# Chapter 1 – The Early Experiments

# Introduction

Chemistry is the science of matter, its properties, and the changes it undergoes. Chemists seek to understand our material universe at a molecular level and to use this understanding to improve our interaction with it, often creating new products that enhance our lives. Chemists often design these products by considering the properties of the desired substance and then proposing reactions of atoms or molecules that might yield the substances of choice. This design process involves particles and processes chemists can imagine but cannot see. They can observe the results of a reaction, such as a color change or the formation of a gas or a solid, but they cannot view directly the collisions of the atoms or molecules in a reaction or the changes these collisions produce. However, chemists are confident that these collisions and changes do take place, and we begin our study of chemistry by examining how we came to the point where we could envision these invisible processes.

# 1.1 The Scientific Method

# Introduction

**Chemistry** is that branch of science that deals with matter and the changes it undergoes, and **science** is that branch of knowledge that is gained by the application of the scientific method. In this section, we explain the scientific method and show an example of its use.

# Objectives

• Apply the scientific method to simple problems.

# 1.1-1. Scientific Method

The entire body of knowledge called science was achieved through the application of the scientific method.

Our understanding of atoms and molecules was gained by repeated application of the scientific method<sup>1</sup>.

There are four steps in the scientific method:

- 1 **Observe:** Observations can be either quantitative or qualitative.
  - *Quantitative observations* involve numbers. "The mass of the substance is 3.0 g and its volume is 36 cm<sup>3</sup>" are quantitative observations.
  - **Qualitative observations** do not involve numbers. "The substance is shiny and reacts with oxygen" are qualitative observations.
- 2 Hypothesize: Form a *hypothesis*; i.e., suggest an explanation for the observation.
  - If the observation is that the substance is shiny and reacts with oxygen, the hypothesis might be that the substance is a metal.
- **3 Predict:** Use the hypothesis to make predictions.
  - If the substance is a metal, then it should conduct electricity.
- **4 Test:** Do the experiment to test the prediction. If the test supports the hypothesis, return to Step 3 and make another prediction to test the hypothesis. If the test does not support the hypothesis, return to Step 2 and modify the hypothesis to include the results of the test.
  - Apply a voltage across the substance to see if it does indeed conduct electricity. If it does, make another prediction based on the first hypothesis. If the first hypothesis fails the test, another hypothesis must be made and a new prediction must be tested.

The above process is repeated over and over again with new predictions and new tests (experiments). If a hypothesis stands up to many such tests and becomes accepted as the explanation for the observation, then the hypothesis becomes a theory. A **theory** is an accepted explanation of an observation. Theories can be supported by experiment, but they cannot be proven.

 $<sup>^{1}</sup> http://www.access$  $excellence.org/AB/BC/Elegant\_Experiments.html$ 

# 1.1-2. Phlogiston

Phlogiston theory, one of the first theories that attempted to explain a property of matter, was proposed in the late 17<sup>th</sup> century to explain fire. The following is an application of the scientific method to phlogiston theory. In it, we examine some chemical and physical properties of magnesium.

- *Chemical property*: a property of one substance that is related to another substance. For example, "magnesium burns in air" is a chemical property because the property of magnesium requires the presence of air.
- *Physical property*: a property of one substance that is independent of other substances. For example, "magnesium is a shiny metal" is a physical property.

#### **OBSERVATIONS**:



Magnesium is a shiny metal.



Magnesium releases something to produce a brilliant white light when it is burned.



Burning the magnesium converts it from a shiny metal to a gray powder.

# HYPOTHESIS:

Magnesium metal contains a substance that is released when the magnesium is burned. The substance was named "phlogiston." The gray powder was the magnesium without its phlogiston, so it was the "dephlogisticated" form of the metal, which was called "calx." Thus, burning magnesium would have been represented as

magnesium  $\rightarrow$  calx of magnesium + phlogiston

#### PREDICTION:

If the metal contains both the calx and phlogiston, then the mass of the metal should be greater than the mass of the calx.

#### TEST:

The mass of the calx was greater than the mass of the metal. The phlogiston hypothesis withstood experiment for over 100 years, but this experiment, which was performed by a scientist named Antoine Lavoisier, destroyed the theory. Although some argued that mass was irrelevant to the study, others agreed with Lavoisier's conclusion that phlogiston theory was incorrect.

Thus, application of the scientific method led to the downfall of phlogiston theory, and its continued application to other hypotheses has led us to our current understanding of the universe.

# 1.2 Lavoisier and the Birth of Modern Chemistry Introduction

Measurements of the ratios in which the masses of substances combined with one another led to the statements of three laws: conservation of mass, constant composition, and multiple proportions. In this section, we briefly examine these three laws because they give us our next clues about the composition of matter.

#### **Objectives**

- Define a law.
- Explain a theory and give an example.

#### 1.2-1. Laws

#### Laws summarize observations.

Lavoisier made many careful measurements of the masses of the reactants and products of reactions, and he observed that the total mass (products plus reactants) never changed during a reaction. He summarized his observation in the law of conservation of mass.

• Law of conservation of mass: The total mass of reactants and products remains constant during a chemical reaction. That is, mass is neither created nor destroyed in a chemical reaction.

Note that the above *law* simply *summarizes* the observations; it does not explain them. The explanation (theory) would not come for another decade.

Lavoisier summarized his observations in the law of conservation of mass, and his work convinced many scientists that phlogiston did not exist. The emerging chemists of the early 19<sup>th</sup> century began testing the concept that matter consisted of elements and compounds and that mass was indeed relevant to chemistry. After a great number of measurements of relative masses had been performed, the following two laws were also accepted:

- *Law of definite proportions*: The elements of a compound are always present in definite proportions by mass. For example,
  - Table salt is always 39% Na and 61% Cl by mass.
  - Water is always 11% H and 89% O by mass.
- Law of multiple proportions: When two different compounds are formed from the same two elements, the masses of one element that combine with a fixed mass of the other are in a ratio of small whole numbers. (If the ratio is one, then the two samples consist of the same compound.)

#### EXAMPLE:

For example, one oxide of iron contains  $\frac{3.490 \text{ g Fe}}{1 \text{ g O}}$ , while another contains  $\frac{2.327 \text{ g Fe}}{1 \text{ g O}}$ . Both amounts of iron are combined with the same mass of oxygen (1 g), and the ratio of the masses is determined as follows:

$$\frac{3.490 \text{ g Fe}}{2.327 \text{ g Fe}} = 1.50 = \frac{3}{2}$$

which is a ratio of small whole numbers.

