1. MATTER AND MEASUREMENTS

1.1 Matter

- Chemistry is the study of matter and the changes it undergoes.
- ***Matter*** is *anything that occupies space and has mass.*
- Matter includes things we can see and touch (such as water, earth, and trees), as well as things we cannot (such as air and atoms).
- Thus, everything in the universe has a "chemical" connection.
- Chemists distinguish among several subcategories of matter based on composition and properties.
- The classifications of matter include:
  Substances
  Mixtures
  Elements
  Compounds
  Atoms
  Molecules

EXAMPLE 1.1
Give two examples of:
(a) matter that can be seen by bare eyes.
(b) matter that cannot be seen by bare eyes.

Solution
(a) A human body and a tree.
(b) A molecule of water and the proton.

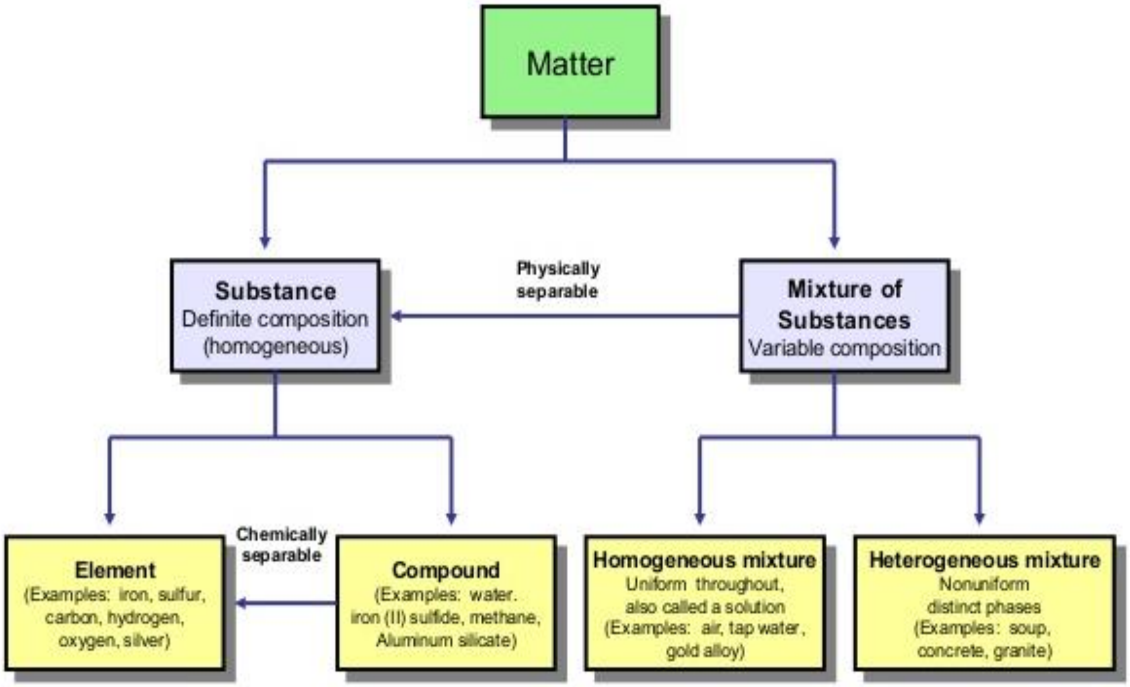
Practice Exercise
Other than mentioned above, give two examples of:
(a) a matter that can be seen by bare eyes.
(b) a matter that cannot be seen by bare eyes.

Classifications of matter

- The following figure summarizes how chemists classify matter.
  - **Substances and mixtures**

Substances

- A ***substance*** is *a form of matter that has a definite (constant) composition and distinct properties.*
- Examples are water, ammonia, table sugar (sucrose), gold, and oxygen.
- Substances differ from one another in composition and can be identified by their appearance, smell, taste, and other properties.



Mixtures

- A ***mixture*** is *a combination of two or more substances in which the substances retain their distinct identities.*
- Examples are air, soft drinks, milk, and cement.
- Mixtures do not have constant composition. Therefore, samples of air collected in different cities would probably differ in composition because of differences in altitude, pollution, and so on.
- Mixtures are either homogeneous or heterogeneous.
- When a spoonful of sugar dissolves in water we obtain a ***homogeneous mixture*** in which *the composition of the mixture is the same throughout.*
- If sand is mixed with iron filings, both the sand grains and the iron filings remain separate.
- This type of mixture is called a ***heterogeneous mixture*** because *the composition is not uniform.*
- Any mixture, whether homogeneous or heterogeneous, can be created and then separated by physical means into pure components without changing the identities of the components. Thus, sugar can be recovered from a water solution evaporating it to dryness.
- To separate the iron-sand mixture, we can use a magnet to remove the iron from the sand.

- After separation, the components of the mixture will have the same composition and properties as they did before.

▪ Elements and Compounds

Substances can be either elements or compounds.

Elements

- An ***element*** is *a substance that cannot be separated into simpler substances by chemical means.*
- To date, 118 elements have been positively identified.
- Most of them occur naturally on Earth. The others have been created by scientists via nuclear processes.


(A) **(B)**

(A) The mixture contains iron and sand. (B) A magnet separates the iron from the mixture.

EXAMPLE 1.2

Give two examples of substances that:

(a) could be present in some refreshment drinks.

(b) are precious.

Solution

(a) Sugar and ginger. **(b)**Diamond and silver.

Practice Exercise

Other than mentioned above, give two examples of substances that:

(a) could be present in some refreshment drinks. substances that are precious.	

EXAMPLE 1.3

Using examples, explain the difference between a the homogeneous and the heterogeneous mixtures.

Solution

A sample of air is a homogeneous mixture because its composition is the same throughout while the composition of a sample of a soil is a heterogeneous mixture because its composition is not the same throughout.

Practice Exercise

Other than mentioned above, give two examples of homogeneous and heterogeneous mixtures.

Symbols of elements

- Symbols of elements are either one or two letters.
- The first letter of a symbol is *always* capitalized, but any following letters are not.
- For example, Co is the symbol for the element cobalt, whereas CO is the formula for the carbon monoxide molecule.
- The table below shows the names and symbols of some of the more common elements.
- A complete list of the elements and their symbols appears in the periodic table.
- The symbols of some elements are derived from their Latin names. For example:
  Au from *aurum* (gold).
  Fe from *ferrum* (iron).
  Na from *natrium* (sodium).
- Whereas most of them come from their English names.
- Many books and internet sites gives the origin of the names and lists the discoverers of most of the elements.

Compounds

- Atoms of most elements interact with one another to form compounds.
- Hydrogen gas, for example, burns in oxygen gas to form water, which has properties that are distinctly different from those of the starting materials.
- Water is always made up of two parts *hydrogen* and one part *oxygen* regardless of where it comes from, Saudi Arabia, China, or Mars.

- Thus, water is a ***compound,*** *a substance composed of atoms of two or more elements chemically united in fixed proportions.*
- Unlike mixtures, compounds can be separated only by chemical means into their pure components.

EXAMPLE 1.4

CO and Co represents two different substances. What are they. Explain why each is represented in this specific way.

Solution

CO represents the carbon monoxide molecule and Co represents the cobalt element.

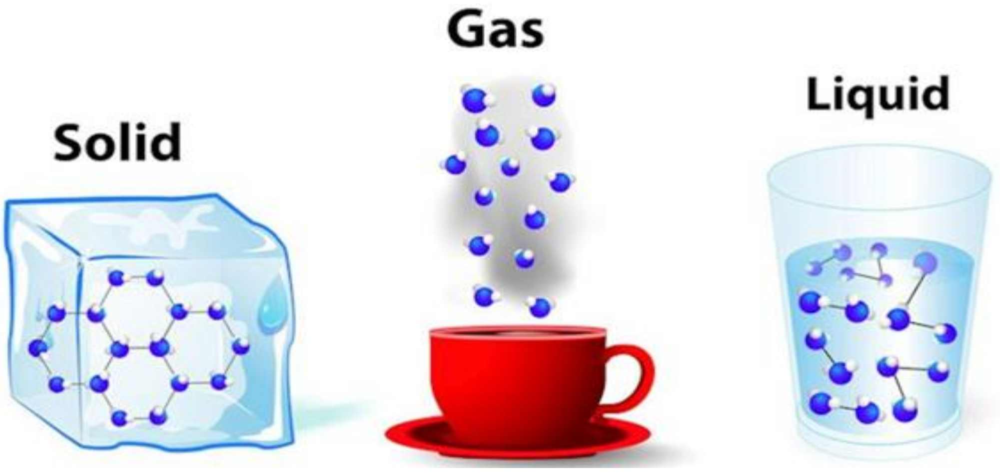
This a result of the convention that the first letter of any element must be capital and its second letter of must be a small letter.

Practice Exercise

BI and Bi represents two different substances. What are they. Explain why each is represented in this specific way.

The three states of matter

- All substances, at least in principle, can exist in three states (solid, liquid and gas).



- As the following figure shows, gases differ from liquids and solids in the distances between the molecules.
- ***In a solid, molecules are*** held close together in an orderly fashion with little freedom of motion.

- ***In a liquid, molecules are*** close together but are not held so rigidly in position and can move past one another.
- ***In a gas, molecules are*** separated by distances that are large compared with the size of the molecules.
- The three states of matter can be interconverted without changing the composition of the substance.
- Upon heating, a solid (for example, ice) ***melts*** to form a liquid (water). (The temperature at which this transition occurs is called the ***melting point*** of the solid.)
- Further heating converts the liquid into a gas. (The temperature at which this transition occurs is called the ***boiling point*** of the liquid.)
- Cooling a gas will cause it to condense into a liquid. When the liquid is cooled further, it will freeze into the solid form.

EXAMPLE 1.5

Name each of the following process:

(a) Changing a liquid substance to a gas.

(b) Changing a liquid substance to a solid.

Solution

(a) Vaporization. (b) Freezing.

Practice Exercise

Name each of the following process:

(a) Changing a solid substance to liquid.

(b) Changing a gaseous substance to liquid.

EXAMPLE 1.6

Would a 100 g of iron have more energy when it is solid or when liquid? Rationalize.

Solution

When it is a liquid it has more energy because when it is a solid it absorbs energy to become liquid and vice versa.

Practice Exercise

Would a 100 g of oxygen have more energy when it is gas or when liquid? Rationalize.

Physical and chemical properties of matter

Physical properties of matter

- Substances are identified by their properties and by their composition.
- Color, melting point, and boiling point are physical properties.

- A ***physical property*** *can be measured and observed without changing the composition or identity of a substance.*
- For example, we can measure the melting point of ice by heating a block of ice and recording the temperature at which it melts to water.
- Liquid water differs from solid water, ice, only in appearance, not in composition, so this is a ***physical change***; we can freeze the water to recover the original ice.
- Therefore, the melting point of a substance is a ***physical property***.
- Similarly, when we say that helium gas is lighter than air, we are referring to a ***physical property***.

Chemical properties of matter

- The statement "Hydrogen gas burns in oxygen gas to form water" describes a ***chemical property*** of hydrogen, because *to observe this property we must carry out a chemical change*, in this case burning.
- After the change, the original chemical substance, the hydrogen gas, will have vanished, and all that will be left is a different chemical substance which is water.
- We ***cannot*** recover the hydrogen from the water by means of a physical change, such as boiling or freezing.
- When an egg is subjected to a temperature of about 100°C, the yolk and the egg white undergo changes that alter not only their physical appearance but their chemical makeup as well.
- When eaten, the egg is changed again in our bodies by *enzymes*.
- This digestive action is a chemical change.

EXAMPLE 1.7

Statement 1: In the earth atmosphere oxygen is a gas.

Statement 2: Iron converts to rust when it is in a humid environment.

Which of the above statements represent a physical property and which represents a chemical property. Rationalize.

Solution

Statements 1 represent a physical property because oxygen wither being a gas, a liquid, or a solid does not mean it differs in its chemical composition.

Statements 2 represent a chemical property because changing iron to rust means that the chemical composition of iron has changed.

Practice Exercise

Give two examples of a physical change and of a chemical change.

Categories of properties of matter

All measurable properties of matter fall into one of two categories:

- ❖ **Extensive properties.**
- The measured value of an ***extensive property*** *depends on how much matter is being considered.*

  Mass, which is *the quantity of matter in a given sample of a substance*, is an extensive property.

  More matter means more mass. Values of the same extensive property can be added together. For example:
  - ✓ Two copper pieces will have a combined mass that is the sum of the masses of each piece.
  - ✓ The length of two rooms is the sum of the lengths of each.
- ***Volume,*** defined as *length cubed*, is another extensive property.
- The value of an extensive quantity depends on the amount of matter.

- ❖ **Intensive properties.**
- The measured value of an ***intensive property*** *does not depend on how much matter is being considered.*
- ***Density,*** defined as *the mass of an object divided by its volume,* is an intensive property. So is temperature.
- Suppose that we have two beakers of water at the same temperature. If we combine them to make a single quantity of water in a larger beaker, the temperature of the larger quantity of water will be the same as it was in the two separate beakers.
- Unlike mass, length, and volume, temperature and other intensive properties are not additive.

EXAMPLE 1.8

Sample 1: 27.0 g of methanol at 23.0 °C.

Sample 2: 72.0 g of methanol at 23.0 °C.

If we mix both samples in one glass, what would the mass and the temperature of the mixture be? Rationalize.

Solution

The mass of the mixture = 27.0 g + 72.0 g = 99.0 g

The temperature of the mixture will be 23.0 °C

Mass is an extensive property and is additive.

Temperature is an intensive property and is not additive

Practice Exercise

Give two examples of extensive properties and of intensive properties.

1.2 Measurements

SI Units

- In 1960, the General Conference of Weights and Measures, the international authority on units, proposed a revised metric system called the ***International System of Units*** (abbreviated ***SI,*** from the French *S* ystème *I* nternationale d'Unites).
- The following table shows the seven SI base units.

Base quantity	**SI base unit**	
	Name	**Symbol**
length	meter	m
mass	kilogram	kg
time	second	s
electric current	ampere	A
Thermodynamic temperature	kelvin	K
amount of substance	mole	mol
luminous intensity	candela	cd

- All other units of measurement can be derived from these base units.
- Like metric units, SI units are modified in decimal fashion by a series of prefixes, as shown in The table below.
- We will use both metric and SI units in this book. Measurements that we will utilize frequently in our study of chemistry include time, mass, volume, density, and temperature.

Prefixes describing the Large		
Prefix (Symbol)	**Power**	**Numeric Representation**
yotta (Y)	10^{24}	1 septillion
zetta (Z)	10^{21}	1 sextillion
exa (E)	10^{18}	1 quintillion
peta (P)	10^{15}	1 quadrillion
tera (T)	10^{12}	1 trillion
giga (G)	10^{9}	1 billion
mega (M)	10^{6}	1 million
kilo (k)	10^{3}	1 thousand

no prefix	10^{0}	1 unit

Prefixes describing the Small		
Prefix (Symbol)	**Power**	**Numeric Representation**
no prefix	10^{0}	1 unit
milli (m)	10^{-3}	1 thousandth
micro (μ)	10^{-6}	1 millionth
nano (n)	10^{-9}	1 billionth
pico (p)	10^{-12}	1 trillionth
femto (f)	10^{-15}	1 quadrillionth
atto (a)	10^{-18}	1 quintillionth
zepto (z)	10^{-21}	1 sextillionth
yocto (y)	10^{-24}	1 septillionth

Mass and weight

- The terms “mass” and “weight” are often used interchangeably, although, strictly speaking, they are different quantities.
- Mass is a measure of the amount of matter in an object, but ***weight,*** is *the force that gravity exerts on an object.*
- An apple that falls from a tree is pulled downward by Earth’s gravity. The mass of the apple is constant and does not depend on its location, but its weight on the surface of the moon would weigh only one-sixth what it does on Earth.
- Chemists determine masses readily with a balance.
- The SI unit of mass is the *kilogram* (kg).
- In chemistry, however, the smaller *gram* (g) is more convenient:

$$1 \text{ kg} = 1000 \text{ g} = 1 \times 10^{-3} \text{ g}$$

Volume

- The SI unit of volume is the *cubic meter* (m^3). Generally, however, chemists work with much smaller volumes, such as the cubic centimeter (cm^3) and the cubic decimeter (dm^3):

$$1 \text{ cm}^3 = (1 \times 10^{-2} \text{ m})^3 = 1 \times 10^{-6} \text{ m}^3$$
$$1 \text{ dm}^3 = (1 \times 10^{-1} \text{ m})^3 = 1 \times 10^{-3} \text{ m}^3$$

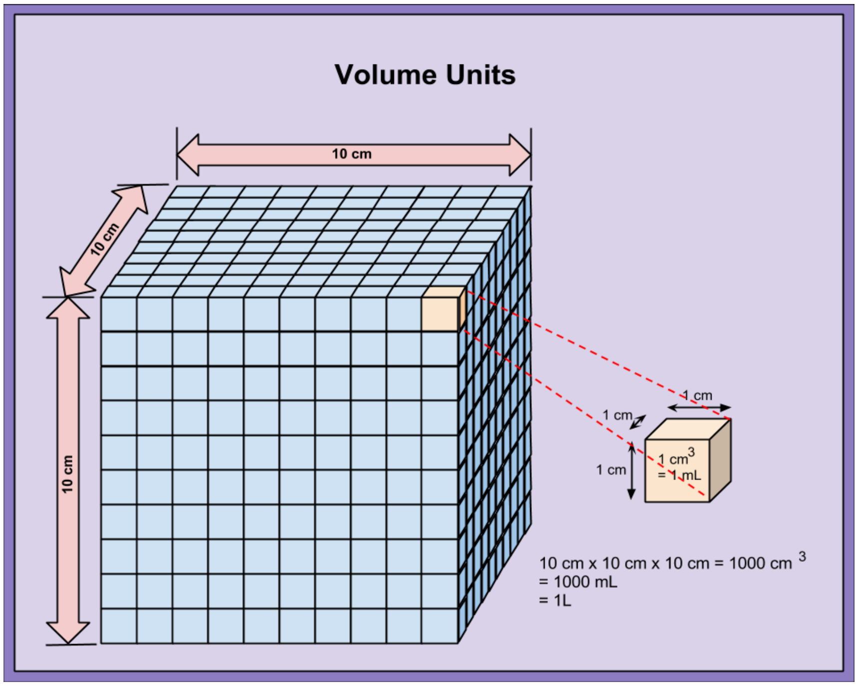
- Another common unit of volume is the liter (L). A ***liter*** is *the volume occupied by one cubic decimeter*. One liter of volume is equal to 1000 milliliters (mL):

$$\begin{aligned} 1 \text{ L} &= 1000 \text{ mL} \\ &= 1 \text{ dm}^3 = 1000 \text{ cm}^3 \end{aligned}$$

and one milliliter is equal to one cubic centimeter:

$$1 \text{ mL} = 1 \text{ cm}^3$$

- Even though the liter is not an SI unit, volumes are usually expressed in liters and milliliters.
- The following figure compares the relative sizes of two volumes.



Density

- The equation for density is

$$\text{density} = \frac{\text{mass}}{\text{volume}}$$

or

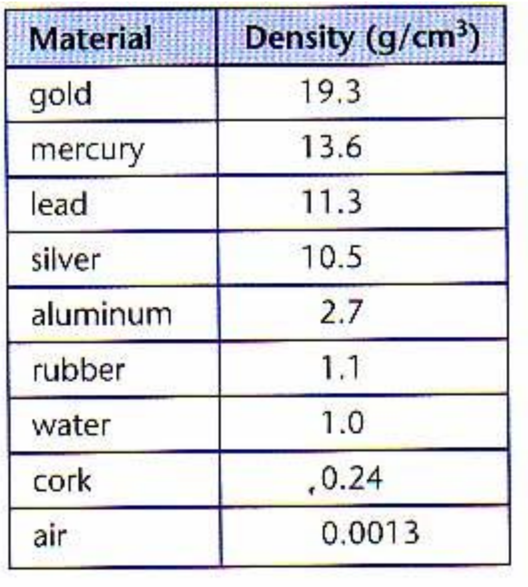
$$d = \frac{m}{V}$$

where d, m, and V denote density, mass, and volume, respectively.
- Because density is an intensive property and does not depend on the quantity of mass present, for a given substance the ratio of mass to volume always remains the same; in other words, V increases as m does.
- Density usually decreases with temperature.
- The SI-derived unit for density is the kilogram per cubic meter (kg/m^3).
- Grams per cubic centimeter (g/cm^3) and its equivalent, grams per milliliter (g/mL), are commonly used for solid and liquid densities.
- Because gas densities are often very low, we express them in units of grams per liter (g/L):

$$1 \text{ g/cm}^3 = 1 \text{ g/mL} = 1000 \text{ kg/m}^3$$

1 g/L = 0.001 g/mL

- The following table lists the densities of several substances.



Material	Density (g/cm³)
gold	19.3
mercury	13.6
lead	11.3
silver	10.5
aluminum	2.7
rubber	1.1
water	1.0
cork	0.24
air	0.0013

EXAMPLE 1.9

Gold is a precious metal that is chemically unreactive. It is used mainly in jewelry, dentistry, and electronic devices. A piece of gold ingot with a mass of 301 g has a volume of 15.6 cm^3. Calculate the density of gold.

Solution

$$d = \frac{m}{V}$$

$$d = \frac{301\ \text{g}}{15.6\ \text{cm}^3}$$

$$d = 19.3\ \text{g/cm}^3$$

Practice Exercise

A piece of platinum metal with a density of 21.5 g/cm^3 has a volume of 4.49 cm^3. What is its mass?

EXAMPLE 1.10

The density of mercury, the only metal that is a liquid at room temperature, is 13.6 g/mL. Calculate the mass of 5.50 mL of the liquid.

Solution

$$m = d \times V$$

$$m = 13.6\ \frac{\text{g}}{\cancel{\text{cm}^3}} \times 5.5\ \cancel{\text{cm}^3}$$

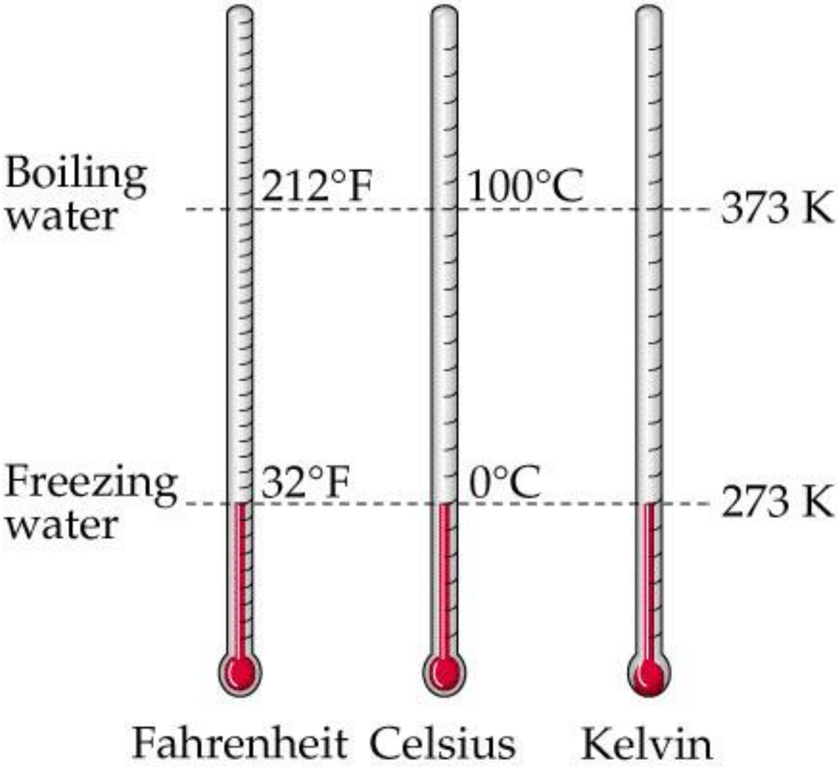
$$m = 74.8\ \text{g}$$

Practice Exercise

The density of sulfuric acid in a certain car battery is 1.41 g/mL. Calculate the mass of 242 mL of the liquid.

Temperature scales

- Three temperature scales are currently in use. Their units are °F (degrees Fahrenheit), °C (degrees Celsius), and K (kelvin).
- The ***Celsius*** scale, which is the most commonly used scale worldwide, divides the range between the freezing point (0°C) and boiling point (100°C) of water into 100 degrees.
- The ***Fahrenheit*** scale, which is the least used scale worldwide but is used in some countries like the United States and the United Kingdom but outside their laboratories, defines the normal freezing and boiling points of water to be exactly 32 °F and 212 °F, respectively.



- We can use the following equations to convert between degrees Celsius and degrees Fahrenheit:

$$\text{Temperature in °C} = (\text{Temperature in °F} - 32\ \text{°F}) \times \frac{5\ \text{°C}}{9\ \text{°F}}$$

$$\text{Temperature in °F} = \left(\frac{9\ \text{°F}}{5\ \text{°C}} \times \text{Temperature in °C}\right) + 32\ \text{°F}$$

- The ***Kelvin*** scale (the ***absolute*** temperature scale) is *the SI base unit of temperature*.

- By absolute we mean that the zero on the Kelvin scale, denoted by 0 K, is the lowest temperature that can be attained theoretically.
- The Celsius and the Kelvin scales have units of equal magnitude; that is, one degree Celsius is equivalent to one Kelvin.
- Experimental studies have shown that:

$$0\ \text{K} = -273.15°\text{C}$$

- We can use the following equations to convert between degrees Celsius and Kelvin:

$$\text{Temperature in K} = (\text{Temperature in °C} + 273.15\ \text{°C}) \times \frac{1\ \text{K}}{1\ \text{°C}}$$

$$\text{Temperature in °C} = (\text{Temperature in K} - 273.15\ \text{K}) \times \frac{1\ \text{°C}}{1\ \text{K}}$$

EXAMPLE 1.11

Mercury melts at − 38.9 °C. Convert its melting point to kelvins and to °F.

Solution

$$\text{Temperature in K} = (\text{Temperature in °C} + 273.15\ \text{°C}) \times \frac{1\ \text{K}}{1\ \text{°C}}$$

$$\text{Temperature in K} = (-\ 38.9\ \text{°C} + 273.15\ \text{°C})\ \frac{\text{K}}{\text{°C}} = 234.3\ \text{K}$$

$$\text{Temperature in °F} = (\frac{9\ \text{°F}}{5\ \text{°C}} \times \text{Temperature in °C}) + 32\ \text{°F}$$

$$\text{Temperature in °F} = (\frac{9\ \text{°F}}{5\ \text{°C}} \times -\ 38.9\ \text{°C}) + 32\ \text{°F} = -\ 38.02\ \text{°F}$$

Practice Exercise

Convert 77 K, (the boiling point of liquid nitrogen) to °C and to °F.

Handling Numbers

- Having surveyed some of the units used in chemistry, we now turn to techniques for handling numbers associated with measurements: scientific notation and significant figures.

Scientific Notation

- Chemists often deal with numbers that are either extremely large or extremely small. For example, in 1 g of the element hydrogen there are roughly

  602,200,000,000,000,000,000,000

  hydrogen atoms. Each hydrogen atom has a mass of only

  0.00000000000000000000000166 g
- Consider the following multiplication:

  0.0000000056 × 0.00000000048 = 0.000000000000000002688
- It would be easy for us to miss one zero or add one more zero after the decimal point.

- Consequently, when working with very large and very small numbers, we use a system called *scientific notation.*
- Regardless of their magnitude, all numbers can be expressed in the form
  $$N \times 10^n$$
  where N is a number between 1 and 10 and n, the exponent, is a positive or negative integer (whole number).
- Any number expressed in this way is said to be written in scientific notation.
- Suppose that we are given a certain number and asked to express it in scientific notation:
  - ✓ We must find n.
  - ✓ We count the number of places that the decimal point must be moved to give the number N (which is between 1 and 10).
  - ✓ If the decimal point has to be moved to the left, then n is a positive integer; if it has to be moved to the right, n is a negative integer.
  - ✓ The following examples illustrate the use of scientific notation:

    (1) $568.762 = 5.68762 \times 10^2$

    n = 2 because the decimal point is moved to the left by two places.

    (2) $0.00000772 = 7.72 \times 10^{-6}$

    n = – 6 because the decimal point is moved to the right by six places.
- Keep in mind the following two points:

  First, n = 0 is used for numbers that are not expressed in scientific notation. For example, 74.6×10^0 (n = 0) is equivalent to 74.6.

  Second, the usual practice is to omit the superscript when n = 1. Thus, the scientific notation for 74.6 is 7.46×10 and not 7.46×10^1.

Addition and Subtraction

- To add or subtract using scientific notation:

  First, write each quantity, say N_1 and N_2, with the same exponent n.

  Second, combine N_1 and N_2; the exponents remain the same.

$$(7.4 \times 10^3) + (2.1 \times 10^3) = 9.5 \times 10^3$$

$$\begin{aligned}(4.31 \times 10^4) + (3.9 \times 10^3) &= (4.31 \times 10^4) + (0.39 \times 10^4) \\ &= 4.70 \times 10^4\end{aligned}$$

$$\begin{aligned}(2.22 \times 10^{-2}) - (4.10 \times 10^{-3}) &= (2.22 \times 10^{-2}) - (0.41 \times 10^{-2}) \\ &= 1.81 \times 10^{-2}\end{aligned}$$

Multiplication and Division

- To multiply numbers expressed in scientific notation:

  First, multiply N_1 and N_2 in the usual way.

Second, add the exponents together.

$$\begin{aligned}(8.0 \times 10^{4}) \times (5.0 \times 10^{2}) &= (8.0 \times 5.0)\,(10^{4+2})\\ &= 40 \times 10^{6}\\ &= 4.0 \times 10^{7}\\ (4.0 \times 10^{-5}) \times (7.0 \times 10^{3}) &= (4.0 \times 7.0)\,(10^{-5+3})\\ &= 28 \times 10^{-2}\\ &= 2.8 \times 10^{-1}\end{aligned}$$

- To divide using scientific notation:
  First, divide N_1 and N_2 as usual.
  Second, subtract the exponents.

$$\begin{aligned}\frac{6.9 \times 10^{7}}{3.0 \times 10^{-5}} &= \frac{6.9}{3.0} \times 10^{7-(-5)}\\ &= 2.3 \times 10^{12}\\ \frac{8.5 \times 10^{4}}{5.0 \times 10^{9}} &= \frac{8.5}{5.0} \times 10^{4-9}\\ &= 1.7 \times 10^{-5}\end{aligned}$$

Significant Figures

- Except when all the numbers involved are integers (for example, in counting the number of students in a class), it is often impossible to obtain the exact value of the quantity under investigation.
- For this reason, it is important to indicate the margin of error in a measurement by clearly indicating the number of ***significant figures***.
- ***Significant figures*** are *the meaningful digits in a measured or calculated quantity*.
- When significant figures are used, the last digit is understood to be uncertain.

  For example,

  ✓ we might measure the volume of a given amount of liquid using a graduated cylinder with a scale that gives an uncertainty of 1 mL in the measurement.
    - ➢ If the volume is found to be 6 mL, then the actual volume is in the range of 5 mL to 7 mL.
    - ➢ We represent the volume of the liquid as (6 ± 1) mL.
    - ➢ In this case, there is only one significant figure (the digit 6) that is uncertain by either plus or minus 1 mL.

  ✓ If we used a graduated cylinder that has finer divisions, so that the volume we measure is uncertain by only 0.1 mL.
    - ➢ If the volume of the liquid is found to be 6.0 mL, we may express the quantity as (6.0 ± 0.1) mL,

  - ➢ The actual value is somewhere between 5.9 mL and 6.1 mL.
- ✓ We can further improve the measuring device and obtain more significant figures, but in every case, the last digit is always uncertain; the amount of this uncertainty depends on the particular measuring device we use.
- The figure below shows a modern balance such as the one available in many general chemistry laboratories.

- Such balance readily measures the mass of objects to four decimal places.
- Therefore, the measured mass typically will have four significant figures (for example, 0.8642 g) or more (for example, 3.9745 g).
- Keeping track of the number of significant figures in a measurement such as mass ensures that calculations involving the data will reflect the precision of the measurement.

Guidelines for Using Significant Figures

- We must always be careful in scientific work to write the proper number of significant figures.
- In general, it is fairly easy to determine how many significant figures a number has by following these rules:
  1. ***Any digit that is not zero is significant***.
     845 cm has three significant figures.
     1.234 kg has four significant figures.
     and so on.
  2. ***Zeros between nonzero digits are significant***.
     606 m contains three significant figures.
     40,501 kg contains five significant figures.

and so on.

3. ***Zeros to the left of the first nonzero digit are not significant***.
   Their purpose is to indicate the placement of the decimal point.
   0.08 L contains one significant figure.
   0.0000349 g contains three significant figures.
   and so on.
4. ***If a number is greater than 1, then all the zeros written to the right of the decimal point count as significant figures***.
   2.0 mg has two significant figures.
   40.062 mL has five significant figures.
   3.040 dm has four significant figures.
   If a number is less than 1, then only the zeros that are at the end of the number and the zeros that are between nonzero digits are significant.
   0.090 kg has two significant figures.
   0.3005 L has four significant figures.
   0.00420 min has three significant figures.
   and so on.
5. ***Numbers that do not contain decimal points, the trailing zeros (zeros after the last nonzero digit) may or may not be significant***.
   400 cm may have one significant figures (the digit 4), two significant figures (40), or three significant figures (400).
   We cannot know which is correct without more information.
   By using scientific notation, however, we avoid this ambiguity.
   We can express the number 400 in three different ways:
   4×10^2 for one significant figure,
   4.0×10^2 for two significant figures,
   4.00×10^2 for three significant figures.

EXAMPLE 1.12

Determine the number of significant figures in the following measurements:

a) 478 cm
b) 6.01 g
c) 0.825 m
d) 0.043 kg
e) 1.310×10^{22} atoms
f) 7000 mL

Solution

a) Three, because each digit is a nonzero digit.
b) Three, because zeros between nonzero digits are significant.
c) Three, because zeros to the left of the first nonzero digit do not count as

significant figures.

d) Two. Same reason as in (c).

e) Four, because the number is greater than one so all the zeros written to the right of the decimal point count as significant figures.

f) This is an ambiguous case. The number of significant figures may be four (7.000×10^3), three (7.00×10^3), two (7.0×10^3) or one (7×10^3). This example illustrates why scientific notation must be used to show the proper number of significant figures.

Practice Exercise

Determine the number of significant figures in each of the following measurements: (a) 24 mL, (b) 3001 g, (c) 0.0320 m^3, (d) 6.4×10^4 molecules, (e) 560 kg.

- A second set of rules specifies how to handle significant figures in calculations.

1. In addition, and subtraction:
   The answer cannot have more digits to the right of the decimal point than either of the original numbers.

$$\begin{array}{rl} 89.332 & \\ \underline{+\ 1.1} & \leftarrow \text{one digit after the decimal point} \\ 90.432 & \leftarrow \text{round off to 90.4} \end{array}$$

$$\begin{array}{rl} 2.097 & \\ \underline{-\ 0.12} & \leftarrow \text{two digits after the decimal point} \\ 1.977 & \leftarrow \text{round off to 1.98} \end{array}$$

   The rounding-off procedure is as follows:

   ✓ To round off a number at a certain point we simply drop the digits that follow if the first of them is less than 5:
   8.724 rounds off to 8.72

   ✓ If we want only two digits after the decimal point. If the first digit following the point of rounding off is equal to or greater than 5, we add 1 to the preceding digit:
   8.727 rounds off to 8.73.
   0.425 rounds off to 0.43.

2. In multiplication and division:

The number of significant figures in the final product or quotient is determined by the original number that has the *smallest* number of significant figures. The following examples illustrate this rule:

$$2.8 \times 4.5039 = 12.61092 \qquad \leftarrow \text{round off to } 13$$

$$\frac{6.85}{112.04} = 0.0611388789 \qquad \leftarrow \text{round off to } 0.0611$$

3. Keep in mind that *exact numbers* obtained from definitions or by counting numbers of objects can be considered to have an infinite number of significant figures.
   For example, the inch is defined to be exactly 2.54 centimeters; that is,

   $$1 \text{ in} = 2.54 \text{ cm}$$

   Thus, the “2.54” in the equation should not be interpreted as a measured number with three significant figures.
   In calculations involving conversion between “in” and “cm,” we treat both “1” and “2.54” as having an infinite number of significant figures.
   Similarly, if an object has a mass of 5.0 g, then the mass of nine such objects is:

   $$5.0 \text{ g} \times 9 = 45 \text{ g}$$

   The answer has two significant figures because 5.0 g has two significant figures. The number 9 is exact and does not determine the number of significant figures.

EXAMPLE 1.13

Carry out the following arithmetic operations to the correct number of significant figures:

(a) 11,254.1 g + 0.1983 g
(b) 66.59 L – 3.113 L
(c) 8.16 m × 5.1355
(d) 0.0154 kg ÷ 88.3 mL
(e) 2.64×10^3 cm + 3.27×10^2 cm.

Solution

a)

$$\begin{array}{rl} & 11{,}254.1 \text{ g} \\ + & \underline{\phantom{11{,}25}0.1983 \text{ g}} \\ & 11{,}254.2983 \text{ g} \end{array} \qquad \leftarrow \text{round off to } 11{,}254.3 \text{ g}$$

b) 66.59 L

$$\begin{array}{r} 66.59 \text{ L} \\ \underline{-\ \ 3.113 \text{ L}} \\ 63.477 \text{ L} \end{array} \quad \leftarrow \text{round off to } 63.48 \text{ L}$$

c) 8.16 m × 5.1355 = 41.90568 m ← round off to 41.9 m

d) $\frac{0.0154 \text{ kg}}{88.3 \text{ mL}}$ = 0.000174405436 kg/mL ←round off to 0.000174 kg/mL

or 1.74×10^{-4} kg/mL

e) First we change 3.27×10^2 cm to 0.327×10^3 cm and then carry out the addition (2.64 cm + 0.327 cm) × 10^3. Following the procedure in (a), we find the answer is 2.97×10^3 cm.

Practice Exercise

Carry out the following arithmetic operations and round off the answers to the appropriate number of significant figures: (a) 26.5862 L + 0.17 L, (b) 9.1 g – 4.682 g, (c) 7.1×10^4 dm × 2.2654×10^2 dm, (d) 6.54 g ÷ 86.5542 mL, (e) (7.55×10^4 m) – (8.62×10^3 m).

- The preceding rounding-off procedure applies to one-step calculations. In *chain calculations*, that is, calculations involving more than one step, we can get a different answer depending on how we round off.
  - ✓ Example:

    First step: A × B = C

    Second step: C × D = E

  - ✓ Let's suppose that A = 3.66, B = 8.45, and D = 2.11.
  - ✓ Depending on whether we round off C to three or four significant figures, we obtain a different number for E:

Method 1	**Method 2**
3.66 × 8.45 = 30.9	3.66 × 8.45 = 30.93
30.9 × 2.11 = 65.2	30.93 × 2.11 = 65.3

  - ✓ However, if we had carried out the calculation as:

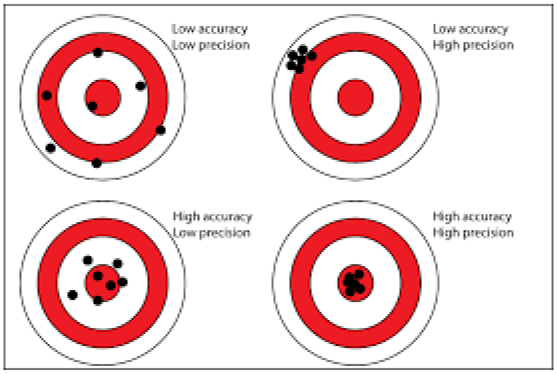
    $$3.66 \times 8.45 \times 2.11 = 65.3$$

    on a calculator without rounding off the intermediate answer, we would have obtained 65.3 as the answer for E.
  - ✓ Although retaining an additional digit past the number of significant figures for intermediate steps helps to eliminate errors from rounding,

this procedure is not necessary for most calculations because the difference between the answers is usually quite small.

Accuracy and precision

- Carefully, look at the following figure:



The distribution of darts on a dart board shows the difference between precise and accurate. The black dots show the positions of the darts.

***Up left**: low accuracy and low precision.*
***Up right** low accuracy and high precision.*
***Down left**: high accuracy and low precision.*
***Down right**: high accuracy and high precision.*

- ***Accuracy*** tells us *how close a measurement is to the true value of the quantity that was measured*.
- ***Precision*** *refers to how closely two or more measurements of the same quantity agree with one another*.
- The difference between accuracy and precision is a subtle but important one. The following figure may ease their concepts.

- Suppose, for example, that the true mass of a copper wire is 2.000 g
  - ✓ Three students are asked to determine the mass of this piece of copper wire.
  - ✓ The results of two successive weighing by each student are:

	Student A	**Student B**	**Student C**
1st weighing	1.964 g	1.972 g	2.000 g
2nd weighing	1.978 g	1.968 g	2.002 g
Average value	**1.971 g**	**1.970 g**	**2.001 g**

- ✓ For student B, the deviation, on 1.972 g and 1.968 g from 1.970 g is less than the deviation of 1.964 g and 1.978 g from 1.971 g for student A. Therefore, we say:
  Results of Student B are more precise than the results of Student A.
  but neither set of results is very *accurate*.
- ✓ Because the average value of Student C is closest to the true value, we say:
  Results of Student C are the most precise and the most accurate.
- ✓ Highly accurate measurements are usually precise too.
- ✓ On the other hand, highly precise measurements do not necessarily guarantee accurate results.
  For example, an improperly calibrated meterstick or a faulty balance may give precise readings that are in error.

