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KOLEJ KOMUNITI MALAYSIA

BASIC PHYSICAL CHEMISTRY

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Basic Physical Chemistry

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Appreciation

Assalamualaikum W.B. T

Be grateful to Allah S.W.T for his abundance and his secret to us in preparing this basic physical chemistry module.

In this regard, we look at both our parents and our families as we always wish for our success in whatever we do.

We also wish to thank the Director, Deputy Director, department heads, and all our colleagues at Tun Syed Nasir Syed Ismail Polytechnic (PTSN) and who always provide guidance to us. We will remember this friendship anytime.

The most special tribute to our students at PTSN is our main model for achieving this mission.

We hope that this module will help the lecturers who teach this course to do their job better. Hopefully, this module will also help students better understand the basic concepts of chemistry for achieving learning objectives.

Finally, thank you to everyone involved in helping us prepare this module. All your services are greatly appreciated.

Preface

Physical Chemistry is the study of matter and the chemical reactions between types of matter. It involves in understanding the basic properties of matter and learning how to predict as well as explain the changes that occur when the matters react to each other to form a product of new substances. The atom and molecules are the basic components of Chemistry. Chemistry is related to everything from the basic elements to complex structures. In a nutshell, it is important for students to study chemistry because they can understand the basics concept of how things work. It plays an essential role in many technological science processes and in daily life activities.

This *First Edition eBook of Basic Physical Chemistry* Module is written for semester one (1) students of Diploma Chemical Technology (Oil and Fat) in Tun Syed Nasir Syed Ismail Polytechnic. This eBook can also be a general reference for any students who enrolled in chemistry programme and it may also be helpful for anyone who would like to gain general overview of the contents in this eBook. The main objective of this eBook is to provide an intensive understanding of the basic concepts in basic physical chemistry. The topics in this eBook are the follow through of the syllabus of DMK10023 Basic Physical Chemistry. The topics include the definition of matter, periodic table, chemical bond, volumetric analysis, acid and bases and oxidation, reduction, chemical kinetics, and equilibrium.

This eBook is presented a simple feature of writing that includes clear figure, table and diagram. Step by step examples with sample question and answers are also provided in this eBook to better understand each topic of basic physical chemistry. Tutorial with answer are also available at the last part of each topic to enhance student mastery of the topics.

Last but not least, it is the author/s hope that Basic Physical Chemistry eBook will cater clear understanding to students for each chapters of this course.

BASIC PHYSICAL CHEMISTRY

Junainah Mustapa
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1.0 Matter

1.1 Concept of Matter

- Matter is all things that have mass and volume.
- Matter is made from elements that have chemical properties and physical properties, respectively.

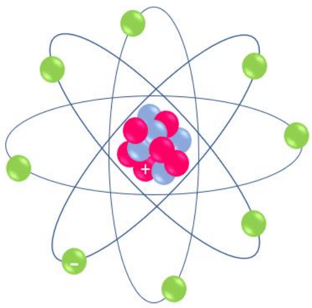


Figure 1.1 Model of atom

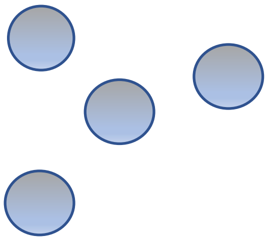


Figure 1.2 Atom of element X

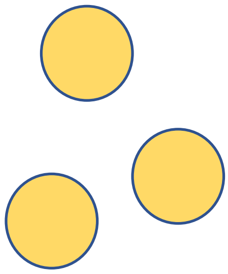


Figure 1.3 Atom of element Y

- An **atom** is the smallest unit of matter.
- Based on Figure *1.1*, an atom consists of a positively charged nucleus of protons and neutrons surrounded by a cloud of negatively charged electrons.
- The nucleus is small and dense compared with the electrons, which are the lightest charged particles in nature.
- Electrons are attracted to any positive charge by their electric force. In an atom, electric forces bind the electrons to the nucleus.
- Element X and Y are composed of very small called atoms. An element is a pure substance consisting only of atoms that all have the same numbers of protons in their atomic nucleus.
- An example of atom *element X* is hydrogen, H and the *element Y* is oxygen, O.

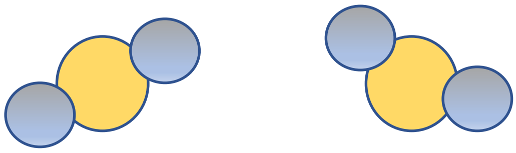
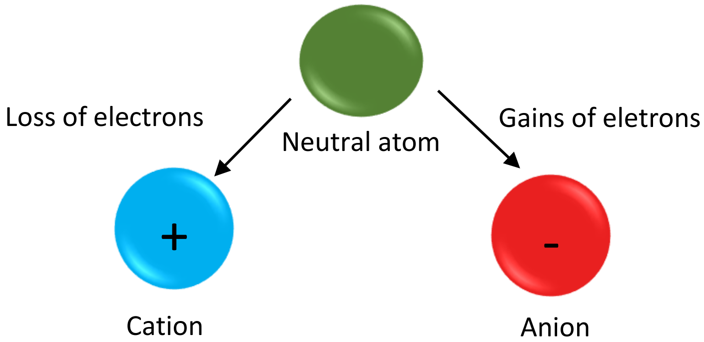


Figure 1.4 Compound of elements of X and Y

- **Molecules** are made up of atoms that are held together by chemical bonds.
- These bonds are formed as a result of the sharing or exchange of electrons among atoms. Based on Figure 1.4 the atoms of certain elements are readily bonded with other atoms to form molecules.



- Electrons can move from one atom to another; when they do, species with overall electric charges are formed. Such species are called **ions**.
- They have the same number of electrons as protons, so the negative charges of the electrons are balanced by the positive charges of the protons. However, this is not always the case.
- Species with overall positive charges are termed cations, while species with overall negative charges are called anions.

1.1.1 Types of matter

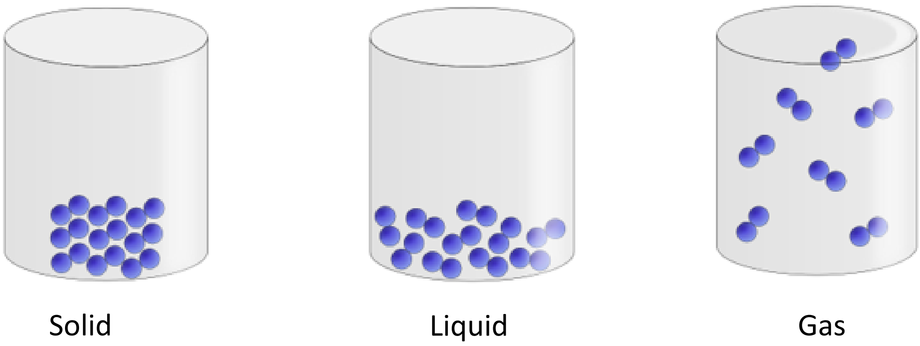
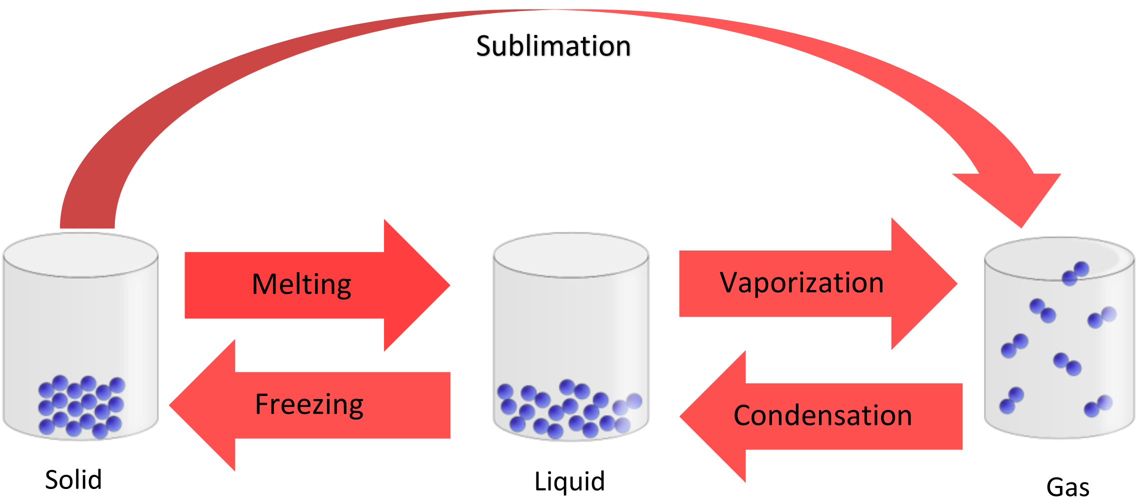


Figure 1.5 Molecules in every type of matter

Table 1.1 Concept multipliers that convert decimals to whole numbers

State of Matter	Volume/Shape	Density	Motion of molecules
Solid	Assumes the volume and shape of its container	Low	Very free motion
Liquid	Has a definite volume but assumes the shape of its container	High	Slide past one another freely
Gas	Has a definite volume and shape	High	Vibrate in fixed positions

1.1.2 Phase changes of matter



- Melting occurs when heat is applied to a solid state, causing it to transform into a liquid.
- When heat is transferred from a liquid state to a solid, the process is known as freezing.
- The process of vaporization occurs in a liquid state when heat transfer occurs and the fluid boils, resulting in the formation of a gas.
- Condensation is the process of heat transfer from a gaseous state to liquid.
- When heat is released from a solid substance to a gaseous substance, the process is known as sublimation.

1.2 Mole Concept

- The **mole** is the base unit of the amount of substance in the International System of Units (SI).
- A **mole** is defined as the amount of substance containing the same number of discrete entities.
- The elementary entities that can be represented in moles can be atoms, molecules, monoatomic/polyatomic ions, and other particles (such as electrons).
- The number $6.02214076 \times 10^{23}$ is popularly known as the Avogadro constant and is often denoted by the symbol 'N_A'.
- Avogadro's number is founded by the Italian chemist named Amadeo Avogadro (1776-1856).
- Avogadro's number is one of the fundamental constants of chemistry.

$$N_A = 6.023 \text{ X } 10^{23}$$

Concept:

1 mole C = $6.023 \text{ X } 10^{23}$ C atom

1 mole H_2O = $6.023 \text{ X } 10^{23}$ H_2O molecules

1 mole NaCl = $6.023 \text{ X } 10^{23}$ NaCl molecules
($6.023 \text{ X } 10^{23}$ Na^+ ions and $6.023 \text{ X } 10^{23}$ Cl^- ions)

- The **molar mass** is defined as the mass in grams of 1 mol of that substance whether the substance is an element, an ionic compound or a covalent compound.

Example 1:

1 mole of C atom = 12 g

1 mole of Mg atom = 24 g

1 mole of Cu atom = 63.5 g

Example 2:

What is the molar mass of the of NaCl?

Answer:

1 mole Na = 23 g

1 mole Cl = 35 g

Molar mass = Na + Cl

= 23 + 35

= 58 g

Example 3:

Calculate the molar mass of the of $Al(OH)_3$?

Answer:

1 mole Al = 27 g

1 mole O = 16 g

1 mole H = 1 g

Molar mass = Al + 3(O + H)

= 27 + 3(16 + 1)

= 27 + 3(17)

= 78 g

1.2.1 Relative atomic mass (R.A.M)

- Atomic mass is the mass of the atom in atomic mass units (amu)
- Relative atomic mass is the mass of an atom or molecule relative to that of 1/12 of a carbon-12 atom.
- Relative atomic mass is unitless.

$$\mathbf{R.A.M} = \frac{\mathbf{mass\ of\ atom\ (amu)}}{\frac{\mathbf{1}}{\mathbf{12}}\ \mathbf{mass\ of\ a\ carbon\ 12\ atom\ (amu)}}$$

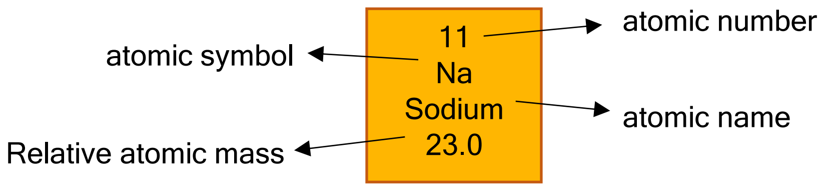
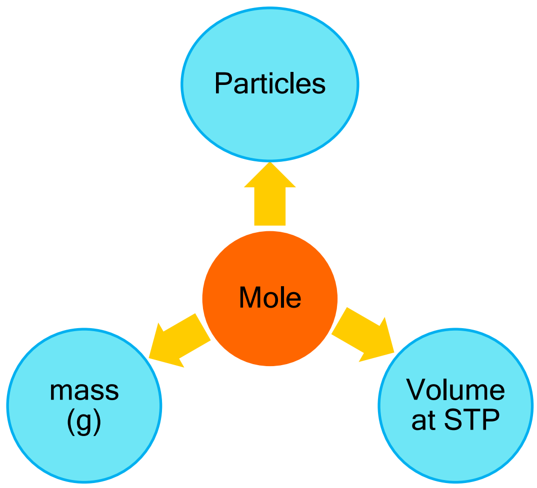


Figure 1.6 Keyword for element in Periodic Table

- Relative atomic mass of any element or atom can be obtained from the Periodic Table as shown in Figure 1.6.

1.2.2 The concept of mole



- Using conversion techniques, we can use the mole to convert back and forth between the number of **particles and moles**. The basic note for this situation is 1 mole element equal to 6.023 X 10^{23} .

$$\boldsymbol{x}\ \mathbf{moles} = \frac{\boldsymbol{x\ particles}}{\mathbf{6.02\ x\ 10^{23}}\ \boldsymbol{particles}}$$

Example 4:

How many moles of carbon atoms is 4.72×10^{24} atoms of carbon?

Answer:

Number of carbon atoms = 4.72×10^{24} atoms

1 mole C = 6.023×10^{23} atoms C

$$x \text{ moles} \quad = \frac{x\ particles}{6.023\ x\ 10^{23}}$$

$$= \frac{4.72\ x\ 10^{24}}{6.023\ x\ 10^{23}}$$

= 7.84 mole

Example 5:

Given sulphuric acid has the chemical formula of H_2SO_4. A quantity of sulphuric acid its contains 4.89×10^{25} atoms of oxygen. Count the moles of sulphuric acid?

Answer:

Number of O atoms = 4.89×10^{25} atoms O

1 mole = 6.023×10^{23} molecules H_2SO_4

$$4.89 \times 10^{25}\ \cancel{\text{atoms O}} \times \frac{1\ \cancel{\text{molecule}\ H_2SO_4}}{4\ \cancel{\text{atoms O}}} \times \frac{1\ \cancel{mole\ H_2SO_4}}{6.02 \times\ 10^{23}\ molecule\ H_2SO_4}$$

$$= \mathbf{20.3\ mole}\ \boldsymbol{H_2SO_4}$$

- The mole can also be found from the **mass** of the substance or compound with this conversion:

1 mole = mass of molar mass (g)

Example 6:

Calculate the moles of Helium(He) atoms are in 7.5 g of He?

Answer:

Molar mass, 1 mole He = 4 g He

x mole He = 7.5 g He

So,

$$7.5 \text{ g He} = x \text{ mole } (4\text{g He})$$

$$x \text{ mole} = \frac{7.5 \; g \cancel{He}}{4 \; g \cancel{He}}$$

= 1.9 mole

- Molar Volume is volume consist of one mole of any gas.
- **Standard temperature and pressure (STP)** with 0°C or 273.15 K and 1 atm pressure.
- STP volume of most gases is around 22.4 L per mole.

$\boxed{\text{1 mole = 22.4 L}}$

Example 7:

A certain reaction produces 86.5L of hydrogen, H_2 gas at STP. How many moles of hydrogen are produced?

Answer:

1 mole H_2 (STP) = 22.4 L

So,

$$86.5 \cancel{L H_2} \; X \; \frac{1 mol \; H_2}{22.4 \cancel{L H_2}}$$

= 3.9 mol H_2

1.3 Chemical Formula, Empirical Formula and Molecular Formula

- **A Chemical formula** is the chemical composition of element. This can be either a molecular formula or empirical formula.
- The chemical formula shows the number of atoms of each element in a compound. It contains the symbols of the atoms of the elements present in the compound as well as how many there are for each element in the form of subscripts.

Name of compound	Chemical Formula
Baking soda	$NaHCO_3$
Sulphuric acid	H_2SO_4

1.3.1 Empirical formula and molecular formula

- The **molecular formula** refers to the number of atoms for each element of the molecule.

Ethanol, C_2H_6O

1 mol C_2H_6O contains:

- 2 moles atom Carbon, C
- 6 moles atom Hydrogen, H
- 1 mole atom Oxygen, O

- The **empirical formula** is the simplest whole-number ratio of atoms in the compound. Its derives from experimental data based on mass (g) or percentage of the compound.
- It is important to remember the concept of some multipliers that convert decimals to whole numbers as in Table 1.2.

Table 1.2: Concept multipliers that convert decimals to whole numbers

Decimal	Multiply by	Example		Whole number
0.20	5	1.20 x 5	=	6
0.25	4	2.25 x 4	=	9
0.33	3	1.33 x 3	=	4
0.50	2	2.50 x 2	=	5
0.67	3	1.67 x 3	=	5

Example 8:

Given Ribose with molecular formula is $C_5H_{10}O_5$. Calculate the empirical formula for Ribose.

Answer:

$C_5H_{10}O_5$

Divide the subscripts in the actual (molecular) formula by a whole number to give the lowest ratio.

C	**H**	**O**
$5 \div 5$	$10 \div 5$	$5 \div 5$
1	2	1

So, empirical formula for Ribose is **CH_2O**

Example 9:

Find the empirical formula for 100g aspirin that contains 60.0% C or 60.0 g C, 4.5% H or 4.5 g H and 35.5% O or 35.5 g O.

Answer:

Atom	**C**	**H**	**O**
Mass	60.0 g	4.5 g	35.5 g
Molar mass	12 g	1 g	16 g
	$\frac{60.0}{12}$	$\frac{4.5}{1}$	$\frac{35.5}{16}$
Mole	5	4.5	2.22
Divide all with the smallest number	$\frac{5}{2.22}$	$\frac{4.5}{2.22}$	$\frac{2.2}{2.22}$
	2.25	2	1
	Based on Table 1.2,	2 x 4 = 8	1 x 4 = 4
	2.25 x 4 = 9		

So, empirical formula for aspirin is $\mathbf{C_9H_8O_4}$

- In the solid state, ionic compounds are in crystal lattice containing many ions each of the cation and anion.
- Cation is a positive ion and anion is a negative ion.
- A balanced formula has a neutral electrical charge or net charge of zero where electrons are shared between cations and anions to complete outer electron shells also known as octets.
- For the determination formula of an ionic compound, the main point is the total of the cation must be equal to the total of the anion which is a chemical compound that is always electrically neutral.

- Many familiar chemicals are ionic compounds. A metal bonded to a non metal is a dead giveaway when dealing with an ionic compound.

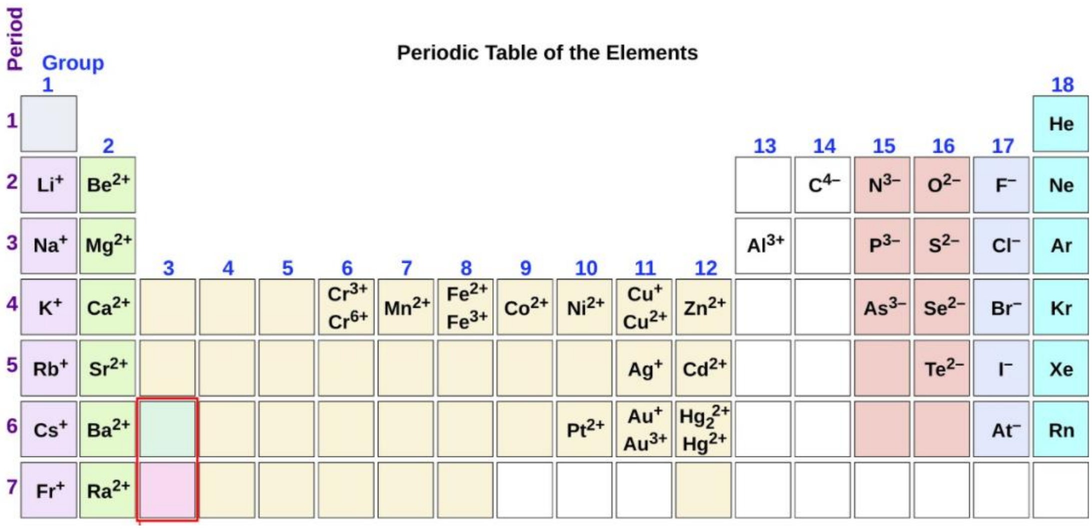


Figure 1.7: Some elements exhibit a regular pattern of ionic charge when they form ions
Photo credit: https://courses.lumenlearning.com/suny- mcc-introductorychemistry/chapter/ions-and-ionic-compounds/

- Steps to write an ionic compounds:
  1. Identify a binary compound – whether the compound is metal or non-metal.
  2. Look up on two elements in Figure 1.7 – first word refers to metal ion with positive ion and second word refers to non-metal with negative ion.
  3. Balance the charge.
  4. Use the multipliers as subscript for each ion.
  5. Write a chemical formula compound.

Example 10:

Predict whether the following compounds are ionic or not:

a) KI
b) H_2O_2
c) $CHCl_3$
d) Li_2CO_3

Answer:

a) Potassium, K (group 1) is a metal, and iodine, I (group 17) is a non-metal; KI is predicted to be ionic compound.
b) Hydrogen, H (group 1) is a non-metal, and oxygen, O (group 16) is a non-metal; H_2O_2 is not ionic compound.
c) Carbon, C (group 14) is a non-metal, hydrogen, H (group 1) is a non-metal, and chlorine

Example 11:

Formula	**Aluminium nitride**	**Calcium Chloride**
1. Identify a binary compound	Al – metal N – non-metal	Ca - metal Cl – non-metal
2. Look up on two elements in Table 1.5	Al^{3+} N^{3-}	Ca^{2+} Cl^{-}
3. Balance the charge.	Al^{3+} N^{3-} 3 3	Ca^{2+} Cl^{-} 1 2
4. Use the multipliers as subscript for each ion.	Al_3N_3 $\div 3$	Ca_1Cl_2
5. Write a chemical formula compound.	Al_1N_1 @ AlN	$CaCl_2$

1.3.2 Balance chemical equations

- A chemical equation is a written description of the occurrence in a chemical reaction.
- A balanced chemical equation tells you the amount of reactants and products needed to satisfy the Law of Conservation of Mass.