#### 1.2-2. Mass Law Exercise

#### EXERCISE 1.1:

Na and O form two compounds. 100 g of each compound contains the following masses of the elements.

```
Compound I: 59 g Na 41 g O
Compound II: 74 g Na 26 g O
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Show that the data is consistent with the Law of Multiple Proportions.

Step 1. Determine the mass of Na that combines with a fixed mass (1 g) of O in each compound.

Compound I mass Na/mass O =\_\_\_\_\_g Na/g O

Compound II	mass $Na/mass O = $	g Na/g O
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Step 2. Determine the ratio of the mass of Na combined with 1 g of O in Compound II to Compound I.

Compound II/Compound I = \_\_\_\_\_

Step 3. Express the result of Step 2 as a reduced fraction of small whole numbers.

numerator

denominator

#### 1.2-3. Theories

Theories explain laws and observations. They can be accepted but not proven.

Theories are valid only as long as they are not disproven by experiment. In general, theories are continually modified or even discarded as more sophisticated experiments are carried out. The work of Antoine Lavoisier discredited phlogiston, so Lavoisier proposed a new hypothesis, which, after acceptance by others, became known as the theory of combustion. After further experiments, he presented the hypothesis that the mass of a metal increased when burned because burning was the combination of two substances, not the release of one. His combustion hypothesis was that burning is the reaction of a substance with oxygen. He named the product "the oxide" of the substance to indicate that the substance had oxygen added to it. Thus, he would have represented the burning of magnesium as

magnesium + oxygen  $\rightarrow$  magnesium oxide

Lavoisier began to classify matter as elements and compounds.

- An element is a pure substance that cannot be broken down into a simpler substance by chemical means.
- A compound is a pure substance that consists of more than one element.

Thus, magnesium and oxygen are elements, and magnesium oxide is a compound that is composed of the two elements magnesium and oxygen. Lavoisier's hypothesis was to be accepted by most other scientists and became the chemical *theory* that was used to *explain* matter and chemical reactions.

# 1.3 John Dalton and Atomic Theory

#### Introduction

We now explore the emergence of atoms and molecules, and examine the meaning of chemical formulas and equations.

The atoms of an element had the same mass, and they combined in fixed ratios in compounds. These two facts allowed scientists to determine the relative numbers of atoms of the elements present in a sample; i.e., they were able to determine chemical formulas.

#### Objectives

- Distinguish between atoms and molecules.
- Convert between the name and symbol of fifty elements.
- Write the formula of a compound given the number and types of atoms that it contains.

#### 1.3-1. Dalton's Atomic Theory

Atomic theory explains the mass relationships in substances and in reactions.

The chemists of the early 19<sup>th</sup> century had three laws (observations) to explain: conservation of mass, definite proportions, and multiple proportions. It was time for a hypothesis to explain the laws. In 1804, John Dalton suggested the explanation. His hypothesis, now known as Dalton's atomic theory, was based on the assumption that elements consisted of tiny spheres, called **atoms**.

Dalton's atomic theory:

- 1 Elements are composed of atoms. The atoms of an element all exhibit identical chemical properties (they all react the same way with other atoms), while atoms of different elements have different chemical properties.
- **2** Atoms are not changed in chemical reactions; they simply change partners.
- **3** Compounds are combinations of atoms of different elements. The number of atoms of each element in the compound is integral and constant.

The second postulate explains the law of mass conservation and is the basis of balancing chemical equations. The third postulate explains the laws of definite and multiple proportions.

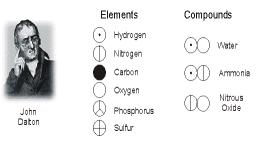
Dalton's theory explained all of the observations of his time and was accepted without change for nearly 100 years.

Dalton used the term "atom" to refer to both a single atom and a combination of atoms. However, a combination of atoms is now called a *molecule*. We will use "molecule" to simplify our discussion. Dalton assumed that an atom was the smallest unit of an element, while a molecule was the smallest unit of a compound. This was not quite correct because, as we shall soon see, some elements exist as molecules.

EXERCISE 1.2:					
Indicate whether each of	Indicate whether each of the following is an atom or a molecule.				
Ar	$O_3$	HCl			
atom	$\operatorname{atom}$	atom			
molecule	molecule	molecule			

# 1.3-3. Naming Atoms

Dalton suggested a series of symbols to represent atoms and molecules. The symbols suggested by Dalton for some atoms and molecules are shown below.



Dalton assumed a 1:1 ratio for the atoms in compounds whose atom ratios were unknown. The figure shows three compounds where this assumption was incorrect.

- Water contains two hydrogen atoms and one oxygen atom.
- Ammonia has three hydrogen atoms and one nitrogen atom.
- Nitrous oxide contains two nitrogen atoms and one oxygen atom.

# 1.3-4. Atom symbols

It is important to know the names and symbols of the fifty most common elements.

Today, the symbols of most of the elements are the first one or two letters of the element's name. You should learn the following table of names and symbols of the fifty most-used elements in this course.

hydrogen	Н	silicon	Si	cobalt	Co	cadmium	Cd
helium	He	phosphorus	Р	nickel	Ni	tin	Sn
lithium	Li	sulfur	S	copper	Cu	iodine	Ι
beryllium	Be	chlorine	Cl	zinc	Zn	xenon	Xe
boron	В	argon	Ar	gallium	Ga	cesium	Cs
carbon	С	potassium	K	germanium	Ge	barium	Ba
nitrogen	Ν	calcium	Ca	arsenic	As	platinum	Pt
oxygen	0	scandium	Sc	selenium	Se	gold	Au
fluorine	F	titanium	Ti	bromine	Br	mercury	Hg
neon	Ne	vanadium	V	krypton	Kr	thallium	Tl
sodium	Na	chromium	Cr	rubidium	Rb	lead	Pb
magnesium	Mg	manganese	Mn	strontium	Sr		
aluminum	Al	iron	Fe	silver	Ag		

EXERCI	EXERCISE 1.3:				
Write the	name of the element from its	symbol.			
Br _	S	Sr	Ar		
Li	S	Sc	Н		
Ca _	(	Cl	Ag		
Be _		Ті	Cd		
В		V	Sn		
С _	(	Cr	I		
N	N	Mn	Xe		
0 _	I	Fe	Cs		
F	(	Co	Ba		
Ne _	I	Ni	Mg		
Zn _	H	Нд	Al		
Pt	I	K	Si		
Ge _	I	Pb	Rb		
He _	I	Na	Cu		
Au _	(	Ga	Tl		
Р		As	S		
Se _	]	Kr			

# 1.3-6. Symbols from Names Exercise

#### EXERCISE 1.4:

Write the symbols of the elements given their names.

• The first letter of each symbol must be upper case, and the second letter in any symbol must be lower case.

bromine	argon	krypton
vanadium	tin	thallium
strontium	lithium	cadmium
boron	cobalt	calcium
aluminum	gallium	barium
neon	carbon	xenon
oxygen	iron	cesium
fluorine	nickel	platinum
sodium	copper	gold
scandium	silver	helium
beryllium	titanium	zinc
mercury	silicon	germanium
lead	phosphorus	arsenic
sulfur	chromium	iodine

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hydrogen	potassium	rubidium
magnesium	nitrogen	manganese
selenium	chlorine	

# 1.3-7. Molecule Symbols

Molecules are represented by their constituent atoms. If there is more than one atom of an element present in a molecule, then the number is given as a subscript in the molecular formula.

water	$H_2O$	two hydrogen atoms + one oxygen atom
ammonia	$NH_3$	one nitrogen atom $+$ three hydrogen atoms
nitrous oxide	$N_2O$	two nitrogen atoms $+$ one oxygen atom
sugar	$C_{12}H_{22}O_{11}$	12  C  atoms + 22  H  atoms + 11  O  atoms

# 1.3-8. Writing Formulas Exercise

#### EXERCISE 1.5:

Use the ball-and-stick models and the atom color codes below to write chemical formulas for the molecules.

- light blue: H
- red: O
- gray: C
- purple: N

Write the symbols in the order C, H, N, O.

hydrogen molecule	water
<b>3</b>	
allene	TNT

# 1.3-9. A Common Misconception

As was evident in the previous exercise, hydrogen atoms are present in many compounds, but  $H_2$  molecules are present only in the hydrogen molecule. Thus, both  $H_2$  and  $H_2O$  contain two H atoms, but there are two H atoms, not a single  $H_2$  molecule in water. As we shall see in the next section, several elements exist as diatomic molecules  $(H_2, N_2, O_2, F_2, Cl_2, Br_2, and I_2)$ . But they are diatomic only as free molecules and never in compounds. Thus, allene  $(C_3H_4)$  contains four H atoms, not two  $H_2$  molecules.

# 1.4 Atoms and Molecules

# Introduction

Atoms and molecules are too small to be seen, so scientists work with large numbers of them. The unit we use to describe this large number is called the mole.

#### Objectives

• Distinguish between elements and compounds.

# 1.4-1. Laws Concerning Gases

In 1808, Joseph Gay-Lussac published the *law of combining volumes*:

• The volumes of reacting gases measured at the same temperature and pressure are always in the ratio of small whole numbers.

Gay-Lussac's law of combining volumes was soon explained by Amedeo Avogadro<sup>2</sup>. His explanation is now known as  $Avogadro's \ law$ :

• Equal volumes of gases at the same temperature and pressure contain equal numbers of molecules.