Dimensional analysis in solving problems (conversion factors)

- The procedure we use to convert between units in solving chemistry problems is called ***dimensional analysis*** (also called the ***factor-label method***).
- Dimensional analysis is based on the relationship between different units that express the same physical quantity.
- For example, by definition 1 in = 2.54 cm (exactly). This equivalence enables us to write a conversion factor as follows:

$$\frac{1\ \text{in}}{2.54\ \text{cm}} \text{ or } \frac{2.54\ \text{cm}}{1\ \text{in}}$$

  Because both the numerator and the denominator express the same length, this fraction is equal to 1.
- Conversion factors are useful for changing units.
- To convert a length expressed in inches to centimeters, we multiply the length by the appropriate conversion factor.

$$12.00\ \cancel{\text{in}} \times \frac{2.54\ \text{cm}}{1\ \cancel{\text{in}}} = 30.48\ \text{cm}$$

- We choose the conversion factor that cancels the unit inches and produces the desired unit, centimeters.
- Note that the result is expressed in four significant figures because 2.54 is an exact number.
- The conversion of 57.8 meters to centimeters is as follows:

$$?\ \text{cm} = 57.8\ \text{m}$$

  By definition,

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

Because we are converting “m” to “cm,” we choose the conversion factor that has meters in the denominator,

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

$$\begin{aligned} ?\ \text{cm} &= 57.8\ \cancel{\text{m}} \times \frac{1\ \text{cm}}{1 \times 10^{-2}\ \cancel{\text{m}}} \\ &= 5780\ \text{cm} \\ &= 5.78 \times 10^{3}\ \text{cm} \end{aligned}$$

Note that scientific notation is used to indicate that the answer has three significant figures.

Again, the conversion factor $\frac{1\ \text{cm}}{1 \times 10^{-2}\ \text{m}}$ contains exact numbers; therefore, it does not affect the number of significant figures.

- In general, to apply dimensional analysis we use the relationship

  given quantity × conversion factor = desired quantity

  and the units cancel as follows:

  $$\cancel{\text{given unit}} \times \frac{\text{desired unit}}{\cancel{\text{given unit}}} = \text{desired unit}$$
- In dimensional analysis, the units are carried through the entire sequence of calculations.
- Therefore, if the equation is set up correctly, then all the units will cancel except the desired one.
- If this is not the case, then an error must have been made somewhere, and it can usually be spotted by reviewing the solution.

A Note on problem solving

- At this point you have been introduced to scientific notation, significant figures, and dimensional analysis.
- These will help you in solving numerical problems.
- Chemistry is an experimental science and many of the problems are quantitative in nature.
- The key to success in problem solving is practice.
- You cannot be sure of your understanding of chemistry without solving problems.
- The following steps will help to improve your skill at solving numerical problems.

  1. **Read** the question carefully.
     Understand the information that is given and what you are asked to solve.
     Make a sketch to help you to visualizing the situation.

2. **Find** the appropriate equation that relates the given information and the unknown quantity.
   Sometimes solving a problem will involve more than one step, and you may be expected to look up quantities in tables that are not provided in the problem.
   Dimensional analysis is often needed to carry out conversions.
3. **Check** your answer for the correct sign, units, and significant figures.
4. **An important** part of problem solving is being able to judge whether the answer is reasonable.
   It is easy to spot a wrong sign or incorrect units.
   If a number (say 9) is incorrectly placed in the denominator instead of in the numerator, the answer would be too small even if the sign and units of the calculated quantity were correct.
5. **One way to quickly check** the answer is to make a “ball-park” estimate. This means making a personal rough estimate.
   The idea here is to round off the numbers in the calculation in such a way so as to simplify the arithmetic.
   This approach can be done easily without using a calculator.
   The answer you get will not be exact, but it will be close to the correct one.

EXAMPLE 1.14

A person’s average daily intake of glucose (a form of sugar) is 0.0833 pound (lb). What is this mass in milligrams (mg)? (1 lb = 453.6 g)

Solution

The sequence of conversions is

$$\text{pounds} \longrightarrow \text{grams} \longrightarrow \text{milligrams}$$

$$\frac{453.6\ \text{g}}{1\ \text{lb}} \text{ and } \frac{1\ \text{mg}}{1 \times 10^{-3}\ \text{g}}$$

$$?\ \text{mg} = 0.0833\ \cancel{\text{lb}} \times \frac{453.6\ \cancel{\text{g}}}{1\ \cancel{\text{lb}}} \times \frac{1\ \text{mg}}{1 \times 10^{-3}\ \cancel{\text{g}}} = 3.78 \times 10^{4}\ \text{mg}$$

Practice Exercise

A roll of aluminum foil has a mass of 1.07 kg. What is its mass in pounds?

EXAMPLE 1.15

An average adult has 5.2 L of blood. What is the volume of blood in m^3?

Solution

$$\frac{1\ \text{m}^3}{1000\ \text{L}} = 1$$

$$5.2\ \text{L} = 5.2\ \cancel{\text{L}} \times \frac{1\ \text{m}^3}{1000\ \cancel{\text{L}}} = 5.2 \times 10^{-3}\ \text{m}^3$$

Practice Exercise

The volume of a room is 1.08×10^8 dm^3. What is the volume in m^3?

EXAMPLE 1.16

Liquid nitrogen is obtained from liquefied air and is used to prepare frozen goods and in low-temperature research. The density of liquid nitrogen at its boiling point (– 196 °C or 77 K) is 0.808 g/cm^3. Convert the density to units of kg/m^3.

Solution

The conversion factors are:

$\frac{1\ \text{cm}^3}{1 \times 10^{-6}\ \text{m}^3} = 1$	$\frac{1\ \text{kg}}{1000\ \text{g}} = 1$

$$0.808\ \frac{\cancel{\text{g}}}{1\ \cancel{\text{cm}^3}} \times \frac{1\ \text{kg}}{1000\ \cancel{\text{g}}} \times \frac{1\ \cancel{\text{cm}^3}}{1 \times 10^{-6}\ \text{m}^3} = 808\ \text{kg/m}^3$$

Practice Exercise

The density of the lightest metal, lithium (Li), is 5.34×10^2 kg/m^3. Convert the density to g/cm^3.

SOLUTIONS OF PRACICE EXERCISES

QUESTIONS AND PROBLEMS

Review Questions

1. Give an example for each of the following terms:
   (a) matter. (b) substance. (c) mixture.
2. Give an example of a homogeneous mixture and an example of a heterogeneous mixture.
3. Using examples, explain the difference between a physical property and a chemical property.
4. How does an intensive property differ from an extensive property?
5. Which of the following properties are intensive and which are extensive?
   (a) length. (b) volume. (c) temperature. (d) mass.
6. Which of the following statements describe physical properties and which describe chemical properties?
   (a) Iron has a tendency to rust.
   (b) Rainwater in industrialized regions tends to be acidic.
   (c) Hemoglobin molecules have a red color.
   (d) When a glass of water is under the sun it gradually disappears.
7. Different from any one mentioned in question number 6 above, give an example of a physical change and of a chemical change.
8. Give an example of an element and a compound. How do elements and compounds differ?
9. What is the number of known elements?
10. Does each of the following describe a physical or a chemical change?
    (a) The helium gas inside a balloon tends to leak out after a few hours.
    (b) A flashlight beam slowly gets dimmer and finally goes out.
    (c) Frozen orange juice is reconstituted by adding water to it.
    (d) In photosynthesis he growth of plants depends on the sun’s energy.
    (e) A spoonful of table salt dissolves in a bowl of soup.
11. Give the chemical symbols for the following elements:
    (a) potassium. (b) tin. (c) chromium.
    (d) boron (e) barium. (f) plutonium.
    (g) sulfur. (h) argon. (i) mercury.
12. Classify each of the following as an element, a compound, a homogeneous mixture, or a heterogeneous mixture:
    (a) seawater. (b) helium gas.
    (c) sodium chloride (table salt). (d) a bottle of soft drink.
    (e) a milkshake. (f) air in a bottle.
    (g) concrete.

13. Name the SI base units that are important in chemistry. Give the SI units for expressing the following:
    (a) length, (b) volume, (c) mass, (d) time, (e) energy, (f) temperature
14. Write the numbers represented by the following prefixes:
    (a) mega-, (b) kilo-, (c) deci-, (d) centi-, (e) milli-, (f) micro-, (g) nano-, (h) pico-.
15. What units do chemists normally use for density of liquids and solids? For gas density? Explain the differences. Describe the three temperature scales used in the laboratory and in everyday life:
    (a) the Fahrenheit scale, (b) the Celsius scale, (c) the Kelvin scale.
16. What is the advantage of using scientific notation over decimal notation?
17. Define significant figure. Discuss the importance of using the proper number of significant figures in measurements and calculations.

Problems

18. Bromine is a reddish-brown liquid. Calculate its density (in g/mL) if 586 g of the substance occupies 188 mL.
19. The density of ethanol, a colorless liquid that is commonly known as grain alcohol, is 0.798 g/mL. Calculate the mass of 17.4 mL of the liquid.
20. Convert the following temperatures to kelvin:
    (a) 113°C, the melting point of sulfur
    (b) 37°C, the normal body temperature
    (c) 357°C, the boiling point of mercury.
21. Convert the following temperatures to degrees Celsius:
    (a) 77 K, the boiling point of liquid nitrogen
    (b) 4.2 K, the boiling point of liquid helium,
    (c) 601 K, the melting point of lead.
22. Express the following numbers in scientific notation:
    (a) 0.000000027 (b) 356 (c) 47,764
    (d) 0.096.
23. Express the following numbers as decimals:
    (a) 1.52×10^{-2} (b) 7.78×10^{-8}.
24. Express the answers to the following calculations in scientific notation:
    (a) $145.75 + (2.3 \times 10^{-1})$ (b) $79{,}500 \div (2.5 \times 10^{2})$
    (c) $(7.0 \times 10^{-3}) - (8.0 \times 10^{-4})$ (d) $(1.0 \times 10^{4}) \times (9.9 \times 10^{6})$
25. Express the answers to the following calculations in scientific notation:
    (a) $0.0095 + (8.5 \times 10^{-3})$ (b) $653 \div (5.75 \times 10^{-8})$
    (c) $850{,}000 - (9.0\ 3\ 10^{5})$ (d) $(3.6 \times 10^{-4}) \times (3.6 \times 10^{6})$
26. What is the number of significant figures in each of the following measurements?

(a) 4867 mi	(b) 56 mL	(c) 60,104 ton
(d) 2900 g	(e) 40.2 g/cm^3	(f) 0.0000003 cm
(g) 0.7 min	(h) 4.6 × 10^{19} atoms	

27.How many significant figures are there in each of the following?

(a) 0.006 L	(b) 0.0605 dm	(c) 60.5 mg
(d) 605.5 cm^2	(e) 960 × 10^{-2} g	(f) 6 kg
(g) 60 m		

28.Carry out the following operations as if they were calculations of experimental results, and express each answer in the correct units with the correct number of significant figures:

(a) 5.6792 m + 0.6 m + 4.33 m

(b) 3.70 g – 2.9133 g

(c) 4.51 cm × 3.6666 cm

(d) (3 3 104 g + 6.827 g) ÷ (0.043 cm^3 – 0.021 cm^3)

29.Three students (A, B, and C) are asked to determine the volume of a sample of ethanol. Each student measures the volume three times with a graduated cylinder. The results in milliliters are:

A (87.1, 88.2, 87.6)
B (86.9, 87.1, 87.2)
C (87.6, 87.8, 87.9)

The true volume is 87.0 mL. Comment on the precision and the accuracy of each student's results.

30.Three apprentice tailors (A, B, and C) are assigned the task of measuring the seam of a pair of trousers. Each one makes three measurements. The results in inches are:

A (31.5, 31.6, 31.4)
B (32.8, 32.3, 32,7)
C (31.9, 32.2, 32.1)

The true length is 32.0 in. Comment on the precision and the accuracy of each tailor's measurements.

31.Carry out the following conversions:

(a) 22.6 m to decimeters	(b) 25.4 mg to kilograms
(c) 556 mL to liters	(d) 10.6 kg/m^3 to g/cm^3

32.The average speed of helium at 25°C is 1255 m/s. Convert this speed to miles per hour (mph).

33.How many seconds are there in a solar year (365.24 days)?

34.How many minutes does it take light from the sun to reach Earth? (The distance from the sun to Earth is 93 million mi; the speed of light = 3.00 × 10^8 m/s.)

35.A slow jogger runs a mile in 13 min. Calculate the speed in

(a) in/s (b) m/min (c) km/h.
(1 mi = 1609 m;1 in = 2.54 cm.)

36. A 6.0-ft person weighs 168 lb. Express this person's height in meters and weight in kilograms.
(1 lb = 453.6 g; 1 m = 3.28 ft.)

37. The car speed limit in some states in the United States is 55 miles per hour. What is the speed limit in kilometers per hour?
(1 mi = 1609 m.)

38. For a fighter jet to take off from the deck of an aircraft carrier, it must reach a speed of 62 m/s. Calculate the speed in miles per hour (mph).

39. The "normal" lead content in human blood is about 0.40 part per million (that is, 0.40 g of lead per million grams of blood). A value of 0.80 part per million (ppm) is considered to be dangerous. How many grams of lead are contained in 6.0×10^3 g of blood (the amount in an average adult) if the lead content is 0.62 ppm?

40. Carry out the following conversions:
(a) 1.42 lightyears to miles (a light-year is an astronomical measure of distance—the distance traveled by light in a year, or 365 days; the speed of light is 3.00×10^8 m/s)
(b) 32.4 yd to centimeters

41. Carry out the following conversions:
(a) 185 nm to meters. (b) 4.5 billion years (roughly the age of Earth) to seconds. (Assume there are 365 days in a year.)
(c) 71.2 cm^3 to m^3. (d) 88.6 m^3 to liters.

42. Aluminum is a lightweight metal (density = 2.70 g/cm^3) used in aircraft construction, high-voltage transmission lines, beverage cans, and foils. What is its density in kg/m^3?

43. The density of ammonia gas under certain conditions is 0.625 g/L. Calculate its density in g/cm^3.

2. ATOMS, MOLECULES AND IONS

Constituent of the atom

The Electron

- Electron was discovered by an English physicist, J. J. Thomson in 1897.
- Electrons are negatively charged atomic particles.
- Thomson determined the ratio of the electric charge to the mass of an individual electron.
- In 1909, an American physicist, R. Millikan measured the charge of an electron to be

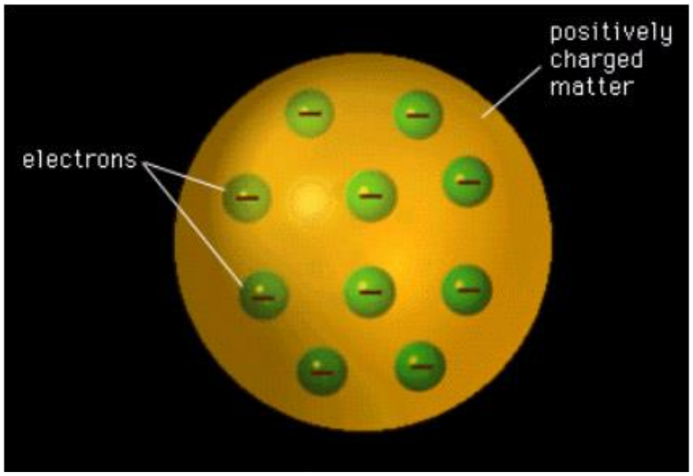
$$1.6022 \times 10^{-19}\ \text{C}$$

- The mass of the electron is found to be

$$9.10 \times 10^{-28}\ \text{g}$$

The Proton and the nucleus

- Earlier in 1900s, it became clear that atoms contain electrons, and they are electrically neutral.
- To maintain electric neutrality, an atom must contain an equal number of positive and negative charges.
- In 1904 Thomson proposed that an atom could be thought of as a uniform, positive sphere of matter in which electrons are embedded like raisins in a cake (Figure 2.1). This so-called "plum-pudding" model was the accepted theory for a number of years.



Thomson's model of the atom, sometimes described as the "plum-pudding" model, after a traditional English dessert containing raisins. The electrons are embedded in a uniform, positively charged sphere.

- The “plum-pudding” is a kind of sweets originally offered in England at Christmas dinner. The following figures display some of its popular kinds and shape.

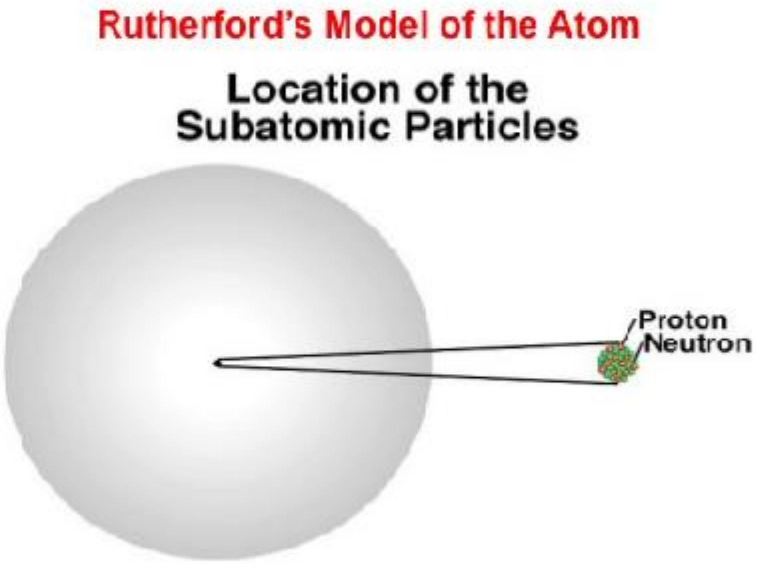
- In 1909, a New Zealander physicist and chemist, Ernest Rutherford discovered the Proton.
- The proton electric charge equals the electron electric charge.
- The proton mass = 1.67262 × 10^{-24} g.
- The proton mass is about 1840 times the mass of the electron.
- The mass of a nucleus constitutes most of the mass of the entire atom.
- The nucleus occupies only about $\frac{1}{1013}$ of the volume of the atom.
- We express atomic (and molecular) dimensions in terms of the SI unit called the *picometer* (pm), where

$$1 \text{ pm} = 1 \times 10^{-12} \text{ m}$$

- A typical atomic radius is about 100 pm, whereas the radius of an atomic nucleus is only about 5 × 10^{-3} pm.
- You can appreciate the relative sizes of an atom and its nucleus by imagining that the size of the nucleus is the same as the size of a ping pong ball, first electron orbiting around it would be 666 m away.
- Although the protons are confined to the nucleus of the atom, the electrons are conceived of as being spread out about the nucleus at some distance from it.
- The concept of atomic radius is useful experimentally, but we should not infer that atoms have well-defined boundaries or surfaces. We will learn later that the outer regions of atoms are relatively “fuzzy.”

The neutron

- James Chadwick, in 1932, showed that atoms consist of a third type of subatomic particles, which he named ***neutrons,*** because they proved to be *electrically neutral particles having a mass slightly greater than that of protons.*
- The following figure shows the location of the elementary particles (protons, neutrons, and electrons) in an atom. The figure shows that electrons are as "clouds" around the nucleus

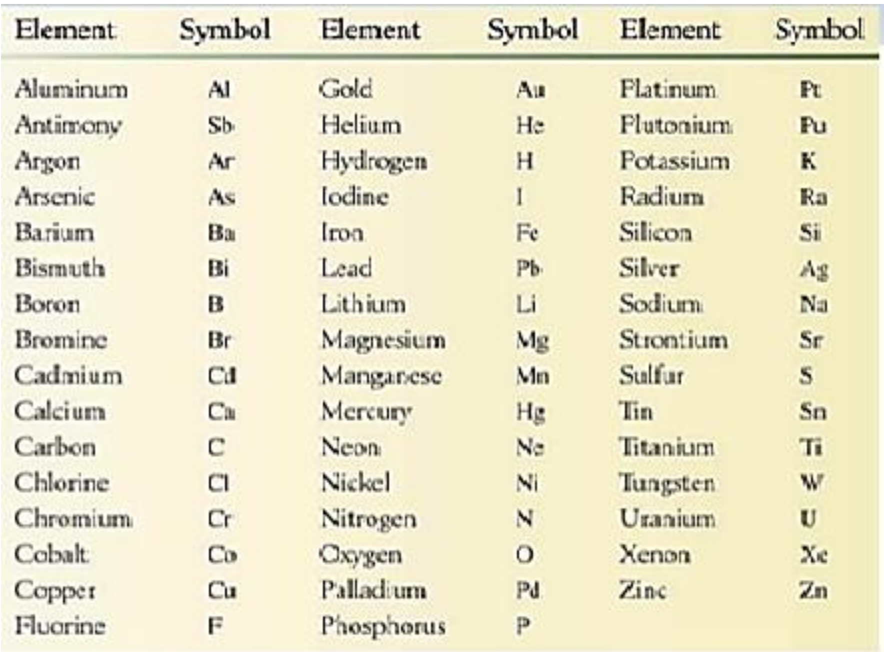


- The table below shows their masses and charges.

Particle	**Mass (g)**	**Electric Charge (C)**
Electron	9.10938×10^{-28}	-1.6022×10^{-19}
Proton	1.67262×10^{-24}	$+1.6022 \times 10^{-19}$
Neutron	1.67493×10^{-24}	0

How to right symbols of elements

- The following table shows the names and symbols of some of the more common elements.



Element	Symbol	Element	Symbol	Element	Symbol
Aluminum	Al	Gold	Au	Platinum	Pt
Antimony	Sb	Helium	He	Plutonium	Pu
Argon	Ar	Hydrogen	H	Potassium	K
Arsenic	As	Iodine	I	Radium	Ra
Barium	Ba	Iron	Fe	Silicon	Si
Bismuth	Bi	Lead	Pb	Silver	Ag
Boron	B	Lithium	Li	Sodium	Na
Bromine	Br	Magnesium	Mg	Strontium	Sr
Cadmium	Cd	Manganese	Mn	Sulfur	S
Calcium	Ca	Mercury	Hg	Tin	Sn
Carbon	C	Neon	Ne	Titanium	Ti
Chlorine	Cl	Nickel	Ni	Tungsten	W
Chromium	Cr	Nitrogen	N	Uranium	U
Cobalt	Co	Oxygen	O	Xenon	Xe
Copper	Cu	Palladium	Pd	Zinc	Zn
Fluorine	F	Phosphorus	P		

- Chemists use symbols of one or two letters to represent the elements.
- The first letter of a symbol is *always* capitalized, but any following letters are not.
- For example, Co is the symbol for the element cobalt, whereas CO is the formula for the carbon monoxide molecule.
- The symbols of some elements are derived from their Latin names, for example,
  Au from *aurum* (gold)
  Fe from *ferrum* (iron)
  Na from *natrium* (sodium).
- Most of the symbols come from their English names.

Atomic number, mass number and isotopes

- The ***atomic number (Z)*** is *the number of protons in the nucleus of each atom of an element.*
- In a neutral atom the number of protons is equal to the number of electrons, so the atomic number also indicates the number of electrons present in the atom.
- The chemical identity of an atom can be determined solely from its atomic number.
- For example,
  The atomic number of fluorine = 9
  This means that each fluorine atom has 9 protons and 9 electrons.

Or, viewed another way,
Every atom in the universe that contains 9 protons is correctly named "fluorine."

- The ***mass number (A)*** is *the total number of neutrons and protons present in the nucleus of an atom of an element.* Except for the most common form of hydrogen, which has one proton and no neutrons, all atomic nuclei contain both protons and neutrons. In general, the mass number is given by

$$\begin{aligned} \text{mass number} &= \text{number of protons} + \text{number of neutrons} \\ &= \text{atomic number} + \text{number of neutrons} \end{aligned}$$

- The number of neutrons in an atom is equal to the difference between the mass number and the atomic number, or

number of neutrons = (*A* – *Z*)

- For example, if the mass number **(*A*)** of a particular boron atom is 12 and the atomic number **(*Z*)** is 5 (indicating 5 protons in the nucleus), then the number of neutrons is 7.

- ***Isotopes*** are *atoms that have the same atomic number but different mass numbers.*
- Atoms of a given element do not all have the same mass.
- Most elements have two or more ***isotopes***.
- For example, there are three isotopes of hydrogen:
  - ✓ first, simply known as hydrogen, has one proton and no neutrons.
  - ✓ *deuterium* isotope contains one proton and one neutron
  - ✓ *tritium* has one proton and two neutrons.

- The accepted way to denote the atomic number (Z) and the mass number (A) of an atom of an element (X) is as follows:

$$\begin{matrix} mass\ number \rightarrow \\ atomic\ number \rightarrow \end{matrix} {}^{A}_{Z}\mathrm{X}$$

- Thus, for the isotopes of hydrogen, we write

$^{1}_{1}\mathrm{H}$	$^{2}_{1}\mathrm{H}$	$^{3}_{1}\mathrm{H}$
hydrogen	deuterium	tritium

- As another example, consider two common isotopes of uranium with mass numbers of 235 and 238, respectively:

$$^{235}_{92}\mathrm{U} \qquad ^{238}_{92}\mathrm{U}$$

The first isotope is used in nuclear reactors and atomic bombs, whereas the second isotope lacks the properties necessary for these applications.

- With the exception of hydrogen, which has different names for each of its isotopes, isotopes of elements are identified by their mass numbers. Thus, the preceding two isotopes are called uranium-235 and uranium-238.
- The chemical properties of an element are determined primarily by the protons and electrons in its atoms; neutrons do not take part in chemical changes under normal conditions. Therefore, isotopes of the same element have similar chemistries, forming the same types of compounds and displaying similar reactivities.
- Example 2.1 shows how to calculate the number of protons, neutrons, and electrons using atomic numbers and mass numbers.

EXAMPLE 2.1

Give the number of protons, neutrons, and electrons in each of the following species:

(a) $^{20}_{11}\mathrm{Na}$

(b) $^{22}_{11}\mathrm{Na}$

(c).$^{17}_{8}\mathrm{O}$

(d) $^{14}_{6}\mathrm{C}$

Solution

(a) number of protons = atomic number = 11
number of neutrons = mass number – number of protons
number of neutrons = 20 – 11 = 9

(b) number of electrons = number of protons = 11
number of protons = atomic number = 11
number of neutrons = mass number – number of protons
number of neutrons = 22 – 11 = 11

(c) number of protons = atomic number = 8
number of electrons = number of protons = 8
number of neutrons = mass number – number of protons
number of neutrons = 17 – 8 = 9

(d) number of protons = atomic number = 6
number of electrons = number of protons = 6
number of neutrons = mass number – number of protons
number of neutrons = 14 – 6 = 8

Practice Exercise

How many protons, neutrons, and electrons are in the following isotope of copper: $^{63}_{29}\mathrm{Cu}$?

Atomic mass

The mass of an atom

- The mass of an atom depends on the number of electrons, protons, and neutrons it contains.
- Knowledge of an atom's mass is important in laboratory work. But atoms are extremely small particles—even the smallest speck of dust that our unaided eyes can detect contains as many as 1×10^{16} atoms!

$$1 \times 10^{16} = 1 \times 10\ 000\ 000\ 000\ 000\ 000$$

- Clearly, we cannot weigh a single atom, but it is possible to determine the mass of one atom *relative* to another experimentally.
- The first step is to assign a value to the mass of one atom of a given element so that it can be used as a standard.
- By international agreement, ***atomic mass*** (sometimes called *atomic weight*) is *the mass of the atom in atomic mass units (amu).*
- One ***atomic mass unit*** is defined as *a mass exactly equal to one-twelfth the mass of one carbon-12 atom.*
- Carbon-12 is the carbon isotope that has six protons and six neutrons.
- Setting the atomic mass of carbon-12 at 12 amu provides the standard for measuring the atomic mass of the other elements.
- For example,
  experiments have shown that, on average, a hydrogen atom is only 8.400 percent as massive as the carbon-12 atom. Thus, if the mass of one carbon-12 atom is exactly 12 amu, the atomic mass of hydrogen must be 0.084×12.00 amu or 1.008 amu.
- Similar calculations show that the atomic mass of oxygen is 16.00 amu and that of iron is 55.85 amu.
- Thus, although we do not know just how much an average iron atom's mass is, we know that it is approximately 56 times as massive as a hydrogen atom.

The average atomic mass

- When you look up the atomic mass of carbon in a table of elements, you will find that its value is not 12.00 amu but 12.01 amu.
- The reason for the difference is that most naturally occurring elements (including carbon) have more than one isotope.
- This means that when we measure the atomic mass of an element, we must generally settle for the *average* mass of the naturally occurring mixture of isotopes.

Average atomic mass = $\sum$percent of isotope × atomic mass of isotope

- For example, carbon:
  98.90% is carbon-12 (The atomic mass of carbon-12 = 12.00000 amu)
  1.10% is carbon-13 (The atomic mass of carbon-13 = 13.00335 amu)
  The atomic mass of carbon-12 and carbon-13 has are 12.00000 amu 13.00335.

$$\begin{aligned}\text{Average atomic mass of natural carbon} &= (0.9890) \times (12.00000\ \text{amu}) \\ &\quad + (0.0110) \times (13.00335\ \text{amu}) \\ &= 12.01\ \text{amu}\end{aligned}$$

- It is important to understand that when we say that the atomic mass of carbon is 12.01 amu, we are referring to the *average* value.
- If carbon atoms could be examined individually, we would find either an atom of atomic mass 12.00000 amu or one of 13.00335 amu, but never one of 12.01 amu.
- Example 2.2 shows how to calculate the average atomic mass of an element.

EXAMPLE 2.2

The atomic masses of its two stable isotopes, ${}^{63}_{29}\text{Cu}$ (69.09%) and ${}^{65}_{29}\text{Cu}$ (30.91%), are 62.93 amu and 64.9278 amu, respectively. Calculate the average atomic mass of copper. The relative abundances are given in parentheses.

Solution

Average atomic mass = $\sum$percent of isotope × atomic mass of isotope
Average atomic mass = (0.6909) × (62.93 amu) + (0.3091) × (64.9278 amu)
Average atomic mass = 63.55 amu

Practice Exercise

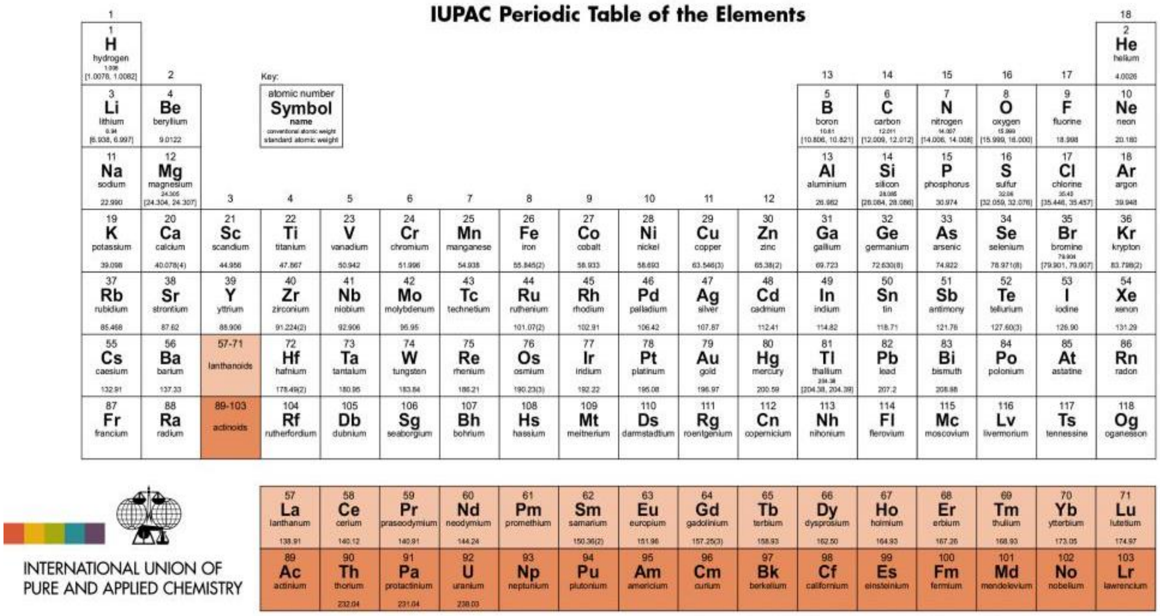
The atomic masses of the two stable isotopes of boron, ${}^{10}_{5}\text{B}$ (19.78%) and ${}^{11}_{5}\text{B}$ (80.22%), are 10.0129 amu and 11.0093 amu, respectively. Calculate the average atomic mass of boron.

- We normally use atomic masses accurate only to four significant figures.
- For simplicity, we will omit the word "average" when we discuss the atomic masses of the elements.

The periodic table

- More than half of the elements known today were discovered between 1800 and 1900.

- Chemists noted that many elements show strong similarities to one another.
- The ***periodic table*** *is a chart in which elements having similar chemical and physical properties are grouped together*.
- The periodic table is a handy tool that correlates the properties of the elements in a systematic way and helps us to make predictions about chemical behavior.
- Figure below shows the modern periodic table in which the elements are arranged by atomic number shown above the element symbol.



IUPAC Periodic Table of the Elements

Key:

atomic number
Symbol
name
conventional atomic weight
standard atomic weight

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 **H** hydrogen 1.008 [1.0078, 1.0082]																	2 **He** helium 4.0026
3 **Li** lithium 6.94 [6.938, 6.997]	4 **Be** beryllium 9.0122											5 **B** boron 10.81 [10.806, 10.821]	6 **C** carbon 12.011 [12.009, 12.012]	7 **N** nitrogen 14.007 [14.006, 14.008]	8 **O** oxygen 15.999 [15.999, 16.000]	9 **F** fluorine 18.998	10 **Ne** neon 20.180
11 **Na** sodium 22.990	12 **Mg** magnesium 24.305 [24.304, 24.307]											13 **Al** aluminium 26.982	14 **Si** silicon 28.085 [28.084, 28.086]	15 **P** phosphorus 30.974	16 **S** sulfur 32.06 [32.059, 32.076]	17 **Cl** chlorine 35.45 [35.446, 35.457]	18 **Ar** argon 39.948
19 **K** potassium 39.098	20 **Ca** calcium 40.078(4)	21 **Sc** scandium 44.956	22 **Ti** titanium 47.867	23 **V** vanadium 50.942	24 **Cr** chromium 51.996	25 **Mn** manganese 54.938	26 **Fe** iron 55.845(2)	27 **Co** cobalt 58.933	28 **Ni** nickel 58.693	29 **Cu** copper 63.546(3)	30 **Zn** zinc 65.38(2)	31 **Ga** gallium 69.723	32 **Ge** germanium 72.630(8)	33 **As** arsenic 74.922	34 **Se** selenium 78.971(8)	35 **Br** bromine 79.904 [79.901, 79.907]	36 **Kr** krypton 83.798(2)
37 **Rb** rubidium 85.468	38 **Sr** strontium 87.62	39 **Y** yttrium 88.906	40 **Zr** zirconium 91.224(2)	41 **Nb** niobium 92.906	42 **Mo** molybdenum 95.95	43 **Tc** technetium	44 **Ru** ruthenium 101.07(2)	45 **Rh** rhodium 102.91	46 **Pd** palladium 106.42	47 **Ag** silver 107.87	48 **Cd** cadmium 112.41	49 **In** indium 114.82	50 **Sn** tin 118.71	51 **Sb** antimony 121.76	52 **Te** tellurium 127.60(3)	53 **I** iodine 126.90	54 **Xe** xenon 131.29
55 **Cs** caesium 132.91	56 **Ba** barium 137.33	57-71 lanthanoids	72 **Hf** hafnium 178.49(2)	73 **Ta** tantalum 180.95	74 **W** tungsten 183.84	75 **Re** rhenium 186.21	76 **Os** osmium 190.23(3)	77 **Ir** iridium 192.22	78 **Pt** platinum 195.08	79 **Au** gold 196.97	80 **Hg** mercury 200.59	81 **Tl** thallium 204.38 [204.38, 204.39]	82 **Pb** lead 207.2	83 **Bi** bismuth 208.98	84 **Po** polonium	85 **At** astatine	86 **Rn** radon
87 **Fr** francium	88 **Ra** radium	89-103 actinoids	104 **Rf** rutherfordium	105 **Db** dubnium	106 **Sg** seaborgium	107 **Bh** bohrium	108 **Hs** hassium	109 **Mt** meitnerium	110 **Ds** darmstadtium	111 **Rg** roentgenium	112 **Cn** copernicium	113 **Nh** nihonium	114 **Fl** flerovium	115 **Mc** moscovium	116 **Lv** livermorium	117 **Ts** tennessine	118 **Og** oganesson

57 **La** lanthanum 138.91	58 **Ce** cerium 140.12	59 **Pr** praseodymium 140.91	60 **Nd** neodymium 144.24	61 **Pm** promethium	62 **Sm** samarium 150.36(2)	63 **Eu** europium 151.96	64 **Gd** gadolinium 157.25(3)	65 **Tb** terbium 158.93	66 **Dy** dysprosium 162.50	67 **Ho** holmium 164.93	68 **Er** erbium 167.26	69 **Tm** thulium 168.93	70 **Yb** ytterbium 173.05	71 **Lu** lutetium 174.97
89 **Ac** actinium	90 **Th** thorium 232.04	91 **Pa** protactinium 231.04	92 **U** uranium 238.03	93 **Np** neptunium	94 **Pu** plutonium	95 **Am** americium	96 **Cm** curium	97 **Bk** berkelium	98 **Cf** californium	99 **Es** einsteinium	100 **Fm** fermium	101 **Md** mendelevium	102 **No** nobelium	103 **Lr** lawrencium

INTERNATIONAL UNION OF
PURE AND APPLIED CHEMISTRY

- *Horizontal rows* of elements are called ***periods***.
- *Vertical columns* of elements are called ***groups***, according to similarities in their chemical properties.
- The elements can be divided into three categories:
  - ✓ Metals, nonmetals, and metalloids.
  - ✓ A ***metal*** is *a good conductor of heat and electricity*.
  - ✓ A **nonmetal** is usually *a poor conductor of heat and* electricity.
  - ✓ A ***metalloid*** *has properties that are intermediate between those of metals and nonmetals*
  - ✓ The majority of known elements are metals; only 17 elements are nonmetals, and 8 elements are metalloids.
  - ✓ From left to right across any period, the physical and chemical properties of the elements change gradually from metallic to nonmetallic.

- ✓ Elements are often referred to collectively by their periodic table group number (Group 1, Group 2, and so on to group 18).
- ✓ However, for convenience, some element groups have been given special names:
  - ➢ ***Alkali metals** are the elements of group 1 (Li, Na, K, Rb, Cs, and Fr).*
  - ➢ ***Alkaline earth metals** are the elements of group 2 (Be, Mg, Ca, Sr, Ba, and Ra).*
  - ➢ ***Halogens** are the elements of group 17 (F, Cl, Br, I, and At).*
  - ➢ ***noble gases**, or **rare gases** are the elements of group 18 (He, Ne, Ar, Kr, Xe, and Rn).*

Molecules and ions

- Of all the elements, only the seven noble gases in group 18 of the periodic table (He, Ne, Ar, Kr, Xe, Rn, and Og) exist as single atoms.
- For this reason, they are called ***monatomic*** (meaning a single atom) gases.
- Most matter is composed of molecules or ions formed by atoms.

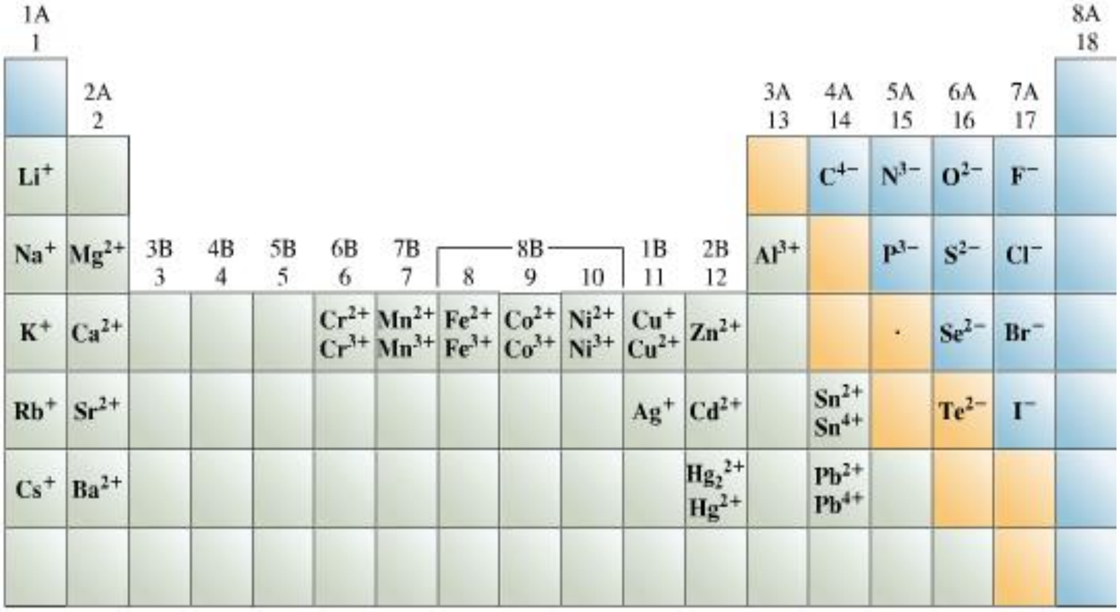
Molecules

- A ***molecule*** is an *aggregate of at least two atoms in a definite arrangement held together by chemical forces* (also called *chemical bonds*).
- A molecule may contain atoms of the same element or atoms of two or more elements joined in a fixed ratio.
- Thus, a molecule is not necessarily a compound, which, by definition, is made up of two or more elements. Hydrogen gas, for example, is a **pure element**, but it consists of molecules made up of two H atoms each.
- Water, on the other hand, is a **molecular compound** that contains hydrogen and oxygen in a ratio of two H atoms and one O atom.
- Like atoms, molecules are electrically neutral.
- The hydrogen molecule, symbolized as H_2, is called a ***diatomic molecule*** because it *contains only two atoms*.
- Other elements that normally exist as ***diatomic molecules*** are nitrogen (N_2) and oxygen (O_2), as well as the group 17 elements, fluorine (F_2), chlorine (Cl_2), bromine (Br_2), and iodine (I_2).
- Of course, a diatomic molecule can contain atoms of different elements. Examples are hydrogen chloride (HCl) and carbon monoxide (CO).
- The vast majority of molecules contain more than two atoms:
  - ✓ They can be atoms of the same element, as in ozone (O_3), which is made up of three atoms of oxygen.
  - ✓ They can be combinations of two or more different elements.

