor (gtt/mL)* can be used to determine drip rates when a prescribed volume of medicine is required over a given time period. Note that drop factors will vary depending on the diameter of the IV tubing that is being used.

$$\left(\frac{\textbf{Volume (mL)}}{\textbf{Time (min)}}\right)\left(\textbf{Drop Factor}\ \left(\frac{\textbf{gtt}}{\textbf{mL}}\right)\right) = \textbf{Flow Rate}\ \left(\frac{\textbf{gtt}}{\textbf{min}}\right) \tag{1.5.8}$$

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1.6: Making Measurements in the Lab

Precision vs. Accuracy

It is important to note the different terminology we use when talking in science. One such set of terminology is precision and accuracy. Although precision and accuracy are often used interchangeably in the non-scientific community, the difference between the terms is extremely important to realize. Precision tells you how close two measurements are to one another, while accuracy tells you how close a measurement is to the known value. A measurement can be precise while not being accurate, or accurate but not precise; the two terms are NOT related. A good analogy can be found in a game of darts (Fig. 1.6.1). A player who always hits the same spot just to the left of the dart board would be precise but not very accurate. However, a dart player who is all over the board but hits the center of the board on average would be accurate but not precise. A good darts player, just like a good scientist, wants to be both precise and accurate.

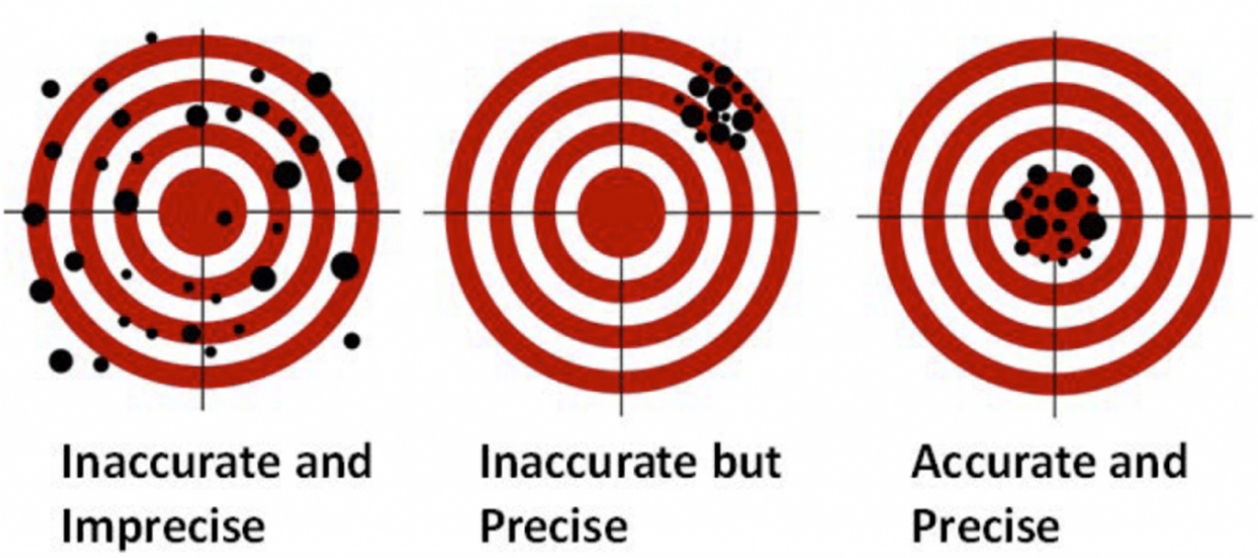


Figure 1.6.1: Difference Between Accuracy and Precision. A game of darts can be used to show the difference between accuracy and precision.

Adapted from: wikipedia

Typically within the laboratory, accuracy is a measure of how well your equipment is calibrated. For example, if your balance is not calibrated correctly, you can make very precise, repeated measurements, but the measurements will not represent the true value. Precision, on the otherhand, is usually determined by how careful the scientist is in making measurements. If you are careless and spill part of your sample on the way, your measurements in repeated experiments will not be precise even if your balance is accurate.

Significant Figures

It is important to realize that values in scientific measurements are never 100% accurate. Our instruments only measure to a certain level of accuracy. Thus, we can pick different instruments to make a measurement based upon the level of accuracy we need for the experiment. Due to the inherent inaccuracy in any measured number we must keep track of the different levels of accuracy each number has with significant figures. Significant figures of a measured quantity are defined as all the digits known with certainty and the first uncertain, or estimated, digit. It makes no sense to report any digits after the first uncertain one, so it is the last digit reported in a measurement. Zeros are used when needed to place the significant figures in their correct

positions. Thus, zeros may or may not be significant figures. Significant figures apply in the real world, as they allow us to quantify the accuracy of any type of measurement. To identify how many numbers in a measurement have significance, you can follow a discreet set of rules, shown below and to the right.

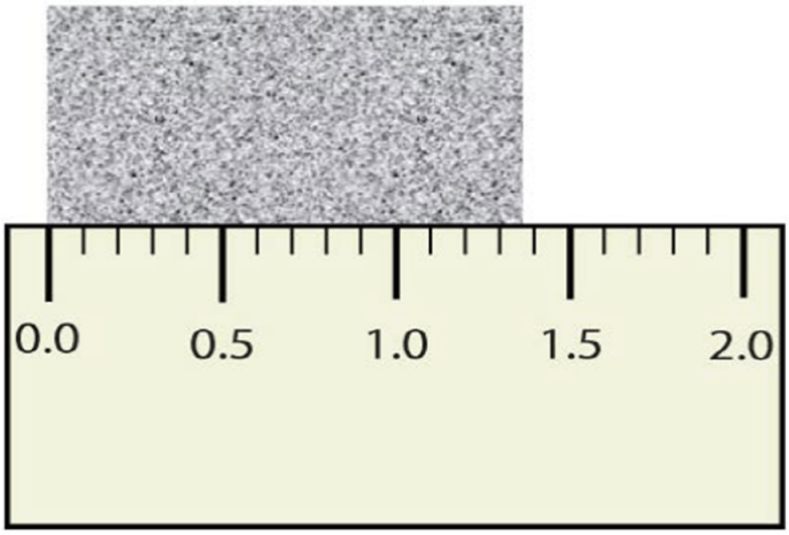


Figure1.6.2**: Measuring an Object to the Correct Number of Significant Figures.** How many digits should be shown in this measurement? The correct answer is 3! The two that you know for sure, plus the estimated position...for this reading it would be close to 1.37

Exact Numbers

Exact numbers are numbers that are not measured by a scientific instrument. They are either used as definitions to define a concept or terminology, or they are made by counting the total of something present. An example of an exact number, would be the number of eggs in a carton or a defined unit such as there are 100 cm in 1 m. Exact numbers, such as the number of people in a room, DO NOT affect the number of significant figures in calculations made with measured values. **Exact number are treated as having infinite number of significant figures in calculations.**

Here is Some Practice Work

Think About This!
1. An oceanographer needs to go out in a boat to collect an important temperature and salinity data logger that is attached to an underwater buoy. How does each of the following situations illustrate the differences between precision and accuracy?
a. The oceanographer check the weather forecast the night before her trip so she knows what to wear on the boat. The TV forecaster says it will be between 26-31 ^{o}C at noon the next day. The actual temperature reading the next day on the boat at noon is 28 ^{o}C

Think About This!
b. When the oceanographer used her Global Positioning System (GPS) to indicate that she is at the location of the underwater buoy, she anchors the boat and jumps in the water to collect the data logger. However, she can't see the buoy. The other GPS units belonging to her colleagues on the boat also indicate that they are at the correct location. After an extensive search, the oceanographer finds the buoy 50 m from the boat.
c. While on the way back to shore, the oceanographer throws in a fishing line to see if she can catch anything for dinner. She is lucky enough to catch a mahi-mahi. When she pulls it out of the water, her colleagues estimate the weight of the fish. Their estimates are 16.1 kg, 16.8 kg, and 15.9 kg. When they weigh the fish upon returning to shore, the actual weight is 18.2 kg
2. Write your own scenario illustrating the difference between accuracy and precision. Swap your scenario with a classmate. Identify your classmate's scenario measurements as accurate or inaccurate and precise or imprecise.
a. A dart player can see how accurate his or her dart throws are by comparing the location of the thrown darts to the target or the bulls-eye of the dart board.
b. How is this model different from scientists who are measuring a natural phenomenon?
c. Is there a way for scientists to determine how accurate their measurements are? Explain your answer.

Rules for Significant Figures:

1. **Trailing zeros at the end of a number but to the left of the decimal point can act as place holders and may or may not be significant**
   - Example: 39,000 may have 2, 3, 4, or 5 significant figures!
   - The researcher that made the measurement must tell you.
   - If there is no indication, you can only use the fewest significant figures, in this case 2.
2. **All non-zero numbers are significant**
   - Example: 171 has 3 significant figures
3. **Trapped zeros between non-zero numbers are significant**
   - Example: 1,007 has 4 significant figures
4. **Leading zeros are not significant**
   - Example: 0.0017 has 2 significant figures, the zeros to the left of the number are insignificant
5. **Trailing zeros are significant after the decimal place**
   - Example: 17.00 has 4 significant figures
6. **When significant figures are in scientific notation all the numbers shown are significant**
   - Example: 1.70×10^7 has 3 significant figures
7. **A decimal place at the end of a whole number indicates that all values to the left are significant**
   - Examples: 100 has 1 significant figure whereas, 100. has 3 significant figures & 100.0 has 4 significant figures.

Rules of Rounding

In scientific operations, the rules of rounding may be a little bit different than the ones you are used to using. Normal rounding

rules suggest that if a number is below 5, it should be rounded down to the lower number, whereas if it is 5 or higher, it should be rounded up. However, note that 5 is right in the middle and causes a problem when using these conventional rounding rules. If you have a large dataset of numbers that you need to round, using this rounding rule will lead to bias in your dataset (i.e. 4/9th of the time you will be rounding down, and 5/9th of the time you will be rounding up). In a large dataset, this bias is unacceptable.

The rules used in this course for rounding numbers are known as 'rounding to the evens', and are implemented as follows:

1. Increase the final digit by one unit if the digit being dropped is greater than 5
2. Leave the final digit unchanged if the digin being dropped is less than 5
3. If the number to be dropped is exactly 5 (with no other numbers following it) then if the preceding number is odd, increase the number by one. If the preceding number is even, it remains the same.

Example 1.6.1

Round 26.65 to three significant figures.

Solution

When you look at the 4^{th} digit, it is a 5 with no numbers following it. So now you must look at the 3^{rd} digit. In this case it is even, so you would round to the even and the final answer would be 26.6

Example 1.6.2

Round 26.652 to three significant figures.

Solution

When you look at the 4^{th} digit, it is a 5 with a number following it. That means that is it greater than 5. In this case both the 5 and the 2 will be dropped and the remaining digit must be increased by one, so you would round the 6 up and the final answer would be 26.7.

Example 1.6.3

Round 26.7500 to three significant figures.

Solution

When you look at the 4^{th} digit, it is a 5 with only zeros following it. This means it is exactly 5. So now you must look at the 3^{rd} digit. In this case it is odd, so you would round up to the even and the final answer would be 26.8

Calculations with Significant Figures

The first thing to realize before performing any calculations in science is that all measured numbers are only as good as the instrument used to measure them. Even with the best instrument available the measured number will never be 100% exact. Scientists use the “good enough” rule of precision, meaning that we accept an inherent amount of imprecision from every measurement we take as long as the final result is close enough to where we want it to be. This concept becomes dangerous when we begin to use these “good enough” numbers for any calculations, if we aren’t careful to keep track of our significant figures our numbers can quickly lose their “good enough” status. To protect their “good enough” numbers, the scientific community has set forth certain rules for performing any calculations; in this section we need only concern ourselves with two very important rules: the Addition/Subtraction rule, and the Multiplication/Division rule.

Addition/Subtraction Rule with an Example:

Rules:

1. Find the number with the least number of decimals and keep track of the number of decimal place
2. Perform the addition/subtraction
3. Round the final answer to the least number of decimals found in Step 1

Example 1.6.4

If you had a beaker weighing 50.27 g and added 2.5 g of calcium carbonate, what would be the total mass of the filled beaker using the correct number of significant figures?

Solution

1. Identify the number with the fewest decimal places: (2.5 g, in this case).
2. Perform the addition: 50.27 g + 2.5 g = 52.77 g
3. Round your answer to the fewest decimal places identified in step 1: 52.8 g

Multiplication/Division Rule with an Example:

Rules:

1. Count the number of significant figures in each number (keep track of the number of significant figures
2. Perform the multiplication/division
3. Round your final answer to the lowest number of significant figures found in step 1

Example 1.6.5

Suppose you were working with 13.76 ml of water mixed with 2.53 ml of cooking oil in a graduated cylinder and your lab instructor asked you to find the ratio of water to oil. What would the final answer be with the correct number of significant figures?

Solution

1. First, recall that ratios represent division (water/oil)
2. Identify the number of significant figures in each measured value:

13.76 ml of water = 4 sig figs

2.53 ml of oil = 3 sig figs

Final answer needs to have 3 significant figures!!

3. Perform the math operation:

(13.76 ml water)/(2.53 ml oil) = 5.4387 water/oil

4. Round the final answer to the correct number of significant figures (ie the lowest identified from the measured values)

5.4387 water/oil = **5.44** water/oil

Calculating Complicated Problems:

1. Using the order of operations, break the problem up into multiple step
2. Perform any addition/subtraction steps following the Addition/Subtraction rule (Do not round yet, just keep track of the correct number of decimals when finding the number of significant figures.)
3. Perform multiplication/division using the Multiplication/Division rule
4. Round the final answer to the correct number of significant figures

---

Conversions and the Importance of Units

The ability to convert from one unit to another is an important skill. For example, a nurse with 50 mg aspirin tablets who must administer 0.2 g of aspirin to a patient, needs to know that 0.2 g equals 200 mg, so that 4 tablets are needed. Fortunately, there is a simple way to convert from one unit to another.

Conversion Factors

If you learned the SI units and prefixes described in Section 1.4 Units of Measurement", then you know that 1 cm is 1/100th of a meter or:

$$100\,\text{cm} = 1\,\text{m} \tag{1.6.1}$$

Suppose we divide both sides of the equation by 1 m (both the number and the unit; Note that it is critically important to always write out your units! This avoids confusion and mistakes when making conversions.):

$$\frac{100\,\text{cm}}{1\,\text{m}} = 1 \tag{1.6.2}$$

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. 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. A fraction that has equivalent quantities in the numerator and the denominator but expressed in different units is called a conversion factor. Note that conversion factors can be written with either term in the numerator or denominator, and used as appropriate for the problem that you want to solve. This is because, both terms are equal to 1.

$$\frac{100\,\text{cm}}{1\,\text{m}} = 1 = \frac{1\,\text{m}}{100\,\text{cm}} \tag{1.6.3}$$

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 100cm/1m and multiply:

$$3.55\ \cancel{\text{m}} \times \frac{100\,\text{cm}}{1\ \cancel{\text{m}}} = 355\,\text{cm} \tag{1.6.4}$$

Because m, the abbreviation for meters, occurs in both the numerator and the denominator of our expression, they cancel out. The final step is to perform the calculation that remains once the units have been canceled. Note that it is CRITICAL to retain the right units in the final answer or it will not make sense. A generalized description of this process is as follows:

$$\text{Quantity (old units)} \times \left(\frac{\text{new units}}{\text{old units}}\right) = \text{Quantity (new units)} \tag{1.6.5}$$

You may be wondering why we use a seemingly complicated procedure for a straightforward conversion. In later studies, the conversion problems you will encounter will not always be so simple. If you can 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 100 cm/1 m as a conversion factor. Does the conversion factor 1 m/100 cm also equal 1? Yes, it does; it has the same quantity in the numerator as in the denominator (except that they are flip-flopped). 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:

$$3.55\,\text{m} \times \frac{1\,\text{m}}{100\,\text{cm}} = \frac{0.0355\,\text{m}^2}{1\,\text{cm}} \tag{1.6.6}$$

INCORRECT USE OF CONVERSION FACTOR!!

You can see that none of the units cancelled out. 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 1.6.3 “A Concept Map for Conversions” shows a concept map for constructing a proper conversion.

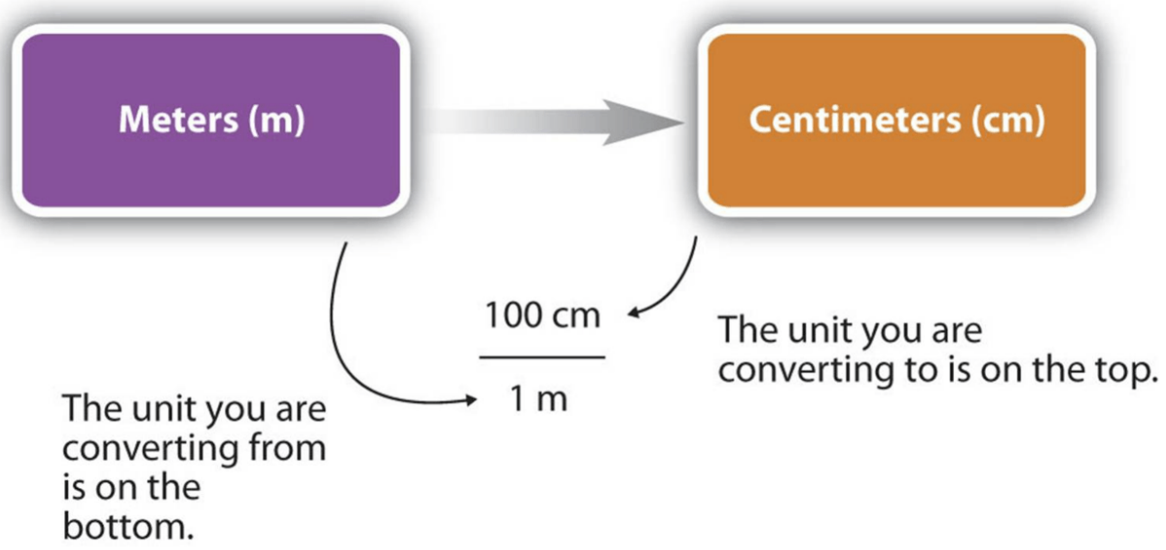


Figure 1.6.3: A Concept Map for Conversions. This is how you construct a conversion factor to convert from one unit to another. The units that you are converting from go on the bottom of your fraction, and the units that you are converting to go on the top of your fraction.

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1.7: Focus on the Environment - Plastics in the Ocean

Plastic Pollution and the World's Ocean

In this section, we present a scientific study published by the Public Library of Science (PLOS) under the Creative Commons License. The original article can be accessed from the PLOS Open Access – Peer Reviewed Online Journal (opens in a new window)

The purpose of presenting this article is to give you experience with science in action. In section 1.2 you learned about the key components of the scientific method and experimental design. Two additional key elements that are critical for scientific studies are ***replicability*** and ***peer review. Replicability*** is defined as the ability of a scientific experiment or trial to be repeated to obtain a consistent result. This is a critical component of a scientific study related to the qualities of precision and accuracy discussed in section 1.6. Peer Review then offers a way for scientists to referee and evaluate the precision and accuracy of scientific studies before they can be published. During ***Scholary Peer Review*** the author's scholarly work, research, or ideas are scrutinized by others who are experts in the same field before a paper describing this work is published within a journal or book.

The typical sections of a scientific article include the ***Abstract*** where the authors summarize the work and their findings, the Introduction where authors describe goal of the research and give background information, the ***Methods*** where authors describe in detail how the research was conducted (note that the methods should be given in enough detail to allow other research groups to repeat the work), The ***Results*** that presents the research data that was collected (usually in the form of figures and tables) and the ***Conclusions or Discussion*** where authors describe the implications of their work in the larger context of science and their field of research. Sometimes when reading research articles it is helpful to read the Abstract, Introduction and Discussion first to acquaint yourself with the purpose of the research and then focus on the Methods and Results to see if the research presented supports the authors conclusions and broader perspectives. Note that some articles also contain supplemental figures that support the article, but are not officially included as part of the article. They can appear with the main article or they may be published at another location and available for download. This article contains supplemental figures at the end of the discussion section. You may follow the provided links to view the supplemental information. In addition, peer reviewed science articles also contain a ***References*** section that provided the location of all source materials that was used to develop the written document.

The research article below focuses on the accumulation of floating plastic debris with the world's oceans. Plastics represent a major pollution problem within our oceans, with the Center for Biological Diversity estimating that plastic floating debris covers approximately 40% of the worlds ocean surfaces. It represents a hazard to birds, fish, sea turtles and marine mammals that mistakenly ingest plastic particles as food or become entangled in plastic debris and drown. Plastics can also release and accumulate toxic substances, such as lead, cadmium, mercury, bisphenol-A, and pthalates, that have been linked with cancer, birth defects, immune system problems, and childhood developmental issues. In the article by Erickson, et al below, researchers are trying to establish a good estimate for how much plastic is currently floating in the ocean.



Figure 1.7.1: **The Effects of Plastic Pollution in the World's Oceans.** *Upper left panel:* Mountain of Plastic. Photo credit: Top News, "Scientists Baffled by Mystery of Missing Ocean Plastic", Jamie Williamson, *Upper right panel:* Location of Plastic Islands in Ocean. Photo credit: Earthly Issues, Charles Welch, *Lower panel:* Bird filled with plastic. Photo courtesy of Simple Green Living, "One Step at a Time"

Homework Assignment: Please download the following CH104 Chapter 1 Environmental Assignment and as you read through the following research article complete the assignment. This is a nice assignment to have a class discussion about the scientific method.

Plastic Pollution in the World's Oceans: More than 5 Trillion Plastic Pieces Weighing over 250,000 Tons Afloat at Sea.

Marcus Eriksen , Laurent C. M. Lebreton, Henry S. Carson, Martin Thiel, Charles J. Moore, Jose C. Borerro, Francois Galgani, Peter G. Ryan, Julia Reisser

Published: December 10, 2014, weblink

Abstract

Plastic pollution is ubiquitous throughout the marine environment, yet estimates of the global abundance and weight of floating plastics have lacked data, particularly from the Southern Hemisphere and remote regions. Here we report an estimate of the total number of plastic particles and their weight floating in the world's oceans from 24 expeditions (2007–2013) across all five sub-tropical gyres, costal Australia, Bay of Bengal and the Mediterranean Sea conducting surface net tows (N = 680) and visual survey transects of large plastic debris (N = 891). Using an oceanographic model of floating debris dispersal calibrated by our data, and correcting for wind-driven vertical mixing, we estimate a minimum of 5.25 trillion particles weighing 268,940 tons. When comparing between four size classes, two microplastic <4.75 mm and meso- and macroplastic >4.75 mm, a tremendous loss of microplastics is observed from the sea surface compared to expected rates of fragmentation, suggesting there are mechanisms at play that remove <4.75 mm plastic particles from the ocean surface.

Introduction

Plastic pollution is globally distributed across all oceans due to its properties of buoyancy and durability, and the sorption of toxicants to plastic while traveling through the environment [1], [2], have led some researchers to claim that synthetic polymers in the ocean should be regarded as hazardous waste [3]. Through photodegradation and other weathering processes, plastics fragment and disperse in the ocean [4], [5], converging in the subtropical gyres [6]–[9]. Generation and accumulation of plastic

pollution also occurs in closed bays, gulfs and seas surrounded by densely populated coastlines and watersheds [10]–[13]

The impact of plastic pollution through ingestion and entanglement of marine fauna, ranging from zooplankton to cetaceans, seabirds and marine reptiles, are well documented [14]. Adsorption of persistent organic pollutants onto plastic and their transfer into the tissues and organs through ingestion [15] is impacting marine megafauna [16] as well as lower trophic-level organisms [17], [18] and their predators [19], [20]. These impacts are further exacerbated by the persistence of floating plastics, ranging from resin pellets to large derelict nets, docks and boats that float across oceans and transport microbial communities [21], algae, invertebrates, and fish [22] to non-native regions [23], providing further rationale to monitor (and take steps to mitigate) the global distribution and abundance of plastic pollution.

Despite oceanographic model predictions of where debris might converge [24] estimates of regional and global abundance and weight of floating plastics have been limited to microplastics <5 mm [19], [25]. Using extensive published and new data, particularly from the Southern Hemisphere subtropical gyres and marine areas adjacent to populated regions [7], [10], [13], [26], corrected for wind-driven vertical mixing [27], we populated an oceanographic model of debris distribution [28] to estimate global distribution and count and weight densities of plastic pollution in all sampled size classes. The oceanographic model assumes that amounts of plastic entering the ocean depend on three principal variables: watershed outfalls, population density and maritime activity. The dataset used in this model is based on expeditions from 2007–2013 (Table S1), surveying all five sub-tropical gyres (North Pacific, North Atlantic, South Pacific, South Atlantic, Indian Ocean) and extensive coastal regions and enclosed seas (Bay of Bengal, Australian coasts and the Mediterranean Sea), and include surface net tows (N = 680) and visual survey transects for large plastic debris (N = 891) totaling 1571 locations in all oceans (Fig 1). We also compared plastic pollution levels between oceans and across four size classes: 0.33–1.00 mm (small microplastics), 1.01–4.75 mm (large microplastics), 4.76–200 mm (mesoplastic), and >200 mm (macroplastic) (Fig. 1).

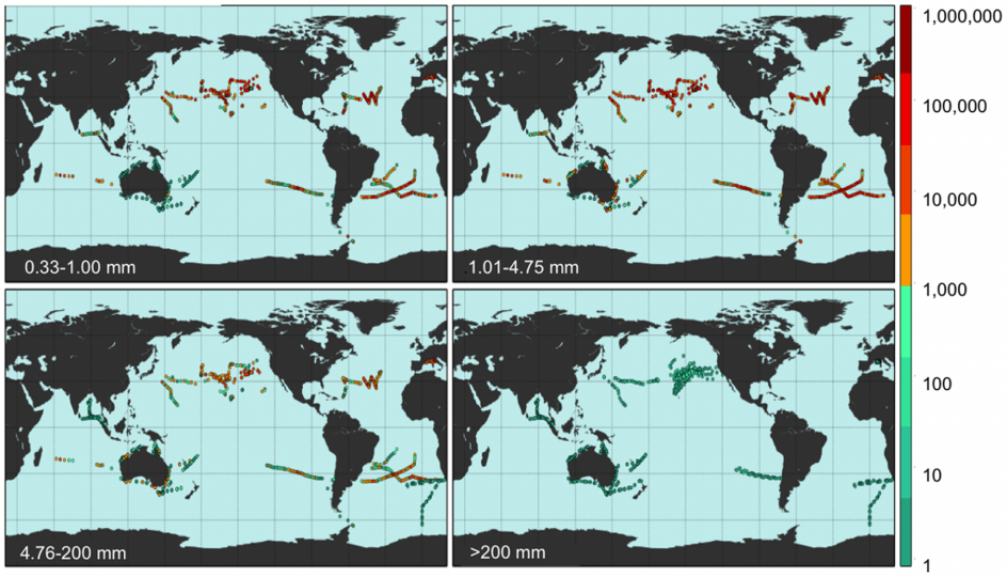


Figure 1.7.2: **Field locations where count density was measured.** Count density (pieces km^{-2}; see colorbar) of marine plastic debris measured at 1571 stations from 680 net tows and 891 visual survey transects for each of four plastic size classes (0.33–1.00 mm, 1.01–4.75 mm, 4.76–200 mm, and >200 mm).

Materials and Methods

Net tow sample collection and analysis

Net tows were conducted using neuston nets with a standard mesh size of 0.33 mm towed between 0.5 and 2 m s^{-1} at the sea surface for 15–60 minutes outside of the vessel's wake to avoid downwelling of debris. Samples were preserved in 5% formalin. Using a dissecting microscope, microplastic was manually separated from natural debris, sorted through stacked Tyler sieves into three size classes [7], [10], [12], then counted individually and weighed together. During sample analysis the identity of smaller microplastics was confirmed with buoyancy and hardness tests. All items were counted and weighed to the nearest 0.01 mg. Using

these data, trawl dimensions and distance traveled, count (pieces km^{-2}) and weight (g km^{-2}) densities were estimated. The slow tow speed and the washing of the net between the tows when needed provided sufficient confidence that any variation in sample collection efficiency due to the net size, difference in tow speed or tow time were negligible.

Visual survey protocol

Visual survey transects of large plastic debris were carried out during expeditions to the South Pacific, North Pacific, South Atlantic, Indian Ocean, and waters around Australia, as well as part of the NOAA Trans-Pacific Marine Debris Survey in the North Pacific. Dedicated observers viewed the ocean surface on one side of the vessel out to 20 meters noting large debris items during timed observation periods [11], [13], [26], with start and stop positions used to calculate the area surveyed. Debris observations were broken into nine categories, four categories for fishing-related debris: buoy, line, net, and other fishing gear, and five categories for other plastics: bucket, bottle, foamed polystyrene, bag/film, or miscelaneous plastics (Table S2). Because observed debris cannot be collected and weighed, similar debris items in similar categories were collected from shorelines in northern-central Chile, South Africa, Atlantic coast of North America and the Hawaiian Archipelago to determine mean weights of items in the nine categories (Table S3). The two categories labeled 'other fishing gear' and 'miscellaneous plastics' were assigned a very conservative weight of 10 g per item. These mean weights were applied to visual survey transects to determine weight densities.

Description of the model

Particle tracking is accomplished in two stages, first a hydrodynamic model describes oceanic circulation and second virtual particles are introduced into the flow field and allowed to move freely through hydrodynamic forcing. For this study, ocean surface currents are extracted from the oceanic circulation modeling system HYCOM/NCODA [29]. The HYCOM model is forced by the US Navy's Operational Global Atmospheric Prediction System (NOGAPS) and includes wind stress, wind speed, heat flux, and precipitation. The model provides systematic archiving of daily ocean circulation on a global scale with output data archived back to mid-2003. While the full HYCOM model contains 32 vertical layers, we only consider velocities in the surface layer as the principal driver of floating particles.

Velocity data extracted from HYCOM are then coupled to the Lagrangian particle-tracking model Pol3DD, which drives the dispersion of floating material. Pol3DD tracks and stores the origin, age, and trajectory information of individual particles [30]. Since wind driven currents are already expressed in the HYCOM hydrodynamic data, no additional wind stress terms were applied to the motion of particles. This model assumes that debris particles are mostly submerged in the water and extra forcing on potentially emerged parts of the debris is neglected.

Model calibration using empirical data from 1571 locations

In this study we determined abundances and mass of microplastics starting at the lowest size of 0.33 mm, which is a commonly used lower limit for pelagic microplastics [31]. The prefixes micro, meso and macro in relation to plastic pollution are poorly defined. Generally accepted microplastic boundaries are based on typical neuston net mesh size (0.33 mm) and an upper boundary of approximately 5.0 mm [31]. We have used 4.75 mm as our upper boundary for microplastic because this is a size for standard sieves used for sample analysis in most of the expeditions contributing data to this manuscript. Mesoplastic has a lower limit of 4.75 mm, and no defined upper limit. In this current study we set the upper boundary of mesoplastic at 200 mm, which represents a typical plastic water bottle, chosen because of its ubiquity in the ocean. Macroplastic has no established lower boundary, though we set it at 200 mm, while the upper boundary is unlimited. There is a clear need for consistent measures in the field [31], and herein we followed a practical approach using commonly employed boundaries and logistic considerations (net and sieve sizes) in order to integrate an extensive dataset that covers the entire global ocean, including areas that have never been sampled before.

Of the 1571 field locations that contributed count data (Fig. 1), a total of 1333 stations also had weight data (Fig. S4). All these data were used to calibrate the numerical model prediction of plastic count and weight density [28]. For the comparison, we fit the model results to measured data by a linear system of equations of the form:

$$\begin{bmatrix} y_1 \\ | \\ y_N \end{bmatrix} = \begin{bmatrix} S_{11} & \cdots & S_{1K} \\ | & & | \\ S_{N1} & \cdots & S_{NK} \end{bmatrix} * \begin{bmatrix} \beta_1 & \cdots & \beta_K \end{bmatrix} + \begin{bmatrix} \varepsilon_1 \\ | \\ \varepsilon_N \end{bmatrix}$$

where y_i is the logarithm of a measured value of plastic count density (pieces km^{-2}) or weight density (g km^{-2}) for each of the N number of samples. K is the number of model output cases with s_{ij} a dimensionless model solution at the location of sample y_i. β_k and ε_N are the computed weighting coefficients and the error terms for a particular dimensionless model solution s_{ij}. This method can be used to fit an arbitrary number of model output cases to any number of measured data points producing a weighting coefficient and error term for each case.

In the model we used a set of three model results (K=3), corresponding to different input scenarios [28]: urban development within watersheds, coastal population and shipping traffic. Values of β and ε are determined for both the concentration distribution (pieces km^{-2}) and the weight distribution (g km^{-2}) of each of the four size classes based on the linear system of equations. To compare the model results directly to the measured data, the weighting coefficient β_k computed above is used to scale the model output for each of the output scenarios.

Adjusting estimated weight and count due to vertical distribution

Wind-driven mixing of the surface layer will drive particles downward, which causes underestimations of plastic in the ocean if relying on surface sampling only. We used a vertical distribution equation from Kukulka et al. [27], relating the ratio of the true number of particles/measured number of particles with the frictional velocity of water ($u_{*w}=[t/r_w]^{1/2}$, where t is the wind stress and r_w is the density of water).

Our data from 680 net tows includes Beaufort Scale sea states, each with a wind speed range. Before using the vertical distribution equation, we transformed these data into wind stress values, by applying the Smith [32] coefficient for sea surface wind stress (N/m^2) as a function of wind speed (m/s). These data were then used in the vertical distribution equation to adjust the total particle count of plastic for each station.

To estimate the increased mass due to vertical distribution, we attributed the same percentage increase in particle count to particle weight.

Estimating expected particle counts based on fragmentation of large particles

We use conservative estimates of fragmentation rates to show that the model results of particle count in each size class differ substantially from our expected particle counts. To estimate fragmentation rates, we assumed that all particles, including the largest ones had a thickness of 0.2 mm. This assumption is conservative, because it is well known that many larger items have a wall thickness substantially larger than this. We assumed smaller particle sizes for the largest size classes, while for the smallest size class (0.33 mm–1.00 mm) we assumed a conservative particle diameter of 0.8 mm – this is substantially larger than most microplastics collected at the sea surface. Thus, our fragmentation estimates are highly conservative because for the macroplastics that generate plastic fragments we consider lower initial mass than commonly found at sea, while for the microplastics in our fragmentation exercise we consider larger particles than typically found at sea. Fragmentation of one macroplastic item (200 mm diameter) into typical mesoplastic fragments (50 mm diameter) would result in 16 particles, fragmentation of one 50 mm diameter mesoplastic item into typical large microplastics (2 mm diameter) results in 625 particles, and fragmentation of one large microplastic item (2 mm diameter) into small microplastics with a diameter of 0.8 mm results in 6.25 particles.

We then used these ratios in a stepwise approach to estimate particle counts in each size class based on the model results of particle count in the next-higher size category. For example, in the North Pacific the modeled data show 0.33×10^{10} particles in the macroplastic size class. Using our estimated fragmentation ratio of 1 : 16 between macro and mesoplastic, we expect 5.33×10^{10} particles in the mesoplastic size class for the entire North Pacific. These fragmentation ratios between size categories are utilized

to estimate the expected particle count for large and small microplastic particles. This stepwise approach is simplistic, because it assumes that the system is close to equilibrium. We recognize that rates of new plastic entering the ocean are unknown, as well as outputs of plastic due to beaching, sinking and mechanisms of degradation, and use these fragmentation estimates as first crude intent to reveal the dynamics of floating plastics in the oceans.

Ethics Statement

During these sampling procedures, no permits were required as we only collected plankton samples, and those samples were collected in international waters.

Results

Based on our model results, we estimate that at least 5.25 trillion plastic particles weighing 268,940 tons are currently floating at sea (Table 1). There was a good correspondence between the model prediction and measured data for particle count and weight (Figs. S1 and S2, Table S4). Our estimates suggest that the two Northern Hemisphere ocean regions contain 55.6% of particles and 56.8% of plastic mass compared to the Southern Hemisphere, with the North Pacific containing 37.9% and 35.8% by particle count and mass, respectively. In the Southern Hemisphere the Indian Ocean appears to have a greater particle count and weight than the South Atlantic and South Pacific oceans combined.

Table 1: Model results for the total particle count and weight of plastic floating in the world's oceans

	Size class	NP	NA	SP	SA	IO	MED	Total
Count	0.33–1.00 mm	68.8	32.4	17.6	10.6	45.5	8.5	183.0
	1.01–4.75 mm	116.0	53.2	26.9	16.7	74.9	14.6	302.0
	4.76–200 mm	13.2	7.3	4.4	2.4	9.2	1.6	38.1
	>200 mm	0.3	0.2	0.1	0.05	0.2	0.04	0.9
	Total	199.0	93.0	49.1	29.7	130.0	24.7	525.0
Weight	0.33–1.00 mm	21.0	10.4	6.5	3.7	14.6	14.1	70.4
	1.01–4.75 mm	100.0	42.1	16.9	11.7	60.1	53.8	285.0
	4.76–200 mm	109.0	45.2	17.8	12.4	64.6	57.6	306.0
	>200 mm	734.0	467.0	169.0	100.0	452.0	106.0	2028.0
	Total	964.0	564.7	210.2	127.8	591.3	231.5	2689.4

Estimated total count ($n \times 10^{10}$ pieces) and weight ($g \times 10^{8}$ g; or $g \times 10^{2}$ tons) of plastic in the North Pacific (NP), North Atlantic (NA), South Pacific (SP), South Atlantic (SA), Indian Ocean (IO), Mediterranean Sea (MED), and the global ocean (Total). Estimates were calculated after correcting for vertical distribution of microplastics [27].

doi:10.1371/journal.pone.0111913.t001

Of the 680 net tows, 70% yielded density estimates of 1000–100,000 pieces km^{-2} and 16% resulted in even higher counts of up to 890,000 pieces km^{-2} found in the Mediterranean. The vast majority of these plastics were small fragments. Although net tow durations varied, the majority of all tows (92.3%) contained plastic, and those locations without plastic were outside the central areas of the subtropical gyres. This pattern is consistent with our model prediction that ocean margins are areas of plastic migration, while subtropical gyres are areas of accumulation. The 891 visual surveys revealed that foamed polystyrene items were the most frequently observed macroplastics (1116 out of 4291 items), while derelict fishing buoys accounted for most (58.3%) of the total macroplastic weight (Table S2). These observations are conservative, recognizing that items with marginal buoyancy, dark color and small size are more difficult to see, especially during challenging environmental conditions (depending on sea state, weather and sun angle).

The data from the four size classes (small microplastics, large microplastics, meso- and macroplastics) were run separately through the model, producing four maps each for count and weight density (Figs. 2 and 3). The mean errors (ε) associated with these predictions can be seen in Table S5. Combining the two microplastic size classes, they account for 92.4% of the global particle count, and when compared to each other, the smallest microplastic category (0.33–1.00 mm) had roughly 40% fewer particles than larger microplastics (1.01–4.75 mm) (Table 1). Most small microplastics were fragments resulting

from the breakdown of larger plastic items; therefore we expected the smallest microplastics to be more abundant than larger microplastics. We observed the opposite in all regions globally except in the S. Pacific where large and small microplastic counts were nearly equal.

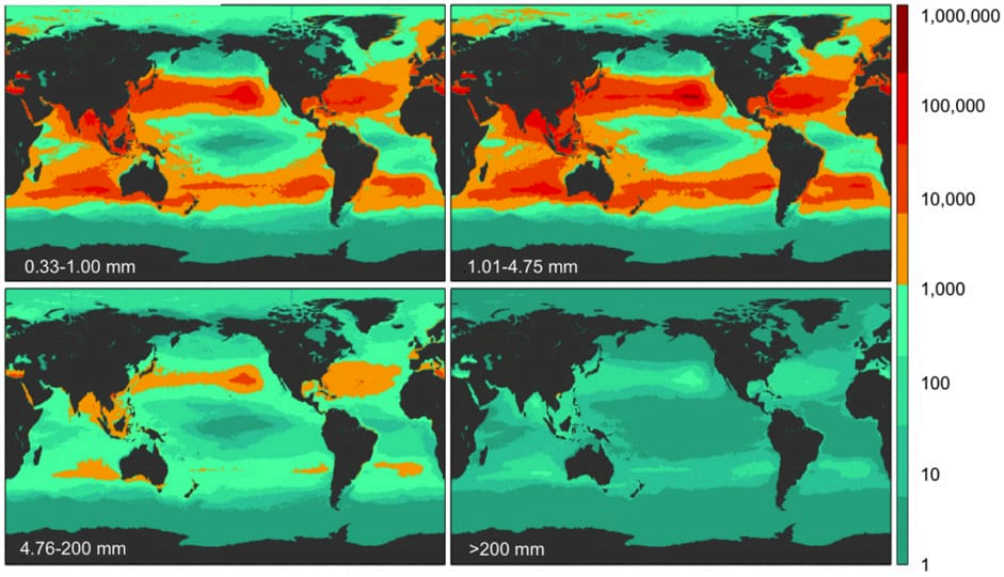


Figure 1.7.3: Model results for global count density in four size classes. Model prediction of global count density (pieces km^{-2}; see colorbar) for each of four size classes (0.33–1.00 mm, 1.01–4.75 mm, 4.76–200 mm, and >200 mm).

The expected numbers of microplastics (large and small) were an order of magnitude larger than the data-calibrated model counts of microplastics in the world's oceans (Fig. S3). The expected numbers were derived from conservative estimates of fragmentation from macroplastic to smaller size classes. In contrast to the apparent dearth of microplastics mesoplastics were observed more frequently than expected by the fragmentation ration. For example, in the North Pacific the modeled data show 0.33×10^{10} particles in the macroplastic size class. Using our estimated fragmentation ratio of 1 : 16 between macro and mesoplastic, we expect 5.33×10^{10} particles in the mesoplastic size class for the entire North Pacific. In this case our modeled data show 13×10^{10} mesoplastic particles, indicating our fragmentation rates underestimated the data-calibrated model results. This discrepancy could be due to lags in the fragmentation of buoyant mesoplastic and macroplastic, or because mesoplastic items, such as water bottles and single-use packaging, enter the ocean in disproportionate numbers when compared to macroplastic. However, the magnitude of the discrepancy between all size classes suggests that there is differential loss of small microplastics from surface waters.

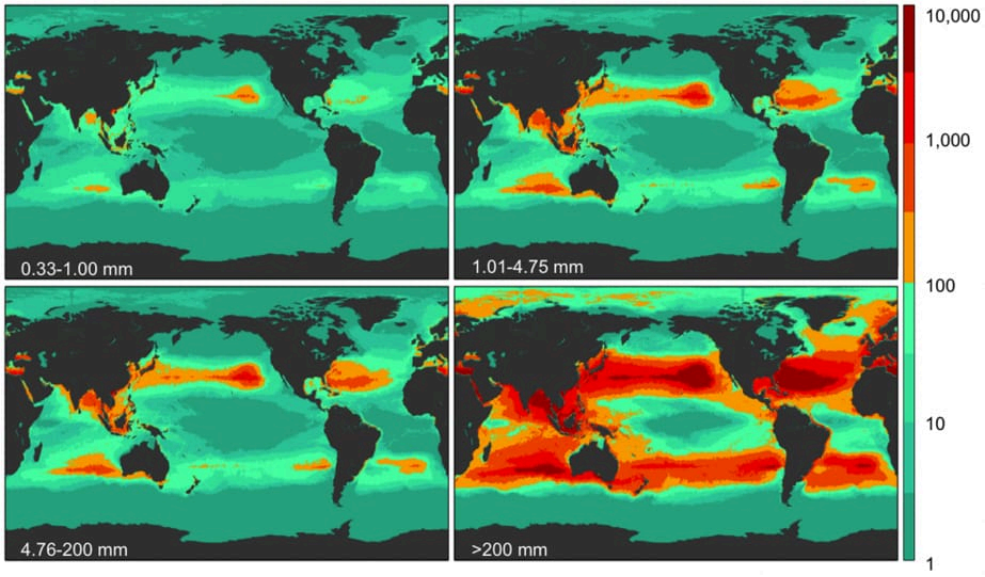


Figure 1.7.3**: Model results for global weight density in four size classes** Model prediction of global weight density (g km^{-2}; see colorbar) for each of four size classes (0.33–1.00 mm, 1.01–4.75 mm, 4.76–200 mm, and >200 mm). The majority of global weight is from the largest size class.

We found a similar pattern of material loss from the sea surface when comparing the weight of the four size classes. The data showed the weight of plastic pollution globally was estimated to comprise 75.4% macroplastic, 11.4% mesoplastic, and 10.6% and 2.6% in the two microplastic size classes, respectively. Our data suggest that a minimum of 233,400 tons of larger plastic items are afloat in the world's oceans compared to 35,540 tons of microplastics.

Discussion

This is the first study that compares all sizes of floating plastic in the world's oceans from the largest items to small microplastics. Plastics of all sizes were found in all ocean regions, converging in accumulation zones in the subtropical gyres, including southern hemisphere gyres where coastal population density is much lower than in the northern hemisphere. While this shows that plastic pollution has spread throughout all the world's oceans, the comparison of size classes and weight relationships suggests that during fragmentation plastics are lost from the sea surface. Simple comparisons across size classes allowed us to suggest possible pathways for oceanic plastics, and below we discuss these pathways and mechanisms involved.

Plastic pollution is moved throughout the world's oceans by the prevailing winds and surface currents. This had been shown for the northern hemisphere where long-term surface transport (years) leads to the accumulation of plastic litter in the center of the ocean basins [6], [7]. Our results confirm similar patterns for all southern hemisphere oceans. Surprisingly, the total amounts of plastics determined for the southern hemisphere oceans are within the same range as for the northern hemisphere oceans (Table 1), which is unexpected given that inputs are substantially higher in the northern than in the southern hemisphere [28]. This could mean that plastic pollution is moved more easily between oceanic gyres and between hemispheres than previously assumed [28], leading to redistribution of plastic items through transport via oceanic currents. Furthermore, there might also be important sources of plastic pollution in the southern hemisphere that had not been accounted for, such as currents from the Bay of Bengal that cross the equator south of Indonesia.

Alternatively, a large proportion of plastics might be lost from the sea surface, more so than considered by previous models, and these losses might be disproportionally higher in the northern hemisphere, leading to similar magnitudes in remaining plastic litter at the sea surface. Indeed, stranding of floating plastics on local seashores seems to be more important in the northern than in the southern hemisphere [28], [33]. Other losses (sinking, degradation) may also be responsible for the fact that northern hemisphere oceans contain relative plastic loads that are lower than expected based on global input scenarios. Herein we applied a correction for vertical distribution to all samples related to wind-driven turbulence [27]. Other hydrodynamic processes including downwelling at convergence zones may also influence the vertical distribution of slightly buoyant particles such as microplastics. We suggest that future sampling campaigns use the spatial distribution of sea surface features to better design their sampling efforts and come up with improved global plastic mass inventories.

Other estimates of global and regional weight of microplastic pollution are within the same order of magnitude as our estimates. A study using an 11-year data set in the North Pacific [9] estimates a weight of 21,290 metric tons of floating microplastic, and ours for the same region is 12,100 metric tons. A recent study on the global distribution of microplastic [25] suggests that the total floating microplastic load ranges between 7,000 and 35,000 metric tons, and ours is 35,500 metric tons. This study [25] also found a 100-fold discrepancy between expected microplastic weight and abundance and their observations, indicating a tremendous loss of microplastics. The similarities between our results and those of this study [25] gives us further confidence in our estimates and support our hypothesis that the ultimate fate of buoyant microplastics is not at the ocean surface.

The observations that there is much less microplastic at the sea surface than might be expected suggests that removal processes are at play. These include UV degradation, biodegradation, ingestion by organisms, decreased buoyancy due to fouling organisms, entrainment in settling detritus, and beaching [4]. Fragmentation rates of already brittle microplastics may be very high, rapidly breaking small microplastics further down into ever smaller particles, making them unavailable for our nets (0.33 mm mesh opening). Many recent studies also demonstrate that many more organisms ingest small plastic particles than previously thought, either directly or indirectly, i.e. via their prey organisms [34]–[36]. Numerous species ingest microplastics, and thereby make it available to higher-level predators or may otherwise contribute to the differential removal of small particles from the sea surface, e.g. by packaging microplastics into fecal pellets [37], thus enhancing sinking. Furthermore, there is increasing evidence that some microbes can biodegrade microplastic particles [38]–[40]. This process becomes more important as plastic particles become smaller since at decreasing particle size the surface area : volume relationship is increased dramatically and oxidation levels are higher, enhancing their biodegradation potential. Thus, bacterial degradation and ingestion of smaller plastic particles by organisms may facilitate their export from the sea surface. In this manner, incorporation of smaller plastics into marine food chains could not only generate impacts on the health of the involved organisms [17]–[20], but also contribute to the removal of small microplastics from the sea surface [37].

Plastics Europe, a trade organization representing plastic producers and manufactures, reported that 288 million tons of plastic were produced worldwide in 2012 [41]. Our estimate of the global weight of plastic pollution on the sea surface, from all size classes combined, is only 0.1% of the world annual production.

However, we stress that our estimates are highly conservative, and may be considered minimum estimates. Our estimates of macroplastic are based on a limited inventory of ocean observations, and would be vastly improved with standardization of methods and more observations. They also do not account for the potentially massive amount of plastic present on shorelines, on the seabed, suspended in the water column, and within organisms. In fact, the larger weight of macroplastic relative to meso- and microplastic, and the global estimate of floating plastic weight relative to the weight of plastic produced annually, indicates that the sea surface is likely not the ultimate sink for plastic pollution. Though significant proportions of meso- and macroplastics may be stranding on coastlines (where some of it could be recovered), removal of microplastics, colonized by biota or mixed with organic debris, becomes economically and ecologically prohibitive, if not completely impractical to recover. This leaves sequestration in sediment the likely resting place for plastic pollution after a myriad of biological impacts along the way, thus reinforcing the need for pre-consumer and post-consumer waste stream solutions to reverse this growing environmental problem.

By generating extensive new data, especially from the Southern Hemisphere, and modeling the plastic load in the world's oceans in separate size classes, we show that there is tremendous loss of microplastics from the sea surface. The question "Where is all the Plastic?" [42] remains unanswered, highlighting the need to investigate the many processes that play a role in the dynamics of macro-, meso- and microplastics in the world's oceans.

Figure S1. **Comparison of mean and modeled densities.** Comparison of data and model predictions for count density (A – pieces km^{-2}) and weight density (B – weight km^{-2}) for four size classes from six ocean regions: North Pacific (NP), North Atlantic (NA), South Pacific (SP), South Atlantic (SA), Indian Ocean (IO), and Mediterranean Sea (MED).

Figure S2. Regression analysis of measured and modeled data. Linear regression of modeled vs. measured values (with correction for vertical distribution) of plastic pollution in terms of count density (A – pieces km^{-2}) and weight density (B – weight km^{-2}) for each of the four size classes.

Figure S3. Comparison of modeled versus expected particle counts ($n \times 10^{10}$ pieces) for the global oceans based on conservative fragmentation estimates. The data-calibrated model results of particle count for the global oceans (see Table 1) in each size class differ substantially from conservative estimates of particle counts based on assumed fragmentation of the number if particles in the next-larger size category. We used simple estimates of particle sizes with 0.2 mm thickness and corresponding diameters, and fragmentation factors of 16 for breakdown of a 200 mm diameter particle into particles of 50 mm diameter, 625 for breakdown of a 50 mm diameter particle into particles of 2 mm diameter, and 6.25 for breakdown of a 2 mm particle into particles of 0.8 mm diameter.

Figure S4. Field locations where weight density was measured. Weight density (g km^{-2}) of marine plastic debris measured at 1333 stations from net tows and survey transects for each of the four size classes (0.33–1.00 mm, 1.01–4.75 mm, 4.76–200 mm, and >200 mm).

Table S1. Expeditions contributing field data. 24 expeditions from 2007–13 contributed data collected at 1571 field locations, with count and weight data in four plastic size classes from six regions: North Pacific (NP), North Atlantic (NA), South Pacific (SP), South Atlantic (SA), Indian Ocean (IO), Mediterranean Sea (MED), and circumnaviating Australia (Au. Cirnav.). Locations marked with an asterisk indicate unpublished data and circles show the type of data collected at each expedition.

Table S2. Percent distribution of items from visual survey transects. 4,291 macroplastic items (>200 mm) in nine categories were observed from all visual survey transects conducted in the North Pacific, South Pacific, South Atlantic, Indian Ocean, and Mediterranean Sea. Mean weights for macroplastic items (Extended Data Table 4) were used to determine percent weight distribution.

Table S3. Using beached macroplastic items to determine mean weight. Mean weight of macroplastic items collected from coastal surveys in Chile (eastern S. Pacific), western South Africa (eastern S. Atlantic), east coast United States (western N. Atlantic), and the Hawaiian Islands, was applied to observed macroplastic items drifting in the ocean and then put through the model to calculate global weight densities. The two categories labeled 'other fishing gear' and 'miscellaneous plastics' were not calculated from weighing items, rather they were assigned a very conservative weight of 10 g.

Table S4. Comparison of measured to modeled means. The measured means of regional count density (pieces km^{-2}) and weight density (g km^{-2}) of plastic in the North Pacific (NP), North Atlantic (NA), South Pacific (SP), South Atlantic (SA), Indian Ocean (IO), Mediterranean Sea (MED), are compared to modeled results. There is generally a good correspondence between the measured and modeled means for each region.

Table S5. Error margins from the linear regression. Average error margin from the linear regression for the count density (pieces km^{-2}) and weight density (g km^{-2}) in the four size classes.

Acknowledgments

We thank the Ocean Research Project for providing microplastic data from the NAG, Diego Miranda and Guillermo Luna-Jorquera for providing the macroplastic data from the SPG, Cat Spina for macroplastic weights from the Hawaiian Islands, and the NOAA Transpacific Marine Debris Survey for macroplastic data from the NPG. The crews and support staff on the expeditions referenced here, specifically the S/V Mir, ORV Alguita, S/V Sea Dragon, and the Stad Amsterdam, were instrumental in sample collection.

Author Contributions

Conceived and designed the experiments: ME LCML HSC MT JCB PGR JR. Performed the experiments: ME LCML HSC MT CJM JCB FG PGR JR. Analyzed the data: ME LCML HSC MT JCB. Contributed reagents/materials/analysis tools: LCML JCB. Wrote the paper: ME LCML HSC MT CJM JCB FG PGR JR. Calculated plastic fragmentation rates: MT. Designed ocean model: LCML JCB. Contributed field data: ME HSC MT CJM FG PGR JR.

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1.8: Chapter Summary

Chemistry is the study of **matter**, which is anything that has mass and takes up space. Chemistry is one branch of **science**, which is the study of the natural universe. Chemistry relies on the **scientific method**, which is the process of learning about the world around us. In the scientific method, a guess or **hypothesis** is tested through experiment and measurement.

Matter can be described in a number of ways. **Physical properties** describe characteristics of a sample that do not change the chemical identity of the material (size, shape, color, density, and so on). Whereas, **chemical properties** describe how a sample of matter changes its chemical composition. A **substance** is any material that has the same physical and chemical properties throughout.

An **element** is a substance that cannot be broken down into chemically simpler components. The smallest identifiable piece of an element is an **atom**. A substance that can be broken down into simpler chemical components is a **compound**. The smallest chemically identifiable piece of a compound is a **molecule**.

Two or more substances combine physically to make a **mixture**. If the mixture is composed of discrete regions that maintain their own identity, the mixture is a **heterogeneous mixture**. If the mixture is so thoroughly mixed that the different components are evenly distributed throughout, it is a **homogeneous mixture**. A special type of homogeneous mixture where the different components cannot be seen by the naked eye is a **solution**.

Substances can also be described by their **phase**: solid, liquid or gas.

Scientists learn about the universe by making measurements of **quantities**, which consist of **numbers** (how many), and **units** (of what). The numerical portion of a quantity can be expressed using **scientific notation**, which is based on powers of ten (exponents). Large numbers have positive powers of ten, while numbers less than one have negative powers of ten.

The **mole** is a counting unit equal to 6.022×10^{23} representative particles, a value known as **Avogadro's number.** Dimensional analysis can be used to convert between moles and representative particles, providing a foundation for later topics in chemistry.

The proper reporting of a measurement requires proper use of **significant figures**, which are all the known digits of a measurement plus the first estimated digit. The number of figures to report in the result of a calculation based on measured quantities depends on the numbers of significant figures in those quantities.

For addition and subtraction, the number of significant figures is determined by position. Whereas, for multiplication and division, the number of significant figures is decided by the least number of significant figures in the original measured values. Nonsignificant digits are dropped from a final answer in accordance with the standard rules of rounding, or rounding to the even when the number to be rounded is exactly five.

Chemistry uses the **International System of Units (SI)** to report numerical findings. This system consists of **seven basic units**. The most important ones for chemistry are the units for mass, length, amount, time, and temperature.

Basic units can be combined with numerical prefixes to change the size of the units. They can also be combined with other units to make **derived units**, which are used to express other quantities such as volume, density or energy.

A formal conversion from one unit to another uses a **conversion factor,** which is constructed from the relationship between the two units. Numbers in a conversion factor may affect the number of significant figures in a calculated quantity, depending on whether the conversion factor is exact. Conversion factors can be applied in separate computations, or several can be used at once in a single, longer computation.

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2: CHAPTER 2 - ATOMS AND THE PERIODIC TABLE

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2.2: Introduction to Elements and the Periodic Table

2.3: Dmitri Medeleev and the Development of the Periodic Table

2.4: Families of the Periodic Table

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2.1: Atomic Theory with Historical Perspectives

The Evolution of Atomic Theory

What are the smallest building blocks of everyday objects? This is a question that has interested man since the age of the Greek philosophers. Like the ancient Greeks we can perform a simple thought experiment that raises a very important question for modern chemistry: suppose you were given a piece of aluminum foil and asked to cut the foil in half over and over. How long could you continue cutting, assuming that you had no limitations based on your own abilities? Is there a limit on how small matter can be broken up into, or could you infinitely divide matter into smaller and smaller pieces? This argument dates as far back as the Greek philosophers. Most, like Aristotle, argued that matter could be divided infinitely. However, one brilliant philosopher, Democritus, argued that there is a limit. He proposed that the smallest piece that any element (like aluminum) can be divided into and still be recognized as that element is an *Atom*, a word derived from the Greek word *atomos,* meaning “indivisible”.

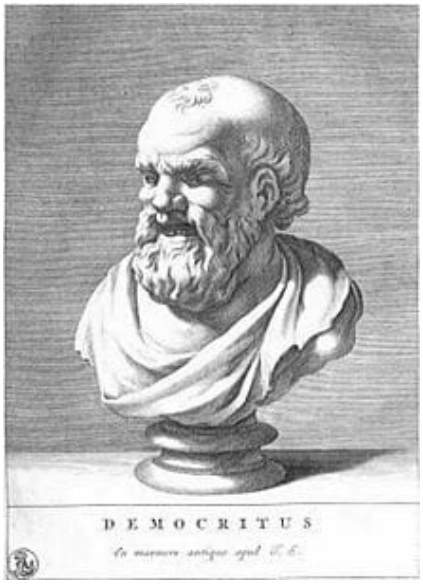


Figure 2.1.1**: Democritus.** Photo taken from: Public Domain

Philosophers, like Democritus, based most of their ideas off of thought experiments like the one above instead of actual observations and experimentation. It is for this reason that Democritus’ ideas on atoms were dismissed until 1808, when John Dalton, an English scientist, proposed four fundamental assumptions based upon observations that we call *Dalton’s Atomic Theory*.

Dalton proposed that:

1. Matter is made up of tiny particles called atoms
2. Atoms cannot be broken into smaller pieces. During a chemical reaction, atoms are rearranged, but they do not break apart, nor are they created or destroyed
3. All atoms of the same element are identical in mass and other properties
4. Atoms of different elements differ in mass and other properties

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2.2: Introduction to Elements and the Periodic Table

Types of Elements

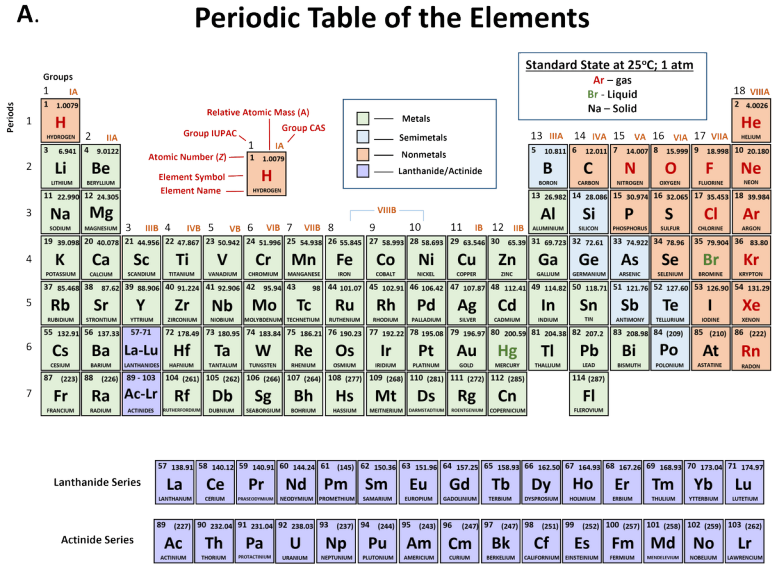
An ***element*** is a substance that cannot be broken down into simpler chemical substances. There are about 90 naturally occurring elements known on Earth. Using technology, scientists have been able to create nearly 30 additional elements that are not readily found in nature. Today, chemistry recognizes a total of 118 elements which are all represented on a standard chart of the elements, called the ***Periodic Table of Elements***. Each element is represented by a one or two letter code, where the first letter is always capitalized and, if a second letter is present, it is written in lowercase. For example, the symbol for Hydrogen is H, and the symbol for carbon is C. Some of the elements have seemingly strange letter codes, such as sodium which is Na. These letter codes are derived from Latin terminology. For example, the symbol for sodium (Na) is derived from the Latin word, natrium, which means sodium carbonate. Elements in the periodic table can be broken up into different general classes based upon similarities in their properties. Going from left to right across the periodic table, the elements can be broken up into ***metals, metalloids, and nonmetals***.

Metals are typically shiny, very dense, and have high melting points. Most metals are ductile (can be drawn out into thin wires), malleable (can be hammered into thin sheets), and good conductors of both heat as well as electricity. All metals are solids at room temperature except for mercury. In chemical reactions, metals easily lose electrons to form positive ions. Examples of metals are silver, gold, and zinc.

Nonmetals are generally brittle, dull, have low melting points, and they are generally poor conductors of heat as well as electricity. In chemical reactions, they tend to gain electrons to form negative ions. Examples of nonmetals are hydrogen, carbon, and nitrogen.

Metalloids have properties of both metals and nonmetals. Metalloids can be shiny or dull. Electricity and heat can travel through metalloids, although not as easily as they can through metals. They are also called ***semimetals***. They are typically semi-conductors, which means that they are elements that conduct electricity better than insulators, but not as well as conductors. They are valuable in the computer chip industry. Examples of metalloids are silicon and boron.

A.



B.

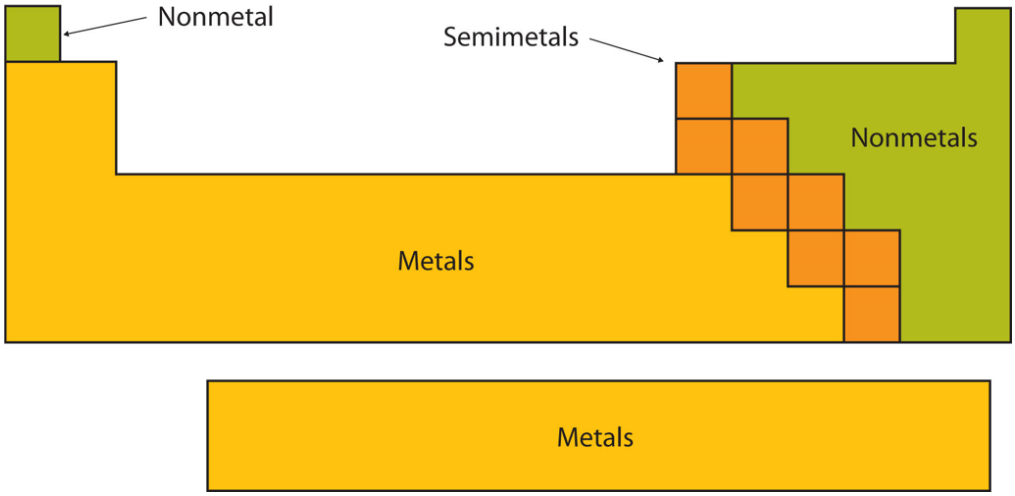


Figure 2.2.1**:Periodic Table of the Elements**. All of the known chemical elements are arranged in the format of a table. The table has been set up in such a way that the characteristics of each different element can be predicted by their position on the table. (A) On this rendition of the periodic table, you can see that the pink elements on the lefthand side of the table are the metals, while the blue elements on the right are the non-metals (Hydrogen is the only exception to this rule and will be explained in the subsequent sections). The metalloids (also termed semi-metals) occur in a stairstep pattern between the metals and nonmetals and are represented in this diagram by the green elements. (B) Shows the positions of the metals, nonmetals and metalloids on the periodic table. During this chapter, you will learn more about these unique characteristics, called *periodic trends*.

Periodic Table Downloadable PDF Version

The elements vary widely in abundance. In the universe as a whole, the most common element is hydrogen (about 90%), followed by helium (most of the remaining 10%). All other elements are present in relatively minuscule amounts, as far as we can detect. On the planet Earth, however, the situation is rather different. Oxygen makes up 46.1% of the mass of Earth's crust (the relatively thin layer of rock forming Earth's surface), mostly in combination with other elements, while silicon makes up 28.5%. Hydrogen, the most abundant element in the universe, makes up only 0.14% of Earth's crust. Table 2.1 lists the relative abundances of elements on Earth as a whole and in Earth's crust. Table 2.2 lists the relative abundances of elements in the human body. If you compare Table 2.1 and 2.2, you will find disparities between the percentage of each element in the human body and on Earth. Oxygen has the highest percentage in both cases, but carbon, the element with the second highest percentage in the body, is relatively rare on Earth and does not even appear as a separate entry in Table 2.1; carbon is part of the 0.174% representing "other" elements. How does the human body concentrate so many apparently rare elements?

The relative amounts of elements in the body have less to do with their abundances on Earth than with their availability in a form we can assimilate. We obtain oxygen from the air we breathe and the water we drink. We also obtain hydrogen from water. On the other hand, although carbon is present in the atmosphere as carbon dioxide, and about 80% of the atmosphere is nitrogen, we obtain those two elements from the food we eat, not the air we breathe.

Table 2.2A: Elemental Composition of the Earth

Earth's Crust		Earth Overall	
Element	Percentage	Element	Percentage
Oxygen	46.1	Iron	34.6
Silicon	28.2	Oxygen	29.5
Aluminum	8.23	Silicon	15.2
Iron	5.53	Magnesium	12.7

Earth's Crust		Earth Overall	
Calcium	4.15	Nickel	2.4
Sodium	2.36	Sulfur	1.9
Magnesium	2.33	All Others	3.7
Potassium	2.09		
Titanium	0.565		
Hydrogen	0.14		
Phosphorous	0.105		
All Others	0.174		

Source: D.R. Lide, ed. CRC Handbook of Chemistry and Physics, 89th ed. (Boca Raton, FL; CRC Press, 2008-9), 14-17.

Table 2.2B Elemental Composition of the Human Body

Human Body		Human Body (Continued)	
Element	Percent by Mass	Element	Percent by Mass
Oxygen	61	Sodium	0.14
Carbon	23	Chlorine	0.12
Hydrogen	10	Magnesium	0.027
Nitrogen	2.6	Silicon	0.026
Calcium	1.4	Iron	0.006
Phosphorous	1.1	Fluorine	0.004
Sulfur	0.20	Zinc	0.003
Potassium	0.20	All Others	0.174

Source: D.R. Lide, ed. CRC Handbook of Chemistry and Physics, 89th ed. (Boca Raton, FL; CRC Press, 2008-9), 7-24.

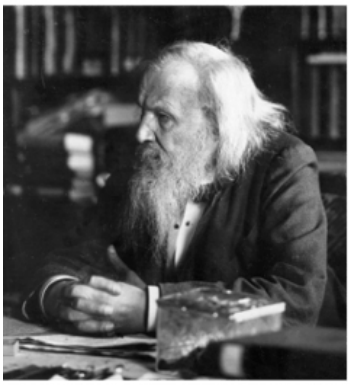
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2.3: Dmitri Medeleev and the Development of the Periodic Table

The First 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. Later, when elements were 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*.


Dmitri Mendeleev

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

Figure 2.3.1: **Dmitri Medeleev's 1871 Early Version of the Periodic Table**

Photo of Dmitri Medeleev provided by: кабинет академика Михаила Михайловича Шульца – фото любезно передано мне в собственность вдовой М.М.Шульца Ниной Дмитриевной Шульц

Periodic Table provided by: Den fjättrade ankan

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2.4: Families of the Periodic Table

Elements that Share Similarities

Remember that Mendeleev arranged the periodic table so that elements with the most similar properties were placed in the same group. A group, or ***family of elements***, is a vertical column of the periodic table. Elements are placed into families due to their similar properties, characteristics, and reactivities. For example, all of the elements in group 1 (except for hydrogen, which has unique properties) are very reactive and form compounds in the same ratios and with similar properties as other 1 elements. Due to the similarities in their chemical properties, Mendeleev put these elements into the same group and they came to be known as the ***alkali metals.*** The ***alkali metals*** include: lithium, sodium, potassium, rubidium, cesium, and francium. Alkali metals are among the most reactive metals. This is due in part to their larger atomic radii and low ionization energies, that will be discussed in more details in section 2.8 below. They get their name from ancient Arabic (al qali) because "scientists" of the time found that the ashes of the vegetation they were burning contained a large amount of sodium and potassium. In Arabic, *al qali* means *ashes*. Although most metals tend to be very hard, alkali metals have a soft texture, are silvery in color and can be easily cut. They also have low boiling and melting points and are less dense than most elements. Figure 2.4.1 shows some of the most common families on the periodic table.

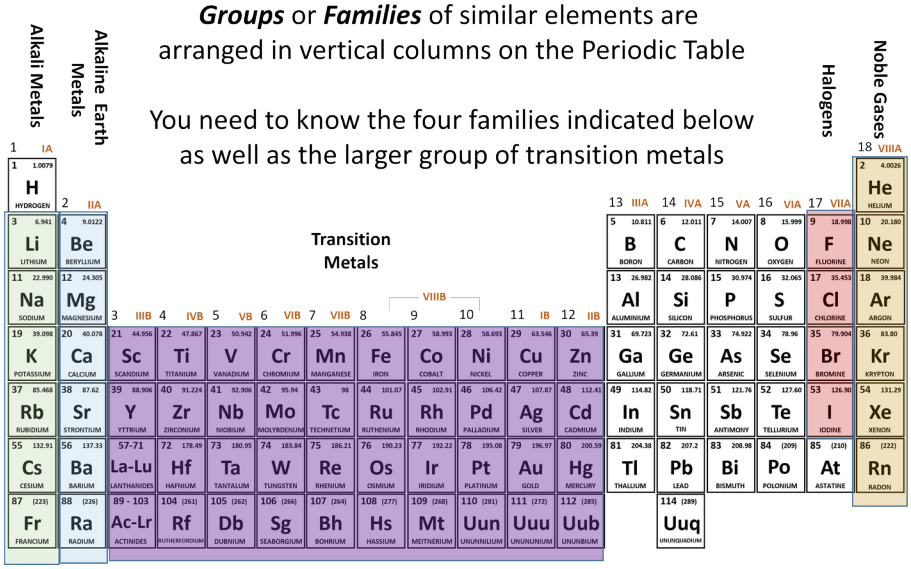


Figure 2.4.1**: Common Families and Groups of the Periodic Table.**

The same pattern is true of other vertical groups on the periodic table. Group 2 is called the ***alkaline earth metals***. Once again these elements have similar properties to each other. ***Alkaline earth metals*** include Beryllium, Magnesium, Calcium, Barium, Strontium and Radium and are soft, silver metals that are less metallic in character than the Group 1 alkali metals. Although many characteristics are common throughout the group, the heavier metals such as Ca, Sr, Ba, and Ra are almost as reactive as the Group 1 alkali metals. They get their name because early "scientists" found that all of the alkaline earth metals were found in the earth's crust.

The ***transition metals*** are the larger block of elements shown in purple on Figure 2.4 extending from Groups 3-12 (also known as the group B elements). Transition elements differ from the main group elements (group A elements) in that they tend to be hard and have high densities. They have high melting points and boiling points and can show various oxidation states when forming chemical bonds (this will be discussed further in chapter 3). They often form colored compounds that are highly stable and they can serve as good *catalysts*. A *catalyst* is an agent that helps to speed up a chemical reaction without itself being changed in the process.

Group 17 elements are also called ***halogens***. This group contains very reactive nonmetals. The ***halogens*** are an interesting group. Halogens are members of Group 17, which is also referred to as 7A. It is the only group in the Periodic Table that contains all of the states of matter at room temperature. Fluorine, F_2 and chlorine, Cl_2 are gases, while Bromine, Br_2, is a liquid and iodine, I_2, and astatine, At, are both solids. Another interesting feature about Group 17 is that it houses four (4) of the seven (7) ***diatomic elements. Diatomic elements*** only exist in nature as a pair of atoms of the same element that are bonded together. The seven diatomic elements are H_2, N_2, O_2, F_2, Cl_2, Br_2, and I_2. Notice that the latter four are Group 17 elements. The word halogen comes from the Greek meaning ***salt forming.*** French chemists discovered that the majority of halogen ions will form salts when combined with metals.

The ***noble gases*** are in group 18. The two most significant properties of noble gases is that they are extremely unreactive, rarely forming compounds, and that they all exist as gases at room temperature. We will learn the reason for their unreactivity when we discuss how compounds form in chapters 3 and 4. The first person to isolate a noble gas was Henry Cavendish, who isolated argon in the late 1700s. The noble gases were actually considered inert gases until the 1960s when a compound was formed between xenon and fluorine which changed the way chemists viewed the “inert” gases. In the English language, inert means to be lifeless or motionless; in the chemical world, inert means *does not react*. Later, the name “noble gas” replaced “inert gas” for the name of Group 18. The elements in this group are also gases at room temperature.

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2.5: Defining the Atom

Basic Atomic Structure – electrons, neutrons, and protons

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

Most elements in their pure form exist as individual atoms. For example, a macroscopic chunk of iron metal is composed, microscopically, of individual iron 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).

Atoms are made up of extremely small subatomic particles called protons, neutrons, and electrons. *Protons* are positively charged particles with a relative mass of 1.672622×10^{-24}g, which form part of the core *nucleus* of an atom. The other part of the atomic nucleus is made up of *neutrons*, electrically neutral particles with a relative mass almost identical to a proton (1.674927×10^{-24}g). *Electrons* are extremely small (9.109328×10^{-28}g) negatively charged particles that form an electron cloud, which orbits the nucleus.Table 2.5A summarizes some of the general properties of subatomic particles.

Table 2.5A: Properties of Subatomic Particles

Particle	Symbol	Mass (kg)	Relative Mass (Proton = 1)	Relative Charge
Proton	p^+	1.673×10^{-27}	1	+1
Neutron	n^0	1.675×10^{-27}	1	0
Electron	e^-	9.109×10^{-31}	0.00055	-1

Experiment have shown that protons and neutrons are concentrated in a central region of each atom called the nucleus (plural, nuclei). Electrons are outside the nucleus and orbit about it because they are attracted to the positive charge in the nucleus. Figures 2.5.1 and 2.5.2 depict the structure of an atom.

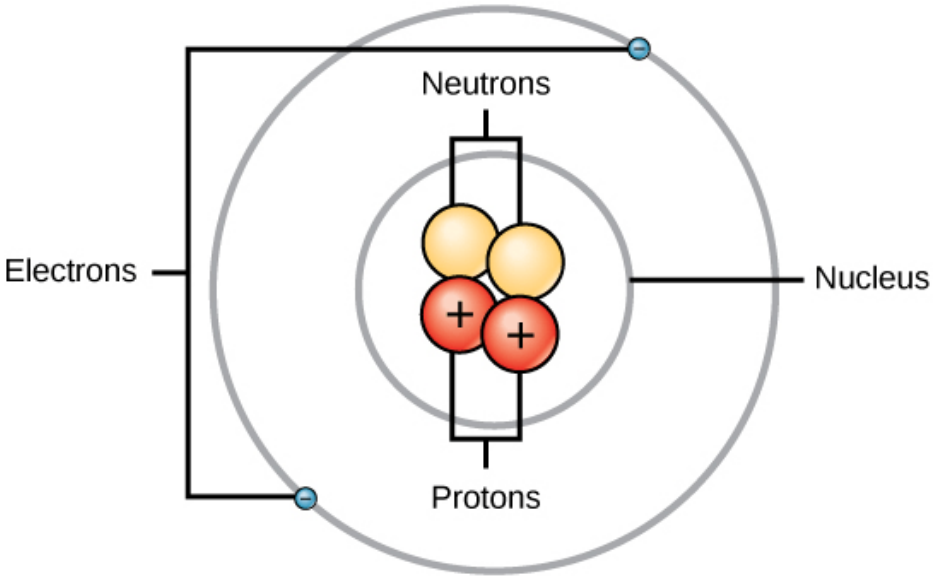


Figure 2.5.1: The Anatomy of an Atom. The protons and neutrons of an atom are found clustered at the center of the atom in a structure called the nucleus. The electrons orbit the nucleus of the atom within an electron cloud, or the empty space that surrounds the atom's nucleus. Note that most of the area of an atom is taken up by the empty space of the electron cloud.

Diagram provided by: CNX OpenStax

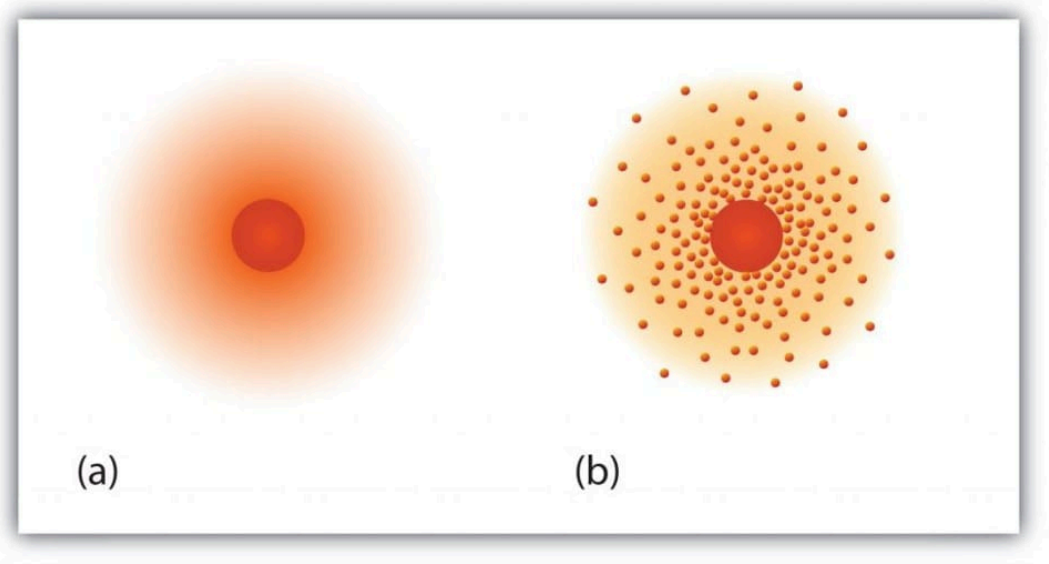


Figure 2.5.2: The path of the electron in a hydrogen atom. Electrons are not in discrete orbits like planets around the sun. Instead there is a probability that an electron may occupy a certain space within the electron cloud (a) The darker the color, the higher the probability that the hydrogen's one electron will be at that point at any given time. (b) Similarly, the more crowded the dots, the higher the probability that hydrogen's one electron will be at that point. In both diagrams, the nucleus is in the center of the diagram.

Most of the mass of an atom is in the nucleus, while the orbiting electrons account for an atom's size. As a result, an atom consists largely of empty space. Atomic particles are so small that it is impractical to measure them in grams, instead we use a relative mass scale which makes the numbers much more manageable. We use *Atomic Mass Units (AMU or u)* to measure the mass of atomic particles, one AMU is equal to 1/12th the mass of an atom of carbon-12. You may also see Atomic Mass Units referred

to as *Daltons (Da)* after John Dalton, the English Chemist that first proposed the atomic theory. Carbon-12 has 6 protons and 6 neutrons in its nucleus, meaning that one amu is equal to the average of the masses of a proton and a neutron. The mass of an atom in AMUs is equal to the number of protons and neutrons making up the atom. For example the atomic mass of bromine is roughly 80 amu and its proton number is 35, meaning that bromine has 35 protons and 45 neutrons in its nucleus.

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2.6: Atomic Number - Protons Determine the Identity of an Atom

Finding the Atomic Number

When looking at the periodic table you might notice that for each element there are two sets of numbers around the symbol. These symbols correspond to important values that give you important information about each element (Figure 2.6.1). The most important value corresponding to characteristics of an element is the proton number, which is also called ***atomic number*** (represented by the mathematical term, *Z*). As it turns out, the number of protons that an atom holds in its nucleus is the key determining feature for its chemical properties. In short, an element is defined by the number of protons found in its nucleus. If you refer back to the Periodic Table of Elements shown in figure 2.2.1, you will see that the periodic table is organized by the number of protons that an element contains. Thus, as you read across each row of the Periodic Table (left to right), each element increases by one proton (or one Atomic Number, *Z*). When atoms are in their elemental states, their overall charge is zero and the atoms are neutral. Since protons are positively charged and electrons are negatively charged, this means that when atoms are in their elemental form, the number of protons equals the number of electrons. Therefore, if you know the atomic number of an atom, you also know how many electrons are present in that atom when it is in its elemental form. When atoms combine with one another to form compounds, like water (H_2O), they will either share or donate/accept electrons from their bonding partners. It is this movement of electrons that facilitates chemical bond formation. Thus, during bond formation the number of electrons around an atom may change, but the atomic number (or number of protons) remains constant and does not change.

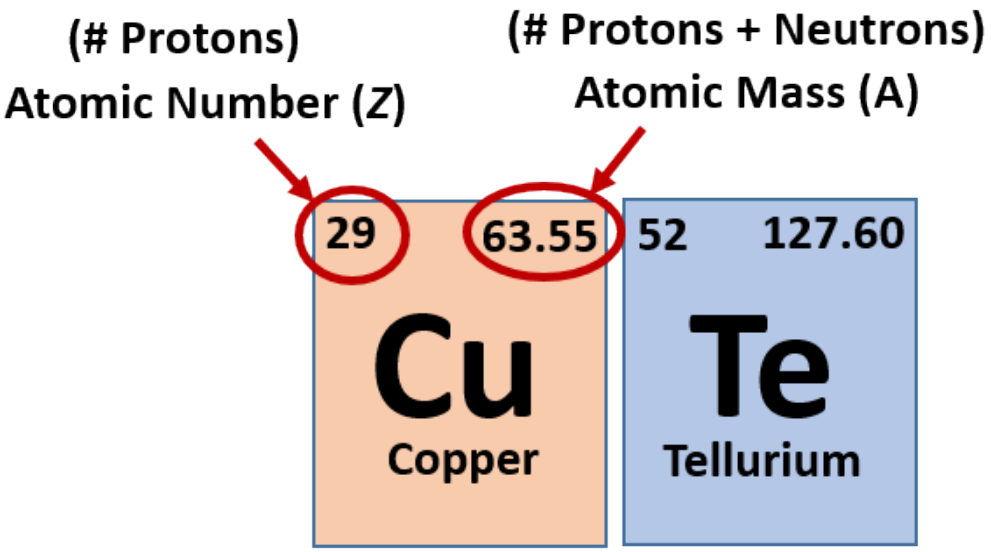


Figure 2.6.1**: Structure of the Periodic Table.** Each element on the periodic table is represented by the atomic symbol (Cu for Copper, and Te for Tellurium). Sometimes the Atomic Number is written in the upper lefthand corner, and the Atomic Mass in the righthand corner, as shown in this figure. Sometimes, periodic tables will show the atomic number above the element symbol and the atomic mass below the element symbol, as shown in the periodic table.

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2.7: Atomic Mass, Isotopes, and Allotropes

Properties of Atoms

Atomic mass (A) is the total mass of an atom of a specific element and can be calculated by adding up the number of protons and neutrons present within an atom. The electrons are ignored in the mass calculation because they are so small that they barely add any mass to the atom.

$$\text{Mass Number} = \#\,\text{Protons} + \#\,\text{Neutrons} \tag{2.7.1}$$

Thus, if you know any two of the the three values (atomic mass, atomic number, or number of neutrons), you can calculate the third value. For example, nitrogen has an atomic mass of 14.007 and an atomic number of 7. Thus, it contains 7 protons, and 7 neutrons (14.007 – 7 = 7.007, which is then rounded to 7). Note that the number of neutrons in an atom does not have to equal the number of protons in the atom. For example, lead (Pb), contains 82 protons and has an atomic mass of 207.2. Thus it contains 125 neutrons (207.2 – 82 = 125). Thus, if you know the atomic mass and the atomic number of an element, you can calculate the number of neutrons present, or if you know the atomic mass and the number of neutrons, you can calculate the atomic number.

So...how many neutrons are in atoms of a particular element? At first it was thought that the number of neutrons in a nucleus was also defining characteristic of an element. However, it was found that atoms of the same element can have different numbers of neutrons. Atoms of the same element that have different numbers of neutrons are called ***isotopes***. An example of the three common isotopes of hydrogen are shown in Figure 2.8. Note that each of the hydrogen isotopes is known by a unique name, hydrogen, deuterium, and tritium. Not all elemental isotopes have such unique names. Many of the isotopes are distinguished from one another by including the atomic mass in the definition. For example, 99% of the carbon atoms on Earth have 6 neutrons and 6 protons in their nuclei, this is known as carbon-12; just under 1% of the carbon atoms have 7 neutrons and 6 protons in their nuclei, which is known as carbon-13, and an even smaller percent is carbon with 8 neutrons and 6 protons, or carbon-14. Carbon-14 is unstable and will decay over time making it a radioactive form of carbon. The half-life of carbon, or the time it takes for half of the isotope to breakdown is 5,700 years. Overall, there are 15 known isotopes of carbon! Thus, naturally occurring carbon on Earth, therefore, is actually a mixture of isotopes, albeit a mixture that is 99% carbon-12. Isotope composition has proven to be a useful method for dating many rock layers and fossils.

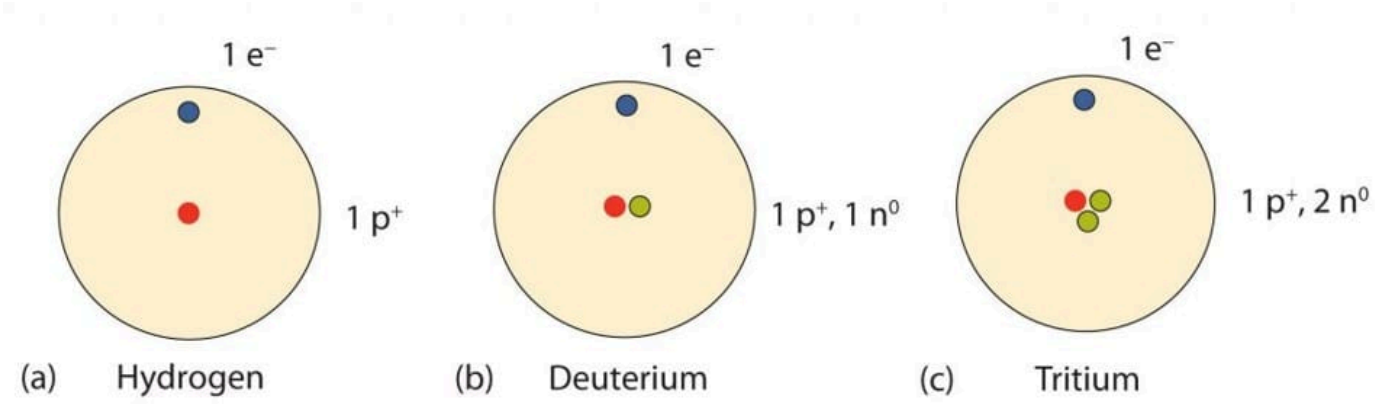
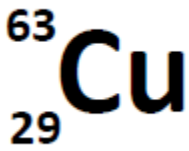


Figure 2.7.1**: Isotopes of Hydrogen.** All hydrogen atoms have one proton and one electron. However, they can differ in the number of neutrons. (a) Most hydrogen atoms only contain one proton and one electron and no neutrons (b) A small amount of hydrogen exists as the isotope deuterium, which has one proton and one neutron in its nucleus, and (c) an even smaller amount contains one proton and two neutrons in its nucleus and is termed Tritium. Note that Tritium is unstable isotope and will breakdown over time. Thus, Tritium is a radioactive element.

Most elements exist as mixtures of isotopes. In fact, there are currently over 3,500 isotopes known for all the elements. When scientists discuss individual isotopes, they need an efficient way to specify the number of neutrons in any particular nucleus. A

simple way of indicating the mass number of a particular isotope is to list it as a superscript on the left side of an element's symbol. Atomic numbers are often listed as a subscript on the left side of an element's symbol. Thus, we might see



which indicates a particular isotope of copper. The 29 is the atomic number, *Z*, (which is the same for all copper atoms), while the 63 is the atomic mass (A) of the isotope. To determine the number of neutrons in this isotope, we subtract 29 from 63: 63 – 29 = 34, so there are 34 neutrons in this atom.

The atomic masses indicated on the periodic table represents an average mass for each element based on the proportion of each isotope present on the Earth. This is why most of the atomic masses on the periodic table are not exact numbers. For example, the atomic mass of copper is 63.546 amu. This mass is an average of an element's atomic masses, weighted by the natural abundance of each isotope. So how could we calculate atomic mass based on the natural abundance of different isotopes of an element?

Example: Calculating Atomic Mass Using Isotope Abundance

Copper has two stable isotopes: ^{63}Cu (A = 62.93 Da) and ^{65}Cu (A = 64.93 Da). On Earth, the abundance of ^{63}Cu is 69.15%, whereas the abundance of ^{65}Cu is 30.85%. From this data, we can calculate the average atomic mass for Cu. Note that the atomic mass values on the periodic table represent the average relative abundance of the isotopes found on Earth.

$$(62.93\,\text{Da})\left(\frac{69.15}{100}\right)+(64.93\,\text{Da})\left(\frac{30.85}{100}\right)=63.55\,\text{Da} \tag{2.7.2}$$

Exercise 2.7.1

Try to work out the atomic mass for boron. Boron exists as a mixture that is 19.9% ^{10}B and 80.1% ^{11}B. Calculate the atomic mass.

Answer available at the end of this section.

Allotropes of an element are different and separate from the term isotope and should not be confused. Some chemical elements can form more than one type of structural lattice, these different structural lattices are known as allotropes. This is the case for phosphorus as shown in Figure 2.9. White or yellow phosphorus forms when four phosphorus atoms align in a tetrahedral conformation (Fig 2.9). The other crystal lattices of phosphorus are more complex and can be formed by exposing phosphorus to different temperatures and pressures. For example, the cage-like lattice of red phosphorus can be formed by heating white phosphorus over 280^{o}C (Fig 2.9). Note that allotropic changes affect how the atoms of the element interact with one another to form a 3-dimensional structure. They do not alter the sample with regard to the atomic isotope forms that are present, and DO NOT alter or affect the atomic mass (A) of the element.

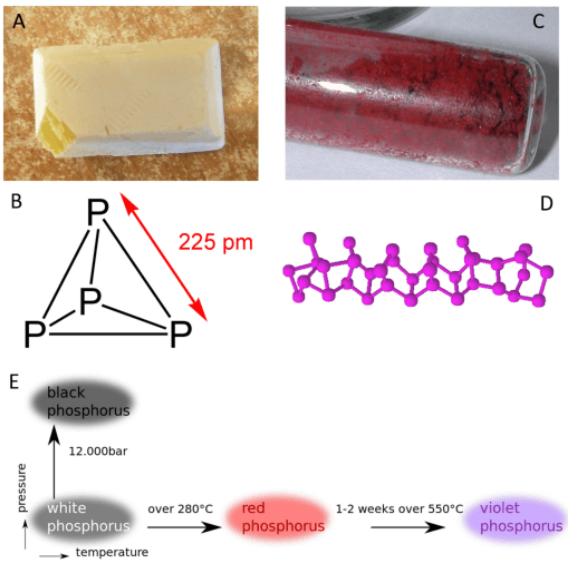


Figure 2.7.2**: Allotropes of Phosphorus.** (A) White phosphorus exists as a (B) tetrahedral form of phosphorus, whereas (C) red phosphorus has a more (D) cage-like crystal lattice. (E) The different elemental forms of phosphorus can be created by treating samples of white phosphorus with increasing temperature and pressure.

Source: Wikipedia: Allotropes of Phosphorous [en.wikipedia.org]

Different allotropes of different elements can have different physical and chemical properties and are thus, still important to consider. For example, oxygen has two different allotropes with the dominant allotrope being the diatomic form of oxygen, O_2. However, oxygen can also exist as O_3, ozone. In the lower atmosphere, ozone is produced as a by-product in automobile exhaust, and other industrial processes where it contributes to pollution. It has a very pungent smell and is a very powerful oxidant. It can cause damage to mucous membranes and respiratory tissues in animals. Exposure to ozone has been linked to premature death, asthma, bronchitis, heart attacks and other cardiopulmonary diseases. In the upper atmosphere, it is created by natural electrical discharges and exists at very low concentrations. The presence of ozone in the upper atmosphere is critically important as it intercepts very damaging ultraviolet radiation from the sun, preventing it from reaching the Earth's surface. Thus, ozone can be a health hazard or a health protector, depending upon where it is found!

Answers

Exercise 2.7.1

Check the Periodic Table for the correct answer!

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2.8: Electronic Structure of Atoms

Quantum Mechanics

Although we have discussed the general arrangement of subatomic particles in atoms, we have said little about how electrons occupy the space about the nucleus. Do they move around the nucleus at random, or do they exist in some ordered arrangement?

The modern theory of electron behavior is predicted by the field of ***quantum mechanics.*** The term ***quantum*** is defined as a discrete quantity or 'packet' of energy. For example, light has qualities of both a wave and a particle. Since it has properties of a particle, the energy of light is said to be quantized into discrete 'packets' of light particles called ***photons.*** Each photon of light, then carries a quantized amount of energy that is dependent on its frequency.

Electrons in atoms are also quantized and can exist at different energy levels depending on how far away from the nucleus of that atom that they are positioned. This is of interest, because the electrons are the mobile part of the atom and they are involved in forming chemical bonds. Understanding their positioning around the nucleus of the atom helps to predict how they will combine with other atoms to form chemical compounds. Electrons typically have higher energy, the farther away they are (on average) from the nucleus. However, the increasing energy of an electron *does not* proceed continuously like a ramp the farther away from the nucleus that it travels. Instead, the energy of an electron is quantized, meaning that the energy of an electron does not increase continuously, but instead increases by levels adding discrete packets of energy. This would be similar to walking up a staircase rather than a ramp. On a staircase, you can step up one step at a time, or maybe two steps at a time, but you can never step up a half of a step. Similarly, electrons travel between energy levels instantly, never having an energy amount in between two levels.

A total of four quantum numbers are used to describe completely the movement and trajectories of each electron within an atom. According to the ***Pauli Exclusion Principle,*** no two electrons can share the same combination of four quantum numbers. Thus, each electron in an atom has a unique set of quantum numbers that helps define the probable location of an electron within an atom. The quantum numbers that help to define electron location exist in a hierarchical order. This would be very similar to finding an address of a friend. If you don't know your friend very well, you may only know the city where your friend lives. This doesn't provide very much information. As you get to know them better, you may find out what neighborhood in the city that they live in. At a deeper level, you may find our what street they live on, and then at the deepest level, what their house number is on that street. However, knowing which house your friend lives in does not tell you where in the house you friend is at, maybe they are in the kitchen or the backyard. Determining the exact location of an electron is not possible. We can only find the approximate location or "address" of the electron.

The Four Electronic Quantum Numbers

There are a total of four quantum numbers: the principal quantum number (n), the orbital angular momentum quantum number (l), the magnetic quantum number (m_l), and the electron spin quantum number (m_s) that are used to describe the major characteristics and spatial distribution of electrons within an atom. The quantum numbers correspond to the following hierarchical layers: the principle quantum number (n) is the broadest classification and corresponds to the energy shell (this would be equivalent to the city in our address analogy), the orbital angular momentum quantum number (l) is the next layer and corresponds to the subshells (this would be the neighborhood in our address analogy), the magnetic quantum number (m_l) corresponds to the electron orbitals (or the street where your friend lives), and electron spin quantum number (m_s) defines the spins of electrons (or the house number in our address analogy).

$$\begin{aligned} n &= \text{Shell} \\ l &= \text{Subshell} \\ m_l &= \text{Orbital} \\ m_s &= \text{Electron Spin} \end{aligned} \tag{2.8.1}$$

The principal quantum number, n, designates the electron shell. Because n describes the most probable distance of the electrons from the nucleus, the larger the number n is, the farther the electron is from the nucleus and the larger the atom. The principal quantum number (n) can be any positive integer between 1 and 7. An n=1 designates the first principal shell (the innermost shell). The first principal shell is also called the ground state, or lowest energy state. When an electron is in an excited state or

gains energy, it may jump to the second principle shell, where n=2. This process is called ***absorption*** because the electron is "absorbing" photons, or gaining energy. Thus, as the energy of the electron increases during absorption, so does the principal quantum number, e.g., if an electron in the $n = 3$ shell absorbs energy, it will jump to the fourth principal shell, $n = 4$. The opposite process is ***emission***, where electrons "emit" or release energy as they fall from higher to lower principle shells. In this case, n decreases by whole numbers (packets or quanta of energy). Within atoms there is a maximum number of seven electron shells ($n = 7$), after which the atom becomes too unstable to hold electrons in place.

At a basic level, the energy shells can be thought of like the layering of an onion, with the first layer being the smallest and closest to the core of the nucleus, and the subsequent layers being larger and farther away from the core. Larger shells have more space and can hold more electrons. The general formula for determining how many electrons can be housed in each shell is $2n^2$ and is shown in Table 2.4. While this table predicts that that outer shells, which are the largest shells can contain 50, 72, and 98 electrons, elements that have this many electrons in those shells have never been discovered. It is likely that they are too big and unstable to exist.

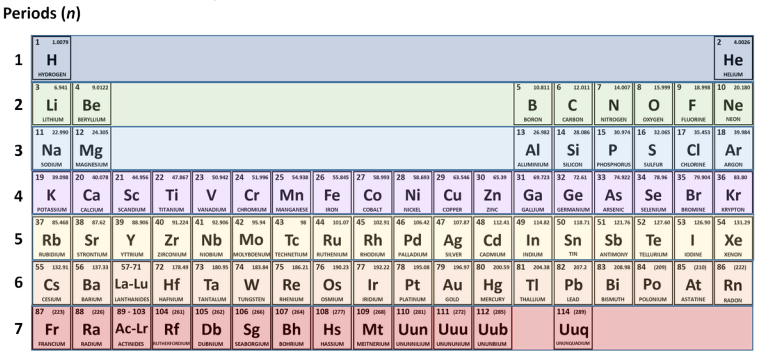
Table 2.8A: Maximum Number of Electrons Per Shell

Electron Shell (*n*)	1	2	3	4	5	6	7
Maximum # Electrons	2	8	18	32	50	72	98

The periodic table allows us to easily determine how many protons (and therefore electrons) an element will have by showing the atomic number (Z) in each element box. Equally useful, the periodic table is set up to represent the different quantum numbers to facilitate the determination of electron configuration of an element. The principle quantum number (n) or number of shells present in an element are shown in the periods or rows of the periodic table (Figure 2.8.1). For example, if we look at the sodium atom, we will see that it is in row 3 of the periodic table. This means that it has three electron shells that can house electrons. As electrons fill their available orbital spaces, they always fill the shells starting at the lowest energy levels and going up to higher levels as needed. This rule can be formally noted as the ***Aufbau principle*** which states that electrons orbiting one or more atoms will fill the lowest available energy levels before filling higher energy levels.

A

The ***Periods*** or horizontal rows on the Periodic Table correspond to the maximum shell or principle quantum number (n) present within an atom in that row



For Example, ***Period 3 elements*** all have three electron shells whereas, ***Period 5 elements*** all have five electron shells
Notice that the Lanthanide and Actinide Series are included in ***Periods 6 and 7***

B.

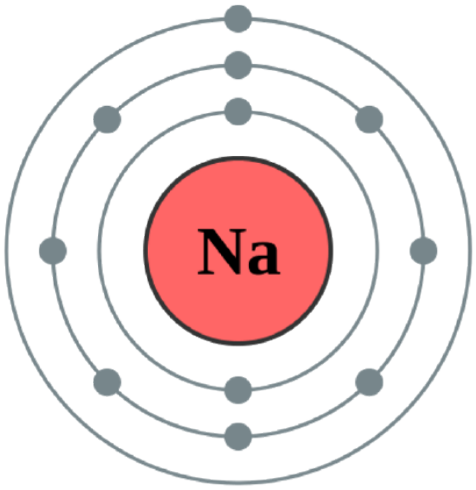


Figure 2.8.1**: The Periods of the Periodic Table Represent Electron Shells** (A) Each electron shell is represented by a row or period on the the periodic table. (B) A representation of the electron shells of the sodium atom. Sodium has an atomic number of 11, thus it has 11 protons and 11 electrons in the elemental form. The first and innermost electron shell can hold a total of 2 electrons, as indicated by the gray circles in the diagram. The second electron shell can hold 8 electrons and is completely full. The third electron shell has the capacity to hold 18 electrons, however, in sodium, there is only one more electron that needs to be placed after filling the first and second electron shells. Thus, the third electron shell of sodium only has 1 electron.

Figure 2.8.1B adapted from Pumbaa

The electron shells are further subdivided into **subshells** that are represented by the second quantum number. There are four major types of subshells that are used to house electrons in known elements. These are termed the *s, p, d*, and *f* subshells. The first electron shell ($n = 1$) is so small that it only contains an *s*-subshell. The second electron shell ($n = 2$) is large enough to house an *s*- and a *p*-subshell. The third electron shell ($n = 3$) contains *s*-, *p*-, and *d*-subshells. The fourth shell and above ($n = 4$, 5, 6, and 7) contain all four electron subshells (*s, p, d, and f*). Shells 5-7 are predicted to have additional subshells, but elements using these subshells have never been discovered, so we will limit our discussion with the *s, p, d,* and *f* subshells.

n = shell #	1	2	3	4	5	6	7
l = subshell #	*s*	*s, p*	*s, p, d*	*s, p, d, f*	*s, p, d, f*	*s, p, d, f*	*s, p, d, f*

Each subshell, in turn, contains a specified number of electron orbitals arranged in unique shapes (Figure 2.8.2). Each orbital can then contain a total of 2 electrons rotating in opposite spin states. The s-subshell only contains 1 circular orbital that can house a total of two electrons. The *p*-subshell contains a total of 3 dumbbell-shaped orbitals that can house a total of 6 electrons. The *d*-subshell contains 5 uniquely shaped orbitals that can house a total of 10 electrons and the *f*-subshell contains 7 orbitals with a potential of housing 14 electrons. While the 5th – 7th shells are predicted to be able to house more electrons in even stranger *g, h,* and *i* subshells, there have never been any atoms discovered that contain enough electrons to utilize these locations. Atoms appear to become too large and unstable after the filling of the *f*-subshell orbitals in the 4th and 5th shell.

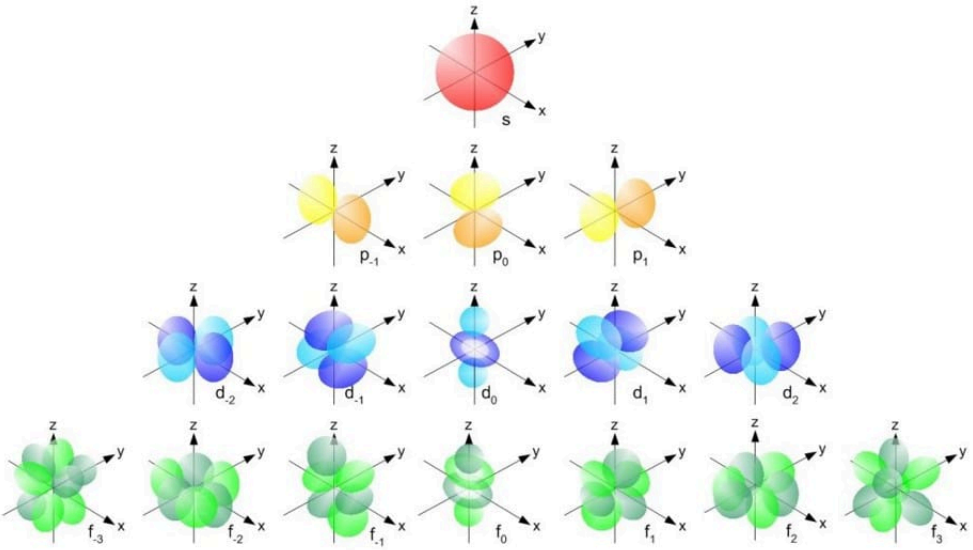


Figure 2.8.2**: Orbital Shape Diagrams for the *s, p, d,* and *f* Subshells.** A pair of electrons with opposite spin can be housed within each of the electron orbitals shown above.