# 1.4-2. Discovering the Formula of Water

We now use the law of combining volumes and Avogadro's law to show how the early scientists discovered the formulas of water, hydrogen, and oxygen.

# **INITIALLY**:

In the absence of any information to the contrary, early scientists assumed that atoms combined in a one-to-one ratio. Thus, water would have been represented as HO. They also believed that the smallest unit of an element was an atom, so the reaction of hydrogen and oxygen to produce water was thought to be the following:

# $\rm H + O \rightarrow \rm HO$

# APPLICATION OF AVOGADRO'S LAW:

Experiments showed that the reacting volume of hydrogen was twice that of oxygen. This fact, combined with Avogadro's law, meant that two hydrogen atoms must react with one oxygen atom, so water must be  $H_2O$ , and the reaction should be written as

 $2~\mathrm{H} + \mathrm{O} \rightarrow \mathrm{H_2O}$ 

# **CURRENT VIEW**:

The volume of water that is produced was later shown to be the same as the volume of hydrogen and one-half the volume of oxygen that react. Therefore, the coefficients of hydrogen and water had to be the same, and each had to be twice that of oxygen. This presented a dilemma until Avogadro concluded that elements did not have to exist as atoms; they could exist as molecules! The equation could be balanced only if hydrogen and oxygen each existed as *diatomic molecules*; i.e., as molecules with two atoms. The following is the way we now view the reaction of hydrogen and oxygen to produce water:

 $2~\mathrm{H_2} + \mathrm{O_2} \rightarrow 2~\mathrm{H_2O}$ 

<sup>&</sup>lt;sup>2</sup>http://www.bulldog.u-net.com/avogadro/avoga.html

# 1.4-3. Elements can be Molecules

Some common elements occur as molecules rather than atoms.

Other elements also exist as diatomic molecules. The diatomic elements are:

- $\mathbf{1}$  H<sub>2</sub>
- **2** N<sub>2</sub>
- **3** O<sub>2</sub>
- **4** F<sub>2</sub>
- **5** Cl<sub>2</sub>
- **6** Br<sub>2</sub>
- **7** I<sub>2</sub>

In addition, some elements exist as molecules with more than two atoms. For example,  $P_4$  and  $S_8$ .

# 1.4-4. Elements or Compounds

Combining Dalton's atomic theory and Avogadro's suggestion that elements did not have to occur as atoms, we can define elements and compounds in terms of their constituent atoms.

- An *element* is a substance that contains only one **type** of atom.
- A *compound* is a substance that contains more than one type of atom.

Note that it is the number of types of atoms, not the number of atoms, that distinguishes an element from a compound.  $S_8$  has more than one atom, so it is a molecule, but it contains only one type of atom (S), so it is an element.

# 1.4-5. Element or Compound Exercise

EXERCISE 1.6:				
Indicate whether each of the	ne following is an element or a comp	oound.		
Ar	$O_3$	HCl		
element	element	element		
compound	compound	compound		

# 1.4-6. Balancing Chemical Equations Video

A video or simulation is available online.

# 1.4-7. Balancing Chemical Equations

The number of each type of atom must be the same on both sides of a balanced chemical equation.

Dalton's atomic theory indicates that atoms change partners in a chemical reaction, but they do not change their identity. Thus, the number of atoms of each type must be the same on both sides of a chemical equation. In other words, chemical equations must be balanced. However, **subscripts cannot be changed as that would change the identity of the molecules**, so chemical equations must be balanced by changing only the coefficients of the molecules.

The following steps should lead to a balanced equation:

1 Pick the molecule with the greatest number of atoms and make its coefficient one unless another choice is obviously better. For example, sometimes a 2 must be used to assure an even number of one of the atoms.

- 2 Determine which atoms are fixed by the coefficient used in Step 1, then balance those atoms on the other side of the equation.
- **3** Determine which atoms are fixed by the coefficient(s) created in Step 2, then balance those atoms on the other side of the equation.
- 4 Repeat Step 3 until the equation is balanced.

Note that ones are not usually included in the balanced equation.

#### EXAMPLE:

As an example, we will follow the steps above to balance the following chemical equation.

 $\underline{\qquad} \operatorname{HCl} + \underline{\qquad} \operatorname{MnO}_2 \rightarrow \underline{\qquad} \operatorname{MnCl}_2 + \underline{\qquad} \operatorname{H}_2 \operatorname{O} + \underline{\qquad} \operatorname{Cl}_2$ 

 $1 \quad {\rm Make \ the \ coefficient \ of \ either \ MnO_2 \ or \ MnCl_2 \ one. \ We \ choose \ MnO_2.}$ 

 $---- \operatorname{HCl}+1 \operatorname{MnO}_2 \rightarrow ---- \operatorname{MnCl}_2 + ---- \operatorname{H}_2 O + ---- \operatorname{Cl}_2$ 

2 The coefficient used in Step 1 fixes the number of Mn atoms at 1 and O atoms at 2, so we balance the Mn atoms with a coefficient of 1 for  $MnCl_2$  and the oxygen atoms with a coefficient of 2 for water.

$$\_$$
 HCl + 1 MnO<sub>2</sub>  $\rightarrow$  **1** MnCl<sub>2</sub> + **2** H<sub>2</sub>O +  $\_$  Cl<sub>2</sub>

3 The coefficient of water fixes the number of hydrogen atoms at four, so we balance the H atoms with a coefficient of 4 for HCl. Note that the coefficient of  $MnCl_2$  does not fix the number of Cl atoms because it is not the only source of Cl.

 $\mathbf{4}~\mathrm{HCl} + 1~\mathrm{MnO_2} \rightarrow \mathbf{1}~\mathrm{MnCl_2} + 2~\mathrm{H_2O} + \underline{\qquad} \mathrm{Cl_2}$ 

4 The coefficient of HCl fixes the number of chlorine atoms at four, but there are already 2 Cl atoms in 1  $MnCl_2$ , so we balance the Cl atoms on the other side of the equation with a coefficient of 1 for  $Cl_2$ .

 $4 \text{ HCl} + 1 \text{ MnO}_2 \rightarrow 1 \text{ MnCl}_2 + 2 \text{ H}_2\text{O} + 1 \text{ Cl}_2$ 

5 Each side of the equation contains 4 H atoms, 1 Mn atom, 2 O atoms, and 4 Cl atoms.

The equation is now balanced, but ones are not usually written. Thus, the balanced equation is usually written as shown in the last step.

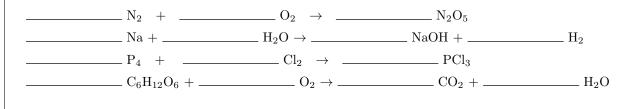
 $4 \ \mathrm{HCl} + \ \mathrm{MnO}_2 \rightarrow \ \mathrm{MnCl}_2 + 2 \ \mathrm{H}_2\mathrm{O} + \ \mathrm{Cl}_2$ 

# 1.4-8. Balanced Equations Exercise

#### EXERCISE 1.7:

Balance the equations in the activity area with smallest integer coefficients. Click "Submit" after all coefficients have been entered. Use the following steps to help:

- 1 Pick the molecule with the greatest number of atoms and make its coefficient one if there is not another obvious choice.
- 2 Determine which atoms have been fixed by the coefficient in Step 1, then balance those atoms on the other side of the equation.
- **3** Determine which atoms are fixed by the coefficient(s) created in Step 2, then balance those atoms on the other side of the equation.
- 4 Continue Step 3 until the equation is balanced.



# 1.5 The Mole and Molar Mass Introduction

Dalton recognized that the mass of an atom is an important characteristic, but individual atoms are much too small to weigh. However, the relative masses of the atoms in a compound can be determined, so Dalton devised a scale of *relative* masses. In this section, we examine these atomic masses or weights and extend them into molecular masses or weights.

#### Objectives

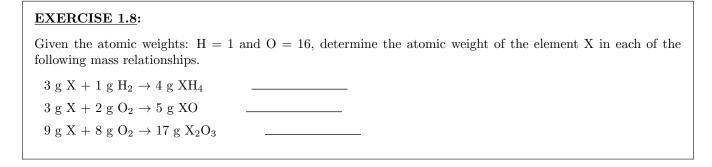
- Determine the molecular mass of a compound from the atomic masses of its constituent atoms.
- Define the term *mole*.
- Use molar mass to convert between mass and moles of a substance.

#### 1.5-1. Atomic mass

Atomic masses (or weights) describe the relative masses of atoms and molecules.

An *atomic mass* is simply a number that indicates the relative mass of an atom. Dalton reasoned that H was the lightest element, so he assigned it a relative mass of 1, which he called its atomic weight. Note that **atomic mass and atomic weight mean the same thing because the masses are relative, so the two terms are used interchangeably**. The atomic weights of the other elements could then be assigned from the experimentally determined masses of the reacting elements and the formulas of the compounds they form. For example, consider the following reaction of  $H_2$  and  $O_2$  to produce  $H_2O$ .

The above data imply that two oxygen atoms (one  $O_2$  molecule) has eight times more mass than four hydrogen atoms (two H<sub>2</sub> molecules), or 1 O atom is sixteen times heavier than 1 H atom. The relative mass of an H atom was established as 1, so the atomic weight of O must be 16. Similarly, two water molecules have nine times more mass than 4 H atoms, or one water molecule is 18 times heavier than a hydrogen atom. Thus, the relative mass of water is 18. The relative mass of a molecule is called its **molecular mass** or weight.



# 1.5-3. Atomic Masses vs. Molecular Masses

A molecular mass equals the sum of the atomic masses of the atoms that comprise the molecule.

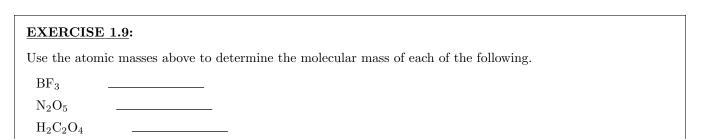
The modern atomic weight scale is no longer based on hydrogen. Instead, it is based on the mass of the most common form of carbon, which is assigned a relative mass (atomic weight) of exactly 12. The masses of individual atoms and molecules are often given in *atomic mass units* (amu) or Daltons (D). 1 amu = 1 D = 1/12 of the mass of a carbon atom. The atomic masses of the ten lightest atoms are given in the accompanying table.