✓ *Molecules containing more than two atoms* are called ***polyatomic molecules***. Examples of ***polyatomic molecules*** are ozone (O_3), water (H_2O) and ammonia (NH_3).

Ions

- An ***ion*** is *an atom or a group of atoms that has a net positive or negative charge.*
- The following figure shows the charges of many monatomic ions.



- The number of positively charged protons in the nucleus of an atom remains the same during ordinary chemical changes (called chemical reactions), but negatively charged electrons may be lost or gained.
- The loss of one or more electrons from a neutral atom results in a ***cation,*** *an ion with a net positive charge.* For example, a sodium atom (Na) can readily lose an electron to become a sodium cation, which is represented by Na^+:

Na Atom	**Na^+ Ion**
11 protons	11 protons
11 electronsons	10 electronsons

- On the other hand, an ***anion*** is *an ion whose net charge is negative* due to an increase in the number of electrons. A chlorine atom (Cl), for instance, can gain an electron to become the chloride ion Cl^-:

Cl Atom	**Cl^- Ion**
17 rotons	17 protons
17 electronsons	18 electronsons

- Sodium chloride (NaCl), ordinary table salt, is called an ***ionic compound*** because it is *formed from cations and anions.*
- An atom can lose or gain more than one electron. Examples are Mg^{2+}, Fe^{3+}, S^{2-}, and N^{3-}.
- These ions, as well as Na^+ and Cl^-, are called ***monatomic ions*** because they *contain only one atom.*
- With very few exceptions, metals form cations and nonmetals form anions.
- In addition, two or more atoms can combine to form an ion that has a net positive or net negative charge.
- ***Polyatomic ions*** such as OH^- (hydroxide ion), CN^- (cyanide ion), and NH_4^+ (ammonium ion) are *ions containing more than one atom.*

Naming Compounds

- When chemistry was a young science and the number of known compounds was small, it was possible to memorize their names.
- Today the number of known compounds is well over 20 million.
- Chemists have devised a clear system for naming chemical substances.
- To begin our discussion of chemical *nomenclature,* the naming of chemical compounds, we must first distinguish between ***inorganic*** and ***organic*** compounds.
- ***Organic compounds*** *contain carbon, usually in combination with elements such as hydrogen, oxygen, nitrogen, and sulfur*.
- All other compounds are classified as ***inorganic compounds***.
- For convenience, some carbon-containing compounds, such as carbon monoxide (CO), carbon dioxide (CO_2), carbon disulfide (CS_2), compounds containing the cyanide group (CN^-), and carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-) groups are considered to be ***inorganic compounds***.
- To organize and simplify our venture into naming compounds, we can divide inorganic compounds into four categories:
  - ✓ ionic compounds,
  - ✓ molecular compounds,
  - ✓ acids and bases,
  - ✓ hydrates.

First: Ionic compounds

- Ionic compounds are made up of cations (positive ions) and anions (negative ions).

- With the important exception of the ammonium ion, NH_4^+, all cations of interest to us are derived from metal atoms.
- Metal cations take their names from the elements.
- The following table shows some of the metal cations:

Element		Name of cation	
Na	sodium	Na^+	sodium ion or cation
K	potassium	K^+	potassium ion or cation
Mg	magnesium	Mg^{2+}	magnesium ion or cation ion
Al	aluminum	Al^{3+}	aluminum ion or cation

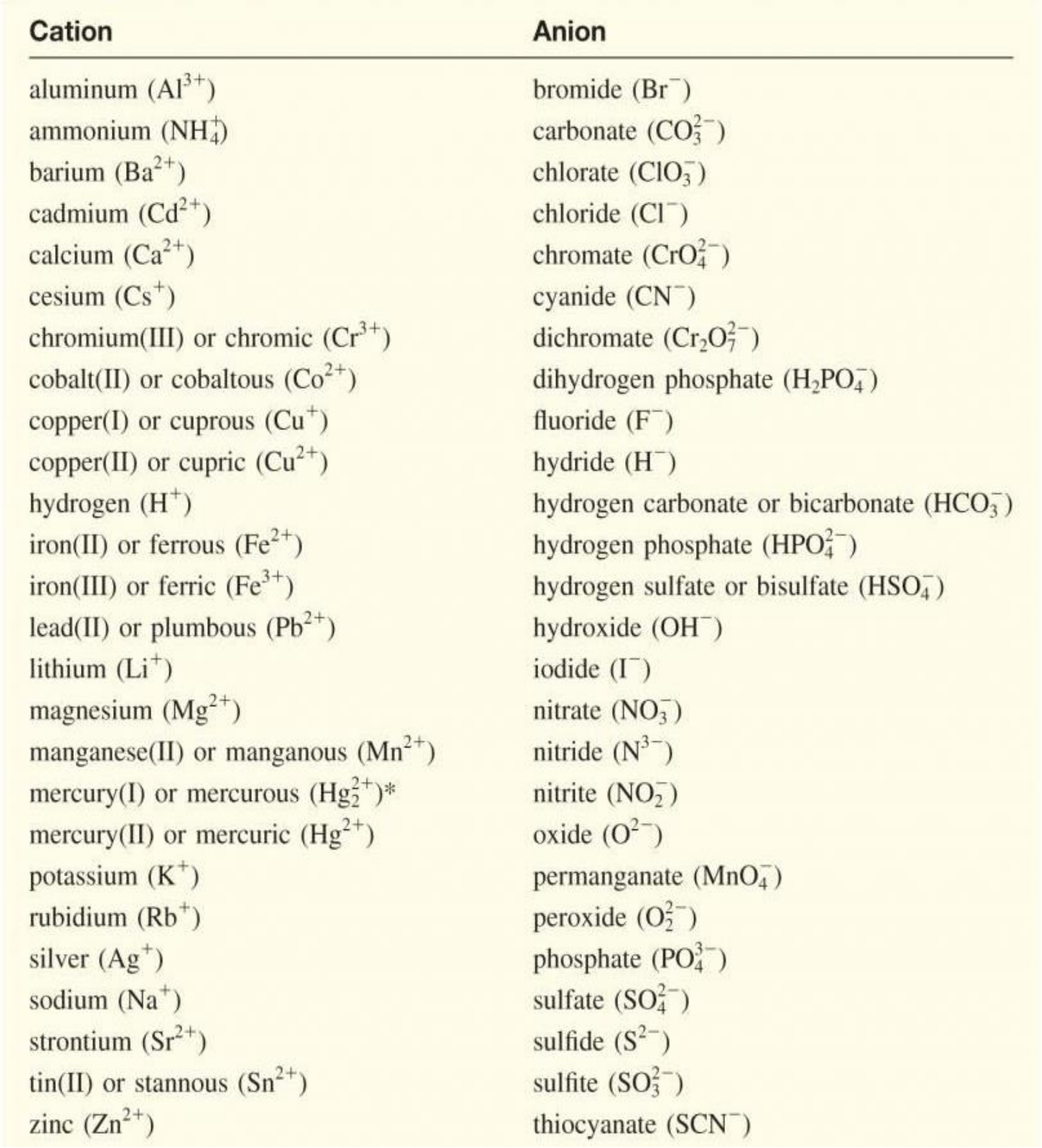
- Many ionic compounds are ***binary compounds,*** or *compounds formed from just two elements*.
- For binary compounds, the first element named is the metal cation followed by the nonmetallic anion.
  - ✓ Thus, NaCl is sodium chloride. The anion is named by taking the first part of the element name (chlorine) and adding "-ide."
  - ✓ Potassium bromide (KBr), zinc iodide (ZnI_2), and aluminum oxide (Al_2O_3) are also binary compounds.
- The following table shows the "-ide" nomenclature of some common monatomic anions according to their positions in the periodic table:

Group 14	Group 15	Group 16	Group 17
C carbide (C^{4-})	N nitride (N^{3-})	O oxide (O^{2-})	F fluoride (F^-)
Si silicide (Si^{4-})	P phosphide (P^{3-})	S sulfide (S^{2-})	Cl chloride (Cl^-)
		Se selenide (Se^{2-})	Br bromide (F^-)
		Te telluride (Te^{2-})	I iodide (I^-)

- The "-ide" ending is also used for certain anion groups containing different elements, such as hydroxide (OH^-) and cyanide (CN^-).
- Thus, the compounds LiOH and KCN are named lithium hydroxide and potassium cyanide, respectively.
- These and a number of other such ionic substances are called ***ternary compounds,*** meaning *compounds consisting of* ***three*** *elements.*
- Certain metals, especially the *transition metals,* can form more than one type of cation.
- Iron can form two cations: Fe^{3+} and Fe^{2+}.
- The old nomenclature system assigns "-ic" and "-ous":

- ✓ the ending “-ic” to the cation with more positive charges:
  Fe^{3+} ferric ion as in ferric chloride, $FeCl_3$.
- ✓ the ending “-ous” to the cation with fewer positive charges
  Fe^{2+}ferrous ion as in ferrous chloride, $FeCl_2$.

- The following table shows names and formulas of some inorganic cations and anions.



Cation	Anion
aluminum (Al^{3+})	bromide (Br^-)
ammonium (NH_4^+)	carbonate (CO_3^{2-})
barium (Ba^{2+})	chlorate (ClO_3^-)
cadmium (Cd^{2+})	chloride (Cl^-)
calcium (Ca^{2+})	chromate (CrO_4^{2-})
cesium (Cs^+)	cyanide (CN^-)
chromium(III) or chromic (Cr^{3+})	dichromate ($Cr_2O_7^{2-}$)
cobalt(II) or cobaltous (Co^{2+})	dihydrogen phosphate ($H_2PO_4^-$)
copper(I) or cuprous (Cu^+)	fluoride (F^-)
copper(II) or cupric (Cu^{2+})	hydride (H^-)
hydrogen (H^+)	hydrogen carbonate or bicarbonate (HCO_3^-)
iron(II) or ferrous (Fe^{2+})	hydrogen phosphate (HPO_4^{2-})
iron(III) or ferric (Fe^{3+})	hydrogen sulfate or bisulfate (HSO_4^-)
lead(II) or plumbous (Pb^{2+})	hydroxide (OH^-)
lithium (Li^+)	iodide (I^-)
magnesium (Mg^{2+})	nitrate (NO_3^-)
manganese(II) or manganous (Mn^{2+})	nitride (N^{3-})
mercury(I) or mercurous (Hg_2^{2+})*	nitrite (NO_2^-)
mercury(II) or mercuric (Hg^{2+})	oxide (O^{2-})
potassium (K^+)	permanganate (MnO_4^-)
rubidium (Rb^+)	peroxide (O_2^{2-})
silver (Ag^+)	phosphate (PO_4^{3-})
sodium (Na^+)	sulfate (SO_4^{2-})
strontium (Sr^{2+})	sulfide (S^{2-})
tin(II) or stannous (Sn^{2+})	sulfite (SO_3^{2-})
zinc (Zn^{2+})	thiocyanate (SCN^-)

- The new nomenclature system done by the German chemist Stock, assigns the Roman numeral:

  (I) means 1 positive charge (II) means 2 positive charges
  (III) means three positive charges (IV) means 4 positive charges
  and so on.

  For example, $FeCl_3$ and $FeCl_2$ are named iron(III) chloride and iron(II) chloride respectively.

  For example, manganese (Mn) atoms can assume several different positive charges:

  Mn^{2+}: MnO manganese(II) oxide, pronounced "manganese-two oxide,"
  Mn^{3+}: Mn_2O_3 manganese(III) oxide, pronounced "manganese-three oxide,"
  Mn^{4+}: MnO_2 manganese(IV) oxide, pronounced "manganese-four oxide,"
- Examples 2.3 and 2.4 illustrate how to name ionic compounds and write formulas for ionic compounds based on the information given in Figures and Tables.

EXAMPLE 2.3

Name the following compounds:

(a) $Cu(NO_3)_2$
(b) KH_2PO_4
(c) NH_4ClO_3

Solution

(a) The nitrate ion (NO_3^-) bears one negative charge, so the copper ion must have two positive charges. Because copper forms both Cu^+ and Cu^{2+} ions, we need to use the Stock system and call the compound **copper(II) nitrate**.

(b) The cation is K^+ and the anion is $H_2PO_4^-$ (dihydrogen phosphate). Because potassium only forms one type of ion (K^+), there is no need to use potassium(I) in the name. The compound is **potassium dihydrogen phosphate**.

(c) The cation is NH_4^+ (ammonium ion) and the anion is ClO_3^-. The compound is **ammonium chlorate**.

Practice Exercise

Name the following compounds: (a) PbO and (b) Li_2SO_3.

EXAMPLE 2.4

Write chemical formulas for the following compounds:

(a) mercury(I) nitrite. (b) cesium sulfide. (c) calcium phosphate.

Solution

(a) The Roman numeral mercury ion wit a +1 charge, but mercury(I) ion is diatomic (that is, Hg_2^{2+}) and the nitrite ion is NO_2^-. Therefore, the formula is **$Hg_2(NO_2)_2$**.

(b) Sulfide ion has two negative charges, and cesium ion has one positive charge. Therefore, the formula is **Cs_2S**.

(c) Calcium ion is Ca^{2+}, and phosphate ion is PO_4^{3-}. Therefore,:

$$3 \times (+2) + 2 \times (-3) = 0$$

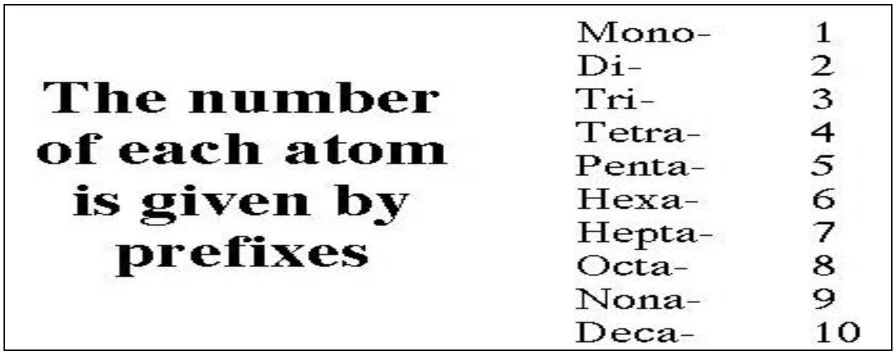
Therefore, the formula is **$Ca_3(PO_4)_2$**.

Practice Exercise

Write formulas for the following ionic compounds: (a) rubidium sulfate and (b) barium hydride.

Second: Molecular compounds

- They are usually composed of nonmetallic elements.
- Many molecular compounds are binary compounds.
- Naming binary ***molecular compounds*** is similar to naming binary ***ionic compounds***.
- We place the name of the first element in the formula first, and the second element is named by adding -ide to the root of the element name. Some examples are
  HCl hydrogen chloride
  HBr hydrogen bromide
  SiC silicon carbide
- In the cases where one pair of elements forms several different compounds (C and O form CO and CO_2) we use of Greek prefixes to denote the number of atoms of each element presents.
- The table below shows these Greek prefixes.

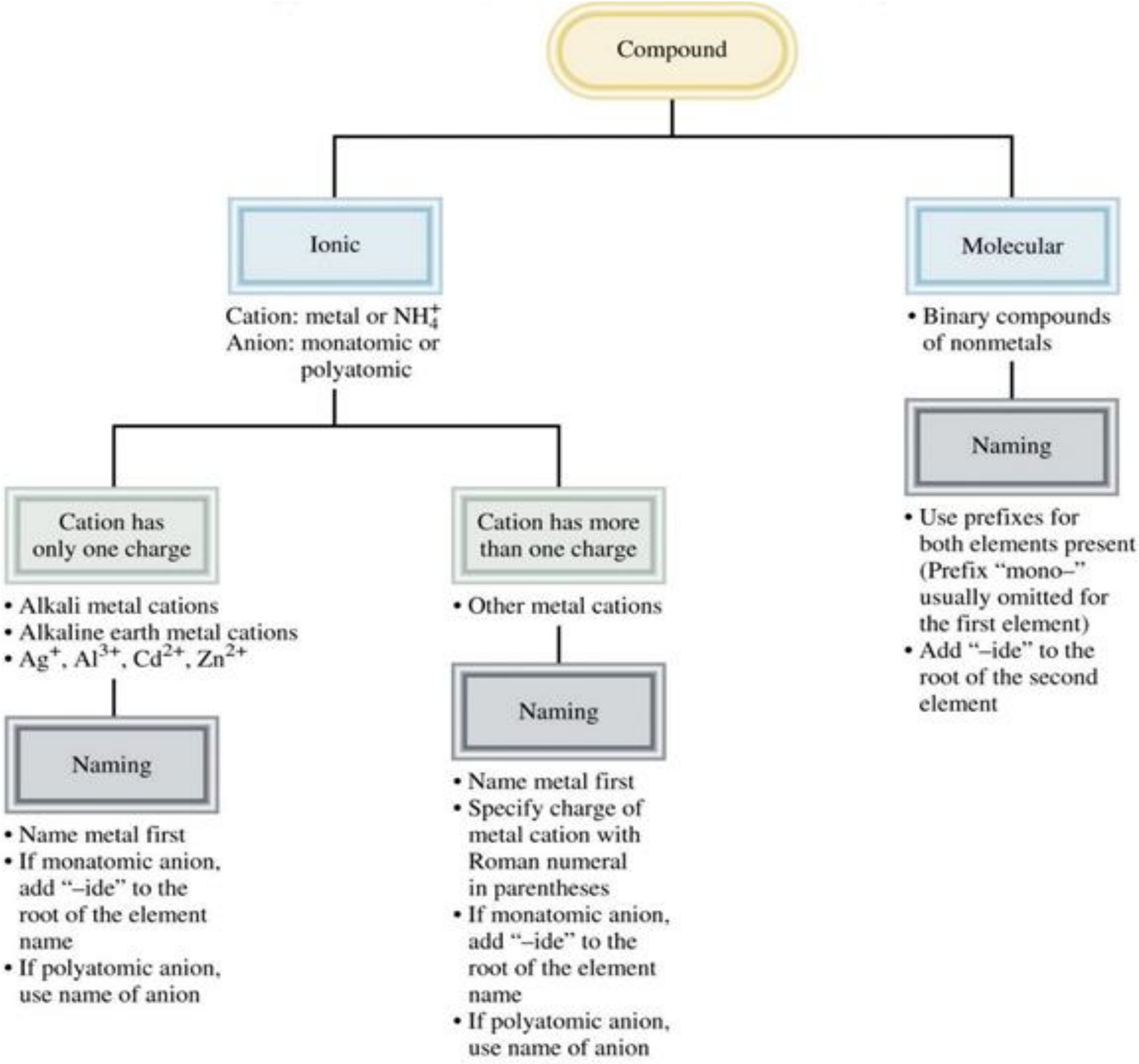


The number of each atom is given by prefixes

Mono-	1
Di-	2
Tri-	3
Tetra-	4
Penta-	5
Hexa-	6
Hepta-	7
Octa-	8
Nona-	9
Deca-	10

- The following are some examples:
  CO carbon monoxide CO_2 carbon dioxide

SO_2 sulfur dioxide
NO_2 nitrogen dioxide
SO_3 sulfur trioxide
N_2O_4 dinitrogen tetroxide



- The following guidelines are helpful in naming compounds with prefixes:
  - ✓ The prefix "mono-" may be omitted for the first element. For example, PCl_3 is named phosphorus trichloride, not monophosphorus trichloride. Thus, the absence of a prefix for the first element usually means there is only one atom of that element present in the molecule.
  - ✓ For oxides, the ending "a" in the prefix is sometimes omitted. For example, N_2O_4 may be called dinitrogen tetroxide rather than dinitrogen tetraoxide.
  - ✓ Exceptions are compounds containing hydrogen. Many of them are called either by their common, nonsystematic names or by names that do not specifically indicate the number of H atoms present:

B_2H_6 diborane	
CH_4 methane	SiH_4 silane
NH_3 ammonia	PH_3 phosphine
H_2O water	H_2S hydrogen sulfide

Even the order of writing the elements is irregular. In water and hydrogen sulfide, H is written first, but it appears last in the others.

- ✓ Writing formulas for molecular compounds is usually straightforward. Thus, the name *arsenic trifluoride* means that there are three F atoms and one As atom in each molecule, and the molecular formula is AsF_3. Note that the order of elements in the formula is the same as in its name.

EXAMPLE 2.5

Name the following molecular compounds:

(a) $SiCl_4$ (b) P_4O_{10}.

Solution

(a) Because there are four chlorine atoms present, the compound is silicon tetrachloride.

(b) There are four phosphorus atoms and ten oxygen atoms present, so the compound is tetraphosphorus decoxide. Note that the “a” is omitted in “deca.”

Practice Exercise

Name the following molecular compounds: (a) NF_3 and (b) Cl_2O_7.

EXAMPLE 2.6

Write chemical formulas for the following molecular compounds:

(a) carbon disulfide (b) disilicon hexabromide.

Solution

(a) Because there are two sulfur atoms and one carbon atom present, the formula is CS_2.

(b) There are two silicon atoms and six bromine atoms present, so the formula is Si_2Br_6.

Practice Exercise

Write chemical formulas for the following molecular compounds: (a) sulfur tetrafluoride and (b) dinitrogen pentoxide.

Third: Acids and bases

Naming Acids

- An ***acid*** can be described as *a substance that yields hydrogen ions (H^+) when dissolved in water.*

- (H^+ is equivalent to one proton, and is often referred to that way.) Formulas for acids contain one or more hydrogen atoms as well as an anionic group.
  - ✓ **Anions whose names end in "-ide"** form acids with a "hydro-" prefix and an "-ic" ending.

    In some cases two different names seem to be assigned to the same chemical formula.

    HCl hydrogen chloride
    HCl hydrochloric acid

    The name assigned to the compound depends on its physical state. In the gaseous or pure liquid state, HCl is a molecular compound called hydrogen chloride. When it is dissolved in water, the molecules break up into H^+ and Cl^- ions; in this state, the substance is called hydrochloric acid.
  - ✓ ***Oxacids*** are acids that *contain hydrogen, oxygen, and another central element.* The formulas of oxoacids are usually written with the H first, followed by the central element and then O. We use the following five common acids as our ***<u>references</u>*** in naming oxoacids:

Reference acids

HNO_3 nitric acid
H_2CO_3 carbonic acid
H_2SO_4 sulfuric acid
H_3PO_4 phosphoric acid
HFO_3 floric acid
$HClO_3$ chloric acid
$HBrO_3$ bromic acid
HIO_3 iodic acid

  - ✓ Often two or more oxoacids have the same central atom but a different number of O atoms. Starting with our reference oxoacids whose names all end with "-ic," we use the following rules to name these compounds.
    1. <u>Addition of one O atom to the "-ic" acid:</u>
       The acid is called "per…….-ic" acid. Thus, adding an O atom to $HClO_3$ changes chloric acid to **perchloric** acid, $HClO_4$.
    2. <u>Removal of one O atom from the "-ic" acid</u>:
       The acid is called "…….-ous" acid. Thus, removing an O atom from $HClO_3$ changes chloric acid to **chlorous** acid $HClO_2$. Other examles are **nitrous** acid, HNO_2, and **phosphorous** acid, H_3PO_3.
    3. <u>Removal of two O atoms from the "-ic" acid:</u>

The acid is called "hypo…….-ous" acid. Thus, removing two O atoms from $HClO_3$ changes chloric acid to **hypochlorous** acid HClO. Other examles are **hyoposulfurous** acid, H_2SO_2, and **hypophosphorous** acid, H_3PO_2.

✓ ***Oxanions,***

anions of oxacids, are named as follows:

1) When all the H ions are removed from the "-ic" acid, the anion's name ends with "-ate." For example, when the two H ions are removed from carbonic acid (H_2CO_3) the anion CO_3^{2-} derived from H_2CO_3 is called carbonate.
2) When all the H ions are removed from the "-ous" acid, the anion's name ends with "-ite." Thus, the anion ClO_2^- derived from chlorous acid ($HClO_2$) is called chlorite.
3) The names of anions in which one or more but not all the hydrogen ions have been removed must indicate the number of H ions present. For example, consider the anions derived from phosphoric acid:

H_3PO_4	phosphoric acid
$H_2PO_4^-$	dihydrogen phosphate
HPO_4^{2-}	hydrogen phosphate
PO_4^{3-}	phosphate

Note that we usually omit the prefix "mono-" when there is only one H in the anion.

4) Below are the names and formulas of the oxacids and oxanions:

Oxacid		Oxanion	
Name	Formula	Name	Formula
Nitric acid	HNO_3	Nitrate ion	NO_3^-
Nitrous acid	HNO_2	Nitrite ion	NO_2^-
Carbonic acid	H_2CO_3	Carbonate ion	CO_3^{2-}
Sulfuric acid	H_2SO_4	Sulfate ion	SO_4^{2-}
Sulfurous acid	H_2SO_3	Sulfuite ion	SO_3^{2-}
Phosphoric acid	H_3PO_4	Phosphate ion	PO_4^{2-}
Phosphorous acid	H_3PO_3	Phosphite ion	HPO_3^{2-}
Perfloric acid	HFO_4	Perflorate ion	FO_4^-
Perchloric acid	$HClO_4$	Perchlorate ion	ClO_4^-
Perbromic acid	$HBrO_4$	Perbromate ion	BrO_4^-

Periodic acid	HIO_4	Periodate ion	IO_4^-
Floric acid	HFO_3	Florate ion	FO_3^-
Chloric acid	$HClO_3$	Chlorate ion	ClO_3^-
Bromic acid	$HBrO_3$	Bromate ion	BrO_3^-
Iodic acid	HIO_3	Iodate ion	IO_3^-
Florous acid	HFO_2	Florite ion	FO_2^-
Chlorous acid	$HClO_2$	Chlorite ion	ClO_2^-
Bromous acid	$HBrO_2$	Bromite ion	BrO_2^-
Iodous acid	HIO_2	Iodite ion	IO_2^-
Hypoflorous acid	HFO	Hypoflorite ion	FO^-
Hypochlorous acid	HClO	Hypochlorite ion	ClO^-
Hypobromous acid	HBrO	Hypobromite ion	BrO^-
Hypoiodous acid	HIO	Hypoiodite ion	IO^-

EXAMPLE 2.7

Name the following oxoacid and oxoanion:

(a) H_3PO_3

(b) IO_4^-

Solution

(a) We start with our reference acid, phosphoric acid (H_3PO_4). Because H_3PO_3 has one fewer O atom, it is called phosphorous acid.

(b) The parent acid is HIO_4. Because the acid has one more O atom than our reference iodic acid (HIO_3), it is called periodic acid. Therefore, the anion derived from HIO_4 is called periodate.

Practice Exercise

Name the following oxoacid and oxoanion: (a) HBrO and (b) HSO_4^-.

Naming bases

1) A ***base*** can be described as *a substance that yields hydroxide ions (OH^-) when dissolved in water*. Some examples are

   NaOH sodium hydroxide
   KOH potassium hydroxide
   $Ba(OH)_2$ barium hydroxide

2) Ammonia (NH_3):
   - ✓ Ammonia is a molecular compound in the gaseous or pure liquid state.
   - ✓ When ammonia dissolves in water, NH_3 reacts partially with water to yield NH_4^+ and OH^- ions.
   - ✓ Thus, it is properly classified as a base.

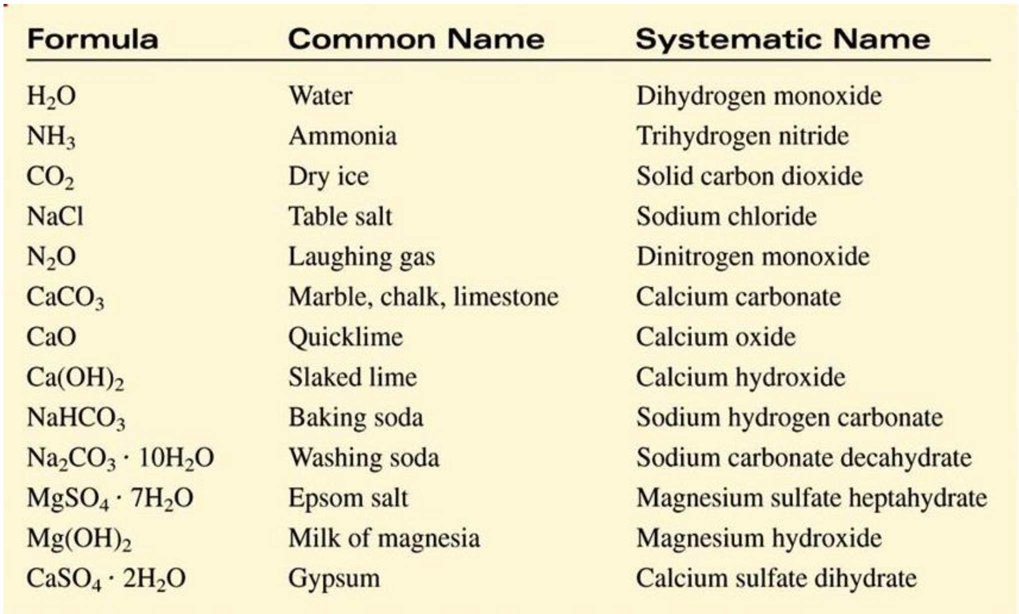
Hydrates

- ***Hydrates*** are *compounds that have a specific number of water molecules attached to* them.
- For example, in its normal state, each unit of copper(II) sulfate has five water molecules associated with it.
- The systematic name for this compound is copper(II) sulfate pentahydrate.
- Its formula is written as $CuSO_4·5H_2O$.
- The water molecules can be driven off by heating.
- When this occurs, the resulting compound is $CuSO_4$, which is sometimes called *anhydrous* copper(II) sulfate.
- "Anhydrous" means that the compound no longer has water molecules associated with it.
- Some other hydrates are

$BaCl_2·2H_2O$ barium chloride dihydrate
$LiCl·H_2O$ lithium chloride monohydrate
$MgSO_4·7H_2O$ magnesium sulfate heptahydrate
$Sr(NO_3)_2·4H_2O$ strontium nitrate tetrahydrate

Familiar inorganic compounds

- Familiar examples are listed in the following table:



Formula	Common Name	Systematic Name
H_2O	Water	Dihydrogen monoxide
NH_3	Ammonia	Trihydrogen nitride
CO_2	Dry ice	Solid carbon dioxide
NaCl	Table salt	Sodium chloride
N_2O	Laughing gas	Dinitrogen monoxide
$CaCO_3$	Marble, chalk, limestone	Calcium carbonate
CaO	Quicklime	Calcium oxide
$Ca(OH)_2$	Slaked lime	Calcium hydroxide
$NaHCO_3$	Baking soda	Sodium hydrogen carbonate
$Na_2CO_3 \cdot 10H_2O$	Washing soda	Sodium carbonate decahydrate
$MgSO_4 \cdot 7H_2O$	Epsom salt	Magnesium sulfate heptahydrate
$Mg(OH)_2$	Milk of magnesia	Magnesium hydroxide
$CaSO_4 \cdot 2H_2O$	Gypsum	Calcium sulfate dihydrate

- Some compounds are better known by their common names than by their systematic chemical names.

SOLUTIONS OF PRACICE EXERCISES

QUESTIONS AND PROBLEMS

1. If the radius of an atom is 10,000 times greater than that of its nucleus, and if an atom was magnified so that the radius of its nucleus became 2.0 cm, what would be the radius of the atom in miles? (1 mi 5 1609 m)
2. Calculate the number of neutrons of ^{239}Pu.
3. For each of the following species, determine the number of protons and the number of neutrons in the nucleus:

   $^{3}_{2}He$, $^{4}_{2}He$, $^{24}_{12}Mg$, $^{25}_{12}Mg$, $^{48}_{22}Ti$, $^{79}_{35}Br$, $^{195}_{78}Pt$
4. Write the appropriate symbol for each of the following isotopes:

   (a) $Z = 74, A = 186$ (b) $Z = 80; A = 201$
5. State two differences between a metal and a nonmetal.
6. Write the names and symbols for four elements in each of the following categories:

   (a) nonmetal. (b) metal. (c) metalloid.
7. Define, with two examples, the following terms:

   (a) alkali metals. (b) alkaline earth metals.

   (c) halogens. (d) noble gases.
8. Describe the changes in properties (from metals to nonmetals or from nonmetals to metals) as we move
   a. down a periodic group.
   b. across the periodic table from left to right.
9. Group the following elements in pairs that you would expect to show similar chemical properties: K, F, P, Na, Cl, and N.
10. What is the difference between an atom and a molecule?
11. Give an example of each of the following:

    (a) a monatomic cation. (b) a monatomic anion.

    (c) a polyatomic cation. (d) a polyatomic anion.
12. Give two examples of each of the following:

    (a) a diatomic molecule containing atoms of the same element.

    (b) a diatomic molecule containing atoms of different elements.

    (c) a polyatomic molecule containing atoms of the same element.

    (d) a polyatomic molecule containing atoms of different elements.
13. Give the number of protons and electrons in each of the following common ions: K^+, Mg^{2+}, Fe^{3+}, Br^-, Mn^{2+}, C^{4-}, Cu^{2+}.
14. Write the formulas for the following ionic compounds:

    (a) copper bromide (containing the Cu^+ ion).

    (b) manganese oxide (containing the Mn^{3+} ion).

    (c) mercury iodide (containing the Hg_2^{2+} ion)/

(d) magnesium phosphate (containing the PO_4^{3-} ion).

15. Which of the following compounds are likely to be ionic? Which are likely to be molecular? CH_4, NaBr, BaF_2, CCl_4, ICl, CsCl, NF_3

16. Name these compounds:

(a) KClO.
(b) Ag_2CO_3.
(c) $FeCl_2$.
(d) $KMnO_4$.
(e) $CsClO_3$.
(f) HIO.
(g) FeO.
(h) Fe_2O_3.
(i) $TiCl_4$.
(j) NaH.
(k) Li_3N.
(l) Na_2O.
m) Na_2O_2.
(n) $FeCl_3{\cdot}_6H_2O$.

17. Write the formulas for the following compounds:

(a) copper(I) cyanide.
(b) strontium chlorite.
(c) perbromic acid.
(d) hydroiodic acid.
(e) disodium ammonium phosphate.
(f) lead(II) carbonate.
(g) tetraphosphorus decasulfide
(h) tin(II) fluoride.
(i) mercury(II) oxide.
(j) mercury(I) iodide.
(k) selenium hexafluoride.

18. Which of the following are elements, which are molecules but not compounds, which are compounds but not molecules, and which are both compounds and molecules?

(a) SO_2.
(b) S_8.
(c) Cs.
(d) N_2O.
(e) O.
(f) O_2.
(g) O_3.
(h) CH_4.
(i) KBr.
(j) S.
(k) P_4.
(l) LiF.

19. Fill the blanks in the following table.

Cation	Anion	Formula	Name
			Magnesium bicarbonate
		$SrCl_2$	
Fe^{3+}	NO^{2-}		
			Manganese(II) chlorate
		$SnBr_4$	
Co^{2+}	PO_4^{3-}		
Hg_2^{2+}	I^-		
		Cu_2CO_3	
			Magnesium bicarbonate
Al^{3+}	S^{2-}		

20. Predict the formula and name of a binary compound formed from the following elements:

(a) Na and H.
(b) B and O.
(c) Al and F.
(d) Sr and Cl.

21. Of the all elements known, only two are liquids at room temperature (25ºC). What are they?
22. List the elements that exist as gases at room temperature.
23. What is wrong with the chemical formula for each of the following compounds:
    (a) $(NH_3)_2CO_3$ (ammonium carbonate).
    (b) CaOH (calcium hydroxide).
    (c) $CdSO_3$ (cadmium sulfide).
    (d) $ZnCrO_4$ (zinc dichromate)?

3. STOICHIOMETRY AND CHEMICAL EQUATIONS

Avogadro's number and the Molar Mass of an Element

- Atomic mass units (amu) provide a relative scale for the masses of the elements.
- Because atoms have such small masses, no usable scale can be devised to weigh them in calibrated units of atomic mass units.
- In any real situation, we deal with macroscopic samples containing enormous numbers of atoms.
- Therefore, it is convenient to have a special unit to describe a very large number of atoms.
- The idea of a unit to denote a particular number of objects is not new. For examples of familiar units are:
  - ✓ the pair = 2 items.
  - ✓ the dozen = 12 items.
  - ✓ And the ***Avogadro's number***.
- ***Avogadro's number (N_A)*** is the number of carbon-12 atoms in 0.012 kg of carbon-12 isotope.
- Chemists measure atoms and molecules in moles.
- The ***mole (mol)*** is *the amount of a substance that contains **Avogadro's number** of its particles (atoms, molecules, ions or any other particles).*
- The actual number of atoms in 12 g of carbon-12 is called ***Avogadro's number*** and its symbol is $\mathbf{N_A}$.
- ***Avogadro's number (*$\mathbf{N_A}$*)*** is determined experimentally.
- The currently accepted value is

  $$N_A = 6.0221415 \times 10^{23}$$

  Generally, we round Avogadro's number to be:

  $$N_A = 6.022 \times 10^{23}$$
- Thus, as one dozen oranges contains 12 oranges, 1 mole of oranges contains 6.022×10^{23} oranges. And as one dozen of hydrogen atoms contains 12 of H atoms, 1 mole of hydrogen atoms contains 6.022×10^{23} H atoms.
- The enormity of Avogadro's number is difficult to imagine.
- For example, spreading 6.022×10^{23} oranges over the entire surface of Earth would produce a layer 9 mi into space!
- Because atoms (and molecules) are so tiny, we need a huge number to study them in manageable quantities.
- We have seen that 1 mole of carbon-12 atoms has a mass of exactly 12 g and contains 6.022×10^{23} atoms.

- This mass (12 g) of carbon-12 is its ***molar mass (*M*)***.
- Molar mass is defined as:

The mass (in grams or kilograms) of one mole of units (such as atoms, molecules or ions) of a substance

- Note that the molar mass of carbon-12 (in grams) is numerically equal to its atomic mass in amu.
- Likewise:
  - ✓ the atomic mass of sodium is 22.99 amu and its molar mass is 22.99 g/mol.
  - ✓ the atomic mass of phosphorus is 30.97 amu and its molar mass is 30.97 g/mol.

  and so on.
- If we know the atomic mass of an element, we also know its molar mass.
- Knowing the molar mass and Avogadro's number, we can calculate the mass of a single atom in grams.
- For example, we know the molar mass of carbon-12 is 12.00 g and there are 6.022×10^{23} carbon-12 atoms in 1 mole of the substance; therefore, the mass of one carbon-12 atom is given by

the mass of one carbon-12 atom $= \dfrac{\mathbf{12.00\ g\ carbon-12\ atoms}}{\mathbf{6.022 \times 10^{23}\ carbon-12\ atoms}} = \mathbf{1.993 \times 10^{-23}\ g}$

- The following equations are so important:

$\mathbf{n = \frac{m}{M}}$	$\mathbf{n = \frac{N}{N_A}}$	$\mathbf{\frac{m}{M} = \frac{N}{N_A}}$

Molar mass of a substance in g/mole units (or kg/mole units) = M
Mass of a substance in g units (or kg units) = m
Number of moles of a substance = n
Number of particles (atoms, molecules or ions, …) of a substance = N
Avogadro's number = N_A
The The following equations are so important:

EXAMPLE 3.1

Helium (He) is a valuable gas used in industry, low-temperature research, deep-sea diving tanks, and balloons. How many moles of He atoms are in 6.46 g of He?

Solution

$$n = \frac{m}{M} = \frac{6.46\ \text{g}}{4.003\ \frac{\text{g}}{\text{mol}}} = 1.61\ \text{mol}$$

Practice Exercise

How many moles of magnesium (Mg) are there in 87.3 g of Mg?

EXAMPLE 3.2

Zinc (Zn) is a silvery metal that is used in making brass (with copper) and in plating iron to prevent corrosion. How many grams of Zn are in 0.356 mole of Zn?

Solution

$$m = n \times M = 0.356 \text{ mole} \times 65.39 \text{ g/mol} = 23.3 \text{ g}$$

Practice Exercise

Calculate the number of grams of lead (Pb) in 12.4 moles of lead.

EXAMPLE 3.3

Sulfur (S) is a nonmetallic element that is present in coal. When coal is burned, sulfur is converted to sulfur dioxide and eventually to sulfuric acid that gives rise to the acid rain phenomenon. How many atoms are in 16.3 g of S?

Solution

$$\frac{m}{M} = \frac{N}{N_A}$$

$$\frac{16.3 \text{ g}}{32.07 \frac{\text{g}}{\text{mol}}} = \frac{N}{6.022 \times 10^{23} \frac{\text{atoms}}{\text{mol}}}$$

$$N = \frac{16.3 \text{ g} \times 6.022 \times 10^{23} \frac{\text{atoms}}{\text{mol}}}{32.07 \frac{\text{g}}{\text{mol}}} = 3.06 \times 10^{23} \text{ atoms}$$

Practice Exercise

Calculate the number of atoms in 0.551 g of potassium (K).

Molecular Mass

- If we know the atomic masses of the component atoms, we can calculate the mass of a molecule.
- The ***molecular mass*** (sometimes called *molecular weight*.) is *the sum of the atomic masses (in amu) in the* molecule.
- For example:
  The molecular mass of H_2O = 2 × (atomic mass of H) + 1 × atomic mass of O
  = 2 × (1.008 amu) + 16.00 amu
  = 18.016 amu
- In general, we need to multiply the atomic mass of each element by the number of atoms of that element present in the molecule and sum over all the elements.

EXAMPLE 3.4

Calculate the molecular masses (in amu) of the following compounds:

(a) Sulfur dioxide (SO_2).

(b) Caffeine ($C_8H_{10}N_4O_2$).

Solution

(a) molecular mass of SO_2 = 1 × 32.07 amu + 2 × 16.00 amu = 64.07 amu

(b) the molecular mass = 8 × 12.01 amu + 10 × 1.008 amu + 4 × 14.01 amu
+ 2 × 16.00 amu = 194.20 amu

Practice Exercise

What is the molecular mass of methanol (CH_4O)?

- From the molecular mass we can determine the molar mass of a molecule or compound. The molar mass of a compound (in grams per mole) is numerically equal to its molecular mass (in amu).
- For example, the molecular mass of water is 18.02 amu, so its molar mass is 18.02 g/mol. Note that 1 mole of water weighs 18.02 g and contains 6.022×10^{23} H_2O *molecules*, just as 1 mole of elemental carbon contains 6.022×10^{23} carbon *atoms*.