We can summarize the availability of electron orbitals below:

n = shell #	1	2	3	4	5	6	7
l = subshell #	*s*	*s, p*	*s, p, d*	*s, p, d, f*	*s, p, d, f*	*s, p, d, f*	*s, p, d, f*
m_l = orbital #	1	1, 3	1, 3, 5	1, 3, 5, 7	1, 3, 5, 7	1, 3, 5, 7	1, 3, 5, 7
m_s = maximum electrons #	2	2, 6	2, 6, 10	2, 6, 10, 14	2, 6, 10, 14	2, 6, 10, 14	2, 6, 10, 14
Total electrons/shell	2	8	18	32	32*	32*	32*

*** Electron amount listed for shells 5, 6, and 7 are not the maximum predicted, however, atoms have never been found in subshells larger than *f*, and thus, additional subshells will not be considered in this text.**

Electron Orbital Filling Rules

Now that we have defined the physical spaces that electrons can occupy, we need to determine the order of electron orbital filling. There are three major rules that we need to follow when filling electron orbitals. Recall that the ***Pauli Exclusion Principle*** excludes electrons from having the same quantum numbers, and thus, they cannot exist in the same place at the same time. Second according to the ***Aufbau principle*****,** electrons orbiting one or more atoms will fill the lowest available energy levels before filling higher energy levels. Thus, the lowest energy levels must be filled with electrons before orbitals with higher energy can house electrons. The final rule that we need to follow is ***Hund's rule*** which states that when electron orbitals have equal energy level, electrons must fill each of those orbitals as single electrons before they can begin to pair with electrons of opposite spin states. This is because electrons are negatively charged and naturally repel each other. Thus, they exist as far apart as possible. This is the most energetically stable way that electrons can fill orbitals.

Due to the strange shapes of the orbitals within the larger subshells, the energy levels of the orbitals don't always correspond directly with their shell level. For example, the *d*-subshell orbitals have a higher energy than the s-subshell orbital from next shell level (i.e. the *d*-subshell orbitals from the 3rd shell have a higher energy and will fill with electrons later that the *s*-subshell from the 4th shell). Figure 2.12 depicts the energy levels from orbitals in the different subshells.

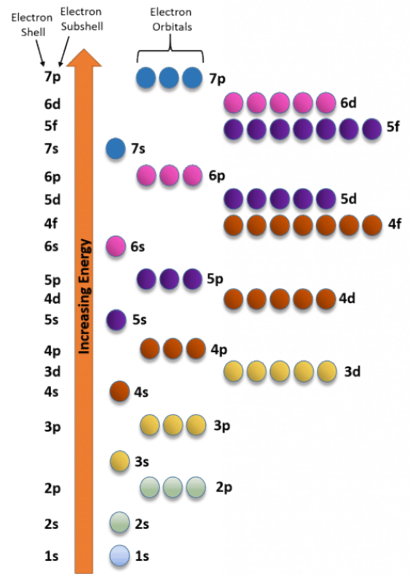


Figure 2.8.3: Electron Energy Filling Diagram. Orbitals with the lowest energy are filled with electrons before orbitals at higher energy levels.

Note that in the energy diagram above that there are many orbitals that share the same energy level. For example the three 2p orbitals have the same energy level. Thus, when these orbitals are filled with electrons, they are filled according to Hund's Rule which states that single electrons will occupy orbitals at the same energy level before they will pair up. (If it helps, you can think to yourself...'electrons find each other repulsive and like to live alone') The following example shows the correct and the incorrect way to fill the 2p orbitals.

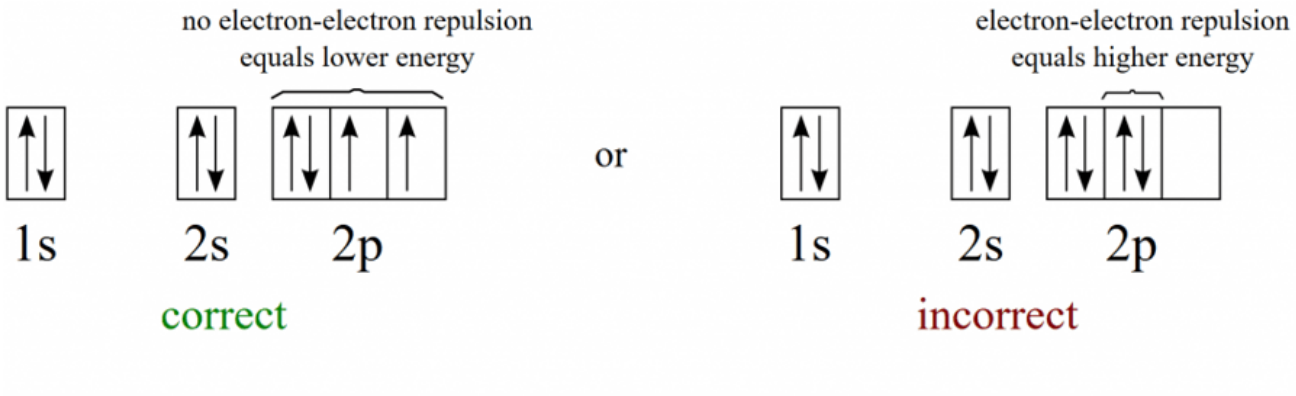


Figure 2.8.4: Electrons fill orbitals according to Hund's Rule. Hund's rule states that single electrons will occupy orbitals at the same energy level before they will pair up.

Image provided by Wikimedia

We can use the electron energy filling diagram to complete an example of how electrons in an element are arranged within the electron orbitals (Figure 2.13). Let's take the example of Iron, (Fe). Iron has an atomic number of 26 or 26 protons. Thus in the elemental state, iron will also have 26 electrons. We will use arrows to represent our electrons within our diagram. Arrows pointing in opposite directions denote electrons that have opposite spin states. Note that the first set of electrons fills the 1s orbital. The next 8 electrons then fill the 2s and 2p orbitals. Note that when filling orbitals that have the same energy level, that the electrons have to follow Hund's Rule, and fill these orbitals as single electrons first, and then pair up when there are no other options to exist in an orbital as a single electron. This filling pattern is noted in the lefthand diagram of the iron electron configuration. The

lefthand diagram shows the active filling of the 2p orbitals with one electron at a time. After all three orbitals receive an electron, they will then pair up before filling the higher energy 3s orbital. Electron filling continues until all 26 electrons are placed. Note that in the case of iron, that the final electrons are placed in the 3d subshell orbitals following Hund's Rule.

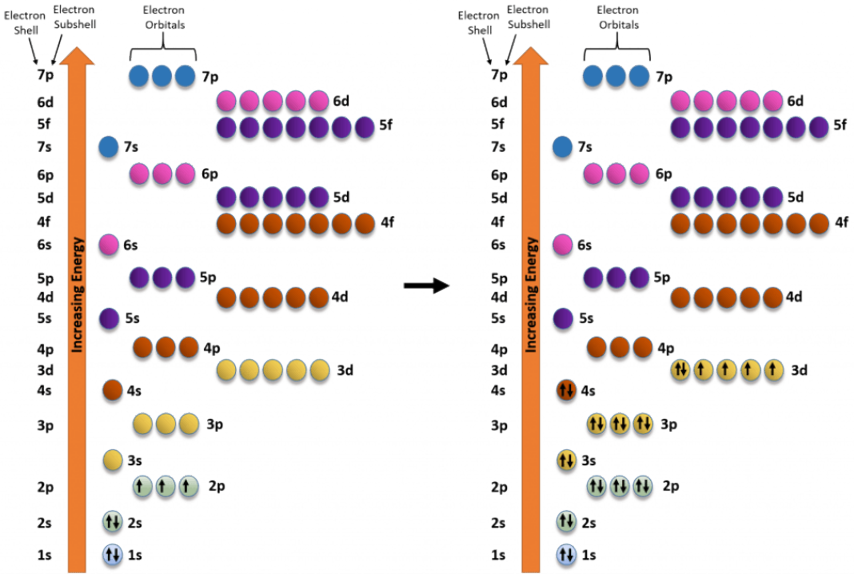
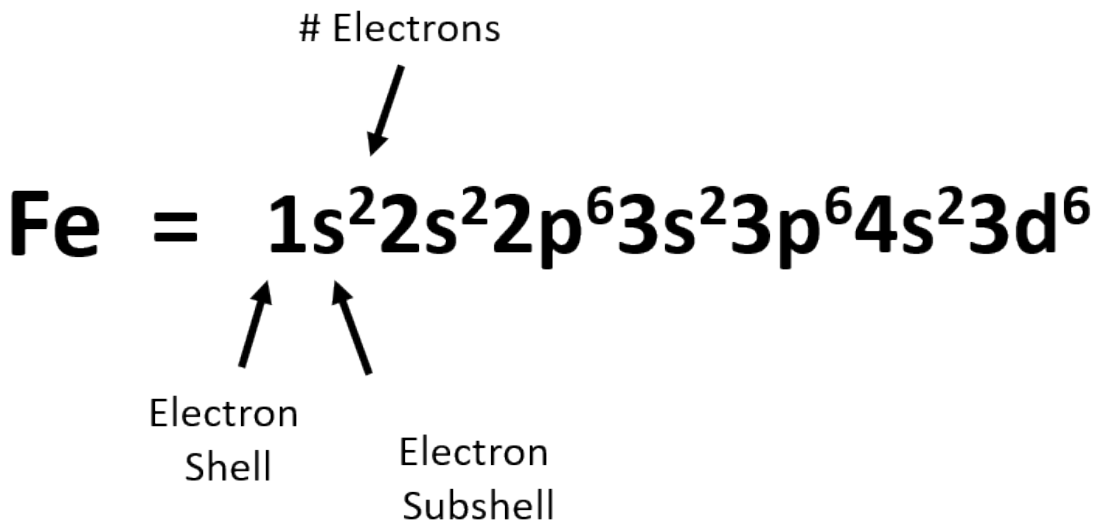


Figure 2.8.5**: Electron Filling Diagram for the Element Iron (Fe).** The lefthand diagram shows the partial filling of the electron orbitals during the assembly of an iron atom. Filling begins with the lowest energy orbital, which is the 1s obital. This is followed by the 2s orbital and the three 2p orbitals. Note that all of the 2p orbitals are at the same energy level. Thus, they are filled according to Hund's Rule: each orbital at the same energy level will fill with one electron alone, until there are no other options. Then the electrons will pair to complete the filling of the 2p orbitals. The figure to the right denotes the completed electron filling diagram for the element iron. Note that the final electrons are placed in the 3d orbitals, and that they are placed to obey Hund's Rule, leaving 4 of the 6 electrons at this energy level in the unpaired state.

We can write the final electron configuration of iron (Fe) using a notation that denotes each electron shell and subshell and the superscript notation that refers the number of electrons present in the orbitals at that energy level. Remember that s-subshells can house 2 electrons, *p*-subshells can house 6 electrons, *d*-subshells can house 10 electrons, and *f*-subshells can house a maximum of 14 electrons.



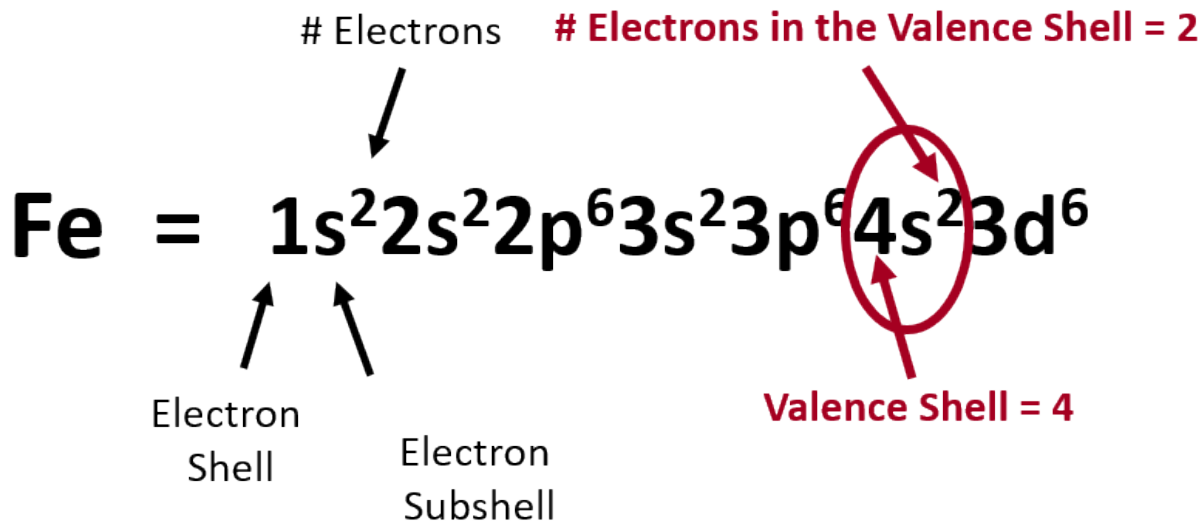
From the diagram above, we can notice a few things. First, if we add up the superscript numbers, this should equal the total number of electrons in that atom. For example if we take the sum of the superscript numbers from the diagram above, we get:

$$(2) \quad + \quad (2+6) \quad + \quad (2+6+6) \quad + \quad (2) \quad = \quad 26 \tag{2.8.2}$$

We can use this as a way to double check and make sure that we have constructed the electron configuration correctly.

The second piece of information that we can find very quickly is the number of electrons present in the outermost shell of the atom. The outermost shell of the atom is referred to as the ***valence shell*****,** and it contains the most available and reactive electrons within the atom. The valence shell will always correspond to the highest shell number present in the atom that contains electrons. The other electron shells are known as inner electron shells. In the case of iron, the valence shell would be the 4th shell (or period on the periodic table). Shells 1-3 would then be the inner shells. Electrons housed in the valence shell are known as the ***valence electrons*****.** Valence electrons are important because they are the ones that are most involved in chemical bonding, although sometimes electrons that are close to the valence electrons in energy, may also participate in bond formation. Most often these exceptions involve electrons in the *d*-subshell.

Note that due to the energy levels of the different subshells, that the only subshells that can exist in the valence shell are the *s*- and *p*-subshells. Both the *d*- and the *f*-subshells only fill after the *s*-orbital of the next higher shell level. Thus, they can never contribute to the number of valence electrons. Since the *s*-orbital can only house 2 electrons, and the *p*-orbitals can house 6 electrons, the maximum number of valence electrons possible for any atom is 8.



Example 2.8.1

How many electrons are in the valence shell of Phosphorus? Phosphorus has an electron configuration of:

$$\mathrm{P} \quad = \quad 1s^2\,2s^2\,2p^6\,3s^2\,3p^3 \tag{2.8.3}$$

Solution

In the analysis of the electron configuration of phosphorus, we can see that the 3rd shell is the valence shell. For phosphorus there are 2 electrons in the 3s orbital, and there are 3 electrons in the 3p orbitals. This is a total of 5 electrons in the outer shell or 5 valence electrons. Note that due to the energy levels of the different subshells, that the only subshells that can exist in the valence shell are the *s*- and *p*-subshells

Exercise 2.8.1

Practice using the electron energy diagram to predict the electron configurations of the following atoms:

Boron, B

Carbon, C

Nitrogen, N

Oxygen, O

Fluorine, F

Neon, Ne

Answer available at the end of this section.

Electron Configurations and the Periodic Table

It is not always convenient to use the energy filling diagram to predict the electron configuration of the elements. Therefore, to

be able to predict electron configurations more easily, the periodic table has been arranged to represent the electron orbital filling patterns. This is what gives the periodic table its stair-step or jagged appearance. Once you know how to read the periodic table for electron configurations, it becomes very easy to write out the electron configuration of any element. Figure 2.14 shows a version of the periodic table that depicts the layout of the electron configurations.

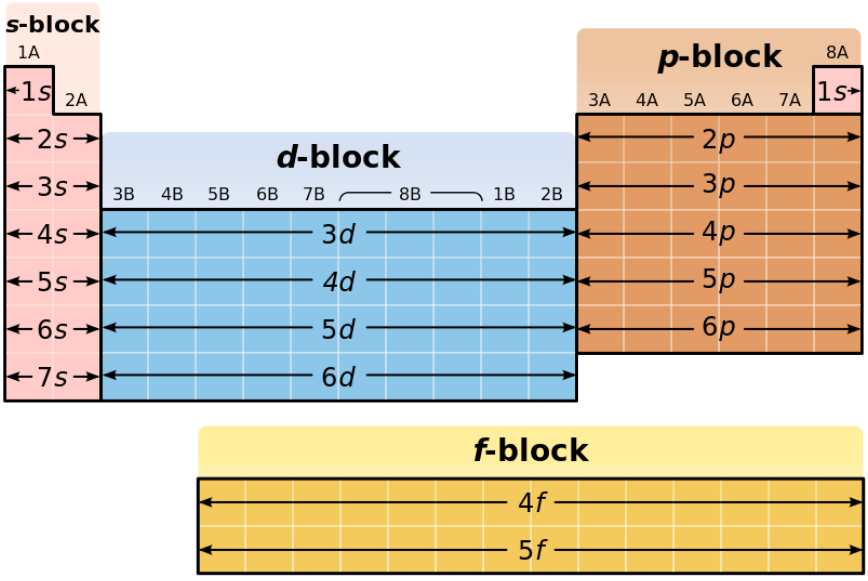


Figure 2.8.6**: The Periodic Table Corresponds to the Filling Patterns of the Electron Shells and Subshells.**

This organization on the periodic table makes it easy to predict where an atom's electron configuration ends and explains why elements within a family share so many similar characteristics! This is because they all share the same outer shell or valence shell electron configuration.

- Group 1A elements are the alkali metals and all have one electron in the outermost energy level because their electron configuration ends in s^1.
- Group 2A elements are the alkaline earth metals and all have two electrons in the outermost energy level because their electron configuration ends in s^2.
- All of the Transition Metals have two electrons in their outermost energy level because their highest shell electron configuration ends in s^2.
- Group 3A elements have three electrons in the outermost energy level because their electron configuration ends in s^2p^1.
- Group 4A elements have four electrons in the outermost energy level because their electron configuration ends in s^2p^2.
- Group 5A elements all have five electrons in the outermost energy level because their electron configuration ends in s^2p^3.
- Group 6A elements all have six electrons in the outermost energy level because their electron configuration ends in s^2p^4.
- Group 7A elements are the halogens and all have seven electrons in the outermost energy level because their electron configuration ends in s^2p^5.
- Group 8A elements are the noble gases and all have eight electrons in the outermost energy level because their electron configuration ends in s^2p^6.
- Elements in group 8A have the most stable electron configuration in the outermost shell because the sub levels are completely filled with electrons.

Let's do some practice problems using the following periodic table:

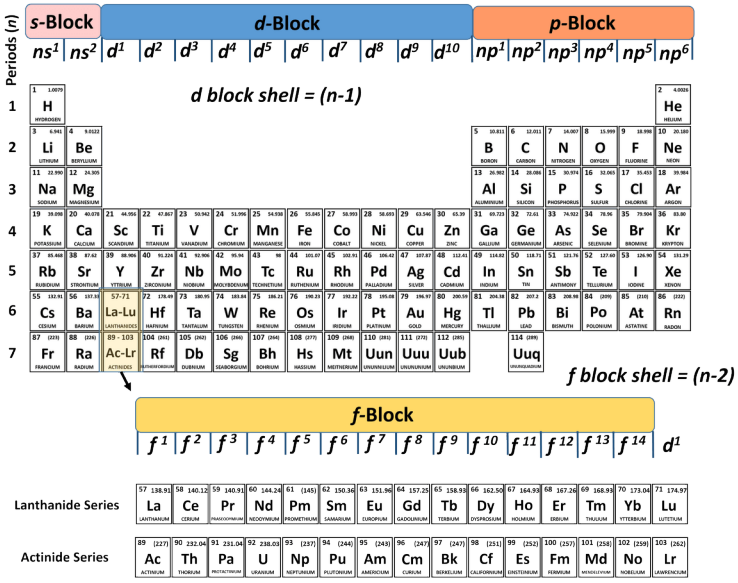


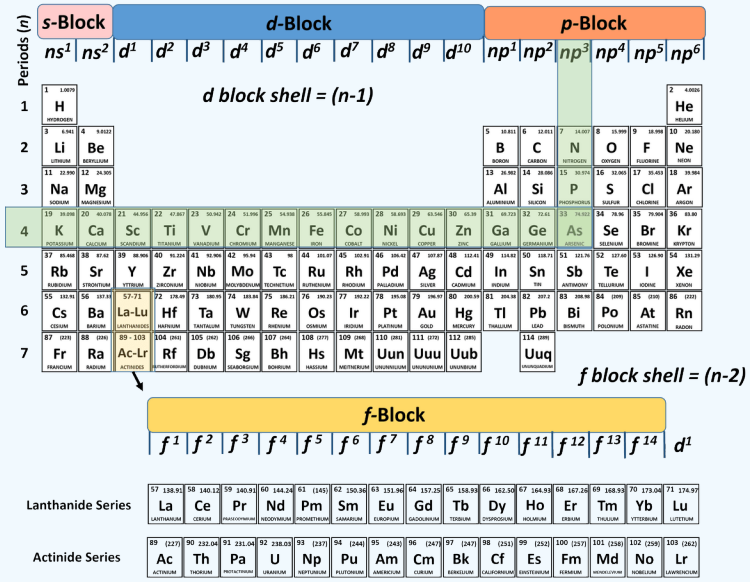
Figure 2.8.6**: The Periodic Table and Electron Configurations.** Note that each of the families on the periodic table corresponds to a specific electron configuration pattern. This makes it easy to determine where the electron configuration ends, and allows us to work backwards to complete the electron configuration.

Example 2.8.2

What is the electron configuration of Arsenic?

Solution

We can use the periodic table like a map and determine where the final electron in Arsenic is placed:



We can see that arsenic ends in the *p*-block at np^3, and if we follow the period back to the left, we can see the *n*=4. Therefore, arsenic ends in $4p^3$. We know that according to Aufbau's principle, that all of the lower energy subshells must be filled with electrons. We can then just walk backwards on the periodic table to read and fill in the lower energy subshells. If we walk backwards from arsenic along the previous periods of the periodic table, we run into the transition metals which represent the *d*-block. Remember that for the *d*-block subshell that the parent shell is (*n*-1). Since we are tracking back from arsenic in row 4, the *d*-block that we run into is *n*-1 or 4-1 = 3. So the next subshell would be $3d^{10}$, followed by $4s^2$, then $3p^6$, $3s^2$, $2p^6$, $2s^2$, and finally $1s^2$. Putting it all together, the electron configuration of arsenic is:

$$\mathbf{As} \quad = \quad \mathbf{1}s^2\,\mathbf{2}s^2\,\mathbf{2}p^6\,\mathbf{3}s^2\,\mathbf{3}p^6\,\mathbf{4}s^2\,\mathbf{3}d^{10}\,\mathbf{4}p^3 \tag{2.8.4}$$

Exercise 2.8.2

What stunning element ends with an electron configuration of $5d^9$? What is the complete electron configuration?

Answer available at the end of this section.

More Review Questions

1. If an element is said to have an outermost electronic configuration of ns^2np^3, it is in what group in the periodic table?
   (a) Group 3A

   (b) Group 4A

   (c) Group 5A

   (d) Group 7A

2. What is the general electronic configuration for the Group 8A elements? (Note: when we wish to indicate an electron configuration without specifying the exact energy level, we use the letter "*n*" to represent any energy level number. That is, ns^2np^3 represents any of the following; $2s^22p^3$, $3s^23p^3$, $4s^24p^3$, and so on.)
   (a) ns^2np^6

   (b) ns^2np^5

   (c) ns^2np^1

   (d) ns^2

3. The group 2 elements are given what name?
   (a) alkali metals

   (b) alkaline earth metals

   (c) halogens

   (d) noble gases

4. Using the diagram below, identify:
   (a) The alkali metal by giving the letter that indicates where the element would be located and write the outermost electronic configuration.

   (b) The alkaline earth metal by giving the letter that indicates where the element would be located and write the outermost electronic configuration.

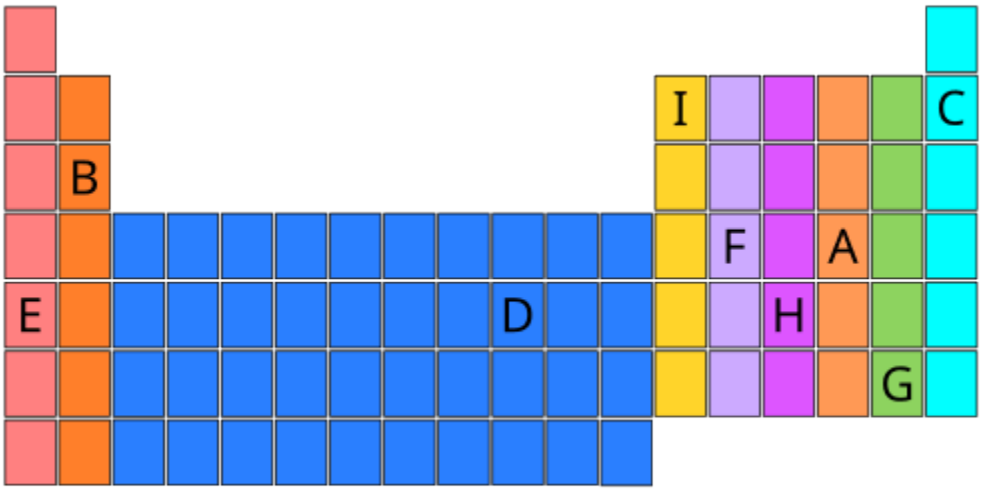
   (c) The noble gas by giving the letter that indicates where the element would be located and write the

outermost electronic configuration.

(d) The halogen by giving the letter that indicates where the element would be located and write the outermost electronic configuration.

(e) The element with an outermost electronic configuration of s^2p^3 by giving the letter that indicates where the element would be located.

(f) The element with an outermost electronic configuration of s^2p^1 by giving the letter that indicates where the element would be located.



5. In the periodic table, name the element whose outermost electronic configuration is found below. Where possible, give the name of the group.

   (a) $5s^2$

   (b) $4s^23d^{10}4p^1$

   (c) $3s^23p^3$

   (d) $5s^24d^{10}5p^2$

   (e) $3s^1$

   (f) $1s^2$

   (g) $6s^25d^{10}6p^5$

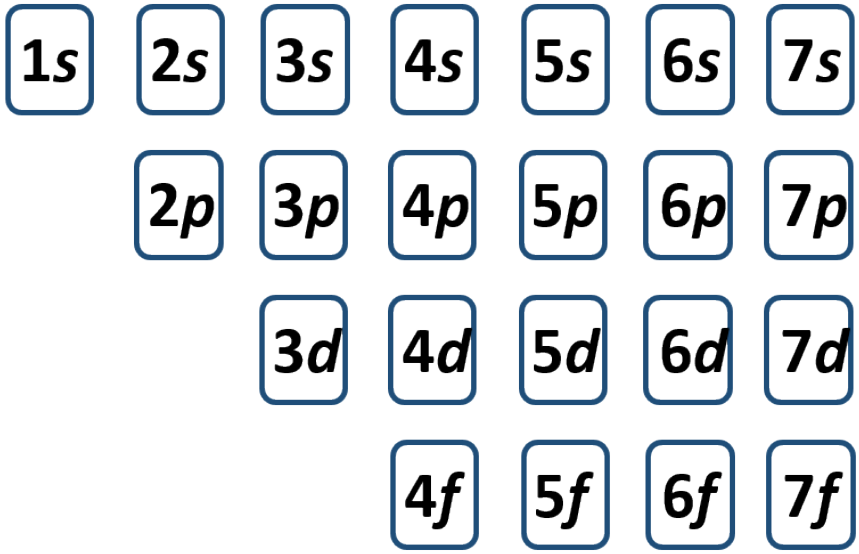
   (h) $4s^24p^4$

Electron Configuration Solitaire

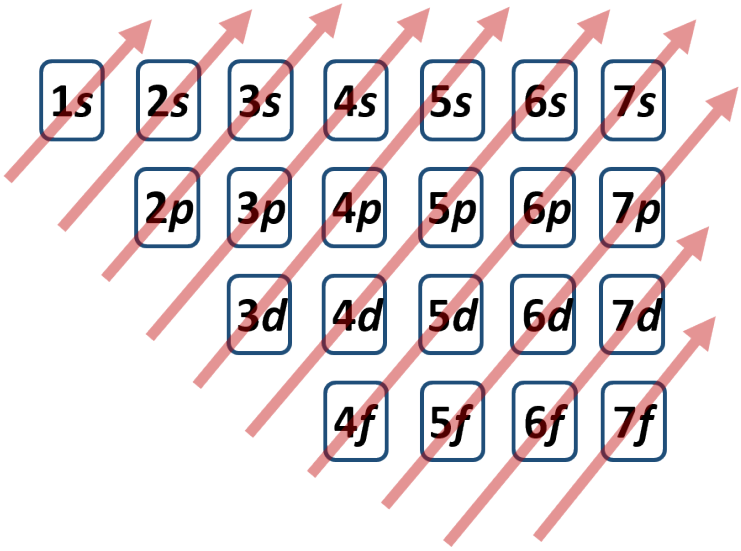
If you are having some trouble using the periodic table to determine electron configurations and don't want to memorize the energy level diagram. There is one more way to help you determine the correct electron configuration of an element. This is also a good method to use to double check you work, when you are using a periodic table to help you determine electron configurations. The method is 'electron configuration solitaire'. I call this method solitaire because that is what it reminds me of every time I draw this chart. Essentially, you are going to lay out all of the electron subshells into neat rows (left to right that are arranged by subshell type (*s, p, d,* and *f*). The first row will contain all of the *s*-subshells arranged from the lowest to the highest shell (*n*) number. So the first row would look like this:



Next align all of the other subshells (*p, d* and *f)* in neat rows directly under their appropriate shell lane. Once your diagram is complete, it will look like you have just dealt yourself a game of solitaire. In reality, you have just created a simple tool to enable you to write out any electron configuration.



To use your chart, you need to draw in diagonal arrows in the direction of electron filling. The final diagram tool should look like this:



It is read from left to right, starting at the bottom of each subsequent arrow.

Example 2.8.3

What is the electronic configuration of Bromine?

Solution

For using the chart above, it is only necessary to determine how many electrons should be present in the element bromine. If we look back at the periodic table, we will see that there are 35 electrons. I find it also really quick to construct the electron configurations if I use a combination of the solitaire method and the periodic table method. I like to use the periodic table to find the end place of my electron configuration. If we look back again at bromine, we see that it is in the *p*-block, ending at $4p^5$. So we can follow the chart above, until we reach $4p^5$. If you don't use the periodic table for this, you should keep track of your electrons and stop the configuration once you have placed all 35 electrons. Either method should give you the same result. Now just read off the appropriate shell/subshells and add in the appropriate amount of electrons for the superscripts:

$$\mathbf{Br} \quad = \quad \mathbf{1}s^2\,\mathbf{2}s^2\,\mathbf{2}p^6\,\mathbf{3}s^2\,\mathbf{3}p^6\,\mathbf{4}s^2\,\mathbf{3}d^{10}\,\mathbf{4}p^5 \tag{2.8.5}$$

Remember also, that adding up your electrons is a good quality check to make sure that the configuration matches the required number of electrons. In this case:

$$(\mathbf{2}) \quad + \quad (\mathbf{2+6}) \quad + \quad (\mathbf{2+6+10}) \quad + \quad (\mathbf{2+5}) \quad = \quad \mathbf{35} \tag{2.8.6}$$

Electron Configuration Shorthand

Writing out electron configurations can fast become tiresome, especially for larger elements like gold. Thus, chemists have made electron configuration shorthands for elements so that they wouldn't have to keep rewriting all of the same subshell beginnings that make up most of the elements. This shorthand uses the Noble Gases as the shorthand reference point. Thus, when you are using the periodic table to determine an electron configuration, you only need to walk back on the periodic table until you run into your first Noble Gas. At that point the shorthand is written by placing the Nobel Gas in a hard bracket followed by the remaining electron configuration. Recall that the electron configuration that we constructed for gold (Au) was quite cumbersome and looked like:

$$\mathbf{Au} \quad = \quad \mathbf{1}s^2\,\mathbf{2}s^2\,\mathbf{2}p^6\,\mathbf{3}s^2\,\mathbf{3}p^6\,\mathbf{4}s^2\,\mathbf{3}d^{10}\,\mathbf{4}p^6\,\mathbf{5}s^2\,\mathbf{4}d^{10}\,\mathbf{5}p^6\,\mathbf{6}s^2\,\mathbf{4}f^{14}\,\mathbf{5}d^9 \tag{2.8.7}$$

With this electron configuration, if we use the periodic table to walk back, we run into our first noble gas at $5p^6$. (*Hint:* All the noble gases end at np^6, so when you are walking back in you electron configurations, you should look for the first np^6 that you see.) The noble gas at this position is Xenon (Xe). Thus, we can shorthand the Au configuration to look like:

$$\mathbf{Au} \quad = \quad [\mathbf{Xe}]\,\mathbf{6}s^2\,\mathbf{4}f^{14}\,\mathbf{5}d^9 \tag{2.8.8}$$

Since xenon has all of the electrons up to $5p^6$, we can replace everything up to that point with the symbol for xenon. Essentially what we are then saying is that the electron configuration for gold looks like xenon + the $6s^2 4f^{14} 5d^9$

Also recall from Exercise 2, we learned that gold rearranges to:

$$\mathbf{Au} \quad = \quad [\mathbf{Xe}]\,\mathbf{6}s^1\,\mathbf{4}f^{14}\,\mathbf{5}d^{10} \tag{2.8.9}$$

where it has greater stability. If you are needing to write out a lot of electron configurations, learning the noble gas shorthand can save you a lot of time!

Exercise 2.8.3

What are the shorthand electron configurations of:

$$\mathrm{Br} = 1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,4s^2\,3d^{10}\,4p^5 \quad (2.8.10)$$

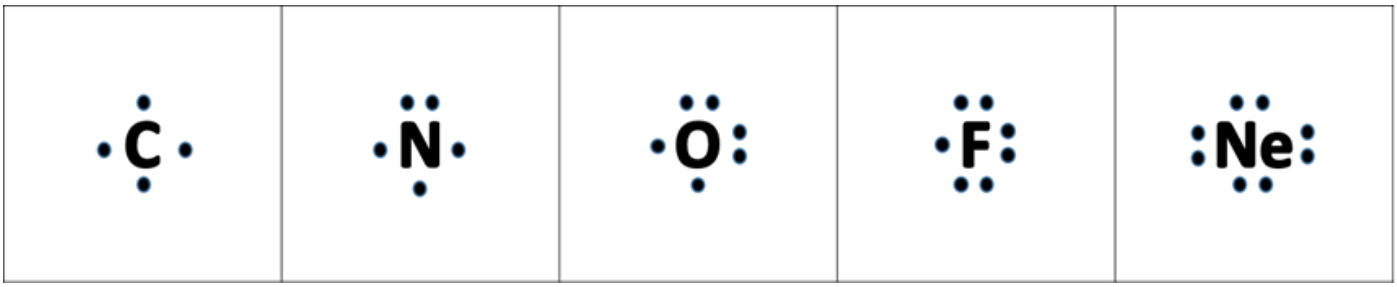
and

$$\mathrm{As} = 1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,4s^2\,3d^{10}\,4p^3 \quad (2.8.11)$$

Answer available at the end of this section.

Electron-Dot Symbols

Although it is entirely possible to define the number of valence electrons in an atom through numbers, sometimes it is helpful to have a graphical representation. The graphical notation used for valence electrons is called an Electron-Dot Symbol. To draw an electron dot symbol, start with the abbreviation for the element of interest as the center, signifying the nucleus of the atom. From there, identify the number of valence electrons the atom has, and then add a single dot for each electron around the nucleus. Students often want to place these electron dots around the nucleus randomly, but it is useful for us to pair electron dots together as we might in an orbital. Following the same rules discussed above about orbital filling, the electron dot symbols for multiple atoms can be seen in the figure below. The easiest way to fill the orbitals is to start at one edge, add a dot, and fill in the rest of the dots one at a time by rotating clockwise on the edges of a square boxing in the nucleus until you have used all of the valence electrons. Note that each side should never have more than two dots, and that you should follow Hund's rule when constructing your Electron-Dot Symbol. Each side should get one electron before the electrons are paired up.

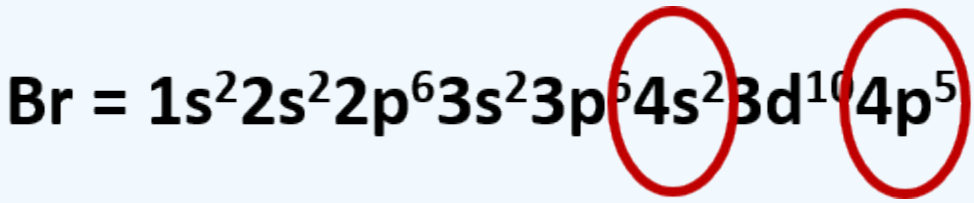


Example 2.8.4

How many valence electrons does bromine have? draw the electron dot representation of bromine?

Solution

For the first part, we need to analyze the electron configuration of bromine and determine the valence shell and the electrons housed there:



We can see that the outer most shell is level 4, and that there are a total of 7 electrons housed there. Thus, bromine has 7 valence electrons. The electron dot symbol should look like:



Notice that this electron dot symbol for bromine looks just like the electron dot symbol for fluorine that is drawn above. This is because they are both in the halogen family. Recall that families share related properties because they have the same valence shell electron configuration. All of the halogens will have 7 electrons in their valence shell.

Since the periodic table is set up so that elements with similar electron configurations are aligned into family groups, it is also easy to use the periodic table to predict the valence electrons and draw the electron dot symbols for each of the family columns. This is shown in Figure 2.16.

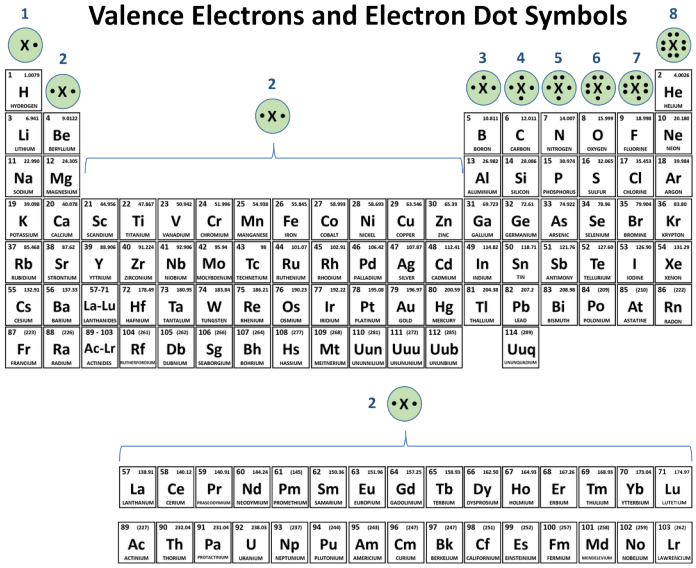


Figure 2.8.7: Identifying Valence Electrons and Electron Dot ymbols from the Periodic Table.

Answers

Exercise 2.8.1

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

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

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

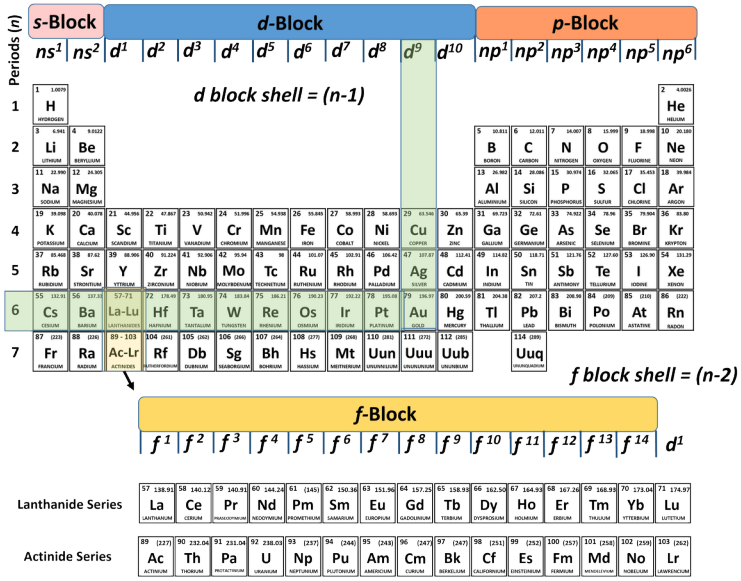
O: $1s^2 2s^2 2p^4$

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

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

Exercise 2.8.2

Again, we can use our knowledge of the periodic table to determine which element that this is represented by this configuration and help us write the full configuration.



The one thing that we have to be careful of when evaluating *d*-block elements, is that we remember that the *d*-block shell is always calculated as *n*-1. So for our problem, we know that our element in question end in $5d^9$. So the shell (*n*) or row that our element is in needs to be calculated using the formula *n* -1 = 5, which gives our final shell number of *n* = 6. Now we can simply follow the nd^9 column down to the 6th row, and we find that Au or gold is our element.

To complete the electron configuration, we would simply walk back along the periodic table to fill in all of the lower energy subshells with electrons. So we start from gold at $5d^9$ and start walking back. What we notice is that the first thing we run into is an *f*-block (the lanthanide series). Note that the *f*-block shell is represented by (*n*-2). Since we are still in the 6th row, this would mean that the 6-2 = 4. The *f*-block is the 4*f* subshell. Recall that the *f*-subshell can hold a total of 14 electrons. Thus, the electron configuration is $4f^{14}$. This is followed by $6s^2$, $5p^6$, $4d^{10}$, $5s^2$, and so on, all the way back to $1s^2$. If we write out the full electron configuration of gold, it would be:

$$\mathbf{Au} \quad = \quad 1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,4s^2\,3d^{10}\,4p^6\,5s^2\,4d^{10}\,5p^6\,6s^2\,4f^{14}\,5d^9 \tag{2.8.12}$$

Interestingly, gold is more stable if it fills the 5d orbitals completely and allows the 6s subshell to only house 1 electron. So it typically rearranges to look like this in its ground-state electron configuration:

$$\mathbf{Au} \quad = \quad 1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,4s^2\,3d^{10}\,4p^6\,5s^2\,4d^{10}\,5p^6\,6s^1\,4f^{14}\,5d^{10} \tag{2.8.13}$$

Transition metals often exhibit this type of flexibility because the s and d orbitals are very close in energy. This flexibility is one reason transition metals commonly form ions with different charges. For this course, however, you will only be expected to predict electron configurations using the Aufbau filling order.

Exercise 2.8.3

Here is Bromine:

$$\mathbf{Br} \quad = \quad [\mathrm{Ar}]\,4s^2\,3d^{10}\,4p^5 \tag{2.8.14}$$

and for Arsenic

$$\mathbf{As} \quad = \quad [\mathrm{Ar}]\,4s^2\,3d^{10}\,4p^3 \tag{2.8.15}$$

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2.9: Periodic Table Trends

Now that you have learned about the organization of the periodic table based on the electron configurations of the elements, we can continue to analyze the periodic table for trends that result from this organization.

Atomic Size

One important trend to be aware of is the way that atomic size changes as you move across a period or down a group in the periodic table. Atomic size is typically measured by the radius of the atom starting at the core of the nucleus, and reaching all the way out to the last valence electron. As you may predict, atomic size will increase as you move down a family group, due to the increased number of electron shells. This substantially increases the size of the electron cloud. What you may not so easily predict is that atomic size decreases as you go across a period. Although this may seem counter-intuitive, the decrease in size can be explained by thinking about the valence electron shell as you go across a period; we see that each element across a period has the same valence electron shell that it is filling with valence electrons. While the valence shell stays the same as you go across a period, the number of protons is increasing. Protons, being positively charged, have a pull on the negatively charged electrons out in the electron cloud. As the number of protons and electrons increases across a period, they have an attractive pull on one another. This results in a tightening of the electron cloud and a reduction in the atomic nuclei. In other words, because the outermost electron shell remains the same across a period, that shell gets pulled progressively closer and closer to the nucleus of the atom as you go across a period. So the overall periodic trend for atomic radius (size) is that atoms get smaller as you go across a period, and they get larger as you go down a family group (Figure 2.9.1).

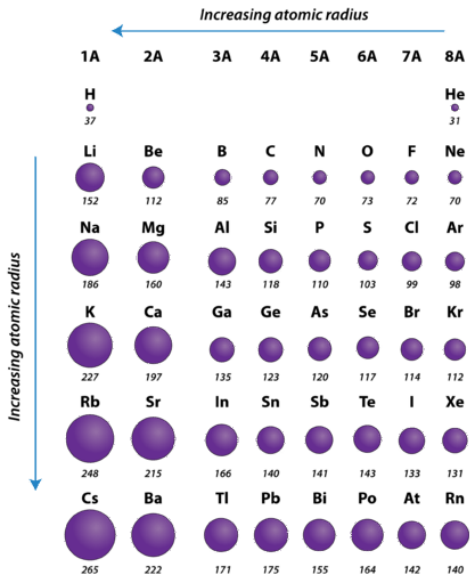


Figure 2.9.1: Atomic Radii of Select Elements Across the Periodic Table

Trends with Atomic Radii

- Atomic radius is determined as half the distance between the nuclei of two identical atoms bonded together.
- The atomic radius of atoms generally decreases from left to right across a period.
- The atomic radius of atoms generally increases from top to bottom within a group.

Electronegativity

Another important periodic trend to be aware of is how electronegativity differences can be identified. *Electronegativity* is the measure of an atom's tendency to attract a bonding pair of electrons. There are various numerical scales for rating electronegativity. Figure 2.9.2 shows one of the most popular—***the Pauling scale***. The Pauling scale assigns fluorine, the most electronegative atom, a 4.0 while less electronegative atoms have smaller grades. We will see in chapters 3 and 4 that electronegativity plays an important role in chemical bonding. The trends for electronegativity in the periodic table are that electronegativity increases as you go across a period, and increases as you go up a group, with fluorine being the most electronegative atom. Noble gases are given an electronegativity rating of 0 due to their inherent stability, which keeps them from forming bonds with other atoms.

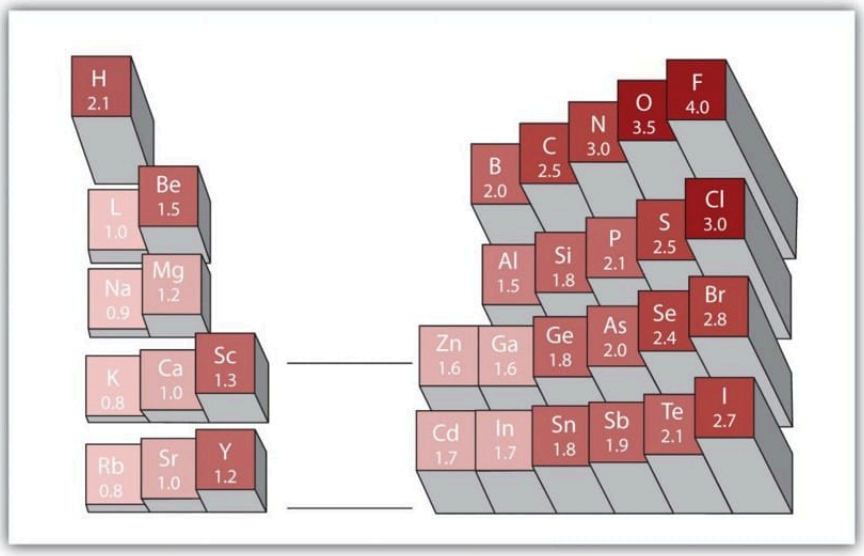
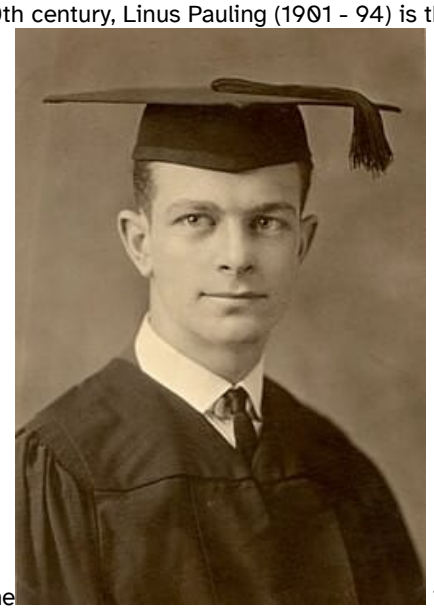


Figure 2.9.2**: Electronegativities of Various Elements.** The Pauling Scale for electronegativities has the value for fluorine atoms set at 4.0, the highest value.

Linus Pauling - A Closer Look

Arguably the most influential chemist of the 20th century, Linus Pauling (1901 - 94) is the only person to have won two



individual (that is unshared) Nobel Prizes. In the 1930s, Pauling used new mathematical theories to enunciate some fundamental principles of the chemical bond. His 1939 book, "*The Nature of the Chemical Bond*", is one of the most significant books every published in chemistry.

By 1935, Pauling's interest turned to biological molecules, and he was awarded the 1954 Nobel Prize in Chemistry for his work on protein structure. (He was also very close to discovering the double helix structure of DNA when James Watson and Francis Crick announced their own discover of its structure in 1953!) He was later awarded the 1962 Nobel Peace Prize for his efforts to ban the testing of nuclear weapons.

In his later years, Pauling became convinced that large doses of vitamin C would prevent disease, including the common cold. Most clinical research failed to show a connection, but Pauling continued to take large doses daily. He died in 1994, having spent a lifetime establishing a scientific legacy that few will ever equal.

Linus Pauling was one of the most influential chemists of the 20th century.

Pauling's Graduation Photo from

Oregon State University in 1922

Ionization Energy

Another periodic trend that you will be expected to know is the trend for ionization energy. ***Ionization energy*** is defined as the amount of energy required to remove the most loosely bound electron of an atom. How tightly bound the electrons of an atom are will affect the amount of energy required to remove one of the valence electrons. Electrons that are closer to the nucleus are going to be more tightly held than those that are further away and will require more energy to pull them off of the atom. For this reason, we see that ionization energy decreases as you go down a family group and the atoms get larger. This same concept can be applied to atoms across a period. We will see that the highest ionization energy will be found on the right side of the period where the atoms are the smallest, and the lowest ionization energy on the left where the atoms have a larger radii. In general, ionization energy decreases as you go down a family group, and increases as you go across a period from left to right (Figure 2.9.3).

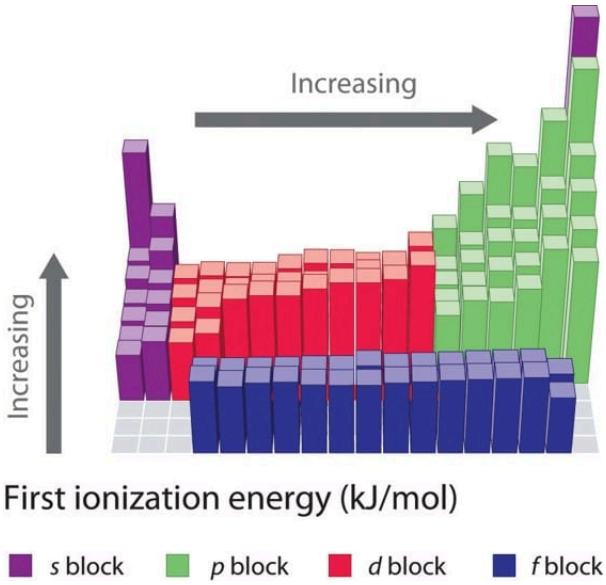


Figure 2.9.3: First Ionization Energies for the Elements of the Periodic Table.

Metallic and Nonmetallic Character

Metallic character refers to the level of reactivity of a metal. Metals tend to lose electrons in chemical reactions, as indicated by their low ionization energies. Within a compound, metal atoms have relatively low attraction for electrons, as indicated by their low electronegativities. By following the trend summary in the figure below, you can see that the most reactive metals would reside in the lower left portion of the periodic table. The most reactive metal is cesium, which is not found in nature as a free element. It reacts explosively with water and will ignite spontaneously in air. Francium is below cesium in the alkali metal group, but is so rare that most of its properties have never been observed.

The metallic character increases as you go down a group. Since the ionization energy decreases going down a group (or increases going up a group), the increased ability for metals lower in a group to lose electrons makes them more reactive. In addition, the atomic radius increases going down a group, placing the outer electrons further away from the nucleus and making that electron less attracted by the nucleus.

Nonmetals tend to gain electrons in chemical reactions and have a high attraction for electrons within a compound. These tendencies are known as ***nonmetallic character***. The most reactive nonmetals reside in the upper right portion of the periodic table. Since the noble gases are a special group because of their lack of reactivity, the element fluorine is the most reactive nonmetal. It is not found in nature as a free element. Fluorine gas reacts explosively with many other elements and compounds and is considered to be one of the most dangerous known substances.

Note that there is no clear division between ***metallic*** and ***nonmetallic*** character. As we move across the periodic table, there is an increasing tendency to accept electrons (nonmetallic) and a decrease in the possibility that an atom would give up one or more electrons.

Metallic and Nonmetallic Character and Periodic Trends:

- Metallic character refers to the level of reactivity of a metal to donate electrons during a chemical reaction.
- Nonmetallic character relates to the tendency of an element to accept electrons during chemical reactions.
- Metallic character increases going down a family group and decreases going across a period.
- Nonmetallic character increases going from left to right across the periodic table and decreases going down a family group.

The following figure summarizes all of the major periodic trends within the periodic table

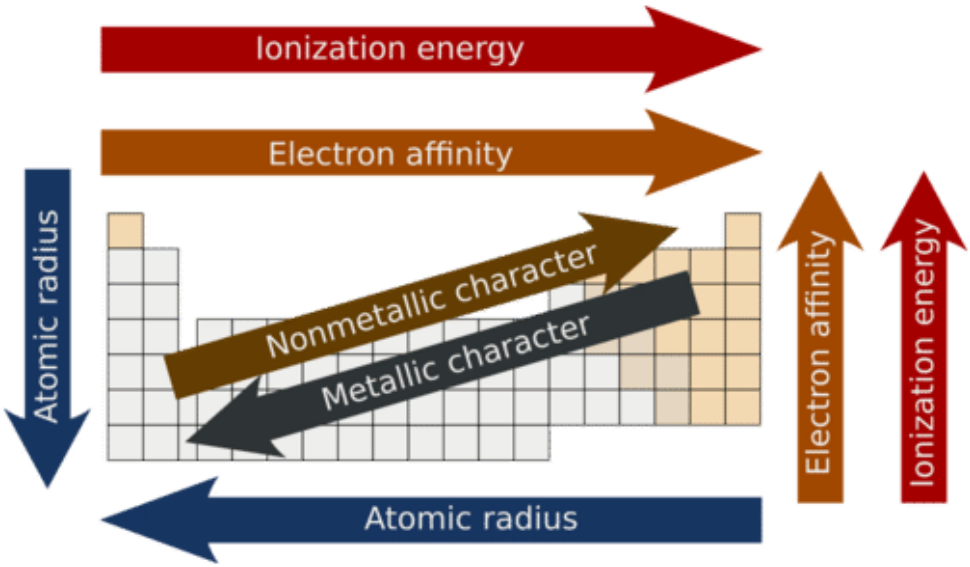


Figure 2.9.4: Summary of Major Periodic Trends

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2.10: Focus on the Environment

Introduction to Radioactivity

In section 2.7 you learned about elemental isotopes and that atoms are defined by the number of protons held within the nucleus. Atomic theory in the nineteenth century presumed that nuclei had fixed compositions. But in 1896, the French scientist Henri Becquerel found that a uranium compound placed near a photographic plate made an image on the plate, even if the compound was wrapped in black cloth. He reasoned that the uranium compound was emitting some kind of radiation that passed through the cloth to expose the photographic plate. Further investigations showed that the radiation was a combination of particles and electromagnetic rays, with its ultimate source being the atomic nucleus. These emanations were ultimately called, collectively, ***radioactivity*.**

There are three main forms of radioactive emissions. The first is called an ***alpha particle***, which is symbolized by the Greek letter α. An *alpha particle* is composed of two protons and two neutrons and is the same as a helium nucleus. (We often use $_2{}^4$He to represent an alpha particle.) It has a 2+ charge. When a radioactive atom emits an alpha particle, the original atom's atomic number decreases by two (because of the loss of two protons), and its mass number decreases by four (because of the loss of four nuclear particles). We can represent the emission of an alpha particle with a chemical equation—for example, the alpha-particle emission of uranium-235 is as follows:

$$^{235}_{92}\mathrm{U} \quad \rightarrow \quad ^{4}_{2}\mathrm{He} \quad + \quad ^{231}_{90}\mathrm{Th} \tag{2.10.1}$$

Rather than calling this equation a chemical equation, we call it a ***nuclear equation*** to emphasize that the change occurs in an atomic nucleus. How do we know that a product of this reaction is Thorium-231? We use the law of conservation of matter, which says that matter cannot be created or destroyed. This means we must have the same number of protons and neutrons on both sides of the nuclear equation. If our uranium nucleus loses 2 protons, there are 90 protons remaining, identifying the element as thorium. Moreover, if we lose four nuclear particles of the original 235, there are 231 remaining. Thus we use subtraction to identify the isotope of the Th atom—in this case, Thorium-231.

Chemists often use the names ***parent isotope*** and ***daughter isotope*** to represent the original atom and the product other than the alpha particle. In the previous example, Uranium-235 is the parent isotope and Thorium-231 is the daughter isotope. When one element changes into another in this manner, it undergoes ***radioactive decay*.**

The second major type of radioactive emission is called a ***beta particle***, symbolized by the Greek letter β. A *beta particle* is an electron ejected from the nucleus (not from the shells of electrons about the nucleus) and has a -1 charge. We can also represent a beta particle as $_{-1}{}^0$e. The net effect of beta particle emission on a nucleus is that a neutron is converted to a proton. The overall mass number stays the same, but because the number of protons increases by one, the atomic number goes up by one. Carbon-14 decays by emitting a beta particle:

$$^{14}_{6}\mathrm{C} \quad \rightarrow \quad ^{0}_{-1}\mathrm{e} \quad + \quad ^{14}_{7}\mathrm{N} \tag{2.10.2}$$

Again, the sum of the atomic numbers is the same on both sides of the equation, as is the sum of the mass numbers. (Note that the electron is assigned an "atomic number" of –1, equal to its charge.)

The third major type of radioactive emission is not a particle but rather a very energetic form of electromagnetic radiation called ***gamma rays***, symbolized by the Greek letter γ. ***Gamma rays*** themselves do not carry an overall electrical charge, but they may knock electrons out of atoms in a sample of matter and make it electrically charged (for which gamma rays are termed ***ionizing radiation***). For example, in the radioactive decay of radon-222, both alpha and gamma radiation are emitted, with the latter having an energy of 8.2×10^{-14} J per nucleus decayed:

$$^{222}_{86}\mathrm{Rn} \quad \rightarrow \quad ^{4}_{2}\mathrm{He} \quad + \quad ^{218}_{84}\mathrm{Po} \quad + \quad ^{0}_{0}\gamma \tag{2.10.3}$$

This may not seem like much energy, but if 1 mol of Rn atoms were to decay, the gamma ray energy would be 4.9×10^7 kJ! That is enough energy to power an average American home for an entire year.

Table 2.10A Characteristics of Radioactive Particles

Characteristic	Alpha Particles	Beta Particles	Gamma Rays
Symbols	$\alpha, {}_2^4He$	$\beta, {}_{-1}^{0}e$	γ
Identity	helium nucleus	electron	electromagnetic radiation
Charge	+2	-1	none
Mass Number	4	0	0
Penetrating Power	minimal (will not penetrate skin)	short (will penetrate skin and some tissues slightly)	deep (will penetrate tissues deeply)

Nuclear Fission Reactions and Energy

Occasionally, an atomic nucleus breaks apart into smaller pieces in a radioactive process called ***spontaneous fission***. Typically, the daughter isotopes produced by fission are a varied mix of products, rather than a specific isotope as with alpha and beta particle emission. Often, fission produces excess neutrons that will sometimes be captured by other nuclei, possibly inducing additional radioactive events. Uranium-235 undergoes spontaneous fission to a small extent. One typical reaction is

$$\mathrm{{}^{235}_{92}U \rightarrow {}^{139}_{56}Ba + {}^{94}_{36}Kr + 2\,{}^{1}_{0}n} \tag{2.10.4}$$

where ${}_0^1$n is a neutron. As with any nuclear process, the sums of the atomic numbers and mass numbers must be the same on both sides of the equation. Spontaneous fission is found only in large nuclei. The smallest nucleus that exhibits spontaneous fission is lead-208. Fission is the radioactive process used in nuclear power plants and one type of nuclear bomb.

When a critical mass of a fissile isotope is achieved, the resulting flux of neutrons can lead to a self-sustaining reaction. Natural uranium is a mixture of isotopes, and includes a small proportion (0.720%) of the fissile isotope, U-235. When the nucleus of a U-235 atom is split by a neutron, it discharges two or three additional neutrons and releases energy in the form of heat (Fig 2.21). The additional neutrons released can react with other U-235 particles and form a sustaining chain reaction. To sustain such a reaction, a critical amount (3-5%) of U-235 is required in the source material. Thus, naturally occurring uranium cannot be used for nuclear fission. The uranium must first be enriched for the U-235 isotope through a complicated and difficult process. Compared to energy grade uranium which is enriched to 3-5% of U-235, bomb grade uranium is highly enriched (>90% U-235).

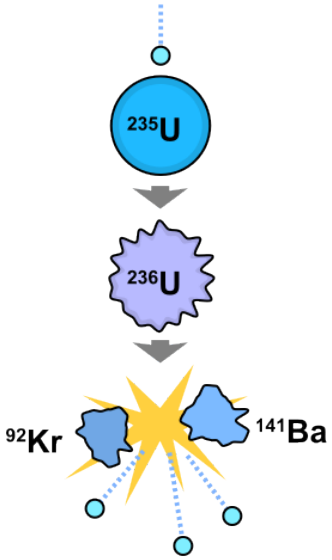


Figure 2.10.1**: Nuclear Fission Reaction of U-235.** The addition of a neutron to U-235 results in the formation of an unstable U-236 atom that splits into Kr-92 and Ba-141 and releases 3 neutrons. This figure was created by Fastfission

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A variety of techniques can be used to control the flow of neutrons from such a reaction, which allows nuclear fission reactions to be maintained at safe levels. With regards to energy production, if the neutron flow in a reactor is carefully regulated so that only enough heat is released to boil water, then the resulting steam can be used to produce electricity. Thus a nuclear reactor is similar in many respects to the conventional power plants, which burn coal or natural gas to generate electricity; the only difference is the source of the heat that converts water to steam. Many levels of control are required, along with a fail-safe design, because otherwise the chain reaction can accelerate so rapidly that it releases enough heat to melt or vaporize the fuel and the container, a situation that can release enough radiation to contaminate the surrounding area. Light-water reactors are the most common type of fission reactor, and are used extensively to produce electricity in countries such as Japan, Israel, South Korea, Taiwan, and France—countries that lack large reserves of fossil fuels. The essential components of a light-water reactor are depicted in Figure 2.22. Approximately 11% of the world's energy is generated by nuclear power, with more than a dozen countries obtaining more than 30% of their energy from nuclear sources.

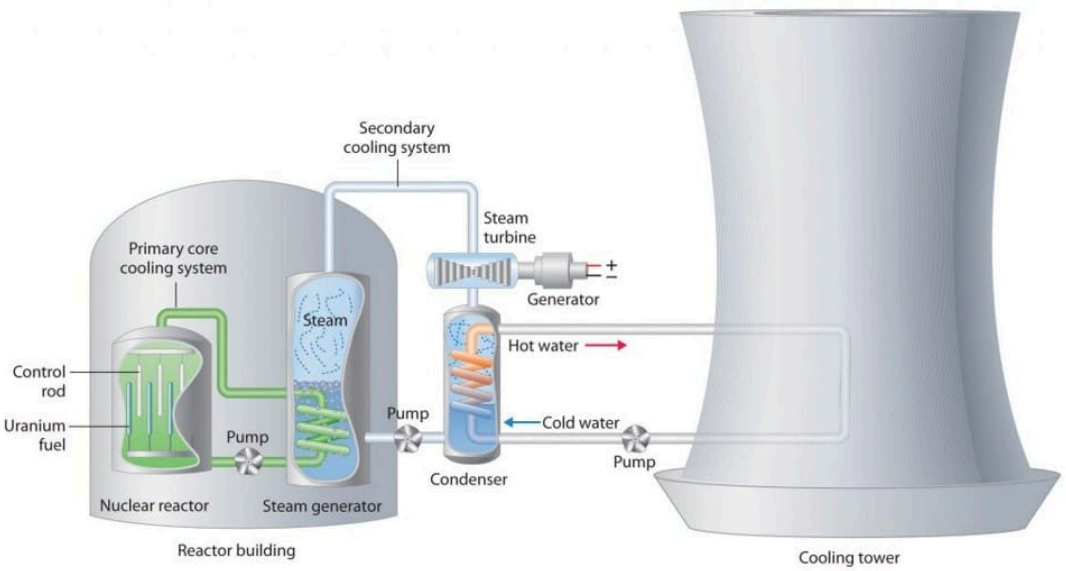


Figure 2.10.2**: A Light-Water Nuclear Fission Reactor for the Production of Electric Power.** The fuel rods are made of a

corrosion-resistant alloy that encases the partially enriched uranium fuel; controlled fission of ^{235}U in the fuel produces heat. Water surrounds the fuel rods and moderates the kinetic energy of the neutrons, slowing them to increase the probability that they will induce fission. Control rods that contain elements such as boron, cadmium, or hafnium, which are very effective at absorbing neutrons, are used to control the rate of the fission reaction. A heat exchanger is used to boil water in a secondary cooling system, creating steam to drive the turbine and produce electricity. The large hyperbolic cooling tower, which is the most visible portion of the facility, condenses the steam in the secondary cooling circuit; it is often located at some distance from the actual reactor.

All existing nuclear power plants have similar components, although different designs use different fuels and operating conditions. *Fuel rods* containing a fissile isotope in a structurally stabilized form (such as uranium oxide pellets encased in a corrosion-resistant zirconium alloy) are suspended in a cooling bath that transfers the heat generated by the fission reaction to a secondary cooling system. The heat is used to generate steam for the production of electricity. In addition, *control rods* are used to absorb neutrons and thereby control the rate of the nuclear chain reaction. Control rods are made of a substance that efficiently absorbs neutrons, such as boron, cadmium, or, in nuclear submarines, hafnium. Pulling the control rods out increases the neutron flux, allowing the reactor to generate more heat, whereas inserting the rods completely stops the reaction, a process called “scramming the reactor.”

All nuclear reactors require a powerful cooling system to absorb the heat generated in the reactor core and create steam that is used to drive a turbine that generates electricity. In 1979, an accident occurred when the main water pumps used for cooling at the nuclear power plant at Three Mile Island in Pennsylvania stopped running, which prevented the steam generators from removing heat. Eventually, the zirconium casing of the fuel rods ruptured, resulting in a meltdown of about half of the reactor core. Although there was no loss of life and only a small release of radioactivity, the accident produced sweeping changes in nuclear power plant operations. The US Nuclear Regulatory Commission tightened its oversight to improve safety.

The main disadvantage of nuclear fission reactors is that the spent fuel, which contains too little of the fissile isotope for power generation, is much more radioactive than the unused fuel due to the presence of many daughter nuclei with shorter half-lives than ^{235}U. The decay of these daughter isotopes generates so much heat that the spent fuel rods must be stored in water for as long as 5 yr before they can be handled. Even then, the radiation levels are so high that the rods must be stored for many, many more years to allow the daughter isotopes to decay to nonhazardous levels. How to store these spent fuel rods for hundreds of years is a pressing issue that has not yet been successfully resolved. As a result, some people are convinced that nuclear power is not a viable option for providing our future energy needs, although a number of other countries continue to rely on nuclear reactors for a large fraction of their energy.

Uncontrolled nuclear fission reactions are relatively rare, but they have occurred at least 18 times in the past. One of the most recent occurred on April 25–26, 1986, at the Chernobyl nuclear power plant in the former Union of Soviet Socialist Republics (USSR; now in the Ukraine). During testing of the reactor’s turbine generator, a series of mechanical and operational failures caused a chain reaction that quickly went out of control, destroying the reactor core and igniting a fire that destroyed much of the facility and released a large amount of radioactivity. Thirty people were killed immediately, and the high levels of radiation in a 20 mile radius forced nearly 350,000 people to be resettled or evacuated. In addition, the accident caused a disruption to the Soviet economy that is estimated to have cost almost $13 billion. It is somewhat surprising, however, that the long-term health effects on the 600,000 people affected by the accident appear to be much less severe than originally anticipated. Initially, it was predicted that the accident would result in tens of thousands of premature deaths, but an exhaustive study almost 20 yr after the event suggests that 4000 people will die prematurely from radiation exposure due to the accident. Although significant, in fact it represents only about a 3% increase in the cancer rate among the 600,000 people most affected, of whom about a quarter would be expected to eventually die of cancer even if the accident had not occurred.

The most recent event resulted from the damaged Fukushima Dai-ichi plant after the March 11, 2011, earthquake and tsunami that devastated Japan. The plant used fresh water for cooling nuclear fuel rods to maintain controlled, sustainable nuclear fission. When the water supply was disrupted, so much heat was generated that a partial meltdown occurred. Radioactive iodine levels in contaminated seawater from the plant were over 4300 times the regulated safety limit. To put this in perspective, drinking one liter of fresh water with this level of contamination is the equivalent to receiving double the annual dose of radiation that is typical for a person. Dismantling the plant and decontaminating the site is estimated to require 30 years at a cost of approximately $12 billion.

Suggested Assignment:

Watch the Frontline Episode: Nuclear Aftershocks (Found here: Frontline Episode [www.pbs.org]Following the video, write a 500 word essay about whether or not you feel that nuclear energy should be used in the United States at the Indian Point Nuclear

Power Plant. Be sure to include pros and cons within your argument.

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2.11: Chapter Summary

Dalton's Atomic Theory proposed that matter is made up of tiny particles called atoms that cannot be broken into smaller pieces. During a chemical reaction, atoms are rearranged, but they do not break apart, nor are they created or destroyed. An ***element*** is a substance that cannot be broken down into simpler chemical substances. There are about 90 naturally occurring elements known on Earth. The smallest unit of an element is the **atom**. All atoms of the same element are identical in mass and other properties, whereas atoms of different elements differ in mass and other properties.

The elements can be divided into three major classes: The ***metals, metalloids,* and *nonmetals***. ***Metals*** are typically shiny, very dense, have high melting points, and are good conductors. ***Nonmetals*** are generally brittle, dull, have low melting points, and they are generally poor conductors. ***Metalloids*** have properties of both metals and nonmetals.

Dmitri Mendeleev organized the elements into a chart based on their similar characteristics and properties. Today this chart is known as the ***periodic table of the elements***. Within the periodic table group, or ***family of elements***, is a vertical column of the periodic table. Elements are placed into families due to their similar properties, characteristics, and reactivities. Group 1 elements are known as the ***alkali metals*** and are the most reactive elements of the metal class. ***Alkaline earth metals*** are found in group 2 and are almost as reactive as the group 1 metals. The ***transition metals*** are the larger block of elements extending from Groups 3-12 (also known as the group B elements). Transition metals have high melting points and boiling points, often form colored compounds that are highly stable, and they can serve as good *catalysts*. A *catalyst* is an agent that helps to speed up a chemical reaction without itself being changed in the process. Group 17 elements, known as ***halogens***, contains very reactive nonmetals that often exist as diatomic elements (F_2, Cl_2, Br_2, I_2). Group 18 elements, the ***noble gases*** are extremely stable, unreactive, and rarely form compounds.

Atoms are made up of extremely small subatomic particles called ***protons, neutrons, and electrons***. ***Protons*** *(*positively charged particles), and ***neutrons*** (electrically neutral particles) form the core or *nucleus* of an atom. ***Electrons*** are extremely small, negatively charged particles that form an electron cloud, which orbits the nucleus. The ***atomic number (Z)*** refers the the number of protons present in an element and is the defining feature of an element. The ***atomic mass (A)*** of an element is the sum of the protons and neutrons within that element.

Atoms of the same element (have the same atomic number) that have different numbers of neutrons are called ***isotopes.*** Most elements exist as isotopes. In fact, over 3,500 isotopes are known for the different elements. The atomic mass reported on the periodic table is the relative mass of the different isotopes of an element based on their abundance on the Earth. Some chemical elements can also form more than one type of structural lattice, these different structural lattices are known as ***allotropes***. Allotropic changes affect how the atoms of the element interact with one another to form a 3-dimensional structure, but *do not* alter the sample with regard to the atomic isotope forms that are present, and *do not* alter or affect the atomic mass (*A*) of the element.

Understanding the electron configuration within an element is important for understanding the reactivity of the element. The modern theory of electron behavior is predicted by the field of ***quantum mechanics***. The term ***quantum*** is defined as a discrete quantity or 'packet' of energy. Electrons in atoms can exist at different energy levels depending on how far away from the nucleus of that atom that they are positioned. Electrons typically have higher energy, the farther away they are (on average) from the nucleus. ***Four quantum numbers (n, l, m_l, and m_s)*** are used to assign the position of an electron within at atom. The principle quantum number (*n*) refers to the electron shells and corresponds to each period or row on the periodic table. The orbital angular momentum quantum number *(l)* refers to the electron subshell classification which can be of the *s, p, d,* or *f* categories. The magnetic quantum number (m_l) refers to the electron orbitals, and the electronic spin number (m_s) refers to the electron spin state of the electrons. Each orbital can house 2 electrons, each of which have an opposite spin. Each subshell can house a specific number of electron orbitals: *s*-subshells have one orbital and can house a total of 2 electrons, *p*-subshells have three obitals and can house a total of 6 electrons, *d*-subshells have five orbitals and can house a total of 10 electrons, and *f*-subshells have seven orbitals and can house a total of 14 electrons.

Electron orbitals are filled according to three major rules. The ***Pauli Exclusion Principle*** states that electrons cannot occupy the same space at the same time, and thus, no two electrons can share the same combination of four quantum numbers. Second according to the ***Aufbau principle***, electrons orbiting one or more atoms will fill the lowest available energy levels before filling higher energy levels. The final rule that we need to follow is ***Hund's rule*** which states that when electron orbitals have equal energy level, electrons must fill each of those orbitals as single electrons before they can begin to pair with electrons of opposite spin states. The periodic table and the electron configuration solitaire tool can be used to determine the electron configuration

of any element. Electron configurations can be written using the noble gas shorthand rules.

The ***valence shell*** of an element is the outermost electron shell. The electrons housed within the valence shell are the most reactive electrons in an atom and are essential for forming chemical bonds with other elements. There are a total of eight electrons that can be housed in the valence shell of any atom. The periodic table can be used to predict the number of valence electrons present within an atom and ***electron dot symbols*** provide a graphic representation of the valence shell electrons.

Due to the organization of the periodic table according to proton and electron configurations, a number of interesting elemental trends can be observed. ***Atomic size*****,** as measured by the atomic radius of an atom, increases and you move down a family group, and decreases as you move from left to right down a period or a row on the periodic table. The ***Electronegativity*** of an atom is the measure of an atom's tendency to attract a bonding pair of electrons, and can be thought of as electron affinity. Electronegativity increases as you go from left to right across the periods of the periodic table and it tends to decrease as you move down family groups. ***Ionization energy*** is defined as the amount of energy required to remove the most loosely bound electron of an atom. Ionization energy tends to increase as you move across the periods of the periodic table from left to right, and decreases as you move down a family group. ***Metallic character*** refers to the level of reactivity of a metal, whereas nonmetallic character refers to the level of reactivity of nonmetals. The metallic character of the elements tends to go up as you move down a family group of elements and goes down as you move from left to right across a row of the periodic table. Concomitantly, nonmetallic character tends to go down as you move down a family group of elements and goes up as you move from the left to the right across the periodic table.

Video Tutorial of Electron Configurations and Ionization Energy By: Paul Anderson and Bozeman Science

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3: CHAPTER 3 - IONS AND IONIC COMPOUNDS

3.1: Introduction to the Octet Rule

3.2: Ions and the Periodic Table

3.3: Ionic Bonding

3.4: Practice Writing Correct Ionic Formulas

3.5: Naming Ions and Ionic Compounds

3.6: Polyatomic Ions

3.7: Naming Polyatomic Ions

3.8: Properties and Types of Ionic Compounds

3.9: Arrhenius Acids and Bases

3.10: Focus on the Environment - Acid Rain

3.11: Chapter Summary

3.12: References

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3.1: Introduction to the Octet Rule

How Atoms Become Stable

Up until now we have been discussing only the elemental forms of atoms which are neutrally charged. This is because the number of electrons (negative in charge) is equal to the number of protons (positive in charge). The overall charge on the atom is zero, because the magnitude of the negative charge is the same as the magnitude of the positive charge. This one-to-one ratio of charges is not, however, the most common state for many elements. Deviations from this ratio result in charged particles called ***ions***.

Throughout nature, things that are high in energy tend to move toward lower energy states. Lower energy configurations are more stable, so things are naturally drawn toward them. For atoms, these lower energy states are represented by the noble gas elements. These elements have electron configurations characterized by full *s* and *p* subshells. This makes them stable and unreactive. They are already at a low energy state, so they tend to stay as they are.

The elements in the other groups have subshells that are not full, so they are unstable when compared to the noble gases. This instability drives them toward the lower energy states represented by the noble gases that are nearby in the periodic table. In these lower energy states, the outermost energy level has eight electrons (an "octet"). The tendency of an atom toward a configuration in which it possesses eight valence electrons is referred to as the "***Octet Rule.***"

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 both 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 with the transfer of electrons the individual atoms acquire a nonzero electric charge. Those that lose electrons become positively charged, and those that gain electrons become negatively charged. Recall that atoms carrying positive or negative charges are called ions. If an atom has gained one or more electrons, it is negatively charged and is called an ***anion.*** If an atom has lost one or more electrons, it is positively charged and is called a ***cation.*** 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.***

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 both atoms. The bond made by electron sharing is called a ***covalent bond.*** Covalent bonding and covalent compounds will be discussed in Chapter 4 "Covalent Bonding and Simple Molecular Compounds".

At the end of chapter 2, we learned how to draw the electron dot symbols to represent the valence electrons for each of the elemental families. This skill will be instrumental in learning about ions and ionic bonding. Looking at Figure 3.1.1, observe the Noble Gas family of elements. The electron dot symbol for the Nobel Gas family clearly indicates that the valence electron shell is completely full with an octet of electrons. If you look at the other families, you can see how many electrons they will need to gain or lose to reach the octet state. Above, we noted that elements are the most stable when they can reach the octet state. However, it should also be noted that housing excessively high negative or positive charge is unfavorable. Thus, elements will reach the octet state and also maintain the lowest charge possible. You will note that for the IA, IIA, IIIA and transition metals groups, it is more economical to lose electrons (1-3 electrons) from their valence shells to reach the octet state, rather than to gain 5-7 electrons. Similarly main group columns VA, VIA, and VIIA tend to gain electrons (1-3) to complete their octet, rather than losing 5-7 electrons. Some atoms, like carbon, are directly in the middle. These atoms don't like to gain or lose electrons, but tend to favor the sharing model of chemical bonding. The remaining sections of this chapter will focus on the formation of ions and the resulting ionic compounds.

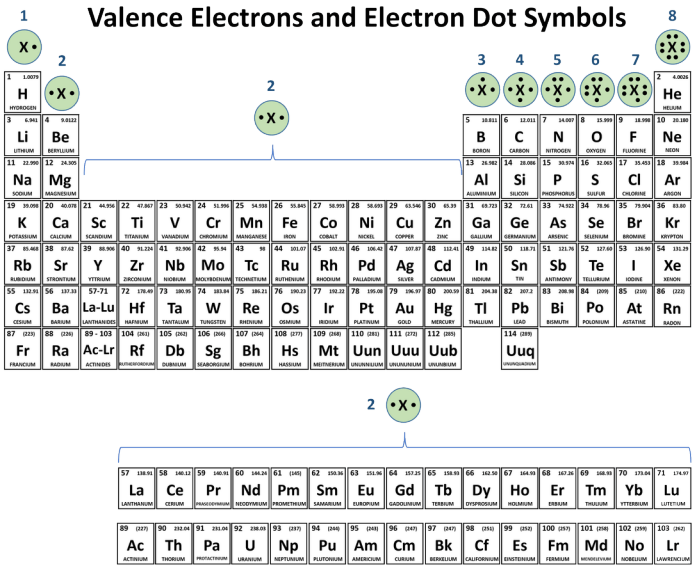


Figure 3.1.1**: Periodic Table with Electron Dot Symbols.**

What is Plasma?

St. Elmo's Fire

When strange, glowing, flame-like projections appeared on the masts of ships during storms, sailors attributed great significance to the unexplained phenomenon they were seeing, naming it after the patron saint of sailors, St. Elmo. The circumstances in which they found themselves and the strangeness of what they were seeing led them to regard these lights as supernatural. What they did not know was that they were watching the process of ionization within and electric field.

During an electric storm, the shape of the electric field at the tip of a pointed object allows enough energy to be transferred to the molecules in the air to overcome their first ionization energy, producing a substance called ***plasma***. This substance is composed of ions and electrons that are at an energy state that is high enough to allow them to move freely. This entirely natural phenomenon produces the light that must have seemed to come from a mysterious or spiritual source.

Source: Wikipedia [en.wikipedia.org]

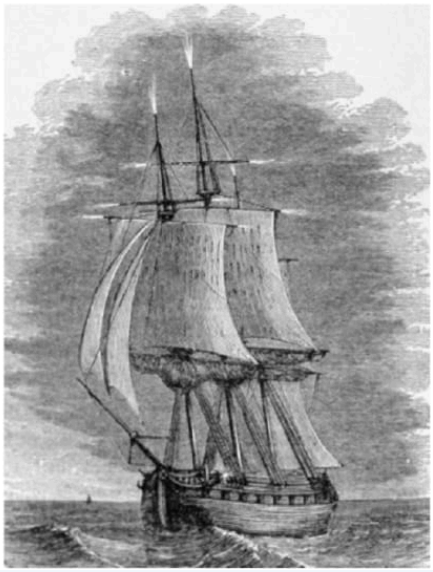




Figure 3.1.2: Ionization Within and Electric Field. (A) Depiction of St. Elmo's Fire at the tips of a ship's masts. (B) In many high voltage applications plasma ionization is an unwanted side effect. Shown is a long exposure photograph of corona discharge on an insulator string of a 500 kV overhead power line. This type of plasma discharge represent a significant power loss for electric utilities.

Photograph depicted in a (A) by: Unknown Author

Photograph depicted in a (B) by: Nitromethane

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3.2: Ions and the Periodic Table

The elements on the right side of the periodic table, nonmetals, gain the electrons necessary to reach the stable electron configuration of the nearest noble gas. Elements on the left side of the periodic table, metals, lose the electrons necessary to reach the electron configuration of the nearest noble gas. Transition elements can vary in how they move toward lower energy configurations.

Common Cations

Group IA elements form ions with a +1 charge. They lose one electron upon ionization, moving into the electron configuration of the previous noble gas. For example as shown in Figure 3.2.1, when a sodium (Na) atom is ionized, it loses one of its 11 electrons, becoming a sodium ion (Na^+) with the electron configuration that looks like the previous noble gas, neon. The sodium ion has one fewer electron than it has protons, so it has a single positive charge and is called a cation.

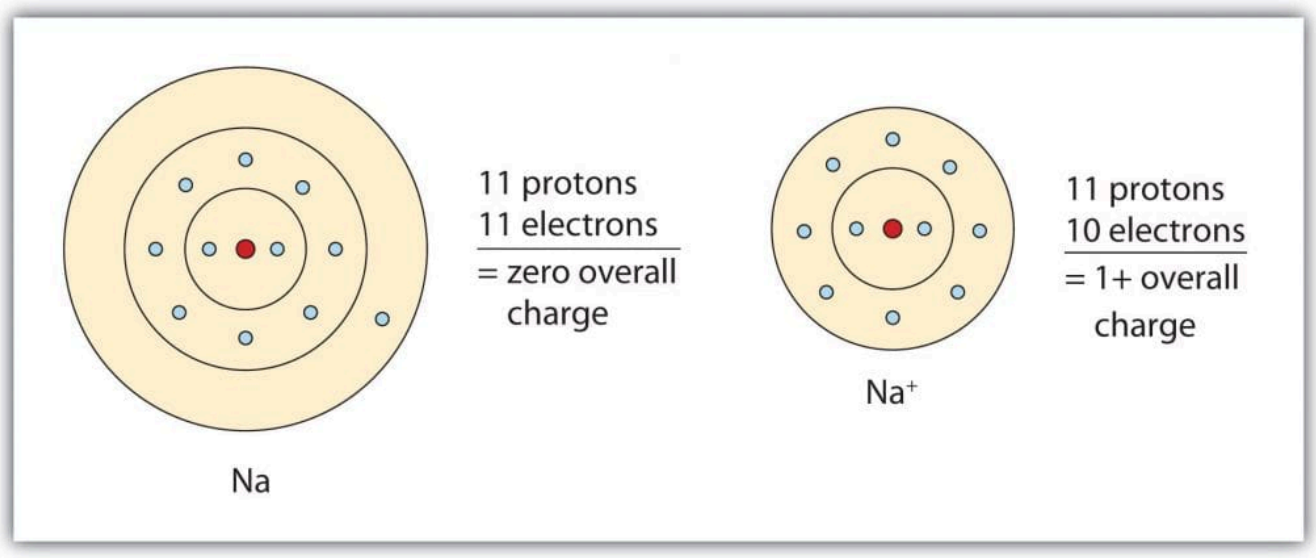


Figure 3.2.1**: Formation of a Sodium Ion.** Sodium tends to lose it's valence shell electron in the third shell during ionic bond formation. It is left with a full octet in the second shell and now has the electron configuration of neon. Note that it still has the same number of protons (11) as the original sodium atom and retains the identity of sodium. However, there are now only 10 electrons within the electron cloud, resulting in a net positive (+1) charge.

Upon losing that electron, the sodium ion now has an octet of electrons from the second principal energy level. The equation below illustrates this process.

$$\begin{aligned} \mathrm{Na} &\longrightarrow \mathrm{Na^+ + e^-} \\ 1s^2\,2s^2\,2p^6\,3s^1 &\longrightarrow 1s^2\,2s^2\,2p^6\ (\text{octet}) \end{aligned} \tag{3.2.1}$$

The electron configuration of the sodium ion 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. Consider a similar process with magnesium and with aluminum:

$$\begin{aligned} \mathrm{Mg} &\longrightarrow \mathrm{Mg^{2+} + 2e^-} \\ 1s^2\,2s^2\,2p^6\,3s^2 &\longrightarrow 1s^2\,2s^2\,2p^6\ (\text{octet}) \end{aligned} \tag{3.2.2}$$

$$\begin{aligned} \mathrm{Al} &\longrightarrow \mathrm{Al}^{3+} + 3\mathrm{e}^- \\ 1s^2\,2s^2\,2p^6\,3s^2\,3p^1 &\longrightarrow 1s^2\,2s^2\,2p^6 \text{ (octet)} \end{aligned} \tag{3.2.3}$$

In this case, the magnesium atom loses its two valence electrons in order to achieve the same noble-gas configuration. The aluminum atom loses its three valence electrons. The Mg^{2+} ion, the Al^{3+} ion, the Na^+ ion, and the elemental Ne atom are all isoelectronic. For most elements under typical conditions, three electrons is the maximum number that will be lost or gained. Only larger atoms, such as lead and uranium, can typically carry larger charge states.

Overall, Group IIA elements lose two valence electrons to reach the electron configuration of the noble gas preceding them in the periodic table and Group IIIA elements lose three electrons to form ions with a +3 charge. This gives them the electron configuration of the noble gas that comes before them in the periodic table.

While hydrogen is in the first column, it is not considered to be an alkali metal, and so it does not fall under the same classification as the elements below it in the periodic table. This is because hydrogen only has an s-subshell and can only house a total of 2 electrons to become filled and obtain the electron configuration of helium. Thus, instead of following the octet rule, it reaches greater stability by gaining a "duet" of electrons through bonding with other atoms. Thus, hydrogen can form both covalent bonds and ionic bonds, depending on the element that it is interacting with. When it participates in ionic bonds, it most often will lose its electron forming a +1 cation. Note, that hydrogen only has one electron to begin with, so when it loses an electron in the ionized state, there is only a single proton left in the nucleus of the atom. Thus, when hydrogen is ionized to H^+ it is often referred to as a *proton*. It can also be ionized, forming a -1 anion. In this case, the H^- anion is named using standard convention forming the hydride ion. During the ionization of hydrogen, the H^+ state is more common than the H^- state. In addition, the H^+ ion is very important in the chemistry of acids. *Acids* are defined as compounds that donate H^+ ions in aqueous solutions, and will be discussed in more detail in Chapter 9.

Note: Despite our focus on the octet rule, we must remember that for small atoms, such as hydrogen, helium and lithium, the first shell is the outermost shell and holds only two electrons. Therefore, these atoms satisfy a ***duet rule***, rather than an octet rule.

Example 3.2.1

A sodium atom has one valence electron in its outer shell. 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 this happens, it becomes an ion with a net positive charge of +1. This can be illustrated as follows:

Analysis of a Sodium Atom vs a Sodium Ion

Sodium Atom		Sodium Ion	
11 Protons	+11	11 Protons	+11
11 Electrons	-11	10 electrons	-10
	Overall Charge = 0		Overall Charge = +1

Common Anions

Elements on the other side of the periodic table, the nonmetals, tend to gain electrons in order to reach the stable electron configurations of the noble gases that come after them in the periodic table.

Group VIIA elements gain one electron when ionized, obtaining a -1 charge. For example as shown in Figure 3.2.2, chlorine (Cl), when ionized, gains an electron to reach the electron configuration of the noble gas that follows it in the periodic table, argon. This gives it a single negative charge, and it is now a chloride ion (Cl^-); note the slight change in the suffix (-ide instead of -ine) to create the name of this anion.

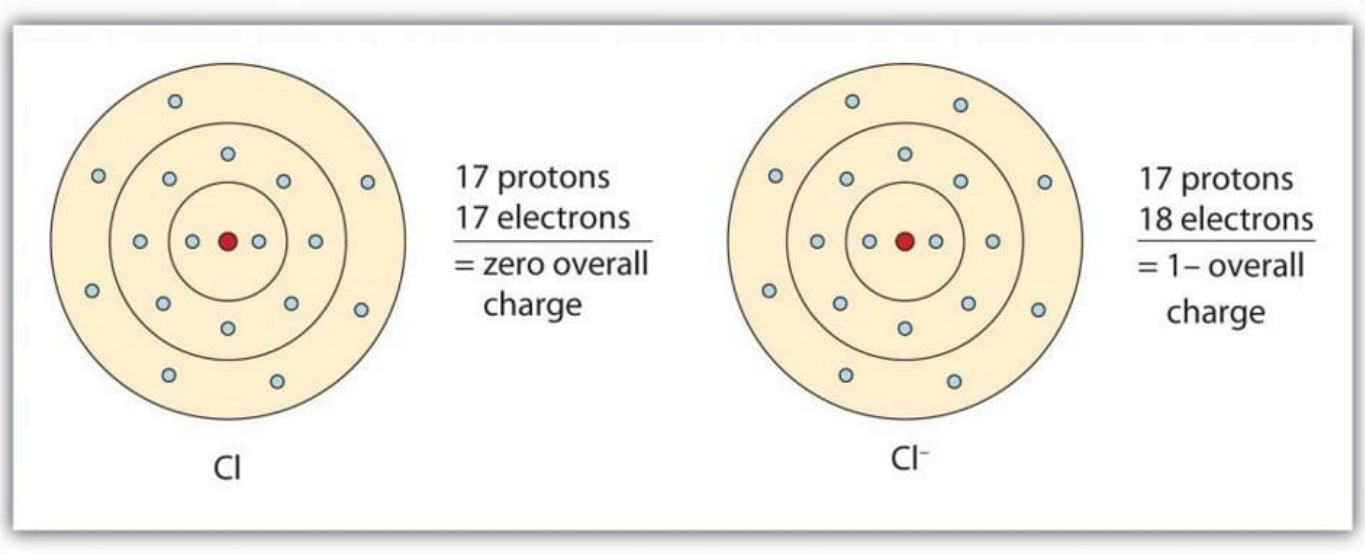


Figure 3.2.2**: The Formation of a Chloride Ion.** On the left, a chlorine atom has 17 electrons. On the right, the chloride ion has gained an extra electron for a total of 18 electrons and a 1^- charge. Note that the chloride ion has now filled its outer shell and contains eight electrons, satisfying the octet rule.

Group VIA elements gain two electrons upon ionization, obtaining -2 charges and reaching the electron configurations of the noble gases that follow them in the periodic table. Whereas, Group VA elements gain three electrons, obtaining -3 charges and also reaching the electron configurations of the noble gases that follow in the periodic table.

When nonmetal atoms gain electrons, they often do so until their outermost principal energy level achieves an octet. This process is illustrated below for the elements fluorine, oxygen, and nitrogen.

$$\begin{aligned} \mathrm{F} + \mathrm{e}^- &\longrightarrow \mathrm{F}^- \\ 1s^2\,2s^2\,2p^5 &\longrightarrow 1s^2\,2s^2\,2p^6\ (\text{octet}) \end{aligned} \tag{3.2.4}$$

$$\begin{aligned} \mathrm{O} + 2\mathrm{e}^- &\longrightarrow \mathrm{O}^{2-} \\ 1s^2\,2s^2\,2p^4 &\longrightarrow 1s^2\,2s^2\,2p^6\ (\text{octet}) \end{aligned} \tag{3.2.5}$$

$$\begin{aligned} \mathrm{N} + 3\mathrm{e}^- &\longrightarrow \mathrm{N}^{3-} \\ 1s^2\,2s^2\,2p^3 &\longrightarrow 1s^2\,2s^2\,2p^6\ (\text{octet}) \end{aligned} \tag{3.2.6}$$

Isoelectronic Species

Notice something interesting about sodium and chlorine, and the other ions that we've been discussing?

Although sodium **loses** an electron and chlorine **gains** an electron, **both achieve stable electron configurations by attaining a full outer electron shell**.

Atoms or ions that possess the **same number and arrangement of electrons** are called **isoelectronic**.

For example, each of the following species contains **10 electrons** and has the same electron configuration as Neon: N^{3-}, O^{2-}, F^-, Ne, Na^+, Mg^{2+}, and Al^{3+}. Although these species have identical electron configurations, they are **not the same element** because they contain different numbers of protons. Figure 3.2.3 shows the **neon isoelectronic series**.

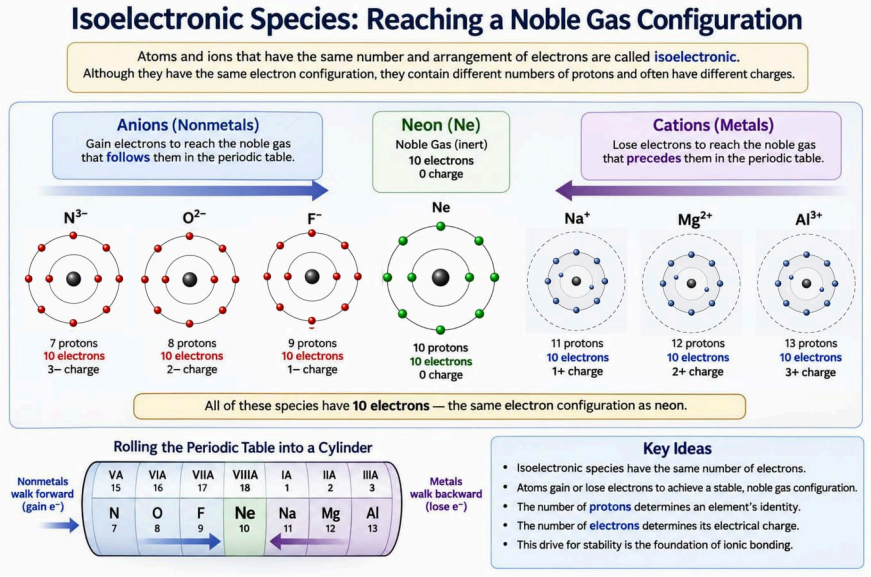


Figure 3.2.3**: The Neon Isoelectronic Series.** Each species contains ten electrons and therefore has the same electron configuration as neon. Although they are isoelectronic, they remain different elements because each contains a different number of protons.

This illustrates an important principle:

> **Key Idea**
>
> The number of **protons** determines an element's identity. The number of **electrons** determines its electrical charge.

Thus, sodium ions are chemically very different from neon atoms, even though they are isoelectronic. Likewise, the other members of the neon isoelectronic series have different identities, chemical properties, and biological roles because each contains a different nucleus.

Using the Periodic Table to Predict Ions

Fortunately, you do not need to memorize every common ion. The periodic table provides a simple way to predict how many electrons an atom is likely to gain or lose.

Figure 3.2.4 illustrates a useful way to visualize this idea by imagining the periodic table rolled into a cylinder so that the metals and nonmetals wrap around toward the noble gases.

Notice the pattern:

- **Metals "walk backward"** by losing the fewest electrons necessary to reach the **preceding noble gas**.
- **Nonmetals "walk forward"** by gaining the fewest electrons necessary to reach the **following noble gas**.

Rather than memorizing individual ions, think about which **noble gas configuration** an atom is trying to achieve.

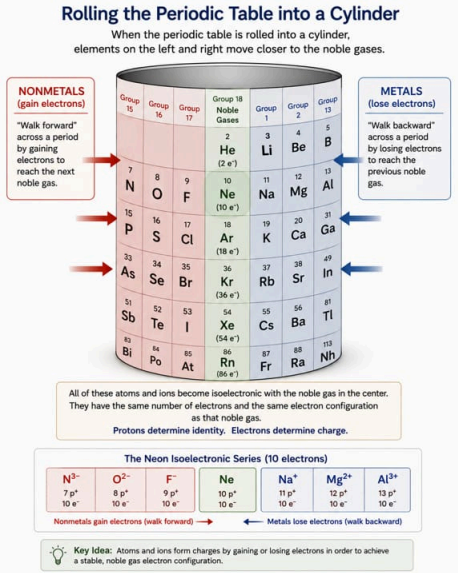


Figure 3.2.4**: Rolling the periodic table into a cylinder highlights a simple trend in ionic bonding.** One way to visualize ion formation is to imagine rolling the periodic table into a cylinder so that the main-group metals and nonmetals wrap toward the noble gases. Main-group metals generally become more stable by **losing the fewest electrons necessary** to reach the preceding noble gas, while main-group nonmetals become more stable by **gaining the fewest electrons necessary** to reach the following noble gas. The resulting ions are **isoelectronic** with the noble gas shown in the center column, meaning they have the same number and arrangement of electrons. Although these ions share the same electron configuration, they remain different elements because **protons determine identity, whereas electrons determine charge.** The "rolling the periodic table into a cylinder" visualization was inspired by a teaching analogy developed by Dr. Ray Dandeneau.

Key Idea

- **Main-group atoms tend to gain or lose the fewest electrons necessary to achieve the electron configuration of the nearest noble gas.** This simple principle explains why many ions form predictable charges and provides a powerful way to understand ionic bonding.

Chemistry Connection

Hydrogen: A Special Case

Hydrogen occupies Group 1 but is **not** an alkali metal. Because it contains only one energy level, hydrogen follows the **duet rule** rather than the octet rule.

Depending on the atoms with which it interacts, hydrogen may:

- lose one electron to form **H**, or
- gain one electron to form **H** (the hydride ion).

The **H ion** is especially important in biology because acids donate hydrogen ions in aqueous solution. We will revisit hydrogen ions and their role in acid-base chemistry later in this textbook.

Key Ideas:

- Cations form when an atom loses one or more electrons.

- The resulting cation has the electron configuration of the noble gas atom in the row above it in the periodic table.
- Anions form when an atom gains one or more electrons.
- The resulting anion has the electron configuration of the noble gas atom in the same row of the periodic table

Ions of Transition Metals

The transition metals are an interesting and challenging group of elements. They have perplexing patterns of electron distribution that don't always follow the electron filling rules. Predicting how they will form ions is also not always obvious.

Transition metals belong to the *d*-block, meaning that the *d*-subshell of electrons is in the process of being filled with up to ten electrons. Many transition metals cannot lose enough electrons to attain a noble-gas electron configuration. In addition, the majority of transition metals are capable of adopting ions with different charges. Iron, which forms either the Fe^{2+} or Fe^{3+} ions, loses electrons as shown below.

$$\begin{aligned} \mathrm{Fe} &\longrightarrow \mathrm{Fe}^{2+} + 2\mathrm{e}^- \\ [\mathrm{Ar}]\, 3d^6\, 4s^2 &\longrightarrow [\mathrm{Ar}]\, 3d^6 \end{aligned} \tag{3.2.7}$$

$$\begin{aligned} \mathrm{Fe} &\longrightarrow \mathrm{Fe}^{3+} + 3\mathrm{e}^- \\ [\mathrm{Ar}]\, 3d^6\, 4s^2 &\longrightarrow [\mathrm{Ar}]\, 3d^5 \end{aligned} \tag{3.2.8}$$

According to the Aufbau process, the electrons fill the 4s sublevel before beginning to fill the 3*d* sublevel. However, the outermost s electrons are always the first to be removed in the process of forming transition metal cations. Because transition metals have two valence electrons, the charge of 2+ is a very common one for their ions. This is the case for iron above. In addition to the 2+ state, iron can also form a 3+ cation. This is because a half-filled *d* subshell (d^5) is particularly stable, which is the result of an iron atom losing a third electron.

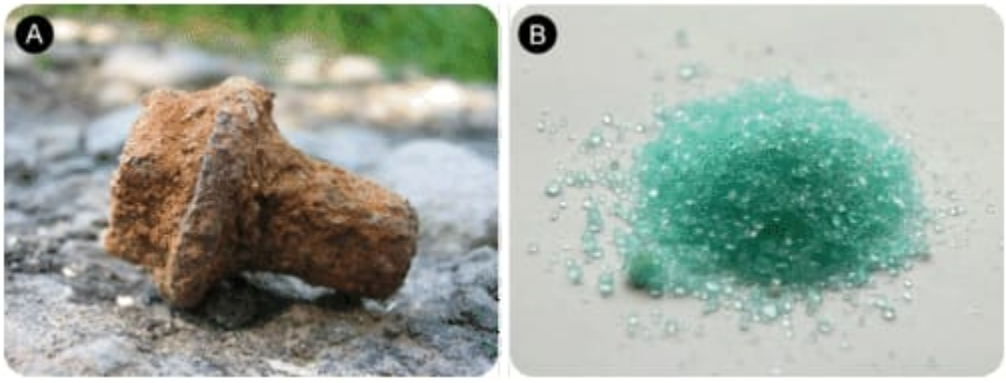


Figure 3.2.5: Iron Compounds and the Formation of Rust. (A). Rust is a complex combination of oxides of iron, among them iron (III) oxide, Fe_2O_3. (B) Iron (II) sulfate, $FeSO_4$ is an example of a compound that contains iron in the 2+ cationic state. It has been known since ancient times as green vitriol and was used for centuries in the manufacture of inks.

Some transition metals that have relatively few *d* electrons may attain a noble gas electron configuration. Scandium is an example.

$$\begin{aligned} \mathrm{Sc} &\longrightarrow \mathrm{Sc}^{3+} + 3\mathrm{e}^- \\ [\mathrm{Ar}]\, 3d^1\, 4s^2 &\longrightarrow [\mathrm{Ar}] \end{aligned} \tag{3.2.9}$$

Others may attain stable configurations with a full d-subshell, such as zinc and copper.

$$\begin{aligned} \mathrm{Zn} &\longrightarrow \mathrm{Zn^{2+} + 2e^-} \\ [\mathrm{Ar}]\,3d^{10}\,4s^2 &\longrightarrow [\mathrm{Ar}]\,3d^{10} \end{aligned} \tag{3.2.10}$$

$$\begin{aligned} \mathrm{Cu} &\longrightarrow \mathrm{Cu^{+} + e^-} \\ [\mathrm{Ar}]\,3d^{10}\,4s^1 &\longrightarrow [\mathrm{Ar}]\,3d^{10} \end{aligned} \tag{3.2.11}$$

The resulting configuration above, with 18 electrons in the outermost principal energy level, is referred to as a *pseudo noble-gas electron configuration*. It gives particular stability to the Zn^{2+} and Cu^{+} ions.

Figure 3.2.6 depicts the most common ionic states of the elements and shows the two most common ionic states for elements that can form more than one ion.

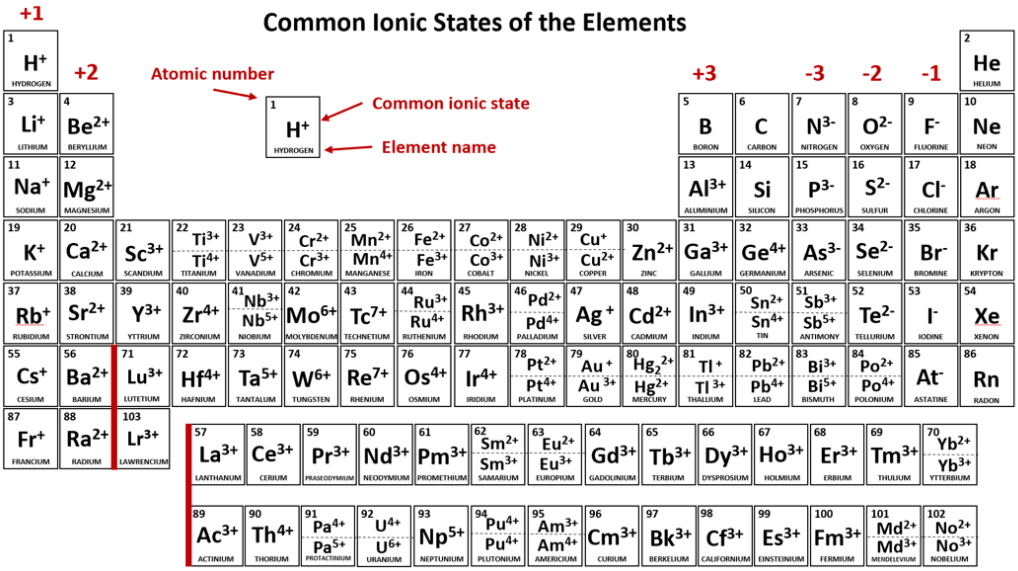


Figure 3.2.6**: Common Ionic States of the Elements.** For elements that have more than one common ionic state, both states are listed. Note that when mercury carries a +1 charge, it forms an uncommon polyatomic ionic state, Hg_2^{2+} where two Hg atoms share electrons and then each also have a +1 charge state (see section XX for more details about polyatomic ions and Hg_2^{2+}). For the printable PDF version of this table (with the common polyatomic ions), click the link below:

Periodic Table with Ions

Key Ideas:

- Transition metal ion formation is more complex than simple cation formation
- Transition metal ions often involve rearrangements of both *d* and s electrons to accomodate different ionic states

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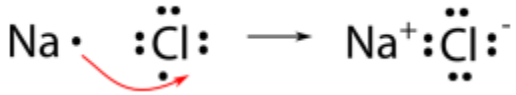
3.3: Ionic Bonding

Donating and Accepting Electrons

Most of the rocks and minerals that make up the Earth's crust are composed of positive and negative ions held together by ionic bonding. An ionic compound is an electrically neutral compound consisting of positive and negative ions. You are very familiar with some ionic compounds such as sodium chloride (NaCl). A sodium chloride crystal consists of equal numbers of positive sodium ions (Na^+) and negative chloride ions (Cl^-).

