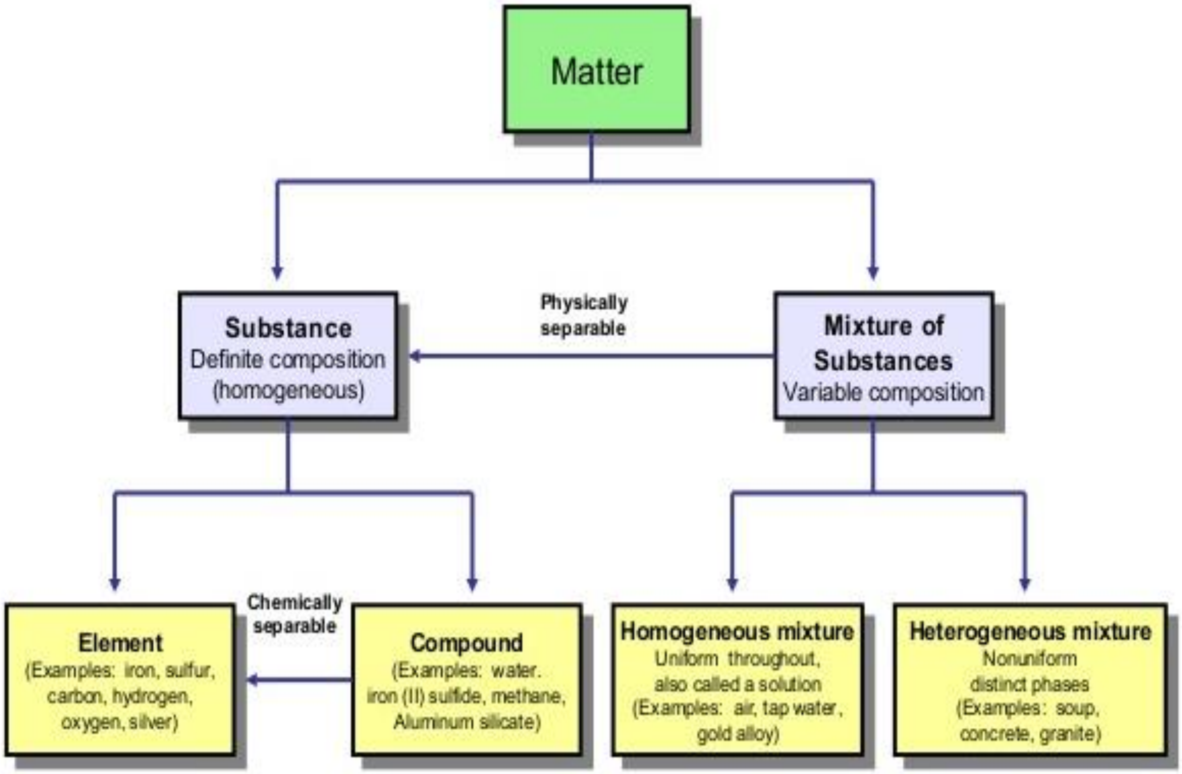
1. MATTER AND MEASUREMENTS

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 and molecules.

1.1.1 Classifications of matter

The following figure summarizes how chemists classify matter.


Matter
Substance
Definite composition
(homogeneous)
Physically
separable
Mixture of
Substances
Variable composition
Element
(Examples: iron, sulfur,
carbon, hydrogen,
oxygen, silver)
Chemically
separable
Compound
(Examples: water.
iron (II) sulfide, methane,
Aluminum silicate)
Homogeneous mixture
Uniform throughout,
also called a solution
(Examples: air, tap water,
gold alloy)
Heterogeneous mixture
Nonuniform
distinct phases
(Examples: soup,
concrete, granite)

First: 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. Substances are 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.

  Symbols of elements: Elements are given symbols that indicate their names:
  - Most of the symbols of elements comes from their English names symbol of carbon is "C" and of oxygen is "O". The symbols of some elements are derived from their Latin names. For example, symbols of gold, iron and sodium are "Au" from *aurum*, "Fe" from *ferrum* and "Na" from *natrium*
  - 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 periodic table contains the names and symbols of all elements
- **Compounds:** A ***compound, is*** *a substance composed of atoms of two or more elements chemically united in fixed proportions.* 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 *hydrogens* and one *oxygen* regardless of where it comes from Saudi Arabia, China, or Mars. Unlike mixtures, compounds can be separated only by chemical means into their pure components.

  Formulas of compounds: Compounds are given formulas that indicate their names:
  - Formula of a compound consists of the symbols of the elements that constitutes the compound. For example, when carbon and oxygen react with each other they, under certain conditions, form a compound that is named "carbon monoxide" and given the formula "CO". However, different conditions they form a different compound that is named "carbon dioxide" and given a different formula "CO_2"
  - The way compounds are named and their formulas are written depends on rules that are well formulated
  - Rules of naming compounds and writing their formula will be discussed in the second chapter

Second: 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:

- **Homogeneous mixture:** A Homogeneous mixture is a mixture in which the composition of the mixture is the same throughout (*the composition is uniform*). Some familiar examples are air, soft drinks, milk, and cement
- **Heterogeneous mixture:** A Heterogeneous mixture is a mixture in which the composition of the mixture is not the same throughout (*the composition is not uniform).* Some familiar examples are the mixture of sand and iron filing, both the sand grains and the iron filing remain separate.

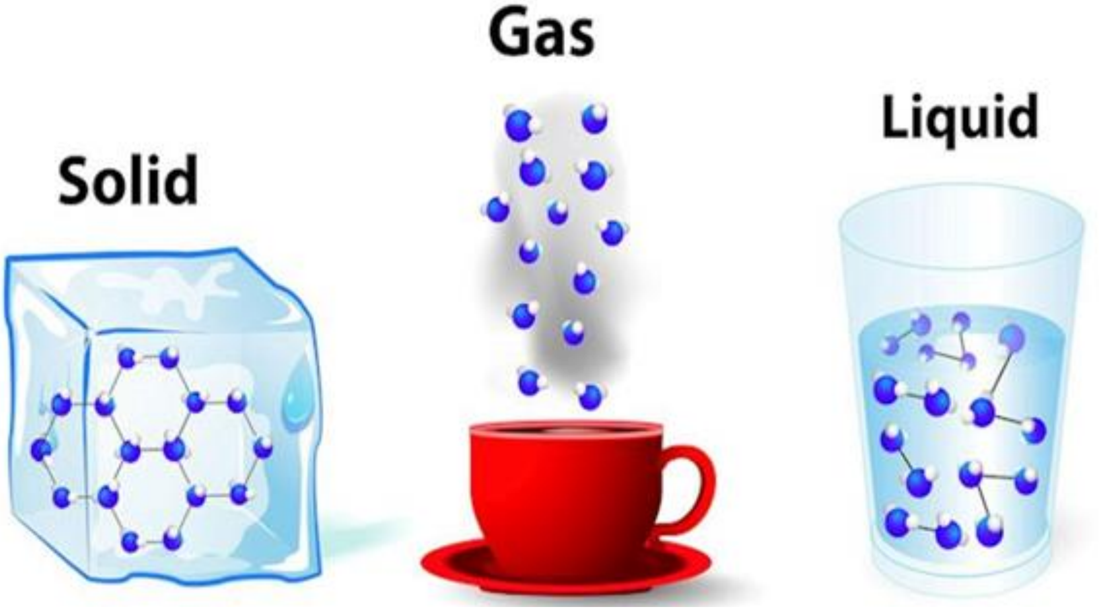
Any mixture, whether homogeneous or heterogeneous, can be created and then separated by physical means into pure components without changing the identities of the components. Thus, sugar or salt can be recovered from a water solution by evaporating the solution to dryness, and to separate the iron-sand 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.

1.1.2 The three states of matter

All substances 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. Cooling a liquid will cause it to freeze into a solid.
- Upon heating, a liquid (for example, water) ***vaporize*** into a gas (vapor). 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.

1.1.3 Physical and chemical properties of matter

Substances differ by their physical properties and chemical composition.

- **Physical properties of matter:** Color, melting point, and boiling point are physical properties. A ***physical property*** *can be measured and observed without changing the chemical 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 liquid 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 and oxygen, because *to observe this property we must carry out a **chemical change***, in this case burning. After the chemical change, the original chemical substance, the hydrogen and the oxygen, 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. Also, 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*, and this digestive action is a chemical change.

1.1.4 Categories of physical properties of matter

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

- **Extensive properties:** If the measured value of the physical property *depends on the amount of the matter then this property is* an ***extensive property***. ***Mass** of a matter*, is an extensive property because its value depends on the amount of matter, more matter means more mass. Values of the same extensive property can be added together. For example:
  a) The mass of two copper pieces is the sum of the masses of each piece.
  b) The length of two adjacent tables is the sum of the lengths of each.
- **Intensive properties:** If the measured value of the physical property does not *depend on the amount of the matter then this property is* an ***intensive property***. Values of the same extensive property cannot be added together. For example:
  a) Density of water filling a 100-cm^3 glass is the same as the density of water filling a 100-cm^3 glass, and if we mix the contents of the two glasses the density of the 1100 cm^3 stays the same.
  b) If we have the two previous glasses at the room temperature (25 °C) then the temperature of each will be 25 °C, and if we mix the contents of the two glasses the temperature of the 1100 cm^3 stays at 25 °C and it will not be 50 °C. Unlike mass, length, and volume, density, temperature and other intensive properties are not additive.

1.2 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).

1.2.1 Base units

Physical quantities are two types, first is the base physical quantities that are given seven base SI units, the second is the derived physical quantities that are given derived SI units. The following table shows the seven base physical quantities and their sven 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

The SI units of length and mass are in decimal fashion.

The table blow shows the prefixes used for large quantities of these two physical properties.

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

The table blow shows the prefixes used for small quantities of these two physical properties.

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

1.2.2 Derived units

Other than the seven base physical quantities all the rest of physical quantities are derived from these seven quantities and their units are derived units. For example, area is the product of a length multiplied by another length, thus area is not a base but derived physical quantity and its unit is not a base unit a derived unit.

1.2.3 Some important units

Below are some important physical quantities and their SI and non-SI Units.

First: Mass and weight

Although they are different quantities, the terms “mass” and “weight” are often used interchangeably. ***Mass*** is a measure of the amount of matter in an object but ***weight*** is *the force that gravity exerts on the object.* An apple with a mass equals 180 g on the surface of the earth has the same mass anywhere in the universe such as the surface of the moon. The mass of the apple is constant and does not depend on its location. However, its weight on the surface of the moon is only one-sixth that on the surface of the earth because the force of gravity of the moon is one-sixth that of the earth. Chemists determine masses with a balance. The SI unit of mass is the *kilogram* (kg). In chemistry, however, the smaller *gram* (g) is more convenient:

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

Pound, abbreviated “lb”, is a non- SI Unit of mass that is used in few countries of our world; it is

$$1 \text{ lb} = 0.4536 \text{ kg} = 453.6 \text{ g}$$
$$1 \text{ kg} = 1000 \text{ g} = 2.2046 \text{ lb}$$

Second: 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):

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

Another common non-SI 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):

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

Even though the liter is not an SI unit, volumes are usually expressed in liters and milliliters.

Third: 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. The SI-derived unit for density is the kilogram per cubic meter ($\frac{kg}{m^3}$). Grams per cubic centimeter ($\frac{g}{cm^3}$) and its equivalent, grams per milliliter ($\frac{g}{mL}$), are commonly used for solid and liquid densities. Because gas densities are often very low, we express them in units of grams per liter ($\frac{g}{L}$):

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

The following table lists the densities of several substances.

Material	Density ($\frac{g}{cm^3}$)
Gold	19.3
Mercury	13.6
Lead	11.3
Silver	10.5
Iron	7.86
Aluminum	2.7
Rubber	1.1
Water	1.0
Cork	0.24
Air	0.0013

EXAMPLE 1.1

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

$$d = \frac{m}{V} = \frac{301\ g}{15.6\ cm^3} = 19.3\ \frac{g}{cm^3}$$

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 1.2

The density of mercury, the only metal that is a liquid at room temperature, is 13.6 $\frac{g}{cm^3}$. Calculate the mass of 5.50 mL of the liquid.

Solution

5.50 mL = 5.50 cm^3

$$m = d \times V = 13.6\ \frac{g}{\cancel{cm^3}} \times 5.5\ \cancel{cm^3} = 74.8\ g$$

Practice Exercise

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

Fourth: Temperature

Temperature is an arbitrary measure of the degree of hotness or coldness of matter. There are three temperature scales are currently in use. Their units are degrees Fahrenheit (°F), degrees Celsius (°C), and Kelvin (K):

- The ***Celsius*** scale, which is the most commonly used scale worldwide, divides the range between the normal freezing point (0°C) and boiling point (100°C) of water into 100 degrees, therefore it is sometimes called "the centigrade scale".
- 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 academic institutions and 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:

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

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

- The ***Kelvin*** scale (also called 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 ***Kelvin*** scale defines the normal freezing and boiling points of water to be exactly 273.15 K and 373 K, respectively. The Celsius and the Kelvin scales have units of equal magnitude; that is, one degree Celsius is equivalent to one Kelvin. To reach 0 K temperature in the Celsius scale must be lowered down to – 273.15°C:

$$0\ \text{K} = -\,273.15\text{°C} = -\,459.67\ \text{°F}$$

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

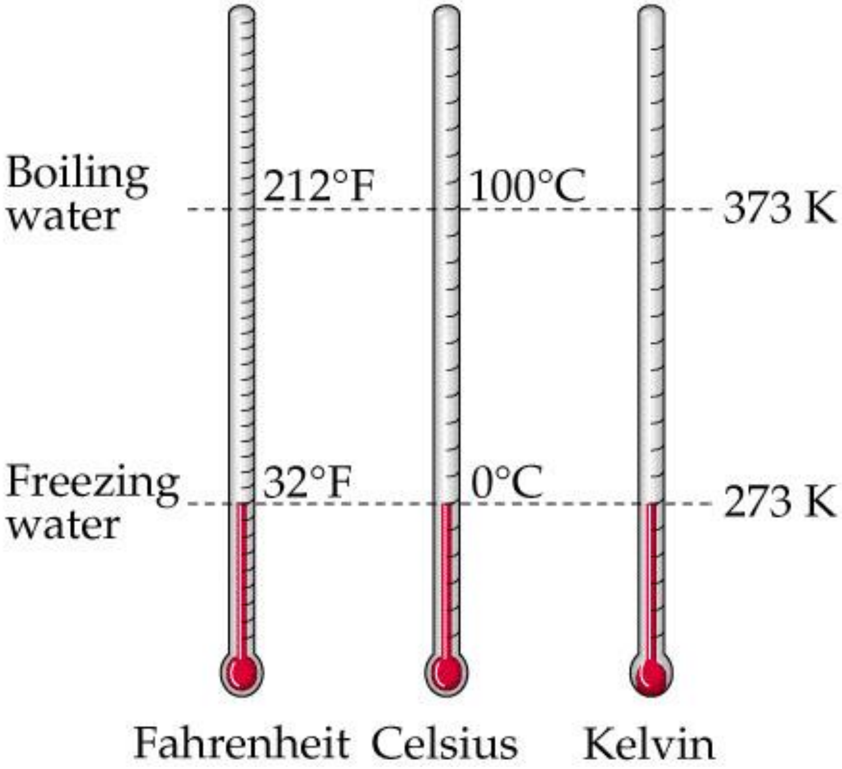
$$\text{Temperature in K} = (\text{Temperature in °C} + 273.15\ \text{°C}) \times \left(\frac{1\ \text{K}}{1\ \text{°C}}\right)$$

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

And we can use the following equations to convert between degrees Fahrenheit and Kelvin:

$$\text{Temperature in K} = (\text{Temperature in °F} + 459.67\ \text{°F}) \times \frac{5\ \text{K}}{9\ \text{°F}}$$

$$\text{Temperature in °F} = (\text{Temperature in K} \times \frac{9\ \text{°F}}{5\ \text{K}}) - (459.67\ \text{°F})$$



EXAMPLE 1.3

A) Mercury melting point is − 38.9 °C. How much is it in Kelvin and °F.

B) Normal human temperature is 98.6 °F. How much is it in Kelvin and °C?

C) Iron boiling point is 3135.35 K. How much is it in °C and °F.

Solution

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

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

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

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

B) Temperature in K = (Temperature in °F + 459.67 °F) × $\frac{5\ \text{K}}{9\ °\text{F}}$

Temperature in K = (98.6 °F + 459.67 °F) × $\frac{5\ \text{K}}{9\ °\text{F}}$ = 310.15 K

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

Temperature in °C = (98.6 °F − 32 °F) × $\left(\frac{5\ °\text{C}}{9\ °\text{F}}\right)$ = 37 °C

C) Temperature in °C = (Temperature in K − 273.15 K) × $\left(\frac{1\ °\text{C}}{1\ \text{K}}\right)$

Temperature in °C = (3135.35 K − 273.15 K) × $\left(\frac{1\ °\text{C}}{1\ \text{K}}\right)$ = 2862.20 °C

Temperature in °F = (Temperature in K × $\frac{9\ °\text{F}}{5\ \text{K}}$) – (459.67 °F)

Temperature in °F = (3135.35 K × $\frac{9\ °\text{F}}{5\ \text{K}}$) – (459.67 °F) = 5183.96 °F

Practice Exercise

A) Convert – 38.83 °C, (the freezing point of mercury) to °F and to K.
B) Convert 346 °F, (the freezing point of nitrogen) to °C and to K.
C) Convert 77 K, (the boiling point of nitrogen) to °C and to °F.

Fifth: Pressure

Pressure is the force applied on unit area:

$$\text{Pressure} = \frac{\text{Fofce}}{\text{Area}}$$

$$\text{Pressure SI Unit} = \frac{\text{Force SI Unit}}{\text{Area SI Unit}} = \left(\frac{\left(\frac{\text{kg m}}{\text{s}^2}\right)}{(\text{m}^2)}\right) = \frac{\text{kg}}{\text{m s}^2}$$

This unit "$\frac{\text{kg}}{\text{m s}^2}$", is called "Pascal" and abbreviated "Pa":

$$1\ \frac{\text{kg}}{\text{m s}^2} = 1\ \text{Pa}$$

Pressure, as any other physical quantity, is measured by other units:

- The ***atmosphere*** unit, which is abbreviated "atm":

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

- The ***centimeter mercury*** unit, which is abbreviated "cmHg":

$$1\ \text{cmHg} = 1333.22\ \text{Pa}$$

The ***millimeter mercury*** unit, which is abbreviated "mmHg" is one-tenth the ***centimeter mercury*** unit:

$$1\ \text{mmHg} = 0.1\ \text{cmHg} = 133.322\ \text{Pa}$$

This unit "mmHg", is called "Torricelli" and abbreviated "Torr":

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

- The ***pound per inch square*** unit, which is abbreviated "psi":

1 psi = 6894.76 Pa

- The ***bar*** unit, which is symbolized as “bar”:

1 bar = 100000 Pa = 750.0617 mmHgm = 14.504 psi

From all of the above units of pressure, chemists mostly use the “Pa” unit, the “atm” unit and the “mmHg” unit which is also called “Torr”.

EXAMPLE 1.4

A) It is found, in a cold day, that the atmospheric pressure in Riyadh is 743 mmHg. How much this pressure in “atm” unit and in the SI Units?

B) If the pressure inside your car tire is 35 psi, how much is this pressure in the SI Units and in bar unit?

C) A balloon full of air at a pressure equals to 0.35 atm. What would its pressure be in “mmHg” unit and in the SI Units?

Solution

A) $\text{Pressure in atm} = \text{Pressure in mmHg} \times \frac{1\ \text{atm}}{760\ \text{mmHg}}$

$\text{Pressure in atm} = 743\ \text{mmHg} \times \frac{1\ \text{atm}}{760\ \text{mmHg}} = 0.978\ \text{atm}$

$\text{Pressure in Pa} = \text{Pressure in mmHg} \times \frac{133.322\ \text{Pa}}{1\ \text{mmHg}}$

$\text{Pressure in Pa} = 743\ \text{mmHg} \times \frac{133.322\ \text{Pa}}{1\ \text{mmHg}} = 99058.2\ \text{Pa}$

B) $\text{Pressure in Pa} = \text{Pressure in psi} \times \frac{6894.76\ \text{Pa}}{1\ \text{psi}}$

$\text{Pressure in Pa} = 35\ \text{psi} \times \frac{6894.76\ \text{Pa}}{1\ \text{psi}} = 241316.6\ \text{Pa}$

$\text{Pressure in bar} = \text{Pressure in psi} \times \frac{1\ \text{bar}}{14.504\ \text{psi}}$

$\text{Pressure in Pa} = 35\ \text{psi} \times \frac{1\ \text{bar}}{14.504\ \text{psi}} = 2.41\ \text{bar}$

C) $\text{Pressure in mmHg} = \text{Pressure in atm} \times \frac{760\ \text{mmHg}}{1\ \text{atm}}$

$\text{Pressure in Pa} = 0.35\ \text{atm} \times \frac{760\ \text{mmHg}}{1\ \text{atm}} = 266\ \text{mmHg}$

Practice Exercise

A) It is found, in a hot day, that the atmospheric pressure in Riyadh is 737 mmHg. How much is this pressure in “mmHg” and in “bar” units?

B) If the pressure inside a gaseous cylinder is 4.6 atm, how much is this pressure in the SI Units in Torr.

C) If the pressure outside an airplane at 40000 ft-altitude reads 0.18 bar. What would this pressure be in “mmHg” unit and in the SI Unit of pressure

Sixth: Energy

Energy is usually defined as the ability to do work. It is manifested by the forms it appears by or by the paths it transfers by. Work and heat are ways of transferring energy from a system to another. Work is the easiest manifestation of energy; it is defined the force causing a movement or displacement. Therefore, mathematical equation of work is written as:

$$\text{Work} = \text{force} \times \text{distance}$$

Accordingly, the SI Units of work is the SI Units of force times the the SI Unit of distance:

$$\text{The SI Units of work} = \frac{\text{kg m}}{\text{s}^2} \times \text{m} = \frac{\text{kg m}^2}{\text{s}^2} = \text{J}$$

This unit of work itself is the unit of energy. This SI Unit, $\frac{\text{kg m}^2}{\text{s}^2}$, is named “Joule” and abbreviated as “J”. The unit “calorie”, abbreviated as “cal” is another unit for energy:

$$1\ \text{cal} = 4.184\ \frac{\text{kg m}^2}{\text{s}^2} = 4.184\ \text{J}$$

It might be useful to mention that when the word “calorie” is written with capital “C” as “Calorie” its value changes:

$$1\ \text{Cal} = 1\ \text{kcal} = 1000\ \text{cal} = 4184\ \text{J}$$

The Calorie” is mostly used in the fields of food, nutrients and physical exercises. If there are 78 Calories in an average-mass apple (150 g), this is equals to 78000 calorie or 18642 J. And a moderate-speed waking for one kilometer burns 55 Calories that is equals to 55000 calorie or 230120 J. Therefore, we should not confuse calorie with Calorie.

1.2.4 Dimensional analysis in solving problems (Conversion factors)

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:

- Because 1 cal = 4.184 J we can covert one of them to the other using the one of the following conversion factors::

$$\frac{1\ \text{cal}}{4.184\ \text{J}} = 1 \text{ or } \frac{4.184\ \text{J}}{1\ \text{cal}} = 1$$

- Because 1 atm = 101325 Pa we can covert one of them to the other using the one of the following conversion factors::

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

- Because 1 in = 2.54 cm we can covert one of them to the other using the one of the following conversion factors:

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

To apply dimensional analysis, we use the relationship

given quantity × conversion factor = desired quantity

The units of the quantity cancel as follows:

$$\boldsymbol{\cancel{\text{given unit}} \times \frac{\text{desired unit}}{\cancel{\text{given unit}}} = \text{desired unit}}$$

- To convert 12 inches to centimeters, we multiply the length by the appropriate conversion factor:

$$12\ \cancel{\text{in}} \times \frac{2.54\ \text{cm}}{1\ \cancel{\text{in}}} = 30.48\ \text{cm}$$

- To convert 57.8 meters to centimeter, we multiply the length by the appropriate conversion factor:

$$57.8\ \cancel{\text{m}} \times \frac{100\ \text{cm}}{1 \times \cancel{\text{m}}} = 5780\ \text{cm}$$

EXAMPLE 1.5

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

$\frac{453.6\ \text{g}}{1\ \text{lb}} = 1$	$\frac{1000\ \text{mg}}{1\ \cancel{\text{g}}} = 1$

$0.0833\ \cancel{\text{lb}} \times \frac{453.6\ \cancel{\text{g}}}{1\ \cancel{\text{lb}}} \times \frac{1000\ \text{mg}}{1\ \cancel{\text{g}}} = 3.78 \times 10^4\ \text{mg}$

Practice Exercise

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

EXAMPLE 1.6

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 $1.08 \times 10^8\ \text{dm}^3$. What is the volume in m^3?

EXAMPLE 1.7

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 $0.808\ \text{g/cm}^3$. Convert the density to units of kg/m^3.

Solution

$\frac{1000000\ \text{cm}^3}{1\ \text{m}^3} = 1$	$\frac{1\ \text{kg}}{1000\ \text{g}} = 1$

$0.808\ \frac{\cancel{\text{g}}}{1\ \cancel{\text{cm}^3}} \times \frac{1\ \text{kg}}{1000\ \cancel{\text{g}}} \times \frac{1000000\ \text{cm}^3}{1\ \text{m}^3} = 808\ \text{kg/m}^3$

Practice Exercise

The density of the lightest metal, lithium (Li), is $5.34 \times 10^2\ \text{kg/m}^3$. Convert the density to g/cm^3.

2. ATOMS, MOLECULES AND IONS

2.1 Constituent of the atom

2.1.1 A brief historical background

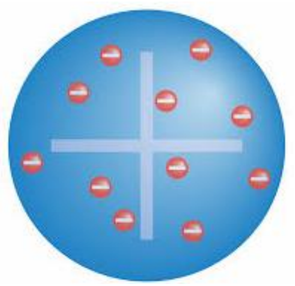
The word “atom” came from the Greek word “atomos” which means “indivisible”. It was chosen by Democritus about 2400 years ago. The theory of Democritus is that atoms are indivisible, infinite in number, uncreated, and eternal. Democritus attributed the properties of matter to the kind of its atoms. Unfortunately, this brilliant vision of Democritus was overlooked because the theory of the four elements (soil, water, air and fire) created by Empedocles was adopted by the greatest Greek philosopher Aristotle. Although the theory of Democritus survived among some Islsmic philosophers, the predomination was in favor of the theory of Empedocles for nothing except that it was adopted by Aristotle. Therefore, we can say that Aristotle adaptation of the theory of the four elements is one of the disastrous event in the sciences of nature. Now, our present understanding of the structure of matter began to take shape in the early nineteenth century with Dalton’s atomic theory in 1808. Dalton resurrected Democritus's theory. Now, we know that all matter is made of atoms, molecules, and ions. All of chemistry is concerned in one way or another with these species.

2.1.2 The structure of the atom

After Dalton’s theory, a series of investigations that began in the 1850s and extended into the twentieth century clearly demonstrated that atoms actually possess internal structure; that is, they are made up of even smaller particles, which are called *subatomic particles.* This led to the discovery of well-known three such subatomic particles namely electrons, protons, and neutrons.