EXAMPLE 3.5

Methane (CH_4) is the principal component of natural gas. How many moles of CH_4 are present in 6.07 g of CH_4?

Solution

$$n = \frac{m}{M} = \frac{6.07\ \mathrm{g}}{4 \times 12.01\,\frac{\mathrm{g}}{\mathrm{mol}} + 4 \times 1.008\,\frac{\mathrm{g}}{\mathrm{mol}}} = 0.378\ \mathrm{mol}$$

Practice Exercise

Calculate the number of moles of chloroform ($CHCl_3$) in 198 g of $CHCl_3$.

- The example below shows that a knowledge of the molar mass enables us to calculate the numbers of moles of individual atoms in a given quantity of a compound.

EXAMPLE 3.6

How many hydrogen atoms are present in 25.6 g of urea [$(NH_2)_2CO$], which is used as a fertilizer, in animal feed, and in the manufacture of polymers? The molar mass of urea is 60.06 g/mol.

Solution

$$\frac{m}{M} = \frac{N}{N_A}$$

$$N = \frac{m \times N_A}{M}$$

$$N_{\text{hydrogen atoms}} = 4 \times N_{\text{urea molecules}}$$

$$N_{\text{hydrogen atoms}} = 4 \times \frac{m \times N_A}{M} = 4 \times \frac{25.6\ \text{g} \times 6.022 \times 10^{23}\ \frac{\text{atoms}}{\text{mol}}}{60.06 \frac{\text{g}}{\text{mol}}} = 1.03 \times 10^{24}\ \text{H atoms}$$

Practice Exercise

How many H atoms are in 72.5 g of isopropanol (rubbing alcohol), C_3H_8O?

- Finally, note that for ionic compounds like NaCl and MgO that do not contain discrete molecular units, we use the term ***formula mass*** instead.
- The formula unit of NaCl consists of one Na^+ ion and one Cl^- ion. Thus, the formula mass of NaCl is the mass of one formula unit:

  formula mass of NaCl = 22.99 amu + 35.45 amu = 58.44 amu

  and its molar mass is 58.44 g/mol.

Percent composition of compounds

First: Percent composition if formula is known

If formula is known, percent composition can be obtained mathematically as follows:

- Percent composition is obtained by dividing the mass of each element in 1 mole of the compound by the molar mass of the compound and multiplying by 100 percent.
- Mathematically, the percent composition of an element in a compound is expressed as:

$$\textbf{percent composition of an element} = \frac{\textbf{n} \times \textbf{molar mass of element}}{\textbf{molar mass of compound}} \times \textbf{100}$$

- Where **n** is the number of moles of the element in 1 mole of the compound.
- For example,

  In 1 mole of hydrogen peroxide (H_2O_2) there are 2 moles of H atoms and 2 moles of O atoms.
- The molar masses of H_2O_2, H, and O are 34.02 g/mol, 1.008 g/mol, and 16.00 g/mol, respectively.
- Therefore, the percent composition of H and O in H_2O_2 is calculated as follows:

$$\text{percent composition of H} = \frac{2 \times 1.008 \frac{\text{g}}{\text{mol}}}{34.02 \frac{\text{g}}{\text{mol}}} \times 100 = 5.926\%$$

$$\text{percent composition of O} = \frac{2 \times 16.00\,\frac{\text{g}}{\text{mol}}}{34.02\,\frac{\text{g}}{\text{mol}}} \times 100 = 94.06\%$$

EXAMPLE 3.7

Phosphoric acid (H_3PO_4) is a colorless, syrupy liquid used in detergents, fertilizers, toothpastes, and in carbonated beverages for a "tangy" flavor. Calculate the percent composition of H, P, and O in this compound.

Strategy

The molar mass of H_3PO_4 is 97.99 g/mol. Each mole of H_3PO_4 contains 3 moles of H atoms, 1 mole of P atoms and 4 moles of O atoms.

Solution

$$\text{percent composition of H} = \frac{3 \times 1.008\,\frac{\text{g}}{\text{mol}}}{97.99\,\frac{\text{g}}{\text{mol}}}\,\text{n} \times 100 = 3.086\%$$

$$\text{percent composition of P} = \frac{1 \times 30.97\,\frac{\text{g}}{\text{mol}}}{97.99\,\frac{\text{g}}{\text{mol}}}\,\text{n} \times 100 = 31.61\%$$

$$\text{percent composition of O} = \frac{4 \times 16.00\,\frac{\text{g}}{\text{mol}}}{97.99\,\frac{\text{g}}{\text{mol}}}\,\text{n} \times 100 = 65.31\%$$

Practice Exercise

Calculate the percent composition by mass of each of the elements in sulfuric acid (H_2SO_4).

Second: Percent composition if formula is unknown

If formula is unknown, percent composition can only be obtained by laboratory experiments.

Empirical and molecular formulas

Empirical formulas

- The empirical formula of a compound is the formula which tells us the numerical ratio of the elements in the formula.
- Usually we seek the ratios that consists of the simplest (smallest) whole numbers.
- The procedure to determine the empirical formula is as follows.
  - ✓ First, from experimental analysis, we know the mass (or the mass percent) of each element present in a given mass of a compound.
  - ✓ Second, we convert the masses to number of moles of each element.

- ✓ Finally, using the method given in the following example, we find the empirical formula of the compound.

EXAMPLE 3.8

Ascorbic acid (vitamin C) cures scurvy. It is composed of 40.92 percent carbon (C), 4.58 percent hydrogen (H), and 54.50 percent oxygen (O) by mass. Determine its empirical formula.

Solution

Each 100 g of ascorbic acid, contains 40.92 g of C, 4.58 g of H, and 54.50 g of O. therefore, we can calculate number of moles of each and the ratios:

$$n = \frac{m}{M}$$

$$n_C = \frac{40.92\ g}{12.01\ \frac{g}{mol}} = 3.407\ mol$$

$$n_H = \frac{4.58\ g}{1.008\ \frac{g}{mol}} = 4.54\ mol$$

$$n_O = \frac{54.50\ g}{16.00\ \frac{g}{mol}} = 3.406\ mol$$

$$\begin{array}{ccccc} C & : & H & : & O \\ 3.407 & : & 4.54 & : & 3.406 \end{array}$$

We need to make the ratios reduced to the simplest (smallest) whole numbers. This can be done by dividing all numbers be the smallest:

$$\begin{array}{ccccc} \frac{3.407}{3.406} & : & \frac{4.54}{3.406} & : & \frac{3.406}{3.406} \\ 1 & : & 1.33 & : & 1 \end{array}$$

The result contains one that is not a whole number. But it will be if multiplied by 3. Therefore, we multiply all by three:

$$\begin{array}{cccccc} 3 \times (& 1 & : & 1.33 & : & 1) \\ & 3 & : & 4 & : & 3 \end{array}$$

The result indicates that C, H and O are in the ratio 3:4:3. We obtain that $C_3H_4O_3$ is the simplest (smallest) empirical formula for ascorbic acid.

Practice Exercise

Determine the empirical formula of a compound having the following percent composition by mass: K: 24.75%; Mn: 34.77%; O: 40.51%.

Molecular formulas

- The formula calculated from percent composition by mass is always the empirical formula because the subscripts in the formula are always reduced to the smallest whole numbers.
- Any multiple of the simplest (smallest) empirical formula is by itself an empirical formula but not the simplest (smallest).

- The molecular formula is that empirical formula with actual number of each element in the compound.
- Knowing the empirical formula is not enough to know the molecular formula (the actual formula).
- To know the molecular formula (the actual formula), we must know the ***approximate molar mass*** of the compound in addition to its empirical formula.
- The molar mass of a compound must be the molar mass of the simplest (smallest) empirical formula or an integral multiple of it.
- We can use the molar mass to find the molecular formula, as the following example demonstrates.

EXAMPLE 3.9

A sample of a compound contains 1.52 g of nitrogen (N) and 3.47 g of oxygen (O). The molar mass of this compound is between 90 g and 95 g. Determine the molecular formula and the accurate molar mass of the compound.

Solution

$$n = \frac{m}{M}$$

$$n_N = \frac{1.52\text{ g}}{14.01\frac{g}{mol}} = 0.108\text{ mol}$$

$$n_O = \frac{3.47\text{ g}}{16.00\frac{g}{mol}} = 0.217\text{ mol}$$

$$\begin{array}{ccc} N & : & O \\ 0.108 & : & 0.217 \end{array}$$

Because ratios did end as whole numbers. we need to make the ratios reduced to the simplest (smallest) whole numbers. This can be done by dividing all numbers be the smallest:

$$\begin{array}{ccc} \frac{0.108}{0.108} & : & \frac{0.217}{0.108} \\ 1 & : & 2 \end{array}$$

The result indicates that N and O are in the ratio 1:2 respectively. We obtain that N_2O is the simplest (smallest) empirical formula for compound.

Empirical formula molar mass = 1 × 14.01 + 2 × 16.00 = 46 g/mol

$$\frac{\text{actual molar mass}}{\text{emperical molar mass}} : \frac{90\frac{g}{mol}}{46\frac{g}{mol}} \approx 2$$

The actual molar mass is twice the empirical molar mass. This means that molecular formula is twice NO_2.

The molecular formula is N_2O_4. Therefore,

the accurate molar mass = 2 × 14.01 + 4 × 16.00 = 92.2 g/mol

Practice Exercise

A sample of a compound consisting of boron (B) and hydrogen (H) contains 6.444 g of B and 1.803 g of H. The molar mass of the compound is about 30 g. What is its molecular formula?

Chemical reactions and chemical equations

- *A **chemical reaction** is a process in which a substance (or substances) is changed into one or more new substances.*
- What happens to atoms and molecules in a ***chemical reaction***?
- To communicate with one another about chemical reactions, chemists have devised a standard way to represent them using **chemical equations**.
- A ***chemical equation*** *uses chemical symbols to show what happens during a chemical reaction.*
- How to write chemical equations and balance them?

Writing chemical equations

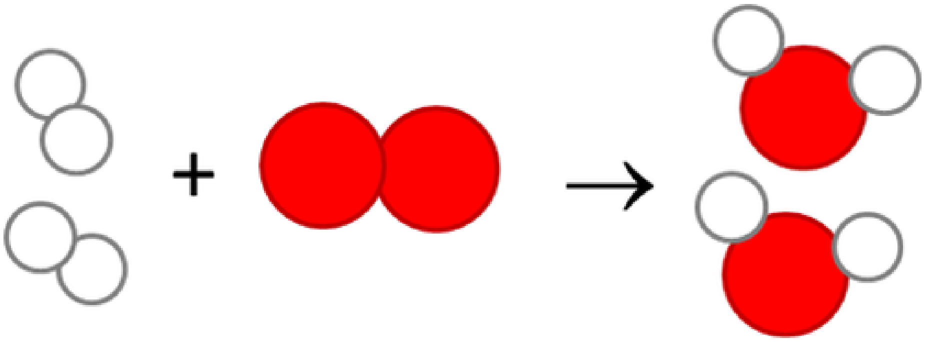
- Consider what happens when hydrogen gas (H_2) burns in air (which contains oxygen, (O_2) to form water (H_2O).
- This reaction can be represented by the chemical equation

$$H_2 + O_2 \rightarrow H_2O$$

- The "plus" sign means "reacts with" and the arrow means "to produce, to give, or to yield."
- Thus, this symbolic expression can be read as follows:
  "Molecular hydrogen reacts with molecular oxygen to produce water."
- The reaction is assumed to proceed from left to right as the arrow indicates.
- If we carefully look at the equation we can notice that it is not complete yet, because there are twice as many oxygen atoms on the left side of the arrow (two) as on its right side (one), and this contradicts the law of conservation of matter.
- To conform with the law of conservation of matter, there must be the same number of each type of atom on both sides of the arrow; that is, we must have as many atoms after the reaction ends as we did before it started.
- We can *balance* the equation by placing the appropriate coefficient (2 in this case) in front of H_2 and H_2O:

$$2H_2 + O_2 \rightarrow 2H_2O$$

- Look at the following figure.



$2H_2$	+	O_2	→	$2H_2O$
Two hydrogen molecules	+	one oxygen molecules	→	Two water molecules

- The figure tells us that this *balanced chemical equation* can be read in three different ways:
    1. "***two hydrogen molecules can combine or react with one oxygen molecule to form two water molecules***."
    2. "***2 moles of hydrogen molecules react with 1 mole of oxygen molecules to produce 2 moles of water molecules***."
       This is because the ratio of the number of molecules is equal to the ratio of the number of moles.
    3. "***4.04 g of*** H_2 ***react with 32.00 g of*** O_2 ***to give 36.04 g of*** H_2O."
       This is because we know the mass of one mole of each of the three substances.
- We refer to H_2 and O_2 as ***reactants,*** which are *the starting materials in a chemical reaction.*
- We refer to H_2O as ***product,*** which is *the substance formed as a result of a chemical reaction*.
- A chemical equation, then, is just the chemist's shorthand description of a reaction.
- In a chemical equation, the reactants are conventionally written on the left and the products on the right of the arrow:

  Reactants → products
- To provide additional information, chemists often indicate the physical states of the reactants and products by using the letters *g*, *l*, and *s* to denote gas, liquid, and solid, respectively.
- For example,

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

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

- To represent what happens when the solid sodium chloride (NaCl) is added to liquid water, we write

$$NaCl(s) \xrightarrow{H_2O} NaCl(aq)$$

where "*aq"* denotes the aqueous environment. ("aqua" means "water"). Writing H_2O above the arrow symbolizes the physical process of dissolving a substance in water, although it is sometimes left out for simplicity.

- Knowing the states of the reactants and products is especially useful in the laboratory.
  - ✓ For example, when potassium bromide (KBr) and silver nitrate ($AgNO_3$) react in an aqueous environment, a solid, silver bromide (AgBr), is formed. This reaction can be represented by the equation:

$$KBr(aq) + AgNO_3(aq) \rightarrow KNO_3(aq) + AgBr(s)$$

  - ✓ If the physical states of reactants and products are not given, an uninformed person might try to bring about the reaction by mixing solid KBr with solid $AgNO_3$.
  - ✓ These solids would react very slowly or not at all.
  - ✓ Imagining the process on the microscopic level, we can understand that for silver bromide to form, the aqueous Ag^+ and Br^- ions would have to come in contact with each other.
  - ✓ However, in the solid KBr and $AgNO_3$ these ions are locked in their positions and have little mobility.

Balancing chemical equations

- Suppose we want to write an equation to describe a chemical reaction that we have just carried out in the laboratory. How should we go about doing it?
- Because we know the identities of the reactants, we can write their chemical formulas.
- The identities of products are more difficult to establish.
- For simple reactions it is often possible to guess the product(s). For more complicated reactions involving three or more products, chemists may need to perform further tests to establish the presence of specific compounds.
- Once we have identified all the reactants and products and have written the correct formulas for them, we assemble them in the conventional sequence, reactants on the left separated by an arrow from products on the right.
- The equation written at this point is likely to be *unbalanced;* that is, the number of each type of atom on one side of the arrow differs from the number on the other side.

- In general, we can balance a chemical equation by the following steps:
  1) Identify all reactants and products and write their correct formulas on the left side and right side of the equation, respectively.
  2) Begin balancing the equation by trying different coefficients to make the number of atoms of each element the same on both sides of the equation.
     - We can change the coefficients (the numbers preceding the formulas) but not the subscripts (the numbers within formulas).
     - Changing the subscripts would change the identity of the substance. For example, $2NO_2$ means "two molecules of nitrogen dioxide," but if we double the subscripts, we have N_2O_4, which is the formula of dinitrogen tetroxide, a completely different compound.
  3) <u>**First**</u>, look for elements that appear only once on each side of the equation with the same number of atoms on each side: The formulas containing these elements must have the same coefficient. Therefore, there is no need to adjust the coefficients of these elements at this point.

     <u>**Next**</u>, look for elements that appear only once on each side of the equation but in unequal numbers of atoms. Balance these elements.

     <u>**Finally**</u>, balance elements that appear in two or more formulas on the same side of the equation.
  4. Check your balanced equation to be sure that you have the same total number of each type of atoms on both sides of the equation arrow.
- Let's consider the following specific example:
  - ✓ In the laboratory, small amounts of oxygen gas can be prepared by heating potassium chlorate ($KClO_3$).
  - ✓ The products are oxygen gas (O_2) and potassium chloride (KCl).
  - ✓ From this information, we write

$$KClO_3 \rightarrow KCl + O_2$$

(For simplicity, we omit the physical states of reactants and products.)

  - ✓ All three elements (K, Cl, and O) appear only once on each side of the equation.
  - ✓ $KClO_3$ and KCl must have the same coefficient because only K and Cl have equal numbers of atoms on both sides.
  - ✓ Because there are three O atoms on the left and two O atoms on the right of the equation, we can balance the O atoms by placing a 2 in front of $KClO_3$ and a 3 in front of O_2.

$$2KClO_3 \rightarrow KCl + 3O_2$$

  - ✓ Finally, we balance the K and Cl atoms by placing a 2 in front of KCl:

$$2KClO_3 \rightarrow 2KCl + 3O_2$$

  - ✓ Note that this equation could also be balanced with coefficients that are multiples of 2(for $KClO_3$), 2(for KCl), and 3(for O 2); for example,

$$4KClO_3 \rightarrow 4KCl + 6O_2$$

- ✓ However, it is common practice to use the *simplest* possible set of whole-number coefficients to balance the equation.

- Let's consider another example:
  - ✓ Now let us consider the combustion (that is, burning) of the natural gas component ethane (C_2H_6) in oxygen, which yields carbon dioxide (CO_2) and water (H_2O).
  - ✓ The unbalanced equation is

$$C_2H_6 + O_2 \rightarrow CO_2 + H_2O$$

  - ✓ We see that the number of atoms is not the same on both sides of the equation for any of the elements (C, H, and O).
    In addition, C and H appear only once on each side of the equation but O appears in two compounds on the right side (CO_2 and H_2O).
  - ✓ To balance the C atoms, we place a 2 in front of CO_2:

$$C_2H_6 + O_2 \rightarrow 2CO_2 + H_2O$$

  - ✓ To balance the H atoms, we place a 3 in front of H_2O:

$$C_2H_6 + O_2 \rightarrow 2CO_2 + 3H_2O$$

  - ✓ At this stage, the C and H atoms are balanced, but the O atoms are not because there are seven O atoms on the right-hand side and only two O atoms on the left-hand side of the equation.
  - ✓ This inequality of O atoms can be eliminated by writing $\frac{7}{2}$ in front of the O_2 on the left-hand side:

$$C_2H_6 + \frac{7}{2}O_2 \rightarrow 2CO_2 + 3H_2O$$

- However, we normally prefer to express the coefficients as whole numbers rather than as fractions. Therefore, we multiply the entire equation by 2 to convert $\frac{7}{2}$ to 7:

$$2C_2H_6 + 7O_2 \rightarrow 4CO_2 + 6H_2O$$

- Note that the coefficients used in balancing the last equation are the smallest possible set of whole numbers.
- The following example is a continuation to practice our equation-balancing skills.

EXAMPLE 3.10

When aluminum metal is exposed to air, a protective layer of aluminum oxide (Al_2O_3) forms on its surface. This layer prevents further reaction between aluminum and oxygen, and it is the reason that aluminum beverage cans do not corrode. [In the case of iron, the rust, or iron(III) oxide that forms is too porous to protect the iron metal underneath, so rusting continues.] Write a balanced equation for the formation of Al_2O_3.

Solution

- The unbalanced equation is:

$$Al + O_2 \rightarrow Al_2O_3$$

- We see that there is one Al atom on the reactants side and there are two Al atoms on the product side. We can balance the Al atoms by placing a coefficient of 2 in front of Al on the reactants side:

$$2Al + O_2 \rightarrow Al_2O_3$$

- There are two O atoms on the reactants side, and three O atoms on the product side of the equation. We can balance the O atoms by placing a coefficient of $\frac{3}{2}$ in front of O_2 on the reactants side:

$$2Al + \frac{3}{2}O_2 \rightarrow Al_2O_3$$

- This is a balanced equation. However, equations are normally balanced with the smallest set of *whole* number coefficients. Multiplying both sides of the equation by 2 gives whole number coefficients:

$$4Al + 3O_2 \rightarrow 2Al_2O_3$$

Practice Exercise

Balance the equation representing the reaction between iron(III)oxide, Fe_2O_3, and carbon monoxide (CO) to yield iron (Fe) and carbon dioxide (CO_2).

Amounts of reactants and products

- "How much product will be formed from a specific amount of a reactant?"

  OR

  "How much reactant must be used to obtain a specific amount of a product?"
- To interpret a reaction quantitatively, we need to apply our knowledge of molar masses and the mole concept.
- ***Stoichiometry*** is *the quantitative study of reactants and products in a chemical reaction.*
- Whether the units given for reactants (or products) are moles, grams, liters (for gases), or some other units, we use moles to calculate the amount of product formed in a reaction.
- This approach is called the ***mole method,*** which means simply that *the stoichiometric coefficients in a chemical equation can be interpreted as the number of moles of each* substance.
- For example, industrially ammonia is synthesized from hydrogen and nitrogen as follows:

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$$

- The stoichiometric coefficients show that one molecule of N_2 reacts with three molecules of H_2 to form two molecules of NH_3.
- The relative numbers of moles are the same as the relative number of molecules:

	$N_2(g)$	+	$3H_2(g)$	→	$2NH_3(g)$
Equation coefficient ⇒	1		3		2
Equation molecules ⇒	1 molecule		3 molecule		2 molecule
Equation moles ⇒	1 mole		3 mol		2 mol

- Thus, this equation can also be read as:
  "1 mole of N_2 combines with 3 moles of H_2 to form 2 moles of NH_3."
- Let's consider a simple example in which 6.0 moles of H_2 react completely with N_2 to form NH_3.
- To calculate the amount of NH_3 produced in moles, we comply with the equation coefficients:

	$N_2(g)$	+	$3H_2(g)$	→	$2NH_3(g)$
Equation moles			3		2
Question moles			6 mol		X

$$X = 6.0\ \text{mol}\ H_2 \times \frac{2\ \text{mol}\ NH_3}{3\ \text{mol}\ H_2} = 4.0\ \text{mol}\ NH_3$$

- Now suppose 16.0 g of H_2 react completely with N_2 to form NH_3. How many grams of NH_3 will be formed?
- To do this calculation, we note that the link between H_2 and NH_3 is the mole ratio from the balanced equation. So, we need to convert grams of H_2 to moles of H_2, then to moles of NH_3, and finally to grams of NH_3:

$$\text{number of moles} = \frac{\text{mass}}{\text{molar mass}}$$

$$n = \frac{m}{M}$$

$$n = \frac{16\ \text{g}}{2.016 \frac{\text{g}}{\text{mol}}} = 7.94\ \text{mol}\ H_2$$

	$N_2(g)$	+	$3H_2(g)$	→	$2NH_3(g)$
Equation moles			3		2
Question moles			7.94 mol		X

$$X = 7.94 \text{ mol } H_2 \times \frac{2 \text{ mol } NH_3}{3 \text{ mol } H_2} = 5.29 \text{ mol } NH_3$$

mass = number of moles × molar mass

$$m = n \times M$$

$$m = 5.29 \text{ mol } NH_3 \times 17.03 \text{ g/mol} = 90.1 \text{ g } NH_3$$

- Similarly, we can calculate the mass in grams of N_2 consumed.
- The general approach for solving stoichiometry problems to calculate the amount of a products from a known amount of a reactant **OR** the amount of a reactant from known amount of a products
  1) Write a balanced equation for the reaction.
  2) Convert the given amount of the substance to number of moles.
  3) Use the mole ratio from the balanced equation to calculate the number of moles of the substance asked for.
  4) Convert the calculated moles to grams of the substance if asked for.

EXAMPLE 3.11

The food we eat is degraded in our bodies to provide energy. The degradation of glucose ($C_6H_{12}O_6$) to carbon dioxide (CO_2) and water (H_2O) is as follows:

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$$

If 856 g of $C_6H_{12}O_6$ is consumed what is the mass of CO_2 produced?

Solution

Number of moles of $C_6H_{12}O_6$

$$n = \frac{m}{M} = \frac{856 \text{ g}}{180.2 \frac{\text{g}}{\text{mol}}} = 4.750 \text{ mol } C_6H_{12}O_6$$

	$C_6H_{12}O_6$	+	$6O_2$	→	$6CO_2$	+	$6H_2O$
Equation moles	1 mole		6 mol		6 mol		6 mol
Question moles	4.750 mol				X		

X = number of moles of CO_2 = 6 ×number of moles of $C_6H_{12}O_6$

number of moles of CO_2 = 6 × 4.750 mol = 28.50 mol CO_2

$m = n \times M = 28.50 \text{ mol} \times 44.01 \text{ g/mol} = 1.25 \times 10^3 \text{ g } CO_2$

Practice Exercise

Methanol (CH_3OH) burns in air according to the equation

$$2CH_3OH + 3O_2 \rightarrow 2CO_2 + 4H_2O$$

If 209 g of methanol are a combusted, what is the mass of H_2O produced?

EXAMPLE 3.12

A typical reaction of alkali metals react with water is that between lithium and water:

$$2Li(s) + 2H_2O(l) \rightarrow 2LiOH(aq) + H_2(g)$$

How many grams of Li are needed to produce 9.89 g of H_2?

Solution

$$\text{Number of moles of } H_2 = \frac{m}{M} = \frac{9.89\ g}{2 \times 1.008\ \frac{g}{mol}} = 5\ mol\ H_2$$

	$2Li$	$+$	$2H_2O$	$\rightarrow$	$2H_2O$	$+$	H_2
Equation moles	2 mole		2 mol		2 mol		1 mol
Question moles	X						5 mol

$$X = \frac{2\ mol\ Li \times 5\ mol\ H_2}{1\ mol\ H_2} = 10\ mol\ Li$$

$$m = n \times M = 10\ mol \times 6.941\ g/mol = 69.41\ g\ Li$$

Practice Exercise

The reaction between nitric oxide (NO) and oxygen to form nitrogen dioxide (NO_2) is a key step in photochemical smog formation:

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$

How many grams of O_2 are needed to produce 2.21 g of NO_2?

Limiting reagents

- When a chemist carries out a reaction, the reactants are usually not present in exact ***stoichiometric amounts,*** that is, *in the proportions indicated by the balanced equation.*
- Because the goal of a reaction is to produce the maximum quantity of a useful compound from the starting materials, frequently a large excess of one reactant is supplied to ensure that the more expensive reactant is completely converted to the desired product.
- Consequently, some reactant will be left over at the end of the reaction.
- *In a reaction, the reactant consumed totally with no left over* is called the ***limiting reagent*** or the ***limiting reactant***.
- It is called so because the maximum amount of product formed is limited by how much of this reactant was originally present. Once this reactant is used up, no more product can be formed.
- *Any reactant present in a quantity greater than necessary to react with the quantity of the limiting reactant i*s called ***excess reagents*** or ***excess reactant***.
- The concept of the limiting reagent is analogous to making sandwiches from slices of chees between pairs of toasts:
  - ✓ If we have ten toasts and seven slices of cheese we can only make five sandwiches.
  - ✓ All the toasts will be consumed. So, they represent the ***limiting reactant***, because the number of sandwiches depended on them.

- ✓ Two cheese slices will be left over. So, they represent the ***excess reactant***, because there are no more toasts for them.

- To determine which reactant is the limiting reactant we follow the steps below for the industrial synthesis of methanol (CH_3OH) from carbon monoxide and hydrogen at high temperatures.
  1) If not given, write the balanced chemical equation of the reaction.
  $$CO(g) + 2H_2(g) \rightarrow CH_3OH(aq)$$
  2) If not given, calculate the number of moles of the initial quantities of the reactants (CO and H_2.)
  Suppose we have 4 moles of CO and 6 moles of H_2
  3) Divide number of moles of each reactant by its coefficient in the chemical equation.
  For CO: $\frac{4}{1} = 4$
  For H_2: $\frac{6}{2} = 3$
  4) The reactant with the least quotient is the limiting reactant, the other is the excess reactant. Therefore, in this reaction H_2 is the limiting reactant, and CO is the excess reactant.
  5) After the limiting reagent has been identified, the rest of the problem can be solved.
  The following example illustrates these steps.

EXAMPLE 3.13

637.2 g of NH_3 are treated with 1142 g of CO_2 to produce urea $(NH_2)_2CO$:

$$2NH_3\,(g) + CO_2(g) \rightarrow (NH_2)_2CO(aq) + H_2O(l)$$

(a) Which of the two reactants is the limiting reagent?

(b) Calculate the mass of $(NH_2)_2CO$ formed.

(c) How much excess reagent (in grams) is left at the end of the reaction?

Solution

a) Number of moles of H_2 and CO_2:

$$n = \frac{m}{M} = \frac{637.2\ g}{17.03\ \frac{g}{mol}} = 37.416\ mol\ NH_3$$

$$n = \frac{m}{M} = \frac{1142\ g}{44.02\ \frac{g}{mol}} = 25.943\ mol\ CO_2$$

	$2NH_3$	+	CO_2	–	$(NH_2)_2CO$	+	H_2O
Equation moles	2 mol		1 mol		1 mol		
Question moles	37.416 mole		25.943 mol		x		
Number of moles	18.708		25.943				

given/coefficient

It is clear from the last row that NH_3 is the limiting reagent.

b)

	$2NH_3$	+	CO_2	$\rightarrow$	$(NH_2)_2CO$	+	H_2O
Equation moles	2 mol		1 mol		1mol		
Question moles	37.416 mole				X		

$$X = \frac{37.416 \text{ mol } NH_3 \times 1 \text{ mol } (NH_2)_2CO}{2 \text{ mol } NH_3} = 18.708 \text{ mol } (NH_2)_2CO$$

$$m = n \times M = 18.708 \text{ mol} \times 60.06 \text{ g/mol} = 1123.6 \text{ g } (NH_2)_2CO$$

c)

	$2NH_3$	+	CO_2	$\rightarrow$	$(NH_2)_2CO$	+	H_2O
Equation moles	2 mol		1 mol				
Question moles	37.416 mole		Y				

$$Y \text{ mol of } CO_2 \text{ reacted} = \frac{37.416 \text{ mol } NH_3 \times 1 \text{ mol } CO_2}{2 \text{ mol } NH_3} = 18.708 \text{ mol } CO_2$$

$$n \text{ mol of } CO_2 \text{ remains} = 25.943 \text{ mol} - 18.708 \text{ mol} = 7.235 \text{ mol}$$

$$m = n \times M = 7.235 \text{ mol} \times 44.02 \text{ g/mol} = 318.5 \text{ g}$$

Practice Exercise

The reaction between aluminum and iron(III) oxide can generate temperatures approaching 3000 °C and is used in welding metals:

$$2Al(g) + Fe_2O_3 \rightarrow Al_2O_3 + 2Fe$$

In one process, 124 g of Al are reacted with 601 g of Fe_2O_3. (a) Calculate the mass (in grams) of Al_2O_3 formed. (b) How much of the excess reagent is left at the end of the reaction?

Reaction yield (Yield percentage)

- The ***theoretical yield*** of the reaction is, *the amount of product that would result if all the limiting reagent reacted*.

  The ***theoretical yield***, is the *maximum* obtainable yield, and cannot be known except by calculations on the balanced equation.

  The amount of limiting reagent present at the start of a reaction determines the ***theoretical yield*** of the reaction
- The ***actual yield*** of the reaction is *the amount of product actually obtained from a reaction*.

  The ***actual yield*** cannot be known by calculations, it can be known only by laboratory experiments.

  The ***actual yield*** is almost always less than the theoretical yield.
- There are many reasons for the difference between actual and theoretical yields.

For instance, many reactions are reversible, and so they do not precede 100 percent from left to right.
Even when a reaction is 100 percent complete, it may be difficult to recover the entire product from the reaction medium (say, from an aqueous solution).
Some reactions are complex in the sense that the products formed may react among themselves or with the reactants to form other products.
These additional reactions will reduce the yield of the first reaction.

- To determine how efficient a given reaction is, chemists often figure the ***percent yield,*** which describes *the proportion of the actual yield to the theoretical yield*.
- It is calculated as follows:

$$\%\textbf{yield} = \frac{\textbf{actual yield}}{\textbf{theoretical yield}} \times \mathbf{100}$$

- The following example shows how to calculate the percent yield of an industrial process.

EXAMPLE 3.14

In an industrial operation 3.54×10^7 g of $TiCl_4$ reacted with 1.13×10^7 g of Mg:

$$TiCl_4(g) + 2Mg(g) \rightarrow Ti(s) + 2MgCl_2(l)$$

(a) Calculate the theoretical yield of Ti in grams.

(b) Calculate the percent yield if 7.91×10^6 g of Ti are actually obtained.

Solution

(a)

First we calculate the number of moles of reactants

$$\text{number of moles of } TiCl_4 = \frac{m}{M} = \frac{3.54 \times 10^7\ g}{189.9\ \frac{g}{mol}} = 1.87 \times 10^5 \text{ mol}$$

$$\text{number of moles of Mg} = \frac{m}{M} = \frac{7.91 \times 10^6\ g}{24.31\ \frac{g}{mol}} = 4.65 \times 10^5 \text{ mol}$$

Second we determine the limiting reactant

	$TiCl_4$	+	$2Mg$	→	Ti	+	$2MgCl_2$
Equation moles	1 mol		2 mol				
Question moles	1.87×10^5		4.65×10^5				
Number of moles given/coefficient	1.87×10^5		2.35×10^5				

It is clear from the last row that $TiCl_4$ is the limiting reagent.

Finally, we calculate the theoretical yield of Ti

	$TiCl_4$	+	$2Mg$	→	Ti	+	$2MgCl_2$
Equation moles	1 mol				1 mol		
Question moles	1.87×10^5 mole				n		

$$\text{Theoretical yield of Ti} = \frac{1.87 \times 10^5 \text{ mol} \times 1 \text{ mol}}{1 \text{ mol}} = 1.87 \times 10^5 \text{ mol}$$

$$m = n \times M = 1.87 \times 10^5 \text{ mol} \times 47.88 \text{ g/mol} = 8.95 \times 10^6 \text{ g}$$

(b)

$$\%\text{yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100$$

$$\%\text{yield} = \frac{7.91 \times 10^6 \text{ g}}{8.95 \times 10^6 \text{ g}} \times 100 = 88.37\%$$

Practice Exercise

Industrially, vanadium metal, which is used in steel alloys, can be obtained by reacting vanadium(V) oxide with calcium at high temperatures:

$$5Ca + V_2O_5 \rightarrow 5CaO + 2V$$

In one process, 1.54×10^3 g of V_2O_5 react with 1.96×10^3 g of Ca. (a) Calculate the theoretical yield of V. (b) Calculate the percent yield if 803 g of V are obtained.

Some kinds of chemical reactions

- **Combination reactions**
  - ✓ In a combination, reactions two or more substances react to form one product. For example, magnesium metal burns brilliantly in air to produce magnesium Oxide:

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

  - ✓ A combination reaction between a metal and a nonmetal produces an ionic solid.
  - ✓ The magnesium loses electrons and forms the magnesium ion, Mg^{2+}. The oxygen gains electrons and forms the oxide ion O^{2-}.
  - ✓ Thus, the reaction product is MgO.
  - ✓ Other examples of combination reactions are:

$$C(s) + O_2(g) \rightarrow CO_2(g)$$
$$N_2(g) + 3H_2 (g) \rightarrow 2NH_3(g)$$
$$CaO(s) + H_2O(L) \rightarrow Ca(OH)_2(s)$$

- **Decomposition reactions**
  - ✓ In a decomposition reaction one substance undergoes a reaction to produce two or more other substances.
  - ✓ Many metal carbonates decompose to form metal oxides and carbon dioxide when heated:

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

- ✓ The decomposition of sodium azide (NaN_3) rapidly releases $N_2(g)$, so this reaction is used to inflate safety air bags in automobiles:

$$2NaN_3(s) \rightarrow 2Na(s) + 3N_2(g)$$

- ✓ The following are more examples of decomposition reaction.

$$2KClO_3(s) \rightarrow 2KCl(s) + 3O_2(g)$$
$$PbCO_3(s) \rightarrow PbO(s) + CO_2\ (g)$$
$$Cu(OH)_2(s) \rightarrow CuO(s) + H_2O(L)$$

- **Combustion reactions**
  - ✓ Combustion reactions are rapid reactions that produce a flame.
  - ✓ Most combustion reactions involve O_2 from air as a reactant.
  - ✓ The most famous combustion reactions are the combustion of $H_2(g)$, C(s), and the compounds containing both H and C:

$$H_2(g) + 0.5O_2(g) \rightarrow H_2O(L)$$
$$C(s) + O_2(g) \rightarrow CO_2(g)$$
$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$$
$$C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(g)$$

Example 3.15

Write a balanced equation for:

a) The combination reaction between lithium metal and fluorine gas.

b) The decomposition reaction that occurs when solid barium carbonate ($BaCO_3$) is heated (two products form, a solid and a gas).

c) The combustion reaction benzene, $C_6H_6(L)$.

Solution

a) $Li(s) + 0.5F_2(g) \rightarrow LiF(s)$ b) $BaCO_3(s) \rightarrow BaO(s) + CO_2(g)$

c) $C_6H_6(g) + 7.5O_2(g) \rightarrow 6CO_2(g) + 3H_2O(g)$

Practice Exercise

Write a balanced equation for:

a) The combination reaction between sodium, carbon and oxygen.

b) The electrical decomposition reaction of water.

c) The combustion reaction ethanol.

SOLUTIONS OF PRACICE EXERCISES

QUESTIONS AND PROBLEMS

Revie questions

1. Define the term “mole.” What does Avogadro’s number represent?
2. What is the molar mass of an atom? What are the commonly used units for molar mass?
3. Use ammonia (NH_3) to explain what is meant by the percent composition by mass of a compound.
4. Describe how the knowledge of the percent composition by mass of an unknown compound can help us identify the compound.
5. In “in empirical formula”, what does the word “empirical” mean?
6. If we know the empirical formula of a compound, what additional information do we need to determine its molecular formula?
7. Use the formation of water from hydrogen and oxygen to explain the following terms: chemical reaction, reactant, product.
8. What is the difference between a chemical reaction and a chemical equation?
9. Why must a chemical equation be balanced? What law is obeyed by a balanced chemical equation? Write the symbols used to represent gas, liquid, solid, and the aqueous phase in chemical equations.
10. Why is the theoretical yield of a reaction determined only by the amount of the limiting reagent?
11. Why is the actual yield of a reaction almost always smaller than the theoretical yield?

Problems

12. How many moles of cobalt (Co) atoms are there in 6.00×10^9 Co atoms?
13. How many grams of gold (Au) are there in 15.3 moles of Au?
14. What is the mass in grams of a single atom of each of the following elements?
    (a) As
    (b) Ni
15. What is the mass in grams of 1.00×10^{12} lead (Pb) atoms?
16. How many atoms are present in 3.14 g of copper (Cu)?
17. Which of the following has a greater mass: 2 atoms of lead or 5.1×102^{23} mole of helium.
18. Calculate the molar mass of the following substances:
    (a) Li_2CO_3
    (b) CS_2
    (c) $CHCl_3$ (chloroform)

(d) $C_6H_8O_6$ (ascorbic acid, or vitamin C)
(e) KNO_3
(f) Mg_3N_2

19. How many molecules of ethane (C_2H_6) are present in 0.334 g of C_2H_6?
20. Urea [$(NH_2)_2CO$] is used for fertilizer and many other things. Calculate the number of N, C, O, and H atoms in 1.68×10^4 g of urea.
21. The density of water is 1.00 g/mL at 4 °C. How many water molecules are present in 2.56 mL of water at this temperature?
22. For many years chloroform ($CHCl_3$) was used as an inhalation anesthetic in spite of the fact that it is also a toxic substance that may cause severe liver, kidney, and heart damage. Calculate the percent composition by mass of this compound.
23. All of the substances listed below are fertilizers that contribute nitrogen to the soil. Which of these is the richest source of nitrogen on a mass percentage basis?
    (a) Urea, $(NH_2)_2CO$
    (b) Ammonium nitrate, NH_4NO_3
    (c) Guanidine, $HNC(NH_2)_2$
    (d) Ammonia, NH_3
24. Peroxyacylnitrate (PAN) is one of the components of smog. It is a compound of C, H, N, and O. Determine the percent composition of oxygen and the empirical formula from the following percent composition by mass: 19.8 percent C, 2.50 percent H, 11.6 percent N. What is its molecular formula given that its molar mass is about 120 g?
25. How many grams of sulfur (S) are needed to react completely with 246 g of mercury (Hg) to form HgS?
26. Calculate the mass in grams of iodine (I_2) that will react completely with 20.4 g of aluminum (Al) to form aluminum iodide (AlI_3).
27. Tin(II) fluoride (SnF_2) is often added to toothpaste as an ingredient to prevent tooth decay. What is the mass of F in grams in 24.6 g of the compound?
28. What are the empirical formulas of the compounds with the following compositions?
    (a) 40.1 percent C, 6.6 percent H, 53.3 percent O
    (b) 18.4 percent C, 21.5 percent N, 60.1 percent K.
29. The empirical formula of a compound is CH. If the molar mass of this compound is about 78 g, what is its molecular formula?
30. Monosodium glutamate (MSG), a food-flavor enhancer, has been blamed for “Chinese restaurant syndrome,” the symptoms of which are headaches and chest pains. MSG has the following composition by mass: 35.51

percent C, 4.77 percent H, 37.85 percent O, 8.29 percent N, and 13.60 percent Na. What is its molecular formula if its molar mass is about 169 g?

