

## **COURSE OUTLINE**

- Particulate nature of matter
- Atomic structure
- Colligative properties
- Bonding and structure
- Phase equilibrium
- Thermochemistry
- Physical equilibrium
- Chemical kinetics
- Chemical equilibrium
- Ionic equilibrium
- Electrochemistry
- Electrochemical cells

### **PARTICULATE NATURE OF MATTER**

Matter is composed of tiny particles and it exists in three forms i.e. Solid, Liquid and Gas. Kinetic theory is concerned in the way in which these particles move and are distributed out hence the three states of matter.

The theory assumes that these particles have energy at all temperatures above zero Kelvin and this energy is in form of Kinetic energy. Increase in temperature increases the Kinetic Energy.

#### **i. SOLIDS**

- Here particles are extremely closed together and this gives the solids compact nature, high density and is compressible.
- Have stationary particles
- Have a definite shape and volume.
- On heating the solids, the particles gain energy and vibrate about the mean of fixed positions. Application of sufficient heat, they expand; eventually their movement is so much that they can't be held together by the forces of attraction, so the particles break and melt to form liquid.

## ii. LIQUIDS

- Particles have more Kinetic energy than in the solid state.
- These particles are far apart and free to move throughout the entire system. At this point, the energy over comes the forces of attraction which makes the particles move in continuous random motion at a greater speed.
- Liquids take up the shape of the container and also have a definite volume.
- Are incompressible.

## iii. GASES

- Take up the shapes of their container and occupy the entire volume of the container
- The particles are independent on one another and the attraction forces are negligible

### EVIDENCE OF EXISTANCE OF MATTER

#### a) Brownian motion;

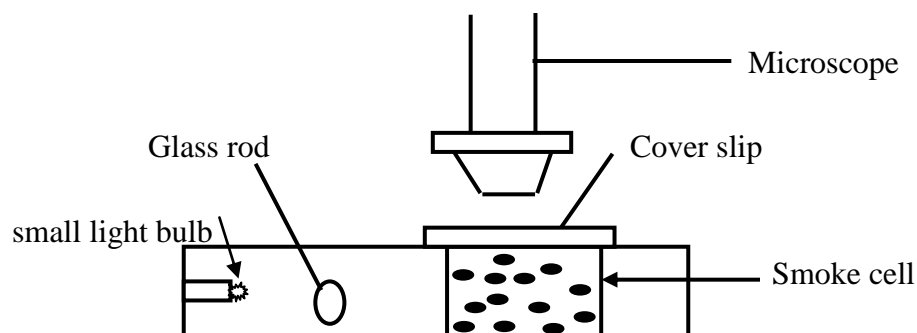
This provides a strong evidence for the presence of moving particles, i.e. in the liquids and gases.

- In gases the movement of particles making up matter can be studied by the **smoke cell experiment**.

In this experiment the smoke cell is illuminated by a beam of light and the smoke particles are seen to move in all directions in a random manner colliding with each other.

This is evident that the smoke particles collide with the invincible air particles hence random motion

#### Illustration



- In liquids suspended pollen grains were observed to be moving in a random motion in a liquid over small distances.

The motion of the suspended pollen grains was caused by water molecules which bombarded them from all sides.

This provides evidence that water molecules are in constant motion

Since the particles are small, few bombardments occur because particles move from one side to another resulting into a random motion.

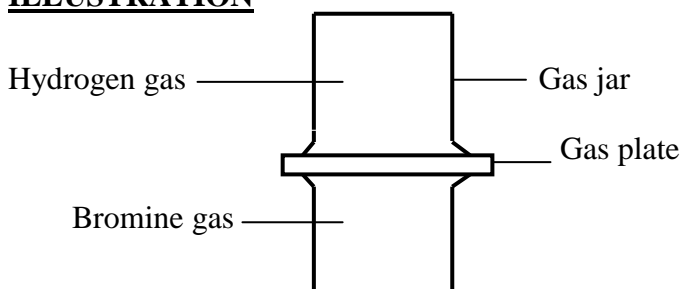
**b) Diffusion;**

This is the uniform spreading of molecules from a region of high pressure to one of low pressure.

In gases and liquids, diffusion can be explained by the idea that liquids and gases have tiny particles. Particles in liquids are able to diffuse but less slowly than those in gases because they have less Kinetic energy.

Diffusion in gases can be investigated by inserting a glass jar full of hydrogen gas over the other full of Bromine gas. After a few seconds, the reddish brown bromine gas spreads throughout the upper gas jar showing that the bromine particles have diffused into the upper jar.

**ILLUSTRATION**



**GRAHAM'S LAW OF DIFFUSION**

States that 'at constant temperature and pressure, the rate of diffusion of a gas is inversely proportion to the square root of its density' i.e.

$$\text{Rate of diffusion} \propto \frac{1}{\sqrt{\text{Density of gas}}}$$

Consider two gases A and B with rates of diffusion  $R_A$  and  $R_B$  respectively and densities  $\rho_A$  and  $\rho_B$  respectively

$$R_A \propto \frac{1}{\sqrt{\rho_A}}$$

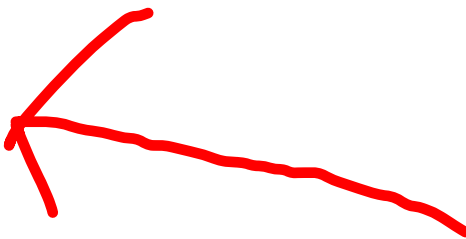
$$R_A = \frac{K}{\sqrt{\rho_A}} \dots\dots\dots(i)$$

$$R_B \propto \frac{1}{\sqrt{\rho_B}}$$

$$R_B = \frac{K}{\sqrt{\rho_B}} \dots\dots\dots(ii)$$

Dividing (i) by (ii)

$$\frac{R_A}{R_B} = \frac{K}{\sqrt{\rho_A}} \div \frac{K}{\sqrt{\rho_B}}$$

$$\frac{R_A}{R_B} = \frac{K}{\sqrt{\rho_A}} \times \frac{\sqrt{\rho_B}}{K}$$


$$\frac{R_A}{R_B} = \sqrt{\frac{\rho_B}{\rho_A}} \dots\dots\dots(*)$$

But also density =  $\frac{\text{mass}}{\text{Volume}}$

If volume is constant, then density is directly proportional to the mass.

Equation (i), becomes

$$R_A \propto \frac{1}{\sqrt{M_A}}$$

$$R_A = \frac{K}{\sqrt{M_A}}$$

$$R_B \propto \frac{1}{M_B}$$

$$R_B = \frac{K}{M_B}$$

$$\frac{R_A}{R_B} = \frac{K}{\sqrt{M_A}} \times \frac{\sqrt{M_B}}{K}$$

$$\frac{R_A}{R_B} = \sqrt{\frac{M_B}{M_A}} \dots\dots\dots(**)$$

Where  $M_A$  = Relative molecular mass of A

$M_B$  = Relative molecular mass of B

Graham's law can also therefore be stated as “**the rate of diffusion of gas at the same conditions of temperature and pressure is inversely proportional to the square root of their relative molecular mass**”

Also rate =  $\frac{1}{\text{time}}$

$$R_A = \frac{1}{t_A}$$

$$R_B = \frac{1}{t_B} \quad \text{Where } t_A \text{ and } t_B = \text{time taken for gas A and B respectively to diffuse.}$$

Substituting for  $R_A$  and  $R_B$  in (\*)

$$\frac{R_A}{R_B} = \sqrt{\frac{\rho_B}{\rho_A}}$$

$$\frac{\frac{1}{t_A}}{\frac{1}{t_B}} = \sqrt{\frac{\rho_B}{\rho_A}}$$

$$\frac{t_B}{t_A} = \sqrt{\frac{\rho_B}{\rho_A}}$$

Also (\*\*) will be;

$$\frac{t_B}{t_A} = \sqrt{\frac{M_B}{M_A}}$$

## Examples

1.(a) State Graham's law

(b) A certain volume of oxygen diffused through a porous membrane in 120s. Under the same condition, the same volume of gas x diffuses in 112s.

Calculate the relative molecular mass of x (UNEB 2004)

### Solution

$$t_{O_2} = 120s, t_x = 112s$$

$$M_{O_2} = (16 \times 2) = 32$$

Let the volume of the gases be  $1\text{cm}^3$

$$R_{O_2} = \frac{1}{120} \text{ cm}^3 \text{ s}^{-1}$$

$$\text{Also } R_x = \frac{1}{112} \text{ cm}^3 \text{ s}^{-1}$$

From Graham's law of diffusion;  $\frac{\text{Rate of diffusion } O_2}{\text{Rate of diffusion of X}} = \sqrt{\frac{M_x}{M_{O_2}}}$

$$\frac{\frac{1}{120}}{\frac{1}{112}} = \sqrt{\frac{M_x}{32}}$$

$$\left(\frac{112}{120}\right)^2 = \left(\sqrt{\frac{M_x}{32}}\right)^2$$

$$\frac{112^2}{120^2} \times 32 = M_x$$

$$M_x = 27.875556$$

$$\approx \mathbf{28}$$

**∴ The relative molecular mass of gas X is = 28.**

2. Nitrogen gas diffuses 1.25 times faster than gases X. calculate the relative molecular mass of gas X.

**Soln**

Let the rate of diffusion of gas X be y

Rate of diffusion of nitrogen = 1.25y

Relative molecular mass of  $N_2 = 14 \times 2$

$$= 28$$

From Graham's law of diffusion;

$$\frac{\text{Rate of diffusion of nitrogen}}{\text{Rate of diffusion of gas X}} = \sqrt{\frac{M_x}{M_{N_2}}}$$

$$\frac{1.25y}{y} = \sqrt{\frac{M_x}{28}}$$

$$(1.25)^2 = \left(\sqrt{\frac{M_x}{28}}\right)^2$$

$$M_x = 1.25^2 \times 28$$

$$= 43.75$$

$$\approx \mathbf{44}$$

**∴ Relative molecular mass of gas X = 44**

3.  $6.3\text{cm}^3$  of gas P diffuses through a porous partition in 5s.  $7.4\text{cm}^3$  of oxygen diffuses through the same partition in the same times. Calculate the molecular mass of P.

**Soln**

From Graham's Law of diffusion;

$$\text{Rate of diffusion of p} = \frac{\text{Volume}}{\text{time}} = \frac{6.3}{5} \text{ cm}^3\text{s}^{-1}$$

$$\text{Rate of diffusion of O}_2 = \frac{7.4}{5} \text{ cm}^3\text{s}^{-1}$$

$$\frac{\text{Rate of diffusion of gas P}}{\text{Rate of diffusion of O}_2} = \sqrt{\frac{M_{O_2}}{M_p}}$$

$$\frac{\frac{6.3}{5}}{\frac{7.4}{5}} = \sqrt{\frac{32}{M_p}}$$

$$\left(\frac{6.3}{5} \times \frac{5}{7.4}\right)^2 = \left(\sqrt{\frac{32}{M_p}}\right)^2$$

$$\frac{31.5}{37} = \frac{32}{M_p}$$

$$\mathbf{M_p = 44}$$

4. The rate of diffusion of gas A: B is in a ratio of 2:1. If the RMM of A is 16, calculate the RMM of B.

**Solution**

$R_A = 2$ , RMM of A = 16,

$R_B = 1$ , RMM B = ?

From Graham's law of diffusion

$$\frac{\text{Rate of diffusion of A}}{\text{Rate of diffusion of B}} = \sqrt{\frac{M_B}{M_A}}$$

$$\left(\frac{2}{1}\right)^2 = \left(\sqrt{\frac{M_B}{M_A}}\right)^2$$

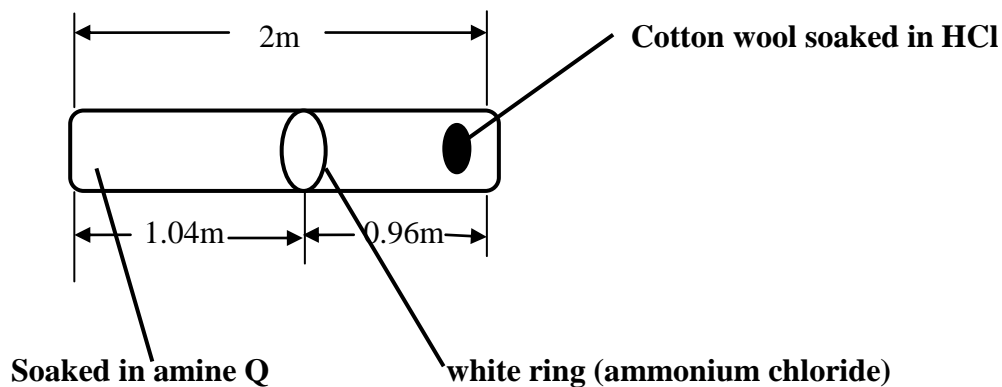
$$4 = \frac{M_B}{16}$$

$$M_B = 64$$

**∴ The Relative molecular mass of B is 64.**

5. Two pieces of cotton wool one soaked in concentrated amine Q and the other in concentrated Hydrochloric acid, were placed at opposite ends of a 2m long glass tube. After some time a white ring was formed at 0.96m from the end containing conc. HCl. Determine the relative molecular mass of amine Q. (H = 1, Cl =35.5)

**Soln:**



If time of diffusion of HCl and Q = x s

$$\text{Rate of diffusion of HCl} = \frac{0.96}{x} \text{ ms}^{-1}$$

$$\text{Rate of diffusion of amine Q} = \frac{1.04}{x} \text{ ms}^{-1}$$

$$\text{From Graham's law of diffusion; } \frac{R_{\text{HCl}}}{R_{\text{Q}}} = \sqrt{\frac{M_{\text{Q}}}{M_{\text{HCl}}}}$$

$$\text{But } M_{\text{HCl}} = 1 + 35.5 = 36.5$$

$$\frac{\frac{0.96}{x}}{\frac{1.04}{x}} = \sqrt{\frac{M_{\text{Q}}}{36.5}}$$

$$\frac{0.96^2}{1.04^2} = \frac{M_{\text{Q}}}{36.5}$$

$$\underline{M_{\text{Q}} \approx 31}$$

**The Relative Molecular Mass of amine Q is 31**

**Trial questions**

1. A given volume of gas Z diffuses through a hole in 14.1s while the same volume of CO<sub>2</sub> diffuses through the same hole in 10s, calculate the RMM of gas Z(C=12, O=16)
2. Oxygen diffuses 1.19 times faster than amine P; determine the RMM of amine P.

**Solution:**

Let the volume of gas Z and CO<sub>2</sub> be 1cm<sup>3</sup>

$$t_z = 14.1\text{s}$$

$$M_{\text{CO}_2} = 12 + (16 \times 2) = 44, M_z = ?$$

$$t_{\text{CO}_2} = 10\text{s}$$

From Graham's law of diffusion;

$$\frac{\text{Rate of diffusion of CO}_2}{\text{Rate of diffusion of gas Z}} = \sqrt{\frac{M_Z}{M_{\text{CO}_2}}}$$

$$\Rightarrow \frac{1}{10} / \frac{1}{14.1} = \sqrt{\frac{M_Z}{44}}$$

$$\left(\frac{14.1}{10}\right)^2 = \left(\sqrt{\frac{M_Z}{44}}\right)^2$$

$$\frac{14.1^2}{10^2} = \frac{M_Z}{44}$$

$$M_Z = \frac{14.1^2}{10^2} \times 44$$

$$= 87.4764$$

$$\approx \mathbf{87.5}$$

**The Relative molecular mass of gas z is 87.5**

2. Let the rate of diffusion of amine P = X

$\Rightarrow$  The rate of diffusion of Oxygen = 1.19x

$$M_{\text{O}_2} = 16 \times 2 = 32$$

$$M_p = ?$$

From Graham's law of diffusion;

$$\frac{\text{Rate of diffusion of gas P}}{\text{Rate of diffusion of Oxygen}} = \sqrt{\frac{M_{\text{O}_2}}{M_p}}$$

$$\Rightarrow \frac{x}{1.19x} = \sqrt{\frac{32}{M_p}}$$

$$\left(\frac{1}{1.19}\right)^2 = \left(\sqrt{\frac{32}{M_p}}\right)^2$$

$$M_p = 1.19^2 \times 32 = 45.3152$$

$$\approx \mathbf{45}$$

**$\therefore$  The relative molecular mass of gas P is 45**

### ***HOMEWORK***

1. The rate of diffusion of a volatile fluoride containing 32.29% fluorine is 13.72 times as slow as that of hydrogen. Establish the formula of this fluoride and the RAM of the metal.
2. A gas X diffuses 4 times as rapidly as Sulphur dioxide under the same condition. If the density of Sulphur dioxide at the given temperature and pressure is  $2.88 \times 10^3 \text{ g/m}^3$ , what is the density of X.
3. Oxygen diffuses 0.9 times faster than a hydrocarbon Q, calculate the relative molecular mass of Q.

4. The time taken for  $0.06\text{cm}^3$  of oxygen to diffuse through a porous partition is 10s. Another gas Z at the same conditions of temperature and pressure diffuses through the partition at the rate of  $0.1\text{cm}^3$  in 20s. Determine the RMM of gas Z

### **FACTORS AFFECTING DIFFUSION**

**i. Density:**

Lighter gases diffuse faster than the heavier ones.

**ii. Temperature:**

The rate of diffusion increases with the increase in temperature because the Kinetic energy of the particles also increases due to the increasing temperatures.

### **APPLICATIONS OF DIFFUSION**

**1. Air bags**

In a car collision, drivers suffer injury or death by being thrown forward onto the dash board.

Now are fitted with air bags in the steering wheel that is inflated between the driver and dash board on impact.

After the driver hits the bag, the gas diffuses out through the small holes in the bag in order for the bag to deflate / reduce in size for the driver to live.

**2. Separation of uranium.**

During the separation of uranium 238, natural uranium consists of both uranium 235 and uranium 238.

In order to separate  $U_{238}$  from  $U_{235}$ , the metal is first converted into  $UF_6$  (hexafluorouranium) The vapor of  $UF_6$  is then allowed to diffuse across porous nickel sheets.

The vapor is then reconverted to the metal and is found to contain mostly of a lighter uranium 235 than uranium 238.

**3. Use of perfumes, tear gas and pesticides.**

When perfumes are sprayed/teargas is released into an area, their molecules are under high pressure.

The high pressures causes them to move thereby diffusing to different regions of lower pressure and hence are able to be smelt / sensed in different places by people and other things.

**4. Extraction of Helium from natural gas.**

Helium may be found in a mixture of hydrocarbons or generally natural gas. In separating the two, the mixture of helium and natural gas is allowed to pass across a very thin sheet of Pyrex glass. Helium being lighter than the other hydrocarbon present in the natural gas will diffuse faster and hence is separated / extracted.

**NOTE:** Effusion is the escape of a gas through a small hole. Graham's law also applies to effusion hence the rate of effusion of a gas is inversely proportional to the square root of its density.

### **FACTORS AFFECTING EFFUSION**

- Density of a gas
- Temperature of the surrounding
- Size of the hole

### **KINETIC THEORY OF GASES**

The theory is mainly useful in accounting for the known properties of gases but it also clarifies many problems concerned with liquids and solids.

#### **Properties of gases:**

- Are compressible: This is because the inter-molecular forces of attraction between the molecules of gases are negligible.
- Diffuse faster because they are lighter than liquids and solids.
- Have low densities / molecular masses
- They expand on heating due to the weakening /breaking of the weak intermolecular forces of attraction.
- Shows a large change in volume with change in pressure
- They are transparent and the degree of transparency depends on density.

#### **ASSUMPTION OF KINETIC THEORY OF GASES:**

- Gases consist of small particles called molecules.
- Molecules are in a state of rapid random motion colliding with one another and with the walls of the container hence constituting pressure.
- The collisions of the molecules are perfectly elastic i.e. there is no loss of Kinetic energy. In perfectly elastic collision, loss of Kinetic Energy by one molecule is balanced by an equal gain by another.
- The average kinetic energy of the molecules is directly proportional to the average Kelvin temperature.

### **GAS LAWS FOR IDEAL GAS.**

#### **Boyle's law:**

States that "at constant temperature, the pressure of a fixed mass of gas is inversely proportional to its volume" i.e.

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

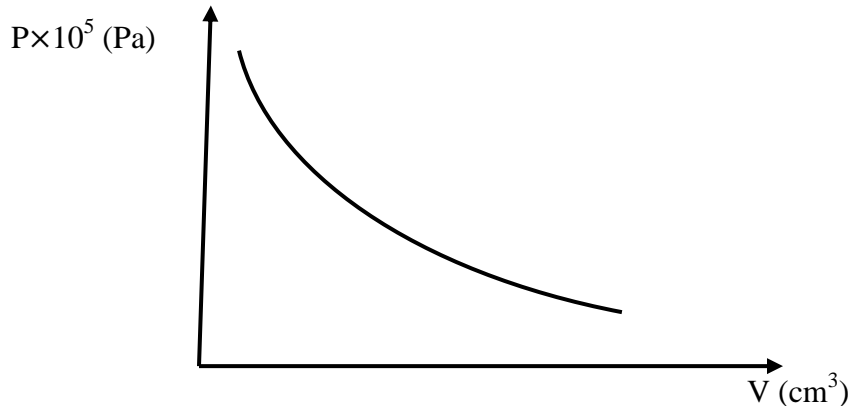
$$P = \frac{K}{V}$$

$$PV = K \text{ (constant)}$$

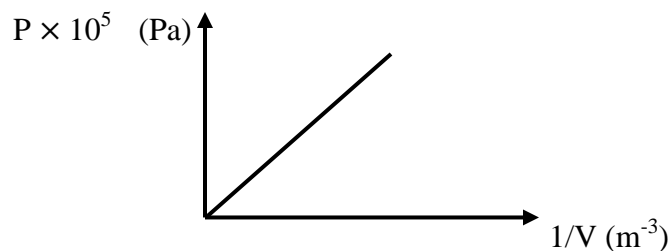
If the pressure of a gas is increased from  $P_1$  to  $P_2$  then the volume decrease from  $V_1$  to  $V_2$

$$P_1 V_1 = P_2 V_2$$

✓ **A plot of pressure of a gas against its volume**



✓ **A plot of pressure of a gas against reciprocal of volume of gas**



### **Charles' law:**

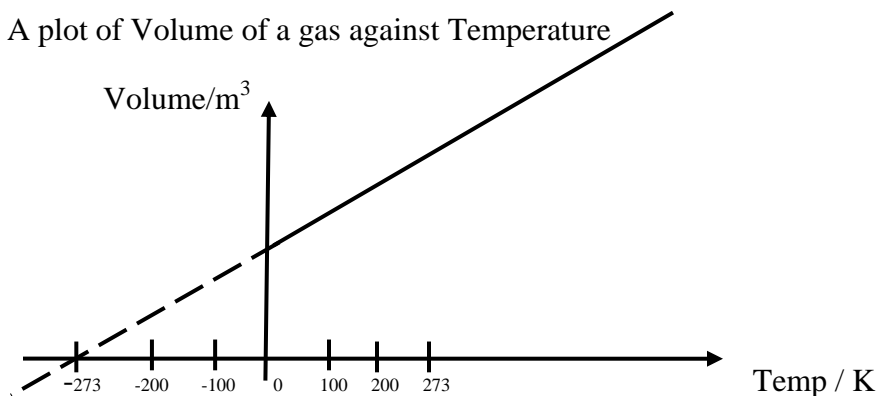
✓ It states that “at constant pressure, the volume of a fixed mass of gas is directly proportional to its temperature” i.e.  $V \propto T$ ;  $V = KT$

$$V/T = K \text{ (constant)}$$

If the temperature of a gas is increased from  $T_1$  to  $T_2$  the volume also increases from  $V_1$  to  $V_2$ .

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

- ✓ A plot of Volume of a gas against Temperature



### Pressure law / Gay Lussac's Law;

- ✓ States that “pressure of a fixed mass of gas is directly proportional to the absolute temperature at constant volume” i.e.  $P \propto T$        $P = KT$

$$\frac{P}{T} = K \text{ (constant)}$$

If the temperature of the gas is increased from  $T_1$  to  $T_2$  at constant volume, the pressure increases from  $P_1$  to  $P_2$

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

Boyles' Law and Charles' law can be combined to give a single equation representing the relation between pressure, volume and Kelvin of a given mass of a gas under different conditions.

If a given mass of gas has a volume,  $V_1$  at a pressure,  $P_1$ ; it will have a volume,  $V_x$  at a pressure,  $P_2$  at constant temperature.

⇒ From Boyle's law;

$$P_1 V_1 = P_2 V_x \text{ _____ (i)}$$

Changing the temperature at which  $V_x$  is measured from  $T_1$  to  $T_2$ , the new volume of a gas  $V_2$  will be given by Charles' law as

$$\frac{V_x}{T_1} = \frac{V_2}{T_2} \text{ _____ (ii)}$$

Making  $V_x$  the subject (ii) and substituting in (i) will obtain.

$$V_x = \frac{V_2 T_1}{T_2} \text{ _____ (*)}$$

Substituting \* into (i)

$$\Rightarrow P_1 V_1 = P_2 \left( \frac{V_2 T_1}{T_2} \right)$$

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

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

$$\text{Generally } \frac{PV}{T} = K \text{ (Constant) _____ (iii)}$$

From (iii)  $PV = \text{constant} \times T$

Constant = R

$PV = RT$  for 1 mole.

**$PV = nRT$**  for n moles.

The constant is the **molar gas constant, R**

For 1 mole of a gas  $PV = RT$

For n moles of a gas;  **$PV = nRT$** : ideal gas equation

### **CALCULATION OF THE VALUE OF MOLAR GAS CONSTANT(R)**

Value of **R** depends on the units adopted for the quantities in the ideal gas equation i.e for 1 mole of a gas at S.T.P,  $P=101325\text{Nm}^{-2}$ ,  $T = 273\text{K}$  and  $V(22.4/1000 = 0.0224\text{m}^3)$   $R = ?$   $n = 1$

From,  $PV = nRT$

$$R = PV/nT = \frac{(101325 \times 0.0224)}{(1 \times 273)}$$

$$\mathbf{R = 8.314J \text{ mole}^{-1} \text{ K}^{-1}}$$

But if pressure is in atmospheres,

$P = 1$  atmospheric pressure

$T = 273\text{K}$

$$\begin{aligned} V = 22.4\text{dm}^{-3}; R = PV/nT &= \frac{(1 \times 22.4)}{(1 \times 273)} \\ &= 0.082051282 \end{aligned}$$

$$\mathbf{R = 0.08205 \text{ atmosphere dm}^3 \text{ mol}^{-1} \text{ K}^{-1}}$$

### **Examples.**

1. A certain mass of a gas has a volume of  $241\text{m}^3$  at  $18^\circ\text{C}$  and  $100400\text{Pa}$ . what would be its volume at s.t.p.

#### **Solution;**

$$\begin{aligned} \text{From } \frac{P_1 V_1}{T_1} &= \frac{P_2 V_2}{T_2} \\ V_2 &= \frac{P_1 V_1 T_2}{P_2 T_1} = \frac{100400 \times 241 \times 273}{291 \times 101325} = 224.03 \approx \mathbf{224 \text{ m}^3} \end{aligned}$$

2. A closed bulb contains a certain volume of a gas at  $21^\circ\text{C}$  and  $100700\text{Pa}$ . find :

- i. the pressure of the gas if the temperature is raised to 51<sup>0</sup>C
- ii. The temperature to which the bulb must be heated to double the pressure.

**Solution:**

(i) Using Pressure Law;

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

$$P_2 = \frac{P_1 T_2}{T_1} = \frac{100700 \times 324}{294} = \mathbf{110975.5Pa}$$

ii) Using Pressure Law;

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

$$T_2 = \frac{P_2 T_1}{P_1} = \frac{(2 \times P_1 \times 294)}{(P_1)} = \mathbf{588K}$$

**Questions**

- 1) 2.20g of carbon dioxide occupies 1166cm<sup>3</sup> at 15<sup>0</sup>C and 12700Pa pressure. calculate the value of the gas constant, R in J mol<sup>-1</sup>K<sup>-1</sup>
- 2) A sealed flask contains oxygen at 17<sup>0</sup> C and 99300Pa pressure. what would be the pressure of oxygen if the temperature was lowered to -23<sup>0</sup> C?

**DENSITY AND MOLAR MASS OF A GAS**

The density of a gas is found by weighing unknown volume of a gas. From PV = nRT, but number of moles (n) =  $\frac{\text{mass of gas (m)}}{\text{molar mass of gas (M)}}$

$$n = m/M$$

$$PV = m/MRT$$

$$PVM = mRT$$

$$PM = \frac{mRT}{V} \dots\dots\dots 1$$

Recall: density of a gas (ρ) = mass of gas /volume of gas = m/v

$$PM = \rho RT$$

$$\mathbf{M = \rho RT/P}$$

### Example :

1. At 273K and  $1.01 \times 10^5 \text{Nm}^{-2}$ , 6.319g of a gas X occupy  $2\text{dm}^3$ . Determine the molar mass of gas X ( $R = 8.314\text{Jmol}^{-1}\text{K}^{-1}$ )

#### Soln

$$T = 273\text{K}, P = 1.01 \times 10^5 \text{Nm}^{-2}, m = 6.319\text{g}, V = 2\text{dm}^3 = 2 \times 10^{-3} \text{m}^3$$

$$\text{From } PV = m/MRT$$

$$M = mRT/PV$$

$$\underline{\underline{M = 71\text{g}}}$$

2. Calculate the molar mass of a gas with a density of  $2.615\text{gdm}^{-3}$  at 298K and  $101\text{Nm}^{-2}$  ( $R = 8.314\text{Jmol}^{-1}\text{K}^{-1}$ )

#### Solution

$$PV = \frac{m}{M}RT$$

$$M = \frac{mRT}{pv} = \frac{2.615 \times 8.314 \times 298}{101 \times 0.001} = 64.15 \approx \underline{\underline{64.2\text{g}}}$$

3. An ideal gas occupies  $225\text{cm}^3$  at 280K and  $4.8 \times 10^5 \text{Nm}^{-2}$  pressure. Determine the number of moles of gas present ( $R = 8.314\text{Jmol}^{-1}$ )

### DALTON'S LAW OF PARTIAL PRESSURE

Partial pressure of a gas *is the pressure which that gas exerts if it occupies a vessel alone which was initially occupied by a mixture of gases.*

Dalton's law states that *"the total pressure of a mixture of gases is equal to the sum of their partial pressures"*.

Consider gases A and B placed in a vessel having partial pressures  $P_A$  and  $P_B$  respectively. According to Dalton's law of partial pressure;

Total pressure ( $P_T$ ) = Partial pressure of A + Partial pressure of B

$$P_T = P_A + P_B \text{ _____ (i)}$$

If gases A and B have their number of moles as  $n_A$  and  $n_B$  respectively,

Total number of moles,  $n_T = n_A + n_B$

## Mole fraction of a gas

Is the ratio of the number of moles of a component of a gas to the total number of moles of the components of the gases in the mixture.

Mole fraction is denoted by X

$$\text{For gas A, } X_A = \frac{n_A}{n_A + n_B} = \frac{n_A}{n_T}$$

$$\text{For gas B, } X_B = \frac{n_B}{n_A + n_B} = \frac{n_B}{n_T}$$

Also applying the ideal gas equation;  $PV = nRT$ .

$$\text{From (i) } P_T V = n_T RT. \quad *$$

$$\text{For gas A: } P_A V = n_A RT. \quad **$$

$$\text{For gas B; } P_B V = n_B RT. \quad ***$$

Dividing \*\* and \*\*\* by \*

$$\frac{P_A V}{P_T V} = \frac{n_A RT}{n_T RT}$$

$$P_A = \frac{n_A}{n_T} P_T \quad (1)$$

$$\frac{P_B V}{P_T V} = \frac{n_B RT}{n_T RT}$$

$$P_B = \frac{n_B}{n_T} P_T \quad (2)$$

From (1) and (2), partial pressure is therefore the *product of the mole fraction of the gas and the total pressure of the gases in the mixture.*

Also from  $P_T = P_A + P_B$

$$P_T = \frac{n_A}{n_T} P_T + \frac{n_B}{n_T} P_T$$

$$P_T = X_A P_T + X_B P_T, \quad P_T = (X_A + X_B) P_T$$

$$\Rightarrow X_A + X_B = 1$$

From the expression above, the **sum of all mole fractions is equal to 1** .

## Examples

1. 12g of Nitrogen, 0.4g of Hydrogen and 9g of Oxygen are put in a 1 litre vessel at a pressure of 22.4 atmospheres. Calculate the partial pressures of the respective gases (N = 14, H = 1, O = 16)

### Soln:

Relative molecular mass of  $H_2 = 1 \times 2 = 2$

$$O_2 = 16 \times 2 = 32$$

$$N_2 = 14 \times 2 = 28$$

$$\begin{aligned} \text{Number of moles of } H_2 &= \frac{0.4}{2} \\ &= 0.2 \text{ moles} \end{aligned}$$

$$\text{Number of moles of } N_2 = \frac{12}{28} = 0.43 \text{ moles}$$

$$\text{Number of moles of } O_2 = \frac{9}{32} = 0.28 \text{ moles}$$

$$\begin{aligned} \text{Total number of moles} &= 0.2 + 0.43 + 0.28 \\ &= 0.91 \text{ moles} \end{aligned}$$

But total pressure = 22.4 atmospheres

Partial pressure of gas = Mole fraction of gas  $\times$  Total pressure

$$\text{Partial pressure of } O_2 = \frac{0.28}{0.91} \times 22.4 = \mathbf{6.89 \text{ atmospheres}}$$

$$\text{Partial pressure of } N = \frac{0.43}{0.91} \times 22.4 = 10.585 = \mathbf{10.59 \text{ atmospheres}}$$

$$\text{Partial pressure of } H = \frac{0.2}{0.91} \times 22.4 = \mathbf{4.92 \text{ atmospheres}}$$

2. 2.6g of Carbon dioxide and 4.8g of Oxygen were mixed in a 1 litre vessel. If the total pressure of the mixture is 100 atmospheres, calculate the partial pressure of each gas present in the container. (C = 12, O = 16)

### Soln

Relative molecular mass of  $CO_2 = 12 + (16 \times 2) = 44$

$$O_2 = (16 \times 2) = 32$$

$$\text{Number of moles of Carbon dioxide} = \frac{2.6}{44} = \mathbf{0.06 \text{ moles}}$$

$$\text{Number of moles of Oxygen} = \frac{4.8}{32} = \mathbf{0.15 \text{ moles}}$$

P = 100 atmospheres and Total number of moles = **0.21 moles**

Partial pressure of a gas = Mole fraction of a gas  $\times$  Total pressure

$$\Rightarrow \text{Partial pressure of } CO_2 = \frac{0.06}{0.21} \times 100 = \mathbf{38.57 \text{ atmospheres}}$$

$$\text{Partial pressure of } O_2 = \frac{0.15}{0.21} \times 100 = \mathbf{71.43 \text{ atmospheres}}$$

3. At constant temperature, a vessel contains two gases, A and B and the pressure of A is  $0.5 \times 10^{-5}$  mmHg and its mole fraction is 0.7.
- Calculate the partial pressure of B.
  - Calculate the total pressure exerted by a mixture of the gasses.

**Soln**

Let the partial pressure of gas A, =  $P_A$ , ( $0.5 \times 10^{-5}$  mmHg)

Mole fraction of A ( $X_A$ ) = 0.7

Let the partial pressure of B =  $P_B$  and mole fraction,  $X_B$

$$X_A + X_B = 1$$

$$\Rightarrow X_B = 1 - X_A$$

$$= 1 - 0.7 = 0.3$$

But partial pressure of A = Mole fraction of A  $\times$  Total pressure

$$\Rightarrow 0.5 \times 10^{-5} = 0.7 \times \text{total pressure}$$

$$\begin{aligned} \text{Total pressure} &= \frac{0.5 \times 10^{-5}}{0.7} \\ &= \mathbf{7.14 \times 10^{-6} \text{ mmHg}} \end{aligned}$$

But  $P_A + P_B = P_{\text{total}}$

$$P_B = P_{\text{total}} - P_A$$

$$= (7.14 \times 10^{-6} - 0.5 \times 10^{-5})$$

$$= \mathbf{2.14 \times 10^{-6} \text{ mmHg}}$$

**$\therefore$  The partial pressure of B is  $2.14 \times 10^{-6}$  mmHg**

4.  $400\text{cm}^3$  of gas A at 2 atmospheres and  $200\text{cm}^3$  of gas B at 1 atmosphere are put in a  $500\text{cm}^3$  container at the same time. Calculate the total pressure in the container.

**Soln:**

Let the partial pressure of A and B be  $P_A$  and  $P_B$  respectively

$400\text{cm}^3$  of gas of A exerts 2 atmospheres

$500\text{cm}^3$  of gas A will exert  $(\frac{2 \times 500}{400})$  atmospheres = 2.5 atmospheres

$200\text{cm}^3$  of gas B exerts 1 atmosphere

$500\text{cm}^3$  of gas B will exert  $(\frac{1 \times 500}{200})$  atmospheres = 2.5 atmospheres

$\therefore$  Total pressure = 2.5 + 2.5, from  $P_A + P_B = P_{\text{total}}$

$$= \mathbf{5 \text{ atmospheres}}$$

## REAL GASES AND IDEAL GASES

**Ideal gas** is one which obeys all gas laws accurately.

Have *no intermolecular forces of attraction* and also *negligible volume*.

**Real (perfect) gas** is one which doesn't obey the ideal gas equation.

This is because intermolecular forces of attraction have a significant effect on the pressure and their volumes are not negligible. e.g. Ammonia, Helium, Nitrogen, Oxygen and Methane.

*Recall the assumptions of the Kinetic theory of an ideal gas;*

An ideal gas is made up of small invisible particles; molecules with negligible intermolecular forces of attraction between them and occupy zero volume.

Gases tend towards ideal behavior at conditions of **high temperature** and **low pressure**.

However, at conditions of **low temperatures** and **high pressures**, deviation from ideal behavior occurs.

### Causes of deviation from ideal gas behavior

#### **i. Intermolecular forces of attraction**

An ideal gas is assumed to have negligible intermolecular forces of attraction, however  
At high pressure;

- Vander Waal forces of attraction become more pronounced/ significant because the molecules have insufficient energy to overcome the forces of attraction.
- Molecules become close together hence resulting into deviation from ideal gas behavior.
- attractive forces between the molecules decreases volume occupied by the gas , gas molecules are very close together; real gas volume < ideal gas volume

At low temperatures;

- Energy of the molecules decreases, collision energy between molecules is therefore low, intermolecular forces of attraction become more significant, molecules become close together hence resulting into deviation from ideal gas behavior.

#### **ii. Co – volume (molecular volume, $V_m$ )**

At very high pressure, repulsive forces between the molecules/molecular sizes molecules themselves become significant, increasing the volume occupied by the gas; real gas volume > ideal gas volume.

## COMPRESSIBILITY FACTOR (Z)

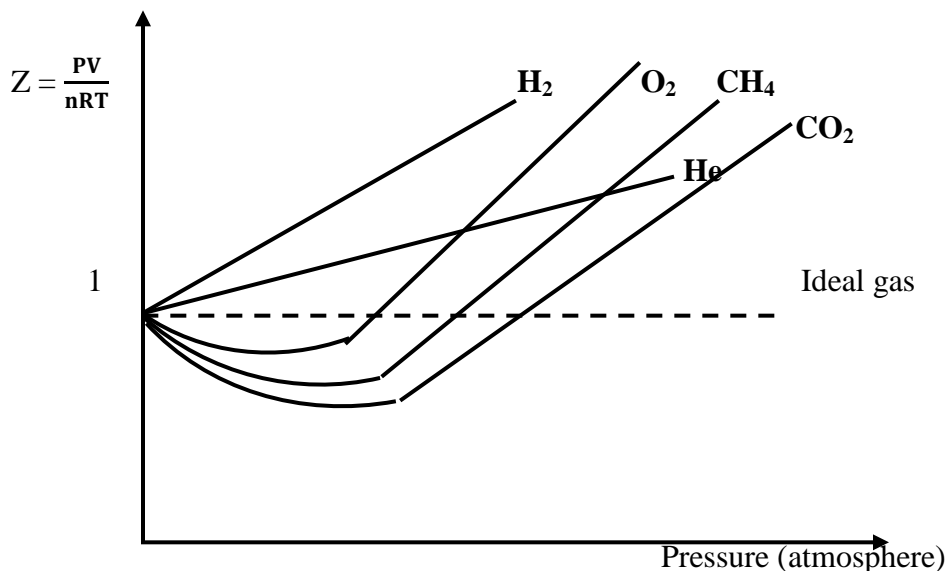
Is a measure of deviation of a real gas from ideal gas behavior.

It is given by  $Z = \frac{PV}{RT}$  where V= volume occupied by one mole of gas at temperature; T and pressure P.

The value of  $Z$  for an ideal gas is one (constant) and it is represented by a straight line parallel to the pressure axis.

For real gases,  $Z$  only approaches the value of 1 at very low pressures. At other pressures  $Z$  may be greater than 1 (meaning that the gas cannot easily be compressed than an ideal gas) or less than 1.

**A graph of  $\frac{PV}{nRT}$  against pressure for different gases at the same temperature**



### Description of the curve

i. **Carbon dioxide**

The curve falls much more than that of methane; because increase in pressure brings about stronger molecular attraction; which is due to the bigger molecular size of  $\text{CO}_2$  compared to the methane molecule.

For both  $\text{CO}_2$  and  $\text{CH}_4$ , the value of  $Z$  increases with increase in pressure because the effect of molecular volume overcomes that of molecular attraction. The deviation of  $\text{CO}_2$  is more significant than that of  $\text{CH}_4$ .

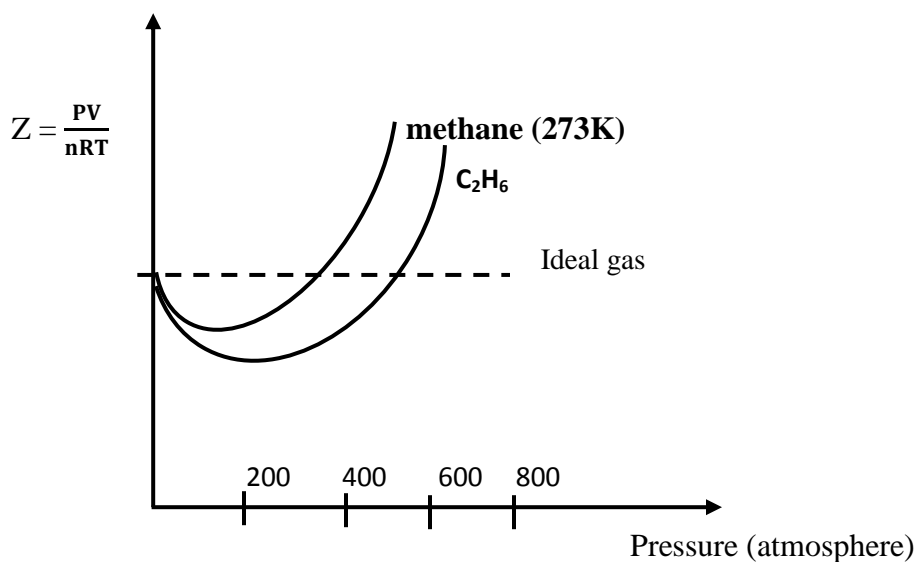
ii. **Hydrogen and noble gases**

For  $\text{H}_2$  and noble/ rare gases,  $Z$  is greater than 1 which makes these gases very difficult to compress.

$Z$  increases from the beginning because deviation due to molecular volume is greater than one due to molecular attraction at all pressures. The molecules of hydrogen repel each other strongly thus this repulsion increases the volume of a gas.

**Example:**

A plot of  $Z$  against pressure for one mole of methane of 273K is as shown below. Use the graph to answer the questions that follow.



**QUESTIONS**

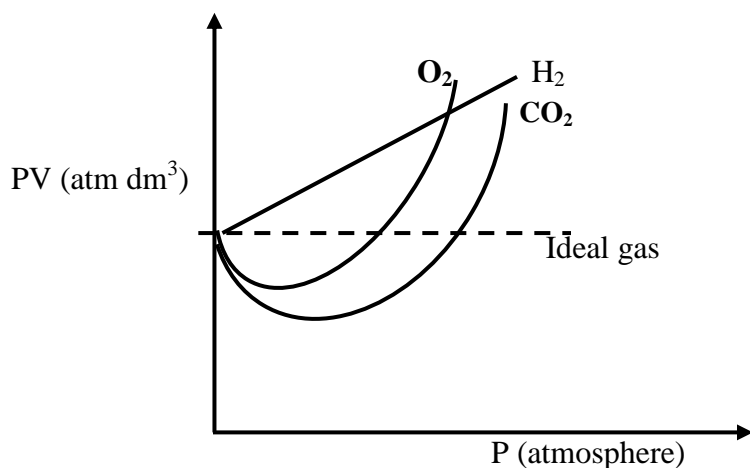
- a) Give reasons for the behavior of methane at 273K when the pressure is;
  - i. Lower than 200 atmospheres
  - ii. Higher than 200 atmospheres
- b) On the same graph, sketch a graph of  $C_2H_6$  at 273K and give reasons for your sketch, label the graph X.

**Solns:**

- (a) i. As pressure increases from Zero atmosphere, Van der Waal's forces of attractions between  $CH_4$  molecules are very significant, due to the closeness of the molecules as compared to molecular volume.  
There is a slight fall in compression factor,  $Z$  due to the effect of molecular attraction.
- ii) As the pressure increases beyond 200 atmospheres, the effect of molecular volume can no longer be ignored and it overcomes that of molecular attraction in the gas. This leads to an increase in the compressibility factor hence the rise of the graph.
- (b) Reasons, having sketched  
The graph falls much more for ethane than for methane ; the molecular size of the molecules of ethane is more than that of  $CH_4$ ; because of increase in pressure, stronger molecular attractions occur in ethane.  
The compressibility factor rises as the pressure increases because the effect of molecular volume in ethane is more significant than that in  $CH_4$ .

### Exercises:

1. The curves below show the deviations of some gases from ideal behavior.



- i) State why Hydrogen shows a small deviation from ideal behavior compared to other gases.
- ii) Compare the deviation of O<sub>2</sub> and CO<sub>2</sub> from ideal behavior.

### Solutions

- i) Since Hydrogen has compressibility factor greater than 1, this makes it very difficult to compress. It therefore shows a small deviation from ideal behavior due to effect of molecular volume (co - volume) is greater than one due to molecular attraction at all pressures since hydrogen molecules repel each other.
- ii) The deviation of Carbon dioxide is more than that of Oxygen because carbon dioxide has a higher relative molecular mass compared to that of Oxygen; increasing the forces of attraction between Carbon dioxide molecules, reducing the volume occupied by carbon dioxide molecules.

### MODIFICATION OF THE IDEAL GAS EQUATION

a) Correction of the finite volume of the molecules.

Gas molecules occupy some volume and therefore space in which the molecules can move is less than total volume of the gases by an equal amount equal to the finite volume of the molecules.

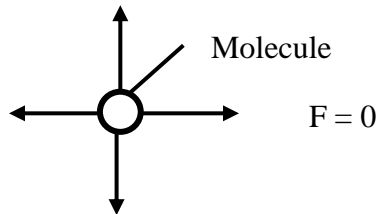
Ideal volume ( $V_i$ ) is obtained by subtracting the volume occupied by the molecules from the total volume of the gas ( $V$ )

If  $b$  is the volume occupied by molecules in 1 mole of gas, the volume occupied by  $n$  molecules of gas is  $nb$ .

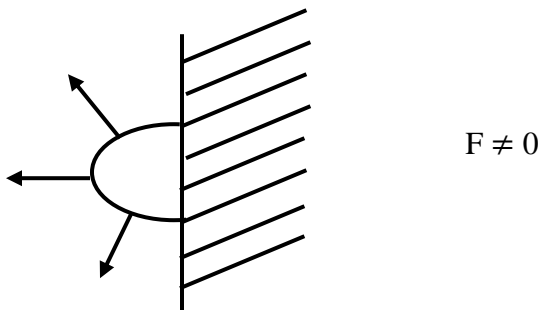
$$V_i = (V - nb) \quad \text{(i)}$$

b) Correction of attractive forces operating between the molecules.

A molecule within the interior of the gas is surrounded by other molecules equally in all directions and thus the net force of attraction on it is zero.



However, when it approaches the wall of the container, it experiences a retarding force due to the attractive forces towards the centre of the vessel by the molecules inside the container.



Due to this one sided molecular attraction, the force with which the molecule strikes the wall will be less than the force if there was no inward pull and thus the measured pressure,  $P$  is less than the Pressure  $P_i$  by an amount  $P'$ . **i.e  $P = P_i - P'$**

$$\Rightarrow P_i = P + P'$$

Force of attraction exerted on the molecule when it is going to strike the wall is directly proportional to the number of molecules per unit volume in the body of the gas. Also, the number of molecules striking the wall is proportional to the number of molecules per unit volume of the gas.

If  $V$  is the volume occupied by  $n$  moles of the gas, then both these factors and hence the correction term  $P'$  is directly proportional to  $\frac{n^2}{V^2}$

Ie  $P' \propto \frac{n^2}{V^2} \Rightarrow P' = \frac{an^2}{V^2}$  where  $a$  – constant characteristic of a particular gas.

From  $P_i = P + P'$

$$\Rightarrow P_i = P + \frac{an^2}{V^2} \text{ (ii)}$$

Therefore from  $PV = nRT$ , the modified equation is

$$\left( P + \frac{an^2}{V^2} \right) (V - nb) = RT$$

$$\text{For one mole, } \left( P + \frac{a}{V^2} \right) (V - b) = RT$$

The constants  $a$  and  $b$  are known as Van der Waals constants and their magnitudes depend on the type of the gas and units which pressure and volume are expressed.

### Examples;

1. Calculate the pressure exerted by 1 mole of  $H_2O$  vapor in 20L at  $27^\circ C$  Using;

- Ideal gas equation
- Van der waals equation.

The values of Van der waals constants  $a$  and  $b$  for water vapor are  $5.464 \text{ l}^2 \text{ atmosphere mole}^{-2}$  and  $0.03049 \text{ l mole}^{-1}$  respectively.

#### Solution

$$T = (23 + 273) = 300K$$

$$\text{Volume} = 20 \text{ liters}$$

$$R = 0.082$$

$$\text{a) } PV = nRT$$

$$P = \frac{nRT}{V} = \frac{0.082 \times 300}{20} = \underline{\underline{1.23 \text{ Atmospheres}}}$$

$$\text{b) } \left( P + \frac{an^2}{V^2} \right) (V - nb) = nRT$$

$$\left( P + \frac{an^2}{V^2} \right) (V - nb) = RT$$

$$P = \left[ \frac{RT}{V-b} \right] - \left( \frac{a}{V^2} \right)$$

$$= \left[ \frac{0.082 \times 300}{20 - 0.03049} \right] - \left( \frac{5.464}{20^2} \right)$$

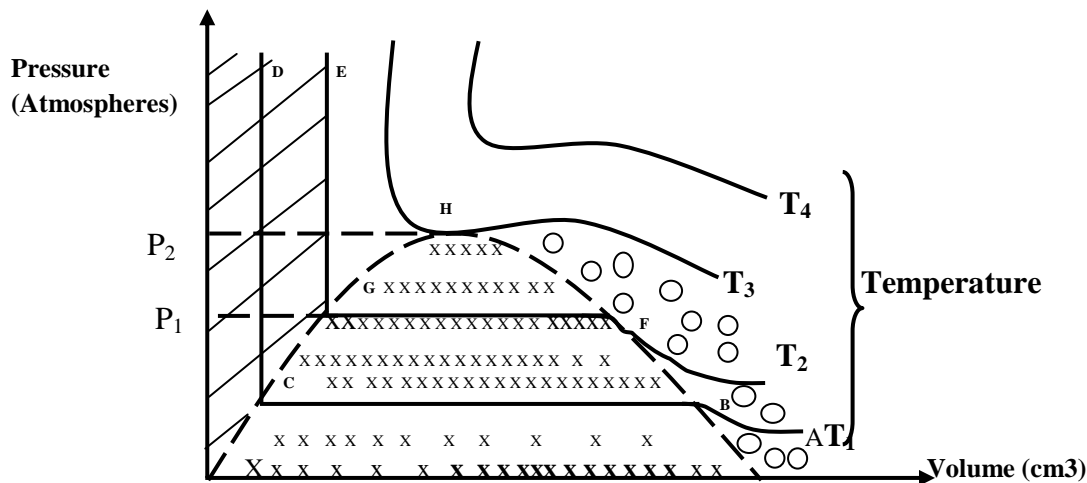
$$= 1.2182 \underline{\underline{\text{Atmospheres}}}$$

## CONDENSATION OF GASES


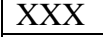
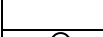

When a gas is sufficiently compressed, it condenses and turns into a liquid. The effect of condensation of gases was studied by Andrews using CO<sub>2</sub> gas subjected to various pressures while changing temperatures.

Curves for a particular temperature (Isotherms were obtained by plotting Pressure against temperature)

### Isotherms for Carbon dioxide



KEY

	Liquid
	Liquid and vapour
	Permanent gas (Ideal gas)
	Vapor

### Points

- i. **A:**  
Carbon dioxide will be in the gaseous state and as pressure is gradually increased the volume decreases hence between A and B, the gas obeys Boyle's law.
- ii. **B:**  
The gas begins to liquefy and there is a constant rapid decrease in volume with very little increase in pressure. This is because the liquid formed has a very high density.
- iii. **C:**  
Liquefaction is complete and any further increase in pressure from C to D results in a slight decrease of volume since liquids cannot be easily compressed compared to gases.
- iv. **Region BCH**

Here the gas is in equilibrium with the liquid. At higher temperatures such as  $T_2$ , a similar path EFG is followed, however above  $T_3$  it is impossible to liquefy the gas however much pressure is exerted.  $T_3$  is known as the **critical temperature** and the pressure  $P_2$  at which it occurs is the **Critical pressure**.

**Definition**

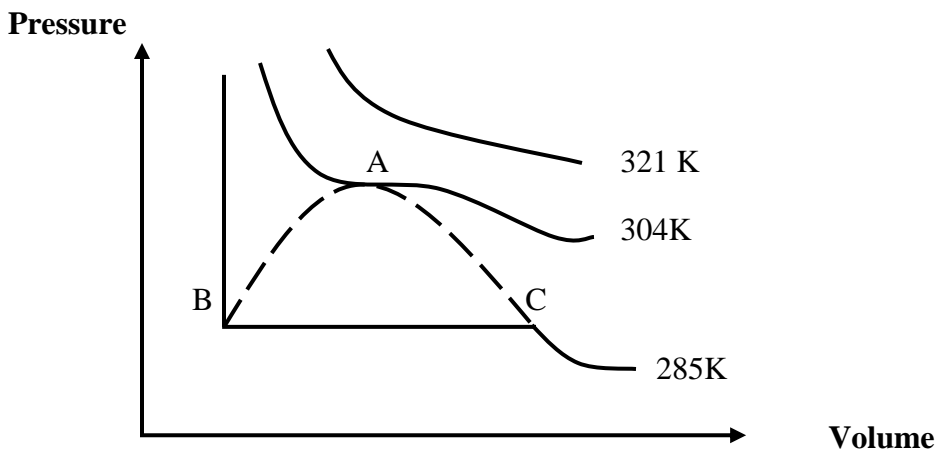
**Critical temperature:** is the temperature above which a gas cannot be liquefied however much pressure is exerted on it or reduced.

**Critical pressure:** is the minimum pressure required to liquefy the gas at critical temperature.

**NOTE:** Liquefaction of a gas only occurs at *low temperature below critical temperature* and at a *high pressure*.

**Qn: UNEB: 1995:**

The diagram shows Isotherms of a gas



i. a) What is the critical temperature of the gas?

**304K**

b) Which Isotherm almost represents the behavior of an ideal gas?

**The Isotherm of 321K**

c) i) What does the region ABC represent?

**Region ABC represents the gas being in Equilibrium with the liquid.**

iii) State **one** condition necessary for liquefying a gas

**A temperature less than the critical temperature (below the critical temperature)**

## MOLE, RELATIVE ATOMIC MASS, RELATIVE MOLECULAR MASS

### a) MOLE

- A mole is the *amount of substance containing  $6.02 \times 10^{23}$  particles. These particles can be atoms, ions or molecules.*  
 $6.02 \times 10^{23}$  is called Avogadro's constant. ( $N_A$ )
- A mole can also be defined as *the amount of substance containing the same number of particles as there carbon atoms in 12g of Carbon – 12 isotope.*
- Therefore the Avogadro's constant  $6.02 \times 10^{23}$  is the number of particles present in 1 mole of a substance. E.g. 1 mole of  $H_2$  (molecule) is  $6.02 \times 10^{23}$  molecules, 2 moles of  $Na^+$  is  $2 \times 6.02 \times 10^{23}$  ions etc.

### b) RELATIVE ATOMIC MASS

On a Carbon scale, the relative atomic mass of an atom is defined as the mass of an atom of element compared to  $\frac{1}{12}$  of mass of 1 atom of C- 12 isotope i.e.

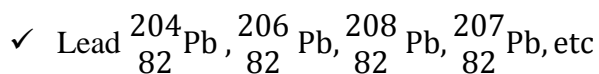
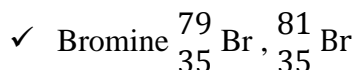
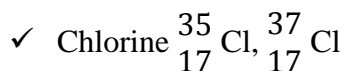
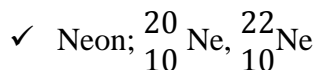
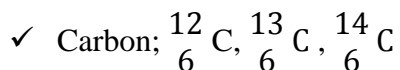
$$\text{R.A.M} = \frac{\text{mass of 1 atom of any substance}}{\frac{1}{12} \times \text{mass of one atom of C-12 isotope}}$$

Thus the R.A.M of an element is the number of times the mass of one atom of an element is heavier than  $\frac{1}{12}$  of the mass of 1 atom of C - 12 isotope.

### Determination of R.A.M by mass spectrometry

#### Isotope:

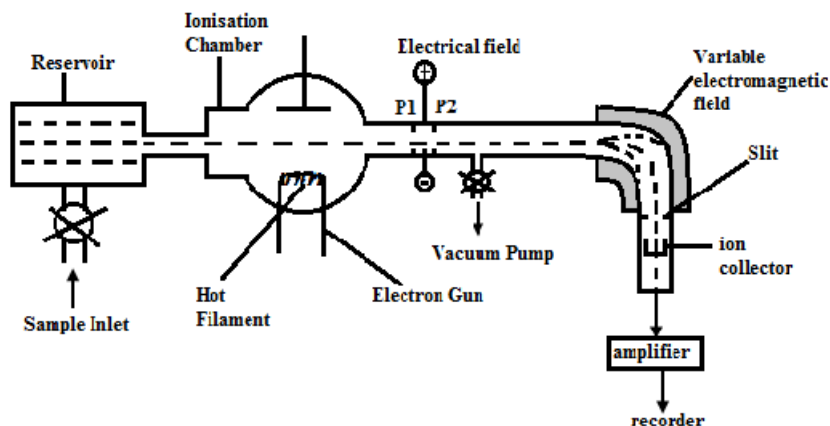
These are atoms of an element with the same number of protons but with different number of neutrons. E.g.



In determining the R.A.M by mass spectrometer, the isotopes are separated by converting them into rays of positive ions and making use of the differences in their masses.

**Reason:** Isotopes of an element have the same chemical properties since they have the same number of electrons which take part in the chemical reaction.

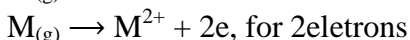
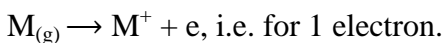
### Structure of a mass Spectrometer



### Operation:

#### 1. Vaporization and Ionisation of the sample:

The Sample is electrically heated through a tungsten film to form vapour. The vapourised sample of an element is then passed into the Ionisation chamber where it is subjected to an electron beam emitted by a hot filament. These electrons bombard the atoms of the vapourised sample from which 1 or 2 electrons are stripped off to become positive ions. i.e.



#### 2. Acceleration stage

The positive ions produced are accelerated by electric field of varying potentials between the plates P<sub>1</sub> and P<sub>2</sub>.

Only positive ions with the same velocity but still with different charge – mass ratio will pass through plate 2.

#### 3. Deflection Stage:

The beam of positive ions emerging from P<sub>2</sub> with the same velocity is deflected into a circular path by strong magnetic field.

The angle of deflection,  $\theta$  is directly proportional to the charge on each ion but inversely proportional to the mass of each ion ie

$$\theta = \frac{e}{m} \text{ where } e - \text{electron charge and } m - \text{mass}$$

#### 4. Deflection stage:

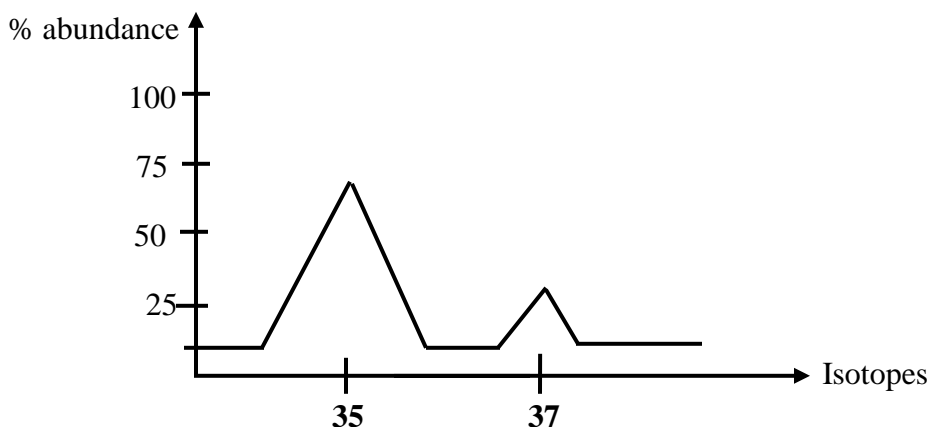
All the positive ions with the same charge to mass ratio are focused at the collector, amplified into sizeable electric current which connects to the recorder at which the electric current separates path which stress the peaks corresponding to the relative abundance of the ions of a particular mass falling on the collector at that instant.

The R.A.M is calculated as the average mass of the isotopes according to their abundances using the formula below

$$\text{R.A.M} = \sum \frac{\% \text{ abundance} \times \text{atomic mass of isotopes}}{100}$$

#### Examples.

1. A mass spectrum of chlorine is as shown below.



Determine the RAM of chlorine.

#### **Solution:**

$$\begin{aligned} \text{R.A.M} &= \sum \frac{\% \text{ abundance} \times \text{atomic mass of isotopes}}{100} \\ &= \frac{(25 \times 37) + (75 \times 35)}{100} \\ &= \underline{\underline{35.5}} \end{aligned}$$

2. An element Y has 3 naturally occurring isotopes whose isotopic masses and relative abundances as shown below.

Isotopic mass	R. abundances
23.98	78.60
24.98	10.11
25.98	11.29

Calculate the average atomic mass

**Solution**

$$\begin{aligned} \text{R.A.M} &= \sum \frac{\% \text{ abundance} \times \text{atomic mass of isotopes}}{100} \\ &= \frac{(78.60 \times 23.98) + (10.11 \times 24.98) + (11.29 \times 25.98)}{100} \\ &= \underline{\underline{24.3}} \end{aligned}$$

3. A mass spectrum of Chlorine shows the molecular peaks at 70, 72 and 74.
- Explain this observation
  - The peaks at 70, 72 and 74 are in the ratio of 9: 6: 1. Calculate the average atomic mass of chlorine.
  - Calculate the relative abundance of Cl -35 and Cl -37

**Solution:**

- a) Chlorine has two isotopes i.e. Cl-35 and Cl- 37. A peak is formed at 70 when two atoms of Cl- 35 combine. A peak is formed at 72 when an atom of Cl – 35 combines with Cl-37.

A peak is formed at 74 when two atoms of chlorine- 37 combine.