Reactant $\longrightarrow$ Product

- Here are the easy steps tobalance the chemical equations:

1. Write the unbalanced equation to show the reactants and products.
2. Write down how many atoms of each element are there on each side of the reaction arrow.
3. Add coefficients (the numbers in front of the formulas) so the number of atoms of each element is the same on both sides of the equation. It is easier to balance the hydrogen and oxygen atoms last.
4. Indicate the state of matter of the reactants and products and check your work.

1.3.3 Balance chemical equations

Example 12:

Balance the equation below:

$Fe + O_2 \rightarrow Fe_2O_3$

Answer:

1. Write the unbalanced equation to show the reactants and products.

   $Fe + O_2 \rightarrow Fe_2O_3$

2. Write down how many atoms of each element are there on each side of the reaction arrow.

Reactant	Product
1 Fe	2 Fe
2 O	3 O

3. Add coefficients (the numbers in front of the formulas) so the number of atoms of each element is the same on both sides of the equation. It is easier to balance the hydrogen and oxygen atoms last.

Reactant	Product
1 Fe x 2	2 Fe
$2Fe + O_2 \rightarrow Fe_2O_3$	
2 O	3O x 2
$2Fe + O_2 \rightarrow 2Fe_2O_3$	

-now balance the product of Fe x 2, and O x 3

4. Indicate the state of matter of the reactants and products and check your work

$4Fe + 3O_2 \rightarrow 2Fe_2O_3$

Example 13:

Balance the equation below:

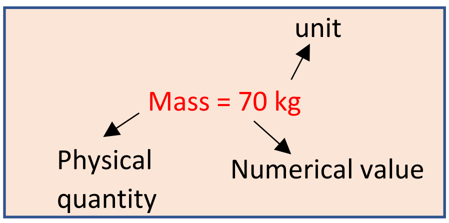
$C_7H_{16} + O_2 \rightarrow CO_2 + H_2O$

Answer:

Reactant	**Product**
7C 16H + 2O	1C 2O + 2H 1O
7C 16H + 2O	(1C 2O) 7 + 2H 1O
$C_7H_{16} + O_2 \rightarrow 7CO_2 + H_2O$	
7C 16H + 2O	7C 14O + (2H 1O)8
$C_7H_{16} + O_2 \rightarrow 7CO_2 + 8H_2O$	
7C 16H + (2O)11	7C 14O + 16H 8O
$C_7H_{16} + 11O_2 \rightarrow 7CO_2 + 8H_2O$	
Now all atoms are balanced for reactant and product.	

1.4 Units And Dimension In Physical Chemistry

- A physical quantity is the product of a numerical value and a unit.
- Physical quantitites is the product of a numerical value and a unit.



1.4.1 Standard international unit

- Standard International, SI is a standard that simplifies the international scientific communication.
- The following are basic SI unit in physical chemistry:

  - Length - meter (m)
  - Time - second (s)
  - Amount of substance - mole (mole)
  - Electric current - ampere (A)
  - Temperature - kelvin (K)
  - Luminous intensity - candela (cd)
  - Mass - kilogram (kg)
  -

1.4.2 Simple conversion of SI unit

Example 14:

Convert 2.5km to SI unit meter.

Answer:

2.5 km x 1000 **= 2500 m**

Example 15:

Convert the volume of 0.5L to SI unit mililitre.

Answer:

0.5 L x 1000 = **500 ml**

1.4.3 Derivation of simple SI unit.

Prefix	Abbreviation	Meaning	Example
Giga	G	10^9	1 gigameter(Gm) = 1 x 10^9 meter
Mega	M	10^6	1 Megameter (Mm) = 1 x 10^6 meter
Kilo	K	10^3	1 Kilometer (Km) = 1 x 10^3 meter
Deci	d	10^{-1}	1 decimeter (dm) = 1 x 10^{-1} meter
Centi	c	10^{-2}	1 centimeter (cm) = 1 x 10^{-2} meter
Milli	m	10^{-3}	1 millimeter (mm) = 1 x 10^{-3} meter
Micro	µ	10^{-6}	1 micrometer (µm) = 1 x 10^{-6} meter
Nano	n	10^{-9}	1 nanometer (nm) = 1 x 10^{-9} meter
Pico	p	10^{-12}	1 picometer (pm) = 1 x 10^{-12} meter

Table 1.3: The prefixes used to designate SI unit

Example 14:

Complete these basic SI system conversions.

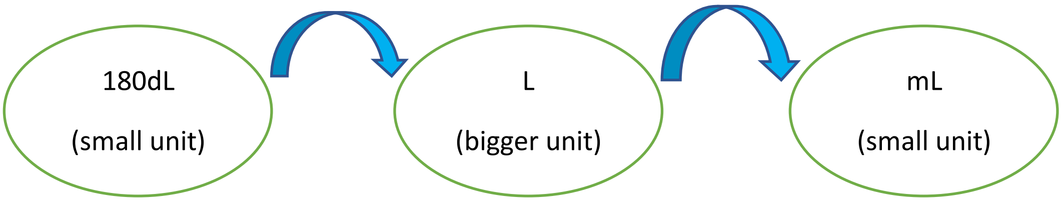
a) 180 dL to mL

b) 0.356 g to nanogram

Answer:

a) 180 dL to L

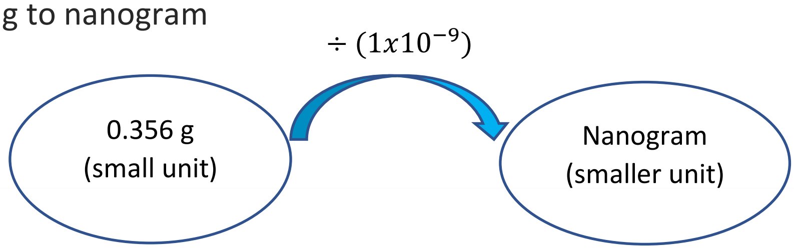
$\times\ (1\ x 10^{-1})$ $\qquad$ $\div\ (1x\ 10^{-3})$



$$= \frac{180\ x\ (1\ x\ 10^{-1})}{(1\ x\ 10^{-3})}$$

$$= \mathbf{18000\ mL}$$

b) 0.356 g to nanogram



$= 0.356\ (1 \times 10^{-9})$

$\boldsymbol{= 3.56\ x\ 10^{-8}\ nanogram}$

Tutorial

1. Write **THREE(3)** states of matter.

2. Calculate the molar mass of:
   i. Hydrochloric acid (HCl)
   ii. Methane (CH_4)
   iii. Sulphur dioxide (SO_2) gas

3. What is the mass of 1.5L (or dm^3) sulphur dioxide gas (measured at s.t.p)?

4. Find the mass of :
   i. 6 moles of CO_2
   ii. 5.467 moles of Na_2SO_4.

5. How many moles are there in:
   i. 1.58g H_2O
   ii. 72 g N_2 gas

6. 10 g of compound A contains 8.23 g nitrogen (N) and the rest is hydrogen (H). Find the empirical formula of compound A.

Answer:

1. solid, liquid, gas

2. i. 36.46 g/mol ii. 16.05 g/mol iii. 64.07 g/mol

3. 0.067 mol

4. i. 264.06 g ii. 776.59 g

5. i. 0.088 mol ii. 2.57 mol

6. NH_3

2.0 Periodic Table

2.1 The Periodic Table and Atomic Structure

2.1.1 Modern atomic model and Bohr's atomic model

- The concept that atoms play a fundamental role in chemistry is formalized by the **modern atomic theory**, first stated by John Dalton, an English scientist, in 1808. It consists of three parts:
  i. All matter is composed of atoms.
  ii. Atoms of the same element are the same; atoms of different elements are different.
  iii. Atoms combine in whole-number ratios to form compounds.
- The modern atomic theory states that atoms of one element are the same, while atoms of different elements are different. What makes atoms of different elements different? The fundamental characteristics that all atoms of the same element shared is the *number of protons*. All atoms of hydrogen have one and only one proton in the nucleus; all atoms of iron have 26 protons in the nucleus. The number of protons is important to identity atom that it is called the atomic number of the element. Thus, hydrogen has an atomic number of 1, while iron has an atomic number of 26. Each element has its own characterised atomic number.
- Atoms of the same element can have different numbers of neutrons. Atoms of the same element (i.e., atoms with the same number of protons) with different numbers of neutrons are called isotopes. Most naturally occurring elements exist as isotopes. For example, most hydrogen atoms have a single proton in their nucleus. However, a small number (about one in a million) of hydrogen atoms have a proton and a neutron in their nuclei. This particular isotope of hydrogen is called deuterium. A very rare form of hydrogen has one proton and two neutrons in the nucleus; this isotope of hydrogen is called tritium. The sum of the number of protons and neutrons in the nucleus is called the mass number of the isotope.

- Niels Bohr is a physicist who proposed a new model to explain the structure of the atom and its behavior.

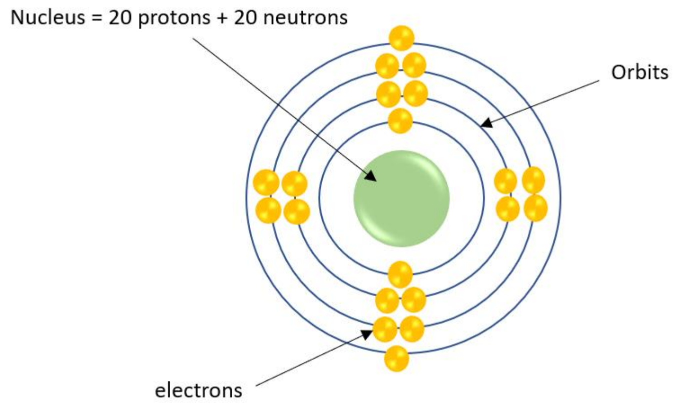


Figure 2.1: Bohr Atomic atom

- The Bohr atomic atom explained:
    i. The electrons in atoms are in the orbits of differing energy around the nucleus (think of planets orbiting around the sun).

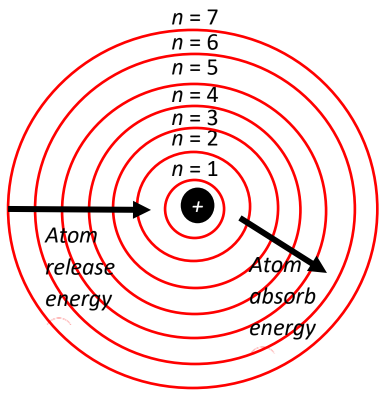


Figure 2.2: Energy condition based on levels or shells of atom.

ii. The term *energy levels* (or *shells*) describe these orbits of differing energy. The energy of an electron is *quantized*, meaning electrons can have one energy level or another but nothing in between.

iii. The energy level an electron normally occupies is called its *ground state* but it can move to a higher-energy and lless-stable level, or shell, by absorbing energy. This higher-energy, less-stable state is called the electron's *excited state*.

iv. After it is done being in the excited state, the electron can return to its original ground state by releasing the energy it has absorbed.

2.1.2 Isotope

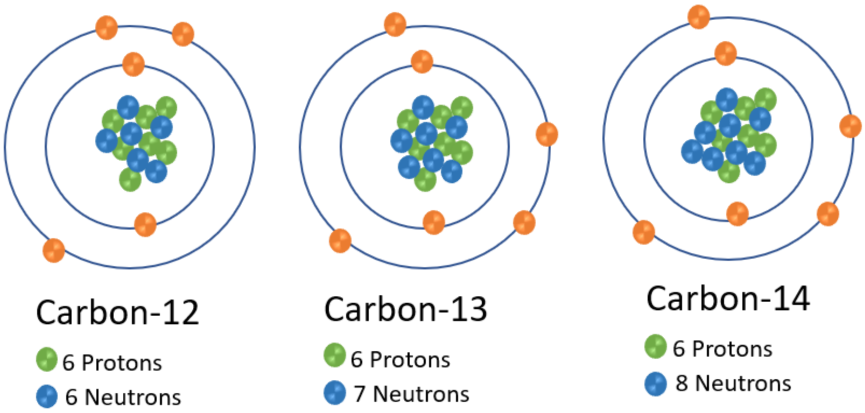
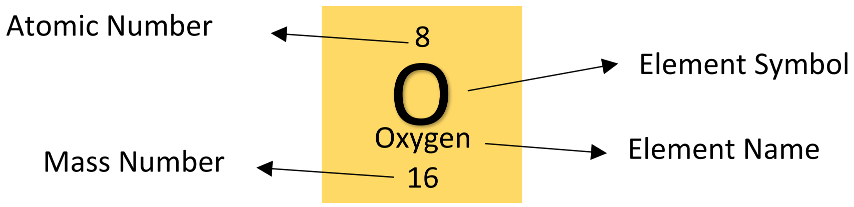


Figure 2.3: Isotopes of Carbon, C

- **Isotope** is one, two or more species of atoms of a chemical element with the same atomic number and position in the periodic table and nearly identical chemical behaviour but with different atomic masses and physical properties. Every chemical element has one or more isotopes such in Figure 2.3.
- Uses of isotopes in the industry:
  i. Radioisotopes are used by manufacturers as tracers to monitor fluid flow and filtration, to detect leaks, and to gauge engine wear as well as corrosion of process equipment.
  ii. Radioactive materials are used to inspect metal parts and the integrity of welds across a range of industries. Industrial gamma radiography exploits the ability of various types of radiation to penetrate materials to different extents.
  iii. Gauges containing radioactive (usually gamma) sources are in wide used in all industries where levels of gases, liquids, and solids must be inspected.
  iv. Analyzing the relative abundance of particular naturally occurring radioisotopes is of vital importance in determining the age of rocks and other materials that are of immense interest to geologists, anthropologists, hydrologists, and archaeologists, among others.

2.1.3 Proton number and mass number



- Proton number
  i. The **proton number** represents the number of protons found in the nucleus of an atom.
  ii. The proton number is equal to the number of protons.
  iii. The proton number is also known as the atomic number.
  iv. In an atom of neutral charge, the number of electrons also equals to the atomic number.
  v. Hence, the proton number of an atom can also represent the number of electrons.
- Mass number
  i. An element's mass number is the sum of the number of protons and the number of neutrons.
  ii. Isotopes of the same element will have the same atomic number but different mass numbers.

2.2 Electron Configuration Related To The Periodic Table

2.2.1 Electron configuration

- The electron configuration of an element describes the way electrons are distributed in its atomic orbitals.
- Electron configurations of atoms follow a standard notation in which all electron-containing atomic subshells are placed in a sequence.

- Two basics methods of writing a configuration electron are orbital diagram and *spdf* notation:

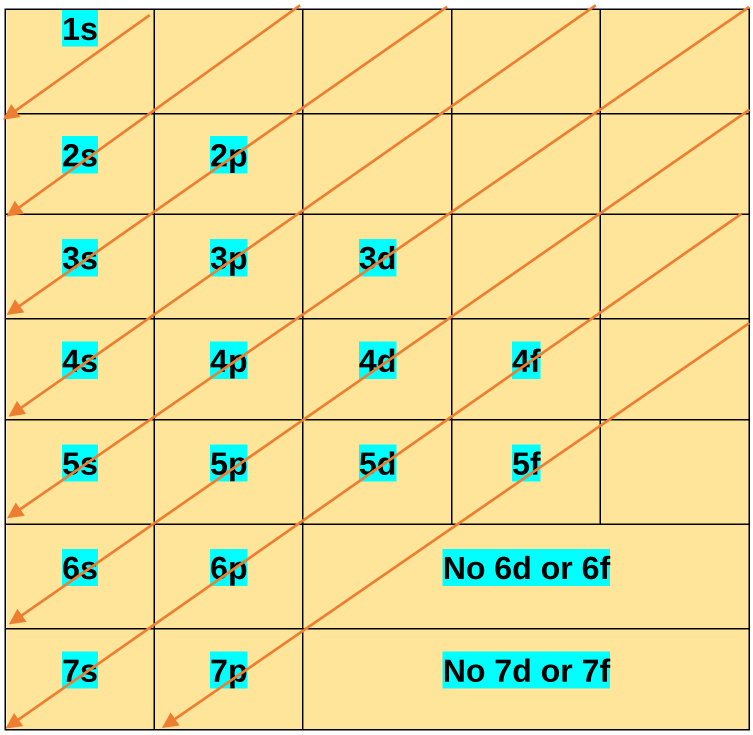


Table 2.1: Orbital order for s = 2 electrons, p = 6 electrons, d = 10 electrons and f = 14 electrons. The Fully written order is 1s2s2p3s3p4s3d4p5s4d5p6s4f5d6p7s5f7p

i. Orbital diagram

The orbital diagram is a type of diagram which shows the distribution of electrons in the orbitals of an atom and it indicates the spin of those electrons. It is a type of notation which shows both filled orbitals and partially filled orbitals.

ii. spdf notation

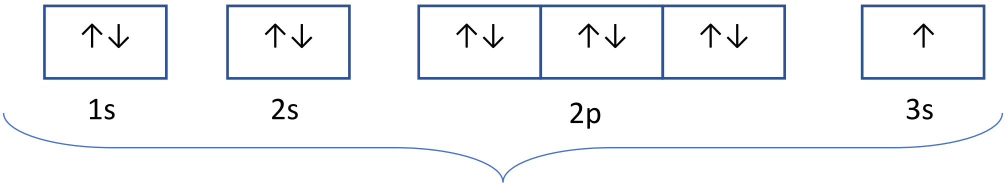
It is an electron configuration, for which there is an obsolete system of categorizing spectral lines as "**s**harp", "**p**rincipal", "**d**iffuse" and "**f**undamental".

Example 1:

Write the electron configuration for Sodium, Na that contains 11 electron.

Answer:

Using table 1,



Orbital diagram

$1s^2 2s^2 2p^6 3s^1$ - spdf notation

2.2.2 The position of the element in the Periodic Table

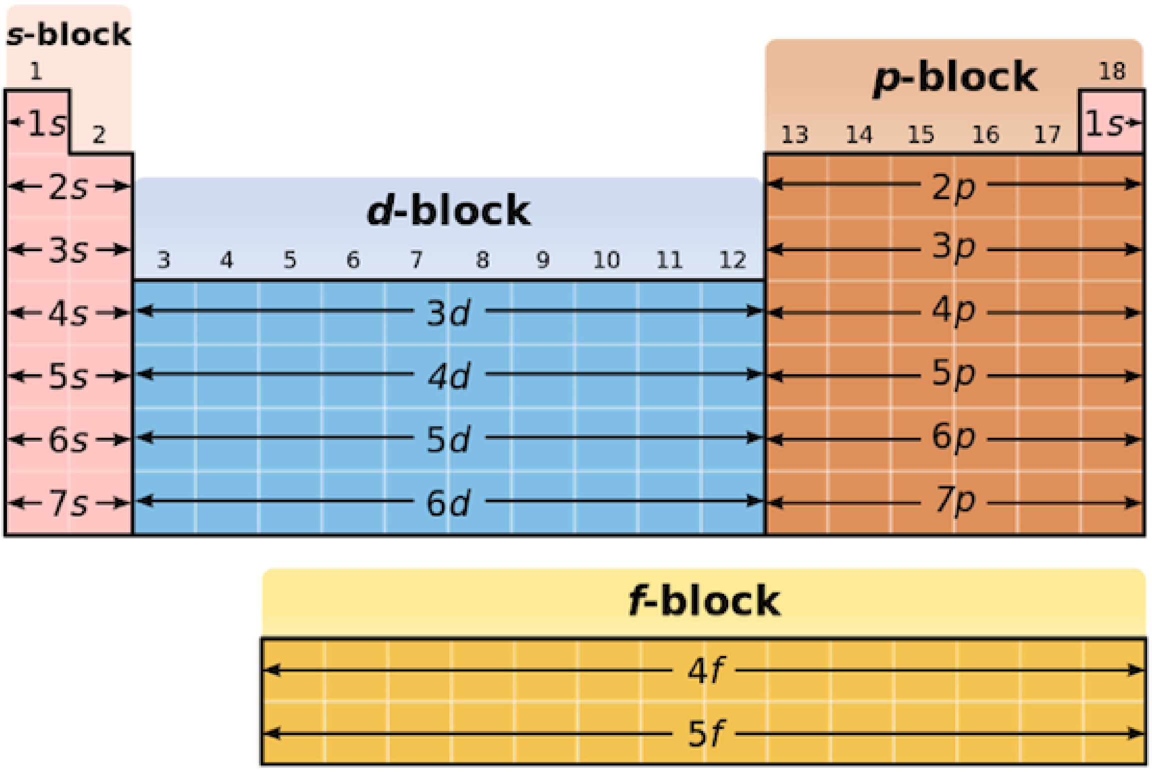


Figure 2.4: s,p,d and f in the Periodic Table

Photo credit, https://courses.lumenlearning.com

- Based on Figure 2.4, the energy level is determined by the period and the number of electrons is given by the atomic number of the element. Orbitals that are on different energy levels are similar to each other, but they occupy different areas in space.

- Both 1s and 2s orbital both have the characteristics of an s orbital but, as they are found on different energy levels, they occupy different spaces around the nucleus.
- Each orbital can be represented by specific blocks on the Periodic Table. The s-block is the region of the alkali metals including helium (Groups 1 & 2), the d-block are the transition metals (Groups 3 to 12), the p-block are the main group elements from Groups 13 to 18, and the f-block are the lanthanides and actinides series.