31. Balance the following:

(a) $N_2O_5 \rightarrow N_2O_4 + O_2$
(b) $KNO_3 \rightarrow KNO_2 + O_2$
(c) $NH_2NO_2 \rightarrow N_2O + H_2O$
(d) $NH_4NO_2 \rightarrow N_2 + H_2O$
(e) $NaHCO_3 \rightarrow Na_2CO_3 + H_2O +$ CO2
(f) $P_4O_{10} + H_2O \rightarrow H_3PO_4$
(g) $HCl + CaCO_3 \rightarrow CaCl_2 + H_2O +$ CO2
(h) $Al + H_2SO_4 \rightarrow Al_2 + SO_4^{2-} + H_2$
(i) $CO_2 + KOH \rightarrow K_2CO_3 + H_2O$
(j) $CH_4 + O_2 \rightarrow CO_2 + H_2O$
(k) $Be_2C + H_2O \rightarrow Be(OH)_2 + CH_4$
(l) $Cu + HNO_3 \rightarrow Cu(NO_3)_2 + NO + H_2O$
(m) $S + HNO_3 \rightarrow H_2SO_4 + NO_2 + H_2O$
(n) $NH_3 + CuO \rightarrow Cu + N_2 + H_2O$

32. Silicon tetrachloride ($SiCl_4$) can be prepared by heating Si in chlorine gas:

$$Si(s) + 2Cl_2(g) \rightarrow SiCl_4(l)$$

In one reaction, 0.507 mole of $SiCl_4$ is produced. How many moles of molecular chlorine were used in the reaction?

33. When baking soda (sodium bicarbonate or sodium hydrogen carbonate, $NaHCO_3$) is heated, it releases carbon dioxide gas, which is responsible for the rising of cookies, donuts, and bread.

(a) Write a balanced equation for the decomposition of the compound (one of the products is Na_2CO_3).
(b) Calculate the mass of $NaHCO_3$ needed to produce 20.5 g of CO_2.

34. Fermentation is a complex chemical process of wine making in which glucose is converted into ethanol and carbon dioxide:

$$C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2$$

Starting with 500.4 g of glucose, what is the maximum amount of ethanol in grams and in liters that can be obtained by this process?
(Density of ethanol = 0.789 g/mL.)

35. For many years the separation of gold from other materials involved the use of potassium cyanide:

$$4Au + 8KCN + O_2 + 2H_2O \rightarrow 4KAu(CN)_2 + 4KOH$$

What is the minimum amount of KCN in moles needed to extract 29.0 g (about an ounce) of gold?

36. Nitrous oxide (N_2O) is also called “laughing gas.” It can be prepared by the thermal decomposition of ammonium nitrate (NH_4NO_3). The other product is H_2O.
    (a) Write a balanced equation for this reaction.
    (b) How many grams of N_2O are formed if 0.46 mole of NH_4NO_3 is used in the reaction?
37. A common laboratory preparation of oxygen gas is the thermal decomposition of potassium chlorate ($KClO_3$). Assuming complete decomposition, calculate the number of grams of O_2 gas that can be obtained from 46.0 g of $KClO_3$. (The products are KCl and O_2.)
38. The depletion of ozone (O_3) in the stratosphere has been a matter of great concern among scientists in recent years. It is believed that ozone can react with nitric oxide (NO) that is discharged from the high altitude jet plane, the SST. The reaction is

$$O_3 + NO \rightarrow O_2 + NO_2$$

    If 0.740 g of O_3 reacts with 0.670 g of NO, how many grams of NO_2 will be produced? Which compound is the limiting reagent? Calculate the number of moles of the excess reagent remaining at the end of the reaction.
39. Consider the reaction

$$MnO_2 + 4HCl \rightarrow MnCl_2 + Cl_2 + 2H_2O$$

    If 0.86 mole of MnO_2 and 48.2 g of HCl react, which reagent will be used up first? How many grams of Cl_2 will be produced?
40. Nitroglycerin ($C_3H_5N_3O_9$) is a powerful explosive. Its decomposition may be represented by

$$4C_3H_5N_3O_9 \rightarrow 6N_2 + 12CO_2 + 10H_2O + O_2$$

    This reaction generates a large amount of heat and many gaseous products. It is the sudden formation of these gases, together with their rapid expansion, that produces the explosion.
    (a) What is the maximum amount of O_2 in grams that can be obtained from 2.00×10^2 g of nitroglycerin?
    (b) Calculate the percent yield in this reaction if the amount of O_2 generated is found to be 6.55 g.
41. Ethylene (C_2H_4), an important industrial organic chemical, can be prepared by heating hexane (C_6H_{14}) at 8008C:

$$C_6H_{14} \rightarrow C_2H_4 + \text{other products}$$

    If the yield of ethylene production is 42.5 percent, what mass of hexane must be reacted to produce 481 g of ethylene?

42. Disulfide dichloride (S_2Cl_2) is used in the vulcanization of rubber, a process that prevents the slippage of rubber molecules past one another when stretched. It is prepared by heating sulfur in an atmosphere of chlorine:

    $$S_8(l) + 4Cl_2(g) \rightarrow 4S_2Cl_2(l)$$

    What is the theoretical yield of S_2Cl_2 in grams when 4.06 g of S_8 are heated with 6.24 g of Cl_2? If the actual yield of S_2Cl_2 is 6.55 g, what is the percent yield?

43. Give oxidation numbers for the underlined atoms in the following molecules and ions:

    (a) $\underline{\mathrm{Cs}}_2\mathrm{O}$
    (b) $\underline{\mathrm{Ca}}\mathrm{I}_2$
    (c) $\underline{\mathrm{Al}}_2\mathrm{O}_3$
    (d) $\mathrm{H}_3\underline{\mathrm{As}}\mathrm{O}_3$
    (e) $\underline{\mathrm{Ti}}\mathrm{O}_2$
    (f) $\underline{\mathrm{Mo}}\mathrm{O}_4^{2-}$
    (g) $\underline{\mathrm{Pt}}\mathrm{Cl}_4^{2-}$
    (h) $\underline{\mathrm{Pt}}\mathrm{Cl}_6^{2-}$
    (i) $\underline{\mathrm{Sn}}\mathrm{F}_2$
    (j) $\underline{\mathrm{Cl}}\mathrm{F}_3$
    (k) $\underline{\mathrm{S}}\mathrm{bF}_6^-$

44. Classify the following redox reactions:

    (a) $P_4 + 10Cl_2 \rightarrow 4PCl_5$
    (b) $2NO \rightarrow N_2 + O_2$
    (c) $Cl_2 + 2KI \rightarrow 2KCl + I_2$
    (d) $3HNO_2 \rightarrow HNO_3 + H_2O + 2NO$

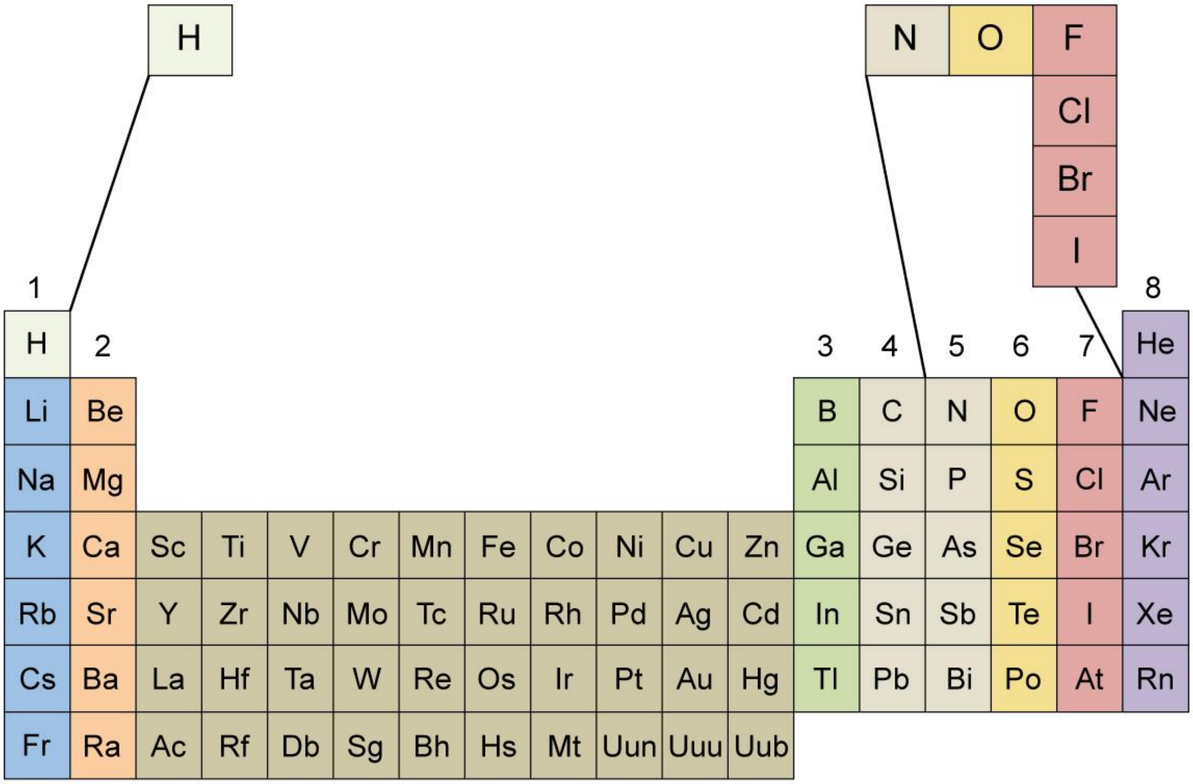
4. GASES

Substances that exist as gases

a. We live at the bottom of an ocean of air whose composition by volume is roughly 78 percent N_2, 21 percent O_2 , and 1 percent other gases, including CO_2.

b. We will focus on the behavior of substances that exist as gases under ***normal atmospheric conditions*** which are defined as ***25 °C and 1 atm (atmosphere)***.

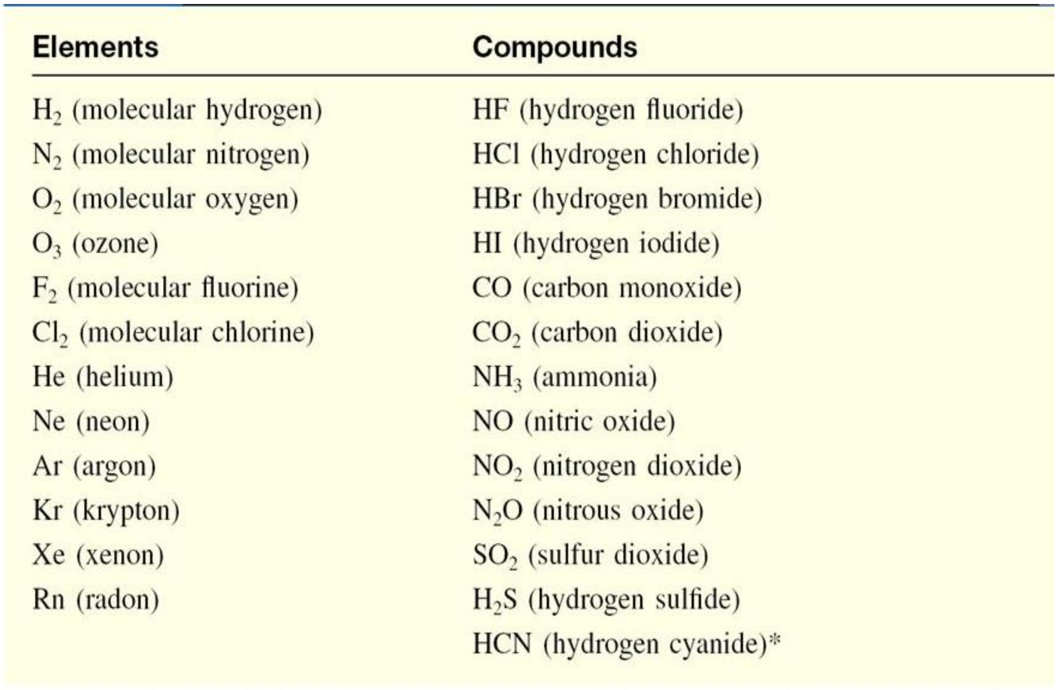
c. The figure below shows the elements that are gases under normal atmospheric conditions.
   - ✓ The periodic table below shows that all the elements in Group 18, the noble gases, are monatomic gases: He, Ne, Ar, Kr, Xe, Rn and Og.
   - ✓ In addition to noble gases, other elements exist as gases. These elements are hydrogen, nitrogen, oxygen, fluorine, and chlorine but they exist as diatomic molecules: H_2, N_2, O_2, F_2, and Cl_2.



   - ✓ Another form of oxygen, ozone (O_3), is also a gas at room temperature.

- Regarding our daily relationship with gases:

- ✓ O_2 is essential for our survival.
- ✓ Hydrogen sulfide (H_2S) and hydrogen cyanide (HCN) are deadly poisons.
- ✓ Several others, such as CO, NO_2, O_3, and SO_2 are somewhat less toxic.
- ✓ The gases He, Ne, and Ar are chemically inert; that is, they do not react with any other substance.
- ✓ Most gases are colorless. Exceptions are F_2, Cl_2, and NO_2.
- ✓ The dark-brown color of NO_2 is sometimes visible in polluted air.



Elements	Compounds
H_2 (molecular hydrogen)	HF (hydrogen fluoride)
N_2 (molecular nitrogen)	HCl (hydrogen chloride)
O_2 (molecular oxygen)	HBr (hydrogen bromide)
O_3 (ozone)	HI (hydrogen iodide)
F_2 (molecular fluorine)	CO (carbon monoxide)
Cl_2 (molecular chlorine)	CO_2 (carbon dioxide)
He (helium)	NH_3 (ammonia)
Ne (neon)	NO (nitric oxide)
Ar (argon)	NO_2 (nitrogen dioxide)
Kr (krypton)	N_2O (nitrous oxide)
Xe (xenon)	SO_2 (sulfur dioxide)
Rn (radon)	H_2S (hydrogen sulfide)
	HCN (hydrogen cyanide)*

*The boiling point of HCN is 26°C, but it is close enough to qualify as a gas at ordinary atmospheric conditions.

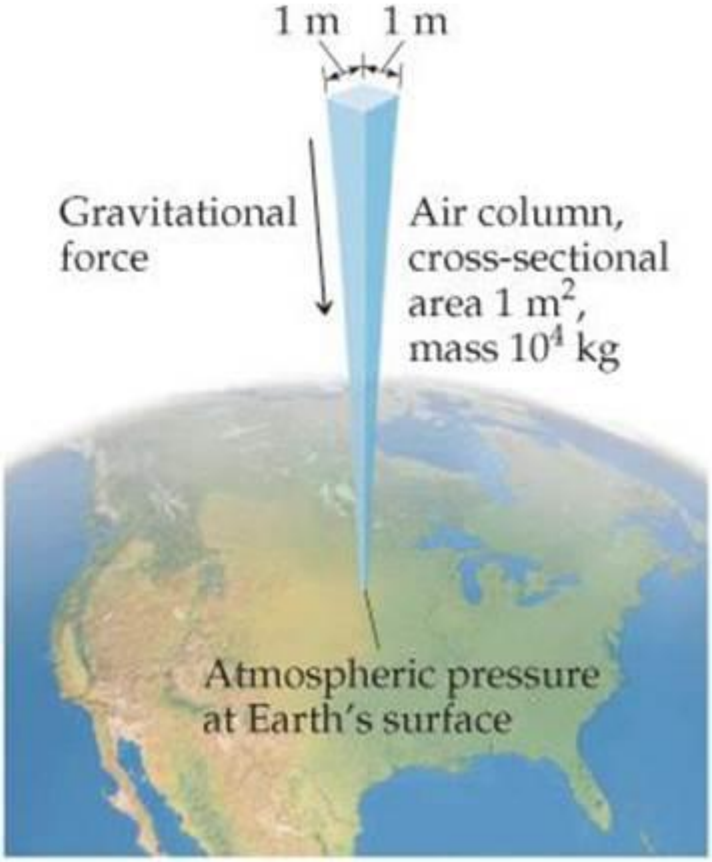
Pressure of a gas and its SI units

- Because gas molecules are constantly in motion, gases exert pressure on any surface with which they come in contact.
- Pressure is defined as the force exerted on unit area. Therefore, the SI unit of pressure is $\frac{\mathrm{N}}{\mathrm{m}^2}$ which is named **Pascal (Pa)**:

$$1\ \mathrm{Pa} = 1\ \mathrm{N/m^2}$$

Atmospheric pressure

- The force experienced by any area exposed to Earth's atmosphere is equal to *the weight of the column of air above it*.
- The figure below explains that ***atmospheric pressure*** is *the pressure exerted by Earth's atmosphere on a unit area of the earth surface*.



- The actual value of atmospheric pressure depends on location, temperature, and weather conditions.
- The magnitude of atmospheric pressure depends on many factors. elevation from sea level, location, weather conditions, and on temperature which is the most important factor affecting pressure.
- The convention is that the value and unit given to atmospheric pressure at sea level and at zero °C is one atmosphere (1 atm).
- In SI units:

$$1 \text{ atm} = 101325 \text{ Pa}$$

- Other non SI units for pressure are common too. The most famous are cmHg and mmHg:

$$1 \text{ atm} = 76 \text{ cmHg} = 760 \text{ mmHg}$$

- Each “mmHg” is called “torr”, after the Italian scientist “Torricelli” who was the first to recognize the pressure of the atmosphere:

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

Standard atmospheric pressure

- Standard atmospheric pressure is its pressure at 0 °C at sea level.

- Standard atmospheric pressure = 101325 Pa = 1 atm = 760 mmHg.

Standard temperature and pressure (STP)

- When studying gases, we encounter the term **Standard Temperature and Pressure** (**STP**).
- STP means that:

Temperature of the gas = 0 °C = 273 K
Pressure of the gas = 1 atm = 101325 Pa

The gas quantity, volume and temperature

In addition to the pressure of the gas there are three other important quantities of the gas, namely quantity, volume and temperature.

- The gas quantity, **n**, is measured by its number of moles.
- The gas volume is measured by the SI unit of volume, m^3.
  Other non SI units for volume are common too. Liter, L, and milliliter, mL, are the most famous:

$$1\ m^3 = 1000\ L$$
$$1\ L = 1000\ mL$$
$$1\ mL = 1\ cm^3$$

- The gas temperature is measured by the SI unit of temperature, Kelvin, K.
  Other non SI units for temperature are common too. Degree Celsius, °C, is the most famous:

$$0\ K = -\ 273\ °C$$

  Conversion from degree Celsius, (t °C) to Kelvin (T K) or vice versa, has already been given on page 6 of chapter one:

$$\text{Temperature in K} = (\text{Temperature in °C} + 273.15\ °C) \times \frac{1\ K}{1\ °C}$$
$$\text{Temperature in °C} = (\text{Temperature in K} + 273.15\ K) \times \frac{1\ °C}{1\ K}$$

The gas laws

__First:__ The ideal gas law

(The relation between n, P, V and T of an ideal gas)

- The mathematical relation between the gas quantity (n), pressure(P), volume (V) and temperature (T) is given by a famous expression called "***the gas law***".
- The gas law is:

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

R is the gas constant.

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

This means that:

$$\frac{P_1 \times V_1}{n_1 \times T_1} = \frac{P_2 \times V_2}{n_2 \times T_2} = \frac{P_3 \times V_3}{n_3 \times T_3} = \ldots$$

- If we have a gas with **n = 1 mole, T = 273 K, P = 1 atm = 101325 Pa it will** occupies a volume (V) that equals 22.4 L = 22.4×10^{-3} m^3.
- We calculate the value of R as follows::

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

1) Using the SI units for P and V:

$$R = \frac{101325 \text{ Pa} \times 22.4 \times 10^{-3} \text{ m}^3}{1 \text{ mol} \times 273 \text{ K}} = 8.314 \text{ Pa} \frac{\text{Pa m}^3}{\text{mol K}}$$

Knowing here that:

Pascal unit × Cubic meter unit = Joule unit

The value of R is as follows:

$$\boxed{\mathbf{R = 8.314 \frac{J}{mol\ K}}}$$

2) Using the non SI units for P and V:

$$R = \frac{1 \text{ atm} \times 22.4 \text{ L}}{1 \text{ mol} \times 273 \text{ K}} = 0.0821 \frac{\text{atm L}}{\text{mol K}}$$

$$\boxed{\mathbf{R = 0.0821 \frac{atm\ L}{mol\ K}}}$$

- The main conclusion here is that **the numerical value of the gas constant, R*, depends on the units the gas pressure and volume*.**

<u>Second:</u> Special cases of the gas law

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

Case (1) The gas law at constant quantity and temperature (<u>Boyle's law</u>)

Boyle studied the relation between the gas pressure and volume when its quantity and temperature are kept constant ($n_1 = n_2$ and $T_1 = T_2$):

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

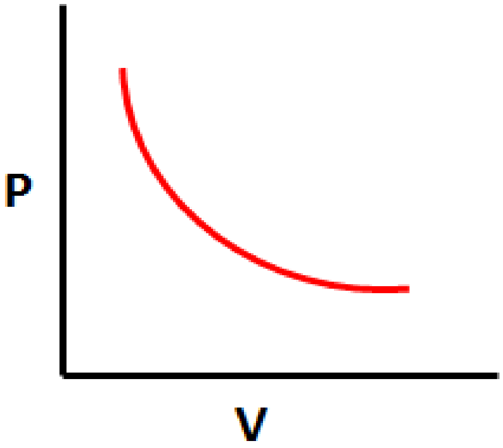
$$P_1 \times V_1 = P_2 \times V_2$$

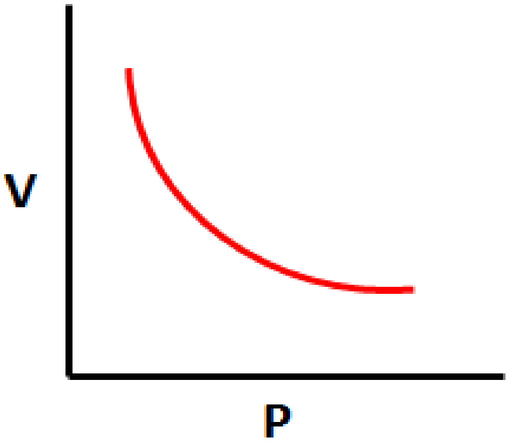
$$P \times V = \text{constant}$$

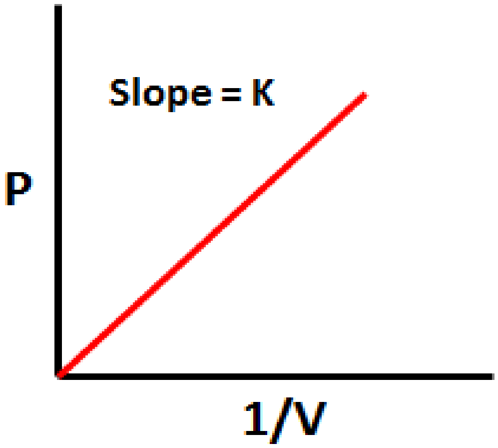
He found that as pressure increases volume decreases:

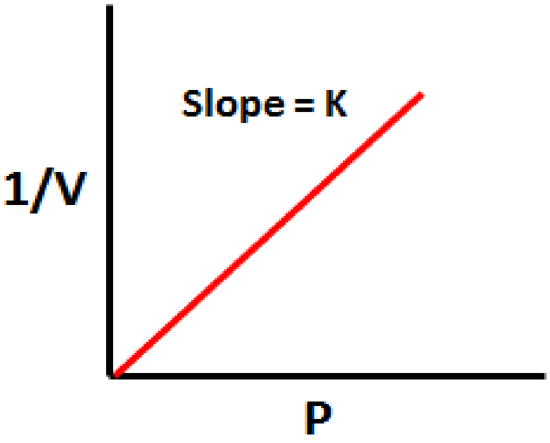
$$P \propto \frac{1}{V}$$

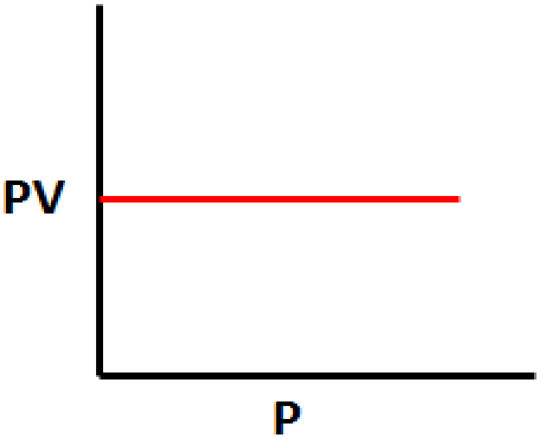
The figures below shows, in different ways, the relationship between the gas P and V at constant n and T.

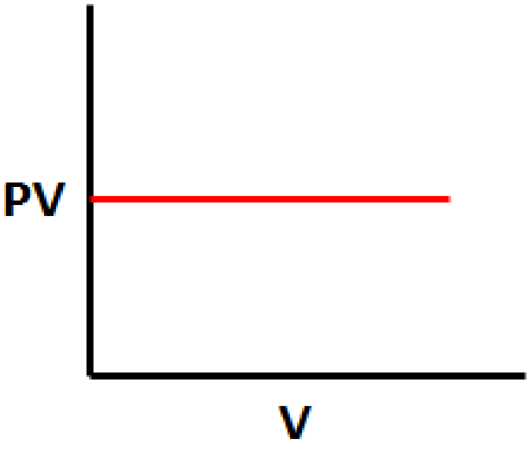












Case (2) The gas law at constant quantity and pressure
(Charles's and Gay Lussac's law)

Charles and Gay Lussac studied the relation between the gas T and V when its n and P are kept constant ($n_1 = n_2$ and $P_1 = P_2$):

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

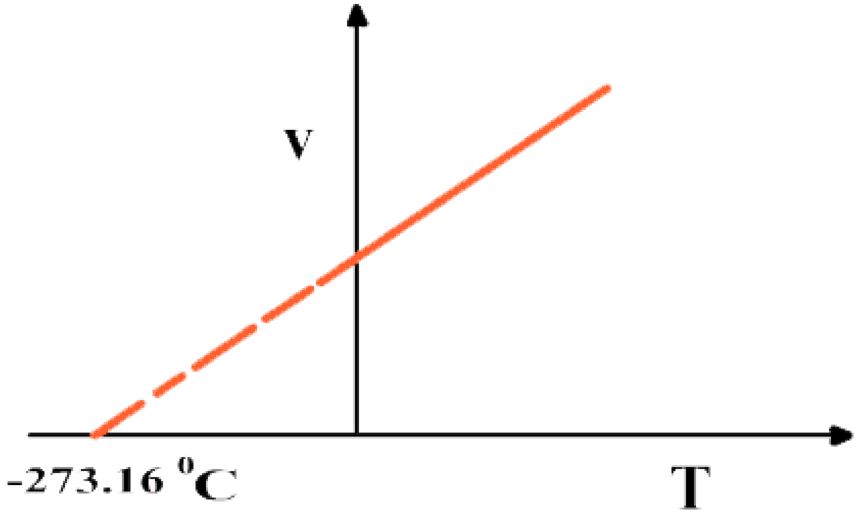
$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$$\frac{V}{T} = \text{constant}$$

They found experimentally that as temperature increases volume increases:

$$V \propto T$$

The figure below shows this relation and that the minimum temperature that can be reached is – 273.16 °C which equals 0 K.



Case (3) The gas law at constant temperature and pressure
(Avogadro's law)

Avogadro studied the relation between the gas n and V when its T and P are kept constant ($T_1 = T_2$ and $P_1 = P_2$):

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

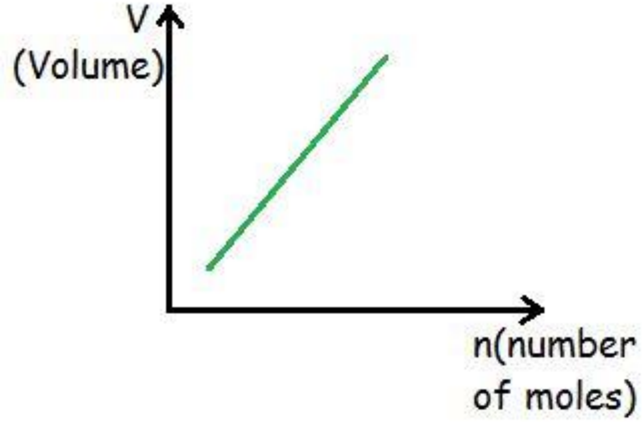
$$\frac{V_1}{n_1} = \frac{V_2}{n_2}$$

$$\frac{V}{n} = \text{constant}$$

He found experimentally that as quantity increases volume increases:

$$V \propto n$$

The figure below shows, the relation between the gas n and V at constant T and P.



Case (4) the gas law at constant quantity

(<u>The cmbined gas law</u>)

Sometimes only n is kept constant. In this case we find:

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

$$\frac{P \times V}{T} = \text{constant}$$

If 1 mole of a gas is at STP its volume is called ***the molar volume at STP*** which equals 22.41 L:

$$V = \frac{n \times R \times T}{P} = \frac{1.0\ \text{mol} \times 0.0821\,\frac{\text{L atm}}{\text{K mol}} \times 273\ \text{K}}{1.0\ \text{atm}} = 22.41\ \text{L}$$

Other cases

$\frac{P_1}{T_1} = \frac{P_2}{T_2}$ (at constant n and V)

$\frac{P_1}{n_1} = \frac{P_2}{n_2}$ (at constant T and V)

$n_1 \times T_1 = n_2 \times T_2$ (at constant P and V)

$\frac{P_1 \times V_1}{n_1} = \frac{P_2 \times V_2}{n_2}$ (at constant T)

$\frac{P_1}{n_1 \times T_1} = \frac{P_2}{n_2 \times T_2}$ (at constant V)

$\frac{V_1}{n_1 \times T_1} = \frac{V_2}{T_2}$ (at constant P)

EXAMPLE 4.1

Sulfur hexafluoride (SF_6) is a colorless, odorless, very unreactive gas. Calculate the pressure (in atm) exerted by 1.82 moles of the gas in a steel vessel of volume 5.43 L at 69.5 °C.

Solution

Because n, V and T are all known, we can use the ideal gas equation to calculate P:

$$P = \frac{n \times R \times T}{V} = \frac{1.82\ \text{mol} \times 0.0821\ \frac{\text{L atm}}{\text{K mol}} \times (69.5\ °\text{C} + 273)\ \text{K}}{5.43\ \text{L}} = 9.42\ \text{atm}$$

Practice Exercise

Calculate the volume (in liters) occupied by 2.12 moles of nitric oxide (NO) at 6.54 atm and 76 °C.

EXAMPLE 4.2

Calculate the volume (in liters) occupied by 7.40 g of NH_3 at STP.

Solution

$$n = \frac{m}{M} = \frac{7.4\ \text{g}}{17.03\ \frac{\text{g}}{\text{mol}}} = 0.435\ \text{mol}$$

$$V = \frac{n \times R \times T}{P} = \frac{0.435\ \text{mol} \times 0.0821\ \frac{\text{L atm}}{\text{K mol}} \times 273\ \text{K}}{1\ \text{atm}} = 9.75\ \text{L}$$

It is also possible to solve the problem using the molar volume atSTP:

Volume of 1 mole at STP ⇒ 22.41

Volume of 0.435 mole at STP ⇒ X

$$X = \frac{0.435\ \text{mol} \times 22.41\ \text{L}}{1\ \text{mol}} = 9.75\ \text{L}$$

Practice Exercise

What is the volume (in liters) occupied by 49.8 g of HCl at STP?

EXAMPLE 4.3

An inflated helium balloon with a volume of 0.55 L at sea level (1.0 atm) is allowed to rise to a height of 6.5 km, where the pressure is about 0.40 atm. Assuming that the temperature remains constant, what is the final volume of the balloon?

Solution

$$P_1 \times V_1 = P_2 \times V_2$$

$$1\ \text{atm} \times 0.55\ \text{L} = 0.4\ \text{atm} \times V_2$$

$$V_2 = 1.4\ \text{L}$$

Practice Exercise

A sample of chlorine gas occupies a volume of 946 mL at a pressure of 726 mmHg. Calculate the pressure of the gas (in mmHg) if the volume is reduced at constant temperature to 154 mL.

EXAMPLE 4.4

Argon is an inert gas used in lightbulbs to retard the vaporization of the tungsten filament. A certain lightbulb containing argon at 1.20 atm and 18 °C is heated to 85 °C at constant volume. Calculate its final pressure.

Solution

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

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

$$\frac{1.2\ \text{atm}}{(18\ °\text{C}\ + 273\ °\text{C}) \times \frac{1\ \text{K}}{1\ °\text{C}}} = \frac{P_2}{(85\ °\text{C}\ +273\ °\text{C}) \times \frac{1\ \text{K}}{1\ °\text{C}}}$$

$$P_2 = 1.48\ \text{atm}$$

Practice Exercise

A sample of oxygen gas initially at 0.97 atm is heated from 21 °C to 268 °C at constant volume. What is its final pressure?

EXAMPLE 4.5

A small bubble rises from the bottom of a lake, where the temperature and pressure are 8 °C and 6.4 atm, to the water's surface, where the temperature is 25 °C and the pressure is 1.0 atm. Calculate the final volume of the bubble if its initial volume was 2.1 mL.

Solution

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

$$\frac{6.4\ \text{atm} \times 2.1\ \text{mL}}{(8\ °\text{C} + 273\ °\text{C}) \times \frac{1\ \text{K}}{1\ °\text{C}}} = \frac{1\ \text{atm} \times V_2}{(25\ °\text{C} + 273\ °\text{C}) \times \frac{1\ \text{K}}{1\ °\text{C}}}$$

$$V_2 = \frac{6.4\ \text{atm} \times 2.1\ \text{L} \times 298\ \text{K}}{281\ \text{K} \times 1\ \text{atm}}$$

$$V_2 = 14.3\ \text{mL}$$

Practice Exercise

A gas initially at 4.0 L, 1.2 atm, and 66 °C undergoes a change so that its final volume and temperature are 1.7 L and 42 °C. What is its final pressure? Assume the number of moles remains unchanged.

Gas density and molar mass calculations

If we rearrange the ideal gas equation, we can calculate the density and the molar mass of a gas, d and M:

$$P \times V = n \times R \times T$$

$$n = \frac{m}{M}$$

$$P \times V = \frac{m}{M} \times R \times T \qquad \text{and} \qquad P \times M = \frac{m}{V} \times R \times T$$

$$P \times M = d \times R \times T$$

Unlike molecules in condensed matter (liquids and solids), gaseous molecules are separated by distances that are large compared with their size. Consequently, the density of gases is very low under atmospheric conditions. For this reason, gas densities are usually expressed in grams per liter (g/L) rather than grams per milliliter (g/mL).

EXAMPLE 4.6

Calculate the density of carbon dioxide (CO_2) in grams per liter (g/L) at 0.990 atm and 55 °C.

Solution

$$P \times M = d \times R \times T$$

$$0.99 \text{ atm} \times 44.1 \text{ g/mol} = d \times 0.0821 \text{ atm L/mol K} \times (55\ °\text{C} + 273) \text{ K}$$

$$d = 1.62 \text{ g/L}$$

Practice Exercise

What is the density (in g/L) of uranium hexafluoride (UF_6) at 779 mmHg and 62 °C?

EXAMPLE 4.7

A chemist has synthesized a greenish-yellow gaseous compound of chlorine and oxygen and finds that its density is 7.71 g/L at 36 °C and 2.88 atm. Calculate the molar mass of the compound.

Solution

To calculate gas molar mass, we need the density, temperature and pressure.

$$P \times M = d \times R \times T$$

$$2.88 \text{ atm} \times M = 7.71 \text{ g/L} \times 0.0821 \text{ atm L/mol K} \times (36\ °\text{C} + 273) \text{ K}$$

$$M = 67.9 \text{ g/mol}$$

Practice Exercise

The density of a gaseous organic compound is 3.38 g/L at 40 °C and 1.97 atm. What is its molar mass?

EXAMPLE 4.8

Chemical analysis of a gaseous compound showed that it contained 33.0 percent silicon (Si) and 67.0 percent fluorine (F) by mass. At 35 °C, 0.210 L of the compound exerted a pressure of 1.70 atm. If the mass of 0.210 L of the compound was 2.38 g, calculate the molecular formula of the compound.

Solution

First, we find the empirical formula and its molar mass

$$\text{Si} : \text{F}$$

$$\frac{33 \text{ g}}{28.09 \frac{\text{g}}{\text{mol}}} : \frac{67 \text{ g}}{19 \frac{\text{g}}{\text{mol}}}$$

$$1.17 \text{ mol} : 3.53 \text{ mol}$$

$$\frac{1.17\ \text{mol}}{1.17\ \text{mol}} : \frac{3.53\ \text{mol}}{1.17\ \text{mol}}$$

$$1 : 3$$

Therefore, the empirical formula is **SiF_3**

Molar mass of the empirical formula SiF_3 = 85.09 g/mol

<u>Second</u>, we find the actual molar mass (molar mass of molecular formula)

$$P \times M = \frac{m}{V} \times R \times T$$

$$1.7\ \text{atm} \times M = \frac{2.38\ \text{g}}{0.21\ \text{L}} \times 0.0821\ \text{atm L/mol K} \times (35\ °\text{C} + 273)\ \text{K}$$

$$M = 169\ \text{g/mol}$$

<u>Third</u>, we divide actual molar mass by the empirical molar mass,

$$\frac{m}{V} = \frac{169\ \frac{g}{mol}}{85.09\ \frac{g}{mol}} = 1.99 = 2$$

The molecular formula = 2 × The empirical formula = 2 × SiF_3 = Si_2F_6

Practice Exercise

A gaseous compound is 78.14 percent boron (B) and 21.86 percent hydrogen (H). At 27 °C, 74.3 mL of the gas exerted a pressure of 1.12 atm. If the mass of the gas was 0.0934 g, what is its molecular formula?

Dalton's law of partial pressures

<u>MOLE FRACTION</u>

Before we discuss this law, we need to know what does the term "*<u>mole fraction</u>*" mean.

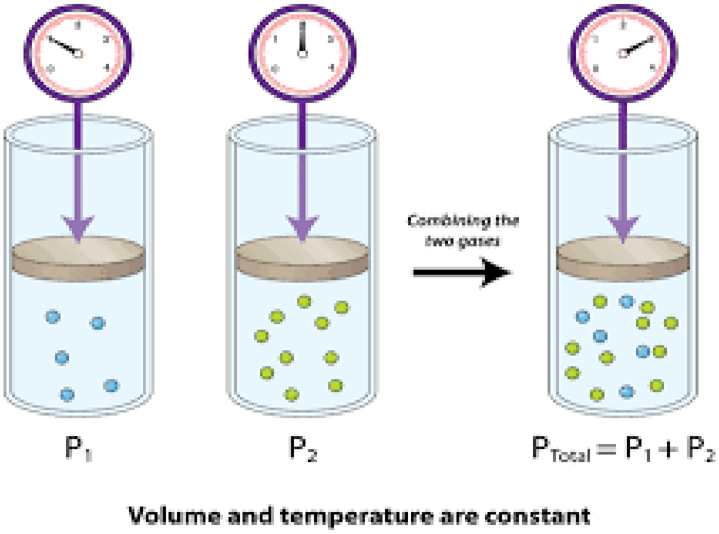
- When more than one substance (for example, two substances "A" and "B") are present together, and we know the number of moles of each "n_A" and "n_B", this means that we know the total number of moles "n_{Total}".
- Now, if we divide n_A or n_B by n_{Total} the quotient will have no unit.
- This quotient represent the mole fraction of each "X_A" and "X_B".
- Therefore, we write:

$$\boxed{\mathbf{X_A} = \frac{\mathbf{n_A}}{\mathbf{n_{Total}}} \text{ and } \mathbf{X_B} = \frac{\mathbf{n_B}}{\mathbf{n_{Total}}}}$$

- In all cases involving mixtures of gases, the total gas pressure is related to ***partial pressures,*** that is, *the pressures of individual gas components in the mixture*.
- In 1801 Dalton formulated a law, now known as ***Dalton's law of partial pressures,*** which states that *the total pressure of a mixture of gases is just*

the sum of the pressures that each gas would exert if it were present alone. The figure below illustrates Dalton's law.

- Consider a case in which two gases, A and B, are in a container of volume V at temperature T as the figure blow shows.
- According to the ideal gas equation, the pressure exerted by gas A and by gas B are:
  - $P_A = n_A \times \frac{RT}{V}$
  - $P_B = n_B \times \frac{RT}{V}$



- Because the two gases are mixed in the same container at the same temperature, the total pressure P_{Total} is:

$$\mathbf{P_{Total} = P_A + P_B}$$

$$P_{Total} = (n_A + n_B) \times \frac{RT}{V}$$

$$P_{Total} = n_{Total} \times \frac{RT}{V}$$

$$\frac{P_A}{P_{Total}} = \frac{n_A}{n_{Total}} \times \frac{RT}{V} = X_A \times \frac{RT}{V}$$

$$\mathbf{P_A = X_A \times P_{Total}}$$

$$\frac{P_B}{P_{Total}} = \frac{n_B}{n_{Total}} \times \frac{RT}{V} = X_B \times \frac{RT}{V}$$

$$\mathbf{P_B = X_B \times P_{Total}}$$

EXAMPLE 4.9

A mixture of 4.46 mol of neon gas, 0.74 mol of argon gas, and 2.15 mol of xenon gas has a total pressure of 2.00 atm. What are the partial pressures of the gases?