- b) Total ratio = 9 + 6 + 1  
= 16

$$\text{Ratio at 70} = \frac{9}{16} \times 100 = \mathbf{56.25\%}$$

$$\text{Ratio at 72} = \frac{6}{16} \times 100 = \mathbf{37.5\%}$$

$$\text{Ratio at 74} = \frac{1}{16} \times 100 = \mathbf{6.25\%}$$

$$\begin{aligned} \text{R.M.M} &= \sum \frac{\% \text{ abundance} \times \text{atomic mass of isotopes}}{100} \\ &= \frac{(56.25 \times 70) + (37.5 \times 72) + (6.25 \times 74)}{100} \end{aligned}$$

$$= 71$$

$$\text{RAM} = \frac{71}{2} = \underline{\underline{35.5}}$$

$$\text{c) } \text{RAM} = \sum \frac{\% \text{ abundance} \times \text{atomic mass of isotopes}}{100}$$

Let the %age abundance of 37 be  $x$

And that of 35 be  $100 - x$

$$\Rightarrow 35.5 = \frac{(x \times 37) + (100 - x) \times 35}{100}$$

$$3550 = 37x + 3500 - 35x$$

$$50 = 2x$$

$$x = 25\%$$

$$100 - x = 100 - 25 = \underline{\underline{75\%}}$$

4. Copper has RAM 63.55 and consists of two isotopes of mass numbers 63 and 65. Calculate the %age abundances of the isotopes. **UNEB 2001**

**Solution:**

Relative atomic mass = 63.55

Mass numbers: 63 and 65

Let the relative % abundance of 63 be  $x$

Let the relative abundance of 65 be  $(100 - x)$

$$\text{Using } \text{RAM} = \sum \frac{\% \text{ abundance} \times \text{atomic mass of isotopes}}{100}$$

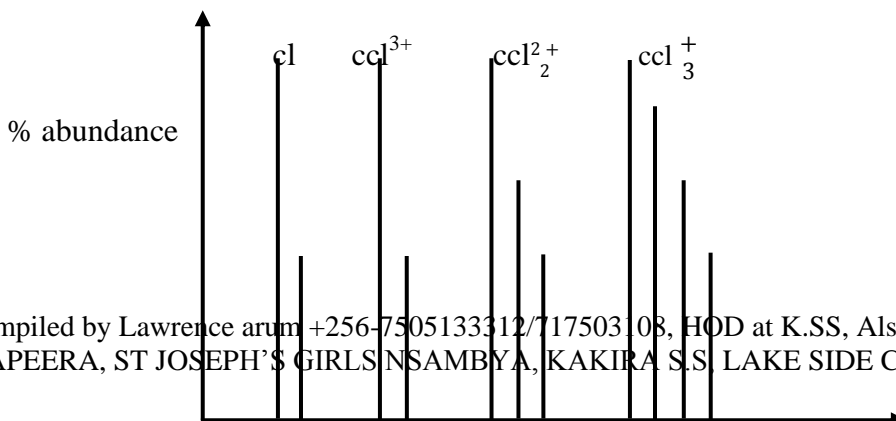
$$63.55 = \frac{(63 \times x) + (100 - x) \times 65}{100}$$

$$6355 = 63x + 6500 - 65x$$

$$x = 72.5\%$$

% abundance of isotope 63 =  $x = 72.5\%$  and % abundance of isotope 65 =  $100 - 72.5 = 27.5\%$

5. On passing tetra chloromethane through a mass spectrometer, we obtain the spectrum below.



1 2    1 2    1 2 3    1 2 3 4    Peaks

### Interpretation

#### Group A:

- Due to one chlorine atom
- Line 1 is due to chlorine 35
- Line 2 is due to chlorine 37

#### Group B:

- Due to  $\text{CCl}^{3+}$
- Line 1 is due to  $\text{CCl}^{35}$ , has a mass of  $(12 + 35) = 47$  (highest peak)
- Line 2 is due to  $\text{CCl}^{37}$ , has a mass of  $(12 + 37) = 49$  (shortest peak)

#### Group C:

- Due to  $\text{CCl}^{2+}$
- Line 1 is due to  $\text{CCl}^{35}$ ,  $\text{Cl}^{35}$ , mass of 82, (highest peak)
- Line 2 is due to  $\text{CCl}^{35}$ ,  $\text{Cl}^{37}$ , mass of 86, the lowest peak.

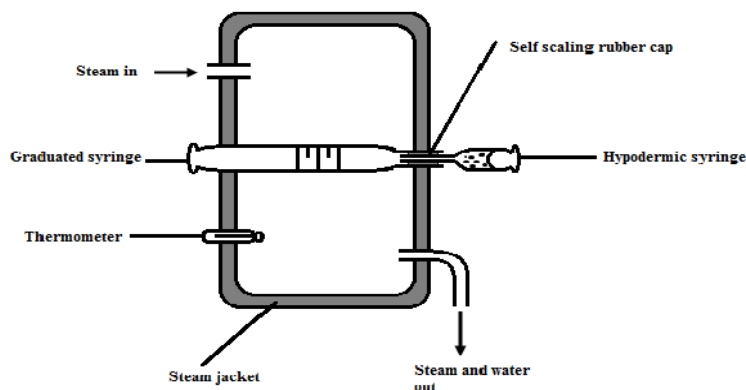
#### Group D:

- Due to  $\text{CCl}_3^+$
- Line 1 is due to  $\text{CCl}^{35}$ ,  $\text{Cl}^{35}$ ,  $\text{Cl}^{35}$ , mass of 117 (highest peak)
- Line 2 is due to  $\text{CCl}^{35}$ ,  $\text{Cl}^{35}$ ,  $\text{Cl}^{37}$ , mass of 119 (second highest peak)
- Line 3 is due to  $\text{CCl}^{35}$ ,  $\text{Cl}^{37}$ ,  $\text{Cl}^{37}$ , mass of 121 (third highest peak)
- Line 4 is due to  $\text{CCl}^{37}$ ,  $\text{Cl}^{37}$ ,  $\text{Cl}^{37}$ , mass of 123 (lowest peak)

## DETERMINATION OF R.M.M OF GASES AND VOLATILE LIQUIDS

### i. Victor Meyer's method for volatile liquids.

#### Set up



#### Procedure:

- Draw a few  $\text{cm}^3$  of air into a graduated syringe
- Pass steam through the outer jacket until the thermometer reading and the volume of the air in the syringe becomes steady.
- Record this temperature,  $T^\circ\text{C}$  and volume of the air in the syringe  $V_1\text{cm}^3$
- Fill the hypodermic syringe with about  $1\text{cm}^3$  of liquid under investigation, ensuring that all air is expelled from the needle being pushed through the self sealing cap of the graduated syringe.
- Weigh the hypodermic syringe and its content
- Inject about  $0.2\text{cm}^3$  of liquid into a larger syringe and withdraw the hypodermic syringe.
- Reweigh the hypodermic syringe and its contents
- The liquid injected into the graduated syringe will evaporate, vapour is formed. The final volume of air + vapour in the graduated syringe should be recorded when the volume becomes steady.
- Finally record the atmospheric pressure  $P$ .

#### Results:

- Mass of hypodermic syringe + volatile liquid before injection into the graduated syringe =  $ag$

- Mass of hypodermic syringe after injection of volatile liquid into the graduated syringe = ***bg***
- Mass of volatile liquid = ***(a - b)g***
- Initial volume of graduated syringe =  $V_1 \text{ cm}^3$
- final volume of graduated syringe =  $V_2 \text{ cm}^3$
- volume of vapour (volatile liquid) =  $(V_2 - V_1) \text{ cm}^3$

### Treatment of results

The RMM of the volatile liquid can then be calculated from

$$PV = nRT, \text{ where } n = \frac{m}{M}$$

$$\Rightarrow PV = \frac{mRT}{M}$$

$$M = \frac{mRT}{PV}$$

### Example

1. A gas syringe containing  $20.6 \text{ cm}^3$  of air at  $48^\circ\text{C}$  was injected with  $0.246 \text{ g}$  of a volatile liquid Q. The volume of the gas in the syringe was found to be  $63.7 \text{ cm}^3$  at a pressure of  $1.01 \times 10^5 \text{ Nm}^{-2}$ . Calculate the R.M.M of volatile liquid Q.

#### Solution

Initial volume of air in the syringe =  $20.6 \text{ cm}^3$

Final volume of air in syringe =  $63.7 \text{ cm}^3$

Volume of vapour =  $(63.7 - 20.6) = 43.1 \text{ cm}^3$

$T = 48 + 273 = 321 \text{ K}$ ,  $m = 0.246 \text{ g}$

Using  $PV = \frac{mRT}{M}$

$$M = \frac{mRT}{PV} = \frac{0.246 \times 8.314 \times 321}{1.01 \times 10^5 \times 43.1 \times 10^{-6}}$$

$$\underline{\underline{M = 151 \text{ g}}}$$

2. When  $0.16 \text{ g}$  of a volatile liquid P was injected into a gas syringe at  $12^\circ\text{C}$  and pressure  $745 \text{ mmHg}$ ,  $51.5 \text{ cm}^3$  of liquid vapour was produced. Calculate the R.M.M of P.

#### Solution:

Initial mass =  $0.16 \text{ g}$      $T = 12 + 273 = 285 \text{ K}$

$P = 745 \text{ mmHg} = 99325.188 \text{ Pa}$

$R = 8.314 \text{ Jmol}^{-1} \text{ K}^{-1}$

$V = 51.5 \text{ cm}^3 = 51.5 \times 10^{-6} \text{ m}^3$

⇒ Using  $PV = \frac{mRT}{M}$

$$M = \frac{mRT}{PV} = \frac{0.16 \times 8.314 \times 285}{99325.188 \times 51.5 \times 10^{-6}} = \underline{\underline{71.12g}}$$

3. By vapourising 0.1g of a liquid at 180°C and  $1.01 \times 10^5$  Pa pressure, 25cm<sup>3</sup> of vapour were obtained. Find the R.M.M of the liquid.

**Solution:**

Mass = 0.1g

T = (180 + 273) = 453K

Pressure =  $1.01 \times 10^5$ Pa

Volume =  $25 \times 10^{-6}$ m<sup>3</sup>

⇒ Using  $PV = \frac{mRT}{M}$

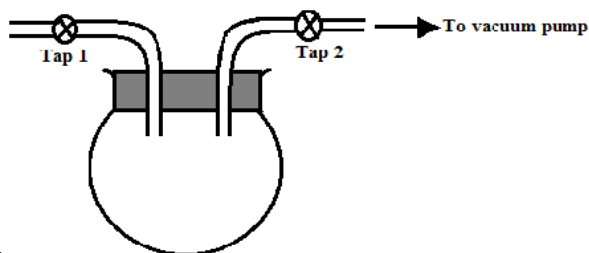
$$M = \frac{mRT}{PV} = \frac{0.1 \times 8.314 \times 453}{1.01 \times 10^5 \times 25 \times 10^{-6}} = \underline{\underline{149.2g}}$$

ii. **Regnault's method for gases.**

This is the modification of Meyer's method.

It involves direct weighing of the gases.

**Setup:**



**Procedure:**

- Tap 1 is closed when tap 2 is open and the vessel is evacuated by connecting tap 2 to the vacuum pump.
- Tap 2 is closed and the mass of the empty vessel is determined
- Tap 1 is then opened while keeping tap 2 closed and the vessel is filled with the gas of known volume.
- The weight of the vessel filled with the gas is then determined

**Results:**

Mass of empty vessel = Xg

Mass of vessel + gas = yg

Mass of the gas alone = (y - x)g

**Treatment of results**

Compiled by Lawrence arum +256-7505133312/717503108, HOD at K.SS, Also taught at KISUBI MAPEERA, ST JOSEPH'S GIRLS NSAMBYA, KAKIRA S.S, LAKE SIDE COLLEGE LUZIRA .

$$\Rightarrow \text{Using } PV = \frac{mRT}{M}$$

$$\therefore M = \frac{mRT}{PV}$$

Where M = Relative Molecular Mass of the gas.

NOTE: In using this method, the following precautions should be taken:

- The gas must be pure
- All weighings should be done at the same temperature and pressure.
- All vessels must be completely evacuated

### EMPIRICAL AND MOLECULAR FORMULAE

The empirical formula of a compound *is the simplest formula which expresses the ratio of the number of atoms of the elements present in the compound.*

Molecular formula *is one which shows the actual number of atoms of the elements present in a molecule/ compound.*

The empirical formula can be obtained from

- i. Percentage composition
- ii. Data obtained from combustion analysis.

Knowing the molecular mass of the compound, then the molecular formula of the compound can also be obtained.

### Relationship between Relative Density and RMM

$$\text{Relative density (vapour density)} = \frac{\text{mass of a given volume of gas}}{\text{mass of an equal volume of hydrogen}}$$

$$= \frac{\text{mass of } n\text{-molecules of a gas}}{\text{mass of } n\text{-molecules of hydrogen}}$$

$$= \frac{\text{mass of 1 molecule of gas}}{\text{mass of 1 molecule of hydrogen}}$$

But RMM = mass of 1 mole of a gas

$$\therefore \text{R.D} = \frac{\text{RMM}}{2}, \text{ mass of 1 molecule of H}_2$$

$$\text{RMM} = \text{R.D} \times 2$$

Molecular formula can either be the same as empirical formula or just a multiple of it i.e. molecular formula = (Empirical formula) $n$ . where  $n = 1$

Molecular formula = empirical formula

## Calculation of Empirical Formula and Molecular Formula

### a) From percentage composition

1. An organic compound Q contains 66.7% Carbon, 11.1% hydrogen and the rest is Oxygen. If the Relative vapour density of Q is 36, determine its molecular formula. (H = 1, O = 16, C = 12)

$$\begin{aligned}\% \text{ composition of O} &= 100 - (66.7 + 11.1) \\ &= 22.2\%\end{aligned}$$

Elements	C	H	O
% composition	66.7	11.1	22.2
Moles of atoms	$66.7/12$	$11.1/1$	$22.2/16$
	5.55833	11.1	1.3875
Simplest Mole ratios	$5.5583/1.3875$	$11.1/1.3875$	$1.3875/1.3875$
	4	8	1

$\therefore$  empirical formula: =  $C_4H_8O$

(Empirical formula) n = molecular mass

$$(C_4H_8O) n = R.D \times 2$$

$$(C_4H_8O) n = 36 \times 2$$

$$48n + 8n + 16n = 72$$

$$n = 1$$

$\therefore$  molecular formula =  $C_4H_8O$

2. A compound W contains Carbon, Hydrogen and Oxygen. Elemental analysis shows that 54.5% is carbon, 9.09% is Hydrogen and the rest is Oxygen.
- Calculate the empirical formula
  - 0.542g of W occupies 148cm<sup>3</sup> at 20°C and 740mmHg. Calculate the molecular mass of W which produces effervescence with NaHCO<sub>3</sub>.

### Solution:

$$\begin{aligned}\% \text{ composition of Oxygen} &= 100 - (54.5 + 9.09) \\ &= 36.41\%\end{aligned}$$

$$\text{Carbon} = 54.5\%$$

$$\text{Hydrogen} = 9.09\%$$

Elements	C	H	O
% composition	54.5	9.09	36.41

Moles of atoms	$54.5/12$	$9.09/1$	$36.41/16$
	4.54167	9.09	2.275625
Mole ratios	$4.54167/2.275625$	$9.09/2.275625$	$2.275625/2.275625$
	$1.9958 \approx 2$	$3.995 \approx 4$	1

Empirical formula =  $C_2H_4O$

b) Mass = 0.542g

$$\text{Volume} = 148\text{cm}^3 = 148 \times 10^{-6}\text{m}^3$$

$$T = 20^\circ\text{C} = 20 + 273 = 293\text{K}$$

$$\text{Pressure} = 740\text{mmHg} = 98658.576\text{Pa}$$

Using  $PV = nRT$

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

$$\Rightarrow PV = \frac{mRT}{M}$$

$$M = \frac{mRT}{PV} = \frac{0.524 \times 8.314 \times 293}{98658.576 \times 148 \times 10^{-6}}$$

$$= \underline{\underline{87.42\text{g}}}$$

From (empirical formula)<sub>n</sub> = molecular mass

$$(C_2H_4O)_n = 87.42$$

$$24n + 4n + 16n = 87.42$$

$$44n = 87.42$$

$$n = 1.987 \approx 2$$

Molecular formula = (E.F) n

$$= (C_2H_4O)_2$$

$$= C_4H_8O_2$$

### UNEB 2007

- Compound R contains Cobalt 24.8% Chlorine, 29.8% and water 45.4%
  - Calculate the empirical formula
  - Determine the molecular formula of R (RFM = 237.9), Co = 58.9, Cl = 35.5, H<sub>2</sub>O = 18)
- Analysis of blue vitriol crystals yielded the following percentage composition, Cu = 25.8%, S = 12.8%, O = 25.6% and H<sub>2</sub>O of crystallization 36.1%. What is the empirical formula of the crystal (Cu = 63.5, S = 32, O = 16, H = 1)
- A compound Q contains 62.1% carbon, 10.3% hydrogen and the rest being Oxygen. (vapour density of Q =  $2.59 \times 10^{-3}$ )g/cm<sup>3</sup> at STP).

- a) Determine the empirical formula of Q  
 (b) Molecular formula of Q

**B) From data from combustion analysis**

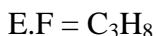
1. (a) When 8.8g of a hydrocarbon Z was burnt in excess air, 14.4g of water and 13.44dm<sup>3</sup> of CO<sub>2</sub> were obtained at STP. Determine the Empirical Formula of Z.  
 (b) The vapor density of Z is 22. Write the name and the molecular formula of Z.

(UNEB 2004)

**Solution:**

- a) Mass of H<sub>2</sub>O = 14.4g  
 Volume of CO<sub>2</sub> = 13.44dm<sup>3</sup>  
 Mass of compound = 8.3g  
 RMM of H<sub>2</sub>O = 2 + 16 = 18  
 Mass of H<sub>2</sub> =  $\frac{2}{18} \times 14.4 = 1.6\text{g}$   
 RMM of CO<sub>2</sub> = 44  
 22.4dm<sup>3</sup> of CO<sub>2</sub> → 44g  
 13.44dm<sup>3</sup> →  $\frac{44}{22.4} \times 13.44$   
 Mass of CO<sub>2</sub> = 26.4g  
 Mass of C =  $\left(\frac{12}{44} \times 26.4\right) \text{g} = 7.2\text{g}$   
 % of Carbon =  $\frac{7.2}{8.8} \times 100 = 81.82\%$   
 % of hydrogen =  $\frac{1.6}{8.8} \times 100 = 18.18\%$

Element	C	H
% composition	81.82	18.18
Moles of atoms	$\frac{81.82}{12}$	$\frac{18.18}{1}$
	6.818	18.18
Mole ratios	$\frac{6.818}{6.818}$	$\frac{18.18}{6.818}$
	(1 = 3	2.66)3 7.98 ≈ 8



- b) RMM = R.D × 2

$$= 22 \times 2 = 44$$

From (E.F)  $n = \text{molecular mass}$

$$(\text{C}_3\text{H}_8)_n = 44$$

$$36n + 8n = 44$$

$$n = 1$$

$\therefore$  Molecular formula =  $\text{C}_3\text{H}_8$

**NB: For fractions/ decimals multiply the simplest ratio by factor to get rid of the decimal numbers.**

1. 0.236g of an organic compound V on combustion gave 0.528g of Carbon dioxide and 0.324g of water. If 0.295g of V at STP gave  $56\text{cm}^3$  of Nitrogen gas, determine the molecular formula of V (RMM of V = 59).

**Solution:**

$$\text{Mass of V} = 0.236\text{g}$$

$$\text{Mass of CO}_2 = 0.528\text{g}$$

$$\text{Mass of H}_2\text{O} = 0.324\text{g}$$

$$\text{Mass of Carbon} = \frac{12}{44} \times 0.528 = 0.144\text{g}$$

$$\text{Mass of hydrogen} = \frac{2}{18} \times 0.324 = 0.036\text{g}$$

$$1 \text{ mole of N}_2 = 14 \times 2 = 28\text{g}$$

$$22400\text{cm}^3 \rightarrow 28\text{g of N}_2$$

$$56\text{cm}^3 \rightarrow \frac{28 \times 56}{22400} \text{ of N}_2 = 0.07\text{g}$$

If 0.295g of V contains 0.07g of  $\text{N}_2$

$$\Rightarrow 0.236\text{g of V contains } \left( \frac{0.07 \times 0.236}{0.295} \right) \text{g of N}_2 = 0.056\text{g}$$

Element	C	H	N
% composition	81.82	18.18	0.056
Moles of atoms	$0.144/12$	$0.036/1$	$0.056/14$
	0.012	0.036	0.004
Mole ratios	$0.012/0.004$	$0.036/0.004$	$0.004/0.004$
	= 3	9	1

$$\text{E.F} = \text{C}_3\text{H}_9\text{N}$$

From (empirical formula) $_n = \text{relative molecular mass}$

$$(\text{C}_3\text{H}_9\text{N})_n = 59$$

$$(12 \times 3)_n + (9 \times 1)_n + (14 \times 1)_n = 59$$

$$59n = 59$$

$$n = 1$$

**Molecular formula, C<sub>3</sub>H<sub>9</sub>N**

2. When 0.13g of a chloride of Fe was vaporized at 600K and 1 atmosphere, 20cm<sup>3</sup> of vapour was formed.
- a) Calculate the relative molecular mass of FeCl (Iron chloride).
- b) i Determine the MF of Iron Chloride.  
ii Write the structural formula of the Iron Chloride. (Fe = 56, Cl = 35.5)

Mass of Iron Chloride = 0.13g

Temperature = 600K.  $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$

Pressure = 1 atmosphere = 101325Pa

Volume of vapour = 20cm<sup>3</sup> =  $2 \times 10^{-5} \text{ m}^3$

Using  $PV = nRT$

$$\text{But } n = \frac{\text{given mass}}{\text{mass number}} = \frac{m}{M}$$

$$\Rightarrow PV = \frac{mRT}{M}$$

$$M = \frac{mRT}{PV} = \frac{0.13 \times 8.314 \times 600}{101325 \times 2 \times 10^{-5}}$$
$$= 320.0059215$$

**≈ 320g**

b) i) (Empirical formula)  $n = \text{molar mass}$

$$\Rightarrow (\text{FeCl}_3) n = 320$$

$$(56 + (35.5 \times 3)) n = 320$$

$$n = 1.969 = 2$$

Molecular formula =  $(\text{FeCl}_3)_2 = \text{Fe}_2\text{Cl}_6$

ii) Structural formula of Iron chloride, Fe<sub>2</sub>Cl<sub>6</sub>

### **DETERMINATION OF MOLECULAR FORMULA OF HYDROCARBON BY EUDIOMETER**

Determination of MF of hydrocarbon by a Eudiometer uses Avogadro's hypothesis,

**“equal volumes of different gases at the same temperature and pressure contain the same number of molecules”.**

i.e. doubling the number of molecules present doubles the volume at constant pressure.

#### **Procedure:**

- Unknown volume of gaseous hydrocarbon is exploded with excess oxygen over mercury in a eudiometer.
- The vapour is then cooled and contraction in volume occurs due to condensation of water vapour to form liquid vapour.
- The resultant volume left is due to CO<sub>2</sub> formed and the unused O<sub>2</sub>

- The volume of CO<sub>2</sub> is determined by adding aqueous NaOH or KOH which absorbs all the CO<sub>2</sub>.

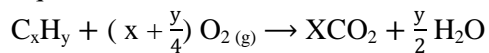
**Examples:**

- 20cm<sup>3</sup> of a gaseous hydrocarbon X were exploded with 120cm<sup>3</sup> of Oxygen. After the explosion, the volume of gases remaining was 90cm<sup>3</sup> and this decreased to 50cm<sup>3</sup> on treatment with aqueous KOH. Calculate the M.F of the hydrocarbon X.

**Solution:**

Let the hydrocarbon be C<sub>x</sub>H<sub>y</sub>

Equation of combustion;



Volume of hydrocarbon = 20cm<sup>3</sup>

Initial volume of Oxygen = 120cm<sup>3</sup>

Residual gas volume = 90cm<sup>3</sup>

Volume of unused O<sub>2</sub> = 50cm<sup>3</sup>

Volume of CO<sub>2</sub> formed = (90 – 50) = 40cm<sup>3</sup>

Volume of O<sub>2</sub> used = (120 – 50) = 70cm<sup>3</sup>

	$C_xH_y + (x + \frac{y}{4}) O_{2(g)} \rightarrow XCO_2 + \frac{y}{2} H_2O$		
Vol. of cpnt.	20cm <sup>3</sup>	70cm <sup>3</sup>	40cm <sup>3</sup>
Mole ratio	$\frac{20}{20}$	$\frac{70}{20}$	$\frac{40}{20}$
	1	$\frac{7}{2}$	2

By comparison; x = 2

$$x + \frac{y}{4} = \frac{7}{2}$$

$$\frac{8+y}{4} = \frac{7}{2}$$

$$8 + y = 14 \Rightarrow y = 2$$

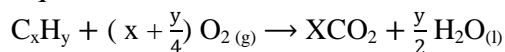
**Molecular formula = C<sub>2</sub>H<sub>6</sub>**

- 15cm<sup>3</sup> of gaseous hydrocarbon Z was exploded with 105cm<sup>3</sup> of excess O<sub>2</sub>. The residual gas occupied 75cm<sup>3</sup>. On addition of conc. KOH, there was a fall in volume to 30cm<sup>3</sup>. Determine the molecular formula of Z.

**Solution:**

Let the hydrocarbon be C<sub>x</sub>H<sub>y</sub>

Equation of combustion:



Volume of hydrocarbon = 15cm<sup>3</sup>

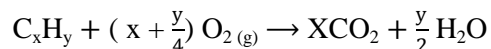
Volume of O<sub>2</sub> (initially) = 105cm<sup>3</sup>

Residual gas volume = 75cm<sup>3</sup>

Volume of Oxygen unused 30cm<sup>3</sup>

Volume of oxygen used =  $(105 - 30) = 75\text{cm}^3$

Volume of carbon dioxide formed =  $(75 - 30) = 45\text{cm}^3$



vol of cpnt	$15\text{cm}^3$	$75\text{cm}^3$	$45\text{cm}^3$
Mole ratio	$\frac{15}{15}$	$\frac{75}{15}$	$\frac{45}{15}$
	1	5	3

By comparing;

$$X = 3$$

$$X + \frac{y}{4} = 5$$

$$3 + \frac{y}{4} = 5$$

$$\frac{12+y}{4} = 5$$

$$Y = 8$$

$\therefore$  **Molecular formula =  $\text{C}_3\text{H}_8$ , Propane.**

3. When  $142\text{cm}^3$  of a hydrocarbon Q of molecular mass 58g was exploded with excess  $\text{O}_2$  and cooled to room temperature, the volume of the residual gas  $694\text{cm}^3$ . On treatment with conc. KOH solution, the volume decreased to  $126\text{cm}^3$ .
- Determine the molecular formula of Q.
  - Write the structural formula and IUPAC name of all possible isomers of Q.

### Solution

a) Let the hydrocarbon =  $\text{C}_x\text{H}_y$

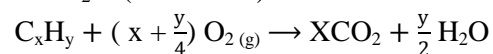
Volume of  $\text{C}_x\text{H}_y = 142\text{cm}^3$

Molecular mass = 58g.

Volume of residual gas =  $694\text{cm}^3$

Volume of  $\text{O}_2 = 126\text{cm}^3$

Volume of  $\text{CO}_2 = (694 - 126)\text{cm}^3 = 568\text{cm}^3$



$$142\text{cm}^3 \qquad \qquad \qquad 568\text{cm}^3$$

Mole ratio	$\frac{142}{142}$	$\frac{568}{142}$
	1	4

By comparison,  $x = 4$

But  $\text{C}_x\text{H}_y = 58$

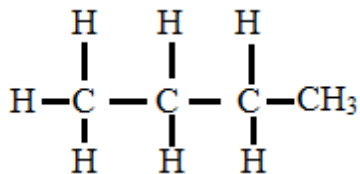
But  $\text{C}_4\text{H}_y = 58$

$$48 + y = 58$$

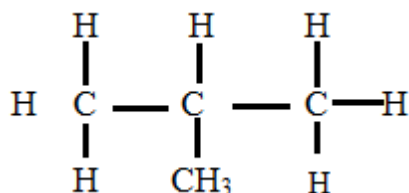
$$y = 10$$

**Molecular formula = C<sub>4</sub>H<sub>10</sub>**

b) i) C<sub>4</sub>H<sub>10</sub> (Butane)



(ii) 2-Methyl Propane.



4. 30cm<sup>3</sup> of a gaseous hydrocarbon W was mixed with 140cm<sup>3</sup> of O<sub>2</sub> and exploded. After cooling to room temperature and pressure, the residual gas occupied 95cm<sup>3</sup>. On absorption with conc. KOH solution there was a fall in volume by 60cm<sup>3</sup>. Determine the molecular formula of W.

**solutions**

**No. 4**

Let the Hydrocarbon be C<sub>x</sub>H<sub>y</sub>

Volume of C<sub>x</sub>H<sub>y</sub> = 30cm<sup>3</sup>

Residual gas = 95cm<sup>3</sup>

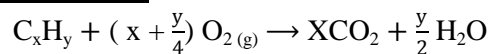
Volume of Carbon dioxide formed = 60cm<sup>3</sup>

Volume of Oxygen initially = 140cm<sup>3</sup>

Volume of oxygen (unused) = (95 - 60) = 35cm<sup>3</sup>

Volume of used oxygen = (140 - 35) = 105cm<sup>3</sup>

**Equation of combustion**



Volumes:      30cm<sup>3</sup>    105cm<sup>3</sup>                  60cm<sup>3</sup>

Mole ratios     $\frac{30}{30}$              $\frac{105}{30}$                      $\frac{60}{30}$

                  1                     $\frac{7}{2}$                     2

By comparison;

$$X = 2$$

Using:

$$x + \frac{y}{4} = \frac{7}{2}$$

$$\Rightarrow 2 + \frac{y}{4} = \frac{7}{2}$$

$$\frac{8+y}{4} = \frac{7}{2}$$

$$y = 6$$

**∴ Molecular formula of W = C<sub>2</sub>H<sub>6</sub>**

## ATOMIC STRUCTURE

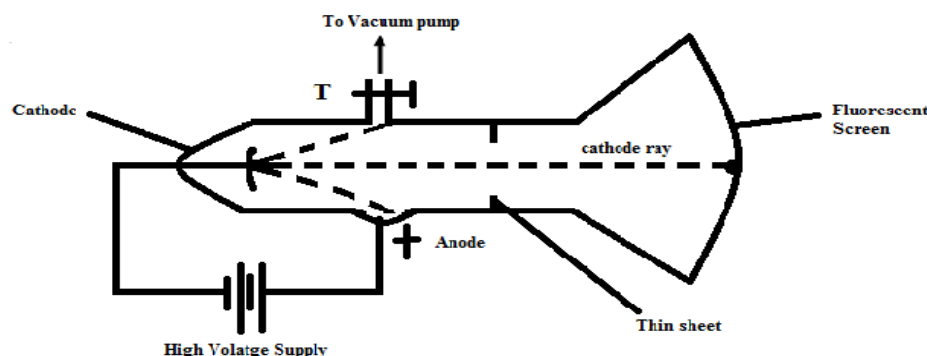
There are **three** fundamental particles within an atom i.e. **protons, neutrons** and **electrons**, each of which differs from the other in terms of mass and charge i.e.

Particle	Symbol	Relative charge	Relative mass
Protons	P	+	1
electrons	E	-	$\frac{1}{1840}$
neutrons	N	0	1

### PRODUCTION OF CATHODE RAYS(ELECTRONS)

- The electric nature of matter was studied by **JJ Thomson** from his study of the phenomenon of discharge through gases at very low pressure.
- At ordinary pressures, gases are electrical insulators but when subjected to very high voltages at very low pressures, they break down and conduct electricity.

#### Illustration:



#### Procedure:

- Two metal electrodes are fitted in a discharge tube containing a gas e.g hydrogen gas.
- A side tube T is also provided to communicate with the vacuum pump.
- With sufficiently high voltage of about 5000V, and the pressure of the gas is reduced to about 700pa, a bright luminous discharge takes place.
- Pressure inside the discharge tube is adjusted by the help of a vacuum pump to less than one pascal (1Pa), the luminous discharge is replaced by only faintly luminous rays which proceed from the cathode; hence are called **Cathode rays**.

### PROPERTIES OF CATHODE RAYS

- Travel in straight lines and cast/give off a sharply defined shadow on the screen of the objects placed in their path.

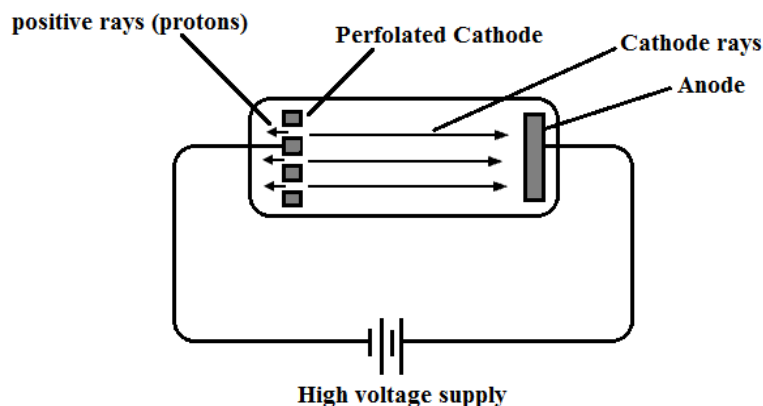
- Produce mechanical effect. This is shown by placing a light paddle wheel in the path of cathode rays; the wheel rotates in the direction away from the cathode. This means that the cathode rays are particles which have mass.
- Deflected by electric field towards the positive plates showing that they are negatively charged.
- Deflected by magnetic fields in the direction that shows that they are negatively charged.
- Causes the screen to fluoresce with a green glow.
- Pass through a thin sheet of aluminum foil which even the smallest gaseous atoms (Helium) or molecules (Hydrogen) cannot penetrate.

NB: *Cathode rays are streams of negatively charged particles, travelling away from the cathode in a straight line.*

### DISCOVERY OF PROTONS

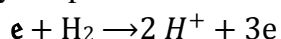
Existence of protons (positively charged particles) in a cathode ray tube was demonstrated by boring small holes in the cathode. When an electric discharge was passed through the cathode ray tube, not only cathode rays are formed ; also rays that originate from the cathode but move in opposite direction.

### ILLUSTRATION



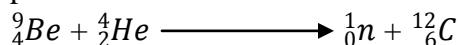
These rays give a red glow; are deflected by both magnetic and electric field in the direction opposite to that of the electrons; showing that they consist of positively charged particles called **Protons**.

They are produced when the electrons are bombarded with gas molecules in the tube i.e.



## DISCOVERY OF NEUTRONS

- Beryllium is bombarded with alpha particles,
- Particles given off were not deflected at all by electric and magnetic fields; therefore possessed no charge.
- Particles are therefore called neutrons; since they were neutral; have the same mass as protons.



## NUCLEUS OF AN ATOM

The nucleus of an atom consists of protons (positively charged) and neutrons (have no charge)

Protons and neutrons are collectively called **nucleons** and the sum of the number of protons and neutrons in the atoms nucleus is called **mass number** or **nucleon number**.

The number of protons in the nucleus of an element is called the **atomic number**.

### Notation for atoms

The notation for an atom X is  ${}^A_Z\text{X}$  where;

X – symbol of an atom

A – mass number

Z – Atomic number

E.g; a symbol for fluorine atom with mass number 19 and Atomic number 9 is;  ${}^{19}_9\text{F}$

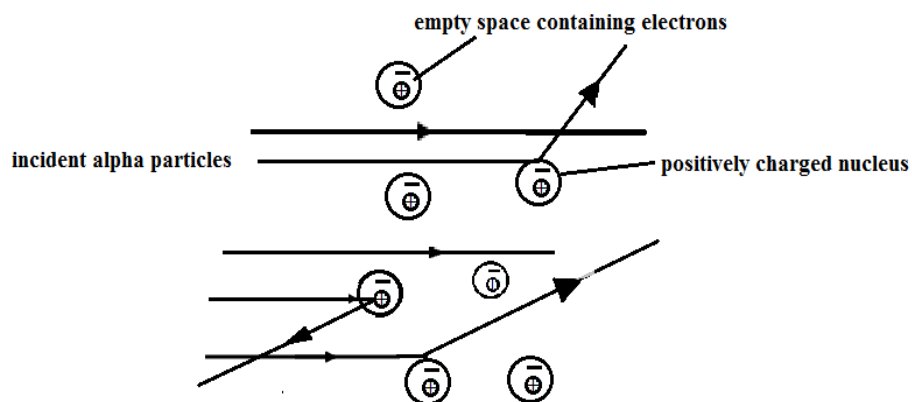
A symbol of fluorine atom can also be written as  ${}^{19}\text{F}$  with the atomic number omitted.

## RUTHERFORD'S MODEL OF AN ATOM

Nuclear model of an atom was studied by;

- passing a stream of positively charged particles (alpha particles) from a Radium source through a thin metal foil of Gold/ platinum.

### Diagram:



### Observations:

1. Most of  $\alpha$  - particles passed through the gold foil undeflected.
2. Few deviated through small angles
3. Extremely very few were scattered through/ deflected back through  $180^\circ$

### Conclusions

1. Most of the atom is an empty space.
2. Atoms contain negative charges (electrons)
3. Alpha particles suffer head on collision with the positive charge concentrated in small fraction of the nucleus.

## RADIOACTIVITY

Is the natural spontaneous disintegration (decay) of unstable nuclei by emission of alpha, beta and gamma rays to form stable nuclei.

Stable nuclei do not undergo radioactive decay while unstable nuclei undergo radioactive decay.

### PROPERTIES OF ALPHA, BETA AND GAMMA RAYS

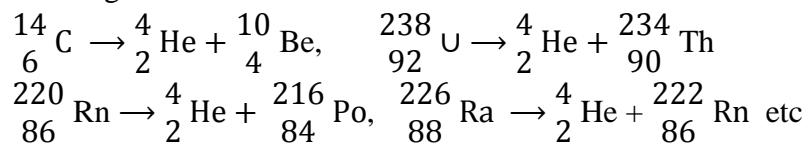
	<u>Properties</u>	<u>Alpha particles</u>	<u>Beta particles</u>	<u>Gamma rays</u>
1	Nature	Essentially a helium nucleus ( ${}^4_2\text{He}$ ) with 2 positive charges and mass number 4 units	Consists of negatively charged electrons each of mass $\frac{1}{1840}$ units. Symbol ${}^0_{-1}\text{e}$	Are electromagnetic radiations without charge but with very short wavelength
2	Deflection by both magnetic and electric fields	Deflected in directions showing they are positively charged i.e. deflected to the negative pole.	Deflected to the positive pole	Not deflected since they are not charged
3	Extent of deflection	Deflected to a less extent since it is heavier.	Deflected to a greater extent since it is lighter.	Not deflected;
4	Extent of penetration	Least penetrating power	Has a fairly high penetrating power. i.e. penetrates a thin sheet of aluminium foil	Have the highest penetrating power as they move with almost the velocity of light and a lot of energy.
5	Ionizing power	Have a high ionizing power such that they can even ionize a gas	Less ionizing power than the alpha particles.	A very low ionising power.

### EFFECTS OF $\alpha$ , $\beta$ AND $\gamma$ EMISSIONS ON ATOMIC AND MASS NUMBERS OF NUCLEI FORMED

Compiled by Lawrence arum +256-7505133312/717503108, HOD at K.SS, Also taught at KISUBI MAPEERA, ST JOSEPH'S GIRLS NSAMBYA, KAKIRA S.S, LAKE SIDE COLLEGE LUZIRA .

a) **Emission of an alpha particle ( ${}^4_2\text{He}$ )**

- All disintegrations by emission/loss of an alpha particle decrease the mass number of the new nucleus by 4 units and atomic number by 2 units.
- This displaces the new nucleus formed by two places backwards/ left in the periodic table e.g.

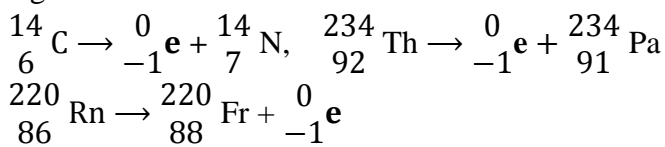


b) **Emission of Beta particles**

Emission / loss of a beta particle increase the atomic number of the new nuclei formed by 1 unit but has no change on the mass number.

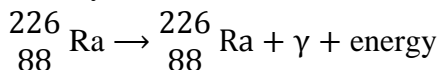
The new nucleus formed is displaced 1 position ahead/ on the right in the periodic table.

e.g.



c) **Emission of a gamma ray**

The loss of gamma rays is accompanied by release of energy but there is no change in the identity of the new nucleus formed. i.e.



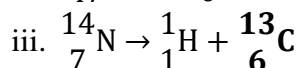
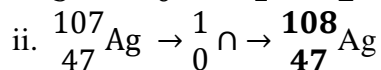
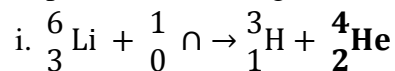
***NB: When the emitted particle is known, the new nucleus formed is identified by its atomic number and NOT mass number.***

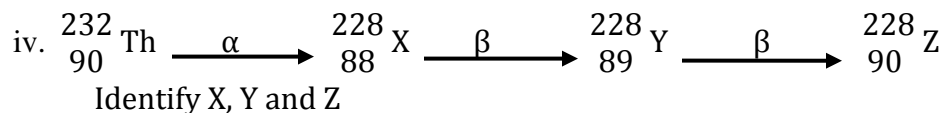
**BALANCING RADIOACTIVE EQUATIONS:**

In balancing radioactive equations, the

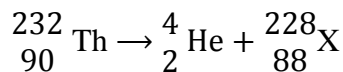
- ***sum of the atomic numbers on the left should equal to the sum of atomic numbers on the right hand side.***
- ***sum of the mass numbers on the left hand side should be equal to that on the right hand side.*** e.g.

1. Complete the following reactions

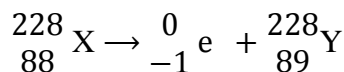




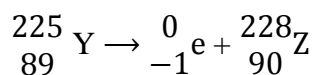
**Solution:**



**X: Radium**

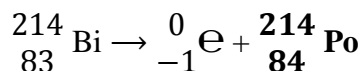


**Y: Actinium**



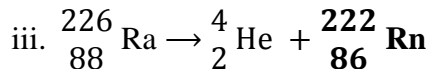
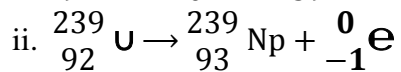
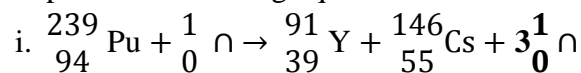
**Z: Thorium**

- Name the three main types of radioactive emissions
- State two properties of any 1 of the emissions named in (a) above. **UNEB 1994:**
- Complete the equation of the decay of Bismuth(**UNEB 2001**)

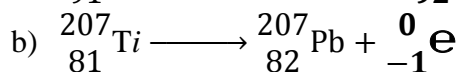
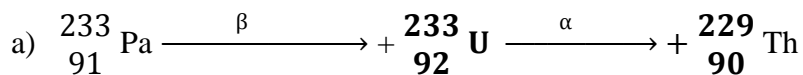


**UNEB 2005(6)**

- Complete the following equations for the nuclear reactions

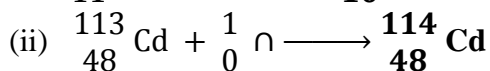
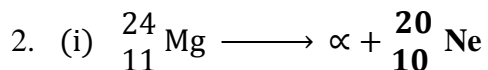
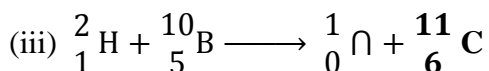
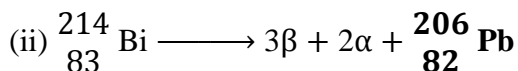
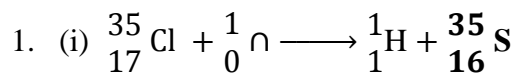


**UNEB 1998 (1)**



## UNEB 2006

Complete the following equations for the nuclear reaction.



## RADIOACTIVE DECAY

Most naturally occurring and manmade heavy isotopes are unstable and hence the nuclei decay spontaneously to form a more stable element after emitting an alpha/ beta particle.

The rate at which a radioactive atom decays is directly proportional to the number of

radioactive atoms/nuclei present at that time i.e. Rate of decay  $\propto$  number of atoms (N)

If  $N_0$  is the initial number of atoms at time  $t = 0$  and  $N_t =$  number of atoms remaining after time  $t = t$ , then

$$\frac{-dN}{dt} \propto N$$

$$\Rightarrow \frac{-dN}{dt} = kN \text{ where } k - \text{Decay constant.}$$

By separating variables;

$$\frac{-dN}{N} = kdt$$

Integrating between limits of  $N_0$  and  $N_t$  and  $t = 0$  to  $t = t$ .

$$\int_{N_0}^{N_t} \frac{-dN}{N} = \int_0^t kdt$$

$$\int_{N_0}^{N_t} \frac{-1}{N} dN = k \int_0^t dt$$

$$-\ln N \Big|_{N_0}^{N_t} = kt \Big|_0^t$$

$$-\ln N_t - -\ln N_0 = kt$$

$$-\ln N_t + \ln N_0 = kt$$

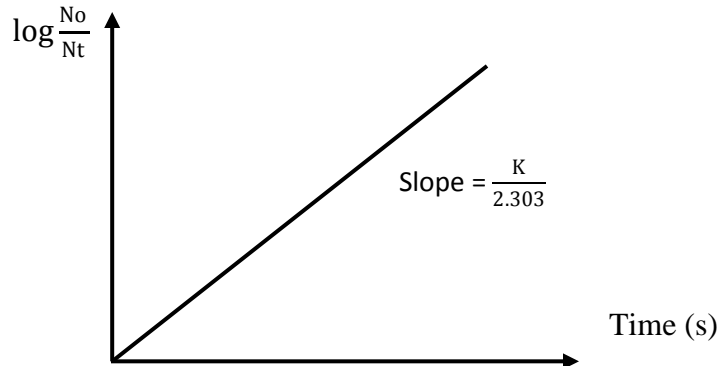
$$\Rightarrow \ln N_0 - \ln N_t = kt$$

$$\ln \frac{N_0}{N_t} = kt$$

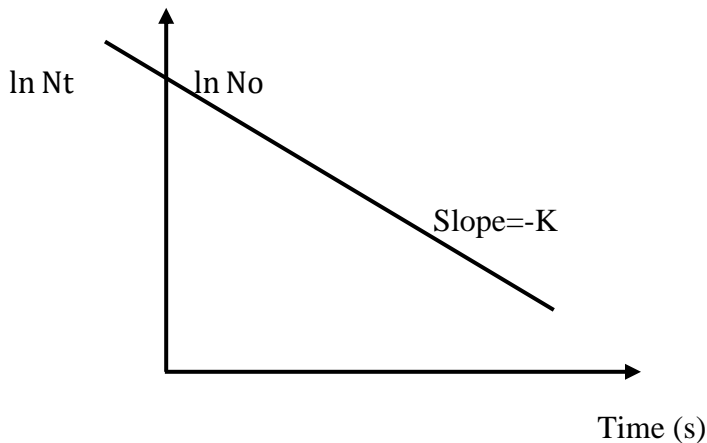
But  $\ln = 2.303 \log_{10}$

$$2.303 \log \frac{N_0}{N_t} = kt$$

**A graph of  $\log \frac{N_0}{N_t}$  against time**



**A graph of  $\ln N_t$  against time**



**NB: If counts are used;**

$$2.303 \log \frac{C_0}{C_t} = kt$$

Where  $C_0$  = counts at time,  $t = 0$

$C_t$  = counts at time,  $t = t$

### **HALF LIFE**

It's the time required for the amount of a radioactive material to be reduced to half its initial value.

Half life is independent of the original concentration i.e. the time taken for 1,000,000 unstable nuclei to disintegrate to half the original amount is the same as the time taken for one nucleus to decay to half the nucleus.

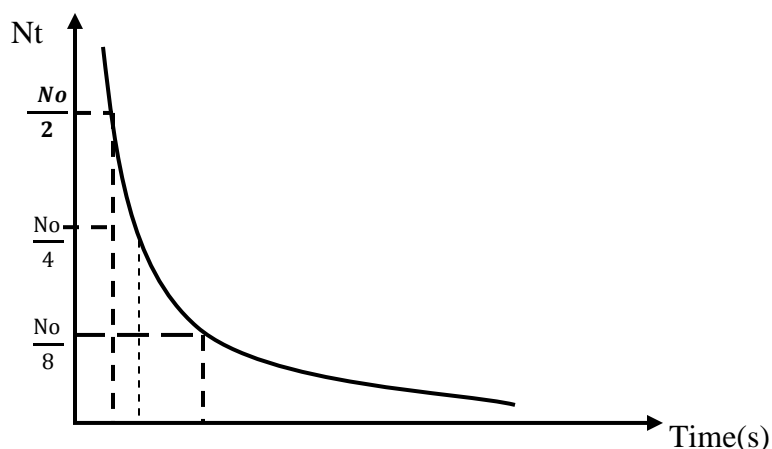
$$\text{From } 2.303 \log \frac{N_0}{N_t} = kt$$

$$\text{At half life; } N_t = \frac{N_0}{2}, t = t_{1/2}$$

$$2.303 \log 2 = k t_{1/2}$$

$$t_{1/2} = \frac{2.303 \log 2}{k}$$

**A graph of  $N_t$  against time has the shape below**



- If  $(t_{1/2} - 0) = (t_{1/4} - t_{1/2}) = \text{half life of } 1^{\text{st}} \text{ order kinetics}$

**NB:** Radioactive decay is a  $1^{\text{st}}$  order process i.e. the rate of decay is proportional to the concentration raised to power 1.

- **Count rate** is the measure of the amount of the nuclide present at each time.
- **Nuclide** is a nuclear species with a specific atomic and mass number.
- **Decay constant** is the number of atoms disintegrating per unit time.

### **Examples**

1. When a radioactive isotope was stored for 42 days, it retained  $\frac{1}{8}$  of its original activity.

Calculate the half life of the isotope.(**UNEB 2006**)

**Solution:**

Time = 42 days

Let the initial activity ( $N_0$ ) be  $x$  at  $t = 0$

At time,  $t = t$ ,  $N_t = \frac{1}{8} x$

Using  $2.303 \log \frac{N_0}{N_t} = kt$

$$2.303 \log \frac{x}{\frac{x}{8}} = k \cdot 42$$

$$2.303 \log 8 = 42k$$

$$k = 0.0495 \text{ day}^{-1}$$

$$\begin{aligned} t_{1/2} &= \frac{0.693}{k} \\ &= \frac{0.693}{0.0495} \\ &= 13.99 \end{aligned}$$

$$t_{1/2} \approx 14 \text{ days}$$

### Assignment.

- The half life of Bismuth is 19.7 minutes. Determine the time taken for 43% by mass of Bismuth to decay. **2009 UNEB**
- Given that  $\lambda = \frac{0.693}{t_{1/2}}$  where  $\lambda$  is a decay constant and  $t_{1/2}$  is the half life. Radium has a half life of 1620 years. Calculate the
  - Value of  $\lambda$
  - The fraction of the sample of Radium remaining after 100 years.
- ${}_{92}^{238}\text{U}$  is radioactive and undergoes an alpha decay to give an isotope for another element.
  - Find the mass number and atomic number of the element formed and hence the element.
  - The half life of Uranium,  ${}_{92}^{238}\text{U}$  is  $4.8 \times 10^9$  years, how many years will be required for 2000 atoms to decay to 497 atoms.
- The disintegration rate constant for the conservation of a radioactive Sodium to Magnesium is  $2.85 \times 10^{-3}$  per second. Calculate the fraction of the original sample after 150s.
- The half life of a radioactive substance Y is 529 minutes. If after 30 minutes, the activity of the sample Y was found to be 285 counts per minute. Calculate initial concentration of Y.
- The beta activity from 1g of Carbon from wood that was cut recently was registered 0.204 counts/ second. 1g of the specimen of Carbon prepared from wood taken from a long strip gave 0.177 counts per second. Estimate the age of the strip to the nearest 50 years. (Half life of Carbon is 5580 years).

### ARTIFICIAL RADIOACTIVITY

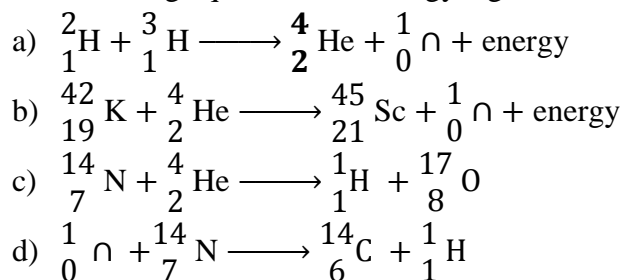
New unstable (radioactive nuclei) is artificially formed by bombarding some stable nuclei with energetic particles e.g. protons, neutrons, alpha particles, etc.

Artificial radioactivity gives rise to two processes namely;

- i. Nuclear fusion
- ii. Nuclear fission

**i. Nuclear fusion;**

Is the process whereby small/light nuclei combine to form heavy nuclei accompanied by release of large quantities of energy e.g.



**ii. Nuclear fission;**

- This is a process which involves splitting/ breaking a heavy nuclei into smaller nuclei accompanied by a large release of energy.
- Fission reactions are usually initiated by fast moving particles such as neutrons e.g.
- ${}_{92}^{235}\text{K} + {}_0^1\text{n} \longrightarrow {}_{36}^{92}\text{K} + {}_{56}^{141}\text{Ba} + 3 {}_0^1\text{n} + \text{energy}$
- The neutrons formed can also bombard more Uranium  ${}_{192}^{235}\text{U}$  nuclei producing more neutrons and therefore the reaction continues until it is stopped. The above type of reaction is called a **chain reaction** since it consists of repeated steps which are initiated by one step.
- The energy released at each step is so large and it is used to *form atomic bombs* and even to form the *nuclear power stations*.
- The energy released is in accordance with Einstein's law.

$$E = mc^2$$

Where E = energy released

M = loss in mass

C = velocity of light

**NUCLEAR STABILITY**

Compiled by Lawrence arum +256-7505133312/717503108, HOD at K.SS, Also taught at KISUBI MAPEERA, ST JOSEPH'S GIRLS NSAMBYA, KAKIRA S.S, LAKE SIDE COLLEGE LUZIRA .

The stability of the nucleus is *the measure of the extent to which the nucleus remains undistorted.*

Stability of the nucleus is attained when the number of protons in an atom is approximately equal to the number of neutrons i.e. ratio of neutrons: protons = 1.

Stable nuclei is one;

- having number of protons approximately equal to the number of neutrons/ neutrons slightly higher than protons.
- does not undergo radioactive disintegration.
- containing adequate number of neutrons to “ dilute” the concentration of positive charges due to proportions which would repel one another and cause instability in the nucleus.

Nuclides with even number of protons/ neutrons/ both are more stable than those with odd number of protons/ neutrons.

Unstable nuclides are atoms;

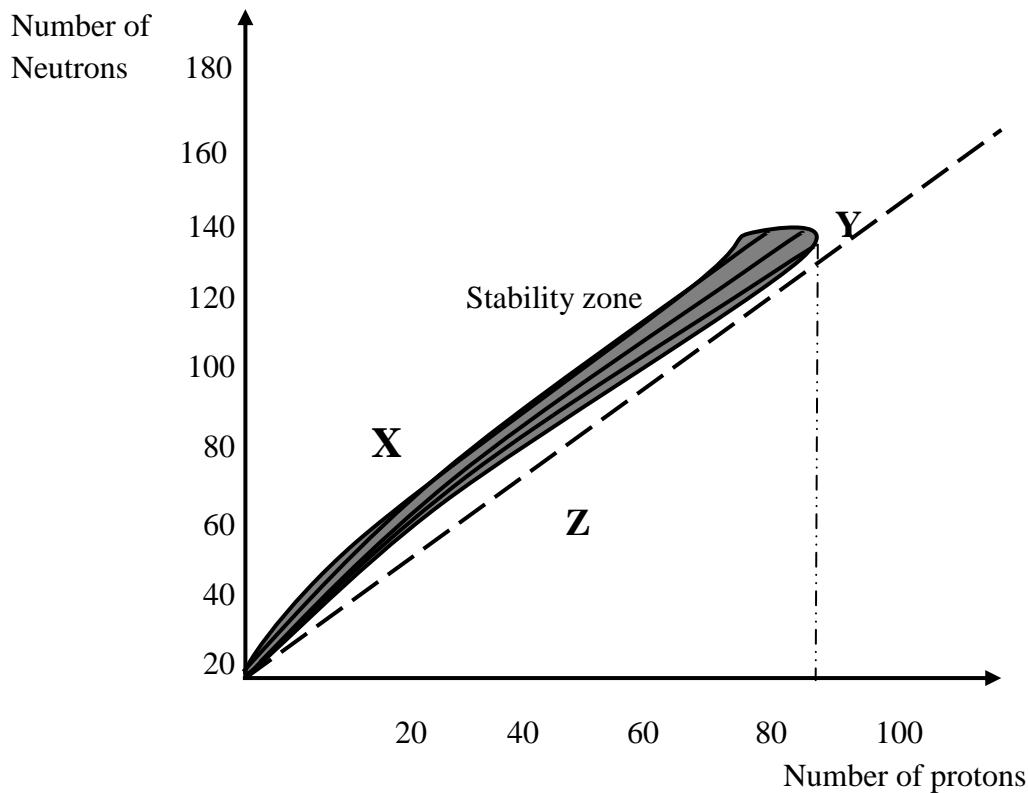
- having number of neutrons much greater than the number of protons/ have a high number of protons than neutrons.
- undergo radioactive decay emitting alpha and beta particles to attain stability.

### **Factors affecting nuclear stability**

#### **i. n: p ratio**

- Stability of a nucleus depends on the neutron proton ratio, because of the exchange of energy between the neutrons and the protons.
- The ratio n : p increases with increase in atomic number and reaches a maximum value when the number of protons is equal to the number of neutrons.

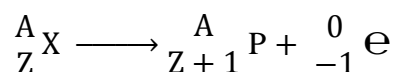
### **A graph showing the r/ship between number of neutrons and the number of protons**



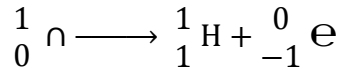
- The graph shows a stable belt (shaded area) or stability region or zone or band running diagonally, starts to curve upwards at atomic number 20 and stops abruptly at atomic number 83.
- All the known stable nuclei lie within the stability zone.
- Along the dotted line, the nuclides have equal number of protons and neutrons i.e.  $n:p \approx 1$ .
- Nuclei at x, y and z outside the stability zone are unstable and therefore undergo radioactive decay to form isotopes which lie in the stability zone, by electron capture, beta emission and alpha emission.

#### Nuclide at x:

- Neutron number  $>$  proton number
- Can lower neutron to proton ratio and move towards the stability zone by **emitting a beta particle**; this decreases the number of neutrons and increases the number of protons in the nucleus i.e.



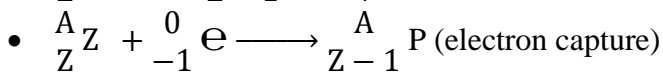
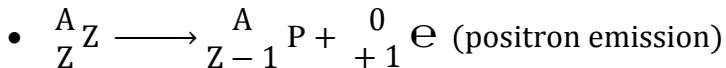
- During emission of a beta particle, one neutron splits up to form a proton and an electron (ejected as a beta particle)



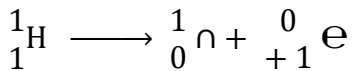
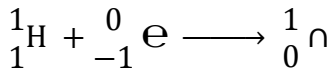
The proton is retained in the nucleus so as the atomic number of the resulting isotope is increased by 1 and thus its nucleus come nearer/ enter the stability zone.

### Nuclide at Z

- Have low n: p ratio i.e. n: p is less than 1, the proton number is greater than the neutron number.
- Such nuclei can lower their ratio and move towards the zone of stability by **electron capture or positron (positive electron) emission**.
- This reduces the number of protons and increases the number of neutrons

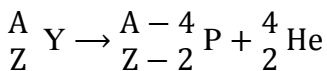


e.g.



### Nuclide at Y.

- Have atomic (proton) number greater or equal to 83 and are heavy, lie beyond the upper right edge of the stability zone.
- Gain stability by **emission of alpha particles** which decreases both number of protons and neutrons.



**NB:** Very heavy nuclei cannot achieve stability with a single emission. Such unstable nuclei undergo a series of emission called *radioactive series or nuclear disintegration series* until a stable nucleus is produced.

#### ii. Half life

The larger the half life the more stable the nuclei and vice-versa

#### iii. Atomic number/ mass number

Stability of the nucleus decreases as the atomic/ mass number increases. Atoms with atomic number 83 are too heavy to be stable.

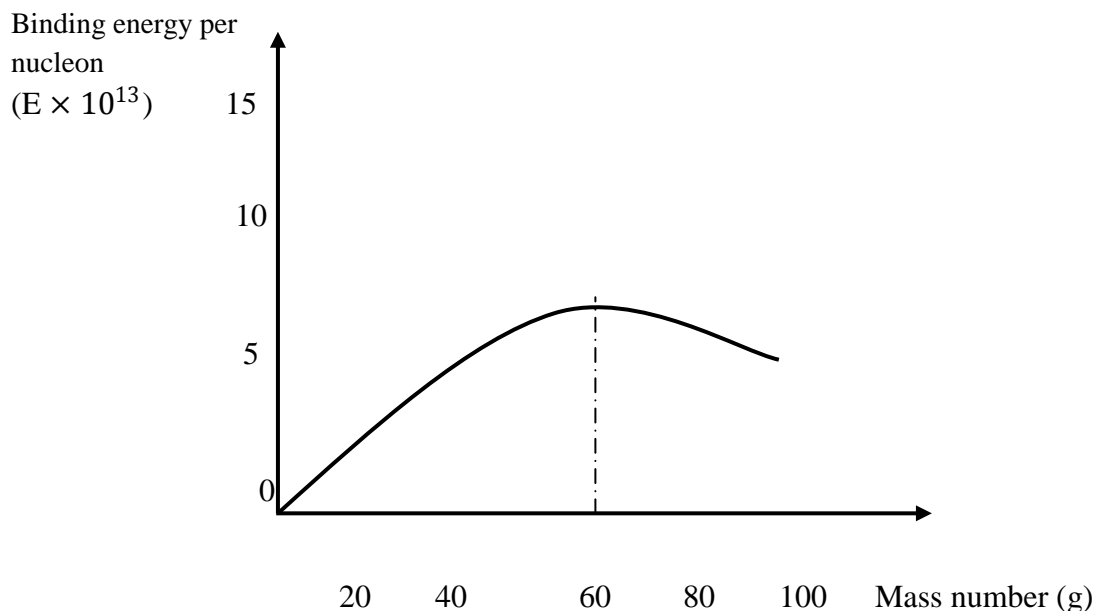
iv. Binding energy.

- This is the energy given out when a nucleus is formed from the individual neutrons and protons or it is required to separate the nucleus into individual nucleons.
- The greater the binding energy, the more stable the nucleus e.g the binding energy of Carbon 14 isotopes is less than binding energy for carbon 12 isotope; thus Carbon-12 isotope is more stable.

**NB:** The mass of the nucleus is slightly less than the masses of the protons and neutrons of which it is composed.

- The difference in mass is called **mass defect** which is transferred into binding energy of the nucleus.
- Einstein's equation gives the relationship between mass and energy.
- The mass defect is the source of binding energy
- Since the constant,  $C^2$  has a large numerical value, even a very small loss in mass is equivalent to release of large amount of energy. This is the origin of the substantial binding energy of the nuclei and the reason why nuclear reactions are an important source of energy.

**A graph showing the relationship between binding energy and mass number**



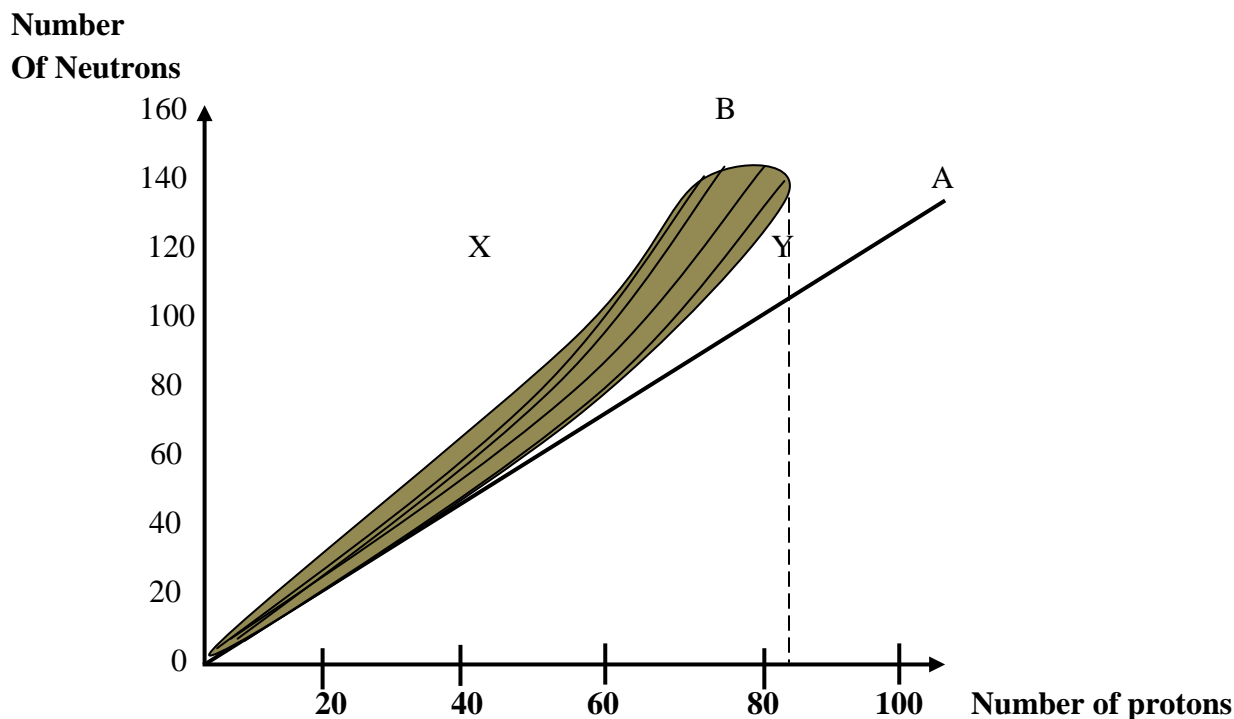
**Interpretation**

- Elements with mass numbers 60 are the most stable.
- Elements with heavier nuclei than this should be able to split into lighter and stable nuclei with release of energy.