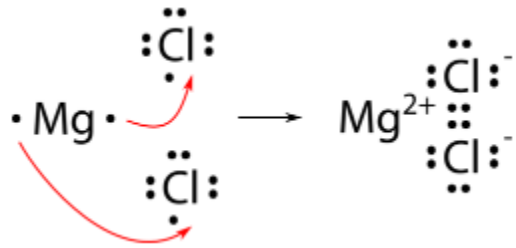
Anions and cations have opposing charges. Because of this, they are attracted to one another. When an anion and a cation are drawn together due to this electrostatic attraction, they can form an *ionic bond*. This kind of bond is the result of opposing charges attracting one another, and is distinct from other types of bonding. Two or more ions bound by electrostatic attraction make an *ionic compound*. The simplest ionic compounds are *binary ionic compounds* or those that only contain two atoms, one acting as the cation, and one acting as the anion. Thus, we will focus on the formation of binary ionic compounds first.

Sodium chloride, or table salt, is an ionic compound. Let's take a look at how it is formed. During the formation of sodium chloride, the electron given off by sodium is taken by chlorine, forming the chloride ion. The chloride ion has one excess electron, giving it a -1 charge. The result of this electron transfer is that the sodium cation and chloride anion become bound through electrostatic attraction, forming sodium chloride, an ionic compound. Note that, electrons cannot be simply "lost" to nowhere in particular, they always end up going to another atom or molecule. Ionic reactions can be represented by electron dot diagrams, as shown below for sodium chloride.



The ionic bond is the attraction of the Na^+ ion for the Cl^- ion. It is conventional to show the cation without dots around the symbol to emphasize that the original energy level that contained the valence electron is now empty. The anion is now shown with a complete octet of electrons. The final formula for sodium chloride is NaCl. Notice that both ions are represented but their charges are not shown. This is because within ionic compounds the overall charge on the compound is zero, i.e. the charge states of the cation(s) and the anion(s) involved in the bond need to be paired in such a way that the number of positive charges equals the number of negative charges. For sodium chloride this is an easy task as one chloride ion has a -1 charge and one sodium ion has a positive charge +1, cancelling each other to zero. Also note that in chemical formulas that the cation always comes first and the anion is always placed second in the formula.

For a compound such as magnesium chloride, it is not quite as simple. Because magnesium has two valence electrons, it needs to lose both to achieve the noble-gas configuration. Therefore, two chlorine atoms will be needed.



The final formula for magnesium chloride is $MgCl_2$. Note that the subscript (2) next to the chloride ion, indicates that there are two chloride ions paired with each magnesium cation. When there is only one ion present in a formula, (i.e the magnesium ion in this case), the subscript of one is implied instead of shown in the formula. As in the case of NaCl, there are no charges shown in the final formula of $MgCl_2$. This is because the positive charge of the magnesium ion (+2) is balanced by the negative charge of the two chloride ions [2 X (-1) = -2] giving the overall molecule a net charge of zero.

Key Ideas

- An ionic compound contains positive and negative ions
- An ionic bond is electrostatic in nature (ie. the oppositely charged ions are attracted to each other, forming the bonded association)
- Electron dot diagrams can be used to illustrate electron movements and ion formation
- Stable ionic compounds have a balanced charge state such that the charge on the overall molecule is zero

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3.4: Practice Writing Correct Ionic Formulas

Predicting the Correct Subscripts

To predict and write correct chemical formulas, the key fundamental steps that are required, are (1) knowing the charge states of the ions and (2) using basic math to help you determine how many cations and anions are needed to reach a zero charge state, (3) writing the chemical forumulas with the cation first followed by the anion, and (4) writing the formula with the lowest ratio of cations and anions to create a net neutral compound.

Overall, ionic bonding occurs between a cation (electron donor) and an anion (electron acceptor) to form a compound that has an overall neutral net charge. Of note, ionic bonds usually occur between a metal and a nonmetal. This will help you recognize ionic compounds more easily, once we learn about covalent bonding (which occurs most commonly between two nonmetals, or between a nonmetal and a semimetal (metalloid).

So, say we want to write the correct chemical formula for a molecule that contains Fe^{3+} as the cation, and Cl^{-} as the anion. What is the correct ionic formula?

To begin this type of problem, I recommend drawing out a charge box or a charge table to help you keep track of the number of ions used, the charges of those ions, and the overall positive and negative charges on the molecule. Drawing out the electron dot symbols can also be helpful. Here is an example of a generic charge box

	CATION	ANION	
CHARGE of ION			
# ATOMS			Total Charge (on the Molecule)
TOTAL ION CHARGE			

Let's try it out for our example of Fe^{3+} and Cl^{-}. First, let's fill in what we know about each element and it's ionic state:

	Fe	Cl	
CHARGE of ION	+3	-1	
# ATOMS			Total Charge (on the Molecule)
TOTAL ION CHARGE			

So now we have our charge box set up with our known information. Now we need to figure out how many atoms of the cation and the anion are required to cancel out the overall positive and negative charge on the resulting molecule. To do this, it is often useful to use the cross-multiplication strategy, where you try using the charge number for the cations, as the number of atoms of anion required, and the charge number for the anion as the number of atoms of the cation required. Multiply each of the ion charges by the number of atoms to calculate the total ion charges of the cation(s) and anion(s) present and then add these numbers together to find the total charge on the compound. This will usually get you to the stable ionic formula that has a net neutral charge of zero.

	Fe	Cl	
CHARGE of ION	+3	-1	
# ATOMS	1	3	Total Charge (on the Molecule)
TOTAL ION CHARGE	+3	-3	= 0

The # of atoms column then becomes the subscripts that you need to use to construct the correct ionic formula. In this case 1 atom of iron (Fe) with 3 atoms of chlorine (Cl) for a formula of $FeCl_3$.

The previous example is pretty straight forward, and you may have been able to construct the formula in you head. However, as the complexity of formula making increases, it is good to be able to use the charge box method to double check your work. For example, what would the correct ionic formula be for aluminum sulfide? First, identify the two atoms involved (Aluminum and Sulfur) and start building your charge box with what you know from the periodic table. From the periodic table in Figure 3.7, you can see that aluminum forms a cation with a +3 charge whereas sulfur forms an anion with a -2 charge state.

	Al	S	
CHARGE of ION	+3	-2	
# ATOMS	2	3	Total Charge (on the Molecule)
TOTAL ION CHARGE	+6	-6	= 0

For step 1: Add in the correct charge for the cation and anion in question, in this case +3 for Al and -2 for S. For Step 2: Use the cross multiply rule to predict how many atoms will be needed from each type and multiply through the total ion charge for both the cation and anion. For Step 3: Add the products together to be sure that your compound is stable and the net charge on the formula is zero. Step 4: Use the # Atoms value to create the subscripts for your chemical formula. In our example, we require 2 atoms of Al and 3 atoms of S. This would be written as Al_2S_3 as the final product.

Key Ideas

- When writing chemical formulas, the cation is always first and the anion is always last
- Stable chemical formulas must be written so that the overall compound has a net neutral charge (ie the total positive charge = the total negative charge)
- Subscripts are used to show how many atoms are present within the ionic formula

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3.5: Naming Ions and Ionic Compounds

Some compounds have common names, like *water* for H_2O. However, there are thousands of other compounds that are uncommon or have multiple names. Also, the common name is usually not recognized internationally. What looks like *water* to you might look like *agua* or *vatten* to someone else. To allow chemists to communicate without confusion, there are naming conventions to determine the systematic name of a chemical. For the chemistry naming system in this text, we will primarily be using the International Union of Pure and Applied Chemistry (IUPAC) naming system. Note that there is also an older and more archaic (-ous and -ic) naming system, in addition to the IUPAC system. In some instances the older naming system is still in high use. These deviations from the IUPAC system will be noted throughout the text, as you will likely still see this older nomenclature still in use within chemical laboratories and the health sciences field.

The convention for naming cations is very easy. It is simply to take the element name and add the term 'ion' to the end of it. So if we are referring to a sodium atom that has lost one electron (Na^+), we would use the term sodium ion. This indicates that sodium is in the +1 charge state, rather than the elemental form of sodium (which has an equal number of protons and electrons and is neutral in charge). Using the ion naming system when referring to ions, rather than the elemental names of atoms is important, as the reactivity of the ion vs the elemental form of a substance can be quite different. For example, if you add the sodium ion to your glass of drinking water in the form of NaCl (or table salt), you will have a nice salty drink on your hands. On the other hand, if you add the elemental form of sodium to your glass of drinking water, it will explode in your face, as the elemental form of sodium is very reactive with water!

For cations that have more than one charge state the name of the atom is followed by a roman numeral and then the term ion, to distinguish the different ionic states. For example, iron has two predominant ionic forms, Fe^{2+} and Fe^{3+}. Thus, in naming these two ions, we would refer to the first one as the iron (II) ion, and the second as the iron (III) ion. This way, there is no confusion about which ion is being referred to when discussing a compound.

Naming anions is a little more complicated. The ending of the element is typically dropped and replaced with the 'ide' ending followed by the term ion. For example, Cl^- is referred to as the chloride ion, rather than the chlorine ion. In this case, the '-ine' ending of chlorine is dropped and replaced with the 'ide' ending. For sufur, the '-ur' ending is dropped and replaced with 'ide' to form the sulfide ion. Similarly phosphorus is converted to the phosphide ion, nitrogen to the nitride ion, and oxygen to the oxide ion. The '-ide' ending is useful because it helps the listener distinguish very quickly between the different types of ions being discussed (the cation which retains the element name vs. the anion which changes the elemental name to the '-ide' ending).

When naming ionic compounds the term ion is dropped and the cation and anion names are placed together, with the cation always listed first and the anion listed last. If the elements involved in the ionic bond only have one possible ionic state, no roman numerals are needed in the name. For example, when the Na^+ and the Cl^- come together to make NaCl, the resulting compound is called sodium chloride. Similary, if Mg^{2+} and Cl^- come together to make $MgCl_2$, the resulting compound is called magnesium chloride. However, if the elements involved in the ionic bond have more than one possible ionic state, the roman numeral system is used to clarify which ion is participating in the bond. For example, if Fe^{3+} and Cl^- come together to form $FeCl_3$, we will need to distinguish it from Fe^{2+} coming together with Cl^- to form $FeCl_2$ in the name so that everyone will understand which ion of iron is being referred to in the reaction. In this case, the first compound will be called iron (III) chloride, and the second compound is iron (II) chloride.

The key feature about naming ionic compounds is that you should be able to draw the structure from the name, and that you should be able to create the name from the structure.

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3.6: Polyatomic Ions

Ions Created by More than One Atom

Up until now, we have been looking at compounds involving monoatomic ions, or ions that occur with a single atom. However, many commonly found ions are composed of multiple atoms that are bound to one another through the sharing of electrons, or covalently. These ions behave as a single unit, bearing a charge and interacting with other ions and compounds just like the monatomic ions discussed above. Because these ions are made of multiple atoms, they are called *polyatomic ions*. It is more common for polyatomic ions to be negatively charged than to be positively charged. Below is a chart showing some commonly encountered polyatomic ions.

Table 3.6A Common Polyatomic Anions

Polyatomic Anions					
acetate	CH_3COO^- or $C_2H_3O_2^-$	dichromate	$Cr_2O_7^{2-}$	orthosilicate	SiO_4^{4-}
asenate	AsO_4^{3-}	dihydrogen phosphate	$H_2PO_4^-$	oxalate	$C_2O_4^{2-}$
arsenite	AsO_3^{3-}	hydrogen carbonate (bicarbonate)	HCO_3^-	perchlorate	ClO_4^-
benzoate	$C_6H_5COO^-$	hydrogen oxalate	$HC_2O_4^-$	periodate	IO_4^-
borate	BO_3^{3-}	hydrogen sulfate	HSO_4^-	permanganate	MnO_4^-
bromate	BrO_3^{3-}	hydrogen sulfide	HS^-	peroxide	O_2^{2-}
carbonate	CO_3^{2-}	hydrogen sulfite	HSO_3^-	phosphate	PO_4^{3-}
chlorate	ClO_3^-	hydroxide	OH^-	pyrophosphate	$P_2O_7^{4-}$
chlorite	ClO_2^-	hypochlorite	ClO^-	sulfate	SO_4^{2-}
chromate	CrO_4^{2-}	iodate	IO_3^-	sulfite	SO_3^{2-}
cyanate	CNO^-	monohydrogen phosphate	HPO_4^{2-}	thiocyanate	SCN^-
cyanide	CN^-	nitrate	NO_3^-	thiosulfate	$S_2O_3^{2-}$
		nitrite	NO_2^-		

Table 3.6B Common Polyatomic Cations

Polyatomic Cations	
ammonium	NH_4^+
hydronium	H_3O^+
mercury I	Hg_2^{2+}

Polyatomic ions can be thought of in a very similar way to monoatomic ions, in that they are ionized by either gaining or losing electrons so that they carry a charge. If they gain electrons, they will become an anion and carry a negative charge, and if they lose electrons, they will become a cation and carry a positive charge. The charge of a polyatomic ion is represented as a supercript that is placed at the upper righthand edge of the ion. For example, for the phosphate ion, the chemical formula is PO_4^{3-}. This indicates that the overall -3 charge is distributed to the entire PO_4 molecule, and that when it is involved in forming an ionic

compound, the entire PO_4^{3-} ion moves as and is treated as a single unit. Let's try making a few compounds using phosphate as an example. First let's build a molecule of sodium phosphate. Note that when you are asked to build molecules from their name, you can often recognize when you have a polyatomic ion due to the name. Recall that monoatomic anions end in the suffix '-ide'. Thus, when you see a different suffix ending, such as '-ate' or '-ite', this should indicate that you are dealing with a polyatomic ion and you should refer to the table above to help you discern the correct ion formula to use. For the sodium phosphate example, we can build this molecule using the same charge box diagram that we used above to construct the simpler biatomic structures above. First we need to place the ions and their charge states into the table. In this case, we know that sodium is a cation with a +1 charge and the phosphate ion is an anion with a -3 charge.

	Na	PO_4	
CHARGE of ION	+1	-3	
# ATOMS			Total Charge (on the Molecule)
TOTAL ION CHARGE			

Note that in our table, we are treating the polyatomic ion as a single unit. We can then continue to use our cross multiplication strategy to determine how many cations and anions are needed to create an overall molecule that is neutral in charge.

	Na	PO_4	
CHARGE of ION	+1	-3	
# ATOMS	3	1	Total Charge (on the Molecule)
TOTAL ION CHARGE	+3	-3	= 0

Thus, we will need 3 atoms of sodium and one molecule of phosphate to complete our structure. Overall the chemical formula of sodium phosphate is written as Na_3PO_4. Note that the naming of the resulting molecule is done in exactly the same way as with other ionic compounds. The name of the cation comes first (using roman numerals when necessary) followed by the name of the anion (in this case phosphate).

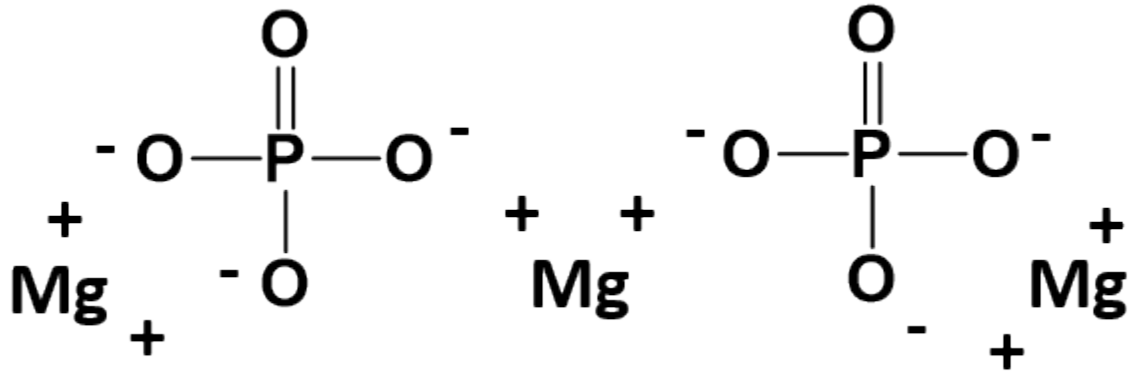
How about a more complicated example? How would we make a molecule of magnesium phosphate? Start building your molecule using the charge box diagram, noting this time that magnesium forms and Mg^{2+} ion.

	Mg	PO_4	
CHARGE of ION	+2	-3	
# ATOMS	3	2	Total Charge (on the Molecule)
TOTAL ION CHARGE	+6	-6	= 0

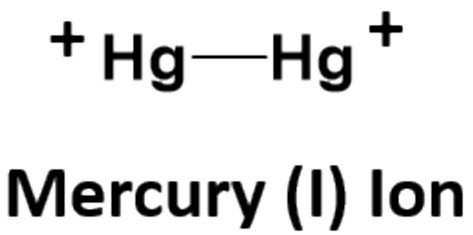
Setting up the charge box for this compound is not more difficult than any other compound. However, one must be careful when writing out compounds that require more than one polyatomic ion within the chemical formula. In this case we need 2 phosphate ions to combine with 3 magnesium ions to form magnesium phosphate. The cation in this case is written the same, however, parentheses are needed when expressing the 2 phosphate ions, as follows:

$$\mathbf{Mg_3\,(PO_4)_2} \tag{3.6.1}$$

The parentheses around the phosphate ion ensure that it is clear that you need two entire PO_4^{3-} ions within this complex. A structural diagram of what this molecule would look like is shown below. Note that each straight line is being used here to indicate a covalent bond within the phosphate ion. Each straight line represents two electrons (or an electron pair) that is being shared between the atoms. Covalent bonding will be described in more detail in chapter 4. For now, it is important to remember that the polyatomic ions move together as a single unit because the atoms that are sharing electrons must stay in close proximity with one another. The ionic bonds are indicated with the (+) and (-) symbols. For magnesium phosphate there are a total of 6 ionic bonds that are formed.

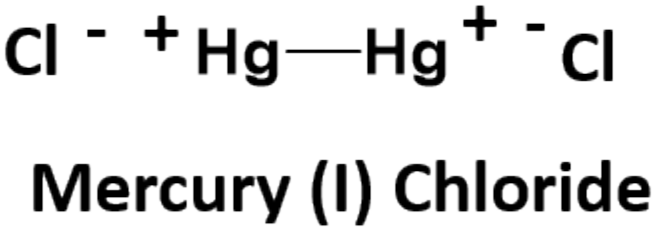


Another strange example is mercury (I) chloride. This one is an exception to our normal bonding rules. You would predict based on charge possibilities that mercury (I) chloride should have the chemical formula of HgCl, as the chloride ion has a charge of -1, and mercury (I) is indicated to have a charge of +1. However, in this unique case, this formula is incorrect. Mercury is unusual in that its singly ionized oxidation state, mercury(I), is found as a dimeric cation, Hg_2^{2+}, where two atoms of mercury are actually covalently bonded to one another as a polyatomic ion. Each mercury atom within the bonded pair has a charge state of +1. This give the overall ion a +2 state, as shown below:



Mercury (I) Ion

Unfortunately, this polyatomic ion does not have a unique name that distinguishes it from normal monoatomic cations. Thus, you will need to remember this unique member. The final mercury (I) chloride chemical formula needs 2 chloride ions to complete the structure, for a minimal chemical formula of Hg_2Cl_2.



Mercury (I) Chloride

While mercury (I) chloride is rarely found in nature, during the 18th and 19th centuries, known as calomel, it was commonly used as medicine to treat infectious diseases like syphilis and yellow fever. It was also used as a general tonic to make patients regurgitate and release their body from 'impurities'. Calomel had extreme side effects and toxicity during its medical use causing both loss of hair and teeth. In fact, calomel was also a common ingredient in teething powders in Britain up until 1954, causing widespread mercury poisoning in the form of pink disease, which at the time had a mortality rate of 1 in 10. Once the cause of pink disease was linked with mercury toxicity, the substance was removed from these powders. In the United States, its use faded in the late 1800's with the discovery of more effective treatments, such as the discovery of penicillin in the late 19th century by Alexander Flemming.

Abraham Lincoln and "Blue Mass"

"Blue mass," a medication that consisted of elemental mercury with various additives, was commonly used for all kinds of complaints in the Civil War-era United States. Though mercury was a known toxin, it was a prominent feature in medical treatment for "hypochondriasis," a condition that may have included various problems we now understand as mood disorders, along with digestive system issues. Abraham Lincoln was known to exhibit the symptoms of hypochondriasis, and he took the blue mass medication. Interestingly, he was known by friends and acquaintances to suffer from insomnia and erratic mood, and there is some evidence that he displayed additional neurological abnormalities. These are symptoms of mercury poisoning. Within the body, elemental mercury, which is uncharged, is oxidized to its mercuric form (Hg^{2+}), which has a +2 charge. This form of mercury is devastating to many body systems, causing dysfunction that may have been responsible for Abraham Lincoln's symptoms. His treatment may have been more harmful than the problems for which it was intended, due to medicine's lack of understanding.

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3.7: Naming Polyatomic Ions

Features of Polyatomic Names

Polyatomic ions have special names. Many of them contain oxygen and are called oxyanions. When only one oxyanion for an element exists, the ending of the primary element is given the '-ate' ending. For example, the oxyanion of carbon is called carbonate (CO_3^{2-}). However, when different oxyanions exist using the same element but have a different number of oxygen atoms, prefixes and suffixes are used to tell them apart. For example, if two oxyanions exist, the one with the lower number of oxygens will be given the '-ite' ending and the one with more oxygens will be given the '-ate' ending. Oxyanions of nitrogen and sulfur are a good example:

$$\begin{aligned} \mathrm{NO_2^-} &= \text{Nitrite} \\ \mathrm{NO_3^-} &= \text{Nitrate} \\ \mathrm{SO_3^{2-}} &= \text{Sulfite} \\ \mathrm{SO_4^{2-}} &= \text{Sulfate} \end{aligned} \tag{3.7.1}$$

Sometimes there may be three or four oxyanions. In this case, the prefix 'hypo-' will be used to indicate one less oxygen than '-ite' form. When four oxyaions exist there is also a 'per-' prefix, meaning one more oxygen that the '-ate' form. The chlorine family of ions is an excellent example where these prefixes are needed.

$$\begin{aligned} \mathrm{ClO^-} &= \text{Hypochlorite} \\ \mathrm{ClO_2^-} &= \text{Chlorite} \\ \mathrm{ClO_3^-} &= \text{Chlorate} \\ \mathrm{ClO_4^-} &= \text{Perchlorate} \end{aligned} \tag{3.7.2}$$

Occasionally, you will see a *bi–* prefix. This is an older prefix, it means the compound can both take up and lose a proton (H^+). IUPAC nomenclature will use *hydrogen* in the name, whereas the older nomenclature uses the *bi*-prefix. In either case, the oxyanion will have a hydrogen in it, decreasing its charge by one. For instance, there is carbonate (CO_3^{2-}) and hydrogen carbonate (HCO_3^-). You may also see hydrogen carbonate referred to as bicarbonate.

One last prefix you may find is *thio-*. It means an oxygen has been replaced with a sulfur within the oxyanion. Cyanate is OCN^-, and thiocyanate is SCN^-.

Naming ionic compounds that contain polyatomic ions is done in exactly the same way as with other binary ionic compounds. The name of the cation comes first (using roman numerals when necessary) followed by the name of the anion.

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3.8: Properties and Types of Ionic Compounds

Common Features of Ionic Compounds

Ionic compounds are held together by the electrostatic forces created by the attraction of the positively charged cations and negatively charged anions. These can be simple ions such as the sodium (Na^+) and chloride (Cl^-) in sodium chloride, or polyatomic species such as the ammonium (NH_4^+) and carbonate (CO_3^{2-}) ions in ammonium carbonate. Individual ions within an ionic compound usually have multiple nearest neighbors, so are not considered to be part of individual molecules, but instead as part of a continuous three-dimensional network or lattice, usually in a crystalline structure. Figure 3.8.1 shows the structure of sodium chloride (NaCl)

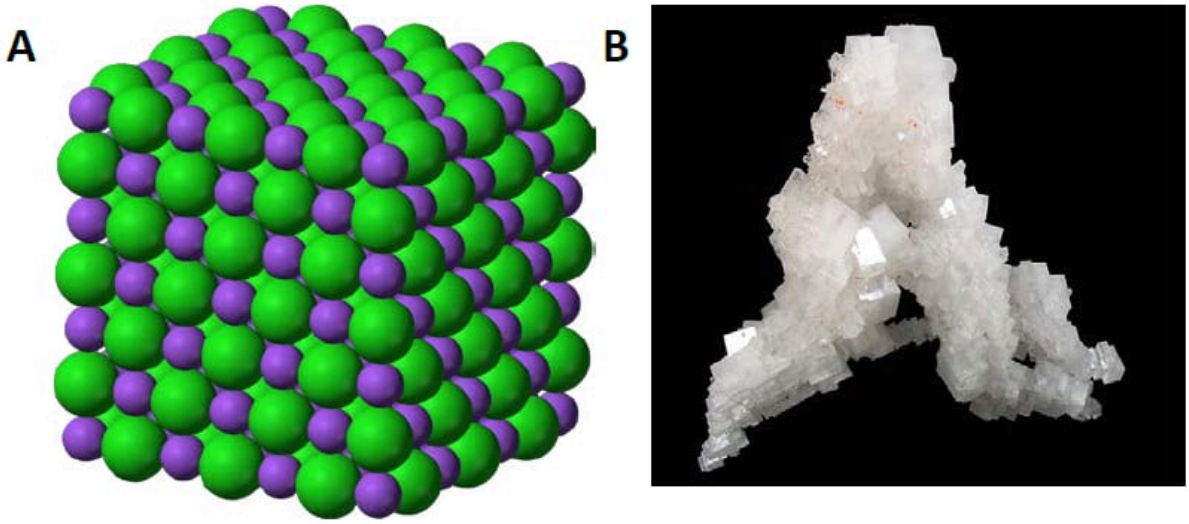


Figure 3.8.1**: Ionic Crystal Lattice.** (A) The crystal structure of sodium chloride, NaCl, a typical ionic compound. The purple spheres represent sodium cations, Na+, and the green spheres represent chloride anions, Cl–. (B) Halite, the mineral form of sodium chloride, forms when salty water evaportates leaving the ions behind.

Source: (A) Benjah-bmm27 (2010). (B) Lavisky, R. (2010) Both (A) and (B) Available at: Wikipedia [en.wikipedia.org]

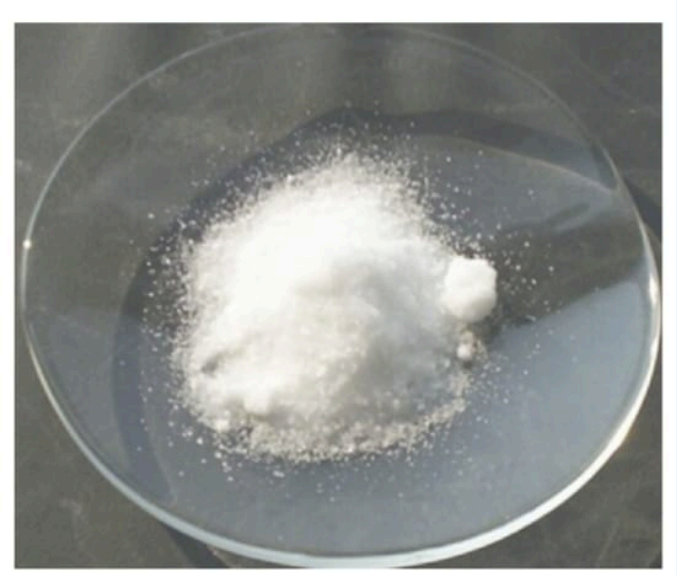
Ionic compounds containing hydrogen ions (H^+) are classified as *acids*, and those containing hydroxide (OH^-) or oxide (O^{2-}) ions are classified as *bases*. All other ionic compounds without these ions are known as *salts*. Ionic compounds typically have high melting and boiling points, and are hard and brittle. As solids, they are most often electrically insulating, but when melted or dissolved they become highly conductive, because the ions are mobilized.

Noticing ionic compounds in our every day lives

Everyday Uses for Ionic Compounds
Ionic compounds have long had a wide variety of uses and applications. Many minerals are ionic. Humans have processed common salt (sodium chloride) for over 8,000 years, using it first as a food seasoning and preservative, and now also in manufacturing, agriculture, water conditioning, for de-icing roads, and many other uses. Many ionic compounds are so widely used in society that they go by common names unrelated to their chemical identity. Examples of this include borax, calomel, mil of magnesia, oil of vitriol, and saltpeter.

Everyday Uses for Ionic Compounds	
 Photo from the Herb Museum	Mercury (I) Chloride (Hg_2Cl_2) or Calomel is a unique compound because the mercury forms a metallic bond with the other mercury atom, and then forms an ionic interaction with the two chloride ions (Cl-Hg-Hg-Cl). Calomel was once used as a treatment for infectious diseases such as syphilis, cholera, and malaria. It was used in the United States from the 1700's until the 1860's. Use was discontinued due to the neurotoxicity of the mercury and the discovery of safer treatments.
  Rio Tinto Borax Mine Pit, Boron, CA. Source: Wichary, M. (2012)	Sodium tetraborate $Na_2B_4O_7 \cdot 10H_2O$ or Borax has many uses. It is used in detergents, cosmetics, and enamel glazes. It is also used in biochemistry to make buffer solutions, has been used as a flame retardent, and as an antifungal compound. It was first discovered in dry lake beds in Tibet where it was transported via the Silk Road. Discovery of Borax in the deserts of California and Nevada in the late 1800's made it readily available in the United States.

Everyday Uses for Ionic Compounds	
 Source: Nosferattus (2022)	Magnesium Hydroxide, $Mg(OH)_2$, or Milk of Magnesia is a basic, ionic compound that is a common component of antacids and laxatives. As an antacid, milk of magnesia simply reduces the acidity of the stomach through a simple acid-base neutralization reaction: $OH^- + H^+ \rightarrow H_2O$ As a laxative, Mg^{2+} is poorly absorbed from the intestinal tract, so it draws water from the surrounding tissue via osmosis.
 Drops of sulfuric acid quickly decompose a cotton towel Source: Toxic Walker	Sulfuric Acid, H_2SO_4, or Oil of Vitriol is a highly corrosive acid that can be derived from a category of glassy minerals originally called green vitriol (iron II sulfate). Sulfuric acid is a highly utilized industrial compound with over 180 million tons produced annually. Most is used in the production of fertilizer (~60%). It is also required for the production of many detergents, synthetic resins, dyes, pharmaceuticals, insecticides, and antifreeze, among others.

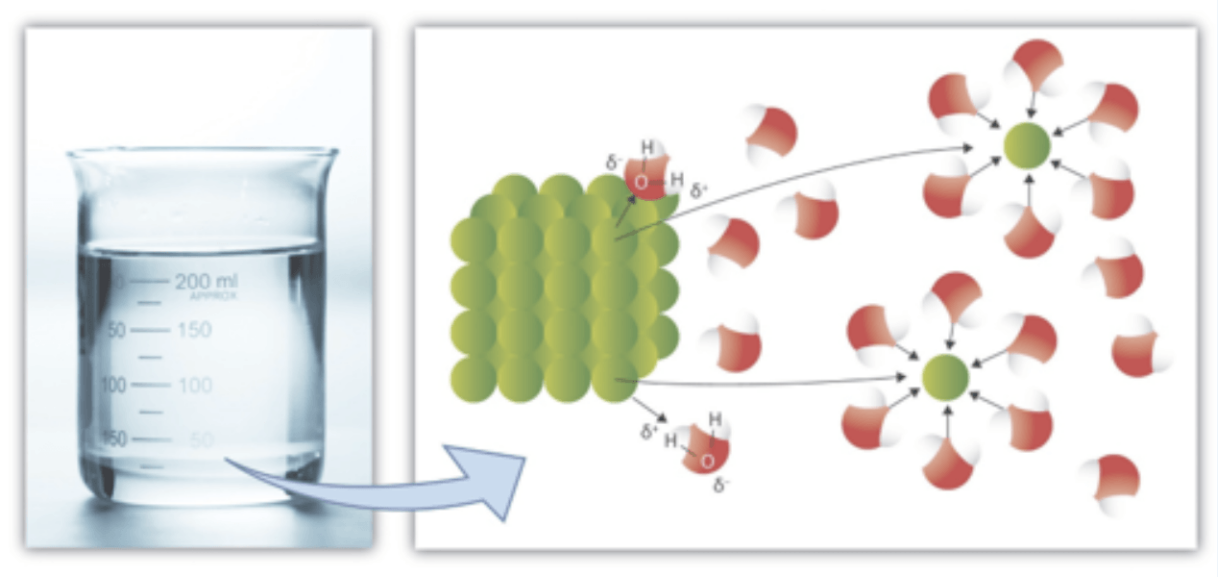
Everyday Uses for Ionic Compounds	
 Saltpeter Powder, KNO_3 Source: Walkerma	Potassium Nitrate (KNO_3) or Saltpeter has found major uses in fertilizers, being a prominent source of nitrogen. As an oxidizing agent it is used in rocket propellant, fireworks and a major propellant of gunpowder (blackpowder). It has also found use as a food preservative. As a preservative, it prevents the germination of the bacteria, C. botulinum, in meat products, reducing the occurance of botulism poisoning. (Although other nitrate preservatives have largely replaced the use of saltpeter for this purpose).

FOR A COOL VIDEO ON THE OXIDATIVE PROPERTIES OF SALTPETER, CLICK HERE!

Noticing ionic compounds in our everyday lives

Everyday Uses for Ionic Compounds
Soluble ionic compounds like table salt (NaCl) can easily be dissolved to provide ***electrolyte solutions*** (solutions that contain charged ions). Rehydration fluids and many sports drinks contain required electrolytes (Na^+, Mg^{2+}, K^+, Ca^{2+} and Cl^-) that are used in nerve impulse conduction and other important biological processes. Infections like cholera can be deadly due to dehydration and loss of electrolyte balance in the body.

Everyday Uses for Ionic Compounds



When salt dissolves in water, the individual ions of the salt become surrounded by water molecules. Eventually, the ion detaches from the remaining solid and floats suspended by the surrounding water molecules in solution. These charged particles floating in solution are known as ***electrolytes.***

Specific properties of solutions depend on the concentration of dissolved particles within the solution. These properties are called ***colligative properties***. They include: (1) Increasing the osmotic pressure, (2) Causing freezing-point depression and boiling-point elevation, and (3) Increasing electrical conductivity of the solution.

Everyday Uses for Ionic Compounds



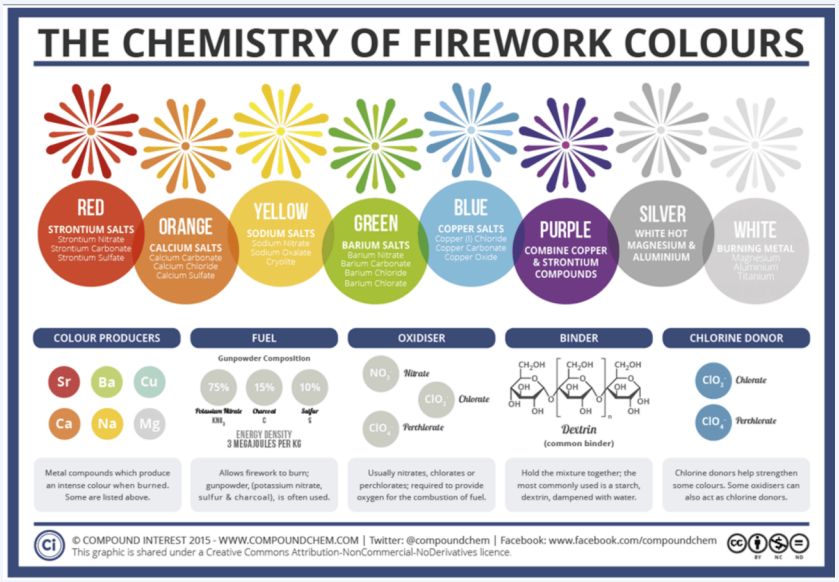
Due to the colligative properties, salts are used for many purposes, including de-icing road ways during the winter. By placing salt on the roadway, the freezing point of water is depressed and the ice will melt.

However, Deicing with salt (primarily sodium chloride) significantly impacts the environment by polluting freshwater ecosystems, degrading soil structure, damaging local vegetation, and threatening drinking water supplies. Once washed away by melting snow, salt accumulates in the environment, causing both short- and

Everyday Uses for Ionic Compounds	
	long-term ecological damage.

The chemical identity of the ions is also important for many uses. For example, fluoride compounds are used in dentistry to help strengthen tooth enamel. Salts containing fluoride are often dissolved in municiple water supplies for water fluoridation. This aims to help prevent tooth decay.

Solid ionic compounds have long been used as pigments in paint and are resistant to organic solvents, but are sensitive to acids and bases. Pyrotechnicians also use various metal ions from ionic compounds as the source of color in their fireworks. Under intense heat, the electrons in the metal ions can be excited. As the electrons return to their normal energy level, they release light with the color spectrum that is characteristic of the metal ion present.



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3.9: Arrhenius Acids and Bases

Recognizing Common Acids and Bases

H^+ and OH^- ions are the key players in acid-base chemistry, under the Arrhenius definitions for acids and bases. Arrhenius defined an *acid* as a compound that increases the concentration of hydrogen cations (H^+) in aqueous solution. Many acids are simple compounds that release a hydrogen cation into solution when they dissolve and can be recognized as ionic compounds that contain H^+ as the cation. Similarly, Arrhenius defined a *base* as a compound that increases the concentration of hydroxide ions (OH^-) in aqueous solution. Many bases are ionic compounds that have the hydroxide ion as their anion, which is released when the base dissolves in water.

Arrhenius bases are named according to standard ionic nomenclature, with the strongest bases being the hydroxides of the alkali metals and the heavier alkaline earth metals. You will be expected to recognize the following strong bases.

Table 3.9A The Most Common Strong Bases

Strong Bases	
Name	**Structure**
Group 1A metal hydroxides	LiOH, NaOH, KOH, RbOH, CsOH
Heavy Group 2A metal hydroxides	$Ca(OH)_2$, $Sr(OH)_2$, $Ba(OH)_2$

Arrhenius acids have a nomenclature system that is a little more complex, since their structures can include both binary compounds as well as polyatomic anions. In naming acids from binary compounds, the prefix 'hydro-' is used to represent the cation H+, and the suffix '-ic' acid is used to indicate that it is an acidic form. The element name of the anion can be used directly, as is the case for H_2S known as hydrosulfuric acid, or more commonly, the anion is modified by dropping the '-ine', '-ous' or '-ogen' ending before replacing with the suffix '-ic acid', as is the case for HCl which is known as hydrochloric acid, H_3P which is known as hydrophosphoric acid and H_3N which is known as hydronitric acid.

If an acid contains a polyatomic ion, no leading prefix is used to indicate the H+ cation. This is implied within the name. For polyatomic anions ending with the suffix '-ate', the acid is named as the [anion name] + the '-ic acid' suffix. For example, when the sulfate ion (SO_4^{2-}) is complexed with H^+ as the cation, the overall formula will be H_2SO_4 and the resulting acid will be named sulfuric acid. Dropping the prefix distinguishes polyatomic acids from the binary acids, in this case sulfuric acid (H_2SO_4) is distinguished from hydrosulfuric acid (H_2S). If a polyatomic anion has the '-ite' ending, the acid name will be written as the [anion name] + the '-ous acid' suffix. For example HNO_2 would be nitrous acid, and HNO_3 would be nitric acid. The prefixes 'hypo-' and 'per-' are also retained in the acid nomenclature for elements that have many oxyanion states. For example the chlorine containing oxyanions can form the following acids:

$$\begin{aligned} ClO^- &= \text{Hypochlorite} \\ ClO_2^- &= \text{Chlorite} \\ ClO_3^- &= \text{Chlorate} \\ ClO_4^- &= \text{Perchlorate} \end{aligned} \tag{3.9.1}$$

These are all distinguished from the binary chlorine-containing acid, by dropping the hydro-prefix:

$$\mathbf{HCl} = \mathbf{Hydrochloric\ Acid} \tag{3.9.2}$$

Strong acids are ones that completely dissociate into their ionic forms in solution. The following table lists common strong acids that you will need to be familiar with.

Table 3.9B The Most Common Strong Acids

Strong Acids	
Name	**Structure**
Perchloric Acid	$HClO_4$
Chloric Acid	$HClO_3$
Hydrochloric Acid	HCl
Hydrobromic Acid	HBr
Hydroiodic Acid	HI
Nitric Acid	HNO_3
Sulfuric Acid	H_2SO_4

Quiz Yourself: More Practice Naming Compounds

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3.10: Focus on the Environment - Acid Rain

How Human Pollution Impacts Our Environment

Acid rain is a term referring to a mixture of wet and dry deposition (deposited material) from the atmosphere containing higher than normal amounts of nitric and sulfuric acids. The precursors, or chemical forerunners, of acid rain formation result from both natural sources, such as volcanoes and decaying vegetation, and man-made sources, primarily emissions of sulfur dioxide (SO_2) and nitrogen oxides (NO_x) resulting from fossil fuel combustion. Acid rain occurs when these gases react in the atmosphere with water, oxygen, and other chemicals to form various acidic compounds. The result is a mild solution of sulfuric acid and nitric acid. When sulfur dioxide and nitrogen oxides are released from power plants and other sources, prevailing winds blow these compounds across state and national borders, sometimes over hundreds of miles.

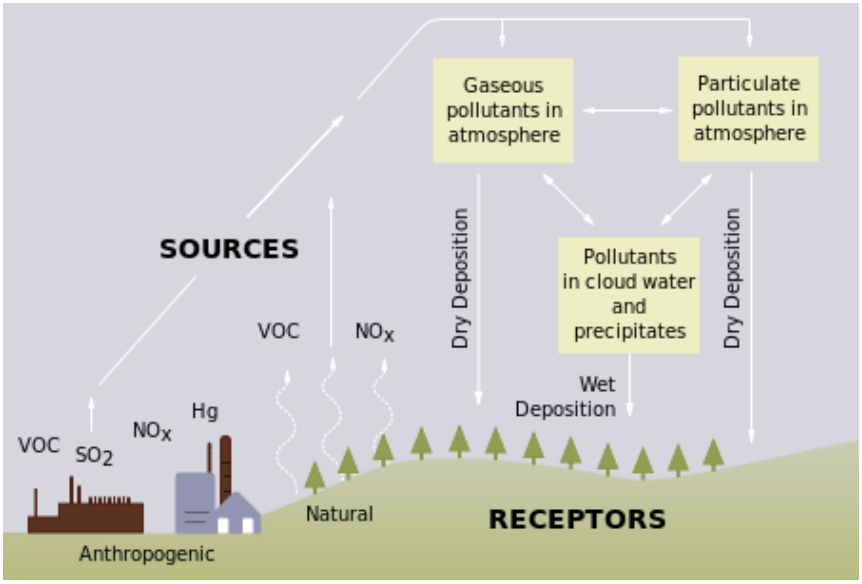


Figure 3.10.1**: Processes involved in acid deposition.** Factories generate pollution that is released into the atmosphere and converted into acidic by-products.

In natural settings when lightning discharges, molecular nitrogen and molecular oxygen react to give nitric oxide:

$$\mathrm{N_2}(g) \quad + \quad \mathrm{O_2}(g) \quad \longrightarrow \quad \mathrm{2\,NO}(g) \tag{3.10.1}$$

Nitric oxide then reacts rapidly with excess oxygen to give nitrogen dioxide. Nitrogen dioxide is also produced by fossil fuel combustion in automobiles, power plants, and industrial facilities. It is one of the primary compounds responsible for the brown color of photochemical smog.

$$\mathrm{2\,NO}(g) \quad + \quad \mathrm{O_2}(g) \quad \longrightarrow \quad \mathrm{2\,NO_2}(g) \tag{3.10.2}$$

When nitrogen dioxide reacts with water droplets in the atmosphere, it initially forms approximately equal amounts of nitrous acid and nitric acid:

$$\mathrm{2\,NO_2}(g) \quad + \quad \mathrm{H_2O}(l) \quad \longrightarrow \quad \mathrm{HNO_2}(aq) \quad + \quad \mathrm{HNO_3}(aq) \tag{3.10.3}$$

As nitrous acid is further oxidized by atmospheric oxygen, the overall process can be summarized by the following net reaction:

$$\mathrm{2\,N_2}(g) \quad + \quad \mathrm{7\,O_2}(g) \quad + \quad \mathrm{2\,H_2O}(l) \quad \longrightarrow \quad \mathrm{4\,HNO_3}(aq) \tag{3.10.4}$$

The nitric acid produced in the atmosphere dissolves in rainwater, lowering its pH. When this acidic precipitation reaches Earth's

surface, it can damage forests, acidify lakes and streams, weather buildings and monuments, and alter soil chemistry.

In addition to nitric acid, large amounts of sulfur dioxide have always been released into the atmosphere by natural sources, such as volcanoes, forest fires, and the microbial decay of organic materials, but for most of Earth's recorded history the natural cycling of sulfur from the atmosphere into oceans and rocks kept the acidity of rain and snow in check. Unfortunately, the burning of fossil fuels seems to have tipped the balance. Many coals contain as much as 5%–6% pyrite (FeS_2) by mass, and fuel oils typically contain at least 0.5% sulfur by mass. Since the mid-19th century, these fuels have been burned on a huge scale to supply the energy needs of our modern industrial society, releasing tens of millions of tons of additional SO_2 into the atmosphere annually. In addition, roasting sulfide ores to obtain metals such as zinc and copper also produces large amounts of SO_2 via reactions such as:

$$\mathbf{2\,ZnS}(s) \quad + \quad \mathbf{3\,O_2}(g) \quad \longrightarrow \quad \mathbf{2\,ZnO}(s) \quad + \quad \mathbf{2\,SO_2}(g) \tag{3.10.5}$$

Regardless of the source, sulfur dioxide can dissolve in atmospheric water and is commonly represented as forming sulfurous acid. Further oxidation ultimately produces sulfuric acid:

$$\mathbf{SO_2}(g) \quad + \quad \mathbf{H_2O}(l) \quad \longrightarrow \quad \mathbf{H_2SO_3}(aq) \tag{3.10.6}$$

$$\mathbf{2\,H_2SO_3}(aq) \quad + \quad \mathbf{O_2}(g) \quad \longrightarrow \quad \mathbf{2\,H_2SO_4}(aq) \tag{3.10.7}$$

Acid rain is measured using a scale called "pH." The lower a substance's pH, the more acidic it is. Pure water has a pH of 7.0. However, normal rain is slightly acidic. CO_2 dissolves in rainwater and establishes an equilibrium that produces a small amount of weak carbonic acid, giving the resulting mixture a pH of approximately 5.6 at typical atmospheric concentrations of CO_2.

$$\mathbf{CO_2}(g) \quad + \quad \mathbf{H_2O}(l) \quad \rightleftharpoons \quad \mathbf{H_2CO_3}(aq) \tag{3.10.8}$$

Acid precipitation can reach pH values near 4 or even lower, making it substantially more acidic than normal rain.

Effects of Acid Rain

Acid rain causes acidification of lakes and streams and contributes to the damage of trees at high elevations (for example, red spruce trees above 2,000 feet) and many sensitive forest soils. In addition, acid rain accelerates the decay of building materials and paints, including irreplaceable buildings, statues, and sculptures that are part of our nation's cultural heritage. Prior to falling to the earth, sulfur dioxide (SO_2) and nitrogen oxide (NO_x) gases and their particulate matter derivatives—sulfates and nitrates—contribute to visibility degradation and harm public health.

The ecological effects of acid rain are most clearly seen in the aquatic, or water, environments, such as streams, lakes, and marshes. Most lakes and streams have a pH between 6 and 8, although some lakes are naturally acidic even without the effects of acid rain. Acid rain primarily affects sensitive bodies of water, which are located in watersheds whose soils have a limited ability to neutralize acidic compounds (called "buffering capacity"). Lakes and streams become acidic (i.e., the pH value goes down) when the water itself and its surrounding soil cannot buffer the acid rain enough to neutralize it. In areas where buffering capacity is low, acid rain releases aluminum from soils into lakes and streams; aluminum is highly toxic to many species of aquatic organisms. Acid rain causes slower growth, injury, or death of forests. Of course, acid rain is not the only cause of such conditions. Other factors contribute to the overall stress of these areas, including air pollutants, insects, disease, drought, or very cold weather. In most cases, in fact, the impacts of acid rain on trees are due to the combined effects of acid rain and these other environmental stressors.

Acid rain and the dry deposition of acidic particles contribute to the corrosion of metals (such as bronze) and the deterioration of paint and stone (such as marble and limestone). These effects significantly reduce the societal value of buildings, bridges, cultural objects (such as statues, monuments, and tombstones), and cars (Figure 3.10.2).



Figure 3.10.2: A gargoyle that has been damaged by acid rain. Over extended time, acid rain can damage building structures and artwork.

Political Tensions

Air pollution and the effects of acid rain are not constrained to the site of origin. Effects of the pollution can impact adjacent lands and create political tensions between neighboring countries. During the 1980's to early 1990's acid rain created a lot of political tension between Canada and the United States. In the late 1970's it became clear that pollution causing acid rain was killing wildlife and damaging forests on both sides of the border, from fish kills in hundreds of lakes in New York's Adirondacks as well as in New England and Eastern Canada.

This resulted in strong protests from Canada to stop acid rain. For example, the first time Ronald Reagan visited Ottawa during his presidency, he was greeted by thousands of Canadian protesters demanding for the United States to "Stop Acid Rain". Full negotiations were underway in 1986 regarding the problem, but it took five additional years of negotiations for President George H. Bush to sign the Acid Rain Accord with Canadian Prime Minister, Brian Mulroney in 1991. The accord provided the following declaration: "States have, in accordance with the Charter of the United Nations and the principles of international law, the sovereign right to exploit their own resources pursuant to their own environmental policies, and the responsibility to ensure that activities within their jurisdiction or control do not cause damage to the environment of other States or of areas beyond the limits of national jurisdiction."

In response to regulatory and public pressure to reduce SO_2 and NO_x emissions, technologies were developed to remove these pollutants before industrial exhaust gases were released to the atmosphere. For example, coal-burning power plants now use SO_2 "scrubbers," which trap SO_2 by its reaction with lime (CaO) to produce calcium sulfite dihydrate. A diagram of this chemical process is provided in Figure 3.10.3.

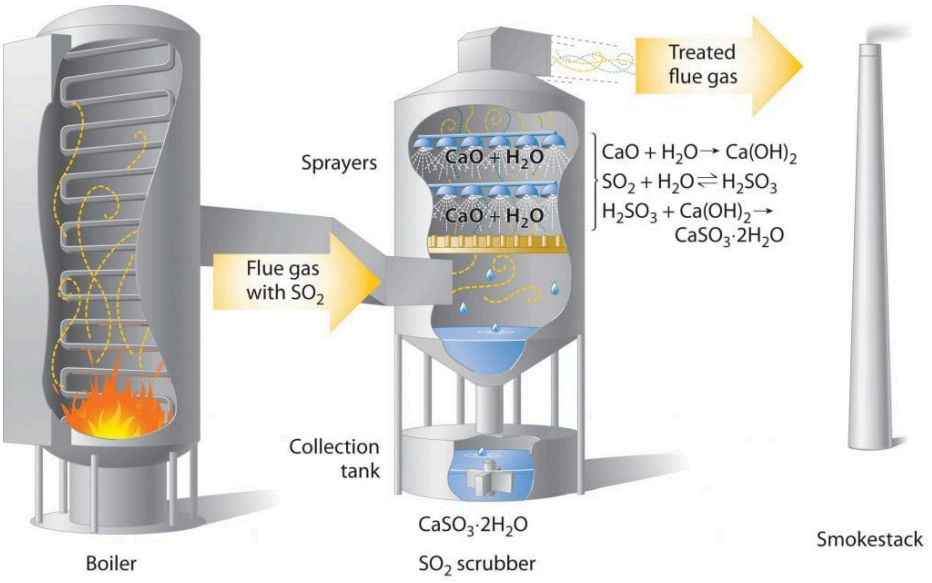


Figure 3.10.3: Schematic Diagram of a Wet Scrubber System. In coal-burning power plants, SO_2 can be removed ("scrubbed") from exhaust gases by its reaction with a lime (CaO) and water spray to produce calcium sulfite dihydrate ($CaSO_3{\cdot}2H_2O$). Removing SO_2 from the gases prevents its conversion to SO_3 and subsequent reaction with rainwater (acid rain). Scrubbing systems are now commonly used to minimize the environmental effects of large-scale fossil fuel combustion.

$$\mathbf{CaO}(s) \quad + \quad \mathbf{SO_2}(g) \quad + \quad \mathbf{2\,H_2O}(l) \quad \longrightarrow \quad \mathbf{CaSO_3 \cdot 2H_2O}(s) \tag{3.10.9}$$

Suggested Practice Assignment:

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3.11: Chapter Summary

If an atom has gained one or more electrons, it is negatively charged and is called an ***anion***. If an atom has lost one or more electrons, it is positively charged and is called a ***cation***. Metals generally form cations while nonmetals generally form anions. 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***. The simplest ionic compounds are ***binary ionic compounds*** or those that only contain two atoms, one acting as the cation, and one acting as the anion.

The tendency of an atom toward a configuration in which it possesses eight valence electrons is referred to as the "***Octet Rule.***" The term ***isoelectronic*** refers to an atom and an ion of a different atom (or two different ions) that have the same electron configuration. Cations lose electrons to become isoelectronic with the noble gas in the previous row (period) on the table. Anions gain electrons to become isoelectronic with the noble gas in the same row as the anion. The periodic table can be used to predict common ion states for the elements

During ionic bond formation, electron dot diagrams can be used to illustrate electron movements. Stable ionic compounds have a balanced charge state such that the charge on the overall molecule is zero. When writing chemical formulas, the cation is always first and the anion is always last. Stable chemical formulas must be written so that the overall compound has a net neutral charge (ie the total positive charge = the total negative charge). Subscripts are used to show how many atoms are present within an ionic formula. Chemical formulas are always reduced to show the lowest number of each cation and anion required for a single compound to form.

Cations are named by using the element name followed by the word 'ion'. Roman numerals are added after the element name if a cation has more than one ionic form. Anions are named by dropping the last part of the element name and replacing it with the suffix '-ide' followed by the word 'ion'. When naming an ionic compound the cation name, including roman numerals when needed, is placed first, followed by the anion name.

Polyatomic ions are ions that form from multiple atoms that are covalently bonded together. Polyatomic ions behave as a single group when participating in ionic bonding. ***Oxyanions*** are polyatomic anions that contain oxygen as one of the elemental components. If only one oxyanion exists for a specific element it is given the '-ate' suffix within the name. If two oxyanions exist for a specific element, the one with fewer oxygens is given the '-ite' ending and the one with more oxygens the '-ate' ending. If three or four oxyanion species exist for a specific element the prefix 'hypo-' and suffix '-ite' are used to show one less oxygen below the '-ite' anion, and the prefix 'per-' and suffix '-ate' are used to show one additional oxygen above the '-ate' anion. Naming ionic compounds that contain polyatomic ions is done in exactly the same way as with other binary ionic compounds. The name of the cation comes first (using roman numerals when necessary) followed by the name of the anion.

Solid ionic compounds typically form a continuous three-dimensional network or lattice, usually in a crystalline structure, rather than individual molecules. Ionic compounds typically have high melting and boiling points, and are hard and brittle. As solids, they are most often electrically insulating, but when melted or dissolved they become highly conductive, because the ions are mobilized.

Using the **Arrhenius definitions**, ionic compounds containing hydrogen ions (H^+) are classified as ***acids***, and those containing hydroxide (OH^-) or oxide (O^{2-}) ions are classified as ***bases***. All other ionic compounds without these ions are known as *salts*. Naming salts and basic ionic compounds follows standard ionic nomenclature rules. In naming acids from binary compounds, the prefix 'hydro-' is used to represent the cation H+, and the suffix '-ic' acid is used to indicate that it is an acidic form. If an acid contains a polyatomic ion, no leading prefix is used to indicate the H+ cation. This is implied within the name. For polyatomic anions ending with the suffix '-ate', the acid is named as the [anion name] + the '-ic acid' suffix. If a polyatomic anion has the '-ite' ending, the acid name will be written as the [anion name] + the '-ous acid' suffix. The prefixes 'hypo-' and 'per-' are also retained in the acid nomenclature for elements that have many oxyanion states.

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4: CHAPTER 4 - COVALENT BONDS AND MOLECULAR COMPOUNDS

4.1: Introduction to Covalent Molecules and Compounds

4.2: Electron Sharing

4.3: Electronegativity and Bond Polarity

4.4: Properties of Covalent Compounds

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4.1: Introduction to Covalent Molecules and Compounds

Chemical bonds are generally divided into two fundamentally different types: ionic and covalent. In reality, however, the bonds in most substances are neither purely ionic nor purely covalent, but lie on a spectrum between these extremes. Although purely ionic and purely covalent bonds represent extreme cases that are seldom encountered in any but very simple substances, a brief discussion of these two extremes helps explain why substances with different kinds of chemical bonds have very different properties. Ionic compounds consist of positively and negatively charged ions held together by strong electrostatic forces, whereas covalent compounds generally consist of molecules, which are groups of atoms in which one or more pairs of electrons are shared between bonded atoms. In a covalent bond, atoms are held together by the electrostatic attraction between the positively charged nuclei of the bonded atoms and the negatively charged electrons they share. This chapter will focus on the properties of covalent compounds.

4.1 Introduction to Covalent Molecules and Compounds

Just as an atom is the simplest unit that has the fundamental chemical properties of an element, *a molecule* is the simplest unit that has the fundamental chemical properties of a covalent compound. Thus, the term *molecular compound* is used to describe elements that are covalently bonded and to distinguish the compounds from ionic compounds. Some pure elements exist as covalent molecules. Hydrogen, nitrogen, oxygen, and the halogens occur naturally as the diatomic ("two atoms") molecules H_2, N_2, O_2, F_2, Cl_2, Br_2, and I_2 (part (a) in Figure 4.1.1). Similarly, a few pure elements exist as polyatomic ("many atoms") molecules, such as elemental phosphorus and sulfur, which occur as P_4 and S_8 (part (b) in Figure 4.1.1).

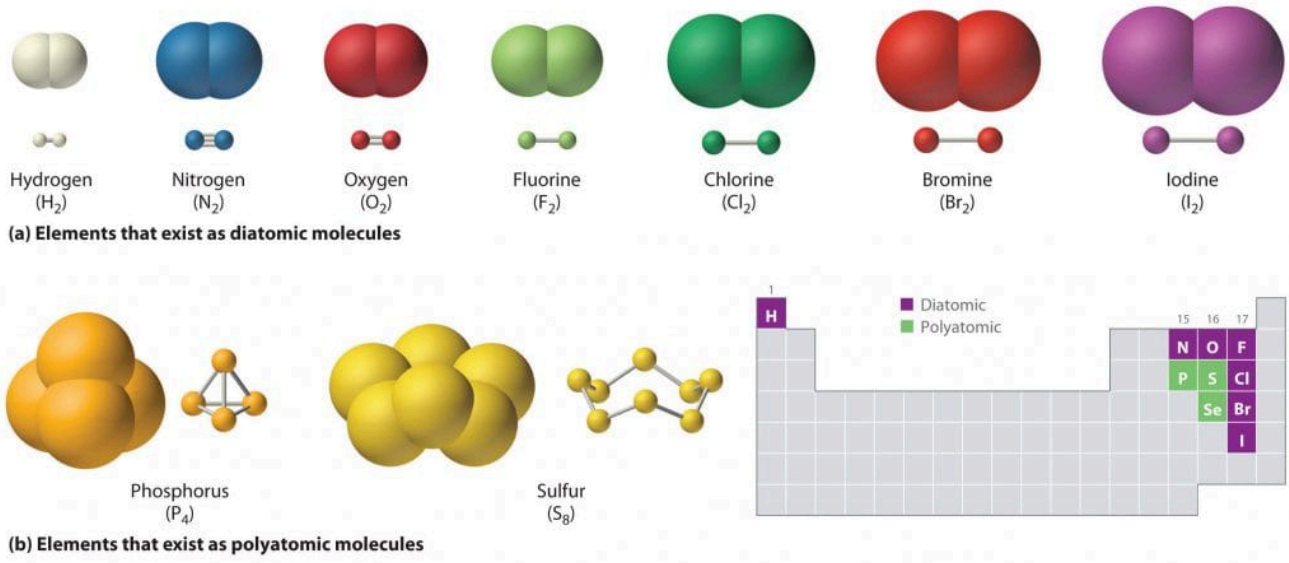


Figure 4.1.1**: Elements That Exist as Covalent Molecules.** (a) Several elements naturally exist as diatomic molecules, in which two atoms (E) are joined by one or more covalent bonds to form a molecule with the general formula E2. (b) A few elements naturally exist as polyatomic molecules, which contain more than two atoms. For example, phosphorus exists as P4 tetrahedra—regular polyhedra with four triangular sides—with a phosphorus atom at each vertex. Elemental sulfur consists of a puckered ring of eight sulfur atoms connected by single bonds. Selenium is not shown due to the complexity of its structure.

Each covalent compound is represented by a molecular formula, which gives the atomic symbol for each component element, in a prescribed order, accompanied by a subscript indicating the number of atoms of that element in the molecule. The subscript is written only if the number of atoms is greater than 1. For example, water, with two hydrogen atoms and one oxygen atom per molecule, is written as H_2O. Similarly, carbon dioxide, which contains one carbon atom and two oxygen atoms in each molecule, is written as CO_2.

Note

Hydrogen, which is placed with the alkali metals on the periodic table, most often forms covalent bonds with other atoms. This is because hydrogen is an exception to the octet rule and only needs one additional electron to fill its valence electron rule. Hydrogen forms an ***Electronic Duet***.

Covalent compounds that predominantly contain carbon and hydrogen are called ***organic compounds***. The convention for representing the formulas of organic compounds is to write carbon first, followed by hydrogen and then any other elements in alphabetical order (e.g., CH_4O is methyl alcohol, a fuel). Compounds that consist primarily of elements other than carbon and hydrogen are called ***inorganic compounds***; they include both covalent and ionic compounds. The convention for writing inorganic compounds, involves listing the component elements beginning with the one farthest to the left in the periodic table, as in CO_2 or SF_6. Those in the same group are listed beginning with the lower element and working up, as in ClF. By convention, however, when an inorganic compound contains both hydrogen and an element from groups 13–15, hydrogen is usually listed last in the formula. Examples are ammonia (NH_3) and silane (SiH_4). Typically this distinguishes when hydrogen is participating in a covalent bond rather than an ionic interaction, as seen in many of the inorganic acids, such as hydrochloric acid (HCl) and sulfuric acid (H_2SO_4), as described in chapter 3. However, compounds such as water, whose compositions were established long before this convention was adopted, are always written with hydrogen first: Water is always written as H_2O, not OH_2.

How to Recognize Covalent Bonds

In Chapter 3, we saw that ionic compounds are composed predominantly of a metal + a nonmetal. Covalent molecules, on the otherhand, are typically composed of two nonmetals or a nonmetal and a metalloid. This is an initial screening method that you can use to categorize compounds into the ionic or the covalent cagetory.

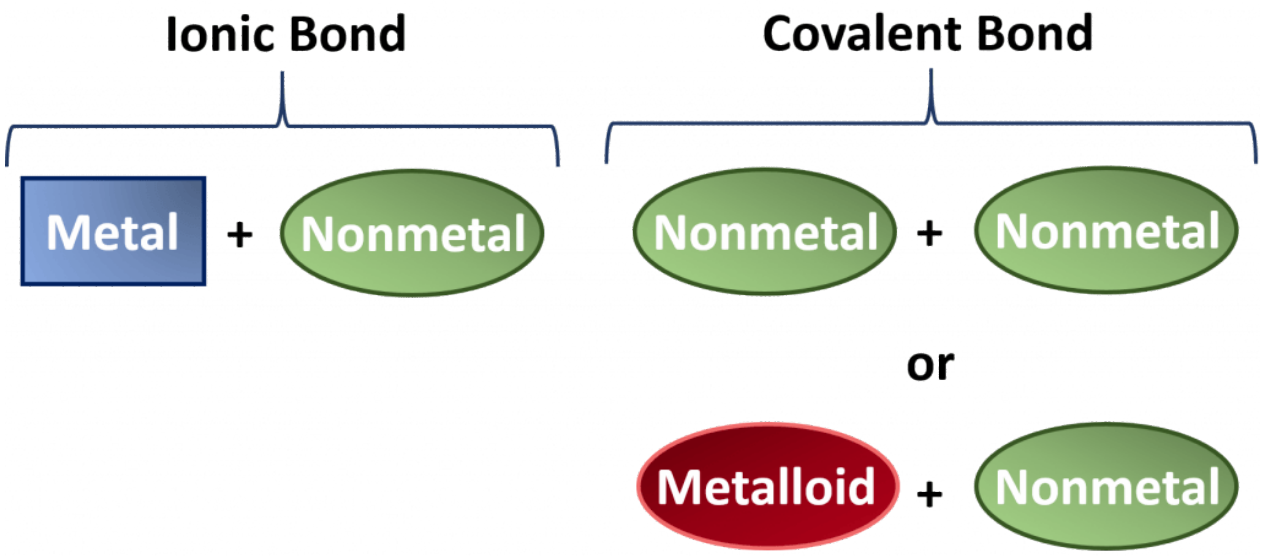


Figure 4.1.2**: Recognizing Ionic vs Covalent Compounds.** Typically compounds that are formed from a combination of a metal with a nonmetal have more ionic bond character whereas compounds formed from two nonmetals or a metalloid and a nonmetal show more covalent character. Although compounds usually lie on a spectrum somewhere between fully ionic and fully covalent character, for naming purposes, this guideline works well.

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4.2: Electron Sharing

Single Covalent Bonds Between the Same Atoms

Chapter 3 described how electrons can be transferred from one atom to another so that both atoms have an energy-stable outer electron shell following the ***octet rule.*** However, there is another way an atom can achieve a full valence shell: atoms can share electrons to reach the octet state (or the ***duet state*** in the case of hydrogen).

This concept can be illustrated by using two hydrogen atoms, each of which has a single electron in its valence shell. (For small atoms such as hydrogen atoms, the valence shell will be the first shell, which holds only two electrons.) We can represent the two individual hydrogen atoms as follows:

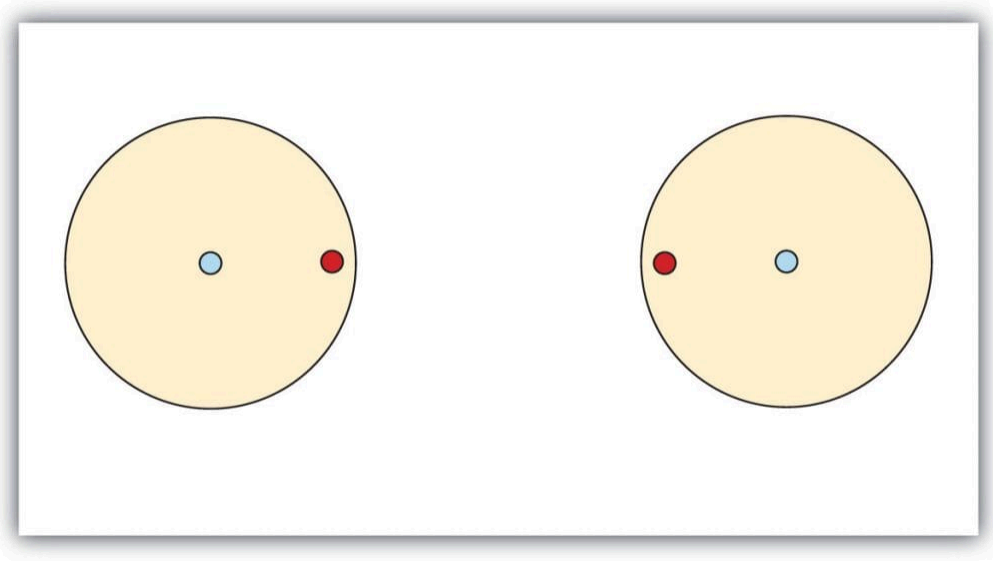


Figure 4.2.1**: Model of Two Hydrogen Atoms.** Image show two hydrogen atoms each with one proton and one electron.

In this situation neither hydrogen can reach the preferred duet state. In contrast, when two hydrogen atoms get close enough together to share their electrons, they can be represented as follows:

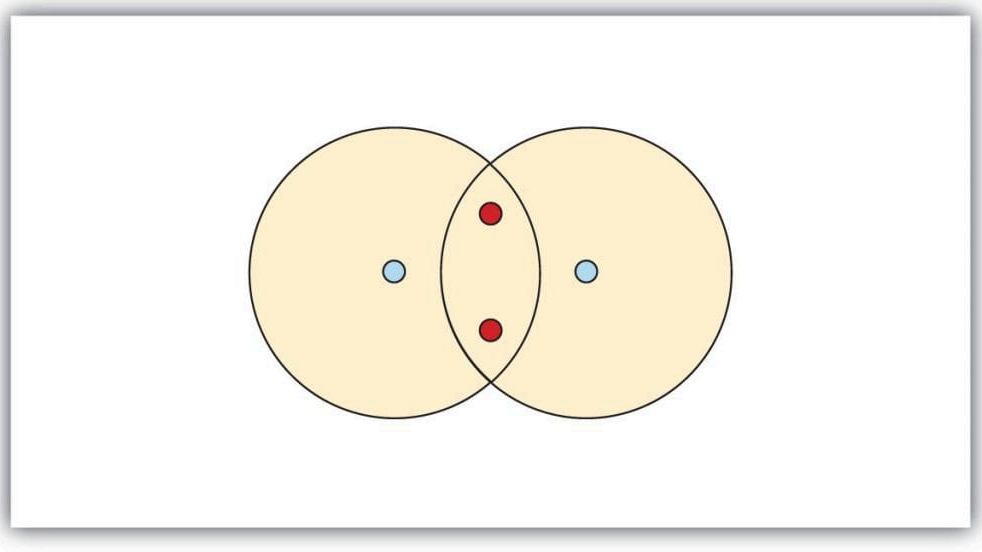


Figure 4.2.2: Model of Molecular Hydrogen. Elemental hydrogen exists as H_2, where each hydrogen shares its electron in a covalent bond with the other forming a duet.

By sharing their valence electrons, both hydrogen atoms now have two electrons in their respective valence shells. Because each valence shell is now filled, this arrangement is more stable than when the two atoms are separate. In this configuration, each hydrogen has an electron configuration equivalent to that of the noble gas, helium. The sharing of electrons between atoms is called a ***covalent bond***, and the two electrons that join atoms in a covalent bond are called a ***bonding pair of electrons***. A discrete group of atoms connected by covalent bonds is called a ***molecule***—the smallest part of a compound that retains the chemical identity of that compound. For example, one molecule of water would contain two hydrogen atoms and one oxygen atom (H_2O).

Chemists frequently use ***Lewis electron dot diagrams*** to represent covalent bonding in molecular substances. For example, the Lewis diagrams of two separate hydrogen atoms are as follows:

$$H\bullet \qquad\qquad \bullet H$$

The Lewis diagram of two hydrogen atoms sharing electrons looks like this:

$$H\!:\!H$$

This depiction of molecules is simplified further by using a dash to represent a covalent bond. The hydrogen molecule is then represented as follows:

$$H—H$$

Remember that the dash, also referred to as a single bond, represents a pair of bonding electrons.

The bond in a hydrogen molecule, measured as the distance between the two nuclei, is about 7.4×10^{-11} m, or 74 picometers (pm; 1 pm = 1×10^{-12} m). This particular bond length represents a balance between several forces: (1) the attractions between oppositely charged electrons and nuclei, (2) the repulsion between two negatively charged electrons, and (3) the repulsion between two positively charged nuclei. If the nuclei were closer together, they would repel each other more strongly; if the nuclei

were farther apart, there would be less attraction between the positive and negative particles.

Fluorine is another element whose atoms bond together in pairs to form diatomic (two-atom) molecules. Two separate fluorine atoms have the following electron dot diagrams:



Each fluorine atom contributes one valence electron, making a single bond and giving each atom a complete valence shell, which fulfills the octet rule:



The circles show that each fluorine atom has eight electrons around it. As with hydrogen, we can represent the fluorine molecule with a dash in place of the bonding electrons:



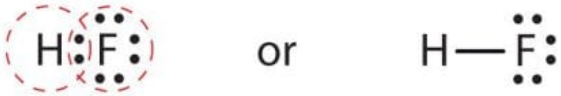
Each fluorine atom has six electrons, or three pairs of electrons, that are not participating in the covalent bond. Rather than being shared, they are considered to belong to a single atom. These are called *nonbonding pairs (or lone pairs)* of electrons.

Single Covalent Bonds Between Different Atoms

Now that we have looked at electron sharing between atoms of the same element, let us look at covalent bond formation between atoms of different elements. Consider a molecule composed of one hydrogen atom and one fluorine atom:

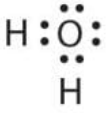


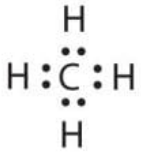
Each atom needs one additional electron to complete its valence shell. By each contributing one electron, they make the following molecule:



In this molecule, the hydrogen atom does not have nonbonding electrons, while the fluorine atom has six nonbonding electrons (three lone electron pairs). The circles show how the valence electron shells are filled for both atoms (recall that hydrogen is filled with two electrons).

Larger molecules are constructed in a similar fashion, with some atoms participating in more than one covalent bond. For example, water, with two hydrogen atoms and one oxygen atom, and methane (CH_4), with one carbon atom and four hydrogen atoms, can be represented as follows:





Atoms typically form a characteristic number of covalent bonds in compounds. Figure 4.2.3 shows valence electron configurations of each element family (or column).

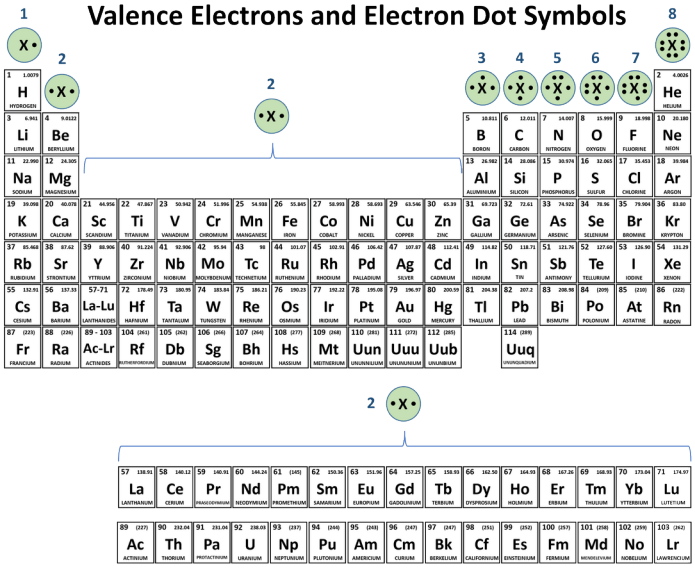


Figure 4.2.3**: Periodic Table with Lewis Structures.** Each family shows a representative lewis structure for that group of elements. For the nonmetals (Families 4A, 5A, 6A, and 7A) they can accept a complementary number of shared bonds to reach the octet state. Family 4A can share 4 covalent bonds (4 + 4 = 8), whereas Families 5A, 6A, and 7A can share 3, 2, and 1 covalent bond(s), respectively, to achieve the octet state. Exceptions to the octet rule do exist. For example, hydrogen can be considered to be in Group 1 or Group 7A because it has properties similar to both groups. Hydrogen can participate in either ionic or covalent bonding. When participating in covalent bonding, hydrogen only needs two electrons to have a full valence shell. As it has one electron to start with, it can only make one covalent bond. Similarly, boron has 3 electrons in its outer shell. This nonmetal typically forms 3 covalent bonds, having a maximum of 6 electrons in its outer shell. Thus, boron can never reach the octet state. Other atoms can have expanded orbitals and accept additional covalent bonds. Two of these that are important for living systems are sulfur and phosphorus. By the octet rule, sulfur can make 2 covalent bonds and phosphorus 3 covalent bonds. Sulfur can also have expanded orbitals to accept 4 or 6 covalent bonds, and phosphorus can expand to 5 covalent bonds.

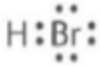
Example 4.2.1

Draw the Lewis structure for each compound:

- A molecule composed of two chlorine atoms
- A molecule composed of a hydrogen atom and a bromine atom

Solution





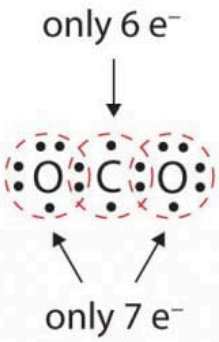
Exercise 4.2.1

Test Yourself: Draw the Lewis structure for each compound:

- A molecule composed of one chlorine and one fluorine atom
- A molecule composed of a hydrogen atom and an iodine atom

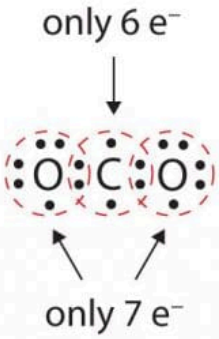
Multiple Covalent Bonds

In many molecules, the octet rule would not be satisfied if each pair of bonded atoms shares only two electrons. Consider carbon dioxide (CO_2). If each oxygen atom shares one electron with the carbon atom, we get the following:

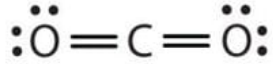


This does not give either the carbon or oxygen atoms a complete octet; The carbon atom only has six electrons in its valence shell and each oxygen atom only has seven electrons in its valence shell. Thus, none of the atoms can reach the octet state in the current configuration. As written, this would be an unstable molecular conformation.

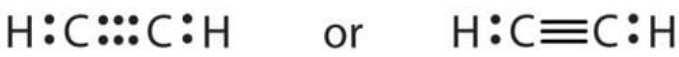
Sometimes more than one pair of electrons must be shared between two atoms for both atoms to have an octet. In carbon dioxide, a second electron from each oxygen atom is also shared with the central carbon atom, and the carbon atom shares one more electron with each oxygen atom:



In this arrangement, the carbon atom shares four electrons (two pairs) with the oxygen atom on the left and four electrons with the oxygen atom on the right. There are now eight electrons around each atom. Two pairs of electrons shared between two atoms make a double bond between the atoms, which is represented by a double dash:



Some molecules contain triple bonds, covalent bonds in which three pairs of electrons are shared by two atoms. A simple compound that has a triple bond is acetylene (C_2H_2), whose Lewis diagram is as follows:

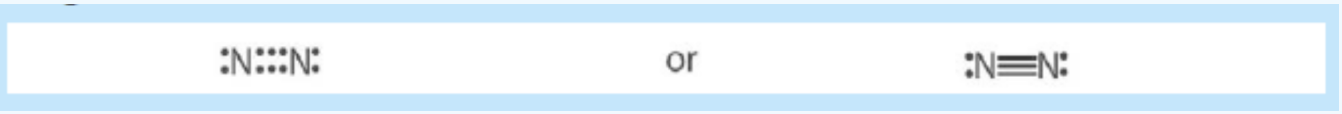


Example 4.2.2

Draw the Lewis Diagram for each molecule:

- N_2
- CH_2O

Solution





Exercise 4.2.1

Test Yourself: Draw the Lewis Diagram for each molecule:

- O_2
- C_2H_4

Coordinate Covalent Bonds

A coordinate bond (also called a dative covalent bond) is a covalent bond (a shared pair of electrons) in which both electrons come from the same atom. A covalent bond is formed by two atoms sharing a pair of electrons. The atoms are held together because the electron pair is attracted by both of the nuclei. In the formation of a simple or ordinary covalent bond, each atom supplies one electron to the bond – but that does not have to be the case. In the case of a coordinate covalent bond, one atom supplies both of the electrons and the other atom does not supply any of the electrons. The following reaction between ammonia and hydrochloric acid demonstrates the formation of a coordinate covalent bond between ammonia and a hydrogren ion (proton).

The reaction between ammonia and hydrochloric acid

If these colorless gases are allowed to mix, a thick white smoke of solid ammonium chloride is formed.

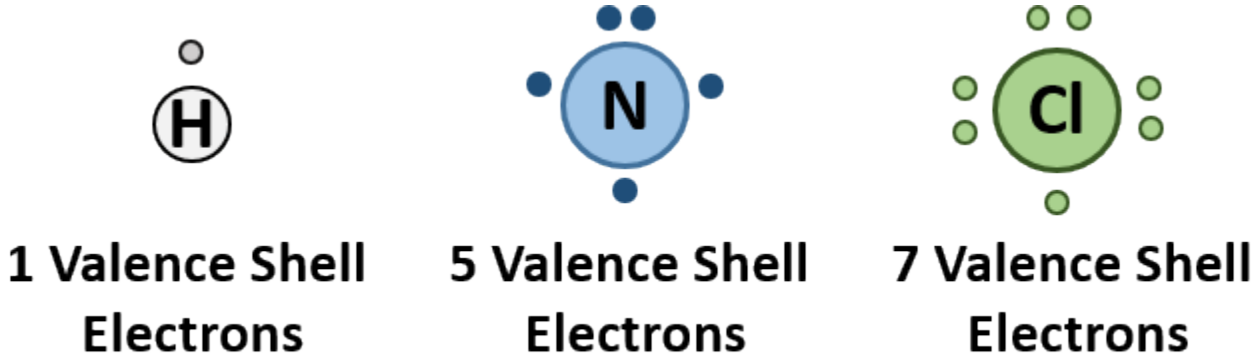


Photo from Wikipedia

The overall reaction is

$$\mathrm{NH_3\,(g) + HCl\,(g) \longrightarrow NH_4Cl\,(s)} \tag{4.2.1}$$

Ammonium ions, NH_4^+, are formed by the transfer of a hydrogen ion (a proton) from the hydrochloric acid molecule to the lone pair of electrons on the ammonia molecule. To visualize this reaction, we can use electron dot configurations to observe the electron movement during the reaction. First recall the valence electron states for all of the atoms involved in the reaction:



On the left side of the equation (to the left of the arrow) are the reactants of the reaction (ammonia and hydrochloric acid). On the right side of the reaction (to the right of the arrow) is the product of the reaction, the ionic compound – ammonium chloride. The diagram below shows the electron and proton movement during the reaction.

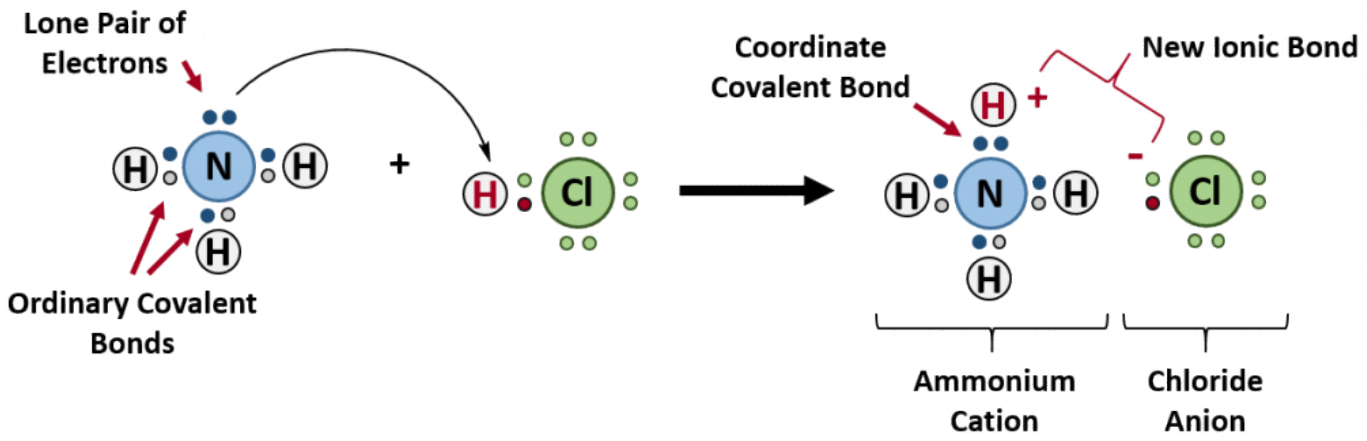


Figure 4.2.4**: Formation of Ammonium Chloride.** When the ammonium ion, NH_4^+, is formed, the fourth hydrogen (shown in red) is attached by a coordinate covalent bond, because only the hydrogen's nucleus is transferred from the chlorine to the nitrogen. The hydrogen's electron is left behind on the chlorine to form a negative chloride ion. Once the ammonium ion has been formed it is impossible to tell any difference between the coordinate covalent and the ordinary covalent bonds, all of the hydrogens are equivalent in the molecule and the extra positive charge is distributed throughout the molecule. Although the electrons are shown differently in the diagram, there is no difference between them in reality. In simple diagrams, a coordinate bond is shown by a curved arrow. The arrow points from the atom donating the lone pair to the atom accepting it.

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4.3: Electronegativity and Bond Polarity

How do Dipoles Form?

Although we defined covalent bonding as electron sharing, the electrons in a covalent bond are not always shared equally by the two bonded atoms. Unless the bond connects two atoms of the same element, there will always be one atom that attracts the electrons in the bond more strongly than the other atom does, as shown in Figure 4.5. When such an imbalance occurs, there is a resulting buildup of some negative charge (called a partial negative charge and designated δ–) on one side of the bond and some positive charge (designated δ+) on the other side of the bond. A covalent bond that has an unequal sharing of electrons, as in part (b) of Figure 4.3.1, is called a *polar covalent bond*. A covalent bond that has an equal sharing of electrons (part (a) of Figure 4.3.1) is called a *nonpolar covalent bond*.

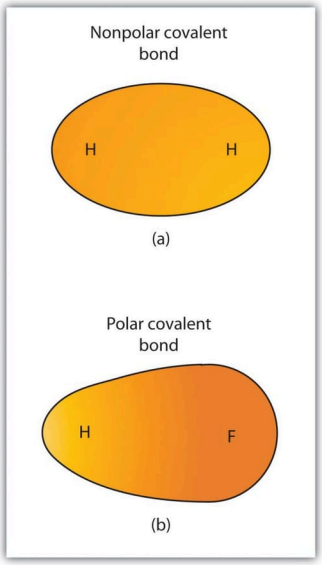


Figure 4.3.1**: Polar versus Nonpolar Covalent Bonds.** (a) The electrons in the covalent bond are equally shared by both hydrogen atoms. This is a nonpolar covalent bond. (b) The fluorine atom attracts the electrons in the bond more than the hydrogen atom does, leading to an imbalance in the electron distribution. This is a polar covalent bond.

Any covalent bond between atoms of different elements is a polar bond, but the degree of polarity varies widely. Some bonds between different elements are only minimally polar, while others are strongly polar. Ionic bonds can be considered the ultimate in polarity, with electrons being transferred completely rather than shared. To judge the relative polarity of a covalent bond, chemists use ***electronegativity***, which is a relative measure of how strongly an atom attracts electrons when it forms a covalent bond.

There are various numerical scales for rating electronegativity. Figure 4.6 shows one of the most popular—***the Pauling scale.*** The polarity of a covalent bond can be judged by determining the difference in the electronegativities between the two atoms making the bond. The greater the difference in electronegativities, the greater the imbalance of electron sharing in the bond.

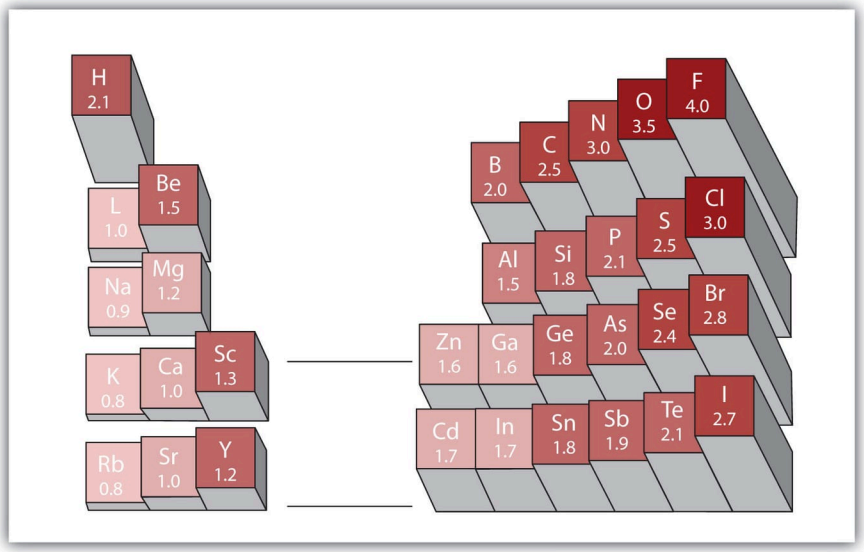


Figure 4.3.2**: Electronegativities of Various Elements.** The Pauling Scale for electronegativities has the value for fluorine atoms set at 4.0, the highest value.

Although there are no hard and fast rules, the general rule is that a difference in electronegativity less than 0.4 indicates the bond is nonpolar; when the difference is greater than 0.4, the bond is considered polar. When the difference in electronegativities is large enough (generally greater than about 1.8), the resulting compound is considered ionic rather than covalent. An electronegativity difference of zero, of course, indicates a nonpolar covalent bond. Examples of electronegativity difference are shown in Figure 4.3.3.

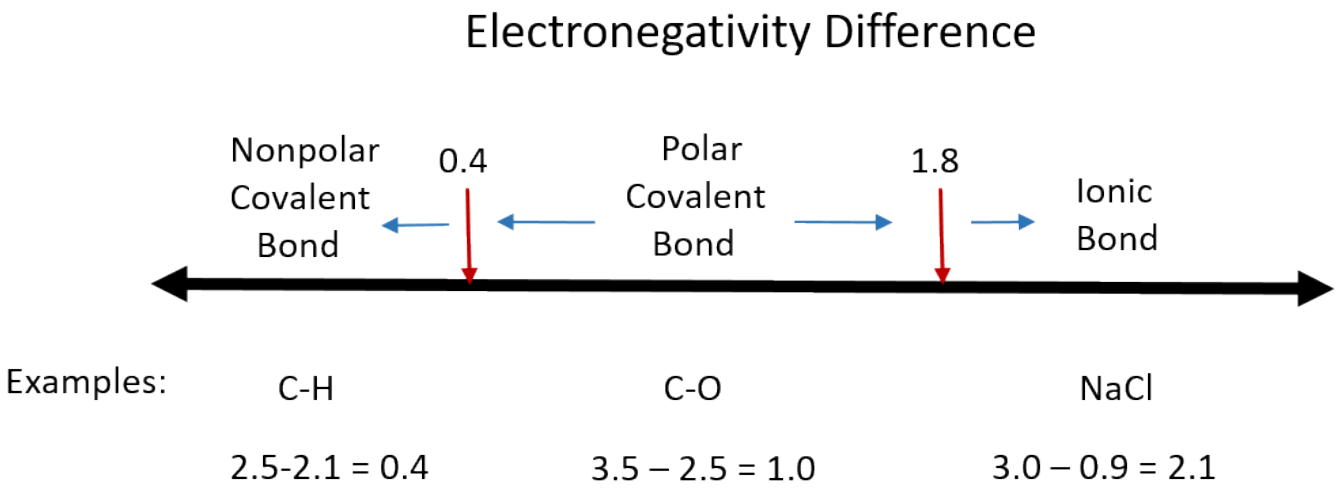


Figure 4.3.3**: Electronegativity Difference Diagram.** The diagram above is a guide for discerning what type of bond forms between two different atoms. By taking the difference between the electronegativity values for each of the atoms involved in the bond, the bond type and polarity can be predicted. Note that full ionic character is rarely reached, however when metals and nonmetals form bonds, they are named using the rules for ionic bonding.

When a molecule's bonds are polar, the molecule as a whole can display an uneven distribution of charge, depending on how the individual bonds are oriented. For example, the orientation of the two O–H bonds in a water molecule (Figure 4.3.4) is bent: one end of the molecule has a partial positive charge, and the other end has a partial negative charge. In short, the molecule

itself is polar. The polarity of water has an enormous impact on its physical and chemical properties. (For example, the boiling point of water [100°C] is high for such a small molecule and is due to the fact that polar molecules attract each other strongly.) In contrast, while the two C=O bonds in carbon dioxide are polar, they lie directly opposite each other in the molecule and so cancel each other's effects. Thus, carbon dioxide molecules are nonpolar overall. This lack of polarity influences some of carbon dioxide's properties. (For example, carbon dioxide becomes a gas at –77°C, almost 200° lower than the temperature at which water boils.)

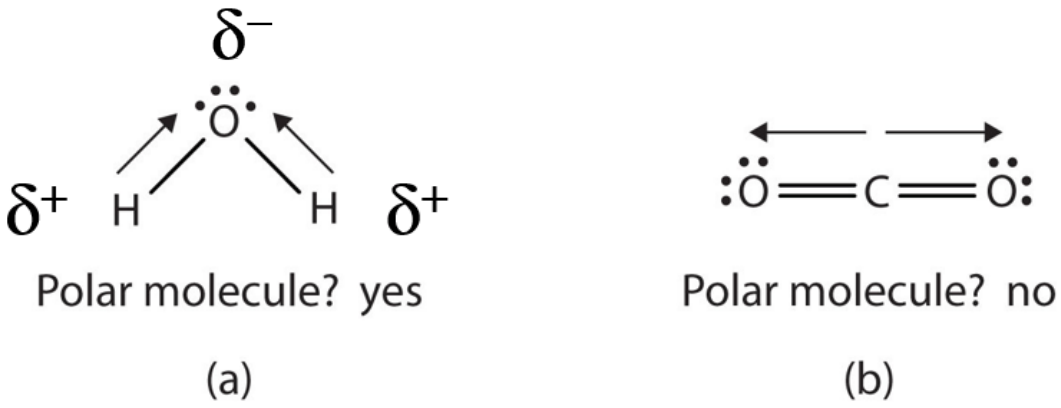


Figure 4.3.4: Physical Properties and Polarity. The physical properties of water (a) and carbon dioxide (b) are affected by their molecular polarities. Note that the arrows in the diagram always point in the direction where the electrons are more strongly attracted. In this diagram, the delta symbol (δ) is used with a (+) or (-) symbol to represent partial positive and partial negative charge distribution in polar covalent bonds. Note that the electrons shared in polar covalent bonds will be attracted to and spend more time around the atom with the higher electronegativity value. When the polarity is equal and directly opposing, as in the case of carbon dioxide (b), the overall molecule will have no overall charge.

Example 4.3.1

Describe the electronegativity difference between each pair of atoms and the resulting polarity (or bond type)

- C and N
- H and H
- Na and F
- O and H

Solution

- The electronegativity difference between Nitrogen (3.0) and Carbon (2.5) is 0.5. Based on our scale, this would represent a Nonpolar to only slightly Polar bond
- Both hydrogen atoms have an electronegativity of 2.1. Thus, the difference is 0 (zero). This bond is nonpolar.
- Sodium has an electronegativity of 0.9 and fluorine's is 4.0. Thus, the difference between the two is 3.1, which falls into the category of ionic bond (ie the most polar bond possible where full charges form).
- Oxygen has an electronegativity of 3.5 and hydrogen is 2.1. The difference between the two is 1.4 which falls into the polar bond category.

Exercise 4.3.1

Test Yourself: Describe the electronegativity difference between each pair of atoms and the resulting polarity (or bond type)

- C and P
- K and Br

- N and N
- Cs and F

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4.4: Properties of Covalent Compounds

Differences Between Ionic and Covalent Compounds

Molecular compounds have many properties that differ from ionic compounds. Some of the generalizations for this group include much lower melting and boiling points when compared with their ionic counterpoints. For example, water (H_2O) has a melting point of 4^oC and a boiling point of 100^oC compared with NaCl that has a melting point of 801^oC and a boiling point of $1{,}413^oC$. This is because the full charges created in ionic bonds have much stronger attractive force than the comparatively weak partial charges created in covalent molecules. thus, ionic compounds tend to form very strong crystalline lattice structures due to the repeating charges of the cation and anion components. Covalent compounds, on the otherhand, do not typically have such well-structured 3-dimensional shapes. Thus they tend to be more brittle and break more easily when in solid form, and many are found in liquid and gas phases. In addition, due to their lack of charges, they tend to be poor electrical and thermal conductors. Many are also insoluble in water due to their nonpolar nature (ie oil and water don't mix).

Table 4.4A shows common differences between covalent and ionic compounds.

Table 4.4A: Comparison of Ionic and Covalent Properties

	Covalent Bonds	Ionic Bonds
State at Room Temperature	Gases, Liquids or Low-Melting Solids	Crystalline Solids
Polarity	Low	High
Solubility	Few are soluble in water; Many are soluble in organic liquids	Many are water soluble; Few are soluble in organic liquids
Formation	A covalent bond is formed between two non-metals that have similar electronegativities. Neither atom is 'strong' enough to attract electrons from the other. For stabilization they share electrons from their outer molecular orbit with others	An ionic bond is formed between a metal and non-metal. Non-metals are more electronegative than metals and will accept electrons donated from the metals. The attraction of the oppositely charged ions results in the formation of the ionic bond.
Conductivity	Do not conduct electricity	Conduct electricity when molten or dissolved in water.
Melting Point	Low	High
Boiling Point	Low	High
Occurs Between	Two nonmetals or a nonmetal and a metalloid	A metal and a nonmetal

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4.5: Naming of Binary Molecular Compounds

Relating the Formula with the Name

Recall that a molecular formula shows the number of atoms of each element that a molecule contains. A molecule of water contains two hydrogen atoms and one oxygen atom, so its formula is H_2O. A molecule of octane, which is a component of gasoline, contains 8 atoms of carbon and 18 atoms of hydrogen. The molecular formula of octane is C_8H_{18}. When writing the chemical formula the element that is the least electronegative (the element that is farther left or further down within the same family group) is written first while the more electronegative element is written second. You will be required to know how to name simple binary covalent compounds (compounds composed of two different elements).



Figure 4.5.1: Nitrogen dioxide (NO_2) is a reddish-brown toxic gas that is a prominent air pollutant produced by internal combustion engines. Gas is captured in a clear glass bottle.

The elements that combine to form binary molecular compounds are both nonmetal atoms or they are a combination of a nonmetal and a metalloid. This contrasts with ionic compounds, which were formed from a metal ion and a nonmetal ion. Therefore, binary molecular compounds are different because ionic charges cannot be used to name them or to write their formulas. Another difference is that two nonmetal atoms will frequently combine with one another in a variety of ratios. Consider the elements nitrogen and oxygen. They combine to make several compounds including

$$\mathrm{NO},\ \mathrm{NO_2},\ \text{and}\ \mathrm{N_2O} \tag{4.5.1}$$

They all can't be called nitrogen oxide. How would someone know which one you were talking about? Each of the three compounds has very different properties and reactivity. A system to distinguish between compounds such as these is necessary.

Prefixes are used in the names of binary molecular compounds to identify the number of atoms of each element. The table below shows the prefixes up to ten.

Table 4.5A: Prefixes used in the Naming of Covalent Molecules

Number of Atoms	Prefixes
1	Mono-
2	Di-
3	Tri-
4	Tetra-
5	Penta-

Number of Atoms	Prefixes
6	Hexa-
7	Hepta-
8	Octa-
9	Nona-
10	Deca-

The rules for using the prefix system of nomenclature of binary compounds can be summarized as follows.

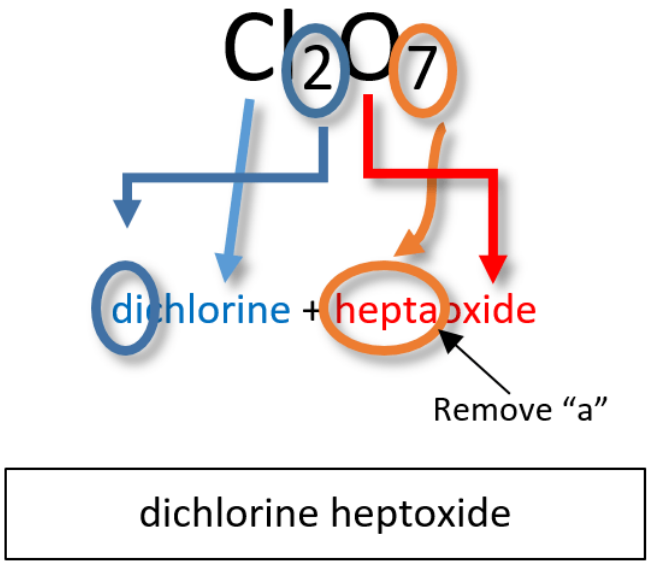
1. Generally, the less-electronegative element is written first in the formula, though there are a few exceptions. *Exception 1*: Carbon is always first in a formula. *Exception 2:* When hydrogen is participating in a covalent bond, it is typically written in the second postion (For example: hydrogen is after nitrogen in a formula such as NH_3) Overall, the order of common nonmetals in binary molecular compounds is C, P, N, H, S, I, Br, Cl, O,
2. When naming the first element, use the full name of the element and the appropriate prefix if there are more than one atom of that element in the formula. If there is only one atom for the first element, the term mono- is NOT used, but is implied. For example, CO is carbon monoxide, not monocarbon monoxide.
3. For the second element the ending of the element's name is typically changed to '*-ide*' and the appropriate prefix is *always* used for the second element.

Note: the *a* or *o* at the end of a prefix is usually dropped from the name when the name of the element begins with a vowel. As an example, four oxygen atoms, is tetroxide instead of tetraoxide. Some examples of molecular compounds are listed in Table 4.5B.

Table 4.5B: Examples of Naming Covalent Molecules

Formula	Names
Cl_2O_7	Dichlorine heptoxide
N_2O	Dinitrogen monoxide
S_2Cl_2	Disulfur dichloride
NO	Nitrogen monoxide

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



dichlorine heptoxide

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4.6: Focus on the Environment - The Love Canal

The Environmental Protection Agency

On December 3rd of 1970 the United States Environmental Protection Agency (EPA) was proposed by President Richard Nixon to be an agency of the federal government charged with protecting human health and the environment. The agency was charged with writing and enforcing regulations based on laws passed by Congress.

The main focus of the EPA as an agency is to conduct research, make environmental assessments, and provide educational materials for use by Congress and the American people regarding environmental and health concerns. The EPA also enforces national standards under a variety of environmental laws, such as the clean air act, and can levy fines, sanctions, and other measures on violators. Within this section, we will learn about creation of the Comprehensive Environmental Response, Compensation, and Liability Act, that is also known as 'Superfund'. The Superfund program was instituted in 1980 and designed to identify and clean up the worst of the hazardous chemical waste sites in the U.S. The first of these sites was the Love Canal described in the next section.

The Love Canal

One of the most famous and important examples of groundwater pollution in the U.S. is the Love Canal tragedy in Niagara Falls, New York (Figure 4.6.1). It is important because the pollution disaster at Love Canal, along with similar pollution calamities at that time (Times Beach, Missouri and Valley of Drums, Kentucky), helped to create Superfund.

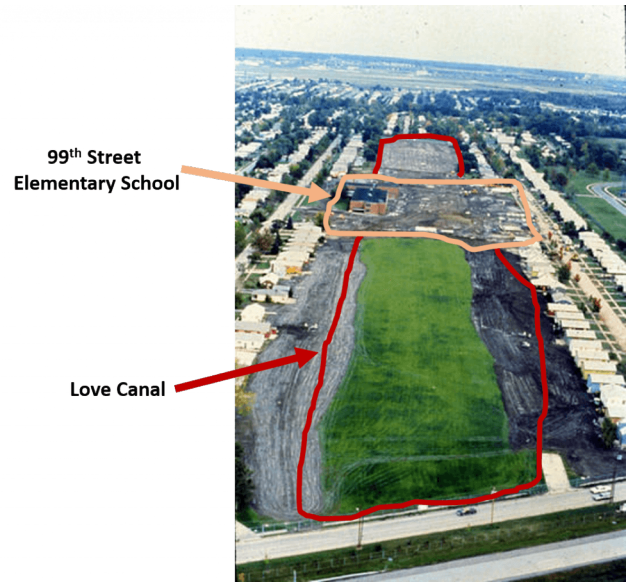


Figure 4.6.1: Love Canal. Source: US Environmental Protection Agency

Love Canal is a neighborhood in Niagara Falls named after a large ditch (approximately 15 m wide, 3–12 m deep, and 1600 m long) that was dug in the 1890s for hydroelectric power. The ditch was abandoned before it actually generated any power and went mostly unused for decades, except for swimming by local residents. In the 1920s Niagara Falls began dumping urban waste into Love Canal, and in the 1940s the U.S. Army dumped waste from World War II there, including waste from the frantic effort to build a nuclear bomb. Hooker Chemical Company purchased the land in 1942 and lined it with clay. Then, the company put into Love Canal an estimated 21,000 tons of hazardous chemical waste, including the carcinogens benzene, dioxin, and polychlorobisphenols (PCBs) in large metal barrels and covered them with more clay (Figure 4.6.2).