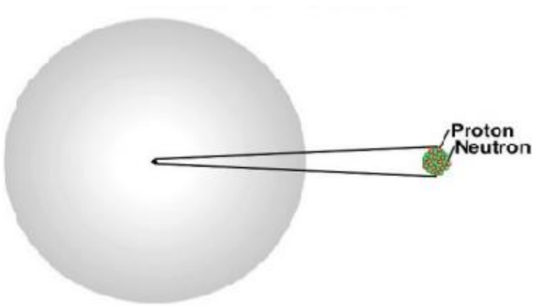
- **The Electron:** Electron was discovered by an English physicist, J. J. Thomson in 1897. Electrons are negatively charged atomic particles. Thomson determined the ratio of the electric charge its mass. In 1909, an American physicist, R. Millikan measured the charge of an electron to be 1.6022×10^{-19} C which allows to determine that the mass of the electron is 9.10×10^{-28} g.
- **The Proton and the nucleus:** Because atoms are neutral, an atom must contain 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. This why Thomson model is called the “plum-pudding model” for “plum-pudding” is a kind of sweets originally offered in England at Christmas dinner. The

following figures display Thompson’s model of the atom (left) and a typical “plum-pudding” (right):



In 1909, the new Zealander physicist and chemist, Ernest Rutherford discovered that the positive particles of the atom constitute the center of te atom. These positive particles in the center of the atom are called the “protons”. The number of protons of any atom equals the number of its electrons and its electric charge equals that of the electron while its mass equals about 1840 times the mass of the electron. The mass of the proton is 1.67262 × 10^{-24} g. Thus, the mass of a nucleus constitutes most of the mass of the entire atom. Regarding the volume of the space that an atom occupies it is found that the nucleus occupies only about $\frac{1}{1013}$ of the entire volume of the atom. Atomic dimensions are expressed in *picometer* (pm), where 1 pm equals 1 × 10^{-12} m. A typical atomic radius is about 100 pm, whereas the radius of an atomic nucleus is only about 5 × 10^{-3} pm. If we imagine that the size of the nucleus is the same as that of a ping pong ball, then the first electron orbiting around it would be 666 m away.

- **The neutron:** In 1932, James Chadwick showed that atoms consist of a third type of subatomic particles, which he named **neutrons,** because they are electrically neutrals. The mass of the neutron is slightly greater than that of protons. The following figure shows the location of the elementary particles (protons, neutrons, and electrons) in an atom. The following figure shows that electrons are as “clouds” around the nucleus.

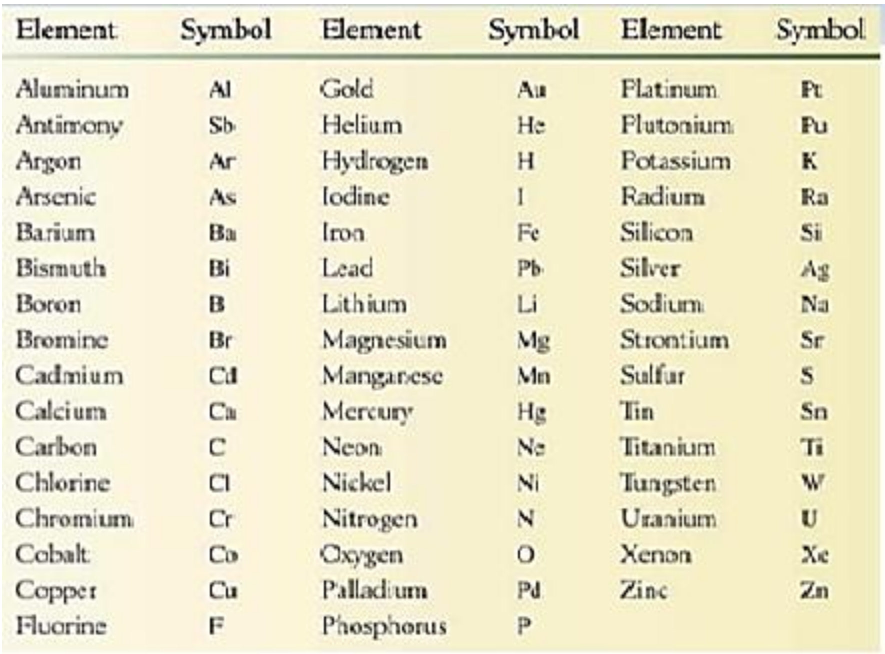


The table below shows their masses and charges.

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

2.2 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. Most symbols are derived from the English names of the elements but some are derived from their Latin names, for example “Au” from *aurum* (gold), “Fe” from *ferrum* (iron) and “Na” from *natrium* (sodium).

2.3 Atomic number, mass number and isotopes

2.3.1 The atomic number (Z): The atomic number 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 oxygen is 8; this means that each oxygen atom has 8 protons and 8 electrons, we can say with confidence that every atom in the universe that contains 6 protons is definitely an oxygen atom.

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

$$\text{mass number} = \text{number of protons} + \text{number of neutrons}$$
$$\text{mass number} = \text{atomic number} + \text{number of neutrons}$$

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

$$\text{number of neutrons} = (A - Z)$$

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

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

$$\begin{array}{r}\text{mass number} \rightarrow \\ \text{atomic number} \rightarrow\end{array} {}^{A}_{Z}X$$

Hydrogen which has only one proton and no neutrons is written as:

$${}^{1}_{1}H$$

Uranium which has 92 protons and 143 neutrons is written as:

$${}^{235}_{92}U$$

2.3.3 Isotopes: 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:

- ✓ **Hydrogen** has one proton and no neutrons. This is written as $^{1}_{1}\mathrm{H}$
- ✓ **Deuterium** has one proton and one neutron. This is written as $^{2}_{1}\mathrm{H}$
- ✓ **Tritium** has one proton and two neutrons. This is written as $^{3}_{1}\mathrm{H}$

Only hydrogen is given different names for each of its isotopes, but isotopes of other elements are identified by their mass numbers. For example, the isotopes of uranium are named "uranium-235" and "uranium-238":

- ✓ Uranium-235 is written as $^{235}_{92}\mathrm{U}$
- ✓ Uranium-235 is written as $^{238}_{92}\mathrm{U}$

The chemical properties of an element are determined 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 and form the same types of compounds.

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 isotope of copper: $^{63}_{29}\mathrm{Cu}$?

2.4 Atomic mass

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

- Hydrogen atom is only 8.4% 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 15.999 amu and that of iron is 55.845 amu.

2.4.1 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 12.0111 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.

$$\text{Average atomic mass} = \sum \text{percent of isotope} \times \text{atomic mass of isotope}$$

For example, carbon has many isotopes but only two are stable:
98.90% is carbon-12 (The atomic mass of carbon-12 = 12.0000 amu)
1.10% is carbon-13 (The atomic mass of carbon-13 = 13.0033 amu)
This means that, in nature, if we have in hand 1000 atom of carbon, we will find 9890 atoms of carbon-12 and 110 atoms of carbon-13. Accordingly, the mass of carbon atom, and any atom of any other element, should be averaged as follows:

$$\text{average atomic mass} = \text{aam}$$
$$\text{aam} = \sum \text{percent of isotope} \times \text{atomic mass of isotope}$$
$$\text{aam of carbon} = (0.9890) \times (12.0000\ \text{amu}) + (0.0110) \times (13.0033\ \text{amu})$$

aam of carbon = 12.011 amu

It is important to understand that when we say that the atomic mass of carbon is 12.011 amu, we are referring to the *average* value.

EXAMPLE 2.2

The abundance of the copper isotope ${}^{63}_{29}\text{Cu}$ is 69.09%) and of the copper isotope ${}^{65}_{29}\text{Cu}$ is 30.91%. Calculate the average atomic mass of copper.

Solution

Average atomic mass = ∑percent of isotope × atomic mass of isotope

Average atomic mass = (0.6909) × (63 amu) + (0.3091) × (65 amu)

Average atomic mass = 63.62 amu

Practice Exercise

The abundance of the boron isotope, ${}^{10}_{5}\text{B}$ is 19.78% and of the boron isotope ${}^{11}_{5}\text{B}$ is 80.22%. Calculate the average atomic mass of boron.

For simplicity, the word “average” is usually omitted when discussing the atomic masses.

2.5 Quantum theory and electronic structure of atoms

After the discoveries of the 19th century, the theories and attempts to understand the finite constituent of atoms were handcuffed by Handcuffed by the disability of traditional physics. The new era in physics started in 1900 with a young German physicist named Max Planck who established the quantum theory which turned physics upside down. Max Planck theory altered our concept of nature forever and opened the door for a flurry of researches and findings by Einstein, Bohr, de Broglie, Heisenberg, Schrodinger and so many others. For electrons, quantum theory solved the puzzle of how electrons present in atoms by the quantum numbers of each electron. The quantum numbers act as identification number acts for us, for electrons, quantum numbers act as thump print acts for us and for electrons, quantum numbers act as home address acts for us. In any atom, no two electrons have the same four quantum numbers.

2.5.1 Quantum numbers

1) **Principal quantum number, n**
   - ✓ The principal quantum number (n) describes the size of the orbital.
   - ✓ Orbitals for which n = 2 are larger than those for which n = 1, for example.
   - ✓ Because they have opposite electrical charges, electrons are attracted to the nucleus of the atom.

- ✓ Energy must therefore be absorbed to excite an electron from an orbital in which the electron is close to the nucleus (n = 1) into an orbital in which it is further from the nucleus (n = 2).
- ✓ The principal quantum number therefore indirectly describes the energy of an orbital.
- ✓ The allowed values of "n" are therefore 1, 2, 3, 4, 5, 6 and 7.

2) Angular quantum number, *l*

The angular quantum number (*l*) describes the shape of the orbital. Orbitals have shapes that are described as:

- spherical (*l* = 0) and this is given the symbol "s"
- dumbbell (*l* = 1) and this is given the symbol "p"
- cloverleaf (*l* = 2) and this is given the symbol "d"
- cloverleaf (*l* = 3) and this is given the symbol "f"

3) Magnetic quantum number, $\mathbf{m}_l$

The magnetic quantum number (m) describes the orientation of an orbital in a magnetic field:

- There is only one way in which the orbital (*l* = 0) can be oriented in space:

$$m_l = 0$$

- There are three ways in which the orbital (*l* = 1) can be oriented in space:

$$m_l = -1,\ m_l = 0,\ m_l = +1$$

- There are five ways in which the orbital (*l* = 2) can be oriented in space:

$$m_l = -2,\ m_l = -1,\ m_l = 0,\ m_l = +1,\ m_l = +2$$

- There are seven ways in which the orbital (*l* = 3) can be oriented in space:

$$m_l = -3,\ m_l = -2,\ m_l = -1,\ m_l = 0,\ m_l = +1,\ m_l = +2,\ m_l = +3$$

4) Spin quantum number, $\mathbf{m}_s$

The spin quantum number (m) describes the direction of an electron spin in its orbital. Spinning can be either clockwise or anticlockwise with no third option:

$$m_s = +\frac{1}{2} \text{ or } m_s = -\frac{1}{2}$$

The following table gives the four quantum numbers of each electron in any orbital. It shows that, in any atom, no two electrons have the same four quantum numbers.

n	***l***	$\mathbf{m}_l$	$\mathbf{m}_s$
1	0 (s)	0	$+\frac{1}{2}$
			$-\frac{1}{2}$

n	***l***	$\mathbf{m}_l$	$\mathbf{m}_s$
2	0 (s)	0	$+\frac{1}{2}$
			$-\frac{1}{2}$
	1 (p)	-1	$+\frac{1}{2}$
			$-\frac{1}{2}$
		0	$+\frac{1}{2}$
			$-\frac{1}{2}$
		$+1$	$+\frac{1}{2}$
			$-\frac{1}{2}$

n	***l***	$\mathbf{m}_l$	$\mathbf{m}_s$
3	0 (s)	0	$+\frac{1}{2}$
			$-\frac{1}{2}$
	1 (p)	-1	$+\frac{1}{2}$
			$-\frac{1}{2}$
		0	$+\frac{1}{2}$
			$-\frac{1}{2}$
		$+1$	$+\frac{1}{2}$
			$-\frac{1}{2}$
	2 (d)	-2	$+\frac{1}{2}$
			$-\frac{1}{2}$
		-1	$+\frac{1}{2}$
			$-\frac{1}{2}$
		0	$+\frac{1}{2}$

			$-\frac{1}{2}$
		+ 1	$+\frac{1}{2}$
			$-\frac{1}{2}$
		+ 2	$+\frac{1}{2}$
			$-\frac{1}{2}$

n	***l***	$\mathbf{m}_{\boldsymbol{l}}$	$\mathbf{m}_{\mathbf{s}}$
4	0 (s)	0	$+\frac{1}{2}$
			$-\frac{1}{2}$
	1 (p)	– 1	$+\frac{1}{2}$
			$-\frac{1}{2}$
		0	$+\frac{1}{2}$
			$-\frac{1}{2}$
		+ 1	$+\frac{1}{2}$
			$-\frac{1}{2}$
	2 (d)	– 2	$+\frac{1}{2}$
			$-\frac{1}{2}$
		– 1	$+\frac{1}{2}$
			$-\frac{1}{2}$
		0	$+\frac{1}{2}$
			$-\frac{1}{2}$
		+ 1	$+\frac{1}{2}$
			$-\frac{1}{2}$
		+ 2	$+\frac{1}{2}$
			$-\frac{1}{2}$
	3 (f)	– 3	$+\frac{1}{2}$
			$-\frac{1}{2}$

		-2	$+\frac{1}{2}$
			$-\frac{1}{2}$
		-1	$+\frac{1}{2}$
			$-\frac{1}{2}$
		0	$+\frac{1}{2}$
			$-\frac{1}{2}$
		$+1$	$+\frac{1}{2}$
			$-\frac{1}{2}$
		$+2$	$+\frac{1}{2}$
			$-\frac{1}{2}$
		$+3$	$+\frac{1}{2}$
			$-\frac{1}{2}$

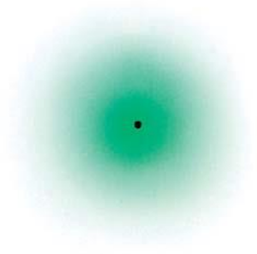
2.5.3 Shapes of orbitals

The letters of subshells go in the order s, p, d and f:

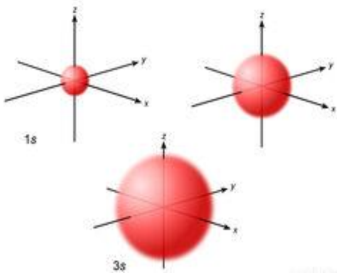
- The “s” subshell has only one orbital.
- The “p” subshell has three orbitals that are equal in energy.
- The “d” subshell has five orbitals that are equal in energy.
- The “f” subshell has seven orbitals that are equal in energy.

Electron occupies all space it moves within. So, it is impossible to draw an orbital. Although, in principle an electron can be found anywhere, we know that during most of the time it is as close as possible to the nucleus. The shape of the space which includes the electron most of its time, say 95% is as follows:

1) **Shape of the “s” Orbitals**



The above figure shows the distribution of electron density in the hydrogen 1s orbital moving outward from the nucleus. The electron density decreases as the distance from the nucleus increases. There is a 90 percent probability of finding the electron within a sphere of radius 100 pm around the nucleus. The following figure shows boundary surface diagrams for the 1s, 2s, and 3s atomic orbitals. All s orbitals are spherical in shape but differ in size, which increases as the principal quantum number increases.



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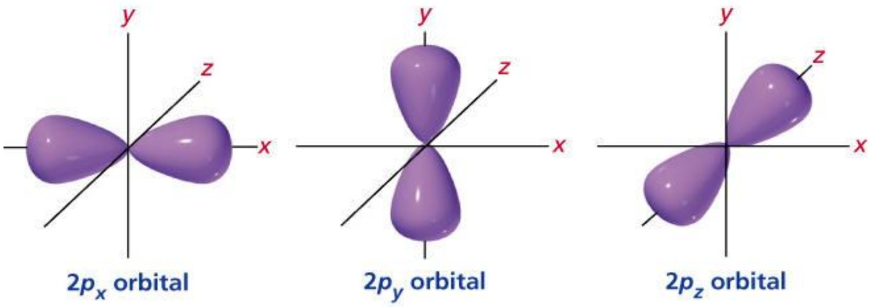
2) Shape of the “p” Orbitals

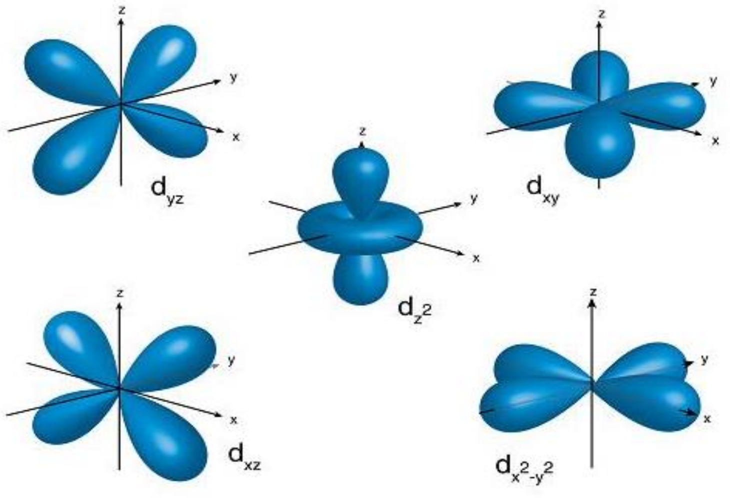
It should be clear that the p orbitals start with the principal quantum number n = 2. When l = 1, the magnetic quantum number m_l can have values of − 1, 0 and + 1. Therefore, there are three p orbitals: p_x , p_y , and p_z as shown by the following figure.



These three p orbitals differ from one another only in orientation. The boundary surface diagrams of p orbitals in the previous figure show that each p orbital can be thought of as two lobes on opposite sides of the nucleus. Like s orbitals, p orbitals increase in size from 2p to 3p to 4p orbital and so on.

3) Shape of the “d” Orbitals

When / = 2, there are five *d* orbitals. The five d orbitals are $3d_{xy}$, $3d_{yz}$, $3d_{xz}$, ,$3d_{x^2-x^2}$ and $3d_{z^2}$, these orbital are equal in energy and shown in the following figure.



4) Shape of the "f" Orbitals

The *f* orbitals are important in elements with atomic numbers greater than 57. In this general chemistry course, we are not concerned with elements having greater than 57 electrons.

2.5.4 The rules of electronic distribution

1) The "Aufbau principle" = The "n + *l*" principle

- This first rule states that electrons occupy the lowest-energy subshell before any other higher-energy subshell.
- Determining which subshell is lower or higher in energy is achieved by the sum of the values of "n" and "*l*" as shown in the following table.

n	***l***	**n + *l***
1	0 (s)	1
2	0 (s)	2
	1 (p)	3
3	0 (s)	3
	1 (p)	4
	2 (d)	5
4	0 (s)	4
	1 (p)	5
	2 (d)	6
	3 (f)	7

- The lowest sum is the lower energy.
- The above table shows that some higher-energy subshells are preceding other subshells that are lower in energy. It also shows the presence of cases where some subshells are having the same value of summation. In these cases, the lowest subshell is the one having the lowest value of "n". Accordingly, the above table is rearranged from left to wright as follows:

1s 2s 2p 3s 3p 4s 3d 4p 4d 4f

- We know that any subshell has a certain number of orientations in the magnetic field. These different orientations do not differ in energy. Therefore, they are shown in the following manner:
- "s" subshell has only one orientation which is represented as:

s = 0

$m_l = 0$

- "p" subshell has three orientations which are represented as:

p

$m_l = -1$	$m_l = 0$	$m_l = +1$

- "d" subshell has five orientations which are represented as:

d

$m_l = -2$	$m_l = -1$	$m_l = 0$	$m_l = +1$	$m_l = +2$

- "f" subshell has seven orientations which are represented as:

f

$m_l = -3$	$m_l = -2$	$m_l = -1$	$m_l = 0$	$m_l = +1$	$m_l = +2$	$m_l = +3$

2) The Pauli principle

- This second rule states that when an electron occupies an orbital it is not possible for another electron to share it the same orbital unless it spins in an opposite direction of the first electron.
- This rule means that, in the same atom, no two electrons can have the same four quantum number (each electron has its own "address").

3) The Hund's rule'

- There is only one orientation in the magnetic field (orbital) in the "s" subshell.
- There are three orientations in the magnetic field (orbitals) in the "p" subshell.
- There are five orientations in the magnetic field (orbitals) in the "d" subshell.

- There are seven orientations in the magnetic field (orbitals) in the "f" subshell.

Hund's rule states that when electrons occupy a subshell which has more than one orientation in the magnetic field (i.e. more than one orbital, this is either p, d or f) they will not pair in the same orbital as long as other orbitals are empty and the unpaired electrons spins in the same direction.

4) **The rule of half-filled and fully-filled subshells**

Half-filled and fully-filled subshells add more stability to electrons and atoms. It is known that starting from the energy level where n = 4 and higher, the difference in energy between subsequent subshells is so small. Therefore, when two consecutive subshells are energetically close to each other, they will seek to be half filled or fully filled even if this requires an electron to be in the slightly-higher energy subshell rather than the slightly lower energy subshell. The following configurations illustrates how electrons distribute themselves within an atom. The table shows this distribution for the first 36 elements in the periodic table of elements.

^{1}H

1s^1
↑↓

^{2}He (Note: its upper shell is full and its electron configuration is symbolized as [He])

1s^2
↑↓

^{3}Li

1s^2	2s^1
↑↓	↑

^{4}B2

1s^2	2s^2
↑↓	↑↓

^{5}B

1s^2	2s^2	2p^1		
↑↓	↑↓	↑		

^{6}C

1s^2	2s^2	2p^2		
↑↓	↑↓	↑	↑	

^{7}N

1s^2	2s^2	2p^3		
↑↓	↑↓	↑	↑	↑

^{8}O

1s^2	2s^2	2p^4		
↑↓	↑↓	↑↓	↑	↑

^{9}F

$1s^2$	$2s^2$	$2p^5$		
↑↓	↑↓	↑↓	↑↓	↑

^{10}Ne (Note: its upper shell is full and its electron configuration is symbolized as [Ne])

$1s^2$	$2s^2$	$2p^6$		
↑↓	↑↓	↑↓	↑↓	↑↓

^{11}Na

$1s^2$	$2s^2$	$2p^6$			$3s^1$
↑↓	↑↓	↑↓	↑↓	↑↓	↑

^{12}Mg

$1s^2$	$2s^2$	$2p^6$			$3s^2$
↑↓	↑↓	↑↓	↑↓	↑↓	↑↓

^{13}Al

$1s^2$	$2s^2$	$2p^6$			$3s^2$	$3p^1$		
↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑		

^{14}Si

$1s^2$	$2s^2$	$2p^6$			$3s^2$	$3p^2$		
↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑	↑	

^{15}P

$1s^2$	$2s^2$	$2p^6$			$3s^2$	$3p^3$		
↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑	↑	↑

^{16}S

$1s^2$	$2s^2$	$2p^6$			$3s^2$	$3p^4$		
↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑	↑

^{17}Cl

$1s^2$	$2s^2$	$2p^6$			$3s^2$	$3p^5$		
↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑

^{18}Ar (Note: its upper shell is full and its electron configuration is symbolized as [Ar])

$1s^2$	$2s^2$	$2p^6$			$3s^2$	$3p^6$		
↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓

^{19}K

$1s^2$	$2s^2$	$2p^6$			$3s^2$	$3p^6$			$4s^1$
↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑

^{20}Ca

$1s^2$	$2s^2$	$2p^6$			$3s^2$	$3p^6$			$4s^2$
↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓

^{21}Sc

$1s^2$	$2s^2$	$2p^6$			$3s^2$	$3p^6$			$4s^2$	$3d^1$				
↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑				

^{22}Ti

$1s^2$	$2s^2$	$2p^6$			$3s^2$	$3p^6$			$4s^2$	$3d^2$				
↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑	↑			

^{23}V

$1s^2$	$2s^2$	$2p^6$			$3s^2$	$3p^6$			$4s^2$	$3d^3$				
↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑	↑	↑		

^{24}Cr

$1s^2$	$2s^2$	$2p^6$	$3s^2$	$3p^6$	$4s^1$	$3d^5$
↑↓	↑↓	↑↓ ↑↓ ↑↓	↑↓	↑↓ ↑↓ ↑↓	↑	↑ ↑ ↑ ↑ ↑

^{25}Mn

$1s^2$	$2s^2$	$2p^6$	$3s^2$	$3p^6$	$4s^2$	$3d^5$
↑↓	↑↓	↑↓ ↑↓ ↑↓	↑↓	↑↓ ↑↓ ↑↓	↑↓	↑ ↑ ↑ ↑ ↑

^{26}Fe

$1s^2$	$2s^2$	$2p^6$	$3s^2$	$3p^6$	$4s^2$	$3d^6$
↑↓	↑↓	↑↓ ↑↓ ↑↓	↑↓	↑↓ ↑↓ ↑↓	↑↓	↑↓ ↑ ↑ ↑ ↑

^{27}Co

$1s^2$	$2s^2$	$2p^6$	$3s^2$	$3p^6$	$4s^2$	$3d^7$
↑↓	↑↓	↑↓ ↑↓ ↑↓	↑↓	↑↓ ↑↓ ↑↓	↑↓	↑↓ ↑↓ ↑ ↑ ↑

^{28}Ni

$1s^2$	$2s^2$	$2p^6$	$3s^2$	$3p^6$	$4s^2$	$3d^8$
↑↓	↑↓	↑↓ ↑↓ ↑↓	↑↓	↑↓ ↑↓ ↑↓	↑↓	↑↓ ↑↓ ↑↓° ↑ ↑

^{29}Cu

$1s^2$	$2s^2$	$2p^6$	$3s^2$	$3p^6$	$4s^1$	$3d^{10}$
↑↓	↑↓	↑↓ ↑↓ ↑↓	↑↓	↑↓ ↑↓ ↑↓	↑	↑↓ ↑↓ ↑↓° ↑↓ ↑↓

^{30}Zn

$1s^2$	$2s^2$	$2p^6$	$3s^2$	$3p^6$	$4s^2$	$3d^{10}$
↑↓	↑↓	↑↓ ↑↓ ↑↓	↑↓	↑↓ ↑↓ ↑↓	↑↓	↑↓ ↑↓ ↑↓° ↑↓ ↑↓

^{31}Ga

$1s^2$	$2s^2$	$2p^6$	$3s^2$	$3p^6$	$4s^2$	$3d^{10}$	$4p^1$
						↑↓ ↑↓ ↑↓ ↑↓ ↑↓	↑

^{32}Ge

$1s^2$	$2s^2$	$2p^6$	$3s^2$	$3p^6$	$4s^2$	$3d^{10}$	$4p^1$
						↑↓ ↑↓ ↑↓ ↑↓ ↑↓	↑ ↑

^{33}As

$1s^2$	$2s^2$	$2p^6$	$3s^2$	$3p^6$	$4s^2$	$3d^{10}$	$3d^{10}$
						↑↓ ↑↓ ↑↓ ↑↓ ↑↓	↑ ↑ ↑

^{34}Se

$1s^2$	$2s^2$	$2p^6$	$3s^2$	$3p^6$	$4s^2$	$3d^{10}$	$3d^{10}$
						↑↓ ↑↓ ↑↓ ↑↓ ↑↓	↑↓ ↑ ↑

^{35}Br

$1s^2$	$2s^2$	$2p^6$	$3s^2$	$3p^6$	$4s^2$	$3d^{10}$	$3d^{10}$
						↑↓ ↑↓ ↑↓ ↑↓ ↑↓	↑↓ ↑↓ ↑

^{36}Kr (**Note: its upper shell is full and its electron configuration is symbolized as [Kr]**)

$\mathbf{1s^2}$	$\mathbf{2s^2}$	$\mathbf{2p^6}$	$\mathbf{3s^2}$	$\mathbf{3p^6}$	$\mathbf{4s^2}$	$\mathbf{3d^{10}}$	$\mathbf{4p^6}$

As it appears from the above configurations, noble gases shells have the maximum number of electrons it can accommodate. Any element comes after a noble gas has the configuration of this noble gas as its core electrons plus the extra electrons in the following shell.

Example 2.3

Give the four quantum numbers for each of the two electrons in a 6 s orbital.

Solution

Quantum number	**n**	***l***	$\mathbf{m}_l$	$\mathbf{m}_s$
First electron	6	0	0	$+\frac{1}{2}$
Second electron	6	0	0	$-\frac{1}{2}$

Practice exercise

Give the four quantum numbers for each of the six electrons in a 3p orbital of an atom.