- Elements with lighter nuclei than 60 should be able to combine if repulsion between nuclear charges can overcome to form heavier nuclei with release of energy. These processes are called fission and fusion respectively.

**QN: UNEB 1996**

- a) i) What is meant by stability of a nucleus?  
 ii) Explain the factors that determine the stability of a nucleus.

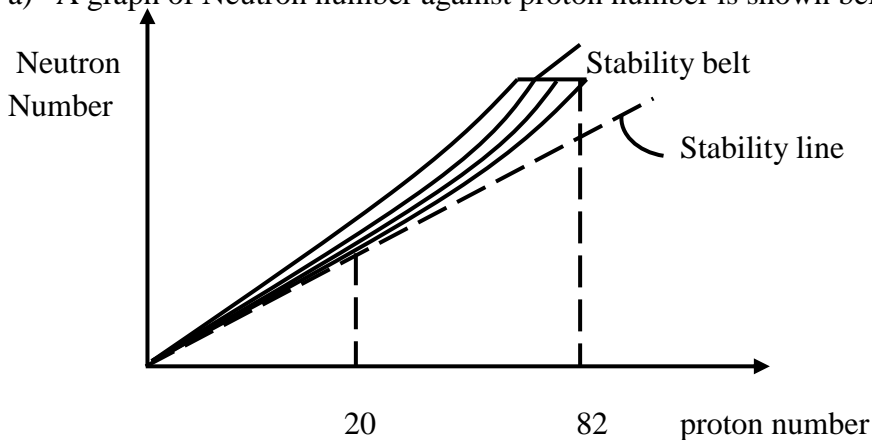


- b) (i) State what lines A and B represent.  
 (ii) Describe briefly how nuclide X and Y can gain stability.

**QN: JJEB 2012**

- Explain what is meant by the term “half life” of the radioactive atom.
  - Write equations for the following nuclear reaction
    - Positive decay of phosphorous  ${}_{15}^{30}\text{P}$
    - Alpha bombardment of aluminum,  ${}_{13}^{37}\text{Al}$
    - Beta decay of Thorium  ${}_{90}^{231}\text{Th}$

a) A graph of Neutron number against proton number is shown below



State how nuclides in region X, Y and Z attain nucleus stability.

b) The activity of a radioactive reduced by  $\frac{7}{8}$  after 42 days. Calculate the half life of the radio isotope

### USES OF RADIOACTIVE ISOTOPES

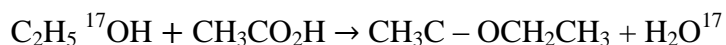
1. Destroying cancer cells ( $^{60}\text{Co}$ ) source is used to radiate cancer patients.
2. Sterilizing surgical instruments (more effective than boiling).
3. Detect leakage in underground water and fuel pipes. Short lived radioactive isotopes are introduced into the pipe and the level of radioactivity on the surface is monitored.
4. Carbon – 14 dating can be used to calculate the age of plants and animal remains. The formed  $^{14}\text{C}$  combines with  $\text{O}_2$  to leave radioactive  $\text{CO}_2$  in the air which is absorbed in green plants during photosynthesis.

The radioactive carbon is then incorporated into the plant tissue and also into the animal tissue since most animals feed on plant materials.

The activity of Carbon – 14 in the living plant/ animal is determined as  $N_0$  and compared with the activity of Carbon – 14 in the dead material as  $N_t$ , which is less than  $N_0$  hence from  $2.303 \log \frac{N_0}{N_t} = kt$ , the age of a dead material can be calculated given  $t_{\frac{1}{2}}$  is  $\approx 5700$  years.

5. Used in tracer studies to trace the path of an element through the body e.g. radioactive iodine is administered to patients with defective thyroids to enable doctors follow the path of iodine through the body and since the half life of iodine is 8 days, the radioactivity soon falls to low levels.
6. Radioactive oxygen,  $^{17}_8\text{O}$  can be used in understanding reaction mechanism of both organic and inorganic ions. E.g. the reaction between ethanoic acid and ethanol can be

studied, when ethanol containing Oxygen – 17, the water formed as a product of the above reaction also contains Oxygen – 17, implying that the O<sub>2</sub> in the water comes from ethanol and not ethanoic acid.



7. In agriculture metabolism of different substances e.g. phosphorus is monitored by radioactive phosphorus i.e. a plant is made to take radioactive phosphorous and its movement within the plant monitored to find out where metabolism takes place.
8. Radioisotopes are also used as tracers to trace the routes of chemicals and physiological reactions such as photosynthesis.

### **DANGERS OF RADIOACTIVE RADIATIONS**

1. Affects living cells and this may lead to death immediately.
- 2.
3. Biological effects on the human body are genetic which appear within an individual for lifetime e.g. skin damage, liver damage, reduced/fertility, cancer and eye cataracts.

### **SAFETY PRECAUTIONS**

- Wear protective gloves, boots and coats when dealing with radioactive substances
- Radioactive source should be held with a pair of tongs and it is advisable not to look at it directly.
- When intensity is high, the users should put on protective badges with monitory gadgets.

### **Assignment.**

**Differentiate between nuclear and chemical reactions**

**(6mks)**

### **ELECTRONIC STRUCTURE OF AN ATOM**

#### **Atomic structure emission**

- When an atom of an element is subjected to heat/electrical discharge, electromagnetic radiations are emitted.

- This means that the atom of the element absorbs energy and emits it in form of electromagnetic radiation.
- When those radiations are passed through a spectrometer, a spectrum consisting of a number of definite lines is obtained.
- Each line consists of a fixed frequency / wavelength of the radiation and the visible parts of the spectrum consists of a series of lines of different colors obtained.

The fact that it is a line spectrum and not a continuous spectrum reveals that only certain energy absorptions and emissions are possible and hence evidence of existence of definite electronic levels. Each absorption is due to movement of an electron from one energy level to a higher energy level and when the electron goes back to the lower energy level, energy is emitted in form of electromagnetic radiations which has a definite energy draw.

### Energy and frequency

Energy and frequency of radiation which can be absorbed or emitted by an electron is known as a quantum of energy

Energy and frequency of radiation can be related by the Planck's equation

$$\Delta E = h\nu; \nu = \frac{c}{\lambda} \quad \text{Where } h \text{ is Planck's constant } (6.6 \times 10^{-34} \text{Js})$$

$\nu$  = frequency (Hz)

$c$  = velocity of light ( $3 \times 10^8 \text{ms}^{-1}$ )

$\lambda$  = wavelength of radiation (m)

## HYDROGEN SPECTRUM

- Each element has its characteristics pattern of lines in its atom and hence its own line spectrum.
- Because hydrogen has only one electron per atom, it has the simplest line spectrum.
- The possible electronic energy levels are denoted by increasing values of  $n$ /principle quantum numbers, whereby the lowest energy level (ground state) is described by  $n = 1$ .
- Emission spectrum of hydrogen consists separate sets of lines or series in ultraviolet, visible, and infra red regions of electromagnetic spectrum.
- Each series is produced by dropping off the electron to a particular energy level from all other energy levels above it i.e **Lyman series**(ultra violet), formed by dropping levels to energy level  $n = 1$ ; **Balmer series**(visible), formed by dropping electrons from higher energy level to energy level  $n = 2$ ; **Paschen series**(infra red), formed by dropping electrons from higher energy levels to energy level  $n = 3$ ; **brackett series**(infra red), formed by dropping electrons from higher energy levels to energy level  $n = 4$ , **P – fund series** (infra red) formed by dropping electrons from higher energy levels to energy level  $n = 5$ .

### Assignment one;

- a) Describe the spectrum of hydrogen atom. Use diagram to illustrate your answer.
- b) Explain how the spectrum of a hydrogen atom

- (i) is formed  
(ii) Provides evidence for existence of energy levels ( 2001, p2)

### **CONVERGENCE SERIES AND IONISATION ENERGY**

a) **The convergence series**

The interval between successive lines in each series gradually becomes smaller as the frequency increase indicating that higher energy levels in the atoms become closer and closer to one another until they finally merge/ converge to form a continuum of light (continuous band of radiation)

b) **Ionization energy**

The energy required to remove an electron completely from an atom. If sufficient energy is given to an atom to excite an electron, that electron will escape and the atom will become a positive ion. i.e. ionization has taken place.

#### **Calculation of ionization energy of Hydrogen atom**

The ionization energy of a hydrogen atom can be calculated from its convergence frequency by using Lyman series of lines i.e. convergence frequency for the Lyman series correspond to the ionisation energy, for Hydrogen, the convergence frequency is  $32.7 \times 10^{14} \text{Hz}$ .

Using Planck's equation;

$$\text{I.E} = hv, \text{ but } h = 4 \times 10^{-13} \text{ KJmol}^{-1}$$

$$\text{I.E} = 4 \times 10^{-13} \times 32.7 \times 10^{14} = \underline{\underline{1308 \text{KJmol}^{-1}}}$$

#### **Energy difference between two energy levels**

The total energy given by an electron in a given energy level is inversely proportional to the square of that principle quantum number, n i.e.

$$E \propto \frac{1}{n^2}$$

For a given atom, the energy possessed by an electron at a given orbit/ energy level is given by;

$$E = hCR_H \left( \frac{1}{n^2} \right) \text{ Where } h = \text{Planck's constant, } C = \text{velocity of light, } R_H = \text{Rydberg's constant.}$$

**Example:** Find the energy of an electron at  $n = 4$ , for a hydrogen atom. Given;

$$n = 4, n^2 = 16$$

#### **Solution:**

Compiled by Lawrence arum +256-7505133312/717503108, HOD at K.SS, Also taught at KISUBI MAPEERA, ST JOSEPH'S GIRLS NSAMBYA, KAKIRA S.S, LAKE SIDE COLLEGE LUZIRA .

$$E = hCR_H \left( \frac{1}{n^2} \right)$$

$$= 6.6 \times 10^{-34} \times 3 \times 10^8 \times 10967800 \times \frac{1}{16} = \underline{\underline{1.357 \times 10^{-19} \text{ Jmol}^{-1}}}$$

When an electron moves from one energy level to another, the energy change will be given by

$$\Delta E = E_i - E_f$$

Where  $E_i$  = initial energy

$E_f$  = final energy

$$\text{For } n = i, E_i = hCR_H \left( \frac{1}{n_i^2} \right) \text{----- (i)}$$

$$\text{For } n = f, E_f = hCR_H \left( \frac{1}{n_f^2} \right) \text{----- (ii)}$$

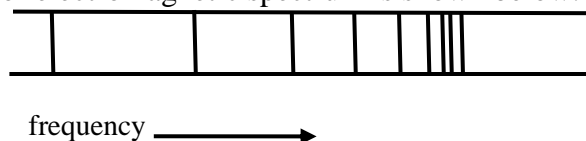
$$\Rightarrow \Delta E = E_i - E_f$$

$$\Delta E = hCR_H \left( \frac{1}{n_i^2} - \frac{1}{n_f^2} \right)$$

N.B The value of  $\Delta E$  is **positive**, when an electron is **moving away** from the nucleus towards a higher energy level but it will have **a negative value** for an electron **moving towards** the nucleus.

### Assignment two;

- Calculate the energy released when an electron drops from an energy level  $n = 5$  to an energy level  $n = 2$  in a hydrogen spectrum.
  - Determine the  $\lambda$  of the photon radiated in this transition.
  - The frequency of hydrogen at the point of ionization is  $32.8 \times 10^{14}$  Hz. Calculate the ionisation energy of hydrogen ( $h = 6.6 \times 10^{-34}$  Js) **UNEB 2001 (P<sub>2</sub>)**
- The sun largely consists of a mixture of hydrogen and helium, presence of each being detected by spectroscopy. The line emission spectrum of atomic hydrogen in the ultra violet region of electromagnetic spectrum is shown below.



- Explain why this spectrum consists of lines which are converging.
- Explain how the ionization energy of atomic hydrogen can be calculated from this spectrum.

### Solution

- a) Lines occur because the atoms have fixed energy levels; and transitions between the upper and lower energy levels; cause emission of light;  
Lines in the ultra violet region end on the energy level with  $n = 1$ ; this forms the Lyman's series, the energy levels get close together as the energy/ frequency increases, so the lines converge.
- b) The convergence limit, where the lines merge, corresponds to an electron at the edge of the atom; the ionization energy is the energy corresponding to that frequency. i.e.  $E = hf$  where  $f$  is convergence frequency.

### **BOHR'S MODEL OF AN ATOM**

It was based on Planck's quantum theory, according to which "*energy can be absorbed/ emitted in certain amounts like separate packets of energy called quantum.*"

Bohr postulated that;

- An electron moving in orbit can have only certain amounts of energy not an infinite number of values, its energy is quantized.
- The energy that an electron needs in order to move in a particular orbit depends on the radius of the orbit i.e. electrons in distant orbits from the nucleus require higher energy than those in orbits near the nucleus.
- If the energy of the electron is quantized, the radius of the orbit must also be quantized i.e. There is a restricted number of orbits with certain radii, not an infinite number of orbit.
- To change from one orbit to another, the electron must absorb or emit a quantity of energy exactly equal to the difference of the energy between the two orbits.

#### **Assignment three**

1.Explain what is meant by the following terms

- a) Quantized
- b) Principle quantum number
- c) Line spectrum
- d) Convergence limit

2.Why do atoms of elements emit discontinuous or line spectrum and not continuous?

## **COLLIGATIVE PROPERTIES OF SOLUTIONS**

A colligative property is that physical property which depends only upon the number of non - volatile solute particles present in the dilute solution and not on the chemical nature of these particles.

Examples include;

- Vapor pressure lowering of the solvent
- Boiling point elevation of the solution.
- Freezing point depression of the solution.
- Osmosis and osmotic pressure of solution.

### **Assumptions/ limitations of colligative properties**

A solution will only exhibit the exact value of a colligative property under the following conditions;

- solute presents should not undergo any association or dissociation.  
Association of solute particles decreases the number of particles lowering the colligative property. Dissociation of solute particles increases the number of particles and the value of colligative property becomes higher.
- There should be no chemical reaction between the solute and the solvent.
- The solutions are assumed to be dilute and ideal. i.e. interaction between the solute particles are negligibly small.
- In case of lowering of vapour pressure and elevation of boiling point, the solute must be non – volatile so that only the solvent particles can exert vapour pressure above the solution (vaporize).

### **COLLIGATIVE PROPERTIES AND DETERMINATION OF RELATIVE MOLECULAR MASSES OF DISSOLVED NON-VOLATILE SUBSTANCES.**

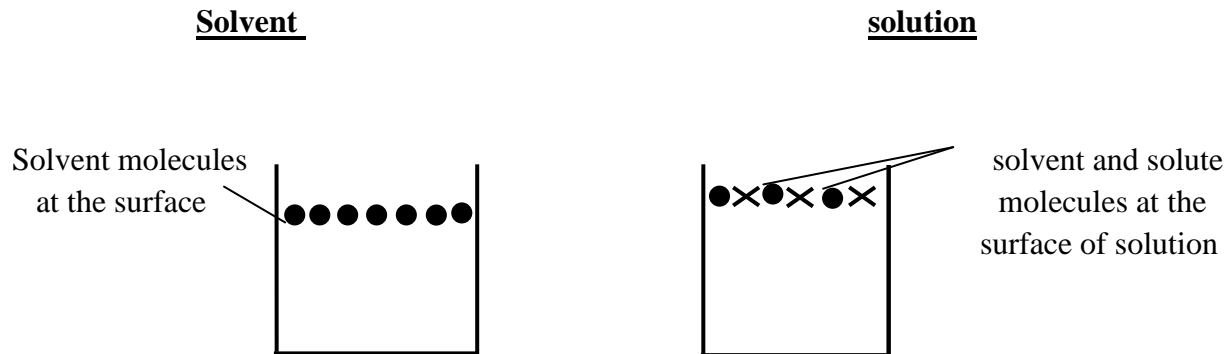
#### **VAPOUR PRESSURE LOWERING OF A SOLVENT**

The vapour pressure of a liquid at a given temperature is the *pressure exerted by the vapour when it is in equilibrium with the liquid*.

Addition of a non – volatile solute lowers the vapour pressure of the solution over that of the pure solvent.

#### **Explanation:**

- Presence of the non- volatile solutes at the surface of the solution reduces the escaping tendency of the otherwise volatile solvent molecules.



- Presence of fewer solvent molecules at the surface of the solution than at the surface of the solvent, few solvent molecules escape into vapour state exerting a small vapour pressure on the solution.
- The lowering of vapour pressure of a solvent is based on **Raoult's law** which states that, "*the relative lowering of the vapour pressure of a solvent is equal to the mole fraction of the non- volatile solute dissolved in that solvent at a given temperature*".

Consider a solution containing some non-volatile solute, let  $X_1$  and  $X_2$  be the mole fractions of the solvent and the solute respectively.

If  $P^0$  is the vapour pressure of the pure solvent and  $P$  is the vapour pressure of the solvent above the solution, then according to;

Vapour pressure of solvent=vapour pressure of pure solvent $\times$  mole fraction of solvent.

$$P = P^0 X_1$$

Addition of a non – volatile solute lowers the Vapour pressure of the solvent,

$$\text{Decrease in Vapour Pressure, } \Delta P = P^0 - (P^0 \cdot X_1), \Rightarrow \Delta P = P_0 (1-X_1) \text{ _____ (i)}$$

$$\text{But } X_1 + X_2 = 1$$

$$X_2 = 1 - X_1$$

$$\text{Substituting in (i) } \Delta P = X_2 \cdot P^0$$

$$\frac{\Delta P}{P^0} = X_2 \text{ (Raoult's law) Where } \frac{\Delta P}{P^0} = \text{Relative lowering of vapour pressure}$$

$$\frac{P^0 - P}{P^0} = X_2$$

Mole fraction of solute  $X_2 = \frac{n_2}{n_1 + n_2}$  where  $n_2$  = mole fraction of solute and  $n_1$  = mole fraction of solvent

But for dilute solution  $n_2 \ll \ll \ll n_1$

$$\Rightarrow n_1 + n_2 = 1$$

$$\Rightarrow \frac{p^0 - p}{p^0} = \frac{n_2}{n_1}$$

$$\text{Number of moles} = \frac{\text{mass of substance}}{\text{RMM of substance}}$$

If  $m_1$  is the mass of the solvent of RMM,  $M_1$  and  $m_2$  is the mass of solute of RMM,  $M_2$

$$\text{Then } \frac{p^0 - p}{p^0} = \frac{\frac{m_2}{M_2}}{\frac{m_1}{M_1}}$$

$$\Rightarrow \frac{p^0 - p}{p^0} = \frac{m_2 \cdot M_1}{M_2 \cdot m_1}$$

$$\Rightarrow \frac{p^0 - p}{p^0} = \frac{\text{mass of solute} \times \text{RMM of solvent}}{\text{RMM of solute} \times \text{mass of solvent}}$$

### **Examples:**

1. Calculate the expected Vapour pressure at  $25^\circ\text{C}$  for a solution prepared by dissolving 158g of a common table sugar, sucrose of molar mass 342.3g in 643.5cm<sup>3</sup> of water at  $25^\circ\text{C}$  (Density of water =  $0.9971\text{gcm}^{-3}$ ), Vapour pressure of water = 23.76Pa)

#### **Solution:**

Vapour pressure of pure  $\text{H}_2\text{O}$ , ( $P^0$ ) = 23.76 Pa

Molar mass of solute = 342.3g

Mass of solute = 158g

RMM of water = 18

Mass of water = Density  $\times$  Volume

$$= 0.9971 \times 643.5$$

$$= 641.63385$$

$$\text{Using } \frac{\Delta P}{p^0} = \frac{\text{mass of solute} \times \text{RMM of solvent}}{\text{RMM of solute} \times \text{mass of solvent}}$$

$$= \frac{158 \times 18}{342.3 \times 641.63385}$$

$$\Delta P = 0.3077\text{Pa}$$

$$\Delta P = p^0 - p$$

$$= 23.76 - 0.3077$$

$$= 23.4523$$

**V.P of solution  $\approx$  23.45Pa**

2. At 290K, the VP of water is  $3.16 \times 10^3$  Pa. calculate the lowering in VP which results when 6g of Urea are dissolved in 1000g of water at the same temperature given that the molecular mass of Urea is 60g.

**Solution:**

VP of water =  $3.16 \times 10^3$  Pa

Mass of solute = 6g

Mass of solvent = 1000g

Molecular mass of solute = 60g

RMM of water = 18g

From Raoult's law;  $\frac{p^0 - P}{p^0} = \frac{\text{mass of solute} \times \text{RMM of solvent}}{\text{RMM of solute} \times \text{mass of solvent}}$

$$\frac{\Delta P}{3.16 \times 10^3} = \left( \frac{6 \times 18}{60 \times 1000} \right)$$

$$\Delta P = 5.688 \text{ Pa}$$

3. The Vapour pressure of  $\text{CS}_2$  at a certain temperature is 53,330 Pa, at the same temperature, a solution of 5g of sulphur in  $63 \text{ cm}^3$  of Carbon disulphide has a VP of 52340 Pa. the density of  $\text{CS}_2$  at this temperature is  $1.27 \text{ g cm}^{-3}$ . Calculate:
- R.F.M of sulphur
  - Molecular formula of sulphur in  $\text{CS}_2$  (C = 12, S = 32)

**SOLUTION**

- a) Vapour Pressure of solute = 53330 Pa ( $\text{CS}_2$ )

Mass of solute = 5g

Volume of solvent =  $63 \text{ cm}^3$

Vapour pressure of solvent = 52340 Pa

Density of solvent =  $1.27 \text{ g cm}^{-3}$

Mass of solvent = Density  $\times$  volume

$$= 1.27 \times 63$$

$$= 80.01 \text{ g}$$

From Raoult's law;

$$\text{RMM} = \frac{p^0 \times \text{mass of solute} \times \text{RMM of solvent}}{(p^0 - P) \times \text{mass of solvent}}$$

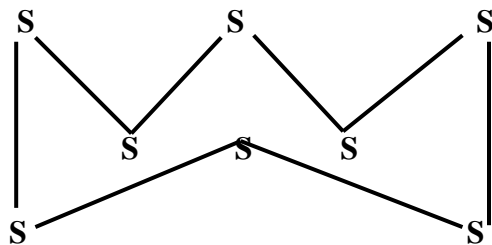
$$= \frac{53330 \times 5 \times 76}{80.01 \times (53330 - 52540)}$$

$$= \underline{\underline{255.844 \text{ g} \approx 256 \text{ g}}}$$

- b) Mass of one atom of sulphur = 32

$$\text{Number of atoms} = \frac{256}{32} = 8$$

$$\Rightarrow \text{S}_8$$



### Assignment

1. A solution of 100g of solute in  $1\text{dm}^3$  of water has a Vapour pressure of  $2.27 \times 10^{-3} \text{Nm}^{-2}$  at  $20^\circ\text{C}$ . The vapour pressure of water at  $20^\circ\text{C}$  is  $2.34 \times 10^{-3} \text{Nm}^{-2}$ . Calculate the molecular mass of the solute.
2. The vapour pressure of Benzene is  $9.97 \times 10^3$  at  $20^\circ\text{C}$ . what is the VP of the solution of 12.8g of naphthalene,  $\text{C}_{10}\text{H}_8$  in 100g of Benzene.

### BOILING POINT ELEVATION OF SOLUTION (EBULLIOSCOPY)

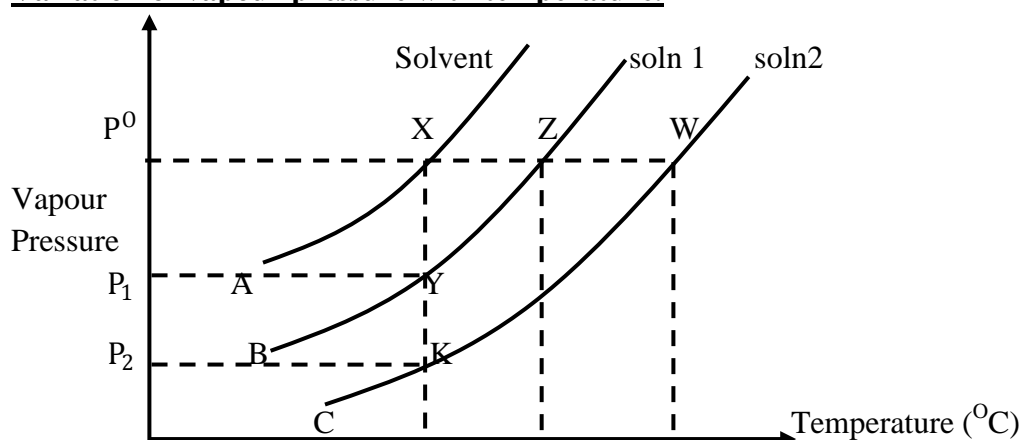
Boiling point of a liquid is the *temperature at which the liquid's vapour pressure becomes equal to the external atmospheric pressure.*

Dissolving a non-volatile solute in a solvent increases/ elevates the boiling point of the solution. The difference between the boiling point of the solution and the boiling point of the solvent is called the *boiling point elevation of the solution.*

#### Explanation:

- The molecule of the non-volatile solute at the surface of the solution reduces the escaping tendency of the volatile solvent molecules into vapour state.
- Hence, the few solvent molecules in the vapour state would only exert a low Vapour pressure onto the solution.
- Thus, this solution has to be heated to a much higher temperature in order for its vapour pressure to be equal to the atmospheric pressure for boiling to occur.

#### Variation of vapour pressure with temperature.



**Curves;**

- i. **AX;**  
Shows the variation of the Vapour Pressure of a pure solvent with temperature
  - ii. **BZ;**  
Shows the variation of vapour pressure of solution 1 with temperature.
  - iii. **CW;**  
Shows the variation of vapour pressure of solution 2 with temperature.
  - iv. **T<sub>0</sub>;**  
Boiling point of pure solvent
  - v. **T<sub>1</sub>**  
Boiling point of solution 1
  - vi. **T<sub>2</sub>;**  
Boiling point of solution 2
- For dilute solutions, the vapour pressure curves are nearly parallel to that of a pure solvent and the curves therefore approximate to straight lines AX, BZ and CW. Therefore triangle XYZ is similar to triangle XWK.

From geometry;

$$\frac{XZ}{XW} = \frac{XY}{XK}$$

$$\text{But } XZ = \Delta T_1 (T_1 - T_0, \text{ for solution 1})$$

$$XW = \Delta T_2 (T_2 - T_0, \text{ for solution 2})$$

$$XY = \Delta P_1 (P^0 - P_1, \text{ For solution 1})$$

$$XK = \Delta P_2 (P^0 - P_2, \text{ for solution 2})$$

$$\text{Therefore } \frac{\Delta T_1}{\Delta T_2} = \frac{P^0 - P_1}{P^0 - P_2} = \frac{\Delta P_1}{\Delta P_2}$$

Dividing the numerator and the denominator of the right hand side by  $P^0$

$$\frac{\Delta T_1}{\Delta T_2} = \frac{\frac{\Delta P_1}{P^0}}{\frac{\Delta P_2}{P^0}}$$

From the above expression, boiling point elevation of a solution is directly proportional to the relative lowering of vapour pressure in dilute solution i.e.

$$\Delta T_b \propto \frac{\Delta P}{P^0} \text{ (i)}$$

But from Raoult's law;  $\frac{\Delta P}{p^0} = X_B$ , mole fraction of the solute.

From (i),  $\Delta T_b \propto X_B$

$\Delta T_b = k X_B$  Where  $k$  = constant of proportionality.

Also  $X_B = \frac{n_B}{n_A + n_B}$  Where  $n_B$  = Number of moles of solute and  $n_A$  = number of moles of solvent.

In dilute solution;  $n_B \llll n_A$

$$\Rightarrow X_B = \frac{n_B}{n_A} = \frac{\frac{m_B}{M_B}}{\frac{m_A}{M_A}}$$

$$= \frac{m_B}{M_B} \times \frac{M_A}{m_A} \text{ Where } m_B = \text{Mass of solute}$$

$m_A$  = mass of solvent

$M_A$  = RMM of solvent

$M_B$  = RMM of solute

$$\therefore \Delta T_B = \frac{K \cdot m_B \cdot M_A}{M_B \cdot m_A}$$

Since  $M_A$  (RMM of solvent) is constant for a particular solvent, both  $k$  and  $M_A = K_b$ ; where  $K_b$  = boiling point elevation constant or ebullioscope constant.

$$\Rightarrow \Delta T_b = \frac{K_b m_B}{M_B m_A} \text{ (ii)}$$

If 1 mole of solute is dissolved in 1000g of the solvent the constant is called **molal boiling point elevation constant**.

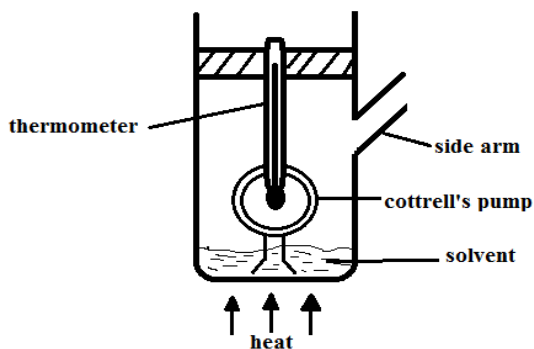
Expression (ii) becomes  $\Delta T_b = k_b \cdot \frac{m_B}{M_B} \times \frac{1000}{m_A}$

### **MOLAL BOILING POINT ELEVATION CONSTANT (EBULLIOSCOPE CONSTANT)**

Is the amount by which the boiling point of 1000g of a solvent is raised by dissolving one mole of a non ionizing and non volatile solute.

### **Determination of R.M.M by boiling point elevation method. (Using Cottrell's method)**

#### **Apparatus:**



2/717503108, HOD at K.S.S, Also taught at KISUBI A, KAKIRA S.S, LAKE SIDE COLLEGE LUZIRA .

### Procedure:

- A known mass of a solvent,  $Xg$  is put in a tube and heated.
- The boiling point of the pure solvent is measured and recorded as  $T_1^{\circ}C$  when the temperature is constant.
- A known mass of solute  $Yg$  is introduced through the side arm.
- The solution is heated and its constant boiling temperature,  $T_2^{\circ}C$  is recorded

### Results:

- Let the boiling point elevation constant be  $K_b$
- Let the elevation in boiling point be  $\Delta T_b (T_2 - T_1)^{\circ}C$
- Mass of solute =  $Yg$
- Mass of solvent =  $Xg$
- Let the R.M.M of the solute be  $M$ .

### Treatment of results

$Xg$  of solvent dissolves  $Yg$  of solute

1000g of solvent dissolves  $(\frac{y}{x} \times 1000)g$  of solute.

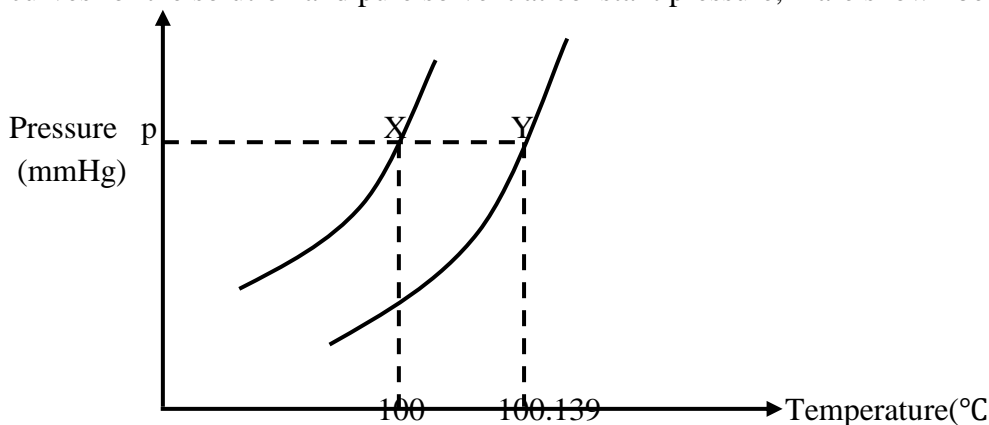
$\Delta T_b$  is the elevation in boiling point caused by  $(\frac{y}{x} \times 1000)g$  of solute

$\Rightarrow K_b$  is the elevation in boiling point caused by  $\frac{1000y}{x \Delta T_b} \times K_b$

$$\boxed{\text{Relative molecular mass of solute} = \frac{1000y}{x \cdot \Delta T_b} \times K_b}$$

### Example

1. 5.5g of a non- volatile substance B was dissolved in 125g of a solvent. The vapour pressure curves for the solution and pure solvent at constant pressure,  $P$  are shown below.



- Identify the curve for the solution.
- Calculate the molecular mass of B, (Boiling point elevation constant for the solvent,  $K_b = 0.52^{\circ}\text{Cmol}^{-1}\text{kg}^{-1}$ )
- State two limitations of your calculation in b)

### **Solution**

- Curve Y
- Mass of solute = 5.5g  
Mass of solvent = 125g  
 $K_b = 0.52$   
Boiling point elevation,  $\Delta T = (100.139 - 100) = 0.139^{\circ}\text{C}$

125g of solvent dissolves 5.5g of solute

1000g of solvent dissolves  $(\frac{5.5 \times 1000}{125})$ g of solute

= 44g of solute

$0.139^{\circ}\text{C}$  boiling point elevation is caused by  $(\frac{44 \times 0.52}{0.139})$  g of solute

= **164.6g**

Molecular mass of solute = **164.6g**

- the solute particles should not associate or dissociate
    - There should be no reaction between solute and solvent
    - The solution is assumed to be dilute
    - The solute should be non volatile.
2. A solution contains 50g of ethane – 1,2 – diol and 40g of water.
- Calculate the boiling point of the solution ( $C = 12$ ,  $O = 16$ ,  $H = 1$ ,  $K_b$  of water =  $0.5\text{Kmol}^{-1}\text{kg}^{-1}$ )
  - State any assumption gas made in the calculation.

### **Soln:**

Let the boiling point of elevation of the solution be  $\Delta T_b$

Molecular mass of the diol,  $\text{C}_2\text{H}_6\text{O}_2 = 62\text{g}$

Mass of solute = 50g

Mass of water =  $0.5\text{Kmol}^{-1}\text{kg}^{-1}$

40g of water dissolves 50g of diol

1000g of water dissolves  $(\frac{250 \times 1000}{40})$  g of diol

$$= 1250\text{g of diol}$$

$\Delta T_b$  is caused by 1250g of diol

0.52 is caused by 62g of diol

$$\Delta T_b = (\frac{1250 \times 0.52}{62}) \text{ K}$$
$$= 10.48\text{K}$$

NB: Boiling point of water =  $100^\circ\text{C}$

$\Rightarrow$  Boiling point of solution =  $373 + 10.48$

$$= \underline{\underline{383.48\text{K}}}$$

3. The addition of 2.01g of glucose to 25g of Benzene caused the boiling point elevation of  $1.204^\circ\text{C}$ , while the boiling point caused by 2.04g of X in 20g of Benzene was  $2.413^\circ\text{C}$ . Calculate

- a)  $K_b$  for Benzene
- b) RMM of X

### Solution

a) Elevation in boiling point caused by glucose =  $1.204^\circ\text{C}$

Mass of Benzene = 25g

Mass of glucose = 25g

$$\text{RMM of glucose, } \text{C}_6\text{H}_{12}\text{O}_6 = (6 \times 12) + (12 \times 1) + (6 \times 16)$$
$$= 180$$

25g of Benzene dissolves 2.01g of glucose

$$1000\text{g of Benzene will dissolve } (\frac{2.01 \times 1000}{25}) \text{ g of glucose}$$
$$= 80.4\text{g of glucose}$$

$1.204^\circ\text{C}$  elevation in boiling point caused by 80.4g of glucose

$$K_b = (\frac{180 \times 1.204}{80.4}) = \underline{\underline{2.6955^\circ\text{C mol}^{-1}\text{kg}^{-1}}}$$

b) Elevation in boiling point caused by X =  $2.415^\circ\text{C}$

Mass of Benzene = 20g

Mass of X is 2.04g

20g of Benzene dissolves 2.04g of X

$$1000\text{g of Benzene will dissolve } (\frac{2.04 \times 1000}{20}) \text{ g of X}$$
$$= 102\text{g.}$$

$2.413^\circ\text{C}$  boiling point elevation is caused by 102g of X

$$\begin{aligned} \Rightarrow 2.6955^{\circ}\text{C boiling point will be caused by } & \left( \frac{102 \times 2.695}{2.413} \right) \\ & = 113.94\text{g} \\ & \approx 114\text{g} \end{aligned}$$

### **RMM of X = 114**

### **UNEB 2003 (2)**

- State what is meant by the term boiling point constant of a liquid.
- Describe an experiment that can be used to determine the R.M.M of a compound using the method of elevation of the boiling point of a liquid.
- Explain why the method you described in b is not used for the determination of R.M.M of ethanoic acid in aqueous solution.
- A solution of 2.8g of Cadmium (II) iodide in 20g of water boils at  $100.2^{\circ}\text{C}$  at a normal pressure. Calculate the RMM of Cadmium (II) iodide (the boiling point elevation constant for water =  $0.52^{\circ}\text{Cmol}^{-1} \text{kg}^{-1}$ )

### **Activity**

- A solution of 5g of X in 100g of water boiled at  $100.42^{\circ}\text{C}$ . Calculate the RMM of X ( $K_b$  of water =  $0.52^{\circ}\text{Cmol}^{-1} \text{kg}^{-1}$ )
- The boiling point of ethanol is  $78^{\circ}\text{C}$ . Calculate the boiling point of solution containing 2.7g of ethanamide ( $\text{CH}_3\text{CONH}_2$ ) in 75g of ethanol ( $K_b$  of ethanol =  $1.15\text{Kmol}^{-1}\text{kg}^{-1}$ , C= 12, O = 16, N = 14, H = 1)
- A solution of 2.8g Cadmium (II) Oxide in 20g of water boils at  $100.2^{\circ}\text{C}$ . Calculate the RMM of Cadmium (II) Oxide. ( $K_b$  of water =  $0.52^{\circ}\text{Cmol}^{-1} 1000 \text{g}^{-1}$ )
- When 0.72g of solute P was in 80g of water, the boiling point of the solution was  $100.16^{\circ}\text{C}$ . Calculate the molecular mass of the solute. ( $K_b$  of water =  $0.52^{\circ}\text{Cmol}^{-1} \text{kg}^{-1}$ )

### **FREEZING POINT DEPRESSION OF SOLUTIONS ( CRYOSCOPY)**

- Freezing point of a solution is the *temperature at which the precipitation of the solid solvent begins (solid solvent crystals begin to separate out of the solution)*  
At this temperature;
- the solid solvent is in equilibrium with the solution ,
- both will have the same Vapour pressure.

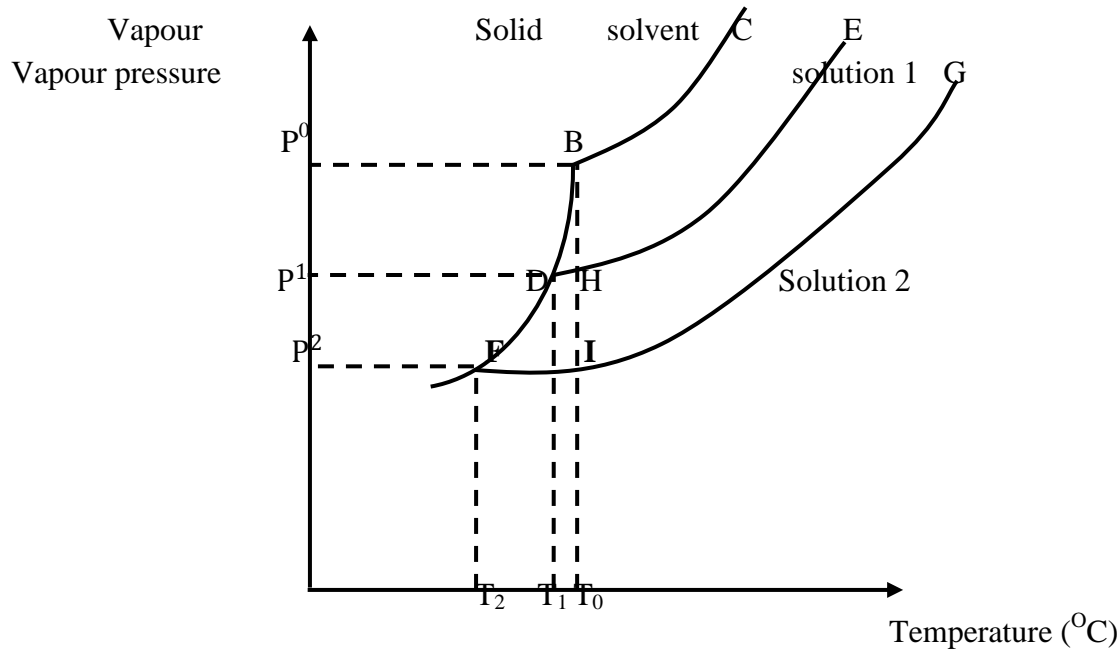
Dissolving a non-volatile solute in a solvent decreases/ depresses the freezing point of the solution. The difference between the freezing point of the solution and the freezing point of the solvent is called the **freezing point depression of the solution.**

### **Explanation;**

- The molecule of the non-volatile solute at the surface of the solution reduces the escaping tendency of the volatile solvent molecules into vapour state.

- Hence, the few solvent molecules in the vapour state would only exert a low Vapour pressure onto the solution.
- Vapour pressure of the solution is therefore lower than that of the pure solvent; and so the vapour pressure of the solution will equal that of the solid solvent at a lower temperature than that of pure solvent; a lower freezing point.

### Variation of Vapour Pressure of solvent and solution with temperature.



#### Curves :

- AB :** - Sublimation curve of solid solvent
  - Solid solvent is in equilibrium with its vapour.
- BC:** Vapour Pressure curve of pure liquid solvent.
  - Liquid solvent is in equilibrium with its vapour.
- DE:** VP curve of solution 1 along which the solution is in equilibrium with its vapour.
- FG:** VP curve of solution 2

#### Points

- B: → Curve AB and BC intersect.
- $T_0$  → Freezing point of the pure solvent
- $T_1$  → Freezing point of solution 1
- $T_2$  → freezing point of solution 2
- D → Curve DE intersects the sublimation curve
  - Both  $T_1$  and  $T_2$  are lower than  $T_0$

- If  $P^O$  is the Vapour pressure of the solid and the liquid solvent at temperature  $T_o$ , and  $P_1$  and  $P_2$  are the Vapour pressures of solution 1 and 2 respectively at the same temperature.
- For dilute solutions, F, D, and B are close to each other and therefore DH and FI approximate to straight lines.  $\rightarrow \Delta BDH$  and FBI are similar.

From Geometry

$$\frac{BH}{BI} = \frac{DH}{FI} \text{ _____ (i)}$$

But  $BH = (P^O - P_1) = \Delta P_1$  (Lowering of VP of solution 1)

$BI = (P^O - P_2) = \Delta P_2$  (Lowering of VP of solution 2)

$DH = (T_o - T_1) = \Delta T_{f1}$  (freezing point of depression of solution 1)

$EI = (T_o - T_2) = \Delta T_{f2}$  (Freezing point depression of solution 2)

Equation (i) becomes

$$\frac{\Delta P_1}{\Delta P_2} = \frac{\Delta T_{f1}}{\Delta T_{f2}} \text{ _____ (ii)}$$

$$\frac{\Delta T_{f1}}{\Delta T_{f2}} = \Delta P_1 / \Delta P_2$$

Dividing the numerator and the denominator of the right hand side of the equation by  $P^O$

$$\Rightarrow \frac{\Delta T_{f1}}{\Delta T_{f2}} = \frac{\Delta P_1}{P^O} / \frac{\Delta P_2}{P^O}$$

$$\text{Or } \Delta T_f \propto \frac{\Delta P}{P^O} \text{ _____ (iii)}$$

But from Raoult's law;  $\frac{\Delta P}{P^O} \propto X_B$

$$\frac{\Delta P}{P^O} = kX_B$$

$$\Delta T_f = kX_B$$

$$X_B = \frac{n_B}{n_A + n_B} \text{ where } n_B = \text{Number of moles of solute.}$$

$n_A = \text{Number of moles of solvent}$

For dilute solutions;  $n_B \ll \ll \ll \ll n_A$

$$\therefore n_B + n_A \approx n_A$$

$$X_B = \frac{n_B}{n_A} \Rightarrow \Delta T_f = \frac{k n_B}{n_A}$$

$$\text{BUT number of moles} = \frac{\text{mass}}{\text{molecular mass}}$$

$$\Rightarrow \Delta T_f = k \left\{ \frac{\left(\frac{m_B}{M_B}\right)}{\left(\frac{m_A}{M_A}\right)} \right\}$$

$$\Delta T_f = \frac{k m_B M_A}{M_B m_A}$$

Where  $M_A$  = Molecular mass of solvent

$M_B$  = Molecular mass of solute

$m_A$  = mass of solvent

$m_B$  = mass of solute

For a given solvent, RMM of a solvent ( $M_A$ ) is constant, therefore both  $k$  and  $M_A$  are replaced by another constant  $k_f$  in equation

$$\Delta T_f = \frac{k_f m_B M_A}{M_B m_A}$$

For a molar solution of 1 mole of solute in 1000g of solvent.

$$\Delta T_f = \frac{k_f m_B \cdot 1000}{M_B m_A} \text{ where } k_f = \text{molal freezing point depression constant / cryoscopic constant}$$

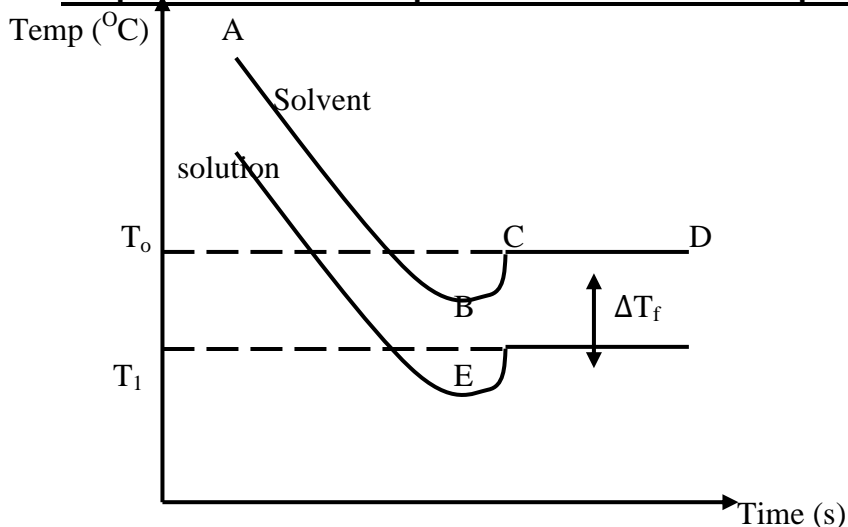
### Molal freezing point lowering constant/cryoscopic constant(K<sub>f</sub>)

Is the amount by which the freezing point of 1000g of solvent is lowered by dissolving 1 mole of solute in it.

### Determination of depression by cooling curves of the solvent and solution

- A known mass of the solvent is placed in the inner glass tube; it is then placed in a freezing mixture.
- Solvent is then stirred continuously; its temperature recorded after known intervals of time until solidification occurs.
- Glass tube then removed and solid solvent melted by warming the glass tube.
- Solute of known mass, is then introduced in the solvent, stirred to dissolve it and whole set up then placed back in the freezing mixture.
- The temperature of the solution is recorded at the same intervals of time until crystals appear.

**Graph of variation of temperature with time are then plotted as below.**



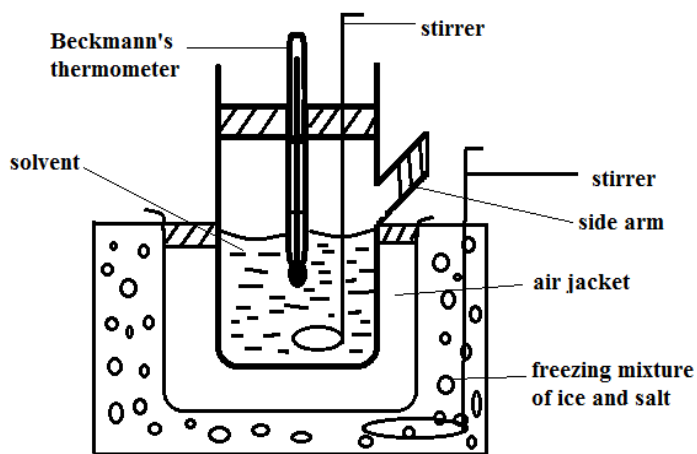
**POINTS**

- B and E represents super cooling
- CD – Temperature remains constant until all the solvent solidify.

NB: Super cooling is the *cooling below the actual freezing point of a liquid resulting from the loss of latent heat of fusion as crystallization starts.*

**DETERMINATION OF RMM OF A SUBSTANCE BY CRYOSCOPY**

**Set up:**



**procedure**

- A known mass,  $W_2$  g of solvent is put in a glass tube containing the Beckmann's thermometer and a stirrer.

- The tube is inserted in the empty vessel which provides an air jacket so as to prevent rapid cooling of the contents of the freezing tube.
- The whole apparatus is then placed in the outer vessel containing the freezing mixture and allowed to cool. As it is cooling, the solvent is constantly stirred in order to avoid super cooling.
- The constant temperature,  $T_0$  °C when the solvent has just solidified is recorded using the Beckmann's thermometer.
- The tube containing the solidified solvent is removed and warmed to melt the solvent.
- A known mass of solute,  $W_1$ g whose MM is under investigation is added into the molten solvent through the side arm.
- The tube is then placed back in the air jacket within the freezing mixture with constant stirring.
- The freezing point,  $T_2$  °C of the solution is determined and recorded.

### **Results**

Mass of pure solvent =  $W_2$ g

Mass of solute =  $W_1$ g

Freezing point of pure solvent =  $T_0$  °C

Freezing point of solution =  $T_1$  °C

Freezing point constant = **K<sub>f</sub>**

Freezing point depression =  $(T_0 - T_1)$  °C =  $\Delta T_f$

Molecular mass of substance = Mr.

### **Treatment of results:**

$W_2$ g of solvent dissolves  $W_1$ g of solute

1000g of solvent dissolves  $\left(\frac{W_1 \times 1000}{W_2}\right)$  g of solute

$\frac{W_1 \times 1000}{W_2}$  g of solute causes a depression of  $\Delta T_f$

RMM of solute causes a depression of  $k_f$

RMM of solute =  $\left(\frac{k_f \times W_1 \times 1000}{W_2 \times \Delta T_f}\right)$

NOTE: Determination of the RMM of a substance by depression of the boiling point is better than by the elevation of boiling point because there is less tendency of the solute decomposing.

### **Examples**

1. 1.5g of a compound Q of molecular mass 90g on dissolving in 30g of water producing a freezing point at  $-1.04$  °C. Calculate the freezing point constant of water.

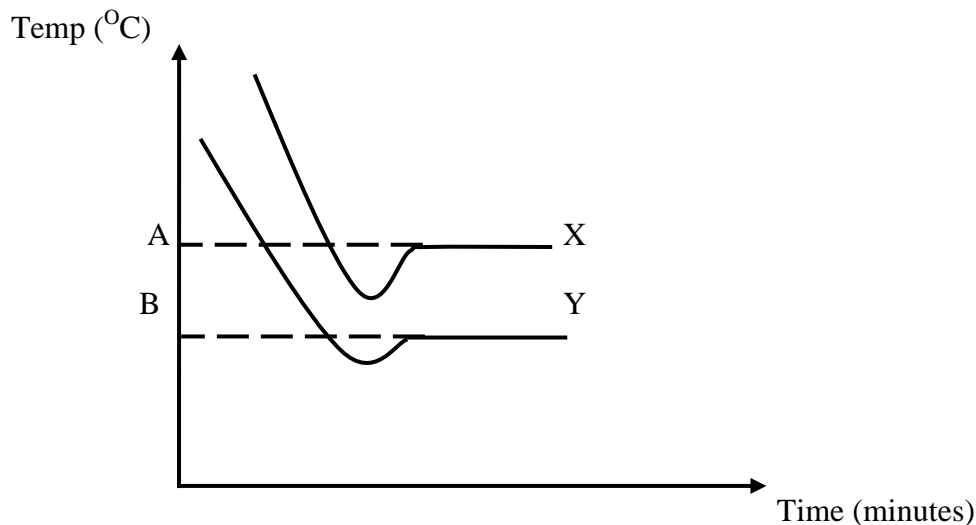
### **Solution:**

Mass of solute = 1.5g



#### 4. UNEB 2007 (10)

The cooling curves of a solution containing 1.2g of sulphur in 20.0g of carbon disulphide and that of pure Carbon disulphide as shown below.



- a) i) Identify curves X and Y.  
ii) State what is represented by points A and B.
- b) i) Calculate the R.M.M of sulphur in Carbon disulphide. (the freezing point depression constant for CS<sub>2</sub> is 6.10 °C mol<sup>-1</sup>kg<sup>-1</sup> and freezing point depression of CS<sub>2</sub> was 1.43°C)  
ii) Comment on your answer.  
iii) Deduce and draw the structure of Sulphur in Carbon disulphide

#### Assumptions/ Limitations of determining R.M.M by depression in Freezing point and elevation in boiling point.

- solution must be dilute
- solute must be highly soluble in the solvent
- solute must be non – volatile
- solute not react with the solvent
- solute should not associate or dissociate.
- solute should not be with a very high R.M.M, because high RMM cause a very small difference in temperature which can not be read off on a thermometer.

#### Questions

UNEB 2003 PAPER 1, No. 1

UNEB 2012 No. 1 PAPER 1

## **QUESTIONS:**

1. a) i) State two advantages of using a mass spectrometer over the depression of freezing point method of determining relative atomic masses.  
ii) Describe how the molecular mass of a substance can be determined using freezing point depression method (diagram not required) (7mks)  
iii) Explain why the method you have described in (ii) is not suitable for determining the molecular mass of a polymer.  
  
b) Calculate the freezing point of solution containing 4.2g of ethane -1, 2 – diol (M.M = 62g) in 30g of water. ( $k_f$  of water =  $1.86^{\circ}\text{C mol}^{-1}\text{kg}^{-1}$ )
2. a) Define the term freezing point constant of a substance.  
b) A solution containing 1.54g of naphthalene ( $\text{C}_{10}\text{H}_8$ ) in 18g of camphor freezes at  $148.3^{\circ}\text{C}$ . Calculate the freezing point constant of camphor (The freezing point of camphor is  $175^{\circ}\text{C}$ )  

**UNEB 2003 PAPER 1**
3. a) The vapour pressure of a solution containing 108.2g of a substance Y in 100g of water at  $20^{\circ}\text{C}$  was reduced by 0.186mmHg (The VP of water at  $20^{\circ}\text{C}$  is 17.54mmHg). Calculate the RMM of substance Y.  
b) State four assumptions made in (a).  
c) Explain why the vapour pressure of a solution containing a non – volatile solute is less than the VP of a pure solvent.
4. A solution containing Xg of cane sugar (RMM = 342) in 105g of water at a pressure of 101.3Pa boiled at  $100.06^{\circ}\text{C}$ . determine X ( $k_b$  of water =  $0.52^{\circ}\text{C mol}^{-1}\text{kg}^{-1}$ ) **UNEB 1993:**

## **OSMOSIS AND OSMOTIC PRESSURE**

### **OSMOSIS**

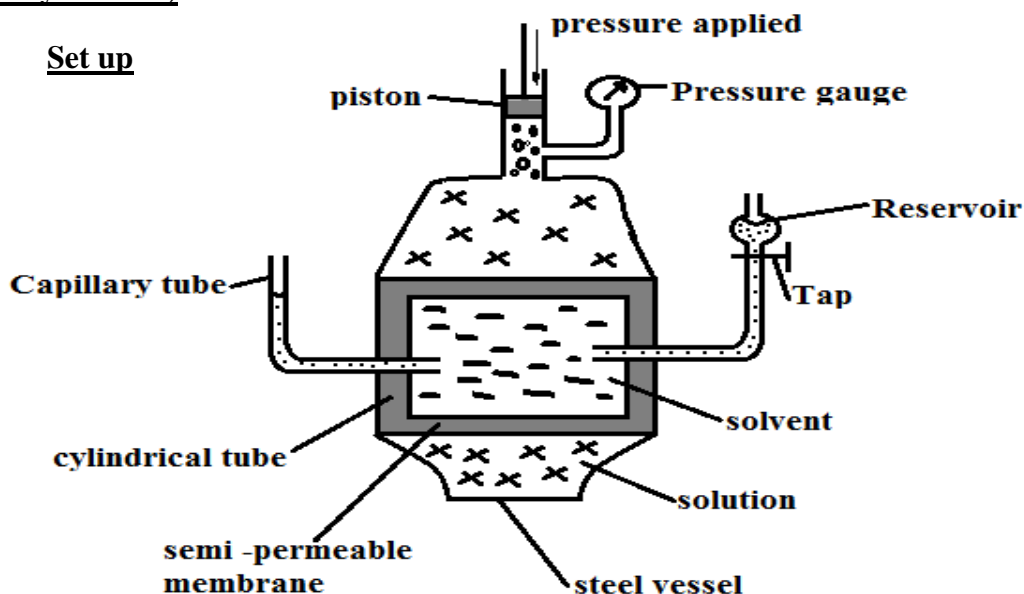
Is the movement of solvent molecules from a dilute solution to a more concentrated solution through a semi – permeable membrane.

### **OSMOTIC PRESSURE ( $\pi$ )**

Is a mechanical pressure which must be applied on a solution to prevent the passage of solvent molecules into the solution through a semi – permeable membrane.

Solutions with the same osmotic pressure at the same temperature are said to be **isotonic**

## DETERMINATION OF OSMOTIC PRESSURE OF THE SOLUTION (By Berkeley and Hartley method)



### Procedure:

- A solution whose Osmotic pressure is to be obtained is put in a steel vessel and separated from the solvent (e.g. water) in a cylinder by a semi-permeable membrane.
- After sometime, the solvent molecules flow through the semi-permeable membrane to the solution hence forcing the solvent levels in the capillary tube to fall slowly.
- The tendency of the solvent molecules to pass into the solution is balanced by pressing the piston until when the solvent in the capillary tube is just at equilibrium i.e. when there is no more solvent molecules passing through the membrane to the side of the solution.
- The pressure at this point is the osmotic pressure of the solution in the steel vessel which is directly read off from the pressure gauge.
- The osmotic pressure is more accurately determined by taking the average readings on the gauge when the levels are slowly rising and falling as is it difficult to adjust the pressure to exactly attain the equilibrium for no movement on either sides.

**NB: Reverse osmosis** is the movement of water from the solution side to the solvent through the semi-permeable membrane on application of too large pressure on the solution side of the membrane.

### Factors affecting Osmotic pressure/ Laws of Osmotic pressure.

#### i. Concentration

- The osmotic pressure of a dilute solution is directly proportional to the molar concentration of the solution at a constant temperature.i.e.

$$\Pi \propto \text{concentration of solution (C)}, \pi = Kc \Rightarrow \frac{\pi}{C} = \text{constant}$$

But  $C \propto \frac{1}{V}$  Where V is the volume of the solution containing one mole of solute.

$$\Rightarrow C = \frac{k}{V}$$

Substituting for C;

$$\frac{\pi V}{k} = \text{constant} \quad \text{_____} \quad \text{(i)}$$

ii. **Temperature:**

- The osmotic pressure of a dilute solution is directly proportional to the absolute temperature of the solution. i.e.

$$\text{I.e. } \pi \propto T$$

$$\Pi = kt$$

$$\frac{\pi}{T} = \text{Constant} \quad \text{_____} \quad \text{(ii)}$$

- Combining the two equations we obtain;  
 $\pi V = nRT$  for n moles of solute
- Equation  $\pi V = nRT$  is called the **Van't Hoff equation** and holds only for dilute solutions.

**Importance of Osmotic pressure**

- Uptake of water by plants through roots and maintains turgidity in plants.
- Used in the determination of Relative molecular mass of polymers.  
This is because high molecular mass solutes (polymers) produce a very small elevation of boiling point/ depression of freezing point that cannot be easily measured.
- Used in many biological processes e.g. distribution of nutrients and release of metabolic waste products.

**Worked example;**

1. Calculate the RMM of sucrose if a solution containing 19.15g of solution per  $\text{dm}^3$  has an osmotic pressure of 136300Pa at  $20^\circ\text{C}$ .

**Solution**

$$\text{Mass of solution} = 19.15\text{g}$$

$$\text{Volume} = 1\text{dm}^{-3} = 10^{-3}\text{m}^3$$

$$\Pi = 136300\text{Pa}$$

$$T = 20^\circ\text{C} = 293\text{K}$$

$$1\text{dm}^3 \text{ contains } 19.15\text{g of solution}$$

$$22.4\text{dm}^3 \text{ contain } (19.15 \times 22.4)$$

$$= \mathbf{428.96\text{g}}$$

$$\text{At } 293\text{K, the osmotic pressure is } 136300\text{Pa}$$

$$\text{At } 273\text{K, the osmotic pressure is } \left(\frac{136300 \times 273}{293}\right)\text{Pa}$$

$$= \mathbf{126996.2457\text{Pa}}$$

126996.2457Pa is caused by 428.96g

$$101325\text{Pa is caused by } \left( \frac{428.96 \times 101325}{126996.2457} \right) \\ = 342.249 \\ \approx \mathbf{342g}$$

2. A solution containing 14g/l of polyvinyl Chloride polymer in 1 litre of dioxane was found to have an osmotic pressure of  $6 \times 10^{-4}$  atmospheres at  $27^{\circ}\text{C}$ . Find the approximate molecular weight of this polymer.
3. The Osmotic pressure of a solution containing 1.24% of a polymer is  $3.1 \times 10^{-3}$  atmospheres of  $25^{\circ}\text{C}$ . Determine the RMM of the polymer.

**Soln**

1.24% = 1.24g in  $100\text{cm}^3$  of solvent

Osmotic pressure =  $3.1 \times 10^{-3}$  atmospheres

Mass of polymer = 1.24g

Volume of solvent =  $100\text{cm}^3$

Temperature =  $25^{\circ}\text{C} = 298\text{K}$

$100\text{cm}^3$  containing 1.24g of polymer

$$22400\text{cm}^3 \text{ will contain } \left( \frac{1.24 \times 22400}{100} \right) \text{ g of polymer} \\ = 277.76\text{g}$$

At 298K, the osmotic pressure is  $3.1 \times 10^{-3}$  atmospheres

$$\Rightarrow \text{At } 273\text{K, the osmotic pressure will be } \left( \frac{3.1 \times 10^{-3} \times 273}{298} \right) \text{ atmospheres} \\ = \mathbf{2.83993 \times 10^{-3} \text{ atmospheres}}$$

$2.83993 \times 10^{-3}$  atmospheres are caused by 277.76g

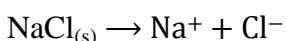
$$1 \text{ atmosphere will be caused by } \left( \frac{277.76 \times 1}{2.83993 \times 10^{-3}} \right) \text{g} \\ = 97805.22\text{g}$$

**$\therefore$  The RMM of the polymer is 97805.22**

**EFFECTS OF DISSOCIATION AND ASSOCIATION OF SOLUTES ON COLLIGATIVE PROPERTY**

**a) Effect of Dissociation:**

Dissociation is the breakdown of ionic compounds into free ions. E.g.