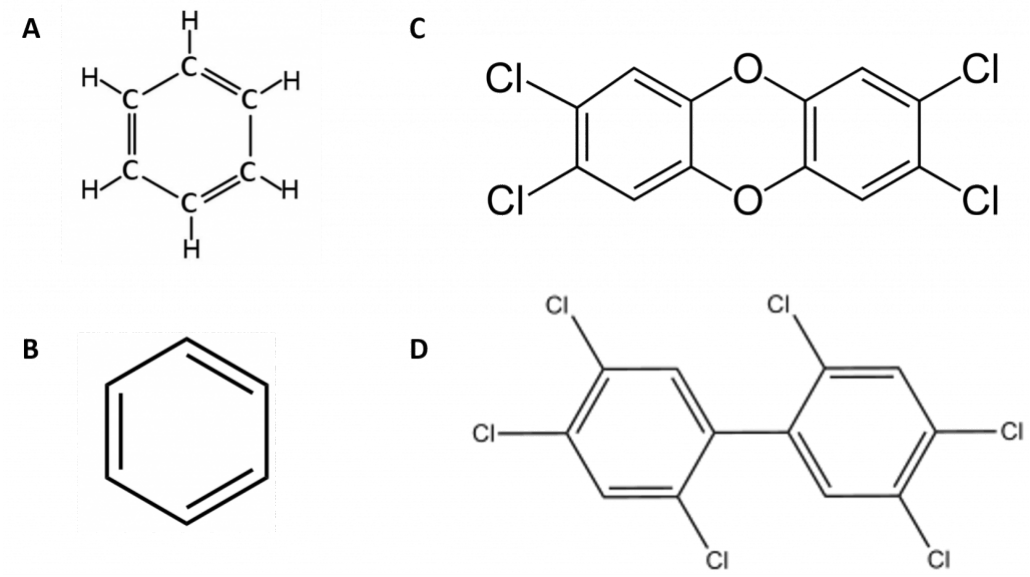


Figure 4.6.2**: Examples of Carcinogens disposed of in the Love Canal.** (A) and (B) are representations of Benzene. In (A) all of the atoms in benzene are shown. (B) is a representative line structure of benzene where carbon atoms are indicated at every bend in every line and hydrogen atoms are implied. (C) line structure of dioxin, and (D) is a line diagram of a representative PCB.

In 1953, Hooker sold the land to the Niagara Falls school board for $1, and included a clause in the sales contract that both described the land use (filled with chemical waste) and absolved them from any future damage claims from the buried waste. The school board promptly built a public school on the site and sold the surrounding land for a housing project that built 200 or so homes along the canal banks and another 1,000 in the neighborhood (Figure 4.6.1). During construction, the canal's clay cap and walls were breached, damaging some of the metal barrels.

Eventually, the chemical waste seeped into people's basements, and the metal barrels worked their way to the surface. Trees and gardens began to die; bicycle tires and the rubber soles of children's shoes disintegrated in noxious puddles. From the 1950s to the late 1970s, residents repeatedly complained of strange odors and substances that surfaced in their yards. Eckardt Beck, the EPA administrator for the region from 1977-1979 recalled in the EPA Journal, "I visited the canal area at that time. Corroding waste-disposal drums could be seen breaking up trough the grounds of backyards. Trees and gardens were turning black and dying. One entire swimming pool had been popped up from its foundation, afloat now on a small sea of chemicals. Puddles of noxious substances were pointed out to be by the residents. Some of these puddles were in their yards, some were in their basements, others yet on the school grounds. Everywhere the air had a faint, choking smell. Children returned from play with burns on their hands and faces. And then there were the birth defects. The New York State Health Department is continuing an investigation into a disturbingly high rate of miscarriages, along with five birth-defect cases detected thus far in the area."[10]

In 1978 President Carter declared a state of emergency at Love Canal, making it the first human-caused environmental problem to be designated that way. The Love Canal incident became a symbol of improperly stored chemical waste. Clean up of Love Canal, which was funded by Superfund and completely finished in 2004, involved removing contaminated soil, installing drainage pipes to capture contaminated groundwater for treatment, and covering it with clay and plastic. In 1995, Occidental Chemical (the modern name for Hooker Chemical) paid $102 million to Superfund for cleanup and $27 million to Federal Emergency Management Association for the relocation of more than 1,000 families. New York State paid $98 million to EPA and the US government paid $8 million for pollution by the Army. The total clean up cost was estimated to be $275 million.

The Love Canal tragedy helped to create Superfund, which has analyzed tens of thousands of hazardous waste sites in the U.S. and cleaned up hundreds of the worst ones. Nevertheless, over 1,000 major hazardous waste sites with a significant risk to human health or the environment are still in the process of being cleaned.

Suggested Assignment:

1. Explore the EPA Superfund Website.

2. Scroll down to the bottom of the page and select ‘Sites Where You Live’

3. Select ‘Your State’ and Show ‘All Sites’.

4. Select a Superfund site within your state and write a 500 word summary describing your chosen site. In the first paragraph, describe the type of toxic waste that is found at the site and what the health and environmental impacts are due to the pollution. In a second paragraphs, describe who is responsible for generating the pollution and what has or is currently being done to restore and clean up the site. Be sure to include the monetary cost of the clean up in your response if it is disclosed and what parties are paying for the clean up.

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4.7: Chapter Summary

Atoms can share pairs of valence electrons to obtain a valence shell octet. This sharing of electrons is a ***covalent bond.*** A species formed from covalently bonded atoms is a molecule and is represented by a ***molecular formula***, which gives the number of atoms of each type in the molecule. The two electrons shared in a covalent bond are called a ***bonding pair of electrons***. The electrons that do not participate in covalent bonds are called ***nonbonding pairs (or lone pairs)*** of electrons. A covalent bond consisting of one pair of shared electrons is called a ***single bond.***

Covalent bonds occur between nonmetal atoms. Naming simple covalent compounds follows simple rules similar to those for ionic compounds. However, for covalent compounds, numerical prefixes are used as necessary to specify the number of atoms of each element in the compound.

In some cases, more than one pair of electrons is shared to satisfy the octet rule. Two pairs of electrons are shared by two atoms to make a ***double bond.*** Three pairs of atoms are shared to make a ***triple bond***. Single, double, and triple covalent bonds may be represented by one, two, or three dashes, respectively, between the symbols of the atoms. In the case of a ***coordinate covalent bond***, one atom supplies both of the electrons and the other atom does not supply any of the electrons.

To judge the relative polarity of a covalent bond, chemists use ***electronegativity,*** which is a relative measure of how strongly an atom attracts electrons when it forms a covalent bond. The greater the electronegativity difference between the atoms involved in the covalent bond, the more polarity the bond displays.

In comparison to ionic compounds, covalent molecules tend to have lower melting and boiling points, are less soluble in water, and are poor conductors of electricity. These major differences are largely due to increased polarity of ionic bonds when compared with covalent bonds.

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5: CHAPTER 5 - MOLECULAR STRUCTURE, POLARITY, AND INTERMOLECULAR FORCES

5.1: Introduction

5.2: Molecular Geometry- Using VSEPR Theory to Predict Molecular Shape

5.3: Molecular Polarity

5.4: Intermolecular Forces and Electrostatic Attractions

5.5: Physical Properties of Intermolecular Forces

5.6: Focus on the Environment

5.7: Chapter Summary

5.8: References

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5.1: Introduction

In the previous chapter, we learned how atoms share electrons to form **covalent bonds** and how to represent those bonds using **Lewis structures**. Lewis structures provide a simple two-dimensional picture of a molecule, showing how atoms are connected and where lone pairs of electrons are located. They also allow us to distinguish between **nonpolar** and **polar covalent bonds** based on differences in electronegativity.

To review, the basic steps for drawing a Lewis structure are:

1. Count the total number of valence electrons for the molecule or polyatomic ion.
2. Identify the central atom and arrange the surrounding atoms around it.
3. Connect the atoms with single bonds.
4. Add lone pairs to the outer atoms to satisfy the octet rule (except for hydrogen).
5. Check whether the central atom has an octet. If necessary, convert lone pairs on surrounding atoms into double or triple bonds.

By following these steps, we can determine how atoms are connected, the types of bonds present, and the locations of lone pairs of electrons. These are essential first steps in understanding the structure of a molecule.

However, Lewis structures have an important limitation—they only show the **connectivity** of atoms, not their actual three-dimensional arrangement in space. In reality, molecules are not flat. Instead, atoms occupy positions in three dimensions that minimize repulsion between regions of electron density.

Each bond and lone pair surrounding the central atom represents a region where electrons are concentrated. These regions, called **electron domains**, repel one another because electrons carry a negative charge. As a result, electron domains arrange themselves as far apart as possible. This simple idea forms the basis of **Valence Shell Electron Pair Repulsion (VSEPR) theory**, which allows us to predict the three-dimensional shape, or **molecular geometry**, of many molecules.

Understanding molecular geometry is about much more than drawing three-dimensional structures. The shape of a molecule determines whether its bond polarities reinforce or cancel one another, which in turn determines whether the molecule is **polar or nonpolar**. Molecular polarity influences how molecules interact with one another, leading to differences in properties such as boiling point, melting point, solubility, and viscosity. By the end of this chapter, you will be able to use a Lewis structure to predict a molecule's geometry, determine whether it is polar, identify its intermolecular forces, and explain many of its physical properties.

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5.2: Molecular Geometry- Using VSEPR Theory to Predict Molecular Shape

Learning Objectives

After completing this section, you should be able to:

- Explain the basic principles of VSEPR theory.
- Distinguish between electron geometry and molecular geometry.
- Predict the molecular geometry of common molecules using a Lewis structure.
- Explain how lone pairs influence molecular shape and bond angles.

From a Lewis Structure to a Molecular Shape

In the previous chapter, you learned how to draw **Lewis structures** to show how atoms are connected within a molecule. Lewis structures provide valuable information about the types of bonds present and the locations of lone pairs of electrons. However, Lewis structures are only **two-dimensional representations** of molecules.

Real molecules exist in **three dimensions**. The arrangement of atoms around the central atom is called the **molecular geometry**, and this three-dimensional shape influences many of a molecule's physical and chemical properties.

To predict molecular geometry, chemists use **Valence Shell Electron Pair Repulsion (VSEPR) theory** (pronounced *vesper*).

The central idea behind VSEPR theory is simple:

Key Idea

- Electron domains repel one another and arrange themselves as far apart as possible.

Because electrons carry a negative charge, regions of high electron density naturally repel one another. The lowest-energy arrangement is therefore the one that minimizes these repulsive forces.

Although VSEPR theory is a simplified model, it accurately predicts the molecular geometry of many small molecules.

Predicting Molecular Geometry

Rather than memorizing dozens of different molecular shapes, it is much easier to follow the same sequence of steps each time to deduce the molecular geometry.

Throughout this chapter, we will use the following five-step strategy.

A Five-Step Strategy for Predicting Molecular Geometry

Step 1. Draw the Lewis structure.



Step 2. Count the electron domains around the central atom.

⬇️

Step 3. Determine the electron geometry.

⬇️

Step 4. Count the number of lone pairs on the central atom.

⬇️

Step 5. Determine the molecular geometry.

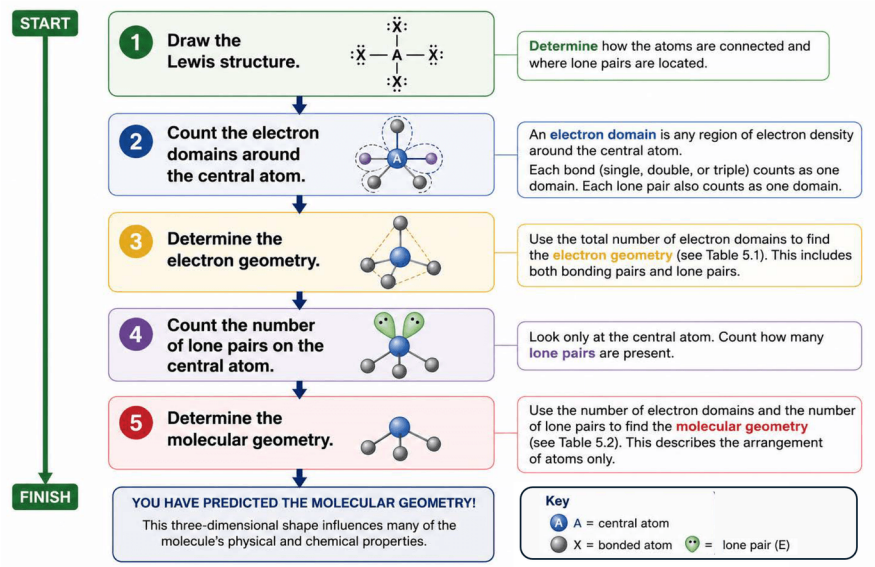


Figure 5.2.1**:** ***Flowchart illustrating the five-step strategy for predicting molecular geometry.*** **1. Draw the Lewis structure** to determine how the atoms are connected and identify the locations of any lone pairs. **2. Count the electron domains** around the central atom. Each single bond, double bond, triple bond, and lone pair counts as one electron domain. **3. Determine the electron geometry** based on the total number of electron domains. Electron geometry includes both bonding pairs and lone pairs. **4. Count the number of lone pairs** on the central atom. **5. Determine the molecular geometry** by combining the electron geometry with the number of lone pairs. Molecular geometry describes the arrangement of the atoms only and does not include lone pairs. The flowchart concludes by noting that the predicted molecular geometry determines many of the molecule's physical and chemical properties.

Step 1: Draw the Lewis Structure

Every molecular geometry problem begins by drawing the **Lewis structure** of the molecule or polyatomic ion. A correct Lewis structure provides the foundation for all of the remaining steps. If the Lewis structure is incorrect, the predicted molecular geometry will also be incorrect.

To draw a Lewis structure:

1. **Count the total number of valence electrons** contributed by all atoms in the molecule or ion. For polyatomic ions, add one

electron for each negative charge or subtract one electron for each positive charge.
2. **Choose the central atom.** In most molecules, the central atom is the least electronegative atom (excluding hydrogen, which is never a central atom).
3. **Connect the surrounding atoms to the central atom** using single covalent bonds.
4. **Complete the octets of the surrounding atoms** by adding lone pairs of electrons.
5. **Place any remaining electrons on the central atom.** If the central atom does not yet have a complete octet, form double or triple bonds as needed by converting lone pairs from surrounding atoms into shared bonding pairs.

Once the Lewis structure is complete, identify the **bonding pairs** and **lone pairs** surrounding the central atom. This information will be used in the remaining steps to predict the molecular geometry.

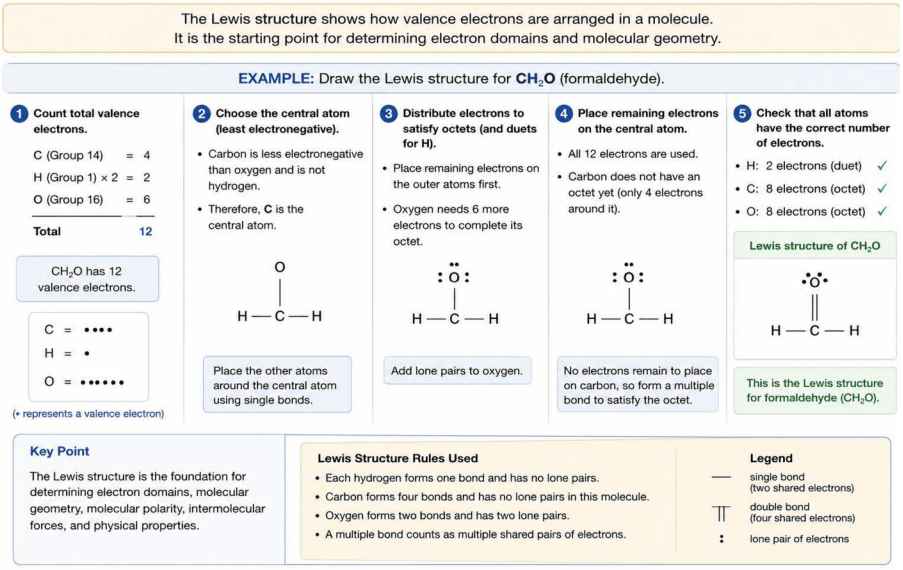


Figure 5.2.2: Drawing the Lewis Structure of Formaldehyde (CH_2O). Five-panel diagram illustrating the steps used to draw the Lewis structure of formaldehyde (CH_2O). Panel 1 counts the total number of valence electrons: carbon contributes 4 electrons, two hydrogen atoms contribute 2 electrons, and oxygen contributes 6 electrons, for a total of 12 valence electrons. Panel 2 identifies carbon as the central atom and connects it to two hydrogen atoms and one oxygen atom with single bonds. Panel 3 places lone pairs on oxygen to satisfy its octet. Panel 4 recognizes that carbon has only six electrons and converts one lone pair on oxygen into a second shared pair, forming a carbon–oxygen double bond. Panel 5 verifies that hydrogen has a duet, while carbon and oxygen each have complete octets. The completed Lewis structure is $H_2C{=}O$, with carbon bonded to two hydrogen atoms by single bonds and to oxygen by a double bond, and oxygen containing two lone pairs.

Note

In VSEPR theory, we are interested only in the electron domains surrounding the **central atom**. Lone pairs located on surrounding atoms do **not** affect the molecular geometry of the central atom.

Step 2: Count the Electron Domains

Next, count the number of **electron domains** surrounding the central atom.

An **electron domain** is any region of electron density around the central atom.

Each of the following counts as **one electron domain**:

- one single bond

- one double bond
- one triple bond
- one lone pair

Notice that double and triple bonds each count as only **one** electron domain because the electrons occupy the same general region of space.

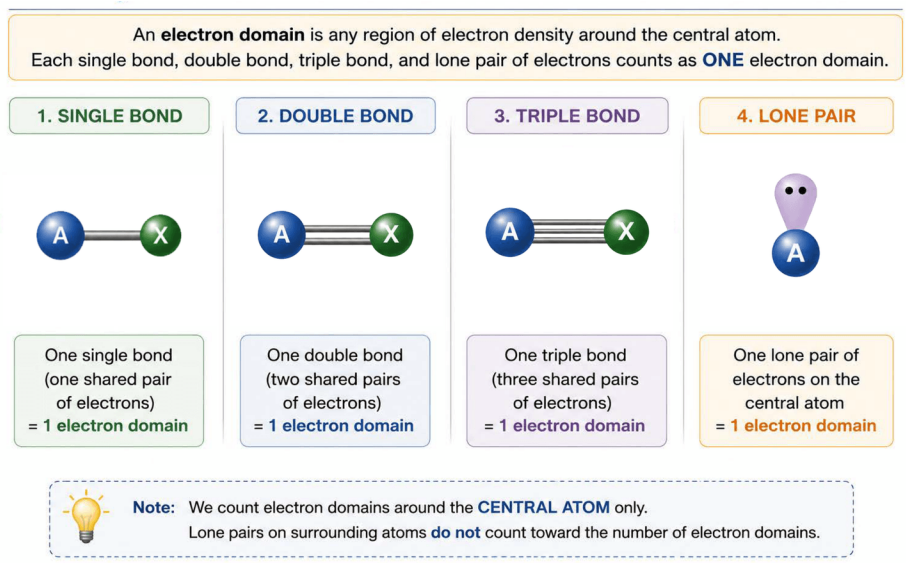


Figure 5.2.3: Each Bond and Lone Pair Counts as One Electron Domain. Four-panel diagram illustrating how electron domains are counted in VSEPR theory. The first panel shows a central atom (A) connected to one bonded atom (X) by a single bond and states that one single bond counts as one electron domain. The second panel shows a double bond between A and X and states that one double bond, although composed of two shared electron pairs, still counts as one electron domain. The third panel shows a triple bond between A and X and states that one triple bond, although composed of three shared electron pairs, also counts as one electron domain. The fourth panel shows a lone pair of electrons (E) on the central atom and states that one lone pair counts as one electron domain. A note at the bottom emphasizes that electron domains are counted only around the central atom; lone pairs on surrounding atoms are not included.

Let's use a water molecule ($\mathbf{H_2O}$) as an example. The oxygen atom is the **central atom** and is bonded to two hydrogen atoms. In addition to these two O–H bonds, the oxygen atom has **two lone pairs of electrons**. Remember that each bond and each lone pair counts as **one electron domain**. Therefore, the oxygen atom in a water molecule has a total of **four electron domains**: two bonding domains and two lone-pair domains (Figure 5.2.4).

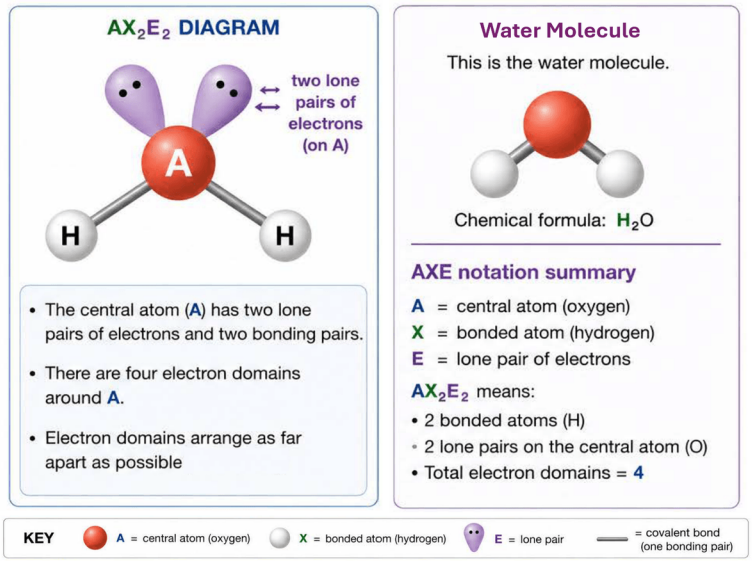
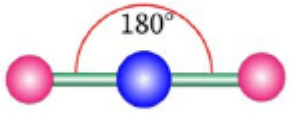
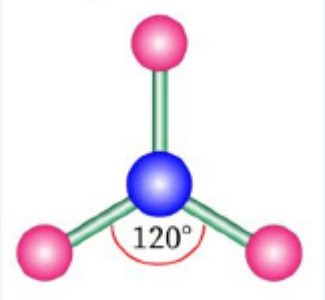


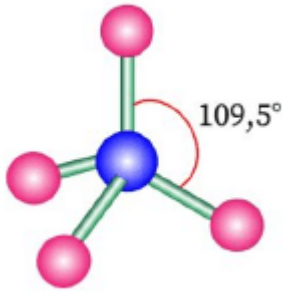
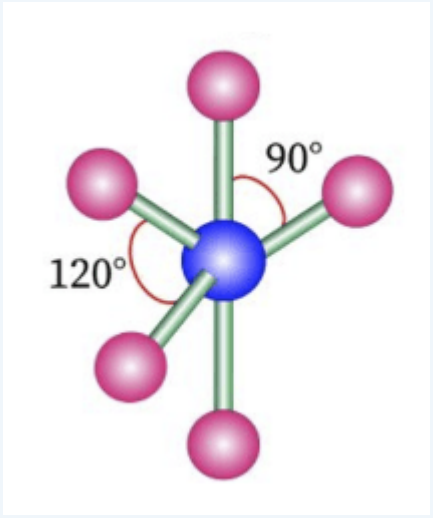
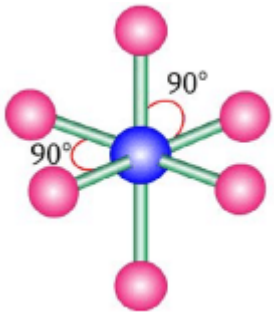
Figure 5.2.4: Identifying Electron Domains in a Water Molecule (H_2O). Diagram of a water molecule (H_2O) illustrating how electron domains are counted using AXE notation. The central oxygen atom (A) is bonded to two hydrogen atoms (X_2) by two single covalent bonds and has two lone pairs of electrons (E_2). The figure explains that A represents the central atom, X represents a bonded atom, and E represents a lone pair of electrons. The notation AX_2E_2 indicates two bonded atoms and two lone pairs surrounding the central atom, for a total of four electron domains. A key identifies the symbols used for the central atom, bonded atoms, lone pairs, and covalent bonds.

Step 3: Determine the Electron Geometry

The number of electron domains determines the **electron geometry**. Electron geometry describes the arrangement of **all electron domains**, including both bonding pairs and lone pairs. Use Table 5.2A to predict the electron geometry of your central atom.

Table 5.2A: Using Electron Domains to Determine Electronic Geometry

Number of Electron Domains	VSEPR Electronic Geometry	Ideal Bond Angle	Visual Representation
2	Linear	180°	
3	Trigonal Planar	120°	

Number of Electron Domains	VSEPR Electronic Geometry	Ideal Bond Angle	Visual Representation
4	Tetrahedral	109.5°	
5	Trigonal Bipyramidal	180°/120°/90°	
6	Octahedral	180°/90°	

Note

To determine the Electronic Geometry, you need to answer one main question: How many **electron domains** are present on the central atom?

Step 4: Count the Lone Pairs

Now count the number of **lone pairs on the central atom**. Lone pairs occupy more space than bonding pairs because their electrons are attracted to only one nucleus rather than being shared between two nuclei. As a result, lone pairs exert stronger repulsive forces than bonding pairs.

The relative strengths of these repulsions are

BP–BP < LP–BP < LP–LP

where

- BP = bonding pair
- LP = lone pair

These stronger repulsions compress nearby bond angles and often change the molecular geometry.

Step 5: Determine the Molecular Geometry

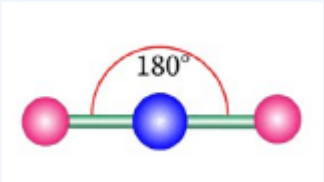
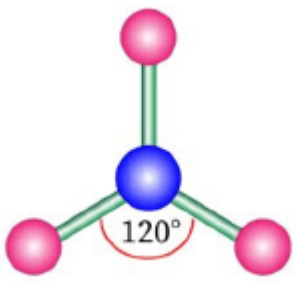
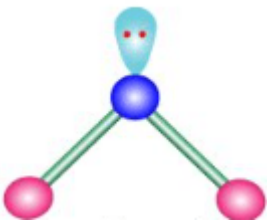
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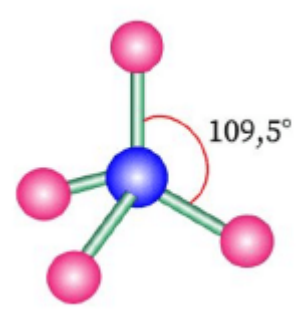
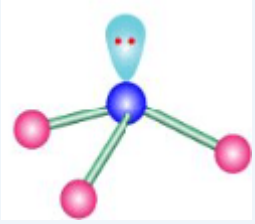
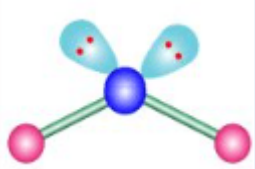
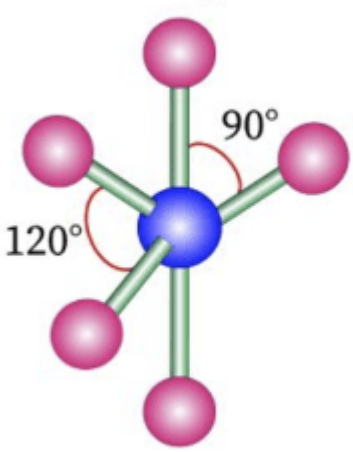
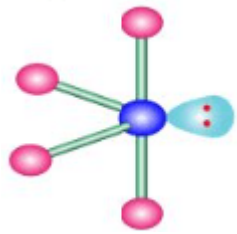
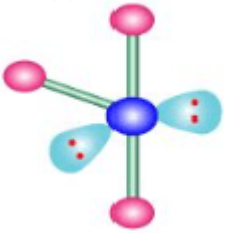
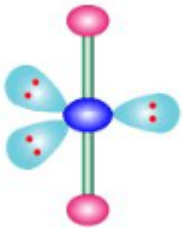
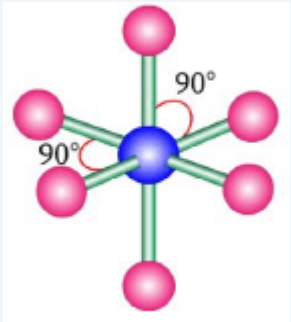
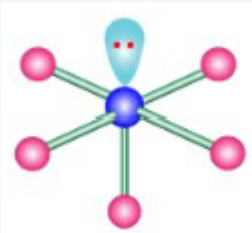
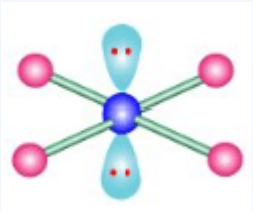
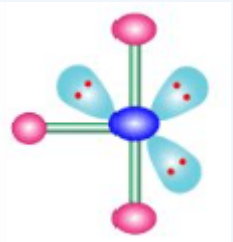
- the number of electron domains, and
- the number of lone pairs

to determine the **molecular geometry**.

Unlike electron geometry, molecular geometry describes only the positions of the **atoms**. Lone pairs influence the shape but are not included when naming the molecular geometry. Table 5.2B summarizes the common molecular geometries. To use this table, slide down the lefthand column to identify the total number of electron domains on your central atom, and then slide across the top row to identify number of lone pairs of electrons on your central atom. Where that row and column meet will identify the appropriate molecular geometry for your central atom.

Table 5.2B: Electron Domains and Lone Pairs of Electrons are Used to Determine Molecular Geometry

	Number of non-bonding electron pairs (or lone pairs) on a central atom			
Total Number of Electron Domains	0	1	2	3
2	Linear 			
3	Trigonal Planar 	Bent 		

Number of non-bonding electron pairs (or lone pairs) on a central atom				
4	Tetrahedral 	Trigonal Pyramidal 	Bent 	
5	Trigonal Bipyramidal 	See-Saw 	T-Shaped 	Linear 
6	Octahedral 	Square Pyramidal 	Square Planar 	T-shaped 

Key Idea

- To determine the Molecular Geometry, follow up with a second question : How many **lone pairs** are attached to the central atom?

Electron Geometry versus Molecular Geometry

One of the most common mistakes students make is confusing **electron geometry** with **molecular geometry**.

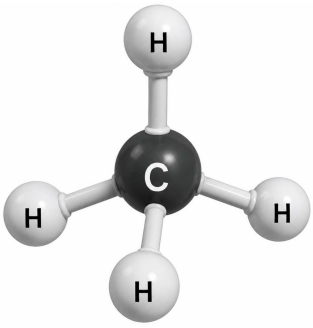
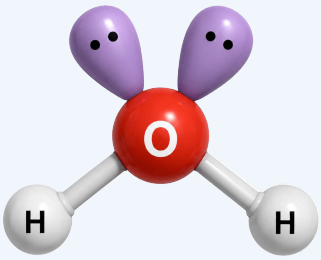
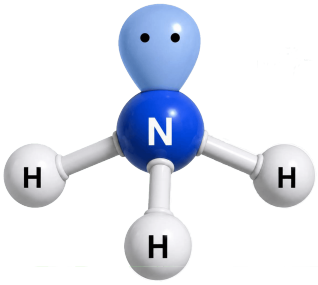
Remember:

Electron geometry includes **all electron domains.**

Molecular geometry includes **only the bonded atoms.**

The difference is illustrated below.

Table 5.2C: Examples of Determining Electronic and Molecular Geometries

Molecule	Visual of Structure	Number of Electron Domains	Number of Lone Pairs	Electron Geometry
CH_4		4	4	Tetrahedral
H_2O		4	2	Tetrahedral
NH_3		4	1	Tetrahedral

Notice that all three molecules contain **four electron domains**. The only difference is the number of lone pairs.

Chemist's Shortcut: AXE Notation

Once you become comfortable predicting molecular geometry, you may find it useful to use **AXE notation** as a shorthand.

- **A** = central atom
- **X** = bonded atoms
- **E** = lone pairs

Table 5.2D: AXE Notation

Molecule	AXE Notation
CO_2	AX_2
BF_3	AX_3
CH_4	AX_4
NH_3	AX_3E
H_2O	AX_2E_2

Notice that the AXE notation simply summarizes the information you already determined using the five-step process. It is not a separate method for predicting molecular geometry.

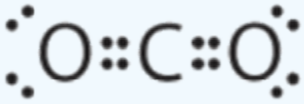
Example 5.2.1

Carbon dioxide is an example of a molecule with **two electron domains** around the central atom. Use the five-step strategy to determine its molecular geometry.

Solution

Step 1: Draw the Lewis Structure

- The Lewis structure for CO_2 is shown below. The central atom, carbon, contributes four valence electrons, and each oxygen atom contributes six. The Lewis electron structure is:



Step 2: Count the Electron Domains

- Around the central carbon atom there are:
  - one carbon–oxygen double bond
  - one carbon–oxygen double bond
- Although each bond is a double bond, each counts as one electron domain.
- Total electron domains = 2

Step 3: Determine the Electron Geometry

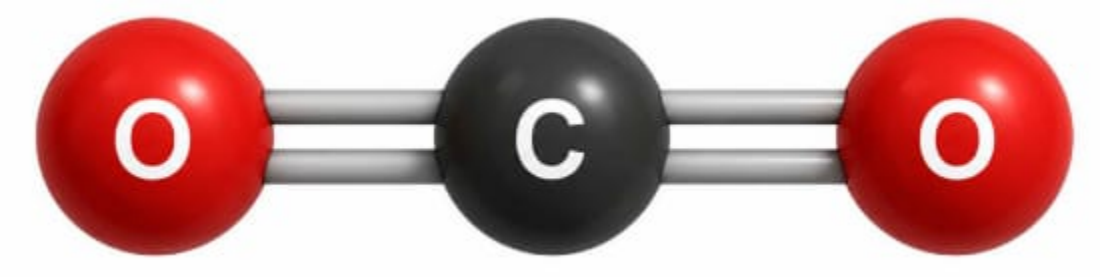
- From Table 5.2A, a central atom with two electron domains has a linear electron geometry.

Step 4: Count the Lone Pairs

- The central carbon atom has no lone pairs.

Step 5: Determine the Molecular Geometry

- Because all electron domains are bonding domains, the molecular geometry is the same as the electron geometry.
- Molecular geometry: Linear



- Carbon dioxide has an ideal bond angle of **180°**.

Key Idea

- Lone pairs on the oxygen atoms do **not** affect the molecular geometry because VSEPR theory considers only the electron domains surrounding the **central atom**.

Exercise 5.2.1

What is the molecular geometry of Boron Trichloride?

Answer available at the end of this section.

Key Idea

- Boron in BCl_3 is an **exception** to the octet rule. It is stable with only six electrons surrounding the central atom.

Exercise 5.2.3

What is the molecular geometry of phosphorous pentachloride?

Answer available at the end of this section.

Key Idea

- Phosphorus is another exception to the octet rule. In PCl_5, the phosphorus atom is surrounded by **10 electrons**, forming an **expanded octet**. Thus, phosphorous can share a total of 3 or 5 bonds
- Sulfur can also support an expanded octet. The normal octet bonding has a total of 2 bonds. Expanded potential for 4 or 6 bonds is also possible.

Molecules Without a Single Central Atom

The five-step VSEPR strategy works best for molecules and polyatomic ions that contain **one central atom**. However, many important molecules—including biological molecules, polymers, and many organic compounds—contain **multiple central atoms** connected together.

Fortunately, VSEPR theory can still be applied to these larger molecules. Instead of analyzing the entire molecule at once, each central atom is considered separately. The local arrangement of atoms around each central atom can be predicted using the same five-step strategy introduced in this chapter.

For example, in ethanol (CH_3CH_2OH), both carbon atoms can be analyzed individually. Each carbon atom has four electron domains, giving each a **tetrahedral electron geometry**. The oxygen atom also has four electron domains but contains two lone pairs, resulting in a **bent molecular geometry** around the oxygen atom.

As molecules become larger and more complex, however, the overall three-dimensional shape depends on more than just the local geometry around each atom. Different parts of the molecule may rotate around single bonds or interact with one another through attractive and repulsive forces. These interactions can change the overall shape of the molecule in ways that VSEPR theory alone cannot predict.

For this reason, VSEPR theory is best viewed as a tool for predicting the **local geometry** around individual atoms. More advanced experimental techniques, such as X-ray crystallography and nuclear magnetic resonance (NMR) spectroscopy, or computational methods are often used to determine the complete three-dimensional structures of large molecules.

Looking Ahead

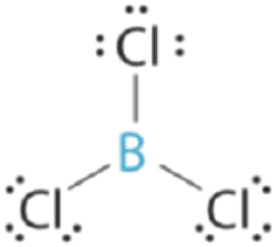
In the next section, we'll build on what you've learned in this chapter by using molecular geometry to determine whether a molecule is **polar or nonpolar**. We'll see that knowing the shape of a molecule is the key to understanding how molecules interact with one another and why substances have different physical properties.

Answers

Exercise 5.2.1

Step 1: Draw the Lewis Structure

- The Lewis structure for BCl_3 is shown below. The central atom, boron, contributes three valence electrons, and each chlorine atom contributes seven valence electrons. The Lewis electron structure is:



Step 2: Count the Electron Domains

- Around the central boron atom there are
  - three boron–chlorine single bonds

Step 3: Determine the Electron Geometry

- According to Table 5.2A, three electron domains produce a trigonal planar electron geometry.

Step 4: Count the Lone Pairs

- The central boron atom has no lone pairs.

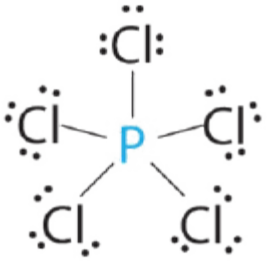
Step 5: Determine the Molecular Geometry

- Because all three electron domains are bonding domains, the molecular geometry is also trigonal planar.
- The ideal bond angle is 120°.
- Each single bond counts as one electron domain.
  - Total electron domains = 3

Exercise 5.2.3

Step 1: Draw the Lewis Structure

- The Lewis structure for PCl_5 is shown below. Phosphorus has five valence electrons, and can form an expanded bonding formation that exceeds the octet rule. Thus, it can form single bonds to each of the five chlorine atoms. Note that each chlorine has seven valence electrons. So, the Lewis electron structure of PCl5 is:



Step 2: Count the Electron Domains

- Around the phosphorus atom there are five phosphorus–chlorine single bonds three equatorial positions, separated by 120° two axial positions, located 90° above and below the equatorial plane

Step 3: Determine the Electron Geometry

- According to Table 5.2A, five electron domains adopt a trigonal bipyramidal electron geometry.

Step 4: Count the Lone Pairs

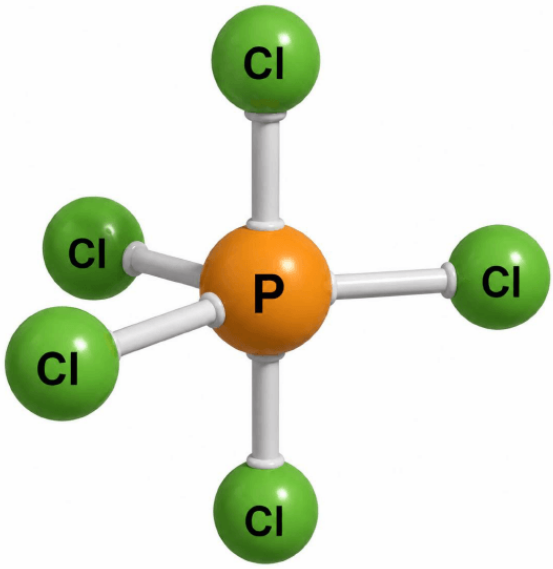
- The phosphorus atom has no lone pairs.

Step 5: Determine the Molecular Geometry

- Because all five electron domains are bonding domains, the molecular geometry is also **trigonal bipyramidal.**

This geometry contains:

- Each bond counts as one electron domain.
- Total electron domains = 5



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5.3: Molecular Polarity

Learning Objectives

After completing this section, you should be able to:

- Distinguish between **bond polarity** and **molecular polarity**.
- Draw bond dipoles for polar covalent bonds.
- Predict whether a molecule is **polar** or **nonpolar** based on its molecular geometry.
- Explain how molecular shape affects the overall distribution of charge.

5.3.1 From Bond Polarity to Molecular Polarity

In Chapter 4, we learned that some covalent bonds are **polar** because electrons are shared unequally between atoms with different electronegativities. The more electronegative atom attracts the shared electrons more strongly, creating a partial negative charge (δ–), while the less electronegative atom develops a partial positive charge (δ+).

However, knowing that a bond is polar does **not** necessarily tell us whether the **entire molecule** is polar.

To determine molecular polarity, we must consider **two factors**:

1. Are the individual bonds polar?
2. How are those bonds arranged in three-dimensional space?

Now that we can predict molecular geometry using VSEPR theory, we have all of the information needed to determine whether an entire molecule is polar or nonpolar.

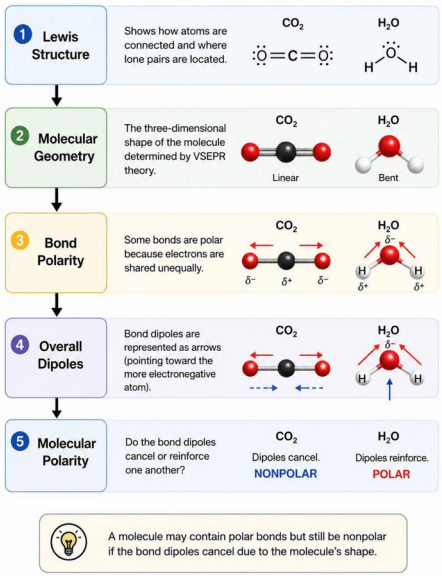


Figure 5.3.1**: Predicting Molecular Polarity from Bond Polarity and Molecular Geometry.** Flowchart illustrating why bond polarity alone does not determine molecular polarity. The diagram presents a five-step process for predicting molecular polarity using carbon dioxide (CO_2) and water (H_2O) as examples. Step 1 begins with drawing the Lewis structure. Step 2 determines the molecular geometry, showing that CO_2 is linear while H_2O is bent. Step 3 identifies the polar bonds in each molecule, with bond dipole arrows pointing toward the more electronegative oxygen atoms.

Step 4 combines the individual bond dipoles to determine the overall molecular dipole. In CO_2, the two bond dipoles are equal in magnitude and point in opposite directions, so they cancel. In H_2O, the bent geometry causes the bond dipoles to reinforce one another, producing a net dipole. Step 5 concludes that CO_2 is a nonpolar molecule, while H_2O is a polar molecule. The figure emphasizes that molecular polarity depends on both bond polarity and molecular geometry.

Key Point: Predicting molecular polarity requires both bond polarity and molecular geometry.

5.3.2 Bond Dipoles

A **bond dipole** forms whenever two atoms with different electronegativities share electrons unequally.

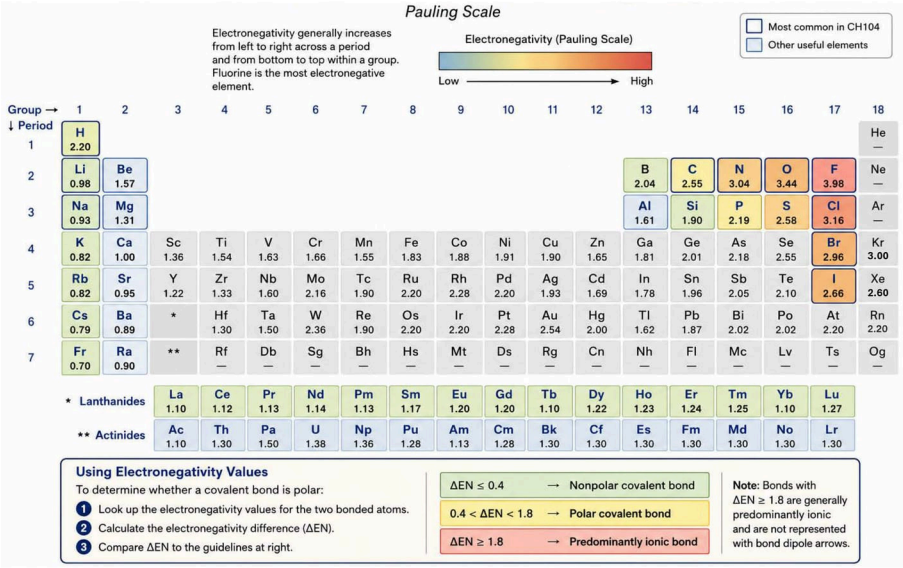
Because the electrons spend more time near the more electronegative atom, one end of the bond becomes slightly negative (δ–) while the other becomes slightly positive (δ+).

Bond dipoles are represented by an arrow that points **toward the more electronegative atom**. The small cross (+) at the tail of the arrow marks the partially positive end of the bond.

Nonpolar covalent bonds do not have bond dipoles because the electrons are shared equally.

As discussed in **Chapter 4**, to determine if a bond is polar or nonpolar, we will use the following Electronegativity Difference (ΔEN) guidelines throughout this textbook:

- ΔEN ≤ 0.4 → nonpolar covalent bond
- 0.4 < ΔEN < 1.8 → polar covalent bond
- ΔEN ≥ 1.8 → predominantly ionic bond



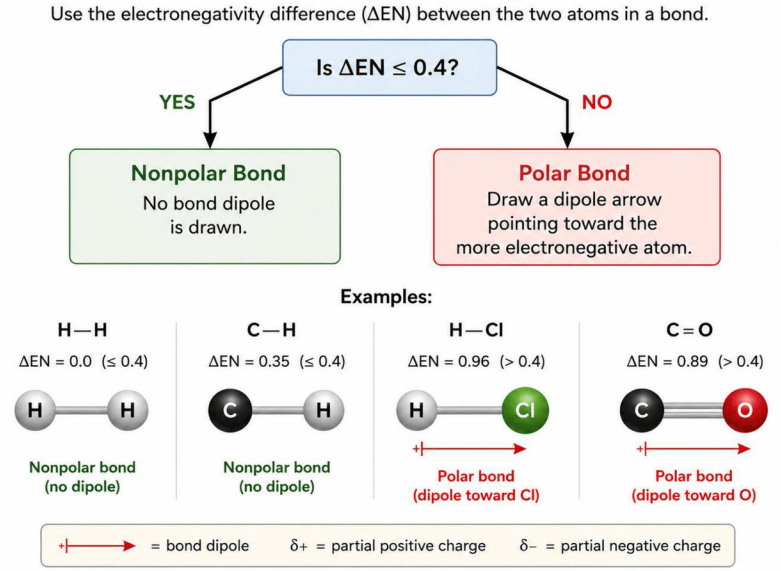


Figure 5.3.2:Determining Whether a Covalent Bond Is Polar. Upper Panel: Periodic table displaying elemental electronegativity values based on the Pauling scale. Each element is labeled with its chemical symbol and electronegativity value and is color-coded to indicate relative electronegativity, with lighter colors representing lower values and darker orange-red colors representing higher values. Electronegativity generally increases from left to right across a period and from bottom to top within a group, with fluorine (3.98) having the highest electronegativity. The table includes the lanthanide and actinide series below the main periodic table. A reference box explains how to use electronegativity values to determine bond polarity by calculating the electronegativity difference (ΔEN) between two bonded atoms. The guidelines indicate that bonds with ΔEN ≤ 0.4 are classified as nonpolar covalent, bonds with 0.4 < ΔEN < 1.8 are classified as polar covalent, and bonds with ΔEN ≥ 1.8 are generally classified as predominantly ionic. A note reminds readers that predominantly ionic bonds are not represented using bond dipole arrows in this chapter. **Lower Panel:** Decision tree for determining whether a covalent bond is polar and whether a bond dipole should be drawn. The process begins by calculating the electronegativity difference (ΔEN) between the two bonded atoms. If ΔEN is **0.4 or less**, the bond is classified as a **nonpolar covalent bond**, and no bond dipole is drawn. If ΔEN is **greater than 0.4**, the bond is classified as a **polar covalent bond**, and a bond dipole arrow is drawn pointing toward the more electronegative atom. Four examples are provided: H–H (ΔEN = 0.0) and C–H (ΔEN = 0.35) are classified as nonpolar covalent bonds with no bond dipoles. H–Cl (ΔEN = 0.96) and C=O (ΔEN = 0.89) are classified as polar covalent bonds, with bond dipole arrows pointing toward chlorine and oxygen, respectively. A legend identifies the bond dipole arrow and the symbols δ⊕ and δ⊖ for partial positive and partial negative charges.

Note: This figure is used to determine **bond dipoles in covalent bonds**. Bonds with an electronegativity difference greater than about **1.8** are generally classified as **ionic** and are not represented using bond dipole arrows.

5.2.3 Five-Step Strategy for Determining Molecular Polarity

Once the molecular geometry has been determined, predicting molecular polarity becomes a straightforward process.

Step 1

Draw the Lewis structure.

Step 2

Determine the molecular geometry using VSEPR theory.

Step 3

Identify the polar bonds.

- Only bonds between atoms with electronegativity differences greater than 0.4 have bond dipoles.

Step 4

Draw the bond dipoles.

- Each dipole points toward the more electronegative atom.

Step 5

Determine whether the bond dipoles cancel.

- If the dipoles cancel completely, the molecule is **nonpolar**.
- If they do not cancel, the molecule is **polar**.

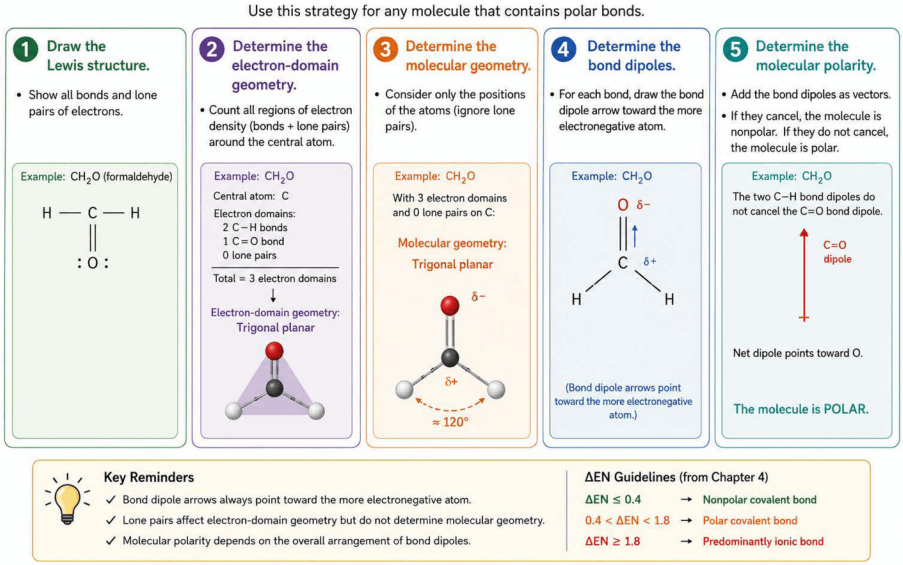


Figure 5.3.3: Five-Step Strategy for Determining Molecular Polarity. Infographic illustrating a five-step strategy for determining molecular polarity using formaldehyde (CH_2O) as an example. Step 1 shows the Lewis structure with carbon as the central atom bonded to two hydrogen atoms by single bonds and to one oxygen atom by a double bond. Step 2 counts the electron domains around the central carbon atom, identifying three bonding domains and no lone pairs, resulting in three electron domains and a trigonal planar electron geometry. Step 3 determines the molecular geometry as trigonal planar with bond angles of approximately 120°. Step 4 identifies the polar bonds and draws bond dipole arrows pointing toward the more electronegative oxygen atom; the carbon–hydrogen bonds are treated as nonpolar and do not have bond dipoles. Step 5 evaluates the overall molecular polarity by combining the bond dipoles. Because the carbon–oxygen bond dipole is not canceled by the surrounding bonds, the molecule has a net dipole directed toward the oxygen atom and is classified as polar. A reminder box notes that bond dipole arrows always point toward the more electronegative atom, lone pairs affect molecular geometry, and molecular polarity depends on the overall arrangement of bond dipoles. A summary box reviews the electronegativity difference guidelines used in the textbook: $\Delta EN \leq 0.4$ indicates a nonpolar covalent bond, $0.4 < \Delta EN < 1.8$ indicates a polar covalent bond, and $\Delta EN \geq 1.8$ indicates a predominantly ionic bond.

5.2.4 Molecular Geometry Determines Molecular Polarity

The three-dimensional arrangement of atoms determines whether the bond dipoles cancel or reinforce one another.

Think of each bond dipole as a small arrow pulling in a particular direction.

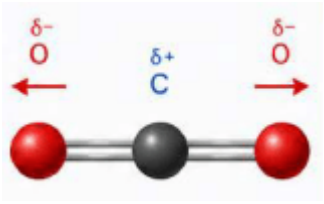
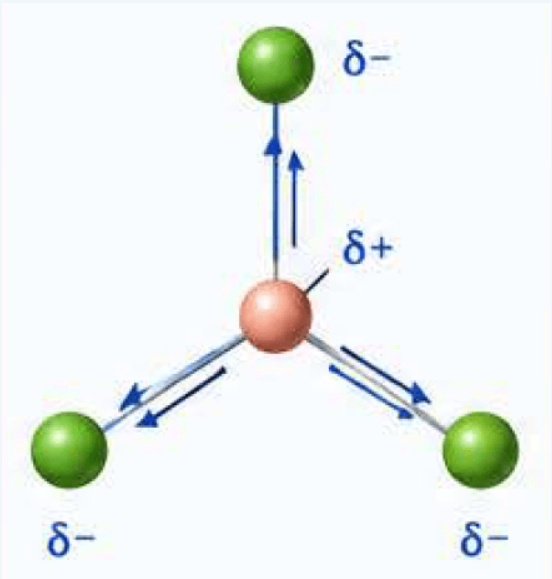
- If the arrows pull equally in opposite directions, they cancel and **the overall molecule is nonpolar**, even if it contains polar bonds within the molecule.
- If one direction is favored, the molecule has a **net dipole** and is polar.

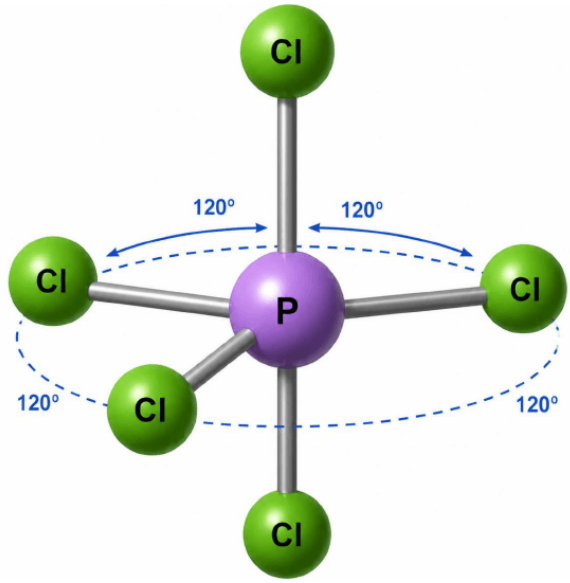
Unlike individual bond dipoles, the **molecular dipole** describes the polarity of the molecule as a whole.

5.2.5 Symmetry Matters

Many molecules can be classified quickly by examining their symmetry. Symmetrical molecules are often nonpolar.

Table 5.3A: Determining Symmetry in Molecules

Chemical Formula	Molecular Geometry	Overall Polarity: Polar? Nonpolar?
CO_2	Linear 	**Nonpolar** - the two carbon-oxygen dipoles are equal in magnitude and opposite in direction, so they cancel.
BCl_3	Trigonal Planar 	**Nonpolar** - the three dipoles are equal in magnitude and each at 120^o from one another. This symmetry causes the forces to cancel out

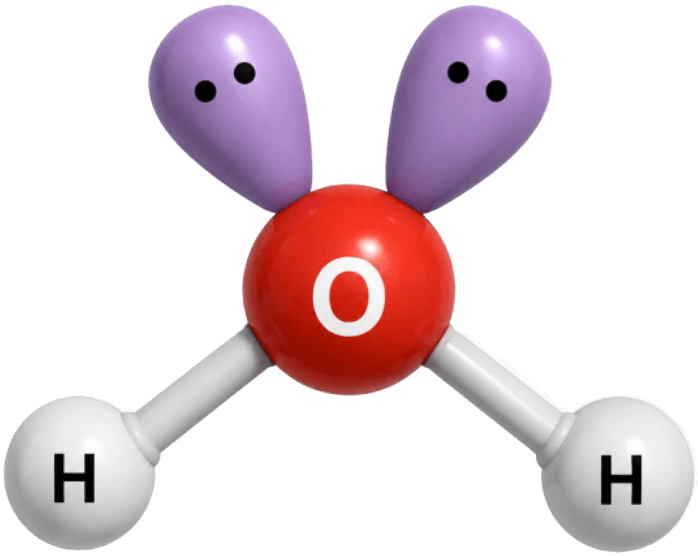
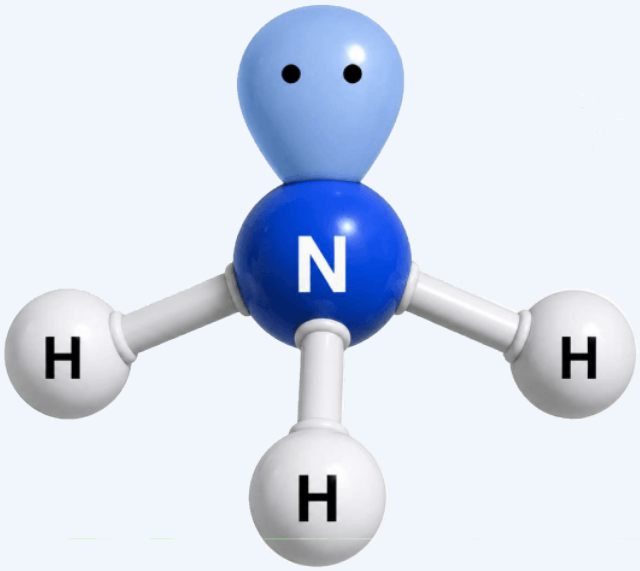
Chemical Formula	Molecular Geometry	Overall Polarity: Polar? Nonpolar?
PCl_5	Trigonal Bipyramidal 	**Nonpolar** - the two axial dipoles are equal in magnitude and are in opposite direction (180^o apart). The three equatorial bond dipoles are also the same magnitude and are at 120^o symmetry. Thus, they also cancel out.

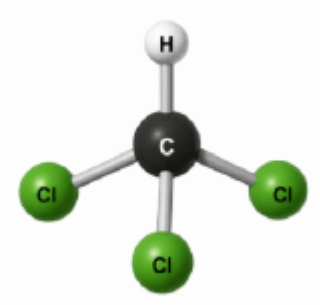
Although these molecules contain polar bonds, their **symmetrical arrangements** cause the **bond dipoles to cancel** completely.

Asymmetrical molecules are often polar. This commonly occurs when:

- lone pairs create an asymmetric shape, or
- the atoms surrounding the central atom are different.

Table 5.3B: Analysis of Assymmetric Molecules

Chemical Formula	Molecular Geometry	Overall Polarity: Polar? Nonpolar?
H_2O	Bent 	**Polar -** The two **O–H bonds** are polar because oxygen is more electronegative than hydrogen. The oxygen atom carries a partial negative charge (δ–), while each hydrogen atom carries a partial positive charge (δ+). The two O–H bond dipoles are equal in magnitude, but because water has a **bent** molecular geometry, they are not arranged directly opposite one another and therefore do not cancel. The two lone pairs of electrons on the oxygen atom contribute to the bent shape of the molecule. As a result, the bond dipoles combine to produce a **net molecular dipole directed toward the oxygen atom**. Consequently, **H_2O is a polar molecule.**
NH_3	Trigonal Pyramidal 	Polar - The three **N–H bonds** are polar because nitrogen is more electronegative than hydrogen. The nitrogen atom carries a partial negative charge (δ–), while each hydrogen atom carries a partial positive charge (δ+). The three N–H bond dipoles are equal in magnitude, but because ammonia has a **trigonal pyramidal** molecular geometry, they are not arranged directly opposite one another and therefore do not cancel. The lone pair of electrons on the nitrogen atom contributes to the asymmetrical shape of the molecule. As a result, the bond dipoles combine to produce a **net molecular dipole directed toward the nitrogen atom**. Consequently, **NH_3 is a polar molecule.**

Chemical Formula	Molecular Geometry	Overall Polarity: Polar? Nonpolar?
$CHCl_3$	Tetrahedral 	**Polar** - The three **C–Cl bonds** are polar because chlorine is more electronegative than carbon. Each chlorine atom carries a partial negative charge (δ–), while the carbon atom carries a corresponding partial positive charge (δ+). The three C–Cl bond dipoles are equal in magnitude. The **C–H bond** is considered **nonpolar** in this textbook because the electronegativity difference between carbon and hydrogen is very small (ΔEN = 0.35). As a result, there is no bond dipole to oppose the three C–Cl bond dipoles. Therefore, the bond dipoles do not cancel, producing a **net molecular dipole directed toward the chlorine atoms**. Consequently, **$CHCl_3$ is a polar molecule.**

In these molecules, the bond dipoles do not cancel, producing a net molecular dipole.

Chemistry in Everyday Life

The polarity of molecules has a tremendous influence on their physical properties. Polar molecules are generally more soluble in water and often have higher boiling points because they experience stronger intermolecular attractions. Nonpolar molecules tend to dissolve in nonpolar substances such as oils and fats.

In the next section, we'll explore how molecular polarity determines the **intermolecular forces** between molecules and how those forces affect melting points, boiling points, solubility, and many other physical properties.

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5.4: Intermolecular Forces and Electrostatic Attractions

Learning Objectives

After completing this section, you should be able to:

- Distinguish between **intramolecular bonds** and **electrostatic attractions between particles**.
- Identify the major types of electrostatic attractions found in introductory chemistry.
- Predict the dominant electrostatic attraction present in a substance.
- Compare the relative strengths of different electrostatic attractions.
- Explain how electrostatic attractions influence physical properties such as melting point, boiling point, solubility, and viscosity.

5.4.1 From Molecules to Materials

So far in this chapter, we have focused on the structure of **individual molecules**. We first learned how to determine molecular geometry using VSEPR theory and then used molecular geometry to predict whether a molecule is polar or nonpolar.

But molecules rarely exist in isolation. Instead, they interact with neighboring particles through a variety of attractive forces. These attractions help explain why some substances are gases at room temperature, while others are liquids or solids. They also influence many familiar physical properties, including melting point, boiling point, viscosity, surface tension, and solubility.

All of these attractions arise from the same fundamental principle:

Opposite charges attract, and like charges repel.

The difference between the various types of attractions lies in **what kinds of particles are interacting** and **whether the charges are full charges or partial charges**.

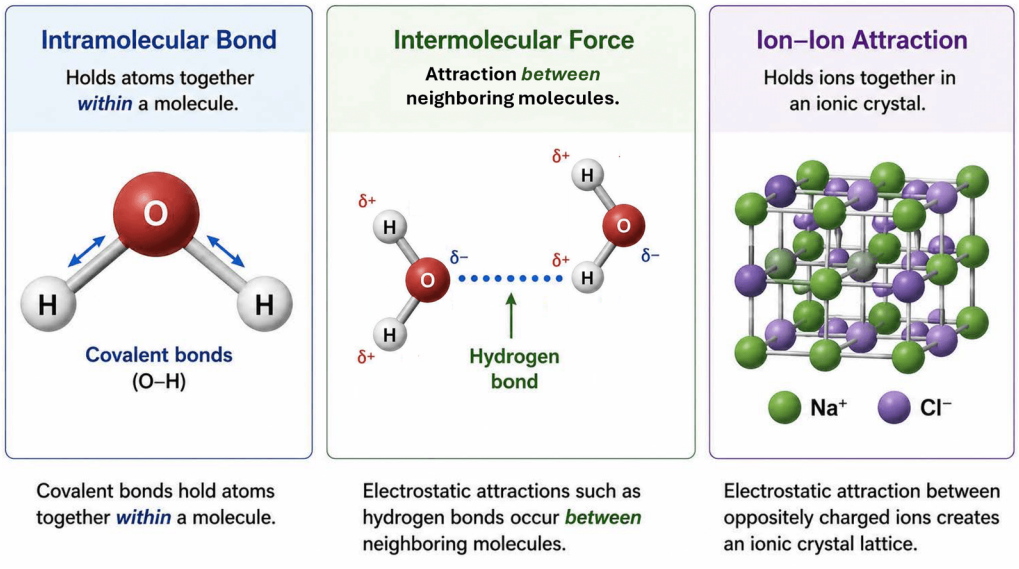


Figure 5.4.1**: Chemical Bonds and Electrostatic Attractions.** Three-panel diagram comparing the types of attractive forces discussed in this chapter. The left panel illustrates an **intramolecular covalent bond** within a single water molecule, showing oxygen covalently bonded to two hydrogen atoms. The panel explains that covalent bonds hold atoms together **within** a molecule. The center panel shows **two neighboring water molecules** connected by a dotted

hydrogen bond between the partially negative oxygen atom of one molecule and the partially positive hydrogen atom of the other. The panel explains that intermolecular forces are electrostatic attractions **between** neighboring molecules. The right panel shows a three-dimensional sodium chloride crystal lattice composed of alternating sodium ions (Na^+) and chloride ions (Cl^-). The panel explains that ion-ion attractions are electrostatic attractions between oppositely charged ions that hold ionic compounds together in an ionic crystal lattice. Together, the three panels distinguish between covalent bonds within molecules, intermolecular forces between molecules, and electrostatic attractions between ions in ionic solids.\

Covalent bonds hold atoms together **within** a molecule and are therefore called **intramolecular bonds**. Electrostatic attractions occur **between** neighboring particles. These attractions include intermolecular forces between molecules, ion-ion attractions between oppositely charged ions, and ion-dipole attractions between ions and polar molecules.

Although electrostatic attractions are generally weaker than covalent bonds, they have a profound effect on the physical properties of matter.

5.4.2 Types of Electrostatic Attractions

Electrostatic attractions can be grouped according to the types of particles involved.

1. Attractions Involving Ions

These attractions occur between positively charged cations and negatively charged anions.

Ion-ion attractions

- Occur between cations and anions.
- Hold ionic compounds together in a repeating three-dimensional crystal lattice.
- Generally represent the strongest type of electrostatic attractions.

Ion-ion attractions occur between **positively charged cations** and **negatively charged anions**. Because ions carry **full positive and negative charges**, the electrostatic attraction between them is much stronger than the attractions that occur between neutral molecules.

Unlike covalent compounds, ionic compounds do **not** exist as individual molecules. Instead, each ion is surrounded by multiple ions of the opposite charge, forming a repeating three-dimensional arrangement called an **ionic crystal lattice** (Figure 5.xx). The crystal lattice extends throughout the entire solid and is responsible for many of the characteristic properties of ionic compounds.

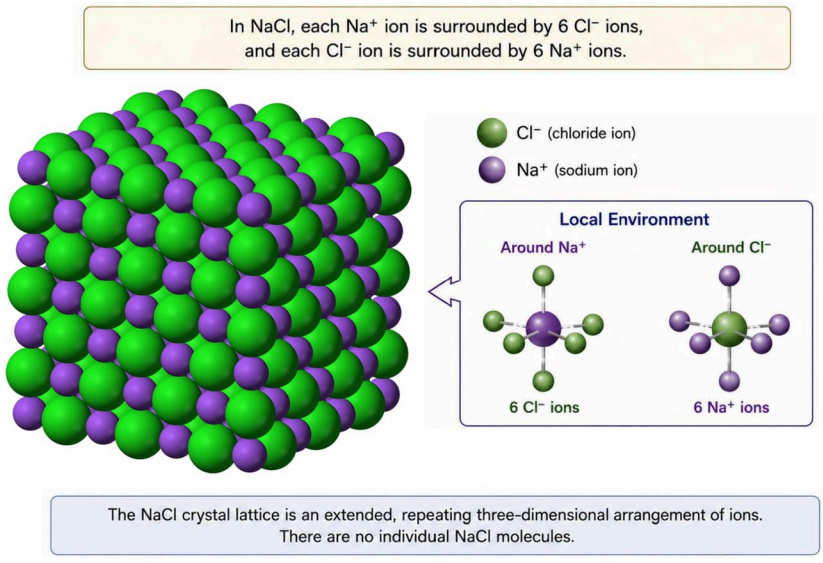


Figure 5.4.2: Sodium Chloride Crystal Lattice. Three-dimensional illustration of the sodium chloride crystal lattice. Purple spheres represent sodium ions (Na^+) and green spheres represent chloride ions (Cl^-) arranged in an alternating, repeating pattern. An inset shows the local coordination environment: each sodium ion is surrounded by six chloride ions, and each chloride ion is surrounded by six sodium ions. The figure emphasizes that solid NaCl is an extended crystal lattice rather than individual NaCl molecules. The formula **NaCl** represents the simplest whole-number ratio of ions in the crystal (a **formula unit**), not an individual molecule.

In sodium chloride (NaCl), each sodium ion (Na^+) is surrounded by chloride ions (Cl^-), and each chloride ion is surrounded by sodium ions. This repeating arrangement maximizes the attractive forces between oppositely charged ions while minimizing repulsions between ions of the same charge. The chemical formula of an ionic compound, such as **NaCl**, represents the **simplest whole-number ratio** of ions present in the crystal and is called a **formula unit**. A formula unit does not represent a single, isolated particle but rather the repeating ratio of ions throughout the crystal lattice.

Because ion-ion attractions are very strong, ionic compounds typically have:

- **High melting points**
- **High boiling points**
- **Hard, crystalline structures**
- **Poor electrical conductivity as solids**
- **Good electrical conductivity when molten or dissolved in water**, because the ions are free to move.

Table 5.4A: The Utility of Ionic Compounds

Ionic Compound	Cation	Anion	Common Use
NaCl	Na^+	Cl^-	Table salt
MgO	Mg^{2+}	O^{2-}	Refractory ceramics, antacids
CaF_2	Ca^{2+}	F^-	Mineral fluorite; source of fluoride
KBr	K^+	Br^-	Laboratory reagent
$NaNO_3$	Na^+	NO_3^-	Fertilizer

Although these compounds contain different ions, they are all held together by **ion-ion electrostatic attractions**.

Key Term: Formula Unit

A **formula unit** is the simplest whole-number ratio of cations and anions in an ionic compound. Unlike a molecular formula, a formula unit does **not** represent an individual molecule but the repeating composition of the ionic crystal lattice.

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2. Attractions Involving Molecules (Intermolecular Forces)

Unlike ion-ion attractions, **intermolecular forces** are electrostatic attractions that occur between **neighboring neutral or uncharged molecules**. These attractions arise from regions of partial positive and negative charge within molecules. Although intermolecular forces are generally weaker than ion-ion attractions, they have a major influence on the physical properties of substances.

The strength of the intermolecular forces between molecules affects many observable properties, including:

- Melting point
- Boiling point
- Viscosity
- Surface tension
- Vapor pressure
- Solubility

In general, **stronger intermolecular forces require more energy to separate neighboring molecules**. As a result, substances with stronger intermolecular forces generally have higher melting points and boiling points than substances with weaker intermolecular forces.

For example, liquids boil when their molecules absorb enough thermal energy to overcome the attractive forces holding neighboring molecules together. Likewise, solids melt when their particles gain enough thermal energy to overcome the attractive forces that hold them in fixed positions.

There are **three major types of intermolecular forces**:

1. Dipole-dipole interactions
2. Hydrogen bonding
3. London dispersion forces

As you read about each type of intermolecular force, remember that **more than one intermolecular force may be present in a substance**. Chemists often identify all of the intermolecular forces that are present and then determine which interaction has the greatest influence on the substance's physical properties.

Dipole-Dipole Interactions

In the previous section, we learned that some molecules are **polar** because they have an unequal distribution of electrons and their bond dipoles do not cancel. Polar molecules possess **permanent dipoles**, meaning one end of the molecule is partially positive (δ⊕) while the other end is partially negative (δ⊖).

When the partially positive end of one polar molecule is adjacent to the partially negative end of a neighboring molecule, an **attractive dipole-dipole interaction** occurs. If like partial charges are adjacent, a **repulsive electrostatic interaction** results (Figure 5.xx).

This behavior is especially apparent in **liquids**, where molecules are constantly moving, rotating, and colliding with one another. As neighboring molecules continually change orientation, they experience both attractive and repulsive interactions. Because attractive orientations are lower in energy, they are favored overall, allowing dipole-dipole interactions to help hold the liquid together.

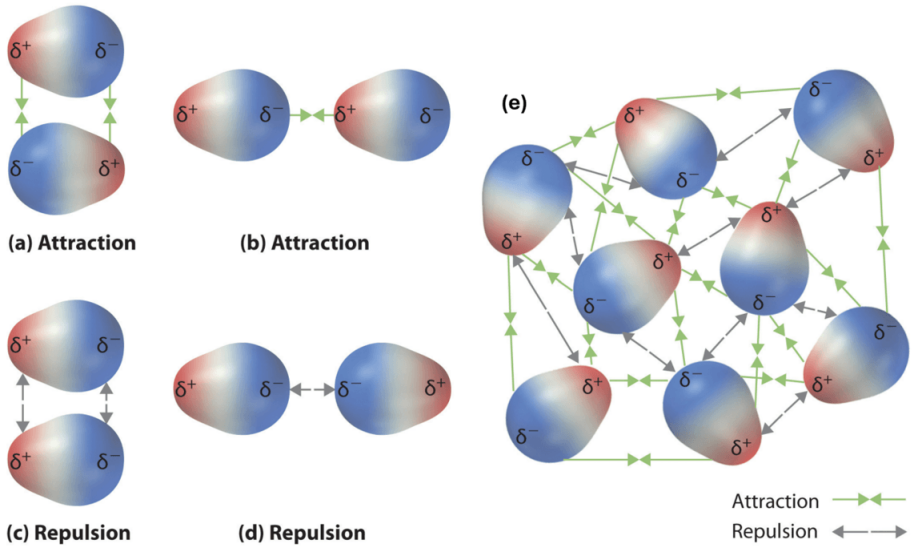


Figure 5.4.3**:Molecular Orientation Determines Dipole-Dipole Interactions (a, b)** When the partially positive end (δ⊕) of one polar molecule is adjacent to the partially negative end (δ⊖) of a neighboring molecule, an **attractive dipole-dipole interaction** occurs. **(c, d)** When like partial charges (δ⊕–δ⊕ or δ⊖–δ⊖) are adjacent, **repulsive electrostatic interactions** occur. **(e)** In a liquid, molecules are in constant motion, continuously rotating, translating,

and colliding with one another. As a result, neighboring molecules continually change orientation, experiencing both attractive and repulsive interactions. Because attractive orientations are lower in energy, they are favored overall, allowing dipole-dipole attractions to help hold the liquid together.

Molecular solids behave differently than liquids. In a molecular solid, intermolecular forces hold neighboring molecules in relatively fixed positions within a crystal. Although the molecules continue to vibrate, they generally cannot translate or rotate freely. As a result, favorable molecular orientations are maintained, producing a stable, ordered arrangement. As the solid is heated, thermal energy eventually overcomes these intermolecular forces, allowing the molecules to move more freely and the solid to melt.

One example of a molecule that exhibits dipole-dipole interactions is **formaldehyde (CH_2O)**. Because formaldehyde is a polar molecule, neighboring molecules align so that the partially negative oxygen atom is attracted to the partially positive carbon atom of a nearby molecule.

Dipole-dipole interactions occur **only between polar molecules**. The strength of the interaction depends on both the magnitude of the molecular dipole and the orientation of neighboring molecules.

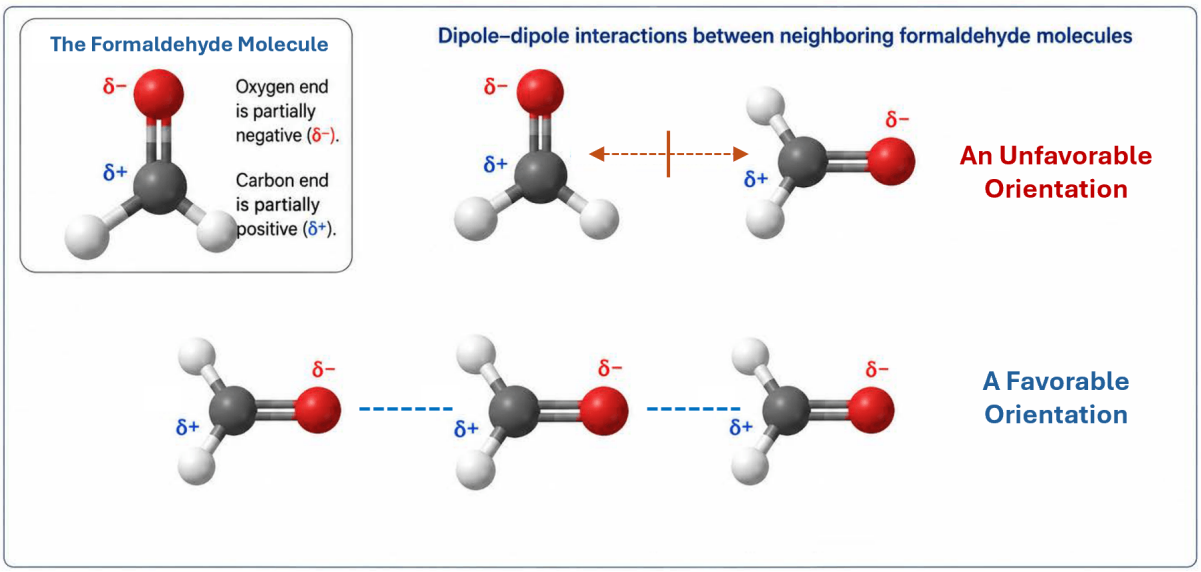


Figure 5.4.4: Dipole-Dipole Interactions Between Formaldehyde Molecules. Diagram illustrating dipole-dipole interactions between formaldehyde (CH_2O) molecules. An inset shows a single formaldehyde molecule with the oxygen atom labeled as partially negative (δ⁻) and the carbon atom labeled as partially positive (δ⁺), indicating the molecule's permanent dipole. The upper example shows an unfavorable orientation in which the partially positive carbon atoms face one another, producing electrostatic repulsion. The lower example shows a favorable orientation in which the partially negative oxygen atom of one molecule is adjacent to the partially positive carbon atom of a neighboring molecule, producing attractive dipole-dipole interactions that can extend throughout the liquid.

Hydrogen Bonding

Hydrogen bonding is a **special type of dipole-dipole interaction** that occurs when a hydrogen atom is covalently bonded to **nitrogen (N), oxygen (O), or fluorine (F).** These highly electronegative atoms pull electron density away from hydrogen, leaving it with a relatively large partial positive charge (δ⁺). A hydrogen bond forms when this partially positive hydrogen is attracted to a **lone pair of electrons on a neighboring nitrogen, oxygen, or fluorine atom** (Figure 5.xx). **Both of these requirements must be present for hydrogen bonding to occur.** Although hydrogen bonds are stronger than ordinary dipole-dipole interactions, they are **still intermolecular forces**, not covalent bonds.

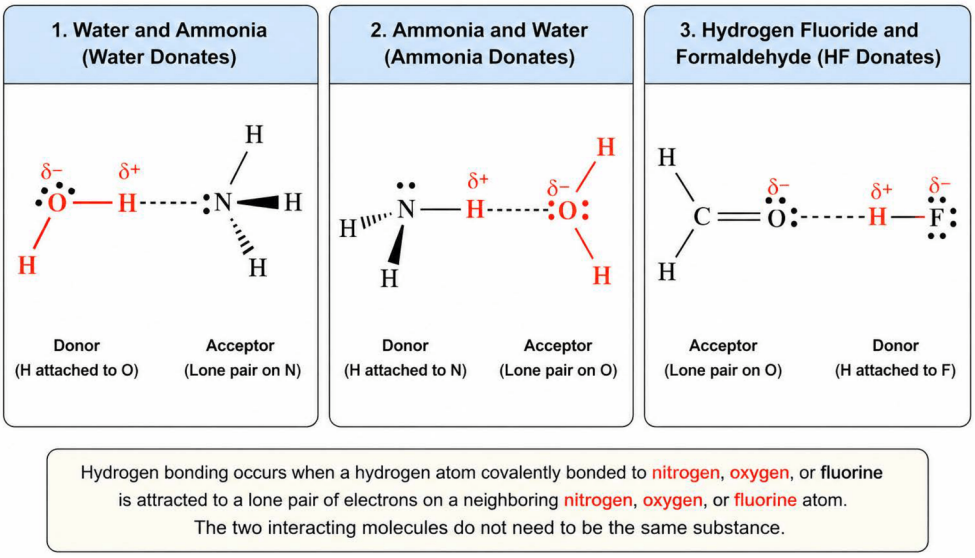


Figure 5.4.5: Requirements for Hydrogen Bonding Between Molecules. Three-panel diagram illustrating the requirements for hydrogen bonding. Hydrogen bonding occurs when a hydrogen atom covalently bonded to **nitrogen (N), oxygen (O), or fluorine (F)** is attracted to a lone pair of electrons on a neighboring nitrogen, oxygen, or fluorine atom. Panel 1 shows a water molecule forming a hydrogen bond to the lone pair on an ammonia molecule. Panel 2 shows an ammonia molecule forming a hydrogen bond to the lone pair on a water molecule. Panel 3 shows hydrogen fluoride forming a hydrogen bond to the carbonyl oxygen of formaldehyde. In each example, the hydrogen bond is represented by a dashed line connecting a hydrogen atom covalently bonded to nitrogen, oxygen, or fluorine with a lone pair of electrons on a neighboring nitrogen, oxygen, or fluorine atom. The figure demonstrates that hydrogen bonding requires both a highly polarized H–N, H–O, or H–F bond and an available lone pair on a neighboring electronegative atom.

Because hydrogen bonding requires a hydrogen atom bonded directly to **N, O, or F**, not all polar molecules are capable of hydrogen bonding. For example, **water (H_2O)**, **ammonia (NH_3)**, and **hydrogen fluoride (HF)** all exhibit hydrogen bonding because they contain hydrogen atoms bonded to highly electronegative atoms. In contrast, **formaldehyde (CH_2O)** is a polar molecule and experiences dipole-dipole interactions, but it cannot form hydrogen bonds with other formaldehyde molecules because its hydrogen atoms are bonded to carbon rather than oxygen (Figure 5.x). However, in mixed solutions, the carbonyl oxygen of formaldehyde can accept hydrogen bonds from neighboring molecules (Figure 5.x.3)

Hydrogen bonding has a profound effect on the physical properties of many substances. Compared with molecules of similar size, substances capable of hydrogen bonding generally have **higher boiling points**, **higher melting points**, and **greater surface tension** because additional energy is required to overcome these stronger intermolecular attractions.

Water (Figure 5.xx) provides one of the best examples of the importance of hydrogen bonding. Each water molecule can form hydrogen bonds with several neighboring water molecules, creating a continuously changing network of intermolecular attractions. Although individual hydrogen bonds continually break and reform as water molecules move, the overall network helps explain many of water's unique properties, including its unusually high boiling point, strong surface tension, and ability to dissolve many ionic and polar substances.

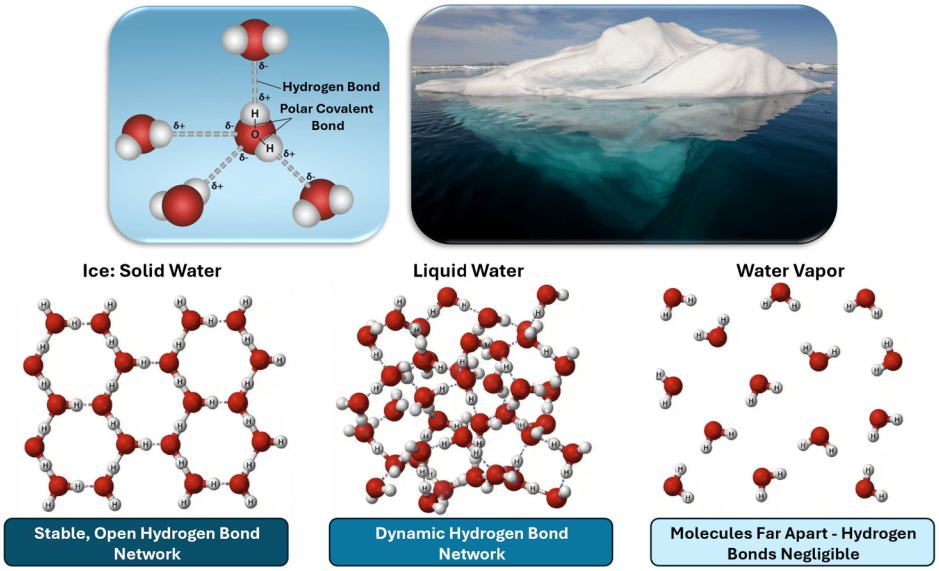


Figure 5.4.6: Hydrogen Bonding Explains the Unique Properties of Water. Composite figure illustrating hydrogen bonding in water across its three phases. The upper left panel shows several water molecules with solid O–H polar covalent bonds within each molecule and dashed hydrogen bonds between neighboring molecules. The upper right panel shows a floating glacier, illustrating that solid ice is less dense than liquid water. The lower panels compare molecular arrangements in the three phases of water. In solid water (ice), hydrogen bonds form a stable, open network that holds molecules in fixed positions. In liquid water, hydrogen bonds continually break and reform as molecules move, creating a dynamic network. In water vapor (gas), molecules are widely separated and hydrogen bonding is negligible.

Photo of Glacial Ice by AWeith - Own work, CC BY-SA 4.0

Chemistry in Action: Why Does Ice Float?

Most substances become **more dense** when they freeze because their particles pack more closely together. Water behaves differently. As water freezes, hydrogen bonds organize the molecules into an open, hexagonal crystal structure that occupies more volume than the liquid. Because the same mass of water now occupies a larger volume, the density decreases, allowing ice to float on liquid water.

This unusual property helps insulate lakes and oceans during the winter, allowing aquatic life to survive beneath the surface.

Connection to Biology

Hydrogen bonding is one of the most important intermolecular forces in living systems. It helps stabilize the three-dimensional structure of proteins, holds the two strands of DNA together, and contributes to the unique properties of water that make life possible

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London Dispersion Forces

Not all molecules are polar. Many molecules have no permanent dipole because their electrons are distributed symmetrically. Yet these substances can still exist as liquids and solids. If no attractive forces existed between their molecules, they would all remain gases under ordinary conditions.

The attraction that allows all atoms and molecules to condense into liquids and solids is called a **London dispersion force**. Unlike dipole-dipole interactions, which arise from permanent molecular dipoles, London dispersion forces arise from **temporary fluctuations in electron density**.

Electrons are constantly moving around the nuclei of atoms. At any instant, the electrons may be distributed slightly unevenly, producing a **temporary (instantaneous) dipole** in an atom or molecule (Figure 5.xx). This temporary dipole can distort the electron cloud of a neighboring atom or molecule, inducing a dipole in that neighbor. The resulting attraction between these temporary, induced dipoles is called a **London dispersion force**.

Video Tutorial on London Dispersion Forces By Bozeman Science.

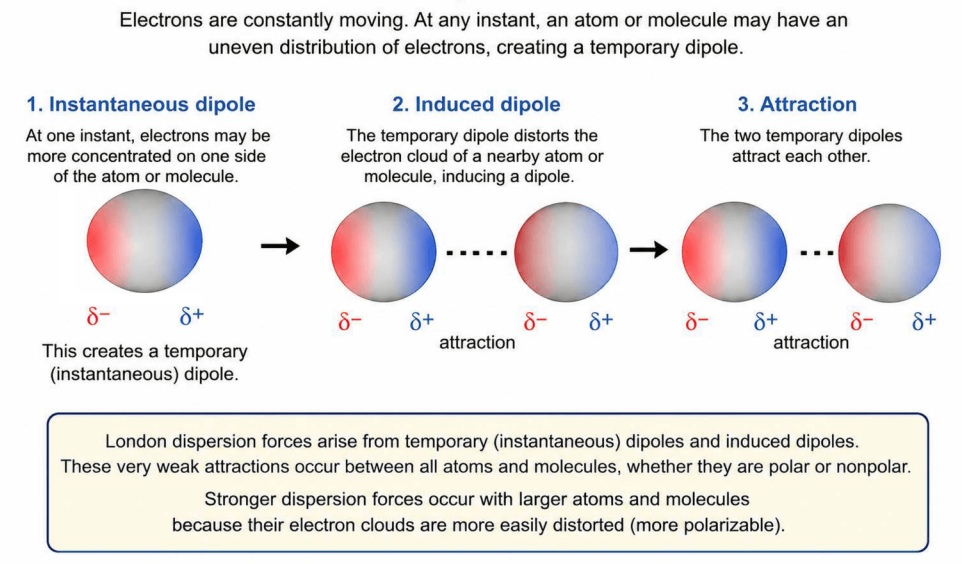


Figure 5.4.7**: Formation of London Dispersion Forces.** Three-panel diagram illustrating the formation of London dispersion forces. Panel 1 shows an atom or molecule developing a temporary (instantaneous) dipole as electrons become unevenly distributed, creating partial negative (δ⁻) and partial positive (δ⁺) regions. Panel 2 shows this temporary dipole inducing an opposite temporary dipole in a neighboring atom or molecule by distorting its electron cloud. Panel 3 shows the two temporary dipoles attracting one another through a London dispersion force. A summary notes that London dispersion forces occur between all atoms and molecules because electrons are always moving, and that these forces become stronger in larger, more polarizable atoms and molecules.

Because electron motion is continuous, these temporary dipoles form and disappear extremely rapidly. Although any single London dispersion force is relatively weak, enormous numbers of these interactions occur simultaneously between neighboring particles. Together, they provide enough attraction to hold many substances together in the liquid and solid phases.

Unlike hydrogen bonding and dipole-dipole interactions, **London dispersion forces occur between all atoms and molecules**, regardless of whether they are polar or nonpolar. Consequently, every molecular substance experiences London dispersion forces. For polar molecules, London dispersion forces act **in addition to** dipole-dipole interactions and hydrogen bonding.

The strength of London dispersion forces depends primarily on **polarizability**, which describes how easily an electron cloud can be distorted. Larger atoms and larger molecules contain more electrons and larger electron clouds, making them more easily polarized. As a result, London dispersion forces generally become stronger as the number of electrons and the size of the molecule increase. As London Dispersion Forces increase due to the increased size of a molecule, the increased binding capacity gives them higher melting and boiling points (Fig 5.xx).

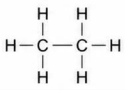
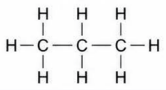
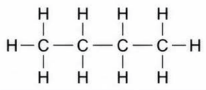
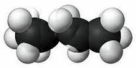
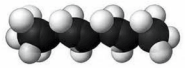
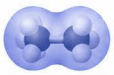
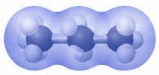
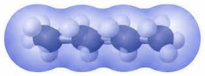
Hydrocarbon	Methane CH_4	Ethane C_2H_6	Propane C_3H_8	Butane C_4H_{10}
Structural formula				
Space-filling model				
Electron cloud (illustration)				
Molar mass (g/mol)	16	30	44	58
Total electrons (in molecule)	10	18	26	34
Relative polarizability (size of electron cloud)	Small	Larger	Even larger	Largest
Relative strength of London dispersion forces	Weak	Stronger	Even stronger	Strongest
Boiling point (°C)	−161.5	−88.6	−42.1	−0.5



Figure 5.4.8**: Molecular Size, Polarizability, and London Dispersion Forces.** Comparison chart of four hydrocarbons—methane (CH_4), ethane (C_2H_6), propane (C_3H_8), and butane (C_4H_{10}). Each column includes the structural formula, a space-filling model, and an illustration of the electron cloud surrounding the molecule. As molecular size increases from methane to butane, the electron cloud becomes larger, the number of electrons and molar mass increase, polarizability increases, London dispersion forces become stronger, and boiling points increase from –161.5 °C to –0.5 °C. A horizontal arrow emphasizes the overall trend of increasing molecular size, electron cloud size, polarizability, and London dispersion force strength.

Polar Bonds Do Not Always Produce a Polar Molecule

For this section, we will use Carbon dioxide as an example in our analysis of intermolecular forces. Carbon dioxide (CO_2) provides an excellent example of the difference between **polar bonds** and a **polar molecule**. Each carbon-oxygen bond is polar because oxygen is more electronegative than carbon. As a result, each bond has a dipole that points toward the oxygen atom.

However, CO_2 has a **linear molecular geometry** (180°). The two identical bond dipoles point in exactly opposite directions and have equal magnitude. As a result, the bond dipoles cancel one another, and the molecule has **no net dipole moment**.

Because CO_2 is **nonpolar**, it does **not** exhibit dipole-dipole interactions or hydrogen bonding. Like all molecules, however, CO_2 experiences **London dispersion forces**. These dispersion forces are the dominant intermolecular force between neighboring carbon dioxide molecules. Thus, when determining the intermolecular forces within a molecule, it is critical to evaluate the polarity of the overall molecule, not just the individual bonds within the molecule.

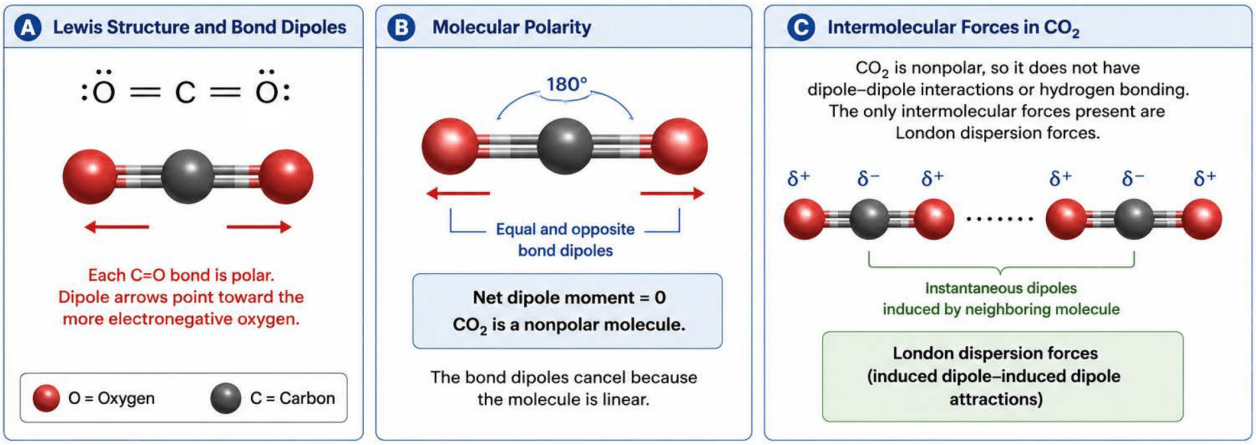


Figure 5.4.9: Carbon Dioxide: Polar Bonds, Nonpolar Molecule. Three-panel diagram illustrating why carbon dioxide is a nonpolar molecule despite containing polar bonds. Panel A shows the Lewis structure and ball-and-stick model of CO_2 with bond dipoles pointing toward each oxygen atom, indicating that each carbon-oxygen bond is polar. Panel B shows the linear (180°) molecular geometry and illustrates that the two equal and opposite bond dipoles cancel, giving the molecule a net dipole moment of zero. Panel C shows two neighboring CO_2 molecules interacting through temporary, induced dipoles, demonstrating that London dispersion forces are the only intermolecular forces present because CO_2 has no permanent molecular dipole.

Polar bonds do not necessarily produce a polar molecule. Molecular geometry determines whether the individual bond dipoles cancel or combine to produce an overall molecular dipole.

Intermolecular forces depend on the polarity of the entire molecule, not the polarity of an individual bond.

Remember

- **London dispersion forces occur between all atoms and molecules.**
- **Intermolecular forces depend on the polarity of the entire molecule, not the polarity of an individual bond.**
- **Polar molecules experience London dispersion forces in addition to dipole-dipole interactions and, when applicable, hydrogen bonding.**
- **Larger atoms and molecules generally exhibit stronger London dispersion forces because their electron clouds are more easily polarized.**

Every atom and every molecule experiences London dispersion forces.

Table 5.4B: Properties of Intermolecular Forces

Property	Dipole-Dipole	Hydrogen Bonding	London Dispersion
Occurs in polar molecules?	✓	✓	✓ (all molecules)
Occurs in nonpolar molecules?	✗	✗	✓
Permanent dipoles required?	✓	✓	✗
Temporary dipoles involved?	✗	✗	✓
Requires H bonded to N, O, or F?	✗	✓	✗
Example	CH_2O	H_2O	I_2

---

3. Attractions Involving Ions and Molecules

After learning about interactions between ions and between molecules, we can now examine what happens when **ions are mixed with polar molecules**.

When an ionic compound dissolves in a polar solvent such as water, the ions separate from the crystal lattice and become surrounded by water molecules. The attractive force between an ion and the partial charges of a polar molecule is called an **ion-dipole interaction**.

Ion-dipole interactions are generally stronger than the intermolecular forces between neutral molecules because they involve the attraction between a full ionic charge and the partial charge of a polar molecule. Although individual ion-dipole interactions are typically weaker than individual ion-ion attractions, many ion-dipole interactions form simultaneously as water molecules

surround each ion during dissolution. These new interactions help stabilize the separated ions in solution and often provide sufficient attraction to overcome the disruption of the crystal lattice and the hydrogen-bonding network of water. As a result, ion-dipole interactions play a critical role in dissolving ionic compounds, transporting ions in biological systems, and many chemical reactions that occur in aqueous solution.

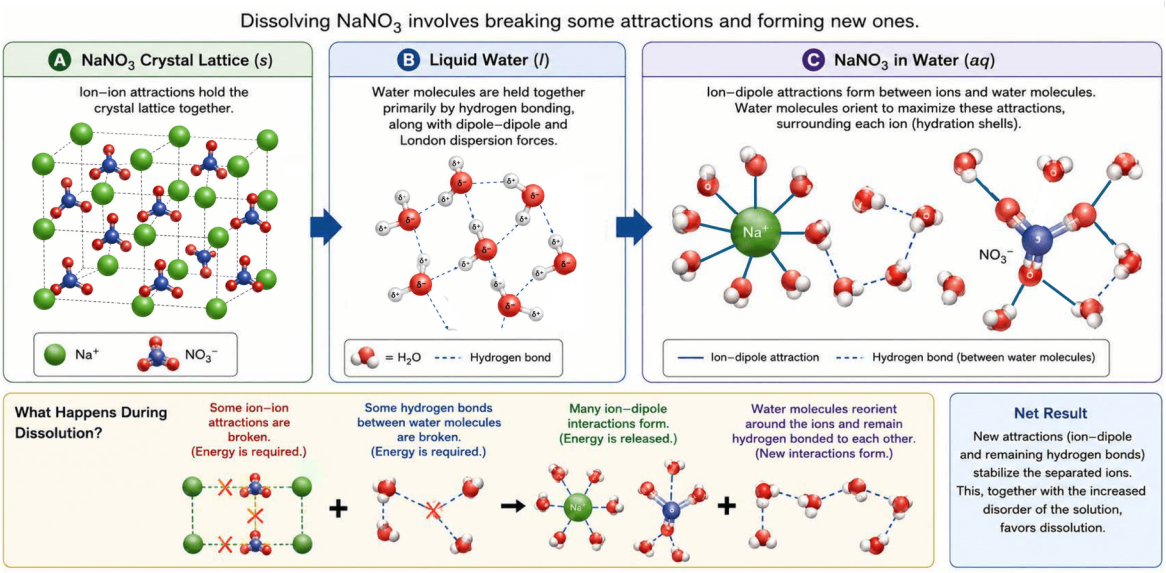


Figure 5.4.10**: Dissolving Sodium Nitrate in Water.** Three-panel diagram illustrating the dissolution of sodium nitrate in water. Panel A shows a solid sodium nitrate crystal lattice held together by ion–ion attractions between sodium ions (Na^+) and nitrate ions (NO_3^-). Panel B shows liquid water in which neighboring water molecules are connected by hydrogen bonds. Panel C shows dissolved sodium nitrate. Water molecules surround each sodium ion with their oxygen atoms directed toward the positive charge and surround each nitrate ion with their hydrogen atoms directed toward the negatively charged oxygen atoms, forming ion–dipole interactions (hydration shells). A summary beneath the panels explains that dissolution involves breaking some ion–ion attractions in the crystal lattice and some hydrogen bonds between water molecules while forming many ion–dipole interactions around the dissolved ions. The combined effect stabilizes the separated ions in solution and favors dissolution.

Ion-dipole attractions replace many of the ion-ion and water-water interactions, allowing the crystal to dissolve.

When sodium nitrate is placed in water, the strong ion-ion attractions that hold the crystal lattice together must first be overcome. At the same time, some of the hydrogen bonds between neighboring water molecules must also be disrupted. Although breaking these attractive forces requires energy, new ion-dipole interactions form as water molecules surround the sodium and nitrate ions.

Water molecules orient themselves according to their partial charges. The partially negative oxygen atoms are attracted to the positively charged sodium ions, while the partially positive hydrogen atoms are attracted to the negatively charged oxygen atoms of the nitrate ion (Figure 5.xx).

When the newly formed ion-dipole interactions are sufficiently favorable, the ions separate from the crystal lattice and become dispersed throughout the solution. Each ion is surrounded by a shell of oriented water molecules called a **hydration shell**.

Table 5.4C: Determining Electrostatic Interactions Between Molecules

Interaction	Present?	Example
Ion-ion	✓	Within $NaNO_3$ crystal
Hydrogen bonding	✓	Between neighboring water molecules

Interaction	Present?	Example
Dipole-dipole	✓	Between water molecules (H-bonding)
London dispersion	✓	Between all molecules
Ion-dipole	✓	Between Na^+/NO_3^- and water

Note

Hydrogen bonding doesn't replace dipole-dipole interactions—it is the strongest, most specific form of dipole-dipole interaction.

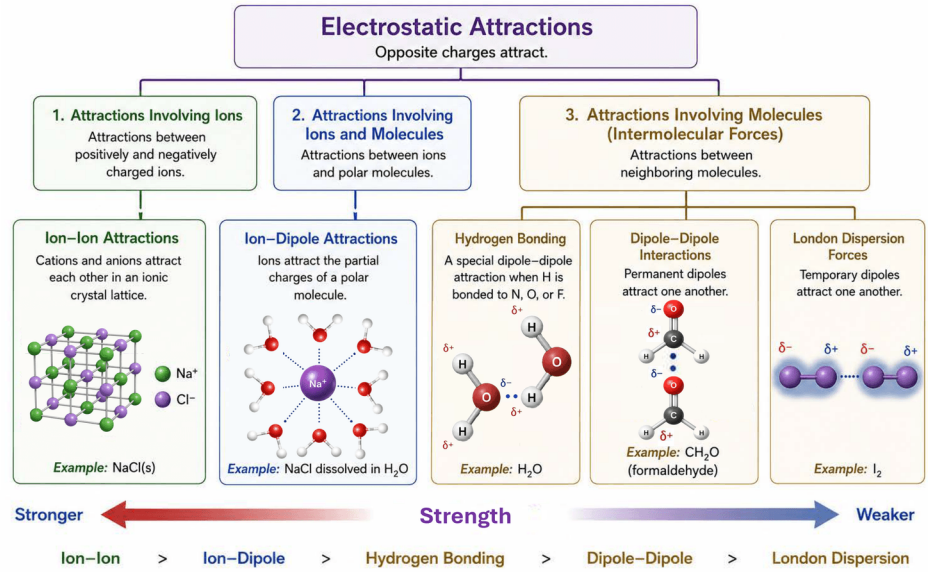


Figure 5.4.11: **Summary of Electrostatic Interactions.** Hierarchy diagram summarizing the major types of electrostatic attractions. Electrostatic attractions are grouped into three categories: **attractions involving ions** (ion-ion attractions in an ionic crystal lattice, illustrated with NaCl), **attractions involving ions and molecules** (ion-dipole attractions between a sodium ion and surrounding water molecules), and **attractions involving molecules** (intermolecular forces), including hydrogen bonding between water molecules, dipole-dipole interactions between formaldehyde (CH_2O) molecules, and London dispersion forces between iodine (I_2) molecules. A strength scale at the bottom indicates the general trend in attraction strength: **ion-ion > ion-dipole > hydrogen bonding > dipole-dipole > London dispersion forces**.

Applying Your Knowledge:

Throughout this section, you have learned how to identify the electrostatic attractions present in different substances.

For each substance below:

1. Determine whether the substance consists of **ions**, **molecules**, or **ions dissolved in molecules**.
2. Identify **all electrostatic attractions** that are present.
3. Identify the **dominant electrostatic attraction**.

(A) SO_2

(B) CH_3Cl

(C) $CaCO_3$

(D) $CoCl_2$ dissolved in water

(E) CH_3OH dissolved in water

(F) CCl_4

Concept Check:

(1) When sodium nitrate dissolves in water, which attraction is responsible for holding the sodium ion inside its hydration shell?

A. Hydrogen bonding

B. Dipole-dipole

C. Ion-dipole

D. London dispersion

(2) Why does carbon dioxide exhibit only London dispersion forces even though each C=O bond is polar?

A. The carbon-oxygen bonds are actually nonpolar.

B. The oxygen atoms cancel each other's electronegativity.

C. The bond dipoles cancel because CO_2 is linear.

D. Carbon dioxide contains too few electrons to be polar.

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5.5: Physical Properties of Intermolecular Forces

Now that we understand **why intermolecular forces exist**, we can use them to explain many of the physical properties of substances. Although molecules differ in size, shape, and polarity, the underlying question is always the same:

How strongly are neighboring particles attracted to one another?

In general, **stronger intermolecular forces require more energy to overcome**. As a result, substances with stronger intermolecular forces tend to have higher boiling points, higher melting points, greater surface tension, and higher viscosity. They also tend to evaporate more slowly and have lower vapor pressures.

Instead of memorizing each property separately, it is often helpful to ask:

What intermolecular force explains this property?

The answer to that question provides the key to understanding the behavior of liquids and molecular solids.