Η	1.01	С	12.01
He	4.00	Ν	14.01
Li	6.94	0	16.00
Be	9.01	$\mathbf{F}$	19.00
В	10.81	Ne	20.18

Molecular masses (or weights) are simply the sum of the atomic masses of the atoms that make up the molecule. For example, the molecular mass of  $CO_2$ ,  $M(CO_2)$ , would be determined as follows:

$$M({\rm CO}_2) = n({\rm C}) \times M({\rm C}) + n({\rm O}) \times M({\rm O}) = 1(12) + 2(16) = 44$$

where n(C) is the number of C atoms in the molecule and M(C) is the atomic mass of a carbon atom.



#### 1.5-4. The Mole

Atoms and molecules react in the ratio specified in a balanced chemical equation, and chemists usually mix the reactants in ratios close to those predicted by the equation. However, chemists convert the ratios of atoms and molecules to ratios of mass in order to quickly deliver the correct amounts of material. The conversion between numbers of atoms or molecules and mass is made with the use of the mole. A mole is the number of molecules or atoms in a sample of a compound or element that has a mass equal to its molecular or atomic mass expressed in grams. It is abbreviated mol. It is a number just as a pair is 2 and a dozen is 12. The number of items in a mole is called Avogadro's number,  $N_A$ .

$$N_A = 6.02 \times 10^{23} \text{ mol}^{-1}$$

Avogadro's number is used to convert between a number of moles and a number of molecules or atoms just as 12 is used to convert between a number of dozens and a number of eggs.

#### EXAMPLE:

For example, determining the number of C atoms in 2 moles of carbon atoms or in 2 dozen carbon atoms is done exactly the same.

$$2 \text{ mol } C \times \frac{6 \times 10^{23} \text{ C atoms}}{1 \text{ mol } C} = 1.2 \times 10^{24} \text{ C atoms}$$
$$2 \text{ doz } C \times \frac{12 \text{ C atoms}}{1 \text{ doz } C} = 24 \text{ C atoms}$$

#### EXAMPLE:

Similarly, the number of ammonia molecules in 8 moles of ammonia is determined as

8 mol NH<sub>3</sub> × 
$$\frac{6 \times 10^{23} \text{ NH}_3 \text{ molecules}}{1 \text{ mol NH}_3} = 4.8 \times 10^{24} \text{ NH}_3 \text{ molecules}$$

Avogadro's number is very large. Consider that one mole of dice that are 1/2" on a side would cover the 48 contiguous states of the USA to a height of 100 miles!

Molecules are very small. A mole of water molecules has a volume of only 18 mL.

#### 1.5-5. Individual Atoms and Molecules

The molar mass has units of g/mol and is used to convert between mass and moles of a substance.

The mass of a mole is called the **molar mass**,  $M_m$ . Molar mass has units of g/mol. The molar mass of H<sub>2</sub> is  $M_m = 2$  g/mol and that of carbon is  $M_m = 12$  g/mol. Thus, 2 g of H<sub>2</sub> contain  $6.02 \times 10^{23}$  H<sub>2</sub> molecules and 12 g of C contain  $6.02 \times 10^{23}$  C atoms.

The *factor label method* uses conversion factors to convert given quantities into desired quantities. Molar mass has units of g/mol, so it is the conversion factor that is used to convert grams into moles or moles into grams. For example, if compound A has a molar mass  $M_m$ , then the number of moles of A present in Z grams of A is

$$Z \ge \mathbf{A} \times \frac{1 \mod \mathbf{A}}{M_m \ge \mathbf{A}} = \frac{Z}{M_m} \mod \mathbf{A}$$

Note that the units of the given quantity (g A) cancel with the denominator of the conversion factor to yield the correct units for the answer. We can determine the mass of n moles of A in a similar manner.

$$n \mod \mathbf{A} \times \frac{M_m \ge \mathbf{A}}{1 \mod \mathbf{A}} = nM_m \ge \mathbf{A}$$

Again, the units of the given quantity are converted into the units of the desired quantity by the conversion factor (molar mass of A).

#### EXERCISE 1.10:

The atomic masses of N, O, and F are 14, 16, and 19, respectively.

The mass of 0.25 mole of  $N_2O_3 =$ \_\_\_\_\_ g  $N_2O_3$ 

The number of moles of  $NF_3$  in 11.8 g = \_\_\_\_ mol  $NF_3$ 

# 1.6 Stoichiometry

#### Objectives

- Determine the number of moles or the mass of one element in a compound from the number of moles or mass of another element in the compound and the chemical formula of the compound.
- Determine the number of moles or mass of one substance that is produced by or reacts with a given amount of another substance in the reaction.

#### 1.6-1. Stoichiometry Video

A video or simulation is available online.

#### 1.6-2. Subscripts as Stoichiometric Factors

The stoichiometric factor used to determine the amount of one atom that is combined with a given mass of another is the ratio of the subscripts of the given to sought elements.

Chemists often need to convert the amount of one substance into the chemically equivalent amount of another substance. The study of such conversions is referred to as **stoichiometry**. The conversion factor that converts one substance into another is called the **stoichiometric factor**. In this and the next section, we use the chemical formula of a compound to derive stoichiometric factors for substances.

The following conversion factors can be written from the formula Na<sub>3</sub>PO<sub>4</sub>.

3 mol Na	3 mol Na	4 mol O
$1 \text{ mol Na}_3 PO_4$	$4 \mod O$	$1 \text{ mol Na}_3 PO_4$

The above ratios and their reciprocals can be used to convert a given number of moles of one substance into the chemically equivalent number of moles of another substance in the formula. For example, the number of moles of oxygen in a sample of  $Na_3PO_4$  that contains 6 mol of sodium can be determined as follows.

$$6 \text{ mol Na} \times \frac{4 \text{ mol O}}{3 \text{ mol Na}} = 8 \text{ mol O}$$

Thus, a sample of  $Na_3PO_4$  that contains 6 mol Na also contains 8 mol O. Note how the stoichiometric factor is derived from the subscripts in the chemical formula.

Once the number of moles of the desired substance is known, its mass can be determined by multiplying the number of moles by the molar mass.

#### 1.6-3. Coefficients as Stoichiometric Factors

The stoichiometric factor used to determine the amount of one substance that reacts with or is formed from another equals the ratio of the coefficients of the sought to given substances in the balanced equation.

The ratios of the coefficients in balanced chemical equations can be used as stoichiometric factors. Consider the following reaction and the factors derived from the coefficients in the balanced equation.

$2 \operatorname{N}_2 + 3 \operatorname{O}_2  ightarrow 2 \operatorname{N}_2\operatorname{O}_3$				
$\frac{2 \text{ mol } N_2 \text{ react}}{2 \text{ mol } N_2 O_3 \text{ forms}}$	$\frac{3 \text{ mol } O_2 \text{ react}}{2 \text{ mol } N_2 O_3 \text{ forms}}$	$\frac{2 \text{ mol } N_2 \text{ react}}{3 \text{ mol } O_2 \text{ react}}$		

Thus, the number of moles of nitrogen that react with 6 mol  $O_2$  in the above reaction can be determined using the factor label method and the balanced equation as follows.

$$6 \ \mathrm{mol} \ \mathrm{O}_2 \times \frac{2 \ \mathrm{mol} \ \mathrm{N}_2}{3 \ \mathrm{mol} \ \mathrm{O}_2} = 4 \ \mathrm{mol} \ \mathrm{N}_2$$

Thus, if 6 mol  $O_2$  are to react then at least 4 mol  $N_2$  must be present. Note that the stoichiometric factor is derived from the coefficients in the balanced equation.

#### 1.6-4. Mole-Mole Substance Stoichiometry Exercise

#### EXERCISE 1.11:

How many moles of NH<sub>3</sub> are in a sample that contains 27 mol of H atoms?

\_\_\_\_\_ mol NH<sub>3</sub>

A sample of  $Al_2O_3$  contains 9 mol of O. How many mol of Al does it contain?

\_\_\_\_ mol Al

# 1.6-5. Mass-Mass Stoichiometry Exercise

#### EXERCISE 1.12:

What is the mass of sulfur is in a 5.00 g sample of  $Ca_2S_3$ ? The atomic mass of Ca is 40 and that of S is 32.

First, convert the amount of given mass into moles.

molar mass of  $Ca_2S_3 = \_\__g/mol$ 

number of moles in a 5.00 g sample = \_\_\_\_\_ mol Ca<sub>2</sub>S<sub>3</sub>

Next, convert the moles of  $Ca_2S_3$  into the chemically equivalent number of moles of sulfur.

\_\_\_\_\_ mol S

Finally, convert the number of moles of sulfur into its mass in grams to obtain the answer.

\_\_\_\_\_ g S

# 1.6-6. Mole-Mole Reaction Stoichiometry Exercise

#### EXERCISE 1.13:

How many moles of each reactant are required to produce 68 g of  $NH_3$  by the following reaction? The atomic weights of N and H are 14 and 1, respectively.

 $N_2 + 3 H_2 \rightarrow 2 NH_3$ 

1. First convert the given amount into moles! The number of moles of NH<sub>3</sub> to be prepared is

 $\_$  mol NH<sub>3</sub>

2. Once the number of moles of the ammonia are known, the number of moles of each reactant can be determined. We first determine the number of moles of  $H_2$  that would be required.

 $\_$  mol H<sub>2</sub>

3. Finally, determine the number of moles of  $N_2$  that are needed.

 $\_$  mol N<sub>2</sub>

#### 1.6-7. Mole-Mass Reaction Stoichiometry Exercise

#### EXERCISE 1.14:

Once the numbers of moles of reactants and products have been determined, the masses can be obtained by multiplying by the molar masses. In this example, we determine the number of moles of  $O_2$  that are required to react with 0.30 mol K and the mass of  $K_2O$  that is produced in the following reaction.