Example 2.4

A person gave the following four quantum numbers for each of the electrons in the "p" subshell of the atom of ^{7}N. Judge the answer.

Quantum number	**n**	***l***	$\mathbf{m}_l$	$\mathbf{m}_s$
First electron	2	0	0	$+\frac{1}{2}$
Second electron	2	1	0	$-\frac{1}{2}$
Third electron	2	1	– 1	+ 1

Solution

- The "n" quantum numbers: they are correct for all the three electrons.
- "*l*" quantum numbers: they are correct for the second and the third electrons but wrong for first electron because it is in the second subshell, p, which always has *l* = 1.
- The "m_l" quantum numbers: according to Hund's rule, all of the electrons must be unpaired and their quantum numbers must be "– 1", "0" and "+ 1".
- The "m_s" quantum numbers: according to Pauli's principle, "m_s" quantum number can be either $+\frac{1}{2}$ or $+\frac{1}{2}$ and nothing else; and according to Hund's rule, they all of them must be either $+\frac{1}{2}$ or $+\frac{1}{2}$.

Practice exercise

A person gave the four quantum numbers for each of the six electrons in the 3p orbitals of an atom. Judge the answer.

Quantum number	**n**	***l***	$\mathbf{m}_l$	$\mathbf{m}_s$
First electron	3	1	– 1	$+\frac{1}{2}$
Second electron	3	1	– 1	$+\frac{1}{2}$

Third electron	3	0	0	$-\frac{1}{2}$
Fourth electron	3	0	0	$-\frac{1}{2}$
Fifth electron	3	– 1	+ 1	$+\frac{1}{2}$
Sixth electron	4	– 1	+ 1	$+\frac{1}{2}$

2.5.4 Electron configurations of anions and cations

1) **First: Anions**

Anions are atoms having one or more than one electrons more than its original electrons. Consider the following examples:

H: $1s^1$	H^-: $1s^2$ or [He]
F: $1s^2\ 2s^2\ 2p^5$	F^-: $1s^2\ 2s^2\ 2p^6$ or [Ne]
O: $1s^2\ 2s^2\ 2p^4$	O^{2-}: $1s^2\ 2s^2\ 2p^6$ or [Ne]
N: $1s^2\ 2s^2\ 2p^3$	N^{3-}: $1s^2\ 2s^2\ 2p^6$or [Ne]

All of these anions also have stable noble gas configurations. Notice that F^-, Na^+, and Ne (and Al^{3+}, O^{2-}, and N^{3-}) have the same electron configuration. They are said to be **isoelectronic** because they have the same number of electrons, and hence the same ground-state electron configuration. Thus, H^- and He are also **isoelectronic**.

2) **Second: Cations**

Cations are atoms having one or more than one electrons more than its original electrons.

✓ **Cations derived from elements that its upper subshell is “p”**

Electrons of cations formed from atoms having “s” or “p” as its upper subshell are removed from the upper subshell and its configuration can be known easily. The electron configurations of some atoms and their corresponding cations are as follows:

Na: [Ne]$3s^1$	Na^+: [Ne]
Ca: [Ar]$4s^2$	Ca^{2+}: [Ar]
Al: [Ne]$3s^2\ 3p^1$	Al^{3+}: [Ne]

As it appears, all configuration becomes similar to the previous noble gas configuration.

✓ **Cations derived from elements that its upper subshell is “d”**

Electrons of cations formed from atoms having “d” as its upper subshell are removed from the upper subshell having the bigger principle quantum number. The electron configurations of some atoms and their corresponding cations are as follows:

Ti: [Ar]$4s^2\ 3d^2$	Ti^{2+}: [Ar]$3d^2$
Fe: [Ar] $4s^2\ 3d^6$	Fe^{3+}: [Ar]$3d^5$
Zn: [Ne]$4s^2\ 3d^{10}$	Zn^{2+}: [Ne]$3d^{10}$

Example 2.5

Write the electron configuration of the following:

A) $^{16}S^{2-}$ B) $^{26}Fe^{3+}$

Solution

A) $^{16}S^{2-}$ has 18 electrons, (16 electrons + 2 electrons):

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$

B) $^{26}Fe^{3+}$ has 23 electrons, (26 electrons – 3 electrons):

First: we write the electron configuration of the Fe atom:

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^6$

Second: we identify which subshell is in the highest "n" quantum number to find that it is 4s which has two electrons. These two electrons and a third electron from the 3d electrons are removed to form Fe^{3+} cation having the following electron configuration

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5$

Practice exercise

Write the electron configuration of the following:

A) $^{15}P^{3-}$ B) $^{31}Ga^{3+}$

2.6 The periodic table of elements

The way electrons are distributed makes element so easy to be arranged depending on the way the electrons of their atoms are distributed. Simply, after knowing how electrons are distributed chemists became able to arrange all elements in a systematic meaningful way called "*the periodic table of elements*".

2.6.1 Blocks, groups and periods

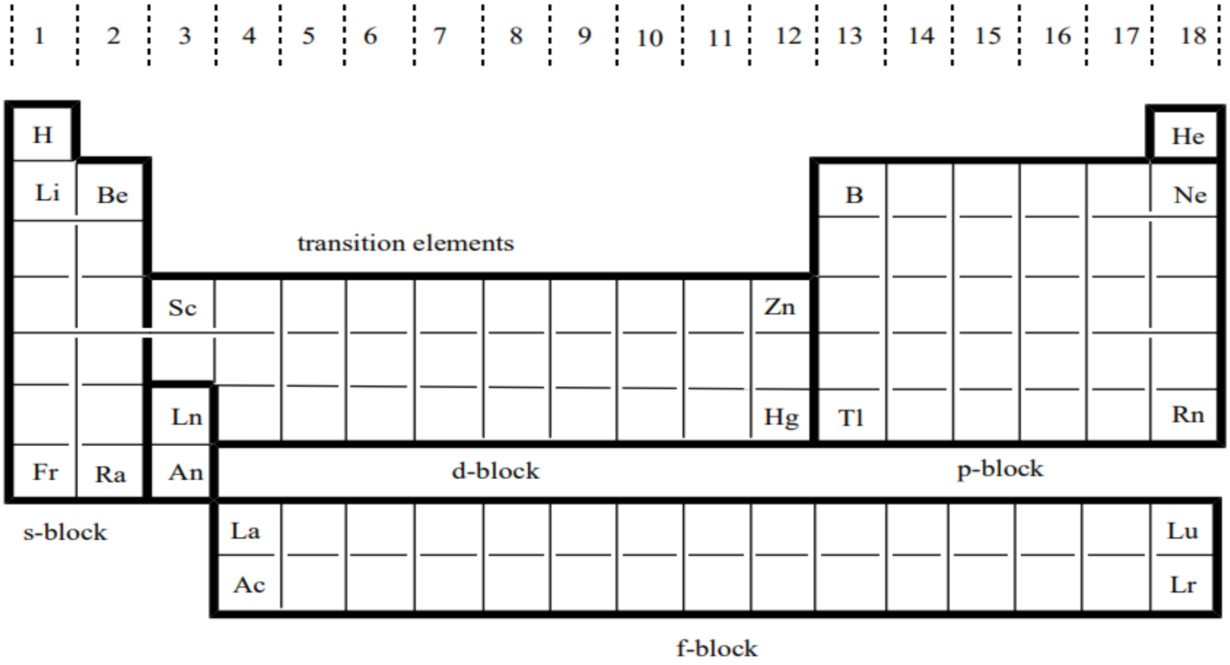
Blocks: The way electrons are distributed reveals that electrons in the highest energy orbitals belong to a specified subshell, either "s", "p", "d", or "f". This fact enables chemists to distribute elements into four blocks:

- s-block elements
- p-block elements
- d-block elements
- f-block elements

Groups: The way electrons are distributed reveals that number of electrons in any subshell varies from an atom of an element to another atom of another element. This fact enables chemists to distribute elements of each block into a number of groups equals the maximum number of electrons for each subshell:

- s-block elements are in two groups
- p-block elements are in six groups
- d-block elements are in ten groups
- f-block elements are in fourteen groups

The International Union of Pure and Applied Chemistry (IUPAC) has recommended numbering the columns (groups) sequentially with Arabic numerals 1 through 18. According to the type of subshell being filled, the elements can be divided into four categories:



1) **The representative elements:**
   The representative elements (also called main group elements) are the elements in Groups 1A through 7A, all of which have incompletely filled s or p subshells of the highest principal quantum number
2) **The noble gases:**
   With the exception of helium, the noble gases (the Group 18 elements) all have a completely filled p subshell. (The electron configurations are $1s^2$ for helium and $ns^2\ np^6$ for the other noble gases, where n is the principal quantum number for the outermost shell.)

3) **The transition elements (or transition metals):**
   The transition metals are ten groups the Groups from groups 3 to group 12. These metals are sometimes referred to as the d -block transition elements.
4) **The lanthanides and the actinides:**
   The lanthanides and actinides are sometimes called f -block transition elements because they have incompletely filled f subshells.

Periods: The way electrons are distributed reveals that number of electrons in any shell varies according to the shell principal quantum number, n. This fact enables chemists to put elements that having the same highest principal quantum number beside each other starting from left to right with the element having only one electron at the far left and ending at the far right with the element having the maximum number of electrons that can be accommodated by the shell. This lead to arranging elements in seven rows called "periods" designated as "period 1, "period 2", "period 3", …to "period 7".

Example 2.6

For each of the four elements having the following atom numbers, determine the block, the period, the group and the group name:

A) 9 B) 10 C) 12 D) 30

Solution

Answering the question requires writing the electron configuration of each:

A) $1s^2\ 2s^2\ 2p^5$

B) $1s^2\ 2s^2\ 2p^6$

C) $1s^2\ 2s^2\ 2p^6\ 3s^2$

D) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}$

	A	B	C	D
Block	p	p	s	d
Period	2	2	3	4
Group	17	18	2	12
Group name	Halogen	Noble gases	Alkali earth	No group name

Practice exercise

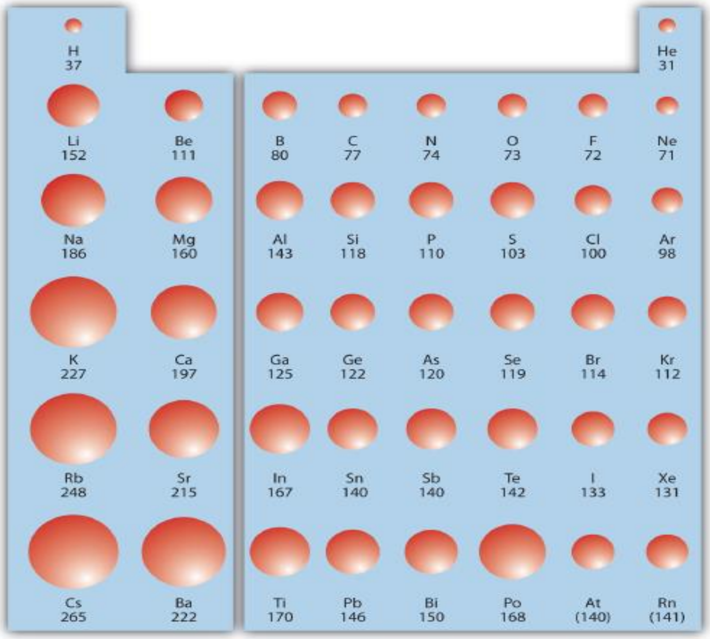
For each of the four elements having the following atom numbers, determine the block, the period, the group and the group name:

A) 8 B) 17 C) 19 D) 40

2.6.2 Periodic variation in physical properties

- **Atomic radius**

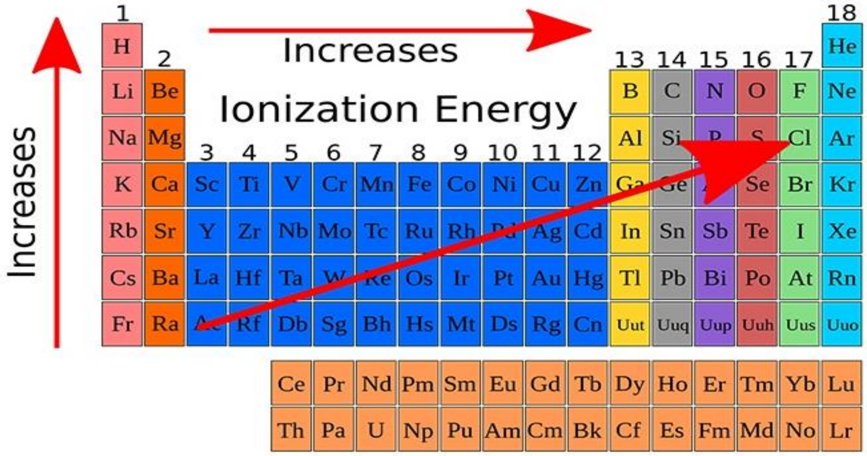
  The atomic radius is one-half the distance between the two nuclei in two adjacent metal atoms or in a diatomic molecule.


H 37
He 31
Li 152
Be 111
B 80
C 77
N 74
O 73
F 72
Ne 71
Na 186
Mg 160
Al 143
Si 118
P 110
S 103
Cl 100
Ar 98
K 227
Ca 197
Ga 125
Ge 122
As 120
Se 119
Br 114
Kr 112
Rb 248
Sr 215
In 167
Sn 140
Sb 140
Te 142
I 133
Xe 131
Cs 265
Ba 222
Tl 170
Pb 146
Bi 150
Po 168
At (140)
Rn (141)

The figure above shows that:

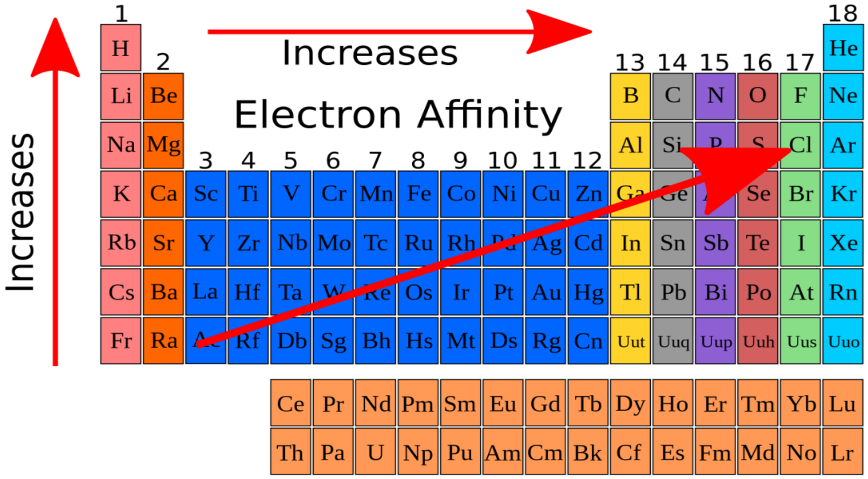
- ✓ The atomic radius of elements decreases from left to wright because number of electrons in the same shell increases from left to right making stronger attractions and diminishing radius.
- ✓ The atomic radius of elements increases from up to down because the same number of electrons is occupying a principal quantum number which its distance from the nucleus increases from up to down.

- **Atomic ionization energy**


Increases
Ionization Energy
Increases
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18

The atomic ionization energy is the energy needed to remove electrons from the atom. If more than one electron is removed we will have “the first ionization energy”, the “second ionization energy”, and so on. Ionization energy increases as the atomic radius decreases. Therefore, ionization energy increases from right to left and from down to up.

- **Atomic electron affinity**



The electron affinity is the energy absorbed or released as a result of attracting electron to an atom. The electron affinity increases as the atomic radius decreases. Therefore, electron affinity increases from left to wright and from down to up.

Example 2.7

A) Which is bigger in radius, the element ^{3}X or the element ^{9}Y? rationalize.

B) Which is higher in ionization energy, the element ^{19}X or the element ^{34}Y? rationalize.

C) Which is higher in electron affinity, the element ^{12}X or the element ^{38}Y? rationalize.

Solution

A) Answering the question requires writing the electron configuration of each:

^{3}**X:** $1s^2\ 2s^1$

^{9}**Y:** $1s^2\ 2s^2\ 2p^5$

Because their upper shell is the same (n = 2) and, in ^{3}X, is occupied be less number of electrons than in ^{9}Y, then the bigger in radius is ^{3}X.

B) Answering the question requires writing the electron configuration of each:

^{19}**X:** $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1$

^{34}**Y:** $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^4$

Because their upper shell is the same (n = 4) and, in ^{19}X, is occupied be less number of electrons than ^{34}Y, then the bigger in radius is ^{19}X. As a result, ionizing ^{34}Y is harder than ionizing ^{9}X making its ionization energy higher.

C) Answering the question requires writing the electron configuration of each:

^{12}X: $1s^2\ 2s^2\ 2p^6\ 3s^2$

^{38}Y: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6\ 5s^2$

Because the upmost electrons of ^{12}X are closer to nucleus than those of ^{38}Y, then the bigger in radius is ^{38}Y. As a result, attracting an electron by ^{12}X is stronger than that by ^{38}Y making its electron affinity higher than that of ^{38}Y.

Practice exercise

A) Arrange the element ^{14}X, ^{17}Y and ^{32}Z in decreasing ionization energy.

B) Arrange the element ^{11}X, ^{12}Y and ^{19}Z in decreasing electron affinity.

2.7 Molecules and ions

Only the noble gases (group 18) of the periodic table (He, Ne, Ar, Kr, Xe, Rn, and Og) exist as single atoms. This why they are called ***monatomic*** gases. Most matter is composed of molecules or ions formed from atoms.

2.7.1 Molecules

A ***molecule*** is at least two atoms in a definite arrangement held together by chemical bonds. Molecules are electrically neutral. A molecule may contain atoms of the same element such as H_2, O_2 and O_3, or atoms of two or more elements bonded in a fixed ratio such as H_2O, Na_2SO_4. Thus, a molecule is not necessarily a compound made up of two or more elements. The hydrogen molecule, H_2, is called a ***diatomic molecule*** because it *contains only two atoms*. Other elements that normally exist as diatomic molecules are N_2, O_2, F_2, Cl_2, Br_2 and I_2. Of course, a diatomic molecule can contain atoms of different elements. Examples are HCl, CO). The vast majority of molecules contain more than two atoms and called ***polyatomic molecules***. Examples of polyatomic molecules are O_3, H_2O and Na_3PO_4.

2.7.2 Ions and ionic compounds

- **Ions:** An ion is an atom or a group of atoms that has an electric charge.
  - ✓ **Positive ions (Cations):** Loss of electrons by an atom is the reason behind the positive charges of cations. The number of protons of an atom remains the same but electrons become less. Also, two or more atoms can combine to form cations and are classified as *polyatomic cations* such as H_3O^+, NH_4^+ and PH_4^+.
  - ✓ **Negative ions (Anions):** Gain of electrons by an atom is the reason behind the negative charges of anions. The number of positive protons remains the same but electrons become more. The following table shows many negative ions.

The following tables shows the most common positive ions (CATIONS) and negative ions (ANIONS).

Hydrogen	H^+	Chromium	Cr^{3+}
Lithium	Li^+	Manganese(II)	Mn^{2+}
Sodium	Na^+	Iron(II)	Fe^{2+}
Potassium	K^+	Iron(III)	Fe^{3+}
Cesium	Cs^+	Cobalt(II)	Co^{2+}
Rubidium	Rb^+	Copper(I)	Cu^+
Magnesium	Mg^{2+}	Copper(II)	Cu^{2+}
Calcium	Ca^{2+}	Zinc	Zn^{2+}
Strontium	Sr^{2+}	Silver	Ag^+
Barium	Ba^{2+}	Cadmium	Cd^{2+}
Aluminum	Al^{3+}	Mercury(I)	Hg_2^{2+}
Tin	Sn^{2+}	Mercury(II)	Hg^{2+}
Lead(II)	Pb^{2+}	Ammonium	NH_4^+

Hydride	H^-
Nitride	N^{3-}
Oxide	O^{2-}
Peroxide	O_2^{2-}
Sulfide	S^{2-}
Fluoride	F^-
Chloride	Cl^-
Bromide	Br^-
Iodide	I^-
Hydroxide	OH^-
Cyanide	CN^-

Carbonate	CO_3^{2-}	Hydrogen carbonate (bicarbonate)	HCO_3^-
Phosphate	PO_4^{3-}	Hydrogen phosphate	HPO_4^{2-}
Nitrate	NO_3^-	Nitrite	NO_2^-
Sulfate	SO_4^{2-}	Sulfite	SO_3^{2-}
		Hydrogen sulfate (bisulfate)	HSO_4^-
Chlorate	ClO_3^-	Chlorite	ClO_2^-
Chromate	CrO_4^{2-}	dichromate	$Cr_2O_7^{2-}$

The above table shows that two or more atoms can combine to form anions that has a net negative charge; these ions are classified as *polyatomic anions* such as OH^- (hydroxide ion), CN^- (cyanide ion) and NO_3^- (nitrate).

- **Ionic compounds:** The chemical substances that are formed from positive ions and negative ions are called ionic compounds. For example, sodium chloride (NaCl), ordinary table salt, is an ionic compound because it is formed from sodium cations, Na^+, and chloride anions, Cl^-. The positive ions (the cations) in ionic compounds are metals such as sodium, calcium, iron…etc. Also, there are some positive ions that are not metals such as those listed on a previous table namely H_3O^+ (hydronium), NH_4^+ (ammonium) and PH_4^+ phosphonium. On the other hand, the negative ions (the anions) are nonmetals such as nitride, oxide and flouride…etc. Also, there are many negative ions that are not nonmetals such as those listed on a previous table, examples are CO_3^{2-} (carbonate), SO_4^{2-} (sulfate) and PO_4^{3-} (phosphate).
- **Naming ionic compounds:** The previous tables gives the names of many cations and anions.
  - ✓ For compounds formed from just two elements (binary compounds) and for compounds formed from more than two elements, the name starts with name of cation followed by the name of the anion. Examples are:
    KBr is potassium bromide
    ZnF_2 is zinc fluoride
    Al_2O_3 is aluminum oxide
    LiOH is lithium hydroxide
    Na_3N is sodium nitride
    KCN is potassium cyanide
    Na_3N is sodium nitride
    $Ca(CN)_2$ is calcium cyanide
    $Mg(OH)_2$ is magnesium hydroxide
  - ✓ Cations of many 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+} is ferric ion as in ferric chloride, $FeCl_3$.
    - ➢ The ending "-ous" to the cation with fewer positive charges: Fe^{2+} is ferrous ion as in ferrous chloride, $FeCl_2$.

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

      "I" means one positive charge
      "II" means two positive charges
      "III" means three positive charges

"IV" means four positive charges

The following are examples:
$FeCl_2$ is iron(II) chloride
$FeCl_3$ is iron(III) chloride
MnO is manganese(II) oxide
Mn_2O_3 is manganese(III) oxide
MnO_2 is manganese(IV) oxide

EXAMPLE 2.8

Name the following compounds:

A) $Cu(NO_3)_2$ B) KH_2PO_4 C) NH_4ClO_3

Solution

A) The nitrate anion (NO_3^-) has only one negative charge, so the copper cation must have two positive charges: the compound **copper(II) nitrate**.

B) The cation is potassium ion and the anion is dihydrogen phosphate: the compound is **potassium dihydrogen phosphate**.

A) The cation is ammonium ion and the anion is chlorate: the compound is **ammonium chlorate**.

Practice Exercise

Name the following compounds:

A) PbO B) Li_2SO_3 C) $Mn(SO_4)_2$

EXAMPLE 2.9

Write chemical formulas for the following compounds:

A) mercury(I) nitrite B) cesium sulfide C) calcium phosphate

Solution

A) The mercury ion has one positive charge, but mercury(I) ion exists as diatomic (that is, Hg_2^{2+}) and the anion is the nitrite ion (NO_2^-): the formula is **$Hg_2(NO_2)_2$**.

B) Sulfide ion has two negative charges, and cesium ion has one positive charge: the formula is **Cs_2S**.

C) The calcium ion has two positive charges (Ca^{2+}), and phosphate ion is PO_4^{3-}: the formula is **$Ca_3(PO_4)_2$**.

Practice Exercise

Write formulas for the following ionic compounds:

A) rubidium sulfate B)) barium hydride C) aluminum carbonate

2.7.3 Molecules and molecular compounds

A molecule is an electrically neutral entity consisting of more than one atom. Molecules are usually composed of nonmetallic elements. Molecular compounds consisting of two different elements are binary compounds while those consisting of three different elements are tertiary compounds.

- **Naming binary molecular compounds:** Binary molecular compounds are named similarly as binary *ionic compounds* by placing 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" is hydrogen chloride
  - ✓ "HBr" is hydrogen bromide
  - ✓ "SiC" silicon carbide.

  There are some cases where two elements form several different compounds (C and O form CO and CO_2); in such cases Greek prefixes are used to denote the number of atoms of each element presents. The table below shows these Greek prefixes.

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

The following are some examples:

- ✓ "CO" is carbon monoxide and "CO_2" is carbon dioxide
- ✓ "SO_2" is sulfur dioxide and "SO_3" is sulfur trioxide
- ✓ "NO_2" is nitrogen dioxide and "N_2O_4" is dinitrogen tetroxide

The following guidelines are helpful in naming compounds with prefixes:

1. The prefix "mono-" may be omitted for the first element. This absence of a prefix for the first element means that there is only one atom of that element in the molecule:
   For example, PCl_3 is phosphorus trichloride not monophosphorus trichloride
2. For oxides, the ending "a" in the prefix is usually omitted. For example, N_2O_4 is dinitrogen tetroxide rather than dinitrogen tetraoxide.
3. 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.
4. Compounds containing hydrogen are named exceptionally. Many of them are called by their common and nonsystematic names or by names that do not indicate the number of hydrogen atoms. In some formulas, hydrogen is written first not like other were it is written last. The following are some examples:
   - ✓ B_2H_6 is diborane not diboron hexahydride
   - ✓ CH_4 is methane not carbon tetrahydride
   - ✓ SiH_4 is silane not silicon tetrahydride
   - ✓ NH_3 is ammonia not nitrogen triahydride

- ✓ PH_3 is phosphine not phosphorus triahydride
- ✓ H_2O is water not dihydrogen oxide
- ✓ H_2S is hydrogen sulfide not dihydrogen sulfide

EXAMPLE 2.10

Name the following molecular compounds:

A) $SiCl_4$ B) P_4O_{10}.

Solution

A) There are one silicon atom and four chlorine atoms: the compound is **silicon tetrachloride**.

B) There are four phosphorus atoms and ten oxygen atoms: the compound is **tetraphosphorus decoxide**.

Practice Exercise

Name the following molecular compounds:

A) NF_3 b**)** Cl_2O_7

EXAMPLE 2.11

Write chemical formulas for the following molecular compounds:

A) carbon disulfide B) disilicon hexabromide

Solution

A) There are one carbon atom and two sulfur atoms: the formula is **CS_2**.

B) There are two silicon atoms and six bromine atoms: the formula is **Si_2Br_6**.