2.3 Groups and Periods in the Periodic Table

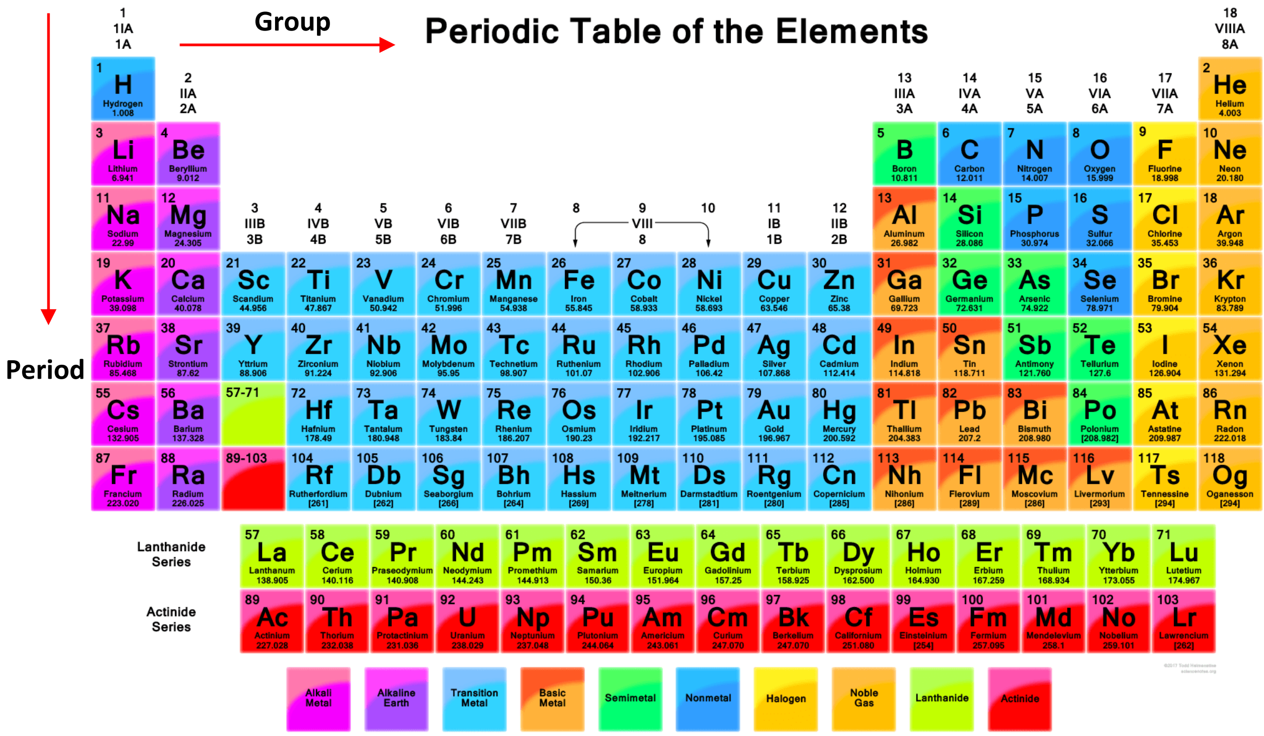


Figure 2.5: Periodic Table
Photo credit, https://sciencenotes.org

- The Periodic Table has undergone extensive changes throughout the time since it was first developed by Mendeleev and Moseley.
- Each square shows the chemical symbol of the element along with its name.
- Most of these elements are known since ancient times and have symbols based on their Latin names.
- The atomic number of each element is written above the symbol.
- **Group:** Elements with similar chemical properties appear at regular intervals, within the vertical columns.

- **Period:** A period is a horizontal row of the periodic table.

2.3.1 Physical and chemical properties for group I and group VII

- Based on Figure 2.5, the physical and chemical properties group I and group VII given on table 1 below:

Criteria	Group I (1)	Group VII (7)
Type of elements	Alkali metals	Non metal (halogens)
Atomic size	Atomic size increases gradually down the group.	Atomic size increases gradually down the group.
Density	Alkali metals have low densities, the densities increase gradually down the group.	Halogens have low densities, the densities increase gradually down the group.
Melting point	The melting point decreases gradually down the group.	The boiling point increases down the group.
Boiling point	The boiling point decreases gradually down the group.	The boiling points increases down the group.
Reactivity	Very reactive. The reactivity increases when going down the group.	The reactivity decreases when going down the group

Table 2.2: Physical and chemical properties of group I and group VII

2.3.2 Physical properties of group VIII elements

- Elements in group 8 in Figure 5 are known as noble gas.

Criteria	Group VIII (8)
Atomic size	Atomic size increases when going down the group.
Density	All noble gases have low densities, the densities increase when going down the group.

Melting point	All noble gases have very low melting points. It increases gradually down the group.
Boiling point	All noble gases have very low boiling points. It increases gradually down the group.
Solubility	All noble gases are insoluble in water.
Conductivity and heat conductivity	All noble gases cannot conduct electricity and poor conduction of heat.

Table 2.3: Physical properties of group VIII

2.3.3 Differences of physical properties group I and group VII to proton number

	Group I (1)	**Group VII (7)**
Outer Shell	*1 electron (+1)*	*7 electron(-1)*

- The number of electrons in a neutral atom is equal to the number of protons.
- The Group I elements have similar properties because of the electronic structure of their atoms - they all have one electron in their outer shell. Atoms of Group VII gain one negative electron (reduction) to be stable.
- An atom of a Group I elements will form an ion with a single positive charge in a reaction and group VII elements will form an ion with a single negative charge to achieve an octet rule.
- The attraction between the nucleus and outer electron gets weaker as go down the group I and group VII because the electrons in the outer shell move further away from the nucleus.

2.3.4 The changes in properties of elements across a period

- Elements are arranged in a series of rows (periods) in the order of atomic number so that those with similar properties appear in vertical columns.
- Elements in the same period have the same number of electron shells. They are moving across a period, elements gain electrons and protons and become less

metallic. This arrangement reflects the periodic recurrence of similar properties as the atomic number increases.

- For example, the alkali metals in Group 1 that share similar properties, such as high reactivity and the tendency to lose one electron to arrive at a noble-gas electron configuration.
- In the s-block and p-block of the periodic table, elements within the same period generally do not exhibit trends and similarities in properties but there is a vertical trend down the groups are more significant. However, in the d-block, trends across periods become significant, and the f-block elements show a high degree of similarity across periods.
- The physical properties of the melting and boiling point, the elements in a given group vary as they move down the table.

2.3.5 Uses of semi metal in the microelectronic industry

- Semimetal or metalloids are oftenly used in the chemical, electronics, and alloying industries.
- Some of the uses of semimetal in the microelectronic industry are:
  i. Germanium and silicon were critical in the development of the first transistors in the late 1940s and to this day, they are considered as an integral part of semiconductors and solid-state electronics.
  ii. Antimony is widely used in alloys such as pewter, while chemical forms of antimony are used as a flame retardant ingredient in plastics and other materials.
  iii. Tellurium is used as an alloying agent to improve the machinability of certain steels, as well as in electro-thermal and photovoltaic applications due to its unique thermal conductivity properties.
  iv. Boron is used as a dopant in semiconductors, as a bonding agent in permanent rare earth magnets, as well as in abrasive and chemical substances. Used as a dopant in some semiconductors, arsenic is more often found in metal alloys with copper and lead where it acts as a strengthening agent.

Tutorial

Figure 1: Part of the Periodic Table

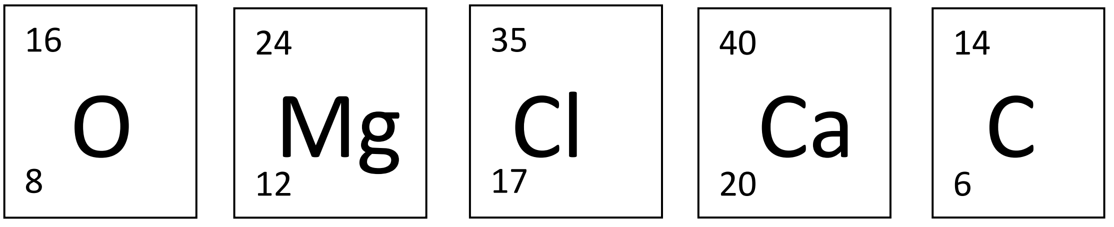
1.

Figure 1 shows part of the Periodic Table and elements, which are represented by symbols A, B, C and D.

a. Write the electron configuration of atom D.

b. State **TWO (2)** physical properties of element B.

2.



Based on the above elements, answer the following questions:

a. State two elements which have similar chemical properties.

b. Write the electron configuration for the ion formed from Ca.

c. What is the number of valency electrons found in atom C?

d. Write the electron configuration for atom O.

Answer:

1.

a) $1s^2 2s^2 2p^6 3s^2 3p^5$, 2.8.7

b) low melting and boiling points, insoluble in water, cannot conduct electricity and poor conduction of heat

2.

a) Mg, Ca

b) $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$, 2.8.8.2

c) 4

d) $1s^2 2s^2 2p^4$, 2.2.4

3.0 Chemical Bond

3.1 Types of Chemical Bonds

- A chemical bond can be defined as a force of attraction that holds groups of two or more atom together and makes them function as a unit (chemical compound).
- For example, the water molecule which consists of hydrogen and oxygen atom is being held together by covalent bond and hydrogen bond.

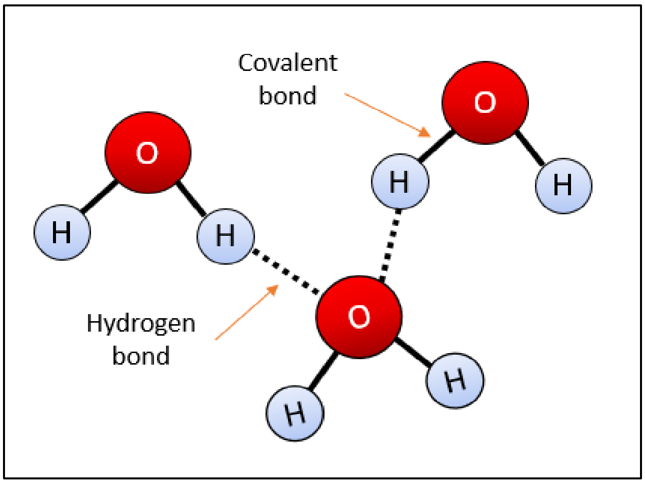


Figure 3.1 Water molecule

- The kind of **chemical bonding** involved in its formation from its elements determines the physical and chemical properties of a **compound**.
- There are three types of chemical bonding;
  - Ionic bond
  - Covalent bond
  - Metallic bond
- In the formation of the ionic and covalent bond, atoms try to achieve the **octet rule.**

The octet rule states that atoms of the elements form bonds to obtain **8 valence electrons**.

3.2 Formation of Ionic Bond

Definition

Ionic bond : The electrostatic force of attraction between positive ion and negative ion that holds them together to create an ionic compound.

- The Ionic bond is also called as an electrovalent bond.
- The attraction usually forms by the **transfer** of valence electrons between **a metal and a non-metal**.
- For example, the attraction between a sodium atom and a chlorine atom to produce sodium chloride.

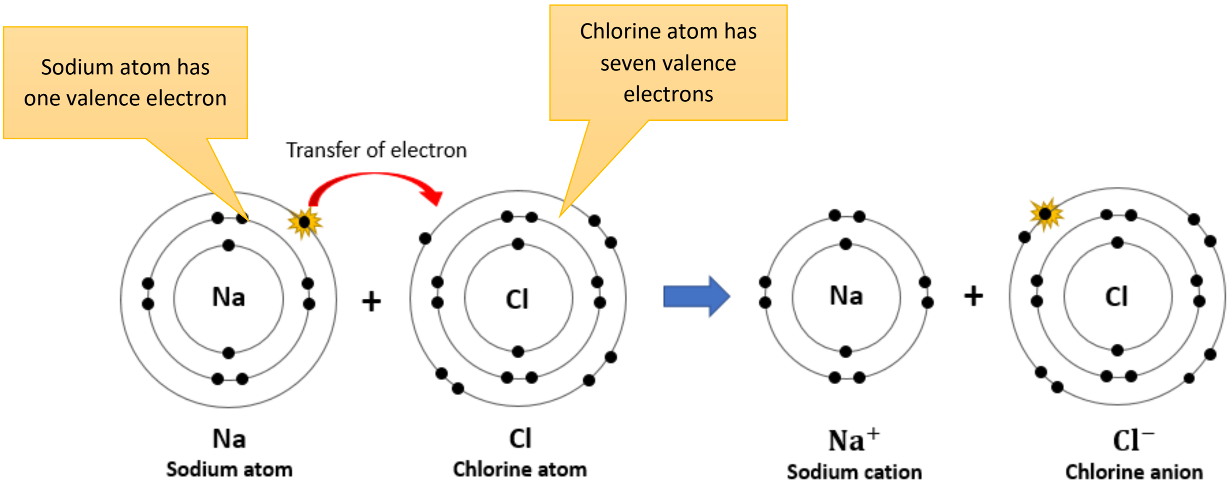


Figure 3.2 Formation of ionic compound

- Atom that loses valence electron becomes a cation (positive charge).
- Atom that gains electrons becomes an anion (negative charge).
- As a result of the oppositely charged cation and anion, the two ions are held together by **a strong electrostatic force called ionic bond**.
- The **dissociation equation** of the ionic compound of NaCl is as follows:-

$$\mathrm{NaCl\ (s)} \rightarrow \mathrm{Na^{+}\ (aq)} + \mathrm{Cl^{-}\ (aq)}$$

- Other examples of the ionic compound,
    a) Magnesium oxide, MgO

Dissociation equation : $MgO (s) \rightarrow Mg^{2+} (s) + O^{2-} (g)$

    b) Lithium flouride, LiF

Dissociation equation : $LiF (s) \rightarrow Li^{+} (s) + F^{-} (g)$

3.2.1 General Properties of Ionic Compound

- In the formation of ionic compounds atoms are bonded to one another by ionic bonds.
- The strong attraction between the positive and negative ions (produced by the transfer of electron) result in a crystal lattice structure (Figure 3.2.1).

(i) **(ii)**

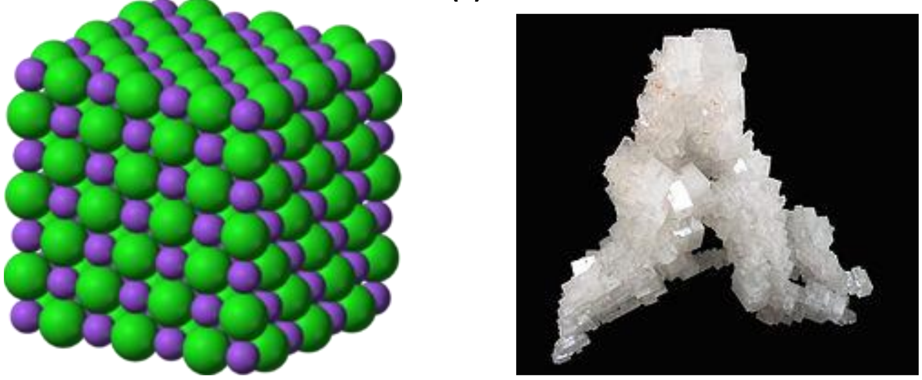


Figure 3.2.1 (a) Crystal Lattice Structure. (i) The crystal structure of sodium chloride, NaCl. The purple spheres represent sodium cations, Na^+, and the green spheres represent chloride anions, Cl^-. (ii) Halite, the mineral form of sodium chloride, forms when salty water evaporates leaving the ions behind.

Sources: https://en.wikipedia.org/wiki/Ionic_compound

- The strength of ionic bond depends on the ;-
    - Ionic charge (higher charge stronger bond)
    - Ionic radius (smaller radiius stronger bond)

Stronger bond

↓

Higher melting point

- The regular and orderly arrangement of ions in the crystal lattice results in the various shapes of the crystals, while transition metal ions give colors to the crystal (Figure 3.2.1).

Figure 3.2.1 (b) (i) Aragonite Crystal is the mineral form of calcium carbonate, $CaCO_3$.
(ii) Fluorite crystal is the mineral form of calcium fluoride, CaF_2.
Sources : https://en.wikipedia.org/wiki

- For some ionic bond, the electronegativity difference between the cation and anion makes the bond polar. Therefore, some compounds are polar. Polar compound dissolve in water (polar solvent). This make the ionic compounds good electrical conductor (in aqueous form).

- Generally, **solid form** of ionic compound is:-
  - Hard and brittle crystal
  - High melting points
  - Good insulators
  - Tend to be soluble in water

- Commonly**, aqueous form** of ionic compound is : -
  - High boiling point
  - Good electrical conductor (because it dissolved in water)

- Examples of ionic compound for everyday use :-

Sodium Chloride, NaCl

(salt)

Sodium Bicarbonate, $NaHCO_3$

(baking soda)

Sodium Hypochlorite, NaOCl

(bleach)

Sodium Hydroxide, NaOH

(drain cleaner)

Figure 3.3 Examples of ionic compound

3.3 Formation of Covalent bond

Definition

Covalent bond: A type of chemical bond that involves the sharing of electron pairs between atoms.

- Covalent bond is typically formed by the sharing of electron **between two non-metals atoms.**
- Atoms that are bonded through covalent bonds produce a molecule.
- In the formation of covalent molecules, each of the atom contributes one, two or three electrons to be shared, to achieve the **octet rule**.

The tendency of an atom toward a configuration in which it possesses **8 valence electrons**.

- Atoms can form three types of covalent bond;-
  - Single bond
  - Double bonds
  - Triple bonds

- <u>**Single bond**</u> forms when two atoms contribute one electron to each other for sharing.
  - ❖ For example, the sharing of electron by two chlorine atoms produces chlorine molecule (Figure 3.4).

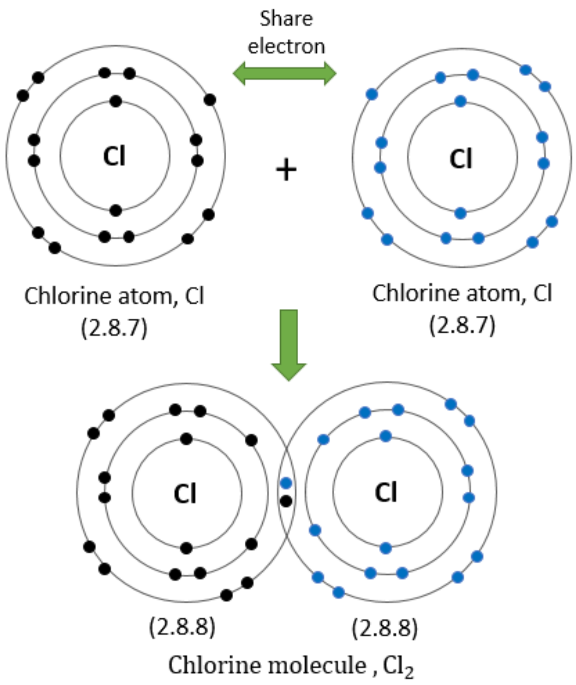


Figure 3.4 Formation chlorine molecule, Cl_2

  - ❖ **Lewis structure** of chlorine molecule formation is represented as below:-

- <u>**Double bond**</u> forms when two atoms contribute two electrons to each other for sharing. Atoms share two pairs of electrons and form the double bond.
  - ❖ For example, the sharing of two pairs of electrons by two oxygen atoms forms oxygen molecule, O_2 (Figure 3.5).

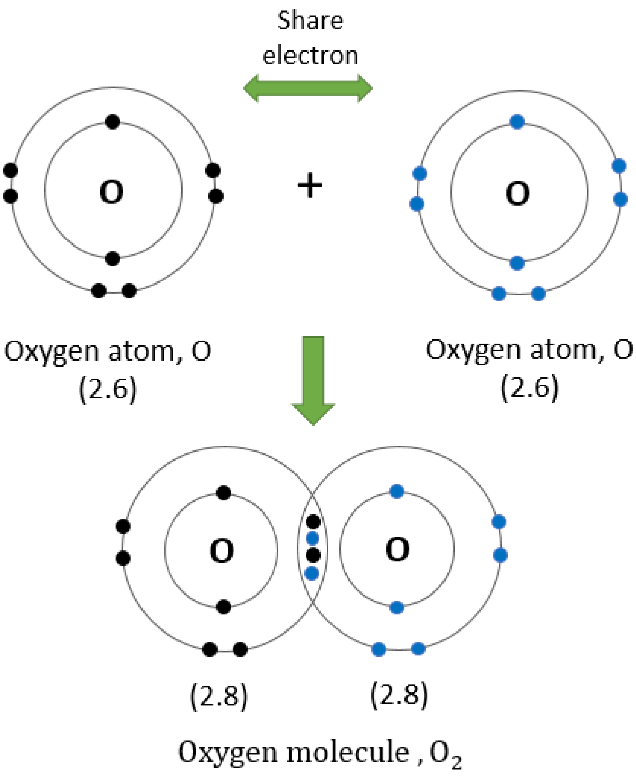
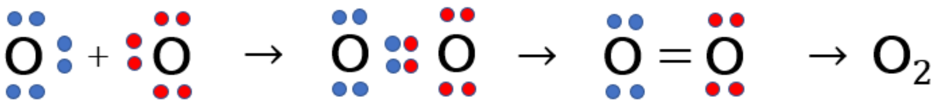


Figure 3.5 Formation of oxygen molecule, O_2

❖ **Lewis structure** of oxygen molecule formation is represented as below;-



- **Triple bond** forms when two atoms contribute three electrons to each other for sharing. Atoms share three pairs of electrons and form the triple bonds.
  ❖ For example, the sharing of three pairs of electrons by nitrogen atoms forms nitrogen molecule, N_2 (Figure 3.6).