- Dissociation increases the number of particles in solution; and since colligative property depends on the number of the non-volatile solutes, the effect is that colligative property will increase.

- Colligative property is inversely proportional to relative molecular mass of the non volatile solute, thus the experimental RMM of the non – volatile solute will decrease.

### Degree of dissociation ( $\alpha$ )

Is the fraction of the original molecule which has undergone dissociation. For solute which dissociates into  $n$  ions, the degree of dissociation,  $\alpha$  is given by

$$\alpha = \frac{i-1}{n-1} \quad \text{Where } i = \frac{\text{observed /experimental colligative property}}{\text{calculated /theoretical /expected colligativeproperty}}$$

### Example:

When 2.150g of  $\text{Ca}(\text{NO}_3)_2$  in 100g of water forms a solution that freezes at  $-0.62^\circ\text{C}$ . Find the apparent degree of dissociation given that  $k_f = 1.86^\circ\text{Cmol}^{-1}\text{kg}^{-1}$

### Solution

Observed Colligative property, freezing point depression =  $0 - -0.62 = 0.62^\circ\text{C}$

RMM of  $\text{Ca}(\text{NO}_3)_2 = 40 + 28 + 96 = 164$

Mass of solute = 2.150g, mass of water (solvent) = 100g

100g of water dissolves  $\left(\frac{2.15 \times 1000}{100}\right)$ g of  $\text{Ca}(\text{NO}_3)_2$

$$= 21.5\text{g of } \text{Ca}(\text{NO}_3)_2$$

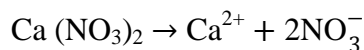
164g of  $(\text{Ca}(\text{NO}_3)_2)$  causes a depression of  $1.86^\circ\text{C}$

21.5g of  $\text{Ca}(\text{NO}_3)_2$  cause a depression of  $\Delta T_f$

$$\Delta T_f = \left(\frac{21.5 \times 1.86}{164}\right)$$

Expected freezing point depression =  $0.24^\circ\text{C}$

Using  $\alpha = \frac{i-1}{n-1}$



$$\therefore \text{Number of moles (n)} = 2 + 1 = 3$$

$$i = \frac{\text{observed colligative property}}{\text{expected colligative property}} = \frac{0.62}{0.24} = 2.5833$$

$$\Rightarrow \alpha = \frac{2.5833-1}{3-1} = \underline{\underline{0.79 \text{ or } 79\%}}$$

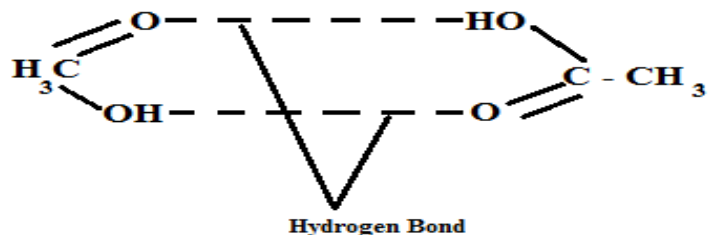
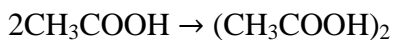
The boiling point of pure water at 760mmHg is  $100^\circ\text{C}$ . At the same pressure, a solution of 0.29g of Sodium chloride in 11g of water boils at a temperature  $0.443^\circ\text{C}$  higher.

- Calculate the boiling point of sodium chloride assuming it did not dissolve in water. ( $k_b$  of water =  $0.52^\circ\text{Cmol}^{-1}\text{kg}^{-1}$ )
- Use your answer in (a) above to calculate the apparent degree of dissociation of sodium chloride in water.

b) **Effects of Association (Dimerisation)**

Association is the combining of smaller solute particles to form larger particles (dimer)

- It lowers the value of colligative property ; increasing the value of RMM of a non volatile solute.
- The solute particles associate through intermolecular hydrogen bonding e.g. Carboxylic acids always associate when dissolved in organic solvents like Benzene. i.e. for ethanoic acid;



For a molecule A which associates,  $2A \longrightarrow A_2$

Initial number of moles	1	0
Moles associated	$\alpha$	$\frac{\alpha}{2}$

At equilibrium	$2(1 - \alpha)$	$\frac{\alpha}{2}$
	$(1 - \alpha)$	$\frac{\alpha}{2}$

Total number of moles	$1 - \alpha + \frac{\alpha}{2}$	
	$= 1 - \frac{\alpha}{2}$	

But colligative property is proportional to the number of particles

$$\frac{\text{Observed colligative property}}{\text{expected colligative property}} = 1 - \frac{\alpha}{2}$$

**Example:**

1. A solution of 3.78g of ethanoic acid in 75g of Benzene boiled at 1.14<sup>o</sup>C above the boiling point of pure solvent.
  - i. Calculate RMM of this acid under this condition and give a comment on your answer.
  - ii. Find the degree of association of this acid given; (kb of Benzene is 2.53<sup>o</sup>Cmol<sup>-1</sup>kg<sup>-1</sup>)

**Solution**

- (i) Mass of solute = 3.78g  
 Mass of ethanoic acid (solute) = 75g  
 $\Delta T_b = 1.14^{\circ}\text{C}$   
 $K_b = 2.53^{\circ}\text{Cmol}^{-1}\text{kg}^{-1}$

75g of solvent dissolves 3.78g of solute

1000g of solvent dissolves  $\left(\frac{3.78 \times 1000}{75}\right)$ g of solute  
= 50.4g of solute

1.14°C elevation in boiling point is caused by 50.4g

2.53°C elevation in boiling point is caused by  $\left(\frac{50.4 \times 2.53}{1.14}\right)$   
= 111.85  
= **112**

### **Comment**

$$\frac{112}{60} = 1.86 \approx 2 \text{ (CH}_3\text{CO}_2\text{H} = 60)$$

The relative molecular mass is almost twice the true value of molecular mass of the acid implying that the acid associated through intermolecular hydrogen bonding in Benzene.

(ii) Observed boiling point elevation = 1.14°C

60g of CH<sub>3</sub>COOH cause an elevation of 2.53

50.4g of acid will cause  $\left(\frac{2.53 \times 50.4}{60}\right)$   
= 2.1252°C

⇒calculated /Expected colligative property = 2.1252°C

$$\frac{\text{Observed Boiling point elevation}}{\text{expected boiling point elevation}} = 1 - \frac{\alpha}{2}$$

$$\frac{1.14}{2.125} = 1 - \frac{\alpha}{2}$$

$$\alpha = 2 \left(1 - \frac{1.14}{2.125}\right)$$

$$\alpha = \mathbf{0.93 = 93\%}$$

## BONDING AND STRUCTURE

- Atoms combine in order to acquire a stable noble gas structure.
- They do this by either transfer of electrons from one atom to another or by sharing electrons contributed by each atom.
- Only electrons in the outermost shell/ valence shells are involved in bonding

### TYPES OF BONDING

There are six types of bonding namely;

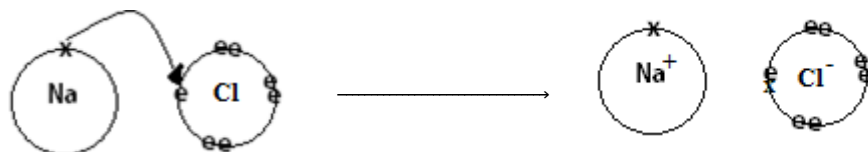
- Ionic/electrovalent/ Heteropolar bonding
- Covalent/ Homopolar bonding
- Dative/ Co-ordinate bond
- Metallic bonding
- Hydrogen bonding
- Van der waal's forces/bonds

#### a) IONIC BONDING

- ✓ An ionic bond is formed by complete transfer of electrons from one atom to another to form oppositely charged ions held together by electrostatic forces of attraction.
- ✓ It is formed between a metal (electropositive) and a non metal (electronegative) e.g. bonding between Na (11) and chlorine atom (17)

Na:  $1S^2 2S^2 2P^6 3S^1$

Cl:  $1S^2 2S^2 2P^6 3S^2 3P^5$



The electron transferred from Sodium atom fits in the singly occupied orbital of the 3P of the Chlorine atom i.e.

#### Sketch

Before transfer

	Px	Py	Pz
Before transfer	↑↓	↑↓	↑

After transfer

	Px	Py	Pz
After transfer	↑↓	↑↓	↑↓

Other examples of compounds formed by electrovalent bonding include

- $CaCl_2$ ,  $MgO$ ,  $KI$ ,  $NaH$  etc

## Factors that affect formation of ions

i. **Ionization energy:**

The lower the ionization energy the most loosely held is an electron and the more electropositive the element.

ii. **Electron affinity:**

Is the ease with which the atoms form anions/negatively charged ions. The greater the value of electron affinity, the easier is negatively charged ion formed.

### COVALENT CHARACTER IN IONIC BOND

The covalent character of the ionic bond depends on the;

- ✓ polarizing power of the positive ion
- ✓ polarisability of the negative ions.

a) **Polarising power of cations**

An ionic bond will acquire a degree of covalent character if the positive ion can attract electrons from the negative ion back into the region between the two nuclei.

The covalent bond character arises because the electrons are partially shared. i.e.



- Polarizing power is the extent to which a positive ion can attract electrons from negative ion back into the region between the nuclei.

### Factors affecting polarizing power.

i. **Charge on the cation:**

The larger the positive charge on the ion, the greater the attraction of the valence electrons.

ii. **Size of the cation**

The smaller the size of the cation, the closer it is to the valence electrons and the larger the force it exerts on them.

iii. **Charge density (charge : radius ratio)**

The greater the charge density of the cation, the greater its polarizing power and therefore the greater the covalent character of the bond it forms with the anion.

**Consider the data below**

Ions	Na <sup>+</sup>	Mg <sup>2+</sup>	Al <sup>3+</sup>
Ionic radius	0.095	0.065	0.05
Polarizing power ( $\frac{Z}{r}$ )	10.5	30.5	60
Melting point of anhydrous chloride	801	712	180

**Interpretation**

- Polarizing power of the cat ions increases in the order of  $\text{Na}^+ < \text{Mg}^{2+} < \text{Al}^{3+}$ .
- $\text{Al}^{3+}$  having a high polarizing power exerts the strongest polarization in Aluminium (III) chloride resulting in a high degree of Covalence in Aluminium chloride, giving aluminium chloride the lowest melting point.
- Low polarizing power of  $\text{Na}^+$ , sodium chloride remains essentially an ionic compound with a very high melting point.

**Questions:**

1. Briefly explain why NaCl melts at 800<sup>0</sup>C where as AlCl<sub>3</sub> sublimes at 180<sup>0</sup>C.

**Solution**

Both NaCl and AlCl<sub>3</sub> have ionic bonding; but because of small size and large charge of Al<sup>3+</sup> ions; which gives it large polarizing power; the electron on the outermost shell of the chloride ions are greatly displaced (polarised) towards the Al<sup>3+</sup>; such that aluminium chloride, AlCl<sub>3</sub> develops some covalent character; making it have low melting point just like covalent compounds;

NaCl is purely ionic hence very high melting point.

**b) Polarisability of the anions**

The extent to which a positive ion can pull electrons back into the space between the two nuclei depends not only on the polarizing power of the cat ion but *also how easily it is to polarize a negative ion.*

The polarisability of a negative ion measures the ease with which its electron density can be distorted.

**Factors affecting polarisability:**

**i. Charge on the negative ion**

Polarisability increases with increase in the charge on the anion.

This is because as the charge on the anion increases, the anion repels its outermost electrons strongly and effectively.

ii. **Size of the anion/number of electrons the anion has**

Polarizability increases with increase in size of the anion / increase in the number of electrons e.g.

- ✓ Fluoride ions have fewer electrons and ;
- ✓ are smaller than the chloride ions; giving it a lower polarisability than chloride ions; decreasing its covalent character.
- ✓ All fluorides have greater ionic character than the corresponding chlorides.
- ✓ This explains why Aluminium fluoride is a crystalline solid melting above  $1000^{\circ}\text{C}$  whereas Aluminium chloride shows covalent character.

**Qn 1:** i) Explain why aluminium fluoride  $\text{AlF}_3$  is ionic and Aluminium chloride is covalent.

ii) Explain why the melting point of  $\text{CaO}$  is higher than that of  $\text{CaCl}_2$

**Qn 2** The ionic radii of Sodium ions,  $\text{Mg}^{2+}$  and  $\text{Al}^{3+}$  are given in the table below

Ion	$\text{Na}^+$	$\text{Mg}^{2+}$	$\text{Al}^{3+}$
Ionic radius (nm)	0.095	0.065	0.050

- a) Calculate the charge to radius ratio for
- i.  $\text{Na}^+$
  - ii.  $\text{Mg}^{2+}$
  - iii.  $\text{Al}^{3+}$
- b) Which of the ions has
- i. Least polarizing power
  - ii. The greater polarizing power
- c) Give a reason for your answer in (b) above.

## **PROPERTIES OF IONIC COMPOUNDS**

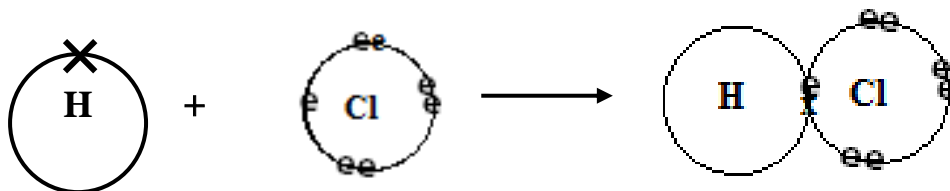
- Are crystalline solids at room temperature.
- Have high melting and boiling points due to strong electrostatic attraction between the oppositely charged ions.
- Soluble in water but are insoluble in organic solvents eg Benzene and ethoxy ethane
- Conduct electricity in their molten state and solution state due to the presence of free ions.
- Oppositely charged ions react together in aqueous solution instantaneously/ rapidly.

b) **COVALENT BONDING**

- A Covalent bond is formed by sharing a pair of unpaired electrons between atoms, each of which donates an electron to the bond.
- It's formed between atoms with either no electronegativity difference or a small electronegativity difference e.g. in chlorine molecule and hydrogen chloride.
- Occurs in non – metals and results into the formation of molecules.

**Illustration:**

i. Hydrogen chloride



**BOND POLARITY IN COVALENT COMPOUNDS**

The covalent bond which holds the two atoms together within the molecule contains a pair of electrons shared between the two atoms.

When the two bonding atoms are not identical, the electrons will be unequally shared.

Unequal sharing of electrons is because different atoms have different power of attraction for electron pairs i.e. **have different electronegativity values**.

**NB:** Electronegativity is the relative ability of an element to attract bonding electrons towards itself.

When unequal sharing of electrons occur, it results in slight separation of charge whereby the more electronegative atom acquires a partial negative charge ( $\delta^-$ ) and the other positive charge ( $\delta^+$ ).

Bond polarity is therefore ***the unequal sharing of electrons in a covalent bond leading to the separation of charge***.

The higher the electronegative difference between two bonding atoms, the greater the separation of charge and hence the bond polarity.

Bond polarity in diatomic molecule results in the separation of charge over the whole molecule and the molecule is thus said to be polar and the overall molecule has an electric dipole (separated charges of opposite signs) quantified as the electric dipole moment, whose magnitude depends on the magnitude of charge and distance separating the charge.

A molecule made up of more than 2 atoms and having polar bonds within itself may not necessarily have an overall dipole moment, if the molecule is symmetrical.

### Reasons:

Symmetrical distribution of atoms about the central atom, creates equal and opposite dipole moment in all directions that cancel out making the molecule non polar e.g;

i. Carbon dioxide;

Resultant dipole moment = 0

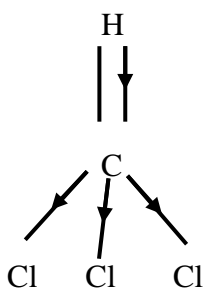
ii. Tetrachloromethane,  $\text{CCl}_4$

Resultant dipole moment = 0

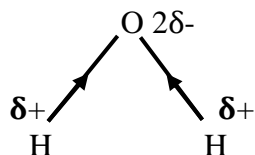
The lack of an overall dipole moment on the molecules makes the molecule non – polar and it is an indicator for the symmetry within that molecule.

Unsymmetrical molecules like water, Ammonia and trichloromethane have an overall dipole moment over the molecule and are said to be polar.

i. Trichloromethane



ii. Water



This explains why trichloromethane is deflected by a charged rod while tetrachloromethane is not, when liquid trichloromethane and tetrachloromethane are passed separately from the beaker closer to the charged rods.

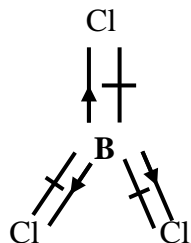
### Example:

Explain why Boron trichloride, is a non – polar molecule while Nitrogen trichloride ( $\text{NCl}_3$ ) is polar.

### Soln:

Boron trichloride has a trigonal planar structure in which the chloride atoms are arranged symmetrically around the central Boron atom.

Therefore because of this symmetry, the net dipole moments cancel out to zero.



However Nitrogen trichloride has a trigonal pyramidal structure in which the chloride ions are not symmetrically arranged.

Therefore there is a net dipole moment in the direction of the more electronegative chlorine atom hence the trichloride is polar.

### PROPERTIES OF COVALENT COMPOUNDS

- More soluble in organic solvents but insoluble in water.
- Do not conduct electricity due to absence of free ions in them except a few which form ions when dissolved in water e.g. hydrogen chloride.
- Consists of discrete molecules and not ions.
- Mainly gases, liquids with very low melting points.

### C.) DATIVE/ CO-ORDINATE BOND

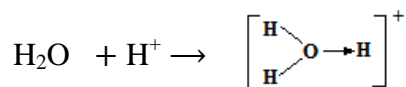
Is a covalent bond whereby an electron rich atom in a molecule gets bonded to another atom/ ion of a species which is electron deficient.

The donor atom donates the non bonding pair of electrons (lone pair) to the acceptor atom which must be either a;

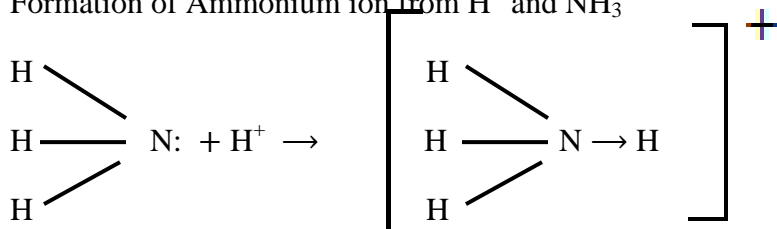
- positively charged species or
- must have an empty orbital.

### Examples;

- Formation of hydroxonium ions from water and acid.



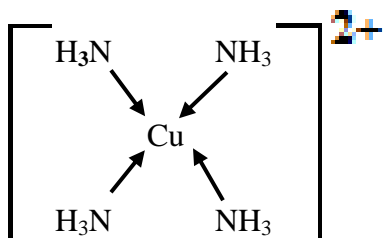
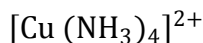
- Formation of Ammonium ion from  $\text{H}^+$  and  $\text{NH}_3$



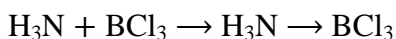
iii. Existence of dimer of  $\text{FeCl}_3$  and  $\text{AlCl}_3$  in vapour state



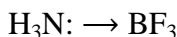
iv. Formation of transition metal complexes; ligands (bonding atoms) donate their lone pairs of electrons to empty d. orbital of transition metal ions. E.g.



v. Between Ammonia and Boron trichloride



For  $\text{BF}_3$



**NB:** Dative bond is;

- weaker than normal covalent bond.
- represented by an arrow which shows direction in which a lone pair of electron is donated.

#### D.) METALLIC BONDING:

- A metal consists of identical atoms closely packed together.
- The outermost electrons are lost control of and uniformly delocalized over the whole metal, ionizing the metal atoms.
- Metallic bonding therefore consists of attraction between the “sea” of mobile delocalized electrons and the positively charged nucleus of metal atoms.
- These delocalized electrons are responsible for the conductivity of heat and electricity by metals.
- Metals have high melting points, the melting points depending on the ***strength of the bond that holds the atoms in a rigid structure.***
- The strength of the metallic bond formed depends on the ***number of valence electrons which each metal atom contributes to the cloud.***

e.g.

- i. Melting point of group II elements is higher than those of group I because they contribute two electrons in forming the metallic bond.

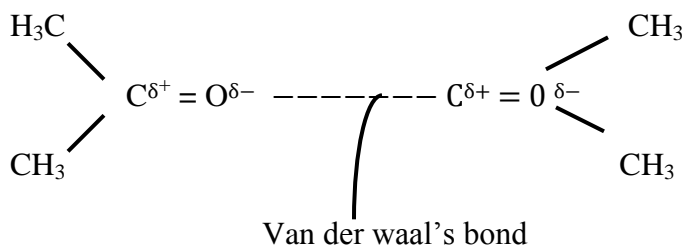
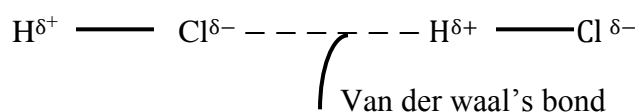
- ii. The melting points of transitional metals are higher than those of higher metals because they use electrons from 4S and 3d to form strong metallic bonds.

**E.) VAN DER WAAL'S FORCES:**

Is the intermolecular force of attraction between two molecules. They include;

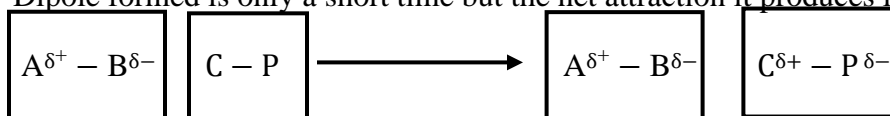
**i. Dipole – Dipole interaction:**

- Electrostatic attraction between the opposite ends of dipole amount for intermolecular bonding in polar compounds.
- These polar molecules have partial charges due to the difference in their electronegativity e.g in HCl and Propanone;



**ii. Dipole – Induced dipole interaction:**

- Consider two nonpolar molecules which are very close to each other.
- Since they are nonpolar the arrangement of electrons on average is symmetrical.
- However at any instant, the electron distribution in one molecule may be unsymmetrical resulting into a dipole at a particular instant.
- This dipole may induce a dipole through a neighbouring molecule.
- Dipole formed is only a short time but the net attraction it produces is permanent.



N.B.

- High relative molecular mass molecules have high van der waal's forces of attraction; because of increase in the number of electrons which are loosely bound in a molecule.
- Energy associated with vanderwaal's bond is small compared to the normal covalent bond.

## Evidence for the existence of Vander waal's forces

- ✓ Increase in boiling and melting points of group VI elements down the group and in alkane.
- ✓ Changing physical states of the halogens down the group i.e. in iodine because of the big size of molecules the forces are strong enough to hold the Iodine molecules in solid state while fluorine and chlorine the forces are weak and are overcome at room temperature.
- ✓ Liquefaction of gases
- ✓ Non -ideal behavior of gases

## F) HYDROGEN BONDING:

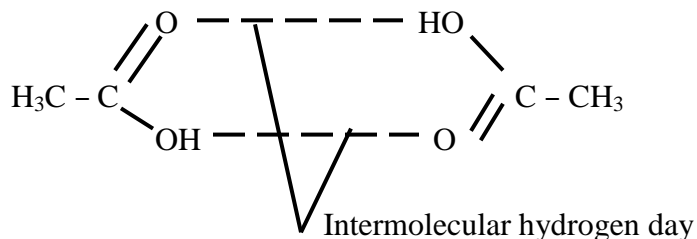
Is a permanent bond formed by dipole interaction/attraction between the hydrogen atom bonded to an electronegative element e.g. oxygen, Nitrogen and fluorine and another highly electronegative atom with at least a lone pair of electrons.

### TYPES OF HYDROGEN BONDING

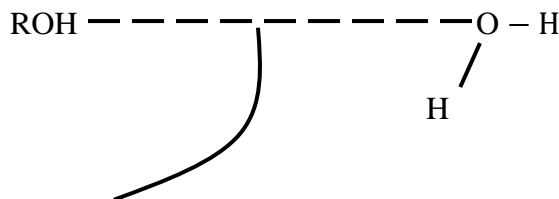
#### 1. Intermolecular hydrogen bond:

Is a hydrogen bond formed between two/more similar or different molecules e.g.

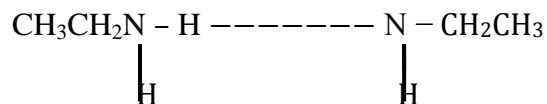
- a) Two similar carboxylic acid. E.g. Ethanoic acid.



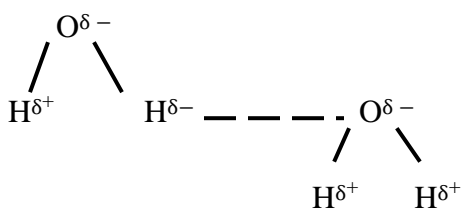
- b) Between two different molecules eg water and alcohol



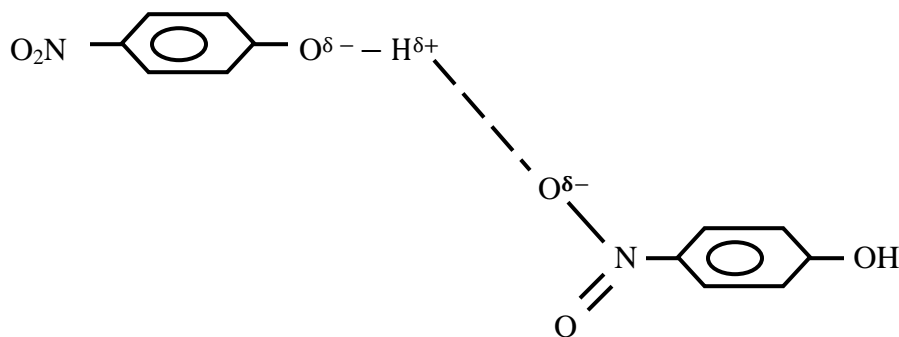
- c) Two similar amines



- d) Water molecules



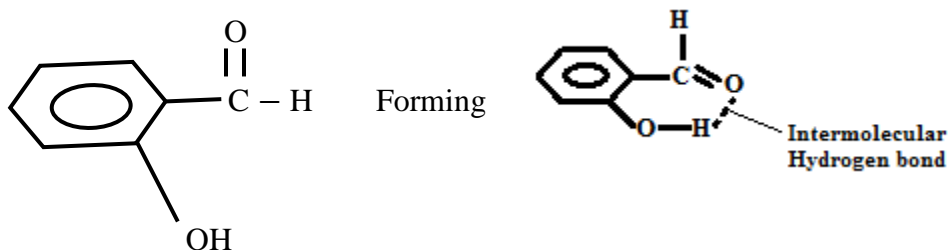
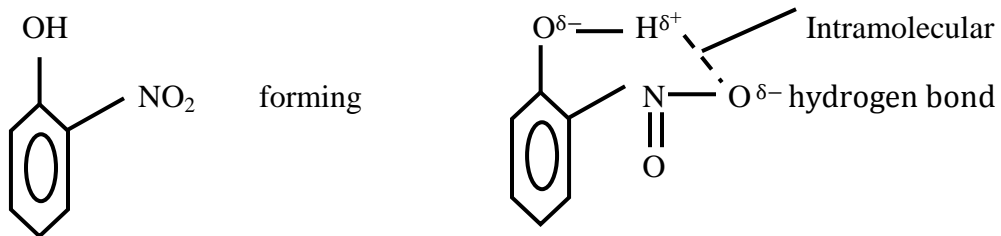
e) 4 – nitrophenol



## 2. Intramolecular hydrogen bond

Is the hydrogen bond formed between atoms of the same molecule e.g

- a) Between the bases of the DNA molecules
- b) Protein molecules
- c) In 2 – nitrophenol
- d) 2 – hydroxyBenzaldehyde. i.e



NB: The energy associated with hydrogen bond is small compared to the normal covalent bond.

### EFFECT OF HYDROGEN BONDING:

Compiled by Lawrence arum +256-7505133312/717503108, HOD at K.SS, Also taught at KISUBI MAPEERA, ST JOSEPH'S GIRLS NSAMBYA, KAKIRA S.S, LAKE SIDE COLLEGE LUZIRA .

✓ **Increased viscosity:**

Hydrogen bonding increases the viscosity of liquids leading to reduced volatility and reduced vapour pressure of that liquid eg in water

✓ **Association of molecules:**

Hydrogen bonding leads to association or dimerisation of carboxylic acids when dissolved in organic solvents like Benzene, doubling the molar mass of the acid.

It also leads to association of hydrogen fluoride molecules forming hydrogen difluoride. This is because of the small size of hydrogen atom which allows the lone pairs of electrons to approach closely the hydrogen nucleus and high electronegativity of fluorine leading to formation of strong hydrogen bond.  $H^{\delta+} \underline{\quad} F^{\delta-} \text{-----} H^{\delta+} \underline{\quad} F^{\delta-}$

✓ **Increased boiling and melting point:**

Hydrogen bonded molecules like Ammonia, water, hydrogen fluoride have abnormally high boiling points compared to those of the hydrides of other elements in group (V), (VI), (VII) respectively, this is because the hydrides of nitrogen, Oxygen and fluorine associate through hydrogen bonding.

Boiling points of alcohols, amines and carboxylic acids are higher than boiling points of corresponding alkanes with similar molar mass because of association through hydrogen bonding and therefore excess energy is needed to break the hydrogen bond.

✓ **Solubility in water:**

Phenols, alcohols and carboxylic acids, primary and secondary amines are more soluble in water than other alkanes of similar molecular mass because of the ability to form hydrogen bonds with water.

2 – nitrophenol and 2 – hydroxyBenzaldehyde are less soluble in water than their corresponding isomers because formation of intramolecular hydrogen bond prevents interaction with neighbouring molecules.

NB: This also explains why 2 – nitrophenol boils at a low temperature than 4 – nitrophenol.

✓ **Increased volume and decreased density of ice:**

Ice is less dense than water and thus floats on it; because the water molecules associate via extensive intermolecular hydrogen bonding; giving ice an open tetrahedral structure; with a bigger volume than that of water with the same mass; and since density is

inversely proportional to volume, then ice will have a less density than water for a given mass.

Therefore when ice is heated, hydrogen bonding is progressively broken giving rise to closely packed liquid structure in the liquid water with decrease in volume and increase in density.

- ✓ A needle covered on the surface of water may float because of surface tension and hydrogen bonding in water.

***Explain the following observations;***

- (i) hydrogen fluoride has a higher boiling point than hydrogen chloride.
- (ii) melting point of 4 – nitrophenol is much higher than that of 2 – nitrophenol.

### **SHAPES OF MOLECULES/IONS**

- Determining shapes of molecules and ions of non –transition elements is based on the **Valence shell Electron pair repulsion theory** (VSEPR Theory) which states “ electron pairs around a central atom repel each other to take up positions as far apart as possible.”
- The electron pairs take up this arrangement so that potential energy due to their electrostatic repulsion is at a minimums.
- The electron pairs can be bonding (shared) pairs which contribute to the covalent bond or unshared (lone pairs) i.e. not used in bonding.
- Lone pairs of electrons give a greater repulsion as they are closer to the nucleus. Electron pair repulsion is in order  $L.P \leftrightarrow L.P > L.P \leftrightarrow B.P > B.P \leftrightarrow B.P$
- According to this theory, ***multiple bonds (double/ triple bonds) act as single shared pairs of electrons.***
- Therefore the shape of a molecule is based on the electron pairs that it has.

<b>Number of electron pairs</b>	<b>Shape of molecule / ion</b>
i. Two pairs	Linear
ii. Three pairs	Trigonal planar
iii. Four pairs	Tetrahedral
iv. Five pairs	Trigonal bipyramidal
v. Six pairs	Octahedral

a) **MOLECULES WITH ONLY BONDING PAIRS**

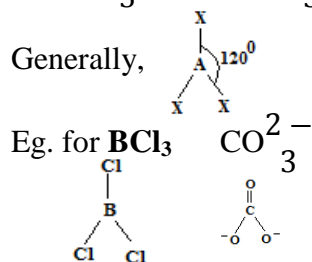
In molecules with only bonding pairs and no lone pairs of electrons on the central atom, the total number of electron pairs equals the number of bonding pairs.

i. **Two bonding electron pairs (AX<sub>2</sub>)**

- Shape of the molecule is *linear* ; because bonding pair around the central atom repel one another as fully as possible at an angle of 180<sup>0</sup> eg  
HgCl<sub>2</sub>, BeCl<sub>2</sub>, CO<sub>2</sub>, CS<sub>2</sub>, HC ≡ CH,  
For CO<sub>2</sub>, O = C =O

ii. **Three bonding electron pairs (AX<sub>3</sub>)**

- Shape of the molecule is *trigonal planar*.
- This is because the 3 bonding electron pairs repel one another equally making the bonds to lie in the same plane at an angle of 120<sup>0</sup> to one another e.g in BCl<sub>3</sub>,  
CO<sub>3</sub><sup>2-</sup>, SO<sub>3</sub>, NO<sub>3</sub><sup>2-</sup>, BF<sub>3</sub>, CH<sub>2</sub> = CH<sub>2</sub>, BBr<sub>3</sub>, etc

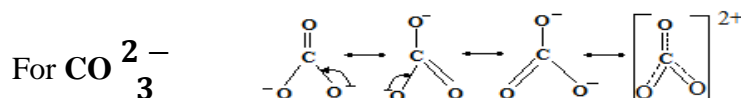
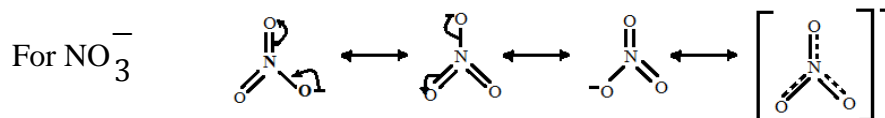


Activity. *Draw the shape of nitrate ion, ethene.*

NB: (i) According to this theory, in determining shape of ions; if

- ✓ the ion has an overall charge of -1, then on top of the number of electrons the central atom has, we add an extra electron.
- ✓ the overall charge on the ion is -2, then add 2 electrons on top of the number of electrons the central atom has.
- ✓ the overall charge on the ion is + 1, number of electrons contributed a central atom is reduced by 1 and if its +2, it is reduced by 2.

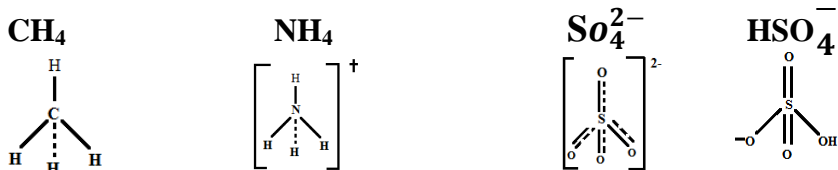
(ii) carbonate and nitrate ions are able to form many resonance structures (are stable) i.e.



(iii)  $\text{CO}_3^{2-}$  and  $\text{NO}_3^-$  are **isoelectronic** (their central atom has the same electronic structure)

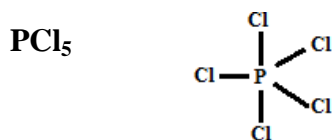
**iii) Four bonding pairs (AX<sub>4</sub>)**

- Shape of molecule is **tetrahedral** as the four electron pairs are distributed tetrahedrally around the central atom with a bond angle of  $109^\circ 28'$ .
- E.g;  $\text{CH}_4$ ,  $\text{CHCl}_3$ ,  $\text{NH}_4^+$ ,  $\text{SO}_4^{2-}$ ,  $\text{CCl}_4$ ,  $\text{PO}_4^{3-}$ ,  $\text{SnCl}_4$ ,  $\text{CrO}_4^{2-}$ , Etc



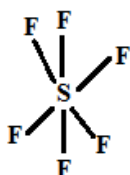
**v) Five electron pairs (AX<sub>5</sub>)**

- Shape of molecule is **trigonal bipyramidal** ;
- because of 5 different regions of electron density (bonds) points towards the five corners of a trigonal pyramid.
- Examples include;  $\text{PF}_5$ ,  $\text{PCl}_5$ ,  $\text{PBr}_5$ ,  $\text{PI}_5$



**vi) Six electron pairs (AX<sub>6</sub>)**

- Shape of molecule is **Octahedral** ;
  - because the 6 bonding pairs repel each other equally; and the 6 bonds point towards the 6 corners of a regular Octahedron.
  - Examples include;  $\text{SF}_6$ ,  $\text{SeF}_6$ ,  $\text{SeCl}_6$ .
- Eg; **SF<sub>6</sub>**



## Activity

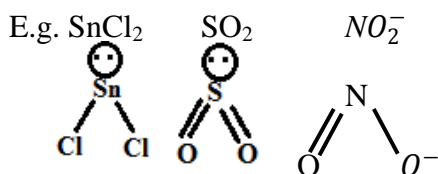
Draw the structures and name the shape of the following species.

Species	Structure	Shape
BF <sub>3</sub>		
CHCl <sub>3</sub>		
ClO <sub>4</sub> <sup>-</sup>		
NO <sub>3</sub> <sup>-</sup>		
SO <sub>3</sub>		

### b) MOLECULES WITH BOTH BONDING AND LONE PAIRS OF ELECTRONS.

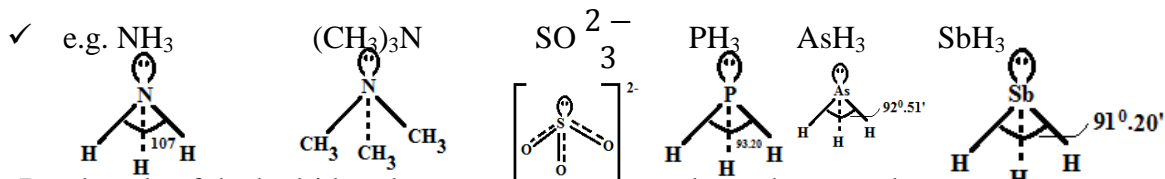
#### i. Three electron pairs (2 bonding and 1 lone pair)

- ✓ Shape of molecule is V – shaped/ Bent.
- ✓ Lone pairs repel bonding pairs more than bonding pairs repel each other.



#### ii. 4 electron pairs (one lone pair and three bonding pairs)

- ✓ 3 bonding pairs and 1 lone pair distribute themselves around the central atom such that the shape is *trigonal pyramidal*.
- ✓ Repulsion is caused by the lone pair and it will lead to a bond angle smaller than tetrahedral angle of 109.5° in methane



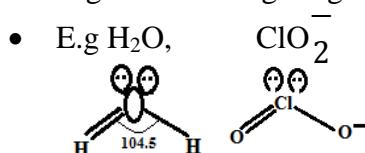
NB. Bond angle of the hydrides, decreases as you move down the group because,

- Decrease in electro negativity ; decreases the attraction for the bonding electrons for the elements as you move down the group.

- Phosphorous has higher electro negativity than Nitrogen so the bonding pairs of electrons are closer to Nitrogen in ammonia than they are to P in PH<sub>3</sub>.
- Closeness of bonding pairs of electrons to the central atom makes them experience greater repulsion giving rise to a bigger bonding angle.
- In SbH<sub>3</sub>, Antimony (Sb) has a much lower electronegativity ; therefore a lower nuclear attraction for bonding electrons and hence bonding pairs of electrons are further away from the central atom making them repel one another to a small extent reducing bond angle further.

iii. **Four electron pairs (2 bonding pairs and 2 lone pairs)**

- The repulsive effect of two lone pairs on the two bonding pairs reduces the bond angle to 104.5° giving rise to a bent/ v- shaped molecule.



**Activity**

- Given the following hydrides HF, NH<sub>3</sub>, H<sub>2</sub>O
  - State the type of intermolecular forces present in the hydrides
  - In which hydride, are the intermolecular forces strongest. Explain your answer.
  - Which of the three hydrides has the highest boiling point?
- Draw the shapes of NH<sub>3</sub> and H<sub>2</sub>O molecules and account for the difference in bond angles in these molecules.

**SOLID STRUCTURES**

Two types of solid structures exist namely;

- ✓ giant structures
- ✓ simple molecular structures.

**(a) Giant structures:**

- consist of a large continuous arrangement of particles (ions or atoms) which makes up a lattice.
- bonding forces in giant lattice maybe *covalent* e.g in diamond, graphite or maybe *ionic* e.g in sodium chloride or *metallic* e.g. in copper.

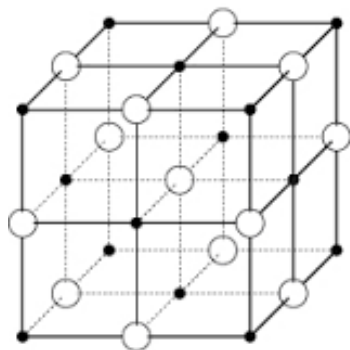
Types of giant structures:

- Giant ionic structure
- Giant metallic structure

- Giant covalent structure
- ❖ **Giant ionic structures:**
  - Negatively charged ions and positively charged ions are held by strong electrostatic forces of attraction.
  - In a NaCl crystal, each ion is surrounded by 6 others of opposite charge. The crystal structure is a regular three dimensional pattern of closed packed Na<sup>+</sup> alternating with chloride ions forming an ionic lattice.
  - structure of NaCl shows 6 – 6 coordination.
  - Na<sup>+</sup> and Cl<sup>-</sup> crystallise in a pattern which is *face centered cubic lattice*

**Note:** Coordination number of the cat ion is the number of anions that can surround one cat ion.

### Structure of NaCl:



- Caesium chloride also shows a giant ionic structure(research the drawing)

### Properties of Giant ionic structure

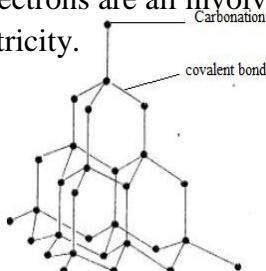
- High melting point due to very strong bonds
- Dissolve in polar solvents as they consist of charged ions
- Conduct electricity in solution or when in molten.
- Very strong but brittle as a shift in the layer split the lattice
- Have a crystalline structure due to ionic lattice.

### ❖ Giant Covalent structure/ Giant molecular structure:

Solid in Giant covalent structure include Diamond , graphite, silicon oxide, silicon carbide and Boron nitride.

### Structure of diamond:

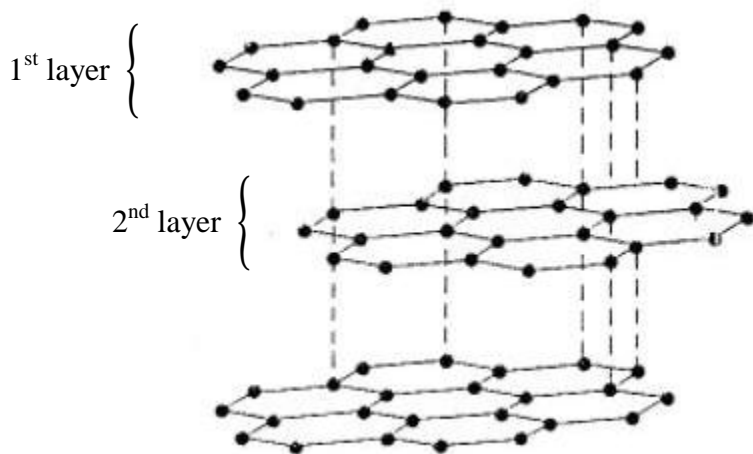
- Each Carbon atom forms 4 bonds to 4 other carbon atoms.
- The 4 atomic orbitals tetrahedrally arrange themselves around the carbon atom which results in a tetrahedral arrangement of carbon atoms in diamond.
- Carbon atoms are attached to each other in a 3 Dimensional arrangement.
- In diamond, the 4 Valence electrons are all involved in bonding therefore no free electrons left to conduct electricity.



- It's the hardest substance known due to the strength of the carbon – carbon bonds and the geometrical rigidity of the structure (very close packed nature of carbon atoms)

### **Structure of graphite:**

- Consists of two dimensional layers of joined hexagonal rings, the layers are held by weak Van der waals forces of attraction.
- Within each layer, each carbon atom is covalently bonded to 3 other carbon atoms.
- remaining valence electrons are delocalized which enable graphite to conduct electricity and responsible for its shiny appearance.
- Weak Van der waals forces between layers result in much wider separation hence graphite has a low density ( $2.3 \text{ gcm}^{-3}$ ) than diamond.
- Weak Van der waals forces of attraction cause these layers to slide past each other thus slippery nature of graphite.



### **Structure of Silicon (IV) oxide (SiO<sub>2</sub>), Silica**

- It forms a 3dimensional structure.
- The Si – O bonds about each Silicon atom are tetrahedrally distributed and each Oxygen atom is bonded to two other Silicon atoms.
- Because of the strong covalent bonds, no ions and free electrons, silica is hard, has a high melting point and boiling point does not dissolve in water and does not conduct electricity.

NB: The strong covalent bonds holding these giant molecules together give the substances high melting point and make them non volatile (having high boiling point)

### **❖ Giant Metallic Structures**

- Metal atoms get closely packed in a 3D arrangement, metal atoms are taken to be individual spheres which touch each other.
- The two main ways in which the spheres can be arranged in a single layer are either square pattern or hexagonal pattern.

- The square/ hexagonal pattern of arrangement gives four main types of metal crystal structures.
  - i. Simple cubic structure e.g. Polonium
  - ii. Body centered cubic structure e.g. group (I) metals such as Caesium.
  - iii. Hexagonal closed packed structures e.g. Mg, Zn, and Titanium etc
  - iv. Face centered cubic structure e.g. Al, Cu, Ag and gold.

**(b) Simple Molecular Structure:**

- Occurs in molecules like Iodine, Solid CO<sub>2</sub> (Dry ice), Bromine and Cl<sub>2</sub> at low temperatures.
- Vander Waals forces of attraction holding molecules are much weaker than forces holding atoms in the molecules.
- Solid CO<sub>2</sub> sublimates above  $-78^{\circ}\text{C}$  on absorbing heat from the surrounding, thus used as a refrigerant in food industry and for laboratory work.

**Question:**

Explain the following observations

- a) Diamond is hard and an electrical insulator.
- b) Graphite is soft and a good electrical conductor
- c) Both Na and Cu are good electrical conductors
- d) CO<sub>2</sub> is a non polar molecule while SO<sub>2</sub> is a polar molecule.
- e) The boiling points of tertiary amines are lower than those of primary amines of the same molecular mass.

## THERMOCHEMISTRY/THERMODYNAMICS.

Thermochemistry is the study of energy changes accompanying chemical reactions.

During chemical reactions, **energy is absorbed to break the bonds** between atoms and **energy is given out when new bonds are formed.**

Thermochemistry investigates the;

- position of equilibrium in the reaction,
- feasibility of the reaction and,
- how far the reaction can go.

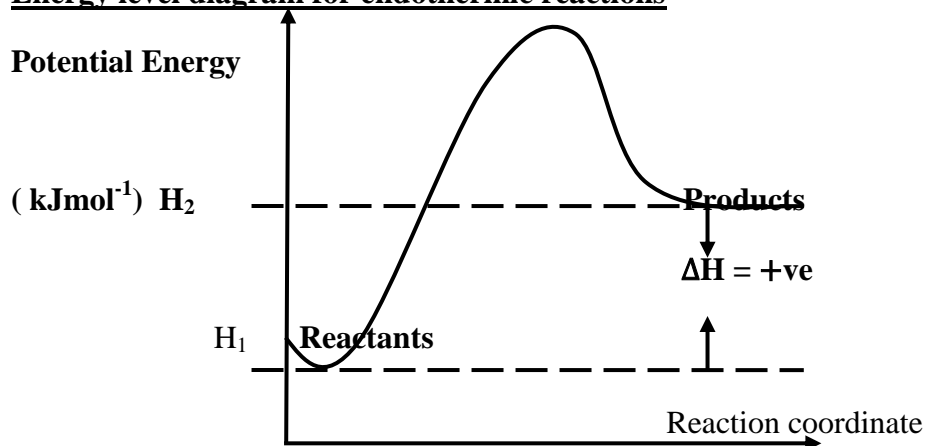
### TYPES OF CHEMICAL REACTIONS

Chemical reactions are grouped according to whether heat is gained/ lost during the reaction.

#### i. Endothermic reactions

- Are reactions which proceed with absorption of heat from the surrounding.
- It is denoted with a positive enthalpy change
- Products are at a higher energy level than the reactants

#### Energy level diagram for endothermic reactions



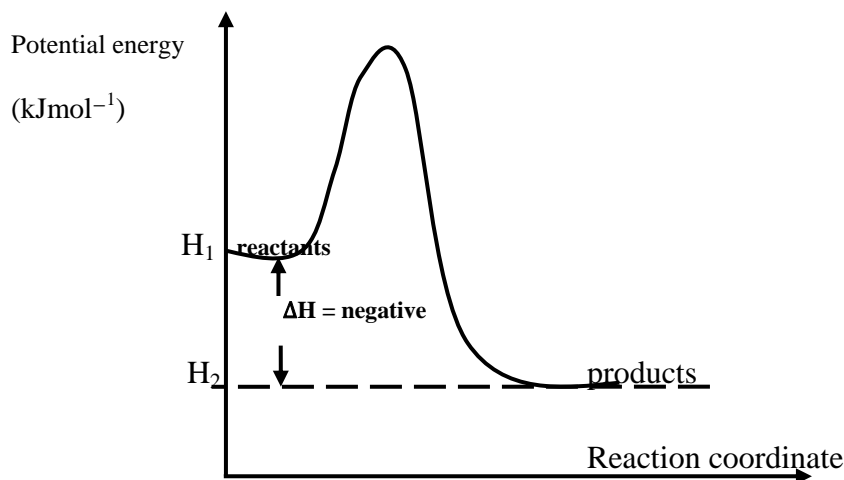
Examples of endothermic reactions include;

- Photosynthesis
- Dissolution of Ammonium nitrate in water
- Change of state e.g. vaporization and melting

#### ii. Exothermic reactions

- Are reactions which proceed with evolution of heat to the surrounding
- Denoted with a negative enthalpy change
- Products are at a lower energy level than the reactants

### Energy level diagram for an exothermic reaction



### Examples include

- Dissolution of Sulphuric Acid in water
- Combustion
- Change of state eg freezing and condensation
- Thermit reaction i.e. reduction of Fe<sub>2</sub>O<sub>3</sub> by aluminium

### ENTHALPY (H)

Is the energy or heat content of a substance.

### Enthalpy change (ΔH)

Is the quantity of heat absorbed at constant pressure.

Enthalpy change = Enthalpy of products – enthalpy of reactant

$$\Delta H = H_2 - H_1$$

Where H<sub>2</sub> = enthalpy of products

H<sub>1</sub> = enthalpy of reactants

### Standard enthalpy change (ΔH°)

Is the heat change when **molar quantities of reactants in their standard states** react to give products.

NB: Standard state of the substance is the pure substance in the specified state (solid, liquid or gas) at 1 atmosphere and 298K.

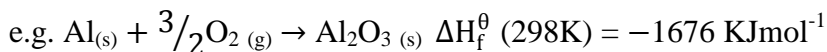
The values of enthalpy change depend on;

- i. Temperature at which reaction is taking place
- ii. Pressure of the gaseous reactants and products
- iii. Physical state of reactants (solid, liquid or gas)
- iv. Amount of reactants and products

## TYPES OF ENTHALPY CHANGES

### a) Standard enthalpy change of formation ( $\Delta H_f^\theta$ )

Is the enthalpy change that occurs when *one mole* of a substance is formed from its elements in their *normal physical state at standard temperature and pressure* (STP)



Enthalpy of formation of substances are **always negative** and cannot be measured experimentally but are determined indirectly using the Born Haber cycle.

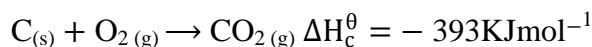
*Standard enthalpy of formation of elements at standard conditions is equal to zero.*

Standard enthalpy of formation is related to the stability of substances i.e.

- ✓ the more negative the value of standard enthalpy change of formation, the more stable the compound will be,
- ✓ and the positive value of  $\Delta H_f^\theta$  indicates that the compound is likely to be thermally unstable or may not form at all.

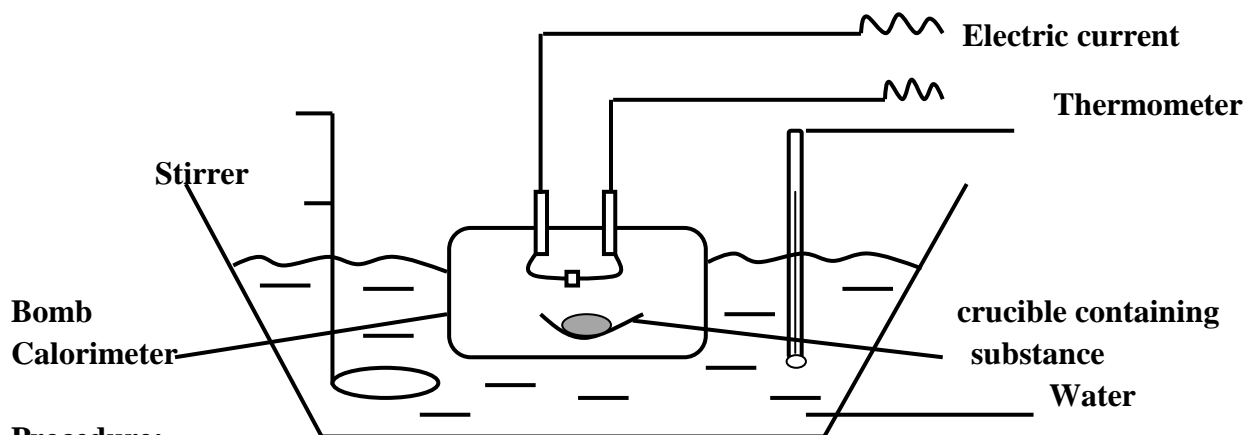
### b) Standard enthalpy change of combustion $\Delta H_c^\theta$

Is the enthalpy change that occurs when *one mole* of a substance is *completely* burnt in  $\text{O}_2$  under standard conditions of temperature and pressure (STP) e.g. heat of combustion of Carbon.



## Experimental determination of enthalpy of combustion of a substance

### Setup:



### Procedure:

- A known mass,  $w_g$  of substance is placed in a crucible suspended in a bomb calorimeter.
- The bomb calorimeter is then filled with oxygen at a pressure of 25 atmospheres and inserted in a calorimeter fitted with thermometer and stirrer containing a fixed volume of water.
- The initial temperature,  $T_1^\circ\text{C}$  of the water is noted, and then the substance is heated by passing electric current through the platinum wire in contact with it.
- Substance burns and the heat generated raise the temperature of water.

- Maximum temperature,  $T_2^{\circ}\text{C}$  of water is then noted.

### Results:

Let

$m$  be the mass of water

$w$  be mass of substance

$M_r$  be the RMM of substance

Temperature rise ( $T_2^{\circ}\text{C} - T_1^{\circ}\text{C}$ ) =  $\Delta T$

$C$  the specific heat capacity of water

$P$  heat produced by heater

### Treatment of results:

#### Assumption:

- Neglecting the heat gained by the calorimeter, then heat evolved by burning the substance and heat produced by the heater is equal to the heat gained by water.

Heat evolved by substance and heater = heat absorbed by water

Heat absorbed by water =  $mc\Delta T$  J

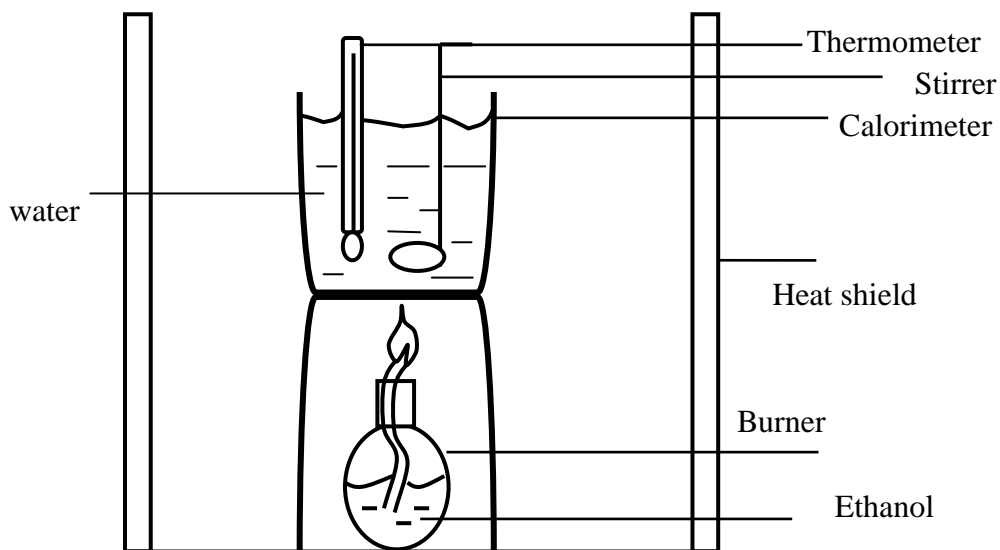
Heat evolved by substance =  $(mc\Delta T - P)$

$w$ g of substance evolves  $(mc\Delta T - P)$  J

$M_r$  will evolve =  $-\frac{(mc\Delta T - P)}{w} \times M_r$

### Experimental determination of enthalpy of combustion of ethanol

#### Setup:



### Procedure:

- A known amount of cold water is weighed into a calorimeter.
- The initial temperature of the cold water is determined,  $T_0^{\circ}\text{C}$
- Some ethanol is added to a burner and the mass of the burner plus the ethanol before burning is determined,  $w_0\text{g}$ .
- The wick is lit and the flame kept steady under water.
- The water is constantly stirred until a reasonable rise in temperature is noted.
- The flame is extinguished and the highest temperature  $T_1^{\circ}\text{C}$  is determined.

### Results

- Mass of water =  $m\text{g}$
- Initial temperature of water =  $T_0^{\circ}\text{C}$
- Final temp. of water =  $T_1^{\circ}\text{C}$
- Mass of burner + ethanol before burning =  $w_0\text{g}$
- Mass of burner + ethanol after burning =  $w_1\text{g}$
- SHC of water =  $C\text{ Jg}^{-1}\text{C}^{-1}$

### Treatment of results:

Assumption:

- Neglecting heat gained by calorimeter; heat evolved by burning ethanol is equal to heat absorbed by water.
- Temperature rise,  $\Delta T = (T_1 - T_0)^{\circ}\text{C}$
- Mass of ethanol burnt =  $(w_0 - w_1)\text{g}$
- Heat evolved = heat absorbed by water
- RMM of ethanol = 46

If  $(w_0 - w_1)\text{g}$  of ethanol evolves  $mc\Delta T\text{ J}$

$$\therefore 46\text{g will evolve } - \frac{mc\Delta T \times 46}{(w_0 - w_1)\text{g}}$$

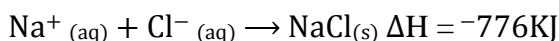
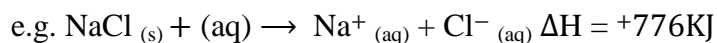
$$\therefore \text{Heat of combustion} = - \left[ \frac{mc\Delta T \times 46}{(w_0 - w_1)} \right] \text{ J}$$

## LAWS OF THERMOCHEMISTRY

There are 2 laws of thermochemistry both of which are based on the **principle of conservation of energy**.

### 1<sup>st</sup> Law:

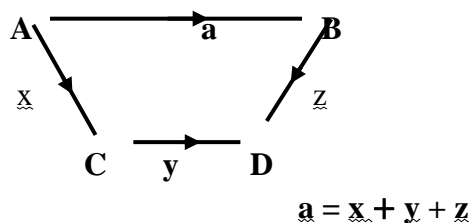
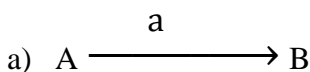
States that, “the amount of heat energy required to decompose a compound into its elements is equal in magnitude but opposite in sign to the amount of heat energy given out when the compound is formed.”



### 2<sup>nd</sup> Law (Hess's law of heat summation)

States that, “enthalpy change of a chemical reaction at constant temperature and pressure is the same irrespective of the number of stages passed but will depend on the initial and final stages of the reaction.

Consider conversion of A to B.



### Applications of Hess's law

- Used to determine heats of reaction which cannot be determined experimentally from given thermochemical data e.g. determining the enthalpy of formation of a compound by using enthalpy of combustion of elements that make up a compound.

When carrying out calculations involving Hess's law;

- All enthalpy changes must have correct signs.
- Reversing the reaction also changes the sign of the enthalpy change
- Multiplying or dividing thermochemical equation by certain number also multiplies or divides the enthalpy change by the same number.
- States of the reactants and products must always be specified.

### Examples:

Compiled by Lawrence arum +256-7505133312/717503108, HOD at K.SS, Also taught at KISUBI MAPEERA, ST JOSEPH'S GIRLS NSAMBYA, KAKIRA S.S, LAKE SIDE COLLEGE LUZIRA .

1. Calculate the enthalpy change of formation of Carbon monoxide given that the enthalpy of combustion of carbon is  $-393\text{kJmol}^{-1}$ , and the enthalpy of combustion of carbon monoxide is  $-286\text{kJmol}^{-1}$

**Solution:**

Expected equation;  $\text{C(s)} + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{CO} \Delta H_f^\theta = ?$

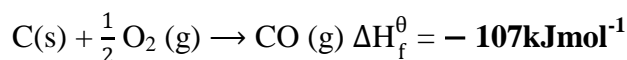
- i.  $\text{C(s)} + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) \Delta H_c^\theta = -393\text{kJmol}^{-1}$   
 ii.  $\text{CO(g)} + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) \Delta H_c^\theta = -286\text{kJmol}^{-1}$

Reversing equation (ii) and adding equation (i)

- i.  $\text{C(s)} + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) \Delta H_c^\theta = -393\text{kJmol}^{-1}$

+

- ii.  $\text{CO}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \Delta H_c^\theta = +286\text{kJmol}^{-1}$
- 



2. Calculate the enthalpy change of formation of methane from the following thermochemical data.

Enthalpy of combustion of Carbon =  $-393\text{kJmol}^{-1}$

Enthalpy of combustion of hydrogen =  $-286\text{kJmol}^{-1}$

Enthalpy of combustion of methane =  $-890\text{kJmol}^{-1}$

**Solution:**

Expected equation;  $\text{C(s)} + 2\text{H}_2(\text{g}) \rightarrow \text{CH}_4(\text{g}) \Delta H_f^\theta = ?$

- i.  $\text{C(s)} + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) \Delta H_c^\theta = -393\text{kJmol}^{-1}$   
 ii.  $\text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l}) \Delta H_c^\theta = -286\text{kJmol}^{-1}$   
 iii.  $\text{CH}_4(\text{g}) + 2\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}) \Delta H = -890\text{kJmol}^{-1}$

Multiplying equation (ii) by 2 and reversing (iii) we obtain,

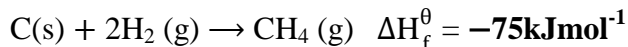
- ii.  $2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O}(\text{l}) \Delta H_c^\theta = -572\text{kJmol}^{-1}$

+

- iii.  $\text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}) \rightarrow \text{CH}_4(\text{g}) + 2\text{O}_2(\text{g}) \Delta H = +890\text{kJmol}^{-1}$
- 

- iv.  $2\text{H}_2(\text{g}) + \text{CO}_2(\text{g}) \rightarrow \text{CH}_4 + \text{O}_2(\text{g}) \Delta H = 318\text{kJmol}^{-1}$

+



**Activity:**

3. Calculate the enthalpy of reaction;  
 $2C(s) + 2H_2(g) \rightarrow C_2H_4(g)$   
Given that enthalpy of combustion of carbon =  $-393kJmol^{-1}$   
Enthalpy of combustion of hydrogen =  $-286kJmol^{-1}$   
Enthalpy of combustion of ethane =  $-1393kJmol^{-1}$
4. Calculate the heat of formation of ethanol given that the heat of combustion of liquid ethanol is  $-649.15kJmol^{-1}$  while the enthalpy of formation of  $CO_2$  gas and water are  $-186.7kJmol^{-1}$  and  $-135.1kJmol^{-1}$  respectively.
5. Calculate the heat change of the reaction  $C_2H_2 + H_2O \rightarrow CH_3CHO$  from the following data.  
Molar heat of combustion of  $C_2H_2 = -1260kJmol^{-1}$   
Molar heat combustion of  $CH_3CHO = -1160kJmol^{-1}$
6. Calculate the enthalpy of combustion of Benzene given that the enthalpy of combustion of Carbon is  $-393kJmol^{-1}$ , enthalpy of formation of Benzene is  $+49kJmol^{-1}$ , and enthalpy of formation of water is  $-285kJmol^{-1}$ .