Boiling Point

The **boiling point** is the temperature at which a liquid changes into a gas. During boiling, molecules must completely overcome the intermolecular forces holding them together in the liquid phase. Consequently, substances with stronger intermolecular forces require more energy to separate the molecules and therefore have **higher boiling points**.

For example, methane (CH_4) experiences only London dispersion forces and boils at a much lower temperature than methanol (CH_3OH), which is capable of hydrogen bonding.

Melting Point

The **melting point** is the temperature at which a solid changes into a liquid. Before molecules can move freely in the liquid phase, some of the intermolecular forces that hold neighboring particles in their fixed positions must be overcome.

In general, stronger intermolecular forces produce **higher melting points**, although crystal structure and molecular shape can also influence how efficiently molecules pack together in the solid state.

Vapor Pressure and Evaporation

Even below the boiling point, some molecules at the surface of a liquid possess enough kinetic energy to escape into the gas phase. This process is called **evaporation**.

Liquids with weak intermolecular forces lose molecules more easily and therefore evaporate more rapidly. Because more molecules enter the gas phase, these liquids also develop a **higher vapor pressure**.

In contrast, liquids with strong intermolecular forces retain their molecules more effectively. They evaporate more slowly and have **lower vapor pressures**.

Thus, vapor pressure and intermolecular force strength are **inversely related**:

- **Stronger intermolecular forces → lower vapor pressure**
- **Weaker intermolecular forces → higher vapor pressure**

Surface Tension

Molecules at the surface of a liquid experience fewer attractive interactions than molecules within the interior of the liquid. As a result, the surface behaves like a stretched elastic film, a property known as **surface tension**.

Liquids with stronger intermolecular forces exhibit **higher surface tension** because the molecules attract one another more strongly. Water is a familiar example. Its extensive hydrogen-bonding network produces an unusually high surface tension, allowing small insects to walk across its surface and causing water droplets to bead together.

Viscosity

Viscosity describes a liquid's resistance to flowing. Molecules that strongly attract one another cannot easily slide past their neighbors, producing a more viscous liquid.

Liquids with weaker intermolecular forces flow readily and have **low viscosity**, whereas liquids with stronger intermolecular forces have **higher viscosity**.

For example, glycerol, which contains three hydroxyl (-OH) groups capable of extensive hydrogen bonding, is much more viscous than ethanol.

Connecting Physical Properties to Intermolecular Forces

Rather than memorizing individual trends, remember the following general relationship:

Table 5.5A: How intermolecular forces shape physical properties

Property	Stronger Intermolecular Forces
Boiling point	↑ Higher
Melting point	↑ Higher
Vapor pressure	↓ Lower
Evaporation rate	↓ Slower
Surface tension	↑ Higher
Viscosity	↑ Higher

Challenge Question:

Which intermolecular force best explains each of the following observations?

- Water beads up on a freshly waxed car.
- Rubbing alcohol evaporates quickly from your skin.
- Honey pours much more slowly than water.
- Methanol has a much higher boiling point than methane.
- Carbon dioxide is a gas at room temperature, whereas iodine is a solid.

Worked Examples:

One of the most useful applications of intermolecular forces is predicting physical properties such as boiling point. In general, molecules with stronger intermolecular forces require more energy to separate from one another and therefore have higher boiling points.

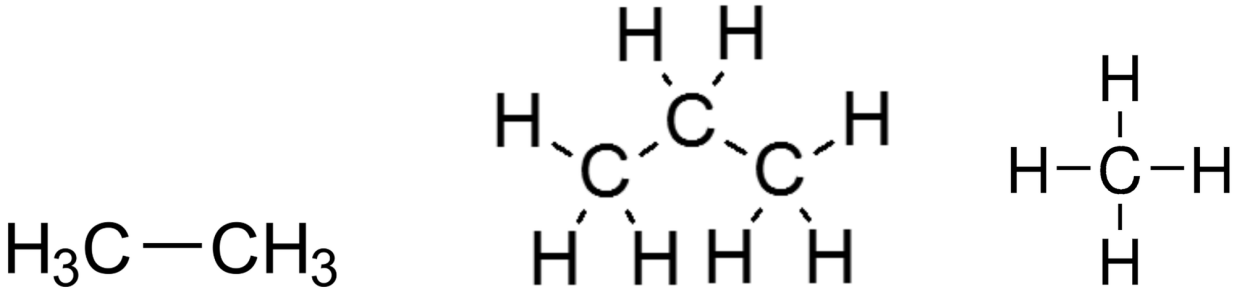
To compare boiling points, first identify the intermolecular forces present in each molecule. Then compare the relative strengths of those forces. If two molecules possess the same dominant intermolecular force, compare their molecular size (molar mass) and shape (surface area), since larger, more polarizable molecules generally exhibit stronger London dispersion forces.

General Guidelines for Comparing Boiling Points

1. All molecules experience London dispersion forces.
2. Polar molecules also experience dipole-dipole interactions.
3. Molecules containing O–H, N–H, or F–H bonds can participate in hydrogen bonding, which generally produces the strongest intermolecular attractions between neutral molecules.
4. If two molecules have the same dominant intermolecular force, the molecule with the larger electron cloud (greater polarizability), higher molar mass, or greater surface area generally has the higher boiling point.

Example 5.5.1

Rank the following molecules from the highest boiling point to the lowest boiling point.



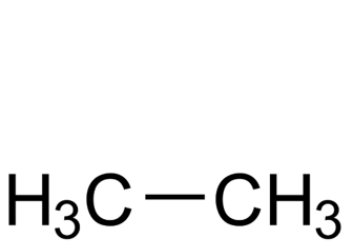
Solution

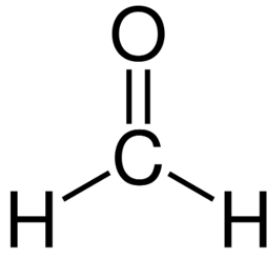
We can start with the assumption that these molecules each have London dispersion forces. To determine the polarity, we could start by drawing Lewis structures. However, these three molecules are made up of only carbon and hydrogen atoms. We know that carbon-hydrogen bonds are nonpolar. So regardless of the molecular geometry, there will be no net dipole. Because all three molecules are nonpolar, London dispersion forces are the only significant intermolecular force present. The larger molecules contain more electrons and are more polarizable, resulting in progressively stronger London dispersion forces. $CH_3CH_2CH_3$ has the highest molecular weight and will have the highest boiling point. CH_4 has lowest molecular weight and will have the lowest boiling point.

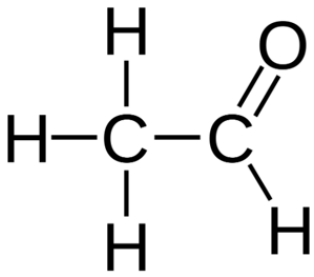
$CH_3CH_2CH_3 > CH_3CH_3 > CH_4$

Exercise 5.5.1

Rank the following molecules from the highest boiling point to the lowest boiling point.



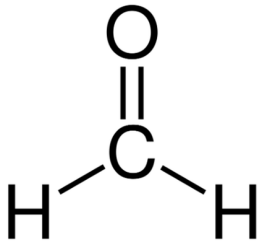


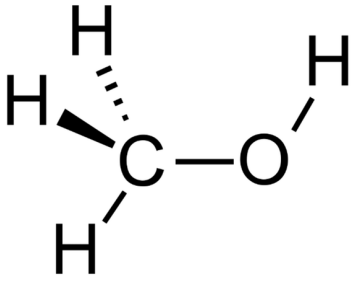


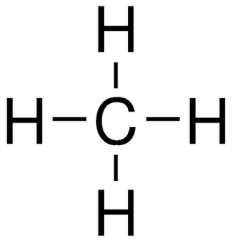
Answer available at the end of this section.

Exercise 5.5.2

Rank the following molecules from the highest boiling point to the lowest boiling point.







Answer available at the end of this section.

Answers

Exercise 5.5.1

Both CH_2O and CH_3CHO contain a polar carbonyl (C=O) bond, making them polar molecules. As a result, they experience both London dispersion forces and dipole-dipole interactions. Neither molecule contains an O–H, N–H, or F–H bond, so neither can hydrogen bond with itself. Since both molecules possess the same dominant intermolecular force (dipole-dipole), the larger molecule, CH_3CHO, has the higher boiling point because it exhibits stronger London dispersion forces. CH_3CH_3 only has London dispersion forces and no permanent dipoles. Thus, it will have the lowest boiling point.

$CH_3CHO > CH_2O > CH_3CH_3$

Exercise 5.5.2

CH_4 only experiences London dispersion forces as it only contains nonpolar C-H bonds. CH_2O experiences London dispersion forces and dipole-dipole interactions, while CH_3OH experiences London dispersion forces, dipole-dipole interactions, and hydrogen bonding. Because hydrogen bonding is the strongest intermolecular force present between these neutral molecules, methanol (CH_3OH) has the highest boiling point.

$CH_3OH > CH_2O > CH_4$

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5.6: Focus on the Environment

Why Are PFAS Called "Forever Chemicals?

Per- and polyfluoroalkyl substances (PFAS) are a family of synthetic chemicals used in products such as nonstick cookware, stain-resistant fabrics, firefighting foams, and food packaging. Because they resist heat, water, and oils, PFAS have been widely used for decades. Unfortunately, these same properties also make them persistent environmental pollutants, earning them the nickname **"forever chemicals."**

In 2015, residents of Hoosick Falls and Petersburgh, New York, discovered that their drinking water had been contaminated with PFAS released from nearby manufacturing facilities. Continued research revealed that long-term exposure to certain PFAS is associated with increased risks of several health problems. As scientific understanding improved, the U.S. Environmental Protection Agency (EPA) lowered the maximum allowable concentration of one common PFAS, perfluorooctanoic acid (PFOA), from hundreds of parts per trillion to just **4 parts per trillion**.



Figure 5.6.1**: Hoosick Falls, New York: A Community Impacted by PFAS Contamination.** Photograph of the downtown area of Hoosick Falls, New York, showing the main street with buildings, businesses, parked vehicles, and surrounding hills in the background. The image represents one of the communities affected by PFAS contamination of its drinking water and serves as a real-world example of how the environmental behavior of chemicals can impact public health. (Photograph by: Daniel Case, CC BY-SA 3.0, Wikimedia).

The EPA estimates that there are more than 15,000 known PFA substances that have been identified and over 10,000 have been cataloged. Thousands have been developed and used commercially, but only relatively few have been extensively tested for their human health effects. The unusual behavior of PFAS can be explained by their molecular structure. Figure 5.6.2 shows example PFA structures.

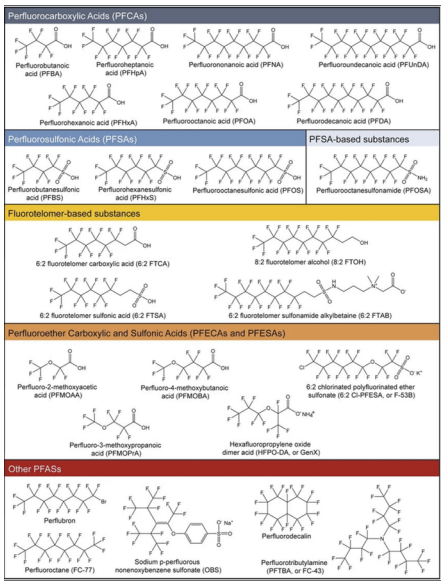


Figure 5.6.2**: Representative Structures of Common PFAS Compounds.** Chart showing representative molecular structures from several families of per- and polyfluoroalkyl substances (PFAS), including perfluorocarboxylic acids (PFCAs), perfluorosulfonic acids (PFSAs), fluorotelomer-based compounds, perfluoroether acids (PFECAs and PFESAs), and other PFAS. Most structures contain a long chain of carbon atoms bonded to fluorine atoms and terminate in a polar functional group, such as a carboxylic acid or sulfonic acid. The figure illustrates the structural diversity of PFAS while highlighting the common combination of a fluorinated tail and a polar head group. (Figure from: Phelps, Drake & Connors, Ashley & Ferrero, Giuliano & DeWitt, Jamie & Yoder, Jeffrey. (2024). Per- and polyfluoroalkyl substances alter innate immune function: evidence and data gaps. Journal of Immunotoxicology. 21. Weblink Here [10.1080])

In most PFAs one end of the molecule contains a **polar head group** that interacts readily with water, while the long fluorinated carbon chain forms a **nonpolar tail**. This combination allows PFAS molecules to dissolve and travel through water while also interacting with many surfaces and biological molecules. At the same time, the carbon-fluorine bonds are among the strongest single bonds in organic chemistry, making PFAS extremely resistant to chemical and biological degradation.

Why do PFAS move so easily through water and yet persist in the environment?

Understanding intermolecular forces helps explain why PFAS are so difficult to remove from the environment. Their polar head allows them to interact with water through dipole and ion-dipole interactions, while the nonpolar fluorinated tail interacts differently with surrounding materials. Combined with their exceptionally strong carbon-fluorine bonds, these intermolecular interactions allow PFAS to spread through groundwater, accumulate in living organisms, and remain in the environment for many years.

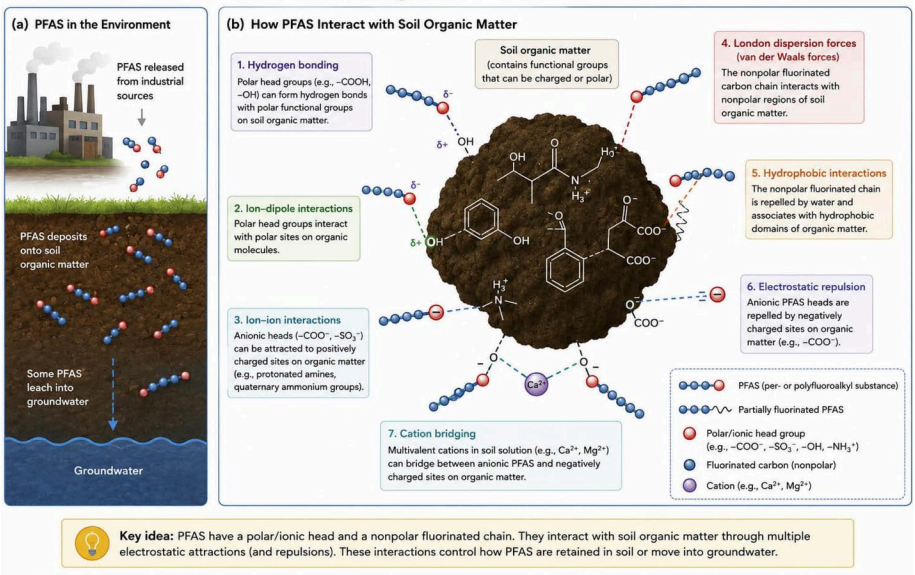


Figure 5.6.3: Intermolecular Forces Between PFAS and Soil Organic Matter. Illustration showing a PFAS molecule interacting with soil organic matter. The polar head group is positioned near charged regions of the soil where ion-ion or ion-dipole attractions can occur. The long fluorinated tail lies alongside nonpolar organic regions of the soil, where London dispersion forces provide additional attraction. Labels identify the different types of electrostatic attractions responsible for PFAS adsorption. The figure emphasizes that both the polar head and the nonpolar fluorinated tail contribute to the environmental behavior of PFAS by influencing how strongly the molecules bind to soil.

After testing showed the contaminated water in New York, people were supplied with bottled water until a filtration system could be installed for the city water. The filtration system is still in place and effectively filters PFAS out of the water. This allows residents of these towns to safely drink the water, but it does not remove the PFAS from the water sources themselves. The environment has been contaminated, and PFAS continue to leach into the water sources. Because of how hardy the PFAS are through their tetrahedral shape, strong C-F bonds, and resistance to water reactions, there are no efficient methods to remove these chemicals from large, contaminated areas. In July of 2017, Hoosick Falls was added to the Superfund National Priorities List, indicating that it was one of the sites most in need of long-term cleanup. In some areas, topsoil has been removed and replaced with soil that is not contaminated. This has helped to reduce the amount of PFAS leaching into water sources, but it does not remove deeper soil that is contaminated. As of 2025, the cleanup continues.

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5.7: Chapter Summary

In this chapter, you learned that the **three-dimensional arrangement of atoms within a molecule influences many of its physical and chemical properties**. Beginning with the electronic and molecular geometry and ending with intermolecular forces, the concepts introduced in this chapter demonstrate how molecular structure determines the behavior of matter.

The shape of a molecule can be predicted using **Valence Shell Electron Pair Repulsion (VSEPR) theory**, which states that electron groups around a central atom arrange themselves to minimize repulsion. By counting bonding pairs and lone pairs of electrons, molecular geometries such as linear, bent, trigonal planar, tetrahedral, trigonal pyramidal, and trigonal bipyramidal can be predicted. Lone pairs occupy more space than bonding pairs and often distort bond angles from their ideal values.

Molecular geometry plays a critical role in determining whether a molecule is **polar or nonpolar**. Bond polarity results from differences in electronegativity between bonded atoms, while molecular polarity depends on both the polarity of individual bonds and the overall three-dimensional arrangement of those bonds. In symmetric molecules such as carbon dioxide, bond dipoles cancel, producing a nonpolar molecule. In asymmetric molecules such as sulfur dioxide or water, the bond dipoles do not cancel, resulting in a permanent molecular dipole.

Once molecular polarity is known, the electrostatic attractions between neighboring particles can be predicted. These attractions can be divided into three broad categories.

Attractions Involving Ions

Ionic compounds consist of positively charged cations and negatively charged anions held together by **ion-ion attractions**. These strong electrostatic attractions produce extended crystal lattices rather than individual molecules. As a result, ionic compounds are represented by **formula units** instead of molecular formulas.

Attractions Involving Molecules (Intermolecular Forces)

Neutral molecules are held together by **intermolecular forces**, which influence the physical properties of molecular substances.

Three major intermolecular forces were discussed:

- **Dipole-dipole interactions** occur between neighboring polar molecules.
- **Hydrogen bonding** is a particularly strong type of dipole-dipole interaction that occurs when hydrogen is covalently bonded to nitrogen, oxygen, or fluorine and is attracted to a lone pair on a neighboring nitrogen, oxygen, or fluorine atom.
- **London dispersion forces** arise from temporary fluctuations in electron density and occur between **all atoms and molecules**. Their strength increases as molecular size and polarizability increase.

Because many substances experience more than one intermolecular force, it is important to identify **all** of the interactions that are present before determining which one is **dominant**.

Attractions Involving Ions and Molecules

When ionic compounds dissolve in water, **ion-dipole interactions** form between dissolved ions and surrounding water molecules. These interactions stabilize ions in solution and help explain the dissolution of many ionic compounds, the transport of ions in biological systems, and numerous chemical processes that occur in aqueous solutions.

Molecular Structure Determines Physical Properties

One of the major themes of this chapter is that **molecular structure determines physical properties**.

The type and strength of electrostatic attractions influence many observable properties of substances.

- Stronger attractions generally produce **higher boiling points** and **higher melting points**.
- Stronger attractions produce **higher surface tension** and **greater viscosity**.
- Stronger attractions result in **lower vapor pressures** and **slower rates of evaporation**.

Rather than memorizing these trends individually, ask a single question:

> **What electrostatic attraction best explains this property?**

Chemistry in the Real World

The concepts introduced in this chapter extend far beyond the classroom. Molecular geometry and intermolecular forces help explain why salts dissolve in water, why oil and water do not mix, why carbon dioxide is a gas while water is a liquid at room temperature, and why some environmental contaminants move easily through groundwater while others remain adsorbed to soil. These same principles also help scientists understand the behavior of pharmaceuticals, biological molecules, and persistent pollutants such as PFAS (Forever Chemicals).

Key Takeaways

After completing this chapter, you should be able to:

- Predict molecular geometry using VSEPR theory.
- Distinguish between electron geometry and molecular geometry.
- Explain how lone pairs influence molecular shape and bond angles.
- Determine whether a molecule is polar or nonpolar using bond polarity and molecular geometry.
- Distinguish between ion-ion, dipole-dipole, hydrogen bonding, London dispersion, and ion-dipole interactions.
- Identify all electrostatic attractions present in a substance and determine the dominant interaction.
- Predict how intermolecular forces influence boiling point, melting point, vapor pressure, evaporation, surface tension, and viscosity.
- Explain how molecular structure influences the behavior of substances in biological and environmental systems.

Final Thought

Throughout this chapter, you developed a framework for connecting molecular structure to observable properties. By asking four simple questions, you can explain the behavior of many substances:

1. What is the molecular geometry?
2. Is the molecule polar or nonpolar?
3. What electrostatic attractions are present?
4. How do those attractions influence the physical properties and behavior of the substance?

These four questions provide a logical pathway from the arrangement of atoms in a molecule to the physical and chemical properties observed in the laboratory, in living systems, and in the environment.

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6: CHAPTER 6 - CHEMICAL REACTIONS

6.1: The Law of Conservation of Matter

6.2: Writing and Balancing Chemical Equations

6.3: Quantitative Relationships Based on Chemical Equations

6.4: Common Types of Chemical Reactions

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6.1: The Law of Conservation of Matter

Chemical change is a central concept in chemistry. The goal of chemists is to know how and why a substance changes in the presence of another substance or even by itself. Because there are tens of millions of known substances, there are a huge number of possible chemical reactions. In this chapter, we will find that many of these reactions can be classified into a small number of categories according to certain shared characteristics.

In science, a ***law*** is a general statement that explains a large number of observations. Before being accepted, a law must be verified many times under many conditions. Laws are therefore considered the highest form of scientific knowledge and are generally thought to be inviolable. Scientific laws form the core of scientific knowledge.

One scientific law that provides the foundation for understanding in chemistry is ***the law of conservation of matter.*** It states that in any given system that is closed to the transfer of matter (in and out), the amount of matter in the system stays constant. A concise way of expressing this law is to say that the amount of matter in a system is conserved, or that matter cannot be created or destroyed during a chemical reaction. It only changes form.

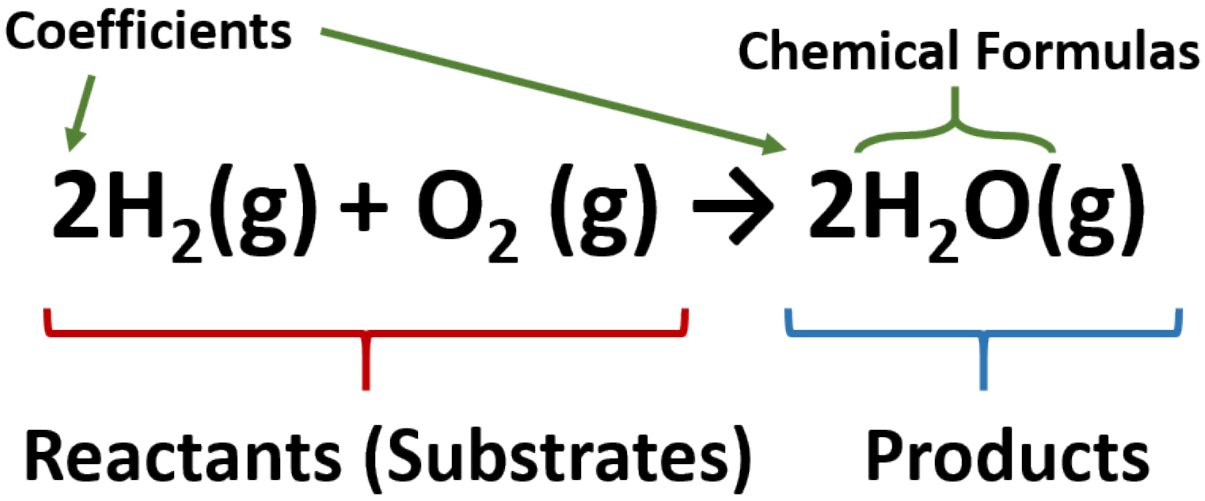
What does this mean for chemistry? In any chemical change, one or more initial substances change into a different substance or substances. Both the initial and final substances are composed of atoms because all matter is composed of atoms. According to the law of conservation of matter, matter is neither created nor destroyed, so we must have the same number and type of atoms after the chemical change as were present before the chemical change.

Before looking at explicit examples of the law of conservation of matter, we need to examine the method chemists use to represent chemical changes.

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6.2: Writing and Balancing Chemical Equations

Water (H_2O) is composed of hydrogen and oxygen. Suppose we imagine a process in which we take some elemental hydrogen (H_2) and elemental oxygen (O_2) and let them react to make water. The chemical equation below is used to express this reaction:



In this chemical reaction, the chemical formulas of the ***reactants (or substrates)*** are written on the left side of the equation, and the chemical formulas of the ***products*** are written on the right side. A plus sign connects the initial substances (and final substances, if there is more than one), and an arrow (→) represents the chemical change (or reaction). In reactions, it is also common to include a phase label with each formula—(s) for solid, (ℓ) for liquid, (g) for gas, and (aq) for a substance dissolved in water, also known as an ***aqueous solution*.**

Due to the law of the conservation of matter, each chemical reaction needs to be balanced to ensure that the same number and types of atoms on the left side of the equation are the same as on the right side of the reaction. To represent this balance, coefficients are placed in front of the chemical formulas on each side to ensure that the same numbers and types of atoms are on each side of the equation. If the coefficient is one, it is not written into the equation, but is assumed. The coefficients represent how many molecules are present in the reaction. In this case, we can see that there are two H_2 molecules (or a total of four hydrogen atoms) of the left side of the equation and that there are two H_2O molecules, which also include four hydrogens on the right side of the equation. Likewise, there are two oxygen atoms in the form of one oxygen molecule (O_2) on the left side, and two oxygen atoms on the right side in the form or two water molecules. A diagram using the Lewis structures is shown below to represent the number of molecules indicated by the coefficients of the equation:

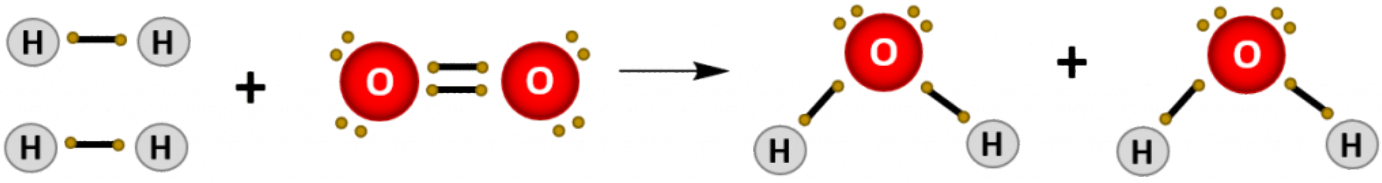


Figure 6.2.1 shows a rather dramatic example of this very reaction.

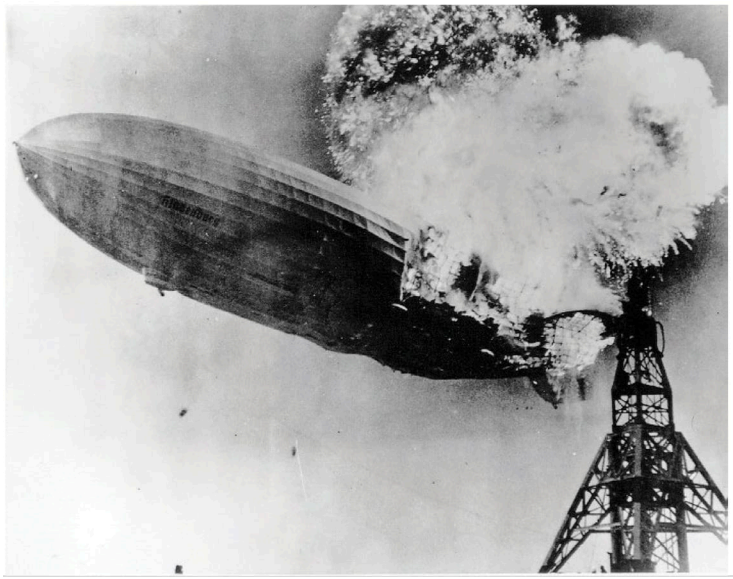
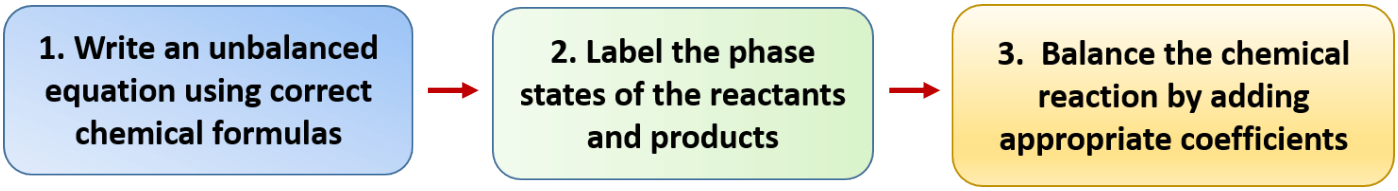


Figure 6.2.1**: Chemical reactions can be violent in nature.** When exposed to a spark or a flame, hydrogen and oxygen react violently to form water. Here the hydrogen gas in the zeppelin, SS Hindenburg, reacts with the oxygen in the air to make water.

The Hindenburg Photo is made available from the US Navy.

Practice Writing and Balancing Equations

To write proper chemical reactions, it is first necessary to write the correct chemical formulas. As you have learned in Chapters 3 and 4, both ionic and covalent compounds combine to either donate/accept electrons or share electrons in ways that enable atoms to reach a stable state, most often following the octet rule. This should be the first consideration when writing a chemical reaction.The second consideration should be the states of the matter involved in the chemical reaction. Label each as a solid (s), a liquid (ℓ), a gas (g), or an aqueous solution (aq). Once the correct chemical formulas have been established, proper chemical equations should then be balanced. Writing balanced reactions is a chemist's way of acknowledging the law of conservation of matter.



How does one balance a chemical equation, starting with the correct formulas of the reactants and products? Basically, a back-and-forth approach is adopted, counting the number of atoms of one element on one side, checking the number of atoms of that element on the other side, and changing a coefficient if necessary. Then check another element, going back and forth from one side of the equation to another, until each element has the same number of atoms on both sides of the arrow. In many cases, it does not matter which element is balanced first and which is balanced last, as long as all elements have the same number of atoms on each side of the equation. However, if elemental forms appear in an equation (i.e. Na, Zn, O_2, H_2, Cl_2, etc), it is often easier to balance the equation, by leaving the elemental forms to be balanced last.

For example, to balance the equation:

$$\mathbf{CH_4 + Cl_2 \longrightarrow CCl_4 + HCl} \tag{6.2.1}$$

the first thing that we notice, is that it contains the elemental form of chlorine (Cl_2). That leaves carbon and hydrogen to balance. We might choose to count the carbon atoms first, finding that both sides are balanced with one carbon atom. Thus, we will not

change the coefficient for the carbon-containing molecules, but instead shift our focus to the number of hydrogen atoms. The reactant side has four hydrogen atoms, however, the product side only has one hydrogen. Thus, we will need to add a coefficient to the product side, such that the product side will also have four hydrogen atoms. We fix this by putting a 4 in front of the HCl:

$$\mathrm{CH_4 + Cl_2 \longrightarrow CCl_4 + 4\,HCl} \tag{6.2.2}$$

Now each side has four hydrogen atoms. Now we can balance the chlorine. The product side has a total of eight chlorine atoms (four from the CCl_4 and four from the four molecules of HCl), so we need eight chlorine atoms on the reactant-side of the equation. Because elemental chlorine is a diatomic molecule, we need a total of four chlorine molecules to get a total of eight chlorine atoms. We add another 4 in front of the Cl_2 reactant:

$$\mathrm{CH_4 + 4\,Cl_2 \longrightarrow CCl_4 + 4\,HCl} \tag{6.2.3}$$

Now we double check: each side has one carbon atom, four hydrogen atoms, and eight chlorine atoms. Yes, the chemical equation is balanced.

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6.3: Quantitative Relationships Based on Chemical Equations

Balancing Chemical Equations

A balanced chemical equation not only describes some of the chemical properties of substances—by showing us what substances react with what other substances to make what products—but also shows numerical relationships between the reactants and the products. The study of these numerical relationships is called *stoichiometry*. The stoichiometry of chemical equations revolves around the coefficients in the balanced chemical equation because these coefficients determine the molecular ratio in which reactants react and products are made. It is very similar to cooking. For example, to make a hamburger, for each hamburger patti, you need to have two slices of bread for the bun. Thus, the ratio of bread to hamburger is 2 to 1.

Consider the following balanced chemical equation:

$$2\,C_2H_2 + 5\,O_2 \longrightarrow 4\,CO_2 + 2\,H_2O \tag{6.3.1}$$

The coefficients on the chemical formulas give the ratios in which the reactants combine and the products form. Thus, we can make the following statements and construct the following ratios:

Statement:

For every 2 molecules of ethyne (C_2H_2), you need 5 molecules of oxygen (O_2), to make 4 molecules of carbon dioxide (CO_2) and 2 molecules of water (H_2O).

This statement can then be represented mathematically into ratios that represent these written relationship statements.

$$\frac{2 \text{ molecules } C_2H_2}{5 \text{ molecules } O_2} \text{ or } \frac{5 \text{ molecules } O_2}{2 \text{ molecules } C_2H_2}$$

$$\frac{2 \text{ molecules } C_2H_2}{4 \text{ molecules } CO_2} \text{ or } \frac{4 \text{ molecules } O_2}{2 \text{ molecules } C_2H_2}$$

$$\frac{2 \text{ molecules } H_2O}{5 \text{ molecules } O_2} \text{ or } \frac{5 \text{ molecules } O_2}{2 \text{ molecules } H_2O}$$

$$\frac{2 \text{ molecules } H_2O}{4 \text{ molecules } CO_2} \text{ or } \frac{4 \text{ molecules } CO_2}{2 \text{ molecules } H_2O}$$

Other relationships are possible; in fact, 12 different ratios can be constructed from this balanced chemical equation. In each ratio, note that the unit is molecules. Chemical reactions describe the number of molecules of one substance required to react with or produce another substance. Any of these fractions can be used as a conversion factor to relate an amount of one substance to an amount of another substance. For example, suppose we want to know how many CO_2 molecules are formed when 26 molecules of C_2H_2 are reacted.

As usual with a conversion problem, we start with the amount we are given — 26 C_2H_2 — and multiply it by a conversion factor that cancels out our original unit and introduces the unit we are converting to—in this case, CO_2.

Thus, we have two choices for our conversion factor

$$\frac{2 \text{ molecules } C_2H_2}{4 \text{ molecules } CO_2} \quad \text{or} \quad \frac{4 \text{ molecules } CO_2}{2 \text{ molecules } C_2H_2}$$

To cancel C_2H_2, we need to make sure that this unit is on the bottom of our convesion factor. Thus, we can set up our conversion equation as follows:

$$26 \text{ molecules } C_2H_2 \quad X \quad \frac{4 \text{ molecules } CO_2}{2 \text{ molecules } C_2H_2} = 52 \text{ molecules } CO_2$$

Essentially, 26 molecules of ethyne can be converted to molecules of carbon dioxide, by multiplying by 4 molecules of carbon dioxide and dividing by 2 molecules of ethyne. This results in the production of 52 molecules of CO_2 when we start with 26 molecules of C_2H_2. Note that with this conversion factor, that we could have simplified our conversion factor prior to completing the multiplication and division steps, as follows:

$$26 \text{ molecules } C_2H_2 \quad X \quad \frac{2 \text{ molecules } CO_2}{1 \text{ molecules } C_2H_2} = 52 \text{ molecules } CO_2$$

This application of stoichiometry is extremely powerful in its predictive ability, as long as we begin with a balanced chemical equation. Without a balanced chemical equation, the predictions made by simple stoichiometric calculations will be incorrect.

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6.4: Common Types of Chemical Reactions

Although there are untold millions of possible chemical reactions, most can be classified into a small number of general reaction types. Classifying reactions has two purposes: it helps us to recognize similarities among them, and it enables us to predict the products of certain reactions. In this chapter, we will discuss five major categories of chemical reactions: (1) Combination (or Synthesis) Reactions, (2) Decomposition Reactions, (3) Single Replacement Reactions, (4) Double Replacement Reactions, and (5) Redox Reactions. Note that a particular reaction may fall into more than one of the categories that we will define in this book.

(1) Combination (or Synthesis) Reactions

A ***combination (or synthesis) reaction*** is a chemical reaction is a building reaction, where two or more elements or compounds combine to make a single compound.

The general equation for a combination reaction is:

$$\mathbf{A + B \longrightarrow AB} \tag{6.4.1}$$

An example of a combination reaction is:

$$\mathbf{4\,Fe\,(s) + 3\,O_2\,(g) \longrightarrow 2\,Fe_2O_3\,(s)} \tag{6.4.2}$$

In this reaction, the elements iron (Fe) and oxygen (O_2) combine to produce iron (III) oxide (Fe_2O_3). Note that combination reactions do not have to combine elements together, however. Combination reactions can also combine compounds together to form larger compounds. The chemical equation:

$$\mathbf{Fe_2O_3\,(s) + 3\,SO_3\,(s) \longrightarrow Fe_2(SO_4)_3\,(s)} \tag{6.4.3}$$

shows a combination reaction in which iron (III) oxide (Fe_2O_3) combines with three molecules of sulfur trioxide (SO_3) to make iron (III) sulfate [$Fe_2(SO_4)_3$].

---

(2) Decomposition Reactions

A ***decomposition reaction*** is the opposite of a combination reaction. In a decomposition reaction, a single substance is converted or broken down into two or more simpler products. A general equation for decomposition reactions is:

$$\mathbf{AB \longrightarrow A + B} \tag{6.4.4}$$

For example, the equation below is a decomposition reaction that occurs when Sodium Bicarbonate ($NaHCO_3$) is exposed to heat:

\[\Large\boldsymbol{ \ce{2NaHCO3(s) -> Na2CO3(s) + CO2(g) + \ce{H2O(l)} \]

Another common decomposition reaction is the thermal decomposition of potassium chlorate ($KClO_3$)

$$\mathbf{2\,KClO_3\,(s) \longrightarrow 2\,KCl\,(s) + 3\,O_2\,(g)} \tag{6.4.5}$$

This reaction can be used to generate small amounts of oxygen in the chemistry lab.

---

(3) Single Replacement (or Single Displacement) Reactions

Single replacement (or displacement) reactions occur when an element (most frequently a metal) replaces another element from a compound. They can occur in two forms: ***cationic exchange*** or ***anionic exchange.*** In ***cationic exchanges,*** the positive ions (cations) of the equation change place. In ***anionic exchanges,*** the negative ions (anions) change place. Note that single

replacement reactions are often also redox reactions, and thus, we will revisit this reaction type in that section.

The general equation for a cationic single replacement reaction is:

$$\mathrm{A + BC \longrightarrow AC + B} \tag{6.4.6}$$

In a cationic single replacement reaction, element A replaces the cation in compound BC. An example of a cationic exchange reaction is:

$$\mathrm{Zn\,(s) + 2\,HCl\,(aq) \longrightarrow H_2\,(g) + ZnCl_2\,(aq)} \tag{6.4.7}$$

In this reaction, the zinc replaces the hydrogen cation in the hydrochloric acid to form zinc chloride in the final product.

For anion exchange reactions, the following general reaction can be used:

$$\mathrm{D + BC \longrightarrow BD + C} \tag{6.4.8}$$

In an anionic single replacement reaction, element D replaces the anion in compound BC. An example of an anionic exchange reaction is:

$$\mathrm{3\,F_2\,(g) + 2\,FeCl_3\,(aq) \longrightarrow 2\,FeF_3\,(aq) + 3\,Cl_2\,(g)} \tag{6.4.9}$$

In this reaction, elemental fluorine replaces chloride ions in iron (III) chloride to produce iron (III) fluoride.

---

(4) Double Replacement (or Displacement) Reactions

Double replacement (or displacement) reactions occur when two chemical groups substitute for each other (change partners) in their respective compounds.

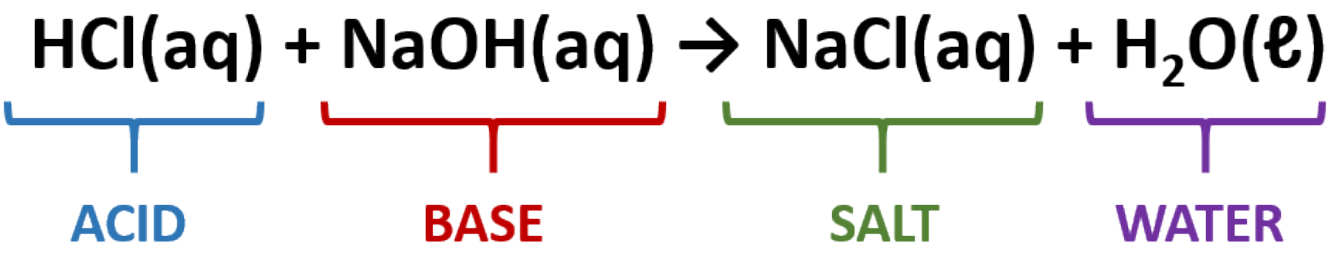
A general equation for a double replacement reaction is:

$$\mathrm{AB + CD \longrightarrow AD + CB} \tag{6.4.10}$$

Two major types of double replacement reactions are Acid-Base Neutralization reactions and Precipitation reactions.

- ### Acid-Base Neutralization Reactions

In an ***acid base neutralization reaction***, an acid is combined with a base to form a salt and water.



- ### Precipitation Reactions

Precipitation reactions occur when cations and anions in aqueous solution combine to form an insoluble ionic solid called a precipitate. Whether or not such a reaction occurs can be determined by using the solubility rules for common ionic solids. Because not all aqueous reactions form precipitates, one must consult the solubility rules before determining the state of the products The ability to predict these reactions allows scientists to determine which ions are present in a solution, and allows

industries to form chemicals by extracting components from these reactions.

Precipitates are insoluble ionic solid products of a reaction, formed when certain cations and anions combine in an aqueous solution. The determining factors of the formation of a precipitate can vary. Some reactions depend on temperature, such as solutions used for buffers, whereas others are dependent only on solution concentration. The solids produced in precipitate reactions are crystalline solids, and can be suspended throughout the liquid or fall to the bottom of the solution. The remaining fluid is called supernatant liquid. The two components of the mixture (precipitate and supernate) can be separated by various methods, such as filtration, centrifuging, or decanting.

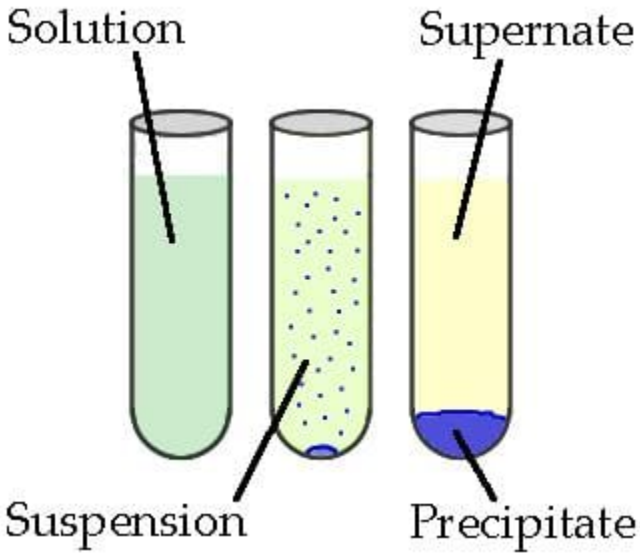


Figure 6.4.1***: Above is a diagram of the formation of a precipitate in solution.*** *In a precipitation reaction a solid forms when the chemicals are mixed and they accumulate at the bottom of the test tube.*

The use of solubility rules require an understanding of the way that ions react. Most precipitation reactions are single replacement reactions or double replacement reactions. A double replacement reaction occurs when two ionic reactants dissociate and bond with the respective anion or cation from the other reactant. The ions replace each other based on their charges as either a cation or an anion. This can be thought of as “switching partners”; that is, the two reactants each “lose” their partner and form a bond with a different partner:

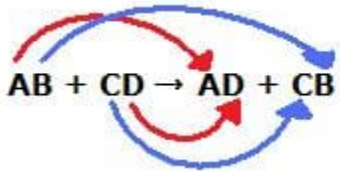


Figure 6.4.2***:*** *A double replacement reaction. This reactions shows the swapping of anions and cations to form the new products*

A double replacement reaction is specifically classified as a precipitation reaction when the chemical equation in question occurs in aqueous solution and one of the of the products formed is insoluble and forms a solid product. An example of a precipitation reaction is given below:

$$\mathbf{CdSO_4\,(aq) + K_2S\,(aq) \longrightarrow CdS\,(s) + K_2SO_4\,(aq)} \tag{6.4.11}$$

Both reactants are aqueous and one product is solid. Because the reactants are ionic and aqueous, they dissociate and are therefore soluble. However, CdS is insoluble and precipitate out of solution to form a solid product. There are six solubility guidelines that you can use to help you predict which molecules will form a solid and enable you to identify a precipitation

reaction.

Solubility Rules

Whether or not a reaction forms a precipitate is dictated by the solubility rules. These rules provide guidelines that tell which ions form solids and which remain in their ionic form in aqueous solution. The rules are to be followed from the top down, meaning that if something is insoluble (or soluble) due to rule 1, it has precedence over a higher-numbered rule.

1. Salts formed with group 1 cations and NH^{4+} cations are soluble.
2. Acetates (CH_3COO^-), nitrates (NO_3^-), and perchlorates (ClO_4^-) are soluble.
3. Bromides, chlorides, and iodides are soluble, except when combined with Ag⦻, Pb^{2}⦻, or Hg_2^{2}⦻.
4. Most sulfates are soluble except those of Ba^{2}⦻, Sr^{2}⦻, Pb^{2}⦻, and Ca^{2}⦻ (slightly soluble).
5. Carbonates (CO_3^{2-}), phosphates (PO_4^{3-}), sulfides, oxides, and hydroxides (OH^-) are insoluble. Exceptions include Group 1 and NH_4⦻ salts. Sulfides of Group 2 metals are generally soluble, and hydroxides of Ca^{2}⦻, Sr^{2}⦻, and Ba^{2}⦻ are slightly soluble.

If the solubility rules indicate that a compound is soluble, it remains dissolved in solution as aqueous ions. If a compound is insoluble, it forms a solid precipitate. If all possible products are soluble, then no precipitation reaction occurs.

Net Ionic Equations

To understand the definition of a ***net ionic equation***, recall the equation for the double replacement reaction. Because this particular reaction is a precipitation reaction, states of matter can be assigned to each variable pair:

$$\mathbf{AB\,(aq) + CD\,(aq) \longrightarrow AD\,(aq) + CB\,(s)} \tag{6.4.12}$$

The first step to writing a net ionic equation is to separate the soluble (aqueous) reactants and products into their respective cations and anions. Precipitates do not dissociate in water, so the solid should not be separated. The resulting equation looks like that below:

$$\mathbf{A^+\,(aq) + B^-\,(aq) + C^+\,(aq) + D^-\,(aq) \longrightarrow A^+\,(aq) + D^-\,(aq) + CB\,(s)} \tag{6.4.13}$$

In the equation above, $\mathbf{A^+}$and $\mathbf{D^-}$ ions are present on both sides of the equation. These are called **spectator ions** because they remain unchanged throughout the reaction. Since the spectator ions appear unchanged on both sides of the equation, they can be canceled to obtain the net ionic equation.

$$\mathbf{C^+\,(aq) + B^-\,(aq) \longrightarrow CB\,(s)} \tag{6.4.14}$$

The net ionic equation only shows the precipitation reaction. A net ionic equation must be balanced on both sides not only in terms of atoms of elements, but also in terms of electric charge. Precipitation reactions are usually represented solely by net ionic equations. If all products are aqueous, a net ionic equation cannot be written because all ions are canceled out as spectator ions. Therefore, **no precipitation reaction occurs.**

Applications and Examples

Precipitation reactions are useful in determining whether a certain element is present in a solution. If a precipitate is formed when a chemical reacts with lead, for example, the presence of lead in water sources could be tested by adding the chemical and monitoring for precipitate formation. In addition, precipitation reactions can be used to extract elements, such as magnesium from seawater. Precipitation reactions even occur in the human body between antibodies and antigens; however, the environment in which this occurs is still being studied.

Example 6.4.1

Complete the double replacement reaction and then reduce it to the net ionic equation:

$$\mathbf{NaOH\,(aq) + MgCl_2\,(aq) \longrightarrow} \tag{6.4.15}$$

Solution

1. First, predict the products of the reaction using your knowledge of double replacement reactions (remember that cations and anions switch partners). In this equation, magnesium will partner with hydroxide to make $Mg(OH)_2$ and sodium will partner with chloride to form NaCl. Note: be sure to build correct chemical formulas for each of the products, based on their ionic charges.

$$\mathbf{NaOH\,(aq) + MgCl_2\,(aq) \longrightarrow Mg(OH)_2 + NaCl} \tag{6.4.16}$$

2. Balance the chemical equation using the appropriate coefficients.

$$\mathbf{2\,NaOH\,(aq) + MgCl_2\,(aq) \longrightarrow Mg(OH)_2 + 2\,NaCl} \tag{6.4.17}$$

3. Next, consult the solubility rules to determine if the products are soluble or have formed a precipitate. From rule 1, group 1 cations are always soluble. Thus, the NaCl is soluble and can be given the (aq) designation. When evaluating the $Mg(OH)_2$, rule 6 states that hydroxides are insoluble, and thus, we can conclude that $Mg(OH)_2$ will form a precipitate and can be given the (s) designation in our equation.

$$\mathbf{2\,NaOH\,(aq) + MgCl_2\,(aq) \longrightarrow Mg(OH)_2\,(s) + 2\,NaCl\,(aq)} \tag{6.4.18}$$

4. Set up the total ionic equation by separating the ions that exist in the aqueous state. Be sure to balance both the electrical charge and the number of atoms.

$$\mathbf{2\,Na^+\,(aq) + 2\,OH^-\,(aq) + Mg^{2+}\,(aq) + 2\,Cl^-\,(aq) \longrightarrow Mg(OH)_2\,(s) + 2\,Na^+\,(aq) + 2\,Cl^-\,(aq}$$

5. To achieve the net ionic equation, cancel out the chemicals that are in the same state on both sides of the equation. For this equation, that includes the 2 Na^+ and the 2 Cl^-.

$$\mathbf{2\ \cancel{Na^+\,(aq)} + 2\,OH^-\,(aq) + Mg^{2+}\,(aq) + 2\ \cancel{Cl^-\,(aq)} \longrightarrow Mg(OH)_2\,(s) + 2\ \cancel{Na^+\,(aq)} + 2}$$

6. Thus, the final net ionic equation is:

$$\mathbf{Mg^{2+}\,(aq) + 2\,OH^-\,(aq) \longrightarrow Mg(OH)_2\,(s)} \tag{6.4.21}$$

Example 6.4.2

Complete the double replacement reaction and then reduce it to the net ionic equation:

$$\mathbf{CoCl_2\,(aq) + Na_2SO_4\,(aq) \longrightarrow} \tag{6.4.22}$$

Solution

1. First, predict the products of the reaction using your knowledge of double replacement reactions (remember that cations and anions switch partners). In this equation, cobalt will partner with the sulfate ion forming CoSO4, and sodium will partner with chloride forming NaCl

$$\mathbf{CoCl_2\,(aq) + Na_2SO_4\,(aq) \longrightarrow CoSO_4 + NaCl} \tag{6.4.23}$$

2. Balance the chemical equation using the appropriate coefficients.

$$\mathrm{CoCl_2\,(aq) + Na_2SO_4\,(aq) \longrightarrow CoSO_4 + 2\,NaCl} \tag{6.4.24}$$

3. Next, consult the solubility rules to determine if the products are soluble or have formed a precipitate. From rule 1, group 1 cations are always soluble. Thus, the NaCl is soluble and can be given the (aq) designation. When evaluating the $CoSO_4$, rule 4 states that sulfates are soluble,with the exception of sulfates formed with Ca^{2+}, Sr^{2+}, and Ba^{2+}. Since our cation in Co^{2+} and not one of the exceptions, we can conclude that the $CoSO_4$ is also soluble and can be given the (aq) designation.

$$\mathrm{CoCl_2\,(aq) + Na_2SO_4\,(aq) \longrightarrow CoSO_4\,(aq) + 2\,NaCl\,(aq)} \tag{6.4.25}$$

4. Since none of the products form a precipitate, we can conclude that no reaction has occured and there will not be any net ionic equation. (ie if you write out the total ionic equation, you will see that all of the ions will cancel eachother out and there will be no net ionic equation left.). If you physically mixed these reagents into a test tube, the solution would remain clear and no precipitate would form. This would also indicate that the ions were still in aqueous form and dissociated from one another. Thus, we can end the problem here by saying:C

Here we can follow out the total ionic equation and prove that all of the reactants cancel out with the products.

$$\mathrm{Co^{2+}\,(aq) + 2\,Cl^-\,(aq) + 2\,Na^+\,(aq) + {SO_4}^{2-}\,(aq) \longrightarrow Co^{2+}\,(aq) + {SO_4}^{2-}\,(aq) + 2\,Na^+\,(aq) +}$$

Then we can see that all of the spectator ions cancel out!

$$\mathrm{\cancel{Co^2+(aq)} + 2\,\cancel{Cl-(aq)} + 2\,\cancel{Na+(aq)} + \cancel{SO4^2-(aq)} \longrightarrow \cancel{Co^2+(aq)} + \cancel{SO4^2-(aq)}}$$

The final result is:

$$\mathrm{NO\ REACTION} \tag{6.4.28}$$

Exercise 6.4.1

Determine if the following reactions result in the formation of a precipitate. Write the net ionic equations for those that occur. Write no reaction, if a reaction does not form a precipitate Make sure to include the states of matter and balance the equations.

1.
$$\mathrm{Fe(NO_3)_3\,(aq) + NaOH\,(aq) \longrightarrow} \tag{6.4.29}$$

2.
$$\mathrm{Al_2(SO_4)_3\,(aq) + BaCl_2\,(aq) \longrightarrow} \tag{6.4.30}$$

3.
$$\mathrm{HI\,(aq) + Zn(NO_3)_2\,(aq) \longrightarrow} \tag{6.4.31}$$

4.
$$\mathrm{CaCl_2\,(aq) + Na_3PO_4\,(aq) \longrightarrow} \tag{6.4.32}$$

5.
$$\mathrm{Pb(NO_3)_2\,(aq) + K_2SO_4\,(aq) \longrightarrow} \tag{6.4.33}$$

Answer available at the end of this section.

(5) Oxidation and Reduction (Redox) Reactions

An *oxidation-reduction (redox) reaction* is a type of chemical reaction that involves a transfer of electrons between two atoms

or compounds. The substance that loses the electrons is said to be oxidized, while the substance that gains the electrons is said to be reduced. The change in electron composition can be evaluated in the change of the *oxidation state (or number)* of an atom. Therefore, an *oxidation-reduction reaction* is any chemical reaction in which the oxidation state (number) of a molecule, atom, or ion changes by gaining or losing an electron. We will learn how to evaluate the oxidation state of a molecule within this section. Overall, redox reactions are common and vital to some of the basic functions of life, including photosynthesis, respiration, combustion, and corrosion or rusting.

As shown in figure 6.4.3, an easy mnemonic for helping you remember which member gains electrons and which member loses electrons is 'LEO the lion says GER', where LEO stands for Lose Electrons = Oxidized and GER stands for Gain Electrons = Reduced.



***Figure** 6.4.3**: Mnemonic for Remembering Oxidation and Reduction.** LEO the lion says GER is a mnemonic for remembering the if an atom loses electrons it is oxidized, and if an atom gains electrons it is reduced.*

Rules for Assigning Oxidation States

The ***oxidation state (or oxidation number)*** of an atom corresponds to the number of electrons an atom loses or gains when forming an ionic compound, or appears to lose or gain when forming covalent compounds. Oxidation states are a bookkeeping tool used to keep track of electron transfer in chemical reactions. In determining the oxidation state of an atom, there are seven guidelines to follow:

1. The oxidation state of an atom in its elemental form is **0**. This includes elements that exist as diatomic molecules. For example, each oxygen atom in $\mathbf{O_2}$ has an oxidation state of **0**.
2. The total oxidation state of all atoms in a *neutral species* is **0** and in an *ion* is equal to the **ion charge**. (For example, the overall oxidation state of NaCl = 0, even though the oxidation state of Na^+ in this bond is +1 and the oxidation state of the chlorine atom, Cl^-, is -1. When you add them together they equal 0. In the case of an ion, the overall charge is always indicated. For example, the overall charge of a OH^- ion is -1, while the oxygen in the OH^- has a -2 oxidation state and the hydrogen has a +1 oxidation state.)
3. Group 1 metals have an oxidation state of **+1**, and Group 2 metals have an oxidation state of **+2** in their compounds.
4. Fluorine always has an oxidation state of **–1** in compounds.
5. Hydrogen generally has an oxidation state of **+1** in compounds
6. Oxygen generally has an oxidation state of **-2** in compounds
7. In binary ionic compounds, Group 17 (7A) elements generally have an oxidation state of –1, Group 16 (6A) elements generally have an oxidation state of –2, and Group 15 (5A) elements generally have an oxidation state of –3.
8. The oxidation states of all other atoms are determined using Rules 1–7.

Rules should be applied in order from top to bottom. If one rule determines the oxidation state of an atom, later rules do not

override it.

Table 6.4A: Summary of the Rules for Evaluating Oxidation States

Rule	Oxidation State
Elemental form	0
Neutral compound	Sum = 0
Polyatomic ion	Sum = ion charge
Group 1	+1
Group 2	+2
F	-1
H	Usually +1
O	Usually -2
Halogens	Usually -1

Example 6.4.3

What is the oxidation state of chromium in the chromate anion, CrO_4^{2-}?

Solution

Looking at all the oxidation state rules, we see that the overall oxidation state is equal to the charge of the ion (-2), and that the oxygen usually takes a -2 oxidation state. So we should assign each oxygen atom in the anion an oxidation state of (-2). There are 4 oxygen atoms, thus the overall charge from all of the oxygens is:

$$(-2) \times 4 = -8 \tag{6.4.34}$$

and the total charge on the anion is (-2). Thus, the oxidation state of chromium can be solved using the following equation, where *X* is the overall positive charge:

$$X + (-8) = -2 \tag{6.4.35}$$

$$X = +6 \tag{6.4.36}$$

Since there is only one Chromium ion within the anion, it must be responsible for the entire positive charge on the molecule. Thus, the chromium ion has an oxidation state of +6.

Exercise 6.4.2

More Practice with Oxidation States:

1. What is the oxidation state of chromium in the dichromate anion, $Cr_2O_7^{2-}$?
2. What is the oxidation state of carbon in $H_2C_2O_4$?
3. What is the oxidation state of sulfur in the $Na_2S_2O_3$?
4. What is the oxidation state of carbon in CO? in CO_2?
5. What is the oxidation state of chlorine in ClO_4^-?

Answer available at the end of this section.

Once you have mastered calculating oxidation states, you can start evaluating chemical reactions to determine if they are oxidation-reduction reactions.

Redox reactions are comprised of two parts, a reduced half and an oxidized half, that *always* occur together. The reduced half gains electrons and the oxidation number decreases (or becomes less positive), while the oxidized half loses electrons and the oxidation number increases (becomes more positive). There is no net change in the number of electrons in a redox reaction. Those given off in the oxidation half reaction are taken up by another species in the reduction half reaction.

A good example of a redox reaction is the thermite reaction, in which iron atoms in ferric oxide lose (or give up) O atoms to Al atoms, producing Al_2O_3.

$$\mathbf{Fe_2O_3\,(s) + 2\,Al\,(s) \longrightarrow Al_2O_3\,(s) + 2\,Fe\,(l)} \tag{6.4.37}$$

To recognize redox reactions, begin by determining the oxidation states of each atom in the reaction on both the left and the right sides of the equation. Then determine of the oxidation state of any of the atoms changes from the reactant to the product side. If so, then the reaction is a redox reaction, and you can determine which compound is oxidized (loses electrons) and which is reduced (gains electrons). For example, if we evaluate the thermite reaction above:

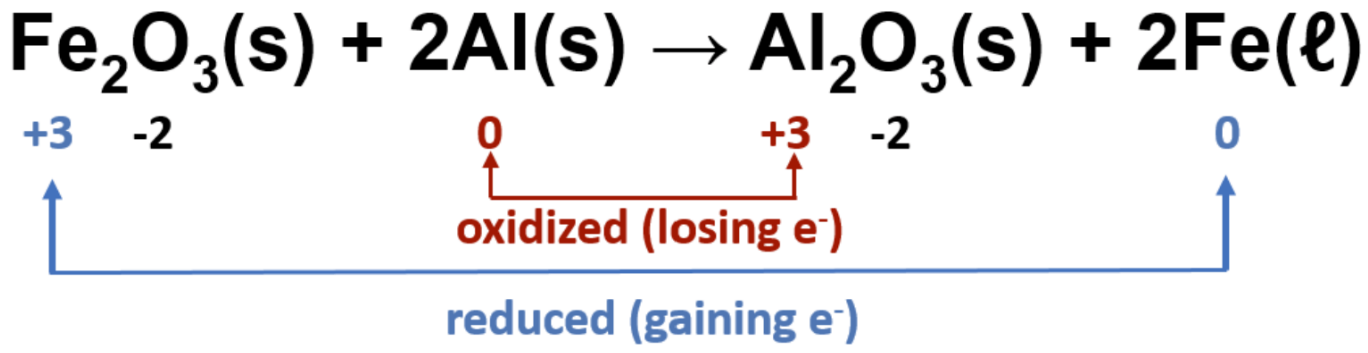
1. First evaluate the reactants side: Start with Fe_2O_3
    - ***Table 6.4B: Evaluating the Oxidation States of Atoms in Iron (III) Oxide***.

Fe_2O_3	Fe	O	Overall Charge
Number of Atoms	2	3	
Oxidation State	+3	-2	
Total Charge	+6	-6	0

2. Then evaluate Aluminum (Al). Since aluminum is in its elemental form, the oxidation state is zero = 0.
3. Then evaluate the product side of the reaction. Start with the Al_2O_3
    - ***Table 6.4C: Evaluating the Oxidation States of Atoms in Aluminum Oxide***.

Al_2O_3	Al	O	Total Charge
Number of Atoms	2	3	
Oxidation State	+3	-2	
Total Charge	+6	-6	0

4. Then evaluate the iron, Fe. Since iron is in its elemental form, the oxidation state is zero = 0.
5. Finally, write in the values on the equation and evaluate the redox states.



Overall in this reaction, the aluminum is oxidized to aluminum oxide, and the iron in the iron III oxide is reduced to elemental iron. Notice that there is no change to the oxidation state of oxygen.

The two species that exchange electrons in a redox reaction are given special names. The ion or molecule that accepts electrons (or becomes reduced during the reaction) is called the oxidizing agent; by accepting electrons it causes the oxidation of another compound or element. In the thermite reaction above, the iron III oxide is the oxidizing agent. Conversely, the species that donates electrons is called the reducing agent; when the reaction occurs, it reduces the other species. Thus, in the thermite reaction, the aluminum is the reducing agent. In other words, the substance that is oxidized is the reducing agent and the substance that is reduced is the oxidizing agent.

Single replacement reactions are often also redox reactions. A good indicator of a redox reaction is the appearance of an elemental form of a substance on one side that is converted into a compound on the other side. Another common redox reaction is a combustion reaction.

Combustion Reactions

$$\mathrm{CxHy + O_2 \longrightarrow CO_2 + H_2O} \tag{6.4.38}$$

Combustion reactions almost always involve oxygen in the form of O_2, and are almost always ***exothermic***, meaning they produce heat. Chemical reactions that give off light and heat are colloquially referred to as “burning.” Complete combustion of carbon compounds results in the production of carbon dioxide (CO_2) and water (H_2O). Note that carbon can exist in a range of oxidation states, typically from -4 to +4. The burning of fuels that provides the energy to maintain our civilization and the metabolism of foods that furnish the energy that keeps us alive both involve redox reactions.

All combustion reactions are also redox reactions.

$$\mathrm{CxHy + O_2 \longrightarrow CO_2 + H_2O} \tag{6.4.39}$$

One example is the burning of acetylene (C_2H_2) in torches:

$$\mathrm{2\,C_2H_2 + 5\,O_2 \longrightarrow 4\,CO_2 + 2\,H_2O} \tag{6.4.40}$$

Oxygen (in its elemental form) is a crucial reactant in combustion reactions, and it is also present in the products. Combustion reactions can be evaluated for their redox potential, as we did for the thermite reaction above.

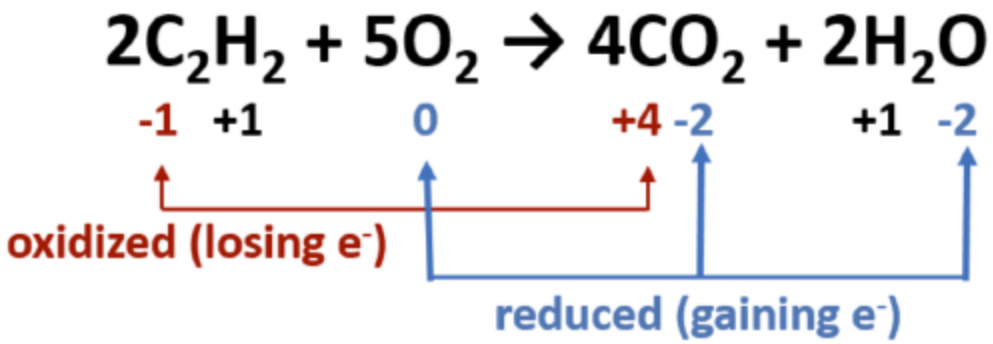
1. First evaluate the reactants side: Start with C_2H_2
    - ***Table 6.4D: Determining Oxidation States of Atoms in Acetylene (Ethyne)***.

C_2H_2	C	H	Overall Charge
Number of Atoms	2	2	
Oxidation State	-1	+1	
Total Charge	-2	+2	0

2. Then evaluate O_2. Since oxygen is in its elemental form, the oxidation state is zero = 0.
3. Then evaluate the products side: Start with the CO_2
    - ***Table 6.4E: Determining the Oxidation States of Atoms in Carbon Dioxide***.

CO_2	C	O	Overall Charge
Number of Atoms	1	2	
Oxidation State	+4	-2	
Total Charge	+4	-4	0

4. Then evaluate H_2O. The Hydrogen takes on the +1 state and the Oxygen takes on the -2 state.
5. Finally, write in the oxidation states on the equation and evaluate the changes.



Overall in combustion reactions, the hydocarbon (in this case, acetylene) is oxidized by molecular oxygen to produce carbon dioxide and water. In the process, oxygen is reduced.

In respiration, the biochemical process by which the oxygen we inhale in air oxidizes foodstuffs to carbon dioxide and water, redox reactions provide energy to living cells. A typical respiratory reaction is the oxidation of glucose ($C_6H_{12}O_6$), a simple sugar. Instead of releasing energy rapidly as heat and light, cells capture the energy from glucose in a controlled series of biochemical reactions to produce ATP.

$$\mathrm{C_6H_{12}O_6 + 6\,O_2 \longrightarrow 6\,CO_2 + 6\,H_2O} \tag{6.4.41}$$

A Closer Look at the Importance of Redox Reactions

Organic chemists use a variety of redox reactions. For example, potassium dichromate ($K_2Cr_2O_7$) is a common oxidizing agent that can be used to oxidize alcohols (symbolized by the general formula R-OH, where R can be any group, and the OH represents the alcohol functional group). The product of the reaction depends on the location of the OH functional group in the alcohol molecule, the relative proportions of alcohol and the dichromate ion, and reaction conditions such as temperature. If the OH group is attached to a terminal carbon atom and the product is distilled off as it forms, the product is an aldehyde, which has a terminal carbonyl group (C=O). One example is the reaction used by the Breathalyzer to detect ethyl alcohol (C_2H_5OH) in a person's breath:

$$\mathrm{3\,C_2H_5OH + Cr_2O_7^{2-} + 8\,H^+ \longrightarrow 3\,CH_3CHO + 2\,Cr^{3+} + 7\,H_2O} \tag{6.4.42}$$

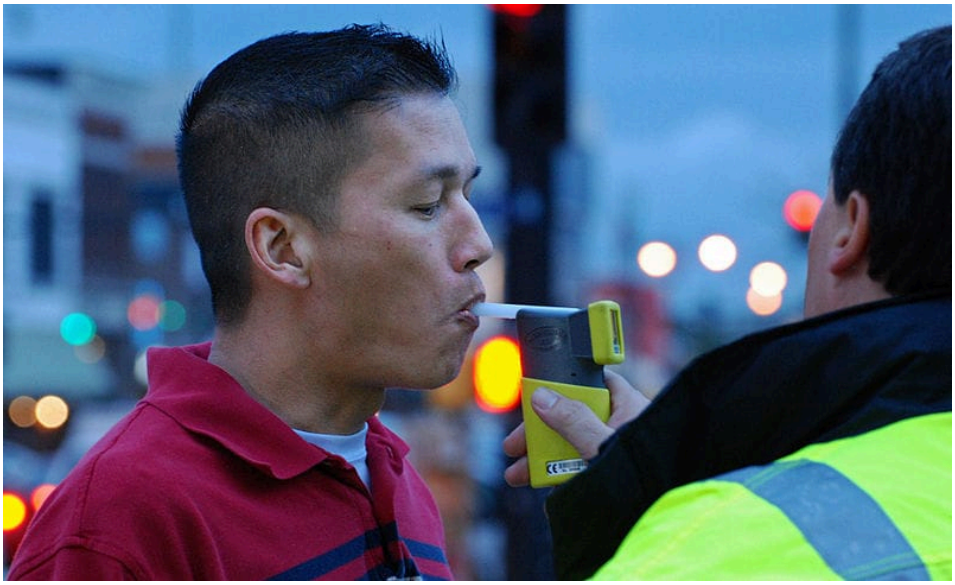
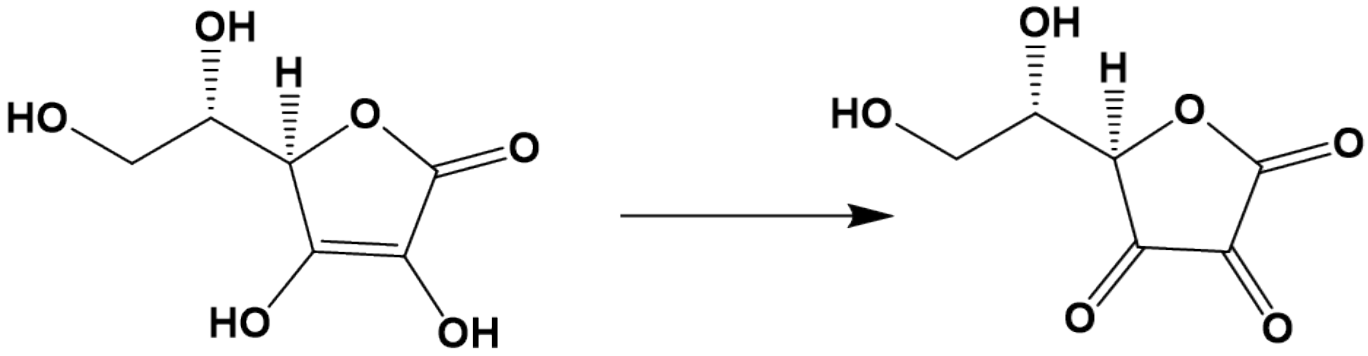


Figure 6.4.4***: Drinkers Learn Their Limit Using a Standard Breathalyzer Test.***

Picture from: KOMUnews

In food chemistry, the substances known as antioxidants are reducing agents. Ascorbic acid (also known as vitamin C; $C_6H_8O_6$) is thought to prevent potentially damaging oxidation of living cells. In the process, it is oxidized to dehydroascorbic acid ($C_6H_6O_6$).

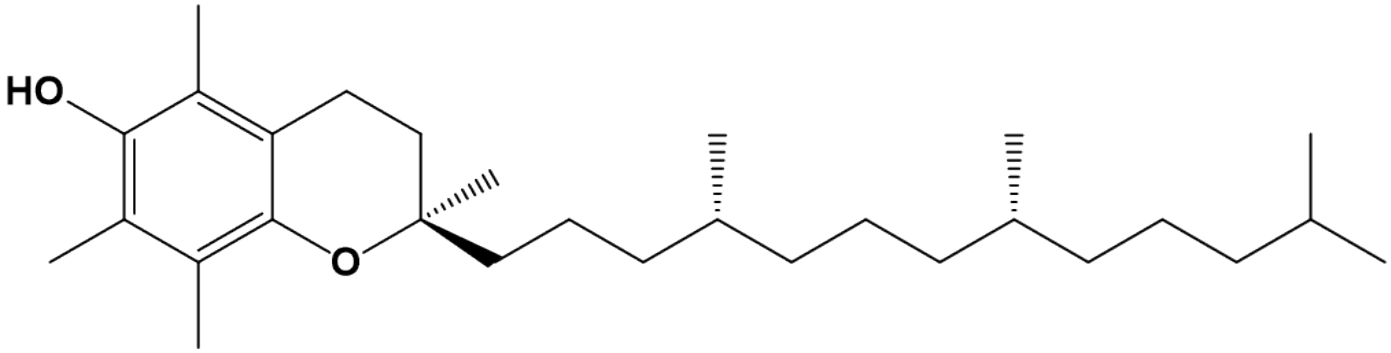


Ascorbic Acid (Reduced Form) **Dehydroascorbic Acid (Oxidized Form)**

In the stomach, ascorbic acid reduces the nitrite ion (NO^{2-}) to nitric oxide (NO):

$$\mathrm{C_6H_8O_6 + 2\,H^+ + 2\,NO_2{}^- \longrightarrow C_6H_6O_6 + 2\,H_2O + 2\,NO} \tag{6.4.43}$$

If this reaction did not occur, nitrite ions from foods would oxidize the iron in hemoglobin, destroying its ability to carry oxygen.



Vitamin E (alpha-Tocopherol)

Tocopherol (vitamin E) is also an antioxidant. In the body, vitamin E is thought to act by scavenging harmful by-products of metabolism, such as the highly reactive molecular fragments called free radicals. In foods, vitamin E acts to prevent fats from being oxidized and thus becoming rancid.

Finally, and of greatest importance, green plants carry out the redox reaction that makes possible almost all life on Earth. They do this through a process called photosynthesis, in which carbon dioxide and water are converted to glucose ($C_6H_{12}O_6$). The synthesis of glucose requires a variety of proteins called enzymes and a green pigment called chlorophyll that converts sunlight

into chemical energy (Figure 6.4.4). In this reaction, carbon dioxide is reduced to form glucose ($C_6H_{12}O_6$), and water is oxidized to oxygen gas. Other reactions convert the glucose ($C_6H_{12}O_6$) to more complex carbohydrates, plant proteins, and oils. The chemical reaction that occurs is as follows:

$$\mathbf{6\,CO_2 + 6\,H_2O \longrightarrow C_6H_{12}O_6 + 6\,O_2} \tag{6.4.44}$$

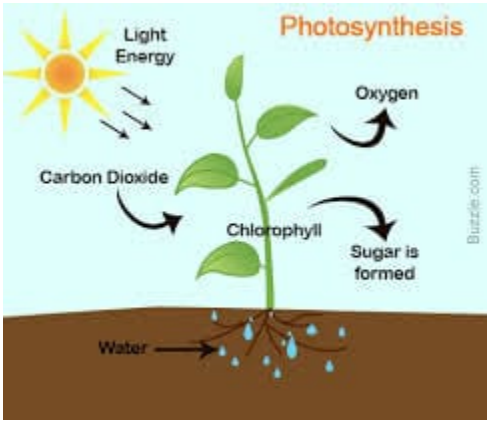


Figure 6.4.4**: Diagram of Photosynthesis.** In photosynthesis, light energy from the sun is harvested by the chlorophyll pigments primarily in the plant leaves where it is used to convert carbon dioxide and water into sugar (glucose).

Image provided from: Masroor.nida.ns

Answers

Exercise 6.4.1

1. The predicted products of this reaction are $Fe(OH)_3$ and $NaNO_3$.

$$\mathbf{Fe(NO_3)_3\,(aq) + 3\,NaOH\,(aq) \longrightarrow Fe(OH)_3\,(s) + 3\,NaNO_3\,(aq)} \tag{6.4.45}$$

The solubility rules predict that $NaNO_3$ is soluble because all nitrates are soluble (rule 2). However, **$Fe(OH)_3$ is insoluble**, because hydroxides are insoluble (rule 6) and Fe is not one of the cations which results in an exception. After dissociation, the total ionic equation is as follows:

$$\mathbf{Fe^{3+}\,(aq) + 3\,NO_3{}^-\,(aq) + 3\,Na^+\,(aq) + 3\,OH^-\,(aq) \longrightarrow Fe(OH)_3\,(s) + 3\,Na^+\,(aq) + 3\,NO_3{}^-\,(aq)} \tag{6.4.46}$$

and after canceling the spectator ions, the net ionic equation is:

$$\mathbf{Fe^{3+}\,(aq) + 3\,OH^-\,(aq) \longrightarrow Fe(OH)_3\,(s)} \tag{6.4.47}$$

2. The predicted products of the reaction are:

$$\mathbf{Al_2(SO_4)_3\,(aq) + 3\,BaCl_2\,(aq) \longrightarrow 2\,AlCl_3\,(aq) + 3\,BaSO_4\,(s)} \tag{6.4.48}$$

Evaluation of the products using the solubility rules shows that $AlCl_3$ is soluble because it contains a chloride (rule 3); however, **$BaSO_4$ is insoluble:** it contains a sulfate, but the Ba^{2+} ion causes it to be insoluble because it is one of the cations that causes an exception to rule 4. The total ionic equation is:

$$\mathbf{2\,Al^{3+}\,(aq) + 3\,SO_4{}^{2-}\,(aq) + 3\,Ba^{2+}\,(aq) + 6\,Cl^-\,(aq) \longrightarrow 2\,Al^{3+}\,(aq) + 6\,Cl^-\,(aq) + 3\,BaSO_4\,(s)} \tag{6.4.49}$$

and the net ionic equation is:

$$\mathbf{Ba^{2+}\,(aq) + SO_4{}^{2-}\,(aq) \longrightarrow BaSO_4\,(s)} \tag{6.4.50}$$

3. From the double replacement reaction, the predicted products are HNO_3 and ZnI_2.

$$\mathbf{2\,HI\,(aq) + Zn(NO_3)_2\,(aq) \longrightarrow 2\,HNO_3\,(aq) + ZnI_2\,(aq)} \tag{6.4.51}$$

Looking at the solubility rules, HNO_3 is soluble because it contains nitrate (rule 2), and ZnI_2 is soluble because iodides are soluble (rule 3). This means that **both the products are aqueous** (i.e. dissociate in water), and thus **no precipitation reaction occurs**.

$$\mathbf{NO\ REACTION} \tag{6.4.52}$$

4. The predicted products of this double replacement reaction are $Ca_3(PO_4)_2$ and NaCl.

$$\mathbf{3\,CaCl_2\,(aq) + 2\,Na_3PO_4\,(aq) \longrightarrow Ca_3(PO_4)_2\,(s) + 6\,NaCl\,(aq)} \tag{6.4.53}$$

Rule 1 states that NaCl is soluble, and according to solubility rule 6, **$Ca_3(PO_4)_2$ is insoluble.** The total ionic equation is:

$$\mathbf{3\,Ca^{2+}\,(aq) + 6\,Cl^-\,(aq) + 6\,Na^+\,(aq) + 2\,PO_4{}^{3-}\,(aq) \longrightarrow Ca_3(PO_4)_2\,(s) + 6\,Na^+\,(aq) + 6\,Cl^-\,(aq)} \tag{6.4.54}$$

and the net ionic equation is:

$$\mathbf{3\,Ca^{2+}\,(aq) + 2\,PO_4{}^{3-}\,(aq) \longrightarrow Ca_3(PO_4)_2\,(s)} \tag{6.4.55}$$

5. The predicted products of this reaction are:

$$\mathrm{Pb(NO_3)_2\,(aq) + K_2SO_4\,(aq) \longrightarrow PbSO_4\,(s) + 2\,KNO_3\,(aq)} \tag{6.4.56}$$

Evaluating potassium nitrate shows that this is soluble based on rule (2). However, **$\mathrm{PbSO_4}$ is insoluble**. Lead(II) is one of the sulfate exceptions in rule (4). So this reaction **does form a precipitate**. The total ionic equation is:

$$\mathrm{Pb^{2+}\,(aq) + 2\,NO_3^-\,(aq) + 2\,K^+\,(aq) + SO_4^{2-}\,(aq) \longrightarrow PbSO_4\,(s) + 2\,K^+\,(aq) + 2\,NO_3^-\,(aq)} \tag{6.4.57}$$

and the net ionic equation is:

$$\mathrm{Pb^{2+}\,(aq) + SO_4^{2-}\,(aq) \longrightarrow PbSO_4\,(s)} \tag{6.4.58}$$

Exercise 6.4.2

1. (+6), 2. (+3), 3. (+2), 4. (+2, +4), 5. (+7)

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6.5: Focus on the Environment - Air Pollution

Understanding and monitoring air quality is essential to atmospheric scientists to help reduce emissions, protect human health and the environment. In this learning module, we will learn about air pollutants, their sources, and the effects on the environment and our respiratory systems.



Figure 6.5.1***: Air Pollution in Hong Kong.*** *On two cloud-free days, the haze situation can differ dramatically depending on the season and on the direction of the wind. Source:* Tokyoahead

Composition of the Atmosphere

The air is made up of many different gases. To give you an idea of what air actually consists of watch this video!

Video Tutorial on the Composition of Air.

The first, nitrogen, is the largest constituent of the atmosphere. If the air were made of 1000 parts, nitrogen would call for 780 parts, or 78%. Nitrogen is really important to us because it helps plants to gain minerals from the soil for plant growth. The next most common gas that is in air is oxygen. Oxygen makes up 209 parts, or 20.9% of our air. Oxygen is important for many things. We need it to breath, but it is also needed for fires. The only problem is with oxygen, if you have too much of it, oxygen is extremely reactive. Things could combust if you have an oxygen-rich environment, so having the nitrogen in our air balances it out and gives us the right percentage of oxygen and nitrogen together to make air safe to breath and be around.

The next gas in the air is called argon. Argon does not do much for us in the atmosphere, but we have 9 parts, or 0.9% in the air. Argon is a gas that can be placed in a tube with an electric current to create a purple hue in a neon sign. Next, we have a gas that we hear a lot about these days, which is carbon dioxide. This gas is one of the trace gases and is found in small concentrations in the atmosphere. Carbon dioxide is a gas that we exhale when we breathe. It is also taken in by plants to create the plant's structure. Carbon dioxide is a greenhouse gas and allows incoming solar radiation to pass through the atmosphere, but traps outgoing or reflected sunlight to cause a warming effect in our atmosphere. Trace gases, including carbon dioxide, make up 1 part, or 0.1% of the air. Other trace gases include ozone, nitrogen oxide, methane, helium, neon, water vapor, and several others.

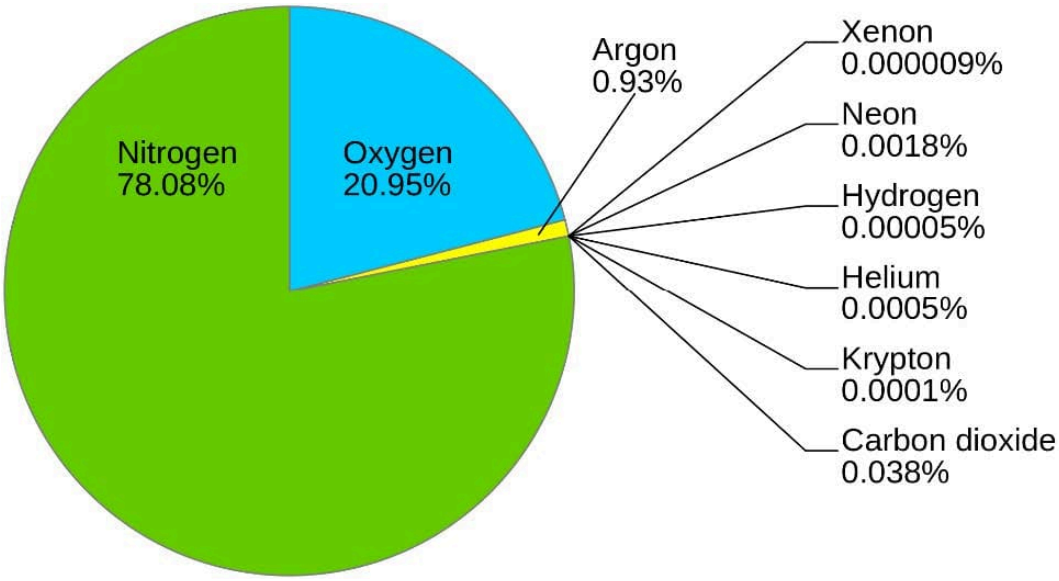


Figure 6.5.2***: Composition of the Atmosphere.*** *Most of our atmosphere, 99%, is made of oxygen (O_2) at 21% and nitrogen (N_2) at 78%. Greenhouse gases, like water vapor, carbon dioxide and methane are vitally important for keeping our planet warm. Although these gases are found in small concentrations, they are vitally important in maintaining a globally averaged temperature of 59^{0}F.*

Pollutants

What is air pollution? It is not only chemicals in the atmosphere, but chemicals that have bad health effects. Since we are breathing it in, it is going to affect our health, lung function, and can lead to increased cancer risks. If the chemicals are affecting us negatively, we call them ***pollutants*****.** Please watch the following video tutorial describing atmospheric pollutants.

Air Pollution Tutorial

Primary pollutants are emitted directly into the atmosphere by a particular source. These include volatile organic compounds (VOCs) such as gases from evaporating gasoline, carbon monoxide (CO), which is an odorless gas that is produced by oxidation reactions, nitrogen oxide (NO), nitrogen dioxide (NO_2), sulfur dioxide (SO_2), particulate matter (PM), and lead (Pb) which used to be a common additive in gasoline and other industrial formulations, such as paint. Lead pollution will be discussed in further detail in Chapter 7.

Primary pollutants can combine with other chemicals in the atmosphere and produce ***secondary pollutants*****.**

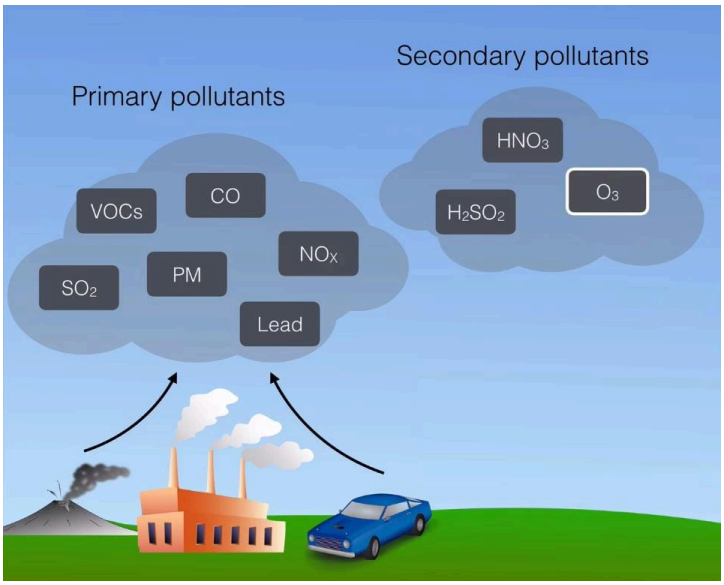


***Figure** 6.5.3**: Diagram of primary and secondary pollutants.** Diagram by*: Paul Anderson

As seen in chapter 3, a number of these primary pollutants can react to form atmospheric acids that are the cause of acid rain. Examples from chapter 3 included NO_x compounds that react to produce nitric acid (HNO_3), and SO_2 that reacts to produce sulfuric acid (H_2SO_4). Ozone is another secondary pollutant that is formed through chemical reactions between NO_2, VOCs, and sunlight.

1. NO_2 from vehicle exhaust, is photolyzed by ultraviolet (UV) radiation (hν) from the sun and decomposes into NO and an oxygen radical:

$$\mathbf{NO_2 + h\nu \longrightarrow NO + O^{\bullet}} \tag{6.5.1}$$

2. The oxygen radical then reacts with an atmospheric oxygen molecule to create ozone, O_3:

$$\mathbf{O^{\bullet} + O_2 \longrightarrow O_3} \tag{6.5.2}$$

3. Under normal conditions, O_3 reacts with NO, to produce NO_2 and an oxygen molecule:

$$\mathbf{O_3 + NO \longrightarrow O_2 + NO_2} \tag{6.5.3}$$

This is a continual cycle that leads only to a temporary increase in net ozone production. To create photochemical smog on the scale observed in Los Angeles, the process must also include volatile organic compounds (VOCs).

4. VOC's (indicated as RH, where R is a placeholder for a more complicated carbon-oxygen containing structures) react with hydroxide in the atmosphere to create water and a reactive VOC molecule:

$$\mathbf{RH + OH^{\bullet} \longrightarrow R^{\bullet} + H_2O} \tag{6.5.4}$$

5. The reactive VOC can then bind with an oxygen molecule to create an oxidized VOC:

$$\mathbf{R^{\bullet} + O_2 \longrightarrow RO_2^{\bullet}} \tag{6.5.5}$$

6. The oxidized VOC can now bond with the nitrogen oxide produced in the earlier set of equations to form nitrogen dioxide and a reactive VOC molecule:

$$\mathbf{RO_2^{\bullet} + NO \longrightarrow RO^{\bullet} + NO_2} \tag{6.5.6}$$

In the second set of equations (6.5.4-6.5.6), the nitrogen oxide, produced in equation 1, is oxidized in equation 6 without the destruction of any ozone. This means that in the presence of VOCs, in equation 3, is essentially eliminated, leading to a large and rapid build up in the photochemical smog in the lower atmosphere.

The EPA has an interactive chart evaluating ground level ozone concentrations over an 8 hour period. Please click on the link below. Once on the site, mouse over the different hours of the day at the top of the page to see how pollution levels change. What is the high point of pollution? Why do you think that this is the case?

Ground Level Ozone Concentrations over an 8 hr Period.

In the morning, NO and VOC concentrations rise, as people fill their cars with gas and drive to work. By midmorning , VOC's begin to oxidize NO into NO_2, thus reducing their respective concentrations. At midday, NO_2 concentrations peak just before solar radiation becomes intense enough to photolyze the NO_2 bond, releasing an oxygen atom that quickly gets converted into O_3. By late afternoon, peak concentrations of photochemical smog are present.

Ozone can be helpful or harmful to our health and the environment. In the stratosphere, ozone is produced naturally where it blocks harmful ultraviolet rays from the sun. This is an example of "good" ozone. In the troposphere, ground-level ozone largely contributes to smog. This is "bad" ozone.

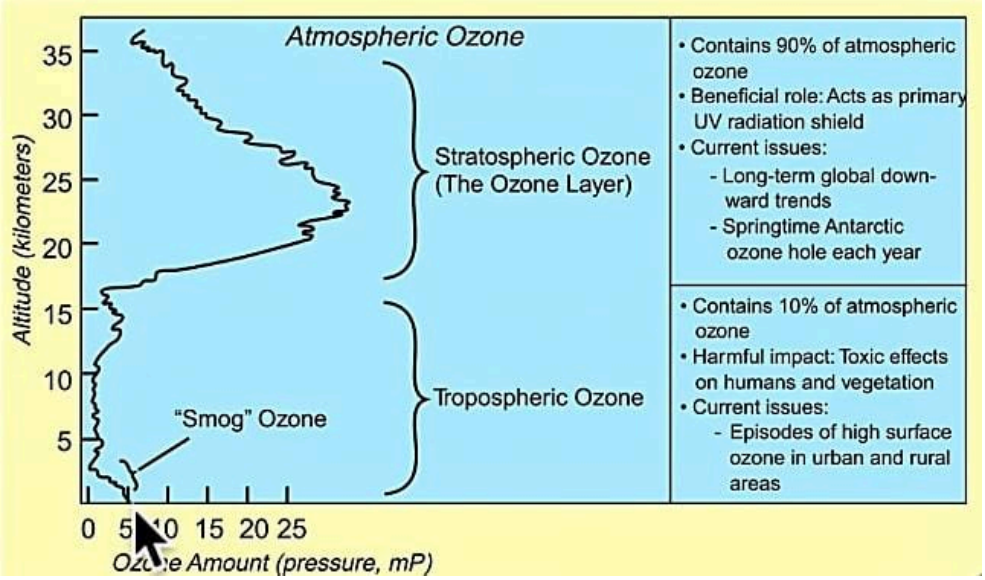


Figure 6.5.4: A vertical profile showing atmospheric ozone, which includes tropospheric and stratospheric ozone levels. *Note that high levels of surface ozone in urban and rural areas are largely due to human pollution.*

Improving Air Quality

A wide array of harmful health effects have been attributed to air pollution including respiratory diseases such as asthma and COPD, cardiovascular diseases, adverse pregnancy outcomes (such as preterm birth) and even death. Air pollution can be improved and controlled air through regulation. The Clean Air Act (1970) in the United States was able to reduce pollutants and save lives. As seen in chapter 3 with the control of acid rain, technology is able to scrub those pollutants out of the air before it is released. The Clean Air Act put strict standards on certain pollutants so that industries are limited on how many pollutants they can put into the atmosphere.

The Clean Air Act requires the Environmental Protection Agency (EPA) to set National Ambient Air Quality Standards (NAAQS) for pollutants considered harmful to public health and the environment. The EPA has set standards for six criteria pollutants which include: carbon monoxide (CO), lead (Pb), nitrogen dioxide (NO_2), ozone (O_3), particulate matter (PM), and sulfur dioxide (SO_2). Follow the link to learn more about the criteria pollutants and the concentrations at which they are considered by the EPA to be unsafe.

Air Quality Index

The Air Quality Index (AQI) is a color-coded scale that ranges from 0 – 500 and evaluates the health quality of the air around us.

A rating below 50 indicates good air quality, whereas over 150 indicates unhealthy conditions for all populations. To learn more about the AQI, watch this next video.

Air Quality Index.

The United States EPA has a real time website entitled **AirNow** where you can look up air quality for any state within the United States. In 2007, the US Embassies in China also established a **World Air Quality Index Project** that is helping monitor air quality world wide region in the world. This project is currently providing air quality information in over 80 countries with over 10,000 monitoring stations. **The United Nations Environment Programme** partners with countries from around the world to address health issues and find solutions for air pollution.

Suggested Activity: Have your students download the following **air_pollution_in class activity**. Introduce the Smog City Program in class and describe how to use the various controls. Have your students complete parts 1 and 2 as homework assignments. Once complete review the assignment with an in-class discussion.

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6.6: Chapter Summary

To ensure that you understand the material in this chapter, you should review the meanings of the following bold terms in the following summary and ask yourself how they relate to the topics in the chapter.

Scientific laws are general statements that apply to a wide variety of circumstances. One important law in chemistry is the ***law of conservation of matter*****,** which states that in any closed system, the amount of matter stays constant.

Chemical equations are used to represent chemical reactions. Reactants change chemically into products. The law of conservation of matter requires that a proper chemical equation be balanced. Coefficients are used to show the relative numbers of reactant and product molecules.

In ***stoichiometry,*** quantities of reactants and/or products can be related to each other using the balanced chemical equation. The coefficients in a balanced chemical reaction are used to devise the proper ratios that relate the number of molecules of one substance to the number of molecules of another substance.

Chemical reactions can be classified by type. ***Combination reactions*** (also called synthesis reactions) build or make a substance from other substances, whereas, ***decomposition reactions*** break one substance down into multiple substances.

Single replacement (or displacement) reactions occur when an element (most frequently a metal) replaces another element from a compound. They can occur in two forms: *cationic exchange* or *anionic exchange*. In ***cationic exchanges*****,** the positive ions (cations) of the equation change place. In ***anionic exchanges*****,** the negative ions (anions) change place. Note that single replacement reactions are often also redox reactions.

Double replacement (or displacement) reactions occur when two chemical groups substitute for each other (change partners) in their respective compounds. Double replacement reactions can be of two major types: **(1)** ***precipitation reactions*** wherein, at least one of the products forms a solid precipitate during the reaction, and **(2)** ***acid-base neutralization reactions,*** wherein an acid is neutralized by a base to form a salt and water. The solubility rules are used to determine if products in a double displacement reaction will be insoluble and precipitate from the reaction mixture. Both precipitation and acid-base neutralization reactions can be written as *net ionic equations*.

Oxidation reactions are reactions in which an atom loses an electron. ***Reduction reactions*** are reactions in which an atom gains an electron. These two processes always occur together, so they are collectively referred to as ***oxidation-reduction (or redox) reactions.*** The species being oxidized it called the ***reducing agent*****,** while the species being reduced is the ***oxidizing agent. Combustion reactions*** are a type of redox reaction that combine molecular oxygen with the atoms of another reactant.

Oxidation-reduction reactions are common in organic and biological chemistry. ***Respiration,*** the process by which we inhale and metabolize oxygen, is a series of redox reactions. In the absence of oxygen, redox reactions still occur in a process called ***anaerobic metabolism***. Antioxidants such as ascorbic acid also play a part in the human diet, acting as reducing agents in various biochemical reactions. ***Photosynthesis,*** the process by which plants convert water and carbon dioxide to glucose, is also based on redox reactions.

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7: CHAPTER 7 - QUANTITIES IN CHEMICAL REACTIONS

7.1: Chapter Introduction

7.2: The Mole

7.3: Atomic and Molar Mass

7.4: Mole-Mass Conversions

7.5: Mole-Mole Relationships in Chemical Reactions

7.6: Mole-Mass and Mass-Mass Problems

7.7: Limiting Reagent and Percent Yield

7.8: Focus on the Environment - Global Climate Change

7.9: Chapter Summary

7.10: References

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7.1: Chapter Introduction

Quantities in Chemistry

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.

Table 7.1A: How to approach solving problems.

When Approaching Problems:
1. Write down what you know (include all compound labels and units!) 2. Write down what you need to find (include all compound labels and units!) 3. Evaluate how the two quantities are related and come up with a ballpark estimate (ie should the answer be larger or smaller? What makes sense?) 4. Write our your conversion factor(s). 5. Do the math! (Make sure that the proper units cancel and that you are left with what you want to find.) 6. Check your work and make sure it makes sense with your ballpark estimate.

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7.2: The Mole

The Mole as a Counting Unit

Figure 7.2.1 “Water Molecules” shows that we need 2 hydrogen atoms and 1 oxygen atom to make 1 water molecule. If we want to make 2 water molecules, we will need 4 hydrogen atoms and 2 oxygen atoms. If we want to make 5 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.

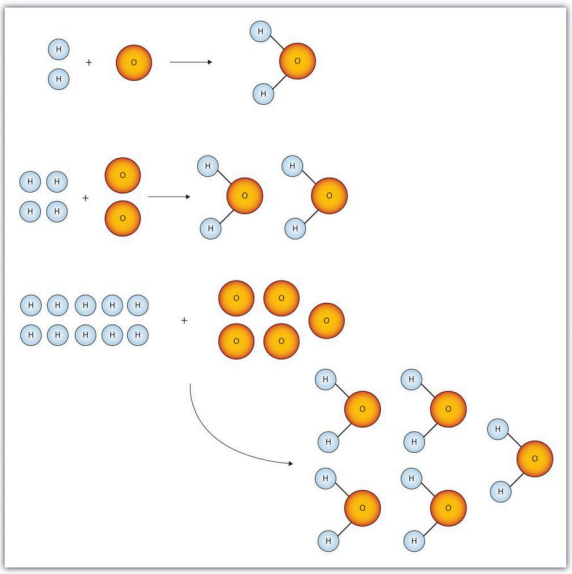


Figure 7.2.1**: Water Molecules.** The ratio of hydrogen atoms to oxygen atoms used to make water molecules is always 2:1, no matter how many water molecules are being made.

One problem we have, however, is that it is extremely difficult, if not impossible, to organize atoms one at a time. As stated in the introduction, we deal with billions of atoms at a time. How can we keep track of so many atoms (and molecules) at a time? We do it by using mass rather than by counting individual atoms.

A hydrogen atom has a mass of approximately 1 u. An oxygen atom has a mass of approximately 16 u. The ratio of the mass of an oxygen atom to the mass of a hydrogen atom is therefore approximately 16:1.

If we have 2 atoms of each element, the ratio of their masses is approximately 32:2, which reduces to 16:1—the same ratio. If we have 12 atoms of each element, the ratio of their total masses is approximately (12 × 16):(12 × 1), or 192:12, which also reduces to 16:1. If we have 100 atoms of each element, the ratio of the masses is approximately 1,600:100, which again reduces to 16:1. As long as we have equal numbers of hydrogen and oxygen atoms, the ratio of the masses will always be 16:1.

The same consistency is seen when ratios of the masses of other elements are compared. For example, the ratio of the masses of silicon atoms to equal numbers of hydrogen atoms is always approximately 28:1, while the ratio of the masses of calcium atoms to equal numbers of lithium atoms is approximately 40:7.

So we have established that the masses of atoms are constant with respect to each other, as long as we have the same number of each type of atom. Consider a more macroscopic example. If a sample contains 40 g of Ca, this sample has the same number of atoms as there are in a sample of 7 g of Li. What we need, then, is a number that represents a convenient quantity of atoms so we can relate macroscopic quantities of substances. Clearly even 12 atoms are too few because atoms themselves are so small. We need a number that represents billions and billions of atoms.

A ***mole*** is defined as 6.02×10^{23} items and thus, it is used by chemists to represent a large number of atoms or molecules. Just as a dozen implies 12 things, a mole (abbreviated *mol*) represents 6.02×10^{23} things. The number 6.02×10^{23}, called ***Avogadro's number***, after the 19th-century chemist Amedeo Avogadro, is the number we use in chemistry to represent macroscopic amounts of atoms and molecules. Thus, if we have 6.02×10^{23} Oxygen atoms, we say we have 1 mole of Oxygen atoms. If we have 2 mol of Na atoms, we have $2 \times (6.02 \times 10^{23})$ Na atoms, or 1.2044×10^{24} Na atoms. Similarly, if we have 0.5 mol of benzene (C_6H_6) molecules, we have $0.5 \times (6.02 \times 10^{23})$ C_6H_6 molecules, or 3.011×10^{23} C_6H_6 molecules.

$$1 \text{ mol} = 6.022 \times 10^{23} \text{ particles} \tag{7.2.1}$$

Note

A mole represents a very large number! If 1 mol of quarters were stacked in a column, it could stretch back and forth between the Earth and the Sun 6.8 billion times!

Notice that we are applying the mole unit to different types of chemical entities. In these examples, we cited moles of atoms *and* moles of molecules. The word *mole* represents a number of things—6.02×10^{23} of them—but does not by itself specify what "they" are. They can be atoms, formula units (of ionic compounds), or molecules. That information still needs to be specified.

Because 1 H_2 molecule contains 2 H atoms, 1 mol of H_2 molecules (6.02×10^{23} molecules) has 2 mol of H atoms. 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 ethanol (C_2H_6O), we can construct the following relationships (Table 7.2A):

Table 7.2A: The Mole in Chemical Equations.

1 Molecule of C_2H_6O has	1 Mole of C_2H_6O has	Molecular Relationships
2 Carbon atoms	2 Moles of Carbon	$\frac{2 \text{ mol C atoms}}{1 \text{ mol } C_2H_6O}$ **or** $\frac{1 \text{ mol } C_2H_6O}{2 \text{ mol C atoms}}$
6 Hydrogen atoms	6 Moles of Hydrogen	$\frac{6 \text{ mol H atoms}}{1 \text{ mol } C_2H_6O}$ **or** $\frac{1 \text{ mol } C_2H_6O}{6 \text{ mol H atoms}}$
1 Oxygen atom	1 Mole of Oxygen	$\frac{1 \text{ mol O atoms}}{1 \text{ mol } C_2H_6O}$ **or** $\frac{1 \text{ mol } C_2H_6O}{1 \text{ mol O atoms}}$

The following example illustrates how we can use these relationships as conversion factors.

Example 7.2.1

If a sample consists of 2.5 mol of ethanol (C_2H_6O), how many moles of carbon atoms, hydrogen atoms and oxygen atoms does it have?

Solution

Using the relationships from Table 7.2A, we apply the appropriate conversion factor for each element:

$$2.5 \text{ mol } C_2H_6O \times \frac{2 \text{ mol C atoms}}{1 \text{ mol } C_2H_6O} = 5.0 \text{ mol C atoms} \tag{7.2.2}$$

and

$$2.5 \text{ mol } C_2H_6O \times \frac{6 \text{ mol H atoms}}{1 \text{ mol } C_2H_6O} = 15.0 \text{ mol H atoms} \tag{7.2.3}$$

and

$$2.5 \text{ mol } C_2H_6O \times \frac{1 \text{ mol O atoms}}{1 \text{ mol } C_2H_6O} = 2.5 \text{ mol O atoms} \quad (7.2.4)$$

Exercise 7.2.1

If a sample contains 6.75 mol of Na_2SO_4, how many moles of sodium atoms, sulfur atoms, and oxygen atoms does it have?

Answer available at the end of this section.

Using Avogadro's Number

Avogadro's number can also be used as a conversion factor, when you need to convert between moles and the number of atoms, ions, molecules or formula units present. Recall that:

$$1 \text{ mol} = 6.022 \times 10^{23} \text{ particles} \quad (7.2.5)$$

This relationship can be used to create a conversion factor:

$$\frac{1 \text{ mol}}{6.022 \times 10^{23} \text{ formula units}} = 1 = \frac{6.022 \times 10^{23} \text{ formula units}}{1 \text{ mol}} \quad (7.2.6)$$

Example 7.2.2

How many formula units are present in 2.34 mol of NaCl? How many ions are present in 2.34 mol of NaCl?