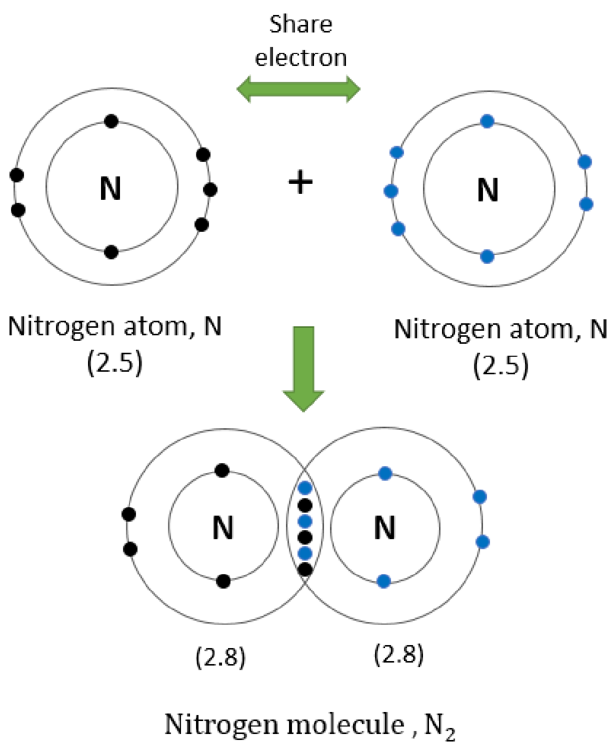


Figure 3.6 Formation of nitrogen molecule, N_2

❖ **Lewis structure** of nitrogen molecule formation can be represented as below:-

3.3.1 General properties of covalent compound

- Covalent compound forms when atoms are bonded with covalent bond.
- The covalent compounds can be in the form of gaseous, liquid or non-crystallize solid.
- It has a poor conductivity in all phases.
- It is soluble in the non-polar solvent and insoluble in the water.
- Bond energy decreases in this order ;
    - triple bond > double bond > single bond
- Bond length decreases in this order;
    - single bond >double bond > triple bond

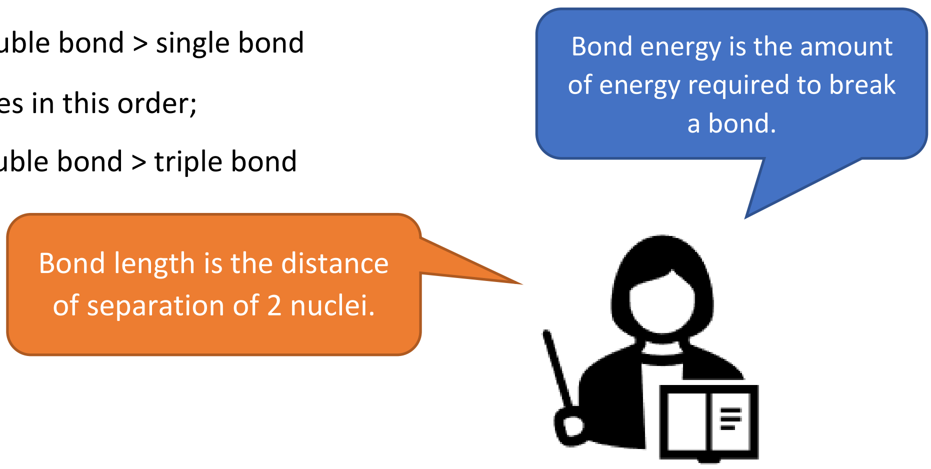
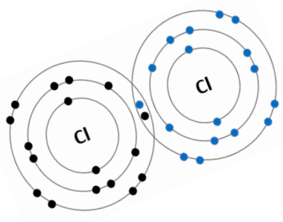
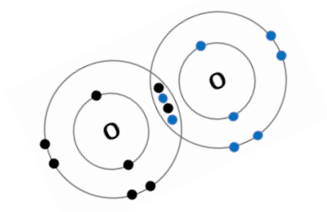
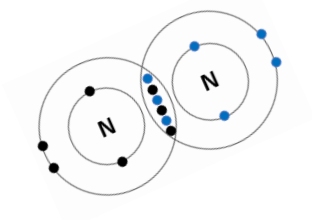


Table 3.1 Comparison of single, double and triple covalent bond

Single Bond	Double Bond	Triple Bond
		
Snares 1 pair valence electrons	Shares 2 pairs valence electrons	Shares 3 pairs valence electrons
Weak bond strength	Intermediate bond strength	Strong bond strength
Long bond length	Medium bond length	Short bond length

3.4 Comparison of Ionic Bond and Covalent Bond

Table 3.4 Comparison of ionic bond and covalent bond.

	Ionic Compound	Covalent Compound
At room temperature	Hard, brittle crystalline solid	Gaseous, liquid, non-crystalline solid
Melting and boiling point	High	Low
Conductivity	Good electrical conductor when in aqueous form	Poor electrical conductor
Solubility	Soluble in water. Insoluble in non-polar solvent	Soluble in non-polar solvent. Insoluble in water.

3.5 Metallic Bond

Definition

Metallic bond : The chemical bonding that results from the electrostatic attraction between a network of positive ions (metal ions) and the ‘sea’ of delocalised electrons.

- Metal atom gives up its **valence electrons** to form positive ions. These electrons no longer belong to any metal atom and they are delocalised. They move freely between atoms in the whole piece of metal.
- The electrons cloud in a metal pull the metal ions together so that they pack as closely as possible. Example of metallic compound structure is in Figure 3.7.
- The phenomenon of delocalised electrons explains the high electrical and thermal conductivity found in metals. As such metals conduct electricity in both the solid and liquid states.

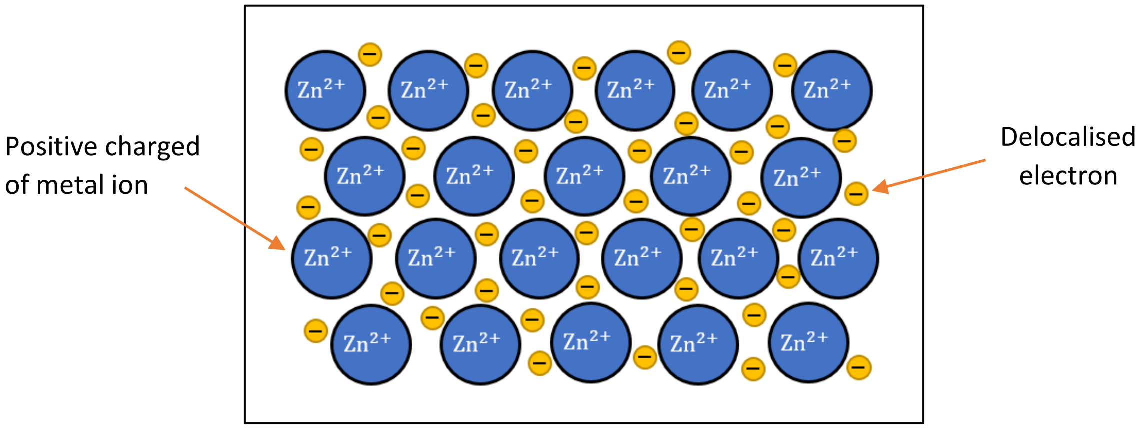


Figure 3.7 Metallic structure of Zinc (Zn)

3.6 Intermolecular Forces

Definition

Intermolecular forces are the interaction forces that act between neighbouring particles (atoms,molecules or ions).

- Intermolecular forces are the kind of intermolecular interactions that explain the way particles interact with other particles around them.
- The intermolecular interactions determine the properties of solids, liquids, and gases, as well as the behavior of particles in solution, chemical reactions, and the organization of biological structures.

- **Van der Waals forces** and **hydrogen bond** are types of intermolecular forces.

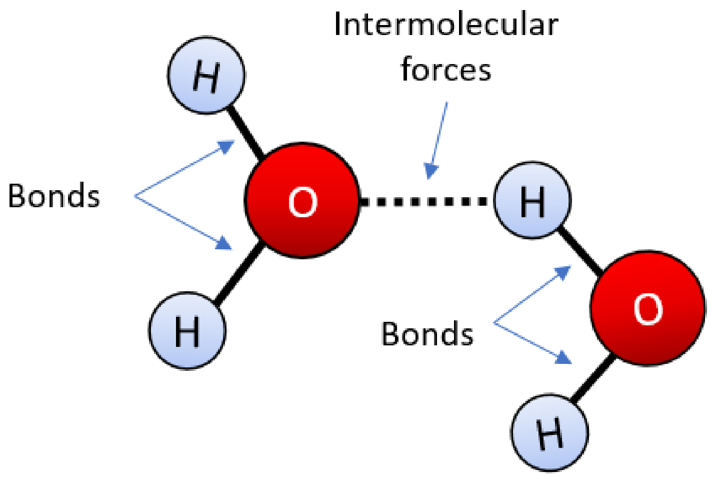


Figure 3.8 Intermolecular forces attraction exist between molecules. Intramolecular (bonding) forces exist between atoms in a molecule.

3.6.1 Van Der Waals Forces

- Van der Waals forces exist either **among non-polar molecules or atoms** (London dispersion forces) or **among polar molecules** (dipole-dipole interactions).

(a) London dispersion forces

- London dispersion forces is the interaction that occurs between **non-polar** molecules or atoms.
- It is the weakest intermolecular force.
- The London dispersion force is a temporary attraction force that results from the uneven electron distributions in molecules (make one side of the atom more negatively chargeg than the other) that later creates a **temporary dipole moment** even on a non-polar molecule.
- This attraction forces that cause non-polar substances to condense to liquids and to freeze into solids when the temperature is decreased sufficiently.

- London dispersion forces are often found in the halogens (Cl_2, F_2, Br_2 and I_2), the noble gases (He, Ne, Ar, Kr and Xe), and in other non-polar molecules, such as methane (CH_4) and carbon dioxide (CO_2).

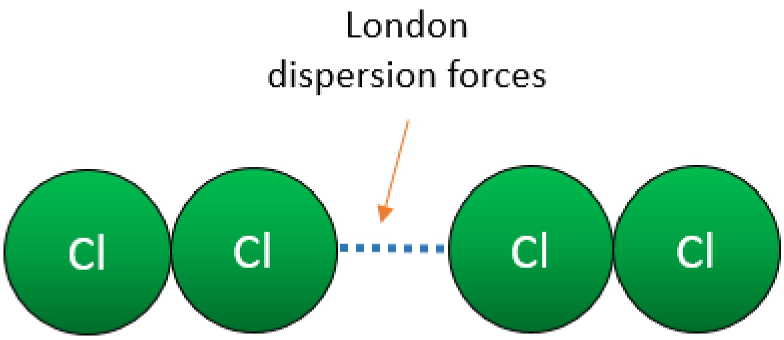


Figure 3.9 London dispersion forces between chlorine molecules (Cl_2).

(b) Dipole-dipole interaction

- Dipole-dipole interaction occurs between **polar** molecules (for example (H_2O and HCl).
- A polar molecule has a dipole moment from a polar bond as a result of an electronegativity differences between the bonded atoms. The larger the difference in electronegativity, the larger the dipole moment.
- Dipole-dipole interaction occurs when the partially negative charged atom in a molecule attracts to the partially positive charged atom of another molecule (Figure 3.10).

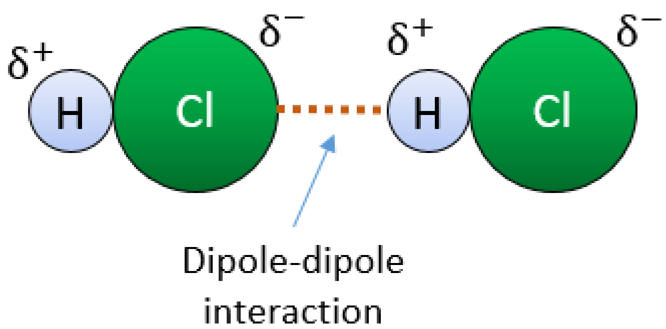


Figure 3.10 Dipole-dipole interaction between hydrogen chloride molecules. The relatively negative charged chlorine atom attracts to the relatively positive charged hydrogen atom of another molecule.

3.6.2 Hydrogen Bond

- A hydrogen bond (H-bond) is a primarily electrostatic force of attraction between a **hydrogen (H) atom** which is bonded to a strongly electronegative atom or group, and **another electronegative atom** with a lone pair of electrons.
- Hydrogen bonds are formed between two molecules, the same or different, that have the following characteristic; -
  - **I.** One molecule has a **hydrogen** atom bonded (covalent bond) to an atom of fluorine (F), oxygen (O) or nitrogen (N).
  - **II.** The other molecule has of fluorine (F), oxygen (O) or nitrogen (N) atom present with lone pairs electrons.

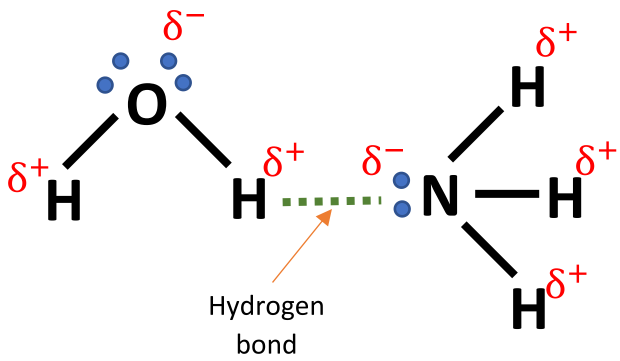


Figure 3.11 Hydrogen bonds between water (H_2O) molecule and ammonia (NH_3) molecule.

- The strength of H-bond is dependent on the electronegativity of F,O or N. The higher electronegativity (F>O>N), the stronger H-bond between molecules.

- The hydrogen bond effect :-
  - the density of liquid
  - the boiling point of liquid
  - the solubility of compound.

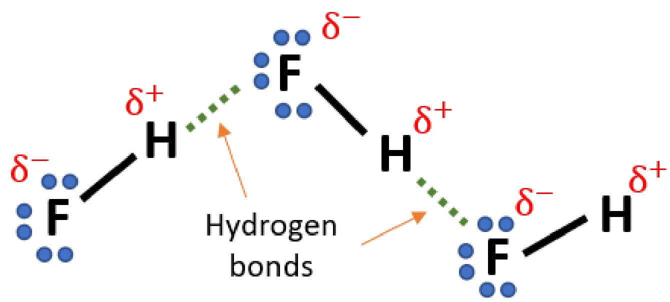


Figure 3.12 Hydrogen bonds between hydrogen flouride (HF) molecules.

Tutorial

1. State **THREE (3)** types of chemical bond.
2. Define the following terms: -
   a. Covalent bond
   b. Ionic bond
3. Write the dissociation equation of ionic compound for Lithium Sulfide , Li_2S.
   [Proton number; Li = 3, S = 16]
4. Draw Lewis structure for the formation of covalent bonding of **TWO (2)** Fluorine (F) atoms.
   [Proton number; F = 9]
5. Give **THREE (3)** differences of the physical properties of ionic compound and covalent compound.

Answer:

1. Covalent bond , ionic bond and metallic bond.

2. (i) **Covalent bond:** A type of chemical bond that involves the sharing of electron pairs between atoms.
   (ii) **Ionic bond** : The electrostatic force of attraction between positive ion and negative ion that holds them together to create an ionic compound.

3. Dissociation equation : **$Li_2S\ (aq) \rightarrow 2\ Li^+\ (aq) + S^{-2}\ (aq)$**

4.

5.

Ionic Compound	**Covalent Compound**
Hard, brittle crystalline solid	Gaseous, liquid, non-crystalline solid
High melting point	Low melting point
Good electrical conductor when in aqueous form	Not electrical conductor
Soluble in water but not in non-polar solvent	Soluble in non-polar solvent but not in water

4.0 Volumetric Analysis

4.0 Introduction

- Volumetric analysis is a general term for a method in quantitative chemical analysis in which the amount of a substance is determined by the measurement of the volume that the substance occupies.

  It is commonly used to determine the unknown concentration of a solution.

4.1 Solution Composition

- Solution is a mixture of a solute and a solvent. The solution concentration is a measure of the amount of solute dissolved in a given quantity of solvent.

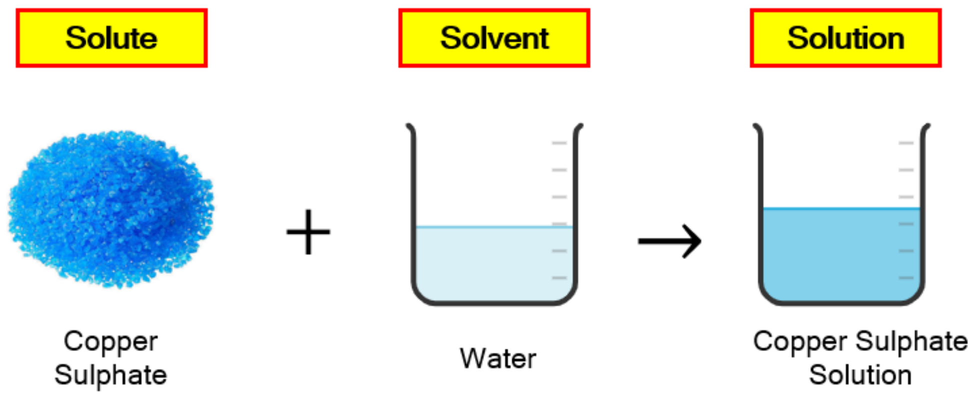


Figure 4.1 Solution formation

Definition

Solute : The substance which is dissolved.

Solvent : The substance in which the solute is dissolved in.

Solution : A homogeneous mixture of two or more substances which do not react with each other.

Aqueous solutions : A solution in which the solvent is water.

4.2 Concept of Molarity, Molality and Normality

- Concentration of solution can be expressed in chemical terms as molarity, molality and normality.

Definition

Molarity or molar concentration (M) is the number of moles of solute (mol) found in one litre (or dm^3) of solution**.**

$$\boldsymbol{Molarity\ (M) = \frac{number\ of\ moles\ of\ solute\ (mol)}{volume\ of\ solution\ in\ litre\ (L)}}$$

Molality (m) is the number of moles of solute in one kilogram(kg) of solvent.

$$\boldsymbol{Molality\ (m) = \frac{number\ of\ moles\ of\ solute\ (mol)}{mass\ of\ solvent\ in\ kilogram\ (kg)}}$$

Normality (N) is the number of equivalent weights of a solute in one litre of solution.

$$\boldsymbol{Normality\ (N) = \frac{number\ of\ equivalent\ weight}{volume\ of\ solution\ in\ litre\ (L)}}$$

@

$$\boldsymbol{= molarity\ (M) \times\ no.of\ mole(n)}$$

Tips

Mass of solute + Mass of solvent = Mass of solution.
Mass of solution = Volume of solution x Density of solution.

4.2.1 Molarity

- Molarity is one of the most common units used to measure the concentration of a solution. It is used to calculate the volume of solvent or the amount of solute. The SI unit for molar concentration is mol/m^3, but mol/L is a more common unit for molarity. 1 mol/L is called ‘one Molar’ or 1 M.

1 mol/L = 1 mol/dm^3 = 1 mol dm^{-3} = 1 M = 1000 mol/m^3

Example 1:

What is the molarity of the solution formed by dissolving 80 g of sodium hydroxide (NaOH) in 0.5 litre of water?

(RAM; Na = 23, O = 16 , H = 1)

$$no.of\ mole\ (n) = \frac{mass}{RMM}$$

$$Molarity\ (M) = \frac{number\ of\ moles\ of\ solute\ (mol)}{volume\ of\ solution\ in\ litre\ (L)}$$

$$No.of\ moles\ of\ NaOH = \frac{80}{(23+16+1)} = \frac{80\ g}{40\ gmol^{-1}} = 2\ mol$$

$$\therefore Molarity\ of\ NaOH\ solution = \frac{2\ mol}{0.5\ L} = 4\ molL^{-1}\ @\ \ 4\ M$$

Example 2:

Determine the molarity of a solution prepared by dissolving 45 g glucose ($C_6H_{12}O_6$) in 85 ml of solution.

(RAM ; C = 12, H = 1, O = 16)

1000 ml = 1 L
85 ml = 0.085 L

$$Molarity\ (M) = \frac{number\ of\ moles\ of\ solute\ (mol)}{volume\ of\ solution\ in\ litre\ (L)}$$

$$No.of\ moles\ of\ glucose\ \ = \frac{45}{((12\times 6)+(1\times 12)+(16\times 6))}$$

$$= \frac{45\ g}{180\ gmol^{-1}} \quad = 0.25\ mol$$

$$\therefore Molarity\ of\ glucose\ solution = \frac{0.25\ mol}{0.085\ L} = \ 2.94\ \ M$$

4.2.2 Molality

- Molality is calculated as the number of moles of a solute divided by the weight (kilograms) of the solvent. Molality depends only on the mass of the solvent. In some situations, using weight is an advantage because mass does not change with ambient conditions (temperature and pressure).

Example 3:

What is the molality of a solution containing 100 g of NaCl in 600 g of water?

(RAM; Na=23, Cl =35.45)

$$Molality\ (m) = \frac{number\ of\ moles\ of\ solute\ (mol)}{mass\ of\ solvent\ in\ kilogram\ (kg)}$$

1000 g = 1 kg
600 g = 0.6 kg

$$No. of\ moles\ of\ NaCl\ = \frac{100}{(23 + 35.45)} = 1.71\ mol$$

$$\therefore Molality\ of\ the\ solution = \frac{1.71\ mol}{0.6\ kg} = 2.85\ molkg^{-1}$$

Example 4:

Determine the molality of a 3.75 M H_2SO_4 solution with a density of 1.230 g/mL.

(RAM; H=1, S=32, O=16)

Mole of solute = 3.75 mol

i) Molarity H_2SO_4 = 3.75 M = 3.75 mol/L

Mass of solute

$$\therefore mass\ of\ H_2SO_4\ = 3.75\ mol\ \times [2(1) + (1)32 + 4(16)] = 367.5\ g$$

ii) Density of solution = 1.23 g/mL

Mass of 1L solution

$$\therefore mass\ of\ 1\ L\ solution\ = \frac{1.23g}{mL} \times 1000mL\ \ = 1230\ g$$

iii) Mass of solvent = mass of solution – mass of solute

$$\therefore mass\ of\ solvent = 1230\ g - 367.5\ g = 862.5\ g$$

1000 g =1 kg
862.5 g = 0.8625 kg

iv)

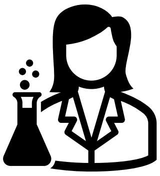
$$Molality\ (m) = \frac{number\ of\ moles\ of\ solute\ (mol)}{mass\ of\ solvent\ in\ kilogram\ (kg)}$$

$$= \frac{3.75\ mol}{0.8625\ kg}$$

$$= 4.35\ molal$$

4.2.3 Normality

- Normality is unit of concentration that mainly used when dealing with acid and base solutions. The use of normality focuses on the H^+ and OH^- available in an acid-base reaction.



- One equivalent of an **acid** is the amount of acid that can furnish 1 mole of $\mathbf{H^+}$ ions.
- One equivalent of a **base** is the amount of base that can furnish 1 mole of $\mathbf{OH^-}$ ions.
- The **equivalent weight** of an acid and a base is the mass in grams of one equivalent of that acid or base.

For the common strong acids of HCl (hydrochloric acid), the molecule produces one H^+ ions, so one mole of HCl can produce 1 mole of H^+ ions.

This means that,

$$\text{1 mol HC1} = \text{1 equivalent of HCl}$$
$$\text{Molar mass HCl} = \text{equivalent weight of HCl}$$

$$HCl \rightarrow H^+ + Cl^-$$

Likewise, for HNO_3 (nitric acid),

$$\text{1 mol HNO}_3 = \text{1 equivalent of HNO}_3$$
$$\text{Molar mass HNO}_3 = \text{equivalent weight of HNO}_3$$

$$HNO_3 \rightarrow H^+ + NO_3{}^-$$

However for H_2SO_4 (sulphuric acid), it furnishes two H^+ ions per molecule.

$$\text{1mol H}_2\text{SO}_4 \xrightarrow{\text{produce}} \text{2 mol H}^+$$
$$\frac{1}{2}\text{mol H}_2\text{SO}_4 \xrightarrow{produce} \text{1 mol H}^+$$
$$\frac{1}{2}\text{mol H}_2\text{SO}_4 = \text{1 equivalent of H}_2\text{SO}_4$$
$$\therefore \frac{1}{2}\text{molar mass H}_2\text{SO}_4 = \text{equivalent weight of H}_2\text{SO}_4$$

$$H_2SO_4 \rightarrow 2H^+ + SO_4{}^{-2}$$

Example 5:

A solution contains 86 g H_2SO_4 per 1 liter of solution. Calculate the normality of the solution.