Practice Exercise

Write chemical formulas for the following molecular compounds:

A) sulfur tetrafluoride B) dinitrogen pentoxide

2.7.2 Acids and bases

- **Acids:** An acid is a substance that has hydrogen atoms in its composition and give them as ions, H^+ when dissolved in water. Also, acids are defined as substances that increases hydrogen ions concentration of water, $[H^+]$, when dissolved in it. When a hydrogen atom loses its electron all left is a proton. Therefore, "H^+" is also called "proton". Acids are classified to two types:
  - ✓ **Naming binary acids:** The following table gives the names anions which ends with the suffix "-ide":

Sulfide	Fluoride	Chloride	Bromide	Iodide	Cyanide
S^{2-}	F^-	Cl^-	Br^-	I^-	CN^-

When one hydrogen ion (or more) is attached to any anion in the above table, the molecular compound formed is named as follows:

Hydrogen sulfide	Hydrogen fluoride	Hydrogen chloride	Hydrogen bromide	Hydrogen iodide	Hydrogen cyanide
H_2S	HF	HCl	HBr	HI	HCN

The ***aqueous*** solution of any one of these compounds is a binary acid and it is named as the following table shows:

Hydrosulfuric acid	Hydrofluoric acid	Hydrochloric acid	Hydrobromic acid	Hydroiodic acid	Hydrocyanic acid
H_2S	HF	HCl	HBr	HI	HCN

✓ **Naming oxacids:**
First: The names of oxoanions which ends with the suffix "-ate":

Nitrate	Carbonate	Sulfate	Phosphate	Fluorate	Chlorate	Bromate	Iodate
NO_3^-	CO_3^{2-}	SO_4^{2-}	PO_4^{3-}	FO_3^-	ClO_3^-	BrO_3^-	IO_3^-

When one hydrogen ion (or more) is attached to any anion listed in the above table, the compound formed is an oxoacid named as follows:

Nitric acid	Carbonic acid	Sulfuric acid	Phosphoric acid	Fluoric acid	Chloric acid	Bromic acid	Iodic acid
HNO_3	H_2CO_3	H_2SO_4	H_3PO_4	HFO_3	$HClO_3$	$HBrO_3$	HIO_3

The last four acids are called "halic acids" because of the presence of "halogen atoms".
All these acids in the table are called "***the reference oxoacids***" because some other oxoacids are derived from them. This derivation comes from adding or removing one or two oxygen atoms to the reference acid:

1. **Addition of one "O" atom to a halic acid:**
   The addition of one "O" atom to a halic acid gives an acid called "perhalic" acid. Thus, adding an "O" atom to (HFO_3) changes chloric acid to perfluoric acid (HFO_4).
2. **Removal of one "O" atom from the halic acid:**
   The removal of one "O" atom from the halic acid gives an acid called "halous" acid. Thus, removing an "O" atom from (HFO_3) changes

fluoric acid to fluorous acid (HFO_2). There are other acids end with "-ous":

- Nitrous acid (HNO_2) derived from nitric acid (HNO_3)
- Sulfurous acid (H_2SO_3) derived from sulfuric acid (H_2SO_3)
- Phosphorous acid (H_3PO_3) derived from phosphoric acid (H_3PO_4)

3. **Removal of two "O" atoms from the "halic" acid:**

The acid is called "hypohalous" acid. Thus, removing two O atoms from (HFO_3) changes fluoric acid to hypofluorous acid ($HClO$). There are other acids end with "-ous":

- Hyposulfurous acid (H_2SO_2) derived from sulfuric acid (H_2SO_4)
- Hypophosphorous acid (H_3PO_2) derived from phosphoric acid (H_3PO_4).

Second: The names of oxoanions which ends with the suffix "-ite":

Nitrite	Sulfite	Phosphite	Fluorite	Chlorite	Bromite	Iodite
NO_2^-	SO_3^{2-}	PO_3^{2-}	FO_2^-	ClO_2^-	BrO_2^-	IO_2^-

When one hydrogen ion (or more) is attached to any anion listed in the above table, the compound formed is an oxoacid named as follows:

Nitrous acid	Sulfurous acid	Phosphorous acid	Fluorous acid	Chlorous acid	Bromous acid	Iodous acid
HNO_2	H_2SO_3	H_3PO_3	HFO_2	$HClO_2$	$HBrO_2$	HIO_2

Third: Removal of hydrogen ions from some oxacids:

The names of anions in which one or more but not all the hydrogen ions have been removed must indicate the number of remaining hydrogen ions. For example:

- The removal of one hydrogen ion from phosphoric acid (H_3PO_4) produces the ion $H_2PO_4^-$, the name of this ion is dihydrogen phosphate.
- The removal of two hydrogen ion from phosphoric acid (H_3PO_4) produces the ion HPO_4^{2-}, the name of this ion is hydrogen phosphate.

Finally, the following table gives the names and formulas of the oxacids and oxanions discussed above:

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^{3-}
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 2.12

Name the following oxoacid and oxoanion:

A) H_3PO_3 B) IO_4^-

Solution

A) The reference acid is phosphoric acid (H_3PO_4). Because H_3PO_3 has one fewer O atom, it is **phosphorous acid**.

B) The reference acid is chloric acid (HIO_3). Because the acid HIO_4 has one more O atom than our reference acid, it is called periodic acid and its oxanion, IO_4^-, is **periodate ion**.

Practice Exercise

Name the following oxoacid and oxoanion:

A) HBrO	B) HSO_4^-.

- **Bases:** A base is a substance that yields hydroxide ions (OH^-) when dissolved in water. Some examples are NaOH, KOH and $Ba(OH)_2$. These compound are named as ionic compounds are named. The name start with metal name snd ends with the anion name which is hydroxide. Therefore, the names of the previous three bases are sodium hydroxide, potassium hydroxide and barium hydroxide respectively.

  Ammonia (NH_3) is a very famous base but it does not have OH^- in its formula. It is a molecular compound in its gaseous state or when it is a pure. When NH_3 is dissolved in water, it reacts partially with water to yield NH_4^+ and OH^- ions:

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

  Thus, its aqueous solution is properly classified as a base.

2.7.3 Hydrates

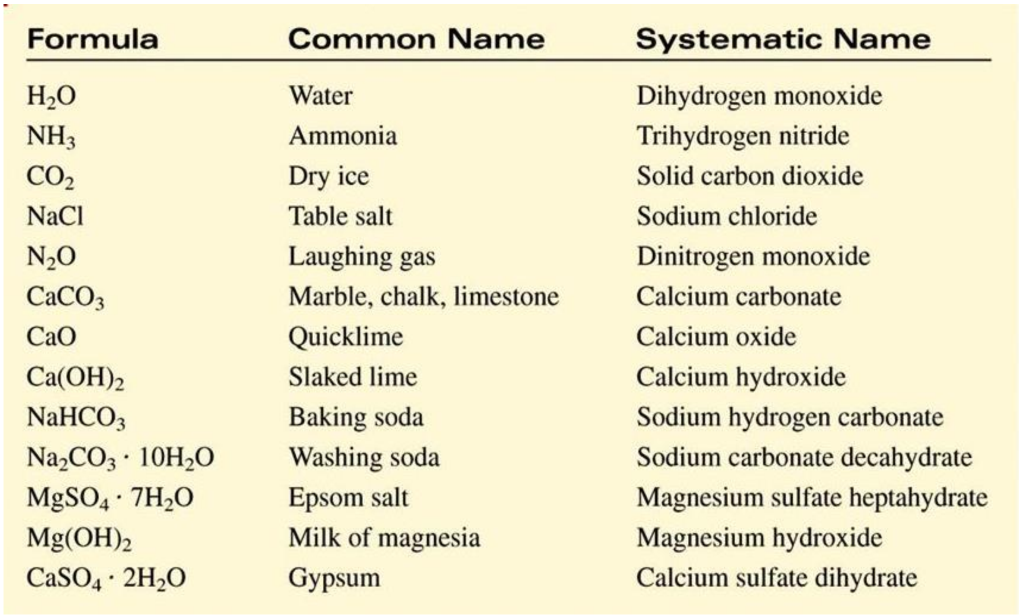
Hydrates are compounds that have a specific number of water molecules attached to them. For example, in its normal state, each unit of copper(II) sulfate has five water molecules associated with it. The systematic name for this compound is copper(II) sulfate pentahydrate. Its formula is written as:

$$CuSO_4 \cdot 5H_2O$$

The water molecules can be driven off by heating. When this occurs, the resulting compound is $CuSO_4$, which is named copper sulfate and sometimes called anhydrous copper(II) sulfate. The word “anhydrous” means that the compound no longer has water molecules associated with it. Some other hydrates are: $BaCl_2 \cdot 2H_2O$, $LiCl \cdot H_2O$, $MgSO_4 \cdot 7H_2O$ and $Sr(NO_3)_2 \cdot 4H_2O$. the names of the previous hydrates are barium chloride dehydrate, lithium chloride monohydrate, magnesium sulfate heptahydrate and strontium nitrate tetrahydrate

2.7.4 Familiar inorganic compounds

There are several compounds acquired their names since remote human history, or have names that are so common among people worldwide and among chemists. These compounds kept their common names. The following table gives the formula and their common and systematic names.



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

3. STOICHIOMETRY AND CHEMICAL EQUATIONS

3.1 Atomic mass unit, Avogadro's number and the mole

3.1.1 Atomic mass unit

The unit used to express the mass of atoms, molecules and nuclear particles is called the "atomic mass unit", abbreviated "amu"; it is also called "Dalton". The atomic mass unit is the of mass which equals to $\frac{1}{12}$ the mass of a single atom of carbon isotope ^{12}C. As expected, its value is so small when compared with the unit "gram":

$$1 \text{ amu} = 1.993 \times 10^{-23} \text{ g}$$

The atomic mass units (amu) provide a relative scale for the masses of the elements. But because this mass is extremely small, no usable scale can be devised to weigh the masses of atoms, molecules and nuclear particles.

3.1.2 Avogadro's number

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. In 1811 a brilliant idea was provided by The Italian scientist, **Avogadro** (1776 – 1856). The idea is that if we express the atomic mass of an element in the unit of "gram" rather than in the unit of "amu" we will have the same number of atoms regardless of the type of the element we chose. Avogadro died before achieving his goal to determine this number. However, the value was first determined in 1865 by the Austrian scientist Josef Loschmidt. This number was named "***Avogadro's number***" by the French scientist Jean Perrin. In its present definition Avogadro's number, N_A, is the number of carbon-12 atoms in 0.012 kg of carbon-12 isotope. Its currently accepted value is

$$N_A = 6.0221415 \times 10^{23} = 6.022 \times 10^{23}$$

Thus, just 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 of no less than 14 km into space!

3.1.3 The mole

The mole (mol) is the amount of a substance that contains Avogadro's number of its particles (atoms, molecules, ions or any other particles). So, having one mole of atoms, oranges or anything means having Avogadro's number of atoms, oranges or anything. We usually give the symbol "N" for the number of particles we have. The value of "N" may equal Avogadro's number, more than Avogadro's number or less than Avogadro's number.

The mole is chosen as the SI unit for the "amount of substance". The IUPAC definition of the mole is that the mole is the ***amount of substance*** of a system which contains as many elementary entities as there are atoms in 0.012 kilogram of carbon-12. When the mole is used, the elementary entities must be specified and may be atoms, molecules, ions, electrons, other particles, or specified groups of such particles.

3.1.3 The molar mass of an element

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. 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 calculated as follows:

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

It is very important to know the mathematical relations between "M", "m", "n", "N" and "N_A".

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

The relations between all of the above are:

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

We can close this discussion saying that the above three equations ar so important and are needed almost in all chemical calculations:

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

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

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

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

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

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

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

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

Practice Exercise

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

3.1.4 Molecular Mass and formula mass

Molecular mass

We know that “H_2O” is the formula water. Therefore, the mass of one mole of water is the sum of the mass, in “amu” unit or in “g” unit, of two moles of hydrogen atoms and one mole of oxygen atoms:

The molar mass of H_2O = 2 × (atomic mass of H) + 1 × atomic mass of O
The molar mass of H_2O = 2 × (1.008 amu) + 1 × (16.00 amu) = 18.016 amu
The molar mass of $H_2O = 2 \times (1.008\ \frac{\text{g}}{\text{mol}}) + 1 \times (16.00\ \frac{\text{g}}{\text{mol}}) = 18.016\ \frac{\text{g}}{\text{mol}}$

Now, because this mass of water is the mass of one mole of water and because water consists of molecules, this mass is also called “the molecular mass”

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) $M_{SO_2} = 1 \times 32.07\ \text{amu} + 2 \times 16.00\ \text{amu} = 64.07\ \text{amu}$

B) $M_{C_8H_{10}N_4O_2} = (8 \times 12.01\ \text{amu}) + (10 \times 1.008\ \text{amu}) + (4 \times 14.01\ \text{amu}) + 2 \times 16.00\ \text{amu} = 194.20\ \text{amu}$

Practice Exercise

What is the molecular mass (in amu) of methanol (CH_4O)?

From the above discussion we conclude that using the unit “amu” or the the unit “$\frac{\text{g}}{\text{mol}}$” gives the same numerical value of the molar mass of the substance. Also, we conclude that the term “molar mass” applies for atomic, ionic and molecular substances, whereas the term “molecular mass” applies only for molecular substances

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

$$n = \frac{m}{M} = \frac{6.07\ \text{g}}{1 \times 12.01\ \frac{\text{g}}{\text{mol}} + 4 \times 1.008\ \frac{\text{g}}{\text{mol}}} = 0.378\ \text{mol}$$

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

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

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

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

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

Practice Exercise

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

Formula mass

Ionic compounds like NaCl and MgO are not consist of molecules. Therefore, for them we do not use the term molecular mass but the term ***formula mass***. 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:

$$\text{formula mass of NaCl} = 22.99 \text{ amu} + 35.45 \text{ amu} = 58.44 \text{ amu}$$

Note that its molar mass is 58.44 g/mol.

3.2 Percent composition of elements in compounds

Any compound is composed of two elements or more. The mass percent of any element in the compound is called the "**percent composition of the element in a compound**" and is obtained by dividing the mass of the element in 1 mole of the compound by the molar mass of the compound and multiplying by 100:

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

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.

Solution

The molar mass of H_3PO_4 is 97.99 g/mol

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

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

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

Practice Exercise

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

3.3 Empirical and molecular formulas

3.3.1 Empirical formulas

The empirical formula of a compound is the formula which tells us the numerical ratios 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 qualitative chemical analysis we know the elements of the compound.
- ✓ Second, from quanitative chemical analysis, we know the mass (or the mass percent) of each element present in a given mass of the compound.
- ✓ Third, we convert the masses to number of moles of each element.
- ✓ Forth, we obtain the mole ratio of elements to each other.
- ✓ Finally, we find the empirical formula of the compound.

EXAMPLE 3.8

Ascorbic acid 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

$$\begin{array}{ccccc}
C & : & H & : & O \\
\frac{40.92\ g}{12.01\ \frac{g}{mol}} & : & \frac{4.58\ g}{1.008\ \frac{g}{mol}} & : & \frac{54.50\ g}{16.00\ \frac{g}{mol}} \\
3.407 & : & 4.54 & : & 3.406 \\
\frac{3.407}{3.406} & : & \frac{4.54}{3.406} & : & \frac{3.406}{3.406} \\
1 & : & 1.33 & : & 1 \\
3 & : & 4 & : & 3
\end{array}$$

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

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%.

3.3.2 Molecular formulas

4 The molecular formula is that empirical formula with actual number of each element in the compound, but the formula calculated from percent composition by mass is 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 one of the many empirical formulas. To know the molecular formula (the actual formula), we must know the molar mass or 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.

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

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

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

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

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

NO_2 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 2 × NO_2

The molecular formula is N_2O_4.

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?

3.4 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. To communicate with one another about **chemical equations**, chemists have devised a standard way to represent what happens to atoms and molecules in a chemical reaction. This way is called The **chemical-reaction equations**, or simply the **chemical equations** the ***chemical equations*** *use chemical symbols to show what happens during a chemical reaction*.

3.4.1 Writing chemical equations

The chemical equation consists of three parts. The first part is the most important and the most to be forgotten or ignored.

- The first part is an arrow "→"
- The second part is the reactants on the left side of the arrow an arrow "→"
- The third part is the products on the right side of the arrow an arrow "→"

The arrow is the speaker of the equation (***The narrator***). It tells us what and how much we had at the beginning and what and how much we had at the end. Consider what happens when hydrogen gas (H_2) burns in oxygen (O_2) of air forming water (H_2O).

This reaction is represented by the chemical equation as:

$$H_2 + O_2 \rightarrow H_2O$$

The "plus" sign means "reacts with" and the arrow tells us the story as follows: "water is produced on the expense of consuming hydrogen and oxygen. Thus, this symbolic expression can be read as follows:

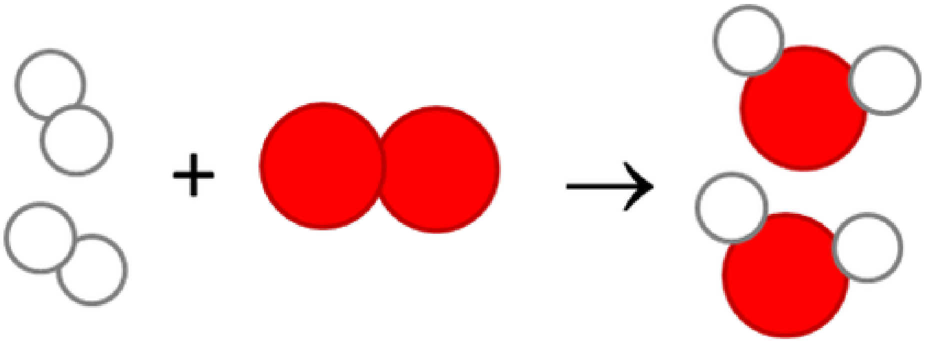
“Molecular hydrogen reacts with molecular oxygen to produce water”

If we carefully look at the equation, we can notice that it violates an important law of nature which is the law of conservation of matter. However, this violation can be simply prevented by ensuring that number of atoms of any element on the right and on the left sides of the arrow are equal. This can be done by balancing the equation. The *balanced* equation previous reaction is:

$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O$$

Usually, we prefer that equation is balanced in a way that gives whole correct numbers without fractions. So, although the last equation is correctly balanced, we prefer the following equation:

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



$2H_2$ + 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. “***2 hydrogen molecules react with 1 oxygen molecule to form 2 water molecules***.”
2. “***2 moles of hydrogen molecules react with 1 mole of oxygen molecules to produce 2 moles of water molecules***.”
3. “***4.016 g of H_2 react with 32.00 g of O_2 to give 36.016 g of H_2O***.”

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.

Balancing chemical equations

You 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.
3) **First**, 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.
   Next, look for elements that appear only once on each side of the equation but in unequal numbers of atoms. Balance these elements.
   Finally, 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:

$$KClO_3 \rightarrow KCl + O_2$$

✓ We balance the O atoms:

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

✓ We balance the K and Cl atoms:

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

- Let’s consider another example:

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

- ✓ We balance the C atoms:

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

- ✓ We balance the H atoms:

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

- ✓ We balance the O atoms:

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

- ✓ We usually prefer the coefficients as whole numbers:

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

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).

3.5 Amounts of reactants and products in chemical reactions

Stoichiometry is *the quantitative study of reactants and products in a chemical reaction.* ***Stoichiometry*** answers questions such as:

- "How much product will be formed as a result of the reaction of a specific amount of a reactant?"
- "How much reactant must be used in a reaction 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.

Whether the units given for reactants (or products) are moles, grams, liters , or any other units, we use the "***mole method***" in which the "***mole***" is the unit used to calculate the amount of reactants consumed or remained and the amount of products formed in a reaction.

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 mole of N_2 reacts with three moles of H_2 to form two moles of NH_3. The relative numbers of moles are the same as the number of coefficients in the balanced chemical equation. The way of representing this fact is usually done in tables like the following table:

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

Let's consider a case 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

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

Now suppose 16.0 g of H_2 reacted completely with N_2 to form NH_3, and we need to know number of grams of NH_3 formed. We do this calculation using the "***mole method***", 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:

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

$$\text{number of moles of } H_2 = \frac{16\ \mathrm{g}}{2.016\frac{\mathrm{g}}{\mathrm{mol}}} = 7.94\ \mathrm{mol\ H_2}$$

Then we construct our table

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

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

$$m = n \times M$$

$$\text{mass of } NH_3 = 5.29\ \mathrm{mol} \times 17.03\ \frac{\mathrm{g}}{\mathrm{mol}} = 90.1\ \mathrm{g\ NH_3}$$

Similarly, we can calculate the mass in grams of N_2 consumed.
The general approach for solving stoichiometry problems is as follows:
Write a balanced equation for the reaction.

1) Write a balanced equation for the reaction
2) Make sure that the amounts of the substances are in the unit of moles
3) Use the mole ratio from the balanced equation to calculate the number of moles of the substance of interest
4) Convert the calculated moles of to any other unit you like

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

	$C_6H_{12}O_6$	+	$6O_2$	$\rightarrow$	$6CO_2$	+	$6H_2O$
Equation moles	1 mole				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

mass of CO_2 produced = n × M = 28.50 mol × 44.01 $\frac{\mathrm{g}}{\mathrm{mol}}$ = 1.25×10^3 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 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

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

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

X = number of moles of Li = 2 mol of Li × $\frac{5\ \mathrm{mol\ H_2}}{1\ \mathrm{mol\ H_2}}$ = 10 mol

mass of Li needed = n × M = 10 mol × 6.941 $\frac{\mathrm{g}}{\mathrm{mol}}$ = 69.41 g

Practice Exercise

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

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

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

3.6 Limiting reactants (reagents)

Let's imagine that some students visiting a friend got hungry and asked him for something to eat. Also, Let's imagine that he has nothing except a bag containing 11 toast breads and 4 slices of cheese. To make a sandwich two toasts and one cheese slice is needed. If we symbolize the toast as "Ts" and the cheese as "Ch", the formula of the sandwich will be "Ts_2Ch":

$$2Ts + Ch \rightarrow Ts_2Ch$$

We know that number "Ch" available is enough to produce only 4 "Ts_2Ch" while some of the "Ts" will remain unreacted because it is present in access. We say that "Ch" is the reactant which ***limits*** the amount of products because it is the one which is consumed completely and we call it "***the limiting reactant***". At the same time, we say that "Ts" is the ***in access reactant*** because some of it will be left over or will remain unreacted.

When a chemist carries out a reaction, the reactants are usually not present in exact ***stoichiometric amounts*** as the balanced equation requires. This is 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 reactant*** or the ***limiting reagent***. It is called so because the maximum amount of product formed is limited by its amount. Once this reactant is used up, no more product can be formed. *Any reactant presents in a quantity greater than necessary to react with the quantity of the limiting reactant i*s called ***excess reactant*** or ***excess reagent***.

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.

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

number of moles of CO_2 = $\frac{m}{M} = \frac{1142\ g}{44.02\,\frac{g}{mol}}$ = 25.943 mol

	$2NH_3$	+	CO_2	→	$(NH_2)_2CO$	+	H_2O
Equation moles	2		1				
Question moles	37.416		25.943				
$\frac{\text{Question moles}}{\text{Equation moles}}$	18.708		25.943				

B) It is clear from the above that NH_3 is the limiting reagent.

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

X = number of moles of $(NH_2)_2CO$ = $\frac{37.416\ mol \times 1\ mol}{2\ mol}$ = 18.708 mol

mass of $(NH_2)_2CO$ = n × M = 18.708 mol × 60.06 g/mol = 1123.6 g

C)

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

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

number of moles of CO_2 remains = 25.943 mol – 18.708 mol = 7.235 mol

mass of CO_2 remains = n × M = 7.235 mol × 44.02 g/mol = 318.5 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?

3.7 Reaction yield (Yield percentage)

The amount of a product that should be produced as a result of a chemical reactions can be calculated theoretically as explained in the previous two section (section 3.5 and section 3.6). this amount of product calculated this way is called “***the theoretical yield***” of the reaction. The theoretical yield is, *the amount of product that would result if all the limiting reagent reacted*. Itis the *maximum* obtainable yield, and cannot be known except by calculations on the balanced equation.

The amount of a product that is produced in reality (not theoretically) as a result of a chemical reactions is different from the ***theoretical yield*** which our calculations give and is called “***the actual yield***”. For many reasons, *the actual yield* is always less than ***the theoretical yield***. Producing an amount of product less than what it should be is not welcomed. As the amount of actual yield get closer to the amount of the theoretical yield as we become more satisfied and feel much successful.

Chemists have created a criterion that could be a measure of their efficiency and success in production of chemicals. This criterion is called “***the yield percent***”, or “***the yield percentage***”

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

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

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				
$\frac{\text{Question moles}}{\text{Equation moles}}$	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		

Theoretical yield of Ti = $\frac{1.87 \times 10^5 \text{ mol} \times 1 \text{ mol}}{1 \text{ mol}} = 1.87 \times 10^5$ 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) %yield = $\frac{\text{actual yield}}{\text{theoretical yield}} \times 100 = \frac{7.91 \times 10^6 \text{ g}}{8.95 \times 10^6 \text{ g}} \times 100 = 88.37\%$

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.

3.8 Some kinds of chemical reactions

3.8.1 Combination reactions

A combination reaction is a reaction in which two or more substances react to form **one** product. For example, magnesium metal burns in oxygen to produce magnesium Oxide:

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

Other examples of combination reactions are:

$$C(s) + O_2(g) \rightarrow CO_2(g)$$

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

$$CaO(s) + H_2O(L) \rightarrow Ca(OH)_2(s)$$

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

$$CuO(s) + H_2O(L) \rightarrow Cu(OH)_2(s)$$

3.8.2 Decomposition reactions

A decomposition reaction is a reaction in which **one** substance undergoes a reaction to produce two or more other substances. For example, magnesium oxide may decompose to produce magnesium metal and oxygen:

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

Other examples of decomposition reactions are:

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$$
$$2NaN_3(s) \rightarrow 2Na(s) + 3N_2(g)$$
$$2KClO_3(s) \rightarrow 2KCl(s) + 3O_2(g)$$
$$PbCO_3(s) \rightarrow PbO(s) + CO_2\ (g)$$
$$Cu(OH)_2(s) \rightarrow CuO(s) + H_2O(L)$$

The above examples clarify that decomposition reactions are the opposites of combination reactions.

3.8.3 Combustion reactions

Combustion reactions is a reaction in which a substance (fuel) reacts (burns) in oxygen O_2 to produce either water or carbon dioxide or both.

First: The combustion reaction of hydrogen

The combustion reaction of hydrogen gas produces water:

$$H_2(g) + 0.5O_2(g) \rightarrow H_2O(l)$$

Second: The combustion reaction of carbon

The combustion reaction of solid carbon produces carbon dioxide:

$$C(s) + O_2(g) \rightarrow CO_2(g)$$

Third: The combustion reaction of a substance containing hydrogen and carbon:

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$$
$$C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l)$$
$$C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$$
$$C_6H_{12}O_6(g) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l)$$
$$C_6H_5NH_2(l) + 7.75O_2(g) \rightarrow 6CO_2(g) + 3.5H_2O(l) + 0.5N_2(g)$$

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 of 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 of ethanol.

4. GASES

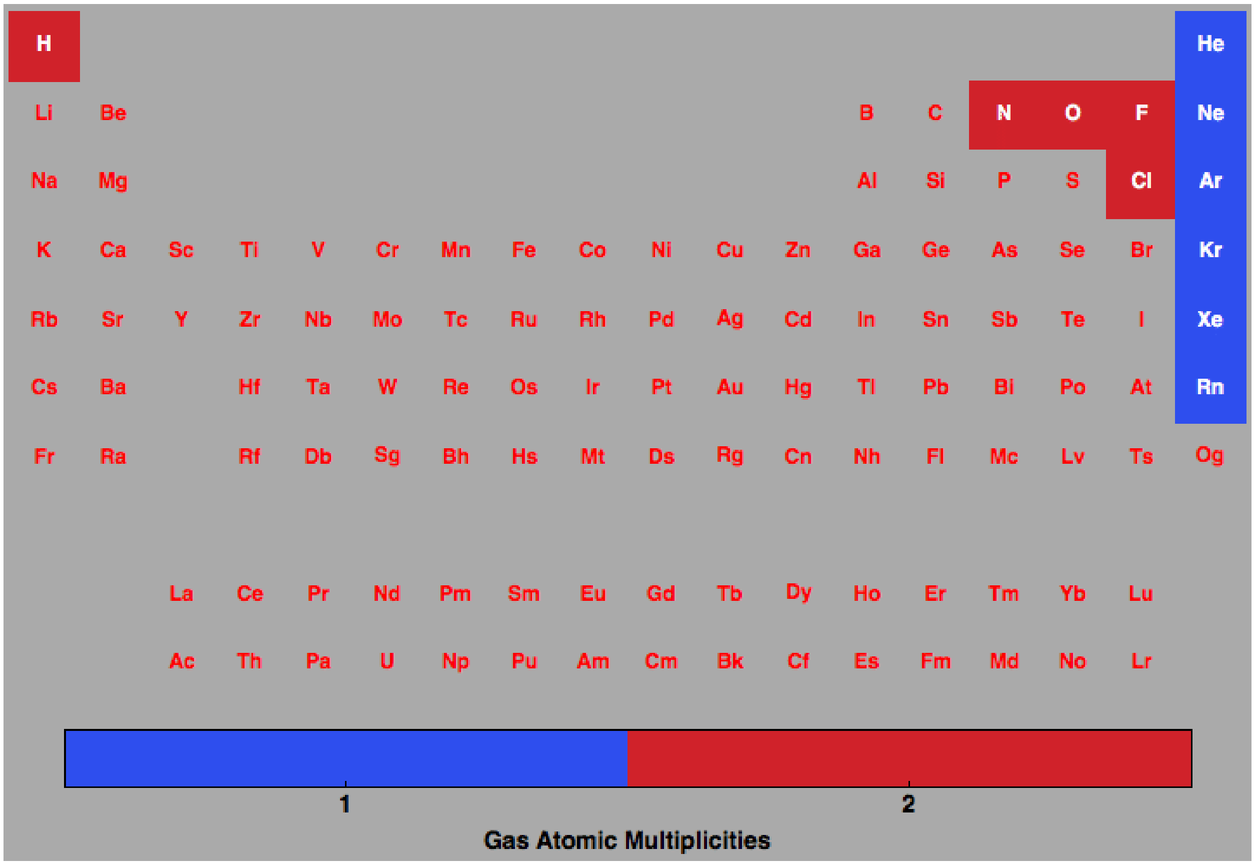
4.1 Substances that exist as gases

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 of CO_2 and other gases. 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)***.