Solution

Using the conversion factor above, we can convert moles into formula units using Avogadro's Number:

$$2.34 \text{ mol NaCl} \times \frac{6.022 \times 10^{23} \text{ formula units NaCl}}{1 \text{ mol NaCl}} = 1.41 \times 10^{24} \text{ formula units NaCl} \quad (7.2.7)$$

To figure out the second part, we need to use a conversion factor between # ions in NaCl compared with the formulat unit. For each formula unit of NaCl, there are two ions (the Na+ cation, and the Cl- anion). Thus, we can convert formula units into ions, as follows:

$$1.41 \times 10^{24} \text{ formula units NaCl} \times \frac{2 \text{ ions}}{1 \text{ formula unit NaCl}} = 2.82 \times 10^{24} \text{ ions} \quad (7.2.8)$$

Exercise 7.2.2

1. How many dozens are in 1 mol? Express your answer in proper scientific notation.
2. A gross is a dozen dozen, or 144 things. How many gross are in 1 mol? Express your answer in proper scientific notation.
3. How many moles of each type of atom are in 1.0 mol of $C_6H_{12}O_6$?
4. How many moles of each type of atom are in 1.0 mol of $K_2Cr_2O_7$?
5. How many moles of each typ of atom are in 2.58 mol of Na_2SO_4?
6. How many moles of each type of atom are in 0.683 mol of heme ($C_{34}H_{32}FeN_4O_4$)?
7. How many molecules are in 16.8 mol of H_2O?
8. How many formula units are in 0.778 mol of iron (III) nitrate?
9. A sample of gold contains 7.02 x 10^{24} atoms. How many moles of gold is this?
10. A flask of mercury contains 3.77 x 10^{22} atoms. How many moles of mercury are in the flask?

11. An intravenous solution of normal saline may contain 1.72 mol of sodium chloride (NaCl). How many sodium and chlorine ions are present in the solution?
12. A lethal dose of arsenic is 1.00 x 10^{21} atoms. How many moles of arsenic is this?

Odd Answers available at the end of this section.

Answers

Exercise 7.2.1

One formula unit of \ceNa2SO4\ce{Na2SO4}\ceNa2SO4 contains **2 sodium atoms**, **1 sulfur atom**, and **4 oxygen atoms**. Therefore, one mole of \ceNa2SO4\ce{Na2SO4}\ceNa2SO4 contains **2 mol Na atoms**, **1 mol S atoms**, and **4 mol O atoms**. Apply the appropriate conversion factor for each element.

Sodium:

$$6.75 \text{ mol } \mathrm{Na_2SO_4} \times \frac{2 \text{ mol Na atoms}}{1 \text{ mol } \mathrm{Na_2SO_4}} = 13.5 \text{ mol Na atoms} \tag{7.2.9}$$

Sulfur:

$$6.75 \text{ mol } \mathrm{Na_2SO_4} \times \frac{1 \text{ mol S atoms}}{1 \text{ mol } \mathrm{Na_2SO_4}} = 6.75 \text{ mol S atoms} \tag{7.2.10}$$

Oxygen:

$$6.75 \text{ mol } \mathrm{Na_2SO_4} \times \frac{4 \text{ mol O atoms}}{1 \text{ mol } \mathrm{Na_2SO_4}} = 27.0 \text{ mol O atoms} \tag{7.2.11}$$

Final Answers:

- Sodium atoms: 13.5 mol Na atoms
- Sulfur atoms: 6.75 mol S atoms
- Oxygen atoms: 27.0 mol O atoms

Exercise 7.2.2

1) 5.018 x 10^{22} dozens

3) 6.0 mol of C atoms, 12.0 mol of H atoms, and 6.0 mol of O atoms

5) 5.16 mol of Na atoms, 2.58 mol of S atoms, and 10.32 mol of O atoms

7) 1.012 x 10^{25} molecules

9) 11.7 moles

11) 1.04 x 10^{24} Na ions and 1.04 x 10^{24} Cl ions

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7.3: Atomic and Molar Mass

The Relationship of Mass and the Mole

Now that we have introduced the mole and practiced using it as a conversion factor, we ask the obvious question: why is the mole *that particular* number of things? Why is it 6.022 × 10^{23} and not 1 × 10^{23} or even 1 × 10^{20}?

The number in a mole, Avogadro's number, is related to the relative sizes of the atomic mass unit and gram mass units. Whereas one hydrogen atom has a mass of approximately 1 amu, 1 mol of H atoms has a mass of approximately 1 *gram*. And whereas one sodium atom has an approximate mass of 23 amu, 1 mol of Na atoms has an approximate mass of 23 *grams*.

One mole of a substance has the same mass in grams that one atom or molecule has in atomic mass units.

$$1 \text{ mol} = 6.022 \times 10^{23} \text{ representative particles} = \text{molar mass (g/mol)} \tag{7.3.1}$$

The numbers in the periodic table that we identified as the atomic masses of the atoms not only tell us the mass of one atom in atomic mass units, but also tell us the mass of 1 mole of atoms in grams! This is because all atoms are made up of the same parts (protons, neutrons, and electrons) with the protons and neutrons having nearly identical masses. Electrons, since they are so light, are negligent in their contribution to atomic mass, even in the largest atoms. Thus, an atomic or molecular mass is indicative of how many atoms or molecules are present. Thus, an important three way relationship is formed: 1 mol = atomic or molecular mass in grams = 6.02 X 10^{23} atoms or molecules. This effectively gives us a way to count molecules in the laboratory using a common balance! Note that in chemical equations and calculations that mole concentrations are abbreviated as mol.

Recall that, the molar mass of an ionic compound (referred to as the *formula mass*) or a covalent molecule (referred to as the *molecular mass*)—is simply the sum of the masses of its atoms. To calculate molar masses, it is important that you keep track of the number of atoms of each element in the formula to obtain the correct molar mass.

For Example:

A molecule of NaCl contains 1 Na^+ and 1 Cl^-. Thus, we can calculate the formula mass of this compound by adding together the atomic masses of sodium and chlorine, as found on the periodic table (Table 7.3A and Figure 7.3.1). What this tells us is that 1 mole of NaCl which has 6.02 x 10^{23} formula units, has a mass of 58.443 g. This is incredibly powerful information, as we now have a feasible way to measure out a known quantity of any substance in the laboratory. We simply need to know the mass (g)!

Table 7.3A: Finding the mass (g) of one mole of sodium chloride.

Na Atom	Cl Atom	Na + Cl
22.990 g	35.453 g	22.990 g + 35.453 g = 58.443 g

A.

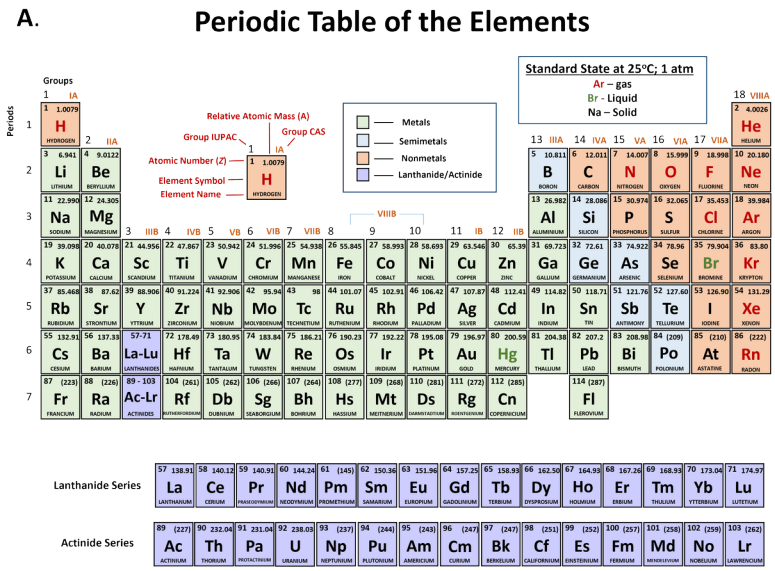


Figure 7.3.1**: Periodic Table of the Elements**.

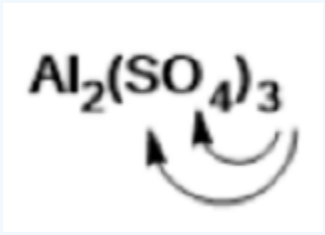
For a larger molecule, like glucose ($C_6H_{12}O_6$), that has multiple atoms of the same type, simply multiply the atomic mass of each atom by the number of atoms present, and then add up all the atomic masses to get the final molecular mass.

Table 7.3B: Using Formula Subscripts Correctly to Calculate Molar Mass.

Atom	Carbon	Hydrogen	Oxygen	Glucose ($C_6H_{12}O_6$)
# atoms	6	12	6	6 + 12 + 6
atomic mass	12.011	1.0079	15.999	6(12.011) + 12(1.0079) + 6(15.999)
total mass/molecule (Da)	72.066	12.095	95.994	**180.155**

Example 7.3.1

Use the atomic masses from the periodic table to calculate the molar mass of each compound. Remember that numbers in parentheses are distributive:



$$\mathrm{Al_2(SO_4)_3 \longrightarrow 2\ Al\ atoms + 3\ S\ atoms + 12\ O\ atoms} \tag{7.3.2}$$

Solution

Step 1: Count the number of atoms of each element.

- Aluminum (Al): 2 atoms
- Sulfur (S): 3 atoms
- Oxygen (O): 12 atoms (3 sulfate ions × 4 oxygen atoms each)

Step 2: Multiply each element's atomic mass by the number of atoms present.

Determining the Contribution of Each Element

Element	Number of Atoms	Atomic Mass (g/mol)	Contribution (g/mol)
Al	2	26.98	53.96
S	3	32.06	96.18
O	12	16.00	192.00

Step 3: Add the contributions together.

53.96 g/mol + 96.18 g/mol + 192.00 g/mol = 342.14 g/mol

Answer

Molar Mass = 342.14 g/mol

The mole concept can be extended to masses of formula units and molecules as well. The mass of 1 mol of molecules (or formula units) in grams is numerically equivalent to the mass of one molecule (or formula unit) in atomic mass units. For example, a single molecule of O_2 has a mass of 32.00 u (the sum of 2 oxygen atoms), and 1 mol of O_2 molecules has a mass of 32.00 g. As with atomic mass unit–based masses, to obtain the mass of 1 mol of a substance, we simply sum the masses of the individual atoms in the formula of that substance. The mass of 1 mol of a substance is referred to as its *molar mass*, whether the substance is an element, an ionic compound, or a covalent compound. Later we will also see that moles can be converted to liters of gas at standard temperature and pressure measurements. Figure 7.3 provides a visual diagram of mole conversions.

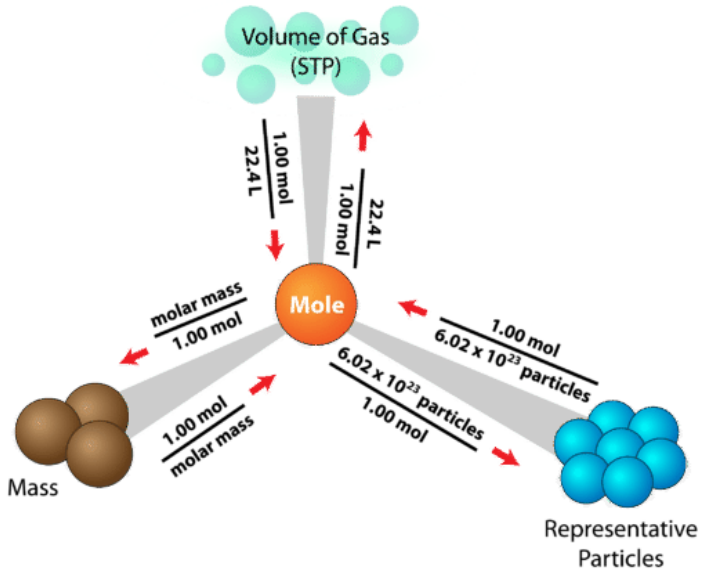


Figure 7.3.2**:** The Amazing Mole. This road map shows the conversion factors needed to interconvert mass, number of particles, and volume of a gas. (CC BY-NC 3.0(opens in new window); Christopher Auyeung via CK-12 Foundation)

The relationship of the mole quantities to gram conversion factors listed above in Figure 6.2 are notably some of the most useful equations in all of chemistry. They make it possible to set up chemical reactions in a safe and efficient manner and they have tremendous impact on the economics of many industrial and manufacturing processes and the production of medicine. If you are a serious student of chemistry, I would recommend printing out table 6.2 and keeping a copy in your notebook. It will be extremely useful in setting up a multitude of word problems and is functionally useful in the laboratory.

So why is the relationship between the mole and compound mass so important? In the microscopic world, chemical equations

are set up on the scale of molecules. Figure 6.3 depicts a typical chemical reaction. As we learned in Chapter 5, the coefficients in front of each compound represent the number of molecules needed for the reaction to proceed. In this combustion reaction, 2 molecules of butane (C_4H_{10}) react with 13 molecules of oxygen to produce 8 molecules of carbon dioxide and 10 molecules of water. In the lab, however, chemists are unable to count out molecules and place them in a reaction flask. Molecules are way too small to be seen by the naked eye and there is no equipment available that is capable of sorting and counting molecules in this way. Mass, on the other hand, can easily be measured using a balance. Thus, the relationship of mass to the number of molecules present becomes a very important conversion. Since the mole represents a fixed number of molecules (6.02×10^{23}), the coefficients used in chemical reactions can also be thought of as molar ratios. Instead of reading our equation in terms of molecules, we can read it in terms of moles. At the macroscopic level, the reaction below reads: 2 moles of butane (C_4H_{10}) react with 13 moles of oxygen to produce 8 moles of carbon dioxide and 10 moles of water.

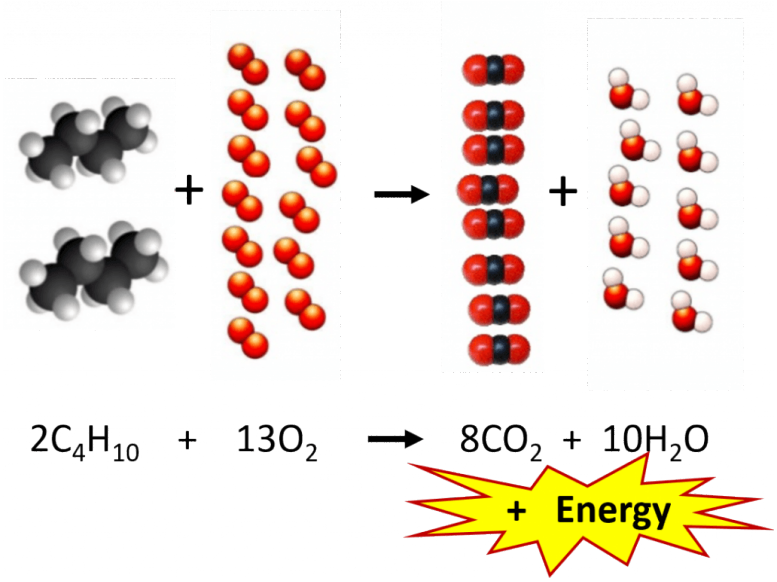


Figure 7.3.3: Combustion Reaction of Butane. The example shows the molecular ratios of the substrates and products of the reaction.

Example 7.3.2

What is the mass of each quantity?

a. 1.5 mol of Al atoms

b. 2.0 mol of U atoms

Solution

a. One mole of Al atoms has a mass in grams that is numerically equivalent to the atomic mass of aluminum. The periodic table shows that the atomic mass of Al is 26.98 grams/mole. Thus, we can use this as a conversion factor to solve this problem:

$$1.5\,\text{mol Al} \times \frac{26.98\,\text{g Al}}{1\,\text{mol Al}} = 40.47\,\text{g Al} \tag{7.3.3}$$

b. Similarly, we can create a conversion factor to use for uranium, based on the molar mass of uranium from the periodic table:

$$2.0\,\text{mol U} \times \frac{238.03\,\text{g U}}{1\,\text{mol U}} = 476.06\,\text{g U} \tag{7.3.4}$$

Example 7.3.3

What is the mass of 1 mol of each substance?

a. NaCl

b. Bilirubin ($C_{33}H_{36}N_4O_6$), the principle pigment present in bile (a liver secretion)

Solution

a. To calculate the molar mass of a substance, you must add together the mass of all the atoms present in the molecule. For NaCl, this is one ion of Na^+ and one ion of Cl^-. Recall that electrons have so little mass, that we ignore them when calculating the molar mass.

Calculating the molar mass of sodium chloride

Na Atom	Cl Atom	Na + Cl
22.990 g	35.453 g	58.443 g

b. For bilirubin, you must add up that masses of all of the components

Calculating the molar mass of billirubin

Atom	Carbon	Hydrogen	Nitrogen	Oxygen	Billirubin
# atoms	33	36	4	6	$C_{33}H_{36}N_4O_6$
atomic mass	12.01 g	1.0079 g	14.01 g	15.99 g	33(12.01) + 36(1.0079) + 4(14.01) + 6(15.99)
total mass/mole	396.33 g	36.36 g	56.04 g	95.94 g	584.67 g

Exercise 7.3.1

More Practice:

1. What is the molar mass of Si? What is the molar mass of U?
2. What is the molar mass of Mn? What is the molar mass of Mg?
3. What is the molar mass of $FeCl_2$? What is the molar mass of $FeCl_3$?
4. What is the molar mass of C_6H_6? What is the molar mass of $C_6H_5CH_3$?
5. What is the molar mass of $(NH_4)_2S$? What is the molar mass of $Ca(OH)_2$?
6. What is the molar mass of $(NH_4)_3PO_4$? What is the molar mass of $Sr(HCO_3)_2$?
7. Aspirin ($C_9H_8O_4$) is an analgesic (pain killer) and an antipyretic (fever reducer). What is the molar mass of aspirin?
8. Ibuprofen ($C_{13}H_{19}NO_3$) is an analgesic. What is the molar mass of ibuprofen?
9. Morphine ($C_{17}H_{19}NO_3$) is a narcotic pain killer. What is the mass of one mole of morphine?
10. Heroin ($C_{21}H_{23}NO_5$) is a narcotic pain killer. What is the mass of one mole of heroin?

Odd Answers available at the end of this section.

Answers

Exercise 7.3.1

1) 28.09 g/mol; 238.03 g/mol
3) 126.75 g/mol; 162.20 g/mol
5) 68.15 g/mol; 74.10 g/mol
7) 180.17 g/mol
9) 285.36 g/mol

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7.4: Mole-Mass Conversions

Moving Between Moles and Mass

The simplest type of manipulation using molar mass as a conversion factor is a mole-mass conversion (or its reverse, a mass-mole conversion), as shown in Figure 7.4.1. In such a conversion, we use the molar mass of a substance as a conversion factor to convert mole units into mass units (or, conversely, mass units into mole units).

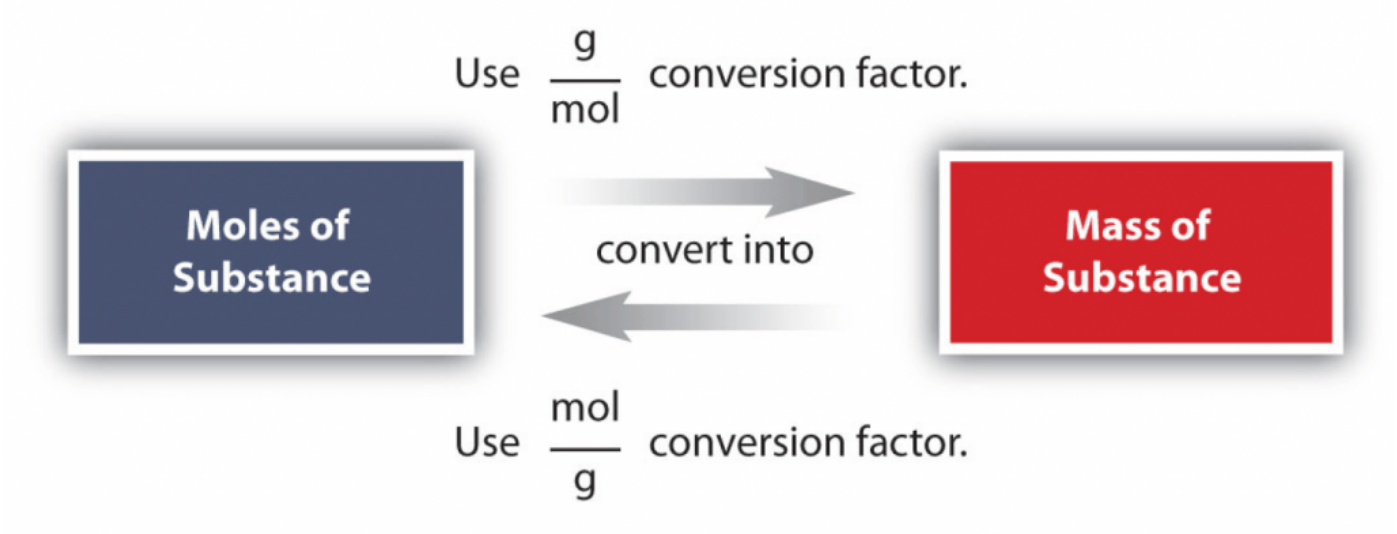
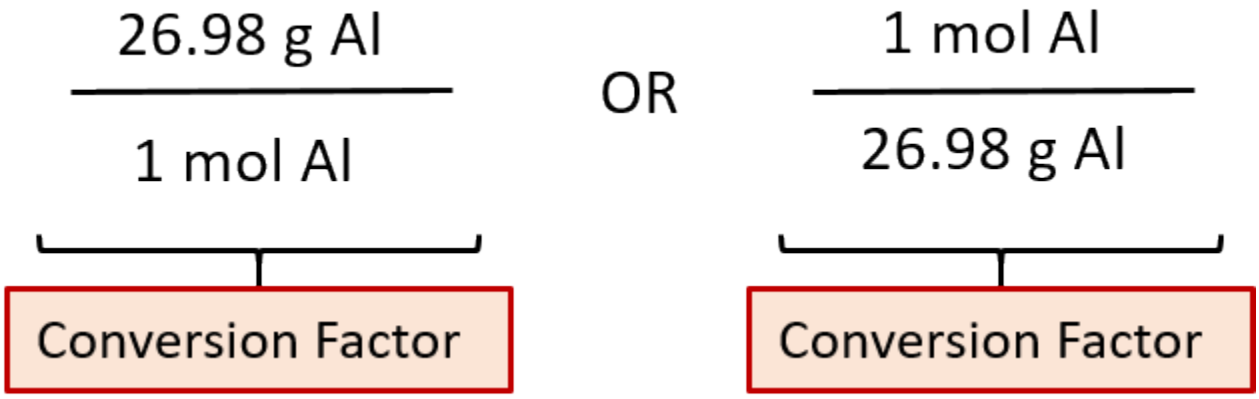


Figure 7.4.1**: A Simple Flowchart for Converting between Mass and Moles of a Substance.**

In section 7.3, we established that 1 mol of Al has a mass of 26.98 g. Stated mathematically,

$$1\,\text{mol Al} \quad = \quad 26.98\,\text{g Al} \tag{7.4.1}$$

We can divide both sides of this expression by either side to get one of two possible conversion factors:



The first conversion factor can be used to convert from moles to mass, and the second converts from mass to moles. Both can be used to solve problems.

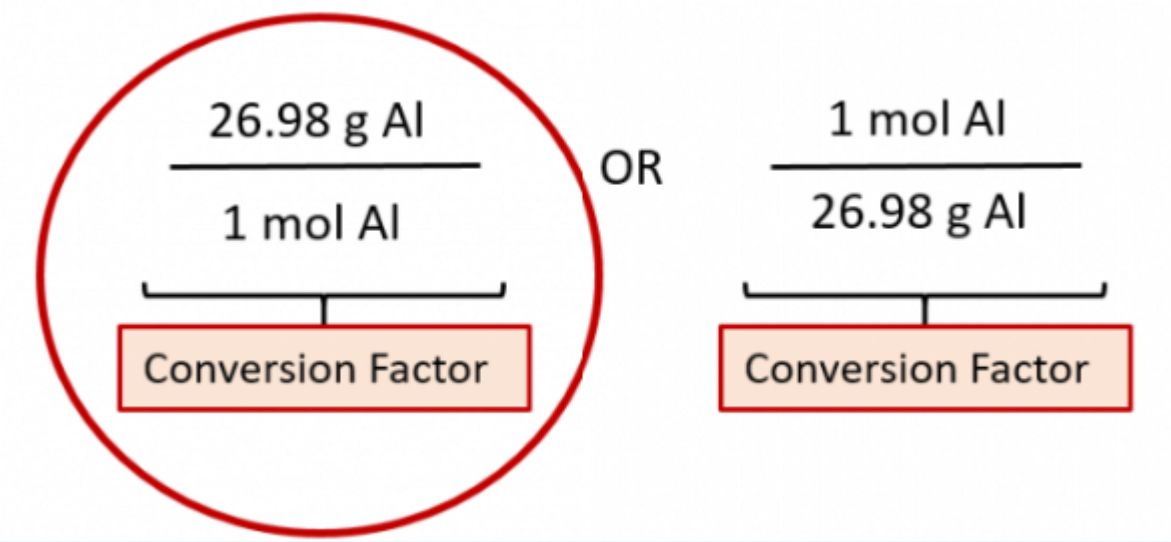
Note

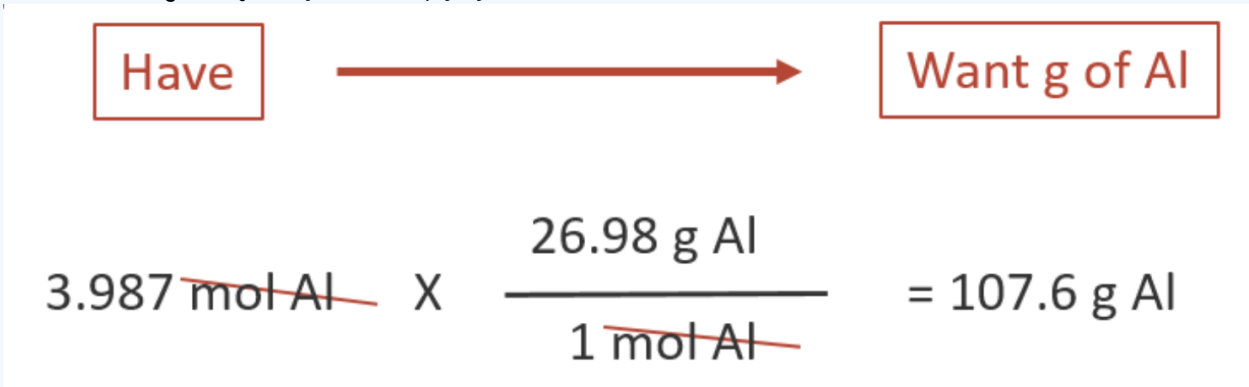
The algebra skills we are using here are the same skills that we used in Chapter 1 to perform unit conversions in the metric system. The important point is to keep track of your units all the way through the problem!

Example 7.4.1

What is the mass of 3.987 mol of Al?

Solution

1. The first step in a conversion problem is to write down what you know. In this case, we know that we have 3.987 mol of Al.
2. Next, write down what you want. In this case, we want grams of Al.
3. Decide which conversion factor to use. Because we are starting with mole units, we want a conversion factor that will cancel the mole unit and introduce the unit for mass in the numerator.
   - 

4. Then start with the given quantity and multiply by the conversion factor.
   - 

   - Final Answer = 107.6 g Al

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 7.4.1 is a chart for determining what conversion factor is needed, and Figure 7.4.2 is a flow diagram for the steps needed to perform a conversion. Note that it takes one mathematical step to convert from moles to mass or from mass to moles.

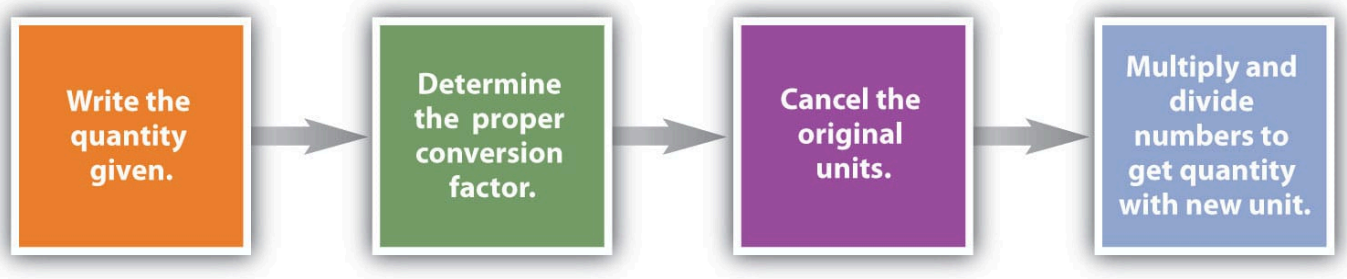


Figure 7.4.2: A Flowchart Illustrating the Steps in Performing a Unit Conversion.

Example 7.4.2

A biochemistry student needs 0.00655 mol of bilirubin ($C_{33}H_{36}N_4O_6$) for an experiment. How many grams will that be?

Solution

1. To convert from moles to mass, we need the molar mass of bilirubin, which we can determine from its chemical formula.

Calculating the molar mass of bilirubin

Atom	Carbon	Hydrogen	Nitrogen	Oxygen	Bilirubin
# atoms	33	36	4	6	$C_{33}H_{36}N_4O_6$
atomic mass	12.01	1.0079	14.01	15.99	33(12.01) + 36(1.0079) + 4(14.01) + 6(15.99)
total mass (g)/mole	396.33	36.36	56.04	95.94	584.67

2. Therefore, 1 mole of bilirubin = 584.67 g

3. Now you can list what you have, what you want, and determine the correct conversion factor needed to get there!

$$\frac{584.73\ \text{g}\ C_{33}H_{36}N_4O_6}{1\ \text{mol}\ C_{33}H_{36}N_4O_6}\ \text{(Conversion Factor)} \quad \text{OR} \quad \frac{1\ \text{mol}\ C_{33}H_{36}N_4O_6}{584.73\ \text{g}\ C_{33}H_{36}N_4O_6}\ \text{(Conversion Factor)}$$

Have → Want g of $C_{33}H_{36}N_4O_6$

$$0.00655\ \cancel{\text{mol}\ C_{33}H_{36}N_4O_6} \times \frac{584.73\ \text{g}\ C_{33}H_{36}N_4O_6}{1\ \cancel{\text{mol}\ C_{33}H_{36}N_4O_6}} = 3.83\ \text{g}\ C_{33}H_{36}N_4O_6$$

4. Final Answer = **3.83 g** of bilirubin

Exercise 7.4.1

A chemist needs 457.8 g of $KMnO_4$ to make a solution. How many moles of $KMnO_4$ is that?

Answer available at the end of this section.

To Your Health: Minerals

For our bodies to function properly, we need to ingest certain substances from our diets. Among our dietary needs are ***minerals***, the non-carbon elements, our body uses for a variety of functions, such developing bone or ensuring proper nerve transmission.

The US Department of Agriculture has established some recommendations for the daily intake (RDIs) of various minerals. The accompanying table lists the RDIs for minerals, both in mass and moles, assuming a 2,000-calorie daily diet.

Table 7.4A: Recommended Daily Intake (RDI) of Mineral Supplements.

Mineral	Male (age 19 - 30 yr)		Female (age 19 - 30 yr)	
Ca	1,000 mg	0.025 mol	1,000 mg	0.025 mol
Cr	0.035 mg	6.7×10^{-7} mol	0.025 mg	4.8×10^{-7} mol
Cu	0.900 mg	1.4×10^{-5} mol	0.900 mg	1.4×10^{-5} mol
F	4 mg	2.1×10^{-4} mol	3 mg	1.5×10^{-4} mol
I	0.150 mg	1.2×10^{-6} mol	0.150 mg	1.2×10^{-6} mol
Fe	8 mg	1.4×10^{-4} mol	18 mg	3.2×10^{-4} mol
K	3,500 mg	9.0×10^{-2} mol	3,500 mg	9.0×10^{-2} mol
Mg	400 mg	1.6×10^{-2} mol	310 mg	1.3×10^{-2} mol
Mn	2.3 mg	4.2×10^{-5} mol	1.8 mg	3.3×10^{-5} mol
Mo	45 mg	4.7×10^{-7} mol	45 mg	4.7×10^{-7} mol
Na	2,400 mg	1.0×10^{-1} mol	2,400 mg	1.0×10^{-1} mol
P	700 mg	2.3×10^{-2} mol	700 mg	2.3×10^{-2} mol
Se	0.055 mg	7.0×10^{-7} mol	0.055 mg	7.0×10^{-7} mol
Zn	0.011 mg	1.7×10^{-4} mol	0.008 mg	1.2×10^{-4} mol

Table 7.4A illustrates several things. First, the needs of men and women for some minerals are different. The extreme case is for iron; women need over twice as much as men do. In all other cases where there is a different RDI, men need more than women.

Second, the amounts of the various minerals needed on a daily basis vary widely—both on a mass scale and a molar scale. The average person needs 0.1 mol of Na a day, which is about 2.5 g. On the other hand, a person needs only about 25–35 µg of Cr per day, which is under one millionth of a mole. As small as this amount is, a deficiency of chromium in the diet can lead to diabetes-like symptoms or neurological problems, especially in the extremities (hands and feet). For some minerals, the body does not require much to keep itself operating properly.

Although a properly balanced diet will provide all the necessary minerals, some people take dietary supplements. However, too

much of a good thing, even minerals, is not good. Exposure to too much chromium, for example, causes a skin irritation, and certain forms of chromium are known to cause cancer (as presented in the movie *Erin Brockovich*).

Exercise 7.4.1

More Practice:

1. What is the mass of 8.603 mol of Fe metal?
2. What is the mass of 0.552 mol of Ag metal?
3. What is the mass of 6.24 x 10^4 mol of Cl_2 gas?
4. What is the mass of 0.661 mol of O_2 gas?
5. What is the mass of 20.77 mol of $CaCO_3$?
6. What is the mass of 9.02 x 10^{-3} mol of the hormone epinephrine ($C_9H_{13}NO_3$)?
7. How many moles are present in 977.4 g of $NaHCO_3$?
8. How many moles of erythromycin ($C_{37}H_{67}NO_{13}$), a widely used antibiotic, are in 1.00 x 10^3 g of the substance?
9. Cortisone ($C_{21}H_{28}O_5$) is a synthetic steriod that is used as an anti-inflammatory drug. How many moles of cortisone are present in one 10.0 mg tablet?
10. Recent research suggests that the daily ingestion of 85 mg of aspirin (also known as acetylsalicylic acid, $C_9H_8O_4$) whill reduce a person's risk of heart disease. How many moles of aspirin is that?

Odd Answers available at the end of this section.

Answers

Exercise 7.4.1

Step 1: Determine the molar mass of potassium permanganate.

Molar Mass of Potassium Permanganate

Element	Number of Atoms	Atomic Mass (g/mol)	Contribution (g/mol)
K	1	39.10	39.10
Mn	1	54.94	54.94
O	4	16.00	64.00

Molar Mass=158.04g/mol

Step 2: Use the molar mass as a conversion factor.

$$457.8\,\text{g}\,\text{KMnO}_4 \times \frac{1\,\text{mol}\,\text{KMnO}_4}{158.04\,\text{g}\,\text{KMnO}_4} = 2.897\,\text{mol}\,\text{KMnO}_4 \tag{7.4.2}$$

Step 3: Apply significant figures.

Since **457.8 g** has **4 significant figures** and the molar mass (**158.04 g/mol**) has **5 significant figures**, the answer should be reported with **4 significant figures**.

Answer

$$2.897\,\text{mol}\,\text{KMnO}_4 \tag{7.4.3}$$

Exercise 7.4.1

1) 480.5 g

3) 4.42 x 10^6 g

5) 2,079 g

7) 11.63 mol

9) 2.77 x 10^{-5} mol

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7.5: Mole-Mole Relationships in Chemical Reactions

Using Stoichiometric Relationships

In this section you will learn how to use a balanced chemical reaction to determine molar relationships between the substances.

In Chapter 5, 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). Here, we will extend the meaning of the coefficients in a chemical equation.

Consider the simple chemical equation

$$\mathbf{2\,H_2 \quad + \quad O_2 \quad \longrightarrow \quad 2\,H_2O} \tag{7.5.1}$$

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

$$\mathbf{4\,H_2 \quad + \quad 2\,O_2 \quad \longrightarrow \quad 4\,H_2O} \tag{7.5.2}$$

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

$$\mathbf{22\,H_2 \quad + \quad 11\,O_2 \quad \longrightarrow \quad 22\,H_2O} \tag{7.5.3}$$

because 22:11:22 also reduces to 2:1:2.

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

$$\mathbf{12.044 \times 10^{23}\,H_2 \quad + \quad 6.022 \times 10^{23}\,O_2 \quad \longrightarrow \quad 12.044 \times 10^{23}\,H_2O} \tag{7.5.4}$$

These coefficients also have the ratio 2:1:2 (check it and see), so this equation is balanced. But 6.022×10^{23} is 1 mol, while 12.044×10^{23} is 2 mol (and the number is written that way to make this more obvious), so we can simplify this version of the equation by writing it as

$$\mathbf{2\,mol\,H_2 \quad + \quad 1\,mol\,O_2 \quad \longrightarrow \quad 2\,mol\,H_2O} \tag{7.5.5}$$

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

$$\mathbf{2\,H_2 \quad + \quad O_2 \quad \longrightarrow \quad 2\,H_2O} \tag{7.5.6}$$

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 in Chapter 5, 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:

$$\mathbf{\frac{2\,mol\,H_2}{1\,mol\,O_2} \quad or \quad \frac{1\,mol\,O_2}{2\,mol\,H_2}} \tag{7.5.7}$$

$$\mathbf{\frac{2\,mol\,H_2O}{1\,mol\,O_2} \quad or \quad \frac{1\,mol\,O_2}{2\,mol\,H_2O}} \tag{7.5.8}$$

$$\mathbf{\frac{2\,mol\,H_2}{2\,mol\,H_2O} \quad or \quad \frac{2\,mol\,H_2O}{2\,mol\,H_2}} \tag{7.5.9}$$

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*.**

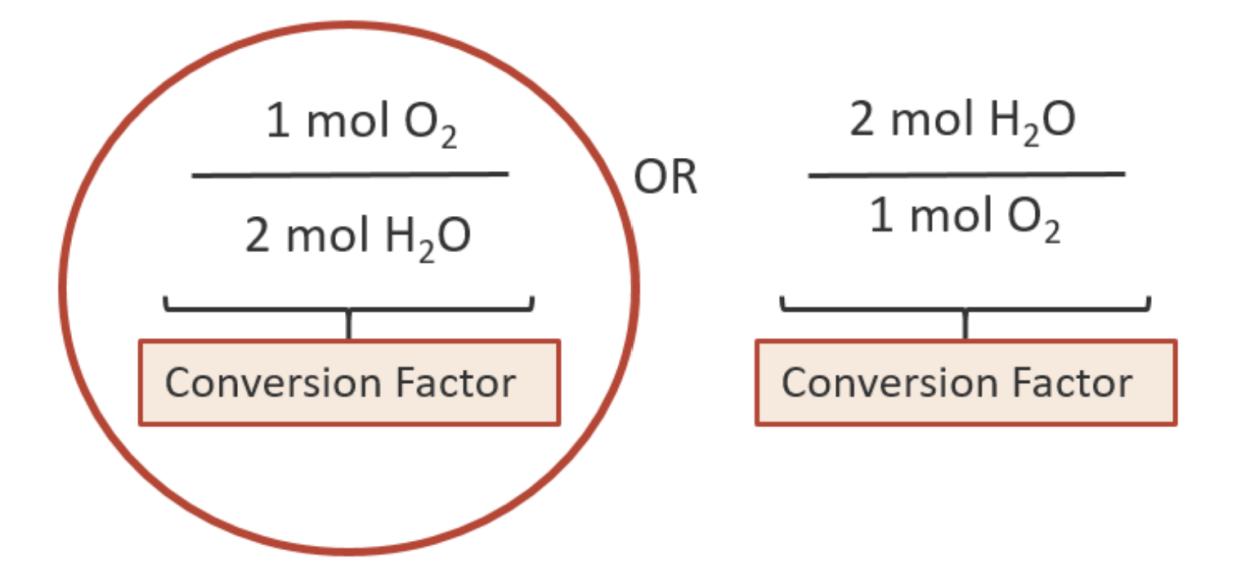
Example 7.5.1

How many moles of oxygen react with hydrogen to produce 27.6 mol of H_2O? The balanced equation is:

$$\mathbf{2\,H_2} \quad + \quad \mathbf{O_2} \quad \longrightarrow \quad \mathbf{2\,H_2O} \tag{7.5.10}$$

Solution

Because we are dealing with quantitites of H_2O and O_2, we will use a ratio that relates those two substances. Because we are given an amount of H_2O and want to determine an amount of O_2, we will use the ratio that has H_2O in the denominator (so that it cancels), and O_2 in the numerator (so it is introduced in the answer). Thus,



1. We start with the given quantity and multiply by the conversion factor as follows:

$$\mathbf{27.6\,mol\,H_2O} \quad \times \quad \frac{\mathbf{1\,mol\,O_2}}{\mathbf{2\,mol\,H_2O}} \quad = \quad \mathbf{13.8\,mol\,O_2} \tag{7.5.11}$$

Exercise 7.5.1

Using **$2H_2 + O_2 \rightarrow 2H_2O$,** how many moles of hydrogen react with 3.07 mol of oxygen to produce water?

Answer available at the end of this section.

Exercise 7.5.2

More Practice.

1. List the molar ratios you can derive from this balanced chemical equation: $NH_3 + 2O_2 \rightarrow HNO_3 + H_2O$
2. List the molar ratios you can derive from this balanced chemical equation: $2C_2H_2 + 5O_2 \rightarrow 4CO_2 + 2H_2O$
3. Given the following balanced chemical equation, $6NaOH + 3Cl_2 \rightarrow NaClO_3 + 5NaCl + 3H_2O$, how many moles of NaCl can be formed if 3.77 mol of NaOH were to react?

4. Given the following balanced chemical equation, $C_5H_{12} + 8O_2 \rightarrow 5CO_2 + 6H_2O$, how many moles of H_2O can be formed if 0.0625 mol of C_5H_{12} were to react?
5. Balance the following unbalanced equation and determine how many moles of H_2O are produced when 1.65 mol of NH_3 react. $NH_3 + O_2 \rightarrow N_2 + H_2O$
6. Trinitrotoluene [$C_6H_2(NO_2)_2CH_3$], also known as TNT, is formed by reacting nitric acid (HNO_3) with toluene ($C_6H_5CH_3$): $HNO_3 + C_6H_5CH_3 \rightarrow C_6H_2(NO_2)_2CH_3 + H_2O$ Balance the equation and determine how many moles of TNT are produced when 4.903 mol of HNO_3 react.
7. Chemical reactions are balanced in terms of molecules and in terms of moles. Are they balanced in terms of dozens? Defend your answer.
8. Explain how a chemical reaction balanced in terms of moles satisfies the law of conservation of matter.

Odd Answers available at the end of this section.

Answers

Exercise 7.5.1

The balanced equation shows that **2 mol H_2 react with 1 mol O_2**. Therefore, use the mole ratio:

$$3.07\,\text{mol O}_2 \times \frac{2\,\text{mol H}_2}{1\,\text{mol O}_2} = 6.14\,\text{mol H}_2 \tag{7.5.12}$$

Final answer:

$$6.14\,\text{mol H}_2 \tag{7.5.13}$$

Exercise 7.5.2

1) 1 mol NH_3:2 mol O_2: 1 mol HNO_3: 1 mol H_2O

3) 3.14 mol

5) $4NH_3 + 3\ O_2 \rightarrow 2\ N_2 + 6\ H_2O$ (2.48 mol)

7) Yes, they are still balanced.

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7.6: Mole-Mass and Mass-Mass Problems

From Writing Chemical Equations to Performing Chemical Reactions

In this section you will learn to convert from mass or moles of one substance to mass or moles of another substance in a chemical reaction.

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, now 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 ability to answer stoichiometry questions in terms of the masses of a particular substance, in addition to moles. This is very powerful, as we can make mass measurements in the laboratory using a simple balance. Stoichiometry allows us to move writing chemical equations, to performing chemical reactions in the lab! We do this using the following sequence:

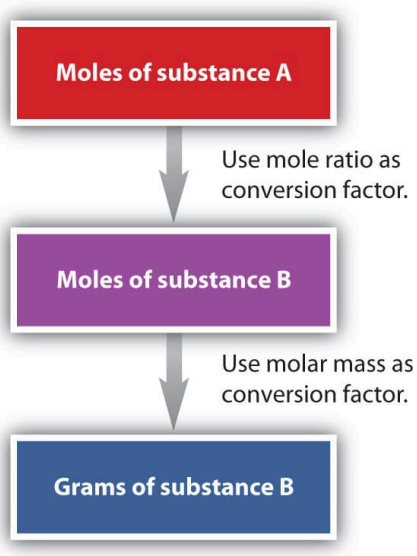


Figure 7.6.1: Flowchart for Calculating Mole to Mass Conversions using Chemical Equations.

Collectively, these conversions are called ***mole-mass calculations***.

Example 7.6.1

Consider the balanced chemical equation

$$\mathbf{Fe_2O_3} \quad + \quad \mathbf{3\,SO_3} \quad \longrightarrow \quad \mathbf{Fe_2\left(SO_4\right)_3} \tag{7.6.1}$$

If we have 3.59 mol of Fe_2O_3, how many grams of SO_3 can react with it?

Solution

Using the mole-mass calculation sequence, we can determine the required mass of 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 SO_3 needed. Then using the molar mass of SO_3 as a conversion factor, we determine the mass that this number of moles of SO_3 has. Graphically, it is represented in these two steps:

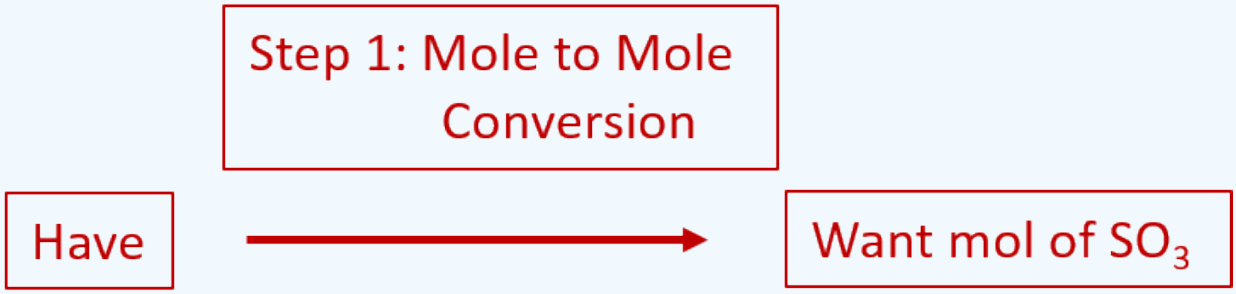
$$Fe_2O_3 + 3SO_3 \rightarrow Fe_2(SO_4)_3$$

Moles ⟶ Moles

↓

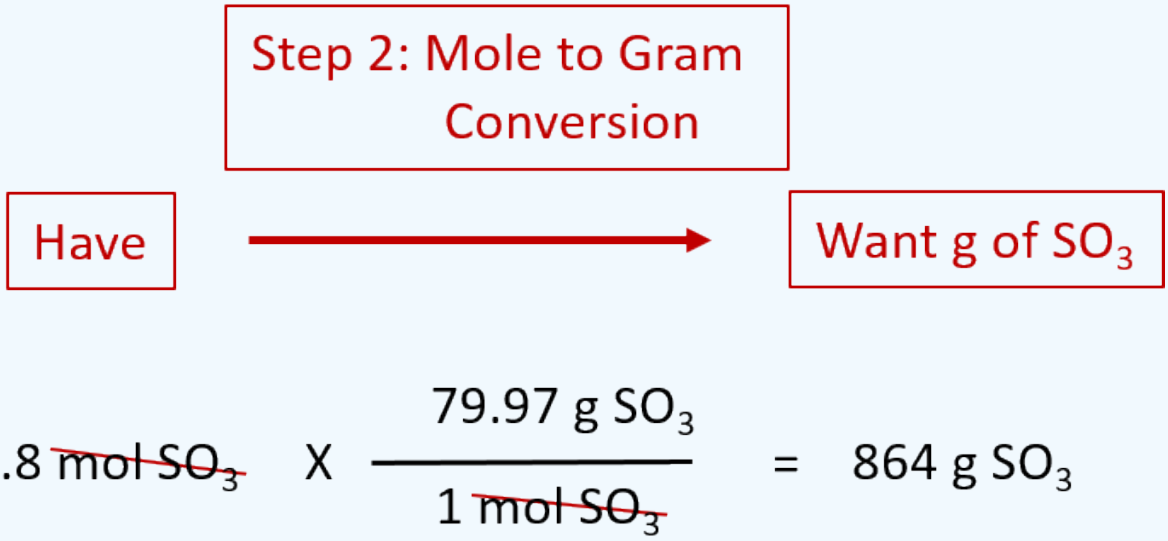
Grams

The first step resembles the exercises we did in Section 7.4 “Mole-Mole Relationships in Chemical Reactions”. As usual, we start with the quantity we were given:



$$3.59 \cancel{\text{ mol } Fe_2O_3} \times \frac{3 \text{ mol } SO_3}{1 \cancel{\text{ mol } Fe_2O_3}} = 10.8 \text{ mol } SO_3$$

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



Our final answer is expressed to three significant figures. Thus, in a two-step process, we find that 864 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:

$$3.59\,\text{mol}\,\text{Fe}_2\text{O}_3 \times \frac{3\,\text{mol}\,\text{SO}_3}{1\,\text{mol}\,\text{Fe}_2\text{O}_3} \times \frac{79.97\,\text{g}\,\text{SO}_3}{1\,\text{mol}\,\text{SO}_3} = 864\,\text{g}\,\text{SO}_3 \quad (7.6.2)$$

We get exactly the same answer when combining all the math steps together as we do when we calculate one step at a time.

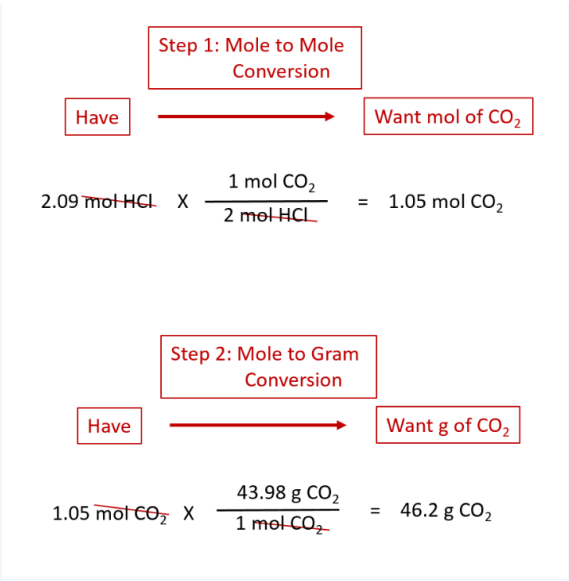
Example 7.6.2

How many grams of CO_2 are produced if 2.09 mol of HCl are reacted according to this balanced chemical equation below?

$$\text{CaCO}_3 + 2\,\text{HCl} \longrightarrow \text{CaCl}_2 + \text{CO}_2 + \text{H}_2\text{O} \quad (7.6.3)$$

Solution

Our strategy will be to convert from moles of HCl to moles of CO_2 and then from moles of CO_2 to grams of CO_2. We will need the molar mass of CO_2 for this second conversion, which is 43.98 g/mol. Performing these two conversions gives 46.2 g of CO2, as seen below:



You can also do these conversions in one processing step as follows:

$$\mathbf{2.09\,mol\,HCl} \times \frac{\mathbf{1\,mol\,CO_2}}{\mathbf{2\,mol\,HCl}} \times \frac{\mathbf{43.98\,g\,CO_2}}{\mathbf{1\,mol\,CO_2}} = \mathbf{46.2\,g\,CO_2} \tag{7.6.4}$$

Exercise 7.6.1

How many grams of glucose ($C_6H_{12}O_6$) are produced if 17.3 mol of H_2O are reacted according to this balanced chemical equation?

$$\mathbf{6\,CO_2} + \mathbf{6\,H_2O} \longrightarrow \mathbf{C_6H_{12}O_6} + \mathbf{6\,O_2} \tag{7.6.5}$$

Answer available at the end of this section.

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:

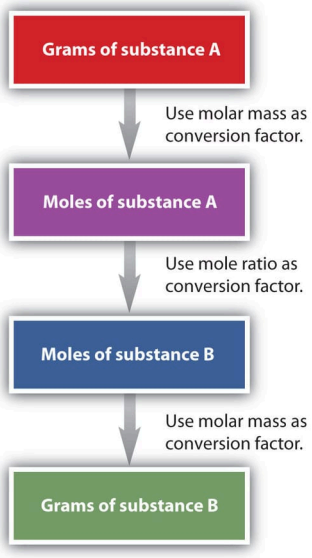


Figure 7.6.2: Flow chart for conducting conversions using chemical equations.

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.

Example 7.6.3

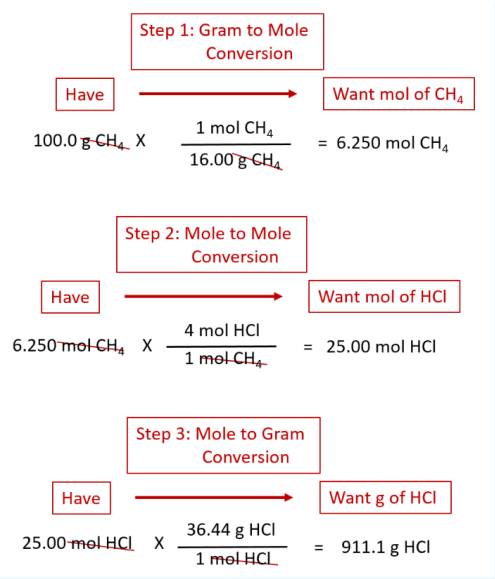
Methane can react with elemental chlorine to make carbon tetrachloride (CCl_4). The balanced chemical equation is as follows:

$$\mathrm{CH_4} + 4\,\mathrm{Cl_2} \longrightarrow \mathrm{CCl_4} + 4\,\mathrm{HCl} \tag{7.6.6}$$

How many grams of HCl are produced by the reaction of 100.0 g of CH_4?

Solution

1. For this problem, we are starting off with grams of a substance. Since we need to convert into another substance using the molar equivalents from our equation, we will need to convert the grams of our known substance, CH_4, into moles.
2. Once in moles we will be able to use the stoichiometry equivalents within our balanced equation to compare molar equivalents of methane (CH_4) with moles of HCl produced.
3. We can then convert moles of HCl produced into grams, using the molar mass of HCl.



Or, you can set it up all at once:

$$100.0\,\text{g CH}_4 \times \frac{1\,\text{mol CH}_4}{16.00\,\text{g CH}_4} \times \frac{4\,\text{mol HCl}}{1\,\text{mol CH}_4} \times \frac{36.44\,\text{g HCl}}{1\,\text{mol HCl}} = 911.1\,\text{g HCl} \quad (7.6.$$

To Your Health: The Synthesis of Taxol

Taxol is a powerful anticancer drug that was originally extracted from the Pacific yew tree (*Taxus brevifolia*). As you can see from the accompanying figure, taxol is a very complicated molecule, with a molecular formula of $C_{47}H_{51}NO_{14}$. Isolating taxol from its natural source presents certain challenges, mainly that the Pacific yew is a slow-growing tree, and the equivalent of six trees must be harvested to provide enough taxol to treat a single patient. Although related species of yew trees also produce taxol in small amounts, there is significant interest in synthesizing this complex molecule in the laboratory.

After a 20-year effort, two research groups announced the complete laboratory synthesis of taxol in 1994. However, each synthesis required over 30 separate chemical reactions, with an overall efficiency of less than 0.05%. To put this in perspective, to obtain a single 300 mg dose of taxol, you would have to begin with 600 g of starting material. To treat the 26,000 women who are diagnosed with ovarian cancer each year with one dose, almost 16,000 kg (over 17 tons) of starting material must be converted to taxol. Taxol is also used to treat breast cancer, with which 200,000 women in the United States are diagnosed every year. This only increases the amount of starting material needed.

Clearly, there is intense interest in increasing the overall efficiency of the taxol synthesis. An improved synthesis not only will be easier but also will produce less waste materials, which will allow more people to take advantage of this potentially life-saving drug.

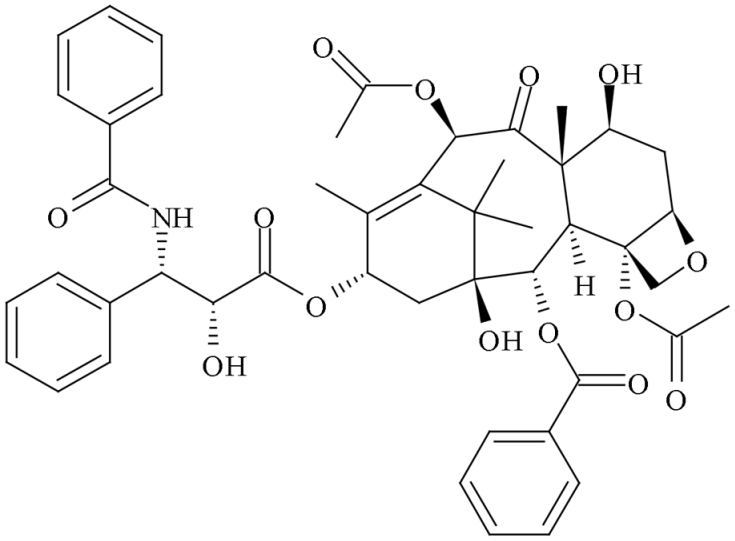


Figure 7.6.3: The Structure of the Cancer Drug Taxol. Because of the complexity of the molecule, carbon atoms and hydrogens bonded to carbon are not shown. Carbon atoms are implied at every line ending or bend.

Key Idea

- A balanced chemical equation can be used to relate masses or moles of different substances in a reaction.

Exercise 7.6.1

More Problems.

1. Given the following unbalanced chemical equation,

$H_3PO_4 + NaOH \rightarrow H_2O + Na_3PO_4$

what mass of H_2O is produced by the reaction of 2.35 mol of H_3PO_4?

2. Given the following unbalanced chemical equation,

$C_2H_6 + Br_2 \rightarrow C_2H_4Br_2 + HBr$

what mass of HBr is produced if 0.884 mol of C_2H_6 is reacted?

3. Certain fats are used to make soap, the first step being to react the fat with water to make glycerol (also known as glycerin) and compounds called fatty acids. One example is as follows:

$C_3H_5(OOC(CH_2)_{14}CH_3)_3 + 3H_2O \rightarrow C_3H_5(OH)_3 + 3CH_3(CH_2)_{14}COOH$

Fat + water → glycerol + fatty acids

How many moles of glycerol can be made from the reaction of 1,000.0 g of $C_3H_5(OOC(CH_2)_{14}CH_3)_3$?

4. Photosynthesis in plants leads to the general overall reaction for producing glucose ($C_6H_{12}O_6$):

$6CO_2 + 6H_2O \rightarrow C_6H_{12}O_6 + 6O_2$

How many moles of glucose can be made from the reaction of 544 g of CO_2?

5. Precipitation reactions, in which a solid (called a precipitate) is a product, are commonly used to remove certain ions from solution. One such reaction is as follows:

$Ba(NO_3)_2(aq) + Na_2SO_4(aq) \rightarrow BaSO_4(s) + 2NaNO_3(aq)$

How many grams of Na_2SO_4 are needed to precipitate all the barium ions produced by 43.9 g of $Ba(NO_3)_2$?

6. Nitroglycerin [$C_3H_5(ONO_2)_3$] is made by reacting nitric acid (HNO_3) with glycerol [$C_3H_5(OH)_3$] according to this reaction:

$C_3H_5(OH)_3 + 3HNO_3 \rightarrow C_3H_5(ONO_2)_3 + 3H_2O$

If 87.4 g of HNO_3 are reacted with excess glycerol, what mass of nitroglycerin can be made?

7. Antacids are bases that neutralize acids in the digestive tract. Magnesium hydroxide [$Mg(OH)_2$] is one such antacid. It reacts with hydrochloric acid in the stomach according to the following reaction:

$Mg(OH)_2 + 2HCl \rightarrow MgCl_2 + 2H_2O$

How many grams of HCl can a 200 mg dose of $Mg(OH)_2$ neutralize?

8. Acid rain is caused by the reaction of nonmetal oxides with water in the atmosphere. One such reaction involves nitrogen dioxide (NO_2) and produces nitric acid (HNO_3):

$3NO_2 + H_2O \rightarrow 2HNO_3 + NO$

If 1.82×10^{13} g of NO_2 enter the atmosphere every year due to human activities, potentially how many grams of HNO_3 can be produced annually?

9. A simplified version of the processing of iron ore into iron metal is as follows:

$2Fe_2O_3 + 3C \rightarrow 4Fe + 3CO_2$

How many grams of C are needed to produce 1.00×10^9 g of Fe?

10. The SS *Hindenburg* contained about 5.33×10^5 g of H_2 gas when it burned at Lakehurst, New Jersey, in 1937. The chemical reaction is as follows:

$2H_2 + O_2 \rightarrow 2H_2O$

How many grams of H_2O were produced?

Odd Answers available at the end of this section.

Answers

Exercise 7.6.1

First, calculate the molar mass of glucose:

6(12.01) + 12(1.008) + 6(16.00) = 180.16g/mol,

Now perform the dimensional analysis:

$$17.3\,\text{mol}\,H_2O \times \frac{1\,\text{mol}\,C_6H_{12}O_6}{6\,\text{mol}\,H_2O} \times \frac{180.16\,\text{g}\,C_6H_{12}O_6}{1\,\text{mol}\,C_6H_{12}O_6} = 519\,\text{g}\,C_6H_{12}O_6 \tag{7.6.8}$$

Final answer:

$$519\,\text{g}\,C_6H_{12}O_6 \tag{7.6.9}$$

Exercise 7.6.1

1) 127 g

3) 1.236 mol

5) 23.9 g

7) 0.251 g

9) 1.61×10^{8} g

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7.7: Limiting Reagent and Percent Yield

Which Reagent Runs Out First?

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

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

The relative amounts of reactants and products represented in a balanced chemical equation are often referred to as *stoichiometric amounts*. All the exercises of the preceding module involved stoichiometric amounts of reactants. For example, when calculating the amount of product generated from a given amount of reactant, it was assumed that any other reactants required were available in stoichiometric amounts (or greater). In this module, more realistic situations are considered, in which reactants are not present in stoichiometric amounts.

Limiting Reagent

Consider another food analogy, making grilled cheese sandwiches (Fig. 7.7.1)

$$\mathrm{1\,slice\ of\ cheese} + \mathrm{2\,slices\ of\ bread} \longrightarrow \mathrm{1\,sandwich} \tag{7.7.1}$$

Stoichiometric amounts of sandwich ingredients for this recipe are bread and cheese slices in a 2:1 ratio. Provided with 28 slices of bread and 11 slices of cheese, one may prepare 11 sandwiches per the provided recipe, using all the provided cheese and having six slices of bread left over. In this scenario, the number of sandwiches prepared has been *limited* by the number of cheese slices, and the bread slices have been provided in *excess*.

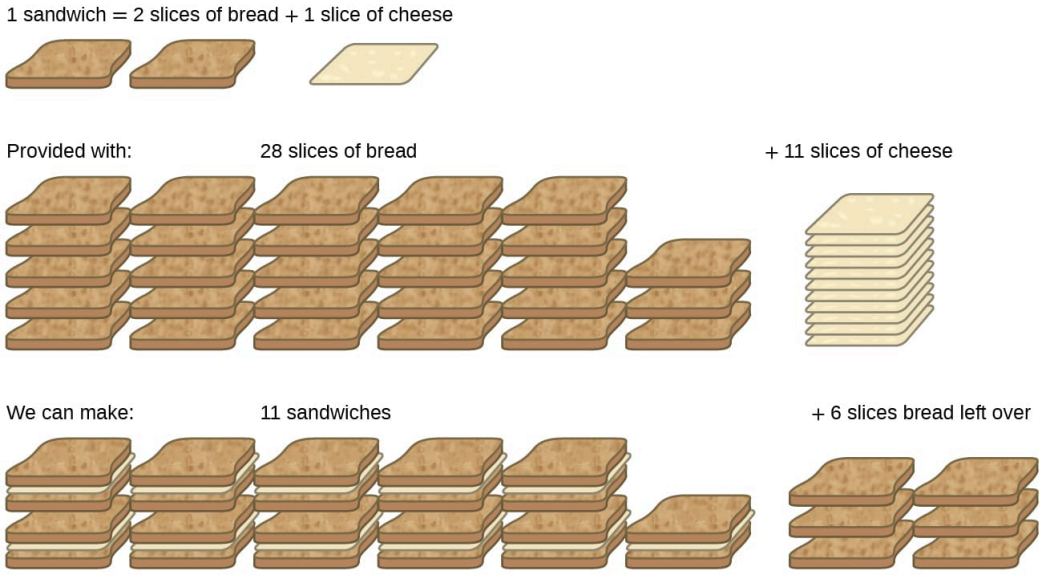


Figure 7.7.1**: Using Cooking to Model Limiting Reagent.** Cheese and bread slices are shown at the top and mimic reactants in a chemical reaction. To form sandwiches, they need to be put together in a 2:1 ratio (2 slices of bread for 1 slice of cheese). The first one to run out as you are making the sandwiches is the limiting reagent (ie. it limits how many sandwiches you can make!) In this case, the cheese runs out first and bread is left over. Cheese is, therefore, the limiting reagent.

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

$$\mathrm{H_2}(g) \quad + \quad \mathrm{Cl_2}(g) \quad \longrightarrow \quad 2\,\mathrm{HCl}(g) \tag{7.7.2}$$

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

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 example, if we had 3 mol H_2 and excess Cl_2, then we would produce 6 mol HCl and fully use up all of the H_2 present:

$$3\,\mathrm{mol\,H_2} \quad \times \quad \frac{2\,\mathrm{mol\,HCl}}{1\,\mathrm{mol\,H_2}} \quad = \quad 6\,\mathrm{mol\,HCl} \tag{7.7.3}$$

However, if we had 2 mol of Cl_2 and excess H_2, then we could produce a total of 4 mol of HCl to fully use up all of the Cl_2 present:

$$2\,\mathrm{mol\,Cl_2} \quad \times \quad \frac{2\,\mathrm{mol\,HCl}}{1\,\mathrm{mol\,Cl_2}} \quad = \quad 4\,\mathrm{mol\,HCl} \tag{7.7.4}$$

Therefore, when we have only 2 mol of Cl_2 and 3 mol of H_2, we can see that we will run out of Cl_2 after 4 mol of HCl have been produced, and there will be leftover H_2 gas that is unreacted. Thus, ***Cl_2 is the limiting reagent*** because it runs out first, and limits the amount of product that can be formed.

As seen above, the chlorine gas will be completely consumed once 4 moles of HCl have been produced. Since enough hydrogen gas was provided to yield 6 moles of HCl, there will be unreacted hydrogen remaining once this reaction is complete. Chlorine gas, therefore, is the limiting reactant and hydrogen gas is the excess reactant (Fig. 7.7.2).

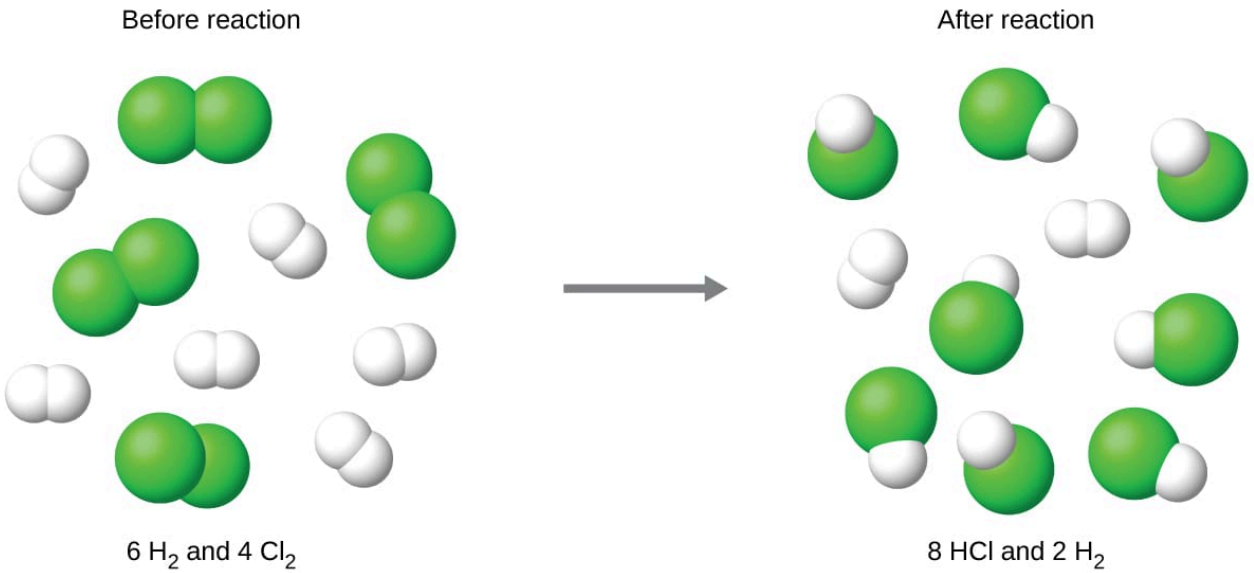
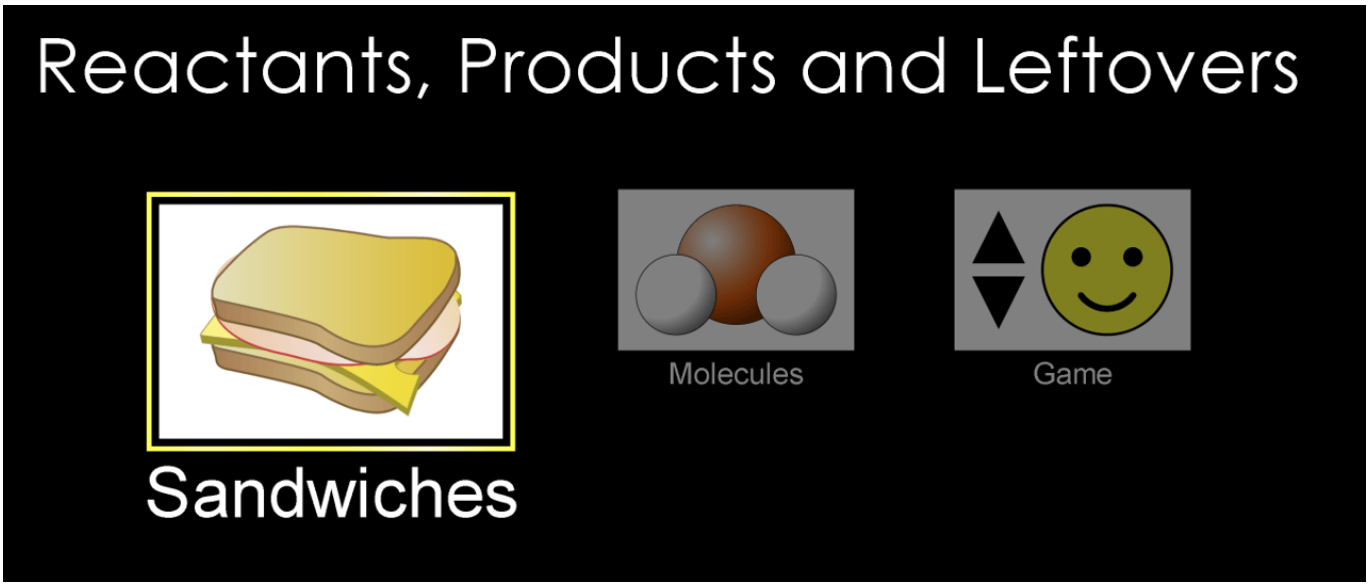


Figure 7.7.2: Finding the Limiting Reagent. When H_2 and Cl_2 are combined in nonstoichiometric amounts, one of these reactants will limit the amount of HCl that can be produced. This illustration shows a reaction in which hydrogen is present in excess and chlorine is the limiting reactant. Figure is from Wacowich-Sgarbi, S. and the Langara Chemistry Dept. (2018) BCCampus.

View this interactive PHET simulation illustrating the concepts of limiting and excess reactants.



Example 7.7.1

Silicon nitride is a very hard, high-temperature-resistant ceramic used as a component of turbine blades in jet engines. It is prepared according to the following equation:

$$3\,\mathrm{Si}(s) \quad + \quad 2\,\mathrm{N_2}(g) \quad \longrightarrow \quad \mathrm{Si_3N_4}(s) \tag{7.7.5}$$

Which is the limiting reactant when 2.00 g of Si and 1.50 g of N_2 react?

Solution

Step 1: Determine how many moles of Si are present.

$$2.00\,\mathrm{g\,Si} \quad \times \quad \frac{1\,\mathrm{mol\,Si}}{28.09\,\mathrm{g\,Si}} \quad = \quad 0.0712\,\mathrm{mol\,Si} \tag{7.7.6}$$

Step 2: Determine how many moles of N_2 are present.

$$1.50\,\mathrm{g\,N_2} \quad \times \quad \frac{1\,\mathrm{mol\,N_2}}{28.02\,\mathrm{g\,N_2}} \quad = \quad 0.0535\,\mathrm{mol\,N_2} \tag{7.7.7}$$

Step 3: Calculate how many moles of Si_3N_4 each reactant could produce.

$$0.0712\,\mathrm{mol\,Si} \quad \times \quad \frac{1\,\mathrm{mol\,Si_3N_4}}{3\,\mathrm{mol\,Si}} \quad = \quad 0.0237\,\mathrm{mol\,Si_3N_4} \tag{7.7.8}$$

From the nitrogen:

$$0.0535\,\mathrm{mol\,N_2} \quad \times \quad \frac{1\,\mathrm{mol\,Si_3N_4}}{2\,\mathrm{mol\,N_2}} \quad = \quad 0.0268\,\mathrm{mol\,Si_3N_4} \tag{7.7.9}$$

Conclusion

Because **silicon produces the smaller amount of product (0.0237 mol Si_3N_4), silicon is the limiting reactant**.

$$\mathrm{Limiting\ Reactant} \quad = \quad \mathrm{Si} \tag{7.7.10}$$

Exercise 7.7.1

Which is the limiting reactant when 5.00 g of H_2 and 10.0 g of O_2 react and form water? (Hint: Start by creating the balanced equation).

Answer available at the end of this section.

Percent Yield

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

$$\textbf{Percent Yield} = \frac{\textbf{Actual Yield}}{\textbf{Theoretical Yield}} \times 100\% \tag{7.7.11}$$

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

Example 7.7.2

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

$$\mathrm{CuSO_4}(aq) + \mathrm{Zn}(s) \longrightarrow \mathrm{Cu}(s) + \mathrm{ZnSO_4}(aq) \tag{7.7.12}$$

What is the percent yield?

Solution

To find the **theoretical yield of Cu**, use the molar mass of $CuSO_4$ (159.61 g/mol) and the 1:1 mole ratio:

$$1.274\,\mathrm{g\,CuSO_4} \times \frac{1\,\mathrm{mol\,CuSO_4}}{159.61\,\mathrm{g\,CuSO_4}} \times \frac{1\,\mathrm{mol\,Cu}}{1\,\mathrm{mol\,CuSO_4}} \times \frac{63.55\,\mathrm{g\,Cu}}{1\,\mathrm{mol\,Cu}} = 0.5073\,\mathrm{g}$$

So the **theoretical yield** is 0.5073 g Cu.

Then apply the percent-yield equation:

$$\textbf{Percent Yield} = \frac{\textbf{Actual Yield}}{\textbf{Theoretical Yield}} \times 100\% \tag{7.7.14}$$

For this problem:

$$\textbf{Percent Yield} = \frac{0.392\,\mathrm{g\,Cu}}{0.5073\,\mathrm{g\,Cu}} \times 100\% = 77.3\% \tag{7.7.15}$$

So the final answer is:

$$\textbf{Percent Yield} = 77.3\% \tag{7.7.16}$$

Exercise 7.7.2

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

$$\mathrm{CCl_4} + \mathrm{2\,HF} \longrightarrow \mathrm{CF_2Cl_2} + \mathrm{2\,HCl} \tag{7.7.17}$$

Answer available at the end of this section.

Green Chemistry and Atom Economy

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

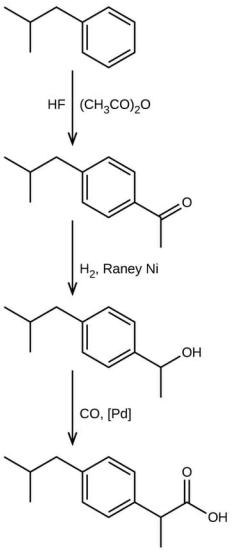
$$\text{Atom Economy} = \frac{\text{Mass of Desired Product}}{\text{Total Mass of Reactants}} \times 100\% \tag{7.7.18}$$

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

The synthesis of the common nonprescription pain medication, ibuprofen, nicely illustrates the success of a green chemistry approach (Fig 7.7.3). First marketed in the early 1960s, ibuprofen was produced using a six-step synthesis that required 514 g of reactants to generate each mole (206 g) of ibuprofen, an atom economy of 40%.



(a)



(b)

Figure 7.7.3: Green Chemistry and Ibuprofen Production. (a) Ibuprofen is a popular nonprescription pain medication commonly sold as 200 mg tablets. (b) The BHC process for synthesizing ibuprofen requires only three steps and exhibits an impressive atom economy. (credit a: modification of work by Derrick Coetzee)Figure from: Wacowich-Sgarbi, S. and the Langara Chemistry Dept. (2018) BCCampusIn the 1990s, an alternative process was developed by the BHC Company (now BASF Corporation) that requires only three steps and has an atom economy of ~80%, nearly twice that of the original process. The BHC process generates significantly less chemical waste; uses less-hazardous and recyclable materials; and provides significant cost-savings to the manufacturer (and, subsequently, the consumer). In recognition of the positive environmental impact of the

BHC process, the company received the Environmental Protection Agency's Greener Synthetic Pathways Award in 1997.

Answers

Exercise 7.7.1

O_2

Exercise 7.7.2

48.3%

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7.8: Focus on the Environment - Global Climate Change

"The thickness of the air, compared to the size of the Earth, is something like the thickness of a coat of shellac on a schoolroom globe. Many astronauts have reported seeing that delicate, thin, blue aura at the horizon of the daylit hemisphere and immediately, unbidden, began contemplating its fragility and vulnerability. They have reason to worry."

Carl Sagan, *Billions and Billions* (New York, NY: Random House 1997), 86.

7.8.1 Current Evidence of Climate Change

Since Charles David Keeling began continuous atmospheric carbon dioxide measurements in 1958, scientists have assembled multiple independent lines of evidence showing that Earth's climate is changing. These observations come from thousands of weather stations, satellites, ocean buoys, ice core records, and long-term ecological monitoring programs. Together, these datasets provide a consistent picture of a warming climate driven primarily by increasing concentrations of greenhouse gases produced by human activities.

Rising Atmospheric Carbon Dioxide

The **Keeling Curve**, initiated by Charles David Keeling at the Mauna Loa Observatory in Hawaii, provides one of the longest continuous records of atmospheric carbon dioxide. Measurements began in 1958 when atmospheric CO_2 concentrations were approximately **315 parts per million (ppm)**. Today, concentrations exceed **430 ppm**, representing the highest atmospheric CO_2 levels experienced by humanity during the entire period of direct measurements. Seasonal fluctuations occur because plants remove CO_2 from the atmosphere during the Northern Hemisphere growing season and release it through respiration and decomposition during the winter. Superimposed on these annual cycles is a persistent long-term upward trend caused primarily by fossil fuel combustion, cement production, and deforestation.

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Video 7.8.1: The Keeling Curve hits 420 ppm. Levels of the greenhouse gas carbon dioxide eclipsed 420 parts per million for the first time in human history. Scripps Institution of Oceanography updated this animation, which explains the rise of carbon dioxide concentration in the atmosphere over the past 300 years and the measurement our researchers collect at Hawaii's Mauna Loa, known as the Keeling Curve. When Scripps Oceanography scientist Charles David Keeling first began taking measurements in 1958, CO2 levels were at 315 parts per million.

Global Temperature Trends

Global average temperatures have increased substantially since the late nineteenth century. Independent analyses by NASA, NOAA, and Berkeley Earth all show that the **last decade has been the warmest since instrumental records began**, with 2023–2025 ranking among the three warmest years on record. Although natural climate cycles such as El Niño and La Niña produce year-to-year variability, the long-term warming trend remains clear and is primarily attributed to increasing greenhouse gas concentrations.

Berkeley Earth has created a summary of global temperature change over time.

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Video 7.8.2: 2022 Temperature Map: Global temperature change from 1850 to 2022 in 90 seconds. It's clear that adding carbon dioxide and other greenhouse gases to the atmosphere by using fossil fuels is transforming the Earth. Learn more in our annual temperature report(opens in new window).

Sea Level Rise and Ocean Change

Rising global temperatures affect Earth's oceans in several important ways. As seawater warms, it expands, while melting glaciers and ice sheets add additional water to the oceans. Satellite observations show that global mean sea level has risen by approximately **9 cm (3.6 inches)** since satellite measurements began in 1993, and the long-term rate of sea-level rise has more than doubled over the past three decades. Approximately two-thirds of this rise now results from melting land ice, with the remainder due to thermal expansion of seawater.

The oceans also absorb roughly **90% of the excess heat** trapped by greenhouse gases and approximately one-quarter of the carbon dioxide emitted by human activities. Although this slows atmospheric warming, dissolved CO_2 reacts with seawater to form carbonic acid, lowering ocean pH through a process known as **ocean acidification** (Figure xx). Increased ocean temperatures and acidification threaten coral reefs, shell-forming organisms, and many marine ecosystems.

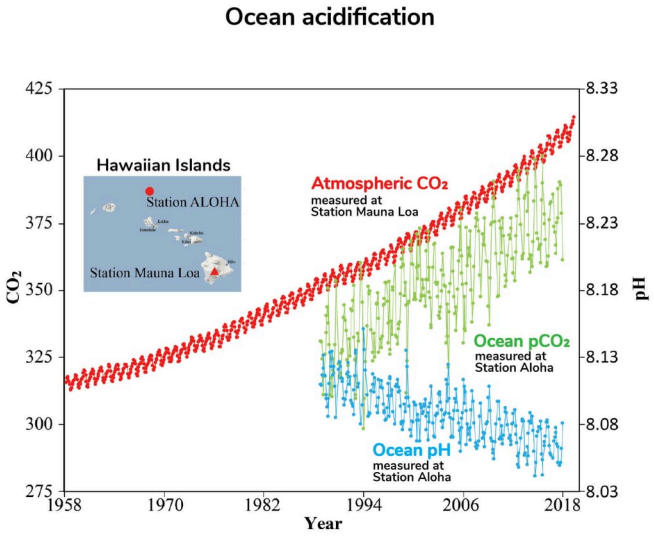


Figure 7.8.1**: Effects of Carbon Dioxide Emissions on the Earth's Oceans.** As human activities have increased CO_2 levels in our atmosphere (red line), about a third of that CO_2 has been absorbed by the ocean (green line), and ocean pH has decreased (blue line). Adapted from NOAA(opens in new window).

Wildfire Activity

Warmer temperatures, prolonged drought, and earlier snowmelt have increased wildfire risk in many regions of the world. Although individual fires result from many interacting factors—including ignition sources, forest management practices, and weather conditions—scientists have documented a substantial increase in the length of fire seasons and the area burned in many western

North American forests. Wildfires release additional carbon dioxide into the atmosphere while simultaneously reducing the ability of forests to remove CO_2 through photosynthesis, creating a positive feedback that can further amplify climate change.

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Video 7.8.3 Are Wildfires Getting Worse? - We Asked a NASA Scientist. Changes in our climate, along with other factors, have led to wildfires increasing in intensity, severity, size and duration. NASA climate and wildfire expert Liz Hoy explains how and why NASA studies these events from the ground, air, and space to better understand the impacts they have on both a local and global scale. NASA Fires. Producers: Jessica Wilde, Scott Bednar Editor: Daniel Salazar

7.8.2 The Chemistry of the Greenhouse Effect

Earth's climate is controlled by a delicate balance between the energy it receives from the Sun and the energy it radiates back into space. The Sun emits most of its energy as **visible light** and **ultraviolet radiation**, which pass relatively easily through Earth's atmosphere. When this solar radiation reaches Earth's surface, it is absorbed by land, oceans, and vegetation, causing the surface to warm.

A warm object continuously emits energy as **infrared (IR) radiation**. Because Earth's surface is much cooler than the Sun, it emits energy primarily in the infrared region of the electromagnetic spectrum rather than as visible light.

The atmosphere does not interact equally with all wavelengths of electromagnetic radiation. Most visible light passes through the atmosphere with little absorption, while certain gases efficiently absorb infrared radiation. These gases are known as **greenhouse gases**.

When a greenhouse gas molecule absorbs infrared radiation, the energy causes the molecule to vibrate. The excited molecule then transfers some of this energy to neighboring molecules through collisions or re-emits infrared radiation in all directions. Some of this re-emitted energy travels back toward Earth's surface, reducing the rate at which heat escapes into space. This process is known as the **greenhouse effect**.

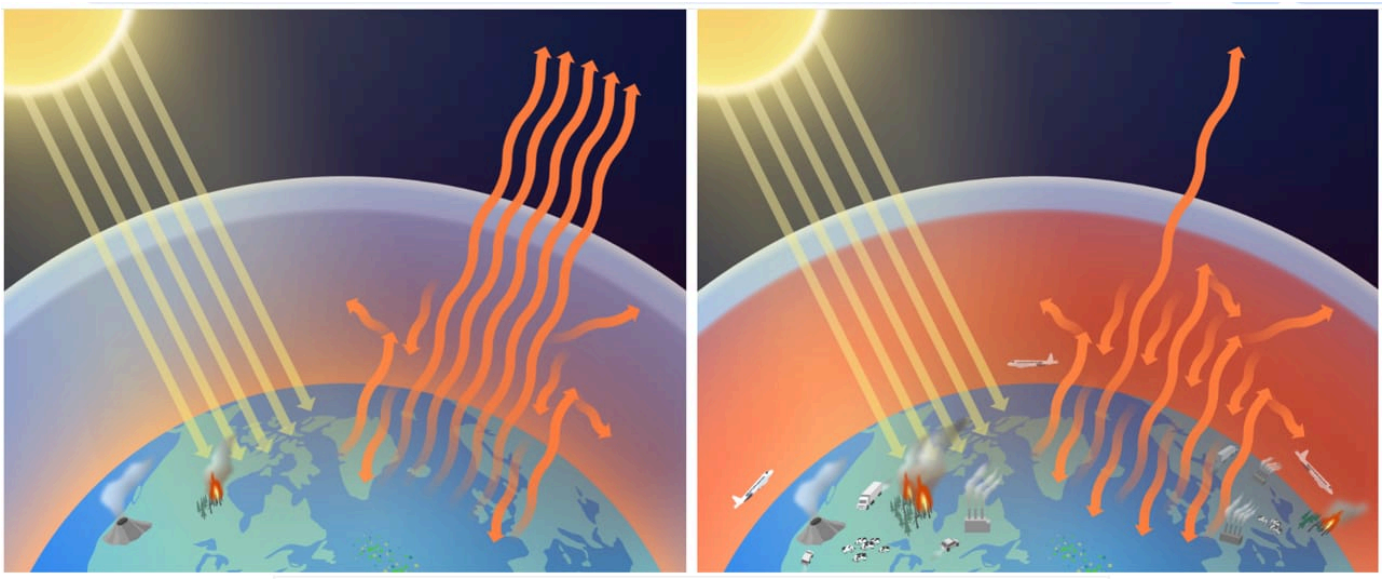


Figure 7.8.2: Model of the Greenhouse Effect. Left Panel - The greenhouse effect is a natural process where certain gases in the Earth's atmosphere trap heat from the sun. Sunlight passes through the air and warms the ground, which then sends heat back up as infrared energy. Greenhouse gases catch this heat and bounce it back, keeping the planet warm enough for life to exist. Right Panel - Human-produced greenhouse gases have intensified Earth's natural greenhouse effect by changing the balance between the amount of sunlight that reaches the surface and the amount of heat that escapes the atmosphere. CREDIT: NOAA Climate Program Office, Graphic by Anna Eshelman

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It is important to recognize that the greenhouse effect is **a natural and essential feature of Earth's atmosphere**. Without naturally occurring greenhouse gases, Earth's average surface temperature would be approximately **–18°C (0°F)** rather than about **15°C (59°F)**. The natural greenhouse effect therefore makes our planet warm enough to support liquid water and life.

Human activities, however, have increased the concentrations of several greenhouse gases since the beginning of the Industrial Revolution. As these concentrations increase, a greater fraction of Earth's outgoing infrared radiation is absorbed within the atmosphere, producing an **enhanced greenhouse effect** and increasing Earth's average surface temperature over time.

You can set up a simple laboratory experiment to see how CO2 can create an enhanced greenhouse effect.

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Video 7.8.4: Greenhouse Effect (II) - Enhanced Greenhouse Effect. Source: Australian Earth Education (AusEarthEd)

Why Do Some Molecules Absorb Infrared Radiation?

The ability of a molecule to absorb infrared radiation depends on its **molecular structure**.

When molecules absorb infrared light, their chemical bonds vibrate by stretching and bending. However, not every molecular vibration can absorb infrared radiation. To interact with infrared light, the vibration must produce a **changing dipole moment** within the molecule.

This concept builds directly upon the ideas of **bond polarity** and **molecular geometry** introduced earlier in this textbook.

Symmetric diatomic molecules such as nitrogen (N_2) and oxygen (O_2) make up approximately 99% of Earth's atmosphere, yet they contribute very little to the greenhouse effect. Because these molecules consist of identical atoms, their bond vibrations do not produce changing dipoles, making them essentially transparent to infrared radiation.

In contrast, molecules such as water (H_2O), carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O), and ozone (O_3) possess vibrational modes that produce changing dipoles. As a result, these molecules efficiently absorb portions of Earth's outgoing infrared radiation.

Notice that this explanation depends on **molecular geometry**, not simply whether a molecule is polar.

For example:

- **Water (H_2O)** has a bent molecular geometry and is highly polar, making it an excellent absorber of infrared radiation.
- **Carbon dioxide (CO_2)** is a linear, nonpolar molecule overall. However, during certain bending and asymmetric stretching vibrations, the electron distribution becomes temporarily asymmetric, allowing carbon dioxide to absorb infrared radiation very effectively.
- **Methane (CH_4)** is a symmetrical tetrahedral molecule and is also nonpolar. Like carbon dioxide, several of its vibrational

modes create temporary dipoles that interact strongly with infrared radiation.

Thus, a molecule **does not need to be permanently polar to act as a greenhouse gas**. Instead, it must possess molecular vibrations that create changing dipoles capable of absorbing infrared radiation. Of note, **Methane (CH_4)** is present in much lower concentrations than carbon dioxide (Table XX), but each methane molecule absorbs infrared radiation more efficiently than a carbon dioxide molecule. Although methane remains in the atmosphere for only about 12 years, it is considered a particularly important greenhouse gas because of its strong warming influence over short time scales. In comparison, a substantial fraction of CO_2 persists for centuries to millennia within the atmosphere.

Major Greenhouse Gases

Only a small fraction of Earth's atmosphere consists of greenhouse gases, yet they have a profound influence on Earth's climate.

Table 7.8A: Common Greenhouse Gases

Gas	Approximate Concentration	Major Human Sources	Comments
Water vapor (H_2O)	Variable (0–4%)	Evaporation	Largest natural greenhouse gas; primarily a climate feedback rather than a direct driver.
Carbon dioxide (CO_2)	>430 ppm	Fossil fuel combustion, cement production, deforestation	Largest contributor to long-term human-caused warming because of its abundance and long atmospheric lifetime.
Methane (CH_4)	~2 ppm	Agriculture, livestock, landfills, natural gas production	More efficient at trapping infrared radiation than CO_2 on a molecule-for-molecule basis but present at much lower concentrations.
Nitrous oxide (N_2O)	~340 ppb	Agricultural fertilizers, industrial processes	Long-lived greenhouse gas with additional effects on stratospheric ozone chemistry.
Fluorinated gases	ppt–ppb	Refrigerants, electronics manufacturing	Extremely effective greenhouse gases, although present in very low concentrations.

Although water vapor is the most abundant greenhouse gas, its atmospheric concentration is largely controlled by temperature through evaporation and condensation. Carbon dioxide therefore plays a particularly important role because increases in atmospheric CO_2 from human activities produce warming, which in turn allows the atmosphere to hold more water vapor. This additional water vapor further amplifies the warming through a **positive climate feedback**.

From Molecular Vibrations to Global Climate

The greenhouse effect provides an excellent example of how chemistry influences Earth's environment. Molecular geometry determines which vibrational motions are possible, while molecular vibrations determine which gases absorb infrared radiation. Changes in the atmospheric concentrations of these molecules alter Earth's energy balance, influencing global temperatures, ocean chemistry, weather patterns, and ecosystems.

Understanding the chemistry of greenhouse gases has enabled scientists to develop increasingly accurate climate models, design technologies that reduce greenhouse gas emissions, and develop new materials for capturing carbon dioxide before it enters the atmosphere.

Chemistry Connection

Earlier in this textbook, you learned that molecular geometry influences a molecule's polarity and physical properties. Here, we see another important application of molecular geometry: it determines how molecules interact with infrared radiation. The same chemical principles used to predict molecular shape also help explain why some gases contribute to Earth's greenhouse effect while others do not.

7.8.3 Future Climate Projections

Climate scientists use sophisticated computer models that incorporate atmospheric chemistry, ocean circulation, ice dynamics, solar radiation, and greenhouse gas emissions to project future climate conditions. Although individual models differ in their details, they consistently predict continued warming if greenhouse gas emissions remain high.

Future projections indicate continued increases in global average temperature, sea level, and the frequency of extreme heat events. Changes in precipitation patterns are expected to increase the risk of drought in some regions while increasing heavy rainfall and flooding in others. Continued warming is also expected to accelerate glacier retreat, reduce Arctic sea ice, and further stress ecosystems already adapting to changing environmental conditions.

Importantly, these projections depend strongly on future greenhouse gas emissions. Scenarios involving rapid reductions in emissions result in substantially less warming than scenarios in which fossil fuel use continues to increase. This demonstrates that future climate conditions remain strongly influenced by societal choices regarding energy production and greenhouse gas emissions.

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Video 7.8.5: What does “climate change” mean? Neil deGrasse Tyson explains under-emphasized elements of climate change and humanity’s relationship to the Earth and our cities. What does the new normal look like?

7.8.4 The Energy Transition

Because most human-produced carbon dioxide originates from the combustion of fossil fuels, reducing emissions requires changes in how energy is generated, transported, and used.

Although coal, petroleum, and natural gas continue to provide most of the world's primary energy, renewable energy technologies have expanded rapidly during the past decade. Solar and wind power now account for much of the world's newly installed electrical generating capacity, while improvements in battery technology have accelerated the adoption of electric vehicles and grid-scale energy storage systems.

At the same time, researchers continue to investigate technologies capable of reducing emissions from existing industrial facilities. **Carbon capture, utilization, and storage (CCUS)** systems remove carbon dioxide from flue gases before release into the atmosphere. Many facilities use chemical absorbents, such as aqueous amine solutions, to selectively capture CO_2, while others employ physical adsorption materials or membrane separation technologies. Captured carbon dioxide may be compressed and injected into deep geological formations for long-term storage or utilized as a feedstock for industrial processes.

Coal-fired power plants have also greatly reduced emissions of sulfur dioxide through the use of **flue-gas desulfurization systems**, commonly known as **scrubbers**. These systems typically react sulfur dioxide with limestone or lime to produce calcium

sulfite or calcium sulfate (gypsum), greatly reducing acid rain compared with earlier generations of power plants.

No single technology is expected to solve the climate challenge. Most energy experts envision a combination of improved energy efficiency, expanded renewable and nuclear power generation, electrification of transportation, carbon capture technologies, improved battery storage, and continued advances in chemistry and materials science working together to reduce greenhouse gas emissions while meeting growing global energy demands.

Suggested References

- NASA Earth Indicators (CO_2, temperature, sea level, ocean warming):
- NASA Global Temperature Analysis (GISTEMP).
- NASA Sea Level Indicator.
- Berkeley Earth.
- NOAA National Centers for Environmental Information (NCEI) (global climate summaries)
- IPCC Sixth Assessment Report (AR6) (physical science basis and mitigation)
- International Energy Agency (IEA) for renewable energy and electric vehicle trends.
- U.S. Department of Energy for carbon capture and storage technologies.

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7.9: Chapter Summary

Using Stoichiometry

To ensure that you understand the material in this chapter, you should review the meanings of the following bold terms in the following summary and ask yourself how they relate to the topics in the chapter.

Chemical reactions relate quantities of reactants and products. Chemists use the ***mole*** unit to represent 6.022×10^{23} things, whether the things are atoms of elements or molecules of compounds. This number, called ***Avogadro's number***, is important because this number of atoms or molecules has the same mass in grams as one atom or molecule has in atomic mass units. ***Molar masses*** of substances can be determined by summing the appropriate masses from the periodic table; the final molar mass will have units of grams.

Because one mole of a substance will have a certain mass, we can use that relationship to construct conversion factors that will convert a mole amount into a mass amount, or vice versa. Such ***mole-mass conversions*** typically take one algebraic step.

Chemical reactions list reactants and products in molar amounts, not just molecular amounts. We can use the coefficients of a balanced chemical equation to relate moles of one substance in the reaction to moles of other substances (stoichiometry). In a ***mole-mass calculation***, we relate the number of moles of one substance to the mass of another substance. In a ***mass-mass calculation***, we relate the mass of one substance to the mass of another substance.

Additional Exercises

1. If the average male has a body mass of 70 kg, of which 60% is water, how many moles of water are in an average male?
2. If the average female is 60.0 kg and contains 0.00174% iron, how many moles of iron are in an average female?
3. How many moles of each element are present in 2.67 mol of each compound?
    1. HCl
    2. H_2SO_4
    3. $Al(NO_3)_3$
    4. $Ga_2(SO_4)_3$
4. How many moles of each element are present in 0.00445 mol of each compound?
    1. HCl
    2. H_2SO_4
    3. $Al_2(CO_3)_3$
    4. $Ga_2(SO_4)_3$
5. What is the mass of one hydrogen atom in grams? What is the mass of one oxygen atom in grams? Do these masses have a 1:16 ratio, as expected?
6. What is the mass of one sodium atom in grams?
7. If 6.63×10^{-6} mol of a compound has a mass of 2.151 mg, what is the molar mass of the compound?
8. Hemoglobin (molar mass is approximately 64,000 g/mol) is the major component of red blood cells that transports oxygen and carbon dioxide in the body. How many moles are in 0.034 g of hemoglobin?

Answers

1) 2,330 mol

3-1) 2.67 mol of H and 2.67 mol of Cl

3-2) 5.34 mol of H, 2.67 mol of S, and 10.68 mol of O

3-3) 2.67 mol of Al, 8.01 mol of N, and 24.03 mol of O

3-4) 5.34 mol of Ga, 8.01 mol of S, and 32.04 mol of O

5) H = 1.66×10^{-24} g and O = 2.66×10^{-23} g; yes, they are in a 1:16 ratio.

7) 324 g/mol

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4. Schmitz, A. (2012) Climate Change Chapter from the book Entrepreneurship and Sustainability (v. 1.0). Published under Creative Commons by-nc-sa 3.0. Available at: Weblink Here [2012books.lardbucket.org]

5. Shaftel, H., Jackson, R. and Callery, S. (2018) Global Climate Change – Vital Signs of the Planet. Published by: Earth Science Communication Team at NASA's Jet Propulsion Laboratory. Retrieved on August 24th, 2018

6. Wacowich-Sgarbi, S. and the Langara Chemistry Department. (2018) CHEM1114 – Introduction to Chemistry. BCcampus. Available at: Weblink Here [pressbooks.bccampus.ca]

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8: CHAPTER 8 - SOLUTIONS

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8.2: Types of Solutions

8.3: Solubility

8.4: Temperature and Solubility

8.5: Effects of Pressure on the Solubility of Gases- Henry's Law

8.6: Solid Hydrates

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8.8: Dilutions

8.9: Ion Concentrations in Solution

8.10: Focus on the Environment- Lead Pollution

8.11: Summary

8.12: References

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8.1: Introduction

Recall from Chapter 1 that *solutions* are defined as homogeneous mixtures that are mixed so thoroughly that neither component can be observed independently of the other. Solutions are all around us. Air, for example, is a solution. If you live near a lake, a river, or an ocean, that body of water is not pure H_2O but most probably a solution. Much of what we drink—for example, soda, coffee, tea, and milk are solutions. Solutions are a large part of everyday life. A lot of the chemistry occurring around us happens in solution. In fact, much of the chemistry that occurs in our own bodies takes place in solution, and many solutions—such as the Ringer's lactate IV solution—are important in healthcare. In our understanding of chemistry, we need to understand a little bit about solutions. In this chapter, you will learn about the special characteristics of solutions, how solutions are characterized, and some of their properties.

Skills to Develop

- Define these terms: solution, solute, and solvent.
- Distinguish solutions, mixtures, and colloids.
- Describe various types of solutions.
- Distinguish unsaturated, saturated, and supersaturated solutions.

The major component of the solution is called ***solvent*****,** and the minor component(s) are called ***solute*****.** If both components in a solution are 50%, the term solute can be assigned to either component. When a gaseous or solid material dissolves in a liquid, the gas or solid material is called the solute. When two liquids dissolve in each other, the major component is called the *solvent* and the minor component is called the *solute*.

Many chemical reactions are carried out in solutions, and solutions are also closely related to our everyday lives. The air we breathe, the liquids we drink, and the fluids in our body are all solutions. Furthermore, we are surrounded by solutions such as the air and waters (in rivers, lakes and oceans).

On the topic of solutions, we include the following sections.

1. Types of Solutions: gaseous, liquid and solid solutions are based on the states of the solution.
2. Solution Stoichiometry: expressing concentration in various units (mass per unit volume, moles per unit volume, percentage and fractions), reaction stoichiometry calculations involving solutions.
3. Solutions of Electrolytes: solutions of acids, bases, and salts in which the solutes dissociate into positive and negative hydrated ions.
4. Metathesis or Exchange Reactions: reaction of electrolytes leading to neutral molecules, gases, and solids.

Solving problems of solution stoichiometry requires the concepts introduced in stoichiometry in Chapter 7, which also provides the basis for the discussion on reactions.

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8.2: Types of Solutions

In Chapter 1, you were introduced to the concept of a ***mixture*****,** which is a substance that is composed of two or more substances. Recall that mixtures can be of two types: Homogeneous and Heterogeneous, where homogeneous mixtures combine so intimately that they are observed as a single substance, even though they are not. Heterogeneous mixtures, on the other hand, are non-uniform and have regions of the mixture that look different from other regions of the mixture. Homogeneous mixtures can be further broken down into two classifications: Colloids and Solutions. A ***colloid*** is a mixture that contains particles with diameters ranging from 2 to 500 nm. Colloids appear uniform in nature and have the same composition throughout but are cloudy or opaque. Milk is a good example of a colloid. ***True solutions*** have particle sizes of a typical ion or small molecule (~0.1 to 2 nm in diameter) and are transparent, although they may be colored. This chapter will focus on the characteristics of true solutions.

Material exists in three states: solid, liquid, and gas. Solutions also exist in all these states:

1. Gaseous mixtures are usually homogeneous and are commonly ***gas-gas solutions***. For quantitative treatment of this type of solutions, we will devote a unit to gases. The atmosphere is a gaseous solution that consists of nitrogen, oxygen, argon, carbon dioxide, water, methane, and some other minor components. Some of these components, such as water, oxygen, and carbon dioxide may vary in concentration in different locations on the Earth depending on factors such as temperature and altitude.
2. When molecules of gas, solid or liquid are dispersed and mixed with those of liquid, the homogeneous (uniform) states are called ***liquid solutions*****.** Solids, liquids and gases dissolve in a liquid solvent to form liquid solutions. In this chapter, most of the chemistry that we will discuss occurs in liquid solutions where water is the solvent.
3. Many alloys, ceramics, and polymer blends are ***solid solutions.*** Within a certain range, copper and zinc dissolve in each other and harden to give solid solutions called brass. Silver, gold, and copper form many different alloys with unique colors and appearances. Alloys and other solid solutions are important in the world of materials chemistry.

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8.3: Solubility

Evaluating Solubility

The maximum amount of a substance that can be dissolved in a given volume of solvent is called *solubility*. Often, the solubility in water is expressed in gram/100 mL. A solution that has not reached its maximum solubility is called an *unsaturated solution*. This means that more solute could still be added to the solvent and dissolving would still occur.

A solution that has reached the maximum solubility is called a *saturated solution*. If more solute is added at this point, it will not dissolve into the solution. Instead it will remain precipitated as a solid at the bottom of the solution. Thus, one can often tell that a solution is saturated if extra solute is present (this can exist as another phase, such as gas, liquid, or solid). In a saturated solution there is no net change in the amount of solute dissolved, but the system is by no means static. In fact, the solute is constantly being dissolved and deposited at an equal rate. Such a phenomenon is called *equilibrium*. For example:

$$\text{Solid Solute} + \text{Liquid Solvent} \rightleftharpoons \text{Dissolved Solute in Solution} \tag{8.3.1}$$

In special circumstances, a solution may be ***supersaturated.*** Supersaturated solutions are solutions that have dissolved solute beyond the normal saturation point. Usually a condition such as increased temperature or pressure is required to create a supersaturated solution. For example, sodium acetate has a very high solubility at 270 K. When cooled, such a solution stays dissolved in what is called a meta-stable state. However, when a *seeding* crystal is added to the solution, the extra solute will rapidly solidify. During the crystallization process, heat is evolved, and the solution becomes warm. Common hand warmers use this chemical process to generate heat.

YouTube Video

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Video 8.3.1: Video showing the crystallization of a supersaturated solution of sodium acetate. Video by : North Carolina School of Science and Mathematics

So how can we predict the solubility of a substance?