Solution

$$\text{Mole fraction of a substance} = \frac{\text{number of moles of the substance}}{\text{number of total moles of all substances}}$$

$$X_{Ne} = \frac{4.46\text{ mol}}{4.46\text{ mol} + 0.74\text{ mol} + 2.15\text{ mol}} = 0.607$$

$$X_{Ar} = \frac{0.74\text{ mol}}{4.46\text{ mol} + 0.74\text{ mol} + 2.15\text{ mol}} = 0.1$$

$$X_{Xe} = \frac{2.15\text{ mol}}{4.46\text{ mol} + 0.74\text{ mol} + 2.15\text{ mol}} = 0.29$$

Pressure of any gas in the mixture = its mole fraction × total pressure

$$P_{Ne} = 0.607 \times 2\text{ atm} = 1.21\text{ atm}$$

$$P_{Ar} = 0.1 \times 2\text{ atm} = 0.2\text{ atm}$$

$$P_{Xe} = 0.29 \times 2\text{ atm} = 0.586\text{ atm}$$

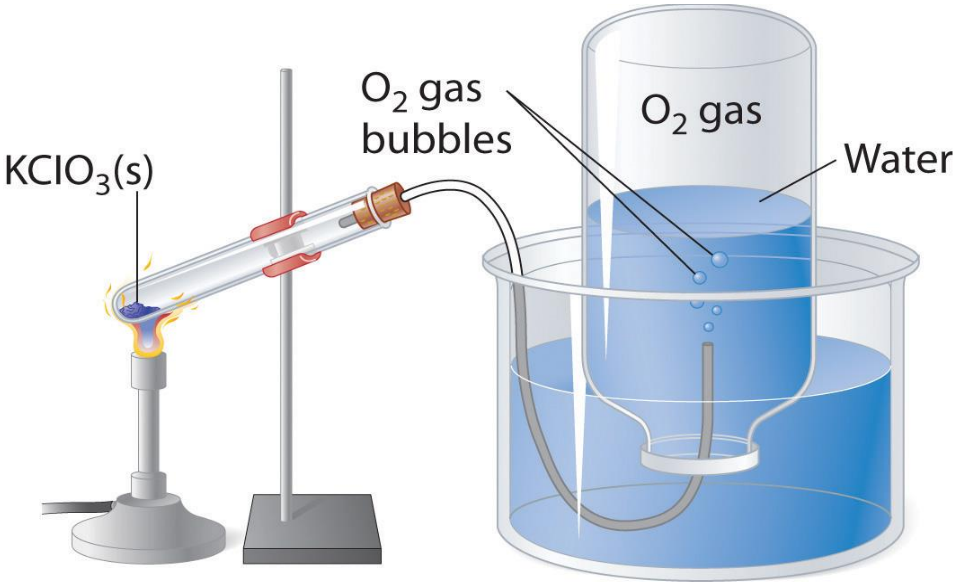
Practice Exercise

A sample of natural gas contains 8.24 moles of methane (CH_4), 0.421 mole of ethane (C_2H_6), and 0.116 mole of propane (C_3H_8). If the total pressure of the gases is 1.37 atm, what are the partial pressures of the gases?

- Collecting a gas over water:
  - ✓ Frequently, chemists need to collect gases over water.
  - ✓ For example, when chemists need $O_2(g)$ in their labs, they heat potassium chlorate ($KClO_3$):

$$2KClO_3(s) \rightarrow 2KCl(s) + 3O_2(g)$$

  - ✓ The produced oxygen is allowed to escape through a hose immersed in water and a flask is flipped over it as shown in the figure below.
  - ✓ Of course, oxygen will not be alone in the space above water surface; water vapor too is occupying this space. (**They become roomates**).



- ✓ The pressure above water is the pressure of both:

$$\mathbf{P_{Total} = P_{oxygen} + P_{water\ vapor}}$$

EXAMPLE 4.10

Oxygen gas generated by the decomposition of potassium chlorate is collected as shown in the previous figure. The volume of oxygen collected at 24°C and atmospheric pressure of 762 mmHg is 128 mL. Calculate the mass (in grams) of potassium chlorate consumed. The pressure of the water vapor at 297 K is 22.4 mmHg.

Solution

$$P_{Total} = P_{oxygen} + P_{water\ vapor}$$

$$762\ mmHg = P_{oxygen} + 22.4\ mmHg$$

$$P_{oxygen} = 762\ mmHg - 22.4\ mmHg = 740\ mmHg$$

$$n = \frac{P \times V}{R \times T} = \frac{740\ mmHg \times \frac{1\ atm}{760\ mmHg} \times 128\ mL \times \frac{1\ L}{1000\ mL}}{0.0821\ \frac{atm\ L}{mol\ K} \times 297\ K} = 5.11 \times 10^{-5}\ mol$$

$$2KClO_3(s) \rightarrow 2KCl(s) + 3O_2(g)$$

		$2KClO_3$	$\rightarrow$	$2KCl$	+	$3O_2$
Equation moles	⇒	2				3
Question moles	⇒	X				5.11×10^{-5}

$$X = 5.11 \times 10^{-5}\ mol\ O_2 \times \frac{2\ mol\ KClO_3}{3\ mol\ O_2} = 3.41 \times 10^{-5}\ mol\ KClO_3$$

$$m = n \times M$$

$$m = 3.41 \times 10^{-5}\ mol \times 123.427\ \frac{g}{mol} = 4.21 \times 10^{-5}\ g$$

Practice Exercise

Hydrogen gas generated when calcium metal reacts with water is collected as shown in the previous figure. The volume of gas collected at 30°C and pressure of 988 mmHg is 641 mL. What is the mass (in grams) of the hydrogen gas obtained? The pressure of water vapor at 30°C is 31.82 mmHg.

SOLUTIONS OF PRACICE EXERCISES

QUESTIONS AND PROBLEMS

Revie questions

1. Name five elements and five compounds that exist as gases at room temperature.
2. List the physical characteristics of gases.
3. Define pressure and give the common units for pressure.
4. Is the atmospheric pressure in a mine that is 500 m below sea level greater or less than 1 atm?
5. List the characteristics of an ideal gas. Write the ideal gas equation and also state it in words. Give the units for each term in the equation.
6. Use the equation ($\frac{P_1 \times V_1}{T_1} = \frac{P_2 \times V_2}{T_2}$) to derive all the gas laws.
7. What are standard temperature and pressure (STP)? What is the significance of STP in relation to the volume of 1 mole of an ideal gas?
8. Why is the density of a gas much lower than that of a liquid or solid under atmospheric conditions? What units are normally used to express the density of gases?
9. State Dalton's law of partial pressures and explain what mole fraction is. Does mole fraction have units?
10. A sample of air contains only nitrogen and oxygen gases whose partial pressures are 0.80 atm and 0.20 atm, respectively. Calculate the total pressure and the mole fractions of the gases.

Problems

11. The atmospheric pressure at the summit of a mountain is 606 mmHg on a certain day. What is the pressure in atm and in kPa?
12. At 46 °C a sample of ammonia gas exerts a pressure of 5.3 atm. What is the pressure when the volume of the gas is reduced to one-tenth (0.10) of the original value at the same temperature?
13. A sample of air occupies 3.8 L when the pressure is 1.2 atm.
    (a) What volume does it occupy at 6.6 atm?
    (b) What pressure is required in order to compress it to 0.075 L? (The temperature is kept constant.)
14. Under constant-pressure conditions a sample of hydrogen gas initially at 88 °C and 9.6 L is cooled until its final volume is 3.4 L. What is its final temperature?
15. Given that 6.9 moles of carbon monoxide gas are present in a container of volume 30.4 L, what is the pressure of the gas (in atm) if the temperature is 62 °C?

16. A certain amount of gas at 25 °C and at a pressure of 0.800 atm is contained in a glass vessel. Suppose that the vessel can withstand a pressure of 2.00 atm. How high can you raise the temperature of the gas without bursting the vessel?
17. The temperature of 2.5 L of a gas initially at STP is raised to 250 °C at constant volume. Calculate the final pressure of the gas in atm.
18. A gas evolved during the fermentation of glucose (wine making) has a volume of 0.78 L at 20.1 °C and 1.00 atm. What was the volume of this gas at the fermentation temperature of 36.5 °C and 1.00 atm pressure?
19. Calculate the volume (in liters) of 88.4 g of CO_2 at STP.
20. Dry ice is solid carbon dioxide. A 0.050-g sample of dry ice is placed in an evacuated 4.6-L vessel at 30 °C. Calculate the pressure inside the vessel after all the dry ice has been converted to CO_2 gas.
21. At 741 torr and 44 °C, 7.10 g of a gas occupy a volume of 5.40 L. What is the molar mass of the gas?
22. Assuming that air contains 78 percent N_2, 21 percent O_2, and 1 percent Ar, all by volume, how many molecules of each type of gas are present in 1.0 L of air at STP?
23. Calculate the density of hydrogen bromide (HBr) gas in grams per liter at 733 mmHg and 46 °C.
24. A compound has the empirical formula SF_4. At 20 °C, 0.100 g of the gaseous compound occupies a volume of 22.1 mL and exerts a pressure of 1.02 atm. What is the molecular formula of the gas?
25. A 2.5-L flask at 15 °C contains a mixture of N_2, He, and Ne at partial pressures of 0.32 atm for N_2, 0.15 atm for He, and 0.42 atm for Ne.
    (a) Calculate the total pressure of the mixture.
    (b) Calculate the volume in liters at STP occupied by He and Ne if the N_2 is removed selectively.
26. A mixture of helium and neon gases is collected over water at 28.0 °C and 745 mmHg. If the partial pressure of helium is 368 mmHg, what is the partial pressure of neon? (Vapor pressure of water at 28 °C = 28.3 mmHg.)

5. THEMOCHEMISTRY

P-V work, specific heat, heat capacity, and quantity of heat

- Thermochemistry is part of a broader subject called *thermodynamics,* which is *the scientific study of the interconversion of heat and other kinds of energy*.
- The first law of thermodynamics is relevant to the study of thermochemistry.
- In thermodynamics, we study changes in the ***state of a system***.
- ***State of a system*** is *the values of all relevant macroscopic properties, for example, composition, energy, temperature, pressure, and volume*.
- Energy, pressure, volume, and temperature are ***state functions***.
- ***State functions*** are *properties that are determined by the state of the system, regardless of how that condition was achieved*.
- In other words, when the state of a system changes, the magnitude of change in any state function depends only on the initial and final states of the system and not on how the change is accomplished.
- The state of a given amount of a gas is specified by its amount, volume, pressure, and temperature.
- Consider a specific quantity of a gas at 2 atm, 300 K is confined in 1 L vessel (the initial state). Suppose a process is carried out on the same quantity at constant temperature such that the gas pressure decreases to 1 atm. According to Boyle's law, its volume must increase to 2 L. The final state of this quantity then corresponds to 1 atm, 300 K, and 2 L. The change in volume (ΔV) is

  $$\Delta V = V_f - V_i$$
  $$\Delta V = 2\ L - 1\ L$$
  $$\Delta V = 1\ L$$

  where V_f and V_i denote the initial and final volumes, respectively.
- No matter how we arrive at the final state (for example, the pressure of the gas can be increased first and then decreased to 1 atm), the change in volume is always 1 L. Thus, the volume of a gas is a state function.
- In a similar manner, we can show that pressure and temperature are also state functions.
- Energy is another state function.

The first law of thermodynamics

- The ***first law of thermodynamics,*** is based on the law of conservation of energy.

- the law of conservation of energy states that *energy can be converted from one form to another, but cannot be created or destroyed.*
- How do we know this is so?
- We can test the validity of the first law by measuring the *change* in the internal energy of a system between its *initial state* and its *final state* in a process. The change in internal energy ΔE is given by

  $$\Delta E = E_f - E_i$$

  where E_i and E_f are the initial and the final internal energies of the system respectively.
- Depending on the values of E_i and E_f, ΔE may be positive, negative or zero.
- The internal energy of a system has two components: kinetic energy and potential energy.

  The kinetic energy component consists of various types of molecular motion and the movement of electrons within molecules.

  Potential energy is determined by the attractive interactions between electrons and nuclei and by repulsive interactions between electrons and between nuclei in individual molecules, as well as by interaction between molecules.
- It is impossible to measure all these contributions accurately, so we cannot calculate the total internal energy of a system with any certainty.
- Changes in energy, on the other hand, can be determined experimentally.
- Consider the reaction between 1 mole of sulfur and 1 mole of oxygen gas to produce 1 mole of sulfur dioxide:

  $$S(s) + O_2(g) \rightarrow SO_2(g)$$
- In this case, our system is composed of the reactant molecules S and O_2 (the initial state) and the product molecules SO_2 (the final state).
- We do not know the internal energy of either the reactant molecules (E_i) or the product molecules (E_f), but we can accurately measure the difference between them (ΔE), given by

  $$\Delta E = E(\text{product}) - E(\text{reactants})$$

$$\Delta E = \text{energy content of 1 mol } SO_2 - \text{energy content of } [1 \text{ mol S} + 1 \text{ mol } O_2]$$

- We find that this reaction gives off heat. Therefore, the energy of the product is less than that of the reactants, and ΔE is negative.
- The release of heat in this reaction means that some of the chemical energy contained in the molecules has been converted to thermal energy, we conclude that the transfer of energy from the system to the surroundings does not change the total energy of the universe.
- That is, the sum of the energy changes must be zero:

  $$\Delta E_{sys} - \Delta E_{surr} = 0$$

OR

$$\Delta E_{sys} = -\Delta E_{surr}$$

where the subscripts "sys" and "surr" denote system and surroundings, respectively.

- Thus, if one system undergoes an energy change ΔE_{sys}, the rest of the universe, or the surroundings, must undergo a change in energy that is equal in magnitude but opposite in sign ($\Delta E_{surr} = -\Delta E_{sys}$); energy gained in one place must have been lost somewhere else.
- Furthermore, because energy can be changed from one form to another, the energy lost by one system can be gained by another system in a different form.
- For example, the energy lost by burning oil in a power plant may ultimately turn up in our homes as electrical energy, heat, light, and so on.
- In chemistry, we are normally interested in the energy changes associated with the system (which may be a flask containing reactants and products), not with its surroundings. Therefore, a more useful form of the first law is

$$\mathbf{\Delta E = q + w}$$

- This equation says that the change in the internal energy, ΔE, of a system is the sum of the heat exchange between the system and the surroundings(q) and the work done on or by the system (w).
- The sign conventions for "q" and "w" are as follows:
  q is positive for an endothermic process
  q is negative for an exothermic process
  w is positive for work done on the system by the surroundings
  w is negative for work done by the system on the surroundings.
- If a system loses heat to the surroundings or does work on the surroundings, we would expect its internal energy to decrease because those are on the expense of the internal energy of the system. For this reason, both "q" and "w" are negative.
- Conversely, if heat is added to the system or if work is done on the system, then the internal energy of the system would increase. In this case, both q and w are positive.
- The table below summarizes the sign conventions

Work and heat

We will now look at the nature of work and heat in more details.

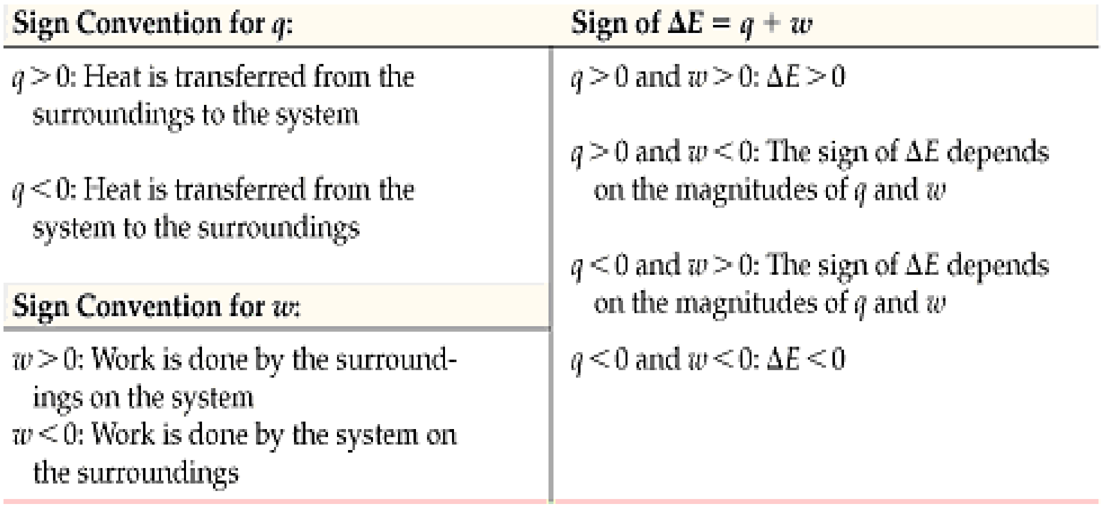
Work

- We know that work is defined as force **F** multiplied by distance **d**:

$$w = F \times d$$

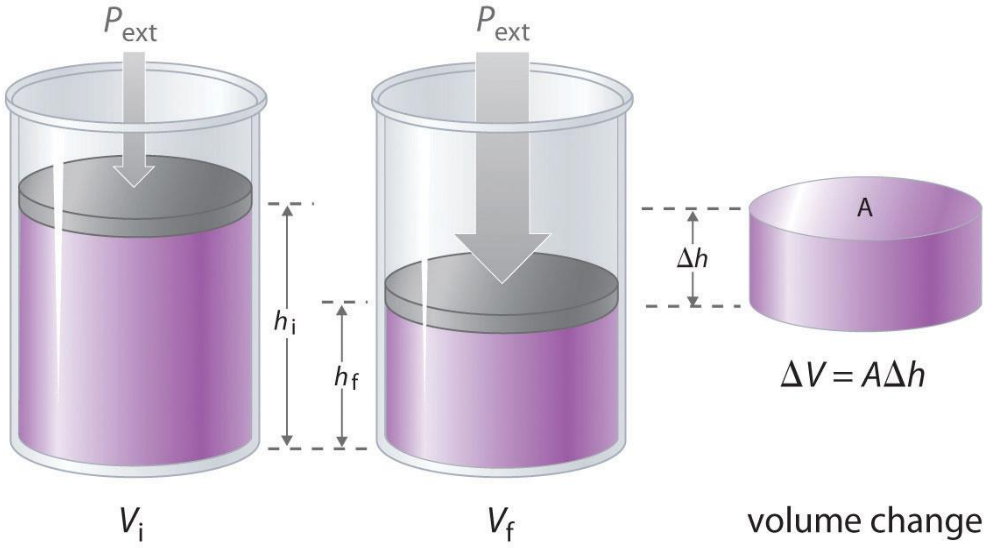
$$\text{work units} = \text{force units} \times \text{distance unit}$$

$$\text{work units} = \frac{\text{kg m}}{\text{s}^2} \times \text{m} = \text{kg m}^2\ \text{s}^{-2} = \text{J}$$



Sign Convention for q:	Sign of $\Delta E = q + w$
$q > 0$: Heat is transferred from the surroundings to the system	$q > 0$ and $w > 0$: $\Delta E > 0$
$q < 0$: Heat is transferred from the system to the surroundings	$q > 0$ and $w < 0$: The sign of ΔE depends on the magnitudes of q and w
Sign Convention for w:	$q < 0$ and $w > 0$: The sign of ΔE depends on the magnitudes of q and w
$w > 0$: Work is done by the surroundings on the system $w < 0$: Work is done by the system on the surroundings	$q < 0$ and $w < 0$: $\Delta E < 0$

- Work is many kind, it includes:
  mechanical work (for example, the expansion or compression of a gas).
  electrical work (a battery supplying electrons to light the bulb of a flashlight).
  surface work (blowing up a soap bubble).
  And many other types.
- We will concentrate only on mechanical work.
- Look and inspect the figure below.



- One way to illustrate mechanical work is to study the expansion or compression of a gas as in the internal combustion engine of the automobile.
- The successive expansion and compression of the cylinders due to the combustion of the gasoline-air mixture provide power to the vehicle.
- The figure shows a gas in a cylinder fitted with a weightless, frictionless movable piston at a certain temperature, pressure, and volume.
- As it expands, the gas pushes the piston upward against a constant opposing external atmospheric pressure P. Here, work is done by the gas and is negative. The work done by or on the gas:

  $$w = -P(V_f - V_i)$$
  $$w = -P\Delta V$$

  For gas expansion (work done *by* the system), $\Delta V > 0$, so $(-P\Delta V)$ is a negative quantity.

  For gas compression (work done *on* the system), $\Delta V < 0$, so $(-P\Delta V)$ is a positive quantity.
- Regarding units:

  $$w = -P \times \Delta V = -\frac{\text{force}}{\text{area}^2} \times \Delta V$$
  $$\text{units of w} = \text{units of P} \times \text{units of V}$$
  $$\text{units of w} = \frac{\text{units of force}}{(\text{units of area})^2} \times \text{units of V}$$
  $$\text{units of w} = \frac{\text{kg} \times \frac{\text{m}}{\text{s}^2}}{\text{m}^2} \times \text{m}^3$$
  $$\text{units of w} = \text{kg m}^{-1}\,\text{s}^{-2} \times \text{m}^3$$
  $$\text{units of w} = \text{Pascal} \times \text{m}^3$$
  $$\text{units of w} = \text{kg m}^2\,\text{s}^{-2} = \text{J}$$

  - ✓ The product of pressure and volume is equal to work.
  - ✓ If "P" is in "Pa" unit and "V" is in "m^3" unit work will be in "J" unit.
  - ✓ If "P" is in "atm" unit and "V" is in "L" unit work will be in "atm L" unts.
  - ✓ 1 atm L = 101.325 J

EXAMPLE 5.1

A certain gas expands in volume from 2.0 L to 6.0 L at constant temperature. Calculate the work done by the gas if it expands

(a) against a vacuum. (b) against a constant pressure of 1.2 atm.

Solution

(a) Because the external pressure is zero, no work is done in the expansion.

$$w = -P\Delta V$$
$$w = -(0 \times \Delta V) = 0$$

(b) The external, opposing pressure is 1.2 atm, so

$$w = -P\Delta V$$

$$w = -\{1.2\ \text{atm} \times 101325\ \frac{\text{Pa}}{\text{atm}}\} \times \{(6-2)\ \text{L} \times 10^{-3}\ \frac{\text{m}^3}{\text{L}}\} = 4.86 \times 10^{-2}\ \text{J}$$

Practice Exercise

A gas expands from 264 mL to 971 mL at constant temperature. Calculate the work done (in joules) by the gas if it expands (a) against a vacuum and (b) against a constant pressure of 4.00 atm.

Heat

- The other component of internal energy is heat, **q**.
- Like work, heat is not a state function.
- For example, it takes 4184 J of energy to raise the temperature of 100 g of water from 20°C to 30°C. This energy can be gained
  (a) directly as heat energy from burner, without doing any work.
  (b) by doing work on the water without adding heat energy (for example, by stirring the water with a magnetic stir bar).
  (c) by some combination of the procedures described in (a) and (b).
- The heat associated with a given process depends on how it is carried out.
- It is important to note that regardless of which procedure is taken, the change in internal energy of the system, ΔE, depends on the sum of (q + w).
- In summary, heat and work are not state functions because they are not properties of a system. They manifest themselves only during a process (during a change).
- Thus, their values depend on the path of the process and vary accordingly.

EXAMPLE 5.2

If the work done on a gas is is 462 J and the heat released by the gas is 128 J, calculate the change in the gas internal energy.

Solution

$$\Delta E = q + w$$

$$\Delta E = (-128\ \text{J}) + (+\ 462\ \text{J}) = +\ 334\ \text{J}$$

Practice Exercise

A gas expands and does P - V work on the surroundings equal to 279 J. At the same time, it absorbs 216 J of heat from the surroundings. What is the change in energy of the system?

Specific heat and heat capacity

- The ***specific heat*** **(s)** of a substance is *the amount of heat required to raise the temperature of* ***one gram*** *of the substance by* ***one degree Celsius****.*

Its units are J/g °C.

- The ***heat capacity*** **(C)** of a substance is *the amount of heat required to raise the temperature of* ***<u>any given mass</u>*** *of the substance by* ***<u>one degree Celsius</u>***. Its units are J/°C.
- Specific heat is an intensive property whereas heat capacity is an extensive property.
- The relationship between the heat capacity and specific heat of a substance is:

$$C = m \times s$$

Where m is the mass of the substance in grams.

- For example, the specific heat of water is 4.184 J/g °C, and the heat capacity of 60.0 g of water is

$$C = 60.0\ \text{g} \times 4.184\ \text{J/g °C} = 251\ \text{J/°C}$$

- The following table shows the specific heat of some common substances.

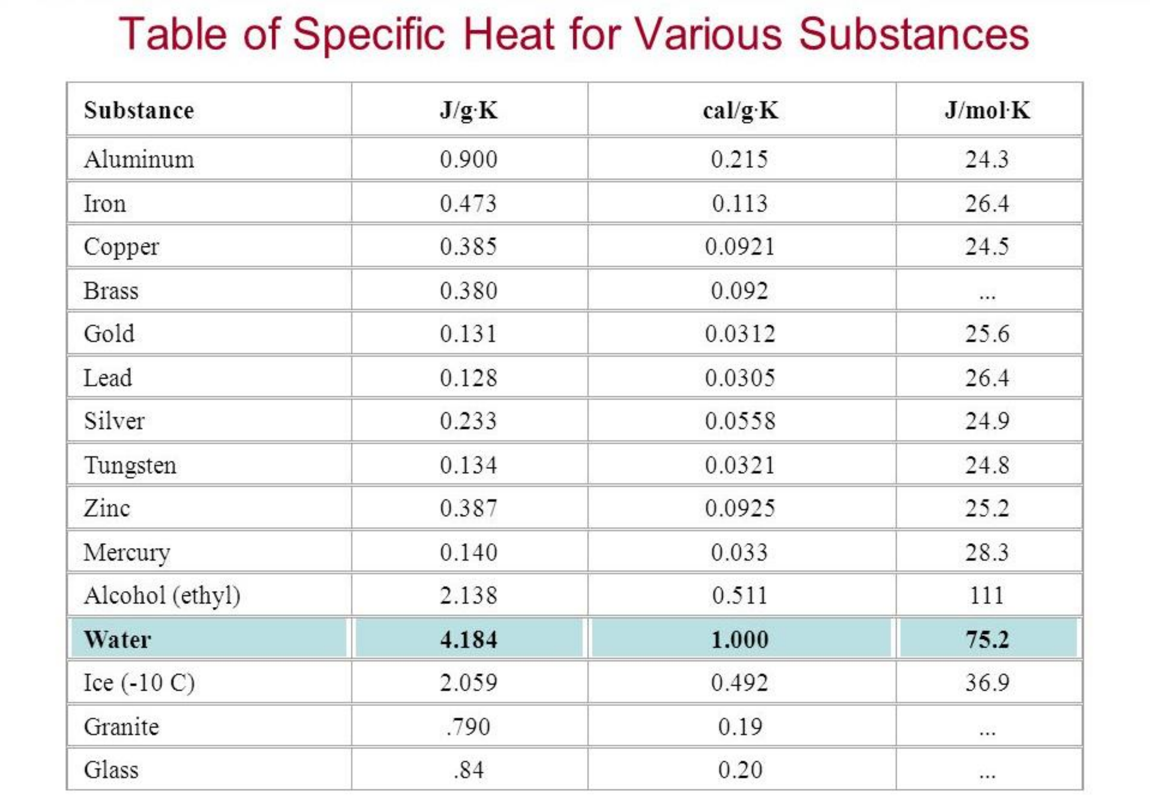


Table of Specific Heat for Various Substances

Substance	J/g·K	cal/g·K	J/mol·K
Aluminum	0.900	0.215	24.3
Iron	0.473	0.113	26.4
Copper	0.385	0.0921	24.5
Brass	0.380	0.092	...
Gold	0.131	0.0312	25.6
Lead	0.128	0.0305	26.4
Silver	0.233	0.0558	24.9
Tungsten	0.134	0.0321	24.8
Zinc	0.387	0.0925	25.2
Mercury	0.140	0.033	28.3
Alcohol (ethyl)	2.138	0.511	111
Water	**4.184**	**1.000**	**75.2**
Ice (-10 C)	2.059	0.492	36.9
Granite	.790	0.19	...
Glass	.84	0.20	...

- If we know **s** and **m**, then **Δt** will tell us the amount **q** that has been absorbed or released in a particular process.
- The equations for calculating the heat change are given by

$$q = m \times s \times \Delta t$$

$$q = C \times \Delta t$$

- **q** is positive for endothermic processes and negative for exothermic processes.

EXAMPLE 5.3

A 466-g sample of water is heated from 8.50 °C to 74.60 °C. Calculate the amount of heat absorbed (in kilojoules) by the water.

Solution

$$q = m \times s \times \Delta t$$

$$q = 466\text{-g} \times 4.184 \text{ J/g °C} \times (74.60 \text{ °C} - 8.50 \text{ °C})$$

$$q = 129000 \text{ J}$$

$$q = 129000 \text{ J} \times 10^{-3} \frac{\text{kJ}}{\text{J}}$$

$$q = 129 \text{ kJ}$$

Practice Exercise

An iron bar (s = 0.45 J/g °C) of mass 869 g cools from 94°C to 5°C. Calculate the heat released (in kilojoules) by the metal.

Enthalpy of reactions

The word ***enthalpy*** is originated from Greek. "***en-***" means "within" and "***thalpein***" means "to heat". Therefore, ***enthalpy*** means "***heat content***". The symbol for enthalpy is "H".

- The heat absorbed or released by a system, at constant temperature, as result of a change in the state of the system is called ***heat of reaction***.
- The heat of the reaction at constant temperature is given a specified name and symbol depending on whether it is also at constant volume or at constant pressure:
  - ✓ If it is at constant temperature and constant volume, it is named "***change in internal energy***" and is given the symbol (**ΔE**).
  - ✓ If it is at constant temperature and constant pressure, it is named "***change in enthalpy***" and is given the symbol (**ΔH**).
- Because most reactions are done at constant temperature and pressure, we became more concerned about changes in enthalpy rather than changes in internal energy.
- For any reaction of the type

  Reactants → products

  Enthalpy of reaction, ΔH, is the change in enthalpy, and it is *the difference between the enthalpies "**the heat content**" of the products and the enthalpies "**the heat content**" of the reactants:*

$$\Delta H = H_{products} - H_{reactants}$$

- There is no way to measure the absolute value of the enthalpy of a substance (H).
- Fortunately, we do not need to know its value because what we care about only is the increase or decrease (the change) in its value, (ΔH).
- The enthalpy of reaction can be positive or negative, depending on the process.
  - ✓ For an endothermic process (heat absorbed by the system from the surroundings), ΔH is positive (that is, $\Delta H > 0$).
  - ✓ For an exothermic process (heat released by the system to the surroundings), ΔH is negative (that is, $\Delta H < 0$).

Thermochemical equations

- At 0°C and a pressure of 1 atm, ice melts to form liquid water.
- Measurements show that for every mole of ice converted to liquid water under these conditions, 6.01 kilojoules (kJ) of heat energy are absorbed by the system (ice).
- Because the pressure is constant, the heat change is equal to the enthalpy change, ΔH.
- Furthermore, this is an endothermic process and ΔH is a positive.
- The equation for this physical change is

  $$H_2O(s) \rightarrow H_2O(l) \qquad \Delta H = 6.01 \text{ kJ}$$

  That is, when 1 mole of ice is converted to 1 mole of liquid water at constant temperature and pressure, ice must have absorbed 6.01 kJ of heat.
- As another example, consider the combustion of methane (CH_4) at constant temperature and pressure:

  $$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l). \qquad \Delta H = -\ 2890.4 \text{ kJ}$$

  - ✓ when 1 mole of CH_4 gas reacts with 2 moles of O_2 gas to produce 1 mole of CO_2 and 2 moles of liquid H_2O, 890.4 kJ of heat energy are released to the surroundings.
  - ✓ It is important to keep in mind that the ΔH value does not refer to a particular reactant or product.
  - ✓ Concerning ΔH for the previous reaction, all the following are true:
    1. $\Delta H = -\ 2890.4$ kJ/ mol CH_4
    2. $\Delta H = -\ 2890.4$ kJ/ 2 mol O_2
    3. $\Delta H = -\ 2890.4$ kJ/ mol CO_2
    4. $\Delta H = -\ 2890.4$ kJ/ 2 mol CH_2O
- A ***thermochemical equation*** cannot be called so unless it satisfies the following conditions:

1) The ***thermochemical equation*** must be balanced.
2) In the ***thermochemical equation***, the states of all substances must be specified.
3) In the ***thermochemical equation***, the value of ΔH must be written.

- If we multiply the ***thermochemical equation*** by a factor, the value of ΔH must also be multiplied by the same factor.
- When we reverse the ***thermochemical equation***, the sign of ΔH must also be reversed.
- When several ***thermochemical equations*** are added together, the values of their ΔH's must also be added together (**This is called Hess's law**).

EXAMPLE 5.4

Given the thermochemical equation

$$2SO_2(g) + O_2\,(g) \rightarrow 2SO_3(g) \qquad \Delta H = -198.2\ \text{kJ}$$

calculate the heat evolved when 87.9 g of SO_2 (molar mass = 64.07 g/mol) is converted to SO_3.

Solution

$$\text{Given moles of } SO_2 = \frac{87.9\ \text{g}}{64.07\frac{\text{g}}{\text{mol}}} = 1.372\ \text{mol}$$

	$2SO_2$	+	O_2	→	$2SO_3$	ΔH
Equation moles	2 mol					− 198.2 kJ
Givnen moles	1.372 mol					X

$$X = \frac{-\ 198.2\ \text{kJ} \times 1.372\ \text{mol}\ SO_2}{2\ \text{mol}\ SO_2} = -\ 135.97\ \text{kJ}$$

Practice Exercise

Calculate the heat evolved when 266 g of white phosphorus (P_4) burns in air according to the equation

$$P_4(s) + 5O_2(g) \rightarrow P_4O_{10}(s) \qquad \Delta H = -\ 3013\ \text{kJ/mol}$$

Relationship between ΔH and ΔE

- We know that $\Delta E = q + w$ and $w = -\ P \times \Delta V$
- We also know that $q = \Delta H$ when T and P are constant
- Therefore, at constant T and P

$$\Delta E = \Delta H - P \times \Delta V$$

- We also know that

$$P \times V = n \times R \times T$$

And at constant T and P,

$$P \times \Delta V = R \times T \times \Delta n_g$$

Therefore,

$$\mathbf{\Delta E = \Delta H - R \times T \times \Delta n_g}$$

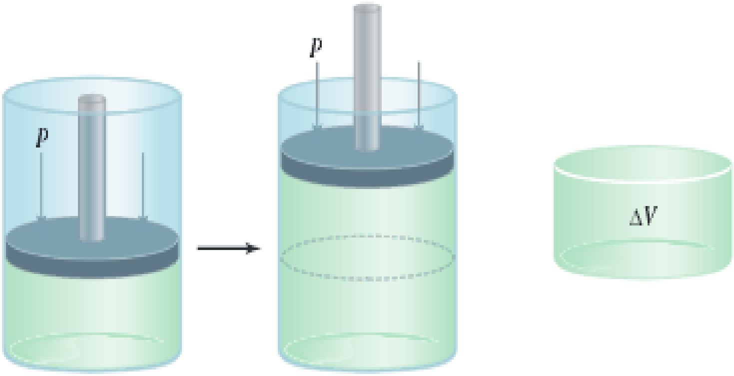
- It is very important to remember that the subscript “g” is to emphasize that when calculating **Δn** only gases count:

$$\mathbf{\Delta n_g = n_{gases\ produced} - n_{gases\ reacted}}$$

- The reaction between sodium metal and water at 1 atm and 298 K is:

$$2Na(s) + 2H_2O(l) \rightarrow 2NaOH(aq) + H_2(g) \qquad \Delta H = -\,367.5\ kJ$$

- This thermochemical equation says that when two moles of sodium react with water, 367.5 kJ of heat are given off. Note that one of the products is hydrogen gas.
- $H_2(g)$ must push back air toward the atmosphere.
- Consequently, some of the energy produced by the reaction is used to do work of pushing back a volume of air (ΔV) against atmospheric pressure (P) as shown by the figure below.



- To calculate the change in internal energy, we apply the previous equation:

$$\Delta E = \Delta H - R \times T \times \Delta n_g$$

$$\Delta E = (-\,367.5\ kJ) - (8.314 \times 10^{-3}\ \frac{kJ}{mol\ K} \times 298\ K \times 1\ mol) = -\,369.98\ kJ$$

EXAMPLE 5.5

Calculate ΔE for the following reaction at 1 atm and 25°C:

$$2CO(g) + O_2(g) \rightarrow 2CO_2(g) \qquad \Delta H = -\,566.0\ kJ$$

Solution

$$\Delta E = \Delta H - R \times T \times \Delta n_g$$

$$\Delta n_g = (2\ mol) - (3\ mol) = -\,1\ mol$$

$$\Delta E = (-\,566.0\ kJ) - (8.314 \times 10^{-3}\ \frac{kJ}{mol\ K} \times 298\ K \times -\,1\ mol) = -\,563.5\ kJ$$

Practice Exercise

What is ΔE for the formation of 1 mole of CO at 1 atm and 258C?

$$\text{C(graphite)} + \frac{1}{2}\text{O}_2(g) \rightarrow \text{CO}(g) \qquad \Delta H = -110.5 \text{ kJ}$$

Some types of Endothermic and exothermic physical changes and chemical reactions

(1) Enthalpies of some physical changes

1.1 Fusion (melting) and enthalpy of fusion

Freezing and enthalpy of freezing

- ***Fusion*** is a physical process in which a substance changes from its solid state to its liquid state.
- ***Fusion*** is an endothermic process.
- The quantity of energy required to fuse (melt) one mole of a solid substance is called ***molar enthalpy of fusion*** **(ΔH_{fus})**.
- The following equations are examples of fusion:

$\text{Ar(s)} \rightarrow \text{Ar}(l)$ $\Delta H = 1.3$ kJ

$\text{C}_6\text{H}_6\text{(s)} \rightarrow \text{C}_6\text{H}_6(l)$ $\Delta H = 10.9$ kJ

$\text{CH}_3\text{CH}_2\text{OH(s)} \rightarrow \text{CH}_3\text{CH}_2\text{OH}(l)$ $\Delta H = 7.61$ kJ

$\text{Hg(s)} \rightarrow \text{Hg}(l)$ $\Delta H = 23.4$ kJ

$\text{H}_2\text{O}(s) \rightarrow \text{H}_2\text{O}(l)$ $\Delta H = 6.01$ kJ

- ***Freezing*** is simply the opposite of fusion.

1.2 Vaporization (evaporation) and enthalpy of vaporization

Condensation and enthalpy of condensation

- ***Vaporization*** is a physical process in which a substance changes from its liquid state to its gaseous state.
- ***Vaporization*** is an endothermic process.
- The quantity of energy required to vaporize one mole of a liquid substance is called ***molar enthalpy of vaporization*** **(ΔH_{vap})**.
- The following equations are examples of vaporization:

$\text{Ar}(l) \rightarrow \text{Ar(g)}$ $\Delta H = 6.3$ kJ

$\text{C}_6\text{H}_6(l) \rightarrow \text{C}_6\text{H}_6\text{(g)}$ $\Delta H = 31.0$ kJ

$\text{CH}_3\text{CH}_2\text{OH}(l) \rightarrow \text{CH}_3\text{CH}_2\text{OH(g)}$ $\Delta H = 39.3$ kJ

$\text{Hg}(l) \rightarrow \text{Hg(g)}$ $\Delta H = 59.0$ kJ

$\text{H}_2\text{O}(l) \rightarrow \text{H}_2\text{O(g)}$ $\Delta H = 40.79$ kJ

- ***Condensation*** is simply the opposite of vaporization.

1.3 Sublimation and enthalpy of sublimation

Deposition and enthalpy of deposition

- ***Sublimation*** is a physical process in which a substance changes directly from its solid state to its gaseous state.
- ***Sublimation*** is an endothermic process.
- The quantity of energy required to sublime one mole of a solid substance is called ***molar enthalpy of sublimation*** **(ΔH_{sub})**.
- ***Sublimation*** is the summation of fusion and vaporization. Therefore,

$$\Delta H_{sub} = \Delta H_{fus} + \Delta H_{vap}$$

- The following equations are examples of sublimation:

$Ar(s) \rightarrow Ar(g)$ $\Delta H = 7.6$ kJ

$C_6H_6(s) \rightarrow C_6H_6(g)$ $\Delta H = 41.9$ kJ

$CH_3CH_2OH(s) \rightarrow CH_3CH_2OH(g)$ $\Delta H = 46.91$ kJ

$Hg(s) \rightarrow Hg(g)$ $\Delta H = 82.4$ kJ

$H_2O(s) \rightarrow H_2O(g)$ $\Delta H = 46.8$ kJ

- ***Deposition*** is simply the opposite of Sublimation.

(2) Enthalpies of some chemical changes

2.1 Combustion and enthalpy of combustion

- A ***combustion reaction*** (also called burning) is the reaction *in which a substance reacts with oxygen* (O_2)*, usually with the release of heat and light to produce a flame*.
- The quantity of energy released as a result of combusting one mole of a substance is called ***molar enthalpy of combustion*** **(ΔH_{com})**.
- The following equations are examples combustion reactions:

$S(s) + O_2(g) \rightarrow SO_2(g)$ $\Delta H = -296.84$ kJ

$Mg(s) + \frac{1}{2}O_2(g) \rightarrow MgO(g)$ $\Delta H = -601.6$ kJ

$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$ $\Delta H = -285.8$ kJ

$C(graphite) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$ $\Delta H = -393.5$ kJ

- The combustion of compounds containing hydrogen and carbon yield CO_2, H_2O and heat:

$CH_3CH_2OH(l) + 5O_2(g) \rightarrow 2CO_2 + 3H_2O(l)$ $\Delta H = -1367$ kJ

$C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l)$ $\Delta H = -2100$ kJ

$C_6H_{12}O_6(s) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l)$ $\Delta H = -22801$ kJ

2.2 Formation and standard enthalpy of formation

- A ***formation reaction*** is the reaction *in which a substance is produced as a result of the reaction of its elements in their standard states*.
- *If an element is in its standard states it has no formation reaction*.