4.1.1 Elements that exist as gases

The figure below shows the elements that are gases under normal conditions.

- ✓ All the elements in Group 18, the noble gases, exist as ***monatomic*** gases: He, Ne, Ar, Kr, Xe, Rn and Og.
- ✓ These elements of hydrogen, nitrogen, oxygen, fluorine, and chlorine exist as ***diatomic*** molecules: H_2, N_2, O_2, F_2, and Cl_2.
- ✓ Ozone is another form of oxygen that exist as ***tritomic*** molecules, O_3.



H
He
Li
Be
B
C
N
O
F
Ne
Na
Mg
Al
Si
P
S
Cl
Ar
K
Ca
Sc
Ti
V
Cr
Mn
Fe
Co
Ni
Cu
Zn
Ga
Ge
As
Se
Br
Kr
Rb
Sr
Y
Zr
Nb
Mo
Tc
Ru
Rh
Pd
Ag
Cd
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Sn
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Rg
Cn
Nh
Fl
Mc
Lv
Ts
Og
La
Ce
Pr
Nd
Pm
Sm
Eu
Gd
Tb
Dy
Ho
Er
Tm
Yb
Lu
Ac
Th
Pa
U
Np
Pu
Am
Cm
Bk
Cf
Es
Fm
Md
No
Lr
1
2
Gas Atomic Multiplicities

4.1.2 Compounds that exist as gases

Poisonous compounds such as hydrogen sulfide (H_2S) and hydrogen cyanide (HCN) and many others such as CO, NO_2, O_3, and SO_2 are gases under ***normal***

atmospheric conditions. The following is a list of the most famous gaseous compounds.

Name	Formula	Name	Formula
Hydrogen fluride	HF	Carbon monoxide	CO
Hydrogen chloride	HCl	Carbon dioxide	CO_2
Hydrogen bromide	HBr	Nitrogen monoxide	NO
Hydrogen iodide	HI	Nitrogen dioxide	NO_2
Hydrogen cyanide	HCN	Dinitrogen tetroxide	N_2O_4
Hydrogen sulfide	H_2S	Sulfur dioxide	SO_2
Ammonia	NH_3	Sulfur trioxide	SO_3

4.2 Four important properties in studying gases

The following table gives the four properties of gases that are so important to know while studying or dealing with gases:

PROPERTY	SYMBOL	UNITS	
		SI Units	Non SI Units
Amount	n	Mole (mol)	--------------
Temperature	T	Kelvin (K)	--------------
Pressure	P	Pascal (Pa)	atm
Volume	V	Cubic meter (m^3)	Liter (L)

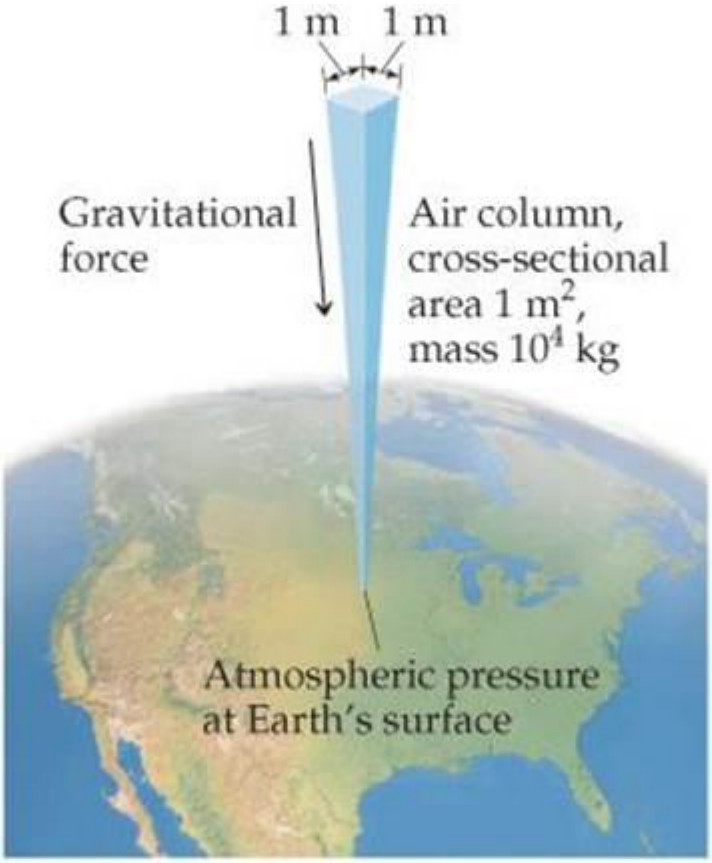
4.3 Atmospheric pressure

4.3.1 Definition of atmospheric pressure

The pressure of the earth atmosphere is the effect of the force (weight) of the Earth's atmosphere on a specified area of the Earth's surface. If we choose an area on the surface of our Earth that equals 1 m^2, there will be above it a column of air extending all the way up to the far end of the Earth atmosphere. The height of this column from sea level is about 90 km. Off course. The height of this column from the sea level is more than from Everest peak (8850 m above sea level) and less than from the level of the dead sea (423 m below sea level).

4.3.2 Definition of standard atmospheric pressure

The pressure of the atmosphere at sea level at 273 K is called "***standard atmospheric pressure***". Its value is 101,325 Pa which equals (1 atm or 760 mmHg). It is less than this value at areas above sea level and lower than this value at areas below sea level.


1 m
1 m
Gravitational force
Air column, cross-sectional area 1 m², mass 10⁴ kg
Atmospheric pressure at Earth's surface

4.4 Standard temperature and pressure (STP)

When studying gases, we encounter the term **S**tandard **T**emperature and **P**ressure (**STP**). STP means that temperature of the gas is 0 °C (273 K) and pressure of the gas is101325 Pa (1 atm).

4.5 The gas laws

4.5.1 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 ideal gas law***" or simply the **gas law**. The gas law is written as follow:

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

R is the gas constant.

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

This means that:

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

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

1) Using the SI units:

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

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:

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

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

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

4.5.2 Special cases of the gas law

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

Case (1) The gas law at constant quantity and temperature (Boyle's law)

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

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

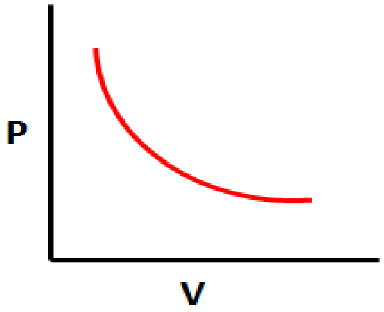
$$P_1 \times V_1 = P_2 \times V_2$$

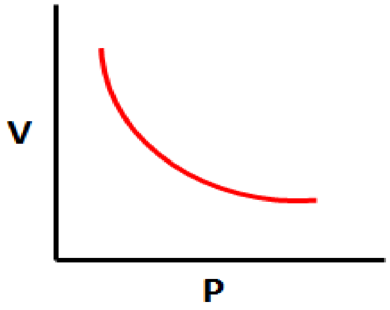
$$P \times V = \text{constant}$$

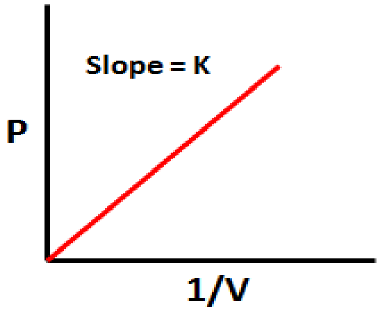
He found that as pressure increases volume decreases:

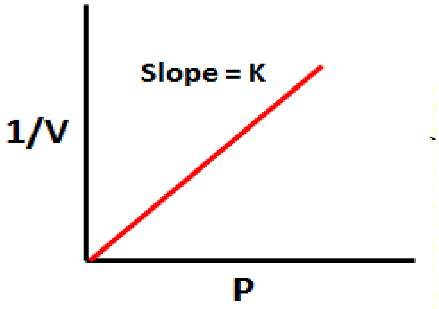
$$P \propto \frac{1}{V}$$

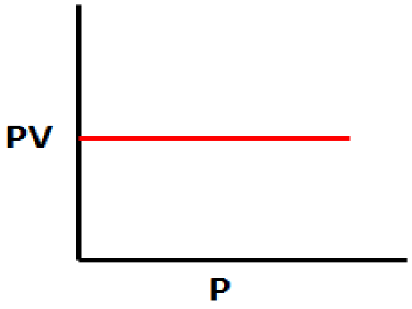
The figures below show, in different ways, the relationship between the gas P and V at constant n and T.

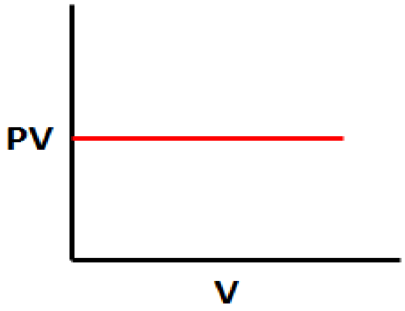












Case (2) The gas law at constant quantity and pressure (Charles's and Gay Lussac's law)

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 $P_1 = P_2$):

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

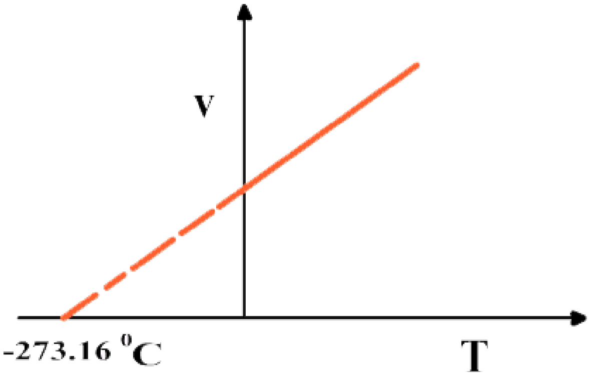
$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

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

They found experimentally that as absolute temperature increases volume directly 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 $P_1 = P_2$):

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

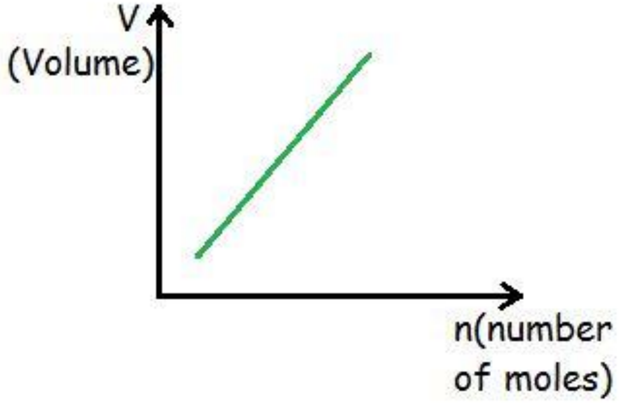
$$\frac{V_1}{n_1} = \frac{V_2}{n_2}$$

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

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 amount
(The cmbined gas law)

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

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

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

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

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

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

$P_2 = 1.48 \text{ atm}$

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

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

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

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

V_2 = 14.3 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.

4.5.3 Calculations of the gas density and molar mass

From the gas law, $P \times V = n \times R \times T$, and from the equation "$m= n \times M$" we can relate the gas density to its molar mass:

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

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

Unlike molecules in liquids and solids, gaseous molecules are separated by distances that are large compared with their size. Consequently, the density of gases is very and are expressed in grams per liter (g/L) rather than in 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 atm × 44.1 g/mol = d × 0.0821 atm L/mol K × (55 °C + 273) K

d = 1.62 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 atm × M = 7.71 g/L × 0.0821 atm L/mol K × (36 °C + 273) K

M = 67.9 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

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

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

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

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

$$1 \quad : \quad 3$$

Therefore, the empirical formula is **SiF_3**

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

Second, we find the actual molar mass (molar mass of molecular formula)

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

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

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

Third, we divide actual molar mass by the empirical molar mass,

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

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?

4.6 Dalton's law of partial pressures

MOLE FRACTION

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

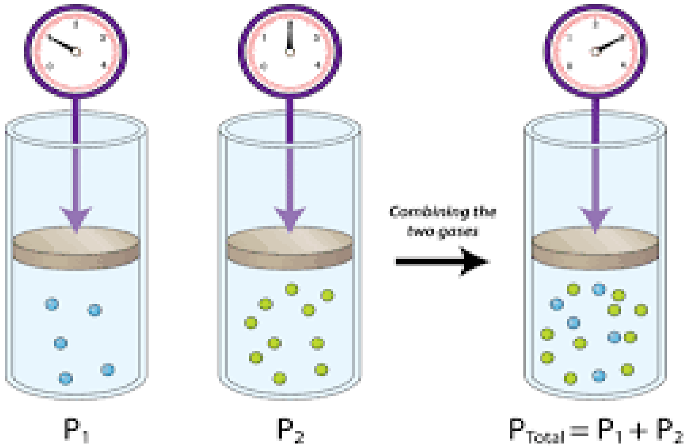
- When more than one substance (for example, two substances "A" and "B") are present together, and we know the number of moles of each "n_A" and "n_B", this means that we know the total number of moles "n_{Total}".

- 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:

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

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

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

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

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

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

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

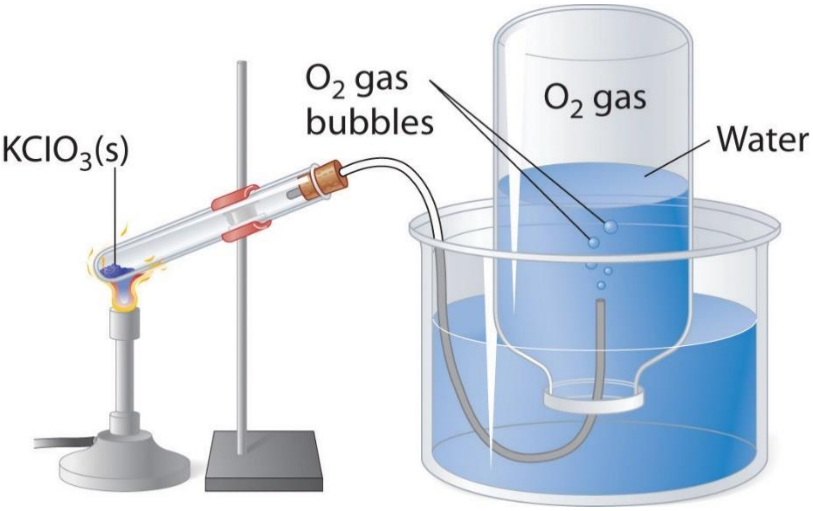
$$P_{Ar} = 0.1 \times 2\text{ atm} = 0.2\text{ atm}$$

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

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:

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

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

$P_{\text{oxygen}} = P_{\text{Total}} - P_{\text{water vapor}} = 762\ \text{mmHg} - 22.4\ \text{mmHg} = 740\ \text{mmHg}$

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

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

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

$\text{Mass of } KClO_3 = n \times M = 3.41 \times 10^{-5}\ \text{mol} \times 123.427\ \frac{\text{g}}{\text{mol}} = 4.21 \times 10^{-5}\ \text{g}$

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.

4.7 Gas stoichiometry

When the reactants and/or products are gases, we can use the relationships between amounts (moles, n) and volume (V) to solve such problems. The following examples show how the gas laws are used in these calculations.

Example 4.11

Calculate the volume of O_2 (in liters) required for the complete combustion of 7.64 L of acetylene (C_2H_2) measured at the same temperature and pressure.

$$2C_2H_2\ (g) + 5O_2(g) \rightarrow 4CO_2(g) + 2H_2O(l)$$

Solution

$$2C_2H_2\ (g) + 5O_2(g) \rightarrow 4CO_2(g) + 2H_2O(l)$$

2 L 5 L

7.64 L V_{oxyg}

$$V_{oxyg} = \frac{5\ L \times 7.64\ L}{2\ L} = 3.056\ L$$

Practice exercise

The equation of the reaction between nitric oxide and oxygen is:

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

If 9.0 L of NO reacted with excess O_2 at STP, calculate the volume and the number of moles of the NO_2 produced?

Example 4.12

Assuming no change in temperature and pressure, calculate the volume of O_2 (in liters) required for the complete combustion of 14.9 L of butane (C_4H_{10}):

$$2C_4H_{10}\ (g) + 13O_2(g) \rightarrow 8CO_2(g) + 10H_2O(l)$$

Solution

$$2C_4H_{10}\ (g) + 13O_2(g) \rightarrow 8CO_2(g) + 10H_2O(l)$$

2 L 13 L

14.9 L V_{oxyg}

$$V_{oxyg} = \frac{13\ L \times 14.9\ L}{2\ L} = 96.85\ L$$

Practice exercise

Sodium azide (NaN_3) is used in some automobile air bags. The impact of a collision triggers the decomposition of NaN_3 as follows:

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

The nitrogen gas produced quickly inflates the bag between the driver and the windshield and dashboard. Calculate the volume of N_2 generated at 80°C and 823 mmHg by the decomposition of 60.0 g of NaN_3.

Example 4.13

The equation for the metabolic breakdown of glucose ($C_6H_{12}O_6$) is the same as the equation for the combustion of glucose in air:

$$C_6H_{12}O_6(s) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l)$$

Calculate the volume of CO_2 produced at 37 °C and 1.00 atm when 5.60 g of glucose is used up in the reaction.

Solution

$$n_{CO_2} = 6 \times n_{C_6H_{12}O_6} = 6 \times \frac{5.6\ \mathrm{g}}{180.156\ \frac{\mathrm{g}}{\mathrm{mol}}} = 0.1865\ \mathrm{mol}$$

$$V = \frac{n \times R \times T}{P} = \frac{0.1865\ \mathrm{mol} \times 0.0821\ \frac{\mathrm{atm\ L}}{\mathrm{mol\ K}} \times (37 + 273)\mathrm{K}}{1\ \mathrm{atm}} = 4.75\ \mathrm{L}$$

Practice exercise

The combustion equation of methane is:

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$$

If 15.0 moles of CH_4 are reacted, calculate the volume of CO_2 produced at 23.0 °C and 0.985 atm?

4.8 The kinetic molecular theory of gases

The gas laws help us to predict the behavior of gases, but they do not explain what happens at the molecular level to cause the changes we observe in the macroscopic world. However, it becomes so clear to physicists and chemists that this macroscopic and sensible behavior of gases is a reflection of the behavior of its atomic and molecular microscopic behavior that opens the door to a deeper understanding of properties such as expansion of gases on heating.

4.8.1 The five hypotheses of the theory

In the nineteenth century, a number of physicists, notably Ludwig Boltzmann and James Clerk Maxwell, found that the physical properties of gases can be explained in terms of the motion of individual molecules. This molecular movement is a kinetic energy (KE). Maxwell, Boltzmann, and others concluded *a number of generalizations about gas behavior* that have since been known as the ***kinetic molecular theory of gases,*** or simply the ***kinetic theory of gases***. This theory is formulated as follows:

1) A gas is composed of molecules that are separated from each other by distances far greater than their own dimensions. The molecules can be considered to be “points”; that is, they possess mass but have negligible volume.
2) Gas molecules exert neither attractive nor repulsive forces on one another.
3) Gas molecules are in constant motion in random directions.
4) Gas molecules frequently collide with one another and with the walls of the container they occupy. Collisions are perfectly elastic (this means that energy is transferred from one molecule to another as a result of a collision). Nevertheless, the total energy of all the molecules in a system remains the same.

5) The average kinetic energy of the molecules is proportional to the temperature of the gas in kelvins. Any two gases at the same temperature will have the same average kinetic energy.

The average kinetic energy of a molecule with a mass equals “m” is given by the following equation:

$$\overline{\text{KE}} = \frac{1}{2}\,\text{m}\,\overline{\text{U}^2}$$

U is the speed of the molecule but $\overline{\text{U}^2}$ is the mean square speed; the bar over U^2 means that it is the average of the square of the speeds of all the molecules and is usually given the symbol U_{rms} which means the root-mean-square speed of all molecules. The value of U_{rms} can be obtained using the following equation:

$$\text{U}_{\text{rms}} = \sqrt{\frac{3\text{RT}}{\text{M}}}$$

Example 4.14

Calculate the root-mean-square speeds of helium atoms and nitrogen molecules in $\frac{\text{m}}{\text{s}}$ at 25°C.

Solution

$$\text{U}_{\text{rms,He}} = \sqrt{\frac{3\text{RT}}{\text{M}_{\text{He}}}} = \sqrt{\frac{3 \times 8.314\,\frac{\text{J}}{\text{mol K}} \times 298\ \text{K}}{4.003\frac{\text{g}}{\text{mol}} \times \frac{1\ \text{kg}}{1000\ \text{g}}}} = 1362.6\,\frac{\text{m}}{\text{s}}$$

$$\text{U}_{\text{rms,N}_2} = \sqrt{\frac{3\text{RT}}{\text{M}_{\text{N}_2}}} = \sqrt{\frac{3 \times 8.314\,\frac{\text{J}}{\text{mol K}} \times 298\ \text{K}}{28.014\,\frac{\text{g}}{\text{mol}} \times \frac{1\ \text{kg}}{1000\ \text{g}}}} = 515.1\,\frac{\text{m}}{\text{s}}$$

Practice exercise

It is found that the value of U_{rms} of an unknown gas is 1.5 times the value of U_{rms} of CO_2(g) at the same temperature. Calculate the molar mass of the unknown gas.

The kinetic molecular theory of gases presents another equation to be used for the calculation of the kinetic energy of a specified quantity of the gas. If the quantity of the gas is one mole, its kinetic energy is called “***the molar kinetic energy***”, with “**KE**” as its symbol:

$$\text{KE} = 1.5 \times \text{R} \times \text{T}$$

This equation enables us to calculate the average kinetic energy of only one molecules "**ke**" by dividing the equation by Avogadro's number:

$$\mathrm{ke} = \frac{\mathrm{KE}}{\mathrm{N_A}} = \frac{1.5 \times \mathrm{R} \times \mathrm{T}}{\mathrm{N_A}} = 1.5 \times \mathrm{k} \times \mathrm{T}$$

$$\mathrm{ke} = 1.5 \times \mathrm{k} \times \mathrm{T}$$

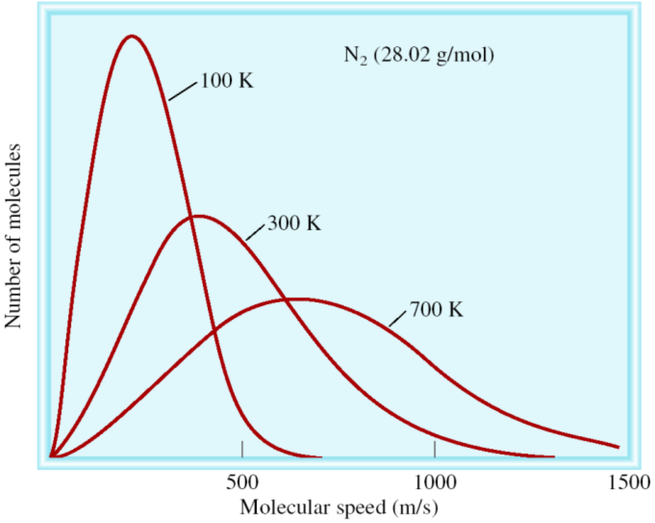
where "k" is Boltzmann constant. Both equations of kinetic energy, either of one mole or of only one molecule of the gas, indicate that the kinetic energy of a specified quantity of the gas depends on nothing except the temperature. This means it's the same for all gases as long as their amounts and temperatures are the same.

4.8.2 Application of kinetic theory to the gas laws

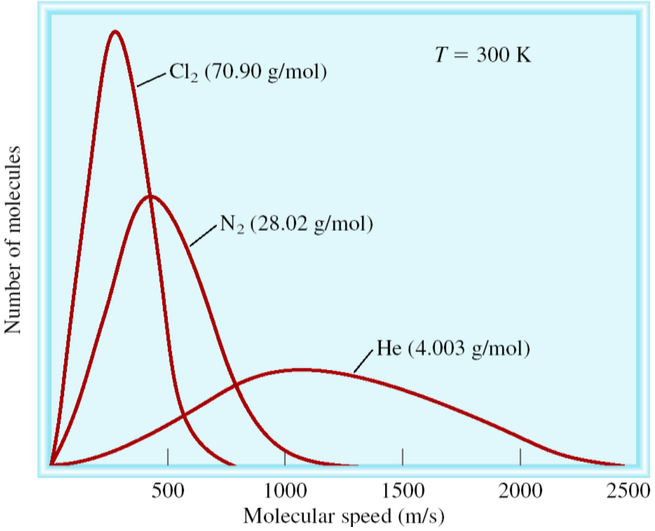
- **Boyle's Law:** The pressure exerted by a gas results from the impact of its molecules on the walls of the container. The number of collisions with the walls per second is proportional to the number of molecules per unit volume. Decreasing the volume of the gas increases its number per unit volume and hence number of collisions. For this reason, the pressure of a gas is inversely proportional to the volume it occupies.
- **Charles's Law:** Because the average kinetic energy of gas molecules is proportional to its absolute temperature, raising the temperature increases the average kinetic energy. Consequently, increasing temperature increases number of collisions and makes collisions stronger, thus the pressure increases, and the volume of gas will expand until the gas pressure is balanced by the constant external pressure.
- **Avogadro's Law:** We have shown that the pressure of a gas is directly proportional to both the amount and the temperature of the gas. In Avogadro's law temperature and pressure must be constant. If we increase the amount of the gas the pressure will remain constant only if the volume increase.
- **Dalton's Law of Partial Pressures:** If molecules do not attract or repel one another, then the pressure exerted by one type of molecule is unaffected by the presence of another gas. Consequently, the total pressure is given by the sum of individual gas pressures.

4.8.2 Distribution of molecular speeds

Maxwell investigated the molecular motion in more detail. If we have a large number of molecules and we hold the temperature constant, the average kinetic energy and the mean square speed will remain unchanged. How many molecules are moving at a particular speed? To answer this question Maxwell analyzed the behavior of gas molecules at different temperatures. The following figure show typical *Maxwell speed distribution curves* for nitrogen gas at three different temperatures.



At any given temperature, the peak of the curve represents the *most probable speed*, that is, the speed of the largest number of molecules at the specified temperature. Note that the most probable speed increases as temperature increases (the peak shifts toward the right). Furthermore, the curve also begins to flatten out with increasing temperature, indicating that larger numbers of molecules are moving at greater speed. The following figure shows the speed distributions of three gases at the *same* temperature.