One useful classification of materials is polarity. As you read about covalent and ionic compounds in Chapters 3 and 4, you learned that ionic compounds have the highest polarity forming full cations and anions within each molecule as electrons are donated from one atom to another. You also learned that covalent bonds could be polar or nonpolar in nature depending on whether or not the atoms involved in the bond share the electrons unequally or equally, respectively. Recall that the electronegativity difference can be used to determine the polarity of a substance. Typically an ionic bond has an electronegativity difference of 1.8 or above, whereas a polar covalent bond is between 0.4 to 1.8, and a nonpolar covalent bond is 0.4 or below.

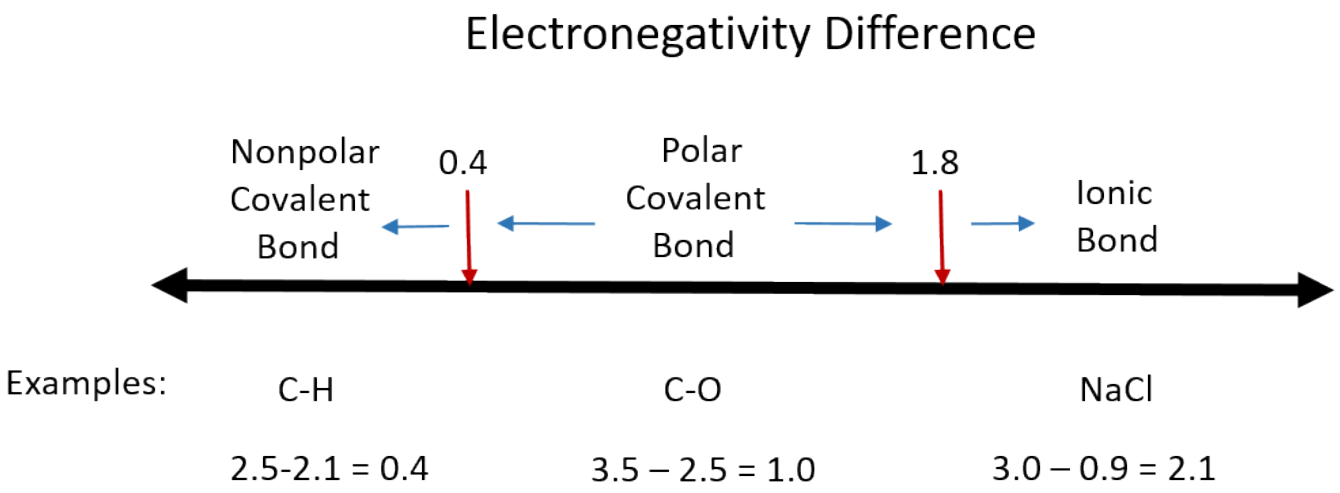


Figure 8.3.1**: Electronegativity Difference Diagram.** The diagram above is a guide for discerning what type of bond forms between two different atoms. By taking the difference between the electronegativity values for each of the atoms involved in the bond, the bond type and polarity can be predicted. Note that full ionic character is rarely reached, however when metals and nonmetals form bonds, they are named using the rules for ionic bonding.

Substances with zero or low electronegativity difference such as H_2, O_2, N_2, CH_4, CCl_4 are nonpolar compounds, whereas H_2O, NH_3, CH_3OH, NO, CO, HCl, H_2S, PH_3 higher electronegativity difference are polar compounds. Typically compounds that have similar polarity are soluble in one another. This can be described by the rule:

Like Dissolves Like.

This means that substances must have similar intermolecular forces to form solutions. When a soluble solute is introduced into a solvent, the particles of solute can interact with the particles of solvent. In the case of a solid or liquid solute, the interactions between the solute particles and the solvent particles are so strong that the individual solute particles separate from each other and, surrounded by solvent molecules, enter the solution. (Gaseous solutes already have their constituent particles separated, but the concept of being surrounded by solvent particles still applies.) This process is called ***solvation*** and is illustrated in Figure 8.2. When the solvent is water, the word ***hydration*****,** rather than solvation, is used.

In general polar solvents dissolve polar solutes whereas nonpolar solvents will dissolve nonpolar solutes. Overall, the solution process depends on the strength of the attraction between the solute particles and the solvent particles. For example, water is a highly polar solvent that is capable of dissolving many ionic salts. Figure 8.2 shows the solution process, where water act as the solvent to dissolve the crystalline salt, sodium chloride (NaCl). Note that when ionic compounds dissolve in a solvent they break apart into free floating ions in solution. This enables the compound to interact with the solvent. In the case of water dissolving sodium chloride, the sodium ion is attracted to the partial negative charge of the oxygen atom in the water molecule, whereas the chloride ion is attracted to the partial positive hydrogen atoms.

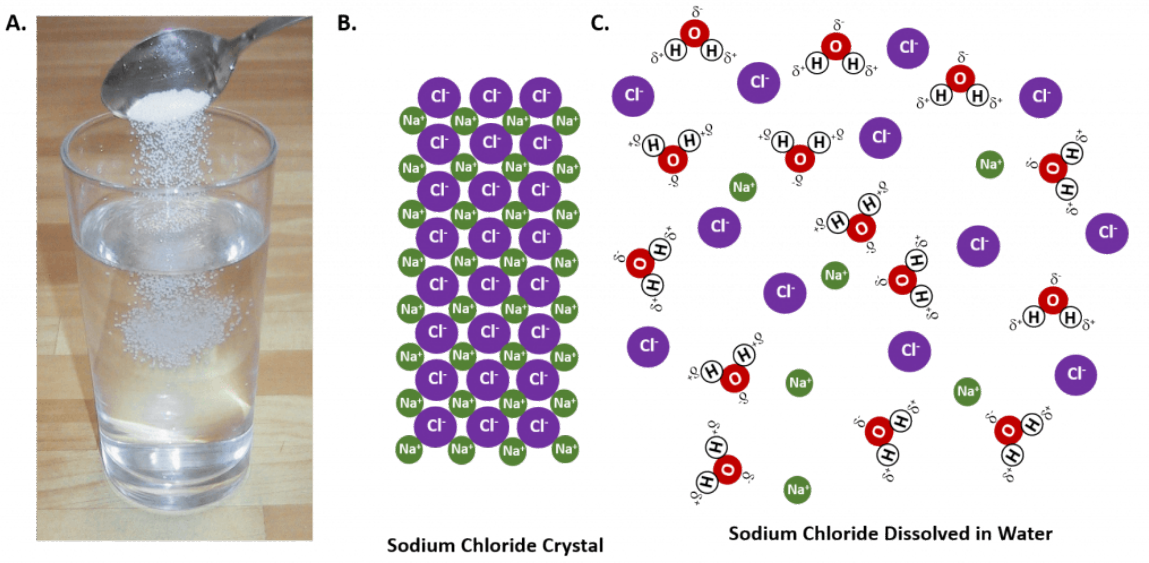


Figure 8.3.2: The Process of Dissolving. When an ionic salt, such as sodium chloride, shown in (A), comes into contact with water, the water molecules dissociate the ion molecules of the sodium chloride into their ionic state, shown as a molecular model in (B) the solid crystalline lattice of sodium chloride, and (C) the sodium chloride dissolved in the water solvent. (Photo of sodium chloride provided by Chris 73).

Many ionic compounds are soluble in water, however, not all ionic compounds are soluble. Ionic compounds that are soluble in water exist in their ionic state within the solution. You will notice in Figure 8.2 that the sodium chloride breaks apart into the sodium ion and the chloride ion as it dissolves and interacts with the water molecules. For ionic compounds that are not soluble in water, the ions are so strongly attracted to one another that they cannot be broken apart by the partial charges of the water molecules. The following table can be used to help you predict which ionic compounds will be soluble in water.

Table 8.3A: Evaluating the Solubility of Ionic Compounds

Solubility Rules
1. All compounds containing Group 1 (alkali metal) cations (Li^+, Na^+, K^+, Rb^+, Cs^+) or the ammonium ion (NH_4^+) are soluble.
2. All nitrates (NO_3^-), acetates (CH_3COO^- or $C_2H_3O_2^-$), chlorates (ClO_3^-), and perchlorates (ClO_4^-) are soluble.
3. Most halide salts (Cl^-, Br^-, I^-) are soluble, except those containing Ag^+, Pb^{2+}, or Hg_2^{2+}.
4. Most sulfate salts (SO_4^{2-}) are soluble, except those containing Ba^{2+}, Sr^{2+}, Pb^{2+}, Ca^{2+}, Ag^+, or Hg_2^{2+}.
5. Most carbonates (CO_3^{2-}), phosphates (PO_4^{3-}), chromates (CrO_4^{2-}), sulfides (S^{2-}), hydroxides (OH^-), and oxides (O^{2-}) are insoluble, except when paired with Group 1 cations or NH_4^+.

Note

These are the same solubility rules introduced in Chapter 6. We will continue to use these rules to predict whether ionic compounds dissolve in water and to determine the ions present in aqueous solutions.

Electrolytes

The dissociation of soluble ionic compounds gives solutions of these compounds an interesting property: they conduct electricity. Because of this property, soluble ionic compounds are referred to as ***electrolytes***. Many ionic compounds dissociate completely and are therefore called ***strong electrolytes***. Sodium chloride is an example of a strong electrolyte. Some compounds dissolve but dissociate only partially, and solutions of such solutes may conduct electricity only weakly. These solutes are called ***weak electrolytes***. Acetic acid (CH_3COOH), the compound in vinegar, is a weak electrolyte. Solutes that dissolve into individual neutral

molecules without dissociation do not impart additional electrical conductivity to their solutions and are called ***nonelectrolytes***. Polar covalent compounds, such as table sugar ($C_{12}H_{22}O_{11}$), are good examples of ***nonelectrolytes***.

The term ***electrolyte*** is used in medicine to mean any of the important ions that are dissolved in aqueous solution in the body. Important physiological electrolytes include Na^+, K^+, Ca^{2+}, Mg^{2+}, and Cl^-. Sports drinks such as Gatoraid have combinations of these key electrolytes, to help replenish electrolyte loss following a hard workout.

Similarly, solutions can also be made by mixing two compatible liquids together. The liquid in the lower concentration is termed the ***solute,*** and the one in higher concentration the ***solvent***. For example, grain alcohol (CH_3CH_2OH) is a polar covalent molecule that can mix with water. When two similar solutions are placed together and are able to mix into a solution, they are said to be ***miscible***. Liquids that do not share similar characteristics and cannot mix together, on the other hand, are termed ***immiscible***. For example, the oils found in olive oil, such as oleic acid ($C_{18}H_{34}O_2$) have mainly nonpolar covalent bonds which do not have intermolecular forces that are strong enough to break the hydrogen bonding between the water molecules. Thus, water and oil do not mix and are said to be ***immiscible***.

Other factor such as temperature and pressure also affects the solubility of a solvent. Thus, in specifying solubility, one should also be aware of these other factors.

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8.4: Temperature and Solubility

When considering the solubility solids, the relationship of temperature and solubility is not simple or predictable. Figure 8.3 shows plots of the solubilities of several organic and inorganic compounds in water as a function of temperature. Although the solubility of a solid generally increases with increasing temperature, there is no simple relationship between the structure of a substance and the temperature dependence of its solubility. Many compounds (such as glucose and CH_3CO_2Na) exhibit a dramatic increase in solubility with increasing temperature. Others (such as NaCl and K_2SO_4) exhibit little variation, and still others (such as Li_2SO_4) become less soluble with increasing temperature.

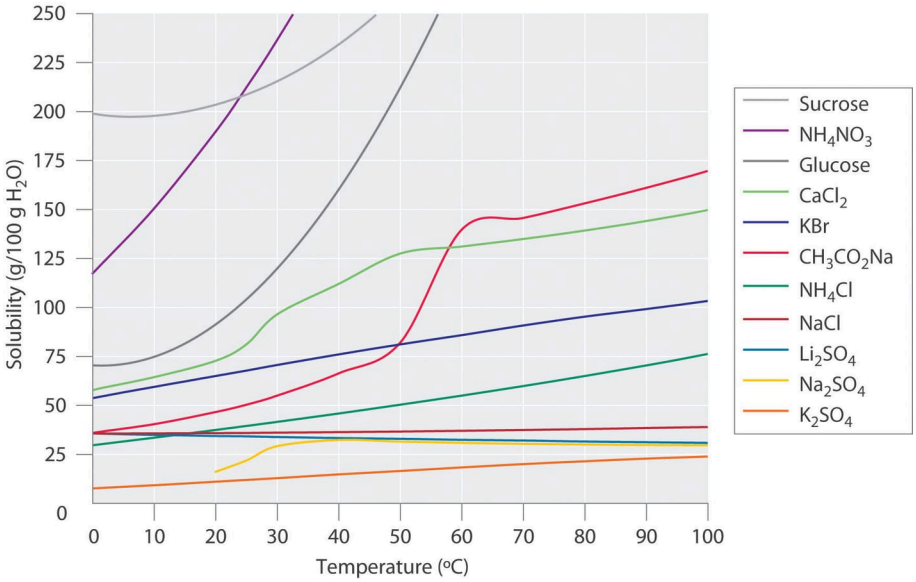


Figure 8.4.1**: Solubilities of Several Inorganic and Organic Solids in Water as a Function of Temperature.** Solubility may increase or decrease with temperature; the magnitude of this temperature dependence varies widely among compounds.

The variation of solubility with temperature has been measured for a wide range of compounds, and the results are published in many standard reference books. Chemists are often able to use this information to separate the components of a mixture by ***fractional crystallization***, the separation of compounds on the basis of their solubilities in a given solvent. For example, if we have a mixture of 150 g of sodium acetate (CH_3CO_2Na) and 50 g of KBr, we can separate the two compounds by dissolving the mixture in 100 g of water at 80°C and then cooling the solution slowly to 0°C. According to the temperature curves in Figure 8.3, both compounds dissolve in water at 80°C, and all 50 g of KBr remains in solution at 0°C. Only about 36 g of CH_3CO_2Na are soluble in 100 g of water at 0°C, however, so approximately 114 g (150 g – 36 g) of CH_3CO_2Na crystallizes out on cooling. The crystals can then be separated by filtration. Thus fractional crystallization allows us to recover about 75% of the original CH_3CO_2Na in essentially pure form in only one step.

Fractional crystallization is a common technique for purifying compounds as diverse as those shown in Figure 8.3 and from antibiotics to enzymes. For the technique to work properly, the compound of interest must be more soluble at high temperature than at low temperature, so that lowering the temperature causes it to crystallize out of solution. In addition, the impurities must be *more* soluble than the compound of interest (as was KBr in this example) and preferably present in relatively small amounts.

The solubility of gases in liquids is much more predictable. The solubility of gases in liquids decreases with increasing temperature, as shown in Figure 8.4.2. Attractive intermolecular interactions in the gas phase are essentially zero for most substances, because the molecules are so far apart when in the gaseous form. When a gas dissolves, it does so because its molecules interact with solvent molecules. Heat is released when these new attractive forces form. Thus, if external heat is added to the system, it overcomes the attractive forces between the gas and the solvent molecules and decreases the solubility of the gas.

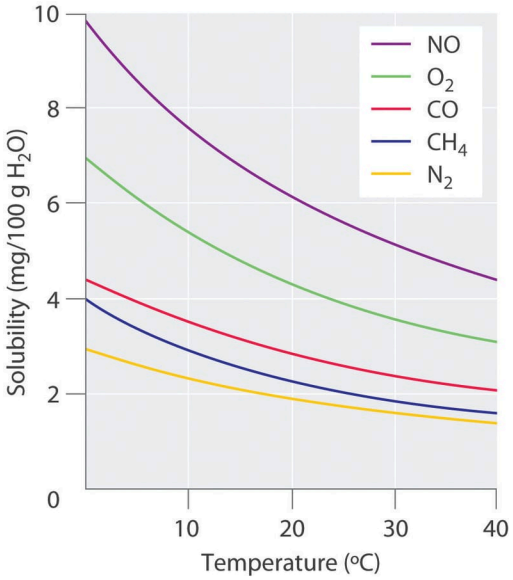


Figure 8.4.2: Solubilities of Several Common Gases in Water as a Function of Temperature at Partial Pressure of 1 atm. The solubilities of gases decrease with increasing temperature.

The decrease in the solubilities of gases at higher temperatures has both practical and environmental implications. Anyone who routinely boils water in a teapot or electric kettle knows that a white or gray deposit builds up on the inside and must eventually be removed. The same phenomenon occurs on a much larger scale in the giant boilers used to supply hot water or steam for industrial applications, where it is called *"boiler scale,"* a deposit that can seriously decrease the capacity of hot water pipes (Figure 7.5). The problem is not a uniquely modern one: aqueducts that were built by the Romans 2000 years ago to carry cold water from alpine regions to warmer, drier regions in southern France were clogged by similar deposits. The chemistry behind the formation of these deposits is moderately complex, but the driving force is the loss of dissolved carbon dioxide (CO_2) from solution. Hard water contains dissolved Ca^{2+} and HCO_3^- (bicarbonate) ions. Calcium bicarbonate [$Ca(HCO_3)_2$] is rather soluble in water, but calcium carbonate ($CaCO_3$) is quite insoluble. A solution of bicarbonate ions can react to form carbon dioxide, carbonate ion, and water:

$$\mathbf{2\,HCO_3^-}(aq) \longrightarrow \mathbf{CO_3^{2-}}(aq) + \mathbf{H_2O}(l) + \mathbf{CO_2}(aq) \tag{8.4.1}$$

Heating the solution decreases the solubility of CO_2, which escapes into the gas phase above the solution. In the presence of calcium ions, the carbonate ions precipitate as insoluble calcium carbonate, the major component of boiler scale.



Figure 8.4.3**: Boiler Scale in a Water Pipe.** Calcium carbonate ($CaCO_3$) deposits in hot water pipes can significantly reduce pipe capacity. These deposits, called boiler scale, form when dissolved CO_2 is driven into the gas phase at high temperatures.

In *thermal pollution*, lake or river water that is used to cool an industrial reactor or a power plant is returned to the environment at a higher temperature than normal. Because of the reduced solubility of O_2 at higher temperatures (Figure 8.4), the warmer water contains less dissolved oxygen than the water did when it entered the plant. Fish and other aquatic organisms that need dissolved oxygen to live can literally suffocate if the oxygen concentration of their habitat is too low. Because the warm, oxygen-depleted water is less dense, it tends to float on top of the cooler, denser, more oxygen-rich water in the lake or river, forming a barrier that prevents atmospheric oxygen from dissolving. Eventually even deep lakes can be suffocated if the problem is not corrected. Additionally, most fish and other nonmammalian aquatic organisms are cold-blooded, which means that their body temperature is the same as the temperature of their environment. Temperatures substantially greater than the normal range can lead to severe stress or even death. Cooling systems for power plants and other facilities must be designed to minimize any adverse effects on the temperatures of surrounding bodies of water. In the Pacific Northwest, salmonid populations are extremely susceptible to changes in water temperature. Within these population, optimal water temperatures are between 12.8 and 17.8 ^{o}C (55-65 ^{o}F). In addition to reduced oxygen levels, salmon populations are much more susceptible to disease, predation, and parasite infections at higher water temperatures. Thus, thermal pollution and global climate change are creating real challenges to the survival and maintenance of these species. For more information on the effects of rising temperatures on salmonid populations visit the State of Washington's Focus Publication.

A similar effect is seen in the rising temperatures of bodies of water such as the Chesapeake Bay, the largest estuary in North America, where global warming has been implicated as the cause. For each 1.5°C that the bay's water warms, the capacity of water to dissolve oxygen decreases by about 1.1%. Many marine species that are at the southern limit of their distributions have shifted their populations farther north. In 2005, the eelgrass, which forms an important nursery habitat for fish and shellfish, disappeared from much of the bay following record high water temperatures. Presumably, decreased oxygen levels decreased populations of clams and other filter feeders, which then decreased light transmission to allow the eelsgrass to grow. The complex relationships in ecosystems such as the Chesapeake Bay are especially sensitive to temperature fluctuations that cause a deterioration of habitat quality.

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8.5: Effects of Pressure on the Solubility of Gases- Henry's Law

Evaluating Pressure

External pressure has very little effect on the solubility of liquids and solids. In contrast, the solubility of gases increases as the partial pressure of the gas above a solution increases. This point is illustrated in Figure 8.5.1, which shows the effect of increased pressure on the dynamic equilibrium that is established between the dissolved gas molecules in solution and the molecules in the gas phase above the solution. Because the concentration of molecules in the gas phase increases with increasing pressure, the concentration of dissolved gas molecules in the solution at equilibrium is also higher at higher pressures.

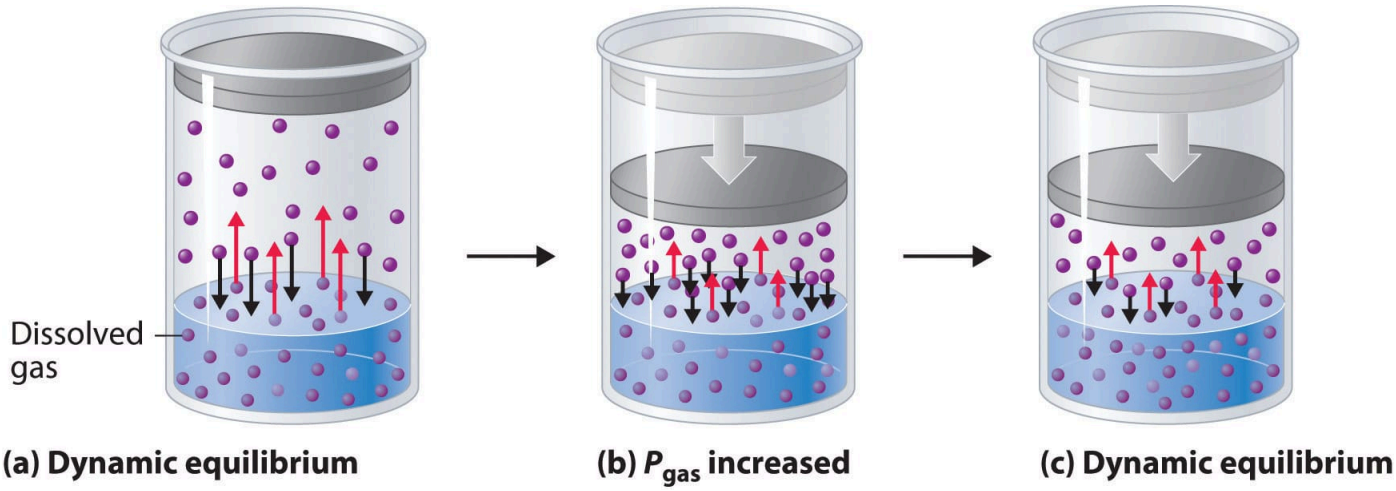


Figure 8.5.1: A Model Depicting Why the Solubility of a Gas Increases as the Partial Pressure Increases at Constant Temperature. (a) When a gas comes in contact with a pure liquid, some of the gas molecules (purple spheres) collide with the surface of the liquid and dissolve. When the concentration of dissolved gas molecules has increased so that the rate at which gas molecules escape into the gas phase is the same as the rate at which they dissolve, a dynamic equilibrium has been established, as depicted here. (b) Increasing the pressure of the gas increases the number of molecules of gas per unit volume, which increases the rate at which gas molecules collide with the surface of the liquid and dissolve. (c) As additional gas molecules dissolve at the higher pressure, the concentration of dissolved gas increases until a new dynamic equilibrium is established.

The relationship between pressure and the solubility of a gas is described quantitatively by Henry's law, which is named for its discoverer, the English physician and chemist, William Henry (1775–1836):

$$C = kP \tag{8.5.1}$$

where *C* is the concentration of dissolved gas at equilibrium, *P* is the partial pressure of the gas, and *k* is the *Henry's law constant*, which must be determined experimentally for each combination of gas, solvent, and temperature. Although the gas concentration may be expressed in any convenient units, we will use molarity exclusively. The units of the Henry's law constant are therefore mol/(L·atm) = M/atm. Values of the Henry's law constants for solutions of several gases in water at 20°C are listed in Table 8.5A

Video Tutorial on Henry's Law from Kahn Academy

All Khan Academy content is available for free at www.khanacademy.org.

As the data in Table 8.5A demonstrate, the concentration of a dissolved gas in water at a given pressure depends strongly on its physical properties. For a series of related substances, London dispersion forces increase as molecular mass increases. Thus among the elements of group 18, the Henry's law constants increase smoothly from He to Ne to Ar. The table also shows that O_2 is almost twice as soluble as N_2. Although London dispersion forces are too weak to explain such a large difference, O_2 is *paramagnetic* and hence more polarizable than N_2, which explains its high solubility. (Note: When a substance is *paramagnetic* it is very weakly attracted by the poles of a magnet, but does not retain any permanent magnetism).

Table 8.5A: Henry's Law Constant is a Physical Property of Elements and Molecules.

Gas	Henry's Law Constant [mol/(L*atm)] x 10^{-4}
He	3.9
Ne	4.7
Ar	15
H_2	8.1
N_2	7.1
O_2	14
CO_2	392

The partial pressure of a gas can be expressed as concentration by writing Henry's Law as $P_{gas} = C/k$. This is important in many aspects of life including medicine where blood gases, like oxygen and carbon dioxide are commonly measured. Since partial pressure and concentration are directly proportional, if the partial pressure of a gas changes while the temperature remains constant, the new concentration of the gas within the liquid can be easily calculated using the following equation:

$$\frac{C_1}{P_1} = \frac{C_2}{P_2} \tag{8.5.2}$$

Where C_1 and P_1 are the concentration and partial pressure, respectively, of the gas at the initial condition, and C_2 and P_2 are the concentration and partial pressure, respectively, of the gas at the final condition. For example:

Example 8.5.1

The concentration of CO_2 in a solution is 0.032 M at 3.0 atm. What is the concentration of CO_2 at 5.0 atm of pressure?

Solution

Henry's Law states that, at a constant temperature, the concentration of a dissolved gas is directly proportional to its partial pressure:

$$\frac{C_1}{P_1} = \frac{C_2}{P_2} \tag{8.5.3}$$

Step 1. Identify the known and unknown values.

- C1=0.032 M
- P1=3.0 atm
- P2=5.0 atm
- C2=?

Step 2. Rearrange the equation to solve for C_2.

$$C_2 = \frac{C_1 P_2}{P_1} \tag{8.5.4}$$

Step 3. Substitute the known values.

$$C_2 = \frac{(0.032\ \text{M})(5.0\ \text{atm})}{3.0\ \text{atm}} \tag{8.5.5}$$

Step 4. Calculate the answer.

$$C_2 = 0.053\ \text{M} \tag{8.5.6}$$

Final Answer:

At a pressure of 5.0 atm, the concentration of dissolved CO_2 is **0.053 M**.

Note

Increasing the pressure from **3.0 atm** to **5.0 atm** increases the concentration of dissolved CO_2 because gas solubility is directly proportional to pressure. This is why carbonated beverages are bottled under high pressure—when the bottle is opened and the pressure decreases, carbon dioxide escapes from solution, producing bubbles.

Exceptions to the Rule:

Interestingly, gases that react chemically with water, such as HCl and the other hydrogen halides, H_2S, and NH_3, do not obey Henry's law; all of these gases are much more soluble than predicted by Henry's law. For example, HCl reacts with water to give H^+(aq) and Cl^-(aq), *not* dissolved HCl molecules, and its dissociation into ions results in a much higher solubility than expected for a neutral molecule. Overall, gases that react with water do not obey Henry's Law.

Note the Pattern

Henry's law has important applications. For example, bubbles of CO_2 form as soon as a carbonated beverage is opened because the drink was bottled under CO_2 at a pressure greater than 1 atm. When the bottle is opened, the pressure of CO_2 above the solution drops rapidly, and some of the dissolved gas escapes from the solution as bubbles. Henry's law also explains why scuba divers have to be careful to ascend to the surface slowly after a dive if they are breathing compressed air. At the higher pressures under water, more N_2 from the air dissolves in the diver's internal fluids. If the diver ascends too quickly, the rapid pressure change causes small bubbles of N_2 to form throughout the body, a condition known as "the bends." These bubbles can block the flow of blood through the small blood vessels, causing great pain and even proving fatal in some cases.

Due to the low Henry's law constant for O_2 in water, the levels of dissolved oxygen in water are too low to support the energy needs of multicellular organisms, including humans. To increase the O_2 concentration in internal fluids, organisms synthesize highly soluble carrier molecules that bind O_2 reversibly. For example, human red blood cells contain a protein called hemoglobin that specifically binds O_2 and facilitates its transport from the lungs to the tissues, where it is used to oxidize food molecules to provide energy. The concentration of hemoglobin in normal blood is about 2.2 mM, and each hemoglobin molecule can bind four O_2 molecules. Although the concentration of dissolved O_2 in blood serum at 37°C (normal body temperature) is only 0.010 mM, the total dissolved O_2 concentration is 8.8 mM, almost a thousand times greater than would be possible without hemoglobin. Synthetic oxygen carriers based on fluorinated alkanes have been developed for use as an emergency replacement for whole blood. Unlike donated blood, these "blood substitutes" do not require refrigeration and have a long shelf life. Their very high Henry's law constants for O_2 result in dissolved oxygen concentrations comparable to those in normal blood.

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8.6: Solid Hydrates

Some ionic solids will accept a small number of water molecules into their crystal lattice structure and remain in a solid state. These solids are called ***solid hydrates.*** Solid hydrates contain water molecules combined in a definite ratio as an integral part of the crystal that are either bound to a metal center or that have crystallized with the metal complex. Such hydrates are also said to contain ***water of crystallization*** or ***water of hydration.***

A colorful example is cobalt(II) chloride, which turns from blue to red upon hydration, and can therefore be used as a water indicator.

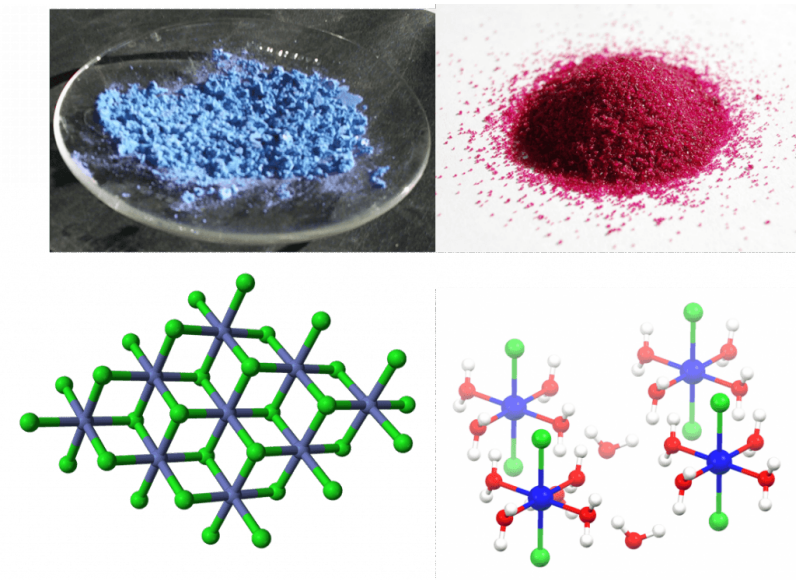


Figure 8.6.1**: Cobalt chloride as an example of a solid hydrate.** Anhydrous cobalt chloride (upper left) and it's crystal lattice structure (lower left) compared with cobalt chloride hexahydrate (upper right) and it's crystal lattice (lower right). Notice that the water molecules shown in red (oxygen) and white (hydrogen) are integrated into the crystal lattice of the cobalt (II) chloride, shown in blue (cobalt) and green (chloride), based on polarity. The partially negative oxygen atoms are attracted to the positively charged cobalt while the partially positive hydrogen atoms are attracted to the negatively charged chloride ions. Images provided by Wikipedia Commons (upper left and lower left), Benjah-bmm27 (upper right), and Smokefoot (lower right).

The notation used to represent a solid hydrate is: "***hydrated compound*** $\cdot$ ***n*** H_2O", where *n* is the number of water molecules per formula unit of the salt. The *n* is usually a low integer, though it is possible for fractional values to occur. For example, in a monohydrate n is one, and in a hexahydrate n is 6. For the example in Figure 8.7, the hydrated cobalt chloride would be designated: "cobalt (II) chloride $\cdot$ $6H_2O$". Numerical prefixes of Greek origin that are used to designate solid hydrates are:

- Hemi – 1/2
- Mono – 1
- Sesqui – 1½
- Di – 2
- Tri – 3
- Tetra – 4
- Penta – 5
- Hexa – 6
- Hepta – 7
- Octa – 8
- Nona – 9
- Deca – 10

- Undeca – 11
- Dodeca – 12

A hydrate which has lost water is referred to as an *anhydride*; the remaining water, if any exists, can only be removed with very strong heating. A substance that does not contain any water is referred to as *anhydrous*. Some anhydrous compounds are hydrated so easily that they will pull water out of the atmosphere and become hydrated. These substances are said to be *hygroscopic* and can be used as drying agents or *desiccants*.

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8.7: Solution Concentrations

In chemistry, *concentration* is defined as the abundance of a constituent divided by the total volume of a mixture. All of us have a qualitative idea of what is meant by *concentration*. Anyone who has made instant coffee or lemonade knows that too much powder gives a strongly flavored, highly concentrated drink, whereas too little results in a dilute solution that may be hard to distinguish from water. Quantitatively, the concentration of a solution describes the quantity of a solute that is contained in a particular quantity of that solution. Knowing the concentration of solutes is important in controlling the stoichiometry of reactants for reactions that occur in solution, and are critical for many aspects of our lives, from measuring the correct dose of medicine to detecting chemical pollutants like lead and arsenic. Chemists use many different ways to define concentrations. In this section, we will cover the most common ways of presenting solution concentration. These include: Molarity and Parts Per Solutions.

8.7.1 Molarity

The most common unit of concentration is ***molarity***, which is also the most useful for calculations involving the stoichiometry of reactions in solution. The ***molarity* (M)** of a solution is the number of moles of solute present in exactly 1 L of solution. Here are the common ways you will see this equation written

$$\text{Molarity} = \frac{\text{moles of solute}}{\text{liters of solution}} \tag{8.7.1}$$

OR

$$M = \frac{\text{mol}}{\text{L}} \tag{8.7.2}$$

OR

$$M = \frac{n}{V} \tag{8.7.3}$$

The units of molarity are therefore moles per liter of solution (mol/L), abbreviated as M. The term moles is also often noted by the letter *n* as seen in equation xxx. Note that the volume indicated is the **total volume of the solution and includes both the solute and the solvent**. For example, an aqueous solution that contains 1 mol (342 g) of sucrose in enough water to give a final volume of 1.00 L has a sucrose concentration of 1.00 mol/L or 1.00 M. In chemical notation, square brackets around the name or formula of the solute represent the concentration of a solute. So

$$[\text{Sucrose}] = 1.00\ \text{M} \tag{8.7.4}$$

is read as “the concentration of sucrose is 1.00 molar.” The equation above can be used to calculate how much solute is required to make any amount of a desired solution.

Exercise 8.7.1: Molarity

Calculate the number of moles of sodium hydroxide (NaOH) needed to make 2.50 L of 0.100 M NaOH.

Answer available at the end of this section.

Preparation of Solutions

Note that in the example above, we still don’t have enough information to actually make the solution in the laboratory. There is no piece of equipment that can measure out the moles of a substance. For this, we need to convert the number of moles of the sample into the number of grams represented by that number. We can then easily use a balance to weigh the amount of substance needed for the solution. For the example above:

1. Calculate the Molar Mass of NaOH

Na = 22.990 g/mol

O = 15.999 g/mol

H = 1.008 g/mol

$$\text{Molar Mass of NaOH} = 22.990\ \text{g/mol} + 15.999\ \text{g/mol} + 1.008\ \text{g/mol} = 39.997\ \text{g/mol} \quad (8.$$

2. Convert mole of NaOH into grams of NaOH

$$0.250\ \cancel{\text{mol NaOH}} \times \frac{39.997\ \text{g NaOH}}{1\ \cancel{\text{mol NaOH}}} = 9.9925\ \text{g NaOH} \quad (8.7.6)$$

Round 9.9925 g NaOH to 3 significant figures, or **9.99 g of NaOH needed** to make 2.50 L of a 0.100 M solution.

To actually make the solution, it is typical to dissolve the solute in a small amount of the solvent and then once the solute is dissolved, the final volume can be brought up to 2.50 L. If you were to add 10 g of NaOH directly to 2.50 L, the final volume would be larger than 2.50 L and the solution concentration would be less than 0.100 M. Remember that the final volume must include both the solute and the solvent.

Figure 8.7.1 illustrates the procedure for making a solution of cobalt(II) chloride dihydrate in ethanol. Note that the volume of the *solvent* is not specified. Since the solute occupies space in the solution, the volume of the solvent needed is *less* than the desired total volume of solution.



(a) An amount of solute is weighed out on an analytical balance and then

(b) A portion of the solvent is added to the volumetric flask.

(c) The mixture is swirled until *all* of the solute is dissolved.

(d) Additional solvent is added up to the mark on the volumetric flask.

Figure 8.7.1**: Preparation of a Solution of Known Concentration Using a Solid Solute.** To make a solution, start by addition a portion of the solvent to the flask. Next, weigh out the appropriate amount of solute and slowly add it to the solvent. Once it is dissolved in the solvent, the volume of the solution can be brought up to the final solution volume. For the volumetric flask shown, this is indicated by the black line in the neck of the flask. In this case, it indicates 500 mL of solution. Volumetric flasks exist in many different sizes to accommodate different solution volumes. Graduated cylinders can also be used to accurately bring a solution to its final volume. Other glassware, including beakers and Erlenmeyer flasks are not accurate enough to make most solutions.

Example 8.7.2: Molarity

The solution in Figure 8.7.1 contains 10.0 g of cobalt(II) chloride dihydrate, $CoCl_2{\cdot}2H_2O$, in enough ethanol to make exactly 500 mL of solution. What is the molar concentration of $CoCl_2{\cdot}2H_2O$?

Solution

We know that Molarity equals moles/Liter. To calculate Molarity, we need to express:

- the mass in the form of moles
- the volume in the form of Liters
- Plug both into the equation above and calculate

1. First, calculate the molar mass of cobalt(II) chloride dihydrate, $CoCl_2 \cdot 2H_2O$:

$$\text{Molar Mass of } CoCl_2 \cdot 2H_2O \quad = \quad 58.93 + 2(35.45) + 2(18.02) \quad = \quad 165.87\,\text{g/mol}$$

2. Next, convert the **10.0 g of $CoCl_2{\cdot}2H_2O$ to moles**:

$$10.0\,\text{g}\,CoCl_2 \cdot 2H_2O \quad \times \quad \frac{1\,\text{mol}\,CoCl_2 \cdot 2H_2O}{165.87\,\text{g}\,CoCl_2 \cdot 2H_2O} \quad = \quad 0.0603\,\text{mol}\,CoCl_2 \cdot 2H_2O \quad (8$$

3. Convert the **solution volume to liters**:

$$500\,\text{mL} \quad \times \quad \frac{1\,\text{L}}{1000\,\text{mL}} \quad = \quad 0.500\,\text{L} \qquad (8.7.9)$$

4. Now use the **molarity equation**:

$$M \quad = \quad \frac{n}{V} \quad = \quad \frac{0.0603\,\text{mol}}{0.500\,\text{L}} \quad = \quad 0.121\,\text{M} \qquad (8.7.10)$$

Therefore,

$$[CoCl_2 \cdot 2H_2O] \quad = \quad 0.121\,\text{M} \qquad (8.7.11)$$

8.7.2 Parts Per Solutions

In the consumer and industrial world, the most common method of expressing the concentration is based on the quantity of solute in a fixed quantity of solution. The "quantities" referred to here can be expressed in mass, in volume, or both (i.e., the *mass* of solute in a given *volume* of solution.) In order to distinguish among these possibilities, the abbreviations (m/m), (v/v) and (m/v) are used.

In most applied fields of Chemistry, (m/m) measure is often used, whereas in clinical chemistry, (m/v) is commonly used, with ***mass expressed in grams* and *volume in mL*.**

One of the more common ways to express such concentrations as "***parts per 100***", which we all know as "***percent***". "***Cent***" is the Latin-derived prefix relating to the number 100 (L. *centum*), as in *century* or *centennial*. It also denotes 1/100th (from L. *centesimus*) as in *centimeter* and the monetary unit *cent*. Percent solutions define the quantity of a solute that is dissolved in a quantity of solution multiplied by 100. Percent solutions can be expressed in terms of mass solute per mass solution (m/m%), or mass solute per volume of solution (m/v%), or volume of solute per volume of solution (v/v%). When making a percent solution, it is important to indicate what units are being used, so that others can also make the solution properly. Also, recall that the solution is the sum of both the solvent and the solute when you are performing percent calculations.

Solution = Solute + Solvent.

Thus, the following equation can be used when calculating percent solutions:

$$\% \text{ Solution} = \frac{\text{Amount of Solute}}{\text{Amount of Solution}} \times 100\% \tag{8.7.12}$$

Example 8.7.3: Percent Solutions

A 7.0% v/v solution of ethanol in water, would contain 7 mL of ethanol in a total of 100 mL of solution. How much water is in the solution?

Solution

For a **percent by volume** solution,

$$\% \ (v/v) = \frac{\text{mL solute}}{\text{mL solution}} \times 100\% \tag{8.7.13}$$

A **7.0% (v/v)** ethanol solution means there are **7.0 mL of ethanol in every 100 mL of solution**.

Since the total solution volume is 100 mL:

$$\text{Volume of Water} = 100.0 \text{ mL} - 7.0 \text{ mL} = 93.0 \text{ mL} \tag{8.7.14}$$

Answer

The solution contains **93.0 mL of water** and **7.0 mL of ethanol**, giving a total solution volume of **100.0 mL**.

Example 8.7.4: Percent Solutions

What is the (m/v)% of a solution if 24.0 g of sucrose is dissolved in a total solution of 243 mL?

Solution

For a **mass/volume percent** solution,

$$\% \ (m/v) = \frac{\text{g solute}}{\text{mL solution}} \times 100\% \tag{8.7.15}$$

Step 1. Identify the known values.

- Mass of sucrose = **24.0 g**
- Volume of solution = **243 mL**

Step 2. Substitute the known values into the equation.

$$\% \ (m/v) = \frac{24.0 \text{ g}}{243 \text{ mL}} \times 100\% \tag{8.7.16}$$

Step 3. Calculate the answer.

$$\% \ (m/v) = 9.88\% \tag{8.7.17}$$

Final Answer:
The solution has a concentration of 9.88% (m/v) sucrose.

Note

A **9.88% (m/v)** sucrose solution contains **9.88 g of sucrose per 100 mL of solution**. Notice that the denominator is the **total volume of the solution**, not the volume of the solvent alone. **Solution = Solute + Solvent**.

Example 8.7.5 Percent Solutions

How many grams of NaCl are required to make 625 mL of a 13.5% solution?

Solution

For a **mass/volume percent** solution,

$$\%\ (m/v) = \frac{\text{g solute}}{\text{mL solution}} \times 100\% \tag{8.7.18}$$

Step 1. Rearrange the equation to solve for the mass of solute.

$$\text{g solute} = \frac{\%\ (m/v) \times \text{mL solution}}{100} \tag{8.7.19}$$

Step 2. Identify the known values.

- Percent solution = **13.5% (m/v)**
- Volume of solution = **625 mL**

Step 3. Substitute the known values.

$$\text{g NaCl} = \frac{(13.5)(625\ \text{mL})}{100} \tag{8.7.20}$$

Step 4. Calculate the answer.

$$\text{g NaCl} = 84.4\ \text{g} \tag{8.7.21}$$

Final Answer:

84.4 g of NaCl are required to prepare **625 mL of a 13.5% (m/v) solution.**

For more dilute solutions, parts per million (10^6 ppm) and parts per billion (10^9; ppb) are used. These terms are widely employed to express the amounts of trace pollutants in the environment.

Like percentage (“part per hundred”) units, ppm and ppb may be defined in terms of masses, volumes, or mixed mass-volume units. There are also ppm and ppb units defined with respect to numbers of atoms and molecules.

The mass-based definitions of ppm and ppb are given here:

For **ppm**:

$$\text{ppm} = \frac{\text{Mass of Solute}}{\text{Mass of Solution}} \times 10^6 \tag{8.7.22}$$

For **ppb**:

$$\text{ppb} = \frac{\text{Mass of Solute}}{\text{Mass of Solution}} \times 10^9 \tag{8.7.23}$$

Both ppm and ppb are convenient units for reporting the concentrations of pollutants and other trace contaminants in water. Concentrations of these contaminants are typically very low in treated and natural waters, and their levels cannot exceed relatively low concentration thresholds without causing adverse effects on health and wildlife. For example, the EPA has identified the maximum safe level of fluoride ion in tap water to be 4 ppm. Inline water filters are designed to reduce the concentration of fluoride and several other trace-level contaminants in tap water (Figure 8.7.2).



(a) (b)

Figure 8.7.2**: Evaluating risk of trace contaminants.** (a) In some areas, trace-level concentrations of contaminants can render unfiltered tap water unsafe for drinking and cooking. (b) Inline water filters inside refridgerators reduce the concentration of solutes in tap water. (credit a: modification of work by Jenn Durfey; credit b: modification of work by "vastateparkstaff"/Wikimedia commons

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When reporting contaminants like lead in drinking water, ppm and ppb concentrations are often reported in mixed unit values of mass/volume. This can be very useful as it is easier for us to think about water in terms of its volume, rather than by its mass. In addition, the density of water is 1.0 g/mL or 1.0 mg/0.001 mL which makes the conversion between the two units easier. For example, if we find that there is lead contamination in water of 4 ppm, this would mean that there are 4 mg of lead in 1,000,000 mg of solution.

However, this is hard for us to think about how much water that is! Since the solution is mostly water, we can calulate the total solution based on the total amount of water (solvent) present, rather than the solvent + the solute, and there will only be negligible error in the total amount of solution present. This allows us to conver the water using from mass into volume, using the density of water as a conversion factor. We know that the density of water is 1 mg per 0.001 mL. This allows us to convert 1,000,000 mg of water int 1,000 mL of water (or more simply, 1 L of water). Thus, 4 ppm of lead, can then be expressed as 4 mg of lead in 1 L of solution. This is more maneagable for us to think about and understand.

A concentration of **4 ppm** means:

$$4\,\text{ppm} = \frac{4\,\text{mg solute}}{1,000,000\,\text{mg solution}} \tag{8.7.24}$$

Although this definition is correct, it is difficult to visualize **1,000,000 mg of water**. Fortunately, most dilute aqueous solutions consist almost entirely of water, so the mass of the solution is approximately equal to the mass of the water present. We can therefore use the density of water to convert the solution mass into a volume.

Using the Density of Water

Because the density of water is approximately **1.00 g/mL**, we know that

$$1.00\,\text{g}\ \text{H}_2\text{O} = 1.00\,\text{mL}\ \text{H}_2\text{O} \tag{8.7.25}$$

Multiplying by the appropriate conversion factor:

$$1,000,000\,\text{mg}\ \text{H}_2\text{O} \quad \times \quad \frac{1.00\,\text{mL}}{1,000\,\text{mg}} \quad = \quad 1,000\,\text{mL} \tag{8.7.26}$$

and we know that there are 1,000 mL in 1.000 L, therefore our equation reduces to:

$$1,000,000\,\text{mg H}_2\text{O} \quad = \quad 1.000\,\text{L} \tag{8.7.27}$$

We can then substitute 1.0 L into our original equation,

For **ppm**:

$$\text{ppm} \approx \frac{\text{mg}}{\text{L}} \tag{8.7.28}$$

Similarly, **ppb** is 1,000 times more dilute and can be represented by,

$$\text{ppb} \approx \frac{\mu\text{g}}{\text{L}} \tag{8.7.29}$$

7.74 Equivalents and Normality

Although **molarity (M)** is the most common concentration unit in chemistry, concentrations of ionic solutions are sometimes expressed in **equivalents (Eq)** or **milliequivalents (mEq)**, particularly in medicine, physiology, and clinical chemistry. Blood electrolyte concentrations, for example, are often reported in **mEq/L**.

One **equivalent (Eq)** represents **one mole of electrical charge**.

- **1 mol Na⊕ = 1 Eq** (one positive charge)
- **1 mol Ca^{2}⊕ = 2 Eq** (two positive charges)
- **1 mol Al^{3}⊕ = 3 Eq** (three positive charges)

Likewise,

- **1 mol Cl⊖ = 1 Eq**
- **1 mol SO_4^{2}⊖ = 2 Eq**
- **1 mol PO_4^{3}⊖ = 3 Eq**

In general,

$$\text{Equivalents} = (\text{moles}) \times (\text{valence}) \tag{8.7.30}$$

where the **valence** is the magnitude of the ionic charge. For example, if **1.00 mol of $CaCl_2$** dissolves in water,

$$\text{CaCl}_2(s) \longrightarrow \text{Ca}^{2+}(aq) + 2\,\text{Cl}^{-}(aq) \tag{8.7.31}$$

the solution contains

- **1 mol Ca^{2}⊕ = 2 Eq**
- **2 mol Cl⊖ = 2 Eq**

Equivalent Weight

The **equivalent weight (Eq Wt)** is the mass of one equivalent of a substance and is calculated by dividing the molar mass by the valence.

$$\text{Equivalent Weight} = \frac{\text{Molar Mass}}{\text{Valence}} \tag{8.7.32}$$

For example, calcium ions have

- Molar mass = **40.08 g/mol**

- Valence = **2**

Therefore,

$$\text{Equivalent Weight} = \frac{40.08\ \text{g/mol}}{2} = 20.04\ \text{g/Eq} \tag{8.7.33}$$

Notice that the units are **grams per equivalent (g/Eq)** rather than g/mol.

Normality

Another concentration unit based on equivalents is **Normality (N)**.

Normality is defined as the **number of equivalents per liter of solution**.

$$N = \frac{\text{Equivalents}}{\text{L of Solution}} \tag{8.7.34}$$

Since

$$\text{Equivalents} = (\text{moles})(\text{valence}) \tag{8.7.35}$$

Normality can also be written as

$$N = M \times z \tag{8.7.36}$$

where

- N = Normality
- M = Molarity
- z = valence factor

Note

Although normality was once widely used in chemistry, **molarity has largely replaced it** in modern laboratory practice because molarity is unambiguous and independent of the type of chemical reaction being studied. Normality and milliequivalents (mEq/L), however, are still commonly used in medicine, physiology, and clinical laboratory testing.

Example 8.7.6: Normality

What is the normality of a 0.100 M solution of $CaCl_2$?

Solution

Step 1. Determine the valence factor.

When calcium chloride dissolves,

$$\text{CaCl}_2(s) \longrightarrow \text{Ca}^{2+}(aq) + 2\,\text{Cl}^-(aq) \tag{8.7.37}$$

Each formula unit produces one calcium ion carrying a **+2 charge**, so

$$z = 2 \tag{8.7.38}$$

Step 2. Use the normality equation.

$$N = M \times z \tag{8.7.39}$$

Step 3. Substitute the known values.

$$N = (0.100\,\mathrm{M})(2) \tag{8.7.40}$$

Step 4. Calculate the answer.

$$N = 0.200\,\mathrm{N} \tag{8.7.41}$$

Final Answer:

A **0.100 M $CaCl_2$** solution has a **normality of 0.200 N**.

Answers

Exercise 8.7.1**: Molarity**

The molarity equation is:

$$M = \frac{n}{V} \tag{8.7.42}$$

where

M = molarity (mol/L) n = moles of solute

Step 1. Rearrange the equation to solve for moles.

$$n = MV \tag{8.7.43}$$

Step 2. Substitute the known values.

$$n = (0.100\ \mathrm{mol/L})(2.50\ \mathrm{L}) \tag{8.7.44}$$

Step 3. Calculate the answer.

$$n = 0.250\ \mathrm{mol\ NaOH} \tag{8.7.45}$$

Final Answer:

A chemist would need **0.250 mol of NaOH** to prepare **2.50 L of a 0.100 M NaOH solution**.

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8.8: Dilutions

Preparing Dilute Solutions from a Stock Solution

A solution of a desired concentration can be prepared by **diluting** a measured volume of a more concentrated solution with additional solvent. A **stock solution** is a solution of known concentration that is used to prepare solutions of lower concentration.

Preparing dilute solutions from a stock solution is often preferred over weighing small amounts of solid solute because very small masses can be difficult to measure accurately. Many chemicals, such as concentrated acids and bases, are also commonly purchased as stock solutions and then diluted to the desired concentration before use.

When a stock solution is diluted, **only the volume of the solution changes**. The amount of dissolved solute remains constant because no solute is added or removed during the dilution process.

Recall that molarity is defined as

$$M = \frac{n}{V} \tag{8.8.1}$$

Rearranging this equation to solve for the number of moles gives

$$n = MV \tag{8.8.2}$$

During a dilution, the number of moles of solute remains constant. Therefore,

$$n_1 = n_2 \tag{8.8.3}$$

Substituting the molarity equation for each solution gives

$$M_1V_1 = M_2V_2 \tag{8.8.4}$$

This relationship is known as the **dilution equation**.

where

- M1 = initial (stock) solution concentration
- V1 = volume of stock solution used
- M2 = final (diluted) solution concentration
- V2 = final volume of the diluted solution

Notice that the dilution equation only works because the **number of moles of solute does not change** during dilution. Adding solvent decreases the concentration by increasing the volume of the solution.



(a) A volume (V_s) containing the desired moles of solute (M_s) is measured from a stock solution of known concentration.

(b) The measured volume of stock solution is transferred to a second volumetric flask.

(c) The measured volume in the second flask is then diluted with solvent up to the volumetric mark [$(V_s)(M_s) = (V_d)(M_d)$].

Figure 8.8.1**: Preparation of a Solution of Known Concentration by Dilution.** (a) A measured volume (V1) of a stock solution with concentration (M1) is transferred to a volumetric flask. (b) Additional solvent is added until the desired final volume (V2) is reached. (c) The resulting solution has a lower concentration (M2), while containing the same number of moles of solute as the original stock solution.

Example 8.8.1: Dilutions

What volume of a 3.00 M glucose stock solution is necessary to prepare 2500 mL of 0.400 M solution?

Solution

During a dilution, the number of moles of solute remains constant, so we use the dilution equation:

$$M_1V_1 = M_2V_2 \tag{8.8.5}$$

Step 1. Identify the known values.

- M1=3.00 M
- V1=?
- M2=0.400 M
- V2=2500 mL

Step 2. Rearrange the equation to solve for V1.

$$V_1 = \frac{M_2V_2}{M_1} \tag{8.8.6}$$

Step 3. Substitute the known values.

$$V_1 = \frac{(0.400\ \text{M})(2500\ \text{mL})}{3.00\ \text{M}} \tag{8.8.7}$$

Notice that the molarity units cancel, leaving the answer in milliliters.

Step 4. Calculate the answer.

$$V_1 = 333\ \text{mL} \tag{8.8.8}$$

Final Answer: A **333 mL** aliquot of the **3.00 M** glucose stock solution should be diluted with water until the **total solution volume is 2500 mL**.

Note

You do **not** add **2167 mL** of water. Instead, you place **333 mL** of the stock solution into a **2500 mL volumetric flask** and then add water **until the total solution volume reaches 2500 mL**. The final volume—not the amount of water added—is what determines the final concentration.

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8.9: Ion Concentrations in Solution

Concentrations of Individual Ions in Solution

Until now, we have described solution concentration in terms of the **total amount of solute** dissolved in a given volume of solution. However, many chemical reactions occur between the **individual ions** present in solution rather than the intact ionic compound.

When an ionic compound dissolves in water, it dissociates into its constituent ions. The resulting cations and anions become surrounded by water molecules through **ion–dipole interactions**. Because these dissolved ions are free to move through solution and carry electrical charge, solutions of soluble ionic compounds are called **strong electrolytes**.

For example, ammonium dichromate dissociates according to the equation

$$(\mathrm{NH_4})_2\mathrm{Cr_2O_7}(s) \longrightarrow 2\,\mathrm{NH_4^+}(aq) + \mathrm{Cr_2O_7^{2-}}(aq) \tag{8.9.1}$$

Notice that **one formula unit** of ammonium dichromate produces **three dissolved ions**:

- two ammonium ions, NH_4^+
- one dichromate ion, $Cr_2O_7^{2-}$

The same relationship applies on the molar scale. Dissolving **1 mole** of ammonium dichromate produces

- **2 moles NH_4^+**
- **1 mole $Cr_2O_7^{2-}$**

for a total of **3 moles of dissolved ions** (Figure 8.9.1)

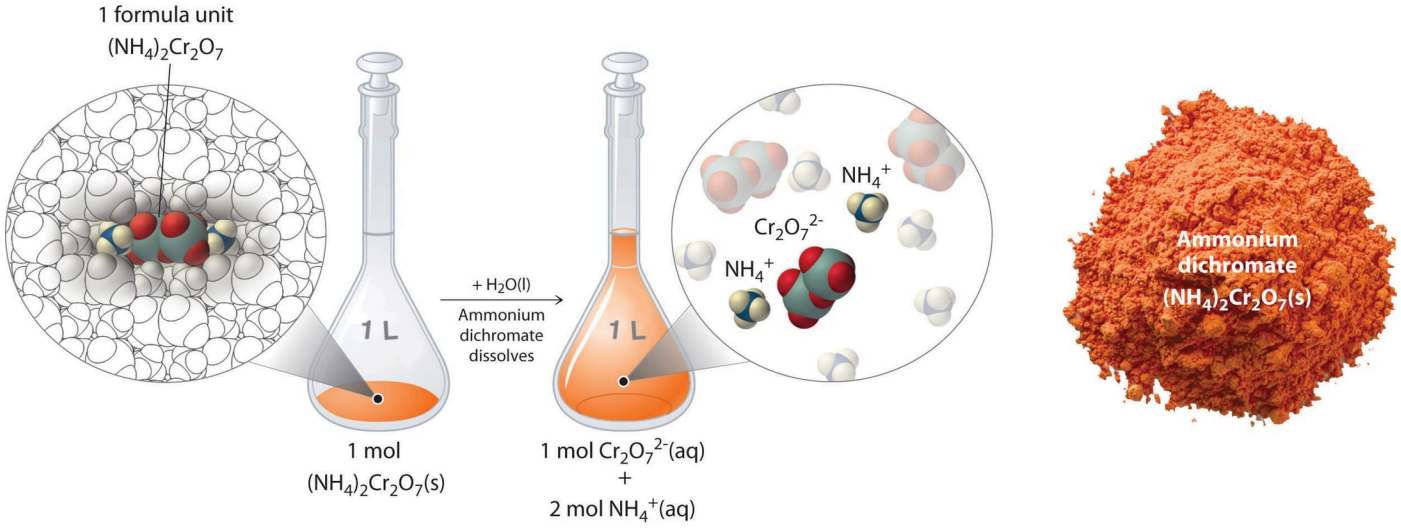


Figure 8.9.1: Dissolution of 1 mol of an Ioncic Compound. Dissoliving 1 mol of ammonium dichromate formula units in water produces 1 mol of $Cr_2O_7^{2-}$ anions and 2 mol of NH_4^+ cations. (Water molecules are omitted from a molecular view of the solution for clarity.)

Calculating Ion Concentrations

The concentration of each ion depends on **how many of that ion are produced** when one formula unit dissolves.

Suppose a solution contains

$$\mathbf{1.43\ M\ (NH_4)_2Cr_2O_7} \tag{8.9.2}$$

Since each formula unit produces **one dichromate ion**,

$$\mathbf{[Cr_2O_7^{2-}] = 1.43\ M} \tag{8.9.3}$$

Each formula unit also produces **two ammonium ions**, so

$$\mathbf{[NH_4^+] = 2(1.43\ M) = 2.86\ M} \tag{8.9.4}$$

Therefore, the **total concentration of dissolved ions** is

$$\mathbf{2.86\ M + 1.43\ M = 4.29\ M} \tag{8.9.5}$$

Note

Notice that the **molarity of the solution remains 1.43 M**, because the solution originally contained 1.43 moles of ammonium dichromate per liter. However, after dissociation there are **4.29 moles of dissolved ions per liter**. It is the individual ions—not the original formula units—that participate in most aqueous chemical reactions.

Example 8.9.1 Ion Concentration

What are the concentrations of all dissolved species in the following aqueous solutions?

- 0.21 M NaOH
- 3.7 M $(CH_3)_2CHOH$
- 0.032 M $In(NO_3)_3$

Solution Strategy

1. Determine whether the solute is an **electrolyte** or a **nonelectrolyte**.
2. If it is a **nonelectrolyte**, the dissolved molecules remain intact.
3. If it is an **electrolyte**, write the dissociation equation and use the coefficients to determine the concentration of each ion.

For NaOH,

$$\mathbf{NaOH}(aq) \rightarrow \mathbf{Na^+}(aq) + \mathbf{OH^-}(aq) \tag{8.9.6}$$

Then,

$$\mathbf{[Na^+]} = \mathbf{0.21\,M} \tag{8.9.7}$$

$$\mathbf{[OH^-]} = \mathbf{0.21\,M} \tag{8.9.8}$$

For Isopropanol (there is no dissociation!),

$$\mathbf{(CH_3)_2CHOH}(aq) \tag{8.9.9}$$

Then,

$$[(CH_3)_2CHOH] = 3.7\,M \tag{8.9.10}$$

For Indium Nitrate,

$$In(NO_3)_3(aq) \rightarrow In^{3+}(aq) + 3\,NO_3^-(aq) \tag{8.9.11}$$

Then,

$$[In^{3+}] = 0.032\,M \tag{8.9.12}$$

$$[NO_3^-] = 3(0.032\,M) = 0.096\,M \tag{8.9.13}$$

The concentrations of individual ions determined in this section can also be used to calculate equivalent concentrations (normality), as described in Section 8.7.4.

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8.10: Focus on the Environment- Lead Pollution

History of Lead Use in the United States

In Chapter 6, you were introduced the EPA and how air quality parameters are monitored to determine pollution levels. One of the six major parameters that is monitored as a result of the Clean Air Act is lead. Lead occurs naturally in the Earth's crust at very low levels, ~ 0.001%, and appears as a blue-gray metal that is soft and dense. It has been used extensively in the United States in many different products, including batteries and metal mixtures, as soldering material for pipes and in pottery, crystal glass, and other familiar commercial products. Lead use was especially high in exterior paints and as an additive in gasoline (Fig 8.10.1). Due to rising health concerns, the use of lead in many products has been phased out and discontinued. However, lead contamination within the soil, water, and air is still problematic and causes increased risk to public health.

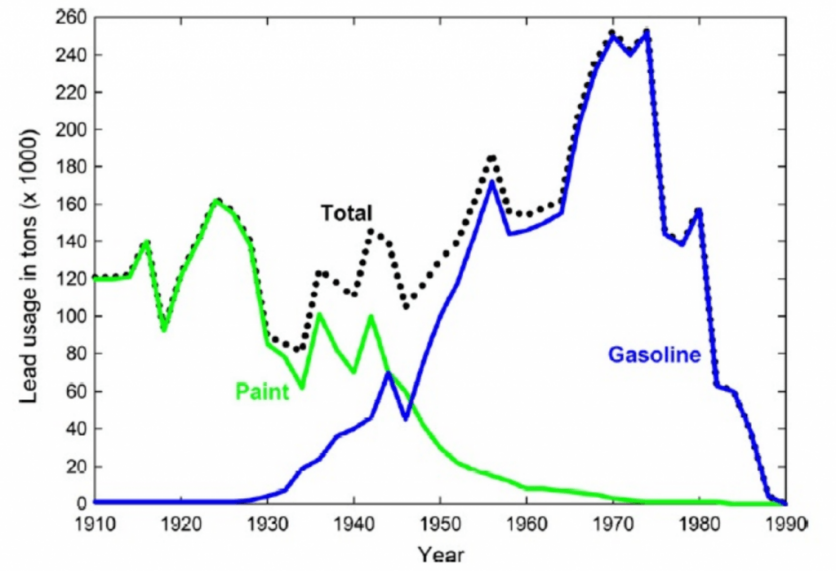


Figure 8.10.1**: History of Lead Usage in Paints and Gasoline During most of the 20th Century.** The graph shows the early dominance of lead-based paints followed by the boom in transportation, resulting in the high use of leaded gasoline. The decline after the mid-1970s was due to controls put in place by the EPA to eliminate leaded gasoline. Source: Filippelli, et al (2005) used by permission.

The National Ambient Air Quality Standards (NAAQS) for lead are set at an upper limit of 0.15 micrograms per cubic meter Pb in total suspended particles as a 3-month average. As you can see from figure 8.10.2, atmospheric lead levels were very high through the mid-1990's after which time we have seen a dramatic drop in atmospheric lead levels. This spike in lead levels is largely due to vehicle emissions when lead was used as an additive in gasoline. In 1970, when the negative health effects of lead were fully recognized, the EPA started a reduction program to eliminate the use of lead in gasoline. The full ban on leaded gasoline when into effect in 1996.

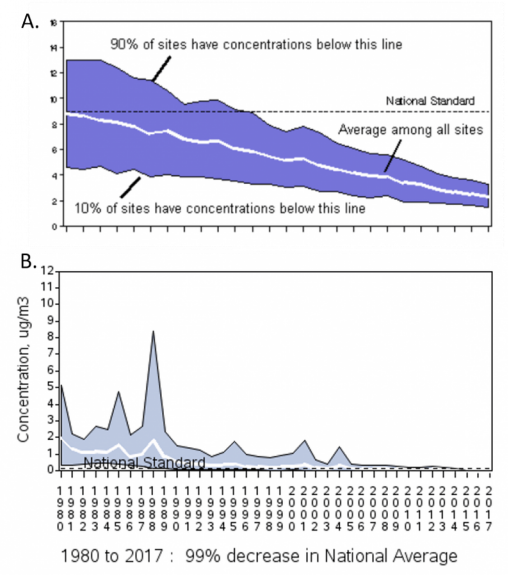


Figure 8.10.2**: Atmospheric Lead Levels from 1980 to 2014.** (A) How to interpret air quality graphs from the EPA. the blue band shows the distribution of air pollution levels among the trend sites, displaying the middle 80 %. The white line represents the average among all the trend sites. Ninety percent of sites have concentrations below the top line, while ten percent of sites have concentrations below the bottom line. (B) Annual maximum 3-month average of atmospheric lead levels, demonstrating a 99% decrease in lead pollution levels from 1980 to 2017. Source: EPA

The use of tetraethyllead (TEL) was identified by General Motors as a fuel additive that increased the overall octane rating of gasoline. This allowed engine compression to be raised substantially leading to increased vehicle performance and greater fuel economy.

TEL is produced by reacting chloroethane with a sodium–lead alloy

$$\mathrm{4\,NaPb} \quad + \quad \mathrm{4\,CH_3CH_2Cl} \quad \longrightarrow \quad \mathrm{(CH_3CH_2)_4Pb} \quad + \quad \mathrm{4\,NaCl} \quad + \quad \mathrm{3\,Pb} \tag{8.10.1}$$

The product is recovered by steam distillation, leaving a sludge of lead and sodium chloride waste materials. Despite decades of research, no reactions were found to improve upon this rather difficult process that involves metallic sodium and converts only 25% of the lead to TEL. TEL is a viscous colorless liquid. Because TEL is charge neutral and contains an exterior of carbon groups, it is highly lipophilic (fat-loving) and soluble in gasoline.

When leaded gasoline is burned, it produces not only carbon dioxide and water, but also lead

$$\mathrm{(CH_3CH_2)_4Pb} \quad + \quad \mathrm{13\,O_2} \quad \longrightarrow \quad \mathrm{8\,CO_2} \quad + \quad \mathrm{10\,H_2O} \quad + \quad \mathrm{Pb} \tag{8.10.2}$$

The lead produced can also become oxidized during combustion forming lead (II) oxide

$$\mathrm{2\,Pb} \quad + \quad \mathrm{O_2} \quad \longrightarrow \quad \mathrm{2\,PbO} \tag{8.10.3}$$

The formation of Pb and PbO inside a car engine will quickly over-accumulate and cause major damage to the engine. Thus, lead scavenging molecules also had to be added to gasoline to react with the lead products produced during combustion. Typically, 1,2-dibromoethane and 1,2-dichloroethane were used for this process. These agents react with the lead by-products and form volatile lead (II) bromide and lead (II) chloride, which can then be flushed into the atmosphere from the engine.

Increased atmospheric levels of lead caused by automobile use correlated strongly with elevated blood levels of lead within the population.

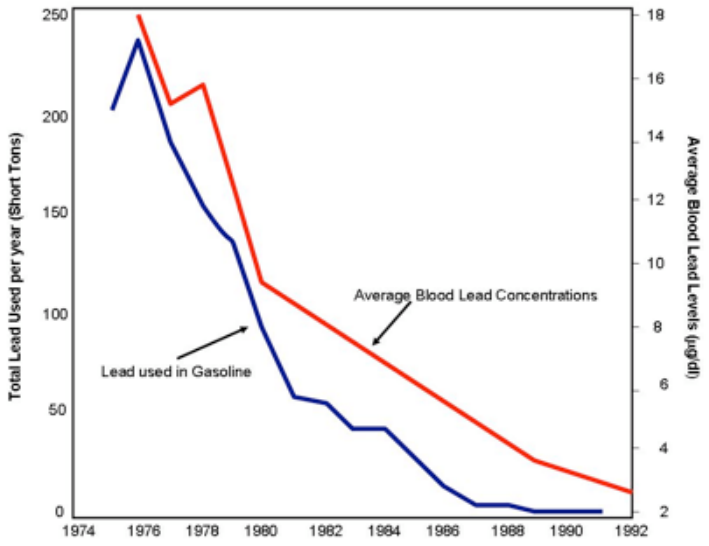


Figure 8.10.3**:** Decline in average blood lead levels in U.S. children and in total led used per year in gasoline for years 1974-1992 (Adapted from U.S.EPA 1999).

The Biological Effects of Lead

Once lead is absorbed into the body it is not excreted. Instead it accumulates in mineralizing tissues such as the bones and the teeth, or in soft tissues such as the liver, kidneys, and brain. The brain is highly sensitive. A Cincinnati lead study demonstrated that childhood exposure to lead causes gray matter loss within the brain, especially in frontal areas involved in executive function and decision making (Figure 8.10.4).

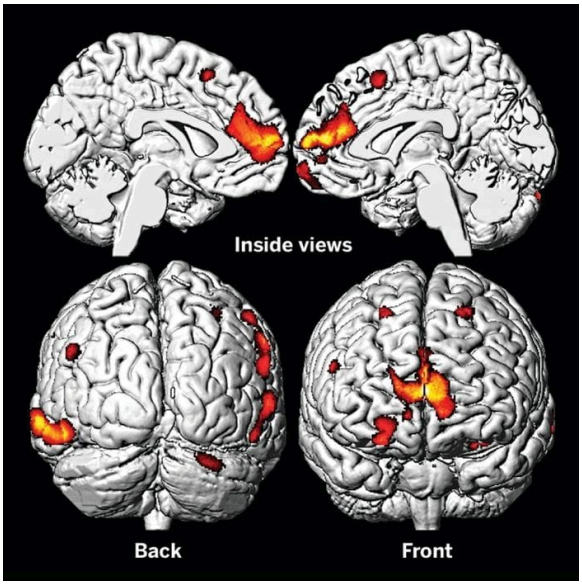


Figure 8.10.4**:** Childhood Exposure to Lead Reduces Brain Size. The brains of adults who were exposed to lead as children show decreased volume, especially in the prefrontal cortex on MRI. Areas of volume loss are shown in color over a template of a normal brain. Source: Cecil, KM, et al.

Acute exposure to lead can cause lead poisoning and result in abdominal pain, constipation, headaches, irritability, memory

problems, inability to have children, and tingling in the hands and feet. It causes almost 10% of intellectual disability of otherwise unknown cause and can result in behavioral problems. Some of the effects are permanent. In severe cases anemia, seizures, coma, or death may occur.

Exposure to lead can occur by contaminated air, water, dust, food, or consumer products Children are at greater risk as they are more likely to put objects in their mouth such as those that contain lead paint and absorb a greater proportion of the lead that they eat. Exposure at work is a common cause of lead poisoning in adults with certain occupations at particular risk. Diagnosis is typically by measurement of the blood lead level. The Centers for Disease Control (US) has set the upper limit for blood lead for adults at 10 µg/dl (10 µg/100 g) and for children at 5 µg/dl.

An Interesting Correlation: Crime and Blood-Levels of Lead

A number of studies over the last decade have shown a strong correlation between preschool blood lead levels and subsequent crime rates, especially violent crimes occurring 20 years later (Figure 8.10.5).

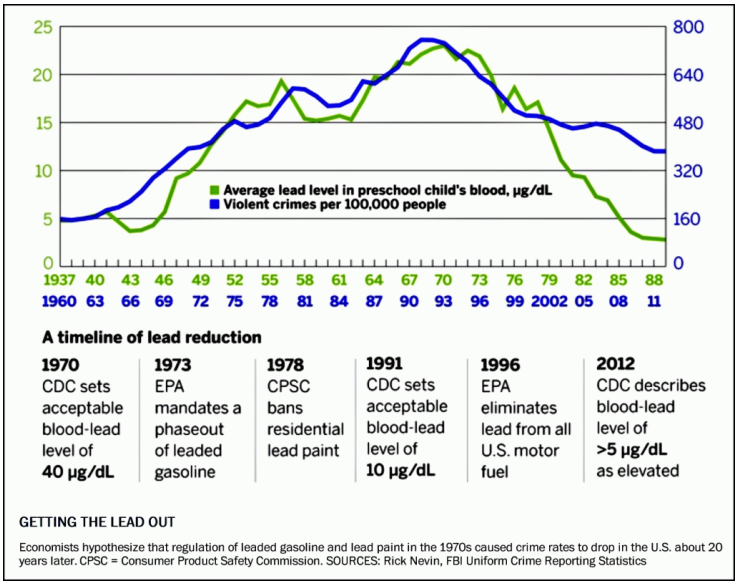


Figure 8.10.5**: Correlation of Preschool Aged Blood Lead Levels and Violent Crimes Committed 23 Years Later**.

In the early 1990's homicide and violent crimes had reached an all time high, with no end in sight. However, by the end of the 1990's there had been a 40% drop in violent crimes throughout the country. Many hypotheses for this rapid decline have been proposed, including an increase in the number of people incarcerated and an increase in the number of police officers. However, blood lead levels show a very strong correlation with the incidence of violent crimes with a lag time of approximately 20 years. In addition, animal studies, including hamsters and cats have shown that lead exposure increases or potentiates aggressive behavior. Furthermore, data compiled by Rick Nevin, from other countries (France, West Germany, Italy, and Australia) that have different incarceration and policing rates, show similar trends in violent crimes with childhood blood lead levels. Thus, there is compelling evidence to suggest that increased exposure to lead in childhood from the use of leaded gasoline, explains, at least in part, the elevation of violent crime rates throughout the 1980's and early 1990's within the United States.

Current Problems and Concerns

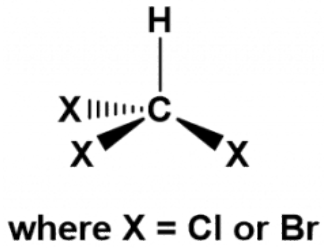
While the use of lead has been extremely curtailed over the last 40 to 50 years, lead can still be found in elevated levels within soils, especially in inner city and industrial areas. In addition, lead was previously used for the construction of water pipes as it is durable and malleable. Lead is not used any more for the construction of pipes, but older cities, such as Flint still have lead piping, as well as copper and iron water pipes that used lead soldering within the pipes joints and connections. In April of 2014, this became a major problem for residents living in Flint, Michigan. The City of Flint, MI was in dire financial problems, and in an effort to save money, decided to build a new water pipeline from Lake Huron to supply drinking water for the area. Cost savings

were estimated to be approximately $10 million/year. However, the pipeline would take a few years to complete. Thus, to save money right away, the City of Flint decided to switch over the town's water temporarily to the Flint River while the new pipeline was being finished. However, river water can be harder to treat due to greater fluctuations in runoff residues, and almost immediately residents of Flint, MI began complaining of foul smelling, off color water coming from their taps (Fig. 8.10.6).



Figure 8.10.6**: LeeAnne Walters displays tap water samples at a public meeting in January 2015.** Source: Ladapo, J.A, et. al. (2017).

Analysis of the water initially showed high levels of fecal coliform bacteria, which caused Flint, MI to issue boil advisories and to increase the amount of chlorine being used to treat the water. This in turn increased the production of trihalomethanes. Trihalomethanes form during a reaction of chlorine disinfectants in the water with organic materials that are present, such as those created by the algae present in the Flint River. Trihalomethanes have been linked with many health concerns, including liver, kidney and lung problems and also create foul smelling and tasting water. They are also dangerous when inhaled, making showering in hot, contaminated water a serious health risk.



Trihalomethanes are produced when added disinfectants react with organic materials (ie algae in the river water)

Thus, in an attempt to reduce the formation of trihalomethane by-products, the City of Flint began adding more $FeCl_3$ to the water to help remove the additional organic materials in this water source. However, they failed to add any corrosion control molecules, such as orthophosphate. Many water treatment facilities use low concentrations of orthophosphates to interact with lead in pipes and form an insoluble lead phosphate lining that does not leach into the water supply (Figure 8.18). The lack of corrosion control by the City of Flint combined with the increased amounts of $FeCl_3$, caused the amount of Cl^- ions present to increase dramatically. The result was an overall increase in the corrosion potential, as measured by a chloride to sulfate mass ratio, from 0.45 for the Detroit Water Supply to 1.60 for the new Flint River Water Supply. With this corrosion potential, oxygen molecules within the water began to oxidize and release soluble forms of lead into the water system (Figure 8.10.7). In addition to oxidized lead by-products, oxidized forms of iron were also released causing more discoloration of the water.

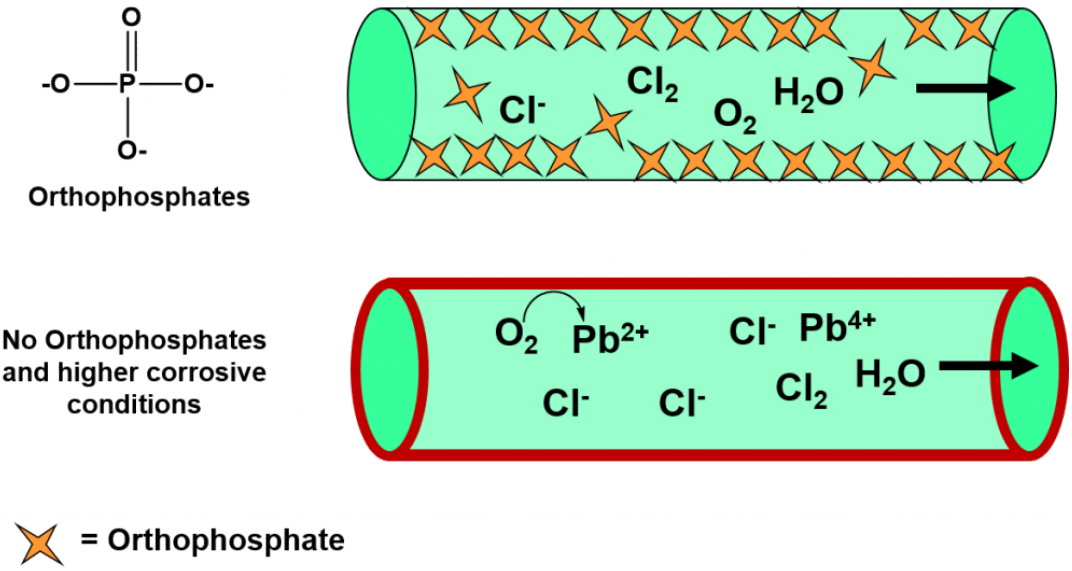


Figure 8.10.7**: The Process of Corrosion during the Flint, Michigan Water Crisis**.

For an interactive animation of this chemical process, watch this

Scientific American Video – Corrosive Chemistry: How Lead Ended Up in Flint's Drinking Water.

Due to public outcry and the refusal of the City of Flint to act on the poor quality of water, Virgina Tech began a water testing program and found extremely high lead levels in many homes in Flint, MI. The CDC states that there are no safe levels of lead that can be consumed and EPA standards limit the lead content of drinking water to 15 ppb. The highest sample recorded by Virginia Tech was 13,000 ppb from a sample at LeeAnne Walters' home (Figure 8.10.8). The City of Flint went back to using Detroit's Water Supply in October of 2015. However, the risk of children in the area to the exposure of lead above the CDC's blood level limits was doubled during this time frame (Figure 8.19). Several pending lawsuits are currently underway due to the negligence of the City of Flint and water quality regulatory institutions in the region.

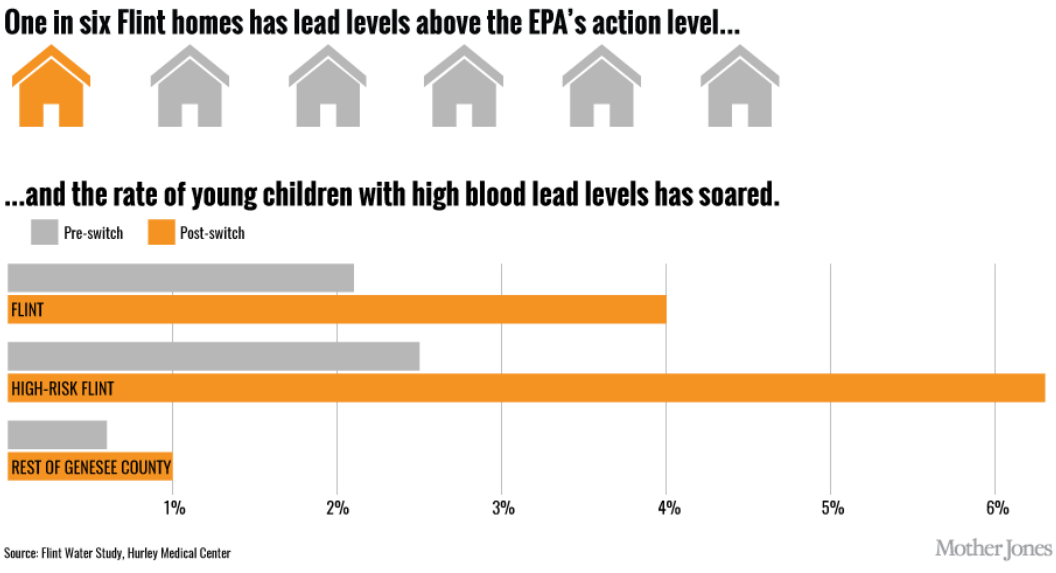


Figure 8.10.8**: Comparison of Lead-Blood Levels in Flint, MI, Pre- and Post-Switching to the Flint River Water Source.** Upper diagram indicates that water quality in 1 out of 6 homes in Flint, MI tested above the EPA safety limits for lead following

the switch to the Flint River water source. Lower panel shows lead-blood levels for children routinely tested for lead-blood levels in the area both pre- and post- the switch to the new water source. Source: Flint Water Study

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Suggested Assignment: Teachers can download a discussion-based assignment on Environmental Injustice and the impact of toxic water pollution in Flint, MI

Flint Water Crisis Environmental Justice Assignment.

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8.11: Summary

To ensure that you understand the material in this chapter, you should review the meanings of the bold terms in the following summary and ask yourself how they relate to the topics in the chapter.

A **solution** is a homogeneous mixture. The major component is the **solvent**, while the minor component is the **solute**. Solutions can have any phase; for example, an **alloy** is a solid solution. Solutes are **soluble** or **insoluble**, meaning they dissolve or do not dissolve in a particular solvent. The terms **miscible** and **immiscible**, instead of soluble and insoluble, are used for liquid solutes and solvents. The statement *like dissolves like* is a useful guide to predicting whether a solute will dissolve in a given solvent.

Dissolving occurs by **solvation**, the process in which particles of a solvent surround the individual particles of a solute, separating them to make a solution. For water solutions, the word **hydration** is used. If the solute is molecular, it dissolves into individual molecules. If the solute is ionic, the individual ions separate from each other, forming a solution that conducts electricity. Such solutions are called **electrolytes**. If the dissociation of ions is complete, the solution is a **strong electrolyte**. If the dissociation is only partial, the solution is a **weak electrolyte**. Solutions of molecules do not conduct electricity and are called **nonelectrolytes**.

The amount of solute in a solution is represented by the **concentration** of the solution. The maximum amount of solute that will dissolve in a given amount of solvent is called the **solubility** of the solute. Such solutions are **saturated**. Solutions that have less than the maximum amount are **unsaturated**. Most solutions are unsaturated, and there are various ways of stating their concentrations. **Mass/mass percent**, **volume/volume percent**, and **mass/volume percent** indicate the percentage of the overall solution that is solute. **Parts per million (ppm)** and **parts per billion (ppb)** are used to describe very small concentrations of a solute. **Molarity**, defined as the number of moles of solute per liter of solution, is a common concentration unit in the chemistry laboratory. **Equivalents** express concentrations in terms of moles of charge on ions. When a solution is diluted, we use the fact that the amount of solute remains constant to be able to determine the volume or concentration of the final diluted solution. Solutions of known concentration can be prepared either by dissolving a known mass of solute in a solvent and diluting to a desired final volume or by diluting the appropriate volume of a more concentrated solution (a **stock solution**) to the desired final volume.

Key Takeaway

- Solution concentrations are typically expressed as molarity and can be prepared by dissolving a known mass of solute in a solvent or diluting a stock solution.

Conceptual Problems

1. Which of the representations best corresponds to a 1 M aqueous solution of each compound? Justify your answers.
    1. NH_3
    2. HF
    3. $CH_3CH_2CH_2OH$
    4. Na_2SO_4
2. Which of the representations shown in Problem 1 best corresponds to a 1 M aqueous solution of each compound? Justify your answers.
    1. CH_3CO_2H
    2. NaCl
    3. Na_2S
    4. Na_3PO_4
    5. acetaldehyde (CH_3CHO)
3. Would you expect a 1.0 M solution of $CaCl_2$ to be a better conductor of electricity than a 1.0 M solution of NaCl? Why or why not?
4. An alternative way to define the concentration of a solution is *molality*, abbreviated *m*. Molality is defined as the number of moles of solute in 1 kg of *solvent*. How is this different from molarity? Would you expect a 1 M solution of sucrose to be more

or less concentrated than a 1 *m* solution of sucrose? Explain your answer.
5. What are the advantages of using solutions for quantitative calculations?

Answer

1a) **NH_3** is a weak base that partially reacts with water by accepting a proton (H^+) from a water molecule, establishing an equilibrium that yields a small amount of NH_4^+ and OH^- ions. Because most of the ammonia remains as neutral molecules alongside a few ions, **beaker #2** is the best representation. **b) HF** is a weak acid. Despite fluorine's high electronegativity, the H-F bond is exceptionally strong, meaning the molecule only partially dissociates into H_3O^+ and F^- ions in water. Since it exists primarily as intact HF molecules in equilibrium with a small concentration of ions, **beaker #2** is the best representation. **c) $CH_3CH_2CH_2OH$, Propanol** is a covalent, non-electrolyte compound. While it dissolves well in water due to hydrogen bonding, it does not dissociate into ions at all. Because it remains entirely in its molecular form, **beaker #3** is the correct choice. **d) Na_2SO_4** is a soluble ionic compound and a strong electrolyte. It dissociates completely into $2Na^+$ and SO_4^{2-} ions when dissolved in water, leaving no intact formula units. Therefore, **beaker #1** is the correct choice.

3) Yes, because when $CaCl_2$ dissociates it will form 3 ions (1 Ca^{2+} and 2 Cl^- ions) whereas NaCl will only dissociate into 2 ions (Na^+ and a Cl^-) for each molecule. Thus, $CaCl_2$ will generate more ions per mole than 1 mole of NaCl and be a better conductor of electricity.

5) If the amount of a substance required for a reaction is too small to be weighed accurately, the use of a solution of the substance, in which the solute is dispersed in a much larger mass of solvent, allows chemists to measure the quantity of the substance more accurately.

Numerical Problems

1. Calculate the number of grams of solute in 1.000 L of each solution.
    1. 0.2593 M $NaBrO_3$
    2. 1.592 M KNO_3
    3. 1.559 M acetic acid
    4. 0.943 M potassium iodate
2. Calculate the number of grams of solute in 1.000 L of each solution.
    1. 0.1065 M BaI_2
    2. 1.135 M Na_2SO_4
    3. 1.428 M NH_4Br
    4. 0.889 M sodium acetate
3. If all solutions contain the same solute, which solution contains the greater mass of solute?
    1. 1.40 L of a 0.334 M solution or 1.10 L of a 0.420 M solution
    2. 25.0 mL of a 0.134 M solution or 10.0 mL of a 0.295 M solution
    3. 250 mL of a 0.489 M solution or 150 mL of a 0.769 M solution
4. Complete the following table for 500 mL of solution.

Practice table for solution concentrations

Compound	Mass (g)	Moles	Concentration (M)
calcium sulfate	4.86		
acetic acid		3.62	
hydrogen iodide dihydrate			1.273
barium bromide	3.92		
glucose			0.983
sodium acetate		2.42	

5. What is the concentration of each species present in the following aqueous solutions?
    1. 0.489 mol of $NiSO_4$ in 600 mL of solution

2. 1.045 mol of magnesium bromide in 500 mL of solution
3. 0.146 mol of glucose in 800 mL of solution
4. 0.479 mol of $CeCl_3$ in 700 mL of solution

6. What is the concentration of each species present in the following aqueous solutions?
   1. 0.324 mol of K_2MoO_4 in 250 mL of solution
   2. 0.528 mol of potassium formate in 300 mL of solution
   3. 0.477 mol of $KClO_3$ in 900 mL of solution
   4. 0.378 mol of potassium iodide in 750 mL of solution
7. What is the molar concentration of each solution?
   1. 8.7 g of calcium bromide in 250 mL of solution
   2. 9.8 g of lithium sulfate in 300 mL of solution
   3. 12.4 g of sucrose ($C_{12}H_{22}O_{11}$) in 750 mL of solution
   4. 14.2 g of iron(III) nitrate hexahydrate in 300 mL of solution
8. What is the molar concentration of each solution?
   1. 12.8 g of sodium hydrogen sulfate in 400 mL of solution
   2. 7.5 g of potassium hydrogen phosphate in 250 mL of solution
   3. 11.4 g of barium chloride in 350 mL of solution
   4. 4.3 g of tartaric acid ($C_4H_6O_6$) in 250 mL of solution
9. Give the concentration of each reactant in the following equations, assuming 20.0 g of each and a solution volume of 250 mL for each reactant.
   1. $BaCl_2(aq) + Na_2SO_4(aq) \rightarrow$
   2. $Ca(OH)_2(aq) + H_3PO_4(aq) \rightarrow$
   3. $Al(NO_3)_3(aq) + H_2SO_4(aq) \rightarrow$
   4. $Pb(NO_3)_2(aq) + CuSO_4(aq) \rightarrow$
   5. $Al(CH_3CO_2)_3(aq) + NaOH(aq) \rightarrow$
10. An experiment required 200.0 mL of a 0.330 M solution of Na_2CrO_4. A stock solution of Na_2CrO_4 containing 20.0% solute by mass with a density of 1.19 g/cm^3 was used to prepare this solution. Describe how to prepare 200.0 mL of a 0.330 M solution of Na_2CrO_4 using the stock solution.
11. Calcium hypochlorite [$Ca(OCl)_2$] is an effective disinfectant for clothing and bedding. If a solution has a $Ca(OCl)_2$ concentration of 3.4 g per 100 mL of solution, what is the molarity of hypochlorite?
12. Phenol (C_6H_5OH) is often used as an antiseptic in mouthwashes and throat lozenges. If a mouthwash has a phenol concentration of 1.5 g per 100 mL of solution, what is the molarity of phenol?
13. If a tablet containing 100 mg of caffeine ($C_8H_{10}N_4O_2$) is dissolved in water to give 10.0 oz of solution, what is the molar concentration of caffeine in the solution?
14. A certain drug label carries instructions to add 10.0 mL of sterile water, stating that each milliliter of the resulting solution will contain 0.500 g of medication. If a patient has a prescribed dose of 900.0 mg, how many milliliters of the solution should be administered?

Answers

1) a. 39.13 g b. 161.0 g c. 93.57 g d. 201.8 g

3) a. 1.40 L of a 0.334 M solution, b. 25.0 mL of a 0.134 M solution, c. 150 mL of a 0.769 M solution

5) a. 0.815 M, b. 2.09 M, c. 0.182 M, d. 0.684 M

7) a. 0.174 M, b. 0.297 M, c. 0.048 M, d. 0.135 M

9) a. $BaCl_2$ = 0.384 M, Na_2SO_4 = 0.563 M, b. $Ca(OH)_2$ = 1.08 M, H3PO4 = 0.816 M, c. $Al(NO_3)_3$ = 0.376 M, H_2SO_4 = 0.816 M, d. $Pb(NO_3)_2$ = 0.242 M, $CuSO_4$ = 0.501 M, e. $Al(CH_3CO_2)$ = 0.392 M, NaOH = 2.00 M

11) 0.48 M ClO^-

13) 1.74×10^{-3} M caffeine

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9: CHAPTER 9 - ACIDS, BASES, AND PH IN AQUEOUS SYSTEMS

9.1: Acids and Bases in Everyday Life

9.2: Arrhenius Acids and Bases (Review)

9.3: Bronsted-Lowry Acids and Bases

9.4: Conjugate Acid-Base Pairs

9.5: Acid and Base Strength

9.6: Autoionization of Water

9.7: pH and pOH

9.8: Neutralization Reactions

9.9: Buffers - Maintaining a Stable pH

9.10: Focus on the Environment - Ocean Acidification

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9.1: Acids and Bases in Everyday Life

Chemistry is all around us, and few topics illustrate this better than acids and bases. Every day, you encounter acidic and basic substances without giving them much thought. The tart flavor of lemonade, the vinegar used in salad dressing, the soap used to wash your hands, the baking soda in cookies, and the antacid tablet used to relieve heartburn all owe their properties to acid-base chemistry.

Although these substances may seem very different, they share a common feature—they participate in chemical reactions involving hydrogen ions (H^+). Understanding how acids and bases behave helps explain countless natural processes, from digestion and food preservation to the chemistry of our oceans and the functioning of every living cell.

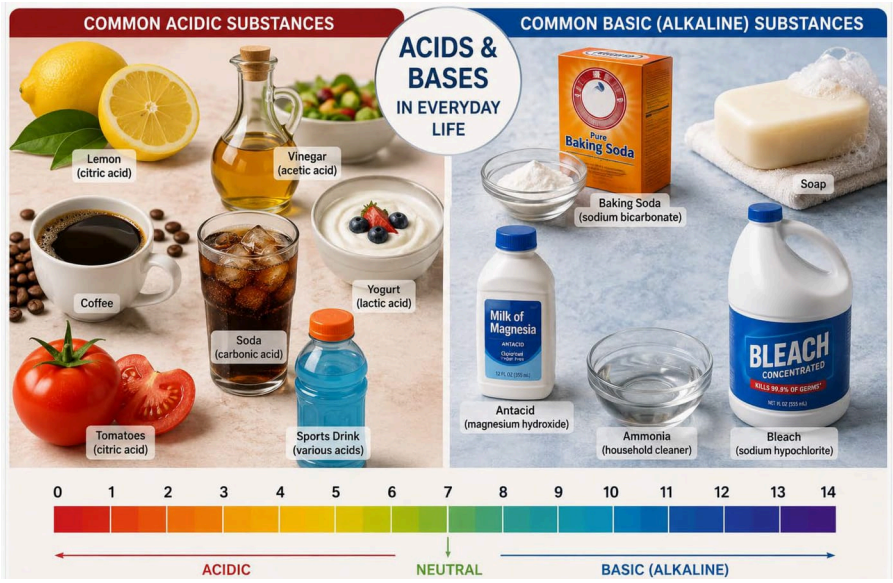


Figure 9.1.1**: Collage of common acidic and basic substances.** Acidic examples include lemon, vinegar, tomatoes, coffee, soda, yogurt, and sports drinks. Basic examples include baking soda, soap, household bleach, ammonia cleaner, and milk of magnesia. A pH scale along the bottom illustrates that acidic substances generally have pH values below 7, neutral solutions have a pH of 7, and basic (alkaline) substances have pH values above 7.

Recognizing Acids and Bases

Long before scientists understood the molecular behavior of acids and bases, people recognized them by their observable properties.

Many acidic foods have a sour taste. Citrus fruits contain citric acid, vinegar contains acetic acid, and yogurt contains lactic acid. These compounds are responsible for the characteristic tang that many people enjoy.

Basic (or **alkaline**) substances often have a bitter taste and may feel slippery to the touch. Soap feels slippery because it is slightly basic, while baking soda has a mildly bitter taste. Although these characteristics can sometimes help identify an acid or base, **you should never taste or touch an unknown chemical.** Many acids and bases can cause serious chemical burns.

Fortunately, chemists have much safer ways to identify these substances.

> **Safety Box**:
>
> Never taste or directly touch chemicals in the laboratory. Many acids and bases are corrosive and can damage skin or eyes. Chemists rely on indicators and laboratory instruments—not taste—to identify unknown substances.

Using Indicators

Certain compounds, called **acid-base indicators**, change color depending on whether they are placed in an acidic or basic solution. These color changes provide a simple way to estimate whether a solution is acidic, basic, or nearly neutral.

One of the oldest indicators is **litmus paper**. Blue litmus paper turns red in an acidic solution, while red litmus paper turns blue in a basic solution.

Another commonly used indicator is **phenolphthalein**, which is colorless in acidic solutions but turns bright pink in basic solutions.

Today, laboratories often use electronic **pH meters**, which measure acidity much more precisely. Later in this chapter, you'll learn what pH means and how it relates to the concentration of hydrogen ions in solution.

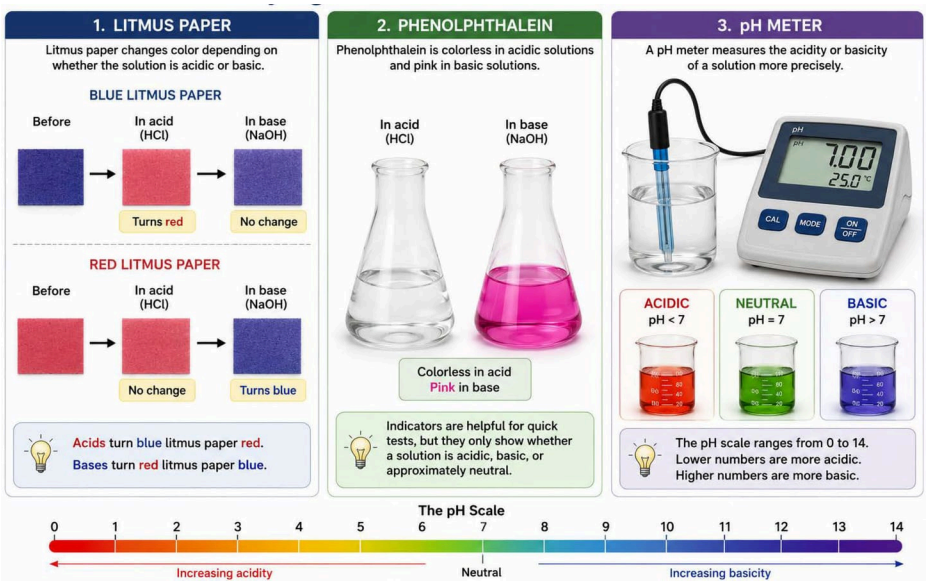


Figure 9.1.2**: Identifying Acids and Bases with Indicators.** Three common methods used to identify acids and bases. Blue litmus paper turns red in acidic solutions but remains blue in basic solutions. Red litmus paper turns blue in basic solutions but remains red in acidic solutions. Phenolphthalein is colorless in acidic solutions and pink in basic solutions. A digital pH meter provides a numerical measurement of solution acidity or basicity, where pH values below 7 are acidic, pH 7 is neutral, and pH values above 7 are basic.

When Acids and Bases Meet

One of the most important properties of acids and bases is that they react with one another in a process called **neutralization**.

For example, your stomach naturally produces hydrochloric acid (HCl), which helps digest food and destroys many harmful microorganisms that enter with your meals. Occasionally, the stomach produces more acid than needed, leading to the familiar burning sensation known as heartburn.

Many antacid tablets contain weak bases such as calcium carbonate ($CaCO_3$) or magnesium hydroxide [$Mg(OH)_2$]. These compounds react with excess stomach acid, reducing its acidity and providing relief.

Neutralization reactions are also widely used outside the human body. Farmers add limestone to acidic soils to improve crop growth, wastewater treatment facilities carefully adjust pH before releasing treated water into rivers, and swimming pools are routinely monitored to keep their pH within a safe range.

Chemists study acids and bases because understanding these reactions allows us to predict and control many important chemical processes.



Figure 9.1.3: When Acids and Bases Meet: Neutralization in Everyday Life. Three examples of acid-base neutralization in everyday life. Antacid tablets neutralize excess stomach acid to relieve heartburn. Agricultural lime is spread on acidic soils to improve conditions for plant growth. Swimming pool chemicals are added to maintain a safe pH range by neutralizing excess acidity or basicity.

Looking Beyond Everyday Observations

The properties we've discussed—sour taste, slippery feel, indicator color changes, and neutralization—allow us to recognize acids and bases in everyday life. However, these observations do not explain *why* acids and bases behave the way they do.

Early chemists developed the **Arrhenius definition** to explain many acid-base reactions in water. Although this model successfully describes many familiar acids and bases, it cannot explain every acid-base reaction. In the next section, you'll briefly review the Arrhenius model before learning the broader Brønsted–Lowry definition, which explains acid-base chemistry in a much wider variety of situations.

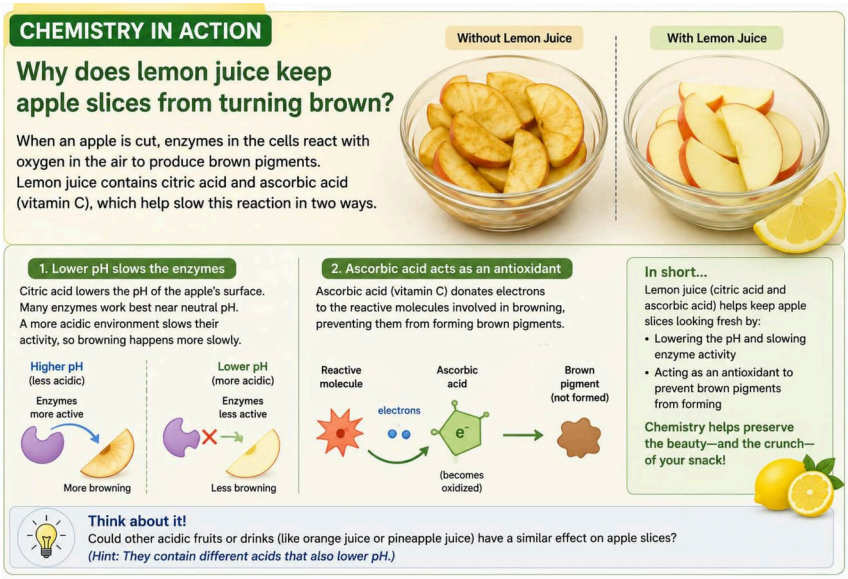


Figure 9.1.4: Chemistry in Action: Why does lemon juice keep apple slices from turning brown? When an apple is cut, enzymes exposed to oxygen begin producing brown pigments. Lemon juice contains citric acid and ascorbic acid (vitamin C), which slow this reaction by lowering the pH and acting as antioxidants. This is one example of how acids influence chemical reactions in everyday life.

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9.2: Arrhenius Acids and Bases (Review)

In Chapter 3, where you were introduced to ionic compounds, you learned that some compounds produce ions when they dissolve in water. Among these are **Arrhenius acids** and **Arrhenius bases**, which were first described by the Swedish chemist Svante Arrhenius in the late 1800s.

According to the **Arrhenius model**, acids and bases are defined by the ions they produce when dissolved in water.

> ***An Arrhenius acid*** increases the concentration of hydronium ions (H_3O^+) in an aqueous solution.
>
> **An Arrhenius base** increases the concentration of hydroxide ions (OH^-) in an aqueous solution.

Because hydrogen ions (H^+) do not exist by themselves in liquid water, they immediately bond to nearby water molecules to form **hydronium ions (H_3O^+)**. Throughout this chapter, you may see either H^+ or H_3O^+ used to represent acidic solutions. Both notations describe the same chemistry, although H_3O^+ is more chemically accurate.

Dissociation in Water

When hydrochloric acid dissolves in water, it completely separates into ions.

$$\mathbf{HCl}(aq) \quad + \quad \mathbf{H_2O}(l) \quad \longrightarrow \quad \mathbf{H_3O^+}(aq) \quad + \quad \mathbf{Cl^-}(aq) \tag{9.2.1}$$

The chloride ion does not participate in the acid-base chemistry. Instead, the important change is the increase in hydronium ions, which makes the solution acidic.

Likewise, sodium hydroxide dissociates in water to produce hydroxide ions.

$$\mathbf{NaOH}(aq) \quad \longrightarrow \quad \mathbf{Na^+}(aq) \quad + \quad \mathbf{OH^-}(aq) \tag{9.2.2}$$

The sodium ion is a spectator ion. The hydroxide ions are responsible for the solution's basic properties.