**CALCULATION OF ENTHALPY OF REACTION FROM;**

a) **Enthalpy of formation:**

Enthalpy of a reaction is the *difference between the total enthalpy of formation of products and the total enthalpies of formation of reactants.*

Consider the reaction;



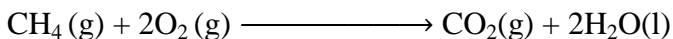
$$\Delta HR = \left[ \begin{array}{c} \text{Total enthalpy of formation} \\ \text{of products} \end{array} \right] - \left[ \begin{array}{c} \text{total enthalpy of formation} \\ \text{of reactants} \end{array} \right]$$

$$\Rightarrow \Delta H_R = \left[ c\Delta H_f^\theta(C) + d\Delta H_f^\theta(D) \right] - \left[ a\Delta H_f^\theta(A) + b\Delta H_f^\theta(B) \right]$$

**Example:**

1. The chemical equation for the combustion of methane is

Compiled by Lawrence arum +256-7505133312/717503108, HOD at K.SS, Also taught at KISUBI MAPEERA, ST JOSEPH'S GIRLS NSAMBYA, KAKIRA S.S, LAKE SIDE COLLEGE LUZIRA .



Calculate the standard enthalpy change of combustion of methane using the values of standard enthalpy change for methane, CO<sub>2</sub> and water given below.

$$\Delta H_f^\theta(\text{CH}_4) = -74.4 \text{ kJmol}^{-1}$$

$$\Delta H_f^\theta(\text{CO}_2) = -393.5 \text{ kJmol}^{-1}$$

$$\Delta H_f^\theta(\text{H}_2\text{O}) = -285.8 \text{ kJmol}^{-1}$$

**solution**

$$\Delta H_c^\theta = [\text{Total enthalpy of formation of products}] - [\text{total enthalpy of formation of reactants}]$$

$$\Delta H_c^\theta = [\Delta H_f^\theta(\text{CO}_2) + 2 \Delta H_f^\theta(\text{H}_2\text{O})] - [\Delta H_f^\theta(\text{CH}_4) + 2\Delta H_f^\theta(\text{O}_2)]$$

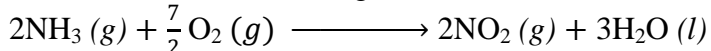
$$= [-393.5 + (2 \times -285.8)] - [-74.4 + 2 \times 0]$$

$$\Delta H_c^\theta = \underline{\underline{-890.7 \text{ kJmol}^{-1}}}$$

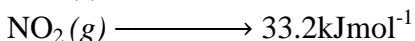
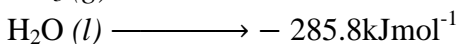
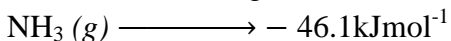
NB. Enthalpy of formation of elements in their standard states is 0, giving  $\Delta H_f^\theta(\text{O}_2) = 0$

**Activity**

1. Calculate the heat change in the reaction;



Given the following standard heats of formation in kJmol<sup>-1</sup>



**b) Bond enthalpy (bond energy)**

- Bond enthalpy is the *standard enthalpy change that occurs when one mole of a covalent bond is formed from its constituent gaseous atoms.*
- Therefore it is referred to as the **bond energy of formation**, denoted by a negative value of enthalpy.
- It can also be defined as *the heat change that occurs when one mole of a covalent bond is broken down into its constituent gaseous atoms*
- Therefore it is referred to as the **bond dissociation energy**, denoted by positive value of enthalpy e.g.
 
$$\text{H}_2(\text{g}) \longrightarrow 2\text{H}(\text{g}) \quad \Delta H = +431 \text{ kJmol}^{-1}$$

$$2\text{H}(\text{g}) \longrightarrow \text{H}_2(\text{g}) \quad \Delta H = -431 \text{ kJmol}^{-1}$$
- The standard enthalpy of a reaction is the *difference between the sum of average standard bond enthalpies of products and sum of the average standard bond enthalpies of reactants.*

$\Delta H^\theta_{\text{reaction}} = \text{summation of bond energies of bonds broken} - \text{summation of bond energies of bonds formed}$

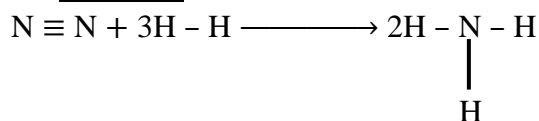
$$\Delta H^\theta_{\text{R}} = \sum \text{Bonds broken} - \sum \text{bonds formed}$$

**Example:**

1. Calculate the enthalpy change for the following reaction;  $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \longrightarrow 2\text{NH}_3(\text{g})$

Bond	Mean of bond enthalpy
$\text{N} \equiv \text{N}$	945
$\text{H} - \text{H}$	436
$\text{N} - \text{H}$	391

**Solution:**



Bonds broken ;  $\text{N} \equiv \text{N}$ ,  $3\text{H} - \text{H}$

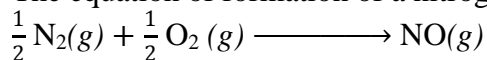
Bonds formed ;  $6\text{N} - \text{H}$

$$\Delta H_{\text{R}} = \sum \text{Bonds broken} - \sum \text{bonds formed}$$

$$= [945 + (3 \times 436)] - [6 \times 391]$$

$$\Delta H_{\text{R}} = \underline{\underline{-93\text{kJmol}^{-1}}}$$

2. The equation of formation of a nitrogen monoxide gas.



Calculate the enthalpy change of formation of nitrogen monoxide using the given bond energies.

Bond	Mean of bond enthalpy
$\text{N} \equiv \text{N}$	$946\text{kJmol}^{-1}$
$\text{H} - \text{H}$	$496\text{kJmol}^{-1}$
$\text{N} - \text{H}$	$630\text{kJmol}^{-1}$

### ENTHALPY OF ATOMISATION AND AVERAGE BOND ENTHALPY

#### a) Enthalpy of Atomisation/sublimation/vapourisation

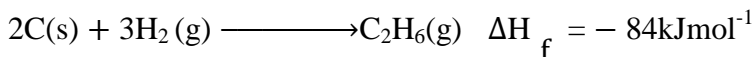
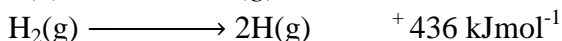
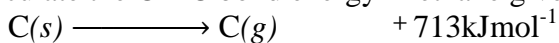
- Is the enthalpy change that occurs when **one mole of gaseous atoms is formed from the elements in their normal physical states at standard conditions.**
- Enthalpy change is always positive. E.g.  
 $\text{Na}(s) \longrightarrow \text{Na}(g)$   
 $\frac{1}{2} \text{Cl}_2(g) \longrightarrow \text{Cl}(g)$   
 $\text{C}(s) \longrightarrow \text{C}(g)$
- For a compound, the standard enthalpy of atomization is **the heat required to convert one mole of a compound in its natural state and under standard conditions into free gaseous atoms.**
- For any di-atomic molecule, enthalpy of atomization is **HALF** the bond energy.

**b) Average bond enthalpy/bond energy term**

- Is the average value of the standard enthalpy changes required to break a particular covalent bond in a full range of molecules in which that bond may be found.
- Calculations based on average standard bond enthalpies give approximate results since true standard bond enthalpies vary from compound to compound.

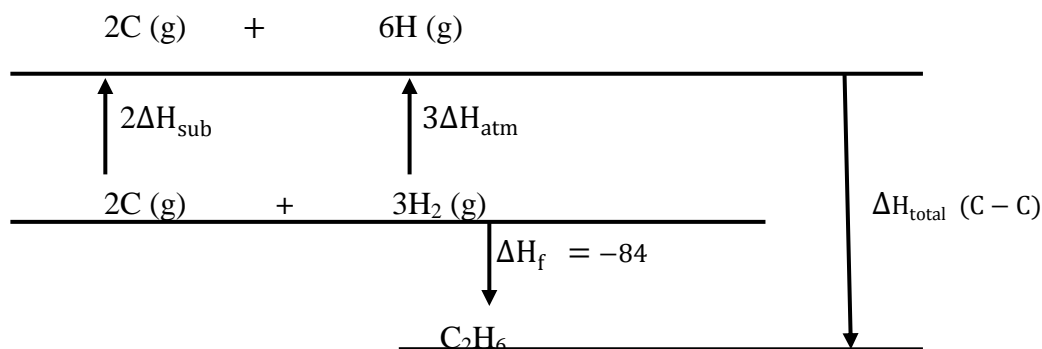
Examples:

1. Calculate the C – C bond energy in ethane given that



**Solution**

Using the energy level diagram.



From Hess' law of constant heat summation

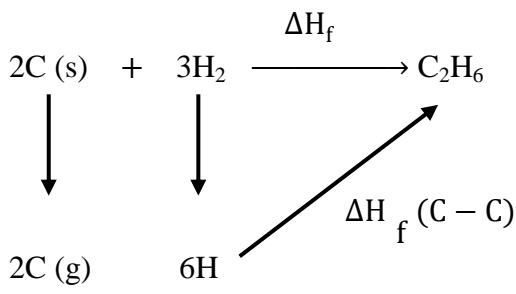
$$(\Delta H_f) = 2\Delta H_{\text{sub}} + 3\Delta H_{\text{atm}} + \text{Total } \Delta H(\text{C} - \text{C})$$

$$\text{Total } \Delta H(\text{C} - \text{C}) = (\Delta H_f) - (2\Delta H_{\text{sub}} + 3\Delta H_{\text{atm}})$$

$$= -(-84) - (2 \times 713) + (3 \times 436)$$

$$= \underline{\underline{-2818 \text{ kJ mol}^{-1}}}$$

**OR:**



$$\Delta H_f = 2 \times \Delta H_a(\text{C}) + 3\Delta H_a(\text{H}) + \Delta H_f(\text{C}-\text{C})$$

$$\Delta H_f(\text{C}-\text{C}) = (\Delta H_f) - (2\Delta H_{\text{sub}} + 3\Delta H_{\text{atm}})$$

$$= -(-84) - (2 \times 713) + (3 \times 436)$$

$$= \underline{\underline{-2818 \text{ kJ mol}^{-1}}}$$

2. (a) The standard enthalpy change of formation of  $\text{SiCl}_4$  is  $-610 \text{ kJ mol}^{-1}$ . The standard enthalpy change of atomization of Si and Cl are  $+338$  and  $+122 \text{ kJ mol}^{-1}$  respectively. Use these values to construct a Born Haber cycle for formation of  $\text{SiCl}_4$  from its elements and indicate the energy changes involved.

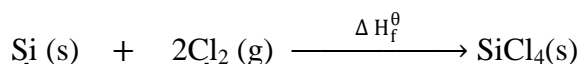
(b) Calculate the average bond energy of the Si-Cl bond. (UNEB 2006 No 9)

**Solution**

$$\text{a) } \Delta H_f^\theta(\text{SiCl}_4) = -610 \text{ kJ mol}^{-1}$$

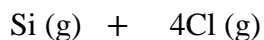
$$\Delta H_a^\theta(\text{Si}) = +338 \text{ kJ mol}^{-1}$$

$$\Delta H_a^\theta(\text{Cl}_2) = +122 \text{ kJ mol}^{-1}$$



$$4\Delta H_f (\text{Si} - \text{Cl})$$

$$\Delta H_a^\theta (\text{Si}) \quad 4\Delta H_a (\text{Cl})$$



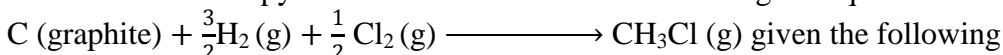
b) From Hess' law of heat summation;

$$\begin{aligned} \Delta H_f^\theta &= \Delta H_a^\theta (\text{Si}) + 4 \text{Ha} (\text{Cl}) + 4\Delta H_f (\text{Si} - \text{Cl}) \\ - (4\Delta H_f (\text{Si} - \text{Cl})) &= \Delta H_f^\theta - \Delta H_a^\theta (\text{Si}) - 4 \text{Ha} (\text{Cl}) \\ &= -610 - 338 - (4 \times 122) \end{aligned}$$

$$4\Delta H_f (\text{Si} - \text{Cl}) = -1436$$

$$\underline{\Delta H_f (\text{Si} - \text{Cl}) = -359 \text{kJmol}^{-1}}$$

3. Calculate the enthalpy of formation of chloromethane using the equation.



given the following thermochemical data;

Bond energy of C - Cl = 336 kJmol<sup>-1</sup>

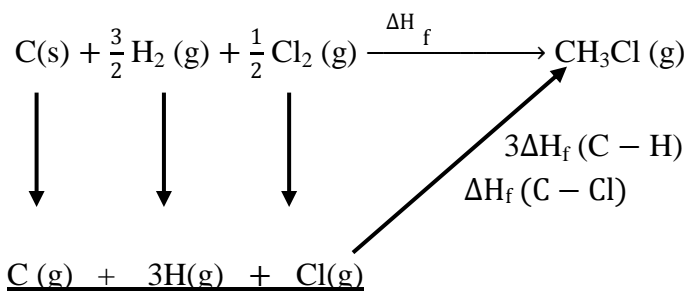
Dissociation energy of H-H = 433 kJmol<sup>-1</sup>

Dissociation energy of Cl - Cl = 248 kJmol<sup>-1</sup>

Bond energy of C-H = 413 kJmol<sup>-1</sup>

Enthalpy of vapourisation of graphite = 715 kJmol<sup>-1</sup>

**Solution**



**NB  $\Delta H_f$  bonds is negative**

From Hess' law of heat summation

$$\begin{aligned} \Delta H_f &= \frac{3}{2}\text{BDE (H)} + \frac{1}{2}\text{BDE (Cl)} + 3\Delta H_f (\text{C} - \text{H}) + \Delta H_f (\text{C} - \text{Cl}) \\ &= \left[ 715 + \left(\frac{3}{2} \times 435\right) + \left(\frac{1}{2} \times 248\right) \right] - (3 \times 413 + 336) \\ &= 1491.5 - 1575 \end{aligned}$$

$$\Delta H_f = -83.5 \text{ kJ mol}^{-1}$$

### Activity

1. Calculate the average (C–H) Bond energy from the following enthalpies of reaction

Enthalpy of formation of  $\text{CO}_2 = -393 \text{ kJ mol}^{-1}$

Enthalpy of formation of  $\text{H}_2\text{O} = -286 \text{ kJ mol}^{-1}$

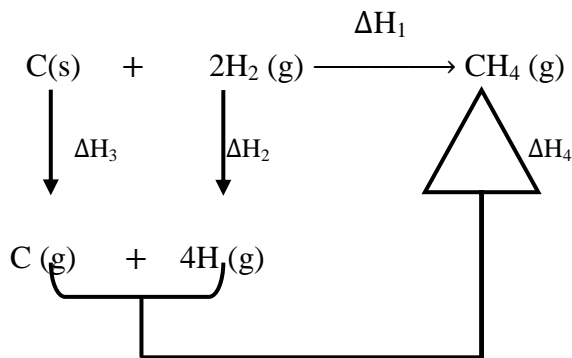
Enthalpy of formation of  $\text{CH}_4 = -890 \text{ kJ mol}^{-1}$

Enthalpy of Atomisation of  $\text{C}_2 = 714 \text{ kJ mol}^{-1}$

Enthalpy of Atomisation of  $\text{H}_2 = 436 \text{ kJ mol}^{-1}$

2. (a) What is meant by Bond energy?

(b) The figure below shows/ represents the energy diagram for formation of  $\text{CH}_4$



Identify the energy changes  $\Delta H_1$ ,  $\Delta H_2$ ,  $\Delta H_3$  and  $\Delta H_4$  given that;

(c)  $\Delta H_1 = -75 \text{ kJ mol}^{-1}$ ,  $\Delta H_2 = +218 \text{ kJ mol}^{-1}$  of  $\text{H}_2$  atom,  $\Delta H_3 = +715 \text{ kJ mol}^{-1}$

Calculate the value of:

- $\Delta H_4$
- Bond energy of C – H bond

3. Calculate the standard enthalpy of formation of  $\text{C}_2\text{H}_4$  in  $\text{kJ mol}^{-1}$  from the following

C = C Bond energy =  $606 \text{ kJ mol}^{-1}$

C – H bond energy =  $410 \text{ kJ mol}^{-1}$

H – H Bond energy =  $435 \text{ kJ mol}^{-1}$

Heat of sublimation of Carbon =  $710 \text{ kJ mol}^{-1}$

## BORN – HABER CYCLE

- Is the enthalpy cycle used to calculate the standard enthalpy changes which occur when an ionic compound is formed from its elements.
- It is an application of Hess' law to ionic compounds.  
Enthalpy changes involved in Born Haber cycle include

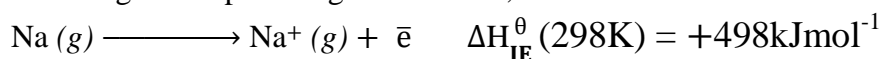
i. Standard enthalpy of Sublimation/ Vaporisation ( $\Delta H_{\text{S}}^{\theta} / \Delta H_{\text{vap}}^{\theta}$ )

ii. Standard enthalpy of atomization ( $\Delta H_{\text{at}}^{\theta}$ ):

Is the enthalpy change when one mole of gaseous atoms is formed from an element in standard state.

iii. Standard enthalpy of ionization ( $\Delta H_{\text{IE}}^{\theta}$ )

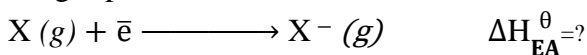
Is the enthalpy change accompanying the removal of one mole of electrons from an atom in gaseous phase e.g. for Sodium;



- When an electron is removed from a singly positively charged ion in the gaseous phase, enthalpy change is described as 2<sup>nd</sup> ionization enthalpy
- i.e.  $\text{Na}^+ \longrightarrow \text{Na}^{2+} + 2\bar{e}$

iv. electron affinity/Electron gain enthalpy

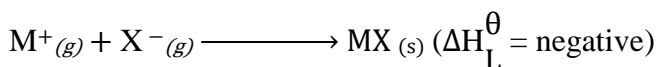
Is the standard enthalpy change accompanying the addition of one electron to an atom in the gas phase. i.e.



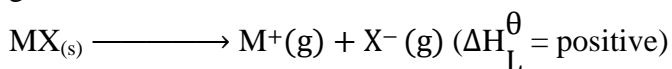
NB: The first electron affinity is **negative** while the 2<sup>nd</sup> electron affinity is **positive** because *work must be done to add the 2<sup>nd</sup> electron against repulsive forces exerted by the first electrons.*

v. Standard lattice enthalpy ( $\Delta H_{\text{L}}^{\theta}$ )

Is the enthalpy change when one mole of an ionic compound is formed from its gaseous ions under standard conditions i.e.

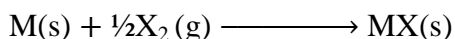


OR: Is the enthalpy absorbed when one mole of an ionic compound is decomposed into its gaseous ions.

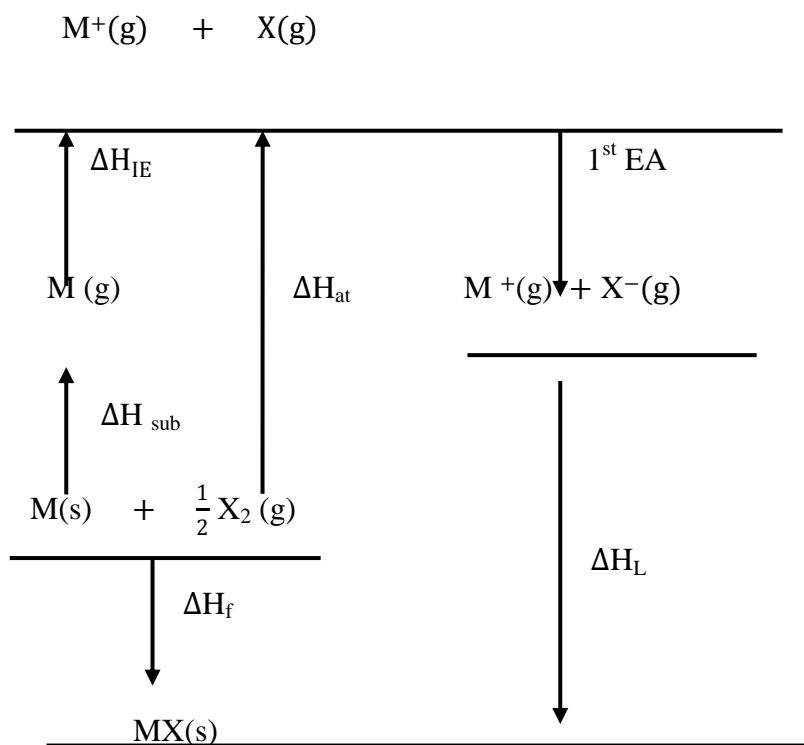


Consider the formation of one mole of MX solid where M is a metal and X is a gas with a diatomic molecule.

### Equation of formation of MX



**Born Haber cycle showing energy changes involved:**



From Hess' law

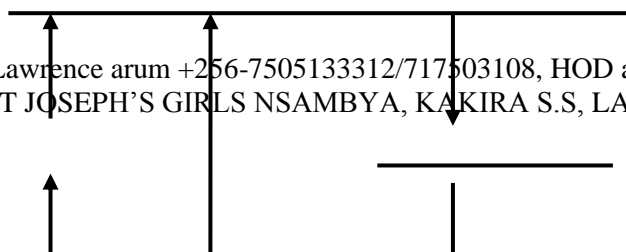
$$\Delta H_f = \Delta H_{sub} + \Delta H_{IE} + \Delta H_{at} + EA + \Delta H_L$$

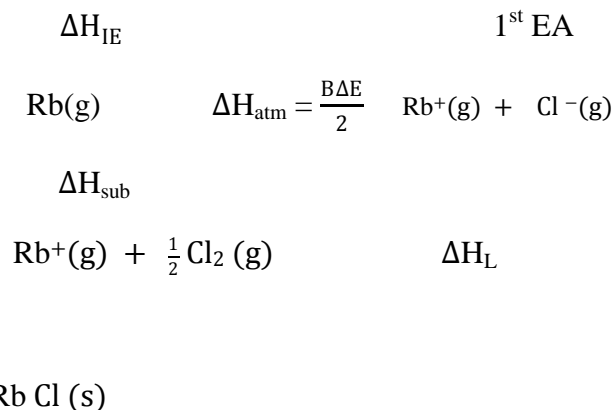
**Example:**

- (a) Draw a Born Haber for the formation of solid Rubidium chloride from its elements  
 (b) Calculate the electron affinity of chlorine atom. Use the following data;  
 Lattice energy of Rubidium chloride =  $-665 \text{ kJmol}^{-1}$   
 Dissociation energy of chlorine gas molecule =  $226 \text{ kJmol}^{-1}$   
 Heat of atomization of Rubidium metal =  $84 \text{ kJmol}^{-1}$   
 Standard heat of formation of solid Rubidium chloride is  $-439 \text{ kJmol}^{-1}$   
 I.E. of Rubidium atom =  $397 \text{ kJmol}^{-1}$

**Solution**

- (a)  $Rb^+(g) + Cl(g)$





(b) From Hess' law;

$$\begin{aligned}
 \Delta H_f &= \Delta H_{\text{sub}} + \Delta H_{IE} + \Delta H_{\text{at}} + \text{E.A} + \Delta H_{\text{L}} \\
 \text{EA} &= \Delta H_f - (\Delta H_{\text{sub}} + \Delta H_{IE} + \Delta H_{\text{at}} + \Delta H_{\text{L}}) \\
 &= -439 - (84 + 397 + \frac{226}{2} + -665) \\
 \mathbf{1^{\text{st}} \text{ EA}} &= \mathbf{-368 \text{ kJmol}^{-1}}
 \end{aligned}$$

### Activity

- Draw a Born Haber cycle for the reaction of Lithium(Solid) and F(g) to form LiF(s) and indicate clearly whether the change is exo/endothermic. using the data below;
  - Enthalpy of atomization of Fluorine molecule = + 150kJmol<sup>-1</sup>
  - Enthalpy of sublimation of Lithium metal = 155kJmol<sup>-1</sup>
  - Ionization energy of Lithium atom = 518kJmol<sup>-1</sup>
  - Standard enthalpy of formation of solid LiF =?
  - Lattice enthalpy = - 1030 kJmol<sup>-1</sup>
  - Electron affinity of F = - 351 kJmol<sup>-1</sup>
- Calculate the lattice energy of CaCl<sub>2</sub> from the following thermochemical data;
  - Standard enthalpy of atomization of CaCl<sub>2</sub> = - 795kJmol<sup>-1</sup>
  - Standard enthalpy of atomization of Chlorine = +717kJmol<sup>-1</sup>
  - First ionization energy of calcium = + 121 kJmol<sup>-1</sup>
  - 2<sup>nd</sup> ionization energy of Calcium = 1100 kJmol<sup>-1</sup>
  - First electron affinity of Cl = - 364 kJmol<sup>-1</sup>
- Using the data below construct an energy level diagram and hence calculate the lattice energy of CuO(s)

Enthalpy kJmol<sup>-1</sup>

Atomization of Cu	+339
1 <sup>st</sup> IE of Cu	+745
Atomization of O <sub>2</sub>	+ 248
2 <sup>nd</sup> IE of Cu	+1960
1 <sup>st</sup> EA of O <sub>2</sub>	-141

## **FACTORS AFFECTING LATTICE ENERGY**

### **Ionic charge**

- The larger the ionic charge, the bigger the lattice energy
- because of the strong electrostatic forces of attraction, between the oppositely charged ions, e.g. the lattice energy of magnesium chloride is larger than that of Sodium Chloride because the greater charge of Mg<sup>2+</sup> strongly attracts the chloride ions.

### **Ionic size/radius:**

- Lattice energy is inversely proportional to the ionic size i.e. large cat ions have less attraction for anions because of the reduced effective nuclear charge. (Large distance of approach) e.g. NaCl has a bigger lattice energy than KCl because the K<sup>+</sup> has a bigger radius than Na<sup>+</sup>.

Consider the halides of Na and their values of lattice energy.

NaF	-795kJmol <sup>-1</sup>
NaCl	-761kJmol <sup>-1</sup>
NaBr	-742kJmol <sup>-1</sup>
NaI	-699kJmol <sup>-1</sup>

### **Trend:**

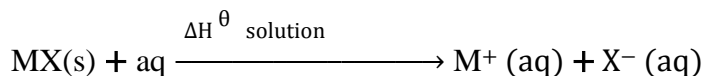
- Lattice energy of the halides decreases down the group

### **Explanation:**

- Lattice energy of NaF is the greatest since there is greater attraction of the F<sup>-</sup> to the Na<sup>+</sup>.
- Lattice energy of NaI is the smallest because I<sup>-</sup> has the biggest size and therefore is least attracted by the Sodium Ion (Na<sup>+</sup>)

## **ENTHALPY OF SOLUTION**

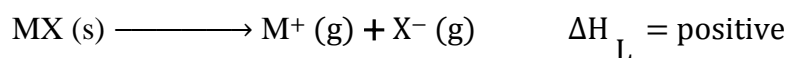
Is the enthalpy change that occurs when one mole of crystal ionic compound is dissolved in a specified number of moles of water at standard conditions.



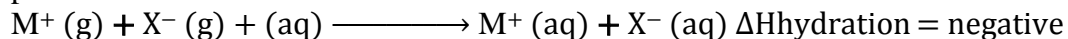
The enthalpy change accompanying the dissolution of an ionic salt in water is either positive or negative

The dissolution of an ionic compound involves two energy terms;

- Separating the ionic lattice into oppositely charged gaseous ions ie



- The energy required is the **lattice dissociation** and is an **endothermic process**
- ii. Hydration/ solvation of the oppositely charged gaseous ions and it's an exothermic process. i.e

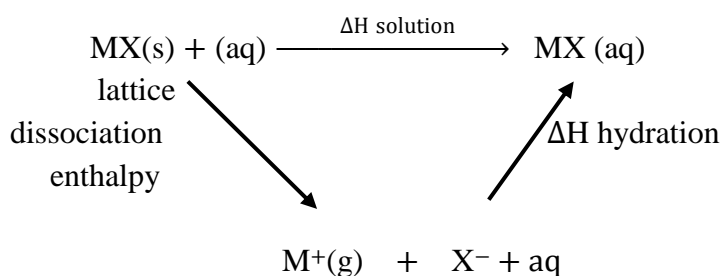


**Definition**

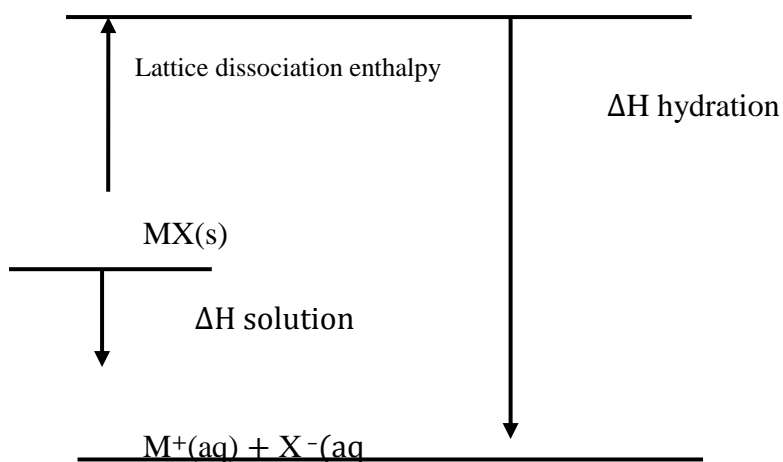
Enthalpy of Hydration/ Solvation is the heat evolved when 1 mole of gaseous ions is completely surrounded by water molecules i.e.

$$\Delta H^{\theta}_{\text{solution}} = \Delta H^{\theta}_{\text{lattice dissociation}} + \Delta H^{\theta}_{\text{solvation (Hydration)}}$$

**Born Haber cycle showing the relationship between the enthalpy of solution, lattice dissociation energy and hydration energy of salt MX**



**OR**



**Factors affecting enthalpy of solution**

- Lattice energy
- Hydration energy

When the

- ✓ lattice dissociation is greater than the hydration, enthalpy of solution is **endothermic**,
- ✓ the hydration energy is greater than lattice dissociation enthalpy, the enthalpy of solution is **exothermic**.

For an ionic compound to dissolve in water, the lattice dissociation energy should be overcome by the hydration enthalpy so that an overall negative enthalpy of solution is obtained i.e. compounds that **dissolve exothermically are more soluble than those which dissolve endothermically**.

### Example:

The enthalpies of hydration and lattice energy of some salts are given below;

Salt	Enthalpy of hydration (kJmol <sup>-1</sup> )	Lattice energy (kJmol <sup>-1</sup> )
KCl	- 692	+ 718
LiCl	- 883	+ 862

- a) Calculate the heats of solution of K and Li Chloride. State whether dissolution is endothermic or exothermic process in each case.
- b) Which of the following two salts will be more soluble in water at a given temperature. Give a reason for your answer.
- c) How would you expect the solubility of these two salts to change with temperature?

### **Solution**

$$\begin{aligned} \text{a) } \Delta H_{\text{soln}} &= \Delta H_{\text{hydration}} + \Delta H_{\text{lattice energy}} \\ \Rightarrow \Delta H_{\text{soln}} (\text{KCl}) &= - 692 + 718 \\ &= + 26\text{kJmol}^{-1} \\ \Delta H_{\text{soln}} (\text{LiCl}) &= - 883 + 862 \\ &= - 21\text{kJmol}^{-1} \end{aligned}$$

KCl, dissolution is endothermic because enthalpy of solution is positive

LiCl dissolution is exothermic because enthalpy of solution is negative

- b) LiCl, because enthalpy of solution is negative
- c) KCl, solubility increases with increase in temperature because it requires more energy to dissolve (enthalpy of solution is positive)  
LiCl, solubility decreases with increase in temperature because enthalpy of solution is exothermic.

- 2 (a) Define the term molar enthalpy of hydration
- (b) The table below shows the enthalpies of Mg<sup>2+</sup> and Cl<sup>-</sup>

Ions	Enthalpy of hydration (kJmol <sup>-1</sup> )
Mg <sup>2+</sup>	1891
Cl <sup>-</sup>	381

- i. State whether the values of enthalpies of hydration given in the table above is positive or negative. Give a reason for your answer
- (ii) Calculate the enthalpy of hydration of MgCl<sub>2</sub> **UNEB 2003**

**Solution**

- i. The values of both enthalpies are negative

**Reason**

- Hydration of both ions involves attraction of water molecules releasing a lot of heat energy.
- $\Delta H$  hydration of MgCl<sub>2</sub> =  $\Delta H$  Hydration of Mg<sup>2+</sup> + 2 $\Delta H$  hydration of Cl<sup>-</sup>  
 $= -1891 + (2 \times -381)$   
 $= -2663 \text{ kJmol}^{-1}$

**Activity**

- a) Explain the term molar enthalpy of solution
- b) Draw a diagram to show the energy changes that takes place when a salt MX (s) is dissolved in water.

**NB**

- (i) Anhydrous salts e.g. Anhydrous CuSO<sub>4</sub> dissolve more exothermically than the hydrated salts (with water of crystallisation) e.g. CuSO<sub>4</sub>.5H<sub>2</sub>O.

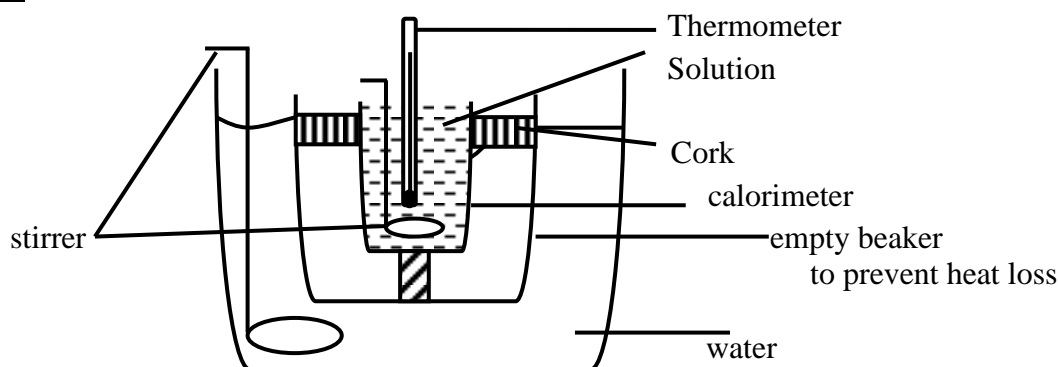
**Reason:**

- ✓ CuSO<sub>4</sub> (hydrated) dissolves endothermically, because ions are already partially hydrated so that when it dissolves its lattice energy outweighs the enthalpy associated with any further hydration.
  - ✓ Anhydrous CuSO<sub>4</sub>, the ions will have to attract more water molecules and become surrounded by the water molecule. This increases its hydration energy more than the lattice energy, the salt will dissolve with evolution of energy.
- ii. Polar solvents like water dissolve in ionic substances because they have large dipoles interacting strongly with solute ions which results in a high negative enthalpy of solvation,
    - Non polar solvents such as hydrocarbons do not dissolve ionic substance because there is no negative enthalpy of solvation to compensate for the positive lattice dissociation enthalpy.

- Qn: a) Predict whether or not KI is likely to be soluble in cyclohexane
- b) Explain your answer in (a) above

**Experimental determination of enthalpy of solution of an ionic compound:**

### Set up



### Procedure:

- A known mass,  $m_1$ g of water is placed in a calorimeter fixed with a stirrer and thermometer and the temperature  $T_1$  is noted.
- A known mass  $m_2$ g of finely powdered sample of an ionic compound is carefully added to the water in the calorimeter.
- The solution is stirred thoroughly until the thermometer shows no more heat change.
- Determine and record the final steady temperature,  $T_2$  °C of the solution.

### Results:

Mass of water =  $m_1$ g

Mass of solute =  $m_2$ g

Initial temperature of water =  $T_1$  °C

Final temperature of solution =  $T_2$  °C

$\Delta$ Temperature =  $\Delta T$  ( $T_1 - T_2$ ) or ( $T_2 - T_1$ )

RFM of compound =  $M_r$

SHC of solution =  $C$

Mass of solution =  $(m_1 + m_2)$  g

### Treatment of results:

#### Assumption:

- Calorimeter has negligible heat loss
  - Density of water =  $1 \text{ g cm}^{-3}$
- Heat evolved = mass of solution  $\times$  SHC  $\times \Delta T$   
 $= (m_1 + m_2) \times C \times \Delta T$

Moles of ionic compound =  $\left(\frac{m_2}{M_r}\right)$  moles

$\therefore \frac{m_2}{M_r}$  evolved  $(m_1 + m_2) \times C \times \Delta T$

1 mole of solution =  $\frac{(m_1 + m_2) \times C \times \Delta T \times M_r}{m_2}$

$$\Delta H_{\text{solution}} = \frac{(m_1 + m_2) \times C \times \Delta T \times Mr}{m_2} \text{ J}$$

**QN: P2 (2006(4))**

### STANDARD ENTHALPY OF NEUTRALISATION

Is the enthalpy change when one mole of  $\text{H}^+$  reacts completely with one mole of  $\text{OH}^-$  to form one mole of water. i.e.  $\text{H}^+(\text{aq}) + \text{OH}^-(\text{aq}) \longrightarrow \text{H}_2\text{O}(\text{l})$

NB: The

- enthalpies of neutralization of strong acids and strong bases are **usually constant and high** because the strong acids and strong bases are fully ionized giving many free hydrogen ions and hydroxyl ions which then react readily to release a lot of heat.
- enthalpies of neutralization of weak acids and weak bases or strong base and vice versa are **usually low and inconsistent** because in the neutralization of weak acids or base, some energy is used first in the ionization and later for neutralization.

### Experimental determination of enthalpy of neutralization (HCL and NaOH)

#### Procedure:

- A known volume  $V\text{cm}^3$  of 2M HCl is measured and placed into a plastic cup, its initial temperature  $T_1$  is noted.
- An equal volume of 2M NaOH is placed into another plastic cup and its initial temperature  $T_2$  is noted.
- NaOH is then carefully added to the cup containing the acid with constant stirring.
- Highest temperature  $T_3$  attained is noted.

#### Results:

- Initial temperature of 2M HCl =  $T_1$  °C SHC of solution = C
- Initial temperature of 2M NaOH =  $T_2$  °C
- Mean initial temperature of mixture =  $\left(\frac{T_1 + T_2}{2}\right)$  °C
- Final temperature of mixture =  $T_3$  °C
- Volume of solution(mixture) =  $2V\text{cm}^3$
- Total mass of mixture =  $2V\text{g}$ , assuming density of solution is  $1\text{gcm}^{-3}$

#### Treatment of results

Heat change = mass of solution X C.ΔT

Heat change =  $(2V \times C \times \Delta T)$  J

Equation:  $\text{NaOH}(\text{aq}) + \text{HCl}(\text{aq}) \longrightarrow \text{NaCl}(\text{aq}) + \text{H}_2\text{O}(\text{l})$

$1000\text{cm}^3$  of solution contain 2 moles of HCl

$V\text{cm}^3$  of solution contains  $\left(\frac{2V}{1000}\right)$  moles

Mole ratio 1 HCl : 1 H<sub>2</sub>O

Moles of water formed  $\left(\frac{2V}{1000}\right)$  moles

$\left(\frac{2V}{1000}\right)$  moles of water evolved  $2V.C.\Delta T$

1 mole of water =  $\frac{2V.C.\Delta T \times 1000}{2V}$

$$\Delta H_{\text{neutralisation}} = -(\Delta T \cdot 1000)J$$

### Example:

When 100cm<sup>3</sup> of 2M HCl was added to 100cm<sup>3</sup> of 2M NaOH, the temperature rose by 13<sup>o</sup>C. Calculate the enthalpy of neutralization assuming density of solution and Specific heat capacity of the resultant solution are 1g/cm<sup>3</sup> and 4.2Jg<sup>-1</sup>K<sup>-1</sup> respectively.

### Solution:

Total volume = 200cm<sup>3</sup>

Mass of solution = 200 × ρ  
= 200g

Heat change = mass of solution × SHC × ΔT  
= 200 × 4.2 × 13  
= 10920J

H<sup>+</sup> (aq) + <sup>-</sup>OH  $\longrightarrow$  H<sub>2</sub>O (l)

1000cm<sup>3</sup> of solution contains 2 moles of HCl

100cm<sup>3</sup> of solution contains  $\left(\frac{2 \times 100}{1000}\right)$  moles of HCl

Mole ratio; 1mole of acid: 1 mole of water

⇒ Moles of water formed = 0.2 moles

0.2 moles of water = 10920 , 1mole of water evolves (10920/0.2)

**Δ Heat of neutralization = - 54600J**

### Exercise

1. 50cm<sup>3</sup> of NaOH solution of concentration 0.4M required 20cm<sup>3</sup> of H<sub>2</sub>SO<sub>4</sub> of concentration 0.5M for neutralization. A temperature rise of 3.4<sup>o</sup>C was realized. If both solutions and calorimeter were at the same temperature, find the standard enthalpy of neutralization of NaOH with H<sub>2</sub>SO<sub>4</sub> (SHC of calorimeter = 39JK<sup>-1</sup> and 4.2Jg<sup>-1</sup>K<sup>-1</sup>)

## HEAT OF PRECIPITATION

Is the heat change when one mole of ionic compound is precipitated from the solution.

### Example

1. When  $50\text{cm}^3$  of 1M NaCl solution and  $50\text{cm}^3$  of 1M  $\text{AgNO}_3$  solution are mixed, there is a temperature rise of  $7.5^\circ\text{C}$ . Calculate the enthalpy of precipitation of AgCl assuming the SHC and density of the resulting solution is  $4.2\text{Jg}^{-1}\text{k}^{-1}$  and  $1\text{gcm}^{-3}$  respectively.

### Solution

Total volume of solution =  $100\text{cm}^3$

Mass of solution = 100g

$$\begin{aligned}\text{Heat produced} &= \text{mass of solution} \times \text{SHC of solution} \times \text{temperature rise} \\ &= 100 \times 4.2 \times 7.5 \\ &= 3150\text{J}\end{aligned}$$

$1000\text{cm}^3$  of NaCl solution contains 1 mole

$50\text{cm}^3$  of NaCl solution contains  $\left(\frac{1 \times 50}{1000}\right)$  moles

Moles of NaCl = 0.05moles

1 mole of NaCl produces 1 mole of AgCl

0.05moles of NaCl will produce 0.05moles of AgCl

0.05moles of AgCl produced 3150J of heat.

1 mole of AgCl produced  $\left(\frac{3150}{0.05}\right)$ J of heat

Enthalpy of precipitation =  $- 63000\text{J}$

### Exercise

2. a) Define the term **heat of precipitation**  
b)  $25\text{cm}^3$  of 0.5M  $\text{AgNO}_3$  solution was added to  $25.0\text{cm}^3$  of 0.5M NaCl solution in an insulated container. The temperature of the resulting mixture rose by  $3^\circ\text{C}$ . Assuming the container has a negligible heat capacity and the SHC of the resulting mixture is  $4.2\text{Jg}^{-1}\text{C}^{-1}$ . Calculate the heat of precipitation of AgCl.

## CHEMICAL KINETICS

Chemical kinetics is the study of rates of reaction and factors affecting rates of reaction.

### Rates of reaction

Is the *rate of change in concentration of one of the products or reactants*.

Rate of reaction decreases as the reaction proceeds and the reactant is gradually used up.

Consider a reaction  $A \rightarrow B$ ;

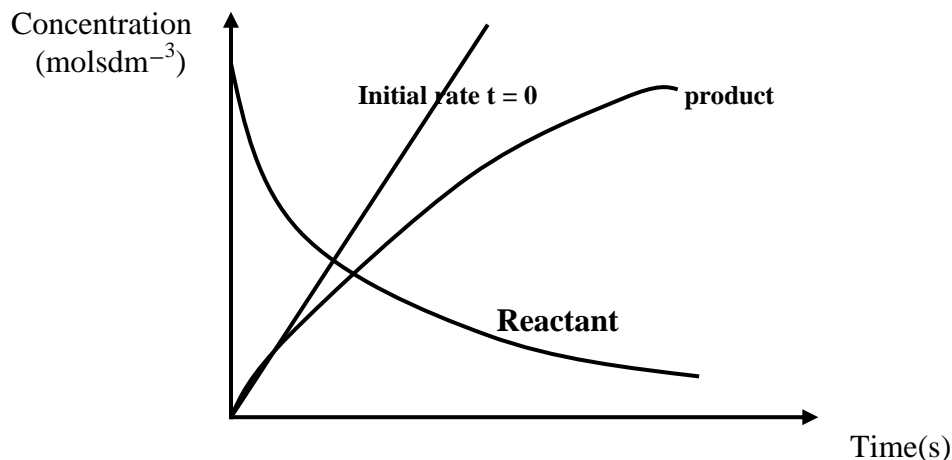
Rate of decrease in concentration of A =  $-\frac{d[A]}{dt}$

Rates of increase in concentration of B =  $\frac{d[B]}{dt}$

Units of reaction rates is **concentration per time** e.g. moles per  $\text{dm}^3$  per second ( $\text{mol dm}^{-3} \text{s}^{-1}$ )

The rate at the start of the reaction, when an infinitesimally small amount of the reactant has been used up is called the **initial rate**.

### Variation of concentration of reactants and products with time



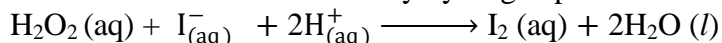
Initial rate of reaction can be obtained by finding the slope/ tangent to the curve at time,  $t = 0$ .

### METHODS OF FINDING THE RATES OF CHEMICAL REACTIONS

#### a) Chemical analysis

- Here, the reaction is carried out in a thermostatically controlled water bath.
- Solutions of the reactants of known concentration are mixed and a stop clock started.
- A sample of a reaction mixture is withdrawn with a pipette and the reaction is stopped/ quenched by either cooling or dilution into a freezing mixture or into an excess of solvent.

- Titration is performed to find the concentration of one of the reactants or products. E.g. oxidation of Iodide to Iodine by hydrogen peroxide.



- Solutions of hydrogen peroxide, acid and Iodine of known concentrations are allowed to reach the temperature of the thermostat bath.
- Solutions are mixed and the time of mixing noted.
- At measured time intervals, sample of reaction mixtures are extracted by pipette.
- Reaction in each sample is quenched by diluting in ice cold water.
- Each sample is titrated against standard aqueous sodium thiosulphite and the concentration of Iodine is calculated.

**b) Electrical conductivity:**

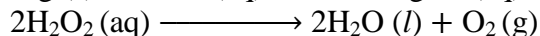
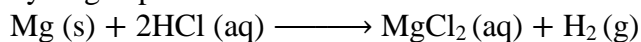
- Conductivity of a reaction mixture may be monitored overtime by carrying out the reaction in a conductivity cell.
- Conductivity apparatus is calibrated with solutions of known concentration
- Conductivity of a solution is proportional to the concentration of its ions and the charges they bear.

**c) Colorimetry**

- Applicable to reaction mixtures that show a steady colour as the reaction as the proceeds.
- Colorimeter indicates concentration by measuring the intensity of light shining through a coloured reaction mixture.
- Photocell is calibrated with solutions of known concentrations
- Light of fixed wavelength is directed through the reaction mixture and into the photocell.
- Photocell develops an emf proportional to the intensity of the light.
- Emf can then be converted to concentration values.

**d) Change in gas volume:**

- For reactions involving gases, the rate of reaction may be monitored by measuring the volume of gas evolved after various time intervals.
- The measured volume of gas may then be used to calculate the corresponding concentration of the reactant. e.g. reaction of a metal with acid and the decomposition of hydrogen peroxide.



**a) Change in pressure**

- An increase or decrease in gaseous pressure can be used to follow many gaseous reactions e.g.
  - The reaction:  $\text{N}_2\text{O}_5(\text{g}) \longrightarrow \text{N}_2\text{O}_4(\text{g}) + \frac{1}{2}\text{O}_2(\text{g})$ 
    - It involves an increase in the number of moles of gas and an increase in pressure can be followed.
  - The reaction:  $\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \longrightarrow \text{H}_2\text{O}(\text{l})$  is accompanied by a decrease in the number of moles, and decrease in pressure at constant volume.

**b) Spectrophotometry**

- Applicable for the reactions which are extremely rapid.
- Uses a very short burst of light from a laser to start reaction that is sensitive to light.

- Spectroscopic techniques then monitor the concentration of the reactive intermediate formed.

### SOME COMMON TERMS

**i. Rate law:**

- States that, “*the rate of any chemical reaction at a constant temperature is directly proportional to the molar concentration of the reactants raised to appropriate power whose value is experimentally determined.*”
- It summarises the relationship between rate of a chemical reaction and the concentration of the reactants.

**ii. Rate equation:**

- Expresses the rate of reaction in terms of the concentration of each reactant raised to a specific power. Consider a reaction  $A + B \longrightarrow \text{Products}$   
From Rate law;  $\text{Rate} \propto [A]^x [B]^y$      $\text{Rate} = k [A]^x [B]^y$

Where  $k$  = rate constant/ coefficient

$X$  = order of reaction with respect to A

$Y$  = Order of reaction with respect to B

**iii. Rate constant / Rate coefficient:**

Is the ratio of the rate of a chemical reaction to the products of the concentration of the reactants raised to appropriate powers as in the rate equation.

Units vary according to the overall order i.e.

From  $\text{Rate} = k [A]^x [B]^y$

$$K = \frac{\text{Rate}}{[A]^x [B]^y}$$

**iv. Order of reaction**

Is the power to which the concentration terms are raised in the experimental rate equation

**v. Overall order equation\**

Is the sum of the powers to which the concentration terms are raised in the experimental rate equation.

From  $\text{Rate} = k [A]^x [B]^y$

Overall order =  $x + y$

**vi. Molecularity of a reaction:**

Is the total number of species (ions/ molecules) involved in a particular reaction i.e the number of species involved in the rate determining step for those reactions occurring in stages.

### Difference between molecularity and order of a reaction

Molecularity	Order of equation
<ul style="list-style-type: none"><li>Only whole numbers and is never zero</li></ul>	Can be a fraction, zero or a whole number
<ul style="list-style-type: none"><li>Determined from a Stoichiometric equation</li></ul>	Experimentally determined
<ul style="list-style-type: none"><li>Number of species that take part in the rate determining state</li></ul>	Power to which the concentration of the reactant is raised in the experimental rate equation

vii. **Rate determining step/Rate limiting step:**

Is the slowest step in a multi step chemical reaction through which the reactants are converted to the products.

viii. **Elementary reactions:**

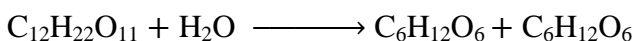
These are reactions that involve one step path or route from reactants to products.

*For elementary reactions, molecularity is equal to the order of reaction.*

However, the reactions which are not elementary, molecularity may not be equal to order of reaction. E.g. in hydrolysis of a reactant such as ester/ sucrose in presence of a large excess of water.

Consider hydrolysis of sucrose;

Sucrose + water  $\longrightarrow$  Glucose + Fructose



Molecularity of above reaction is two because both sucrose and water are involved in the rate determining step.

However, the overall order of this reaction is *first order* when experimentally determined.

**Reason**

- Water is present in large excess, its concentration remains unaffected and hence doesn't contribute to the order of the reaction.
- Only sucrose concentration changes during the course of a reaction, affecting the rate of reaction with an order one.

NB: *Such reactions where water is in excess making its concentration zero is referred to as pseudo – first order reaction.*

### **DETERMINATION OF ORDER OF REACTION FROM INITIAL RATE METHOD**

In this method, the order of reaction with respect to a given reactant is determined by comparing the initial rate for the experiments in which the concentration of only the reactant

whose order of reaction is to be determined is changing while the other reactant concentrations are kept constant.

It therefore requires more than one reactant.

For zero order reaction;

- ✓ the rate of reaction is not affected by change in initial concentration of the reactant e.g. doubling the concentration of the reactant has no effect on the rate.

For all 1<sup>st</sup> order reactions;

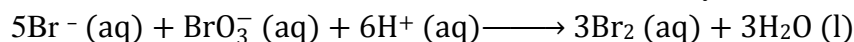
- ✓ doubling the initial concentration of the reactant also doubles the rate,
- ✓ Trebling it also trebles the rate i.e. increasing the concentration of reactant by factor y also increases the rate by some factor y.

For second order reactions;

- ✓ doubling or trebling initial concentration of the reactant increases the rate by 4 or 9 times respectively.

**Example:**

The result shown refers to oxidation of Bromine ion by Bromate ion in acidic solution.



[5Br <sup>-</sup> ](mol dm <sup>-3</sup> )	BrO <sub>3</sub> <sup>-</sup> (mol dm <sup>-3</sup> )	H <sup>+</sup> (mol dm <sup>-3</sup> )	Initial rate (mol dm <sup>-3</sup> )
i. 0.10	0.10	0.10	$8 \times 10^{-4}$
ii. 0.10	0.20	0.10	$1.6 \times 10^{-3}$
iii. 0.20	0.20	0.10	$3.2 \times 10^{-3}$
iv. 0.10	0.10	0.20	$3.2 \times 10^{-3}$

- Find the order of the reaction with respect to Br<sup>-</sup>, Br O<sub>3</sub><sup>-</sup>, H<sup>+</sup>
- State the overall order of reaction
- Write the rate equation
- Calculate the value of rate constant and state its units.
- Calculate the rate reaction when concentration of all three reactants is 0.2mol dm<sup>-3</sup>

**Solution**

a) (i) Br<sup>-</sup>

Let the order of the reaction with respect to Br<sup>-</sup> be x

Let the order of reaction with respect to Br O<sub>3</sub><sup>-</sup> be y

Let the order of reaction with respect to H<sup>+</sup> be z

Taking experiments (ii) and (iii)

$$\text{Rate} = K[\text{Br}^-]^x [\text{Br}_3^-]^y [\text{H}^+]^z$$

$$1.6 \times 10^{-3} = K [0.10]^x [0.2]^y [0.10]^z \text{ ----- (i)}$$

$$3.2 \times 10^{-3} = K [0.2]^x [0.2]^y [0.1]^z \text{ _____ (ii)}$$

Dividing equation (ii) by (i)

$$\frac{3.2 \times 10^{-3}}{1.6 \times 10^{-3}} = \frac{K[0.2]^x [0.2]^y [0.1]^z}{K [0.10]^x [0.2]^y [0.10]^z}$$

$$\frac{3.2 \times 10^{-3}}{1.6 \times 10^{-3}} = \left(\frac{0.2}{0.1}\right)^x$$

$$2^1 = 2^x$$

$$\mathbf{X = 1}$$

**Order of reaction with Br<sup>-</sup> is 1**

**Reason:**

Doubling the concentration of Br<sup>-</sup> doubles the initial rate

(ii) BrO<sub>3</sub><sup>-</sup>

Taking experiments (i) and (ii)

$$\text{Rate} = K[\text{Br}^-]^x [\text{Br}_3^-]^y [\text{H}^+]^z$$

$$\text{For (i); } 8 \times 10^{-4} = K [0.1]^x [0.1]^y [0.1]^z \text{ _____ (i)}$$

$$\text{For (ii); } 1.6 \times 10^{-3} = K[0.1]^x [0.2]^y [0.1]^z \text{ _____ (ii)}$$

Dividing equation (ii) by (i)

$$\frac{1.6 \times 10^{-3}}{8 \times 10^{-4}} = \frac{K[0.1]^x [0.2]^y [0.1]^z}{K [0.1]^x [0.1]^y [0.1]^z}$$

$$\frac{1.6 \times 10^{-3}}{8 \times 10^{-4}} = \left(\frac{0.2}{0.1}\right)^y$$

$$2^1 = 2^y$$

$$\mathbf{Y = 1}$$

**The order of reaction with respect to BrO<sub>3</sub><sup>-</sup> is 1**

**Reason:**

Doubling the concentration of BrO<sub>3</sub><sup>-</sup> doubles the rate.

(iii) H<sup>+</sup>

Taking experiment (i) and (iv)

$$\text{Rate} = K[\text{Br}^-]^x [\text{Br}_3^-]^y [\text{H}^+]^z$$

$$\text{For (i); } 8 \times 10^{-4} = K [0.1]^x [0.1]^y [0.1]^z \text{ _____ (i)}$$

$$\text{For (iv); } 3.2 \times 10^{-3} = K [0.1]^x [0.1]^y [0.2]^z \text{ _____ (ii)}$$

Dividing (ii) by (i)

$$\frac{3.2 \times 10^{-3}}{8 \times 10^{-4}} = \frac{K [0.1]^x [0.1]^y [0.2]^z}{K [0.1]^x [0.1]^y [0.1]^z}$$

$$4 = 2^z$$

$$2^2 = 2^z$$

**Z = 2;** Order of reaction with respect to H<sup>+</sup> is 2

**Reason:**

Doubling the reaction with respect to H<sup>+</sup> rate increases by factor four (4) (rate quadruples)

$$\text{b) Rate} = K[\text{Br}^-]^1 [\text{Br}_3^-]^1 [\text{H}^+]^2$$

$$\text{Overall order} = 2 + 1 + 1 = 4$$

c) Rate =  $K[\text{Br}^-]^1 [\text{Br}_3^-]^1 [\text{H}^+]^2$

d) From rate =  $K[\text{Br}^-]^1 [\text{Br}_3^-]^1 [\text{H}^+]^2$

$$K = \frac{\text{Rate}}{[\text{Br}^-]^1 [\text{Br}_3^-]^1 [\text{H}^+]^2} = \frac{3.2 \times 10^{-3} \text{ (mol dm}^{-3}\text{)}}{(0.2)(0.2)(0.1)^2 \text{ (mol dm}^{-3}\text{)(mol dm}^{-3}\text{)(mol dm}^{-3}\text{)}} \\ = \mathbf{8 \text{ mol}^{-3} \text{ dm}^4 \text{ s}^{-1}}$$

e) Rate =  $8 (0.2)(0.2) (0.2)^2$   
 $= \mathbf{0.0128 \text{ mol dm}^{-3} \text{ s}^{-1}}$

### Example

2. For the reaction  $\text{A} + \text{B} \longrightarrow \text{C}$ , the following results were obtained for kinetic run at the same temperature.

[A] (mol dm <sup>-3</sup> )	[B] (mol dm <sup>-3</sup> )	Initial rate (mol dm <sup>-3</sup> s <sup>-1</sup> )
0.20	0.10	0.2
0.40	0.20	0.8
0.40	0.20	0.8

Find:

- Rate equation of reaction
- Rate constant
- Initial rate of reaction when  $[\text{A}] = 0.6 \text{ mol dm}^{-3}$  and  $[\text{B}] = 0.3 \text{ mol dm}^{-3}$

### Solution:

- Doubling the concentration of **A** quadruples the rate giving order 2.  
 For B, doubling the concentration has no effect on rate hence zero order.

$$\text{Rate} = k [\text{A}]^2$$

(b)  $K = \frac{\text{rate}}{[\text{A}]^2} = \frac{0.20}{(0.20)^2} = \mathbf{5 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}}$

(c) Rate =  $k [\text{A}]^2 [\text{B}]^0$   
 $= 5[0.6]^2$   
 $= \mathbf{1.8 \text{ mol dm}^{-3} \text{ s}^{-1}}$

### Exercise

1. The table below shows some data for the reactions;

[A] (mol dm <sup>-3</sup> )	[B] (mol dm <sup>-3</sup> )	Initial rate (mol dm <sup>-3</sup> s <sup>-1</sup> )
$1.00 \times 10^{-2}$	$2.8 \times 10^{-3}$	2.2

$5.00 \times 10^{-3}$	$2.8 \times 10^{-3}$	1.1
$1.00 \times 10^{-2}$	$5.6 \times 10^{-3}$	4.4

- Determine the order of reaction with respect A and B, giving reasons for your answers.
  - Write the rate equation of reaction
  - Calculate the rate constant and find its unit
  - Calculate the rate reaction when concentration of A and B is  $A = 8.5 \times 10^{-3} \text{ moldm}^{-3}$ ,  $B = 3.83 \times 10^{-3} \text{ moldm}^{-3}$
2. 2 - Bromo - 2 - methylpropane,  $(\text{CH}_3)_3\text{CBr}$  and NaOH react together according to the following equation
- $$(\text{CH}_3)_3\text{CBr} + \text{OH}^- \longrightarrow (\text{CH}_3)_3\text{COH} + \text{Br}^-$$
- The following data gives the results of three experiments used to determine the rate equation from the reaction at  $25^\circ\text{C}$ .

Experiment	Initial $(\text{CH}_3)_3\text{CBr}$ ( $\text{moldm}^{-3}$ )	Initial $[\text{OH}^-]$ ( $\text{moldm}^{-3}$ )	Initial rate of reaction ( $\text{moldm}^{-3}$ )
1	$1.0 \times 10^{-3}$	$2.0 \times 10^{-1}$	$3.0 \times 10^{-3}$
2	$4.0 \times 10^{-3}$	$2.0 \times 10^{-1}$	$6.0 \times 10^{-3}$
3	$5.0 \times 10^{-3}$	$4.0 \times 10^{-1}$	$6.0 \times 10^{-3}$

From these results, it can be deduced that the rate equation is;

$$\text{Rate} = K [(\text{CH}_3)_3\text{CBr}]$$

- Show how the data can be used to determine/ deduce that the reaction is 1<sup>st</sup> order with respect to  $(\text{CH}_3)_3\text{CBr}$  and zero order with respect to  $\text{OH}^-$ .
  - Calculate the value of the rate constant at this temperature and state its units.
  - Calculate the initial rate of reaction when the initial concentration of  $(\text{CH}_3)_3\text{CBr}$  is  $4.0 \times 10^{-3} \text{ moldm}^{-3}$  and the initial concentration of  $\text{OH}^-$  is  $1.0 \times 10^{-1} \text{ moldm}^{-3}$
- b) Name and outline a mechanism for the reaction of tertiary haloalkane  $(\text{CH}_3)_3\text{CBr}$  with aqueous NaOH.

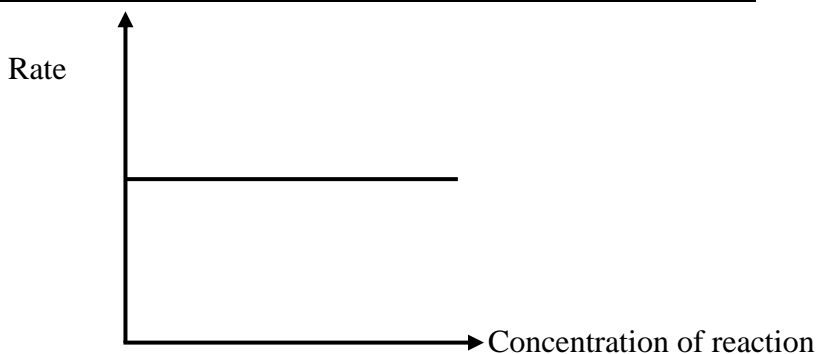
## CLASSIFICATION OF CHEMICAL REACTIONS ACCORDING TO OVERALL ORDER

### Zero Order Reactions

- Rate of reaction is independent of the concentration of the reactant
- The rate equation for the zero order reaction is given by;  

$$\text{Rate} = K [\text{A}]^0 \Rightarrow \text{Rate} = K (\text{constant})$$
 Where A is a constant in the determining step.