- The quantity of energy released or absorbed as a result of the formation of one mole of a substance from the reaction between its elements in their standard states is called ***standard molar enthalpy of formation*** **(ΔH_f°)**.
- The following equations are examples formation reactions:

  $$S(s) + O_2(g) \rightarrow SO_2(g) \qquad \Delta H = -296.84\ kJ$$

  Note that this reaction can also be called a combustion reaction.

  $$Mg(s) + \frac{1}{2}O_2(g) \rightarrow MgO(g) \qquad \Delta H = -601.6\ kJ$$

  Note that this reaction can also be called a combustion reaction.

  $$2C(graphite) + 3H_2(g) + \frac{1}{2}O_2(g) \rightarrow CH_3CH_2OH(l) \qquad \Delta H = -277.6\ kJ$$

  $$3C(graphite) + 4H_2(g) \rightarrow C_3H_8(g) \qquad \Delta H = -104.7\ kJ$$

  $$6C(graphite) + 6H_2(g) + 3O_2 \rightarrow C_6H_{12}O_6(s) \qquad \Delta H = -1271\ kJ$$
- So far, we have learned that we can determine the enthalpy change "ΔH" that accompanies a reaction by measuring the heat absorbed or released at constant temperature and pressure.
- S***tandard change in enthalpy*** is the change in enthalpy at standard pressure (1 atm). The symbol for ***standard change in enthalpy*** is **ΔH°**.
- Change in enthalpy becomes standard only when the change in substances occurs while they are at their standard states. Therefore, the superscript "°" indicates that substances are in their standard states.
- Substances are in their standard states only when they are at 1 atm.
- ***The standard enthalpy of formation*** **(ΔH_f°)** is the change in enthalpy as a result of producing a substance from its elements while they are in their standard states.
- Therefore, any element in its standard state has no formation reaction and its (ΔH_f°), by definition, is zero:

  When any element is in its standard state its $\Delta H_f^\circ = 0$
- At 1 atm and 25°C, O_2 is more stable than O_3. Thus, we have:

  $$\Delta H_f^\circ(O_2) = 0 \text{ and } \Delta H_f^\circ(O_3) = 142.2\ kJ/mol$$

  Also at 1 atm and 25°C, graphite is a more stable form of carbon than diamond:

  $$\Delta H_f^\circ(C,graphite) = 0 \text{ and } \Delta H_f^\circ(C,diamond) = 1.90\ kJ/mol$$
- Based on this reference for elements, we can now define the standard enthalpy of formation of a compound as ***the heat change that results when 1 mole of the compound is formed from its elements at a pressure of 1 atm.***
- The standard state does not specify a temperature, but we will always use ΔH_f° values measured at 25°C as most of the thermodynamic data are collected at this temperature.

- ***The importance*** of the standard enthalpies of formation is that once we know their values, we can readily calculate the *standard enthalpy* of any reaction, ΔH°_{rxn} defined as *the enthalpy of a reaction carried out at 1 atm*.
- For example, consider the hypothetical reaction

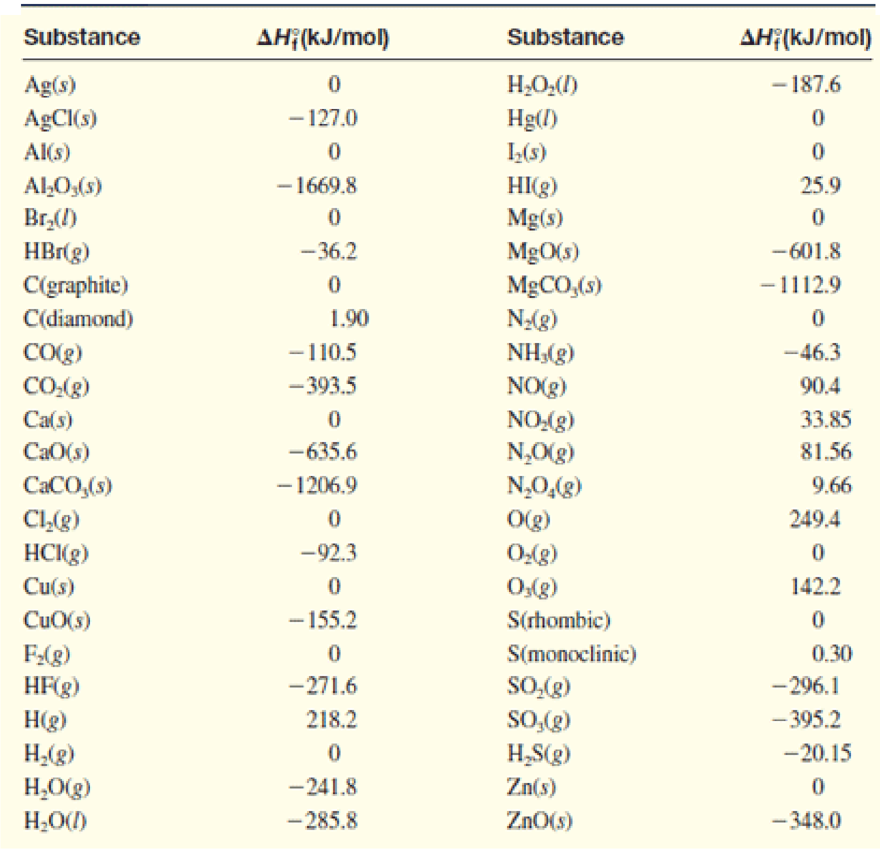
  $$aA + bB \rightarrow cC + dD$$

  For this reaction ΔH°_{rxn} is given by:

  $$\Delta H^{\circ}_{rxn} = [c \times \Delta H^{\circ}_{f,C} + d \times \Delta H^{\circ}_{f,D}] - [a \times \Delta H^{\circ}_{f,A} + b \times \Delta H^{\circ}_{f,B}]$$
- The generalized equation is:

  $$\Delta H^{\circ}_{rxn} = \Sigma\Delta H^{\circ}_{f,products} - \Sigma\Delta H^{\circ}_{f,reactants}$$

  Where Σ (sigma) means "the sum of."
- The table below lists the standard enthalpies of formation for a number of elements and compounds at 25 °C.



Substance	ΔH°_f(kJ/mol)	Substance	ΔH°_f(kJ/mol)
$Ag(s)$	0	$H_2O_2(l)$	−187.6
$AgCl(s)$	−127.0	$Hg(l)$	0
$Al(s)$	0	$I_2(s)$	0
$Al_2O_3(s)$	−1669.8	$HI(g)$	25.9
$Br_2(l)$	0	$Mg(s)$	0
$HBr(g)$	−36.2	$MgO(s)$	−601.8
C(graphite)	0	$MgCO_3(s)$	−1112.9
C(diamond)	1.90	$N_2(g)$	0
$CO(g)$	−110.5	$NH_3(g)$	−46.3
$CO_2(g)$	−393.5	$NO(g)$	90.4
$Ca(s)$	0	$NO_2(g)$	33.85
$CaO(s)$	−635.6	$N_2O(g)$	81.56
$CaCO_3(s)$	−1206.9	$N_2O_4(g)$	9.66
$Cl_2(g)$	0	$O(g)$	249.4
$HCl(g)$	−92.3	$O_2(g)$	0
$Cu(s)$	0	$O_3(g)$	142.2
$CuO(s)$	−155.2	S(rhombic)	0
$F_2(g)$	0	S(monoclinic)	0.30
$HF(g)$	−271.6	$SO_2(g)$	−296.1
$H(g)$	218.2	$SO_3(g)$	−395.2
$H_2(g)$	0	$H_2S(g)$	−20.15
$H_2O(g)$	−241.8	$Zn(s)$	0
$H_2O(l)$	−285.8	$ZnO(s)$	−348.0

EXAMPLE 5.6

The thermite reaction involves aluminum and iron(III) oxide

$$2Al(s) + Fe_2O_3(s) \rightarrow Al_2O_3(s) + 2Fe(l)$$

This reaction is highly exothermic and the liquid iron formed is used to weld metals. Calculate the heat released in kilojoules per gram of Al reacted with Fe_2O_3.

$\Delta H^\circ_{f,Al_2O_3(l)}$/kJ/mol = – 1669.8, $\Delta H^\circ_{f,Fe(l)}$ = 12.40, $\Delta H^\circ_{f,Fe_2O_3(s)} = -$ 822.2

Solution

$$\Delta H^\circ_{rxn} = \Sigma\Delta H^\circ_{f,products} - \Sigma\Delta H^\circ_{f,reactants}$$

$$\Delta H^\circ_{rxn} = [\Delta H^\circ_f(Al_2O_3) + 2\Delta H^\circ_f(Fe)] - [2\Delta H^\circ_f(Al) + \Delta H^\circ_f(Fe_2O_3)]$$

$$\Delta H^\circ_{rxn} = [(-1669.8\text{ kJ/mol}) + (2\text{ mol} \times 12.40\text{ kJ/mol})]$$

$$-[(2\text{ mol} \times 0) + (-822.2\text{ kJ/mol})]$$

$$\Delta H^\circ_{rxn} = -822.8\text{ kJ/2 mol of Al reacted}$$

Mass of Al reacted = n × M = 2 mol × 26.98 g/mol = 53.96 g

– 822.8 kJ per 53.96 g Al

X kJ per 1 g Al

$$X = \frac{-822.8\text{ kJ} \times 1\text{ g}}{53.96\text{ g}} = -15.25\text{ kJ/g}$$

Practice Exercise

Benzene (C_6H_6) burns in air to produce carbon dioxide and liquid water. Calculate the heat released (in kilojoules) per gram of the compound reacted with oxygen. The standard enthalpy of formation of benzene is 49.04 kJ/mol.

Hess's law

- Many reactions cannot be done easily. Therefore, changes in their enthalpies (ΔH°_{rxn}) cannot be known easily. In these cases, ΔH°_{rxn} can be determined by an indirect approach,
- Germain Henri Hess (1802–1850) is a Swiss chemist. born in Switzerland but spent most of his life in Russia. For formulating what is known as "**Hess's law**", he is called the father of thermochemistry
- Hess's law of heat summation (simply **Hess's law**) can be stated as follows: *When reactants are converted to products, the change in enthalpy is the same whether the reaction takes place in one step or in a series of steps*.
- Hess's law is based on the fact that because H is a state function, ΔH depends only on the initial and final state.
- The general rule in applying Hess's law is to arrange a series of chemical equations in such a way that, when added together, all species will cancel except for those that appear in the overall desired reaction.
- Further, we often need to multiply some or all of the equations representing the individual steps by the appropriate coefficients.
- Let's say we are interested in the standard enthalpy of formation of carbon monoxide (CO):

$$\text{C(graphite)} + \frac{1}{2}O_2(g) \rightarrow CO(g)$$

- ✓ We know that:
  $C(\text{graphite}) + O_2(g) \rightarrow CO_2(g) \qquad \Delta H^{\circ}_{rxn} = -\,393.5\ \text{kJ}$
  $CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g) \qquad \Delta H^{\circ}_{rxn} = -\,283.0\ \text{kJ}$
- ✓ Now we reverse the second equation and add the resultant to the first:
  $C(\text{graphite}) + O_2(g) \rightarrow CO_2(g) \qquad \Delta H^{\circ}_{rxn} = -\,393.5\ \text{kJ}$
  $CO_2(g) \rightarrow CO(g) + \frac{1}{2}O_2(g) \qquad \Delta H^{\circ}_{rxn} = +\,283.0\ \text{kJ}$
  $C(\text{graphite}) + \frac{1}{2}O_2(g) \rightarrow CO_2(g) \qquad \Delta H^{\circ}_{rxn} = -\,110.5\ \text{kJ}$

- Note that when an equation is multiplied by a number its ΔH must also be multiplied by the same number. And when an equation is reversed the sign of the value of its ΔH must also be reversed.

EXAMPLE 5.7

Calculate the standard enthalpy of formation of acetylene (C_2H_2) from its elements:

$$2C(\text{graphite}) + H_2(g) \rightarrow C_2H_2(g)$$

The equations for each step and the corresponding enthalpy changes are:

(a) $C(\text{graphite}) + O_2(g) \rightarrow CO_2(g) \qquad \Delta H^{\circ}_{rxn} = -\,393.5\ \text{kJ/mol}$
(b) $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l) \qquad \Delta H^{\circ}_{rxn} = -\,285.8\ \text{kJ/mol}$
(c) $2C_2H_2(g) + 5O_2(g) \rightarrow 4CO_2(g) + 2H_2O(l) \qquad \Delta H^{\circ}_{rxn} = -\,2598.8\ \text{kJ/mol}$

Solution

Careful look at the desired equation indicates that the first equation must be multiplied by 2; and the third equation must be revered and multiplied by $\frac{1}{2}$. So we will have

$2C(\text{graphite}) + 2O_2(g) \rightarrow 2CO_2(g) \qquad \Delta H^{\circ}_{rxn} = -\,787.0\ \text{kJ}$
$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l) \qquad \Delta H^{\circ}_{rxn} = -\,285.8\ \text{kJ}$
$2CO_2(g) + H_2O(l) \rightarrow C_2H_2(g) + 2.5O_2(g) \qquad \Delta H^{\circ}_{rxn} = +\,1299.4\ \text{kJ}$
$2C(\text{graphite}) \rightarrow H_2(g) \rightarrow C_2H_2(g) \qquad \Delta H^{\circ}_{rxn} = +\,226.6\ \text{kJ}$

Practice Exercise

Calculate the standard enthalpy of formation of carbon disulfide (CS_2) from its elements, given that:

$C(\text{graphite}) + O_2(g) \rightarrow CO_2(g) \qquad \Delta H^{\circ}_{rxn} = -\,393.5\ \text{kJ}$
$S(\text{rhombic}) + O_2(g) \rightarrow SO_2(g) \qquad \Delta H^{\circ}_{rxn} = -\,296.4\ \text{kJ}$
$CS_2(l) + 3O_2(g) \rightarrow CO_2(g) + 2SO_2(g) \qquad \Delta H^{\circ}_{rxn} = -\,1073.6\ \text{kJ}$

SOLUTIONS OF PRACICE EXERCISES

Questions and Problems

Revie questions

1. Define these terms: thermochemistry, exothermic process, endothermic process.
2. Stoichiometry is based on the law of conservation of mass. On what law is thermochemistry based?
3. Describe two exothermic processes and two endothermic processes.
4. Decomposition reactions are usually endothermic, whereas combination reactions are usually exothermic. Give a qualitative explanation for these trends.
5. Explain what is meant by a state function. Give two examples of quantities that are state functions and two that are not.
6. Consider these changes.
   (a) $Hg(l) \rightarrow Hg(g)$
   (b) $3O_2(g) \rightarrow 2O_3(g)$
   (c) $CuSO_4 \cdot 5H_2O(s) \rightarrow CuSO_4(s) + 5H_2O(g)$
   (d) $H_2(g) + F_2(g) \rightarrow 2HF(g)$
   At constant pressure, in which of the reactions is work done by the system on the surroundings? By the surroundings on the system? In which of them is no work done?
7. A gas expands in volume from 26.7 mL to 89.3 mL at constant temperature. Calculate the work done (in joules) if the gas expands
   (a) against a vacuum.
   (b) against a constant pressure of 1.5 atm.
   (c) against a constant pressure of 2.8 atm.
8. The work done to compress a gas is 74 J. As a result, 26 J of heat is given off to the surroundings. Calculate the change in energy of the gas.
9. Calculate the work done in joules when 1.0 mole of water vaporizes at 1.0 atm and 100°C.
10. What is the difference between specific heat and heat capacity? What are the units for these two quantities? Which is the intensive property and which is the extensive property?
11. What is meant by the standard-state condition?
12. How are the standard enthalpies of an element and of a compound determined?
13. What is meant by the standard enthalpy of a reaction?
14. State Hess's law. Explain, with one example, the usefulness of Hess's law in thermochemistry.

15. Describe how chemists use Hess's law to determine the ΔH_f° of a compound by measuring its enthalpy of combustion.
16. Define these terms: enthalpy, enthalpy of reaction.
17. Under what condition is the heat of a reaction equal to the enthalpy change of the same reaction?
18. In writing thermochemical equations, why is it important to indicate the physical state of each substance?
19. For which of the following reactions does $\Delta H_{rxn}^\circ = \Delta H_f^\circ$?
    (a) $H_2(g) + S(\text{rhombic}) \rightarrow H_2S(g)$
    (b) $C(\text{diamond}) + O_2(g) \rightarrow CO_2(g)$
    (c) $H_2\ (g) + CuO(s) \rightarrow H_2O(l) + Cu(s)$
    (d) $O(g) + O_2(g) \rightarrow O_3(g)$
20. The ΔH° f values of the two forms of oxygen, O_2 and O_3 , are 0 and 142.2 kJ/mol, respectively, at 25°C. Which is the more stable form at this temperature?
21. Predict the value of ΔH_f° (greater than, less than, or equal to zero) for these elements at 25°C:
    (a) $Br_2(g)$; $Br_2(l)$.
    (b) $I_2(g)$; $I_2(s)$.

problems

22. A piece of silver of mass 362 g has a heat capacity of 85.7 J/°C. What is the specific heat of silver?
23. Calculate the amount of heat liberated (in kJ) from 366 g of mercury (specific heat = 0.139 J/g °C) when it cools from 77.0 °C to 12.0 °C.
24. Explain the meaning of this thermochemical equation:
    $4NH_3(g)\ 1\ 5O_2(g) \rightarrow 4NO(g) + 6H_2O(g) \qquad \Delta H = -904\ kJ$
25. Consider this reaction:
    $2CH_3OH(l) + 3O_2(g) \rightarrow 4H_2O(l) + 2CO_2(g) \qquad \Delta H = -1452.8\ kJ$
    What is the value of ΔH if
    (a) the equation is multiplied throughout by 2?
    (b) the direction of the reaction is reversed so that the products become the reactants and vice versa?
    (c) water vapor instead of liquid water is formed as the product?
26. The first step in the industrial recovery of zinc from the zinc sulfide ore is roasting, that is, the conversion of ZnS to ZnO by heating:
    $2ZnS(s) + 3O_2(g) \rightarrow 2ZnO(s) + 2SO_2(g) \qquad \Delta H = -879\ kJ/mol$
    Calculate the heat evolved (in kJ) per gram of ZnS roasted.

27. Determine the amount of heat (in kJ) given off when 1.26×10^4 g of NO_2 are produced according to the equation

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g) \qquad \Delta H = -114.6 \text{ kJ/mol}$$

28. Consider the reaction:

$$H_2(g) + Cl_2(g) \rightarrow 2HCl(g) \qquad \Delta H = -184.6 \text{ kJ/mol}$$

If 3 moles of H_2 react with 3 moles of Cl_2 to form HCl, Calculate the work done (in joules) against a pressure of 1.0 atm at 25°C. What is ΔE for this reaction?

29. Calculate the heats of combustion for the following reactions from the standard enthalpies of formation listed in your textbook:

(a) $C_2H_4(g) + 3O_2(g) \rightarrow 2CO_2(g) + 2H_2O(l)$

(b) $2H_2S(g) + 3O_2(g) \rightarrow 2H_2O(l) + 2SO_2(g)$

30. The standard enthalpy change for the following reaction is 436.4 kJ/mol:

$$H_2(g) \rightarrow H(g) + H(g)$$

Calculate the standard enthalpy of formation of atomic hydrogen (H).

31. Pentaborane-9, B_5H_9, is a colorless, highly reactive liquid that will burst into flame when exposed to oxygen. The reaction is

$$2B_5H_9(l) + 12O_2(g) \rightarrow 5B_2O_3(s) + 9H_2O(l)$$

Calculate the kilojoules of heat released per gram of the compound reacted with oxygen. The standard enthalpy of formation of $B_5H_9(l)$ is 73.2 kJ/mol.

32. At 850 °C, $CaCO_3$ undergoes substantial decomposition to yield CaO and CO_2. Assuming that the ΔH_f° values of the reactant and products are the same at 850°C as they are at 25°C, calculate the enthalpy change (in kJ) if 66.8 g of CO_2 are produced in one reaction.

33. From the following data,

$$C(graphite) + O_2(g) \rightarrow CO_2(g) \qquad \Delta H^\circ_{rxn} = -393.5 \text{ kJ/mol}$$

$$H_2(g) + \tfrac{1}{2}O_2(g) \rightarrow H_2O(l) \qquad \Delta H^\circ_{rxn} = -285.8 \text{ kJ/mol}$$

$$2C_2H6(g) + 7O_2(g) \rightarrow 4CO_2(g) + 6H_2O(l) \qquad \Delta H^\circ_{rxn} = -3119.6 \text{ kJ/mol}$$

calculate the enthalpy change for the reaction

$$2C(graphite) + 3H_2(g) \rightarrow C_2H6(g)$$

34. From the following data,

$$2Al(s) + \tfrac{3}{2}O_2(g) \rightarrow Al_2O_3(s) \qquad \Delta H^\circ_{rxn} = -1669.8 \text{ kJ/mol}$$

$$2Fe(s) + \tfrac{3}{2}O_2(g) \rightarrow Fe_2O_3(s) \qquad \Delta H^\circ_{rxn} = -822.2 \text{ kJ/mol}$$

Calculate the standard enthalpy change for the reaction

$$2Al(s) + Fe_2O_3(s) \rightarrow 2Fe(s) + Al_2O_3(s)$$

35. From the following data,

$H_2(g) \rightarrow 2H(g)$	$\Delta H° = 436.4$ kJ/mol
$Br_2(g) \rightarrow 2Br(g)$	$\Delta H° = 192.5$ kJ/mol
$H_2(g) + Br_2(g) \rightarrow 2HBr(g)$	$\Delta H° = -72.4$ kJ/mol

Calculate ΔH° for the reaction

$$H(g) + Br(g) \rightarrow HBr(g)$$

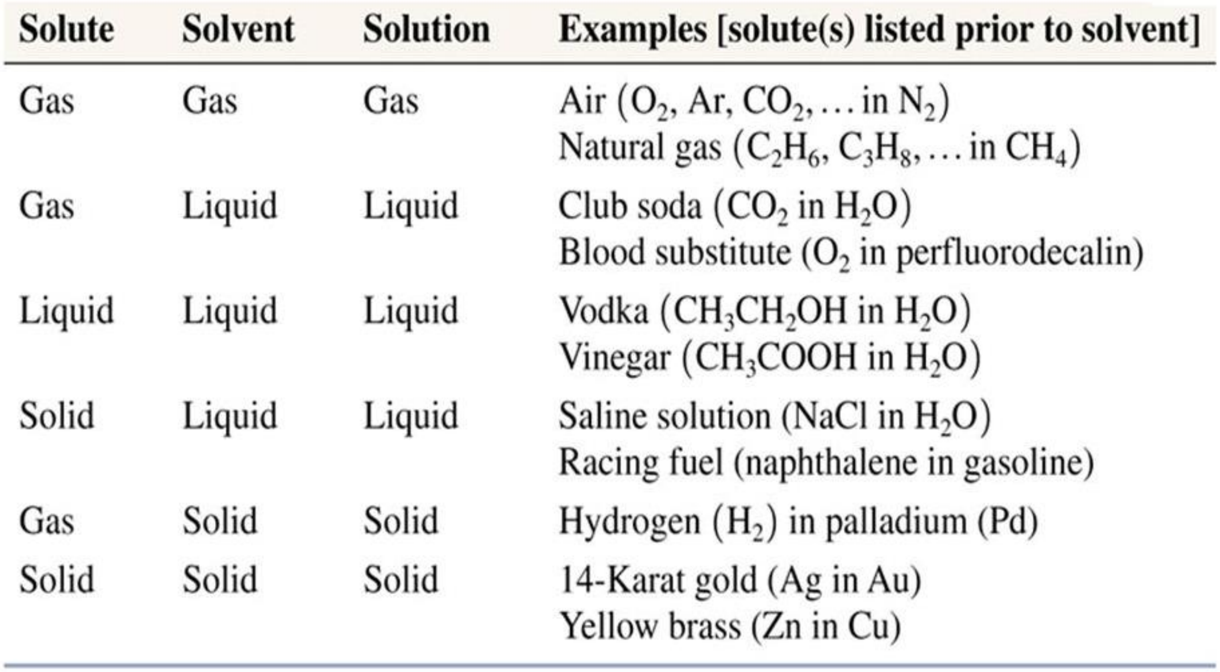
6. SOLUTIONS

Types of Solutions

- Any solution consists of two components, solvent and solute.

Solvent + Solute = Solution

- The table below gives some common types of solutions.



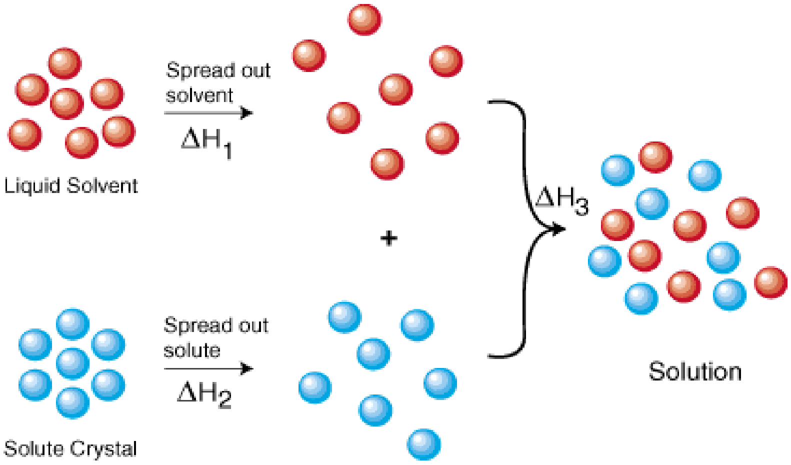
Solute	Solvent	Solution	Examples [solute(s) listed prior to solvent]
Gas	Gas	Gas	Air (O_2, Ar, CO_2, … in N_2) Natural gas (C_2H_6, C_3H_8, … in CH_4)
Gas	Liquid	Liquid	Club soda (CO_2 in H_2O) Blood substitute (O_2 in perfluorodecalin)
Liquid	Liquid	Liquid	Vodka (CH_3CH_2OH in H_2O) Vinegar (CH_3COOH in H_2O)
Solid	Liquid	Liquid	Saline solution (NaCl in H_2O) Racing fuel (naphthalene in gasoline)
Gas	Solid	Solid	Hydrogen (H_2) in palladium (Pd)
Solid	Solid	Solid	14-Karat gold (Ag in Au) Yellow brass (Zn in Cu)

- Our focus will be on solutions involving a liquid the solvent:
  - ✓ liquid - gas solutions.
  - ✓ Liquid - liquid solutions.
  - ✓ liquid - solid solutions.
- Chemists characterize solutions by their capacity to dissolve a solute.
- A solution is called ***saturated solution*** *when it contains the maximum amount of a solute dissolved in the solvent at a specific temperature.*
- A solution is called ***unsaturated solution*** *when it contains less than its capacity to dissolve a solute*.
- There are also solutions that are called ***supersaturated solution*** but they will not be discussed here.

A Molecular view of the solution process

- The intermolecular attractions between molecules of any gas are extremely weak or nonexistent to which justifies neglecting any effect they may have.

- The intermolecular attractions that hold molecules together in liquids and in solids play a central role in the formation of solutions of solids in liquids and of liquids in liquids.
- When one substance (the solute) dissolves in another (the solvent), particles of the solute disperse throughout the solvent.
- The solute particles occupy positions that are originally taken by solvent molecules.
- The ease with which a solute particle replaces a solvent molecule depends on the relative strengths of three types of interactions:
  - ✓ solvent-solvent interaction.
  - ✓ solute-solute interaction.
  - ✓ solvent-solute interaction.
- For simplicity and as figures below show, we can imagine the solution process taking place in three distinct and ***<u>simultaneous</u>*** actions:
  - ✓ Action 1 the separation of solvent molecules.
  - ✓ Action 2 the separation of solute molecules.
  - ✓ Action 3 the attraction between solvent and solute molecules.



- The first and the second **require** energy to break attractive intermolecular forces; therefore, they are endothermic ($\Delta H_1 > 0$ and $\Delta H_2 > 0$). The third **releases** energy as a result of attractions; therefore, it is exothermic ($\Delta H_3 < 0$).

  The enthalpy (heat) of solution ΔH_{soln} is given by:

  $$\mathbf{\Delta H_{soln} = \Delta H_1 + \Delta H_2 + \Delta H_3}$$

  - ✓ If the solute-solvent attraction is **stronger** than the solvent-solvent attraction and the solute-solute attraction, the solution process is exothermic ($\Delta H_{soln} > 0$).

- ✓ If the solute-solvent attraction is **weaker** than the solvent-solvent attraction and the solute-solute attraction, the solution process is endothermic and ($\Delta H_{soln} < 0$).
- ✓ If the solute-solvent attraction is **equal to** the solvent-solvent attraction and the solute-solute attraction, the solution process is not endothermic or exothermic. In this case the solution is described as an ***ideal solution.***

EXAMPLE 6.1

What does make a solution ideal or non-ideal?

Solution

The types of the attractions between the particles of the solvent and the solute determines whether the solution is an ideal or non-ideal solution. If they are of the same type the solution is ideal otherwise the solution is non-ideal.

Practice Exercise

Illustrate by your own drawing the actions of the solution process. Show on your drawing the enthalpies of each action and the overall enthalpy.

Solubility

Solubility is a measure of how much solute will dissolve in a solvent at a specific temperature.

- The saying "*like dissolves like*" is helpful in predicting the solubility of a substance in a given solvent. If solvent and solute have similar type intermolecular forces then the solvent dissolves the solute. For example, both carbon tetrachloride (CCl_4) and benzene (C_6H_6) are nonpolar liquids. Therefore, these two liquids dissolve in each other.
- **Ionic compounds** (such as the ionic solid sodium chloride NaCl or the ionic solid sodium nitrate $NaNo_3$) and **polar compounds** (such as the liquid ammonia NH_3 or the liquid hydrogen fluoride HF) are all soluble in **polar** solvents (such as water H_2O) rather in nonpolar solvents (such as benzene and carbon tetrachloride).
  - ✓ **Nonpolar solvents** cannot dissolve ionic compounds like sodium chloride and cannot dissolve polar compounds such as ammonia.
  - ✓ **Polar solvents** cannot dissolve nonpolar compounds like benzene.
- The next example illustrates how to predict solubility based on a knowledge of the intermolecular forces in the solute and the solvent.

EXAMPLE 6.2

Knowing that:

- Molecules of Br_2, C_6H_6, CCl_4, CH_2O and CS_2 are nonpolar.

- Molecules of H_2O, CH_2O and liquid NH_3 are polar.
- KCl is an ionic compound.
- Molecules of H_2O and of CH_2O can form hydrogen bonds.

Predict the solubility in the following cases:

(a) Bromine (Br_2) in benzene (C_6H_6), and in water (H_2O).

(b) Potassium chloride (KCl) in (CCl_4) and in liquid ammonia (NH_3).

(c) Formaldehyde (CH_2O) in carbon disulfide (CS_2), and in water (H_2O).

Solution

(a) Br_2 is a nonpolar molecule. Therefore, it is soluble C_6H_6 more than in H_2O.

(b) KCl is an ionic compound. Therefore, it is soluble in NH_3 more than in CCl_4.

(c) CH_2O is polar and can form hydrogen bonds. Therefore, it is soluble in H_2O which also can form hydrogen bonds, but not in CS_2.

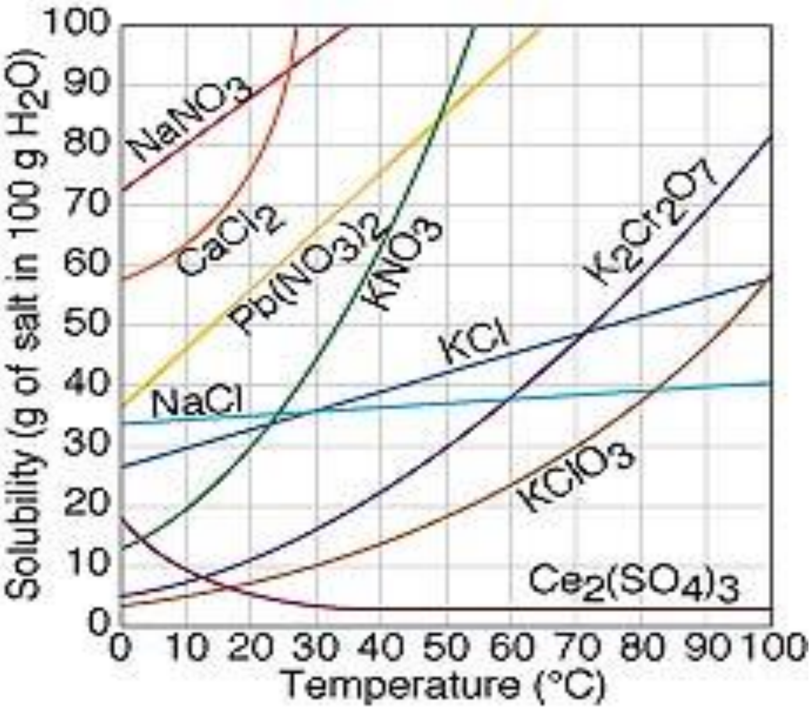
Practice Exercise

Knowing that I_2 and CS_2 are nonpolar and H_2O is polar, is iodine (I_2) more soluble in water or in carbon disulfide (CS_2)?

The effect of temperature on solubility

First: Solid solubility and temperature

- First, let's look and inspect the following figure.



- The figure shows clearly that:

- ✓ Solubility of most ionic solid salts in water increases as temperature increases.
- ✓ Solubility of a few ionic solid salts in water increases as temperature decreases.
- ✓ Solubility of very rare solid salts in water is almost the same at all temperatures.
- ✓ The solubility differs from a salt to another.
- ✓ The solubility for all salts can be determined and compared.

EXAMPLE 6.3

Using the curves of the solubility versus temperature,

1) At 40 °C, which is more soluble KCl or $K_2Cr_2O_7$?
2) At 90 °C, which is more soluble KCl or $K_2Cr_2O_7$?

Solution

1) At 40 °C, KCl is more soluble than $K_2Cr_2O_7$.
2) At 90 °C, $K_2Cr_2O_7$ is more soluble than KCl.

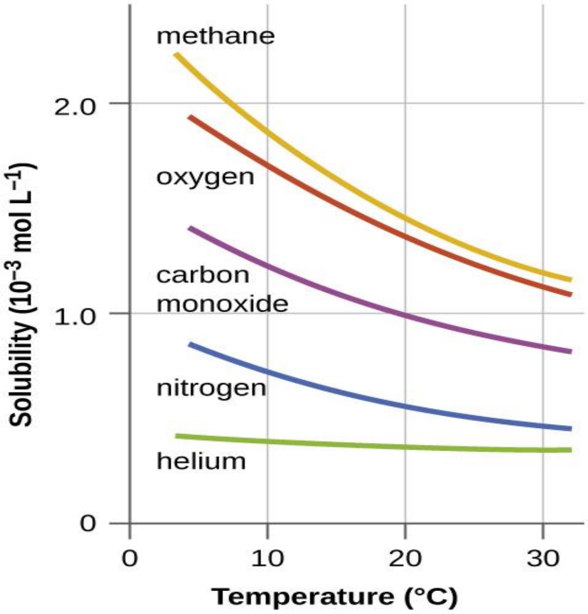
Practice Exercise

Using the curves of the solubility versus temperature,

1) At what temperature will the solubility of KCl equalizes that of $KClO_3$?
2) At 47 °C, the solubility of KNO_3 is 80 g/100 g of water. At what temperature would the solubility of $NaNO_3$ be the same?

Second: Gas solubility and temperature

- Again, let's look and inspect the following figure.



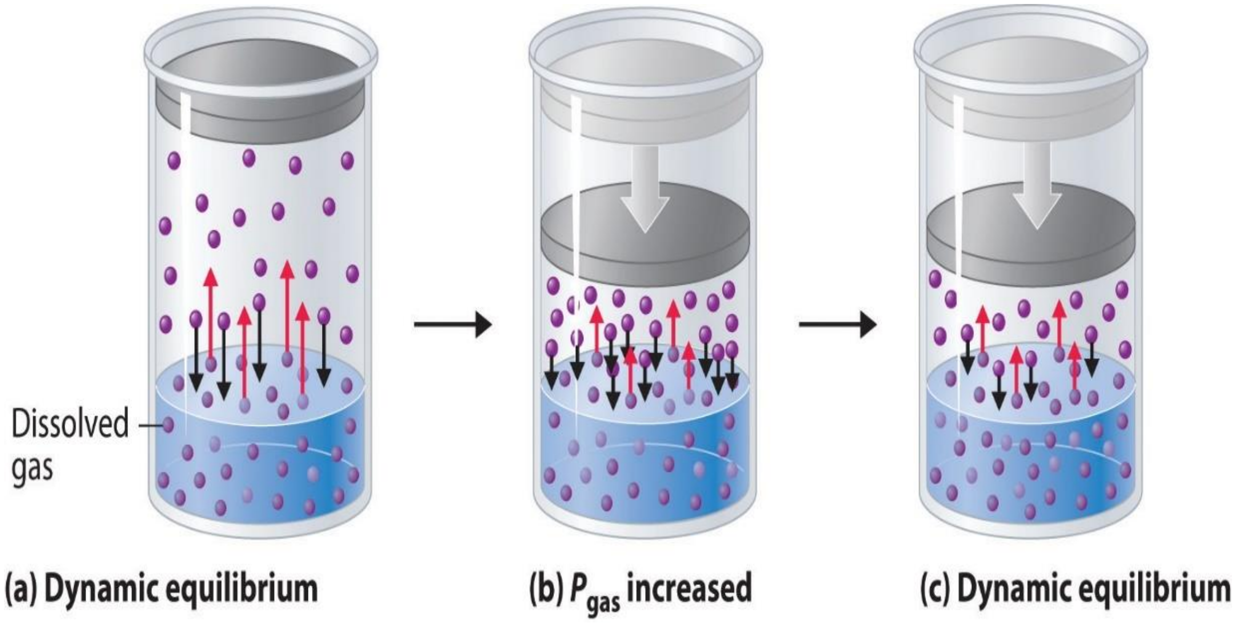
- The figure shows clearly that:
  - ✓ In ***all*** cases and with no single exception, the solubility of any gas decreases as temperature increases.
  - ✓ The solubility differs from a gas to another.
  - ✓ The solubility for all gases can be determined and compared.

The effect of pressure on solubility

- Due to the closeness between particles of solids and of liquids, **pressure has no effect** on the solubility of a liquid in a liquid or a solid in a liquid.
- Due to the spacing between particles of gases, **pressure has a great effect** on the solubility of gases.
- as the following figure shows that as we increase the pressure of the gas above the liquid it is forced to dissolve more.
- The quantitative relationship between gas solubility and pressure is given by ***Henry's law,*** which states that ***the solubility of a gas in a liquid is proportional to the pressure of the gas over the solution***:

$$\mathbf{c = kP}$$

- If several gases are present, P is the partial pressure of each gas.



- In ***Henry's law,*** (c = kP):
  c is the molar concentration (mol/L) of the dissolved gas.

P is the pressure (in atm) of the gas over the solution
k is a constant for each gas and is called ***Henry's constant***.
k differs from gas to another.
k also differs for the same gas from temperature to another.
k units are $\frac{\text{mol}}{\text{L} \times \text{atm}}$.

- Henry's law can be understood qualitatively in terms of a theory called "the kinetic molecular theory of gases".
  - ✓ The amount of gas that will dissolve in a solvent depends on how frequently the gas molecules collide with the liquid surface and become trapped.
  - ✓ A bottle of a refreshment drink is sealed at high pressure of CO_2.
  - ✓ The amount of CO_2 dissolved in these drinks is many times the amount that would dissolve under normal atmospheric pressure.
  - ✓ When the cap of the bottle is removed the excess dissolved CO_2 comes out of solution, causing the effervescence, and the pressure in the bottle falls to atmospheric pressure and the amount of CO_2 remaining in the beverage inside the bottle is then determined only by the normal atmospheric partial pressure of CO_2, 0.0003 atm.
- The following example applies Henry's law to nitrogen gas.

EXAMPLE 6.4

The solubility of nitrogen gas (N_2) in water at 25 °C and 1 atm of N_2 is 6.8×10^{-4} mol/L. What is the molarity of nitrogen dissolved in water under atmospheric conditions? The partial pressure of nitrogen gas in the atmosphere is 0.78 atm.

Solution

$$c = k \times P$$

$$6.8 \times 10^{-4}\ \text{mol/L} = k \times 1\ \text{atm}$$

$$k = \frac{6.8 \times 10^{-4}\ \frac{\text{mol}}{\text{L}}}{1\ \text{atm}} = 6.8 \times 10^{-4}\ \text{mol/L atm}$$

Therefore,

$$c = 6.8 \times 10^{-4}\ \frac{\text{mol}}{\text{L} \times \text{atm}} \times 0.78\ \text{atm} = 5.3 \times 10^{-4}\ \text{mol/L}$$

The decrease in solubility from 6.8×10^{-4} mol/L to 5.3×10^{-4} mol/L is the result of lowering the nitrogen pressure from 1 atm to 0.78 atm.

Practice Exercise

Calculate the molar concentration of oxygen in water at 25°C for a partial pressure of 0.22 atm. The Henry's constant for oxygen is 1.3×10^{-3} mol/L atm.

Concentrations of solutions

- The term concentration is used to designate the amount of solute dissolved in a given quantity of solvent of solution.
- The greater the amount of solute, the more concentrated the resulting solution.
- Below we review the many ways of expressing concentration.
- The concentration units we will discuss are only four:
  Mass percent
  Molality
  Mole fraction
  Molarity
- At the end we will see that ***knowing only one of these concentration units makes all other units able to be calculated.***

Mass percent of solute (Solute%)

- The mass percent of the solute in a solution (**Solute%**) is given by:

$$\textbf{Solute\%} = \frac{\mathbf{m_{solute}}}{\textbf{total mass of solution}} \times \mathbf{10^2}$$

- What does 25% $C_6H_{12}O_6$ solution mean?
  It means that:
  - ✓ Solvent is water and solyte is glucose.
  - ✓ $m_{solution}$ = 100 g.
  - ✓ m_{solute} = 25 g.
  - ✓ $m_{solvent}$ = 75 g.
  - ✓ $n_{solvent}$ and n_{solute} can be calculated.
  - ✓ $V_{solution}$ can be calculated if density of the solution ($d_{solution}$) is given.

Example 6.5

Calculate glucose mass% in a solution containing 131.4 g of glucose in 0.50 kg of water.

Solution

$$\text{Glucose mass\%} = \frac{m_{glucose}}{\text{total mass of solution}} \times 10^2$$

$$\text{Glucose mass\%} = \frac{131.4\ \text{g}}{131.4\ \text{g} + 0.5\ \text{kg} \times 1000\frac{\text{g}}{\text{kg}}} \times 10^2 = 20.81\%$$

Calculate glucose mass% in a solution containing 131.4 of glucose in 0.50 kg of water.

Practice Exercise

A solution is made by dissolving 8.74 g sodium nitrate ($NaNO_3$) in 75.0 g of water. Calculate the mass percent of of sodium nitrate in the solution.