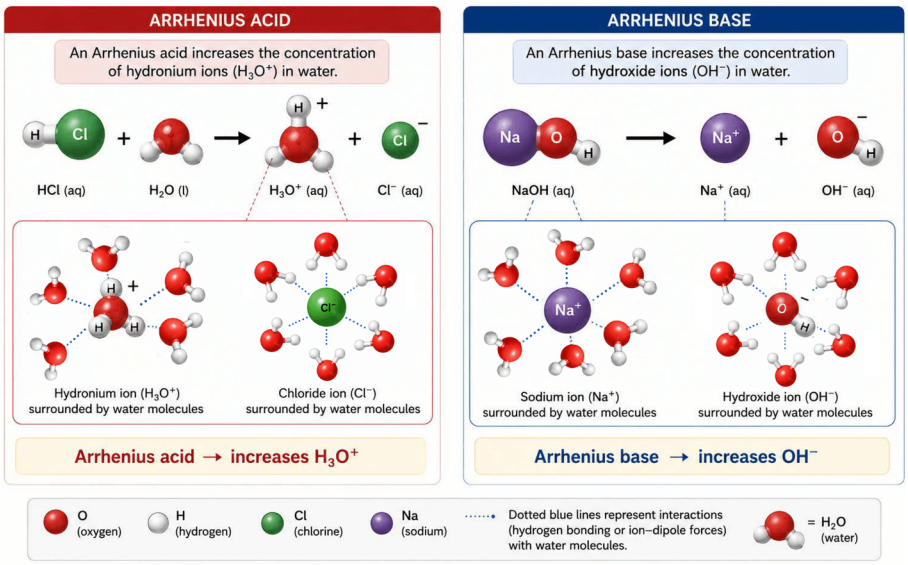


Figure $\mathrm{PageIndex1}$: Arrhenius Acids and Bases Produce Ions in Water. Two-panel diagram comparing an Arrhenius acid and an Arrhenius base in water. The left panel shows hydrochloric acid (HCl) reacting with water to

form hydronium ions ($H_3O^⊕$) and chloride ions ($Cl^⊖$), illustrating that an Arrhenius acid increases the concentration of hydronium ions in aqueous solution. The right panel shows sodium hydroxide (NaOH) dissociating into sodium ions ($Na^⊕$) and hydroxide ions ($OH^⊖$), illustrating that an Arrhenius base increases the concentration of hydroxide ions. Molecular illustrations show the ions surrounded by water molecules, emphasizing that these ions exist in aqueous solution rather than as isolated particles.

Many of the acids and bases encountered in everyday life fit the Arrhenius definition.

Table 9.2A: Common Arrhenius Acids and Bases.

Arrhenius Acids	Arrhenius Bases
Hydrochloric acid (HCl)	Sodium hydroxide (NaOH)
Nitric acid (HNO_3)	Potassium hydroxide (KOH)
Sulfuric acid (H_2SO_4)	Calcium hydroxide [$Ca(OH)_2$]

Notice that all Arrhenius bases contain the hydroxide ion ($OH^⊖$), while Arrhenius acids produce hydronium ions when dissolved in water.

Limitations of the Arrhenius Model

The Arrhenius definition successfully explains many familiar acids and bases, but it has important limitations.

First, it only applies to reactions that occur in **water**. Chemists eventually discovered acid-base reactions that take place in other solvents—and even in the gas phase.

Second, not every base contains hydroxide ions.

For example, ammonia (NH_3) is commonly used in household cleaning products and behaves as a base when dissolved in water. However, its chemical formula contains **no hydroxide ions**.

When ammonia dissolves, it reacts with water to produce hydroxide ions.

$$\mathbf{NH_3}(aq) \quad + \quad \mathbf{H_2O}(l) \quad \rightleftharpoons \quad \mathbf{NH_4^+}(aq) \quad + \quad \mathbf{OH^-}(aq) \tag{9.2.3}$$

Although ammonia behaves as a base, it does not fit neatly into the original Arrhenius definition.

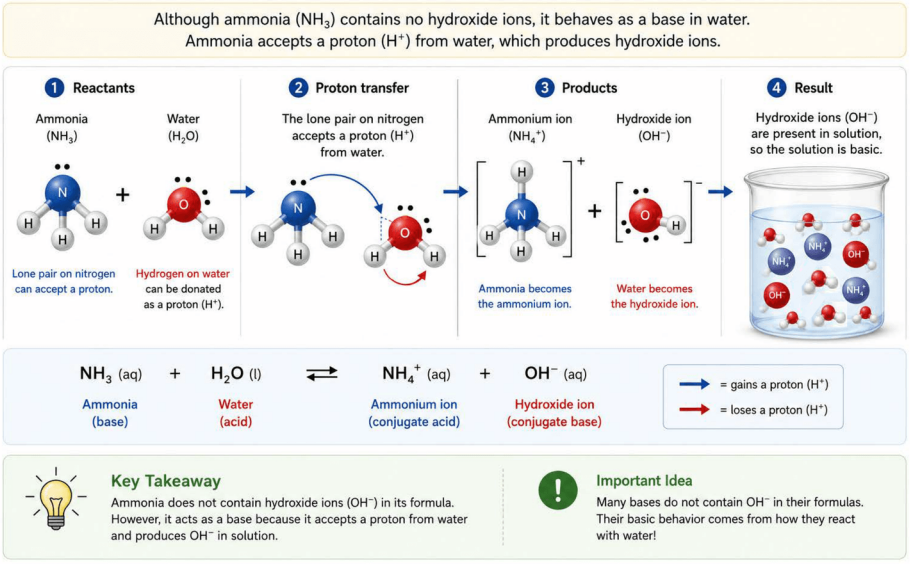


Figure $\text{Page}Index2$: Ammonia behaves as a base even though it contains no hydroxide ions. Step-by-step diagram illustrating how ammonia (NH_3) acts as a Brønsted–Lowry base in water. Ammonia, which contains no hydroxide ions (OH^-), uses its lone pair of electrons to accept a proton (H^+) from a water molecule. This proton transfer produces an ammonium ion (NH_4^+) and a hydroxide ion (OH^-). The overall reaction is $NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$. Because hydroxide ions are produced during this reaction, the solution becomes basic even though ammonia itself does not contain OH^-.

Looking Ahead

As chemists studied more reactions, they realized that acids and bases could not simply be defined by the ions they produced in water. A broader explanation was needed—one that could describe acid-base reactions in many different environments and explain why substances like ammonia behave as bases.

In the next section, you'll learn the **Brønsted–Lowry model**, which defines acids and bases by the transfer of a proton (H^+). This model not only includes all Arrhenius acids and bases but also explains many reactions that the Arrhenius definition cannot.

Chemistry Connection

Did You Know?

Svante Arrhenius proposed his theory of acids and bases in 1884, when scientists were just beginning to understand ions in solution. His work helped establish modern physical chemistry and earned him the **1903 Nobel Prize in Chemistry**. Although chemists now use broader definitions of acids and bases, the Arrhenius model remains an excellent starting point for understanding acid-base behavior in aqueous solutions.

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9.3: Bronsted-Lowry Acids and Bases

In the previous section, you reviewed the Arrhenius model, which defines acids and bases by the ions they produce in water. While this model explains many familiar substances, it cannot describe every acid-base reaction.

For example, ammonia (NH_3) behaves as a base even though it contains no hydroxide ions. In addition, many acid-base reactions occur in solvents other than water or even in the gas phase.

To explain these reactions, chemists Johannes Brønsted and Thomas Lowry independently proposed a broader model in 1923. Instead of focusing on the ions present in solution, they focused on what actually happens during an acid-base reaction—the **transfer of a proton**.

Proton Transfer: The Heart of Acid-Base Chemistry

The Brønsted–Lowry model defines acids and bases according to how they behave during a chemical reaction.

> **A Brønsted–Lowry acid is a proton (H⊕) donor**.
>
> **A Brønsted–Lowry base is a proton (H⊕) acceptor**.

Rather than thinking of acids and bases as substances that simply produce certain ions, imagine a proton being passed from one molecule to another, much like passing a baton in a relay race. One molecule donates the proton, while another accepts it.

Every Brønsted–Lowry acid-base reaction involves this transfer of a proton.

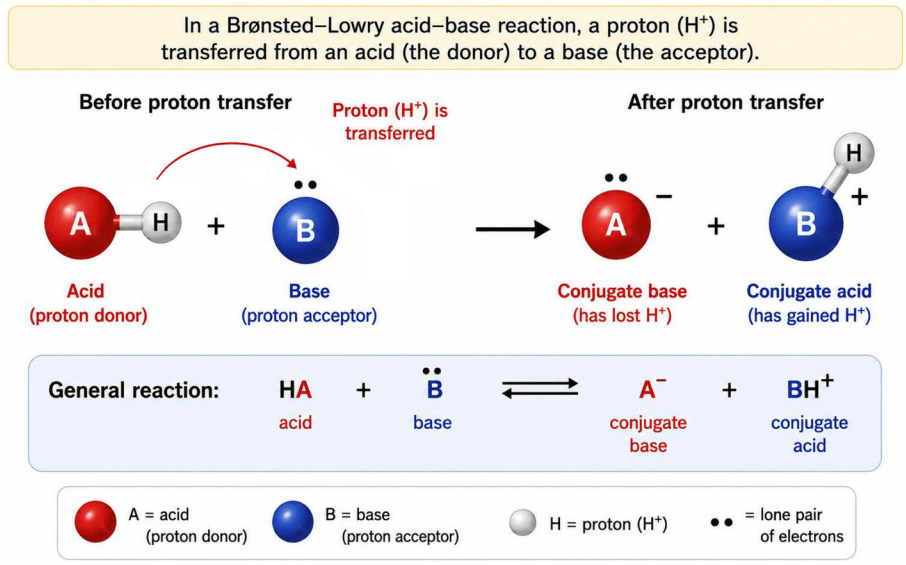


Figure 9.3.1: Acid-Base Reactions Involve the Transfer of a Proton. Generalized diagram of a Brønsted–Lowry acid-base reaction. Before the reaction, an acid (HA) contains a proton (H⊕), and a base (B) has a lone pair of electrons that can accept the proton. During the reaction, the proton is transferred from the acid to the base. After the transfer, the acid becomes its conjugate base (A⊕), and the base becomes its conjugate acid (BH⊕). The figure emphasizes that Brønsted–Lowry acid-base reactions are defined by the transfer of a proton from a proton donor (acid) to a proton acceptor (base).

One remarkable feature of the Brønsted–Lowry model is that **water can behave as either an acid or a base**, depending on the reaction taking place.

When hydrochloric acid dissolves in water, water accepts a proton.

$$\mathbf{HCl}(aq) \quad + \quad \mathbf{H_2O}(l) \quad \longrightarrow \quad \mathbf{H_3O^+}(aq) \quad + \quad \mathbf{Cl^-}(aq) \tag{9.3.1}$$

In this reaction,

- HCl donates a proton, so it acts as the **acid**.
- Water accepts the proton, so it acts as the **base**.

Notice that the hydronium ion (H_3O^+) forms because a water molecule gains the proton released by HCl.

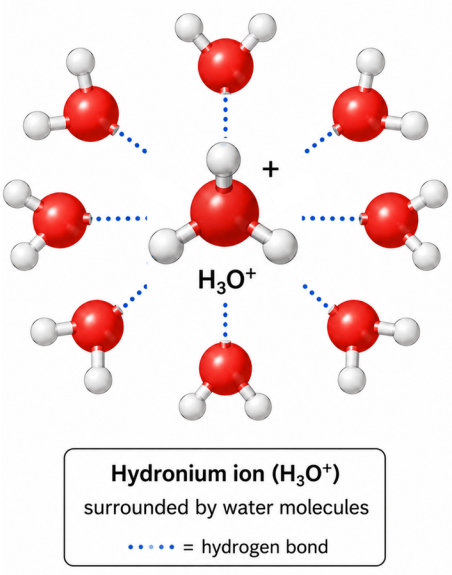


Figure 9.3.2: Formation of a hydronium ion after water accepts a proton from an acid. Water molecules surrounding the hydronium ion are attracted through hydrogen bonding.

Water Can Also Act as an Acid

Now consider the reaction you saw in the previous section involving ammonia.

$$\mathbf{NH_3}(aq) \quad + \quad \mathbf{H_2O}(l) \quad \rightleftharpoons \quad \mathbf{NH_4^+}(aq) \quad + \quad \mathbf{OH^-}(aq) \tag{9.3.2}$$

This time, water **loses** a proton.

Ammonia accepts that proton and becomes an ammonium ion (NH_4^+). The water molecule that lost the proton becomes a hydroxide ion (OH^-).

Now the roles are reversed.

- Water donates a proton, so it acts as the **acid**.
- Ammonia accepts the proton, so it acts as the **base**.

The Brønsted–Lowry model explains ammonia's behavior naturally. Unlike the Arrhenius definition, it does not require bases to contain hydroxide ions—they simply need to accept a proton from water.

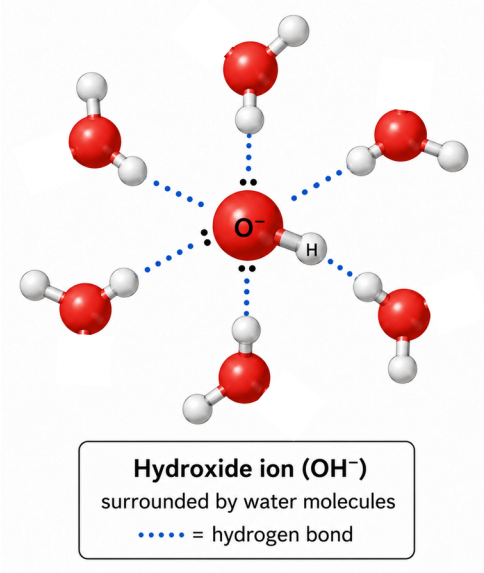


Figure 9.3.3: Formation of a hydroxide ion after water donates a proton to a base. Water molecules surrounding the hydroxide ion are attracted through hydrogen bonding.

Water Is Amphoteric

Because water can either donate or accept a proton, it is described as ***amphoteric***.

Amphoteric substances can behave as either acids or bases depending on the reaction.

This property makes water especially important in biological systems, where it participates in thousands of acid-base reactions every second.

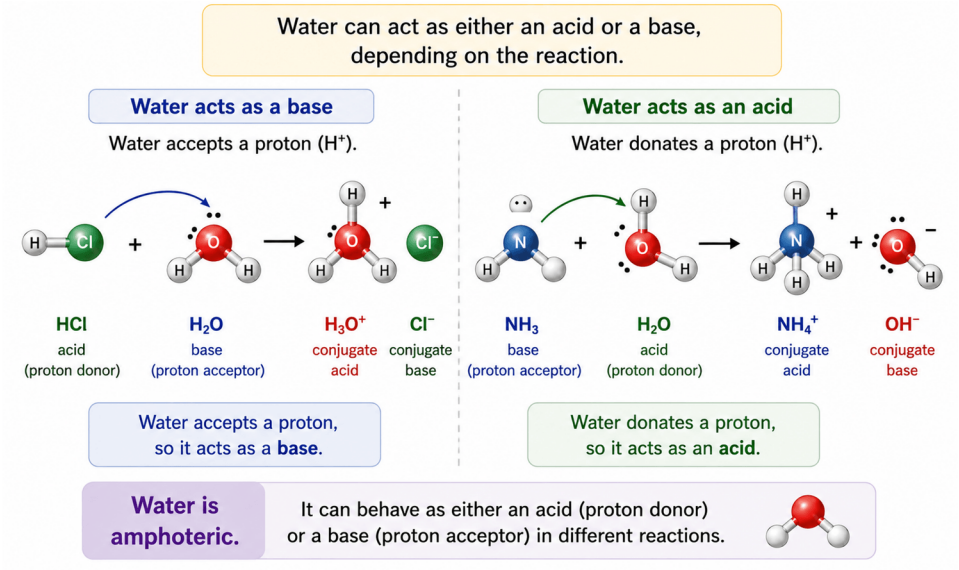


Figure 9.3.4: Water is amphoteric. Depending on the circumstance, water can act as proton donor or a proton acceptor and behave as either an acid or a base. On the left hand side of the diagram, water acts as a base and accepts a proton from hydrochloric acid forming the hydronium ion. On the right hand side, water acts as an acid and donates a proton to ammonia forming the hydroxide ion.

A New Way to Think About Acids and Bases

The Brønsted–Lowry model includes every Arrhenius acid and base you've learned so far, but it also explains many reactions that the Arrhenius model cannot.

Rather than asking,

"Does this substance contain OH? "

chemists instead ask,

"Is this molecule donating or accepting a proton? "

That simple question explains an enormous variety of chemical reactions, making the Brønsted–Lowry model the foundation of modern acid-base chemistry.

Chemistry in Action

Why is ammonium nitrate an effective fertilizer?

Plants require nitrogen to build proteins, DNA, and chlorophyll. One common fertilizer, **ammonium nitrate (NH_4NO_3)**, provides nitrogen in two forms: ammonium ions (NH_4^+) and nitrate ions (NO_3^-). Soil bacteria can convert ammonium into nitrate, and plant roots can absorb both forms. Because ammonium is the conjugate acid of ammonia, it also participates in acid-base reactions in soils, influencing soil pH and nutrient availability. Understanding proton transfer helps explain why different nitrogen fertilizers can affect both plant growth and soil chemistry.

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9.4: Conjugate Acid-Base Pairs

In the previous section, you learned that every Brønsted–Lowry acid-base reaction involves the transfer of a proton (H⊕). But what happens to the molecules after the proton has been transferred?

When an acid donates a proton, it does not disappear. Instead, it becomes a new species that is capable of accepting a proton again. Likewise, when a base accepts a proton, it becomes a new species that can donate that proton back.

These related substances are known as **conjugate acid-base pairs**.

Conjugate Acid–Base Pairs

A **conjugate acid-base pair** consists of two substances that differ by exactly one proton (H⊕).

- When an acid loses a proton, it becomes its **conjugate base**.
- When a base gains a proton, it becomes its **conjugate acid**.

Notice that only **one hydrogen ion** changes. All of the other atoms remain exactly the same.

For example,

$$\mathbf{HCl}(aq) \quad + \quad \mathbf{H_2O}(l) \quad \longrightarrow \quad \mathbf{H_3O^+}(aq) \quad + \quad \mathbf{Cl^-}(aq) \tag{9.4.1}$$

contains two conjugate acid-base pairs.

Table 9.4A: Conjugate Acid-Base Pairs

Acid	Conjugate Base
HCl	Cl⊕

Table 9.4B: Conjugate Base-Acid Pairs

Base	Conjugate Acid
H_2O	H_3O⊕

The chloride ion is the conjugate base of hydrochloric acid because it is what remains after HCl donates a proton. Likewise, the hydronium ion is the conjugate acid of water because it forms after water accepts a proton.

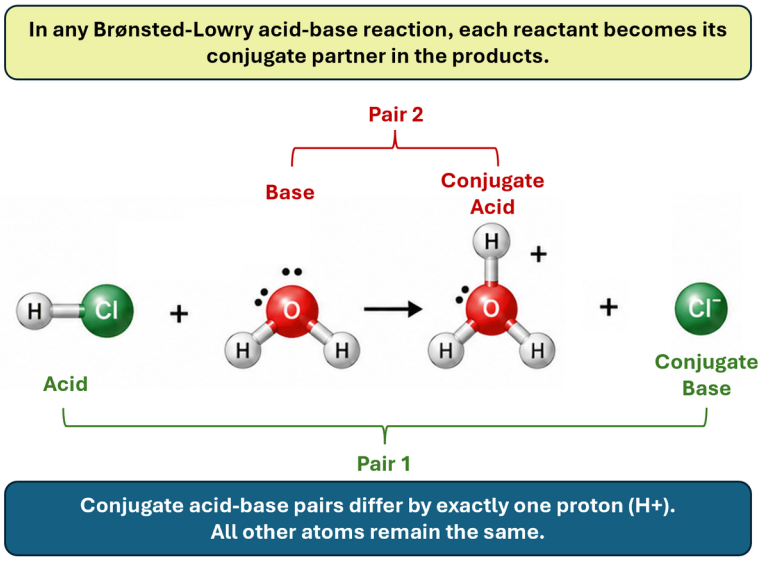


Figure 9.4.1: Every Acid-Base Reaction Produces Two Conjugate Acid-Base Pairs. Diagram of the Brønsted–Lowry reaction between hydrochloric acid and water: HCl + H_2O → $H_3O^⊕$ + $Cl^⊖$. The figure identifies two conjugate acid-base pairs. Hydrochloric acid (HCl) donates a proton to become its conjugate base, chloride ($Cl^⊖$). Water (H_2O) accepts the proton to become its conjugate acid, hydronium ($H_3O^⊕$). Each conjugate acid-base pair differs by one proton ($H^⊕$), while all other atoms remain unchanged.

Another Example

Now consider the reaction between ammonia and water.

$$\mathbf{NH_3}(aq) \quad + \quad \mathbf{H_2O}(l) \quad \rightleftharpoons \quad \mathbf{NH_4^+}(aq) \quad + \quad \mathbf{OH^-}(aq) \tag{9.4.2}$$

Again, there are two conjugate acid-base pairs.

Table 9.4C: Conjugate Acid-Base Pairs

Acid	Conjugate Base
H_2O	$OH^⊕$

Table 9.4D: Conjugate Acid-Base Pairs

Base	Conjugate Acid
NH_3	$NH_4^⊕$

Notice that water acts as the acid because it donates the proton. Ammonia acts as the base because it accepts the proton.

Once again, each conjugate pair differs by only one proton.

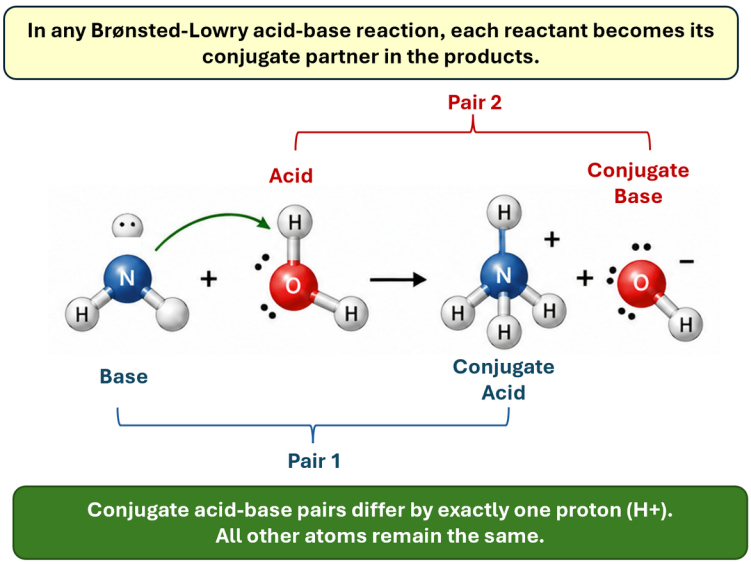


Figure 9.4.2: Every Acid-Base Reaction Produces Two Conjugate Acid-Base Pairs. The Brønsted–Lowry reaction $NH_3 + H_2O \rightarrow NH_4^+ + OH^-$ illustrating two conjugate acid-base pairs. Ammonia (NH_3) acts as the base by accepting a proton and becomes its conjugate acid, ammonium (NH_4^+). Water (H_2O) acts as the acid by donating a proton and becomes its conjugate base, hydroxide (OH^-). Each conjugate acid-base pair differs by exactly one proton (H^+).

Amphoteric Substances

Some substances can behave as either an acid or a base depending on the reaction they are participating in. These substances are called **amphoteric**.

As noted in the previous section, water is the most familiar amphoteric substance.

When reacting with hydrochloric acid,

$$\mathbf{HCl}(aq) \quad + \quad \mathbf{H_2O}(l) \quad \longrightarrow \quad \mathbf{H_3O^+}(aq) \quad + \quad \mathbf{Cl^-}(aq) \tag{9.4.3}$$

water accepts a proton and acts as a **base**.

When reacting with ammonia,

$$\mathbf{NH_3}(aq) \quad + \quad \mathbf{H_2O}(l) \quad \rightleftharpoons \quad \mathbf{NH_4^+}(aq) \quad + \quad \mathbf{OH^-}(aq) \tag{9.4.4}$$

water donates a proton and acts as an **acid**.

Its role depends entirely on the other substance in the reaction.

Bicarbonate: An Amphoteric Ion

Water is not the only amphoteric substance.

The **bicarbonate ion (HCO_3^-)** can also either donate or accept a proton.

When bicarbonate accepts a proton, it forms carbonic acid.

$$\mathbf{HCO_3^-}(aq) \quad + \quad \mathbf{H^+}(aq) \quad \longrightarrow \quad \mathbf{H_2CO_3}(aq) \tag{9.4.5}$$

In this reaction, bicarbonate acts as a **base**.

However, bicarbonate can also donate a proton.

$$\mathrm{HCO_3^-}(aq) \quad \rightleftharpoons \quad \mathrm{CO_3^{2-}}(aq) \quad + \quad \mathrm{H^+}(aq) \tag{9.4.6}$$

Now bicarbonate acts as an **acid**.

Because bicarbonate can behave in both ways, it is also amphoteric.

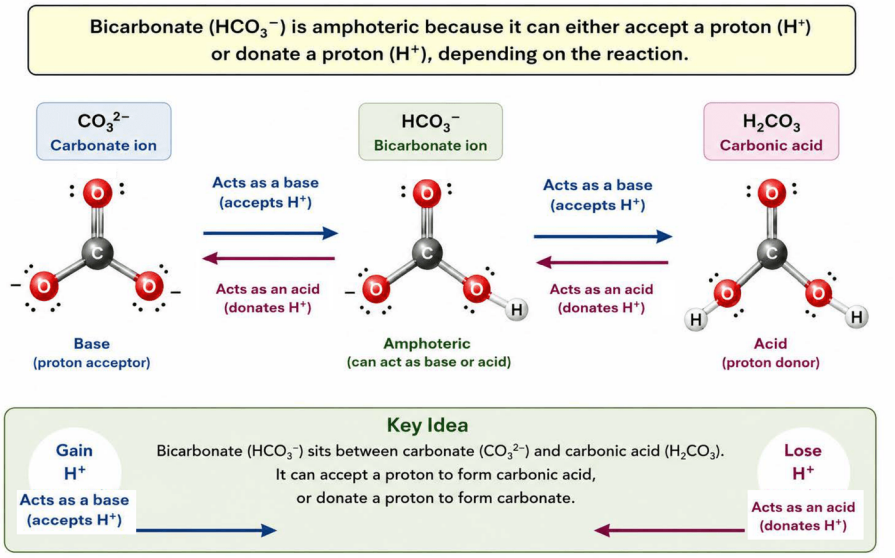


Figure 9.4.3: Bicarbonate Can Either Accept or Donate a Proton. Diagram showing the relationship among the carbonate ion (CO_3^{2-}), bicarbonate ion (HCO_3^-), and carbonic acid (H_2CO_3). Bicarbonate is amphoteric because it occupies the middle of the series and can either accept a proton (H^+) to form carbonic acid or donate a proton to form carbonate. Carbonate acts as a base, carbonic acid acts as an acid, and bicarbonate can behave as either depending on the reaction.

Why Is Bicarbonate Important?

Bicarbonate plays a vital role in the human body.

One of its most important functions is helping to maintain the pH of blood within a very narrow range. As you'll learn later in this chapter, bicarbonate is part of one of the body's most important **buffer systems**, helping resist large changes in pH as acids or bases are added.

Bicarbonate also plays an important role in natural waters and the oceans, where it helps regulate pH and is involved in the chemistry of dissolved carbon dioxide. We'll return to this topic in the **Focus on the Environment** section at the end of the chapter when we discuss **ocean acidification**.

Concept Check

Identify the conjugate acid and conjugate base in each reaction.

1)

$$\mathrm{HF}(aq) \quad + \quad \mathrm{H_2O}(l) \quad \rightleftharpoons \quad \mathrm{H_3O^+}(aq) \quad + \quad \mathrm{F^-}(aq) \tag{9.4.7}$$

2)

$$\mathbf{NH_3}(aq) \quad + \quad \mathbf{H_2O}(l) \quad \rightleftharpoons \quad \mathbf{NH_4^+}(aq) \quad + \quad \mathbf{OH^-}(aq) \tag{9.4.8}$$

3) Is water acting as an acid or a base in each reaction?

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9.5: Acid and Base Strength

In the previous sections, you learned that acids donate protons (H⊕) and bases accept protons. However, not all acids donate their protons equally well, and not all bases accept protons to the same extent.

Some acids transfer nearly every available proton to water, while others transfer only a small fraction. This difference is known as **acid strength**.

Similarly, some bases readily accept protons, while others react only to a limited extent. Understanding acid and base strength helps explain why different substances produce different concentrations of hydronium and hydroxide ions, even when prepared at the same concentration.

Strong and Weak Acids

The strength of an acid depends on **how completely it donates its proton to water**, not on how much acid is present.

A **strong acid** ionizes essentially completely in water. Nearly every acid molecule transfers its proton to a water molecule, producing hydronium ions.

For example, when hydrochloric acid, HCl, reacts with water:

$$\mathbf{HCl}(aq) \quad + \quad \mathbf{H_2O}(l) \quad \longrightarrow \quad \mathbf{H_3O^+}(aq) \quad + \quad \mathbf{Cl^-}(aq) \tag{9.5.1}$$

Almost every HCl molecule undergoes this reaction.

A **weak acid**, on the other hand, ionizes only partially. Most of the acid molecules remain unchanged, while only a small fraction donate their protons.

For example, when acetic acid, CH_3COOH, reacts with water:

$$\mathbf{CH_3COOH}(aq) \quad + \quad \mathbf{H_2O}(l) \quad \rightleftharpoons \quad \mathbf{H_3O^+}(aq) \quad + \quad \mathbf{CH_3COO^-}(aq) \tag{9.5.2}$$

Only a few acetic acid molecules ionize, fewer hydronium ions are produced. This means that the acid is not as strong as the HCl in the previous example, even if both are provided in the same concentration.

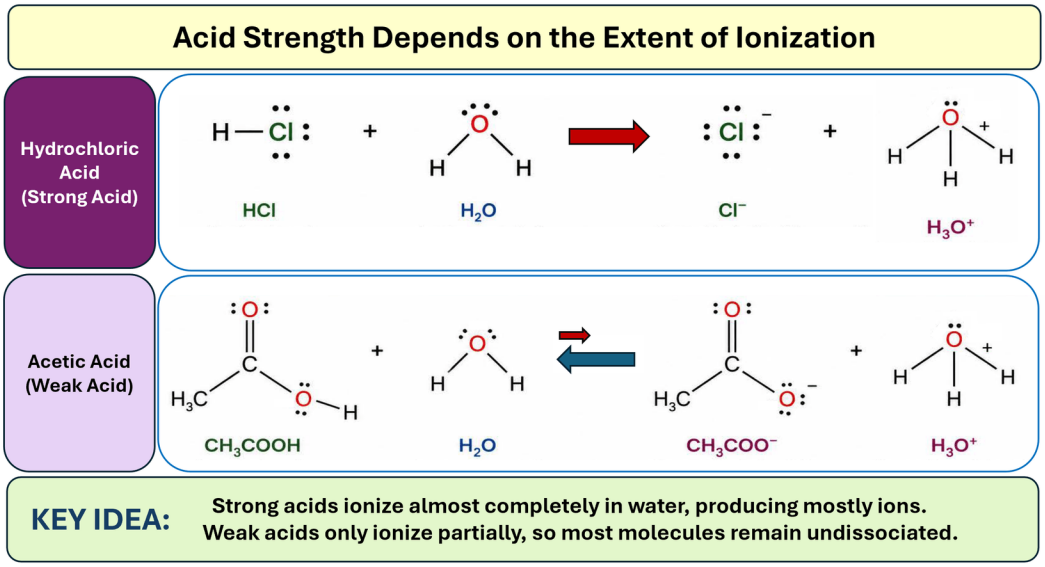


Figure 9.5.1***: Strong and weak acids differ in the extent of ionization.*** Comparison of the ionization of a strong acid (hydrochloric acid, HCl) and a weak acid (acetic acid, CH_3COOH) in water. Hydrochloric acid reacts essentially completely with water, producing chloride ions (Cl^-) and hydronium ions (H_3O^+), and is represented by a single forward reaction arrow. Acetic acid reacts only partially with water, producing acetate ions (CH_3COO^-) and hydronium ions while most acetic acid molecules remain un-ionized. This reaction is represented by equilibrium arrows, indicating that both reactants and products are present. The figure illustrates that strong acids ionize almost completely, whereas weak acids ionize only partially.

Strong and Weak Bases

Bases also differ in their strength. Strong bases, such as sodium hydroxide (NaOH), dissociate completely in water, producing hydroxide ions.

$$\mathbf{NaOH}(aq) \longrightarrow \mathbf{Na}^+(aq) + \mathbf{OH}^-(aq) \tag{9.5.3}$$

Weak bases, such as ammonia (NH_3), react with water only to a limited extent.

$$\mathbf{NH_3}(aq) + \mathbf{H_2O}(l) \rightleftharpoons \mathbf{NH_4^+}(aq) + \mathbf{OH}^-(aq) \tag{9.5.4}$$

Only a fraction of the ammonia molecules accept a proton, so fewer hydroxide ions are produced.

Strong Does Not Mean Concentrated

One of the most common misconceptions is that **strong** and **concentrated** mean the same thing. They do not. **Strength** describes **how completely an acid or base ionizes**. **Concentration** describes **how much acid or base is dissolved in a given volume of solution**. For example, a dilute hydrochloric acid solution is still a **strong acid** because every HCl molecule ionizes. Likewise, a concentrated acetic acid solution is still a **weak acid** because only a fraction of its molecules ionize. Strength and concentration describe two completely different properties.

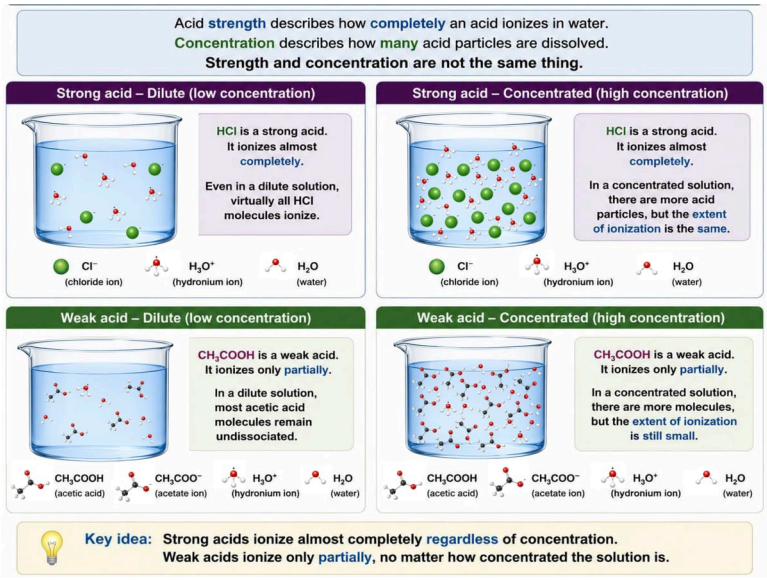


Figure $9.5.2$***: Strong Does Not Mean Concentrated.*** Four beakers compare acid strength and concentration. The top row shows dilute and concentrated solutions of hydrochloric acid (HCl), a strong acid. Although the concentrated solution contains more acid particles than the dilute solution, nearly all HCl molecules ionize in both cases, producing hydronium (H_3O^+) and chloride (Cl^-) ions. The bottom row shows dilute and concentrated solutions of acetic acid (CH_3COOH), a weak acid. In both solutions, most acetic acid molecules remain un-ionized, with only a small number forming acetate ions (CH_3COO^-) and hydronium ions. The figure illustrates that **acid strength describes the extent of ionization, while concentration describes the amount of acid dissolved in solution.** A strong acid can be either dilute or concentrated, and a weak acid can also be either dilute or concentrated.

Ionization and Chemical Equilibrium

Did you notice something different about the equations for hydrochloric acid and acetic acid?

Hydrochloric acid is written with a single reaction arrow.

$$\mathbf{HCl}(aq) \quad + \quad \mathbf{H_2O}(l) \quad \longrightarrow \quad \mathbf{H_3O^+}(aq) \quad + \quad \mathbf{Cl^-}(aq) \tag{9.5.5}$$

Acetic acid is written with a double arrow.

$$\mathbf{CH_3COOH}(aq) \quad + \quad \mathbf{H_2O}(l) \quad \rightleftharpoons \quad \mathbf{H_3O^+}(aq) \quad + \quad \mathbf{CH_3COO^-}(aq) \tag{9.5.6}$$

The double arrow indicates that the reaction is **reversible**.

As acetic acid molecules donate protons, some acetate ions accept those protons and reform acetic acid. Eventually, the forward and reverse reactions occur at the same rate. At this point, the system has reached **chemical equilibrium**.

Although both reactions continue to occur, the concentrations of reactants and products remain constant.

For weak acids and weak bases, equilibrium lies far toward the reactants, meaning that most molecules remain un-ionized.

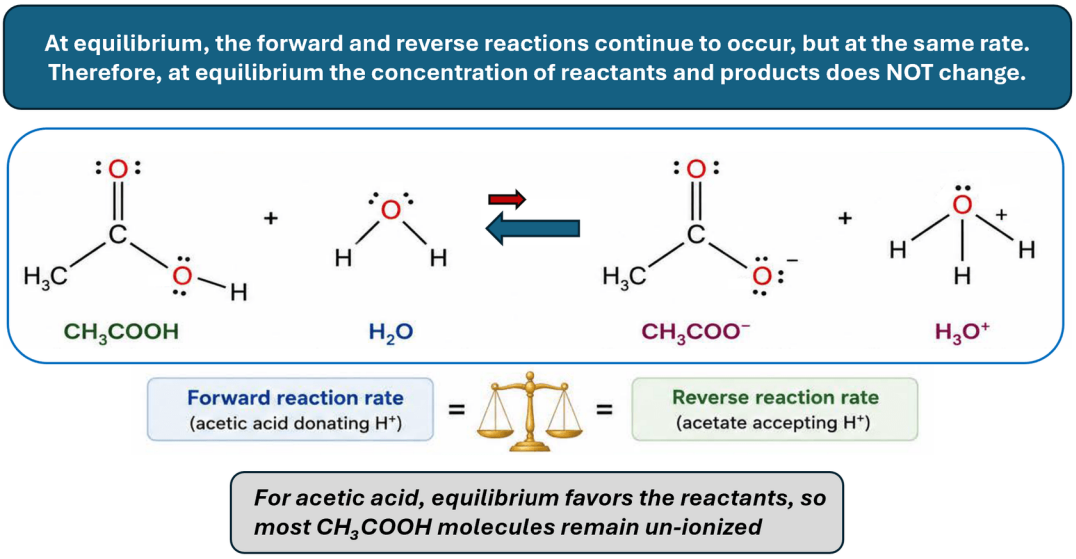


Figure* 9.5.3*: Chemical Equilibrium is Dynamic. The ionization of acetic acid in water is shown as a reversible reaction: $CH_3COOH + H_2O \diamondsuit CH_3COO^- + H_3O^+$. Larger forward and smaller reverse arrows indicate that the equilibrium lies toward the reactants, so most acetic acid molecules remain un-ionized. A balance scale below the reaction illustrates that, at equilibrium, the forward and reverse reaction rates are equal. Because the forward and reverse reactions occur at the same rate, the concentrations of reactants and products remain constant over time, even though both reactions continue to occur.

Conjugate Acid–Base Strength

The strength of an acid is closely related to the strength of its conjugate base.

A **strong acid** has a **very weak conjugate base**.

For example,

$$\mathrm{HCl}(aq) \longrightarrow \mathrm{Cl}^-(aq) \tag{9.5.7}$$

The chloride ion has very little tendency to accept a proton, so HCl readily donates it. Thus, the reaction of a strong acid is to go to completion and achieve full ionization.

In contrast, a **weak acid** has a **stronger conjugate base**.

For example,

$$\mathrm{CH_3COOH}(aq) \rightleftharpoons \mathrm{CH_3COO}^-(aq) \tag{9.5.8}$$

Because acetate ions readily accept protons, many acetic acid molecules reform. Thus, most of the acetic acid molecules remain in the un-ionized state.

A similar relationship exists for bases. Strong bases have weak conjugate acids, while weak bases have stronger conjugate acids.

The stronger the acid, the weaker its conjugate base.

The weaker the acid, the stronger its conjugate base.

Chemistry in Action

Why does vinegar taste sour if it is a weak acid?

Household vinegar contains acetic acid, a **weak acid** that ionizes only partially in water. Even though only a small fraction of acetic acid molecules donate protons, vinegar is often sold as a **5% solution**, meaning it contains a relatively high concentration of acetic acid molecules. Because so many molecules are present, enough hydronium ions are produced to give vinegar its characteristic sour taste and make it useful for cooking, cleaning, and food preservation. This example highlights the important distinction between **acid strength** and **acid concentration**.

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9.6: Autoionization of Water

How can pure water contain both acids and bases?

In the previous sections, acids donated protons to water and bases accepted protons from water. But what happens when **only water molecules are present?**

Surprisingly, water molecules can react with one another. In this process, one water molecule donates a proton (H⊕) to another water molecule. As a result, one molecule becomes a **hydronium ion ($H_3O^⊕$)** while the other becomes a **hydroxide ion ($OH^⊖$).**

This process is called the **autoionization** (or **self-ionization**) of water.

$$2\,\mathrm{H_2O}(l) \quad \rightleftharpoons \quad \mathrm{H_3O^+}(aq) \quad + \quad \mathrm{OH^-}(aq) \tag{9.6.1}$$

Although this reaction occurs continuously, only a very small fraction of water molecules are ionized at any given time. Most water molecules remain unchanged.

> **One water molecule donates a proton while the other accepts it**.

Water Is Amphoteric

The autoionization of water demonstrates that water is **amphoteric**. Depending on the reaction, water can behave as either an acid or a base.

In the autoionization reaction:

- One water molecule **donates** a proton and acts as a Brønsted–Lowry acid.
- The other water molecule **accepts** that proton and acts as a Brønsted–Lowry base.

This reaction provides another example of how proton transfer is the central idea of Brønsted–Lowry acid–base chemistry.

The Ion-Product Constant for Water

Because the concentrations of hydronium and hydroxide ions remain constant in pure water at a given temperature, chemists define a special equilibrium constant called the **ion-product constant for water**, represented by K_w.

At **25°C**,

$$K_w = [\mathrm{H_3O^+}][\mathrm{OH^-}] = 1.0 \times 10^{-14} \tag{9.6.2}$$

The small value of K_w reflects the fact that only a tiny fraction of water molecules are ionized.

Unlike other equilibrium constants, K_w applies specifically to the autoionization of water and is used throughout acid–base chemistry.

> **Note:** Pure liquid water is omitted from the expression for K_w because its concentration remains essentially constant.

Neutral Water

In pure water, every hydronium ion produced by autoionization is accompanied by one hydroxide ion.

Therefore,

$$[\mathbf{H_3O^+}] = [\mathbf{OH^-}] \tag{9.6.3}$$

At **25°C**, each concentration is

$$[\mathbf{H_3O^+}] = [\mathbf{OH^-}] = \mathbf{1.0 \times 10^{-7}\ M} \tag{9.6.4}$$

Because the concentrations of hydronium and hydroxide ions are equal, pure water is described as **neutral**.

A neutral solution does **not** mean that it doesn't contain any ions. Instead, it contains **equal concentrations** of positive and negative ions, such that they cancel each other out.

Chemistry in Action

Why doesn't pure water conduct electricity very well?

Pure water contains hydronium and hydroxide ions formed through autoionization, but their concentrations are extremely small. Because there are so few charged particles available to carry electric current, pure water is a very poor electrical conductor. When acids, bases, or salts dissolve in water, they produce many more ions, dramatically increasing the solution's ability to conduct electricity.

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9.7: pH and pOH

Measuring Acidity and Basicity

In the previous section, you learned that pure water contains a small concentration of hydronium ions (H_3O^+) and hydroxide ions (OH^-) produced by the autoionization of water. Acidic solutions contain **more hydronium ions than hydroxide ions**, while basic solutions contain **more hydroxide ions than hydronium ions**.

Although hydronium ion concentration provides a direct measure of acidity, these concentrations are often extremely small and inconvenient to write. For example, a neutral solution at 25°C contains

$$[\mathrm{H_3O^+}] = 1.0 \times 10^{-7}\,\mathrm{M} = 0.0000001\,\mathrm{M} \tag{9.7.1}$$

while a strongly acidic solution may contain

$$[\mathrm{H_3O^+}] = 1.0 \times 10^{-1}\,\mathrm{M} = 0.10\,\mathrm{M} \tag{9.7.2}$$

Rather than writing numbers with many zeros or large negative exponents, chemists use the **pH scale**, which provides a convenient way to describe the acidity of a solution.

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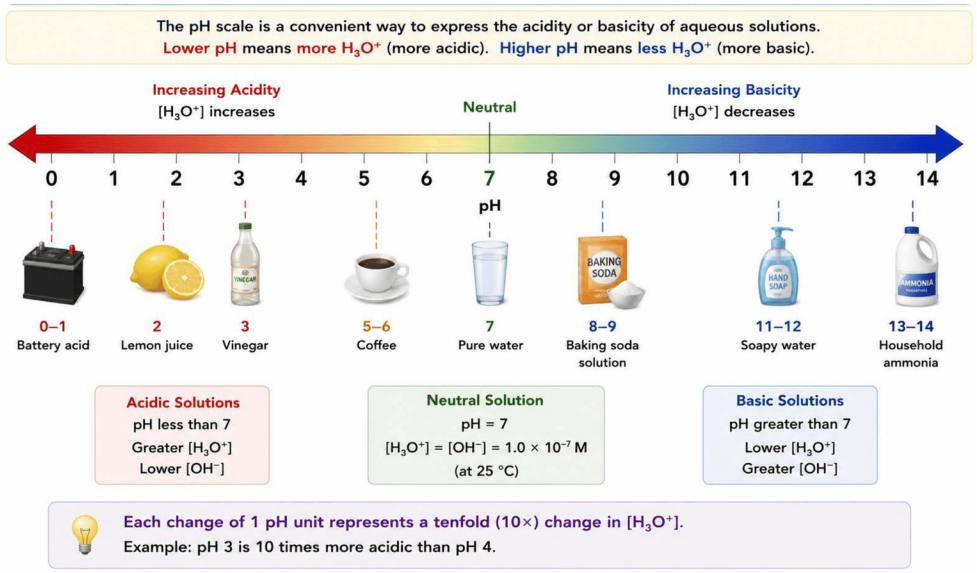


Figure 9.7.1: The pH Scale Measures the Concentration of Hydronium Ions. The pH scale ranges from 0 to 14 and provides a convenient way to express the acidity or basicity of aqueous solutions. Lower pH values correspond to higher hydronium ion (H_3O^+) concentrations and greater acidity, while higher pH values correspond to lower hydronium ion concentrations and greater basicity. A pH of 7 represents a neutral solution, where the concentrations of hydronium and hydroxide ions are equal. The scale includes approximate pH values for common substances: battery acid (0–1), lemon juice (2), vinegar (3), coffee (5–6), pure water (7), baking soda solution (8–9), soapy water (11–12), and household ammonia (13–14). The figure also emphasizes that each decrease of one pH unit corresponds to a tenfold increase in hydronium ion concentration.

The pH Scale

The pH of a solution is defined as

$$\mathrm{pH} = -\log[\mathrm{H_3O^+}] \tag{9.7.3}$$

The negative logarithm converts very small hydronium ion concentrations into simple numbers that are easier to compare. As the concentration of hydronium ions increases, the pH decreases. Conversely, as the concentration of hydronium ions decreases, the pH increases.

Because the pH scale is logarithmic, a change of **one pH unit** represents a **tenfold change** in hydronium ion concentration.

For example,

- A solution with a pH of 3 contains ten times more hydronium ions than a solution with a pH of 4.
- A solution with a pH of 2 contains one hundred times more hydronium ions than a solution with a pH of 4.

This logarithmic relationship explains why relatively small changes in pH correspond to large differences in acidity.

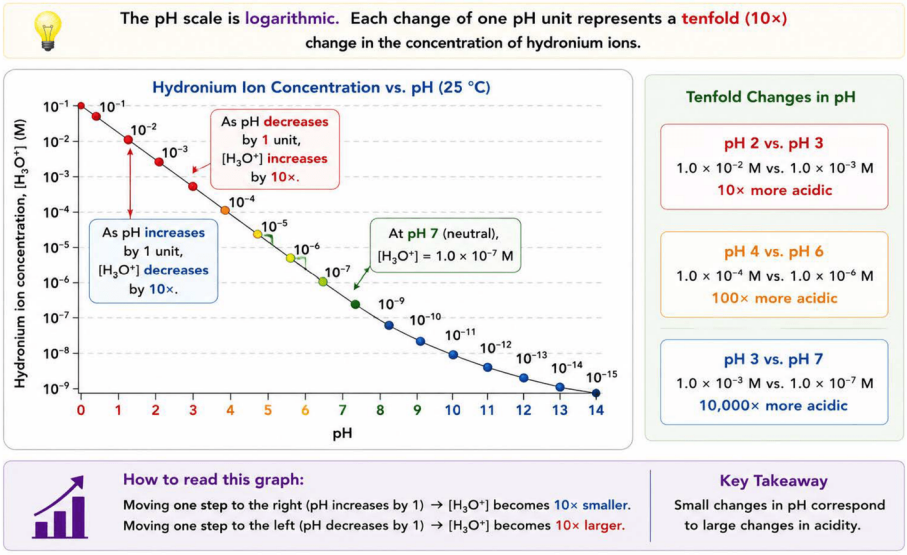


Figure 9.7.2: Each pH unit represents a tenfold change in hydronium ion concentration. Graph showing the relationship between pH and hydronium ion concentration (H_3O^+) at 25°C. The horizontal axis shows pH values from 0 to 14, and the vertical axis shows hydronium ion concentration on a logarithmic scale ranging from 10^{-1} to 10^{-9} moles per liter. As pH increases, hydronium ion concentration decreases by a factor of ten for each increase of one pH unit. For example, pH 2 corresponds to 10^{-2} M H_3O^+, pH 3 to 10^{-3} M, and pH 7 (neutral) to 1.0×10^{-7} M. Callout boxes emphasize that increasing pH by one unit decreases hydronium ion concentration tenfold, while decreasing pH by one unit increases hydronium ion concentration tenfold. Additional examples show that a difference of one pH unit corresponds to a tenfold difference in hydronium ion concentration, two pH units correspond to a hundredfold difference, and four pH units correspond to a ten-thousandfold difference. The figure illustrates that small changes in pH correspond to large changes in acidity.

Converting pH to Hydronium Ion Concentration

The pH equation can also be rearranged to calculate the hydronium ion concentration.

$$\mathrm{pH} = -\log[\mathrm{H_3O^+}] \tag{9.7.4}$$

Rearranging gives

$$[\mathrm{H_3O^+}] = 10^{-\mathrm{pH}} \tag{9.7.5}$$

Notice that this equation uses **10 raised to the negative pH**, which is sometimes called taking the **antilogarithm (antilog)**.

Chemistry Tip: Significant Figures in pH Calculations

Because pH is calculated using a logarithm, the rules for significant figures are different than for multiplication, division, addition, or subtraction.

When calculating pH from a concentration:

- The **digits after the decimal point** in the pH value equal the **number of significant figures** in the concentration.

Significant figures in pH calculations

Hydronium concentration [H_3O^+] (M)	Significant figures from the Hydronium concentration	pH
1.0×10^{-3}	2	3.00
2.35×10^{-5}	3	4.629
8.1×10^{-9}	2	8.09

When calculating concentration from pH:

- The **number of decimal places** in the pH equals the **number of significant figures** in the calculated concentration.

Significant figures in pH calculations

pH	Decimal places	Hydronium Concentration [H_3O^+] M
4.62	2	2.4×10^{-5}
7.000	3	1.00×10^{-7}
2.10	2	7.9×10^{-3}

Key Idea

> **For logarithms, the digits to the right of the decimal point in the pH (or pOH) are the significant figures. Why?** The whole-number portion of a pH (called the *characteristic*) tells you the order of magnitude of the concentration. Only the digits after the decimal point contain information about the precision of the measurement.

Neutral, Acidic, and Basic Solutions

At 25°C,

- **Acidic solutions** have

$$[\mathrm{H_3O^+}] > [\mathrm{OH^-}] \tag{9.7.6}$$

and

$$\mathrm{pH} < 7 \tag{9.7.7}$$

- **Neutral solutions** have

$$[\mathrm{H_3O^+}] = [\mathrm{OH^-}] \tag{9.7.8}$$

and

$$\mathrm{pH} = 7 \tag{9.7.9}$$

- **Basic solutions** have

$$[\mathrm{OH^-}] > [\mathrm{H_3O^+}] \tag{9.7.10}$$

and

$$\mathrm{pH} > 7 \tag{9.7.11}$$

Although pH values below 7 are acidic and values above 7 are basic at 25°C, remember that the exact pH of a neutral solution changes slightly with temperature because K_w changes with temperature.

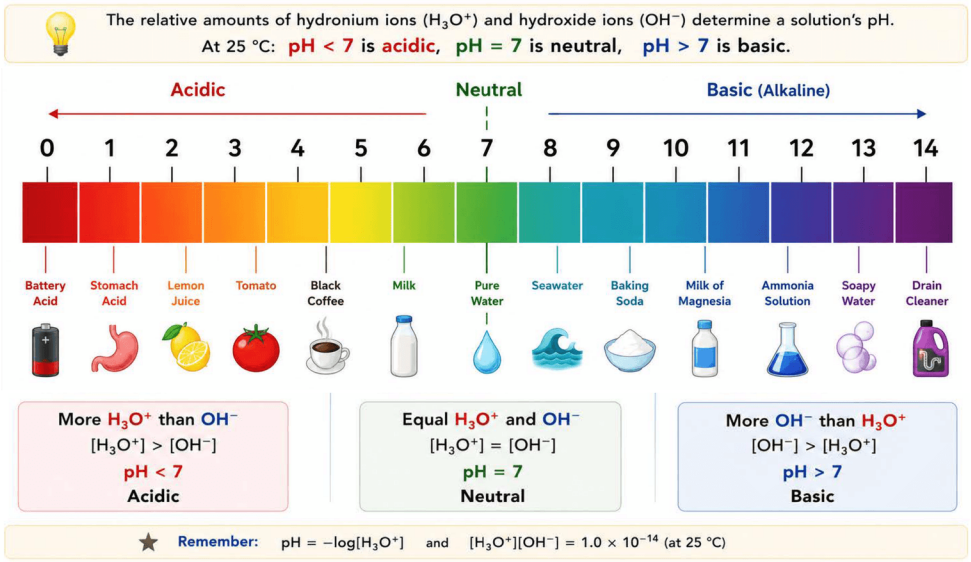


Figure 9.7.3: Hydronium and hydroxide concentrations determine whether a solution is acidic, neutral, or basic. The pH scale ranges from 0 to 14 at 25°C and relates pH to the relative concentrations of hydronium ions (H_3O^+) and hydroxide ions (OH^-). Solutions with **pH less than 7** are **acidic** because the concentration of hydronium ions is greater than the concentration of hydroxide ions $[H_3O^+]>[OH^-]$. A **neutral** solution has **pH = 7**, where the concentrations of hydronium and hydroxide ions are equal $[H_3O^+]=[OH^-]$. Solutions with **pH greater than 7** are **basic** because the concentration of hydroxide ions is greater than the concentration of hydronium ions $[OH^-]>[H_3O^+]$. The figure also shows approximate pH values for common substances, including battery acid, stomach acid, lemon juice, tomato, black coffee, milk, pure water, seawater, baking soda solution, milk of magnesia, ammonia solution, soapy water, and drain cleaner. A reminder at the bottom shows the pH equation, $pH=-\log [H_3O^+]$

The pOH Scale

Just as pH describes the concentration of hydronium ions, the **pOH** scale describes the concentration of hydroxide ions.

$$\mathbf{pOH} = -\mathbf{log}[\mathbf{OH}^-] \tag{9.7.12}$$

At 25°C,

$$\mathbf{pH} + \mathbf{pOH} = \mathbf{14.00} \tag{9.7.13}$$

Knowing either the pH or the pOH allows the other value to be determined easily.

For example, if the pH of a solution is 4, then the pOH is 14 - 4 or 10. Likewise, if the pOH is 2, then the pH is 14 - 2 or 12.

Example 9.7.1

Find the pOH of a solution with a pH of 3.5.

Solution

Step 1. Use the relationship between pH and pOH:

$$\mathbf{pH} + \mathbf{pOH} = \mathbf{14.00} \tag{9.7.14}$$

Step 2. Substitute in the value given for pH and solve for pOH:

$$\mathbf{pOH} = \mathbf{14.0} - \mathbf{pH} = \mathbf{14.0} - \mathbf{3.5} = \mathbf{10.5} \tag{9.7.15}$$

Final Answer: pOH is 10.5

Example 9.7.2

What is the pH of a solution that has a concentration of [$H3O^+$] of 0.00346 M or 3.46 x 10^{-3} M?

Solution

The pH of a solution is calculated using the pH equation:

$$\mathbf{pH} = -\mathbf{log}[\mathbf{H_3O^+}] \tag{9.7.16}$$

Step 1. Identify the known value.

$$[\mathbf{H_3O^+}] = \mathbf{3.46 \times 10^{-3}\,M} \tag{9.7.17}$$

Step 2. Substitute the known value into the pH equation.

$$\mathbf{pH} = -\mathbf{log}\left(\mathbf{3.46 \times 10^{-3}}\right) \tag{9.7.18}$$

Step 3. Calculate the answer.

$$\mathbf{pH} = \mathbf{2.46} \tag{9.7.19}$$

Final Answer: The solution has a **pH of 2.46**.

Example 9.7.3

What is the pH of a solution that contains 0.0010 M hydrochloric acid?

Solution

Hydrochloric acid is a **strong acid**, meaning it dissociates completely in water.

$$\mathrm{HCl}(aq) \quad + \quad \mathrm{H_2O}(l) \quad \longrightarrow \quad \mathrm{H_3O^+}(aq) \quad + \quad \mathrm{Cl^-}(aq) \tag{9.7.20}$$

Because one mole of HCl produces one mole of hydronium ions,

$$[\mathrm{H_3O^+}] = 0.0010\,\mathrm{M} = 1.0 \times 10^{-3}\,\mathrm{M} \tag{9.7.21}$$

Step 1. Write the pH equation.

$$\mathrm{pH} = -\log[\mathrm{H_3O^+}] \tag{9.7.22}$$

Step 2. Substitute the known value.

$$\mathrm{pH} = -\log\left(1.0 \times 10^{-3}\right) \tag{9.7.23}$$

Step 3. Calculate the answer.

$$\mathrm{pH} = 3.00 \tag{9.7.24}$$

Final Answer: The solution has a **pH of 3.00**.

Example 9.7.4

A solution has a pH of 5.41. Calculate the hydronium ion concentration, $[H_3O^+]$.

Solution

To calculate the hydronium ion concentration from a known pH, use the inverse pH equation:

$$[\mathrm{H_3O^+}] = 10^{-\mathrm{pH}} \tag{9.7.25}$$

Step 1. Identify the known value.

$$\mathrm{pH} = 5.41 \tag{9.7.26}$$

Step 2. Substitute the known value into the equation.

$$[\mathrm{H_3O^+}] = 10^{-5.41} \tag{9.7.27}$$

Step 3. Calculate the answer.

$$[\mathrm{H_3O^+}] = 3.89 \times 10^{-6}\,\mathrm{M} \tag{9.7.28}$$

Final Answer: The hydronium ion concentration is

$$[\mathrm{H_3O^+}] = 3.9 \times 10^{-6}\,\mathrm{M} \tag{9.7.29}$$

Note

Notice the relationship between **significant figures** and **decimal places**:

- The pH is reported as **5.41**, which has **two decimal places**.
- Therefore, the hydronium ion concentration should be reported with **two significant figures**

Chemistry in Action

Why do swimming pools need their pH monitored?

The pH of pool water affects both swimmer comfort and the effectiveness of disinfectants such as chlorine. If the pH becomes too low, the water can irritate the eyes and skin and may corrode metal equipment. If the pH becomes too high, chlorine becomes less effective at killing microorganisms, and mineral deposits may begin to form. Most swimming pools are maintained between **pH 7.2 and 7.8**, providing a balance between effective sanitation and swimmer comfort.

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9.8: Neutralization Reactions

When Acids and Bases React

In **Chapter 6**, you learned that many aqueous ionic compounds undergo **double-displacement (double-replacement)** reactions, in which ions exchange partners to form new products. One important type of double-displacement reaction is the **acid-base neutralization reaction**.

When an acid reacts with a base, hydronium ions (or hydrogen ions, H⊕) react with hydroxide ions to form water. At the same time, the remaining ions combine to form an ionic compound called a **salt**.

Although the products of neutralization vary depending on the acid and base, the fundamental proton-transfer process is always the same.

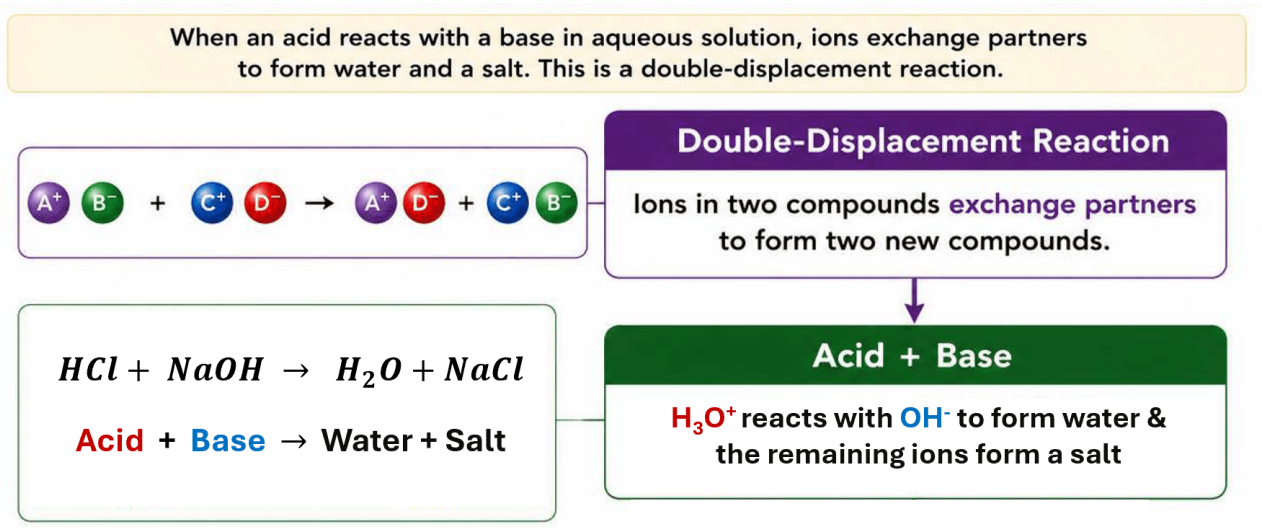


Figure 9.8.1: Acid–base neutralization is a special type of double-displacement reaction. Acid–base neutralization is shown as a special type of double-displacement reaction. At the top, a generalized double-displacement reaction illustrates two ionic compounds exchanging partners to form two new compounds. A text box explains that ions exchange partners during this type of reaction. Below, the neutralization reaction **HCl(aq) + NaOH(aq) → H₂O(l) + NaCl(aq)** is presented as a specific example, followed by the general form **Acid + Base → Water + Salt**. A second text box explains that during neutralization, hydronium ions (or H⊕) react with hydroxide ions (OH⊕) to form water, while the remaining ions combine to form a salt. The figure connects the general concept of double-displacement reactions introduced in Chapter 6 with acid–base neutralization reactions. Reviewed from Chapter 6

Molecular Equations

A **molecular equation** shows all reactants and products as complete chemical formulas.

For example, hydrochloric acid reacts with sodium hydroxide to produce sodium chloride and water.

$$\mathrm{HCl}(aq) \quad + \quad \mathrm{NaOH}(aq) \quad \longrightarrow \quad \mathrm{NaCl}(aq) \quad + \quad \mathrm{H_2O}(l) \tag{9.8.1}$$

Notice that both the acid and the base have been converted into new substances.

Total Ionic Equations

Strong acids, strong bases, and soluble ionic compounds exist as ions in aqueous solution.

The **total or complete ionic equation** shows these dissolved ions separately.

$$\mathrm{H^+}(aq) \quad + \quad \mathrm{Cl^-}(aq) \quad + \quad \mathrm{Na^+}(aq) \quad + \quad \mathrm{OH^-}(aq) \quad \longrightarrow \quad \mathrm{Na^+}(aq) \quad + \quad \mathrm{Cl^-}(aq) \quad + \quad \mathrm{H}$$

Notice that sodium ions and chloride ions appear unchanged on both sides of the equation. These ions do not participate directly in the chemical reaction. They are called **spectator ions**.

Net Ionic Equations

By removing the spectator ions from the complete ionic equation, we obtain the **net ionic equation**, which shows only the species that actually undergo chemical change.

For the neutralization of a strong acid and a strong base,

$$\mathrm{H^+}(aq) \quad + \quad \mathrm{OH^-}(aq) \quad \longrightarrow \quad \mathrm{H_2O}(l) \tag{9.8.3}$$

or, equivalently,

$$\mathrm{H_3O^+}(aq) \quad + \quad \mathrm{OH^-}(aq) \quad \longrightarrow \quad 2\,\mathrm{H_2O}(l) \tag{9.8.4}$$

Both equations describe the same proton-transfer process. Throughout this text, we often use the hydronium ion (H_3O^+) because it more accurately represents acids in aqueous solution.

The net ionic equation emphasizes that all strong acid–strong base neutralization reactions involve the same essential chemistry, regardless of the particular acid or base.

Chemistry in Action

How Antacids Relieve Heartburn

Stomach acid is composed primarily of hydrochloric acid. When too much acid is present, it can cause the burning sensation known as **heartburn**. Antacid tablets contain weak bases such as calcium carbonate or magnesium hydroxide that react with excess stomach acid.

For example,

$$\mathrm{CaCO_3}(s) \quad + \quad 2\,\mathrm{HCl}(aq) \quad \longrightarrow \quad \mathrm{CaCl_2}(aq) \quad + \quad \mathrm{CO_2}(g) \quad + \quad \mathrm{H_2O}(l) \tag{9.8.5}$$

or

$$\mathrm{Mg(OH)_2}(s) \quad + \quad 2\,\mathrm{HCl}(aq) \quad \longrightarrow \quad \mathrm{MgCl_2}(aq) \quad + \quad 2\,\mathrm{H_2O}(l) \tag{9.8.6}$$

These reactions consume excess hydronium ions, raising the pH of the stomach contents and providing relief. Students often recognize these active ingredients from familiar products such as calcium carbonate chewable tablets or milk of magnesia.

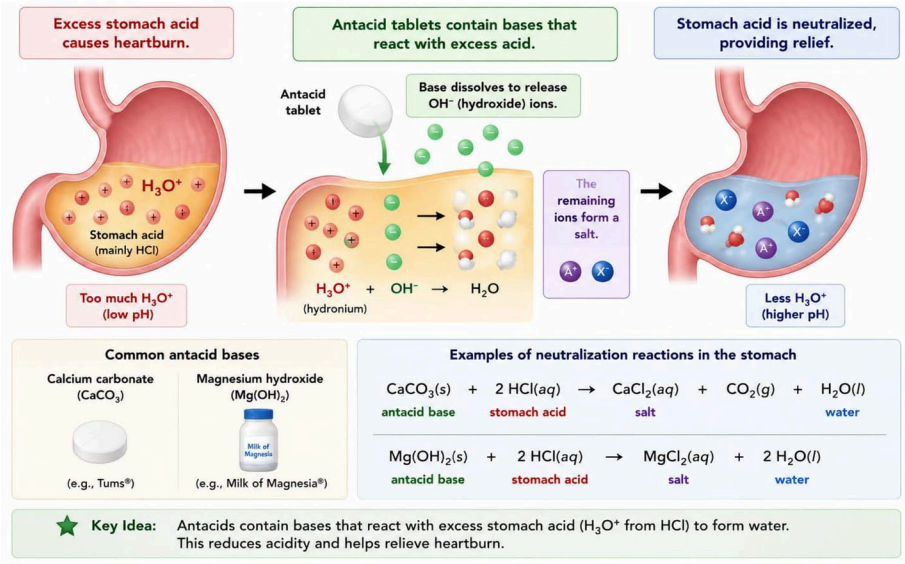


Figure 9.8.2: Antacids neutralize excess stomach acid through acid–base neutralization reactions. An infographic illustrates how antacids relieve heartburn by neutralizing excess stomach acid. The left panel shows a stomach containing excess hydronium ions (H_3O^+) produced by hydrochloric acid (HCl), representing an acidic environment with a low pH. The center panel shows an antacid tablet dissolving and releasing hydroxide ions (OH^-), which react with hydronium ions to form water. Remaining ions combine to form dissolved salts. The right panel shows fewer hydronium ions in the stomach after neutralization, indicating a higher pH and relief from excess acidity. The lower portion of the figure lists two common antacid ingredients, calcium carbonate ($CaCO_3$) and magnesium hydroxide [$Mg(OH)_2$], along with example neutralization reactions:

- $CaCO_3(s) + 2\ HCl(aq) \rightarrow CaCl_2(aq) + CO_2(g) + H_2O(l)$
- $Mg(OH)_2(s) + 2\ HCl(aq) \rightarrow MgCl_2(aq) + 2\ H_2O(l)$

The key idea emphasizes that antacids contain basic compounds that react with excess stomach acid, reducing acidity and helping relieve heartburn.

Introduction to Acid–Base Titrations

One of the most common laboratory techniques for studying acids and bases is the **acid–base titration**. A titration is used to determine the concentration of an unknown acid or base by reacting it with a solution of known concentration.

During a titration, the solution of **known concentration**, called the **titrant**, is added slowly from a buret to a measured volume of the **unknown solution**, called the **analyte**. As the titrant is added, the acid and base react in a neutralization reaction.

The pH of the solution changes throughout the titration. By monitoring this change, chemists can determine when enough titrant has been added to completely react with the analyte.

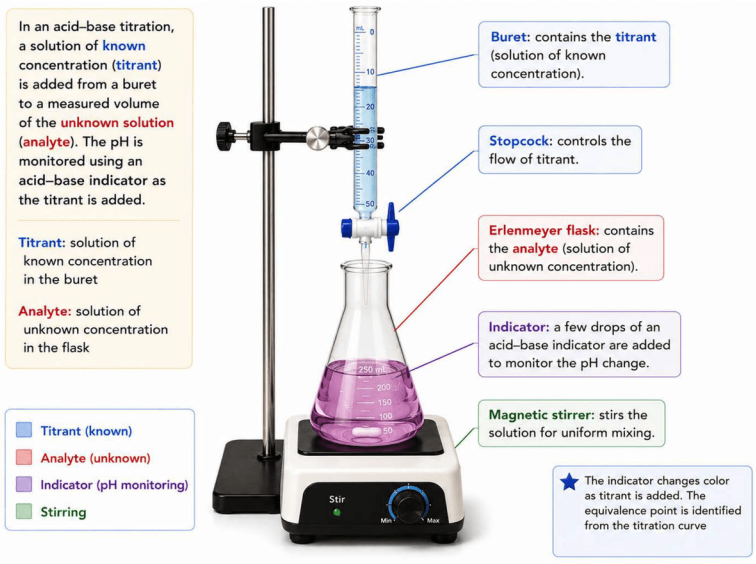


Figure 9.8.3: A typical acid–base titration setup. A labeled diagram of a typical acid–base titration apparatus. A buret containing the **titrant**, a solution of known concentration, is clamped vertically above an Erlenmeyer flask containing the **analyte**, a measured volume of solution with an unknown concentration. A stopcock at the bottom of the buret controls the addition of the titrant to the flask. The flask sits on a magnetic stirrer to ensure the solution mixes continuously as the titrant is added. A few drops of an acid–base indicator are added to the analyte before the titration begins. As the titrant is added, the indicator changes color near the endpoint, signaling that the equivalence point has been reached or is very close. The figure identifies the major components of the apparatus, including the buret, stopcock, Erlenmeyer flask, magnetic stirrer, titrant, analyte, and indicator.

The Equivalence Point

As titrant is added, the acid and base continuously neutralize one another.

Eventually, a point is reached where the **amount of acid added is chemically equivalent to the amount of base originally present**. This is called the **equivalence point**.

At the equivalence point:

- all of the acid has reacted,
- all of the base has reacted,
- neither reactant is present in excess.

For a titration involving a **strong acid and a strong base**, the solution is approximately **neutral (pH ≈ 7)** at the equivalence point.

It is important to distinguish the **equivalence point** from the **endpoint**. The equivalence point is determined by the reaction stoichiometry, whereas the endpoint is the point at which an indicator changes color. A well-chosen indicator changes color very close to the equivalence point.

The Titration Curve

As titrant is added, the pH changes gradually at first. Near the equivalence point, however, a very small addition of titrant causes a **large change in pH**. Plotting the pH as a function of the volume of titrant added produces a **titration curve**. The steep vertical region of the curve identifies the equivalence point. For a strong acid–strong base titration, the equivalence point occurs at approximately **pH 7**.

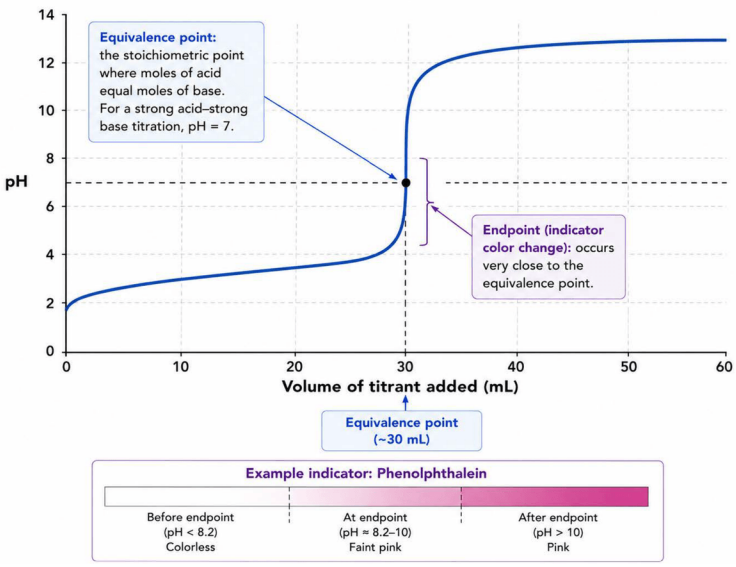


Figure 9.8.4: A titration curve identifies the equivalence point of an acid–base titration. A graph illustrates the pH changes during a strong acid–strong base titration. The vertical axis shows pH from 0 to 14, and the horizontal axis shows the volume of titrant added (mL). The titration curve begins at a low pH, increases gradually as titrant is added, then rises steeply near the equivalence point before leveling off at a high pH. The **equivalence point** is marked near 30 mL of titrant added at **pH = 7**, indicating the stoichiometric point where equivalent amounts of acid and base have reacted. A note explains that, for a strong acid–strong base titration, the equivalence point occurs at approximately pH 7. A second annotation identifies the **endpoint**, the point at which an acid–base indicator changes color, and notes that it occurs very close to the equivalence point. Beneath the graph, a color bar illustrates the behavior of **phenolphthalein**: colorless before the endpoint, faint pink near the endpoint (approximately pH 8.2–10), and pink after the endpoint.

Why Titrations Matter

Acid–base titrations are widely used in chemistry, biology, medicine, environmental science, and industry.

Some common applications include:

- determining the concentration of an unknown acid or base,
- measuring the acidity of foods and beverages,
- monitoring the quality of drinking water,
- analyzing pharmaceuticals,
- determining the acidity of soil and agricultural products.

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9.9: Buffers - Maintaining a Stable pH

Learning Objectives

After completing this section, you should be able to:

- Explain what a buffer is.
- Describe how a weak acid and its conjugate base resist changes in pH.
- Explain the role of the bicarbonate buffer system in blood.
- Describe why buffers are essential for living organisms.

What Is a Buffer?

Many chemical and biological processes require the pH to remain within a narrow range. Although acids and bases are continually added to biological systems, the pH often changes very little.

A **buffer** is a solution that **resists changes in pH** when small amounts of acid or base are added.

Most buffers consist of

- a **weak acid**, and
- its **conjugate base**.

Because both species are present in solution, the buffer can react with either added acid or added base.

Unlike a strong acid or strong base, a buffer does not completely neutralize added chemicals. Instead, it minimizes changes in pH by shifting equilibrium between the weak acid and its conjugate base.

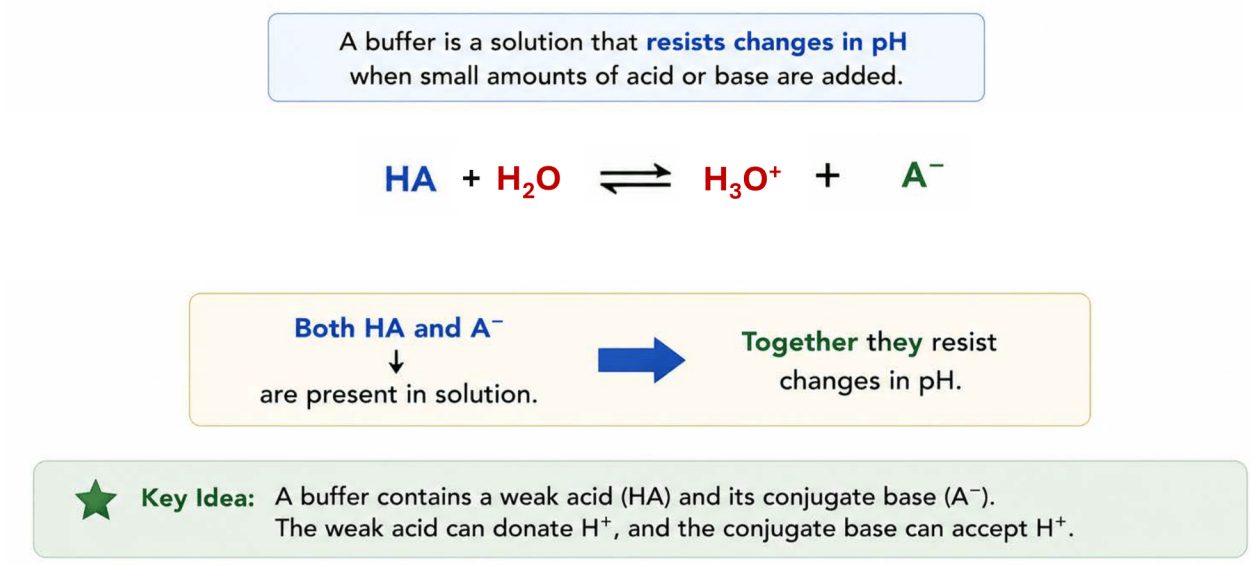


Figure 9.9.1: A buffer contains a weak acid and its conjugate base. A buffer is defined as a solution that resists changes in pH when small amounts of acid or base are added. The equilibrium equation **HA + H_2O ⇌ H_3O^+ + A^-** illustrates the partial ionization of a weak acid (HA) to produce hydronium ions (H_3O^+) and its conjugate base (A^-). A highlighted statement explains that both the weak acid (HA) and its conjugate base (A^-) are present together in

solution, allowing them to work together to resist changes in pH. A key idea summarizes that a buffer contains a weak acid and its conjugate base; the weak acid can donate H⊕, and the conjugate base can accept H⊕.

How Buffers Work

Suppose a small amount of acid is added to a buffer. The added hydronium ions react with the **conjugate base**, forming more weak acid.

$$\mathbf{A^-}(aq) \quad + \quad \mathbf{H_3O^+}(aq) \quad \longrightarrow \quad \mathbf{HA}(aq) \quad + \quad \mathbf{H_2O}(l) \tag{9.9.1}$$

Because the added acid is converted into a weak acid, the pH changes only slightly.

Now suppose a small amount of base is added. The hydroxide ions react with the **weak acid**, producing water and more conjugate base.

$$\mathbf{HA}(aq) \quad + \quad \mathbf{OH^-}(aq) \quad \longrightarrow \quad \mathbf{A^-}(aq) \quad + \quad \mathbf{H_2O}(l) \tag{9.9.2}$$

Again, most of the added base is consumed, so the pH changes only slightly. In both cases, the weak acid and its conjugate base work together to resist large changes in pH.

The Bicarbonate Buffer System

One of the most important buffers in the human body is the **bicarbonate buffer system**.

It consists primarily of

- **carbonic acid, H_2CO_3,**
- **bicarbonate ion, HCO_3⊕**

These substances help maintain the pH of blood near **7.4**, despite the continual production of acids during metabolism.

When excess acid enters the bloodstream,

$$\mathbf{HCO_3^-}(aq) \quad + \quad \mathbf{H_3O^+}(aq) \quad \longrightarrow \quad \mathbf{H_2CO_3}(aq) \quad + \quad \mathbf{H_2O}(l) \tag{9.9.3}$$

When excess base is added,

$$\mathbf{HCO_3^-}(aq) \quad + \quad \mathbf{H^+}(aq) \quad \longrightarrow \quad \mathbf{H_2CO_3}(aq) \tag{9.9.4}$$

In this way, the buffer continually adjusts to maintain a nearly constant blood pH.

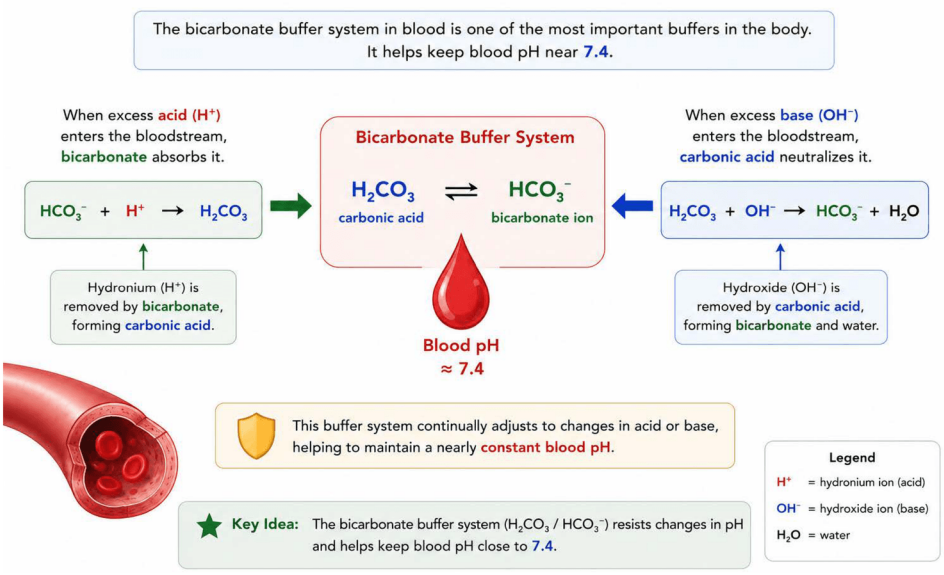


Figure 9.9.2: The bicarbonate buffer system helps maintain blood pH. The bicarbonate buffer system is illustrated as the primary buffer that helps maintain blood pH near **7.4**. At the center of the figure, carbonic acid (H_2CO_3) and bicarbonate ion (HCO_3^-) are connected by a reversible equilibrium arrow, representing the buffer system. On the left, the figure shows how excess acid (H^+) is removed from the bloodstream by bicarbonate ions:

HCO_3^- + H^+ → H_2CO_3 forming carbonic acid. On the right, the figure shows how excess base (OH^-) is neutralized by carbonic acid: **H_2CO_3 + OH^- → HCO_3^- + H_2O** producing bicarbonate ions and water. A blood drop icon emphasizes that these reactions help maintain a blood pH of approximately **7.4**. A key idea states that the bicarbonate buffer system (H_2CO_3/HCO_3^-) resists changes in pH by removing excess acid or base, helping keep blood pH nearly constant.

Why Buffers Matter

Living organisms are extremely sensitive to changes in pH. Even small changes in blood pH can affect the structure and function of proteins, including enzymes that control essential biochemical reactions. Buffers help maintain the stable environment required for normal cellular function. Buffers are also important in many other systems, including:

- lakes and rivers,
- soils,
- industrial chemical processes,
- pharmaceutical formulations,
- foods and beverages.

Without buffers, even small additions of acids or bases could produce large changes in pH.

Key Idea

Buffers contain a **weak acid and its conjugate base**.

Together, they react with added acids and bases to minimize changes in pH and help maintain stable conditions in living organisms and the environment.

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9.10: Focus on the Environment - Ocean Acidification

Learning Objectives

After completing this section, you should be able to:

- Explain how increasing atmospheric carbon dioxide changes ocean chemistry.
- Describe the chemical reactions responsible for ocean acidification.
- Explain why carbonate ions are important for marine organisms.
- Relate acid–base chemistry, equilibrium, and buffers to an environmental issue.

Ocean Chemistry Is Changing

Throughout this textbook, we have learned that carbon dioxide dissolves in water to form **carbonic acid**, a weak acid. The same chemistry occurs naturally in Earth's oceans.

The ocean absorbs approximately **25–30% of the carbon dioxide released into the atmosphere by human activities**, helping reduce atmospheric CO_2 concentrations. However, this also changes seawater chemistry.

For hundreds of thousands of years, the average surface ocean had a pH of approximately **8.2**, making it slightly basic. Since the beginning of the Industrial Revolution, the average surface ocean pH has decreased to about **8.1**. Although this change appears small, the logarithmic nature of the pH scale means it represents roughly a **30% increase in acidity**.

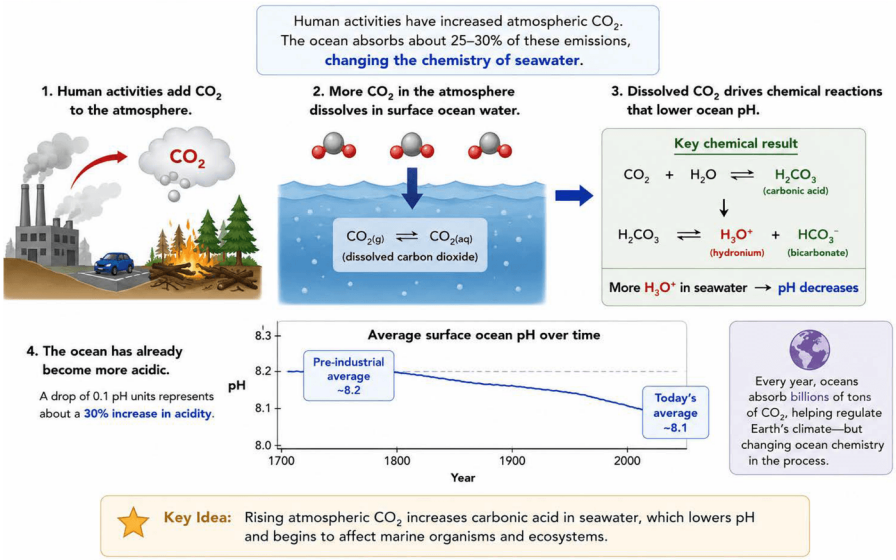


Figure 9.10.1: Increasing atmospheric carbon dioxide changes ocean chemistry. An infographic summarizes how increasing atmospheric carbon dioxide (CO_2) changes ocean chemistry. The figure begins by showing human activities, such as burning fossil fuels and wildfires, increasing the amount of carbon dioxide in the atmosphere. Approximately 25–30% of this atmospheric CO_2 dissolves into surface ocean water. Dissolved carbon dioxide reacts with water to form carbonic acid (H_2CO_3), which partially ionizes to produce hydronium ions (H_3O^+) and bicarbonate ions (HCO_3^-). The increase in hydronium ions lowers ocean pH. A graph shows that the average surface ocean pH has decreased from approximately 8.2 before the Industrial Revolution to about 8.1 today, corresponding to roughly a 30% increase in acidity. A concluding statement emphasizes that rising atmospheric CO_2 increases carbonic acid in seawater, lowering pH and beginning to affect marine organisms and ecosystems.

Carbon Dioxide Forms Carbonic Acid

When atmospheric carbon dioxide dissolves into seawater, it reacts with water.

$$\mathrm{CO_2}(g) \quad + \quad \mathrm{H_2O}(l) \quad \rightleftharpoons \quad \mathrm{H_2CO_3}(aq) \tag{9.10.1}$$

Carbonic acid is a weak acid that partially ionizes.

$$\mathrm{H_2CO_3}(aq) \quad + \quad \mathrm{H_2O}(l) \quad \rightleftharpoons \quad \mathrm{H_3O^+}(aq) \quad + \quad \mathrm{HCO_3^-}(aq) \tag{9.10.2}$$

As more CO_2 dissolves into seawater, more hydronium ions are produced. More hydronium ions lower the pH of the ocean's waters.

Notice that this is the **same carbonic acid equilibrium** discussed earlier in this chapter when learning about buffers.

Carbonate Ions Become Less Available

One consequence of increasing hydronium ion concentration is often overlooked. The added hydronium ions react with carbonate ions already dissolved in seawater.

$$\mathrm{H_3O^+}(aq) \quad + \quad \mathrm{CO_3^{2-}}(aq) \quad \rightleftharpoons \quad \mathrm{HCO_3^-}(aq) \quad + \quad \mathrm{H_2O}(l) \tag{9.10.3}$$

This reaction removes carbonate ions from solution. Although bicarbonate ions increase, **carbonate ions decrease**. This distinction is important because many marine organisms require carbonate ions to build calcium carbonate.

Why Carbonate Matters

Many marine organisms build shells or skeletons from **calcium carbonate ($CaCO_3$).**

Examples include

- corals
- oysters
- clams
- sea urchins
- pteropods ("sea butterflies")
- many plankton species

These organisms use dissolved calcium ions and carbonate ions to build calcium carbonate.

$$\mathrm{Ca^{2+}}(aq) \quad + \quad \mathrm{CO_3^{2-}}(aq) \quad \rightleftharpoons \quad \mathrm{CaCO_3}(s) \tag{9.10.4}$$

When fewer carbonate ions are available, shell formation becomes more difficult. Existing shells are generally not expected to dissolve under current ocean conditions, but growth can slow and newly formed shells may be thinner or weaker.

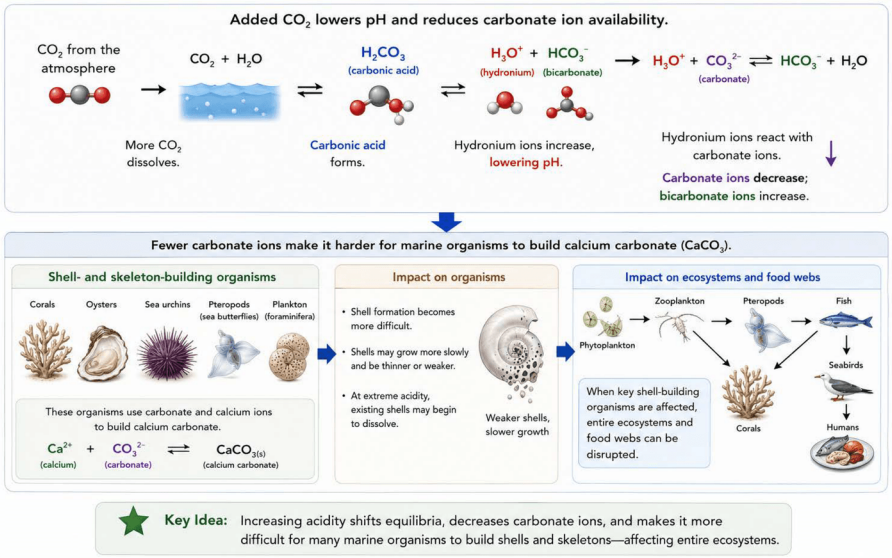


Figure 9.10.2: Ocean acidification decreases carbonate ions, making shell formation more difficult for marine organisms. An infographic illustrates how ocean acidification reduces the availability of carbonate ions and affects marine organisms. The **upper portion** of the figure shows atmospheric carbon dioxide (CO_2) dissolving into seawater, where it reacts with water to form carbonic acid (H_2CO_3). Carbonic acid partially ionizes to produce hydronium ions (H_3O^+) and bicarbonate ions (HCO_3^-). The added hydronium ions then react with carbonate ions (CO_3^{2-}), converting them into additional bicarbonate ions. As a result, carbonate ion concentration decreases while bicarbonate concentration increases, lowering the amount of carbonate available in seawater. The **lower portion** of the figure explains the biological consequences. Shell- and skeleton-building organisms—including corals, oysters, sea urchins, pteropods, and planktonic foraminifera—use calcium ions (Ca^{2+}) and carbonate ions (CO_3^{2-}) to produce calcium carbonate ($CaCO_3$), the material used to build shells and skeletons. When carbonate ions become less available, shell formation becomes more difficult, and shells may grow more slowly or be thinner and weaker. The figure also illustrates that changes to shell-building organisms can affect marine food webs, influencing larger organisms such as fish, seabirds, and ultimately humans. The key idea emphasizes that increasing ocean acidity shifts chemical equilibria, decreases carbonate ion availability, and affects marine ecosystems by making calcium carbonate shell formation more difficult.

Effects on Marine Ecosystems

Changes in ocean chemistry affect more than individual organisms. Coral reefs provide habitat for thousands of marine species. If coral growth slows, the entire ecosystem may be affected. Some organisms, such as cold-water pteropods, may be especially vulnerable because carbon dioxide dissolves more readily in cold water, leading to greater decreases in pH.

Ocean acidification can also affect organisms that do not build shells. Changes in seawater chemistry have been shown to alter the behavior of some fish and other marine organisms, influencing predator avoidance and habitat selection.

Chemistry in Action

In the laboratory, ocean acidification can be modeled by gently blowing through a straw into artificial seawater.

The carbon dioxide in your breath dissolves into the water, forming carbonic acid and lowering the pH. This simple investigation demonstrates the same chemical processes that occur naturally as atmospheric carbon dioxide dissolves into the oceans.

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9.11: Summary

In this chapter, you learned that **acids** and **bases** are substances that transfer protons (H^+) in chemical reactions. According to the **Brønsted–Lowry theory**, acids donate protons and bases accept protons. When an acid donates a proton, it forms its **conjugate base**, while a base that accepts a proton forms its **conjugate acid**. Some substances, such as bicarbonate (HCO_3^-), are **amphoteric**, meaning they can act as either an acid or a base depending on the reaction.

Strong acids and bases **ionize almost completely** in water, whereas weak acids and bases ionize only partially and establish an **equilibrium** between reactants and products. Acid strength depends on the extent of ionization, not on how much acid is present. Therefore, **strong** and **concentrated** describe different properties: strength refers to ionization, while concentration describes the amount of dissolved solute.

Water undergoes **autoionization**, producing small, equal amounts of **hydronium ions (H_3O^+)** and **hydroxide ions (OH^-)**. The product of their concentrations is the **ion-product constant for water (K_w)**, which equals 1.0×10^{-14} at 25 °C. In a neutral solution, the concentrations of hydronium and hydroxide ions are equal.

The **pH scale** provides a convenient way to express hydronium ion concentration. Solutions with pH values less than 7 are acidic, solutions with a pH of 7 are neutral, and solutions with pH values greater than 7 are basic. Because pH is logarithmic, a one-unit change in pH corresponds to a tenfold change in hydronium ion concentration.

When acids and bases react, they undergo a **neutralization reaction**, producing water and a salt. Neutralization reactions are a special type of **double-displacement reaction** and can be represented using molecular, complete ionic, and net ionic equations. These reactions have many practical applications, including the use of **antacids** to relieve heartburn and **titrations** to determine the concentration of an unknown solution.

Many biological systems rely on **buffers**, which are solutions containing a weak acid and its conjugate base. Buffers resist large changes in pH by reacting with added acids or bases. One of the most important biological buffers is the **bicarbonate buffer system**, which helps maintain the pH of human blood near 7.4.

Finally, you explored **ocean acidification**, a real-world example that integrates many of the concepts in this chapter. As atmospheric carbon dioxide dissolves into seawater, it forms carbonic acid, increasing the hydronium ion concentration and lowering ocean pH. The resulting decrease in carbonate ions makes it more difficult for many marine organisms to build calcium carbonate shells and skeletons, demonstrating how acid–base chemistry influences Earth's ecosystems.

Big Picture

Throughout this chapter, you learned that acids, bases, and buffers are connected by the transfer of protons and the principles of chemical equilibrium. These concepts explain everyday phenomena—from heartburn relief and blood pH regulation to laboratory titrations and the effects of rising atmospheric carbon dioxide on Earth's oceans. Understanding acid–base chemistry provides a foundation for studying biological systems, environmental science, medicine, and many industrial processes.

Key Terms

Acid – A substance that donates a proton (H^+) to another substance.

Base – A substance that accepts a proton (H^+) from another substance.

Brønsted–Lowry acid – A proton donor.

Brønsted–Lowry base – A proton acceptor.

Conjugate acid – The species formed when a base gains a proton.

Conjugate base – The species formed when an acid loses a proton.

Conjugate acid–base pair – Two species that differ by the gain or loss of one proton.

Amphoteric – A substance that can act as either an acid or a base.

Strong acid – An acid that ionizes almost completely in water.

Weak acid – An acid that ionizes only partially in water.

Strong base – A base that dissociates almost completely in water.

Weak base – A base that ionizes only partially in water.

Ionization – The process by which a neutral molecule forms ions in solution.

Equilibrium – A dynamic state in which the forward and reverse reactions occur at the same rate, so concentrations remain constant.

Autoionization of water – The reaction in which water molecules transfer protons to one another, producing hydronium and hydroxide ions.

Hydronium ion (H_3O^+) – The ion formed when water accepts a proton; responsible for the acidic properties of aqueous solutions.

Hydroxide ion (OH^-) – The ion formed when water loses a proton; responsible for the basic properties of aqueous solutions.

Ion-product constant for water (K_w) – The equilibrium constant describing the autoionization of water, equal to 1.0×10^{-14} at 25 °C.

pH – A logarithmic measure of hydronium ion concentration, defined as $pH = -\log[H_3O^+]$.

pOH – A logarithmic measure of hydroxide ion concentration, defined as $pOH = -\log[OH^-]$.

Neutralization reaction – A reaction in which an acid and a base react to produce water and a salt.

Salt – An ionic compound produced during many neutralization reactions.

Titration – A laboratory technique used to determine the concentration of an unknown solution by reacting it with a solution of known concentration.

Equivalence point – The point in a titration at which stoichiometrically equivalent amounts of acid and base have reacted.

Endpoint – The point in a titration at which the indicator changes color, signaling that the equivalence point has been reached or is very near.

Indicator – A substance that changes color over a specific pH range and is used to identify the endpoint of a titration.

Buffer – A solution containing a weak acid and its conjugate base that resists changes in pH when small amounts of acid or base are added.

Bicarbonate buffer system – The carbonic acid/bicarbonate equilibrium that helps maintain the pH of blood and many natural waters.

Ocean acidification – The decrease in ocean pH caused by the absorption of atmospheric carbon dioxide, which forms carbonic acid and shifts acid–base equilibria in seawater.

Chapter Review Problems

1. Identifying Acids and Bases:

For each reaction below, identify the **Brønsted–Lowry acid**, **Brønsted–Lowry base**, **conjugate acid**, and **conjugate base**.

a) $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$

b) $HF + H_2O \rightleftharpoons H_3O^+ + F^-$

c) $HSO_4^- + H_2O \rightleftharpoons H_3O^+ + SO_4^{2-}$

---

2. Conjugate Acid–Base Pairs:

Complete the table below.

Identification of conjugate acid-base pairs

Species	Conjugate Acid	Conjugate Base
H_2O		
HCO_3^-		
NH_4^+		
HSO_4^-		

---

3. Amphoteric Species:

Hydrogen Phosphate (HPO_4^{2-}) is amphoteric.

a. Write a reaction showing hydrogen phosphate acting as an **acid**.

b. Write a reaction showing hydrogen phosphate acting as a **base**.

---

4. Strong vs. Weak Acids:

Two solutions each contain **0.10 M acid**.

- Solution A contains HCl.
- Solution B contains CH_3COOH.

Which solution contains the higher concentration of hydronium ions? Explain why.

---

5. Strength vs. Concentration:

Determine whether each statement is **True** or **False**. If the statement is false, rewrite it to make it correct.

a. A strong acid always has a lower pH than a weak acid.

b. Strong acids ionize almost completely in water.

c. Concentration tells how much acid is dissolved in a solution.

d. Strength tells how completely an acid ionizes in water.

6. pH Calculations:

Calculate the pH of each solution.

a. $[H_3O^+] = 2.5\times10^{-3}\ M$

b. $[H_3O^+] = 4.0\times10^{-9}\ M$

---

7. Hydronium Concentration:

Calculate the hydronium ion concentration for each solution.

a. pH = 2.75

b. pH = 8.40

Express each answer in scientific notation using the correct number of significant figures.

---

8. Classifying Solutions:

For each solution, indicate whether it is **acidic**, **neutral**, or **basic**.

Identifying Solutions as Acidic or Basic

Solution	pH	Acidic? Neutral? Basic?
1	3.4	
2	7.0	
3	9.8	
4	12.1	
5	6.9	

---

9. Neutralization:

Complete and balance the following molecular equation.

$HNO_3\ (aq) + Ca(OH)_2\ (aq) \rightarrow$

Then write the **total ionic equation** and the **net ionic equation**.

---

10. Buffers:

Complete the following statements.

a. A buffer contains a _____ and its _____.

b. When a small amount of acid is added to a buffer, the _____ reacts with the added H^+.

c. When a small amount of base is added to a buffer, the _____ reacts with the added OH^-.

d. Buffers help maintain a relatively _____ pH.

---

11. Titration:

A student performs a titration by slowly adding NaOH to a flask containing HCl and an indicator.

a. What is the purpose of the indicator?

b. Define the **equivalence point**.

c. Why is the equivalence point not necessarily identical to the endpoint?

---

12. Bicarbonate Buffer:

Explain how the bicarbonate buffer system responds when:

a. Acid is added to the blood.

b. Base is added to the blood.

---

13. Ocean Acidification:

Use the following reactions to explain why increasing atmospheric CO_2 makes it more difficult for many marine organisms to build calcium carbonate shells.

$CO_2 + H_2O \diamond H_2CO_3$

$H_2CO_3 + H_2O \diamond H_3O^+ + HCO_3^-$

$H_3O^+ + CO_3^{2-} \diamond HCO_3^- + H_2O$

---

14. Chapter Challenge:

A patient takes an antacid tablet containing calcium carbonate after eating a large meal.

Explain, in complete sentences, how this tablet relieves heartburn using the concepts of:

- acids
- bases
- neutralization
- pH

Answers to Odd-Numbered Practice Problems:

1. Identifying Acids, Bases, and Conjugate Acid–Base Pairs

(a) $NH_3 + H_2O \diamond NH_4^+ + OH^-$

- **Brønsted–Lowry acid:** H_2O
- **Brønsted–Lowry base:** NH_3
- **Conjugate acid:** $NH_4\diamond$
- **Conjugate base:** $OH\diamond$

b) $HF + H_2O \diamond H_3O^+ + F^-$

c) $HSO_4^- + H_2O \diamond H_3O^+ + SO_4^{2-}$

(b) $HF + H_2O \diamondsuit H_3O^+ + F^-$

- **Brønsted–Lowry acid:** HF
- **Brønsted–Lowry base:** H_2O
- **Conjugate acid:** $H_3O\diamondsuit$
- **Conjugate base:** $F\diamondsuit$

(c) $HSO_4^- + H_2O \diamondsuit H_3O^+ + SO_4^{2-}$

- **Brønsted–Lowry acid:** $HSO_4\diamondsuit$
- **Brønsted–Lowry base:** H_2O
- **Conjugate acid:** $H_3O\diamondsuit$
- **Conjugate base:** $SO_4{}^2\diamondsuit$

---

3. Amphoteric Species:

(a) Hydrogen phosphate acting as an acid

$HPO_4^{2-} + H_2O \diamondsuit PO_4^{3-} + H_3O^+$

(b) Hydrogen phosphate acting as a base

$HPO_4^{2-} + H_3O^+ \diamondsuit H_2PO_4^- + H_2O$

---

5. Strength vs. Concentration:

a. False. A strong acid does **not always** have a lower pH than a weak acid because pH depends on **both acid strength and concentration**.

b. True

c. True

d. True

---

7. Hydronium Ion Concentration:

Use

$[H_3O^+] = 10^{-pH}$

(a) pH = 2.75

$[H_3O^+] = 10^{-2.75} = 1.8\times10^{-3}$ M

(two significant figures)

(b) pH = 8.40

$[H_3O^+] = 10^{-8.40} = 4.0\times10^{-9}$ M

(two significant figures)

9. Neutralization:

Balanced Molecular Equation

$2HNO_3\,(aq) + Ca(OH)_2\,(aq) \rightarrow Ca(NO_3)_2\,(aq) + 2H_2O\,(l)$

Total Ionic Equation

$2H^+(aq) + 2NO_3^-(aq) + Ca^{2+}\,(aq) + 2OH^-\,(aq) \rightarrow Ca^{2+}\,(aq) + 2NO_3^-\,(aq) + 2H_2O\,(l)$

Net Ionic Equation

Either of the following is acceptable:

$H^+\,(aq) + OH^-\,(aq) \rightarrow H_2O\,(l)$

or

$H_3O^+\,(aq) + OH^-\,(aq) \rightarrow 2H_2O\,(l)$

---

11. Titration:

a. The indicator changes color near the endpoint, signaling that the titration is complete.

b. The **equivalence point** is reached when stoichiometrically equivalent amounts of acid and base have reacted.

c. The **endpoint** is the observed color change of the indicator. A properly chosen indicator changes color very close to, but not necessarily exactly at, the equivalence point.

---

13. Ocean Acidification:

As atmospheric carbon dioxide increases, more CO_2 dissolves into seawater and reacts with water to form **carbonic acid**. Carbonic acid partially ionizes to produce **hydronium ions**, increasing the acidity of seawater and lowering the pH. The added hydronium ions react with **carbonate ions** to form bicarbonate ions, reducing the amount of carbonate available in solution. Because many marine organisms use carbonate ions to build **calcium carbonate ($CaCO_3$)** shells and skeletons, shell formation becomes more difficult as carbonate ion availability decreases.

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9.12: References

Open Educational Resources

- Chemistry LibreTexts. *Introduction to General Chemistry* (Malik), Chapter 6: Acids and Bases.(opens in new window)

Educational Resources

- Howard Hughes Medical Institute (HHMI) BioInteractive. Ocean Acidification Student Handout.(opens in new window)

Figures and Original Illustrations

- Unless otherwise noted, figures in this chapter were created by the author for this Open Educational Resource.

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1.4: Avogadro's Number and the Mole

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GLOSSARY

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Sample Word 1 | Sample Definition 1

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