(RAM; H = 1, S =32, O=16)

$$Normality\ (N) = \frac{number\ of\ equivalent\ weight}{volume\ of\ solution\ in\ litre\ (L)}$$

$$No. of\ equivalent\ weight\ of\ 86\ g = \frac{86}{\left(\frac{98}{2}\right)} = 1.8$$

$$\therefore Normality\ of\ the\ solution = \frac{1.8}{1\ L} = 1.8\ N$$

RMM H_2SO_4= 1 + 32 + (16x4) = 98

$$H_2SO_4 \rightarrow 2H^+ + SO_4^{-2}$$

$$1\text{mol } H_2SO_4 \xrightarrow{\text{produce}} 2\text{ mol } H^+$$

$$\therefore Equivalent\ weigth\ (H_2SO_4) = \frac{98}{2}$$

Example 6:

Calculate the normality of LiOH solution that contains 48 g LiOH in 1 L solution.

(RAM; Li = 7, O = 16, H = 1)

$$Normality\ (N) = \frac{number\ of\ equivalent\ weight}{volume\ of\ solution\ in\ litre\ (L)}$$

$$No. of\ equivalent\ weight\ of\ 48\ g = \frac{48}{24} = 2$$

$$\therefore Normality\ of\ the\ solution = \frac{2}{1\ L} = 2\ N$$

RMM LiOH = 7 + 16 +1 = 24

$$LiOH \rightarrow Li^+ + OH^-$$

$$1\text{mol LiOH} \xrightarrow{\text{produce}} 1\text{ mol } OH^-$$

$$\therefore Equivalent\ weight\ (LiOH) = \frac{24}{1}$$

4.3 Concentration in Unit % w/w, % w/v, %v/v and ppm.

4.3.1 Measurement of concentration by mass, % w/w

- Percentage by mass is usually measured for solids dissolved in liquids.

$$Percentage\ by\ mass, \%\frac{w}{w} = \frac{Mass\ of\ solute\ (g)}{Mass\ of\ solution\ (g)} \times 100\%$$

Tips

Mass of solute + Mass of solvent = Mass of solution.
Mass of solution = Volume of solution x Density of solution.

Example 7:

A solution with a mass of 355 g has 36.5 g of NaCl dissolved in it. What is the mass percent concentration of the solution?

$$Percentage\ by\ mass, \%\frac{w}{w} = \frac{mass\ of\ solute\ (g)}{mass\ of\ solution\ (g)} \times 100\%$$

$$= \frac{36.5\ g}{355\ g} \times 100\%$$

$$= 10.28\ \%$$

4.3.2 Measurement of concentration by volume, % v/v

- Percentage by volume is usually used to measure the mixing of two liquids to form a solution.

$$Percentage\ by\ volume, \%\frac{v}{v} = \frac{Volume\ of\ solute\ (mL)}{Volume\ of\ solution\ (mL)} \times 100\%$$

Example 8:

A 500 mL of solution contains of 50 mL of alcohol. Calculate the concentration of alcohol by volume in the solution.

$$Percentage\ by\ volume, \%\frac{v}{v} = \frac{Volume\ of\ solute\ (mL)}{Volume\ of\ solution\ (mL)} \times 100\%$$

$$= \frac{50\ mL}{500\ mL} \times 100\% \ = 10\ \%$$

4.3.3 Measurement of concentration by weight/volume, % w/v

- The concentration is measured by the percentage of quantity of solute (in weight unit) in a volume of solution (volume unit). Percent weight/volume is often used when a **dry solute** is weighed out and added to a **liquid solvent**.

$$Percentage\ \ weight/volume\ , \%\frac{w}{v} = \frac{Mass\ of\ solute\ (g)}{Volume\ of\ solution\ (mL)} \times 100\%$$

Example 9:

What is the % w/v of a solution that has 7.5 g of sodium chloride diluted to 100 mL deionized water?

$$\%\frac{w}{v} = \frac{Mass\ of\ solute\ (g)}{Volume\ of\ solution\ (mL)} \times 100\%$$

$$= \frac{7.5\ g}{100\ mL} \times 100\% = 7.5\ \%$$

4.3.4 Measurement of concentration by part per million (ppm)

- Part per million (ppm) is a way of expressing very dilute concentration of substances. It is the ratio of one part of solute per million parts of solution.
  - 1 ppm = 1 milligram of something per liter (mg/l) or
  - 1 ppm = 1 milligram of something per kilogram (mg/kg).

$$Part\ per\ million\ (ppm) = \frac{Mass\ of\ solute(g)}{Mass\ of\ solution\ (g)} \times 10^6$$

Example 10:

What is the number of ppm of sodium chloride (NaCl) in the solution with 117g of NaCl dissolved in 500 mL of water?

$$Part\ per\ million\ (ppm) = \frac{Mass\ of\ solute(g)}{Mass\ of\ solution\ (g)} \times 10^6$$

$$= \frac{117\ g}{(500\ g + 117\ g)} \times 10^6$$

$$= 19\ \times 10^4\ ppm$$

$$Water\ density = 1\ g/mL$$
$$\therefore 1\ mL = 1\ g$$
$$500\ mL = 500\ g$$

4.4 Dilution of Solution

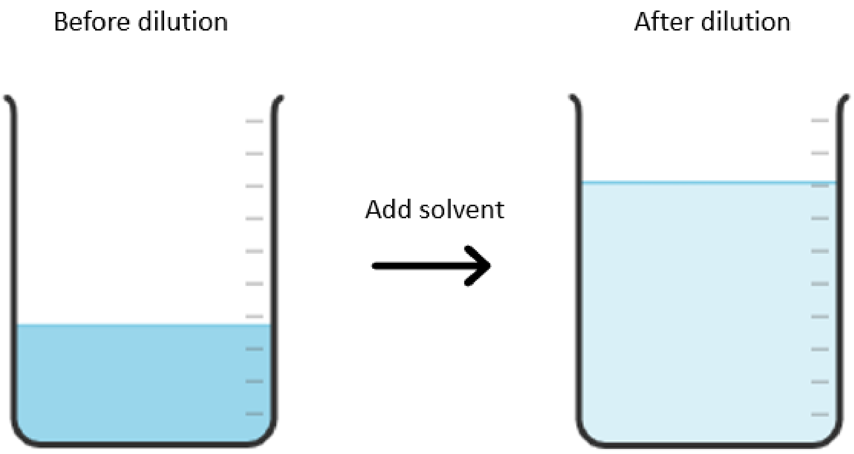
- Dilution is a process of adding more solvent to a solution. Dilution increases the volume of solution. As a result, the concentration of the solution decreases.

  In a dilution, the amount (moles or gram) of solute does not change.

$$Moles\ of\ solute\ before\ dilution, n_1 = Moles\ of\ solute\ after\ dilution, n_2$$

$$M_1V_1 = M_2V_2$$

$$n = Molarity \times Volume$$



Solution before and after dilution has the same quantity of solute

Figure 4.2 Solution before and after dilution

Example 11:

A concentrated sulfuric acid (H_2SO_4) has a molarity of 16 M. What is the amount of the concentrated H_2SO_4 must be used to prepare 1.5 L of 0.1 M H_2SO_4 solution?

$$M_1V_1 = M_2V_2$$

$$16\ (V_1) = 0.1\ (1.5)$$

$$V_1 = \frac{0.1\ (1.5)}{16}$$

$$V_1 = 9.4\ \times 10^3\ L$$

$$1\ L = 1000\ mL$$

$$9.4\ \times 10^3\ L = 9.4\ mL$$

$$\therefore V_1 = 9.4\ mL$$

To make 1.5 L of 0.1 M H_2SO_4, we must take 9.4 mL of the 16 M H_2SO_4 and dilute it with water to a final volume of 1.5 L.

4.5 Calculation of Molarity Using Stoichiometry of Solution Reactions

- A chemical reaction (solution reaction) represents by a chemical equation whereas the chemical present before reaction (reactant) is shown to the left of an arrow and the chemical formed by the reaction (product) is shown to the right of an arrow.
- For example, the reaction between hydrochloric acid (HCl) and sodium hydroxide (NaOH) is represented by this chemical equation: -

$$\underbrace{HCl\,(aq) \;+\; NaOH\,(aq)}_{\text{reactants}} \;\rightarrow\; \underbrace{H_2O\,(l) + \;NaCl\,(aq)}_{\text{products}}$$

This equation can be interpreted in terms of moles as follows: -

$\boxed{\text{1 mol of HCl reacts with 1 mol of NaOH to give 1 mol of } H_2O \text{ plus 1 mol NaCl}}$

- The chemical equation tells us the formula of the reactants and products.
- The number of coefficients in the balanced chemical equation shows the relative numbers of molecules of each product and reactant that participates in the reaction.
- Solution stoichiometry utilizes molarity as a conversion factor between volume and moles of the products and reactants in a solution reaction.
- Solution stoichiometry commonly applies in a neutralization reaction by **acid-base titration**.

Definition

Acid-base titration is a technique to determine the concentration of acid or base solution by neutralizing the unknown concentration of solution (acid/base).

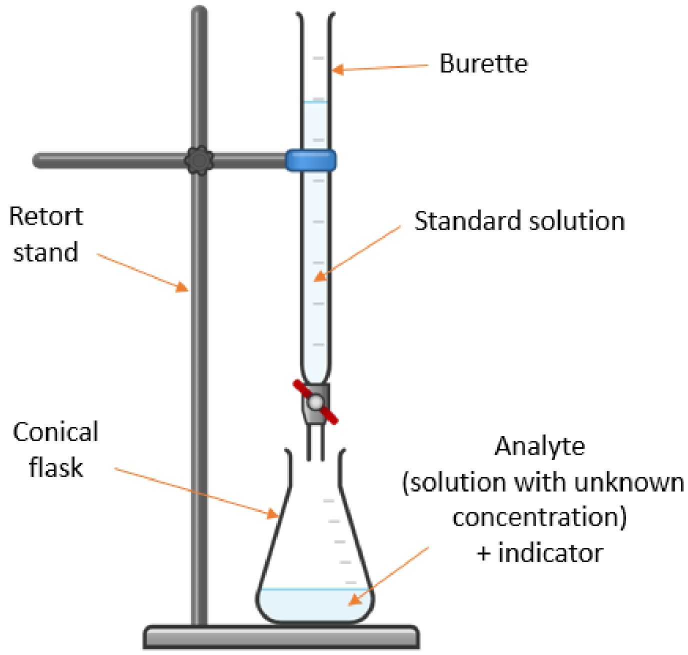


Figure 4.3 Titration apparatus set up

- Acid-base titration involves neutralization reactions between acid and base to form salt and water. Examine the neutralization reaction between acid A and base B as shown below:-

$$\boldsymbol{a\,Acid + b\,Base \rightarrow salt + water}$$

Stoichiometry coefficients

The quantitative relationship between acid A and base B is:-

$$\boxed{\frac{M_a V_a}{M_b V_b} = \frac{a}{b}}$$

M_a = Molarity of acid, V_a = Volume of acid,

M_b = Molarity of base, V_b = Volume of base

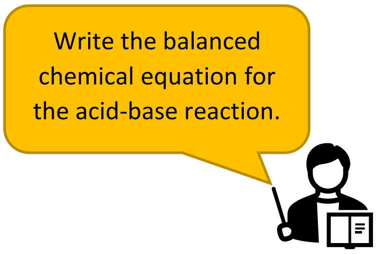
a/b = Stoichiometry ratio

By using that relationship, the acid and base molarity can be determined.

Example 12:

In a titration, 16 cm^3 aqueous sodium hydroxide (NaOH) solution is required to neutralize 20 cm^3 sulphuric acid (H_2SO_4) with a concentration of 0.25 M. Calculate the molarity of the NaOH.

$$\underset{\text{Acid}}{H_2SO_4} + \underset{\text{Base}}{2\,NaOH} \rightarrow \underset{\text{Salt}}{Na_2SO_4} + \underset{\text{Water}}{2\,H_2O}$$



*Mole ratio of acid to base is 1:2

This can be expressed as :-

$$\frac{\boldsymbol{M_aV_a}}{\boldsymbol{M_bV_b}} = \frac{\boldsymbol{a}}{\boldsymbol{b}}$$

$$\frac{0.25\,M\,(20\,cm^3)}{M_B\,(16\,cm^3)} = \frac{1}{2}$$

$$\therefore M_B = 0.63\,M$$

Example 13:

A 50ml 0.2 M HCl solution (containing phenolphthalein) is titrated with 0.1 M NaOH solution to the end point which changes the solution from colourless to light pink. Determine the volume of NaOH solution that causes the HCl solution colour change.

$$\underset{\text{Acid}}{\mathrm{HCl\,(aq)}} + \underset{\text{Base}}{\mathrm{NaOH\,(aq)}} \rightarrow \underset{\text{Salt}}{\mathrm{NaCl\,(aq)}} + \underset{\text{Water}}{\mathrm{H_2O\,(l)}}$$

*Mole ratio acid to base is 1:1

$$\frac{\boldsymbol{M_aV_a}}{\boldsymbol{M_bV_b}} = \frac{\boldsymbol{a}}{\boldsymbol{b}}$$

$$\frac{0.2\,M\,(50\,ml)}{(0.1\,M)V_b} = \frac{1}{1}$$

$$V_b = \frac{0.2(50)}{0.1} = 100\,ml$$

Tutorial

1. Name **TWO (2)** compositions of solution.
2. Define the following terms: -
   a. Solution
   b. Molarity
3. A glucose solution with a mass of 2×10^2 g has 15.8 g of glucose dissolved in it. What is the mass/mass percent concentration of the solution?
4. A solution contains 75 g of sodium hydroxide, NaOH in 600 ml of distilled water. Calculate the molarity of the solution? [RAM; Na = 23, O = 16, H= 1]
5. Determine the concentration of the diluted hydrochloric acid (HCl) if 75 cm3 water is added to 25 cm3 of 2 M HCl solution.

Answer:

1. Solvent and Solute
2. (a) **Solution :** A homogeneous mixture of two or more substances which do not react with each other.
   (b) **Molarity** : The number of moles of solute (mol) found in one litre (or dm^3) of solution.
3. 7.9 %
4. 3.13 mol/L
5. 0.5

5.0 Acid and Base.

5.1 Theories related to acid and base.

- The first person to recognize the essential nature of acid and base is Svante Arrhenius. In his studies of solutions, he observed that when the substances HCl, HNO_3, H_2SO_4 are dissolved in the water, they behave as strong electrolytes. He suggested that this is the result of ionization reaction of water.

Example 1:

$$HCl \xrightarrow{Water} H^+ + Cl^-$$

$$HNO_3 \xrightarrow{Water} H^+ + NO_3^-$$

$$H_2SO_4 \xrightarrow{Water} H^+ + HSO_4^-$$

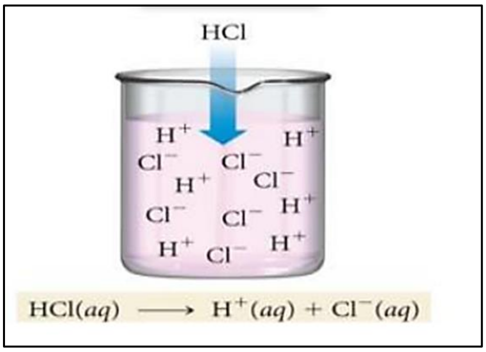


Figure 5.1 Dissociation of HCl in water.

5.1.1 Arrhenius Theory and Bronsted Lowry Theory of acid and base.

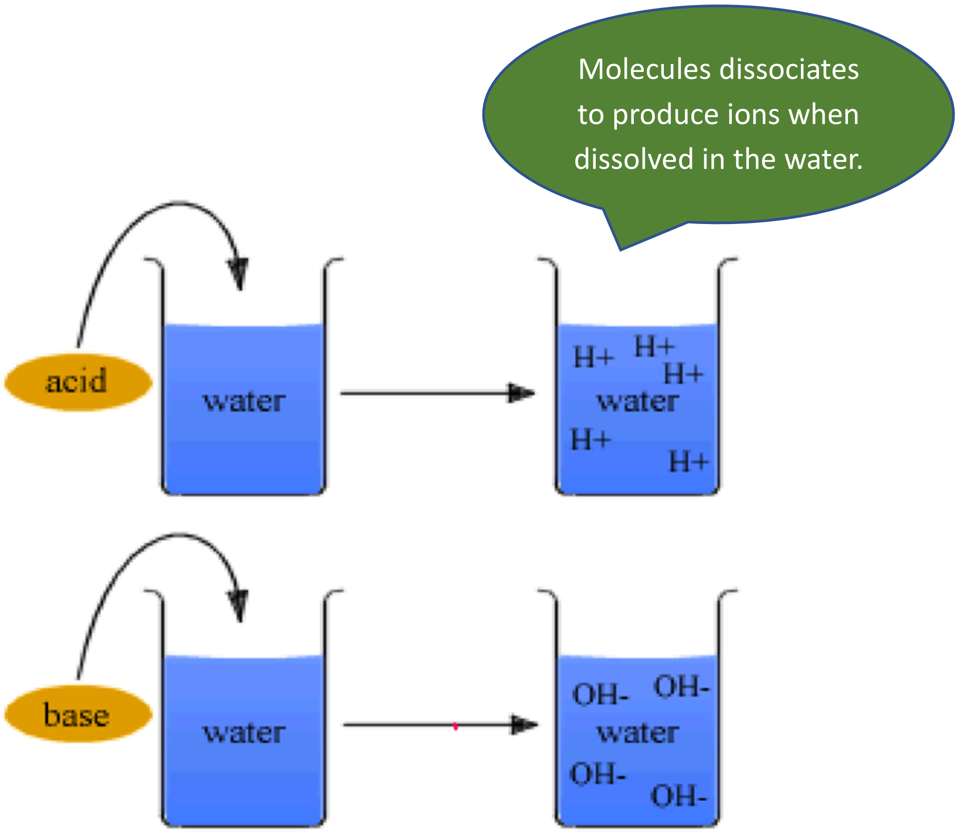
1. <u>Arrhenius Theory</u>

- **Acid** is a substance that produces hydrogen ion (H^+) when dissolved in water. The concentration of H^+ ions is high in the solution.

$HCl(aq) \rightarrow H^+ (aq) + Cl^- (aq)$
HCl ionizes in water, producing H^+ and Cl^- ions.

- **Base** is a substance that produce hydroxide ions (OH^-) when dissolved in the water. The concentration of OH^- is high in the solution.

$NaOH (aq) \rightarrow Na^+ (aq) + OH^- (aq)$
NaOH dissociates in the water, producing Na^+ and OH^- ions.



- However, some substances could not be classified using Arrhenius theory. They are bases but do not dissociate to produce OH^-. For example:

  Sodium ethanoate (C_2H_5ONa)

  Ammonia (NH_3)

2. Bronsted-Lowry Theory

- **Acid** is a proton donor (gives away hydrogen ion (H^+)).
- **Base** is a proton acceptor (gains hydrogen ion (H^+)).

Acids donate protons (H^+)

$HCl \rightarrow H^+ + Cl^-$

Bases accept protons (H^+)

$NH_3 + H^+ \rightarrow NH_4^+$

Water behaves as acid or base depending on the reactions (Amphoteric substances). Because water can be a donor or accept H^+

Example 2:

HCl	+	H_2O	$\rightleftharpoons$
	H_3O^+	+	Cl^-
Hydrogen Chloride	Hydronium	Water Chloride ion	

- HCl donates an H^+ to water and, therefore, acts as an acid. Water accepts an H^+ from HCl and, therefore, acts as a base.
- Note that the hydrogen ions (H^+) that are transferred to the water molecule will form hydronium ions (H_3O^+).
- HCl is a strong acids that is completely ionized in the aqueous solution.

Example 3:

NH_3	+	H_2O	$\rightleftharpoons$	NH_4^+	+	OH^-
Ammonia		Water		Ammonium ion		Hydroxide ion
Base (H⁺ acceptor)		**Acid (H⁺ donor)**		**Basic Solution**		

- Water donates an H^+ to NH_3 and, therefore, acts as an acid.
- NH_3 accepts an H^+ from water and, therefore, acts as a base.
- This is because, nitrogen atom has a stronger attraction for H^+ than oxygen.
- Ammonia is a weak base that is partially ionized in the aqueous solution.

5.1.2 Conjugate acid and conjugate base of acid and base.

- In any acid-base reaction there are two conjugate acid-base pairs

Acid and conjugate base pair

$$HA + B \rightleftharpoons A^- + BH^+$$

Base and conjugate acid pair

- A conjugate acid is a species that is formed by adding a proton to a base.

Base		Conjugate Acid
NH_3	$\longrightarrow$	NH_4^+
OH^-	$\longrightarrow$	HOH
H_2O	$\longrightarrow$	H_3O^+
CO_3^{2-}	$\longrightarrow$	HCO_3^-

Figure 5.3 Example of bases and their conjugate acids.

- A conjugate base is a species that is formed by removing a proton from an acid.

Acid		Conjugate Base
HCl	$\longrightarrow$	Cl^-
HBr	$\longrightarrow$	Br^-
HNO_3	$\longrightarrow$	NO_3^-
$HC_2H_3O_2$	$\longrightarrow$	$C_2H_3O_2^-$

Figure 5.4 Example of acids and their conjugate bases.

Example 4:

Acid-base
Conjugate pair

$$\underset{\text{acid}}{CH_3COOH(aq)} + \underset{\text{base}}{H_2O\ (aq)} \rightleftharpoons \underset{\text{Conjugate base}}{CH_3COO^-\ (aq)} + \underset{\text{Conjugate acid}}{H_3O^+\ (aq)}$$

Acid-base
Conjugate pair

Acetic acid gives a proton to the base "water".	**Water** acts as a base by accepting the proton from the acid.	**Acetate ion** Conjugate Base of the acid.	**Hydronium Ion** Conjugate Acid of the base.

Figure 5.5 Acid-base conjugate pair. Water acts as a base.

- Based on Figure 5.5, the hydrogen atom in acetic acid goes to the water molecule as a proton leaving the lone pair of electrons to the H_3O^+ anion. The proton forms a covalent bond with the lone pairs of electrons on the hydronium ion.

Example 5:

Acid-base
Conjugate pair

$$\underset{\text{acid}}{H_2O\ (aq)} + \underset{\text{base}}{NH_3\ (aq)} \rightleftharpoons \underset{\text{Conjugate base}}{OH^-\ (aq)} + \underset{\text{Conjugate acid}}{NH_4^+\ (aq)}$$

Acid-base
Conjugate pair

Water gives a proton to the base "water".	**Ammonia** acts as a base by accepting the proton from the acid.	**Hydroxide ion** Conjugate Base of the acid.	**Ammonium Ion** Conjugate Acid of the base.