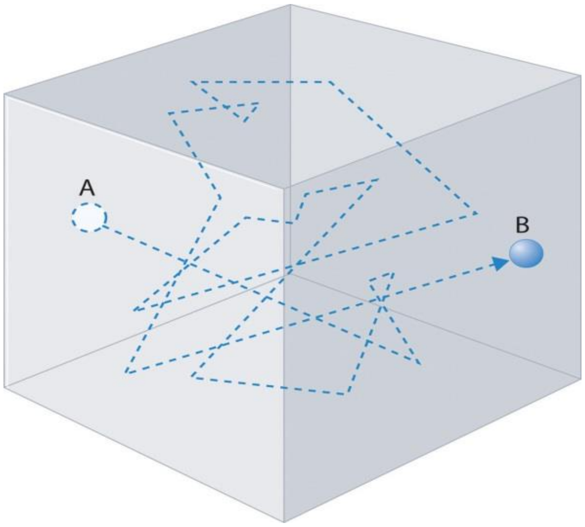


The difference in the curves can be explained by noting that lighter molecules move faster, on average, than heavier ones.

4.9 Gas diffusion and effusion

4.9.1 Gas diffusion

Diffusion is the gradual mixing of molecules of one gas with molecules of another by virtue of their kinetic properties. Despite the fact that molecular speeds are very great, the diffusion process takes a relatively long time to complete because diffusion of gases always happens gradually. For example, when a bottle of concentrated ammonia solution is opened at one end of a lab bench, it takes some time before a person at the other end of the bench can smell it. The following figure shows that the reason is that a molecule experiences numerous collisions while moving from one point “A” to point “B”:

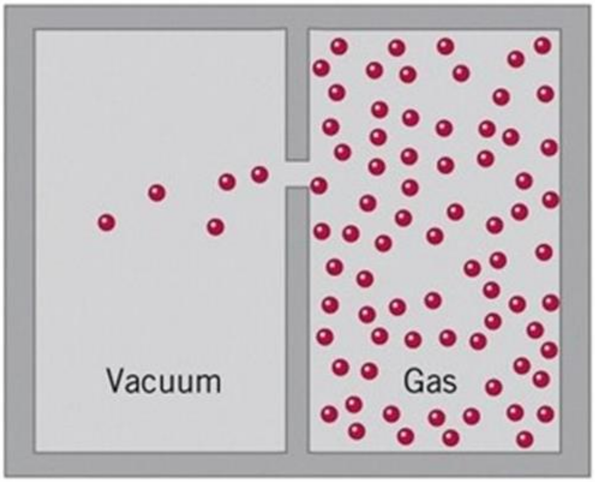


In 1832 the Scottish chemist Thomas Graham found that under the same conditions of temperature and pressure, rates of diffusion for gases (r) are inversely proportional to the square roots of their molar masses. This statement, now known as Graham’s law of diffusion:

$$\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}$$

4.9.2 Gas effusion

Gas effusion is the process by which a gas under pressure escapes from one compartment of a container to another by passing through a small opening. The following figure the effusion of a gas into a vacuum:



Although effusion differs from diffusion in nature, the rate of effusion of a gas has the same form as Graham's law of diffusion. A helium-filled rubber balloon deflates faster than an air-filled one because the rate of effusion through the pores of the rubber is faster for the lighter helium atoms than for the air molecules.

Example 4.15

A flammable gas made up only of carbon and hydrogen is found to effuse through a porous barrier in 1.50 min. Under the same conditions of temperature and pressure, it takes an equal volume of bromine vapor 4.73 min to effuse through the same barrier. Calculate the molar mass of the unknown gas, and suggest what this gas might be.

Solution

$$\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}$$

$r_1 = \frac{V_1}{Time_1}$ and $r_2 = \frac{V_2}{Time_2}$ but $V_1 = V_2$ therefore, $\frac{\frac{V_1}{Time_1}}{\frac{V_1}{Time_2}} = \sqrt{\frac{M_2}{M_1}}$

$\frac{Time_2}{Time_1} = \sqrt{\frac{M_2}{M_1}}$

$\frac{4.73 \text{ min}}{1.50 \text{ min}} = \sqrt{\frac{159.808}{M_1}}$

$(3.153)^2 = \frac{159.808}{M_1}$

$M_1 = 16.07 \frac{g}{mol}$

This gas is methane, because methane molar mass is 16.04 $\frac{\mathrm{g}}{\mathrm{mol}}$, methane is flammable and is formed from carbon and hydrogen.

Practice exercise

A gas evolved from the fermentation of glucose is found to effuse through a porous barrier in 15.0 min. Under the same temperature and pressure, it takes 12.0 min for an equal volume of N_2 to effuse through the same barrier. Calculate the molar mass of the gas and suggest what the gas might be.

4.10 Deviation from ideal behavior

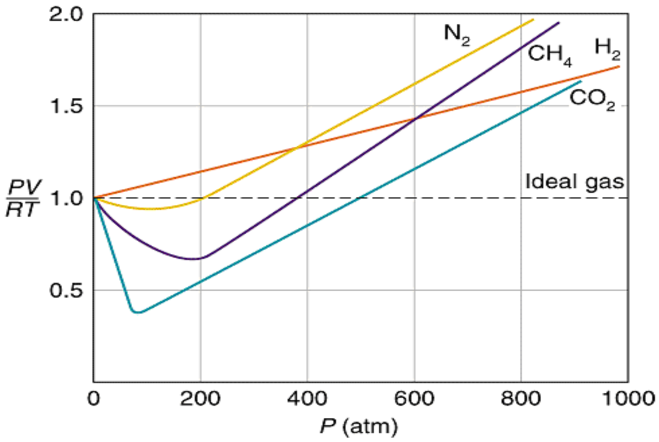
The gas laws and the kinetic molecular theory assume that:

1) Attractive and repulsive forces between molecules of the gas are so small and therefore can be ignore.
2) The volume occupied by the molecules of the gas is so small and therefore ignored.

These two assumptions are in fact not true and cannot be accepted except under strict conditions. When a gas obeys these strict conditions it is honored as the "***perfect gas***" and rewarded with a law bearing its name "***the perfect gas law***":

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

The question now is: "Under what conditions will not real gases exhibit perfect behavior?" The following curves shows "$\frac{PV}{RT}$" plotted against "P" for one mole of each of the four real gases and the ideal gas all at the same temperature.



For the one mole of the ideal gas $\frac{PV}{RT} = 1$ regardless of its pressure but for one mole of any one of the real gases, $\frac{PV}{RT} = 1$ only at zero or extremely small pressures and significant deviations occur as pressure increases. The following is the interpretation to these observations:

> **Attractive forces operate among molecules at relatively short distances. therefore, at low pressures the molecules in a gas are far apart and they experience no attractive and repulsive forces. But at high pressures, the molecules are much closer to one another and intermolecular forces are significant enough to affect the motion of the molecules, and the gas will not behave perfectly. This nonperfect behavior can be observed much significantly at lower temperature because cooling a gas decreases the molecules' average kinetic energy, which makes molecules movement less freely.**

To study real gases accurately, we need to modify the ideal gas equation to take into account intermolecular forces and finite molecular volumes. this was made by the Dutch physicist J. D. van der Waals in 1873. The following is his logic:

1) The intermolecular attractions exerted between a molecule and its neighbors tend to soften the collisions made by this molecule against the wall which makes the gas pressure lowers than if it is ideal. Van der Waals suggested that to correct the deviation, resulting from lowering the pressure, a certain correction value must be added to the real pressure. This value he determined to be "$a \times \frac{n^2}{V^2}$". This means that the gas pressure must be corrected to be $(P + a \times \frac{n^2}{V^2})$. "a" is constant for each gas, and it is related to the strength of the forces between the molecules of the gas
2) Another correction concerns the volume occupied by the gas molecules. In the perfect gas equation, "V" represents the volume of the container as a free space that is occupied by nothing. However, each molecule does occupy a finite, although small, volume, so the effective volume of the gas is less than the volume of the container by a certain value. This value is determined by van der Waals to be "n × b". This means that the gas volume must be corrected to be $(V - n \times b)$. "b" is constant for each gas, and it is related to the volume occupied by the molecules of the gas.
3) From the previous two corrections the law of the real gas is written as:

$$(P + a \times \frac{n^2}{V^2}) \times (V - n \times b) = n \times R \times T$$

This equation is called the “**van der Waals equation**”, the “**real gas equation**” and the “**nonperfect gas equation**”

4) From van der Waals equation it is so easy to understand that if the gas is a perfect gas its values of the two constants “a” and “b” are zero.

Example 4.16

Given that 3.50 moles of NH_3 occupy 5.20 L at 47° C, calculate the pressure of the gas (in atm) using (A) the ideal gas equation and (B) the van der Waals equation. ($a = 4.17\ \text{atm L}^2/\text{mol}^2$, $b = 0.0371\ \text{L/mol}$)

Solution

A) $$P = \frac{n \times R \times T}{V} = \frac{3.5\ \text{mol} \times 0.0821\ \frac{\text{atm L}}{\text{mol K}} \times 320\ \text{K}}{5.2\ \text{L}} = 17.7\ \text{atm}$$

B) $$P = \left(\frac{n \times R \times T}{V - n \times b}\right) - \left(a \times \frac{n^2}{V^2}\right)$$

$$P = \left(\frac{3.5\ \text{mol} \times 0.0821\ \frac{\text{atm L}}{\text{mol K}} \times 320\ \text{K}}{5.2\ \text{L} - 3.5\ \text{mol} \times 0.0371\ \frac{\text{L}}{\text{mol}}}\right) - \left(4.17\ \frac{\text{atm L}^2}{\text{mol}^2} \times \frac{(3.5\ \text{mol})^2}{(5.2\ \text{L})^2}\right) = 16.2\ \text{atm}$$

Practice exercise

At 27°C, 10.0 moles of a gas in a 1.50-L container exert a pressure of 130 atm. Is this an ideal gas?

5. THEMOCHEMISTRY

5.1 System, state of the system and state function

5.1.1 System

A “**system**” is a part of the universe confined in a container and is the focus of our interest. Everything outside the system is called the “***surroundings***”. What separate the system from its surroundings is the “***boundaries***” of the system.

5.1.1 State of the system

The “**state of a system**” is the values of all properties of the system such as its composition, energy, temperature, pressure, and volume. Thus if we have 100 g of liquid water at 30 °C and 1.0 atm and someone are asked us “what the state of this system”, then our correct answer will be “the state of the system is that it is 100 g of water in its liquid state at 30 °C and 1.0 atm”.

5.1.3 State function of the System

The “**State function of the System**” is any property of the system that indicates the state of the system and depend on its it such as its composition, energy, temperature, pressure, and volume. Any property of the system depends on its specified state not on the **path** which brought the system to this specified state. We can change a gas state function, such as its volume, from an initial value, V_i = 1 L to a final value, V_f = 3 L. If we manage to make the amount and the temperature of the gas at the final state the same as it was at the initial state, then the change in the volume can be achieved by changing the pressure. This change in volume, ΔV = 2 L, will be the same regardless of how we did this change, no matter how we arrive at the final state (for example, the pressure of the gas can be increased then decreased, or it can be increased then decreased then increased), the change in volume is always 2 L. Thus, the volume of the gas is a state function.

5.2 PV-work and heat

5.2.1 PV-work

Work is many kinds, it includes **mechanical work, electrical wor**k, **surface work** and many other types. Work is a way of transferring energy from a place to another. It is not a property of the system. We can say that the temperature of a substance is, for example, 25° C, but we cannot say that the work of the system is, for example, 250 J.

We will concentrate only on the mechanical work of expansion and compression of gases. The work done by or on the gas is given by the following equation:

$$w = -P \times (V_f - V_i)$$
$$w = -P \times \Delta V$$

In the equation, the negative sign was intentionally placed. This is to make the sign of work negative in cases of expansion (energy of the system decreases) and positive in cases of compression (energy of the system increases).

Regarding units of the PV-work:

$$w = -P \times \Delta V$$
$$\text{units of w} = \text{units of P} \times \text{units of V}$$
$$\text{units of w} = \frac{\text{units of force}}{(\text{units of area})^2} \times \text{units of V}$$
$$\text{units of w} = \frac{\text{kg} \times \frac{\text{m}}{\text{s}^2}}{\text{m}^2} \times \text{m}^3$$
$$\text{units of w} = \text{kg m}^{-1}\ \text{s}^{-2} \times \text{m}^3$$
$$\text{units of w} = \text{Pascal} \times \text{m}^3$$
$$\text{units of w} = \text{kg m}^2\ \text{s}^{-2} = \text{J}$$

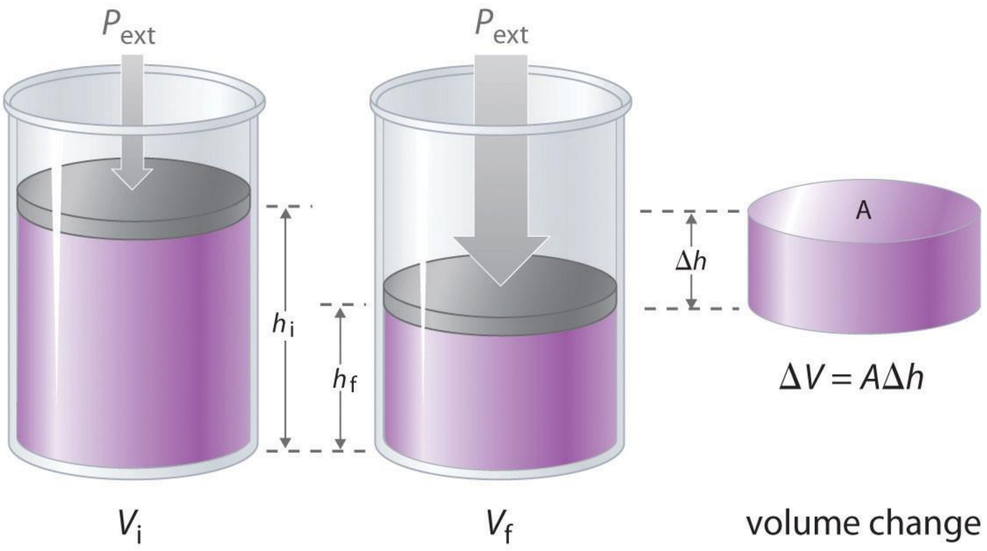
As it appears, the product of pressure and volume equals the work done:

✓ If "P" is in "Pa" and "V" is in "m^3", the unit of the work will be "J"

✓ If "P" is in "atm" and "V" is in "L" the unit of the work will be "atm L"

✓ 1 atm L = 101.325 J

One way to illustrate this type of work is using a cylinder with its piston. The figure below shows a gas in a cylinder fitted with a weightless, frictionless movable piston at a certain temperature, pressure, and volume. It shows that the gas expands by pushing the piston upward against a constant opposing external atmospheric pressure, P.



Because $w = -P \times (V_f - V_i)$, the work done by the gas: $w = -P \times (V_f - V_i)$ has a negative quantity indicating that work done causes a decrease in the energy of the gas. For gas expansion (work done on the system), $\Delta V < 0$, so $(-P\Delta V)$ is a positive quantity indicating that work done causes an increase in the energy of the gas.

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) $w = -P\Delta V = -(0 \times \Delta V) = 0$

B) $w = -P\Delta V = -\{1.2\text{ atm} \times 101325\,\frac{\text{Pa}}{\text{atm}}\} \times \{(6-2)\text{ L}\,\frac{\text{m}^3}{1000\text{ L}}\} = -4.86 \times 10^{-2}\text{ J}$

Practice Exercise

A gas expands from 264 mL to 971 mL at constant temperature. Calculate the work done by the gas if it expands against a constant pressure of 4.00 atm.

5.2.2 Heat

Like work, heat is not a state function. Heat is a way of transferring energy from a place to another. It is not a property of the system. We can say that the temperature of a substance is, for example, 25° C, but we cannot say that the heat of the system is, for example, 250 J. 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 in different ways such as:

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.

Calculation of heat absorbed by a system requires understanding the effect of how mass the substance is and how many degrees its temperature increases on the amount of heat absorbed. This can be understood by knowing what specific heat (s), heat capacity (C) and quantity of heat (q) mean.

First: specific heat (s)

The specific heat of a substance is the amount of heat required to raise the temperature of only ***one gram*** of the substance by only ***one degree Celsius***. Its units are $\frac{\text{J}}{\text{g °C}}$.

Second: heat capacity (C)

The ***heat capacity*** of a substance is the amount of heat required to raise the temperature of ***any given mass***, (m), of the substance by only ***one degree Celsius***. Its units are $\frac{J}{°C}$.

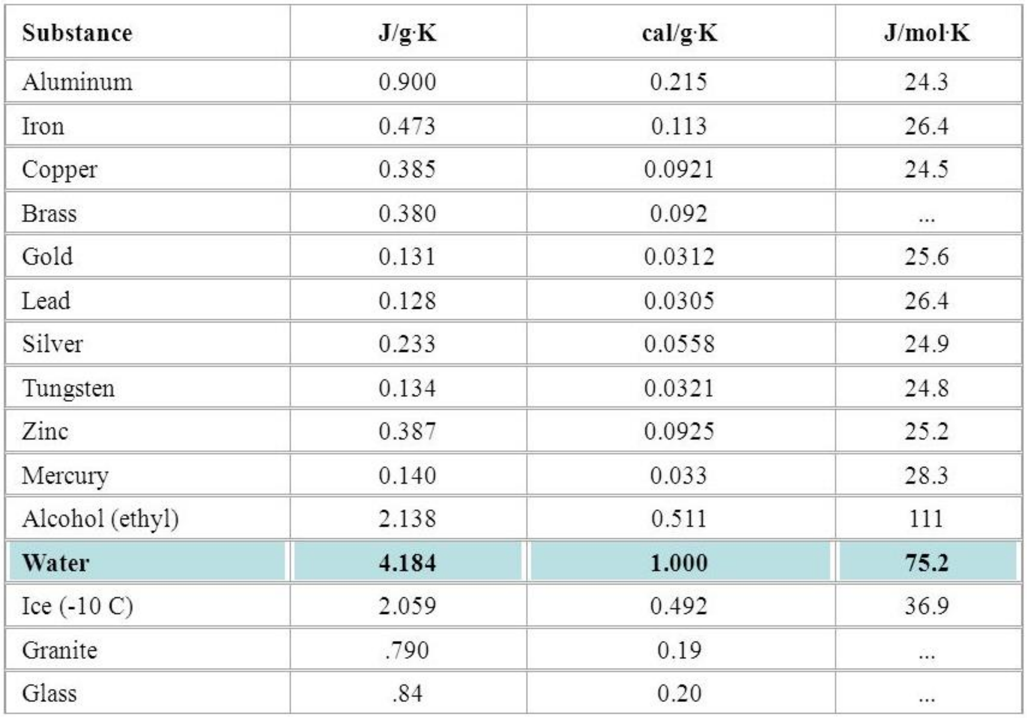
The relationship between the heat capacity and specific heat of a substance is:

$$C = m \times s$$

For example, the specific heat of water is 4.184 $\frac{J}{g\,°C}$, and the heat capacity of 60.0 g of water is

$$C = 60.0\ g \times 4.184\ J/g\ °C = 251\ \frac{J}{°C}$$

The following table shows the specific heat of some common 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	...

Third: quantity of heat (q)

The ***quantity of heat*** is the amount of heat required to raise the temperature of ***any given mass***, (m), of the substance by ***any Celsius degrees***. Its unit is J.

If we know **s** and **m**, then **Δt** we can calculate the amount **q** that has been absorbed or released in a particular process. The equations for calculating the quantity of heat is:

$$q = C \times \Delta t = m \times s \times \Delta t$$

EXAMPLE 5.2

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. ($s_{H_2O} = 4.184 \frac{J}{g\,°C}$)

Solution

$q = m \times s \times \Delta t = 466\ g \times 4.184 \frac{J}{g\,°C} \times (74.60\ °C - 8.50\ °C) = 129000\ J$

$q = 129000\ J \times 10^{-3} \frac{kJ}{J} = 129\ kJ$

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.

5.3 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.* 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 the following equation:

$$\Delta E = E_f - E_i$$

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:

1) **The kinetic energy component:** The kinetic energy consists of various types of molecular motion and the movement of electrons within molecules.
2) **Potential energy component:** The 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.

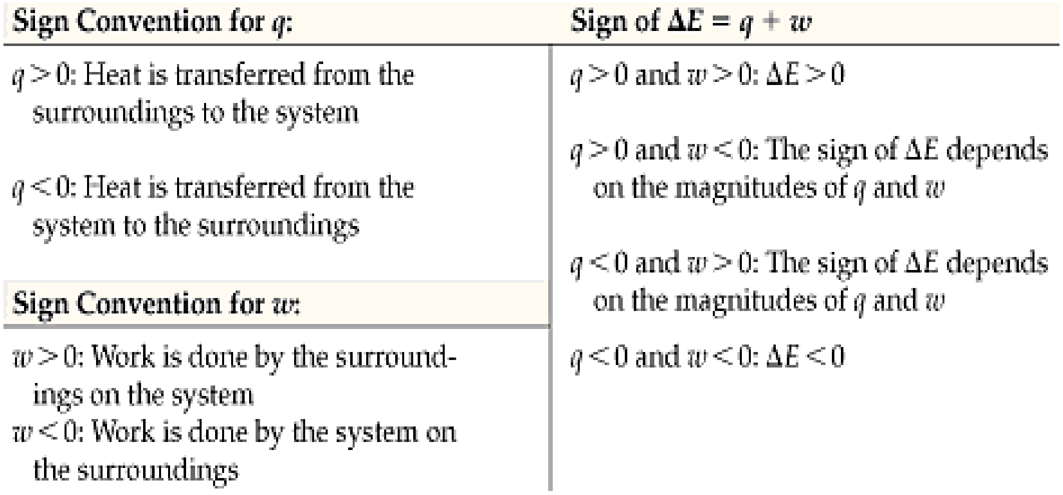
It is impossible to measure all these contributions accurately, so we cannot calculate the total internal energy of a system with any certainty. Changes in energy, on the other hand, can be determined experimentally. Consider the following reaction

$$S(s) + O_2(g) \rightarrow SO_2(g)$$

Our system is initially composed of S and O_2 and finally composed of SO_2. We do not know the initial or the final internal energy, E_i and E_f, but the first law of thermodynamic assures 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:

$$\Delta E = q + w$$

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.
The table below summarizes the sign conventions



Sign Convention for q:	**Sign of $\Delta E = q + w$**
$q > 0$: Heat is transferred from the surroundings to the system	$q > 0$ and $w > 0$: $\Delta E > 0$
	$q > 0$ and $w < 0$: The sign of ΔE depends on the magnitudes of q and w
$q < 0$: 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:	
$w > 0$: Work is done by the surroundings on the system	$q < 0$ and $w < 0$: $\Delta E < 0$
$w < 0$: Work is done by the system on the surroundings	

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 5.3

If the work done on a gas is 462 J and the heat released by the gas is 128 J, calculate the change in the gas internal energy.

Solution

$\Delta E = q + w = (-128 \text{ J}) + (+ 462 \text{ J}) = + 334 \text{ J}$

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?

5.4 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:

$$\text{Reactants} \rightarrow \text{products}$$

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*:

$$\Delta H = H_{\text{products}} - H_{\text{reactants}}$$

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, $\Delta H < 0$).

5.5 Thermochemical equations

At 0°C and a pressure of 1 atm, ice melts to form liquid water. Measurements show that for every mole of solid water (ice) converted to liquid water under these conditions, 6.01 kilojoules (kJ) of heat are absorbed by the system (ice). Because the pressure is constant, the heat change is 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.

Thermochemical equations can be manipulated with as follows:

- Multiplying a thermochemical equation by a number or a fraction produces a correct thermochemical equation as long as the value of ΔH is multiplied by the same number.
- Reversing a thermochemical equation produces a correct thermochemical equation as long as the sign of ΔH is changed to its opposite.
- Adding several thermochemical equations together produces a correct thermochemical equation as long as all values of ΔH are 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

Given moles of SO_2 = $\frac{87.9 \text{ g}}{64.07 \frac{\text{g}}{\text{mol}}}$ = 1.372 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

$$P_4(s) + 5O_2(g) \rightarrow P_4O_{10}(s) \qquad \Delta H = -3013 \text{ kJ/mol}$$

5.6 Relationship between ΔH and ΔE

We know that:

$$\Delta E = q + w \text{ and } w = -P \times \Delta V$$

$$q = \Delta H \text{ when "T" and "P" are constant}$$

$$\Delta E = \Delta H - P \times \Delta V \text{ when "T" and "P" are constant}$$

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

$$P \times \Delta V = R \times T \times \Delta n_g$$

Therefore:

$$\boxed{\Delta E = \Delta H - R \times T \times \Delta n_g}$$

It is very important not to forget that the subscript "g" is to emphasize that when calculating **Δn** only gases count:

$$\Delta n_g = n_{\text{gases produced}} - n_{\text{gases reacted}}$$

To understand the equation "$\Delta E = \Delta H - R \times T \times \Delta n_g$" let's consider 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 2 moles of solid Na react with 2 moles of liquid water, 367.5 kJ of heat is released. The H_2 gas produced needs a space to occupy. Therefore, it pushes the air toward the atmosphere. This means that some of the energy produced by the reaction as heat is used to do work of pushing back a volume, ΔV, against atmospheric pressure, P. To calculate the change in internal energy, we apply the previous equation:

$$\Delta E = \Delta H + w = \Delta H - R \times T \times \Delta n_g$$

$$\Delta E = (-\ 367.5\ kJ) - (8.314 \times 10^{-3}\ \frac{kJ}{mol\ K} \times 298\ K \times 1\ mol) = -\ 369.98\ kJ$$

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?

$$C(graphite) + \frac{1}{2}O_2(g) \rightarrow CO(g) \qquad \Delta H = -110.5\ kJ$$

5.6 Enthalpies of changes

5.6.1 Enthalpies of some physical changes

First: Main physical changes

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. It 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:

$Ar(s) \rightarrow Ar(l)$ $\Delta H = 1.3$ kJ

$C_6H_6(s) \rightarrow C_6H_6(l)$ $\Delta H = 10.9$ kJ

$CH_3CH_2OH(s) \rightarrow CH_3CH_2OH(l)$ $\Delta H = 7.61$ kJ

$Hg(s) \rightarrow Hg(l)$ $\Delta H = 23.4$ kJ

$H_2O(s) \rightarrow H_2O(l)$ $\Delta H = 6.01$ kJ

Freezing is simply the opposite of fusion.

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. It 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:

$Ar(l) \rightarrow Ar(g)$ $\Delta H = 6.3$ kJ

$C_6H_6(l) \rightarrow C_6H_6(g)$ $\Delta H = 31.0$ kJ

$CH_3CH_2OH(l) \rightarrow CH_3CH_2OH(g)$ $\Delta H = 39.3$ kJ

$Hg(l) \rightarrow Hg(g)$ $\Delta H = 59.0$ kJ

$H_2O(l) \rightarrow H_2O(g)$ $\Delta H = 40.79$ kJ

Condensation is simply the opposite of vaporization.

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. It 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}).

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.

Second: Relation between the main physical changes

A simple inspection and a quick glance to the three sets of thermochemical equations given above should reveal that sublimation is the summation of fusion and vaporization and $\Delta H_{sub} = \Delta H_{fus} + \Delta H_{vap}$.

5.6.1 Enthalpies of some chemical changes

1) Combustion reaction 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 heat 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

The most important combustion reactions are the combustion are:

- The combustion of hydrogen to produce H_2O:

  $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$ $\Delta H = -285.8$ kJ

- The combustion of carbon to produce CO_2:

  $C(\text{graphite}) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$ $\Delta H = -393.5$ kJ

- The combustion of compounds containing both hydrogen and carbon yield both H_2O and CO_2:

  $CH_3CH_2OH(l) + 5O_2(g) \rightarrow 2CO_2 + 3H_2O(l)$ $\Delta H = -1367$ 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) Formation reaction and standard enthalpy of formation

A ***formation reaction*** is the reaction *in which* ***one*** *substance is produced as a result of the reaction of its* ***elements in their standard states***. 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°**). From the definition of the formation reaction, it appears that if the substance we have is an element in its standard state, it has no formation reaction and therefore its standard enthalpy of formation equals **zero**.