$$4 \mathrm{K} + \mathrm{O}_2 \rightarrow 2 \mathrm{K}_2\mathrm{O}$$

The number of moles of  $O_2$  required = \_\_\_\_\_ mol

The number of moles of  $K_2O$  produced = \_\_\_\_\_ mol

The mass of potassium oxide that forms =  $\_\__g$ 

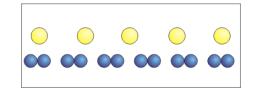
#### 1.6-8. Limiting Reactants Video

A video or simulation is available online.

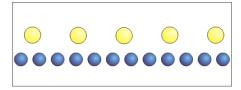
#### 1.6-9. Limiting Reactants

When reactants are not added in the required stoichiometric ratio, the amount of reaction is dictated by the limiting reactant.

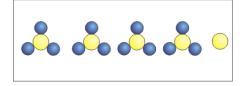
Chemists seldom add chemicals in the exact stoichiometric ratio, so the amount of product that forms depends upon the amount of the reactant, called the limiting reactant, that is consumed first. In the following, we examine the reaction of 5 mol S and 6 mol  $O_2$  to produce  $SO_3$ .



Initially there are 5 mol S, the five yellow spheres in the figure, and 6 mol  $O_2$ , the six pairs of blue spheres.



There are 12 mol O atoms in 6 mol  $O_2$ , so there are 5 mol S and 12 mol O.



Each mole of  $SO_3$  requires one mole of S, so there is enough S present to produce 5 mol  $SO_3$ . Each mole of  $SO_3$  also requires 3 mol of O, so there are enough oxygen atoms to make only

 $12/3 = 4 \mod SO_3$ . Since less  $SO_3$  can be made with the oxygen, it is the limiting reactant. Consumption of 6 mol  $O_2$  produces 4 mol  $SO_3$ , so that is all that can be made. Initially, there were 5 mol S, but making 4 mol  $SO_3$  requires only 4 moles. Therefore, there is 1 mol S left over.

#### 1.6-10. Limiting Reactants 2

Typically, the limiting reactant is determined by applying the stoichiometric factors for the reaction to the given numbers of moles of reactant to determine which reactant produces the least amount of product; i.e., to determine the limiting reactant. Consider the reaction of 5 mol S with 6 mol  $O_2$  as discussed in the previous section. The chemical equation for the reaction is

 $2 \text{ S} + 3 \text{ O}_2 \rightarrow 2 \text{ SO}_3$ . The amount of SO<sub>3</sub> that can be produced from 5 mol S and 6 mol O<sub>2</sub> is then determined to be

$$5 \mod S \times \frac{2 \mod SO_3}{2 \mod S} = 5 \mod SO_3$$

and

$$6 \text{ mol } O_2 \times \frac{2 \text{ mol } SO_3}{3 \text{ mol } O_2} = 4 \text{ mol } SO_3$$

Oxygen produces less product, so it is the limiting reactant and the amounts of all products that form and the amounts of reactants that react are based on the number of moles of  $O_2$  that react.

#### 1.6-11. Limiting Reactant Exercise

#### EXERCISE 1.15:

What mass of  $Al_2O_3$  can be produced from 10.0 mol Al and 9.0 mol  $O_2$ ?

4 Al + 3 O<sub>2</sub> 
$$\rightarrow$$
 2 Al<sub>2</sub>O<sub>3</sub>

The number of moles of  $Al_2O_3$  produced from 10.0 mol Al =\_\_\_\_\_ mol

The number of moles of  $Al_2O_3$  produced from 9.0 mol  $O_2 = \_$ \_\_\_\_ mol

The limiting reactant is \_\_\_\_\_

The maximum number of moles of  $Al_2O_3$  that can be produced = \_\_\_\_\_ mol

The molar mass of  $Al_2O_3 =$ \_\_\_\_\_g/mol

The mass of  $Al_2O_3$  that can be produced = \_\_\_\_\_ g

# 1.7 Energy

# Introduction

Chemical processes are driven by energy differences, which result from changes in the interactions between charges. We now examine two types of energy and the energy of interaction between charged particles.

#### **Objectives**

- Distinguish between kinetic and potential energy.
- State the direction of energy change in most processes in nature.

# 1.7-1. Energy

There are two forms of energy: kinetic energy and potential energy.

In simple terms, energy is the capacity to move something. The energy of an object is the sum of two terms.

- *Kinetic energy* is energy due to motion.
- *Potential energy* is energy due to position.

An object that is moving can make another object move by colliding with it. The kinetic energy of a particle of mass m moving with a velocity v is  $KE = \frac{1}{2}mv^2$ . Molecules and atoms are in constant motion, and their speed (kinetic energy) is dictated by their temperature.

An object that has the capacity to move due to its position has potential energy. Two examples of potential energy:

- 1 A truck parked at the top of a hill has potential energy because it will move and gain kinetic energy if its brake is released.
- **2** A compressed spring has potential energy because the ends of the spring move and gain kinetic energy when the force that compresses the spring is removed and the spring returns to its uncompressed state.

Molecules and atoms have potential energy because they interact with one another. The change in potential energy caused by these interactions is responsible for the formation of chemical bonds and the condensation and freezing of molecules.

# 1.7-2. Energy Change

Systems in nature seek to minimize their energy, so energy changes for most processes are negative.

The energy of an object is a relative quantity and cannot be measured absolutely. For example, a ball at rest on the floor has neither kinetic nor potential energy relative to the floor, but it does have kinetic energy relative to the sun and potential energy relative to the center of the Earth. Consequently, it is energy **change**, not absolute energy, that is typically measured. The symbol  $\Delta$  (Delta) is used to represent change and the symbol E is used for energy, so the energy change is expressed as  $\Delta E$ . By convention, energy change is the final energy minus the initial energy.

$$\Delta E = E_{\text{final}} - E_{\text{initial}}$$

Thus,  $\Delta E < 0$  means that the object loses energy because its final energy is less than its initial energy. A very important concept in chemistry is that systems naturally seek the position of lowest energy; i.e., nature favors processes for which  $\Delta E < 0$ . Although energy change in chemical processes is not discussed in detail until Chapter 9, we will use the concept that molecules undergo chemical processes in order to reduce their potential energy in every chapter of this text.

# EXAMPLE:

As an example of the amount of energy that can be released in a common reaction, consider the combustion of octane, a component of gasoline. The chemical equation for the combustion is

 $\mathrm{C_8H_{18}+12.5~O_2} \rightarrow 8~\mathrm{CO_2+9~H_2O}$ 

 $\Delta E < 0$  for this reaction, and the energy that is released is used to power many automobiles. The amount of energy released in the reaction can be better appreciated by considering the following:

• In order to deliver the same amount of energy as all of the kinetic energy of a 2200 pound (1000 kg) car moving at 40 mph (18 m/s), you would have to burn only 3 g of octane (~0.0008 gal).

# 1.8 Electromagnetism and Coulomb's Law Introduction

The attraction of opposite charge and the repulsion of like charge are the result of the electromagnetic force. The electromagnetic force, which is responsible for all of the interactions between atoms and molecules discussed in this course, is the topic of this section.

#### Objectives

- Use Coulomb's law to predict the sign and relative magnitude of the energy change resulting when two charged particles approach one another.
- Explain the role of the medium in the magnitude of the interaction between two charged particles.

# 1.8-1. Electromagnetism and Coulomb's Law

Coulomb's law describes the force exerted between two charged particles. The Coulombic force is responsible for the forces in molecules.

In the 1800's, scientists recognized that charged particles interacted, but Charles Coulomb was the first to measure the electromagnetic force.



Charles Coulomb 1736 - 1806

He observed that the force of interaction between two charged particles was

- **1** proportional to the charges on the particles,
- 2 inversely proportional to the square of the distance between them,
- 3 attractive when the charges were of opposite sign and repulsive when they had the same sign.

His observations are summarized by **Coulomb's law**: Two particles with charges  $q_1$  and  $q_2$  and separated by a distance r experience the following force F.

$$F = \frac{kq_1q_2}{\epsilon r^2} \qquad \text{The Coulombic Force} \tag{1.1}$$

- $k = 8.9875 \times 10^9 \text{ N} \cdot \text{m}^2 \cdot \text{C}^{-2}$  and is called Coulomb's constant.
- $\epsilon$  is the *dielectric constant* of the medium separating the charges. The dielectric constant indicates how well the medium shields the charges from one another.
- When the charges are of the same sign, F > 0 and the force is repulsive. When the charges are of opposite sign, F < 0 and the force is attractive.

#### **1.8-2.** Energy of Interaction

Opposite charges attract and like charges repel because doing so lowers their potential energy (energy of interaction).

Energy is a force exerted through a distance (E = Fr). Consequently, the potential energy of two charged particles separated by a distance r is determined by multiplying Equation 1.1 by r:

$$\Delta E = \frac{kq_1q_2}{\epsilon r} \qquad \text{Energy of Interaction of 2 Charged Particles} \tag{1.2}$$