Figure 5.6 Acid-base conjugate pair. Water acts as an acid.

- Based on Figure 5.6, the hydrogen atom in the water goes to ammonia molecule as a proton leaving the lone pair of electrons to the NH_4^+ anion. The proton forms a covalent bond with the lone pairs of electrons on the ammonium ion.

5.2 Concept of acid and base.

5.2.1 Strong acid and base, weak acid and base.

- The strength of an acid (or base) is determined by the degree of ionization (degree of dissociation) which is represented as α.

Strong Acid and Strong Base.

- **Strong acid** is acid that is completely ionized in the aqueous solution. The degree of dissociation, α equals to 1 ($\alpha = 1$), that is almost 100% dissociated. As a result, the concentration of **H^+ ions** are **high**. HNO_3, HCl, H_2SO_4 and $HClO_4$ are some of the known strong acids.

strong acid:

$$HCl + H_2O \longrightarrow H^+ + Cl^-$$

- Strong base is base that is completely ionized in the aqueous solution. The degree of dissociation, α equals to 1 (α=1), that is almost 100% dissociated. As a result, the concentration of OH^- ions is high. Examples of bases are NaOH, KOH, Ba $(OH)_2$.

strong base:

$$NaOH + H_2O \longrightarrow Na^+ + OH^-$$

Table 5.1 Example of the common strong acids & bases.

6 Strong Acids		6 Strong Bases	
$HClO_4$	perchloric acid	$LiOH$	lithium hydroxide
HCl	hydrochloric acid	$NaOH$	sodium hydroxide
HBr	hydrobromic acid	KOH	potassium hydroxide
HI	hydroiodic acid	$Ca(OH)_2$	calcium hydroxide
HNO_3	nitric acid	$Sr(OH)_2$	strontium hydroxide
H_2SO_4	sulfuric acid	$Ba(OH)_2$	barium hydroxide

Weak Acid and Weak Base.

- Weak acid is acid that is partially ionized in the aqueous solution. The degree of dissociation, α is less than 1 (α<1), that is less than 100% dissociated. As a result, the concentration of H^+ ions is low. Examples are CH_3COOH, HCOOH, HCN.

weak acid:

$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H^+$$

- Weak base is base that is partially ionized in the aqueous solution. The degree of dissociation, α is less than 1 (α<1), that is less than 100% dissociated. As a result, the concentration of OH^- ions is low. Examples are NH_3, CH_3NH_2.

weak base:

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

Table 5.2 Examples **of common weak acids & bases.**

Common Weak Acids	
Acid	**Formula**
Formic	$HCOOH$
Acetic	CH_3COOH
Trichloroacetic	CCl_3COOH
Hydrofluoric	HF
Hydrocyanic	HCN
Hydrogen sulfide	H_2S
Water	H_2O
Conjugate acids of weak bases	NH_4^+

Common Weak Bases	
Base	**Formula**
ammonia	NH_3
trimethyl ammonia	$N(CH_3)_3$
pyridine	C_5H_5N
ammonium hydroxide	NH_4OH
water	H_2O
HS^- ion	HS^-
conjugate bases of weak acids	e.g.: $HCOO^-$

5.2.2 The concept of pH and pOH.

- A pH scales represents the acidity and the basicity of a solution. The pH scale is a way of expressing the strength of acids and bases. Instead of using very small numbers, use the NEGATIVE power of 10 (-log) on the molarity of the H^+ (or OH^-) ion.

- pH is the negative log of hydrogen ion concentration in solution ;-

$$\boxed{\mathrm{pH} = -\log[\mathrm{H^+}]}$$

- pOH is the negative log of hyroxide ion concentration in solution;-

$$\boxed{\mathrm{pOH} = -\log\ [\mathrm{OH^-}]}$$

pH Scale		Example
Strong	1	Battery acid
	2	Lemon Juice
	3	Range Juice
Acid	4	Tomato Juice
	5	Black Coffee
Weak	6	Tea
Neutral	7	Distilled water
Weak	8	Egg whites
	9	Baking Soda
	10	Mild Detergent
Base	11	Ammonia
	12	Soapy water
	13	Bleach
Strong	14	Liquid drain cleaner

Figure 5.7 pH scale with reference to the pH of common substances

5.2.3 The pH and pOH value of strong acids and bases.

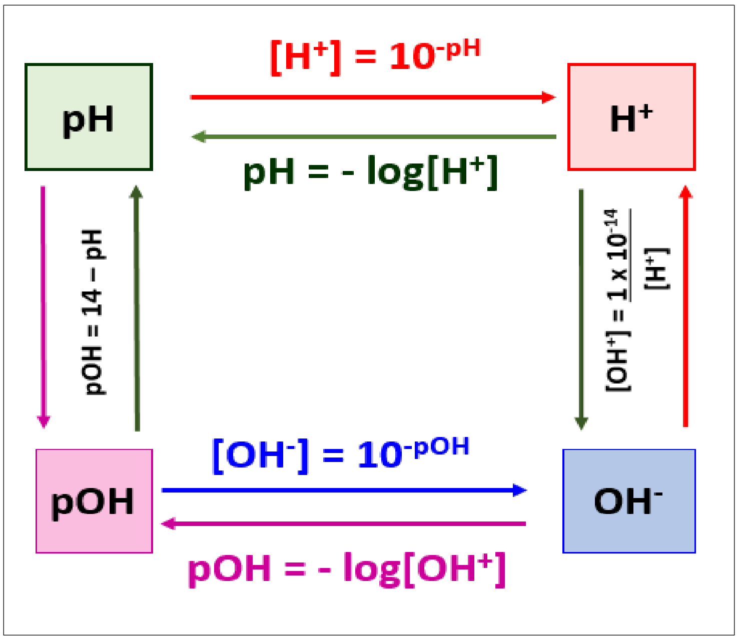


Figure 5.8 Formula for calculating $[H^+]$, $[OH^-]$, pH and pOH.

Example 6:

Calculating the pH/pOH from [OH^-] / [H^+] .

What is the pOH of a solution that has a hydroxide ion concentration of 4.82 x 10^{-5} M? (Note that pH + pOH = 14)

pOH = - log [OH-]

pOH = - log [4.82 x 10^{-5}]

pOH = 4.32

Example 7:

Calculating the [OH^-] / [H^+] from pH / pOH

A solution has a pH of 8.5. What is molarity of hydrogen ions in the solution?

pH = - log [H^+]

8.5 = - log [H^+]

- (8.5) = - (-log [H^+])

Antilog -8.5 = Antilog (log [H^+])

3.16 x 10^{-9} M = [H^+]

Example 8:

Calculating pH of Strong Acid Solutions

In the case of a solution of strong acid, although on the bottle stated 1.0 M HCl, the solution virtually contains no HCl molecules. The solution contains H^+ and Cl^- ions rather than HCl molecules.

$$1.0 \text{ M HCl} \rightarrow 1.0 \text{ M H}^+ + 1.0 \text{ M Cl}^-$$

Therefore, the [H^+] in the solution is 1.0 M and the pH is then,

pH = - log [H^+]

pH = - log 1.0

pH = 0

Example 9:

A strong base is one that dissociates completely in the water to form hydroxide ions:

lithium hydroxide, LiOH → $OH^-(aq)$ + $Li^+(aq)$

sodium hydroxide, NaOH → $OH^-(aq)$ + $Na^+(aq)$

potassium hydroxide, KOH → OH-(aq) + $K^+(aq)$

Find the pOH of 0.2 mol L^{-1} $KOH_{(aq)}$.

$[KOH_{(aq)}]$ = 0.2 mol L^{-1}

$[KOH_{(aq)}]$ = $[OH^-]$ = 0.2 mol L^{-1}

pOh = $-\log[OH^-]$

= -log 0.2

= 0.7

5.2.4 The strength of weak acid and weak base to the respective dissociation constant K_a and K_b.

- A reversible reaction is a chemical reaction that can proceed to the forward and reverse directions. At an equilibrium, the rate of the forward reaction equals to the rate of the reverse reaction. The quantitative measurement of the strength of weak acid/base can be determined from its equilibrium constant K_c/ K_b .
- For example, the general equation for the ionization of a weak acid in the water, in which HA is the parent acid and A− is its conjugate base, is as follows:

$$HA_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + A^-_{(aq)}$$

The equilibrium constant for this dissociation is as follows

$$K = \frac{[H_3O^+][A^-]}{[H_2O][HA]}$$

The acid ionization constant (K_a), is also called the acid dissociation constant:

$$K_a = K[H_2O] = \frac{[H_3O^+][A^-]}{[HA]}$$

- $[H_2O]$ is a constant.
- Weak acid has $K_a < 1$.
- Leads to small $[H_3O+]$ and a pH of 2 – 7.

Weak bases react with water to produce the hydroxide ion, as shown in the following general equation, in which B is the parent base and BH^+ is its conjugate acid:

$$B_{(aq)} + H_2O_{(l)} \rightleftharpoons BH^+_{(aq)} + OH^-_{(aq)}$$

The equilibrium constant for this reaction is the base ionization constant (K_b), also called as the base dissociation constant:

$$K_b = K[H_2O] = \frac{[BH^+][OH^-]}{[B]}$$

- $[H_2O]$ is a constant.
- Weak base has $K_b < 1$.
- Leads to small [OH-] and pH of 12 – 7.

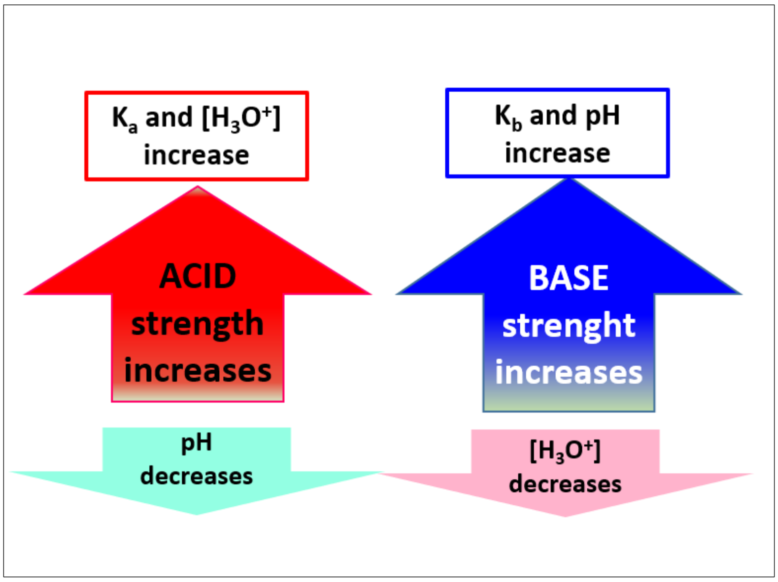


Figure 5.9 The relation between K_a, $[H_3O^+]$, K_b and pH.

5.2.5 pH and pOH values of weak acid and weak base.

What is the pH of 1.0 M solution of acetic acid (CH_3COOH)? Given $K_a = 1.8 \times 10^{-5}$.

$$CH_3COOH \leftrightharpoons H^+ + CH_3COO^-$$

Step 1. Define equilibrium concentration in ICE table.

	$[CH_3COOH]$	$[H^+]$	$[CH_3COO^-]$
Initial concentration	1.00	0	0
Change	$-\alpha$	$+\alpha$	$+\alpha$
Concentration at equilibrium	$1.00 - \alpha$	α	α

Step 2. Write Ka expression.

$$K_a = 1.8 \times 10^{-5} = \frac{[H_3\, O^+][OAc^-]}{HOAc} = \frac{\alpha^2}{1.00 - \alpha}$$

Step 3. Solve Ka expression.

First, assume x is very small because Ka is also small.

$$K_a = 1.8 \times 10^{-5} = \frac{\alpha^2}{1.00}$$

$\alpha = [H^+] = [CH_3COO^-] = 4.2 \times 10^{-3}M$

pH = - log $[H^+]$ = -log (4.2×10^{-3}) = 2.37

Water Equilibrium Constant, Kw

H_2O is a the most common amphoteric substances. It can behave either as an acid or a base. In the ionization of water (autoionization) as follows:

$$H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

At 25 °C, the actual concentration is:

$[H^+] = [OH^-] = 1x10^{-7}$ mol/L

In a neutral solution, [H+] = [OH]

The expression of equilibrium constant for the ionization of water, Kw

$$K_w = [H^+][OH^-] = 1 \times 10^{-14} \text{ mol/L}$$

Kw is called an ion-product constant for water. In any aqueous solution, no matter what it contains, the product of $[H^+]$ and $[OH^-]$ of water must always equal to 1×10^{-14} mol/L. If an acid is added to water, added source of $[H^+]$, the $[H^+]$ will be greater than $[OH^-]$, therefore it is an acidic solution. If a base is added to water, we have added source of $[OH^-]$, the $[OH^-]$ will be greater than $[H^+]$, therefore it is an basic solution.

$\boxed{\text{acids: } [H^+] > [OH^-]}$

$\boxed{\text{bases: } [OH^-] > [H^+]}$

5.3 Concept of buffer and preparing samples of buffer solutions.

5.3.1 Definition of buffer.

- A solution that does not change in its pH significantly with the addition of small amount of a strong acid or base (the resisting change of pH). There are two types of buffer solutions: -
  - **i. Acidic buffer solution**, which consists of weak acid and its conjugates base salt.

    Example: CH_3COOH and CH_3COONa

    (Weak Acid) (Conjugate Base Salt)
  - **ii. Basic buffer solution,** which consists of a weak base and its conjugates acid salt.

    Example: NH_3 and NH_4Cl

    (Weak Base) (Conjugate Acid Salt)

- Buffer solution is important to living organisms that can survive only in a very narrow pH range, namely the as pH of goldfish aquarium and pH of human blood.

5.3.2 Calculation pH of a buffered solution using Henderson-Hasselbalch equation.

- The Henderson–Hasselbalch equation is developed independently by an American biological chemist, L. J. Henderson and a Swedish physiologist, K. A. Hasselbalch for relating the pH to the bicarbonate buffer system of the blood (see below). In its general form, the Henderson-Hasselbalch equation is a useful expression for buffer calculations. It derives from the equilibrium constant expression for a dissociation reaction of the general weak acid (HA).

$$HA \rightleftharpoons H^+ + A^-$$

$$Ka = \frac{[H^+][A^-]}{[HA]}$$

$$[H^+] = K_a \frac{[HA]}{[A^-]}$$

$$[H^+] = K_a \frac{[Acid]}{[Salt]}$$

Taking the negative logarithms throughout:

$$-\log [H^+] = -\log K_a - \log \frac{[HA]}{[A-]}$$

$$-\log [H^+] = -\log K_a - \log \frac{[Acid]}{[Salt]}$$

Substituting -log K_a = pK_a and pH= -log [H^+],

$$pH = pK_a - \log \frac{[Acid]}{[Salt]} \quad \text{or} \quad pH = pK_a + \log \frac{[Salt]}{[Acid]}$$

Similarly for basic buffer solution:

$$[OH] = K_b \frac{[Base]}{[Salt]}$$

Taking negative logarithms throughout,

$$pOH = pK_b - \log \frac{[Base]}{[Salt]} \quad \text{or} \quad pOH = pK_b + \log \frac{[Salt]}{[Base]}$$

Example 10:

A solution contains 0.15 M HCOOH and 0.12 M HCOONa. What is the pH of the solution? [K_a = 1.8 x 10^{-4}]

Answer:

$$pH = pK_a - \log \frac{[Weak\ Acid]}{[Salt]}$$

$$= -\log 1.8 \times 10^{-4} - \log \frac{0.15}{0.12}$$

$$= 3.74 - \log 1.25$$

$$= 3.74 - 0.0969$$

$$= 3.64$$

Example 11:

What is the pH of a buffer solution containing 0.1 M ammonia and 0.1 ammonium chloride? [K_b= 1.8 x 10^{-5}].

Answer:

$$pOH = pK_b - \log\frac{[\text{Weak Base}]}{[\text{Salt}]}$$

$$= -\log 1.8 \times 10^{-5} - \log\frac{0.1}{0.1}$$

$$= 4.74 - \log 1.25$$

$$= 4.74 - 0$$

$$= 4.74$$

$$pH = 14 - pOH$$

$$= 14 - 4.74$$

$$= 9.26$$

Tutorial

1. Classify the following as acid, base, conjugated acid , conjugate base.

   i) HCl (aq) + H_2O (l) $\rightarrow$ H_3O^+(aq) + Cl^- (aq)

   ii) KOH(s) + H_2O (l) $\rightarrow$ K (aq) + OH^- (aq)

2. Calculate:

   i) pH given $[H^+] = 1.8 \times 10^{-4}$ M.

   ii) pOH of the solution if $[H^+] = 1.2 \times 10^{-5}$ M.

   iii) pOH if $[OH^-] = 4.0 \times 10^{-12}$ M.

3. Calculate:

   i) pOH value of a solution $Ba(OH)_2$ which has a concentration of 0.3 M.

   ii) pOH value of solution 0.25 mol dm^{-3} trimethylamine $(CH_3)_3N$.

   [K_b $(CH3)_3N$= $7.4 \text{ X } 10^{-5}$ mol dm^{-3}].

4. Find:

   i. pH value of a 0.5 M HNO_3 solution.

   ii. pOH value of a 0.03 M H_2SO_4 solution.

   iii. pH value of a 0.5M NaOH solution.

5. A buffer is found to contain 1.74 M of ammonia and 1.0 M of ammonium chloride in a solution. What is the pH of the solution? [pK_b of ammonia = 4.74].

6. Calculate the pH of a buffer solution that has 0.15 mol dm^{-3} CH_3COOH and 0.45mol dm^{-3} CH_3COONa. (K_a for CH_3COOH is 1×10^{-5} mol dm^{-3})

Answer:

1. i) HCl (aq) = acid; H_2O (l) = base; H_3O^+(aq) = conjugate acid; Cl^- (aq) = conjugate base

   ii) KOH(s) = base; H_2O (l) = acid; K (aq) = conjugate acid; OH^- (aq) = conuugate base

2. i) pH = 3.74

   ii) pOH = 9.08

   iii) pOH = 11.40

3. i) pOH = 0.22

   ii) pOH = 2.37

4. i) pH = 0.3

   ii) pOH = 12.78

   iii) pOH = 13.7

5. pH = 9.50

6. pH = 5.34

6.0 Oxidation and Reduction, Chemical Kinetics and Equilibrium

6.1 Redox reactions and electron transfer.

- The redox reaction is a reaction in which oxidation and reduction take place together. The term 'redox' derives from combination of reduction and oxidation reaction. The reaction involves a change in the oxidation number of specific elements in the reactants.
- An example of redox reaction is the iron rusting process of an iron nail to form rust nail. Based on the equation in Figure 6.1, iron is oxidized to form iron (II) ions The electrons that are released by the iron atom flow through the water droplets in which contain plenty of dissolved oxygen. The electrons are received by oxygen of the air in the presence of moisture to form hydroxide ions. Iron (II) ions and hydroxide ions are combined to form iron (II) hydroxide. The iron (II)hydroxide reacts with oxygen in the water to form hydrated iron (III) oxide. Hydrated iron (III) oxide is the rust which forms a reddish-brown coating over the iron.

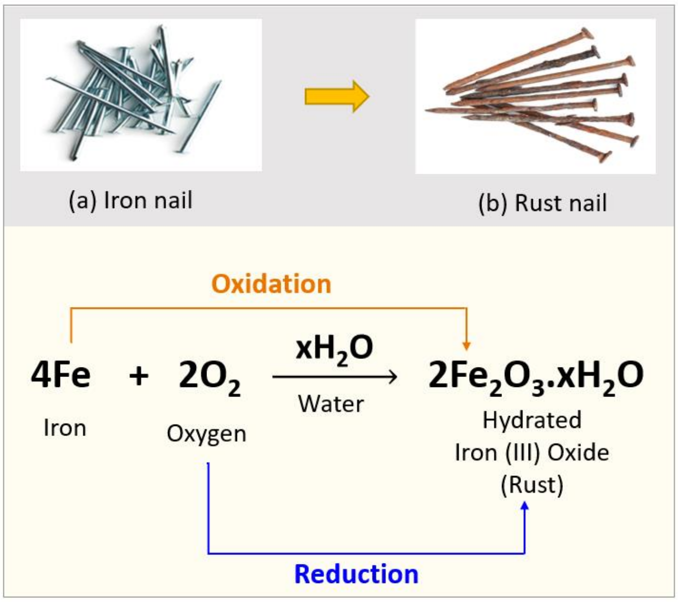


Figure 6.1 The iron rusting process.

6.1.1 The oxidation and reduction reactions.

- The oxidation and reduction reactions can be separated into two half-reactions. The separated oxidation and reduction reactions form a single oxidation and reduction reactions that are known as half-reactions.
- **The oxidation reaction** is a chemical process in which a **reactant loses or releases one or more electrons and shows an increase in its oxidation number**.
- **The reduction reaction** is a chemical process in which **a reactant gains or receives one or more electrons and shows a decrease in its oxidation number.**

6.1.2 The oxidizing and reducing agents.

Example 1:

Consider the following reaction:

$Fe^{2+} + Ce^{4+} \rightarrow Fe^{3+} + Ce^{3+}$ (Redox Reaction)

In this reaction,

(i) Fe^{2+} is oxidized to form Fe^{3+}

$Fe^{2+} \rightarrow Fe^{3+} + \bar{e}$ (Oxidation Reaction)

- In this reaction, Fe2+ has lost an electron, so it is said to have been oxidised and as a **reducing agent.** This electron is given to Ce^{4+}, and so Fe^{2+} is considered the reducing agent for Ce^{4+}.

(ii) Ce^{4+} is reduced to form Ce^{3+}

$Ce^{4+} + e \rightarrow Ce^{3+}$ (Reduction Reaction)

- In this reaction, Ce^{4+} has received an electron, so it is said to have been reduced and as an **oxidising agent**. This electron is from Fe^{2+}, and so Ce^{4+} is considered the oxidising agent for Fe^{2+}.

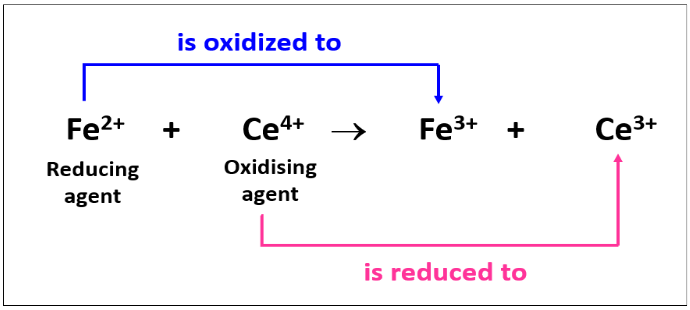


Figure 6.2 The summary of the reaction for Example 1.