When any element is in its standard state its $\Delta H^\circ_f = 0$

The following reaction equations are examples formation reactions:

$S(s) + O_2(g) \rightarrow SO_2(g)$ $\Delta H = -\ 296.84$ kJ

(*Note: this reaction can also be called a combustion reaction*)

$Mg(s) + \frac{1}{2}O_2(g) \rightarrow MgO(g)$ $\Delta H = -\ 601.6$ kJ

(Note: this reaction can also be called a combustion reaction)

$2C(graphite) + 3H_2(g) + \frac{1}{2}O_2(g) \rightarrow CH_3CH_2OH(l)$ $\Delta H = -\ 277.6$ kJ
$3C(graphite) + 4H_2(g) \rightarrow C_3H_8(g)$ $\Delta H = -\ 104.7$ kJ
$6C(graphite) + 6H_2(g) + 3O_2 \rightarrow C_6H_{12}O_6(s)$ $\Delta H = -\ 1271$ kJ

The standard enthalpies of formation are one of the most important tools chemists use to determine the standard enthalpy of any physical or chemical change, ΔH°_{rxn}. This can be accomplished simply by the following equation:

$$\boxed{\Delta H^\circ_{rxn} = \Sigma\Delta H^\circ_{f,products} - \Sigma\Delta H^\circ_{f,reactants}}$$

The equation says that the standard enthalpy of any change equals the sum of the standard enthalpies of formation of products minus the sum of the standard enthalpies of formation of reactants. For example, knowing that the standard enthalpies of formation for gaseous carbon monoxide and gaseous carbon dioxide are $-\ 110.5\ \frac{kJ}{mol}$ and $-\ 393.5\ \frac{kJ}{mol}$ respectively enables us to calculate the standard oxidation of carbon monoxide to carbon dioxide as follows:

$$CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$$

$$\Delta H^\circ_{rxn} = \Sigma\Delta H^\circ_{f,products} - \Sigma\Delta H^\circ_{f,reactants}$$

$$\Delta H^\circ_{rxn} = (\Sigma 1 \times \Delta H^\circ_{f,CO_2}) - (\Sigma 1 \times \Delta H^\circ_{f,CO} + \frac{1}{2}\ \Sigma\Delta H^\circ_{f,O_2})$$

$$\Delta H^\circ_{rxn} = (\Sigma 1\ mol \times -\ 393.5\ \frac{kJ}{mol}) - (\Sigma 1\ mol \times -\ 110.5\ \frac{kJ}{mol} + \frac{1}{2} \times 0)$$

$$\Delta H^\circ_{rxn} = -\ 283\ kJ$$

Standard enthalpies of formation are determined almost for all known substances and are presented in thermodynamic tables found in references, textbooks and internet sights. The following table gives some.

Compound	$\mathbf{\Delta H_f^\circ} (\frac{\mathbf{kJ}}{\mathbf{mol}})$	**Compound**	$\mathbf{\Delta H_f^\circ} (\frac{\mathbf{kJ}}{\mathbf{mol}})$
AgBr(s)	– 99.5	C_2H_2(g)	+ 226.7
AgCl(s)	– 127.0	C_2H_4(g)	+ 52.3
AgI(s)	– 62.4	C_2H_6(g)	– 84.7
Ag_2O(s)	– 30.6	C_3H_8(g)	– 103.8
Ag_2S(s)	– 31.8	n– C_4H_{10}(g)	– 124.7
Al_2O_3(s)	– 1669.8	n– C_5H_{12}(l)	– 173.1
$BaCl_2$(s)	– 860.1	C_2H_5OH(l)	– 277.6
$BaCO_3$(s)	– 1218.8	CoO(s)	– 239.3
BaO(s)	– 558.1	Cr_2O_3(s)	– 1128.4
$BaSO_4$(s)	– 1465.2	CuO(s)	– 155.2
$CaCl_2$(s)	– 795.0	Cu_2O(s)	– 166.7
$CaCO_3$	– 1207.0	CuS(s)	– 48.5
CaO(s)	– 635.5	$CuSO_4$(s)	– 769.9
$Ca(OH)_2$(s)	– 986.6	Fe_2O_3(s)	– 822.2
$CaSO_4$(s)	– 1432.7	Fe_3O_4(s)	– 1120.9
CCl_4(l)	– 139.5	HBr(g)	– 36.2
CH_4(g)	– 74.8	HCl(g)	– 92.3
CH_3OH(l)	– 238.6	HI(g)	+ 25.9
CO(g)	– 110.5	HNO_3(l)	– 173.2
CO_2(g)	– 393.5	H_2O(g)	– 241.8
H_2O(l)	– 285.8	NH_4Cl(s)	– 315.4
H_2O_2(l)	– 187.6	NH_4NO_3(s)	– 365.1
H_2S(g)	– 20.1	NO(g)	+ 90.4
H_2SO_4(l)	– 811.3	NO_2(g)	+ 33.9
HgO(s)	– 90.7	NiO(s)	– 244.3
HgS(s)	– 58.2	$PbBr_2$(s)	– 277.0
KBr(s)	– 392.2	$PbCl_2$(s)	– 359.2
KCl(s)	– 435.9	PbO(s)	– 217.9
$KClO_3$(s)	– 391.4	PbO_2(s)	– 276.6
KF(s)	– 562.6	Pb_3O_4(s)	– 734.7
$MgCl_2$(s)	– 641.8	PCl_3(g)	– 306.4
$MgCO_3$(s)	– 1113	PCl_5(g)	– 398.9
MgO(s)	– 601.8	SiO_2(s)	– 859.4
$Mg(OH)_2$(s)	– 924.7	$SnCl_2$(s)	– 349.8
$MgSO_4$(s)	– 1278.2	$SnCl_4$(l)	– 545.2
MnO(s)	– 384.9	SnO(s)	– 286.2
MnO_2(s)	– 519.7	SnO_2(s)	– 580.7
NaCl(s)	– 411.0	SO_2(g)	– 296.1
NaF(s)	– 569.0	So_3(g)	– 395.2
NaOH(s)	– 426.7	ZnO(s)	– 348.0
NH_3(g)	– 46.2	ZnS(s)	– 202.9

EXAMPLE 5.6

The thermite reaction involves aluminum and iron(III) oxide

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

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.

$\Delta H^\circ_{f,Al_2O_3(s)} = -1669.8\ \frac{kJ}{mol}$, $\Delta H^\circ_{f,Fe(l)} = 12.40\ /\frac{kJ}{mol}$, $\Delta H^\circ_{f,Fe_2O_3(s)} = -822.2\ /\frac{kJ}{mol}$

Solution

$$\Delta H^\circ_{rxn} = \Sigma\Delta H^\circ_{f,products} - \Sigma\Delta H^\circ_{f,reactants}$$

$$\Delta H^\circ_{rxn} = [\Delta H^\circ_f(Al_2O_3) + 2\Delta H^\circ_f(Fe)] - [2\Delta H^\circ_f(Al) + \Delta H^\circ_f(Fe_2O_3)]$$

$$\Delta H^\circ_{rxn} = [(-1669.8\ kJ/mol) + (2\ mol \times 12.40\ kJ/mol)]$$

$$-[(2\ mol \times 0) + (-822.2\ kJ/mol)]$$

$$\Delta H^\circ_{rxn} = -822.8\ kJ/2\ mol\ of\ Al\ reacted$$

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

$$X = \frac{-822.8\ kJ \times 1\ g}{53.96\ g} = -15.25\ kJ/g$$

Practice Exercise

Benzene (C_6H_6) burns in air to produce carbon dioxide gas and liquid water. Calculate the heat released (in kilojoules) per gram of the compound reacted with oxygen. $\Delta H^\circ_{f,CO_2(g)} = -393.5\ \frac{kJ}{mol}$, $\Delta H^\circ_{f,H_2O(l)} = -285.8\ \frac{kJ}{mol}$, and $\Delta H^\circ_{f,C_6H_6(l)} = 49.04\ \frac{kJ}{mol}$.

5.7 Hess's law of heat summation

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 known as the father of thermochemistry 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 as follows:

1) 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.
2) Multiply any reaction by the appropriate factor as needed. Do not forget to multiply ΔH by the same factor.

3) Reverse any reaction as needed. Do not forget to change the sign of the ΔH to the opposing sign.

From the following equations:

$$\begin{array}{ll}
\mathrm{C(graphite)} + \mathrm{O_2}(g) \rightarrow \mathrm{CO_2}(g) & \Delta H^{\circ}_{rxn} = -\ 393.5\ \mathrm{kJ} \\
\mathrm{CO}(g) + \frac{1}{2}\mathrm{O_2}(g) \rightarrow \mathrm{CO_2}(g) & \Delta H^{\circ}_{rxn} = -\ 283.0\ \mathrm{kJ}
\end{array}$$

Our simple inspections suggest that the second equation should be reversed then added to the first:

$$\begin{array}{ll}
\mathrm{C(graphite)} + \mathrm{O_2}(g) \rightarrow \mathrm{CO_2}(g) & \Delta H^{\circ}_{rxn} = -\ 393.5\ \mathrm{kJ} \\
\mathrm{CO_2}(g) \rightarrow \mathrm{CO}(g) + \frac{1}{2}\mathrm{O_2}(g) & \Delta H^{\circ}_{rxn} = +\ 283.0\ \mathrm{kJ} \\
\hline
\mathrm{C(graphite)} + \frac{1}{2}\mathrm{O_2}(g) \rightarrow \mathrm{CO}(g) & \Delta H^{\circ}_{rxn} = -\ 110.5\ \mathrm{kJ}
\end{array}$$

EXAMPLE 5.7

Calculate the standard enthalpy of formation of acetylene (C_2H_2) from its elements:

$$2\mathrm{C(graphite)} + \mathrm{H_2(g)} \rightarrow \mathrm{C_2H_2(g)}$$

The equations for each step and the corresponding enthalpy changes are:

$$\begin{array}{ll}
\text{(a) } \mathrm{C(graphite)} + \mathrm{O_2(g)} \rightarrow \mathrm{CO_2(g)} & \Delta H^{\circ}_{rxn} = -\ 393.5\ \mathrm{kJ/mol} \\
\text{(b) } \mathrm{H_2(g)} + \frac{1}{2}\mathrm{O_2(g)} \rightarrow \mathrm{H_2O}(l) & \Delta H^{\circ}_{rxn} = -\ 285.8\ \mathrm{kJ/mol} \\
\text{(c) } 2\mathrm{C_2H_2(g)} + 5\mathrm{O_2(g)} \rightarrow 4\mathrm{CO_2(g)} + 2\mathrm{H_2O}(l) & \Delta H^{\circ}_{rxn} = -\ 2598.8\ \mathrm{kJ/mol}
\end{array}$$

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

$$\begin{array}{ll}
2\mathrm{C(graphite)} + 2\mathrm{O_2(g)} \rightarrow 2\mathrm{CO_2(g)} & \Delta H^{\circ}_{rxn} = -\ 787.0\ \mathrm{kJ} \\
\mathrm{H_2(g)} + \frac{1}{2}\mathrm{O_2(g)} \rightarrow \mathrm{H_2O}(l) & \Delta H^{\circ}_{rxn} = -\ 285.8\ \mathrm{kJ} \\
2\mathrm{CO_2(g)} + \mathrm{H_2O}(l) \rightarrow \mathrm{C_2H_2(g)} + 2.5\mathrm{O_2(g)} & \Delta H^{\circ}_{rxn} = +\ 1299.4\ \mathrm{kJ} \\
\hline
2\mathrm{C(graphite)} \rightarrow \mathrm{H_2}(g) \rightarrow \mathrm{C_2H_2}(g) & \Delta H^{\circ}_{rxn} = +\ 226.6\ \mathrm{kJ}
\end{array}$$

Practice Exercise

Calculate the standard enthalpy of formation of carbon disulfide (CS_2) from its elements, given that:

$$\begin{array}{ll}
\mathrm{C(graphite)} + \mathrm{O_2(g)} \rightarrow \mathrm{CO_2(g)} & \Delta H^{\circ}_{rxn} = -\ 393.5\ \mathrm{kJ} \\
\mathrm{S(rhombic)} + \mathrm{O_2(g)} \rightarrow \mathrm{SO_2(g)} & \Delta H^{\circ}_{rxn} = -\ 296.4\ \mathrm{kJ} \\
\mathrm{CS_2}(l) + 3\mathrm{O_2(g)} \rightarrow \mathrm{CO_2(g)} + 2\mathrm{SO_2(g)} & \Delta H^{\circ}_{rxn} = -\ 1073.6\ \mathrm{kJ}
\end{array}$$

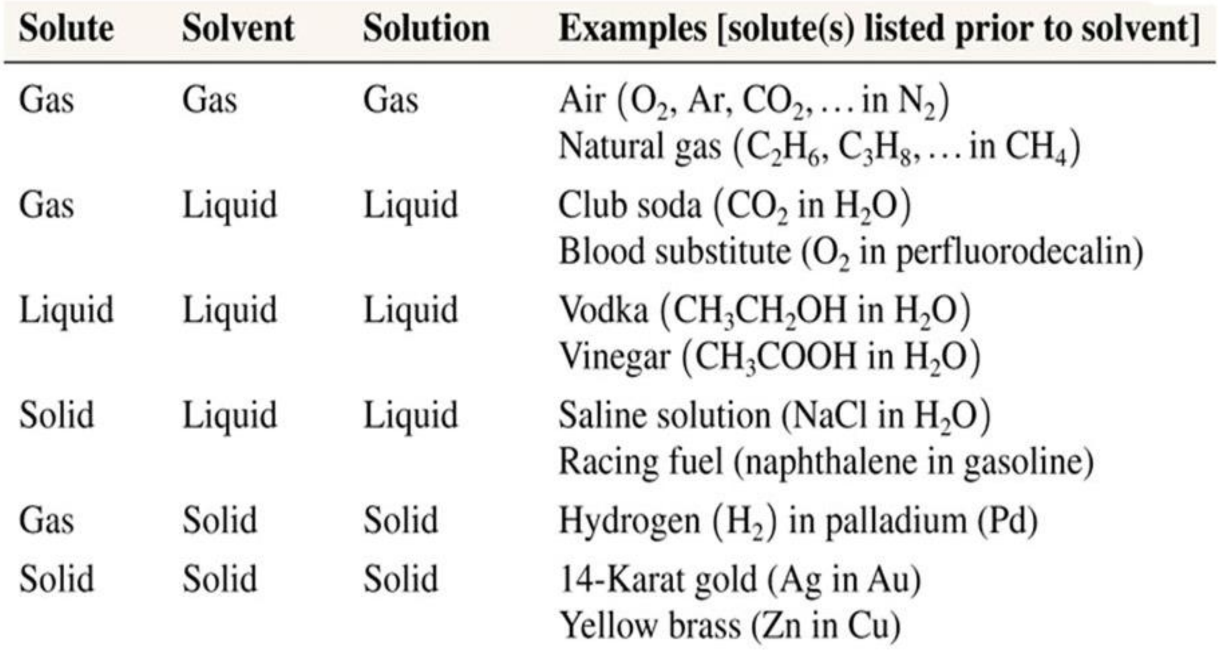
6. SOLUTIONS

6.1 Definition and types of solutions

A solution is a mixture of two or more components. One of the components is called “**solvent**” the other (or the others) is (are) called “**solute**” (“solutes”):

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 liquid solutions:

- ✓ Solutions of gases in liquids
- ✓ Solutions of liquids in liquids
- ✓ Solutions of solids in liquids

6.2 Degrees of saturation of solutions

Chemists characterize solutions by their capacity to dissolve a solute. Depending on the amount of solute dissolved we can differentiate between three cases:

1) **saturated solution:** a solution is described as saturated when it contains the maximum amount of a solute dissolved in the solvent at a specific temperature.
2) **unsaturated solution:** a solution is described as supersaturated when it contains less than its capacity to dissolve a solute.

3) **supersaturated solution:** a solution is described as saturated when it contains more than its capacity to dissolve a solute.

6.3 How solution is formed?

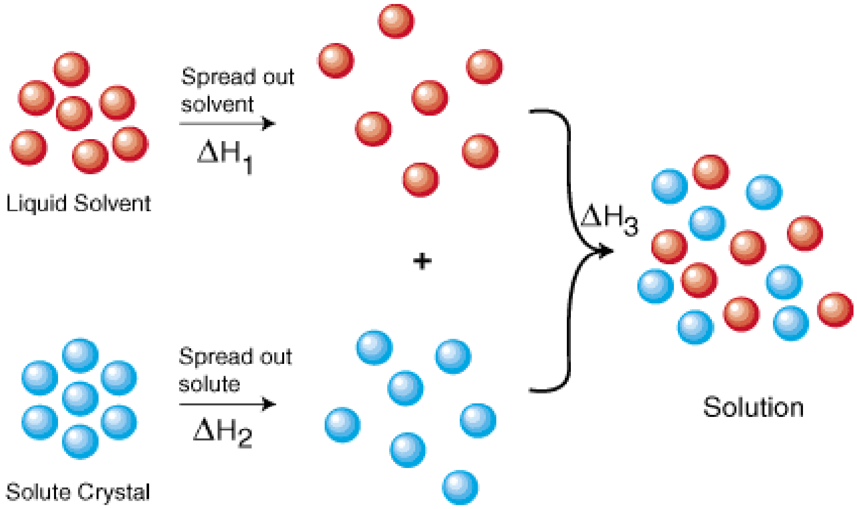
6.3.1 A Molecular view of the solution process

The intermolecular attractions between particles of a substance depends on its state. Particles of gases has extremely weak intermolecular attractions or none. But particles of liquid or a solid has considerable intermolecular attractions that hold molecules together. Therefore, intermolecular attractions have an important role in the formation of solutions of solids in liquids and of liquids in liquids. When the liquid or the solid solute dissolves in the liquid solvent particles of the solute disperse throughout the solvent and 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:

1) solvent-solvent interaction
2) solute-solute interaction
3) solvent-solute interaction

For simplicity and as figures below show, we can imagine the solution process taking place in three distinct and ***simultaneous*** actions:

1) the separation of solvent molecules
2) the separation of solute molecules
3) the attraction between solvent and solute molecules.



The first and the second actions are endothermic because breaking attractive forces requires energy ($\Delta H_1 > 0$ and $\Delta H_2 > 0$). The third action is exothermic because forming attractive forces releases energy ($\Delta H_3 < 0$). The enthalpy of solution ΔH_{soln} is given by:

$$\Delta H_{soln} = \Delta H_1 + \Delta H_2 + \Delta H_3$$

It is clear that there are three distinguished cases:

First case: If the solute-solvent attractions are **stronger** than the solvent-solvent and the solute-solute attractions, the solution process is exothermic ($\Delta H_{soln} > 0$)

Second case: If the solute-solvent attractions are **weaker** than the solvent-solvent and the solute-solute attractions, the solution process is endothermic ($\Delta H_{soln} < 0$).

Third case: If the solute-solvent attractions are **equal to** the solvent-solvent and the solute-solute attractions, the solution process is not endothermic or exothermic. In this case the solution is described as an ***ideal solution.***

6.3.2 The "like dissolve like" proverb

What does "**Like** dissolve **like**" mean? It means the following: **"THE SOLUTE CAN DISSOLVE IN THE SOLVENT IF THE ATTRACTIVE FORCES BETWEEN ITS PARTICLES ARE LIKE THOSE IN THE SOLVENT PARTICLES, BUT IF THEY ARE NOT, THE SOLUTE CANNOT DISSOLVE IN THE SOLVENT**". This is exactly what "**Like** dissolve **like**" means. Therefore, focusing on the attractive forces of the solvent will be so helpful. Investigations revealed with proven reliability that they are so many. So, we will not consider, at our level here, except two types. The first is called "polar solvents" in which any ionic or polar solute can dissolve but any nonionic or nonpolar solute cannot dissolve. The second is called "nonpolar solvents" in which any nonionic or nonpolar solute can dissolve but any ionic or polar solute cannot dissolve. The following table gives some of the important polar and nonpolar solvents that are widely used:

POLAR SOLVENTS		NONPOLAR SOLVENTS	
Water	H_2O	Hexane	$CH_3CH_2CH_2CH_2CH_2CH_3$
Formic acid	HCO_2H	Benzene	C_6H_6
Acetic acid	CH_3CO_2H	Toluene	$C_6H_5CH_3$
Methanol	CH_3OH	1,4-dioxene	$(CH_3CH_2O)_2$
Ethanol	CH_3CH_2OH	Chloroform	$CHCl_3$
n-butanol	$CH_3CH_2CH_2CH_2OH$	Diethyl ether	$(CH_3CH_2)_2O$

EXAMPLE 6.1

Knowing that:

A) Molecules of Br_2, C_6H_6, CCl_4, CH_2O and CS_2 are nonpolar

B) Molecules of H_2O, CH_2O and liquid NH_3 are polar

C) KCl is an ionic compound

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 soluble C_6H_6 not in H_2O

B) KCl is soluble in NH_3 not in CCl_4

C) CH_2O is soluble in H_2O not in CS_2.

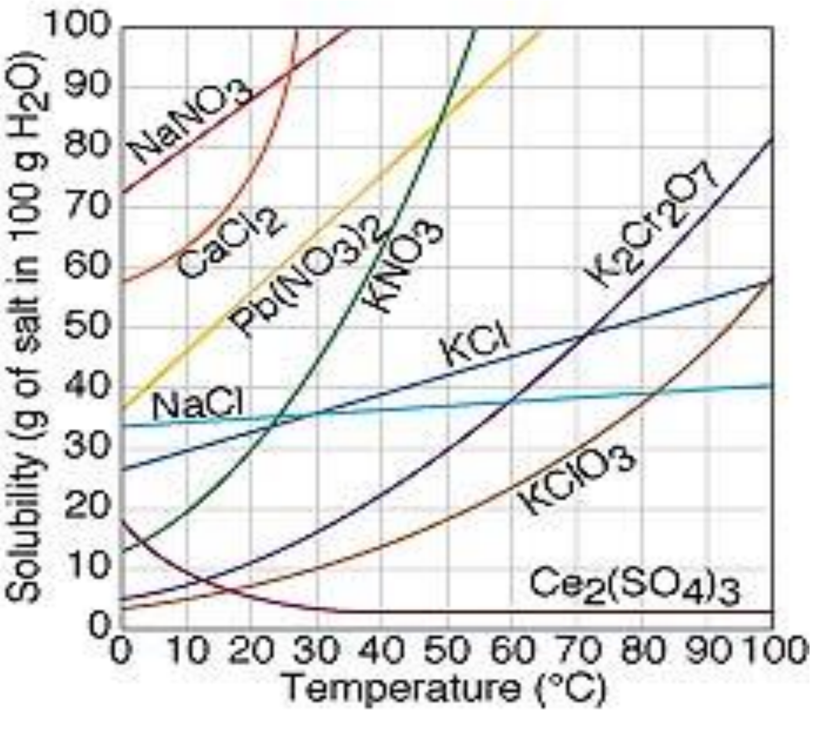
Practice Exercise

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)?

6.4 The effect of temperature on solubility

6.4.1 Solid solubility and temperature

First, let's carefully look and inspect the following figure:



The figure clearly shows that:

1) Solubility of most ionic solid salts in water increases as temperature increases
2) Solubility of a few ionic solid salts in water increases as temperature decreases
3) Solubility of very rare solid salts in water is almost the same at all temperatures
4) The solubility differs from a salt to another
5) The solubility for all salts can be determined and compared

EXAMPLE 6.2

Using the above curves answer the following questions:

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

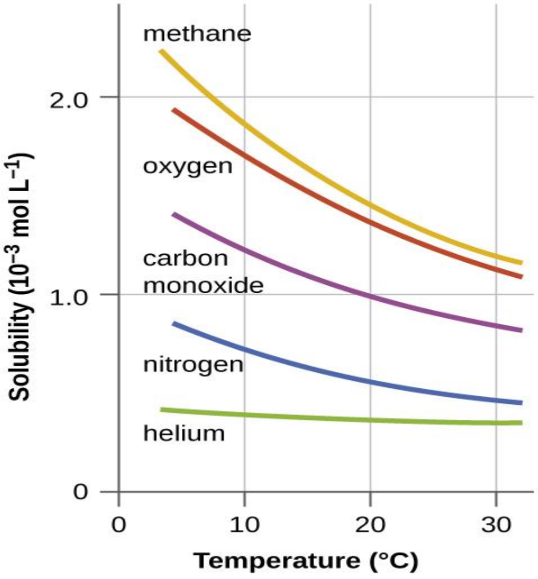
Practice Exercise

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?

6.4.2 Gas solubility and temperature

First, let's carefully look and inspect the following figure:

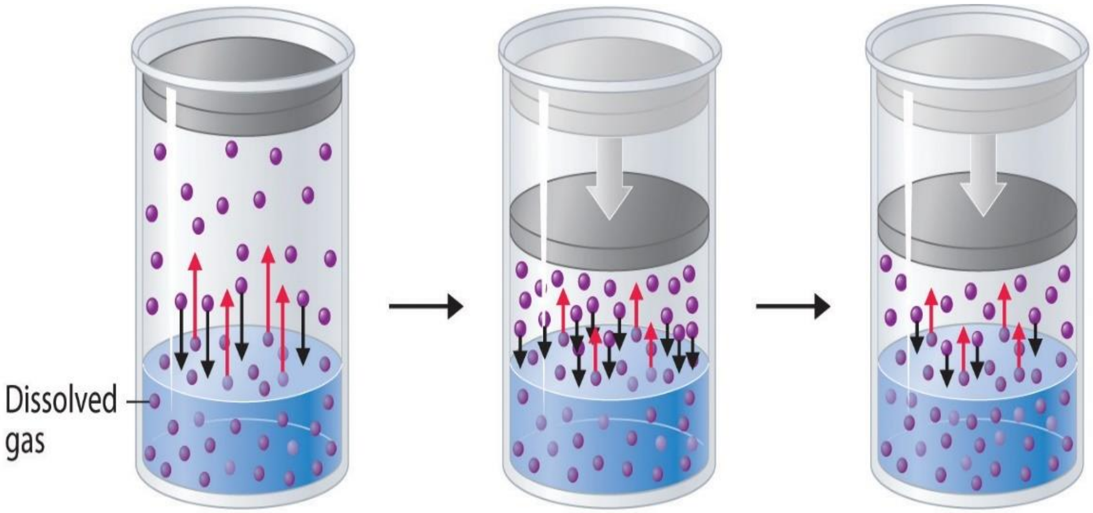


The figure clearly shows that:

1) In ***all*** cases and with no single exception, the solubility of any gas decreases as temperature increases
2) The solubility differs from a gas to another
3) The solubility for all gases can be determined and compared

6.5 The effect of pressure on solubility

Due to the closeness between particles of solids and liquids, **pressure has no effect** on the solubility of a liquid in a liquid or a solid in a liquid. However, due to the spacing between particles of gases, **pressure has a great effect** on the solubility of gases. Let's look at the following figure:



The 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 its pressure is given by **Henry's law,** which states that **the solubility of a gas in a liquid is proportional to its pressure of over the solution**. It is presented by the following law:

$$\mathbf{c = kP}$$

"**c**" is the molar concentration (the number of moles of gas in one liter of the solution, ($\frac{\text{mol}}{\text{L}}$).

"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***. Henry's constant differs from a gas to another and its 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 the liquid depends on how frequently the gas molecules collide with the liquid surface and become trapped. We can understand this matter when we think about a bottle of a refreshment drink:

1) The bottle is sealed at high pressure of CO_2. This means that amount of CO_2 dissolved in these drinks is many times the amount dissolved under normal atmospheric pressure.
2) 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 finally 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.