 $\Delta E$ , which is referred to as the *energy of interaction*, is the potential energy of the two particles separated by a distance r relative to their potential energy when they are separated by an infinite distance (i.e., not interacting).

$$\Delta E = E_r - E_\infty = E_r - 0 = E_r = E$$

Consequently, the energy of interaction is often written without the  $\Delta$ . Note that the energy change is negative (the energy decreases) as r decreases when  $q_1$  and  $q_2$  have opposite signs, therefore particles of opposite charge lower their energy as they get closer. Systems strive to lower their energy, so particles of opposite sign are attracted. However, the energy change is positive (the energy increases) when  $q_1$  and  $q_2$  have the same sign, which means that the energy of two particles of the same sign increases as they get closer. Consequently, particles of the same charge move apart to lower their energy; i.e., particles of like charge are repelled. The energy of interaction of two charged particles as a function of the distance between them is shown in Figure 1.1.

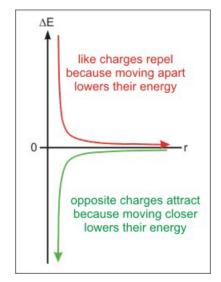
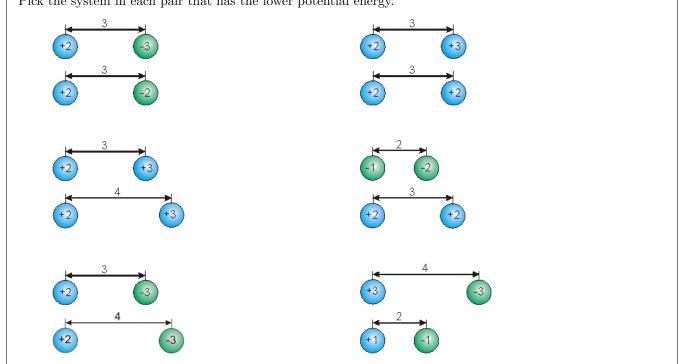


Figure 1.1 Energy of Interaction: The energy of like-charged particles increases as they get closer, while the energy of oppositely-charged particles decreases as they get closer. Thus, particles of like charge avoid (are repelled by) one another, while particles of opposite charge are attracted to one another.

# 1.8-3. Coulomb's Law Exercise

# EXERCISE 1.16:

Pick the system in each pair that has the lower potential energy.



# **1.9 Atomic Structure** Introduction

New technology led to new experiments at the end of the 19<sup>th</sup> century, experiments that Dalton's atomic theory could not explain. We now examine three of the most important of those experiments and take the atom to the next step.

#### **Objectives**

- Describe Thomson's cathode ray experiment and his conclusions. •
- Describe Millikan's oil drop experiment and his conclusions. •
- Describe Rutherford's gold foil experiment and his conclusions. .
- Describe the Rutherford model of the atom.

# 1.9-1. Thomson Experiment



J. J. Thomson 1856 - 1940

In 1897, the British physicist J. J. Thomson discovered the electron while he was exploring the nature of the "cathode rays." In his experiment, which is demonstrated schematically below, he examined the effect of electric fields on cathode rays.

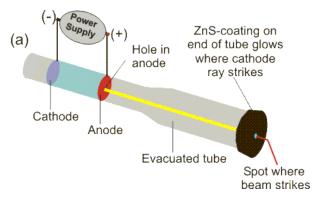


Figure 1.2a: Cathode Ray Tube

Two metal plates, which are connected to a power supply, are sealed into an evacuated glass tube. One of the plates has a small hole in its center. When a high voltage is applied across the metal plates, a "ray" originating at the cathode (-) (hence their name "cathode rays") passes through the hole in the other plate, which is the anode (+) and hits the end of the tube, which is coated with ZnS. ZnS glows when struck with cathode rays to produce the dot in the end of the tube. The yellow line represents the trajectory of the ray, but cathode rays are not visible, which is why ZnS was necessary.

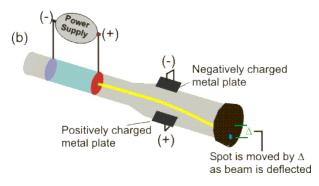


Figure 1.2b: Deflected Cathode Ray

The "ray" was deflected when an electric field was applied. The extent of deflection is given by the value of  $\Delta$ , the amount by which the spot moves from its position in the absence of the electric field. Thomson noted the direction of the deflection and carefully measured the value of  $\Delta$  at several field strengths.

#### 1.9-2. Thomson Observations

Cathode rays are beams of negatively-charged particles.

Thomson made the following observations and conclusions:

#### **Observation:**

• The "rays" were deflected by electric and magnetic fields.

Conclusion:

• Cathode rays are not light rays because light rays are not deflected by these fields. Therefore, the "rays" were actually charged particles, which are now called *electrons*.

#### **Observation:**

• The deflection was away from the negative plate and toward the positive plate.

#### **Conclusion:**

• The particles were negatively charged.

#### **Observation:**

• The deflection was large.

#### Conclusion:

The amount of deflection depended upon the strength of the field and on the charge and mass of the particles. The greater the charge on the particle (q), the greater the deflection, but the greater its mass (m), the smaller the deflection. Thus, Δ ∝ q/m. Thus, the large deflection meant that either the particle had a very high charge or a very small mass. He was familiar with charges observed by others in different experiments and reasoned that the charge could not be the reason for the large deflection. He concluded that the mass of the particle must be less than one-thousandth that of the hydrogen atom. He was shocked! This meant that the hydrogen atom was not the smallest unit of matter as Dalton had suggested nearly a century earlier.

#### **Observation:**

• The value of  $\Delta$ 

#### Conclusion:

• Thomson used the experimental value of  $\Delta$  as shown in Figure 1.2b and the strength of the electric field that caused the deflection to determine the charge-to-mass ratio for the electron.

 $\frac{q_e}{m_e} = -1.76 \times 10^{11} \text{ kg} \cdot \text{ C}^{-1}$ 

# 1.9-3. Millikan Experiment

Robert Millikan, an American physicist at the University of Chicago, was the first to accurately determine the charge on the electron.

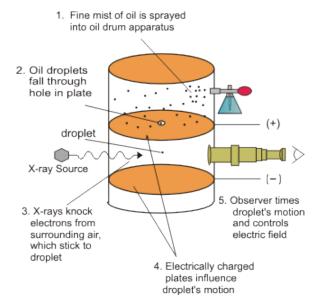


Figure 1.3: Oil Drop Experiment

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- Two plates were welded into an oil drum as shown in the figure. The upper plate had a small hole drilled into it.
- Above the hole, he created a fine mist of oil droplets. Individual oil droplets passed randomly through the hole one-by-one to descend toward the lower plate.
- He used a microscope to observe the fall of an individual droplet. Initially, the drop accelerated due to gravity, but eventually the resistance due to the air stopped its acceleration and the drop began to fall at a constant speed called its terminal speed. He determined the droplet's terminal speed and used it to determine the mass of the droplet.
- He then fired X-rays into the drum, which removed electrons from some of the molecules in the air. Some of the released electrons attached to the oil droplet, creating a negative charge (q) on its surface.
- Next, he applied an electric field (E) across the two plates, creating a positive charge on the top plate and a negative charge on the bottom plate. As the electric field increased, the rate of descent of the droplet slowed as it was increasingly attracted to the positive upper plate and repelled by the lower plate.
- Millikan adjusted the voltage across the two plates until the droplet became suspended, moving neither up nor down.

#### 1.9-4. Millikan Observations

The mass of an electron is only 1/1800 the mass of a hydrogen atom.



Robert Millikan 1868 - 1953

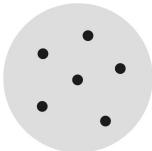
At the point where the particle moved neither up nor down, the electrostatic force (qE) that pulled the droplet up equaled the gravitational force (mg) that pulled it down, so  $q = \frac{mg}{E}$ . E, m, and g were all known, so he was able to determine the charge on the droplet. Various experiments yielded different values of q for different droplets, but all of the measured charges were multiples of the same charge,  $-1.6 \times 10^{-19}$  C. Millikan reasoned that the charges on the droplets were different because each droplet had a different number of electrons; i.e.,  $q = nq_e$ , where n is the number of electrons and  $q_e$  is the charge on each electron. In this way he was able to determine that the charge on an electron must be  $q_e = 1.6 \times 10^{-19}$  C. With this charge and Thomson's charge-to-mass ratio, Millikan was able to determine the mass of the electron to be  $9.1 \times 10^{-31}$  kg, which is approximately 1/1800 the mass of the hydrogen atom.

charge on the electron	mass of electron
$q_e = 1.6 \times 10^{-19} \text{ C}$	$m_e = 9.1 \times 10^{-31} \text{ kg}$

#### 1.9-5. Kelvin-Thomson Model

Clearly, it was time to refine Dalton's atomic model. One proposed model was the "**raisin pudding**" model of Lord Kelvin and J. J. Thomson. They reasoned that because atoms are uncharged themselves, they must contain enough positive charge to balance the negative charge of the electrons. In the Kelvin-Thomson model, the atom resembled raisin pudding with the negatively-charged electrons (the raisins) embedded in a mass of diffuse positive charge (the pudding).

In the accompanying figure of the raisin pudding model, six electrons or raisins are embedded in a mass of positive charge. The raisins carry very little mass but all of the negative charge, while the pudding carries almost all of the mass and all of the positive charge in a (grey area). Since the positive charge was thought to be spread over a relatively large volume, it was thought to be diffuse. Atoms are neutral, so the positive charge in the bulk of the mass must equal the negative charge of the electrons.



Raisin-Pudding model of an atom with six electrons.

#### 1.9-6. Rutherford Experiment

Almost all of the mass and all of the positive charge in an atom is concentrated in its nucleus.



1871 - 1937 Figure also shows his equipment