Example 12:

$$Sn^{2+} + 2Fe^{3} \rightarrow Sn^{4+} + 2Fe^{2+} \qquad (1)$$

The reaction is made up of two processes, which are:

Oxidation : $Sn^{2+} \rightarrow Sn^{4+} + 2\bar{e}$ (2)

Reduction : $2Fe^{3+} + 2\bar{e} \rightarrow 2Fe^{2+}$ (3)

Equation (1) is a redox reaction known as **ionic equation** that are formed by combining the two **half reactions of Equation (2) and (3).**

In the redox reaction, Sn^{2+} (oxidising agent) donates an electron. Then, the electron is gained by Fe^{3+} (reducing agent).

Table 6.1 The summary of oxidation and reduction processes

Oxidation (Reducing agent)		**Reduction (Oxidising agent)**
Gains oxygen	← Oxygen	Donates / Loses oxygen
Donates / Loses Hydrogen	Hydrogen →	Gains Hydrogen
Donates / Loses Electron	Electron →	Gains Electron

6.2 The Concept of Oxidation Number.

- The oxidation number is the total number of electrons that an atom either gains or losses to form a chemical bond with another atom.

- The oxidation number of an atom is equal to the total number of electrons that have been removed from an element (producing a positive oxidation number) or added to an element (producing a negative oxidation number) to reach its present state. The oxidation process involves an increase in oxidation state or number whereas the reduction process involves a decrease in oxidation state or number.

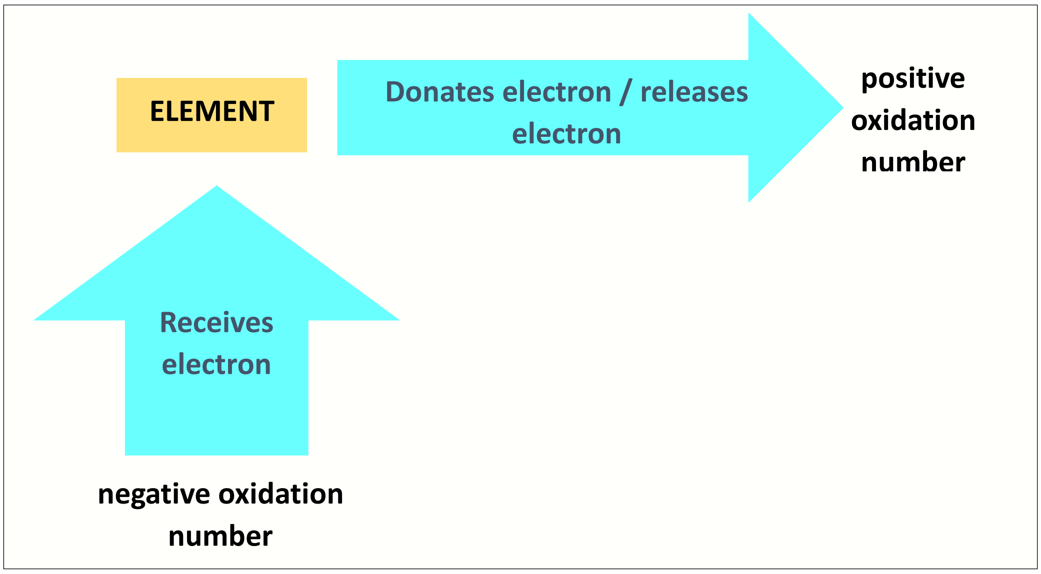


Figure 6.3 The diagram of the oxidation number concept.

Table 6.2 The concept of electron transfer and the change of oxidation number.

REACTION	ELECTRONS	OXIDATION NUMBER
Oxidation	Donated	Increases
Reduction	Received	Decreases

6.2.1 Calculation the oxidation number.

Table 6.3 Oxidation number rules.

Rule	Situation	Example	Oxidation Number
Rule 1	All elements in uncombined element (Example: Sodium, Na)	Na = 0, K = 0,	0
Rule 2	All monoatomic ions.	Ca^{2+} = +2 Cl^{-} = -1	Same as their charge
Rule 3	Hydrogen in all compounds		+1
Rule 4	Hydrogen in hydrides	NaH, MgH_2	-1
Rule 5	Oxygen in all compounds		-2
Rule 6	Oxygen in all peroxides (H2O2) and fluorine.		-1
Rule 7	All group 1 elements in compounds		+1
Rule 8	All group 2 elements in compounds.		+2
Rule 9	All halogens in group 1 and 2 compounds.		-1
Rule 10	The more electronegativity element in a binary compound is assigned.	O in NO = -2	Same as its charge. (negative)
Rule 11	An element that is less electronegativity,		Positive charge
Rule 12	The sum of oxidation numbers in a compound.		0
Rule 13	The sum of oxidation numbers in a polyatomic ion.	H in OH^{-} = +H P in $H_2PO_4^{-}$ = +5	Same as its charge.
Rule 14	Fluorine in a compound.	F in LiF	-1
Rule 15	Hydrogen is combined with a metal.	H in LiH	-1

Table 6.3 The oxidation numbers of some reference elements.

H	**+1 (except in metal hydride)**					
Group I	Na	+1		K	+1	
Group II	Mg	+2		Ca	+2	
Group XIII	B	+3		Al	+3	
Group XVI	O	-2 (except in fluoride and peroxide)				
Group XVII	F	-1		Cl	-1 (Except when bonded to O and F)	
Group XVIII	He	0		Ne	0	

In ionic compounds, the oxidation number = with the charge on the ion.

Example 3:

$FeCl_2$; Fe = +2, Cl = -1

The sum of oxidation numbers of all the atoms or ions in a compound is always zero.

Example 4:

$FeCl_3$, the sum of all the oxidation numbers.

$+3 + 3(-1) = 0$.

The sum of oxidation numbers of all the atoms in an ion is equal to the charge on that ion.

Example 5:

SO_4^{2-}

$+6 + 4\ (-2) = -2$

Free elements and the elements found within molecules which are made up of the same kind of atoms.

Example 6:

H_2 gas, O_2 and others, oxidation number = 0.

6.2.2 Determination the oxidation and reduction reactions using the oxidation number concept.

- The following equation is given:

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

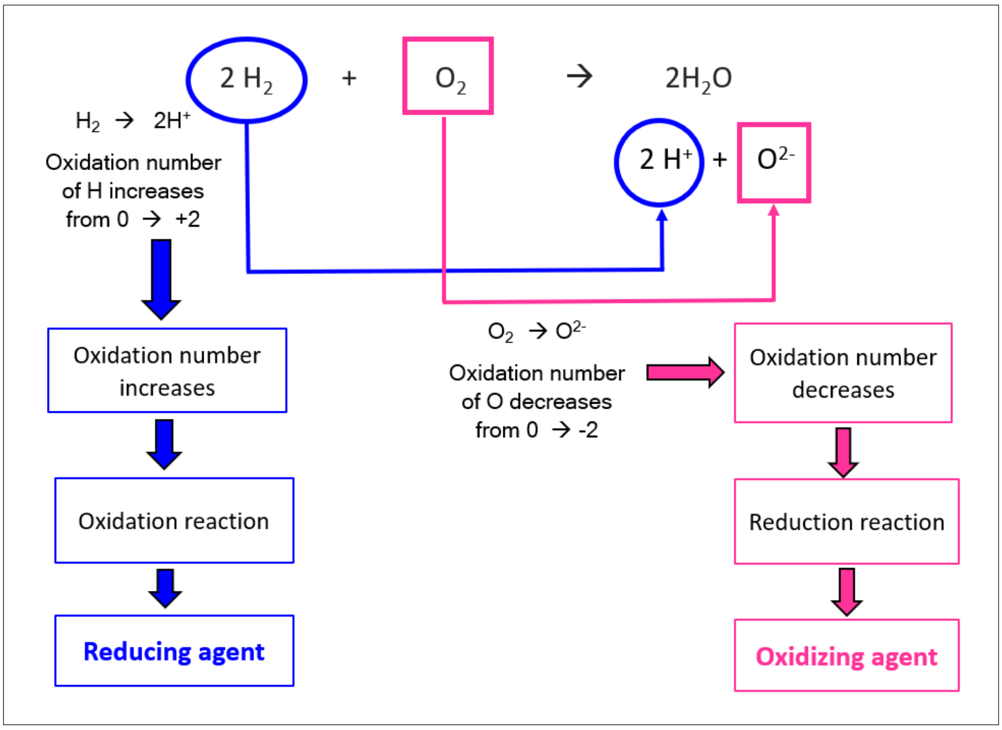


Figure 6.4 The diagram of oxidation and reduction reaction using oxidation number concept.

6.3 Balance redox equation by using the ion-electron method.

6.3.1 Consider the redox reaction between oxalic acid and the permanganate ion:

$$MnO_4^- + C_2O_4^{2-} \longrightarrow CO_2 + Mn^{2+}$$

MnO^{4-} is the oxidising agent. The oxidation number of manganese drops from +7 in MnO^{4-} to +2 in Mn^{2+}. Manganese is reduced.	The oxalate ion, $C_2O_4^{2-}$ is the reducing agent. The oxidation number of carbon increases from +3 in $C_2O_4^{2-}$ to +4 in CO_2. Carbon is oxidized.

Example 7:

Given the simple unbalanced redox reaction:

$$Zn + Cu^{+} \rightarrow Zn^{2+} + Cu$$

STEP 1 : Divide the reaction into half reactions.

$Zn \rightarrow Zn^{2+}$

$Cu+ \rightarrow Cu$

STEP 2 : Balance the charges by adding $\bar{e}$.

$Zn \rightarrow Zn^{2+} + 2\bar{e}$

$1e^{-} + Cu^{+} \rightarrow Cu$

STEP 3 : Multiply both half-equations by a suitable factor that's have the same number of electrons in them.

$Zn \rightarrow Zn^{2+} + 2\bar{e}$

$2(1e^{-} + Cu^{+} \rightarrow Cu)$

STEP 4 : Cancel out the electron on both sides, then the two reactions can be added.

$$\begin{array}{ll} & Zn \rightarrow Zn^{2+} + 2\bar{e} \\ + & 2(1\bar{e} \ + Cu^{+} \rightarrow Cu) \\ \hline & \end{array}$$

$Zn + 2Cu^{+} \rightarrow Zn^{2+} + 2Cu$

- The summary of the steps for balancing redox reactions in acidic solution is as follows:
  1. Divide the reaction into half-reactions
  2. Balance the charges by adding $\bar{e}$.
  3. Multiply both half-equations by a suitable factor that has the same number of electrons in them.
  4. Cancel out the electron on both sides, then the two reactions can be added.

6.3.2 Consider the unbalanced redox reaction

Example 8:

$MnO_4^-\ (aq) + Zn(s) \rightarrow MnO_2(s) + Zn(OH)_4^{2-}\ (aq)$

STEP 1 : Divide the reaction into half reactions.

$MnO_4^- \rightarrow MnO_2$

$Zn \rightarrow Zn\ (OH)_4^{\ 2}$

STEP 2 : Balance the elements other than H and O. H and O are already balanced.

STEP 3 : Balance the O atoms by adding $\mathbf{H_2O}$.

$MnO_4^- \rightarrow MnO_2 + \mathbf{2H_2O}$

$Zn + \mathbf{4H_2O} \rightarrow Zn\ (OH)_4^{\ 2-}$

STEP 4 : Balance the H atoms by adding $\mathbf{H^+}$

$MnO_4^- + \mathbf{4H^+} \rightarrow MnO_2 + 2H_2O$

$Zn + 4H_2O \rightarrow Zn\ (OH)_4^{\ 2-} + \mathbf{4H^+}$

STEP 5 : Balance the charges by adding $\bar{e}$.

$MnO_4^- + 4H^+ + 3\bar{e} \rightarrow MnO_2 + 2H_2O$

$Zn + 4H_2O \rightarrow Zn\ (OH)_4^{\ 2-} + 4H^+ + 2\bar{e}$

STEP 6 : Cancel out the electron on both sides, then the two reactions can be added.

The number of electrons in the first half reaction ($3\bar{e}$) does not equal the number of electrons in the second half reaction ($2\bar{e}$).

The reactions must be multiplied by the coefficients so that the electrons can be cancelled out when they are added.

In this case, the first reaction should be multiplied by 2 to yield $6\bar{e}$, and the second reaction multiplied by 3 to yield $6\bar{e}$ as well.

$$2\,(MnO_4^- + 4H^+ + 3\bar{e} \rightarrow MnO_2 + 2H_2O)$$

$$3\,(Zn + 4H_2O \rightarrow Zn\,(OH)_4^{\,2-} + 4H^+ + 2\bar{e}\,)$$

Carrying this out, then get:

$$2MnO_4^- + 8H^+ + 6\bar{e} \rightarrow 2MnO_2 + 4H_2O$$

$$3Zn + 12H_2O \rightarrow 3Zn\,(OH)_4^{\,2-} + 12H^+ + 6\bar{e}$$

STEP 7 : The electron on both sides can be cancelled out, now the two reactions can be added.

$$2MnO_4^- + \cancel{8H^+} + \cancel{6\bar{e}} \rightarrow 2MnO_2 + \cancel{4H_2O}$$

$$3Zn + \underset{8H_2O}{\cancel{12H_2O}} \rightarrow 3Zn\,(OH)_4^{2-} + \underset{4H^+}{\cancel{12H^+}} + 6\bar{e}$$

Thus, the balanced reaction is:

$$2MnO_4^- + 3Zn + 8H_2O \rightarrow 2MnO_2 + 3Zn\,(OH)_4^{2-} + 4H^+$$

- The summary of the steps for balancing redox reactions in acidic solution are as follows:
  1. Divide the reaction into half reactions.
  2. Balance the elements other than H and O.
  3. Balance the O atoms by adding H2O.
  4. Balance the H atoms by adding H^+.
  5. Balance the charges by adding $\bar{e}$.
  6. Multiply both half-equations by a suitable factor that has the same number of electrons in them.
  7. Cancel out the electron on both sides, then the two reactions can be added.

6.4 Rate of reaction in chemical kinetics

CHEMICAL KINETIC is the area of chemistry concerns with the speed or rate, at which a chemical occurs.

KINETIC is the movement/ change (general) and the rate of a reaction, which is a speed at which the reaction happens.

RATE OF REACTION is determined by measuring the change in a selected quantity of a reactant or a product during a reaction with time (m/s).

- Reactions progress at different speeds, depending on the substance(s) involved as well as the various factors in the environment or speed at which a chemical reaction happens.
  - Rate of reaction is high → short time is taken for a complete reaction
  - Rate of reaction is slow → time taken is long for a complete reaction
  - Rate of reaction = 0 → complete reaction

- **Slow Reactions:**

  Chemical reactions that take a long time for completion are called slow reactions.

Example 9:

$4Fe + 3O_2 \rightarrow 2Fe_2O_3$

(Iron) (Oxygen) (Rust – Iron Oxide)

- **Fast Reactions:**

  Chemical reactions that are completed in a very short time, such as less than 10^{-6} seconds are called fast reactions.

  Example: A neutralization reaction between acids and bases is a fast reaction.

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

(Acid) (Base) (Common Salt) (Water)

6.4.1 Reaction rate, average rate and instantaneous rate

- **Reaction Rate** is the change in a selected quantity of a reactant or a product during a reaction per unit of time (m/s).
- **Average Rate:** The speed of the entire reaction from start to finish.
- **Instantaneous Rate:** The speed of the reaction at one moment in time. Some reactions can happen quickly at the start and then slow down.

Measuring the rate of reaction

Any reaction can be represented by the general equation:

Reactants $\longrightarrow$ **Product**

Example 10:

N_2 + $3H_2$ $\rightarrow$ $2NH_3$

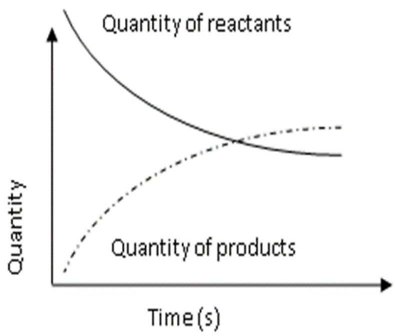
(Reactants) (Product)

- When the reaction takes place, reactants are consumed while products are formed.
- When the reaction runs, the number of reactants decreases while the amount of products increases.

Formula:

$$\text{The rate of reaction} = \frac{\text{change in a selected quantity}}{\text{time taken for the change to occur}}$$

- The 'quantity' mentioned above can be any easily observable or measurable quantity, such as:
  - number of moles of a reactant / product,
  - mass of a solid
  - volume of a gas
  - concentration of a solution
  - pH of the solution



Example 11:

0.2 g magnesium **reacts completely** with diluted hydrochloric acid in 40 seconds.

i. What is the average rate of reaction?

$$\text{Rate of reaction} = \frac{\text{total mass of magnesium reacted}}{\text{time taken}}$$

$$= \frac{0.2\ \text{g}}{40\ \text{s}} = 0.005\ \text{g s}^{-1}$$

If the mass of Mg is measured regularly through the 40 seconds, the following graph could be obtained.

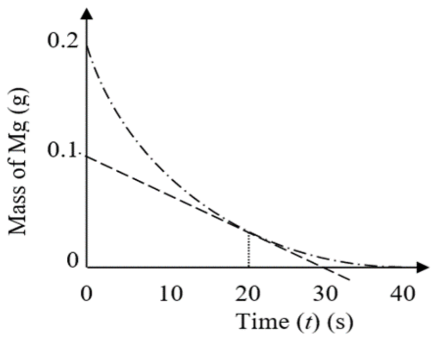
ii. What is the rate of the reaction at 20 seconds?

The instantaneous rate of the reaction at 20 s is required here, and can be found from the same graph, by drawing a tangent at t = 20.

Rate of reaction at 20s, = gradient of tangent at t = 20

$$= \frac{0.1 - 0}{30 - 0} = \frac{0.1}{30}$$

$$= 0.0033\ \text{g s}^{-1}$$



6.4.2 Factors affecting the rate of reaction

- The rate of a reaction is the speed at which a chemical reaction happens. If a reaction has a low rate, that means the molecules combine at a slower speed than a reaction with a high rate.

- **Collision Theory**

  The collision theory suggests that as more collisions in a system occur, there will be **more combinations** of molecules bouncing into each other. If there were more possible combinations, there will be a higher chance for the molecules to complete the reaction. The reaction will happen faster which means the rate of that reaction will increase.

- Factors that affect the rate of reaction

  i. Size of the molecules

  ii. Concentration of the reactant(s)

  iii. Pressure of the reaction involving gaseous reactant(s)

  iv. Temperature of the reaction

  v. Catalyst

i. Size of molecules

When the size of molecules is small, the surface area of a solid reactant increases, and the rate of reaction increases. According to the Collision Theory, when the exposed surface area is wider, the frequency of collision among the reactants increases, and so the frequency of effective collisions increases. Therefore, the rate of reaction rises.

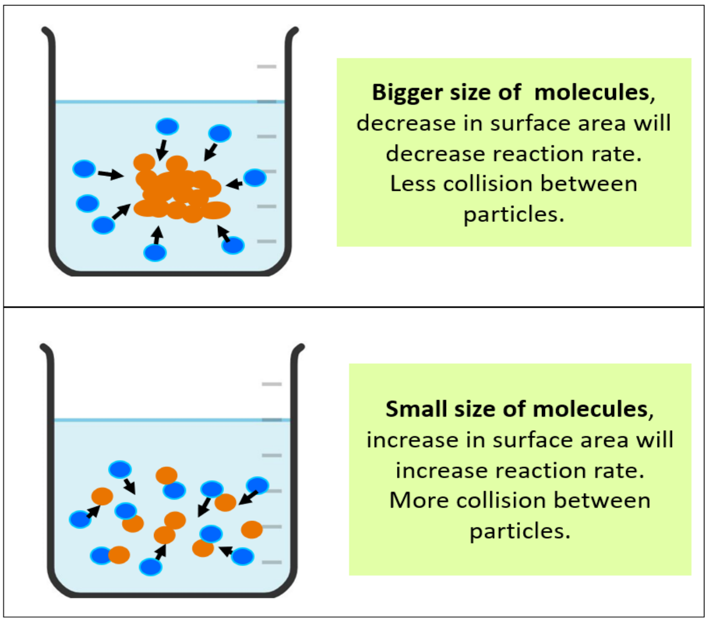


Figure 6.5 The effects of the molecule size to the reaction rate.

ii. Concentration of reactant(s)

When more of a substance and the concentration in a system is increases, there is a greater chance that molecules will collide and speed up the rate of the reaction. Hence, the frequency of effective collision is correspondingly higher.

When less of a substance, there will be fewer collisions and the reaction will probably happen at a slower speed.

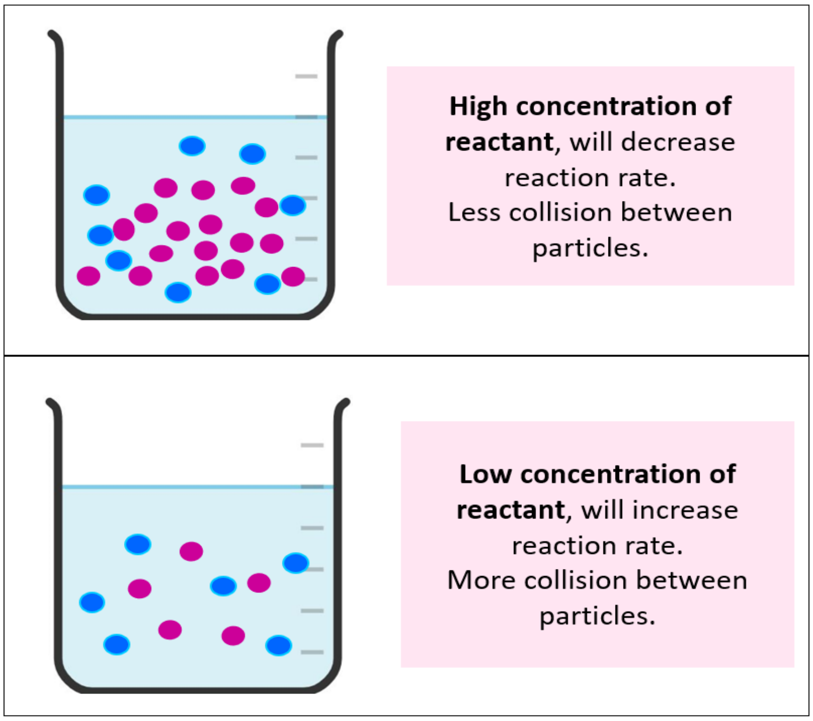


Figure 6.6 The effects of the concentration of reactant to the reaction rate.

iii. Pressure of reaction involving gaseous reactant(s)

Pressure affects the rate of a reaction. When pressure is increase, the molecules have less space in which they can move. That greater **density** of the molecules increases the number of collisions. When pressure decreases, the molecules do not hit each other as often and the rate of the reaction decreases.