EXAMPLE 6.3

The solubility of nitrogen gas in water at 25 °C and 1 atm of N_2 is $6.8 \times 10^{-4}\ \frac{\text{mol}}{\text{L}}$. 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

$c = k \times P$

6.8×10^{-4} mol/L $= k \times 1$ atm

$k = \frac{6.8 \times 10^{-4}\ \frac{\text{mol}}{\text{L}}}{1\ \text{atm}} = 6.8 \times 10^{-4}$ mol/L atm

Therefore,

$c = 6.8 \times 10^{-4}\ \frac{\text{mol}}{\text{L} \times \text{atm}} \times 0.78\ \text{atm} = 5.3 \times 10^{-4}$ mol/L

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.

6.6 Concentrations of solutions

In any solution, the term "concentration" is used to compare the amount of the solute with the amount of the solvent. The greater the amount of solute, the more concentrated the solution is. Below we review four of the many ways of expressing concentration. They are called: "mass percent", "mole fraction", "molality", and "molarity". At the end we will see that ***knowing one of these concentration units makes all other units able to be calculated.***

6.6.1 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:
1) The solute mass percent has no units
2) Water is the solvent and glucose is the solute
3) $m_{solution}$ = 100 g
4) m_{solute} = 25 g
5) $m_{solvent}$ = 75 g
6) $n_{solvent}$, n_{solute} and n_{total} can be calculated
7) $V_{solution}$ can be calculated if density of the solution ($d_{solution}$) is given

Example 6.4
A solution contains 131.4 g of glucose in 0.5 kg of water. Calculate glucose mass%.
Solution

$$\text{Glucose mass\%} = \frac{m_{glucose}}{\text{total mass of solution}} \times 10^2$$

$$\text{Glucose mass\%} = \frac{131.4\ \text{g}}{131.4\ \text{g} + 0.5\ \text{kg} \times 1000\frac{\text{g}}{\text{kg}}} \times 10^2 = 20.81\%$$

Practice Exercise
A solution contains 8.74 g $NaNO_3$ in 75 g of water. Calculate the $NaNO_3$%.

6.6.1 Mole fraction (X)

Mole fraction of a component of a solution (**$X_{component}$**) is given by:

$$\mathbf{X_{component}} = \frac{\mathbf{n_{component}}}{\textbf{total moles of componants}} = \frac{\mathbf{n_{component}}}{\mathbf{n_t}}$$

In an aqueous solution, the mole fraction is 0.25 for $C_6H_{12}O_6$, what does this mean?
It means that:
1) The mole fraction has no units
2) Water is the solvent and glucose is the solute
3) $n_{C_6H_{12}O_6}$ = 0.25 mol.
4) $n_{solvent}$ = 0.75 mol.
5) $m_{C_6H_{12}O_6}$ can be calculated.
6) $m_{solvent}$ can be calculated.
7) $m_{solution}$ can be calculated.
8) $V_{solution}$ can be calculated if density of the solution ($d_{solution}$) is given.

Example 6.5

Calculate the mole fraction of 281 g of glucose ($C_6H_{12}O_6$) in 450 mL aqueous solution ($d_{solution} = 0.998\ \frac{g}{mL}$).

solution

Mass = density × volume

Mass of solution = $0.998\ \frac{g}{mL} \times 450\ mL = 449.1\ g$

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.

6.6.3 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:

1) The molality units are $\frac{mol}{kg}$ which is usually called “molal” which is abbreviated as “m”
2) Solvent is water and solute is glucose
3) $n_{C_6H_{12}O_6} = 0.25\ mol$
4) $m_{solvent} = 1\ kg = 1000\ g$
5) m_{solute} can be calculated
6) $n_{solvent}$ can be calculated
7) $m_{solution}$ can be calculated
8) $V_{solution}$ 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

$m_{solvent} = d_{solvent} \times V_{solvent} = 25\ mL \times 1\ \frac{g}{mL} = 25\ g = 0.025\ kg$

$$molality = \frac{n_{solute}}{mass_{solv}(kg)} = \frac{\frac{4.35\ g}{180\frac{g}{mol}}}{0.025\ kg} = 0.097\ \frac{mol}{kg} = 0.097\ molal = 0.097\ m$$

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.

6.6.4 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 (solution):

$$\textbf{Molarity (M)} = \frac{\mathbf{n_{solute}}}{\mathbf{V_{solution}\ (L)}}$$

What does 0.25 molar $C_6H_{12}O_6$ solution mean?
It means that:

1) The molarity units are $\frac{mol}{L}$ which is usually called "molar" which abbreviated as "M"
2) Solvent is water and solute is glucose
3) $n_{C_6H_{12}O_6} = 0.25\ mol$
4) $V_{solution} = 1L = 1000\ mL$
5) m_{solute} can be calculated
6) $m_{solution}$ can be calculated if density of the solution ($d_{solution}$) is given
7) $m_{solvent}$ can be calculated
8) $n_{solvent}$ can be calculated

Example 6.7

Calculate the molarity of 19.6 g of glucose ($C_6H_{12}O_6$) in 650 mL aqueous solution.

Solution

$$Molarity = \frac{n_{solute}}{V_{soln}\ (L)} = \frac{\frac{19.6\ g}{180\frac{g}{mol}}}{\frac{650\ mL}{1000\frac{mL}{L}}} = 0.168\ \frac{mol}{L} = 0.168\ molar = 0.168\ M$$

Practice Exercise

Calculate the molarity of 8.74 g sodium nitrate ($NaNO_3$) in 750 mL aqueous solution.

The dilution law

Solutions used routinely in the laboratory are often purchased or prepared in a very concentrated form (called stock solutions). Solutions of lower concentrations can then be prepared by adding water to the stock concentrated solution, this process is 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 solution of $CuSO_4$ with a concentration of 0.1 M from a stock solution having a concentration of 1 M $CuSO_4$:

$$\mathbf{n_{solute,diluted\ solution} = n_{solute,diluted\ solution}}$$

$$\mathbf{M_{conc} \times V_{conc} = M_{dil} \times V_{dil}}$$

$$\mathbf{1 \times V_{conc} = 0.1 \times 250}$$

$$\mathbf{V_{conc} = 25\ mL}$$

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 6.8

How many milliliters of 3.0 M H_2SO_4 are needed to make 450 mL of 0.1 M H_2SO_4?

Solution

$M_{conc} \times V_{conc} = M_{dil} \times V_{dil}$

$3\ \frac{mol}{L} \times V_{conc} = 0.1\ \frac{mol}{L} \times 450\ mL$

$V_{conc} = 15\ mL$

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 6.9

How many milliliters of water must be added to 60 mL of 18 M HCl to get a solution that is 0.2 M?

Solution

$M_{conc} \times V_{conc} = M_{dil} \times V_{dil}$

$18\ M \times 60\ mL = 0.2\ M \times V_{dil}$

$V_{dil} = 5400\ mL$

$V_{dil} = V_{conc} + V_{water}$

$5400\ mL = 60\ mL + V_{water}$

$V_{water} = 5340\ mL$

Practice Exercise

How many milliliters of water must be added to 15 mL of 5.5 $\frac{mol}{L}$ $NaNO_3$ stock solution to get a solution that is 0.15 $\frac{mol}{L}$?

6.7 Interconversion between concentration's units

The above discussion was an illustration to the main four types of concentration units: solute mass%, mole fraction, molality and molarity. It was mentioned that knowing any one of them enables us to determine the other three. The following exercises shows how this can be done.

Example 6.10

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) $n_{solute} = \frac{m_{solute}}{M_{solute}} = \frac{36\ g}{36.45\ \frac{g}{mol}} = 0.988\ mol$

$m_{solvent} = 100\ g - 36\ g = 64\ g$

$n_{solvent} = \frac{m_{solvent}}{M_{solvent}} = \frac{64\ g}{18\ \frac{g}{mol}} = 3.556\ mol$

$X_{solute} = \frac{n_{solute}}{n_t} = \frac{0.988\ mol}{(0.988\ mol + 3.556\ mol)} = 0.217$

B) $molality = \frac{n_{solute}}{mass_{solv}\ (kg)} = \frac{0.988\ mol}{0.064\ kg} = 15.44\ molal$

Practice Exercise

Calculate the molality of a sodium nitrate ($NaNO_3$) aqueous solution in which the mass percent of $NaNO_3$ is 43%.

Example 6.11

A solution with a density of 0.876 g/mL contains 5 g of toluene (C_7H_8) dissolved in 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 6.12

Calculate the glucose mass% in a 0.73 molal solution of glucose in water.

Solution

$Glucose\% = \frac{m_{glucose}}{\text{total mass of solution}} \times 10^2$

$n_{glucose} = 0.73\ mol$,, $m_{water} = 1\ kg = 1000\ g$

$m_{glucose} = n_{glucopse} \times M_{glucose} = 0.73 \times 180 = 131.4\ g$

$m_{solution} = m_{glucose} + m_{water} = 131.4 + 1000 = 1131.4\ g$

$Solute\% = \frac{131.4\ g}{1131.4\ g} \times 10^2 = 11.61\%$

Practice Exercise

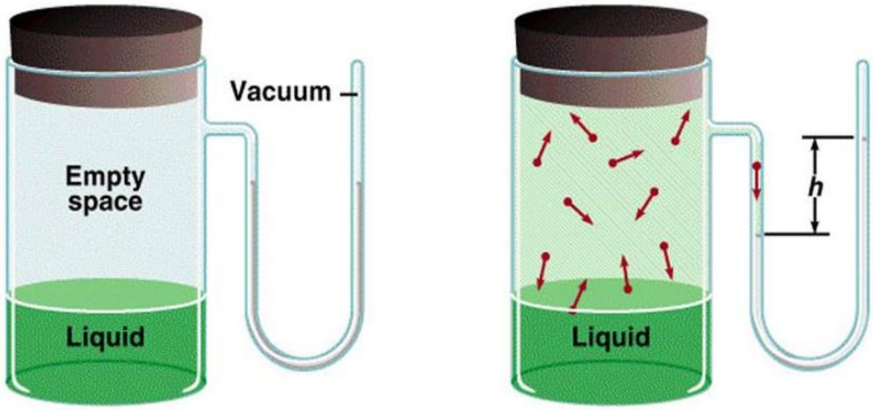
If the molality of a solution of urea (NH_2CONH_2) in water is 0.14 mol/kg, calculate the mass percent of urea in the solution.

THE PROPERTIES OF A PURE LIQUID CHANGE AFTER IT BECOMES NOT PURE

6.7 Vapor pressures, boiling points, and freezing points of pure liquids

6.7.1 Vapor pressures of pure liquids

The liquid molecules that evaporate become gaseous molecules and are called "**vapor**" and 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 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 and any liquid molecule that is not at the surface of the liquid will not vaporize even if it has high energy and speed. Let’s look carefully to the following figure:



Before Evaporation

At Equilibrium

The figure 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 and 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. 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***. Vapor pressure of many liquids at different temperatures are available in tables achieved by physicists and chemists.

6.7.2 Boiling points of pure liquids

As cleared out above, when liquid temperature increases its vapor pressure increases. When the temperature increases the vapor pressure of the liquid will equalize the external pressure at a ***certain temperature***. At this certain temperature the whole liquid molecules become in a situation of transition from the liquid state to the gaseous state, and the surface of the liquid disappears. This particular situation of evaporation at this ***certain temperature*** is given a particular name. It is called ***boiling***. And the temperature at which this happens is called "***the boiling point***." If the external pressure is the standard pressure (1 atm) it is called "***the standard boiling point***". For example, the boiling point of water is 100 °C only if the pressure is 1 atm.

- If the external pressure is higher than standard pressure the boiling point becomes higher than standard boiling point (for example, at 1.5 atm water will boil at 110.5 °C).
- If the external pressure is lower than standard pressure the boiling point becomes lower than standard boiling point (for example, at 0.4 atm water will boil at 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.

6.7.3 Freezing points of pure liquids

Decreasing the temperature of liquid molecules will decrease their energies and speeds and consequently the attractive forces between them increase. At a ***certain temperature***, the liquid molecules start to be tightly bonded to their neighboring molecules and cannot leave their positions. When this starts to happen, we say: liquid ***freezes***. We call the temperature at which the liquid freezes "***the freezing point***." If the pressure at which liquid freezes is 1 atm this temperature is called "***the standard freezing point***". For example, the standard freezing point of water is 0 °C.

6.8 Vapor pressures of mixed liquids (Raoult's law)

Here we do not have a **pure liquid** but two liquids. Suppose we have liquid "A" and liquid "B", and the number of moles we have are "n_A and "n_B" and 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° but when they are mixed together, we will symbolize their vapor pressure in the mixture as P_A and P_B. If we mix the n_A mole of A with 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?*** ($P_{solution}$). "Raoult" had proven that:

$$P_{solution} = P_A + P_B$$

$$(P_A = \times P^{\circ}_{A}) \qquad \text{and} \qquad (P_B = X_B \times P^{\circ}_{B})$$

Therefore, he proved that:

$$P_{solution} = (X_A \times P^{\circ}_{A}) + (X_B \times P^{\circ}_{B})$$

Because $X_A + X_B = 1$, the last equation can be modified to be:

$$P_{solution} = X_A \times (P^{\circ}_{A} - P^{\circ}_{B}) + P^{\circ}_{B}$$

OR

$$P_{solution} = X_B \times (P^{\circ}_{B} - P^{\circ}_{A}) + P^{\circ}_{A}$$

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 at our level here.

Example 6.13

Calculate the vapor pressure of a solution of 252 g of pentane and 1400 g of heptane at 20°C.

$(M_{pentane} = 72\ \frac{g}{mol}$ and $P^{\circ}_{pentane} = 420$ mmHg)

$(M_{heptane} = 100\ \frac{g}{mol}$ and $P^{\circ}_{heptane} = 36$ mmHg)

Solution

$$P_{solution} = (X_{pentane} \times P^{\circ}_{pentane}) + (X_{heptane} \times P^{\circ}_{heptane})$$

$$n_{pentane} = \frac{m_{pentane}}{M_{pentane}} = \frac{252\ g}{72\ \frac{g}{mol}} = 3.5\ mol$$

$$n_{heptane} = \frac{m_{heptane}}{M_{heptane}} = \frac{1400\ g}{100\ \frac{g}{mol}} = 14\ mol$$

$$X_{pentane} = \frac{n_{pentane}}{n_{pentane} + n_{heptane}} = \frac{3.5}{3.5 + 14} = 0.2$$

$$X_{pentane} = 1 - X_{pentane} = 1 - 0.2 = 0.8$$

$$P_{solution} = (0.2 \times 420\ mmHg) + (0.8 \times 36\ mmHg) = 112.8\ mmHg$$

Practice Exercise

Calculate the vapor pressure of a solution of 50 g of methanol and 50 g of ethanol at 20°C.

$(M_{methanol} = 32\ \frac{g}{mol}$ and $P^{\circ}_{methanol} = 94$ mmHg)

$(M_{ethanol} = 46\ \frac{g}{mol}$ and $P^{\circ}_{ethanol} = 44$ mmHg)

6.9 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* ***do not depend*** *on their nature*. These properties are four:

1) **Vapor pressure**
2) **Boiling point**
3) **Freezing point**
4) **Osmotic pressure**

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. Later on, we will explain the ***osmotic pressure*** of the solution.

6.9.1 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 value of **ΔP** depends solely on the amount of the solute not on its nature. 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, $P_{solution}$ is given as follows:

$$P_{solution} = X_{solvent} \times P^{\circ}_{solvent}$$
$$P_{solution} = (1 - X_{solute}) \times P^{\circ}_{solvent}$$
$$P_{solution} = P^{\circ}_{solvent} - (X_{solute} \times P^{\circ}_{solvent})$$
$$P^{\circ}_{solvent} - P_{solution} = X_{solute} \times P^{\circ}_{solvent}$$
$$\Delta P = X_{solute} \times P^{\circ}_{solvent}$$

The presence of this kind of solutes makes the vapor pressure of the solution less than that when the solvent is pure by a value equals to ΔP which depends on the amount of the solute in the solution. This is why ΔP is considered a ***colligative property***.

EXAMPLE 6.14

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

$n_{water} = \frac{460\ g}{18.016\ \frac{g}{mol}} = 25.53\ mol$	$n_{glucose} = \frac{218\ g}{180.15\ \frac{g}{mol}} = 1.21\ mol$
$X_{water} = \frac{25.5\ mol}{25.5\ mol + 1.21\ mol} = 0.995$	

$P_{solution} = X_{solvent} \times P^{\circ}_{solvent}$

$P_{solution} = 0.995 \times 31.82\ mmHg = 30.4\ mmHg$

$\Delta P = P^{\circ}_{solvent} - P_{solution} = 31.82\ mmHg - 30.4\ mmHg = 1.42\ mmHg$

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).

6.9.2 Boiling point elevation

Boiling point (t_b) *is the temperature at which the vapor pressure of the liquid equalizes the external pressure. And the* ***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 temperature at which the pure liquid boils***, will be less than that needed for the solution to boil. 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).

7 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.

$$\Delta T_b = \frac{K_b \times n_{solute}}{m_{solvent}\ (kg)}$$

If we prefer for masses as we usually are, using the gram unit rather than the kilogram, then the conversion factor from kilogram unit to gram unit has to be introduced in the equation:

$$\Delta T_b\ (^{\circ}C) = \frac{K_b\ (\frac{\frac{^{\circ}C}{mol}}{kg}) \times \frac{m_{solute}\ (kg)}{M_{solute}\ (\frac{kg}{mol})}}{m_{solvent}\ (kg)} = \frac{K_b\left(\frac{^{\circ}C\ kg}{mol}\right) \times m_{solute}\ (g) \times (\frac{1000\ g}{1\ kg})}{M_{solute}\left(\frac{g}{mol}\right) \times m_{solvent}\ (g)}$$

$$\Delta T_b = \frac{K_b \times m_{solute} \times 1000}{M_{solute} \times m_{solvent}}$$

The last equation is used to determine “ΔT_b” but with its restriction that the unit of “M_{solute}” is “$\frac{g}{mol}$” and the unit of “$m_{solvent}$” is “g”.

6.9.3 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 the liquid substance changes its state to solid at the standard external pressure (= 1 atm).* As mentioned before, at a particular low temperature, the liquid molecules start to be tightly bonded to their neighboring molecules and cannot leave their positions, and once this starts start happening, 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 tightly 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.

$$\Delta T_f = \frac{K_f \times n_{solute}}{m_{solvent}\ (kg)}$$

Again, if we prefer for masses as we usually are, using the gram unit rather than the kilogram, then the conversion factor from kilogram unit to gram unit has to be introduced in the equation:

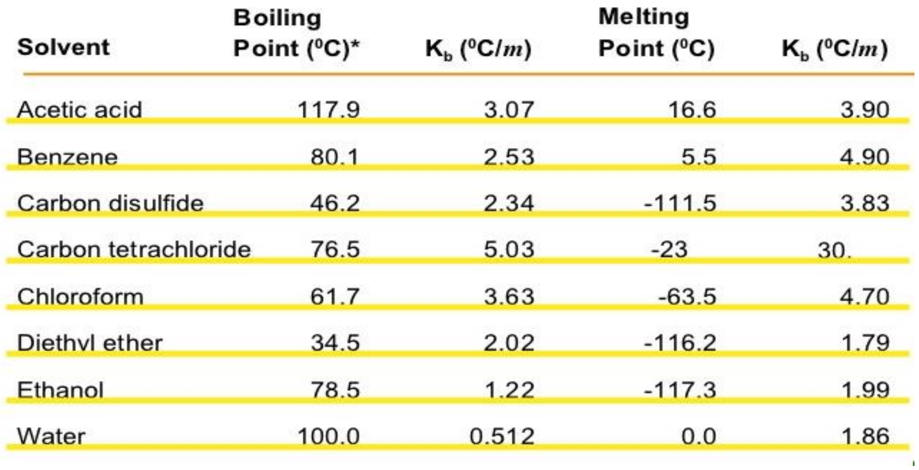
$$\Delta T_f\ (^{\circ}C) = \frac{K_f\ (\frac{\frac{^{\circ}C}{mol}}{kg}) \times \frac{m_{solute}\ (kg)}{M_{solute}\ (\frac{kg}{mol})}}{m_{solvent}\ (kg)} = \frac{K_f\left(\frac{^{\circ}C\ kg}{mol}\right) \times m_{solute}\ (g) \times 1000\ (\frac{g}{kg})}{M_{solute}\left(\frac{g}{mol}\right) \times m_{solvent}\ (g)}$$

$$\Delta T_f = \frac{K_f \times m_{solute} \times 1000}{M_{solute} \times m_{solvent}}$$

And again, the last equation is used to determine “ΔT_f” but with its restriction that the unit of “M_{solute}” is “$\frac{g}{mol}$” and the unit of “$m_{solvent}$” is “g”.

The following table of some common liquids provides their;

1) standard boiling points (t_b°)
2) molal boiling point elevation constant (K_b)
3) standard freezing points (t_f°)
4) molal boiling point elevation constant (K_b)



Solvent	Boiling Point (⁰C)*	K_b (⁰C/*m*)	Melting Point (⁰C)	K_b (⁰C/*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 6.15

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 made of 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 °C and $T^\circ_{\text{boiling,water}}$ = 100 °C

$K_{f,\text{water}}$ = 1.86 °C/m and $K_{b,\text{water}}$ = 0.52 °C/m

Solution

$$\text{molality} = \frac{n_{\text{solute}}}{m_{\text{solvent}}\,(\text{kg})} = \frac{\frac{m_{\text{solute}}}{M_{\text{solute}}}}{m_{\text{solvent}}\,(\text{kg})} = \frac{\frac{651\ \text{g}}{62.01\frac{\text{g}}{\text{mol}}}}{2505\ \text{g} \times 10^{-3}\,\frac{\text{kg}}{\text{g}}} = 4.19\,\frac{\text{mol}}{\text{kg}}$$

A) $\mathbf{\Delta T_b = K_b\, m}$

$\Delta T_b = 0.52$ °C/m × 4.19 m = 2.2 °C

$\Delta T_b = T_{b,\text{solution}} - T^\circ_{b,\text{water}}$

2.2 °C = $T_{b,\text{solution}}$ – 100 °C

$T_{b,\text{solution}}$ = 102.2 °C

$\mathbf{\Delta T_f = K_f\, m}$

$\Delta T_f = 1.86$ °C/m × 4.19 m = 7.8 °C

$\Delta T_f = T^\circ_{f,\text{water}} - T_{f,\text{solution}}$

$7.8\ °C = 0\ °C - T_{f,solution}$

$T_{f,solution} = -7.8\ °C$

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 boiling.

Practice Exercise

Calculate the boiling and freezing points of a solution containing 478 g of ethylene glycol (Molar mass = 62.01 g/mol) in 3202 g of water.

$(T^{\circ}_{\text{boiling,water}} = 100\ °C,\ K_{b,water} = 0.52\ °C/m)$

$(T^{\circ}_{\text{freezing,water}} = 0\ °C,\ K_{f,water} = 1.86\ °C/m)$

EXAMPLE 6.16

A 7.85-g sample of an unknown compound is dissolved in 301 g of benzene. The freezing point of the solution is 1.05 °C below that of pure benzene. Calculate the molar mass of this compound. ($K_f = 5.12\ \frac{°C\ kg}{mol}$)

Solution

$\Delta T_f = 1.05\ °C$

$$\Delta T_f = \frac{K_f\ \frac{°C\ kg}{mol} \times m_{solute}\ (g) \times 1000 \frac{g}{kg}}{M_{solute}\left(\frac{g}{mol}\right) \times m_{solvent}\ (g)}$$

$$1.05\ °C = \frac{5.12\ \frac{°C\ kg}{mol} \times 7.85\ (g) \times 1000\ (\frac{g}{kg})}{M_{solute} \times 301\ (g)}$$

$M_{solute} = 127\ \frac{g}{mol}$

Practice Exercise

Calculate the boiling and freezing points of a solution containing 478 g of ethylene glycol (Molar mass = 62.01 g/mol) in 3202 g of water.

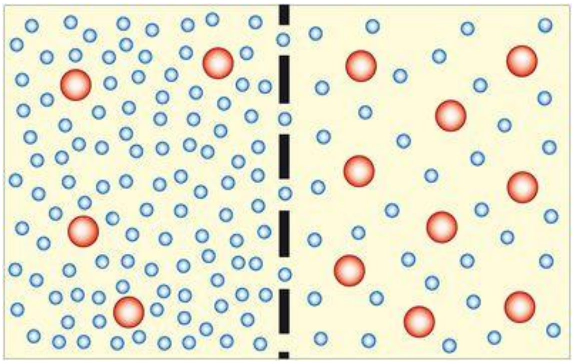
$(T^{\circ}_{\text{boiling,water}} = 100\ °C,\ K_{b,water} = 0.52\ °C/molal)$

$(T^{\circ}_{\text{freezing,water}} = 0\ °C,\ K_{f,water} = 1.86\ °C/molal)$

6.9.4 Osmotic pressure

Semipermeable membranes?

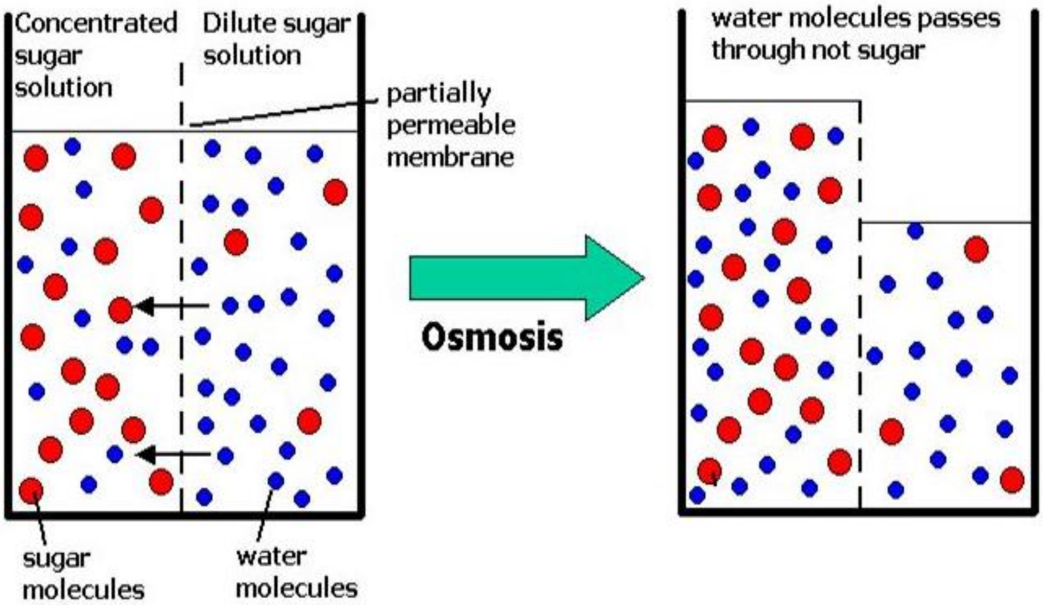
Old way to cool water is to put it in a pottery pot similar to the one shown in the figure below. The walls of the pottery pots permit water inside the pot to pass through its walls. This allows water to be in contact with the colder atmosphere outside the pot. This way was one of the ancient technologies 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 depicted below, 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.

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.


Concentrated sugar solution
Dilute sugar solution
partially permeable membrane
sugar molecules
water molecules
Osmosis
water molecules passes through not sugar

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 6.17

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 6.18

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

$$M = \frac{\pi}{R \times T} = \frac{10\ \text{mmHg} \times \frac{1\ \ \ \text{atm}}{760\ \text{mmHg}}}{0.0821\ \frac{\text{atm L}}{\text{mol K}} \times 298\ \text{K}} = 5.38 \times 10^{-4}\ \text{mol/L}$$

$$n_{\text{Hb}} = M \times V\ (\text{L}) = 5.38 \times 10^{-4}\ \text{mol/L} \times \text{I L} = 5.38 \times 10^{-4}\ \text{mol}$$

$$M_{\text{Hb}} = \frac{m_{\text{Hb}}}{n_{\text{Hb}}} = \frac{35\ \text{g}}{5.38 \times 10^{-4}\ \text{mol}} = 6.51 \times 10^{4}\ \text{g/mol}$$

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.