In another classic experiment, Ernest Rutherford tested the raisin pudding model in 1911 and discovered the nucleus of the atom.

Rutherford bombarded a very thin gold foil with  $\alpha$  particles (particles with

atomic mass = 4 and charge = +2) moving at 10,000 mi/s. If the raisin pudding model was correct, most of the particles would pass through the foil undeflected because the positive charge of the atom was assumed to encompass the entire atom, which would make it diffuse. Some particles were expected to experience minor deflection. Consistent with the predictions, most of the particles did indeed pass through undeflected or with only minor deflection. However, a few (1 in 20,000) were deflected back at acute angles, and these few showed that the raisin pudding model could not be correct!

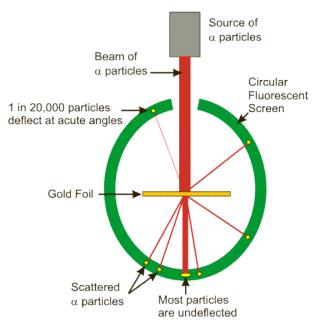


Figure 1.4: The Rutherford Experiment

#### 1.9-7. Rutherford Observations

His experiment showed that the raisin pudding model was incorrect, so Rutherford had to view his observations in light of a new model. The following observations had to be explained.

#### **Observation:**

• Most particles passed through undeflected.

#### Explanation:

Most of the volume of the atom contained very little mass to deflect the massive, positively-charged α particles.

#### **Observation:**

• Some minor deflections were observed.

#### Explanation:

• Small deflections of the  $\alpha$  particles were caused by near misses with a massive particle within the atom.

#### **Observation:**

• One particle in 20,000 was deflected at an acute angle.

#### Explanation:

• Only a very massive and highly, positively-charged particle could cause the high-energy, positivelycharged  $\alpha$  particles to reverse direction. The fact that only one particle in 20,000 was deflected meant that the cross-sectional area of this positive charge was only 1/20,000 of the cross section of the atom. Thus, most of the mass and all of the positive charge of the atom was concentrated in a very small particle, which is called the **nucleus**.

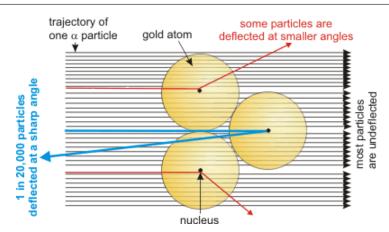


Figure 1.5 Rutherford's Nuclear Model of the Atom: The positive charge and most of the mass resides in the nucleus as represented by the black dots. Only near-collisions with the very small, massive, and highly-positively-charged nuclei resulted in acute deflections.

#### 1.9-8. Nuclear Model of the Atom

As a result of the work of Thomson, Millikan, and Rutherford, we had a very different view of the atom. It was no longer the "billiard ball" put forth by Dalton 100 years earlier. Based on his experiments and those of his contemporaries, Rutherford presented his nuclear model of the atom: All of the positive charge and most of the mass of the atom was contained in the very small nucleus at its center. The negative charge, but almost none of the mass, was carried by electrons, which orbited the nucleus much like the planets

*orbit the sun.* His model was a giant step forward, but Rutherford was not satisfied with it because he could not understand why the electromagnetic force between the negatively-charged electrons and the positively-charged nucleus would not cause them to combine. The answer, which would dramatically alter the way we understand matter and the universe, would not be forthcoming for another decade.

# 1.10 Subatomic Particles, Isotopes, and Ions Introduction

A third subatomic particle, the neutron, was discovered about 20 years after Rutherford introduced the nuclear model of the atom. The atom now consisted of three particles: neutrons and protons in the nucleus and electrons surrounding it. We now examine the effect that each of these particles has on the characteristics of the atom.

Objectives

- Name the major subatomic particles and give their masses and their charges.
- Define an isotope.
- Convert between the symbol and charge of a species and the number of protons and electrons that it contains.
- Distinguish between atoms, anions, and cations.

# 1.10-1. Subatomic Particles

The major *subatomic* particles are:

particle	mass (amu)	charge
electron	$5 \times 10^{-4}$	-1
proton	1.0073	+1
neutron	1.0087	0

The **proton** is the source of the positive charge that balances the negative charge of the electrons to produce neutral atoms; i.e., the number of electrons equals the number of protons in an atom. The **neutron** is slightly more massive than the proton, but it carries no charge. Neutrons somehow keep the positively charged protons together in the nucleus.

# 1.10-2. Atomic Number, Z

It is the number of protons in the nucleus (the atomic number) that characterizes an atom.

The *atomic number*, Z, is the number of protons in the nucleus. It is the number that characterizes the element. Sulfur is the element that has sixteen protons in its nucleus; i.e., Z = 16 for sulfur. The number of neutrons determines the mass, and the number of electrons determines its charge. The atomic numbers of the first ten elements are:

Η	He	Li	Be	В	С	Ν	0	F	Ne
1	2	3	4	5	6	7	8	9	10

# 1.10-3. Mass Number, A

The mass number, A, is the number of protons plus neutrons in the nucleus.

The **mass number**, A, is the number of protons plus the number of neutrons in the nucleus. It is sometimes given as a superscript preceding the symbol. For example, an atom of <sup>19</sup>F (read "fluorine-19") has 9 protons because it is fluorine and 10 neutrons because its mass is 19

(10 + 9 = 19). The mass of a neutron and a proton are each ~1 amu, so the atomic mass is close to 19 amu, the mass number. Note that the symbol <sup>19</sup>F does not include the atomic number because the number of protons is known if the element (F) is known. However, it is sometimes included to aid in balancing nuclear reactions. In these cases, the atomic number is found as a subscript preceding the symbol.

# 1.10-4. Isotopes

Isotopes have the same Z but different A.

*Isotopes* are atoms with the same atomic number but different mass numbers. For example, naturally occurring chlorine is a mixture of two isotopes: <sup>35</sup>Cl and <sup>37</sup>Cl (chlorine-35 and chlorine-37). They are both chlorine atoms, so they both contain 17 protons, but they differ in the number of neutrons.

- ${}^{35}$ Cl contains 18 neutrons (35 17).
- ${}^{37}$ Cl contains 20 neutrons (37 17).

Elements that have atomic masses that are not nearly integers exist in more than one isotope.

#### EXAMPLE:

For example, the atomic mass of chlorine is 35.5 because naturally occurring chlorine is 75.8%  $^{35}$ Cl and 24.2%  $^{37}$ Cl. That is, one mole of chlorine contains 0.758 mol  $^{35}$ Cl and 0.242 mol  $^{37}$ Cl. The mass of one mole of chlorine atoms is therefore

 $\frac{0.758 \text{ mol}^{-35} \text{Cl}}{\text{mol Cl}} \times \frac{35.0 \text{ g Cl}}{\text{mol}^{-35} \text{Cl}} + \frac{0.242 \text{ mol}^{-37} \text{Cl}}{\text{mol Cl}} \times \frac{37.0 \text{ g Cl}}{\text{mol}^{-37} \text{Cl}} = \frac{35.5 \text{ g Cl}}{\text{mol Cl}}$ 

# 1.10-5. Ions

An ion is a charged particle. The charge is shown as a superscript after the symbol.

Atoms are neutral because they have an equal number of protons and electrons. However, electrons can be added to or removed from atoms to produce *ions*.

- *Cations* are positively-charged ions because the number of protons exceeds the number of electrons.
- Anions are negatively-charged ions because the number of electrons exceeds the number of protons.

Ion charge = number of protons - number of electrons

The charge of the ion is given as a superscript with the number and then the sign as in the  $F^{1-}$  anion and the  $Ca^{2+}$  cation. (The "1" in 1– and 1+ ions is normally not written; however, it is included in this course because a superscript of "–" is too easily missed.) Remember that it is the number of protons that characterizes the element, and the number of protons does not change when an ion is formed from its elements. Thus, F and  $F^{1-}$  each have 9 protons, but F has 9 electrons while  $F^{1-}$  has 10. Similarly, Ca and  $Ca^{2+}$  each have 20 protons, but Ca has 20 electrons while  $Ca^{2+}$  has only 18 electrons.

EXERCISE 1.17:		
Indicate whether each species neutrons present.	is an atom, a cation, or an anion, ar	nd give the number of electrons, protons, and
The atomic numbers of the ele	ements can be found in the Elements	s resource.
<sup>27</sup> Al <sup>3+</sup> Type: atom cation anion		
Protons =	Neutrons =	Electrons =
<sup>32</sup> S <sup>2–</sup> Type: atom cation anion		
Protons =	Neutrons =	Electrons =
<sup>56</sup> Fe <sup>2+</sup> Type: atom cation anion		
Protons =	Neutrons =	Electrons =
<sup>80</sup> Br Type atom cation anion		
Protons =	Neutrons =	_ Electrons =

# 1.10-7. Exercise on Writing Symbols

EXERCISE 1.18:	
Determine the symbol for the listed specie The atomic numbers of the elements can be	
6 protons, 8 electrons, 6 neutrons	
$28\ {\rm protons}, 26\ {\rm electrons}, 32\ {\rm neutrons}$	
$32\ {\rm protons}, 32\ {\rm electrons}, 40\ {\rm neutrons}$	
$15\ {\rm protons}, 18\ {\rm electrons}, 16\ {\rm neutrons}$	

EXERCISE 1.19:		
Determine the number of protons, ne	eutrons and electrons for the species b	pelow.
(a) ${}^{16}O^{2-}$		
Protons =	Neutrons =	Electrons =