**A plot of rate of reaction against concentration of reactant**



$$\text{From Rate} = -\frac{d[A]}{dt} = K[A]^0$$

$$= -\frac{d[A]}{dt} = K$$

$$-d[A] = Kdt$$

Integrate from  $A_0$  at  $t = 0$  to  $A_t$  at time  $t = t$

$$-\int_{A_0}^{A_t} d[A] = K \int_{t=0}^{t=t} dt$$

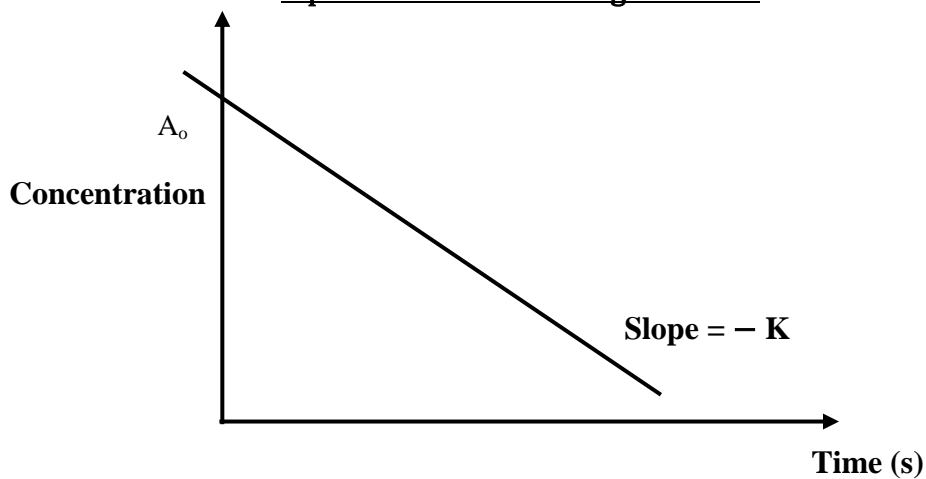
$$- [A] \Big|_{A_0}^{A_t} = Kt \Big|_{t=0}^{t=t}$$

$$- A_t - (-A_0) = Kt$$

$$- A_t + A_0 = Kt$$

$$A_t = -Kt + A_0 \quad (y = mx + c)$$

**A plot of concentration against time**



### Examples of zero order reactions

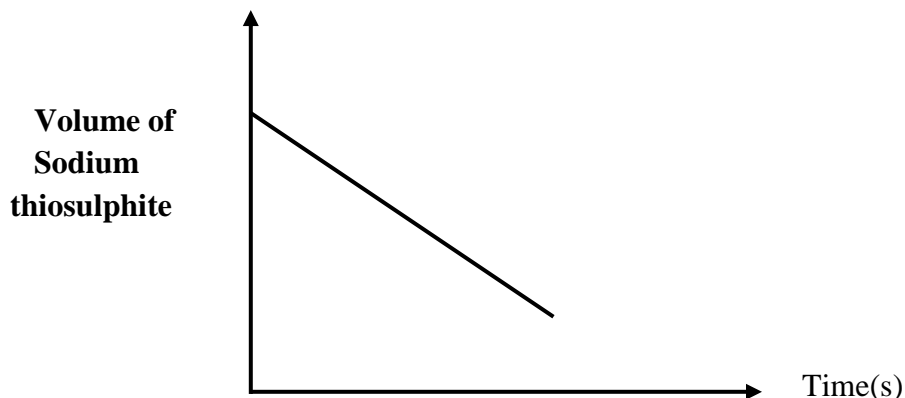
- ✓ *Iodination of Propanone*; in which the reaction is zero order with respect to Iodine.
- ✓ *Reactions between gases*; where rate of reaction with respect to one of the reactants is zero order; indicating that this reactant has been adsorbed on the surface of the vessel and the rate only depends on the frequency of collision between the non adsorbed gas with the inside of the vessel e.g. decomposition of  $\text{NH}_3$  (g) to Nitrogen and Hydrogen in the presence of a hot tungsten wire.

### Experiment: To determine order of reactions with respect to Iodine in the Iodination of propanone catalysed by $\text{H}_2\text{SO}_4$

#### Procedure:

- Fixed volumes of propanone and sulphuric acid are measured into a clean flask.
- A fixed volume of standard solution of iodine is then added to the flask. The time at which the iodine is added is being noted.
- After a few minutes, a sample of the reacting mixture is pipetted into a conical flask and added a solution of Sodium hydrogen Carbonate solution to stops the reaction instantly by neutralizing the acid.
- The time at which the reaction stops is noted.
- The resultant mixture is then titrated with a standard solution of Sodium thiosulphite to determine the amount of Iodine that remains.
- The procedure is repeated at intervals of 5 minutes to determine the amount of Iodine that has remained.
- Initial concentration of iodine is determined
- Since titre values at various times will be proportional to the concentration of iodine left at those times, a plot of volume of thiosulphite against the time elapsed since the start of reaction, gives a straight line from which the value of rate constant(K) can be determined.

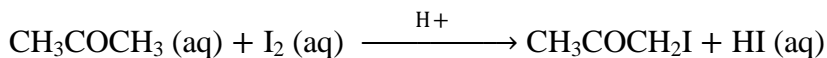
#### A plot of volume of Sodium thiosulphite against time



Rate of the reaction remains constant as the iodine concentration decreases.

#### Example (QUIZ)

- a) Describe an experiment to show Iodination of Propanone follows a zero order reaction with respect to Iodine. (7mks)
- b) Propanone reacts with Iodine in the presence of an acid catalyst according to the equation



The reaction is first order with respect to Propanone and independent of the concentration of Iodine. Briefly describe how the order of reaction with respect to Iodine can be determined.

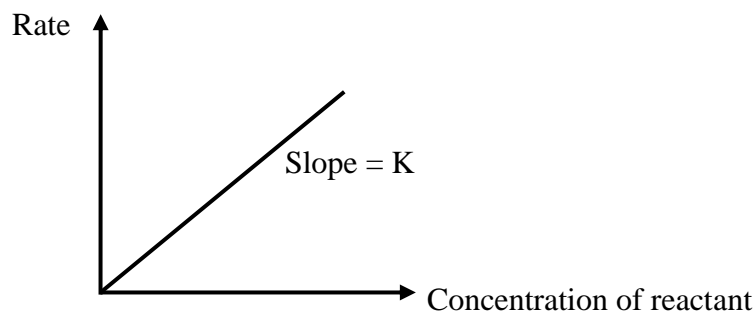
## 2. First Order Reactions

- Rate of reaction is proportional to the first power of concentration of single reactants.
- Consider a reaction,  $\text{A} \longrightarrow \text{products}$

$$\text{Rate} = -\frac{d[\text{A}]}{dt} = k [\text{A}]^1$$

$$\text{Rate} = k [\text{A}], \text{ from } y = mx + c, c = 0$$

### A graph of rate against concentration of reactants



### Examples of first order reactions

- Hydrolysis of sucrose in presence of acid.
- Acid catalysed hydrolysis of an ester.
- Radioactive decay
- Decomposition of nitrogen pentaoxide,  $\text{N}_2\text{O}_5$
- Decomposition of Benzene diazonium chloride.

### Radioactive decay and half life

#### Half life:

Is the time taken for the concentration to fall to half its original value.

$$\text{Rate of reaction} = -\frac{d[\text{A}]}{dt} = k [\text{A}]$$

Separating variables;

$$-\frac{d[A]}{[A]} = K dt$$

Integrating between the limits  $A_0$  at times  $t = 0$  to  $A_t$  at  $t = t$

$$-\int_{A_0}^{A_t} \frac{d[A]}{[A]} = k \int_{t=0}^{t=t} dt$$

$$-\ln[A] \Big|_{A_0}^{A_t} = kt \Big|_{t=0}^{t=t}$$

$$-\ln A_t - (-\ln A_0) = kt$$

$$\ln \left( \frac{A_0}{A_t} \right) = kt$$

$$\text{But } \ln = 2.303 \log_{10} \Rightarrow \boxed{2.303 \log \frac{A_0}{A_t} = kt} \text{ ----- (i)}$$

$$\text{At } t = t_{1/2}; A_t = \frac{A_0}{2}$$

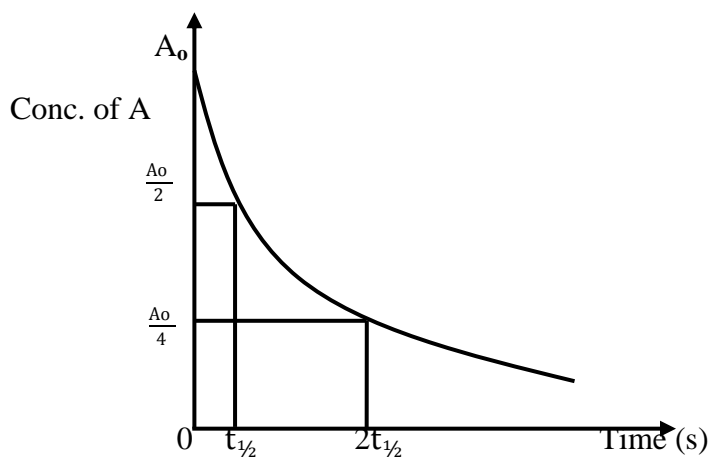
$$2.303 \log \frac{A_0}{\frac{A_0}{2}} = kt_{1/2}$$

$$t_{1/2} = 2.303 \log 2 = \frac{0.693}{K}$$

$$\therefore \boxed{t_{1/2} = \frac{0.693}{K}} \text{ ----- (ii)}$$

For 1<sup>st</sup> order reactions, *half life is constant and independent of the initial concentration of the reactant.*

**A graph of concentration of A against time**

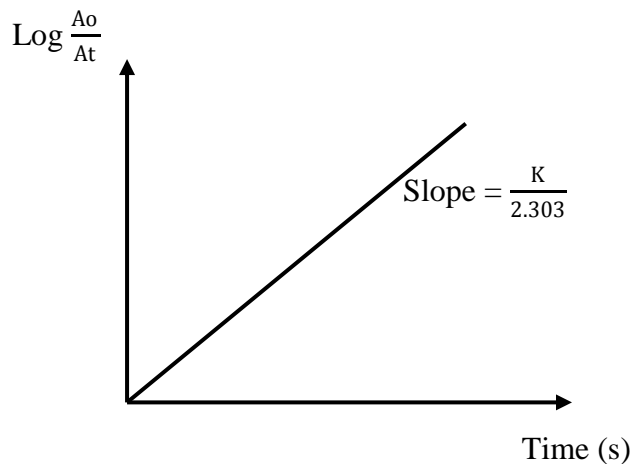


First order reaction  $(t_{1/2} - 0) = (2t_{1/2} - t_{1/2})$

Also from  $2.303 \log \frac{A_0}{A_t} = kt$

$$\Rightarrow \text{Log } \frac{A_o}{A_t} = \frac{kt}{2.303}$$

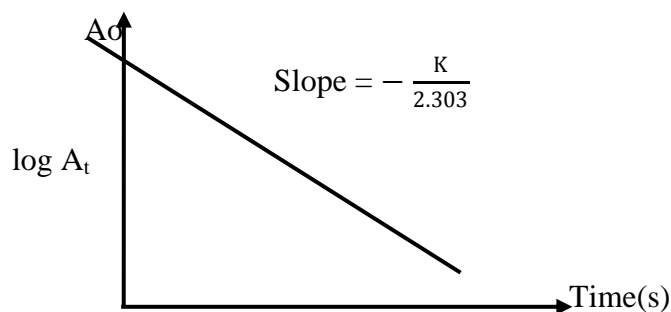
A plot of  $\frac{A_o}{A_t}$  against time



Also from  $\log \frac{A_o}{A_t} = \frac{K}{2.303}$

$$\log A_o - \log A_t = \frac{K}{2.303}$$

$$\log A_t = \log A_o - \frac{K}{2.303}$$



### UNEB 2011

- The table below shows the kinetic data that was obtained for the conversion of sucrose to glucose in acid solution.

Conc. of sucrose ( $\text{mol dm}^{-3}$ )	0.08	0.06	0.04	0.02	0.01
Rate of reaction ( $\text{mol dm}^{-3}$ )	0.004	0.003	0.002	0.001	0.0005

- Plot a graph of rate of reaction against the concentration of sucrose.

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- ii. State the order of the reaction. Give a reason for your answer.
  - iii. Determine the rate constant for the reaction and indicate its units.
  - iv. Calculate the rate of the reaction when the concentration of sucrose was  $0.12\text{mol dm}^{-3}$ .
2. Compound B undergoes a reaction to form compound W. The course of the reaction can be followed by adding excess KI solution to a fixed volume of the reactant. B reacts with a standard solution of Sodium thiosulphate. The volume of the Sodium thiosulphate solution is a measure of the concentration of B remaining at time T. The table below shows the volume of Sodium thiosulphate, V required at various times.

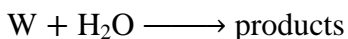
V( $\text{cm}^3$ )	24.70	17.80	12.90	9.25	5.50	3.60
t (mins)	0	60	120	180	240	300

- a) Plot a graph of V against time
- b) From the graph in (a), deduce the time for B; to
  - i. be reduced to half the original value
  - ii. be reduced to  $\frac{1}{4}$  the original value
- c) What is the order of the reaction with respect to B?
- d) Write the rate equation for the reaction in which B is converted to W.
- e) Determine the rate constant for the reaction.

NB: When only time and the concentration of the product is given, the concentration of the reactant at each time is got by subtracting the concentration of the product at that time from the concentration of the product at the end of the reaction. i.e.

$$[\text{Reactants}]_t = [\text{product}]_{\text{end}} - [\text{product}]_t$$

A plot of the concentration of reactant and time is then made e.g. given;



Time(s)	0	20	40	60	$\infty$
[products]/ $\text{mol dm}^{-3}$	30	90	120	135	150

### **Solution:**

Time (s)	0	20	40	60	$\infty$
[Product] ( $\text{mol dm}^{-3}$ )	30	90	120	135	150
[reactant] ( $\text{mol dm}^{-3}$ )	(150 – 30)	(150– 90)	(150– 120)	(150– 135)	(150– 150)

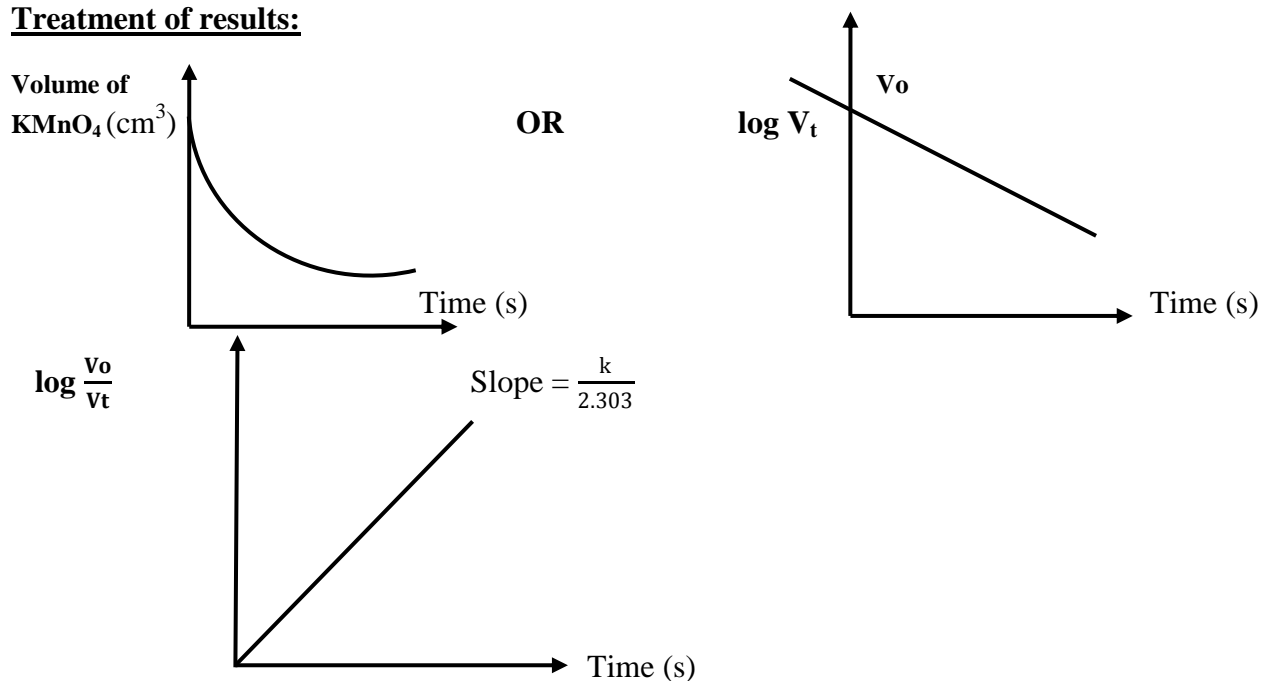
	120	60	30	15	0
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### Experimental determination of order of catalyzed decomposition of H<sub>2</sub>O<sub>2</sub>

#### Procedure:

- A known fixed volume of H<sub>2</sub>O<sub>2</sub> solution is pipette.
- NaOH solution is added to it followed by FeCl<sub>3</sub> solution and the stop clock simultaneously started.
- Mixture is shaken and allowed to stand for 3 minutes.
- A known volume reaction mixture is withdrawn, excess dilute H<sub>2</sub>SO<sub>4</sub> is added to it stop the decomposition.
- The resultant mixture is then titrated with a standard solution of KMnO<sub>4</sub>.
- The procedure is repeated at intervals of 3 minutes before adding H<sub>2</sub>SO<sub>4</sub> and the titre values V<sub>t</sub> noted.
- Initial concentration of H<sub>2</sub>O<sub>2</sub> before decomposition is obtained by titrating the original H<sub>2</sub>O<sub>2</sub>, with KMnO<sub>4</sub> and volume of the potassium permanganate used V<sub>o</sub> is recorded.
- A graph of  $\log \left(\frac{V_o}{V_t}\right)$  against time is plotted, a straight line is obtained.

#### Treatment of results:



#### UNEB 2011

1. Describe an experiment to show that catalytic decomposition of H<sub>2</sub>O<sub>2</sub> is a first order reaction.
2. A certain volume of H<sub>2</sub>O<sub>2</sub> solution was decomposed in the presence of platinum. The amount of H<sub>2</sub>O<sub>2</sub> after time t was found by withdrawing aliquot portions of solution, adding dilute

sulphuric acid and titrating with Potassium manganate (VII) solution. The volume  $V_t$  of Potassium manganate (VII) solution were as follows;

t (min)	0	5	10	15	20	25	30	35	40	45
$V_t$ (cm <sup>3</sup> )	12.30	9.20	6.90	5.20	3.90	2.90	2.20	1.60	1.20	1.15

- Tabulate values of  $\log V_t$
- Plot a graph of  $\log V_t$  against time
- State order of reaction with respect hydrogen peroxide. Give reason for your answer.
- Determine the rate constant for the reaction
- Calculate the half life for the reaction

### **NB: Conditions for first order reaction**

- If one of the reactants is in large excess that only a small fraction of it will be used up in the reaction.
- Use of acid as catalyst; where its concentration doesn't change during the course of the reaction e.g acid catalysed hydrolysis of esters and sucrose.

### **3. SECOND ORDER REACTION**

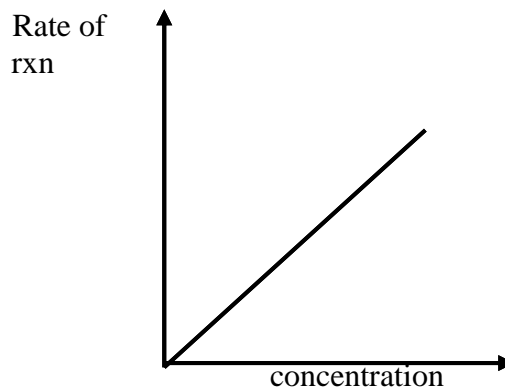
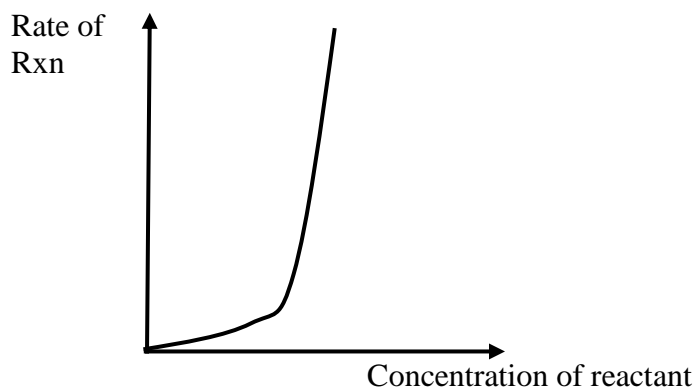
Rate of reaction is proportional to the ,

- ✓ products of the concentration of reactants each raised to power one
- ✓ square of the concentration of a single reactant.

For  $A \longrightarrow$  Products , rate =  $k[A]^2$

For  $A + B \longrightarrow$  Products, Rate =  $k[A]^1 [B]^1$

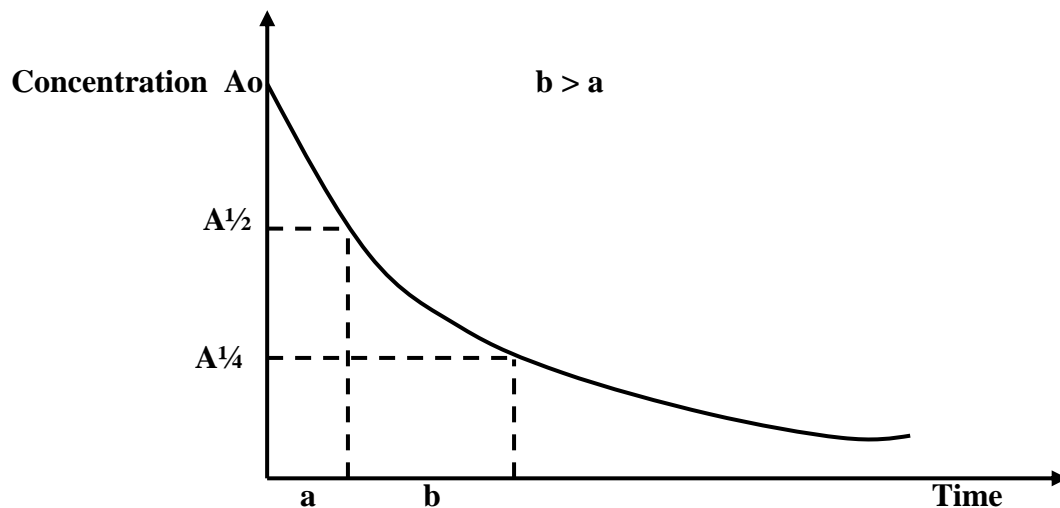
#### **Graphs of second order reactions**



#### **Half life:**

For second order reactions, half life is inversely proportional to the concentration. i.e . It almost doubles for every successive decrease in concentration of the reactant by half.

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### Examples of 2<sup>nd</sup> order reactions

- Hydrolysis of ethyl ethanoate by aqueous NaOH
- Oxidation of  $I^-$  to  $I_2$  by  $H_2O_2$

### FACTORS AFFECTING RATES OF REACTION

These include

- i. Concentration of reactants in solution
- ii. Temperature
- iii. Pressure of gaseous reactants
- iv. Light
- v. Catalyst
- vi. Surface area/size of particle of a solid reactant.

#### Surface area:

- For reactions involving solids, breaking the solid into smaller pieces increases its total surface area.
- Increase in SA of the reactants increases the rate of reaction by exposing more reactant molecules to react with another.

#### Light:

- Photosensitive reactions e.g. photosynthesis and formation of Ag and Ag salts which take place when a photographic film is exposed to light, their rates increase with exposure to light.
- Light of sufficient energy breaks the bonds in one of the reactants creating a reactive intermediate from which the products are formed.

### **Pressure of gaseous reactants:**

Increase in pressure of gases pushes the gaseous molecules close together; increasing on their frequency of collision and thus reacting more rapidly.

### **Concentration:**

- Increasing the concentration of the reactants increases the rate of reaction and vice versa
- This is because at greater concentration, there are more molecules in a given volume, close distance between these molecules are reduced and there is an increased number of collisions per unit volume.

### **Example:**

- The rate equation for  $2A + B \longrightarrow C$  is given by  $\text{Rate} = k[A][B]^2$ . How will the rate of reaction alter if concentration of
  - A is doubled but concentration of B is kept constant
  - Concentration of B is halved but concentration of A is kept constant
  - Both Concentration of A and concentration of B are doubled

### **Solution:**

- $$\begin{aligned} \text{Rate} &= k[A][B]^2 \\ &= k[2A][B]^2 \\ &= 2k[A][B]^2 \end{aligned}$$

**New rate is twice the initial rate**

- $$\begin{aligned} \text{Rate} &= k[A][\frac{1}{2}B]^2 \\ &= (\frac{1}{2})^2 k[A][B]^2 \\ &= \frac{1}{4} k[A][B]^2 \end{aligned}$$

**New rate is  $\frac{1}{4}$  times the initial rate**

- $$\begin{aligned} \text{From Rate} &= k[A][B]^2 \\ \text{Rate} &= k[2A][2B]^2 \\ &= (2)(4) k[A][B]^2 \\ &= 8 k[A][B]^2 \end{aligned}$$

**new rate is 8 times the initial rate**

### **ACTIVITY**

The rate of a certain reaction is  $\text{Rate} = k[\text{A}][\text{B}]^2[\text{C}]$  where [ ] is the concentration in moles per litre and  $k$  is the rate constant. State how the rate of the reaction will change if;

- Concentration of B and C is doubled and A is kept constant
- Concentration of A and C were kept constant and concentration of B is halved
- [A] and [C] were kept constant and [B] was doubled.
- Concentration of A, B and C were doubled.

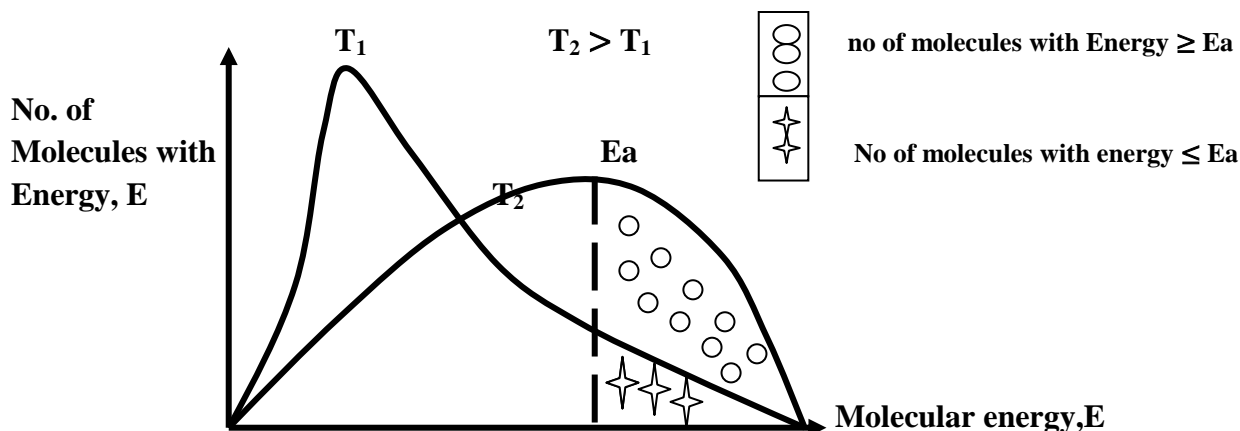
### Temperature:

- Increasing the temperature of the reactants increases the rate of a reaction.
- At higher temperatures, the ions/ molecules of the reactants have more energy moving with greater average velocity and collide more frequently and with more force.
- Increased collision frequency results in a higher rate of reaction.

### MAXWELL – BOLTZMANN DISTRIBUTION OF MOLECULAR ENERGY, E

- Maxwell – Boltzmann stated that; *Rate of reaction doubles for every  $10^0\text{C}/10k$  rise in temperature* as shown below.

#### A plot of fraction of number of molecules with energy E against molecular energy E



### Interpretation

- At lower temperature ( $T_1$ ), a very large fraction of the molecules have energy close to the average energy, only a very small fraction of the molecules having very high or very low energies.
- At higher temperature ( $T_2$ ), there is a wide range of molecular energies; proportion of molecules with energy greater than or equal to average is greater; increasing the likelihood of successive collision increasing the rate of reaction.

Qn: Explain with the help of Maxwell - distribution diagram why the rate of some reactions approximately doubles when the temperature is increased by  $10^0\text{C}$  around room temperature.

### Relationship between the rate constant, K and temperature

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- Arrhenius equation relates the magnitude of the rate constant and the temperature
- The equation can be used to calculate the activation energy from the rates of reactions at different temperatures.

$$K = Ae^{-E_a/RT}$$

$$\ln K = \ln A - \frac{E_a}{RT}$$

Where A = Arrhenius factor (pre exponential factor)

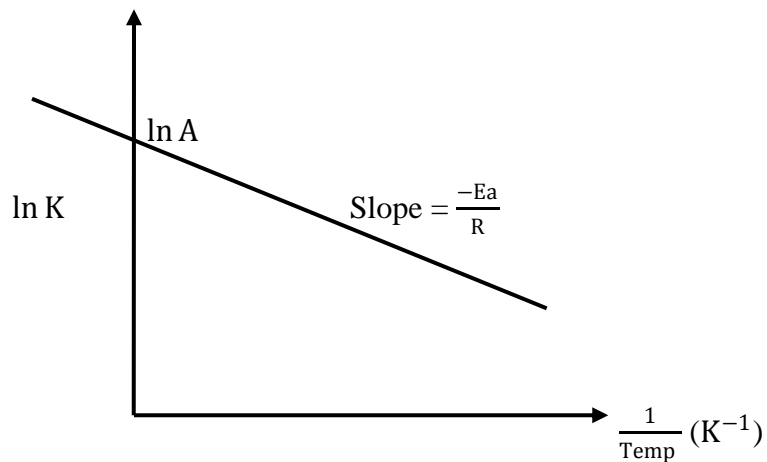
K = Rate constant

E<sub>a</sub> = Activation energy

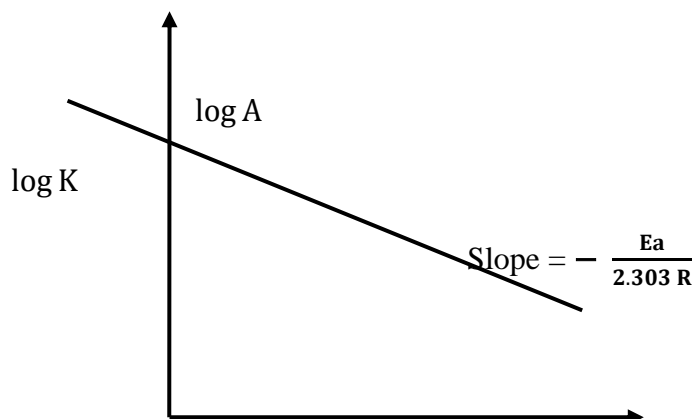
T = absolute temperature

R = Gas constant

### A plot of ln K against temperature



### A Plot of log K against 1/T (log K = log A - $\frac{E_a}{2.303 RT}$ )



$$\frac{1}{T} \text{ (K}^{-1}\text{)}$$

- If  $K_1$  is the rate constant at temperature  $T_1$  and  $K_2$  is the rate constant at temperature  $T_2$

$$\text{From } \ln K = \ln A - \frac{E_a}{RT}$$

$$K_1 \rightarrow T_1, K_2 \rightarrow T_2$$

$$\ln K_1 = \ln A - \frac{E_a}{RT_1} \text{----- (i)}$$

$$\ln K_2 = \ln A - \frac{E_a}{RT_2} \text{----- (ii)}$$

$$(i) - (ii)$$

$$\ln K_1 - \ln K_2 = - \frac{E_a}{RT_1} - \left( - \frac{E_a}{RT_2} \right)$$

$$\ln \frac{K_1}{K_2} = \frac{E_a}{RT_2} - \frac{E_a}{RT_1}$$

$$\Rightarrow \ln \frac{K_1}{K_2} = \frac{E_a}{R} \left( \frac{T_1 - T_2}{T_2 T_1} \right) \text{----- (i)}$$

**OR**

$$\ln \frac{K_2}{K_1} = \frac{E_a}{R} \left( \frac{T_2 - T_1}{T_2 T_1} \right) \text{----- (ii)}$$

$$\text{But } \ln = 2.303 \log_{10}$$

$$\log \frac{K_1}{K_2} = \frac{E_a}{2.303R} \left( \frac{T_1 - T_2}{T_2 T_1} \right)$$

### Example

1. The activation energy for a certain reaction is  $50 \text{ kJ mol}^{-1}$ . What is the effect on the rate constant of increasing the temperature by 10K around room temperature (assumed to be  $15^\circ \text{C}$ )

### Solution:

$$T_1 = (15 + 273) = 288 \text{K}$$

$$T_2 = 288 + 10 = 298 \text{K}$$

$$\text{From } \log \frac{K_2}{K_1} = \frac{E_a}{2.303R} \left( \frac{T_2 - T_1}{T_2 T_1} \right)$$

$$\log \frac{K_2}{K_1} = \frac{5000}{2.303 \times 8.314} \left( \frac{298 - 288}{298 \cdot 288} \right)$$

$$\log \frac{K_2}{K_1} = 0.30426871$$

$$\frac{K_2}{K_1} = \log^{-1} (0.30426871) = \underline{\underline{2.0149}}$$

$$\frac{K_2}{K_1} \approx 2$$

**The final rate is twice the initial rate**

### **ACTIVITY**

The rate  $2\text{N}_2\text{O}_5 \longrightarrow 2\text{N}_2\text{O}_4(\text{g}) + \text{O}_2(\text{g})$  was studied at various temperatures and the rate constants were determined at those temperatures as shown in the table below.

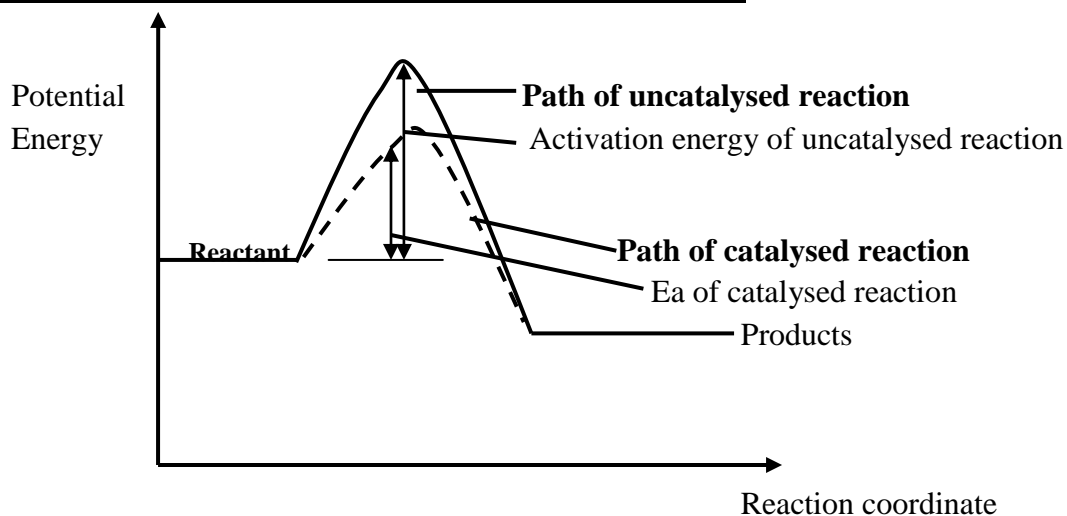
Temp <sup>o</sup> C	20	35	45	65
Rate constant	$1.76 \times 10^{-4}$	$1.35 \times 10^{-4}$	$4.94 \times 10^{-4}$	$4.87 \times 10^{-3}$

Calculate the activation energy  $E_a$  for the reaction.

### **Vi) Catalyst:**

- Is a substance that alters the rate of chemical reaction but remains chemically unchanged at the end of the reaction.
- They speed up the rate of chemical reaction by providing an alternative route of lower activation energy from reactants to products

### **Reaction profile of uncatalysed and catalysed reactions**



### UNEB 2012 (5) d

- i. Using the same axis, draw a labeled diagram for energy – reaction coordinate for a catalysed and uncatalysed. reactions
- ii. State the difference in your diagrams
- iii. State how a catalyst increases the rate of a reaction.

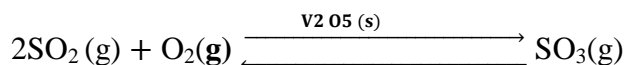
### Classification of catalyst

Classified according to the physical state it is in compared to the reactant namely.

- a) Heterogeneous catalyst
- b) Homogenous catalyst

#### a) Heterogeneous catalyst

- Catalysts and reacting substances are in different states
- Examples include.
  - i. Using of Fe in the Haber Process
  - ii. Nickel catalyst in the in the hardening of vegetable oils in the production of Margarine.
  - iii. Vanadium (v) oxide in the contact process



Heterogeneous catalyst takes place at the surface of the Catalyst.

Reactants are adsorbed onto the surface of the catalyst, bonds are broken and new bonds formed. The products are desorbed from the surface

#### b) Homogenous catalyst

- Catalyst and reacting substances are in the same physical states. E.g. include
  - i. Acid catalysed hydrolysis
  - ii. Peroxidase enzyme in the mammalian liver.
  - iii. Use of Aq.  $\text{CoCl}_2$  in the reaction between  $\text{H}_2\text{O}_2$  and aqueous solution of Sodium – Potassium 2, 3 – dihydroxybutandioate.

### Features of Catalysts

- i. Very specific to a single reaction or to class of very similar reactions.
- ii. Catalyse both forward and backward reaction at the same extent and therefore have no effect on equilibrium constant or equilibrium position.
- iii. Small quantities can usually achieve a huge increase in rate of reaction.
- iv. Catalyst maybe poisoned by some other substances e.g. lead, Arsenic and cyanide.

## Determination of a mechanism of a reaction

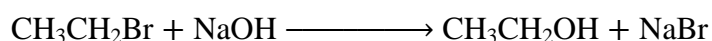
- Reaction mechanism is a detailed step by step description of the pathways followed by reactants in forming products.
- It specifies all intermediate stages and all intermediate species formed.

### Examples:

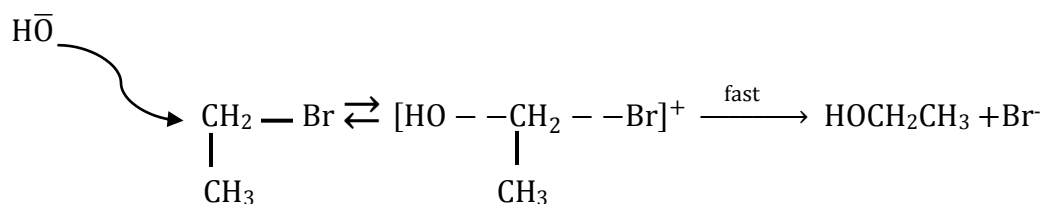
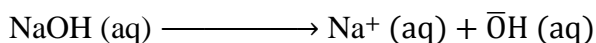
#### i. Hydrolysis of primary alkyl halide.

- The reaction is first order with respect to Hydroxyl ion and also first order with respect Bromoethane ; giving an overall order of 2.

### Equation:



### Mechanism:



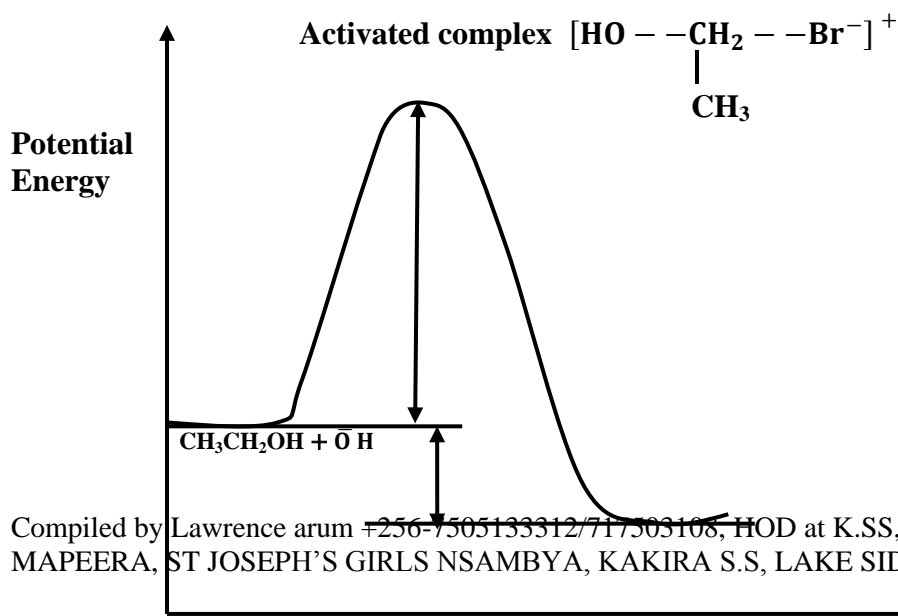
Reactants

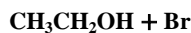
activated complex

products

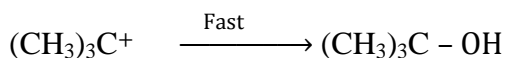
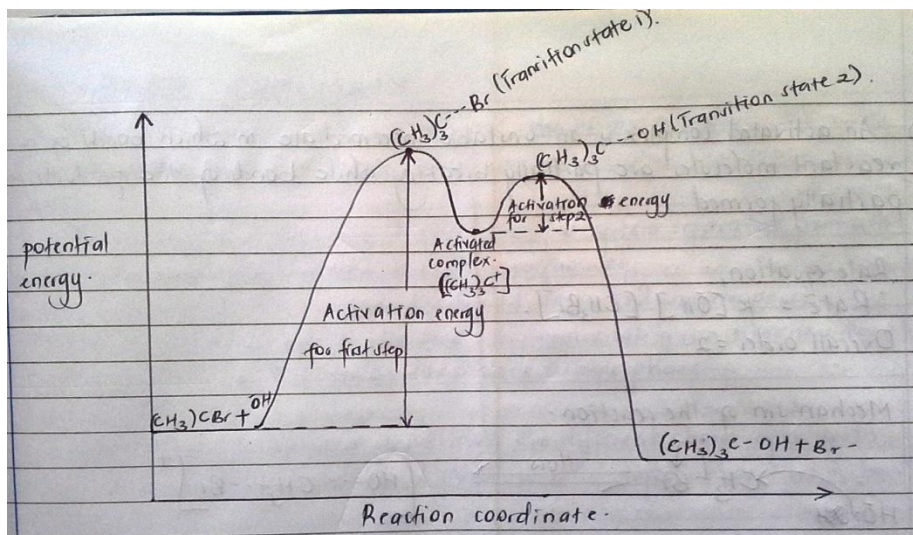
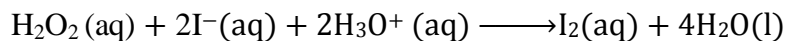
$$\text{Rate} = k [\bar{\text{O}}\text{H}] [\text{CH}_3\text{CH}_2\text{Br}]$$

### Reaction profile for substitution Nucleophilic (SN<sub>2</sub>)



$\Delta H$ **NB:**

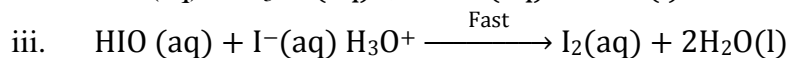
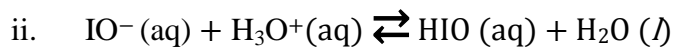
Activated complex is an “*unstable intermediate in which bonds of the reactant molecules are partially breaking while the new bonds of the product molecules are partially being formed.*”

**ii. Hydrolysis of tertially alkyl halides (2 - Bromo - 2 - methyl propane)****Equation:****Reaction profile of substitution Nucleophilic Unimolecular (SN<sub>1</sub>)****iii. Oxidation of Iodide to Iodine by H<sub>2</sub>O<sub>2</sub>****Mechanism**

slow



Fast



$$\text{Rate} = k [\text{H}_2\text{O}_2][\text{I}] \quad \text{Overall order} = 2$$

### **Questions (UNEB 1999 QN 14)**

- 2 - Bromo - 2- methyl propane reacts with aqueous NaOH to form 2 - methyl - propan - 2 - ol
  - Write the rate equation for the reaction.
  - Draw an energy diagram for the reaction  
Write the mechanism for the reaction
  - State the;
    - Rate determining step of the reaction
    - Technique which was used to study the reaction
- Bromo - methane reacts with aqueous NaOH according to the following equations  
 $\text{CH}_3\text{Br} + \text{OH}^- (\text{aq}) \longrightarrow \text{CH}_3\text{OH} (\text{aq}) + \text{Br}^- (\text{aq}) \quad \Delta H = -\text{VE}.$   
The overall order is 2
  - Draw a fully labeled diagram of energy versus reaction pathway for the reaction.
  - Explain what is meant by the term activated complex.
    - Write the rate equation for the reaction
    - Outline a mechanism for the reaction.

### **NOTE:**

- Transition state is a state of maximum potential energy during a chemical reaction in which the substance present at that state can now form the products of the reaction or can give back the reactants.
- Activation energy is the minimum energy which colliding molecules need in order to react forming products.

### **Assignment**

Theories of reaction rates

- Collision theory( **Ramsden, 287-290, 307-308; understanding chem., 165-166**)
- Transition state theory(**Ramsden, 308-310; understanding chem.; 166-167**)

# PHASE EQUILIBRIUM

Is the study of conditions under which different phases are in equilibrium.

## Common terms:

### a) Phase:

- ✓ Is a homogenous and physically distinct part of a system separated from other parts of the system by definite boundary surfaces e.g.,
  - i. Water system containing 3 phases (ice, liquid water and water vapour)
  - ii. Mixture of chloroform and water owing to immiscibility constitutes two phases
  - iii. Mixture of gases due to diffusion constitutes a single phase.

### b) Boundary:

- ✓ Is a physical part of a system separating the different phases e.g. in water system liquid – vapour interface, solid – liquid interface, solid- vapour interface are in boundaries.

### c) Component:

- ✓ Refers to a single pure substance e.g. water

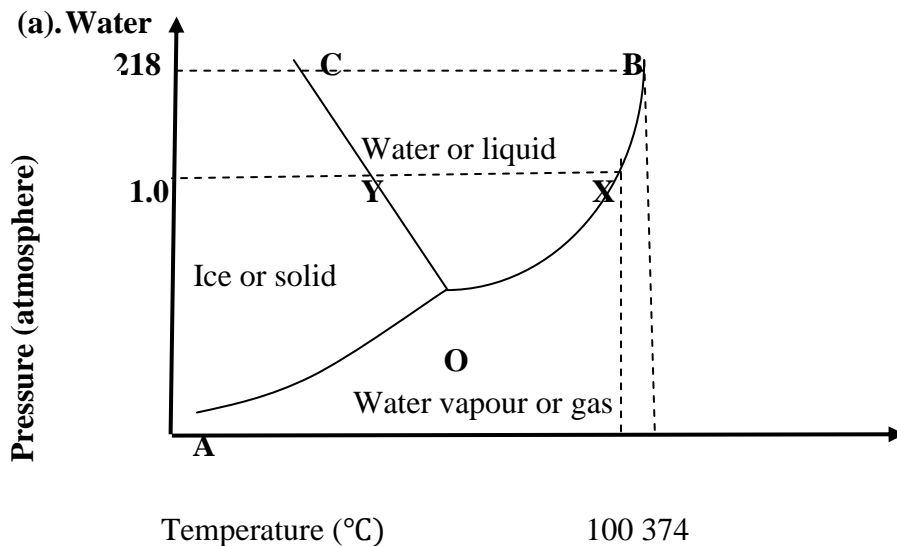
### d) Phase diagram:

A graphical plot of the effects of various temperatures and pressures on phase equilibria.

In a phase diagram;

- ❖ a phase is represented by a region separated from each other regions by lines or curves.
- ❖ Lines or curves represent a condition under which a phase can exist.

## PHASE DIAGRAMS OF SINGLE PURE SUBSTANCES



## POINTS

Compiled by Lawrence arum +256-7505133312/717503108, HOD at K.SS, Also taught at KISUBI MAPEERA, ST JOSEPH'S GIRLS NSAMBYA, KAKIRA S.S, LAKE SIDE COLLEGE LUZIRA .

**O: Triple point of water**

- ❖ At this point, pure ice, liquid and vapour are in equilibrium or co- exist

**B; Critical point of water; (corresponds to critical temperature)**

- ❖ Critical temperature is the temperature above which vapour cannot be converted into liquid water no matter how much pressure is exerted.
- ❖ Beyond this temperature, the vapour and liquid become indistinguishable.

**X on OB; Boiling point of water;**

- ❖ Liquid water and water vapour are in equilibrium at 100°C and a pressure of one atmosphere.

**Y on C; Freezing point of water;**

- ❖ Ice is in equilibrium with water at a temperature of 273K (0°C) and the pressure of 1 atmosphere.

**CURVES**

**AO; Vapour pressure curve of ice (sublimation curve)**

- ❖ Describes the effect of the temperature on saturated vapour pressure of ice.

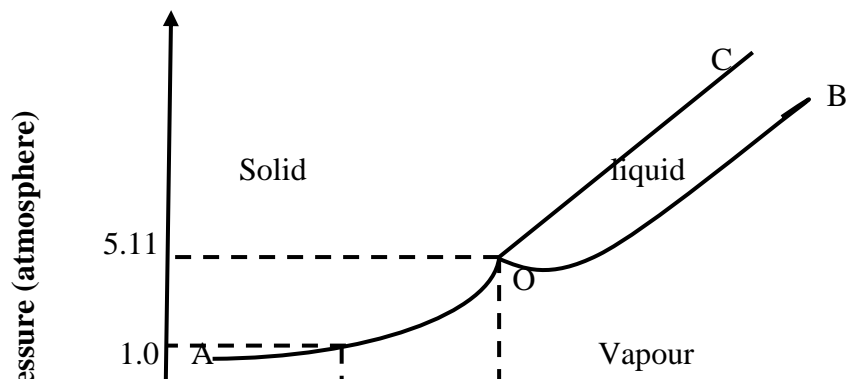
**OB; VP curve of liquid water (Vaporisation curve)**

- ❖ Shows variation of vapour pressure of water in equilibrium with its vapour with temperature.

**OC; Melting temperature/ Freezing temperature curve of ice (Fusion curve of ice)**

- ❖ Slopes towards the pressure axis indicating that melting point of ice is lowered by increasing in pressure. (Formation of ice is favoured)

**(b). Carbon dioxide**



NB; 195 217 Temperature(K)

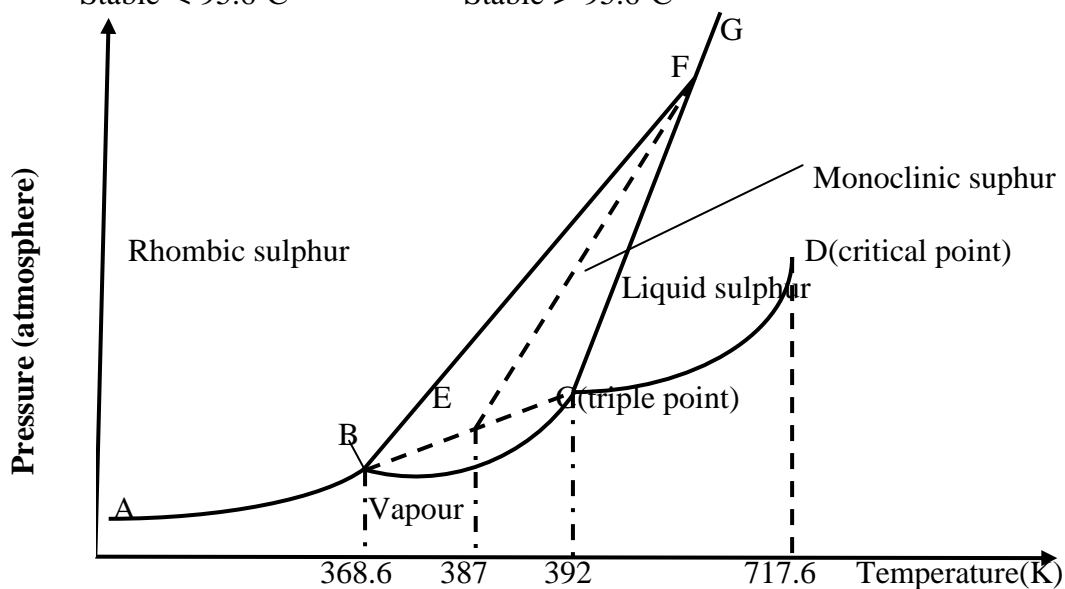
*Phase diagram for CO<sub>2</sub> is similar to that of water with two notable exceptions;*

- Triple point lies much above 1 atmosphere.  
At all pressures below its triple point, if solid carbon dioxide is warmed it sublimes.
- Curve OC slopes towards the right or away from the pressure axis.  
Molecules of CO<sub>2</sub> in the solid phase are packed more closely than in liquid phase where unlike water, Solid CO<sub>2</sub> is denser than the liquid i.e. increase in pressure favours formation of liquid.  
Melting points of solid CO<sub>2</sub> is increased with increase in pressure.

### (c) Sulphur system:

- ✓ Exhibits *allotropy* (existence of an element in more than one crystalline form)
- ✓ Exists in two allotropic forms; **Alpha sulphur** which has a rhombic crystalline form and **Beta Sulphur** which has a monoclinic crystalline form.
- ✓ Sulphur molecules, S<sub>8</sub> in rhombic sulphur are more densely packed than in the monoclinic sulphur.
- ✓ Sulphur exhibits *enantiotropy* (when an element can exist in two or more allotropic forms each of which is stable over a range of conditions).
- ✓ Monoclinic sulphur is stable above 95.6<sup>0</sup>C until a temperature of 119<sup>0</sup>C when it melts.
- ✓ On cooling, monoclinic sulphur changes to rhombic sulphur at 95.6<sup>0</sup>C.
- ✓ Temperature at which the two forms are in equilibrium is called the **transition temperature and its 95.6<sup>0</sup>C**.

Rhombic sulphur  $\rightleftharpoons$  Monoclinic sulphur  
Stable < 95.6<sup>0</sup>C                      Stable > 95.6<sup>0</sup>C



### POINTS

B; Transition temperature (368.6K); Rhombic sulphur changes to monoclinic sulphur

C; Melting point of monoclinic sulphur ( $119^{\circ}\text{C}$ )

F; Equilibrium point between Rhombic sulphur, monoclinic sulphur and liquid sulphur.

### CURVES

**AB;**

- Sublimation curve of Rhombic sulphur:
- Shows the Vapour Pressure of Rhombic sulphur at various temperatures.

**BC;**

- Sublimation curve of monoclinic sulphur
- Shows variation of vapour pressure of monoclinic sulphur in equilibrium with its vapour with temperature.

**CD;**

- Vaporisation curve of liquid sulphur
- Shows variation of vapour pressure of liquid sulphur in equilibrium with its vapour with temperature.

**CF;**

- Fusion curve of monoclinic sulphur.
- Shows variation of melting point of monoclinic sulphur with pressure.

**BF;**

- Transition curve;
- Shows the effect of pressure on the transition point

**FG;**

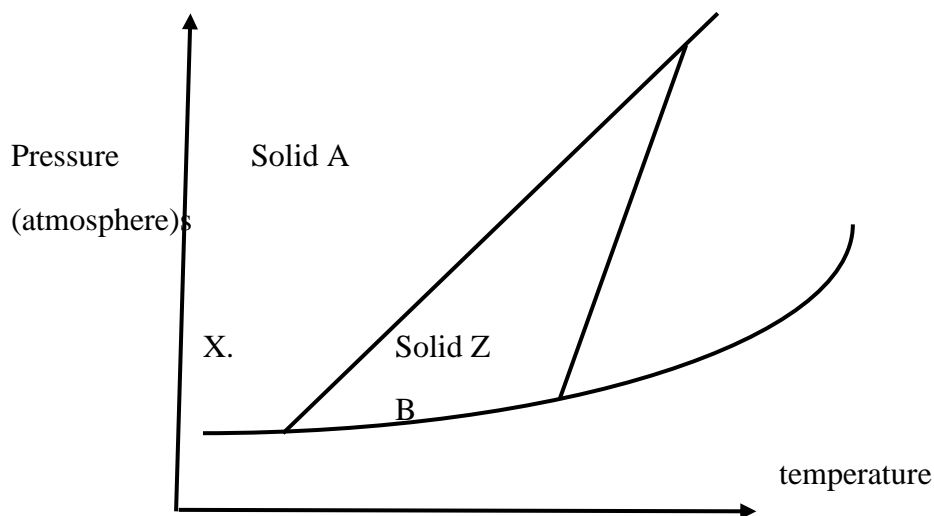
- melting point/ fusion curve of rhombic sulphur.
- Shows variation of melting point of rhombic sulphur with pressure.
- Slants towards the right signifying that the melting point of rhombic sulphur increases with temperature.

**NB:**

- ✓ Curves **BG** and **CG** slope to the right indicating the melting points of monoclinic and rhombic sulphur increase with pressure.
- ✓ When sulphur is rapidly heated, melting occurs without conversion into monoclinic sulphur.
- ✓ When it is slowly heated, it changes slowly from rhombic to monoclinic sulphur at  $95.5^{\circ}\text{C}$  and then converts to liquid sulphur at  $119^{\circ}\text{C}$  and finally to vapour at  $444^{\circ}\text{C}$

**QUESTIONS UNEB 1999 P2 (No. 17)**

1. The figure below is a phase diagram for a certain substance;

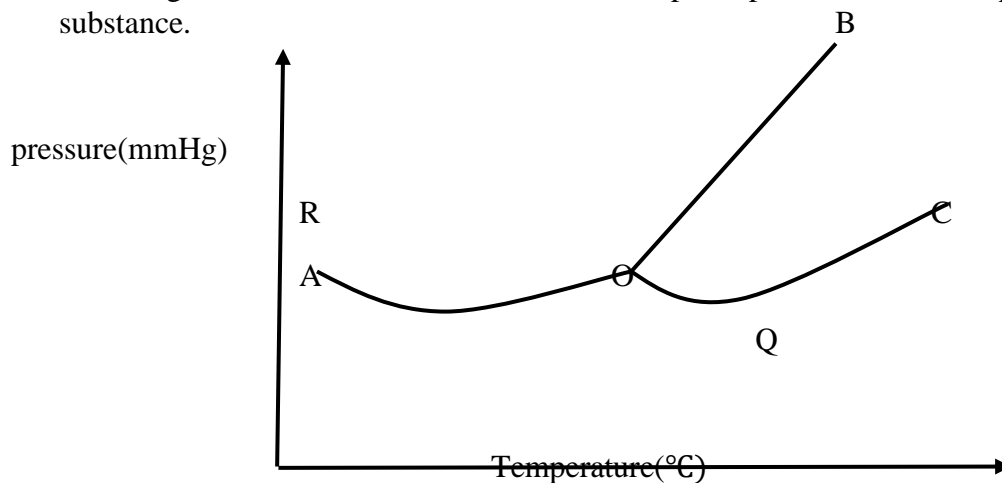


- a) Label the following on the diagram;
  - i. Axes (ii) Phases present (iii) Critical point (iv) Triple point
- b) Define the following terms
  - i. Critical temperature (ii) Triple point
- c) Explain what would happen when the substance at point X changes to point B

**Solution (part c).**

❖ Gradual decrease in pressure in X; solid A changes to solid Z and pressure drops below solid Z vapour line and solid z changes to vapour B.

2. The diagram below shows Variation of Vapour pressure with temperature of a pure substance.



(a) (i) On the diagram indicate the different phases of the substance

(ii) State what happens at O

(b). High pressure was applied at the constant temperature to the phase at Q. Describe the changes that took place.

(c) The temperature of the phase at point R was increased at constant pressure. State what was observed. (ANS. Volume of the vapour decreases until a point on the curve OC, when it starts to turn into liquid)

## SOLIDIFICATION OF SOLUTION

### Common terms

i) Eutectic mixture

- Is a liquid mixture of two or more substances which at constant pressure will solidify at constant temperature below the freezing point of the components in it forming a heterogeneous solid of the same composition as the liquid mixture.

ii) Eutectic temperature:

- Is the constant temperature at which a liquid mixture of two or more components solidifies at a given pressure without change in composition.

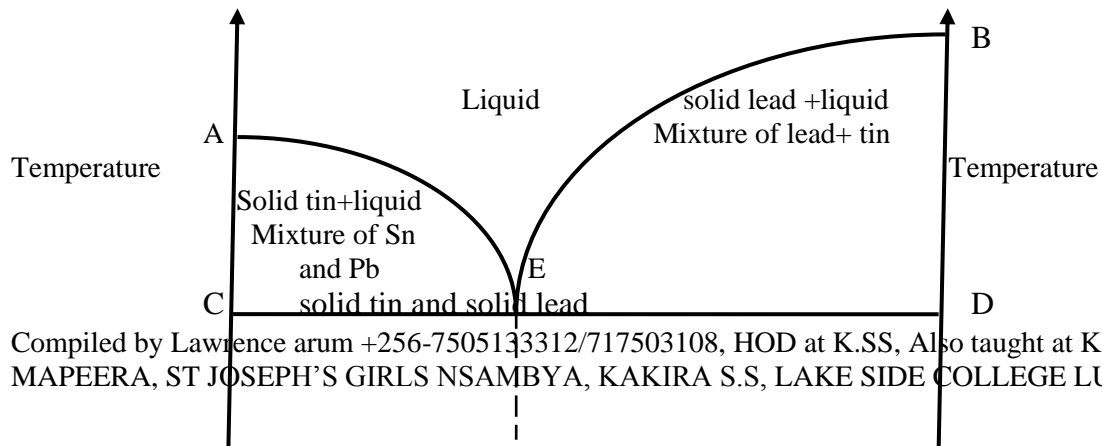
### A. Solidification of a mixture of two liquids without compound formation

- ✓ Tin and lead mixture, Silver and lead mixture, Lead and Antimony, Zinc and Cadmium, Bromomethane and Benzene mixture, Camphor and Naphthalene, Copper and Zinc etc

### TIN AND LEAD SYSTEM

- Pure tin will melt on heating and solidify on cooling at a temperature of  $232^{\circ}\text{C}$
- Pure lead will melt on heating and solidify on cooling at a temperature of  $327^{\circ}\text{C}$
- Addition of a little Lead to a molten Tin will lower the melting point/ freezing point of Tin such that on cooling, pure Tin will separate out as a solid.
- Freezing point of Tin will be lowered as more and more lead is added; more and more Tin separates out until finally a solid mixture of Tin and Lead separates out.
- The reverse is true i.e. as Tin is added to molten Lead

### Temperature composition diagram for a Tin lead mixture



## POINTS

100% Tin

mass (%)

100% Lead

**A:** Melting point of Lead

0% Tin

**B:** Melting / freezing point of Lead

**E:** Eutectic point (point at which solid Tin and Lead separate)

## CURVES

### AE:

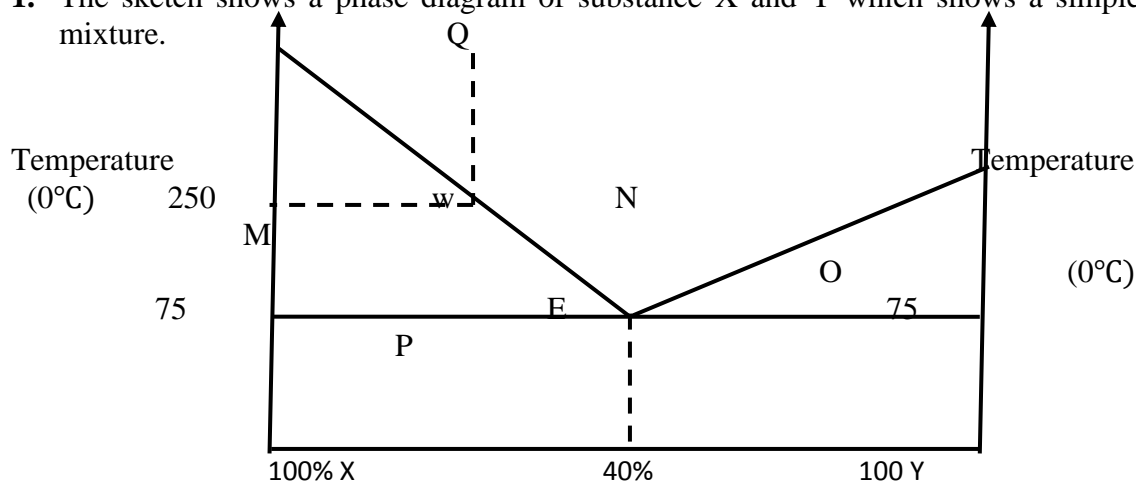
Shows how the freezing point in Tin is lowered by adding Lead

### BE:

Shows how the freezing point of Lead is lowered by addition of Sn

## Questions

1. The sketch shows a phase diagram of substance X and Y which shows a simple Eutectic mixture.



- Which one is the eutectic point?
- Identify the following regions
  - M
  - P
  - N
  - O
- Explain what happens when a mixture corresponding to the composition at Q is cooled.