Pressure is also related to concentration and volume. By decreasing the volume available to the molecules of gas, the concentration of molecules will increase in a specific space. Changing the pressure of a system only works well for gases. Generally, reaction rates for solids and liquids remained unaffected by increases in pressure.

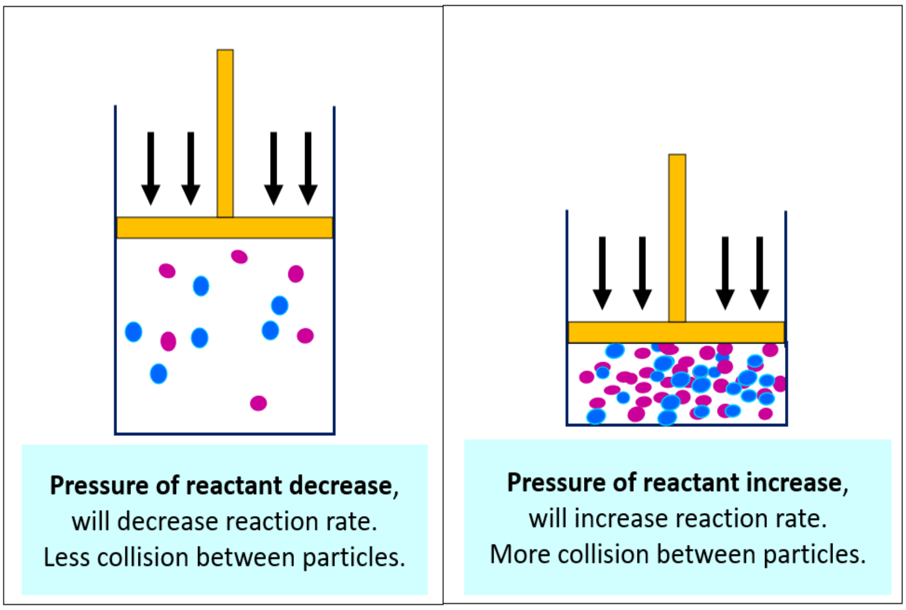


Figure 6.7 The effects of the pressure of reactant to the reaction rate.

iv. <u>Temperature of reaction</u>

The kinetic energy associated with particles increases with temperature. The high temperature will supply additional heat energy to the reactant particles. This increases their kinetic energy and causes them to move faster and so collide more frequently and with higher energy. Hence, an increase in temperature would increase the frequency of effective collision. The rate of the reaction increases greatly with temperature. On the other hand, it decreases as the temperature decreases.

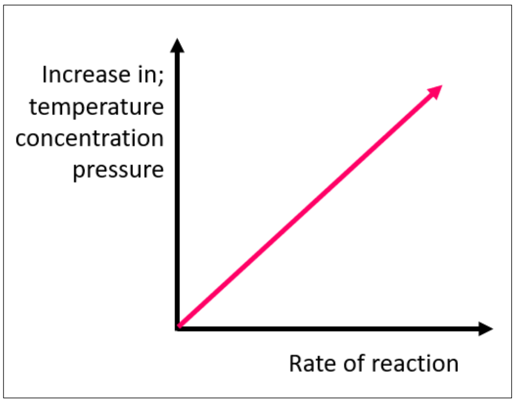


Figure 6.8 Graph of the effect of the temperature, concentration, and pressure of reactant to the reaction rate.

v. Catalyst

Catalysts always speed up a reaction. They are substances that participate in a chemical reaction by increasing the rate of reaction but are unchanged by the reaction itself. Catalysts act by lowering the activation energy or the distance to the transition state.

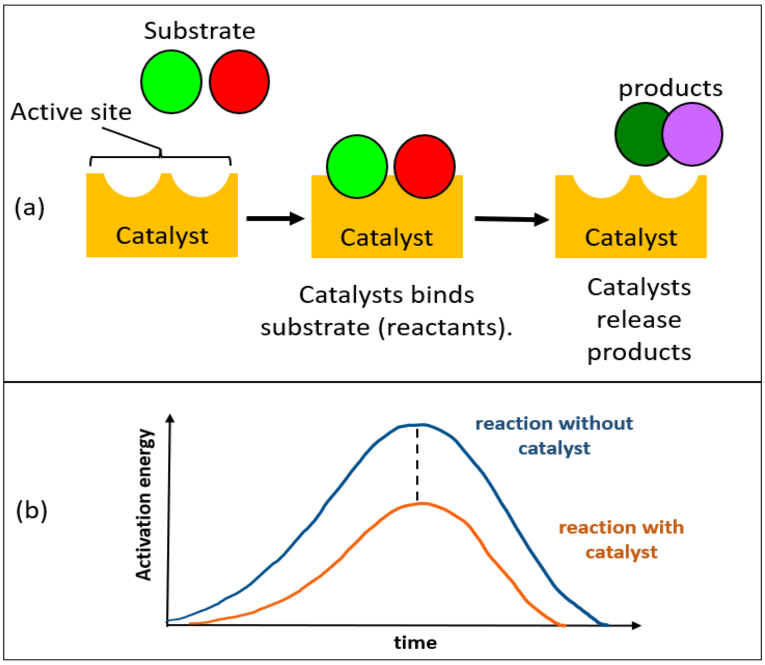


Figure 6.8 (a) Illustration of the catalyst reaction; (b) Graph of the activation versus time.

6.5 Dynamic Equilibrium

- The concept of dynamic equilibrium holds that forward and reverse reactions both o ccur at equal rates at equilibrium to the extent allowed by kinetic considerations.
- The reaction stops when one or more reactants are completely used up. As soon as some product molecules are formed, they (product) react with one another to form reactant molecules. Such reactions are called **reversible reactions** and are represented by a **symbol.**

Take a look at an example is the reaction between zinc carbonate and dilute sulphuric acid.

$$ZnCO_3\ (s) + H_2SO_4\ (aq) \rightarrow ZnSO_4\ (aq) + CO_2\ (g) + H_2O\ (l)$$

- There are also reactions that do not go to completion.

$$A + B \rightleftharpoons C + D$$

(Reactants) (Products)

In the reaction above, A and B react to form C and D which in turn react together to form A and B again. At the end of the reaction, both the reactants A and B and products C and D are present. The reaction going from left to right is called the **forward reaction** while the reaction going from right to left is called the **reverse rea ction**.

A **reversible reaction** is a chemical reaction in which the conversion of reactants to products and the conversion of products to reactants co-occur. Therefore, in a reversible reaction, the reactants and the products are never fully consumed, nor is the reaction complete. Instead, the reaction will come to equilibrium if the concentrations of the reactants and products remained constant.

- According to **Le Chatelier's principle**, a **reversible reaction** is self-correcting. Suppose there is a change in the concentration, temperature, or pressure. In that case, the system will naturally shift towards equilibrium. This equilibrium is a **dynamic equilibrium.**

Example 12 :

Example of reversible reactions:

$H_2 (g) + I_2 (g) \leftrightharpoons 2\ HI (g)$

Hydrogen Iodine Hydrogen Iodide

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

Nitrogen Hydrogen

Ammonia

$CaCo_3 (s) \leftrightharpoons CaO (s) + CO_2 (g)$

Calcium carbonate Calcium oxide Carbon dioxide

6.5.1 Characteristics of a dynamic equilibrium system

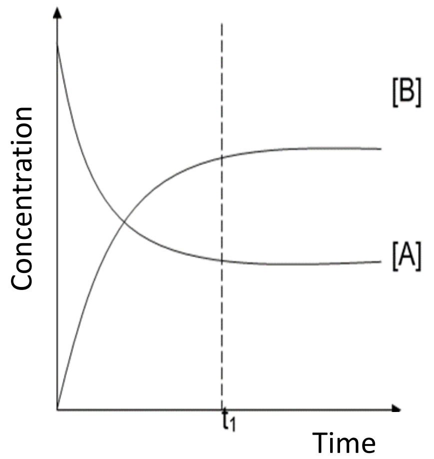


Figure 6.9

Figure 6.9 shows the graph of the concentration versus time. The concentration of A and B are plotted against time at constant temperature. The concentration of A decreases with time, while the concentration of B increases with time. But after time t_1, the concentration of A and B remained constant. The system is said to have achieved equilibrium.

After the system achieved equilibrium, what is the relationship between the concentrations of the reactants and that of the products?

For systems involving concentration:

$$aA + bB \rightleftharpoons cC + dD$$

- When equilibrium is reached, the following ratio is a constant irrespective of the starting concentration of the substances.

$$\text{Constant, } K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

- The constant is called equilibrium constant in terms of molar concentration.

[A], [B], [C] and [D] = molar equilibrium concentration of A, B, C, and D.

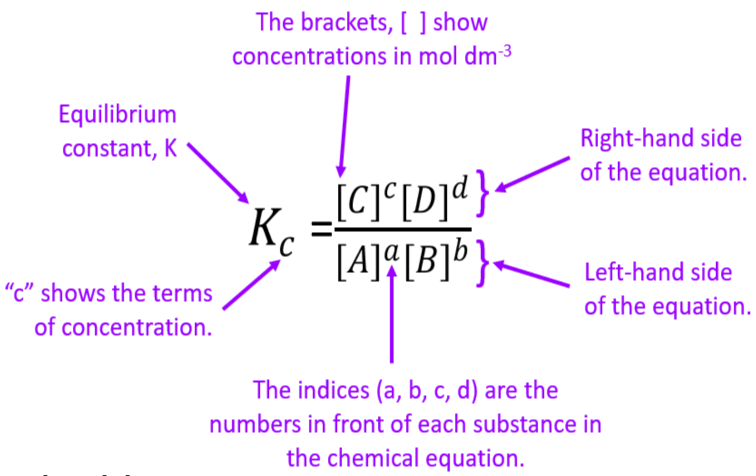


Figure 6.10 The explanation of the terms for each symbol.

For systems involving gases:

$$aA + bB \rightleftharpoons cC + dD$$

- The equilibrium constant can also be expressed in terms of the equilibrium partial pressure of the gases present.

$$\frac{(PC)_c\ (PD)_d}{(PA)_a\ (PB)_b} = Kp$$

P is equilibrium partial pressure of the gas in the equilibrium mixture, K_p equilibrium constant in terms of pressure. The characteristics of a dynamic equilibrium are:

(a) The reaction does not stop completely

(b) The rate of the forward reaction and the rate of the reverse reaction is the same

(c) There is no net change in the concentration of the species involved

(d) Equilibrium can be achieved from either direction

6.6 Equilibrium Conditions and Constants

6.6.1 Homogeneous and heterogeneous equilibrium

Homogeneous Equilibrium

- Homogeneous equilibrium applies to reactions in which all **reactant species are in the same physical state**. The concentration of all the species is included in the expression for equilibrium constants.

Example 13:

The dissociation of N_2O_4 is an example of gas-phase equilibrium.

$$N_2O_4\ (g) \leftrightharpoons 2NO_2\ (g)$$

The equilibrium constant, $Kc = \frac{[NO_2]^2}{[N_2O_4]}$

In Kc, the **subscript c** indicates the **concentrations of the reacting species** are expressed in molarity or moles per liter. The concentrations of reactants and products in gaseous reactions can be expressed in terms of their **partial pressure**.

$$K_p = \frac{P^2_{N_2}}{P_{N_2O_4}}$$

where P_{NO_2} and $P_{N_2O_4}$ are equilibrium partial pressures (in atmospheres) of NO_2 and N_2O_4 respectively.

Heterogeneous Equilibrium

- **Heterogeneous** equilibrium results from a reversible reaction **involving reactants and products that are in different phases.**

Example 14:

Carbon with Steam.

$$H_2O(g)+C(s) \rightleftharpoons H_2(g)+CO(g)$$

The equilibrium constant expression is written the same way as in previous examples, by omitting the solid carbon term:

$$K_c = \frac{[H_2]\,[CO]}{[H_2O]}$$

Example 15:

Copper with Silver Ions.

Consider the redox reaction between solid copper and silver ions in a solution:

$$Cu(s)+2Ag^+(aq) \rightleftharpoons Cu^{2+}(aq)+2Ag(s)$$

Both the copper on the left-hand side and the silver on the right are solids. Both are left out of the equilibrium constant expression:

$$K_c = \frac{[Cu^{2+}]}{[Ag^+]^2}$$

Example 16:

Heating $CaCO_3$.

This equilibrium is only established if calcium carbonate is heated in a closed system, preventing carbon dioxide from escaping:

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

The only non-solid species in this system is carbon dioxide, so it is the only term in the equilibrium constant expression:

$$Kc = [CO_2]$$

6.7 Le Chatelier's Principle

6.7.1 Definition of the Le Chatelier's principle

- When an external stress (a change in pressure, temperature or concentration) is applied to a system in a chemical equilibrium, the equilibrium will change in such a way as to reduce the effect of the stress.

6.7.2 Factors affecting chemical equilibrium

- Concentration
- Pressure
- Temperature

1. **Changes of the Concentration.**

If the concentration of a reactant increases the equilibrium will shift in the direction of the reaction that uses the reactants, so that the reactant concentration decreases. The forward reaction is favoured and it is also favoured if the concentration of the product is decreased, so that more product is formed. If the concentration of a reactant decreases the equilibrium will shift in the direction of the reaction that produces the reactants, so that the reactant concentration increases. The reverse reaction is favoured and it is also favoured if the concentration of the product is increased, so that product is used. For **example**, in the reaction between sulfur dioxide and oxygen to produce sulfur trioxide:

$$2SO_2(g)+O_2(g)\leftrightharpoons 2SO_3(g)$$

If the SO_2 or O_2 concentration increases:

Le Chatelier's principle predicts that equilibrium will shift to decrease the concentration of reactants. An increase in the rate of the forward reaction means a decrease in the reactants. So some of the sulfur dioxide or oxygen are used to produce sulfur trioxide.

Equilibrium shifts to the right. That is, when a new equilibrium is achieved (when the rate of forward and reverse reactions are equal again), there will be more products than before.

If $[SO_3]$ decreases:

Le Chatelier's principle predicts that the equilibrium will shift to increase the concentration of products. An increasing in the rate of the forward reaction means an increase in the products. Thus, some sulfur dioxide or oxygen are used to produce sulfur trioxide. Equilibrium shifts to the right. That is, when a new equilibrium is achieved, there will be more products than before.

If $[SO_3]$ increases:

Le Chatelier's principle predicts that the equilibrium will shift to decrease the concentration of products. Increasing the rate of the reverse reaction means a decrease in the products. Thus, some of the sulfur trioxide would change back to sulfur dioxide and oxygen to restore equilibrium. Equilibrium shifts to the left. That is, when a new equilibrium is achieved there will be less products than before.

2. Changes of the volume and the pressure

If the pressure of a gaseous reaction mixture is changed, the equilibrium will shift to minimize that change. If the pressure is increased, the equilibrium will shift to favor a decrease in the pressure. If the pressure is decreased, the equilibrium will shift to favor an increase in the pressure.

When the volume of a system is decreased (and the temperature is constant), the pressure increases. There will be more collisions with the walls of the container. If there are fewer gas molecules there will be fewer collisions, and therefore lower pressure. The equilibrium will shift in a direction that reduces the number of gas molecules so that the pressure is also reduced. Therefore, to predict in which direction the equilibrium will shift to change the pressure, you need to look at the number of gas molecules in the balanced reactions.

For example, the equation for the reaction between nitrogen and hydrogen is shown below:

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

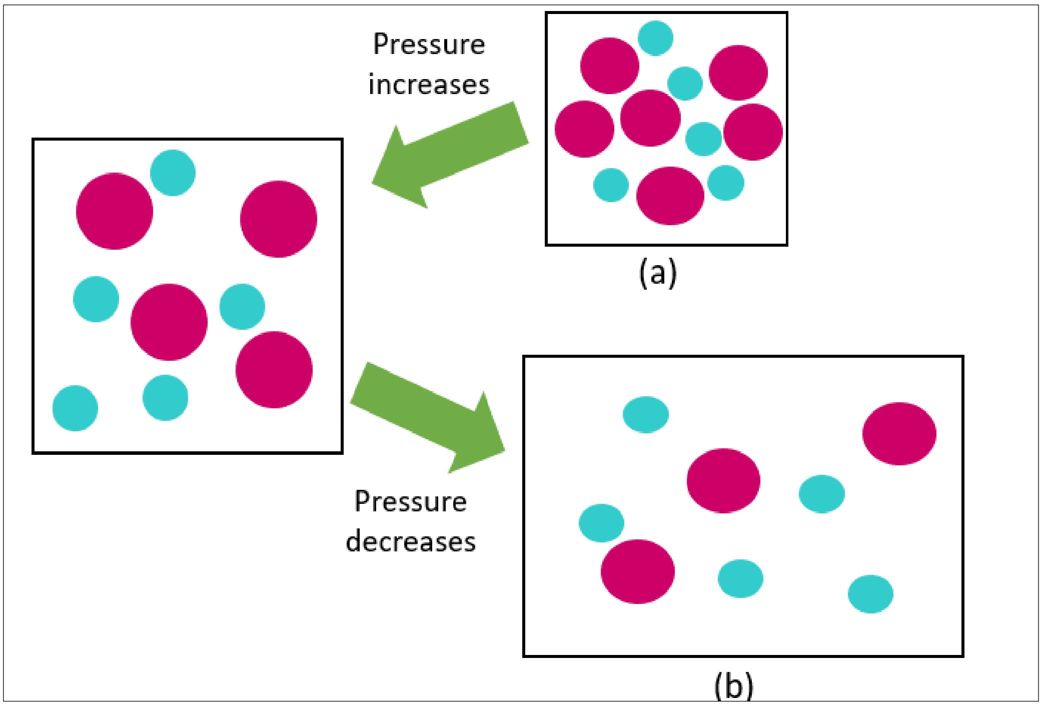


Figure 6.11 (a) The decrease in the pressure of this reaction favours the reverse reaction (more gas molecules); the equilibrium shifts to the left. (b) The increase in the pressure of this reaction favours the forward reaction (fewer gas molecules), the equilibrium shifts to the right.

3. Changes of the temperature

If the temperature of a reaction mixture is changed, the equilibrium will shift to minimise that change. If the **temperature is increased** the equilibrium will shift to favour the reaction which reduces the temperature. The **endothermic reaction** is favoured. If the **temperature is decreased** the equilibrium will shift to favour the reaction which increases the temperature. The **exothermic reaction** is favoured.

For example, the forward reaction shown below is exothermic (shown by the negative value for ΔH). This means that the forward reaction, where nitrogen and hydrogen react to form ammonia, gives off heat, causing an increase in the temperature (the forward reaction is exothermic). In the reverse reaction, in which the ammonia decomposes into hydrogen and nitrogen gas, heat is taken in by the reaction, cooling the vessel (the reverse reaction is endothermic).

SUMMARY

Table 6.4 The summary of effects of concentration, pressure, temperature and catalyst toward the rate of reactions, equilibrium constant and equilibrium composition.

Change	Rate	Rate Constant	Equilibrium Constant	Equilibrium Composition
Concentration	Changes	Unchanged	Unchanged	Changes
Pressure	Changes	Unchanged	Unchanged	Changes
Temperature	Changes	Changes	Changes	Changes
Catalyst	Changes	Changes	Unchanged	Unchanged

Tutorial

1. Identify an oxidising agent and a reducing agent of the following reaction. Then, explain your answer in terms of the oxidation number.

   $Sn^{2+} + 2Fe^{3+} \rightarrow Sn^{4+} + 2Fe^{2+}$

2. Calculate the oxidation number of the following chemical substances:
   i) Thallium (Tl) in $TlCl_3$
   ii) Chlorine (Cl) in Cl_2O_7
   iii) Iron (Fe) in $Fe(CN)_6^{3-}$
   iv) Sulfur (S) in $H_2S_2O_8$
   v) Arsenic (As) in AsO_4^{3-}

3. Construct a balanced equation of a redox reaction to represent the reaction.

   $Co^{3+} (aq) \quad + \quad Ni (s) \rightarrow \quad Co^{2+} (aq) \quad + \quad Ni^{2+} (aq)$

4. Draw a possible graph of concentration versus time for a reactant.

5. Explain why the rate of disappearance of NO and the rate of formation of N_2 are not the same in the reaction, $2CO(g) + 2NO(g) \rightarrow 2CO_2(g) + N_2(g)$.

6. For the reaction $A + 3B \rightarrow 2C$, explain the rate of disappearance of B compared to the rate of production of C.

7. If the rate of the appearance of O_2 in the reaction: $2O_3(g) \rightarrow 3O_2(g)$ is 0.250 M/s over the first 5.50 s, calculate the concentration of oxygen that is formed during this time.

8. Explain the factor that affect the rate of a reaction based on Collision theory.

Answer:

1. Fe^{3+} = oxidising agent, $Fe^{3+}$is reduced, forming Fe^{2+}.

   Sn^{2+} = reducing agent, Sn^{2+} is oxidised to form Sn^{4+}.

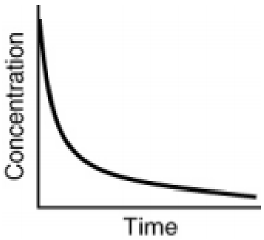
2. i) Oxidation number of Tl = +3

   ii) Oxidation number of Cl = +7

   iii) Oxidation number of Fe = +3

   iv) Oxidation number of S = +7

3. $$2Co^{3+} (aq) + Ni (s) \rightarrow 2Co^{2+} (aq) + Ni^{2+} (aq)$$

4. 

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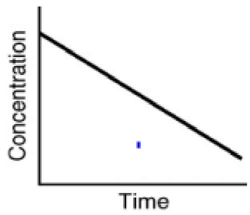

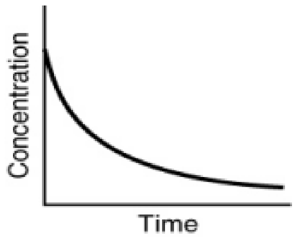

5. Because of the 2:1 stoichiometric ratio between NO and N_2, the NO must use 2 moles for each mole of N_2 produced. This means that the rate of consumption of NO is twice as fast as the rate of production of N_2.

6. 1.38 M

7. The rate of disappearance of B is 3/2 the rate of appearance of C.

The energy of collisions and the orientation of colliding molecules.

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