(b) ${}^{27}\text{Al}^{3+}$		
Protons =	Neutrons =	Electrons =
(c) $^{25}$ Mg		
Protons =	Neutrons =	Electrons =
(d) ${}^{19}F$		
Protons =	Neutrons =	Electrons =
(e) $^{48}$ Ti <sup>4+</sup>		
Protons =	Neutrons =	Electrons =

# 1.11 Dimitri Mendeleev and The Periodic Law Introduction

As the number of known elements and the properties grew, it became clear that there had to be some way of organizing all of the information if chemistry was to grow as a science. The organization came in what is now called the *periodic law*. We now turn our study to this very powerful tool.

# Objectives

- Define chemical groups and periods.
- Distinguish between metals and nonmetals based on their properties.
- Determine whether an element is a metal, a metalloid, or a nonmetal from its position in the periodic table.
- Describe the meaning of the numbers and symbols found in the periodic table.
- Distinguish a main group element from a transition element.
- Identify the alkali metals, the alkaline earth metals, the halogens, and the noble gases.

# **Periodic Trends**

Arranged in the order of their atomic numbers, the elements exhibit periodicity in their chemical and physical properties.



Sixty years after Dalton published his atomic theory but 28 years before Thomson's discovery of the electron, Dimitri Mendeleev, a Russian chemist, was writing a textbook. As he tried to determine how best to break the book into chapters, he placed all of the elements in order of increasing atomic mass. He noticed that both the physical and chemical properties of the elements varied in a periodic manner. In order to maintain the periodicity, he had to reverse order of two elements (Te and I) and insert some spaces for yet undiscovered elements. His observations were summarized as the periodic law in 1869: The elements, if arranged in an order that closely approximates that of their atomic weights, exhibit an obvious periodicity in their properties.

The reason some elements had to be reversed is that it is the atomic number, not atomic weight, that characterizes an element, but atomic numbers were unknown when he discovered this relationship. Today, the periodic law is stated slightly differently.

• **Periodic law:** Arranged in the order of their atomic numbers, the elements exhibit periodicity in their chemical and physical properties.

Mendeleev arranged the elements in rows of a length such that elements of similar properties fell directly beneath one another. Elements that fell in the same column had similar properties and formed chemical families or **groups**. Elements that fell in the same row formed a **period**. The properties of the elements in a period changed gradually in going from left to right in the period. This behavior is demonstrated for a physical property (melting points) and a chemical property (formula of oxides) in the following section.

#### 1.11-2. Examples

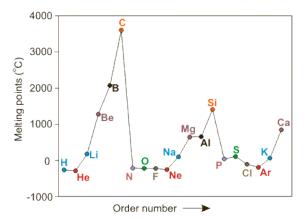


Figure 1.6: Periodicity of Physical Properties

Figure 1.6 shows a plot of the melting points of the elements. Elements in the same family or group share the same color. Note that K and Ar have been reversed from the order of mass.

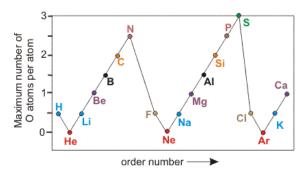


Figure 1.7: Periodicity of Chemical Properties

Figure 1.7 represents the **maximum** number of oxygen atoms that combine with one atom of each element. For example, nitrogen is at 2.5 because it forms an oxide with the formula  $N_2O_5$ , so there are 2.5 oxygen atoms for each nitrogen atom. Oxygen itself has been omitted. Also, K and Ar have been reversed from the order of mass.

# 1.11-3 Periodicity Exercise

#### EXERCISE 1.20:

Identify each formula.

What is the formula of potassium sulfide if that of sodium sulfide is Na<sub>2</sub>S?

What is the formula of calcium chloride if that of sodium chloride is NaCl and that of aluminum chloride is AlCl<sub>3</sub>?

What is the formula of fluoride of nitrogen if those of carbon and oxygen are  $CF_4$  and  $OF_2$ ?

What is the formula of aluminum oxide given the formulas Na<sub>2</sub>O, MgO and SiO<sub>2</sub>?

What is the formula of phosphorus oxide given the information in the previous question?

#### 1.11-4. Metals and Nonmetals

Elements on the left side of the periodic table are metallic, and elements on the right side are nonmetallic.

Elements fall into three classes:

- **Metals** tend to be lustrous (shiny) solids (only mercury is a liquid at room conditions) that are ductile (can be drawn into wires) and malleable (can be beaten into a form). Metals are good conductors of both heat and electricity. They comprise about 75% of the elements.
- *Nonmetals* tend to be gases or dull, brittle solids that are poor conductors of electricity or heat. Seventeen elements are nonmetals.

• *Metalloids* have properties intermediate between the metals and nonmetals. They are shiny but brittle. They are not good conductors of heat or electricity. Indeed, they are semiconductors. Eight elements are metalloids.

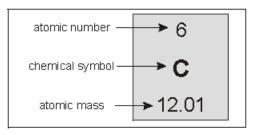
The elements on the left side of a period are metallic, those on the right are nonmetallic, and those lying between the two broader classes are metalloid. Thus, the elements start out metallic and become less metallic and more nonmetallic as you move from lower order number to higher order number (left to right) within a period.

Order numb	er within a peric	id —
Metallic	Metalloid	Nonmetallic

In the above image, the gradual change of colors from blue to yellow represents the manner in which the elements change gradually in a period from metallic on the left to nonmetallic on the right. There are one or two elements between the two larger classes in each period that have properties of both. These elements are called metalloids.

# 1.11-5. Information Available in the Periodic Table

The periodic table not only gives the order of the elements, it also gives important information about each element. Indeed, some periodic tables can show a large amount of data for each element. However, the periodic table found in the resource titled Periodic Table gives the information as shown in the figure.



# 1.11-6. Other Periodic Tables

Mendeleev's arrangement of the elements has become known as the periodic chart or the *periodic table* and is the source of a great deal of information about the physical and chemical properties of the elements. The columns define groups, which consist of elements with similar properties. The rows define periods, which contain elements whose properties change gradually. There are two methods of numbering the groups in the periodic table, the American method, 1A–8A and 1B–8B, and the newer method, which numbers the groups as 1–18. Both numbering schemes are shown on the Periodic Table. However, we use the older method in discussions in this text.

The elements discussed in this course can also be classified in the following way:

- Main Group Elements are the elements in Groups 1A–8A or Groups 1–2 and 13–18.
- Transition Metals or Transition Elements are the elements in Groups 1B–8B or Groups 3–12.

A current periodic table that includes chemical symbols, atomic masses, and atomic numbers can be found by going to the "Resources Menu" above and selecting "Periodic Table." For more information about the elements, click "WebElements" below and to see the use of the elements in comic books, click "Comic Books."

# 1.11-7. Some Commonly Named Groups

Several chemical groups have common names that we will use throughout the course. Note that the last element in each group is radioactive and not included in the figure.

Alkali	Alkaline	l.		6	8A	0
Metals	Earths				2	
1A	2A		7A		He 4.00	
3	4		9		10	
Li	Be		F		Ne	
6.94	9.01		19.00		20.18	
10	11		17		18	
Na	Mg		CI		Ar	
22.99	24.31		35.45		39.95	
19	20		35		36	
ĸ	Ca		Br		Kr	
39.10	40.08		79.90		83.80	
37	38		53		54	
Rb	Sr		I.		Xe	
85.48	87.62		126.9		131.3	
55	56				Nabla	
Cs	Ba	Halogens		Noble		
132.9	137.3				Gases	
Meta	als		N	onm	etals	

Figure 1.8: Common Named Chemical Groups

- **Alkali metal**: a Group 1A element. They are the first members of a period. They are all very reactive metals and readily lose an electron to form +1 ions.
- **Alkaline earth metal**: a Group 2A element. They are the second member of a period. They are all also reactive, but not as reactive as the alkali metals. The alkaline earth metals lose two electrons to form +2 ions.
- *Halogen*: a Group 7A element. They are the next-to-last elements of each period. They all exist as diatomic nonmetals (the elements are all of the form  $X_2$ ). They are reactive and tend to gain one electron to become -1 ions.
- *Noble gas*: a Group 8A element. As their name implies, they are unreactive and are all gases. They are the last elements in each period.

# 1.11-8. Periodic Table Exercise

# EXERCISE 1.21:

Use the Periodic Table to identify each element by symbol.

The halogen in the third period

The alkaline earth in the fourth period

The Group 4 metalloid in the fourth period

The noble gas in the fifth period

The third transition metal in the first row transition metals

# 1.12 Exercises and Solutions

Links to view either the end-of-chapter exercises or the solutions to the odd exercises are available in the HTML version of the chapter.