### **SOLUTION (part c)**

- Q cools up to 250°C without change in phase.
- At 250°C and below; solid X begins to separate out from the mixture.
- As the mixture is cooled further, more and more X crystallise out of the mixture, until a temperature of 75°C, where solid X and solid Y are formed.
- Any further cooling below 75°C, will give the eutectic mixture (solid X and solid Y)

## **ACTIVITY**

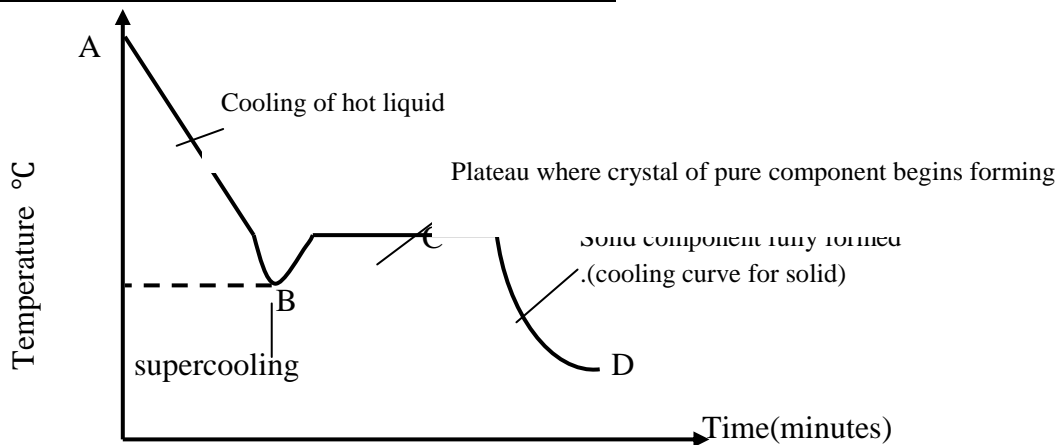
1. Two components A and B form an Eutectic mixture in which the freezing temperature of A and B and the Eutectic mixture are  $320^{\circ}\text{C}$ ,  $260^{\circ}\text{C}$  and  $140^{\circ}\text{C}$  respectively.
  - a) Using the above data, sketch a well labeled diagram of the system, assuming the eutectic mixture forms at 50% A
  - b) Explain what happens if a mixture at 40% B is cooled to room temperature,  $25^{\circ}\text{C}$
2. a) Naphthalene – biphenyl system forms an Eutectic mixture at  $41^{\circ}\text{C}$ .

The Eutectic mixture contains 0.47 moles fraction of Naphthalene. The melting points of various compositions of Naphthalene system are shown in the table below.

Mole fraction of Naphthalene	0.125	0.275	0.625	0.800
Melting point ( $^{\circ}\text{C}$ )	63.0	53.0	54.0	64.0

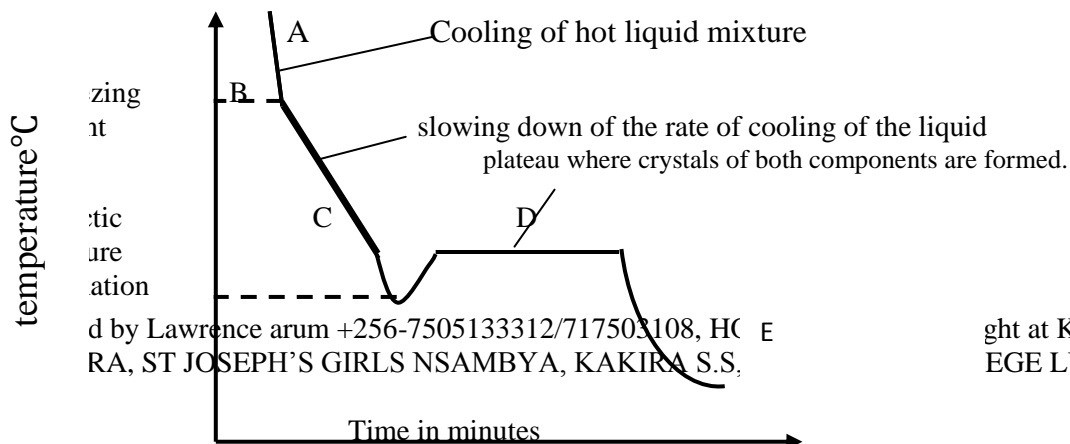
- (i). Draw an accurate phase diagram for Naphthalene – Biphenyl system and label all the regions of the diagram (melting point of Naphthalene,  $86^{\circ}\text{C}$ , Melting point of biphenyl,  $71^{\circ}\text{C}$ )
- (ii). Explain what would happen if a liquid mixture containing 80% Naphthalene was gradually cooled.

### COOLING CURVES OF A PURE SUBSTANCE



NB: *Super cooling is the cooling below the freezing point without crystal formation.*

### COOLING CURVE OF A MIXTURE



## COMPARISON BETWEEN EUTECTIC MIXTURE AND A COMPOUND

### (a) Similarities

- Have fixed melting points at constant atmospheric pressures
- Have similar cooling curves

### (b) Differences

Eutectic mixtures	Compound
<ul style="list-style-type: none"><li>• Can be separated by physical means</li></ul>	<ul style="list-style-type: none"><li>• Separated by chemical means</li></ul>
<ul style="list-style-type: none"><li>• Composition varies with pressure</li></ul>	<ul style="list-style-type: none"><li>• Composition doesn't vary with pressure</li></ul>
<ul style="list-style-type: none"><li>• Properties are simply the sum of properties of its components</li></ul>	<ul style="list-style-type: none"><li>• Properties are completely different from those of the components in it</li></ul>
<ul style="list-style-type: none"><li>• Is heterogeneous</li></ul>	<ul style="list-style-type: none"><li>• Is homogenous</li></ul>

**QN:** Mention three tests that can be carried out on a eutectic mixture to show that it is not a pure compound.

- ✓ Microscopy shows a heterogeneous mixture of separate distinct crystals that make up the mixture.
- ✓ X-ray diffraction pattern does not conform to a pure compound.
- ✓ Melting point and composition of eutectic mixture change with pressure.
- ✓ Composition of eutectic does not correspond to any known compound e.g Calcium-magnesium system.

## APPLICATION OF EUTECTICS.

Used in ;

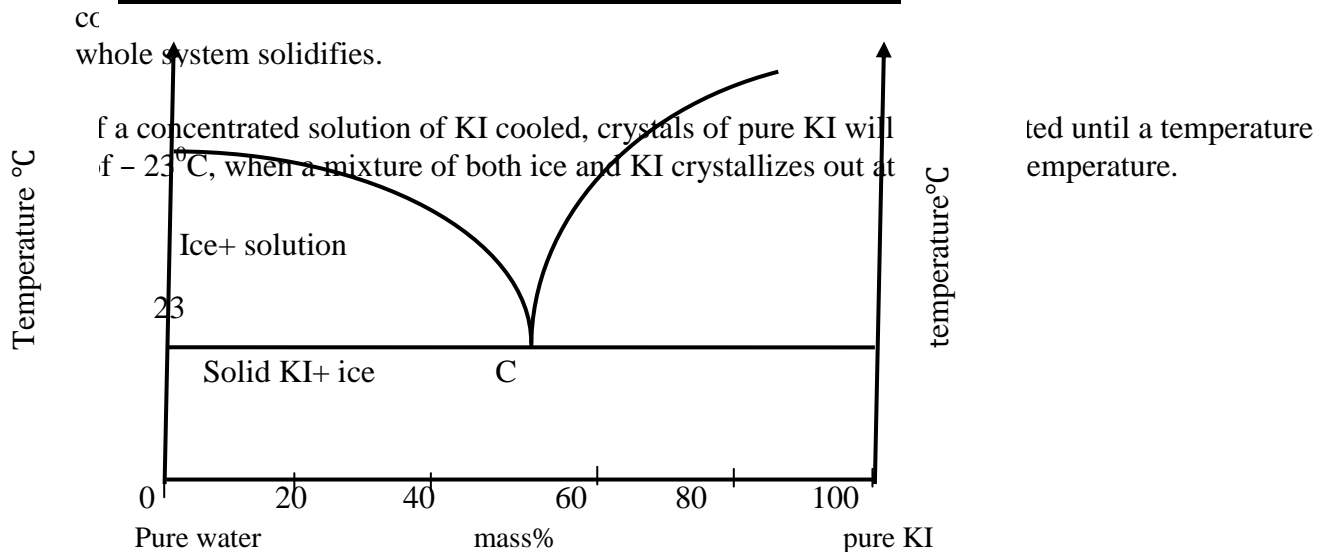
- ✓ formation of alloys e.g. solder which is used for joining other metals at temperatures which are not so high to melt the pure metal.
- ✓ Industries where it is desirable to lower the melting point of a substance e.g.
  - (i).Extraction of Aluminium from the bauxite ( $\text{Al}_2\text{O}_3$ ), cryolite is added to lower the melting point.
  - (ii)Extraction of Sodium, Calcium chloride is added to Sodium chloride to lower its melting point from  $800^\circ\text{C}$  to  $600^\circ\text{C}$ .
- ✓ Used as safety appliances such as plugs.

## SALT-WATER SYSTEM

- If a dilute solution of KI is cooled below  $0^\circ\text{C}$ , pure ice will form when the freezing point of the solution is reached. Its freezing point will be less than  $0^\circ\text{C}$ , because the added KI lowers the freezing point of water.

- As ice is formed, the solution becomes more concentrated so that its freezing point becomes lower still with more ice deposited.

• A **Temperature composition diagram for KI - water system**



**POINT**

**A:** Melting point of ice / freezing point of water

**C** Eutectic point

- Corresponds to lowest temperature which must be reached before the whole system solidifies.
- Three phases are in equilibrium, ice, KI and solution and there is no compound formation.
- Crystals deposited from the solution have the same composition as the solution mixture, and is called eutectic mixture or the **cryohydric mixture**

**CURVES:**

**AC**

- Describes the way the freezing point of water is lowered by addition of KI.

**BC**

- Solubility curve of KI in water
- Steep rise shows that solubility of KI increases slowly with increase in temperature.

**Questions:**

- Define the term eutectic mixture
- The table shows the melting points of various mixtures of Lead and Tin.

% Tin	0	20	40	70	80	100
Melting point ( $^{\circ}\text{C}$ )	327	280	234	193	206	232

- Draw a fully labeled diagram for a Tin and Lead system
- Determine the eutectic temperature and the composition of the eutectic mixture

- c) Describe changes that could take place when a liquid mixture of the above system containing 40% Tin is cooled from 400<sup>0</sup>C to 100<sup>0</sup>C.
- d) (i) State one application of Tin- Lead eutectic mixture  
(ii) Name one other pair of metals which can give a similar phase diagram as in b (i)  
(iii) State one similarity between a eutectic mixture and a pure metal.

### THERMOCHEMISTRY/THERMODYNAMICS.

Thermochemistry is the study of energy changes accompanying chemical reactions.

During chemical reactions, energy is absorbed to break the bonds between atoms and energy is given out when new bonds are formed.

Thermochemistry investigates the position of equilibrium in the reaction, feasibility of the reaction and how far the reaction can go.

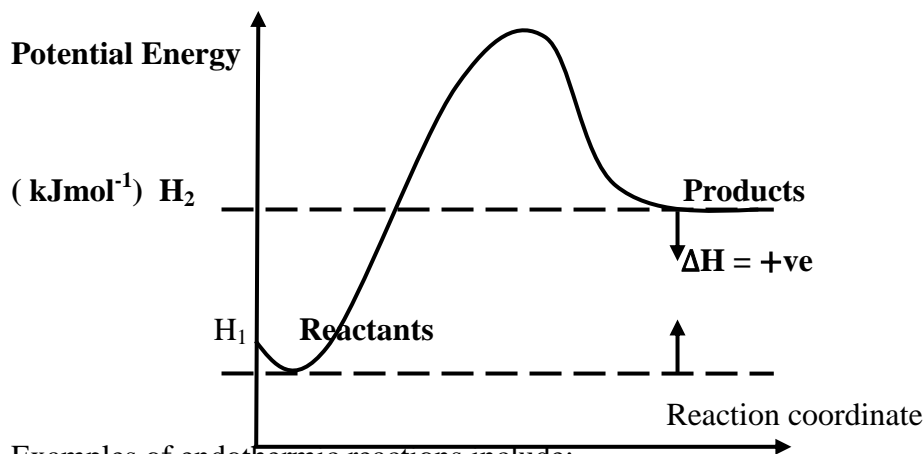
### TYPES OF CHEMICAL REACTIONS

Chemical reactions are grouped according to whether heat is gained/ lost during the reaction.

#### iii. Endothermic reactions

- Are reactions which proceed with absorption of heat from the surrounding.
- It is denoted with a positive enthalpy change
- Products are at a higher energy level than the reactants

#### Energy level diagram for endothermic reactions

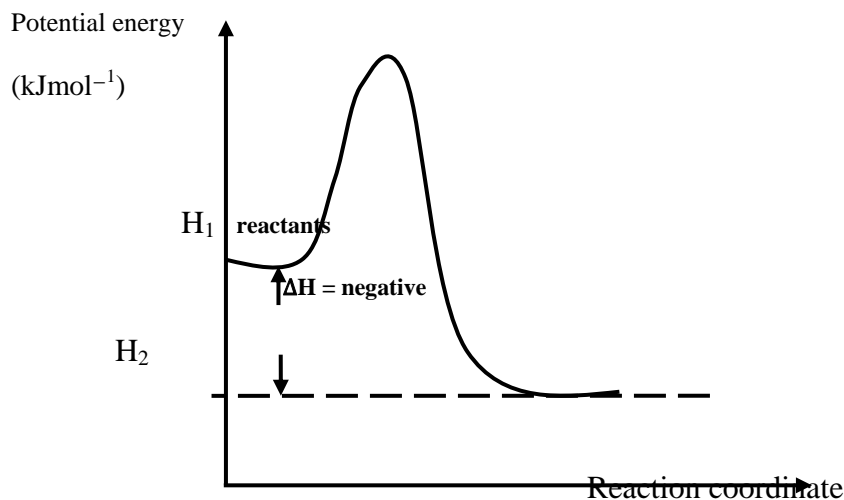


- Photosynthesis
- Dissolution of Ammonium nitrate in water
- Change of state e.g. vaporization and melting

#### iv. Exothermic reactions

- Are reactions which proceed with evolution of heat to the surrounding
- Denoted with a negative enthalpy change
- Products are at a lower energy level than the reactants

#### Energy level diagram for an exothermic reaction



#### Examples include

- Dissolution of Sulphuric Acid in water
- Combustion
- Change of state eg freezing and condensation
- Thermit reaction i.e. reduction of Fe<sub>2</sub>O<sub>3</sub> by aluminium

### ENTHALPY (H)

Is the energy or heat content of a substance

#### Enthalpy change (ΔH)

Is the quantity of heat absorbed at constant pressure.

Enthalpy change = Enthalpy of products – enthalpy of reactant

$$\Delta H = H_2 - H_1$$

Where H<sub>2</sub> = enthalpy of products

H<sub>1</sub> = enthalpy of reactants

### STANDARD ENTHALPY CHANGE (ΔH<sup>θ</sup>)

Is the heat change when molar quantities of reactants in their standard states react to give products.

NB: Standard state of the substance is the pure substance in the specified state (solid, liquid or gas) at 1 atmosphere and 298K.

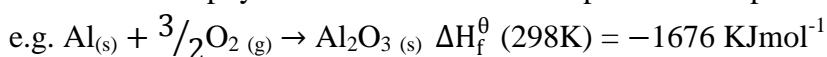
The values of enthalpy change depend on;

- v. Temperature at which reaction is taking place
- vi. Pressure of the gaseous reactants and products
- vii. Physical state of reactants (solid, liquid or gas)
- viii. Amount of reactants and products

### TYPES OF ENTHALPY CHANGES

#### c) Standard enthalpy change of formation ( $\Delta H_f^\theta$ )

Is the enthalpy change that occurs when one mole of a substance is formed from its elements in their normal physical state at standard temperature and pressure (stp)



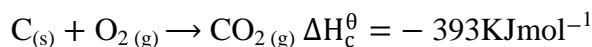
Enthalpy of formation of substances are always negative and cannot be measured experimentally but are determined indirectly using the Born Haber cycle.

Standard enthalpy of formation of elements at standard conditions are equal to zero.

Standard enthalpy of formation is related to the stability of substances i.e. the more negative the value of standard enthalpy change of formation, the more stable the compound will be and the positive value of  $\Delta H_f^\theta$  indicates that the compound is likely to be thermally unstable or may not form at all.

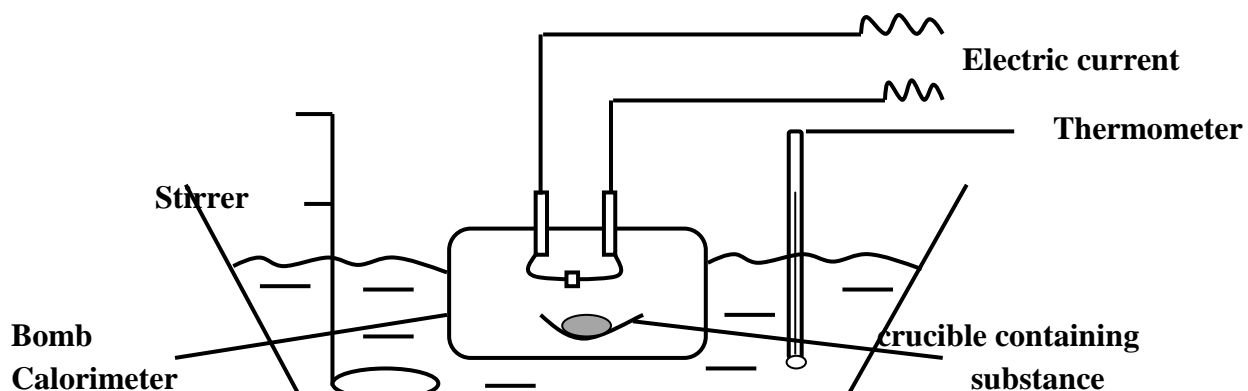
#### d) Standard enthalpy change of combustion ( $\Delta H_c^\theta$ )

Is the enthalpy change that occurs when one mole of a substance is completely burnt in  $\text{O}_2$  under standard conditions of temperature and pressure (STP) e.g. heat of combustion of Carbon.



### Experiment: To determine enthalpy of combustion of a substance

#### Setup:



## Water

### Procedure:

- A known mass of substance is placed in a crucible suspended in a bomb calorimeter.
- The bomb calorimeter is then filled with O<sub>2</sub> at a pressure of 25 atmospheres and increased in a calorimeter fitted with thermometer and stirrer containing a fixed volume of water.
- The initial temperature of the water is noted. T<sub>1</sub><sup>0</sup>C and then the substance is heated by passing electric current through the platinum wire in contact with it.
- Substance burns and the heat generated raises the temperature of H<sub>2</sub>O.
- Maximum temperature T<sub>2</sub><sup>0</sup>C of water is then noted.

### Results:

- Let **m** be the mass of water in grams  
**w** be mass of substance in grams  
**M<sub>r</sub>** be the RMM of substance  
Temperature rise (T<sub>2</sub><sup>0</sup>C – T<sub>1</sub><sup>0</sup>C) = ΔT  
C the specific heat capacity of water  
P heat produced by heater

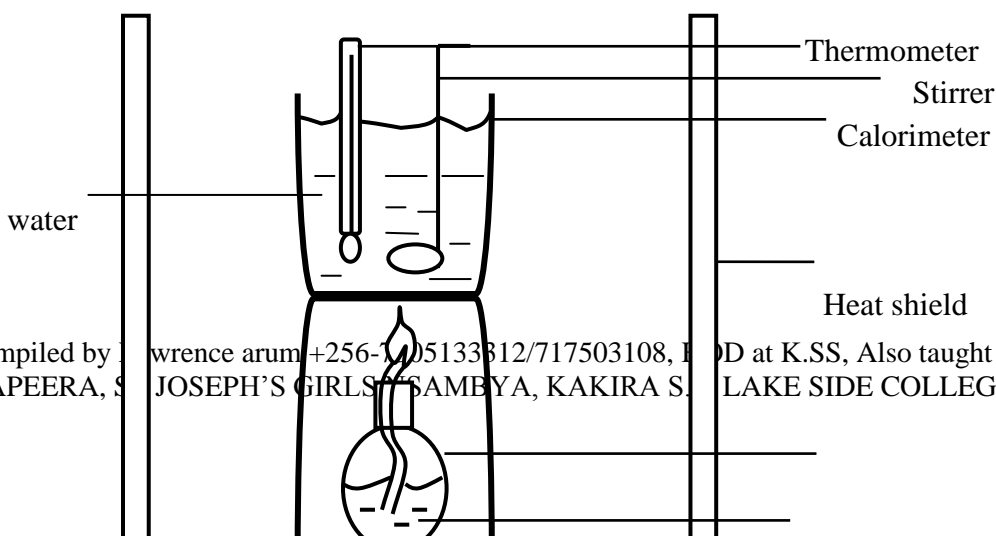
### Treatment of results:

#### Assumption:

- Neglecting the heat gained by the calorimeter, then heat evolved by burning the substance and heat produced by the heater is equal to the heat gained by water.  
Heat evolved by substance and heater = heat absorbed by water  
Heat absorbed by water = mcΔT J  
Heat evolved by substance = (mcΔT – P)  
Wg of substance evolves (mcΔT – P) J  
M<sub>r</sub> will evolve  $\frac{(mc\Delta T - P)}{w} \times M_r$

### Expt: To determine enthalpy of combustion of ethanol

#### Setup:



Burner

-

Ethanol

### Procedure:

- A known amount of cold water is weighed into a calorimeter.
- The initial temperature of the cold water is determined,  $T_0^{\circ}\text{C}$
- Some ethanol is added to a burner and the mass of the burner plus the ethanol before burning is determined,  $w_0\text{g}$ .
- The wick is lit and the flame kept steady under water.
- The water is constantly stirred until a reasonable rise in temperature is noted.
- The flame is extinguished and the highest temperature  $T_1^{\circ}\text{C}$  is determined.

### Results

- Mass of water =  $m\text{g}$
- Initial temperature of water =  $T_0^{\circ}\text{C}$
- Final temp. of water =  $T_1^{\circ}\text{C}$
- Mass of burner + ethanol before burning =  $w_0\text{g}$
- Mass of burner + ethanol after burning =  $w_1\text{g}$
- SHC of water =  $C\text{ Jg}^{-1}\text{C}^{-1}$

### Treatment of results:

Assumption:

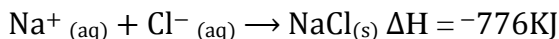
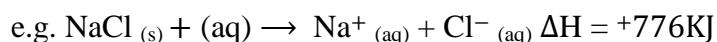
- Neglecting heat gained by calorimeter; heat evolved by burning ethanol is equal to heat absorbed by water.
  - Temperature rise,  $\Delta T = (T_1 - T_0)^{\circ}\text{C}$
  - Mass of ethanol burnt =  $(w_0 - w_1)\text{g}$
  - Heat evolved = heat absorbed by water
  - RMM of ethanol = 46
- If  $(w_0 - w_1)$  g of ethanol evolves  $mc\Delta T$  J
- $$\therefore 46\text{g will evolve } - \frac{mc\Delta T \times 46}{(w_0 - w_1)\text{g}}$$
- $$\therefore \text{Heat of combustion} = - \left[ \frac{mc\Delta T \times 46}{(w_0 - w_1)} \right] \text{ J}$$

## LAWS OF THERMOCHEMISTRY

There are 2 laws of thermochemistry both of which are based on the principle of conservation of energy.

### i. 1<sup>st</sup> Law:

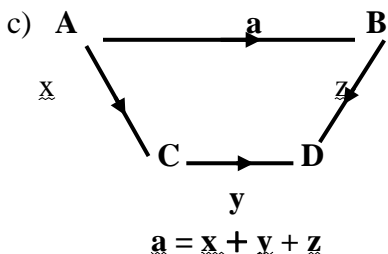
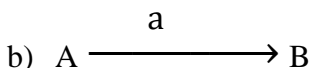
States that, “the amount of heat energy required to decompose a compound into its elements is equal in magnitude but opposite in sign to the amount of heat energy given out when the compound is formed.”



### ii. 2<sup>nd</sup> Law (Hess's law of heat summation)

States that, “enthalpy change of a chemical reaction at constant temperature and pressure is the same irrespective of the number of stages passed but will depend on the initial and final stages of the reaction.

Consider conversion of A to B.



### Applications of Hess's law

- Used to determine heats of reaction which can not be determined experimentally from given thermochemical data e.g. determining the enthalpy of formation of a compound by using enthalpy of combustion of elements that make up a compound.

When carrying out calculations involving Hess's law;

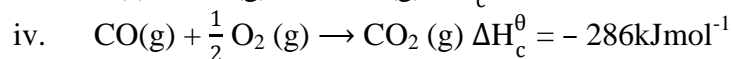
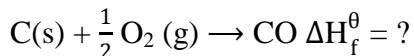
- All enthalpy changes must have correct signs.
- Reversing the reaction also changes the sign of the enthalpy change
- Multiplying or dividing an equation by certain number also multiplies/ divides the enthalpy change by the same number.

- States of the reactants and products must always be specified.

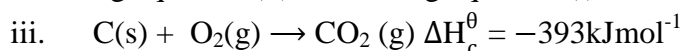
**Examples:**

3. Calculate the enthalpy change of formation of Carbon monoxide given that the enthalpy of combustion of carbon is  $-393\text{kJmol}^{-1}$ , and the enthalpy of combustion of carbon monoxide is  $-286\text{kJmol}^{-1}$

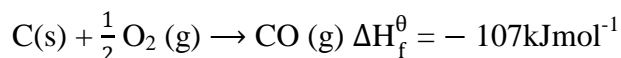
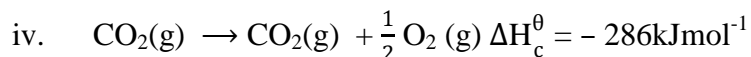
**Solution:**



Reversing equation (ii) and adding equation (i)



+



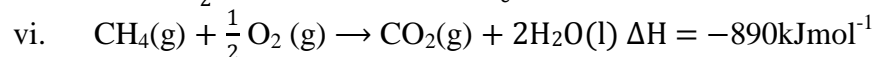
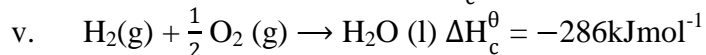
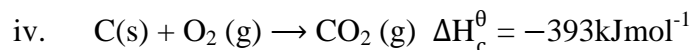
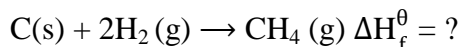
4. Calculate the enthalpy change of formation of methane from the following thermochemical data.

Enthalpy of combustion of Carbon =  $-393\text{kJmol}^{-1}$

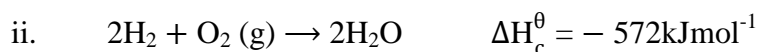
Enthalpy of combustion of hydrogen =  $-286\text{kJmol}^{-1}$

Enthalpy of combustion of methane =  $-890\text{kJmol}^{-1}$

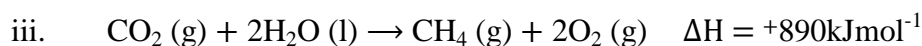
**Solution:**

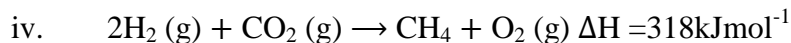


Multiplying equation (ii) by 2 and reversing (iii) we obtain

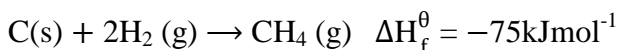


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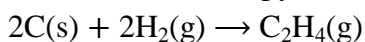


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**Activity:**

3. Calculate the enthalpy of reaction;



Given that enthalpy of combustion of carbon =  $-393\text{kJmol}^{-1}$

Enthalpy of combustion of hydrogen =  $-286\text{kJmol}^{-1}$

Enthalpy of combustion of ethane =  $-1393\text{kJmol}^{-1}$

4. Calculate the heat of formation of ethanol given that the heat of combustion of liquid ethanol is  $-649.15\text{kJmol}^{-1}$  while the enthalpy of formation of  $\text{CO}_2$  gas and water are  $-186.7\text{kJmol}^{-1}$  and  $-135.1\text{kJmol}^{-1}$  respectively.
5. Calculate the heat change of the reaction  $\text{C}_2\text{H}_2 + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{CHO}$  from the following data.  
 Molar heat of combustion of  $\text{C}_2\text{H}_2 = -1260\text{kJmol}^{-1}$   
 Molar heat combustion of  $\text{CH}_3\text{CHO} = -1160\text{kJmol}^{-1}$
6. Calculate the enthalpy of combustion of Benzene given that the enthalpy of combustion of Carbon is  $-393\text{kJmol}^{-1}$ , enthalpy of formation of Benzene is  $+49\text{kJmol}^{-1}$ , and enthalpy of formation of water is  $-285\text{kJmol}^{-1}$ .

**CALCULATION OF ENTHALPY OF REACTION FROM:**

- c) **Enthalpy of formation:**

Enthalpy of a reaction is the difference between the total enthalpy of formation of products and the total enthalpies of formation of reactants.

Consider the reaction;

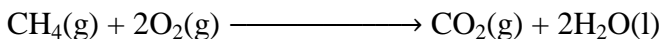


$\Delta\text{H}_R = [\text{Total enthalpy of formation of products}] - [\text{total enthalpy of formation of reactants}]$

$\Rightarrow \Delta\text{H}_R = [c\Delta\text{H}_f^\theta(\text{C}) + d\Delta\text{H}_f^\theta(\text{D})] - [a\Delta\text{H}_f^\theta(\text{A}) + b\Delta\text{H}_f^\theta(\text{B})]$

**Example:**

2. The chemical equation for the combustion of methane is



Calculate the standard enthalpy change of combustion of methane using the values of standard enthalpy change for methane, CO<sub>2</sub> and water.

$$\Delta H_f^\theta(\text{CH}_4) = -74.4 \text{ kJmol}^{-1}$$

$$\Delta H_f^\theta(\text{CO}_2) = -393.5 \text{ kJmol}^{-1}$$

$$\Delta H_f^\theta(\text{H}_2\text{O}) = -285.8 \text{ kJmol}^{-1}$$

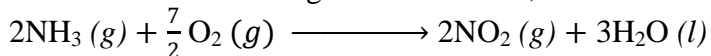
$$\Delta H_c^\theta = [\text{Total enthalpy of formation of products}] - [\text{total enthalpy of formation of reactants}]$$

$$\Delta H_c^\theta = [\Delta H_f^\theta(\text{CO}_2) + 2 \Delta H_f^\theta(\text{H}_2\text{O})] - [\Delta H_f^\theta(\text{CH}_4) + 2\Delta H_f^\theta(\text{O}_2)]$$

$$= [-393.5 + (2 \times -285.8)] - [-74.4 + 2 \times 0]$$

$$\Delta H_c^\theta = \underline{\underline{-890.7 \text{ kJmol}^{-1}}}$$

3. Calculate the heat change in the reaction;



Given the following standard heats of formation in kJmol<sup>-1</sup>

$$\text{NH}_3(\text{g}) \longrightarrow -46.1 \text{ kJmol}^{-1}$$

$$\text{H}_2\text{O}(\text{l}) \longrightarrow -285.8 \text{ kJmol}^{-1}$$

$$\text{NO}_2(\text{g}) \longrightarrow 33.2 \text{ kJmol}^{-1}$$

#### d) BOND ENTHALPY (BOND ENERGY)

- Bond enthalpy is the standard enthalpy change that occurs when one mole of a covalent bond is formed from its constituent gaseous atoms.
  - Therefore it is referred to as the **bond energy of formation** and it is denoted by a negative value of enthalpy.
  - It can also be defined as the heat change that occurs when one mole of a covalent bond is broken down into its constituent gaseous atoms
  - Therefore it is referred to as the bond dissociation energy and denoted by positive value of enthalpy e.g.
- $$\text{H}_2(\text{g}) \longrightarrow 2\text{H}(\text{g}) \quad \Delta H = +431 \text{ kJmol}^{-1}$$
- $$2\text{H}_2(\text{g}) \longrightarrow \text{H}_2(\text{g}) \quad \Delta H = -431 \text{ kJmol}^{-1}$$
- The standard enthalpy of a reaction is the difference between the sum of average standard bond enthalpies of products and sum of the average standard bond enthalpies of reactants.

$\Delta H^\theta_{\text{reaction}} = \text{summation of bond energies} - \text{summation of bond energies of bonds formed}$

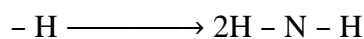
$$\Delta H^\theta_{\text{R}} = \sum \text{Bonds broken} - \sum \text{bonds formed}$$

Example:

3. Calculate the enthalpy change for the following reaction;  $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \longrightarrow 2\text{NH}_3(\text{g})$

Bond	Mean of bond enthalpy
$\text{N} \equiv \text{N}$	945
$\text{H} - \text{H}$	436
$\text{N} - \text{H}$	391

**Solution:**  
 $\text{N} \equiv \text{N} + 3\text{H}$



H

Bonds broken =  $\text{N} \equiv \text{N}$ ,  $\text{H} - \text{H}$

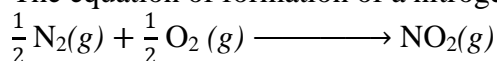
Bonds formed =  $\text{N} - \text{H}$

$$\Delta H_{\text{R}} = \sum \text{Bonds broken} - \sum \text{bonds formed}$$

$$= [945 + (3 \times 436)] - [6 \times 391]$$

$$\Delta H_{\text{R}} = \underline{\underline{-93\text{kJmol}^{-1}}}$$

4. The equation of formation of a nitrogenmonoxide gas.



Calculate the enthalpy change of formation of nitrogenmonoxide using the given bond energies.

Bond	Mean of bond enthalpy
$\text{N} \equiv \text{N}$	$946\text{kJmol}^{-1}$
$\text{H} - \text{H}$	$496\text{kJmol}^{-1}$
$\text{N} - \text{H}$	$630\text{kJmol}^{-1}$

### ENTHALPY OF ATOMISATION AND AVERAGE BOND ENTHALPY

#### c) Enthalpy of Atomisation

- Also called enthalpy of sublimation/ vapourisation

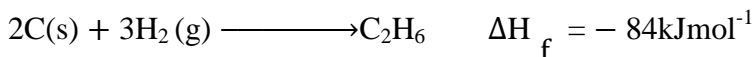
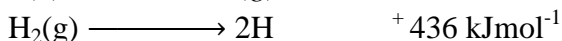
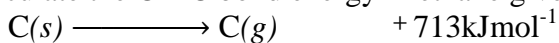
- Is the enthalpy changes that occurs when one mole of gaseous atoms is formed from the elements in its normal physical state at standard conditions.
- Enthalpy change is always positive. E.g.  
 $\text{Na}(s) \longrightarrow \text{Na}(g)$   
 $\frac{1}{2} \text{Cl}_2(g) \longrightarrow \text{Cl}(g)$   
 $\text{C}(s) \longrightarrow \text{C}(g)$
- For a compound the standard enthalpy of atomization is the heat required to convert 1 mole of a compound in its natural state and under standard conditions into free gaseous atoms.
- For any di-atomic molecule, enthalpy of atomization is half the bond energy.

d) **Average bond enthalpy/bond energy term**

- Is the average value of the standard enthalpy changes required to break a particular covalent bond in a full range of molecules in which that bond may be found.
- Calculations based on average standard bond enthalpies give approximate results since true standard bond enthalpies vary from compound to compound.

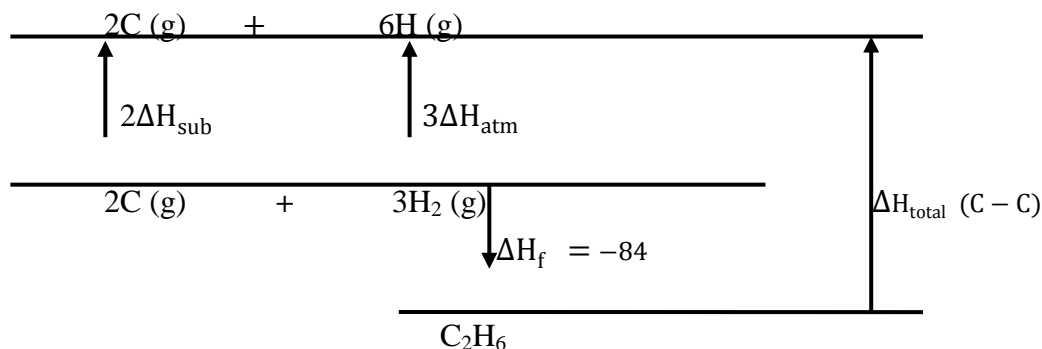
**Examples:**

4. Calculate the C – C bond energy in ethane given that



**Solution**

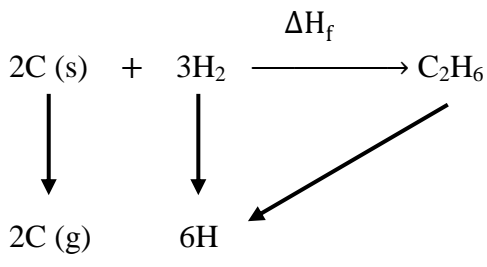
Using the energy level diagram.



From Hess' law of constant heat summation

$$\begin{aligned} \text{Total } \Delta H (\text{C} - \text{C}) &= - (\Delta H_f) + 2\Delta H_{\text{sub}} + 3\Delta H_{\text{atm}} \\ &= - (- 84) + (2 \times 713) + (3 \times 436) \\ &= \underline{\underline{2818 \text{kJmol}^{-1}}} \end{aligned}$$

**OR:**



$$\Delta H_f = 2 \times \Delta H_a(\text{C}) + 3\Delta H_a(\text{H}) - \Delta H_f(\text{C}-\text{C})$$

$$\begin{aligned}
 \Delta H_f(\text{C}-\text{C}) &= 2 \times \Delta H_a(\text{C}) + 3\Delta H_a(\text{H}) - \Delta H_f \\
 &= (2 \times 713) + (3 \times 436) - (-84) \\
 &= \underline{\underline{2818\text{kJmol}^{-1}}}
 \end{aligned}$$

**Example (UNEB 2006 No 9)**

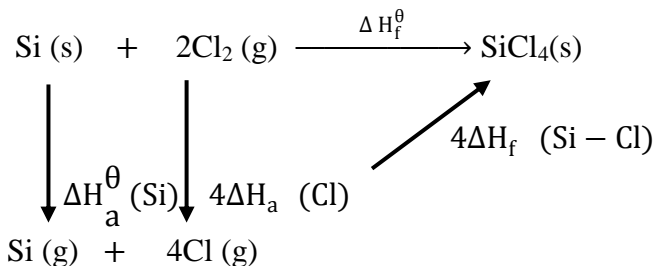
5. (a) The standard enthalpy change of formation of  $\text{SiCl}_4$  is  $-610\text{kJmol}^{-1}$ . The standard enthalpy change of atomization of Si and Cl are  $+338$  and  $+122\text{kJmol}^{-1}$  respectively. Use these values to construct a Born Harber cycle for formation of  $\text{SiCl}_4$  from its elements and indicate the energy changes involved.  
 (b) Calculate the average bond energy of the Si-Cl bond

**Solution**

c)  $\Delta H_f^\theta(\text{SiCl}_4) = -610\text{kJmol}^{-1}$

$$\Delta H_a^\theta(\text{Si}) = +338\text{kJmol}^{-1}$$

$$\Delta H_a^\theta(\text{Cl}_2) = +122\text{kJmol}^{-1}$$



d) From Hess' law of heat summation;

$$\Delta H_f^\theta = \Delta H_a^\theta(\text{Si}) + 4\text{Ha}(\text{Cl}) - 4\Delta H_f(\text{Si}-\text{Cl})$$

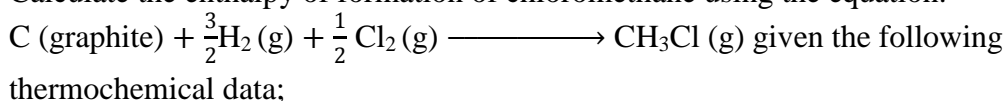
$$\Delta H_f^\theta = +338 + (4 \times 122) - (4\Delta H_f(\text{Si}-\text{Cl}))$$

$$- 610 = 826 - 4\Delta H_f (\text{Si} - \text{Cl})$$

$$4\Delta H_f (\text{Si} - \text{Cl}) = - 1436$$

$$\underline{\Delta H_f (\text{Si} - \text{Cl}) = 359\text{kJmol}^{-1}}$$

6. Calculate the enthalpy of formation of chloromethane using the equation.



$$\text{Bond energy of C} - \text{Cl} = 336\text{kJmol}^{-1}$$

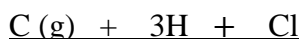
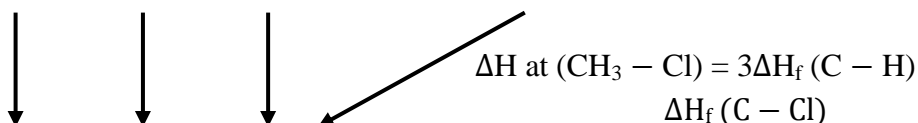
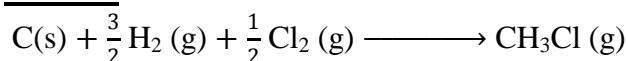
$$\text{Dissociation energy of H} - \text{H} = 433\text{kJmol}^{-1}$$

$$\text{Dissociation energy of Cl} - \text{Cl} = 248\text{kJmol}^{-1}$$

$$\text{Bond energy of C} - \text{H} = 413\text{kJmol}^{-1}$$

$$\text{Enthalpy of vapourisation of graphite} = 715\text{kJmol}^{-1}$$

**Solution**



From Hess' law of heat summation

$$\begin{aligned} \Delta H_f &= \frac{3}{2}\text{B}\Delta\text{E} (\text{H}) + \frac{1}{2}\text{B}\Delta\text{E} (\text{Cl}) - 3\Delta H_f (\text{C} - \text{H}) + \Delta H_f (\text{C} - \text{Cl}) \\ &= \left[ 715 + \left(\frac{3}{2} \times 435\right) + \left(\frac{1}{2} \times 248\right) \right] - (3 \times 413 + 336) \\ &= 1491.5 - 1575 \\ &= \underline{\underline{- 83.5\text{kJmol}^{-1}}} \end{aligned}$$

7. Calculate the average (C– H) Bond energy from the following enthalpies of reaction

$$\text{Enthalpy of formation of CO}_2 = - 393\text{kJmol}^{-1}$$

$$\text{Enthalpy of formation of H}_2\text{O} = - 286\text{kJmol}^{-1}$$

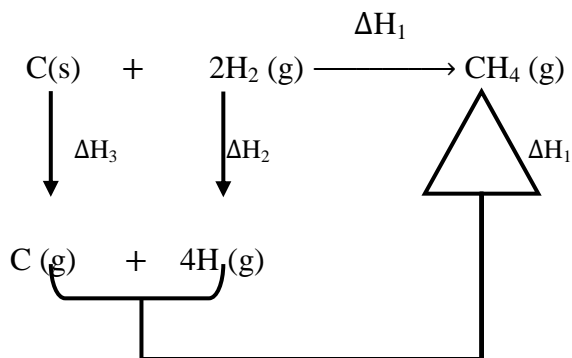
$$\text{Enthalpy of formation of CH}_4 = - 890\text{kJmol}^{-1}$$

$$\text{Enthalpy of Atomisation of C}_2 = 714\text{kJmol}^{-1}$$

$$\text{Enthalpy of Atomisation of H}_2 = 436\text{kJmol}^{-1}$$

**EXERCISE**

1. (a) What is meant by Bond energy?
- (b) The figure below shows/ represents the energy diagram for formation of CH<sub>4</sub>



Identify the energy changes  $\Delta H_1$ ,  $\Delta H_2$ ,  $\Delta H_3$  and  $\Delta H_4$  given that;

(c)  $\Delta H_1 = -75\text{kJmol}^{-1}$ ,  $\Delta H_2 = +218\text{kJmol}^{-1}$  of  $\text{H}_2$  atom,  $\Delta H_3 = +715\text{kJmol}^{-1}$

Calculate the value of:

- iii.  $\Delta H_4$
- iv. Bond energy of C - H bond
2. Calculate the standard enthalpy of formation of  $\text{C}_2\text{H}_4$  in  $\text{kJmol}^{-1}$  from the following
  - C = C Bond energy =  $606\text{kJmol}^{-1}$
  - C - H bond energy =  $410\text{kJmol}^{-1}$
  - H - H Bond energy =  $435\text{kJmol}^{-1}$
  - Heat of sublimation of Carbon =  $710\text{kJmol}^{-1}$

## BORN - HABER CYCLE

- Is the enthalpy cycle used to calculate the standard enthalpy changes which occur when an ionic compound is formed from its elements.
  - It is an application of Hess' law to ionic compounds.
- Enthalpy changes involved in Born Haber cycle include

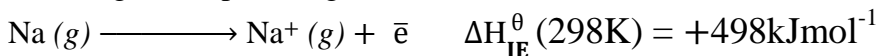
vi. Standard enthalpy of Sublimation/ Vaporisation ( $\Delta H_s^\theta / \Delta H_{\text{vap}}^\theta$ )

vii. Standard enthalpy of atomization ( $\Delta H_{\text{at}}^\theta$ ):

Is the enthalpy change when one mole of gaseous atoms is formed from an element in standard state.

viii. Standard enthalpy of ionization ( $\Delta H_{\text{IE}}^\theta$ )

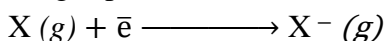
Is the enthalpy change accompanying the removal of one mole of electrons from an atom in gaseous phase e.g. for Sodium;



- When an electron is removed from a singly positively charged ion in the gaseous phase, enthalpy change is described as 2<sup>nd</sup> ionization enthalpy
- i.e.  $\text{Na}^+ \longrightarrow \text{Na}^{2+} + 2\bar{e}$

**ix. electron affinity/Electron gain enthalpy**

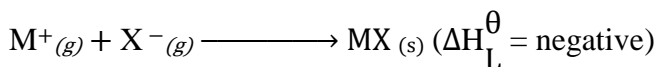
Is the standard enthalpy change accompanying the addition of one electron to an atom in the gas phase. i.e.



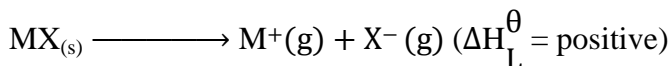
NB: The first electron affinity is **negative** while the 2<sup>nd</sup> electron affinity is **positive** because work must be done to add the 2<sup>nd</sup> electron against repulsive forces exerted by the first electrons.

**x. Standard lattice enthalpy ( $\Delta H_{\text{L}}^{\theta}$ )**

Is the enthalpy change when one mole of an ionic compound is formed from its gaseous under standard conditions i.e.

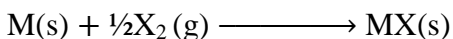


OR: Is the enthalpy absorbed when one mole of an ionic compound is decomposed into its gaseous ions.

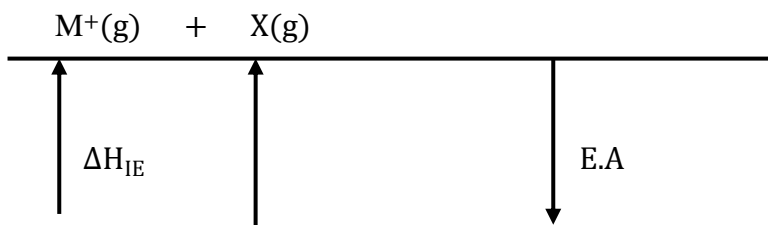


Consider the formation of one mole of MX solid where M is a metal and X is a gas with a diatomic molecule.

**Equation of formation of MX**

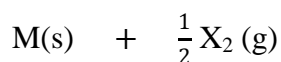


**Born Harber cycle showing energy changes involved:**





$$\Delta H_{sub}$$



$$\Delta H_L$$

$$\Delta H_f$$



From Hess' law

$$\Delta H_f = \Delta H_{sub} + \Delta H_{IE} + \Delta H_{at} + EA + \Delta H_L$$

**Example:**

2. (a) Draw a Born Harber for the formation of solid Rubidium chloride from its elements  
 (b) calculate the electron affinity of chlorine atom. Use the following data;

Lattice energy of Rubidium chloride =  $-665 \text{kJmol}^{-1}$

Dissociation energy of chlorine gas molecule =  $226 \text{kJmol}^{-1}$

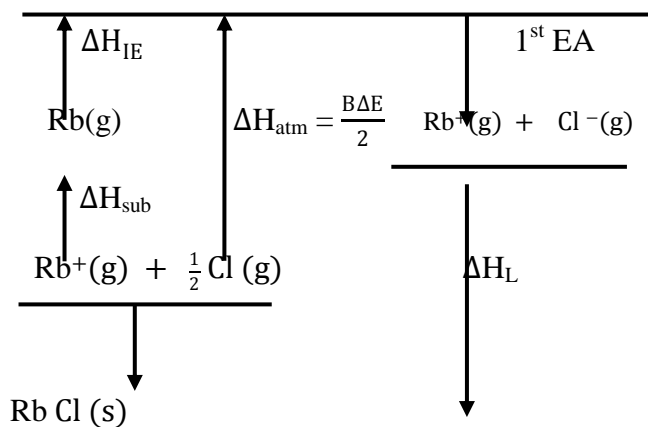
Heat of atomization of Rubidium metal =  $84 \text{kJmol}^{-1}$

Standard heat of formation of solid Rubidium chloride is  $-439 \text{kJmol}^{-1}$

I.E. of Rubidium atom =  $397 \text{kJmol}^{-1}$

**Solution**

2. (a)  $Rb^+(g) + Cl(g)$



- (b) From Hess' law;

$$\Delta H_f = \Delta H_{sub} + \Delta H_{IE} + \Delta H_{at} + E.A + \Delta H_L$$

$$\begin{aligned}
 EA &= \Delta H_f - (\Delta H_{\text{sub}} + \Delta H_{\text{IE}} + \Delta H_{\text{at}} + \Delta H_L) \\
 &= -439 - (84 + 397 + \frac{226}{2} + -665) \\
 &= \underline{\underline{-368 \text{kJmol}^{-1}}}
 \end{aligned}$$

### Activity

4. Draw a Born Haber cycle for the reaction of Lithium(Solid) and F(g) to form LiF(s) and indicate clearly whether the change is exo/endothermic. using the data below;

Enthalpy of atomization of Fluorine molecule = + 150kJmol<sup>-1</sup>

Enthalpy of sublimation of Lithium metal = 155kJmol<sup>-1</sup>

Ionization energy of Lithium atom = 518kJmol<sup>-1</sup>

Standard enthalpy of formation of solid LiF =?

Lattice enthalpy = - 1030 kJmol<sup>-1</sup>

Electron affinity of F = - 351 kJmol<sup>-1</sup>

5. Calculate the lattice energy of CaCl<sub>2</sub> from the following thermochemical data;

Standard enthalpy of atomization of CaCl<sub>2</sub> = - 795kJmol<sup>-1</sup>

Standard enthalpy of atomization of Chlorine = +717kJmol<sup>-1</sup>

First ionization energy of calcium = + 121 kJmol<sup>-1</sup>

2<sup>nd</sup> ionization energy of Calcium = 1100 kJmol<sup>-1</sup>

First electron affinity of Cl = - 364 kJmol<sup>-1</sup>

6. Using the data below construct an energy level diagram and hence calculate the lattice energy of CuO(s)

<u>Enthalpy</u>	<u>kJmol<sup>-1</sup></u>
Atomization of Cu	+339
1 <sup>st</sup> IE of Cu	+745
Atomization of O <sub>2</sub>	+ 248
2 <sup>nd</sup> IE of Cu	+1960
1 <sup>st</sup> EA of O <sub>2</sub>	-141

### FACTORS AFFECTING LATTICE ENERGY

These include:

i. Ionic charge

- The larger the ionic charge, the bigger the lattice energy
- This is because of the strong electrostatic forces of attraction between the oppositely charged ions, e.g. the lattice energy of magnesium chloride is larger than that of Sodium Chloride because the greater charge of Mg<sup>2+</sup> strongly attracts the chloride ions.

ii. **Ionic size/radius:**

- Lattice energy is inversely proportional to the ionic size i.e. large cations have less attraction for anions because of the reduced effective nuclear charge. (Large distance of approach) e.g. NaCl has a bigger lattice energy than KCl because the K<sup>+</sup> has a bigger radius than Na<sup>+</sup>.

Consider the halides of Na and their values of lattice energy.

NaF	-795kJmol <sup>-1</sup>
NaCl	-761kJmol <sup>-1</sup>
NaBr	-742kJmol <sup>-1</sup>
<b>NaI</b>	<b>-699kJmol<sup>-1</sup></b>

**Trend:**

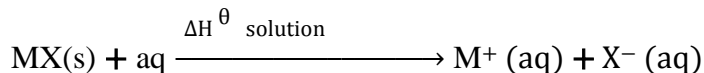
- Lattice energy of the halides decreases down the group

**Explanation:**

- Lattice energy of NaF is the greatest since there is greater attraction of the F<sup>-</sup> to the Na<sup>+</sup>.
- Lattice energy of NaI is the smallest because I<sup>-</sup> has the biggest size and therefore is least attracted by the Sodium Ion (Na<sup>+</sup>)

## **ENTHALPY OF SOLUTION**

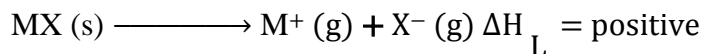
Is the Enthalpy change that occurs when one mole of crystal ionic compound is dissolved in a specified number of moles of water at standard conditions.



The enthalpy change accompanying the dissolution of an ionic salt in water is either positive or negative

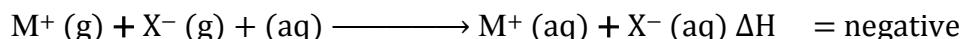
The dissolution of an ionic compound of an ionic compound involves two energy terms;

- iii. Separating the ionic lattice into oppositely charged gaseous ions ie



The energy required is the lattice dissociation and is an endothermic process

- iv. Hydration/ solvation of the oppositely charged gaseous ions and its an exothermic process.ie

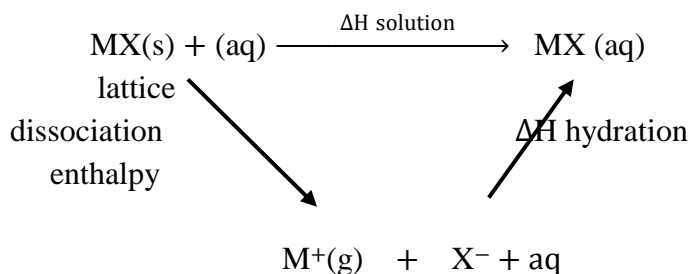


**Definition**

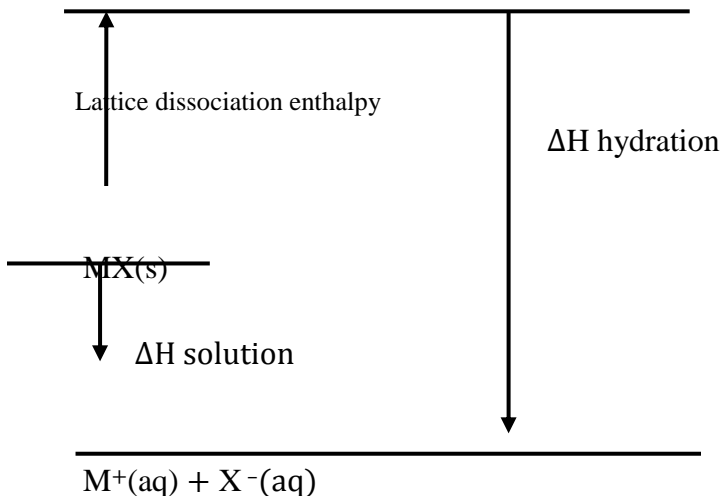
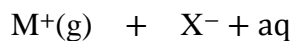
Enthalpy of Hydration/ Solvation is the heat evolved when 1 mole of gaseous ions is completely surrounded by water molecules i.e.



**Born harber cycle showing the relationship between the enthalpy of solution, lattice dissociation energy and hydration energy of salt MX**



**OR**



**Factors affecting enthalpy of solution**

- Lattice energy
- Hydration energy

When the lattice dissociation is greater than the hydration, enthalpy of solution is endothermic, whereas when the hydration energy is greater than lattice dissociation enthalpy, the enthalpy of solution is exothermic.

For an ionic compound to dissolve in water, the lattice dissociation energy should be overcome by the hydration enthalpy so that an overall negative enthalpy of solution is obtained i.e. compounds that dissolved exothermically are more soluble than those which dissolve endothermically.

**Example:**

The enthalpies of hydration and lattice energy of some salts are given below;

Salt	Enthalpy of hydration (kJmol <sup>-1</sup> )	Lattice energy (kJmol <sup>-1</sup> )
KCl	- 692	+ 718
LiCl	- 883	+ 862

- d) Calculate the heats of solution of K and Li Chloride. State whether dissolution is endothermic or exothermic process in each case.
- e) Which of the following two salts will be more soluble in water at a given temperature. Give a reason for your answer.
- f) How would you expect the solubility of these two salts to change with temperature?

**Solution**

$$d) \Delta H_{\text{soln}} = \Delta H_{\text{hydration}} + \Delta H_{\text{lattice energy}}$$

$$\Rightarrow \Delta H_{\text{soln}} (\text{KCl}) = - 692 + 718$$

$$= + 26\text{kJmol}^{-1}$$

$$\Delta H_{\text{soln}} (\text{LiCl}) = - 883 + 862$$

$$= - 21\text{kJmol}^{-1}$$

KCl, dissolution is endothermic because enthalpy of solution is positive

LiCl dissolution is exothermic because enthalpy of solution is negative

- e) LiCl, because enthalpy of solution is negative
- f) kCl, solubility increases with increase in temperature because it requires more energy to dissolve (enthalpy of solution is positive)  
LiCl, solubility decreases with increase in temperature because enthalpy of solution is exothermic.

**UNEB 2003**

2 (a) Define the term molar enthalpy of hydration

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(b) The table below shows the enthalpies of  $\text{Mg}^{2+}$  and  $\text{Cl}^-$

Ions	Enthalpy of hydration ( $\text{kJmol}^{-1}$ )
$\text{Mg}^{2+}$	1891
$\text{Cl}^-$	381

- ii. State whether the values of enthalpies of hydration given in the table above is positive or negative. Give a reason for your answer
- iii. Calculate the enthalpy of hydration of  $\text{MgCl}_2$

**Solution**

- iii. The values of both enthalpies are negative

**Reason**

- Hydration of both ions involves attraction of water molecules releasing a lot of heat energy.
- $\Delta H$  hydration of  $\text{MgCl}_2 = \Delta H$  Hydration of  $\text{Mg}^{2+} + 2\Delta H$  hydration of  $\text{Cl}^-$   
 $= -1891 + (2 \times -381)$   
 $= -2663 \text{kJmol}^{-1}$

**Revision:**

- c) Explain the term molar enthalpy of solution
- d) Draw a diagram to show the energy changes that takes place when a salt  $\text{MX}$  (s) is dissolved in water.

**NB**

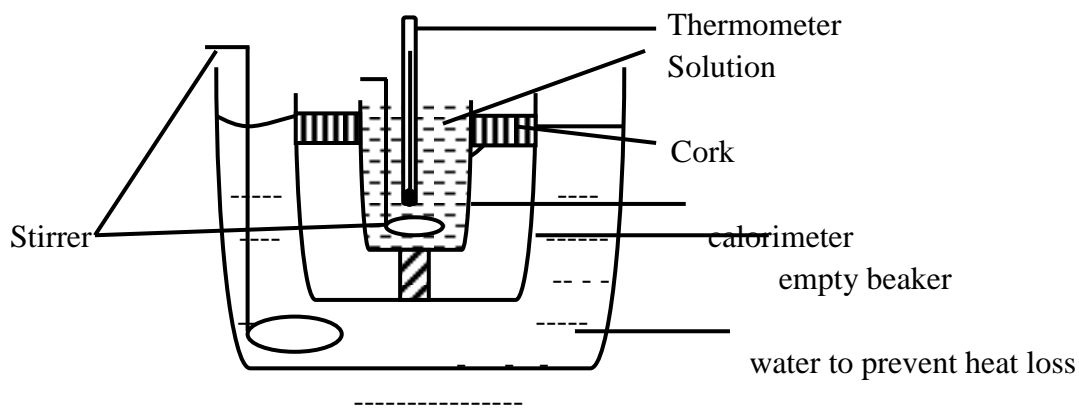
- (ii) Anhydrous salts e.g. Anhydrous  $\text{CuSO}_4$  dissolve more exothermically than the hydrated salts (with water of crystallisation) e.g.  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ .

**Reason:**  $\text{CuSO}_4$  (hydrated) dissolves endothermically because ions are already partially hydrated so that when it dissolves its lattice energy outweighs the enthalpy associated with any further hydration.

- In Anhydrous  $\text{CuSO}_4$ , the ions will have to attract more water molecules and become surrounded by the water molecule. This increases its hydration energy more than the lattice energy, the salt will dissolve with evolution of energy.
- iv. Polar solvents like water dissolve in ionic substances because they have large dipoles interacting strongly with solute ions which results in a high negative enthalpy of solvation,
- Non polar solvents such as hydrocarbons do not dissolve ionic substance because there is no negative enthalpy of solvation to compensate for the positive lattice dissociation enthalpy.

- Qn: a) Predict whether or not KI is likely to be soluble in (cyclohexane)
- b) Explain your answer in (a) above

**EXPT: To determine enthalpy of solution of an ionic compound:**



**Procedure:**

- A known mass,  $m_1$ g of water is placed in a calorimeter fixed with a stirrer and thermometer and the temperature  $T_1$  is noted.
- A known mass  $m_2$ g of finely powdered sample of an ionic compound is carefully added to the water in the calorimeter.
- The solution is stirred thoroughly until the thermometer shows no more heat change.
- Determine and record the final steady temperature of the solution.

**Results:**

Mass of water =  $m_1$ g

Mass of solute =  $m_2$ g

Initial temperature of water =  $T_1$ °C

Final temperature of solution =  $T_2$ °C

$\Delta$ Temperature =  $\Delta T$  ( $T_1 - T_2$ ) or ( $T_2 - T_1$ )

RFM of compound =  $M_r$

SHC of solution =  $C$

Mass of solution =  $(m_1 + m_2)$  g

**Treatment of results:**

**Assumption:**

- Calorimeter has negligible heat loss
- Density of water =  $1\text{gcm}^{-3}$   
Heat evolved = mass of solution  $\times$  SHC  $\times \Delta T$   
 $= (m_1 + m_2) \times C \times \Delta T$

Moles of ionic compound =  $\left(\frac{m_2}{M_r}\right)$  moles

$$\therefore \frac{m_2}{M_r} \text{ evolved } (m_1 + m_2) \times C \times \Delta T$$

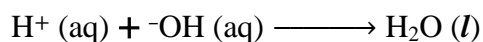
$$1 \text{ mole of solution} = \frac{(m_1 + m_2) \times C \times \Delta T \times M_r}{m_2}$$

$$\Delta H_{\text{solution}} = \frac{(m_1 + m_2) \times C \times \Delta T \times M_r}{m_2}$$

QN: P2 (2006(4))

### **STANDARD ENTHALPY OF NEUTRALISATION**

Is the enthalpy change when one mole of  $H^+$  reacts completely with one mole of  $OH^-$  to form one mole of water. i.e.



NB: The enthalpies of neutralization of strong acids and strong bases are usually constant and high because the strong acids and strong bases are fully ionized giving many free hydrogen ions and hydroxyl ions which then react readily to release a lot of heat.

However, enthalpies of neutralization of weak acids and weak bases or strong base and vice versa are usually low and inconsistent because in the neutralization of weak acids or base, some energy is used first in the ionization and later for neutralization.

### **EXPT: To determine enthalpy of neutralization (HCL and NaOH)**

#### **Procedure:**

- A known volume  $V \text{ cm}^3$  of 2M HCl is measured and placed into a plastic cup, its initial temperature  $T_1$  is noted.
- An equal volume of 2M NaOH is placed into another plastic cup and its initial temperature  $T_2$  is noted.
- NaOH is then carefully added to the cup containing the acid with constant stirring.
- Highest temperature  $T_3$  attained is noted.

#### **Results:**

- Initial temperature of 2M HCl =  $T_1$  °C
- Initial temperature of 2M NaOH =  $T_2$  °C
- Mean initial temperature of mixture =  $\left(\frac{T_1 + T_2}{2}\right)$  °C
- Final temperature of mixture =  $T_3$  °C

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- Volume of solution(mixture) =  $2V\text{cm}^3$
- Total mass of mixture =  $2V\text{g}$ , assuming density of solution is  $1\text{gcm}^{-3}$

### Treatment of results

Heat change = mass of solution  $\times C \cdot \Delta T$

Heat change =  $(2V \times C \times \Delta T)$  J

Equation:  $\text{NaOH (aq)} + \text{HCl (aq)} \longrightarrow \text{NaCl (aq)} + \text{H}_2\text{O (l)}$

$1000\text{cm}^3$  of solution contain 2 moles of HCl

$V\text{cm}^3$  of solution contains  $\left(\frac{2V}{1000}\right)$  moles

Mole ratio 1 HCl : 1  $\text{H}_2\text{O}$

Moles of water formed  $\left(\frac{2V}{1000}\right)$  moles

$\left(\frac{2V}{1000}\right)$  moles of water involved  $2V \cdot C \cdot \Delta T$

1 mole of water =  $\frac{2V \cdot C \cdot \Delta T \times 1000}{2V}$

$$\boxed{\Delta H \text{ neutralisation} = -(\Delta T \cdot 1000)\text{J}}$$

### Example:

When  $100\text{cm}^3$  of 2M HCl was added to  $100\text{cm}^3$  of 2M NaOH, the temperature rose by  $13^\circ\text{C}$ .