Molality (m)

- Molality (**m**) expresses the concentration of a solution as the number of moles of solute (n_{solute}) in one kilogram of the solvent (solv):

$$\textbf{Molality (m)} = \frac{\mathbf{n_{solute}}}{\mathbf{mass_{solv}(kg)}}$$

- What does 0.25 molal $C_6H_{12}O_6$ solution mean?
  It means that:
  - ✓ Solvent is water and solyte is glucose.
  - ✓ $n_{C_6H_{12}O_6}$ = 0.25 mol.
  - ✓ $m_{solvent}$ = 1 kg = 1000 g.
  - ✓ $n_{solvent}$ can be calculated.
  - ✓ $m_{solution}$ can be calculated.
  - ✓ $V_{solution}$ can be calculated if density of the solution ($d_{solution}$) is given.

Example 6.6

A solution is made by dissolving 4.35 g glucose ($C_6H_{12}O_6$) in 25.0 mL of water. Calculate the molality of glucose in the solution. Water has a density of 1 g/mL.

Solution

$$m_{solvent} = d_{solvent} \times V_{solvent} = 25 \times 1 = 25 \text{ g} = 0.025 \text{ kg}$$

$$\text{molality} = \frac{n_{solute}}{mass_{solv}(kg)} = \frac{\frac{4.35}{180}}{0.025} = 0.097 \text{ molal}$$

Practice Exercise

A solution is made by dissolving 8.74 g sodium nitrate ($NaNO_3$) in 75.0 g of water. Calculate the molality of sodium nitrate in the solution.

Mole fraction (X)

- Mole fraction of a component of a solution ($\mathbf{X_{component}}$) is given by:

$$\mathbf{X_{component}} = \frac{\mathbf{n_{component}}}{\textbf{total moles of componants}} = \frac{\mathbf{n_{component}}}{\mathbf{n_t}}$$

- In a solution of a mole fraction of 0.25 for $C_6H_{12}O_6$, what does $X_{C_6H_{12}O_6}$ mean?
  It means that:
  - ✓ Solvent is water and solyte is glucose.

- ✓ $n_{C_6H_{12}O_6}$ = 0.25 mol.
- ✓ $n_{solvent}$ = 0.75 mol.
- ✓ $m_{C_6H_{12}O_6}$ can be calculated.
- ✓ $m_{solvent}$ can be calculated.
- ✓ $m_{solution}$ can be calculated.
- ✓ $V_{solution}$ can be calculated if density of the solution ($d_{solution}$) is given.

Example 6.7

Calculate the mole fraction of 281 g of glucose ($C_6H_{12}O_6$) in 450 mL aqueous solution ($d_{solution}$ = 0.998 g/mL).

Mass = dencity × volume

Mass of solution = 0.998 g/mL × 450 mL = 449.1 g

Mass of water = 449.1 g – 281 g = 168.1 g

$$n_{glucose} = \frac{m_{glucose}}{M_{glucose}} = \frac{281\ g}{180\frac{g}{mol}} = 1.56\ mol$$

$$n_{water} = \frac{m_{water}}{M_{water}} = \frac{168.1\ g}{18\ \frac{g}{mol}} = 9.34\ mol$$

$$n_t = n_{glucose} + n_{water} = 1.56\ mol + 9.34\ mol = 10.9\ mol$$

$$X_{glucose} = \frac{n_{glucose}}{n_t} = \frac{1.56}{10.9} = 0.143$$

Practice Exercise

A solution is made by dissolving 8.74 g sodium nitrate ($NaNO_3$) in 75.0 g of water. Calculate the mole fraction of sodium nitrate in the solution.

Molarity (M)

- Molarity (**M**) expresses the concentration of a solution as the number of moles of solute (n_{solute}) in one liter of the solution (soln):

$$\textbf{Molarity (M)} = \frac{\mathbf{n_{solute}}}{\mathbf{V_{soln}(L)}}$$

- Unit of molarity is "**mol/L**". mol/L is symbolized "**M**" and called "**molar**". Therefore, "**mol/L**", "**M**", and "**molar**" are all the same.
- What does 0.25 molar $C_6H_{12}O_6$ solution mean?
  It means that:
  - ✓ Solvent is water and solyte is glucose.
  - ✓ $n_{C_6H_{12}O_6}$ = 0.25 mol.
  - ✓ $V_{solution}$ = 1L = 1000 mL.
  - ✓ m_{solute} can be calculated.
  - ✓ $m_{solution}$ can be calculated if density of the solution ($d_{solution}$) is given.

- ✓ $m_{solvent}$ and $n_{solvent}$ can be calculated.

Example 6.8

Calculate the molarity of 19.6 g of glucose ($C_6H_{12}O_6$) in 650 mL aqueous solution.

Solution

$$\text{Molarity} = \frac{n_{solute}}{V_{soln}(L)} = \frac{\frac{19.6\ g}{180\frac{g}{mol}}}{\frac{650\ mL}{1000\frac{mL}{L}}} = 0.168\ \text{mol/L}$$

Practice Exercise

Calculate the molarity of 8.74 g sodium nitrate ($NaNO_3$) in 750 mL aqueous solution.

- **Dilution law**
  - ✓ Solutions used routinely in the laboratory are often purchased or prepared in concentrated form (called stock solutions).
  - ✓ Solutions of lower concentrations can then be prepared by adding water, a process called dilution.
  - ✓ The main point to remember is that when solvent is added to a solution, the number of moles of solute remains unchanged:

The number of moles of solute remains the same
in the concentrated solution and in the in the diluted solution

$$\mathbf{n_{solute,concentrated\ solution} = n_{solute,diluted\ solution}}$$

- ✓ Because:

$$\mathbf{n_{solute,concentrated\ solution} = n_{solute,diluted\ solution}}$$

The dilution law is:

$$\boxed{\mathbf{M_{conc} \times V_{conc} = M_{dil} \times V_{dil}}}$$

- Suppose we want to prepare 250 mL of 0.1 M $CuSO_4$ solution by diluting a 1 M $CuSO_4$ stock solution:

$$\mathbf{n_{solute,diluted\ solution} = n_{solute,diluted\ solution}}$$

$$\mathbf{M_{conc} \times V_{conc} = M_{dil} \times V_{dil}}$$

$$\mathbf{1 \times V_{conc} = 0.1 \times 250}$$

$$\mathbf{V_{conc} = 25\ mL}$$

- The procedure is to take 25 mL from the 1 M CuSO4 stock solution and add water to it until the volume becomes 250 mL. the resultant solution is 0.1 molar.

Example 6.9

How many milliliters of 3.0 M H_2SO_4 are needed to make 450 mL of 0.1 M

H_2SO_4?

Solution

$$M_{conc} \times V_{conc} = M_{dil} \times V_{dil}$$
$$3\ \text{mol/L} \times V_{conc} = 0.1\ \text{mol/L} \times 450\ \text{mL}$$
$$V_{conc} = 15\ \text{mL}$$

Practice Exercise

Calculate the molarity of a sodium nitrate ($NaNO_3$) solution which was prepared by diluting 15 mL of a 5.5 mol/L $NaNO_3$ stock solution to a volume equals to 150 mL.

Example 6.10

How many milliliters of water must be added to 60 mL of 18 M HCl to get a solution tha is 0.2 M?

Solution

$$M_{conc} \times V_{conc} = M_{dil} \times V_{dil}$$
$$18 \times 60 = 0.2 \times V_{dil}$$
$$V_{dil} = 5400\ \text{mL}$$
$$V_{dil} = V_{conc} + V_{water}$$
$$5400 = 60 + V_{water}$$
$$V_{water} = 5340\ \text{mL}$$

Practice Exercise

How many milliliters of water must be added to 15 mL of 5.5 mol/L $NaNO_3$ stock solution to get a solution that is 0.15 mol/L?

Interconversion between concentration's units

- The above discussion is an illustration to the main four types of concentration units: solute mass%, molality, mole fraction and molarity.
- The following exercises shows that knowing one of these four types enables us to calculate the other three.

Example 6.11

An aqueous solution of hydrochloric acid contains 36% HCl by mass:

a) Calculate the mole fraction of HCl.

b) Calculate the molality of HCl.

Solution

a) $n_{solute} = \frac{m_{solute}}{M_{solute}} = \frac{36\ g}{36.45\ \frac{g}{mol}} = 0.988\ \text{mol}$

$m_{solvent} = 100 - 36 = 64\ g$

$n_{solvent} = \frac{m_{solvent}}{M_{solvent}} = \frac{64}{18} = 3.556\ \text{mol}$

$$X_{solute} = \frac{n_{solute}}{n_t} = \frac{0.988\ mol}{0.988\ mol + 3.556\ mol} = 0.217$$

b) $m = \frac{n_{solute}}{mass_{solv}(kg)} = \frac{0.988\ mol}{0.064\ kg} = 15.44$ molal

Practice Exercise

Calculate the molality of a sodium nitrate ($NaNO_3$) aqueous solution in which the mass percent of $NaNO_3$ is 43%.

Example 6.12

A solution with a density of 0.876 g/mL contains 5.0 g of toluene (C_7H_8) and 225 g of benzene. Calculate the molality and molarity of the toluene solution.

Solution

$$n_{solute} = \frac{m_{solute}}{M_{solute}} = \frac{5\ g}{92\frac{g}{mol}} = 0.054\ mol$$

$$m = \frac{n_{solute}}{mass_{solv}(kg)} = \frac{0.054\ mol}{0.225\ kg} = 0.34\ molal$$

$$V_{soln} = \frac{m_{son}}{d_{soln}} = \frac{5\ g + 225\ g}{0.876\frac{g}{mL}} = 262.56\ mL = 0.263\ L$$

$$Molarity = \frac{n_{solute}}{V_{soln}(L)} = \frac{0.054\ mol}{0.263\ L} = 0.205\ molar$$

Practice Exercise

A solution with a density of 0.998 g/mL contains 281 g of glucose ($C_6H_{12}O_6$) and 168.1 g of water. Calculate the molality and molarity of the glucose solution.

Example 6.14

Calculate the glucose mass% in a 0.73 molal solution of glucose in water.

Solution

$$Glucose\% = \frac{m_{glucose}}{total\ mass\ of\ solution} \times 10^2$$

$$n_{glucose} = 0.73\ mol \qquad ,, \qquad m_{water} = 1\ kg = 1000\ g$$

$$m_{glucose} = n_{glucopse} \times M_{glucose} = 0.73 \times 180 = 131.4\ g$$

$$m_{solution} = m_{glucose} + m_{water} = 131.4 + 1000 = 1131.4\ g$$

$$Solute\% = \frac{131.4}{1131.4} \times 10^2 = 11.61\%$$

Practice Exercise

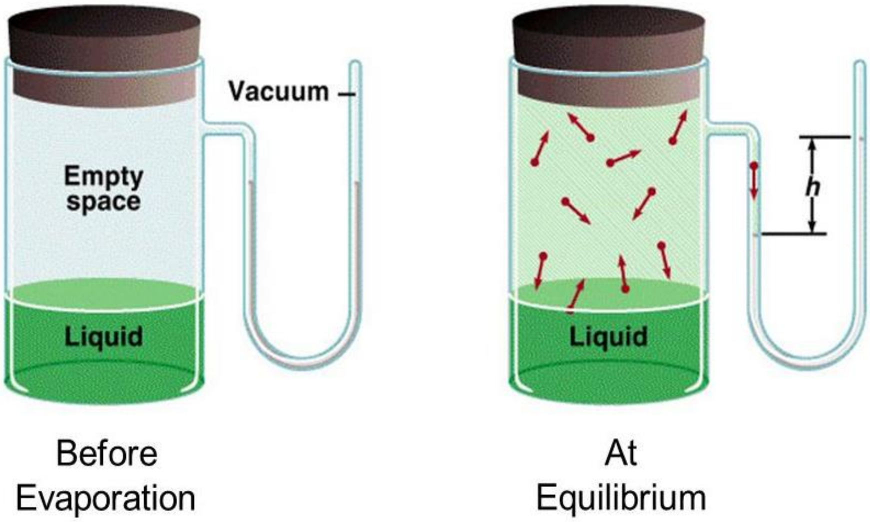
If the molality of a solution of urea (NH_2CONH_2) in water is 0.14 mol/kg, calculate the mass percent of urea in the solution.

THE PROPERTIES OF A PURE LIQUID CHANGE WHEN IT BECOMES NOT BURE

Vapor pressures, boiling points, and freezing points of <u>pure liquids</u>

Vapor pressures of <u>pure liquids</u>

- Let's look and inspect the following figure.



- The liquid molecules that evaporate become gaseous molecules and are called "**vapor**" and they exert a pressure called "**vapor pressure**".
- The only liquid molecules that can escape (free themselves) from its liquid state and become gaseous (vapor) are those which are at the surface of the liquid, and at the same time having the highest energies and speeds.
  - ✓ Any liquid molecule that does not have high energy and speed will not vaporize even if it is at the surface of the liquid.
  - ✓ Any liquid molecule that is not at the surface of the liquid will not vaporize even if it has high energy and speed.
- Increasing temperature increases not only the energy and speed of molecules but also increases the number of molecules having high energy and speed. Therefore, ***as temperature increases vapor pressure increases***.
- The figure above shows that before the evaporation process starts, the mercury levels in the U-shaped manometer tube are equal.
- As soon as some molecules leave the liquid, a vapor phase is established and its pressure is called ***the vapor pressure***.
- However, the process of evaporation does not continue indefinitely. Eventually, the mercury levels stabilize and no further changes in pressure are seen.

- As the concentration of molecules in the vapor phase increases, some molecules start to *condense from the gas phase to the liquid phase*.
- Vapor molecules differ in their energies and speeds.
- The only vapor molecules that can condense back to liquid (trapped by the liquid molecules at the liquid surface) are those which collide the surface of the liquid, and at the same time having the lowest energies and speeds.
    - ✓ Any vapor molecule that does not have low energy and speed will not condense even if it collides the surface of the liquid.
    - ✓ Any vapor molecule that does not collide the surface of the liquid will not condense even if it has low energy and speed.
- As condensation rate rises evaporation rate falls down until the two rates become equal.
- When the two rates become equal we say that a state of ***dynamic equilibrium*** is reached.
- The *vapor pressure measured when this dynamic equilibrium exists between condensation and evaporation* is called ***equilibrium vapor pressure***. We often use the simpler term "***vapor pressure***" when we talk about the equilibrium vapor pressure of a liquid.
- It is important to note that the equilibrium vapor pressure is the *maximum* vapor pressure of a liquid at a given temperature and that it is constant at a constant temperature.
- Remember that the vapor pressure of a liquid increases with temperature.
- Vapor pressure of liquids at different temperatures are available in tables achieved by physicists and chemists.

Boiling points of <u>pure liquids</u>

- As cleared out above, when liquid temperature increases its vapor pressure increases.
- When the temperature increases to a ***certain temperature*** the vapor pressure of the liquid will equalize the external pressure
- At this ***certain temperature*** the whole liquid molecules become in a situation of transition from the liquid state to the gaseous state.
- When all molecules are in the situation of transition to the gaseous state, the surface of the liquid disappears.
- This particular situation of evaporation at this ***certain temperature*** is given a particular name. It is called ***boiling***.
- This ***certain temperature*** is also given a particular name, it is called "***the boiling point***."

- If the external pressure is the standard pressure (1 atm) it is called "***the standard boiling point***."
- The value of this particular temperature is directly proportional to the external pressure.
  - ✓ If the external pressure is the standard pressure the boiling point is the standard boiling point (for example, it is 100 °C for water).
  - ✓ If the external pressure is higher than standard pressure the boiling point becomes higher than standard boiling point (for example, if the external pressure is 1.5 atm water will not boil before its temperature reaches 110.5 °C).
  - ✓ If the external pressure is lower than standard pressure the boiling point becomes lower than standard boiling point (for example, if the external pressure is 0.4 atm water will boil once its temperature reaches 84 °C).
- Off course, the value of this particular temperature differs from liquid to liquid.
- The liquid which vaporizes easier has the lesser boiling point and vice versa.

Freezing points of <u>pure liquids</u>

- Decreasing the temperature of liquid molecules will decrease their energies and speeds.
- As the energies and speeds of the liquid molecules decrease the attraction forces between them increase.
- At a ***certain temperature***, the liquid molecules start to be tightly bonded to their neighboring molecules and cannot leave each other. When this starts to happen, we say: liquid ***freezes***.
- We call the temperature at which the liquid freezes "***the freezing point***."
- If the liquid freezes at the standard pressure (1 atm) it is called "***the standard freezing point***."

Vapor pressures of mixed liquids (Raoult's law)

- Here we do not have a **<u>pure liquid</u>**.
- Suppose we have two liquids, A and B, and the number of moles we have are n_A and n_B.
- Also, suppose that the forces of attractions between the particles of both liquids are of the same type.
- When both of them are pure, we will symbolize their vapor pressure as P_A° and P_B°.
- When they are not pure but mixed together, we will symbolize their vapor pressure as P_A and P_B.

- If we mix the n_A mole of A with the n_B mole of B, we will get a liquid solution with a known molar fraction of each, X_A and X_B.
- The question now is: "***what is the value of the vapor pressure of the solution?* (P$_{soln}$)**"
- "Raoult" had proven that:

$$P_{soln} = P_A + P_B$$

$$(P_A = X_A \times P^{\circ}_A) \qquad \text{and} \qquad (P_B = X_B \times P^{\circ}_B)$$

Therefore, he proved that:

$$P_{soln} = (X_A \times P^{\circ}_A) + (X_B \times P^{\circ}_B)$$

Because it is known that $X_A + X_B = 1$, the last equation can be modified to be:

$$P_{soln} = X_A \times (P^{\circ}_A - P^{\circ}_B) + P^{\circ}_B$$

OR

$$P_{soln} = X_B \times (P^{\circ}_B - P^{\circ}_A) + P^{\circ}_A$$

- All of these previous equations are known as ***Raoult's law***.
- Raoult's law is applicable only if ***the forces of attractions between the particles of the mixed liquids are of the same type***.
- Any solution obeys Raoult's law is called "***ideal solution***"; if not it is called "***nonideal solution***".
- Nonideal solution will not be discussed.

The colligative properties of liquid solutions

Vapor pressures, boiling points, and freezing points of nonpure liquids

IN OUR DISCUSSION HERE,
THE SOLUTES ARE STRICTLY *NONVOLATILE* AND *NONELECTROLYTIC*.

- ***Colligative properties*** (or collective properties) are *properties of the solution that depend only on the number of solute particles and* **not** *on their nature*.
- These properties are four:
  Vapor pressures
  Boiling points
  Freezing points
  Osmotic pressures

- Suppose we have a known amount of a liquid solvent, and a known amount of a nonvolatile and nonelectrolytic solute; and suppose we make a solution of this solute in this solvent.

  Below, we will see what happens to the ***vapor pressure***, ***boiling point*** and ***freezing point*** of the liquid. We will explain also the ***osmotic pressure*** of the solution.

Vapor-pressure lowering

- The vapor above the solution is the vapor of only the solvent.
- We can calculate the molar fractions ($X_{solvent}$ and X_{solute}).
- The question now is: "***what is the value of the vapor pressure of the solution* (P_{soln})*?***".
- When the solvent was pure its vapor pressure was $P^{\circ}_{solvent}$. However, the solvent molecules after dissolving solute particles, become attached to the solute particles. These attachments hinder the evaporation of the solvent particles which in turn makes the vapor pressure of the liquid lower than its value when it was pure by an amount of **ΔP** which is called "***vapor pressure lowering***".
- The lowering of the vapor pressure by an amount equals to (ΔP) depends solely on the amount of the solute.
- According to Raoult's law:

$$P_{solvent} = X_{solvent} \times P^{\circ}_{solvent}$$

- Because the vapor pressure of the solution belongs only to the vapor pressure of the solvent, P_{soln} is P_A. Therefore,

$$P_{soln} = X_{solvent} \times P^{\circ}_{solvent}$$
$$P_{soln} = (1 - X_B) \times P^{\circ}_{solvent}$$
$$P_{soln} = P^{\circ}_{solvent} - (X_B \times P^{\circ}_{solvent})$$
$$P^{\circ}_{solvent} - P_{soln} = X_B \times P^{\circ}_{solvent}$$
$$\Delta P = X_B \times P^{\circ}_{solvent}$$

- The presence of this kind of solutes makes the vapor pressure of the solution less than that when solvent was pure by a value equals to ΔP which depends on the amount of the solute in the solution. Therefore, ΔP is a ***colligative property***.

EXAMPLE 6.15

Calculate the vapor pressure of a solution made by dissolving 218 g of glucose (molar mass = 180.2 g/mol) in 460 mL of water at 30 °C. What is the vapor-pressure lowering? The vapor pressure of pure water at 30 °C is 31.82 torr.

Assume the density of the solution is 1.00 g/mL.

Solution

$n_{water} = \frac{460\text{ g}}{18.016\,\frac{\text{g}}{\text{mol}}} = 25.53\text{ mol}$	$n_{glucose} = \frac{218\text{ g}}{180.15\,\frac{\text{g}}{\text{mol}}} = 1.21\text{ mol}$
$X_{water} = \frac{25.5\text{ mol}}{25.5\text{ mol} + 1.21\text{ mol}} = 0.995$	

$$P_{soln} = X_{solvent} \times P^{\circ}_{solvent}$$

$$P_{soln} = 0.995 \times 31.82\text{ mmHg} = 30.4\text{ mmHg}$$

$$\Delta P = P^{\circ}_{solvent} - P_{soln} = 31.82\text{ mmHg} - 30.4\text{ mmHg} = 1.42\text{ mmHg}$$

Practice Exercise

Calculate the vapor pressure and the vapor-pressure lowering at 35°C of a solution of 82.4 g of urea in 212 mL of water. (P°_{water}= 42.2 mmHg).

Boiling point elevation

- ***Boiling point*** *is the temperature at which the vapor pressure of the liquid equalizes the external pressure.*
- ***Standard boiling point*** *(*t°_{b}*)is the temperature at which the vapor pressure of the liquid equalizes the standard external pressure (= 1 atm).*
- As mentioned above, the vapor pressure of the solution became less than that of the pure liquid.
- So, the vapor pressure of the solution at the boiling point of the pure liquid will be less than that needed for boiling.
- So, we will find that the temperature at which the vapor pressure of the solution equalizes the external pressure is elevated by a certain value (ΔT_b).
- The value of ΔT_b is proportional to the solution molality (m):

$$\Delta T_b \propto m$$

$$\Delta T_b = K_b\, m$$

- K_b is the ***molal boiling-point elevation constant***; its value differs from liquid to another.

$$\Delta T_b = \frac{K_b \times n_{solute}}{m_{solvent}\,(kg)}$$

$$\Delta T_b\,(^{\circ}C) = \frac{K_b\left(\frac{^{\circ}C}{\frac{mol}{kg}}\right) \times \frac{m_{solute}\,(kg)}{M_{solute}\,\left(\frac{kg}{mol}\right)}}{m_{solvent}\,(kg)} = \frac{K_b\left(\frac{^{\circ}C\,kg}{mol}\right) \times m_{solute}\,(g) \times 1000\,\left(\frac{g}{kg}\right)}{M_{solute}\left(\frac{g}{mol}\right) \times m_{solvent}\,(g)}$$

$$\Delta T_b = \frac{K_b \times m_{solute} \times 1000}{M_{solute} \times m_{solvent}}$$

Freezing point depression

- ***Freezing point*** *is the temperature at which the liquid substance changes its state to solid.*

- ***Standard freezing point*** (t_f°) *is the temperature at which liquid substance changes its state to solid at the standard external pressure (= 1 atm).*
- As mentioned above, at a particular low temperature, the liquid molecules start to be tightly bonded to their neighboring molecules and cannot leave each other, and once this starts to happen, we say: liquid freezes.
- But because the liquid we have here is not pure but contains a solute that is nonvolatile, its molecules cannot bond to each other at the same temperature when the liquid is pure.
- Temperature of the solution must be lowered by a certain value (ΔT_f) in order to freeze.
- The value of ΔT_f is proportional to the solution molality (m):

$$\Delta T_f \propto m$$

$$\Delta T_f = K_f\, m$$

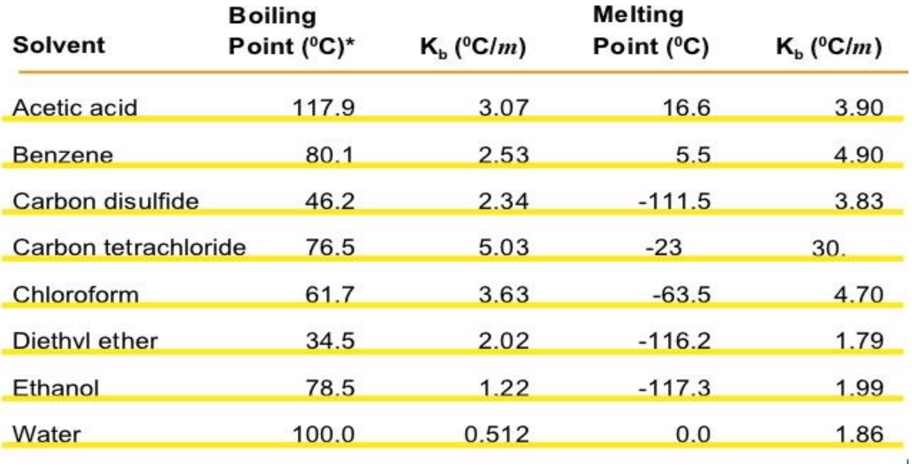
- K_f is the ***molal freezing-point depression constant***; its value differs from liquid to another.

$$\Delta T_f = \frac{K_f \times n_{solute}}{m_{solvent}\,(kg)}$$

$$\Delta T_f\,(^oC) = \frac{K_f\,(\frac{\frac{^\circ C}{mol}}{kg}) \times \frac{m_{solute}\,(kg)}{M_{solute}\,(\frac{kg}{mol})}}{m_{solvent}\,(kg)} = \frac{K_f\left(\frac{^\circ C\ kg}{mol}\right) \times m_{solute}\,(g) \times 1000\,(\frac{g}{kg})}{M_{solute}\left(\frac{g}{mol}\right) \times m_{solvent}\,(g)}$$

$$\Delta T_f = \frac{K_f \times m_{solute} \times 1000}{M_{solute} \times m_{solvent}}$$

- In addition to the standard freezing points of some common liquids (t_f°), the table provided above gives their molal freezing point elevation constant (K_f).
- In addition to the standard boiling (t_b°) and the standard freezing points (t_f°) of some common liquids, the table below also gives their molal boiling point elevation constant (K_b) and their molal freezing point depression constant (K_f).



Solvent	Boiling Point (ºC)*	K_b (ºC/*m*)	Melting Point (ºC)	K_b (ºC/*m*)
Acetic acid	117.9	3.07	16.6	3.90
Benzene	80.1	2.53	5.5	4.90
Carbon disulfide	46.2	2.34	-111.5	3.83
Carbon tetrachloride	76.5	5.03	-23	30.
Chloroform	61.7	3.63	-63.5	4.70
Diethyl ether	34.5	2.02	-116.2	1.79
Ethanol	78.5	1.22	-117.3	1.99
Water	100.0	0.512	0.0	1.86

EXAMPLE 6.16

Ethylene glycol, $CH_2(OH)CH_2(OH)$, is an automobile antifreeze. It is water soluble and nonvolatile. (Molar mass = 62.01 g/mol).

(a) Calculate the boiling point and the freezing point of a solution containing 651 g of this substance in 2505 g of water.

(b) Would you keep this substance in your car radiator during the summer?

$T^{\circ}_{\text{freezing,water}} = 0\ °\text{C}$ and $T^{\circ}_{\text{boiling,water}} = 100\ °\text{C}$

$K_{f,\text{water}} = 1.86\ °\text{C/m}$ and $K_{b,\text{water}} = 0.52\ °\text{C/m}$

Solution

$$\text{molality} = \frac{n_{\text{solute}}}{m_{\text{solvent}}\ (\text{kg})} = \frac{\frac{m_{\text{solute}}}{M_{\text{solute}}}}{m_{\text{solvent}}\ (\text{kg})} = \frac{\frac{651\ \text{g}}{62.01\frac{\text{g}}{\text{mol}}}}{2505\ \text{g} \times 10^{-3}\ \frac{\text{kg}}{\text{g}}} = 4.19\ \text{mol/kg}$$

(a)

$$\mathbf{\Delta T_b = K_b\ m}$$

$$\Delta T_b = 0.52\ °\text{C/m} \times 4.19\ \text{m} = 2.2\ °\text{C}$$

$$\Delta T_b = T_{b,\text{solution}} - T^{\circ}_{b,\text{water}}$$

$$2.2\ °\text{C} = T_{b,\text{solution}} - 100\ °\text{C}$$

$$T_{b,\text{solution}} = 102.2\ °\text{C}$$

$$\mathbf{\Delta T_f = K_f\ m}$$

$$\Delta T_f = 1.86\ °\text{C/m} \times 4.19\ \text{m} = 7.8\ °\text{C}$$

$$\Delta T_f = T^{\circ}_{f,\text{water}} - T_{f,\text{solution}}$$

$$7.8\ °\text{C} = 0\ °\text{C} - T_{f,\text{solution}}$$

$$T_{f,\text{solution}} = -\ 7.8\ °\text{C}$$

(b) Because the solution will boil at 102.2 °C, it would be preferable to leave the antifreeze in my car radiator in summer to prevent the solution from boiling.

Practice Exercise

Calculate the boiling point and the freezing point of a solution containing 478 g of ethylene glycol in 3202 g of water.

EXAMPLE 6.17

A 7.85-g sample of a compound with the empirical formula C_5H_4 is dissolved in 301 g of benzene. The freezing point of the solution is 1.05 °C below that of pure benzene. What are the molar mass and molecular formula of this compound?

Solution

$$\Delta T_f = \frac{K_f\ \frac{°\text{C kg}}{\text{mol}} \times m_{\text{solute}}\ (\text{g}) \times 1000 \frac{\text{g}}{\text{kg}}}{M_{\text{solute}} \left(\frac{\text{g}}{\text{mol}}\right) \times m_{\text{solvent}}\ (\text{g})}$$

$$1.05\ °\text{C} = \frac{5.12\ \frac{°\text{C kg}}{\text{mol}} \times 7.85\ (\text{g}) \times 1000\ (\frac{\text{g}}{\text{kg}})}{M_{\text{solute}} \times 301\ (\text{g})}$$

$$M_{\text{solute}} = 127 \text{ g/mol}$$

$$\text{Empirical formula molar mass} = (5 \times 12.02) + (4 \times 1.008) = 64 \text{ g/mol}$$

$$\frac{\text{empirical formula molar mass}}{\text{real formula molar mass}} = \frac{127\,\frac{\text{g}}{\text{mol}}}{64\,\frac{\text{g}}{\text{mol}}} = 1.98$$

$$\text{Molecular formula} = 2 \times \text{empirical formula} = 2 \times C_5H_4 = C_{10}H_8$$

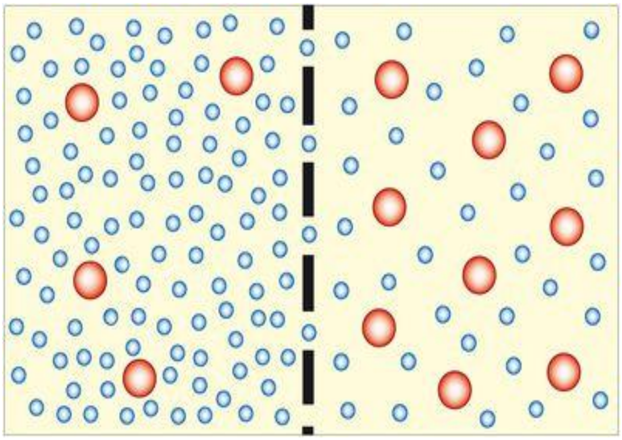
Practice Exercise

A solution of 0.85 g of an organic compound in 100.0 g of benzene (t_f° = 5.5 °C, K_f = 5.12 $\frac{°C\ kg}{mol}$) has a freezing point of 5.16 °C. What are the molar mass of the solute and the molality of the solution?

Osmotic pressure

Semipermeable membranes

- Old way to cool water is to put it in a pottery pot similar to the one shown in the figure below.
- The walls of the pottery pot permits water inside the pot to pass through its walls. This allows water to be in contact with the colder atmosphere outside the pot. This way was one of the ancient technologies to cool drinking water. these walls do not allow other substances such as ions of other materials to pass through. It only allows water.

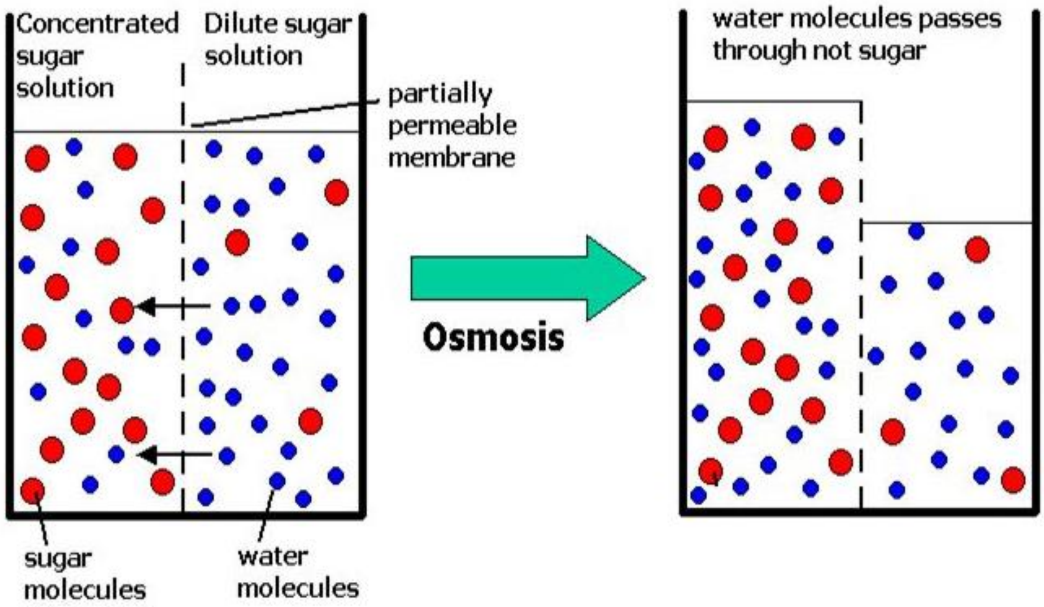


- Cells' wall of the living creatures is depicted in the figure below.
- These walls allow the passage of water from outside to inside and vice versa but not any other materials.
- Walls of the pottery pot and of the cells of living creatures are named "semipermeable membranes".
- Any ***semipermeable membrane*** allows the passage of solvent molecules but blocks the passage of any solute molecules.

The osmosis phenomenon

***Osmosis** is the selective passage of solvent molecules through a porous membrane or a wall from a dilute solution to a more concentrated one.*

- First look and inspect the following figure.



- At the middle, there is a ***semipermeable membrane***.
- Into each compartment a sugar solution is poured.
- The volume and temperature of the two sugar solutions are the same but their concentrations are not.
- The pressure of water on the right side of the membrane is more than its pressure on the left side.
- The amount of water passing through the membrane from right to left will be more than that from left to right.
- The surface of the solution in the left side will rise up and that of the right side will falls down.
- Eventually, equilibrium is reached, that is when amounts water passing through both sides are the same.
- Once this happens the two pressures exerted on both sides of the membrane become equal.
- The name of this pressure is ***osmotic pressure*** and its symbol is **π**.
- **The *osmotic pressure (π)* of a solution is *the pressure required to stop osmosis*.**
- This osmotic pressure of the solution is calculated by the following equation:

$$\boldsymbol{\pi = M \times R \times T}$$

M is the molarity of the solution and T is the temperature.

$$\text{Molarity} = \frac{\text{number of moles of solute}}{\text{Volume of solution in liter}}$$

Therefore,

$$\boldsymbol{\pi} = \frac{n}{V} \times R \times T$$

$$\boldsymbol{\pi \times V = n \times R \times T}$$

EXAMPLE 6.18

Calculate the molar concentration of an aqueous solution of sucrose ($C_{12}H_{22}O_{11}$) that has an osmotic pressure of 30.0 atm at 25 °C.

Solution

$$M = \frac{\pi}{R \times T} = \frac{30\ \text{atm}}{0.0821\ \frac{\text{atm L}}{\text{mol K}} \times 298\ \text{K}} = 1.23\ \text{mol/L}$$

Practice Exercise

What is the osmotic pressure (in atm) of a 0.884 M urea solution at 16 °C?

EXAMPLE 6.19

A I L of hemoglobin solution contains 35.0 g of hemoglobin. The osmotic pressure is 10.0 mmHg at 25 °C, calculate the molar mass of hemoglobin.

Solution

$$M = \frac{\pi}{R \times T} = \frac{10\ \text{mmHg} \times \frac{1\ \ \text{atm}}{760\ \text{mmHg}}}{0.0821\ \frac{\text{atm L}}{\text{mol K}} \times 298\ \text{K}} = 5.38 \times 10^{-4}\ \text{mol/L}$$

$$n_{\text{Hb}} = M \times V\ (L) = 5.38 \times 10^{-4}\ \text{mol/L} \times \text{I L} = 5.38 \times 10^{-4}\ \text{mol}$$

$$M_{\text{Hb}} = \frac{m_{\text{Hb}}}{n_{\text{Hb}}} = \frac{35\ \text{g}}{5.38 \times 10^{-4}\ \text{mol}} = 6.51 \times 10^{4}\ \text{g/mol}$$

Practice Exercise

A 202-mL benzene solution containing 2.47 g of an organic polymer has an osmotic pressure of 8.63 mmHg at 21 °C. Calculate the molar mass of the polymer.

SOLUTIONS OF PRACICE EXERCISES

QUESTIONS AND PROBLEMS

Revie questions

1. Distinguish between unsaturated and saturated solutions.
2. Use the dissolution of a solid in a liquid as an example to describe the solution process at the molecular level.
3. Provide a molecular interpretation for the difference between endothermic and exothermic solution processes.
4. How do the solubility of most ionic compounds in water change with temperature? And with pressure?
5. Discuss the factors that influence the solubility of a gas in a liquid.
6. What is Henry's law? Define each term in the equation, and give its units.
7. A student is observing two beakers of water. One beaker is heated to 30 °C, and the other is heated to 100 °C. In each case, bubbles form in the water. Are these bubbles of the same origin? Explain.
8. Write the equation representing Raoult's law, and express it in words.
9. Use a solution of benzene in toluene to explain what is meant by an ideal solution. Write the equations relating boiling-point elevation and freezing-point depression to the concentration of the solution. Define all the terms, and give their units.
10. How is vapor-pressure lowering related to a rise in the boiling point of a solution?
11. What is osmosis? What is a semipermeable membrane?
12. Write the equation relating osmotic pressure to the concentration of a solution. Define all the terms and specify their units.
13. Explain why molality is used for boiling-point elevation and freezing-point depression calculations and molarity is used in osmotic pressure calculations.
14. Describe how you would use freezing-point depression and osmotic pressure measurements to determine the molar mass of a compound. Why are boiling-point elevation and vapor-pressure lowering normally not used for this purpose?

Problems

15. The solubility of KNO_3 in 100 g of water at 75 °C is 155 g and at 25 °C is 38.0 g. What mass (in grams) of KNO_3 will crystallize out of solution if exactly 100 g of its saturated solution at 75°C is cooled to 25°C?
16. Calculate the mass of KI in grams required to prepare 5.00×10^2 mL of a 2.80 M solution.

17. How many moles of $MgCl_2$ are present in 60.0 mL of 0.100 M $MgCl_2$ solution?
18. Calculate the molarity of each of the following solutions 29.0 g of ethanol (C_2H_5OH) in 545 mL of solution.
19. Calculate the volume in mL of a solution required to provide the following 2.14 g of sodium chloride from a 0.270 M solution.
20. How many grams of solutes would be needed to make 2.50×10^2 mL of a 0.100 M solution cesium iodide (CsI).
21. A miner working 260 m below sea level opened a carbonated soft drink during a lunch break. To his surprise, the soft drink tasted rather “flat.” Shortly afterward, the miner took an elevator to the surface. During the trip up, he could not stop belching. Why?
22. The solubility of N_2 in blood at 37 °C and at a partial pressure of 0.80 atm is 5.6×10^{-4} mol/L. A deep-sea diver breathes compressed air with the partial pressure of N_2 equal to 4.0 atm. Assume that the total volume of blood in the body is 5.0 L. Calculate the amount of N_2 gas released (in liters at 37 °C and 1 atm) when the diver returns to the surface of the water, where the partial pressure of N_2 is 0.80 atm.
23. How many grams of sucrose ($C_{12}H_{22}O_{11}$) must be added to 552 g of water to give a solution with a vapor pressure 2.0 mmHg less than that of pure water at 20 °C? (The vapor pressure of water at 20 °C is 17.5 mmHg.)
24. The vapor pressures of ethanol (C_2H_5OH) and 1-propanol (C_3H_7OH) at 35 °C are 100 mmHg and 37.6 mmHg, respectively. Assume ideal behavior and calculate, at 35 °C, the partial pressures of each over a solution of both, in which the mole fraction of ethanol is 0.300.
25. How many grams of urea [$(NH_2)_2CO$] must be added to 450 g of water to give a solution with a vapor pressure 2.50 mmHg less than that of pure water at 30 °C? (The vapor pressure of water at 30°C is 31.8 mmHg.)
26. The analysis of gum arabic (a substance used in adhesives, inks, and pharmaceuticals) showed that it contained 40.0% C, 6.7 % H, and 53.3 % O. A solution of 0.650 g of it in 27.8 g of the diphenyl gave a freezing-point depression of 1.56 °C. Calculate the molar mass and molecular formula of the solid. (K_f for diphenyl is 8.00 °C/m.)
27. A solution of 2.50 g of a compound having the empirical formula C_6H_5P in 25.0 g of benzene is observed to freeze at 4.3 °C. Calculate the molar mass of the solute and its molecular formula. (Freezing point of benzene is 5.5 °C)
28. A solution containing 0.8330 g of a polymer of unknown structure in 170.0 mL of an organic solvent was found to have an osmotic pressure of 5.20 mmHg at 25 °C. Determine the molar mass of the polymer.

29. A solution of 6.85 g of a carbohydrate in 100.0 g of water has a density of 1.024 g/mL and an osmotic pressure of 4.61 atm at 20.0 °C. Calculate the molar mass of the carbohydrate.