Calculate the enthalpy of neutralization assuming density of Specific heat capacity of the resultant solution are  $1\text{g/cm}^3$  and  $4.2\text{Jg}^{-1}\text{K}^{-1}$  respectively.

### Solution:

Total volume =  $200\text{cm}^3$

Mass of solute =  $200 \times 1$   
=  $200\text{g}$

Heat change = mass of solution  $\times \text{SHC} \times \Delta T$   
=  $200 \times 4.2 \times 13$   
=  $10920\text{J}$

$\text{H}^+ (\text{aq}) + \text{OH}^- \longrightarrow \text{H}_2\text{O (l)}$

$1000\text{cm}^3$  of solution contains 2 moles of HCl

$100\text{cm}^3$  of solution contains  $\left(\frac{2 \times 100}{1000}\right)$  moles of HCl

Mole ratio 1mole of acid: 1 mole of water

$\Rightarrow$  Moles of water formed = 0.2 moles

0.2 moles of water =  $10920$

**$\Delta$  Heat of neutralization =  $- 54600\text{J}$**

### Exercise

2.  $50\text{cm}^3$  of NaOH solution of concentrated 0.4M required  $20\text{cm}^3$  of  $\text{H}_2\text{SO}_4$  of concentration 0.5M for neutralization. A temperature rise of  $3.4^\circ\text{C}$  was realized. If both solutions and

calorimeter were at the same temperature, find the standard enthalpy of neutralization of NaOH with H<sub>2</sub>SO<sub>4</sub> (SHC of calorimeter = 39JK<sup>-1</sup> and 4.2Jg<sup>-1</sup>K<sup>-1</sup>)

### HEAT OF PRECIPITATION

Is the heat change when one mole of ionic compound is precipitated from the solution.

#### Example

3. When 50cm<sup>3</sup> of 1M NaCl solution and 50cm<sup>3</sup> of 1M AgNO<sub>3</sub> SOLUTION are mixed, there is a temperature rise of 7.5<sup>0</sup>C. Calculate the enthalpy of precipitation of AgCl assuming the SHC and density of the resulting solution is 4.2Jg<sup>-1</sup>k<sup>-1</sup> and 1gcm<sup>-3</sup> respectively.

#### Solution

Total volume of solution = 100cm<sup>3</sup>

Mass of solution = 100g

Heat produced = mass of solution × SHC of solution × temperature rise  
= 100 × 4.2 × 7.5  
= 3150J

1000cm<sup>3</sup> of NaCl solution contains 1 mole

50cm<sup>3</sup> of NaCl solution contains  $\left(\frac{1 \times 50}{1000}\right)$  moles

Moles of NaCl = 0.05moles

1 mole of NaCl produces 1 mole of AgCL

0.05moles of NaCl will produce 0.05moles of AgCl

0.05moles of AgCl produced 3150J of heat.

1 mole of AgCl produced  $\left(\frac{3150}{0.05}\right)$ J of heat

Enthalpy of precipitation = - 63000J

#### Exercise

4. a) Define the term heat of precipitation  
b) 25cm<sup>3</sup> of 0.5M AgNO<sub>3</sub> solution was added to 25.0cm<sup>3</sup> of 0.5M NaCl solution in an insulated container. The temperature of the resulting mixture rose by 3<sup>0</sup>C. Assuming the container has a negligible heat capacity and the SHC of the resulting mixture is 4.2 Jg<sup>-1</sup>O<sup>-1</sup>. Calculate the heat of precipitation of AgCl.

## CHEMICAL KINETICS

Chemical kinetics is the study of rates of reaction and factors affecting rates of reaction.

### Rates of reaction

Is the rate of change in concentration of one of the products or reactants.

Rate of reaction decreases as the reaction produced and the reactant is gradually used up.

Consider a reaction  $A \rightarrow B$ ; rate of decrease in concentration of A;

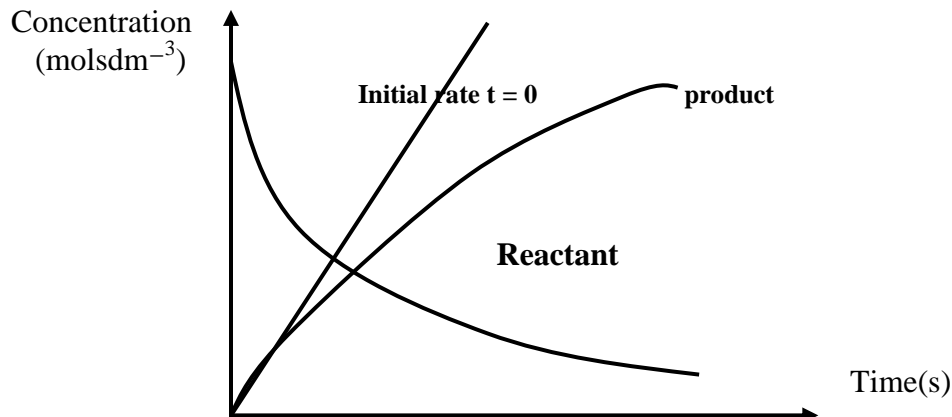
$$\text{Rate of decrease in concentration of A} = -\frac{d(A)}{dt}$$

$$\text{Rates of increase in concentration of B} = -\frac{d(B)}{dt}$$

Units of reaction rates is **concentration per time** e.g. moles per  $\text{dm}^3$  per second ( $\text{mol dm}^{-3} \text{s}^{-1}$ )

The rate at the start of the reaction, when an infinitesimally small amount of the reactant has been used up is called the **initial rate**.

### Variation of concentration of reactants and products with time



Initial rate of reaction can be obtained by finding the slope/ tangent to the curve at time,  $t = 0$ .

### METHODS OF FINDING THE RATES OF CHEMICAL REACTIONS

**d) Chemical analysis**

- Here, the reaction is carried out in a thermostatically controlled water bath.
- Solutions of the reactants of known concentration are mixed and a stop clock started.
- A sample of a reaction mixture is withdrawn with a pipette and the reaction is stopped/quenched by either cooling or dilution into a freezing mixture or into an excess of solvent.
- Titration is performed to find the concentration of one of the reactants or products. E.g. oxidation of Iodide to Iodine by hydrogen peroxide.  
$$\text{H}_2\text{O}_2(\text{aq}) + \text{I}^-_{(\text{aq})} + 2\text{H}^+_{(\text{aq})} \longrightarrow \text{I}_2(\text{aq}) + 2\text{H}_2\text{O}(\text{l})$$
- Solutions of hydrogen peroxide, acid and Iodine to known concentrations are allowed to reach the temperature of the thermostat bath.
- Solutions are mixed and the time of mixing noted.
- At measured time intervals, sample of reaction mixtures are extracted by pipette.
- Reaction in each sample is quenched by diluting in ice cold water.
- Each sample is titrated against standard aqueous sodiumthiosulphate and the concentration of Iodine is calculated.

**e) Electrical conductivity:**

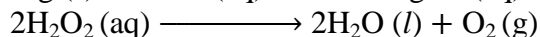
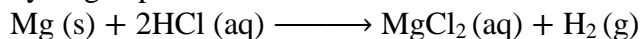
- Conductivity of a reaction mixture may be monitored overtime by carrying out the reaction in a conductivity cell.
- Conductivity apparatus is calibrated with solutions of known concentration
- Conductivity of a solution is proportional to the concentration of its ions and the charges they bear.

**f) Colorimetry**

- Applicable to reaction mixtures that show a steady colour as the reaction proceeds.
- Colorimeter indicates concentration by measuring the intensity of light shining through a coloured reaction mixture.
- Photocell is calibrated with solutions of known concentrations
- Light of fixed wavelength is directed through the reaction mixture and into the photocell.
- Photocell develops an emf proportional to the intensity of the light.
- Emf can then be converted to concentration values.

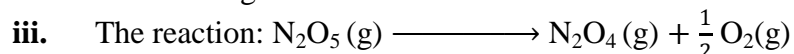
**d) Change in gas volume:**

- For reactions involving gases, the rate of reaction may be monitored by measuring the volume of gas evolved after various time intervals.
- The measured volume of gas may then be used to calculate the corresponding concentration of the reactant. e.g. reaction of a metal with acid and the decomposition of hydrogen peroxide.



**c) Change in pressure**

- An increase or decrease in gaseous pressure can be used to follow many gaseous reactions e.g.



- It involves an increase in the number of moles of gas and an increase in pressure can be followed.
- iv. The reaction:  $\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \longrightarrow \text{H}_2\text{O}(\text{l})$  is accompanied by a decrease in the number of moles, and decrease in pressure at constant volume.
- d) **Spectrophotometry**
- Applicable for the reactions which are extremely rapid.
  - Uses a very short burst of light from a laser to start reaction that is sensitive to light.
  - Spectroscopic techniques then monitor the concentration of the reactive intermediate formed.

### **SOME COMMON TERMS**

ix. **Rate law:**

- States that, “the rate of any chemical reaction at a constant temperature is directly proportional to the molar concentration of the reactants raised to appropriate power whose value is experimentally determined.”
- It summarises the relationship the rate of a chemical reaction and the concentration of the reactants.

x. **Rate equation:**

- Expresses the rate of reaction in terms of the concentration of each reactant raised to a specific power. Consider a reaction  $\text{A} + \text{B} \longrightarrow \text{Products}$   
From Rate law;  $\text{Rate} \propto [\text{A}]^x [\text{B}]^y$

Where  $k$  = rate constant/ coefficient

$X$  = order of reaction with respect to A

$Y$  = Order of reaction with respect to B

xi. **Rate constant / Rate coefficient:**

Is the ratio of the rate of a chemical reaction to the products of the concentration of the reactants raised to appropriate powers as in the rate equation.

Units vary according to the overall order i.e.

From  $\text{Rate} = k [\text{A}]^x [\text{B}]^y$

$$K = \frac{\text{Rate}}{[\text{A}]^x [\text{B}]^y}$$

xii. **Order of reaction**

✓ Is the power to which the concentration term of a single reactant is raised in the experimental rate equation.

OR

✓ Is the sum of the powers to which the concentration terms of reactants are raised in the experimental rate equation .

xiii. **Overall order equation\**

Is the sum of the powers to which the concentration terms are raised in the experimental rate equation.

From Rate =  $k [A]^x [B]^y$

Overall order =  $x + y$

xiv. **Molecularity of a reaction:**

Is the number of species (atoms/ molecules) which participate in a reaction as given by the stoichiometric equation

**Difference between molecularity and order of a reaction**

Molecularity	Order of equation
<ul style="list-style-type: none"><li>Only whole numbers and is never zero</li></ul>	Can be a fraction, zero or a whole number
<ul style="list-style-type: none"><li>Determined from a Stoichiometric equation</li></ul>	Experimentally determined
<ul style="list-style-type: none"><li>Number of species that take part in the rate determining state</li></ul>	Power to which the concentration of the reactant is raised in the experimental rate equation

xv. **Rate determining step/Rate limiting step:**

Is the slowest step in a multi step chemical reaction through which the reactants are converted to the products.

xvi. **Elementary reactions:**

These are reactions that involve one step path or route from reactants to products.

For elementary reactions, molecularity is equal to the order of reaction.

However, the reactions which are not elementary, molecularity may not be equal to order of reaction. E.g. in hydrolysis of a reactant such as ester/ sucrose in presence of a large excess of water.

Consider hydrolysis of sucrose;

Sucrose + water  $\longrightarrow$  Glucose + Fructose

$C_{12}H_{22}O_{11} + H_2O \longrightarrow C_6H_{12}O_6 + C_6H_{12}O_6$

Molecularity of above reaction is two because both sucrose and water are involved in the rate determining step.

However, the overall order of this reaction is first order when experimentally determined.

**Reason**

- Water is present in large excess, its concentration remains unaffected and hence doesn't contribute to the order of the reaction.
- Only sucrose concentration changes during the course of a reaction, affecting the rate of reaction with an order one.

NB: Such reactions where water is in excess making its concentration zero is referred to as pseudo – first order reaction.

### **DETERMINATION OF ORDER OF REACTION FROM INITIAL RATE METHOD**

In this method, the order of reaction in respect to a given reactant is determined by comparing the initial rate for the experiments in which the concentration of only the reactant whose order of reaction is to be determined is changing while the other reactant concentration are kept constant. It therefore requires more than one reactant.

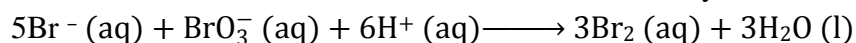
For zero order reaction, the rate of reaction is not affected by change in initial concentration of the reactant e.g. doubling the concentration of the reactant has no effect on the rate.

For all 1<sup>st</sup> order reactions, doubling the initial concentration of the reactant also doubles the rate, Trebling it also trebles the rate i.e. increasing the concentration of reactant of factor y also increases the rate by some factor y.

For second order reactions, doubling or trebling initial concentration of the reactant increases the rate by 4 or 9 times respectively.

#### **Example:**

The result shown refers to oxidation of Bromine ion by Bromate ion in acidic solution.



[5Br <sup>-</sup> ](mol dm <sup>-3</sup> )	BrO <sub>3</sub> <sup>-</sup> (mol dm <sup>-3</sup> )	H <sup>+</sup> (mol dm <sup>-3</sup> )	Initial rate (mol dm <sup>-3</sup> )
v. 0.10	0.10	0.10	$8 \times 10^{-4}$
vi. 0.10	0.20	0.10	$1.6 \times 10^{-3}$
vii. 0.20	0.20	0.10	$3.2 \times 10^{-3}$
iii. 0.10	0.10	0.20	$3.2 \times 10^{-3}$

- f) Find the order of the reaction with respect to;
  - i. Br<sup>-</sup>
  - ii. Br O<sub>3</sub><sup>-</sup>
  - iii. H<sup>+</sup>
- g) State the overall order of reaction
- h) Write the rate equation
- i) Calculate the value of rate constant and state its units.
- j) Calculate the rate reaction when concentration of all three reactants is 0.2mol dm<sup>-3</sup>

#### **Solution**

- f) (i) Br<sup>-</sup>

Let the order of the reaction with respect to Br<sup>-</sup> be x

Let the order of reaction with respect to Br O<sub>3</sub><sup>-</sup> be y

Let the order of reaction with respect to H<sup>+</sup> be z

Taking experiments (ii) and (iii)

$$\text{Rate} = K[\text{Br}^-]^x [\text{Br}_3^-]^y [\text{H}^+]^z$$

$$1.6 \times 10^{-3} = K [0.10]^x [0.2]^y [0.10]^z \text{----- (i)}$$

$$3.2 \times 10^{-3} = K [0.2]^x [0.2]^y [0.1]^z \text{----- (ii)}$$

Dividing equation (ii) by (i)

$$\frac{3.2 \times 10^{-3}}{1.6 \times 10^{-3}} = \frac{K[0.2]^x [0.2]^y [0.1]^z}{K [0.10]^x [0.2]^y [0.10]^z}$$

$$\frac{3.2 \times 10^{-3}}{1.6 \times 10^{-3}} = \left(\frac{0.2}{0.1}\right)^x$$
$$2^1 = 2^x$$

$$\mathbf{X = 1}$$

### Order of reaction with Br<sup>-</sup> is 1

#### Reason:

Doubling the concentration of Br<sup>-</sup> doubles the initial rate

(ii) BrO<sub>3</sub><sup>-</sup>

Taking experiments (i) and (ii)

$$\text{Rate} = K[\text{Br}^-]^x [\text{Br}_3^-]^y [\text{H}^+]^z$$

$$\text{For (i); } 8 \times 10^{-4} = K [0.1]^x [0.1]^y [0.1]^z \text{----- (i)}$$

$$\text{For (ii); } 1.6 \times 10^{-3} = K [0.1]^x [0.2]^y [0.1]^z \text{----- (ii)}$$

Dividing equation (ii) by (i)

$$\frac{1.6 \times 10^{-3}}{8 \times 10^{-4}} = \frac{K[0.1]^x [0.2]^y [0.1]^z}{K [0.1]^x [0.1]^y [0.1]^z}$$

$$\frac{1.6 \times 10^{-3}}{8 \times 10^{-4}} = \left(\frac{0.2}{0.1}\right)^y$$

$$2^1 = 2^y$$

$$\mathbf{Y = 1}$$

### The order of reaction with respect to BrO<sub>3</sub><sup>-</sup> is 1

#### Reason:

Doubling the concentration of BrO<sub>3</sub><sup>-</sup> doubles the rate.

(iii) H<sup>+</sup>

Taking experiment (i) and (iv)

$$\text{Rate} = K[\text{Br}^-]^x [\text{Br}_3^-]^y [\text{H}^+]^z$$

$$\text{For (i); } 8 \times 10^{-4} = K [0.1]^x [0.1]^y [0.1]^z \text{----- (i)}$$

$$\text{For (iv); } 3.2 \times 10^{-3} = K [0.1]^x [0.1]^y [0.2]^z \text{----- (ii)}$$

Dividing (ii) by (i)

$$\frac{3.2 \times 10^{-3}}{8 \times 10^{-4}} = \frac{K [0.1]^x [0.1]^y [0.2]^z}{K [0.1]^x [0.1]^y [0.1]^z}$$

$$4 = 2^z$$

$$2^2 = 2^z$$

$$\underline{\mathbf{Z = 2}}$$

Order of reaction with respect to H<sup>+</sup> is 2

**Reason:**

Doubling the reaction with respect to H<sup>+</sup> rate increases by factor four (4) (rate quadruples)

g) Rate = K[Br<sup>-</sup>]<sup>1</sup> [Br<sub>3</sub><sup>-</sup>]<sup>1</sup> [H<sup>+</sup>]<sup>2</sup>

Overall order = 2 + 1 + 1 = 4

h) Rate = K[Br<sup>-</sup>]<sup>1</sup> [Br<sub>3</sub><sup>-</sup>]<sup>1</sup> [H<sup>+</sup>]<sup>2</sup>

i) From rate = K[Br<sup>-</sup>]<sup>1</sup> [Br<sub>3</sub><sup>-</sup>]<sup>1</sup> [H<sup>+</sup>]<sup>2</sup>

$$K = \frac{\text{Rate}}{[\text{Br}^-]^1 [\text{Br}_3^-]^1 [\text{H}^+]^2} = \frac{3.2 \times 10^{-3} \text{ (mol dm}^{-3}\text{)}}{(0.2)(0.2)(0.1)^2 \text{ (mol dm}^{-3}\text{)(mol dm}^{-3}\text{)(mol dm}^{-3}\text{)}} \\ = \mathbf{8 \text{ mol}^{-3} \text{ dm}^4 \text{ s}^{-1}}$$

j) Rate = 8 (0.2)(0.2) (0.2)<sup>2</sup>  
 $= \underline{\mathbf{0.0128 \text{ mol dm}^{-3} \text{ s}^{-1}}}$

**Example**

2. For the reaction A + B → C, the following results were obtained for kinetic run at the same temperature.

[A] (mol dm <sup>-3</sup> )	[B] (mol dm <sup>-3</sup> )	Initial rate (mol dm <sup>-3</sup> s <sup>-1</sup> )
0.20	0.10	0.2
0.40	0.20	0.8
0.40	0.20	0.8

Find:

- d) Rate equation of reaction  
 e) Rate constant  
 f) Initial rate of reaction when [A] = 0.6 mol dm<sup>-3</sup> and [B] = 0.3 mol dm<sup>-3</sup>

**Solution:**

- b) Doubling the concentration of A quadruples the rate giving order 2.  
 For B, doubling the concentration has no effect on rate hence zero order.

c) Rate = k[A]<sup>2</sup>  
 $K = \frac{\text{rate}}{[\text{A}]^2} = \frac{0.20}{(0.20)^2} = \underline{\mathbf{5 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}}}$

$$\begin{aligned} \text{Rate} &= k [A]^2 [B]^0 \\ &= 5[0.6]^2 \\ &= \underline{\underline{1.8 \text{ mol dm}^{-3} \text{ s}^{-1}}} \end{aligned}$$

### Exercise

3. The table below shows some data for the reactions;

[A] (mol dm <sup>-3</sup> )	[B] (mol dm <sup>-3</sup> )	Initial rate (mol dm <sup>-3</sup> s <sup>-1</sup> )
1.00 × 10 <sup>-2</sup>	2.8 × 10 <sup>-3</sup>	2.2
5.00 × 10 <sup>-3</sup>	2.8 × 10 <sup>-3</sup>	1.1
1.00 × 10 <sup>-2</sup>	5.6 × 10 <sup>-3</sup>	4.4

- e) Determine the order of reaction with respect A and B  
 f) Write the rate equation of reaction  
 g) Calculate the rate constant and find its unit  
 h) Calculate the rate reaction when concentration of A and B is A = 8.5 × 10<sup>-3</sup> moldm<sup>-3</sup>, B = 3.83 × 10<sup>-3</sup> moldm<sup>-3</sup>
4. 2 - Bromo - 2 - methylpropane, (CH<sub>3</sub>)<sub>3</sub>CBr and NaOH react together according to the following equation  
 (CH<sub>3</sub>)<sub>3</sub>CBr + OH<sup>-</sup> → (CH<sub>3</sub>)<sub>3</sub>COH + Br<sup>-</sup>

The following data gives the results of three experiments used to determine the rate equation from the reaction at 25°C.

Experiment	Initial (CH <sub>3</sub> ) <sub>3</sub> CBr (moldm <sup>-3</sup> )	Initial [OH <sup>-</sup> ] (moldm <sup>-3</sup> )	Initial rate of reaction (moldm <sup>-3</sup> )
1	6.0 × 10 <sup>-3</sup>	7.0 × 10 <sup>-1</sup>	8.0 × 10 <sup>-3</sup>
2	9.0 × 10 <sup>-3</sup>	2.0 × 10 <sup>-1</sup>	6.0 × 10 <sup>-3</sup>
3	10.0 × 10 <sup>-3</sup>	4.0 × 10 <sup>-1</sup>	6.0 × 10 <sup>-3</sup>

From these results, it can be deduced that the rate equation is;

$$\text{Rate} = K [(CH_3)_3CBr]$$

- iv. Show how the data can be used to determine/ deduce that the reaction is 1<sup>st</sup> order with respect to (CH<sub>3</sub>)<sub>3</sub>CBr and zero order with respect to OH<sup>-</sup>.
- v. Calculate the value of the rate constant at this temperature and state its units.
- vi. Calculate the initial rate of reaction when the initial concentration of (CH<sub>3</sub>)<sub>3</sub>CBr is 4.0 × 10<sup>-3</sup> moldm<sup>-3</sup> and the initial concentration of OH<sup>-</sup> is 1.0 × 10<sup>-1</sup> moldm<sup>-3</sup>
- b) Name and outline a mechanism for the reaction at primary haloalkane (CH<sub>3</sub>)<sub>3</sub>CBr with .aqueous NaOH.

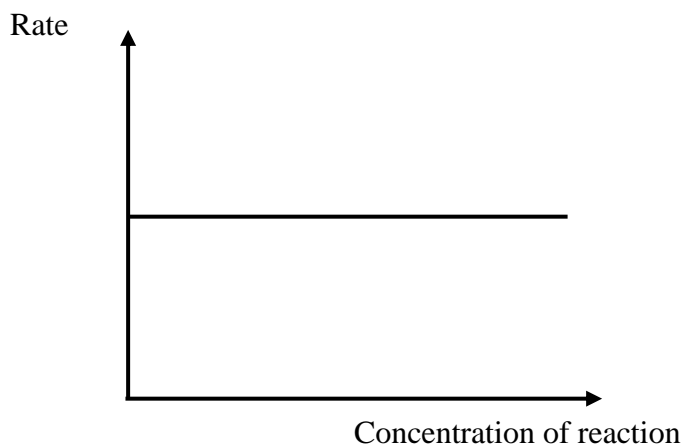
## CLASSIFICATION OF CHEMICAL REACTIONS ACCORDING TO OVERALL ORDER

### 1. Zero Order Reactions

- Rate of reaction is independent of the concentration of the reactant
- The rate equation for the zero order reaction is given by;  
Rate =  $K [A]^0 \Rightarrow$  Rate =  $K$  (constant)

Where  $K$  is a constant in the determining step.

#### A plot of rate of reaction against concentration of concentration of reactant



$$\text{From Rate} = -\frac{d[A]}{dt} = K[A]^0$$

$$= -\frac{d[A]}{dt} = K$$

$$-d[A] = Kdt$$

Integrate from  $A_0$  at  $t = 0$  to  $A_t$  at time  $t = t$

$$-\int_{A_0}^{A_t} d[A] = K \int_{t=0}^{t=t} dt$$

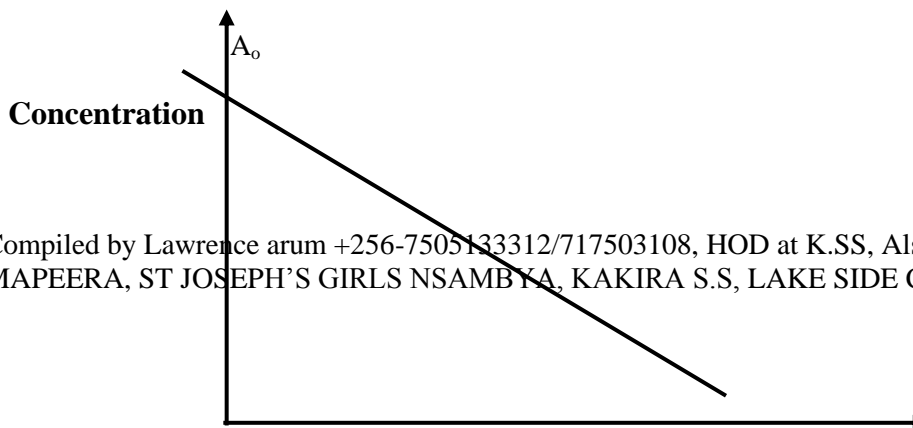
$$- [A] \Big|_{A_0}^{A_t} = Kt \Big|_{t=0}^{t=t}$$

$$- A_t - (-A_0) = Kt$$

$$- A_t + A_0 = Kt$$

$$A_t = -Kt + A_0 \quad (y = mx + c)$$

#### A plot of concentration against time



$$\text{Slope} = -K$$

Time (s)

### Examples of zero order reactions

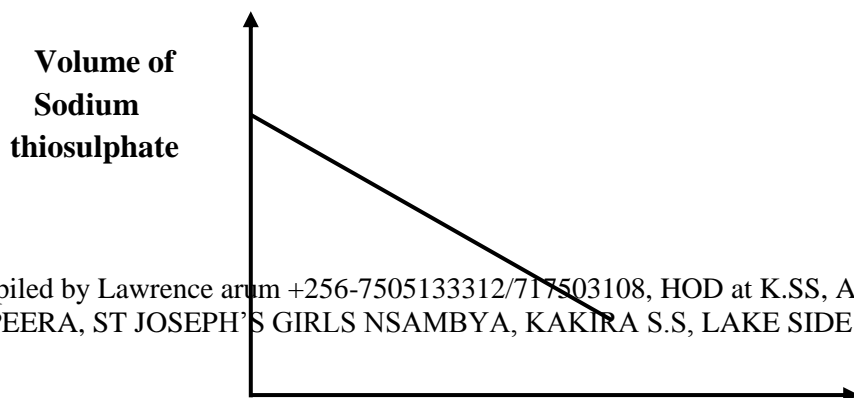
- Iodination of Propanone in which the reaction is zero order with respect to Iodine.
- Reactions between gases, where rate of reaction with respect to one of the reactants is zero order. This indicates that this reactant has been absorbed on the surface of the vessel and the rate only depends on the frequency of collision between the non absorbed gas with the inside of the vessel e.g. decomposition of  $\text{NH}_3$  (g) to Nitrogen to Hydrogen in the presence of a hot tungsten wire.

### Experiment: To determine order of reactions with respect to Iodine in the Iodination of propanone catalysed by $\text{H}_2\text{SO}_4$

#### Procedure:

- Solutions of known concentration of Propanone, Iodine in KI and  $\text{H}_2\text{SO}_4$  of known pH are prepared and brought to a required temperature in a thermostat bath.
- A fixed volume of this mixture is pipetted into a flask and a stop watch is started.
- After a few minutes, a sample of the reacting mixture is pipetted from the solution into Sodium hydrogen Carbonate solution. This stops the reaction instantly by neutralizing the acid.
- The time at which the reaction stops is noted.
- The resultant mixture is then titrated with a standard solution of Sodium thiosulphate ( $\text{S}_2\text{O}_3$ ) to determine the amount of Iodine that remains.
- The procedure is repeated at intervals of 5 minutes to determine the amount of Iodine that has remained.
- The volume of thiosulphate ( $\text{S}_2\text{O}_3$ ) required is plotted against the time elapsed since the start of reaction.

#### A plot of volume of Sodium thiosulphate against time

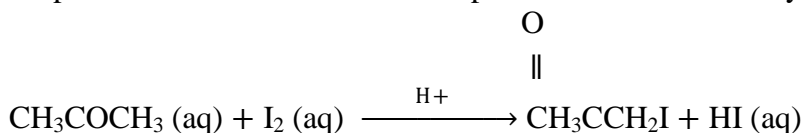


Time(s)

Rate of the reaction remains constant as the iodine concentration decreases.

### Example (QUIZ)

- c) Describe an experiment to show Iodination of Propanone follows a zero order reaction with respect to Iodine. (7mks)
- d) Propanone reacts with Iodine in the presence of an acid catalyst according to the equation



The reaction is first order with respect to Propanone and independent of the concentration of Iodine. Briefly describe how the order of reaction with respect to Iodine can be determined.

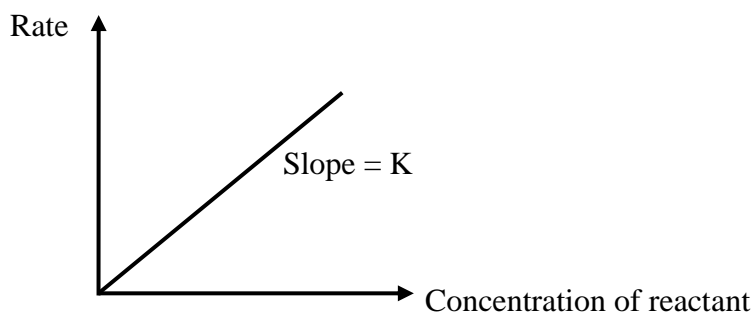
## 2. First Order Reactions

- Rate of reaction is proportional to the first power of concentration of single reactants.
- Consider a reaction A going to products;  $\text{A} \longrightarrow \text{products}$

$$\text{Rate} = -\frac{d[\text{A}]}{dt} = k [\text{A}]^1$$

$$\text{Rate} = k [\text{A}], \text{ from } y = mx + c, c = 0$$

### A graph of rate against concentration of reactants



### Examples of first order reactions

- Hydrolysis of sucrose in presence of acid.
- Acid catalysed hydrolysis of an ester.
- Radioactive decay
- Decomposition of nitrogen pentaoxide  $\text{N}_2\text{O}_5$
- Decomposition of Benzene diazonium chloride.

Compiled by Lawrence arum +256-7505133312/717503108, HOD at K.SS, Also taught at KISUBI MAPEERA, ST JOSEPH'S GIRLS NSAMBYA, KAKIRA S.S, LAKE SIDE COLLEGE LUZIRA .

## Radioactive decay and half life

### Half life:

Is the time taken from the concentration to fall to half its original value.

$$\text{Rate of reaction} = -\frac{d[A]}{dt} = K [A]$$

Separating variables;

$$-\frac{d[A]}{[A]} = K dt$$

Integrating between the limits  $A_0$  at times  $t = 0$  to  $t = t$

$$- \int_{A_0}^{A_t} \frac{d[A]}{[A]} = k \int_{t=0}^{t=t} dt$$

$$- \ln[A] \Big|_{A_0}^{A_t} = kt \Big|_{t=0}^{t=t}$$

$$- \ln A_t - (- \ln A_0) = kt$$

$$\ln \left( \frac{A_0}{A_t} \right) = kt$$

$$\text{But } \ln = 2.303 \log_{10} \Rightarrow \boxed{2.303 \log \frac{A_0}{A_t} = kt} \text{ ----- (i)}$$

$$\text{At } t = A_{1/2}; A_t = \frac{A_0}{2}$$

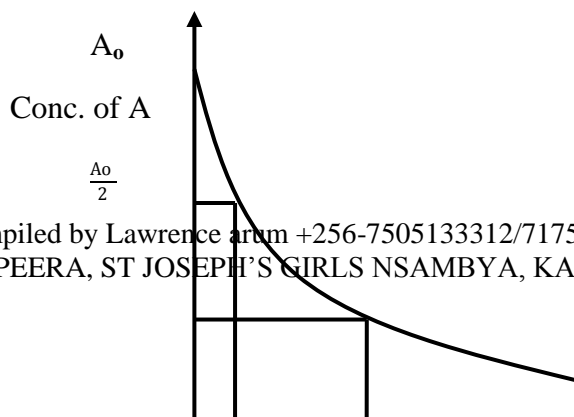
$$2.303 \log \frac{A_0}{A_{1/2}} = kt_{1/2}$$

$$t_{1/2} = 2.303 \log 2 = \frac{0.693}{K}$$

$$\therefore \boxed{t_{1/2} = \frac{0.693}{K}} \text{ ----- (ii)}$$

For 1<sup>st</sup> order reactions, half life is constant and independent of the initial concentration of the reactant.

### A graph of concentration of A against time



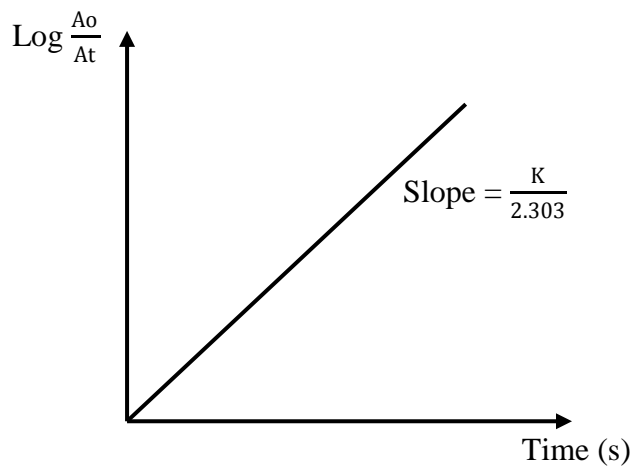
$$\frac{A_0}{4}$$

0     $t_{1/2}$      $2t_{1/2}$     Time (s)  
 First order reaction  $(t_{1/2} - 0) = (2t_{1/2} - t_{1/2})$

Also from  $2.303 \log \frac{A_0}{A_t} = kt$

$\Rightarrow \log \frac{A_0}{A_t} = \frac{kt}{2.303}$  ( $y = mx + c$ )

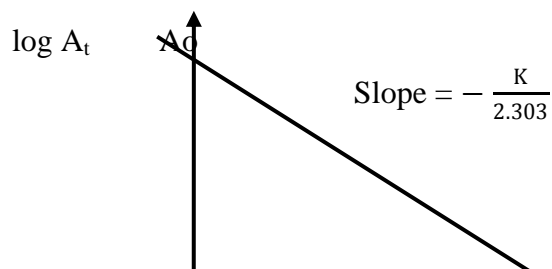
**A plot of  $\frac{A_0}{A_t}$  against time**



Also from  $\log \frac{A_0}{A_t} = \frac{K}{2.303}t$

$\log A_0 - \log A_t = \frac{K}{2.303}t$

$\log A_t = \log A_0 - \frac{K}{2.303}t$



Time

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3. The table below shows the kinetic data that was obtained for the conversion of sucrose to glucose in acid solution.

Time (s)	0	20	40	60	$\infty$	
Conc. of sucrose ( $\text{mol dm}^{-3}$ )		0.08	0.06	0.04	0.02	0.01
Rate of reaction ( $\text{mol dm}^{-3}$ )		0.004	0.003	0.002	0.001	0.0005

- v. Plot a graph of rate of reaction against the concentration of sucrose.  
vi. State the order of the reaction. Give a reason for your answer.  
vii. Determine the rate constant for the reaction and indicate its units.  
viii. Calculate the rate of the reaction when the concentration of sucrose was  $0.12 \text{ mol dm}^{-3}$ .
4. Compound B undergoes a reaction to form compound W. the course of the reaction Can be followed by adding excess KI solution to a fixed volume of the reactant. B reacts with a standard solution of Sodium thiosulphate. The volume of the Sodium thiosulphate solution is a measure of the concentration of B remaining at time T. THE TABLE BELOW shows the volume of Sodium thiosulphate, V required at various times.

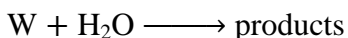
V( $\text{cm}^3$ )	24.70	17.80	12.90	9.25	5.50	3.60
t (mins)	0	60	120	180	240	300

- f) Plot a graph of V against time  
g) From the graph in (a), deduce the time for B; to  
iii. be reduced to half the original value  
iv. be reduced to  $\frac{1}{4}$  the original value  
h) What is the order of the reaction with respect to B?  
i) Write the rate equation for the reaction in which B is converted to W.  
j) Determine the rate constant for the reaction.

NB: When only time and the concentration of the product is given, the concentration of the reactant at each time is got by subtracting the concentration of the product at that time from the concentration of the product at the end of the reaction. i.e.

$$[\text{Reactants}]_t = [\text{product}]_{\text{end}} - [\text{product}]_t$$

A plot of the concentration of reactant and time is then made e.g. given;



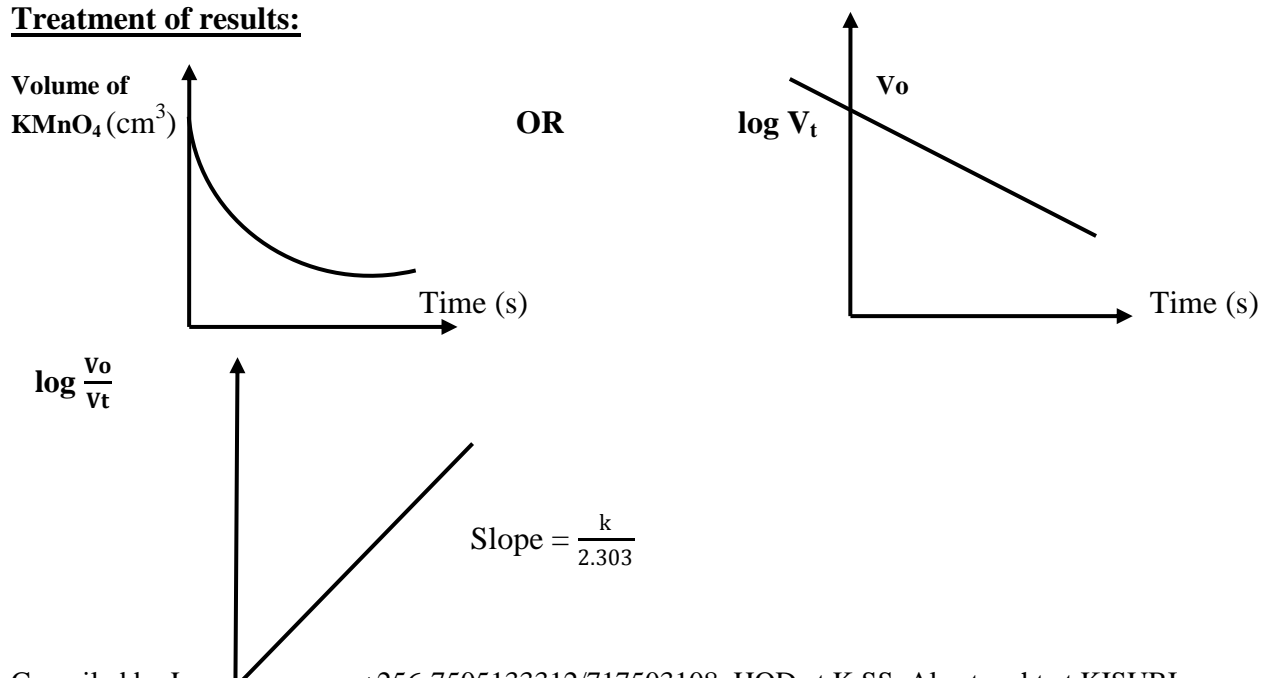
	Product (mol dm <sup>-3</sup> )	30	90	120	135	150
Time (s)	0	20	40	60	∞	
[Product] (mol dm <sup>-3</sup> )	30	90	120	135	150	
[reactant] (mol dm <sup>-3</sup> )	(150 - 30) = 120	(150 - 90) = 60	(150 - 120) = 30	(150 - 135) = 15	(150 - 150) = 0	

### Experimental determination of order of catalyzed decomposition of H<sub>2</sub>O<sub>2</sub>

#### Procedure:

- A fixed volume of H<sub>2</sub>O<sub>2</sub> solution is pipette
- About 1cm<sup>3</sup> of NaOH solution followed by 1cm<sup>3</sup> of FeCl<sub>3</sub> solution is added. The time for which the FeCl<sub>3</sub> is added is noted.
- Mixture is shaken and allowed to stand for 3 minutes.
- 20cm<sup>3</sup> of 1M H<sub>2</sub>SO<sub>4</sub> is added to stop the decomposition.
- The resultant mixture is then titrated with a standard solution of KMnO<sub>4</sub> to determine the amount of H<sub>2</sub>O<sub>2</sub> undecomposed.
- The procedure is repeated at intervals of 3 minutes before adding H<sub>2</sub>SO<sub>4</sub> and the titre values V<sub>t</sub> noted.
- The initial concentration of H<sub>2</sub>O<sub>2</sub> before decomposition is obtained by titrating the original H<sub>2</sub>O<sub>2</sub> with KMnO<sub>4</sub> and titre value V<sub>0</sub> is noted.
- Volumes of KMnO<sub>4</sub> required is plotted against time elapsed since the start of the reaction.

#### Treatment of results:



Time (s)

**UNEB 2011**

4. Describe an experiment to show that catalytic decomposition of  $\text{H}_2\text{O}_2$  is a first order reaction.
5. A certain volume of  $\text{H}_2\text{O}_2$  solution was decomposed in the presence of platinum. The amount of  $\text{H}_2\text{O}_2$  after time  $t$  was found by withdrawing a liquid of small portions of solution, adding dilute  $\text{H}_2\text{SO}_4$  and titrating with Potassium manganate (VII) solution. The volume  $V_t$  of Potassium manganate (VII) solution were as follows;

t (min)	0	5	10	15	20	25	30	35	40	45
$V_t$ ( $\text{cm}^3$ )	12.30	9.20	6.90	5.20	3.90	2.90	2.20	1.60	1.20	1.15

- vi. Tabulate values of  $\log V_t$
- vii. Plot a graph of  $\log V_t$  against time
- viii. State order of reaction with respect  $\text{H}_2\text{O}_2$ . Give reason for your answer.
- ix. Determine the rate constant for the reaction
- x. Calculate the half life for the reaction

**NB: Conditions for first order reaction**

- If one of the reactants is in large excess that only a small fraction of it will be used up in the reaction.
- Use of acid catalyst; where its concentration doesn't change during the course of the reaction e.g acid catalysed hydrolysis of esters and glucose.

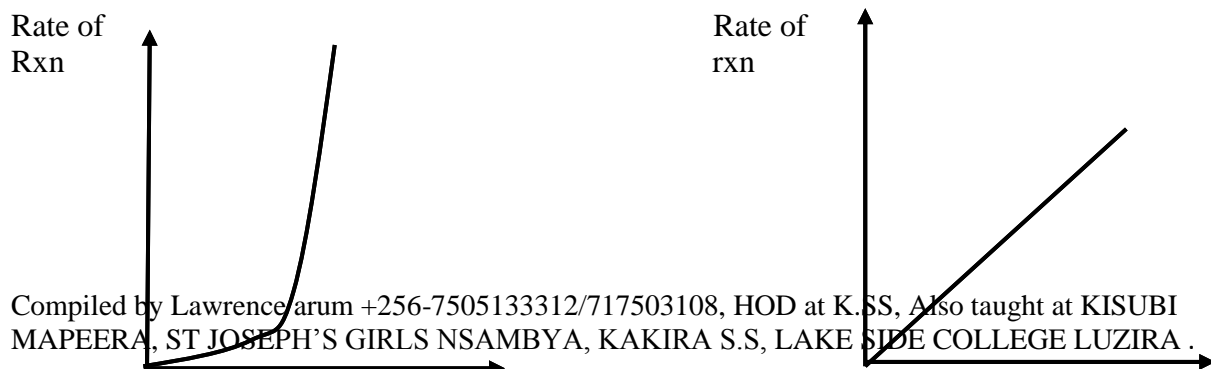
**6. SECOND ORDER REACTION**

Rate of reaction is proportional to the products of the concentration of reactants each raised to power 1 or to the square of the concentration of a single reactant.

For  $\text{A} \longrightarrow \text{Products}$ , rate =  $k[\text{A}]^2$

For  $\text{A} + \text{B} \longrightarrow \text{Products}$ , Rate =  $k[\text{A}]^1 [\text{B}]^1$

**Graphs of second order reactions**

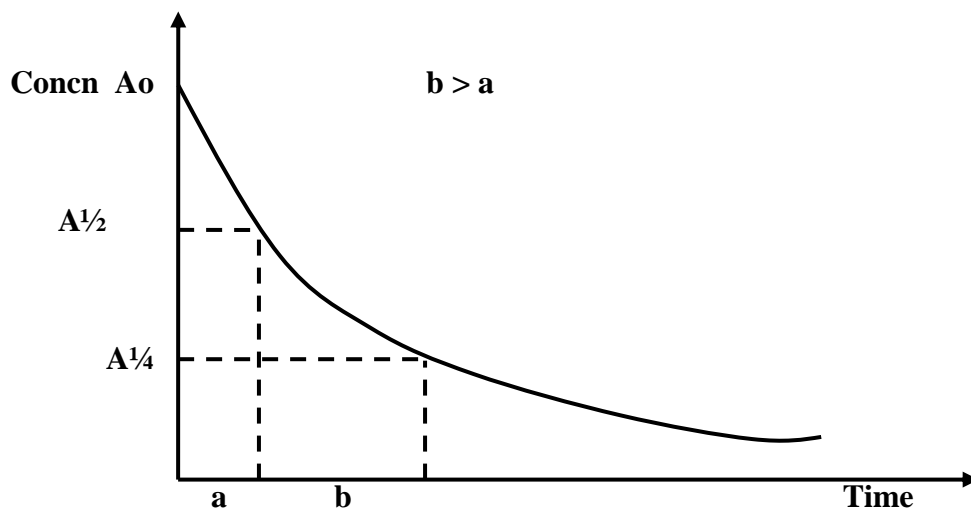


Concentration of reactant

concentration<sup>2</sup>

**Half life:**

For second order reactions, half life is inversely proportional to the concentration. Ie. It almost doubles for every successive decrease in concentration of the reactant by 1/2



**From** Rate =  $-\frac{d[A]}{dt} = k[A]^2$

$$\frac{-d[A]}{[A]^2} = Kdt$$

$$-\int_{A_0}^{A_t} \frac{d[A]}{[A]^2} = \int_{t=0}^{t=t} kdt$$

$$-\left[\frac{-1}{[A]}\right]_{A_0}^{A_t} = kt \Big|_{t=0}^{t=t}$$

$$\frac{1}{A} \Big|_{A_0}^{A_t} = kt$$

$$\frac{1}{A_t} - \frac{1}{A_0} = kt$$

$$\frac{1}{A_t} = kt + \frac{1}{A_0}$$

$$\text{At } t_{1/2}; A_t = \frac{A_0}{2}$$

$$\frac{1}{\frac{A_0}{2}} = kt + \frac{1}{A_0}$$

$$\frac{2}{A_0} - \frac{1}{A_0} = kt_{1/2}$$

$$\Rightarrow t_{1/2} = \frac{1}{A_0 k}$$

### Examples of 2<sup>nd</sup> order reactions

- Hydrolysis of ethyl ethanoate by aqueous NaOH
- Oxidation of I<sup>-</sup> to I<sub>2</sub> by H<sub>2</sub>O<sub>2</sub>

### FACTORS AFFECTING RATES OF REACTION

These include

- vii. Concentration of reactants in solution
- viii. Temperature
- ix. Pressure of gaseous reactants
- x. Light
- xi. Catalyst
- xii. Surface area/size of particle of a solid reactant.

#### Surface area:

- For reactions involving solids, breaking the solid into smaller pieces increases its total surface area.
- Increase in SA of the reactants increases the rate of reaction by exposing more reactant molecules to react with another.

#### Light:

- Photosensitive reactions e.g. photosynthesis and formation of Ag and Ag salts which take place when a photographic film is exposed to light, their rates increase with exposure to light.
- Light of sufficient energy breaks the bonds in one of the reactants creating a reactive intermediate from which the products are formed.

### **Pressure of gaseous reactants:**

Increase in pressure of gases pushes the gaseous molecules close together; increasing on their frequency of collision and thus reacting more rapidly.

### **Concentration:**

- Increasing the concentration of the reactants increases the rate of reaction and vice versa
- This is because at greater concentration, there are more molecules in a given volume, close distance between these molecules are reduced and there is an increased number of collisions per unit volume.

### **Example:**

2. The rate equation for  $2A + B \longrightarrow C$  is given by  $\text{Rate} = k[A][B]^2$ . How will the rate of reaction alter if concentration of
- A is doubled but concentration of B is kept constant
  - Concentration of B is halved but concentration of A is kept constant
  - Both Concentration of A and concentration of B are doubled

### **Solution:**

$$\begin{aligned} \text{iv. Rate} &= k[A][B]^2 \\ &= k[2A][B]^2 \\ &= 2k[A][B]^2 \end{aligned}$$

**New rate is twice the initial rate**

$$\begin{aligned} \text{v. Rate} &= k[A][\frac{1}{2}B]^2 \\ &= (\frac{1}{2})^2 k[A][B]^2 \\ &= \frac{1}{4} k[A][B]^2 \end{aligned}$$

**New rate is  $\frac{1}{4}$  times the initial rate**

$$\begin{aligned} \text{vi. From Rate} &= k[A][B]^2 \\ \text{Rate} &= k[2A][2B]^2 \\ &= (2)(4) k[A][B]^2 \\ &= 8 k[A][B]^2 \end{aligned}$$

**NEW rate is 8 times the initial rate**

### **Exercise**

The rate of a certain reaction is  $\text{Rate} = k[\text{A}][\text{B}]^2[\text{C}]$  where  $[\text{C}]$  is the concentration moles per litre and  $k$  is the rate constant. State how the rate of the reaction will change if;

- v. Concentration of B and C is doubled and A is kept constant
- vi. Concentration of A and C were kept constant and concentration of B is halved
- vii.  $[\text{A}]$  and  $[\text{C}]$  were kept constant and  $[\text{B}]$  was doubled.
- viii. Concentration of A, B and C were doubled.

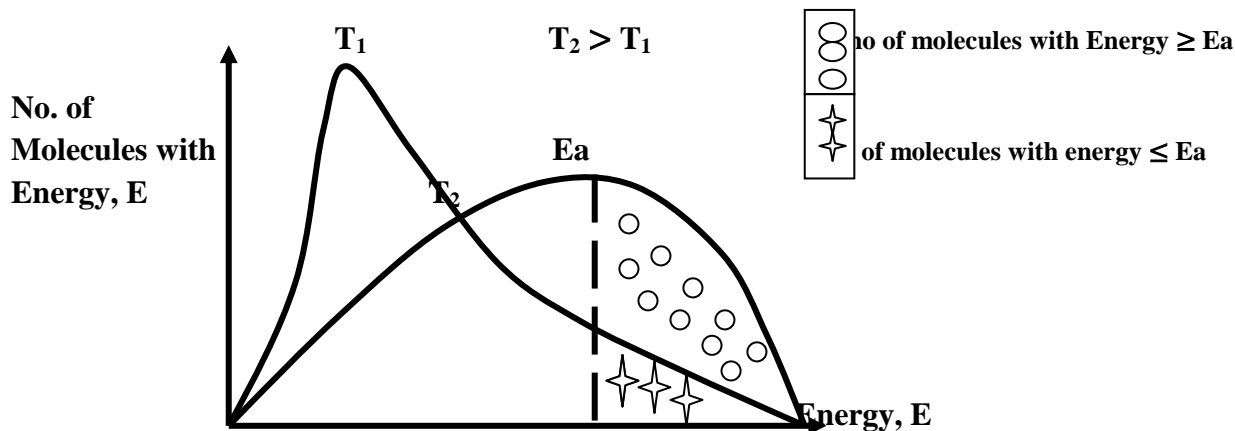
### Temperature:

- Increasing the temperature of the reactants increases the rate of a reaction.
- At higher temperatures, the ions/ molecules of the reactants have more energy moving with greater average velocity and collide more frequently and with more force.
- Increased collision frequency results in a higher rate of reaction.

### MAXWELL – BOLTZMANN DISTRIBUTION OF MOLECULAR ENERGY, E

- It shows activation energy the key to the dependence of the rate reaction on temperature.
- **Activation energy:** is the minimum energy with colliding molecules need in order to react to form products.
- Maxwell – Boltzman started that; Rate of reaction doubles for every  $10^0\text{C}$  rise in temperature as shown below.

### A Plot of fraction of number of molecules with energy E against energy E



### Interpretation

- At lower temperature ( $T_1$ ), a very large fraction of the molecules have energy close to the average energy, only a small fraction of the molecules having very high energies.
- At higher temperature ( $T_2$ ), there is a wide range of molecular energies.
- At higher temperatures therefore, the many more – energetic molecules increase the likelihood of successive collision increasing the rate of reaction.

Qn: Explain with the help of Maxwell - distribution diagram why the rate of some reactions approximately doubles when the temperature is increased by 10<sup>0</sup>C around room temperature.

### Relationship between the rate constant, K and temperature

- Arrhenius equation relates the magnitude of the rate constant and the temperature
- The equation can be used to calculate the activation energy from the rates of reactions at different temperatures.

$$K = Ae^{-E_a/RT}$$

$$\ln K = \ln A - \frac{E_a}{RT}$$

Where A = Arrhenius factor (pre exponential factor)

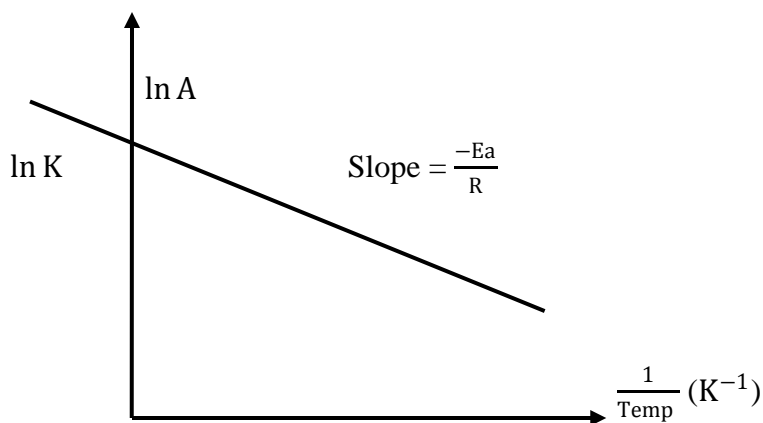
K = Rate constant

E<sub>a</sub> = Activation energy

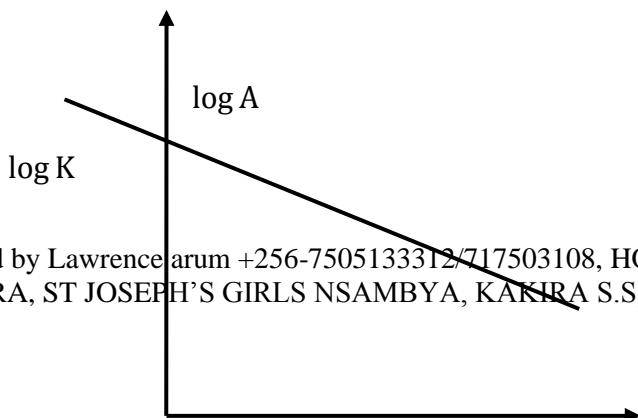
T = absolute temperature

R = Gas constant

### A plot of ln K against temperature



**A Plot of log K against 1/T (log K = log A -  $\frac{E_a}{2.303 RT}$ )**



$$\text{Slope} = - \frac{E_a}{2.303 R}$$

$$\frac{1}{T} \text{ (K}^{-1}\text{)}$$

- If  $K_1$  is the rate constant at temperature  $T_1$  and  $K_2$  is the rate constant at temperature  $T_2$

$$\text{From } \ln K = \ln A - \frac{E_a}{RT}$$

$$K_1 \rightarrow T_1, K_2 \rightarrow T_2$$

$$\ln K_1 = \ln A - \frac{E_a}{RT_1} \text{----- (i)}$$

$$\ln K_2 = \ln A - \frac{E_a}{RT_2} \text{----- (ii)}$$

$$(i) - (ii)$$

$$\ln K_1 - \ln K_2 = - \frac{E_a}{RT_1} - \left( - \frac{E_a}{RT_2} \right)$$

$$\ln \frac{K_1}{K_2} = \frac{E_a}{RT_2} - \frac{E_a}{RT_1}$$

$$\Rightarrow \ln \frac{K_1}{K_2} = \frac{E_a}{R} \left( \frac{T_1 - T_2}{T_2 T_1} \right) \text{----- (i)}$$

**OR**

$$\ln \frac{K_2}{K_1} = \frac{E_a}{R} \left( \frac{T_2 - T_1}{T_2 T_1} \right) \text{----- (ii)}$$

$$\text{But } \ln = 2.303 \log_{10}$$

$$\log \frac{K_1}{K_2} = \frac{E_a}{2.303R} \left( \frac{T_1 - T_2}{T_2 T_1} \right)$$

**Example**

2. The activation energy for a certain reaction is  $50 \text{ kJ mol}^{-1}$ . What is the effect on the rate constant of increasing the temperature by 10K around room temperature (assumed to be  $15^\circ\text{C}$  which is 288K)

**Solution:**

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$$T_1 = (15 + 273) = 288\text{K}$$

$$T_2 = 288 + 10 = 298\text{K}$$

$$\text{From } \log \frac{K_2}{K_1} = \frac{E_a}{2.303R} \left( \frac{T_2 - T_1}{T_2 T_1} \right)$$

$$\log \frac{K_2}{K_1} = \frac{5000}{2.303 \times 8.314} \left( \frac{298 - 288}{298 \cdot 288} \right)$$

$$\log \frac{K_2}{K_1} = 0.30426871$$

$$\frac{K_2}{K_1} = \log^{-1} (0.30426871) = \underline{\underline{2.0149}}$$

$$\frac{K_2}{K_1} \approx 2$$

### The final rate is twice the initial rate

3. The rate  $2\text{N}_2\text{O}_5 \longrightarrow 2\text{N}_2\text{O}_4(\text{g}) + \text{O}_2(\text{g})$  was studied at various temperatures and the rate constants were determined at those temperatures as shown in the table below.

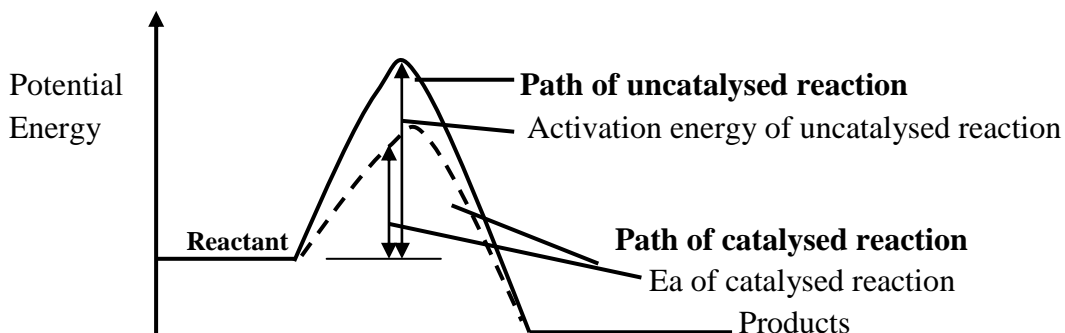
Temp <sup>o</sup> C	20	35	45	65
Rate constant	$2.76 \times 10^{-4}$	$1.35 \times 10^{-4}$	$4.94 \times 10^{-4}$	$4.87 \times 10^{-3}$

Calculate the activation energy  $E_a$  for the reaction.

### Vi) Catalyst:

- Is a substance that alters the rate of chemical reaction but remains chemically at the end of the reaction.
- They speed up the rate of chemical reaction by providing an alternative route of lower activation energy from reactants to products.

### Reaction profile and uncatalysed reactions

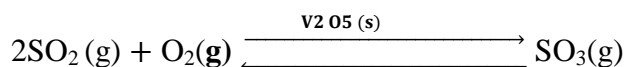


**UNEB 2012 (5) d**

- iv. Using the same axis, draw a labeled diagram for energy – reaction coordinate for a catalysed and uncatalysed.
- v. State the difference in your diagrams
- vi. State how a catalyst increases the rate of a reaction.

**Classification of catalyst**

- A catalyst is classified according to the physical state it is in compared to the reactant namely.
  - c) Heterogeneous catalyst
  - d) Homogenous catalyst.
- c) **Heterogeneous catalyst**
  - Catalysts and reacting substances are in different states
  - Examples include
    - iv. Combination of hydrogen and Oxygen under the influence of platinum
    - v. Using of Fe in the Haber Process
    - vi. Nickel catalyst in the in the hardening of vegetable oils in the production of Margarine.
    - vii. Vanadium (v) oxide in the contact process



Heterogeneous catalyst takes place at the surface of the Catalyst.

Reactants are absorbed onto the surface of the catalyst, bonds are broken and new bonds formed. The products are absorbed from the surface

**d) Homogenous catalyst**

- Catalyst and reacting substances are in the same physical states. E.g.s include
  - iv. Acid catalysed hydrolysis
  - v. Peroxidase enzyme in the mammalian liver.
  - vi. Use of Aq.  $\text{CoCl}_2$  in the reaction between  $\text{H}_2\text{O}_2$  and aqueous solution of Sodium – Potassium 2, 3 – dihydroxybutandioate.

**Features of Catalysts**

- v. Very specific to a single reaction or to class of very similar reactions.
- vi. Catalyst both forward and backward reaction at the same extent and therefore have no effect on equilibrium constant or equilibrium position.
- vii. Small quantities can usually achieve a huge increase in rate of reaction.
- viii. Catalyst maybe poisoned by some other substances e.g. lead, Arsenic and cyanide.

**Experiment Determination of a mechanism of a reaction**

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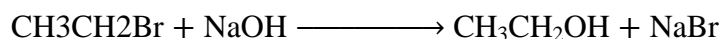
- Reaction mechanism is a detailed step by step description of the pathways followed by reactants in forming products.
- It specifies all intermediate stages and all intermediate species formed.

**Examples:**

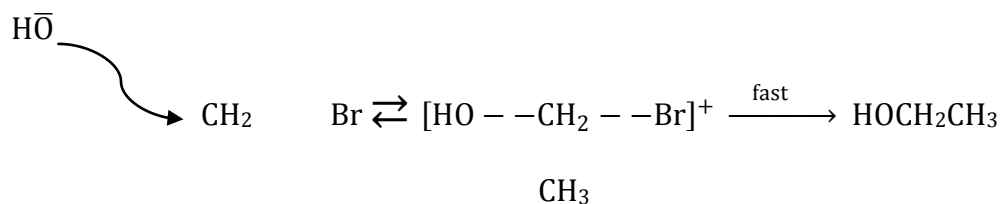
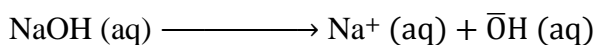
iv. **Hydrolysis of primary alkyl halide.**

- The reaction is first order with respect to Hydroxyl ion and also first order with respect Bromoethane giving an overall order of 2.

**Equation:**



**Mechanism:**



Reactants

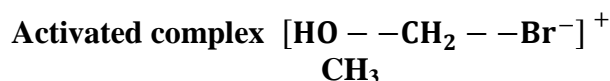
Activated complex

$$\text{Rate} = K [\text{OH}^-] [\text{CH}_3\text{CH}_2\text{Br}]$$

**Reaction profile for substitution Nucleophilic (SN<sub>2</sub>)**

Potential

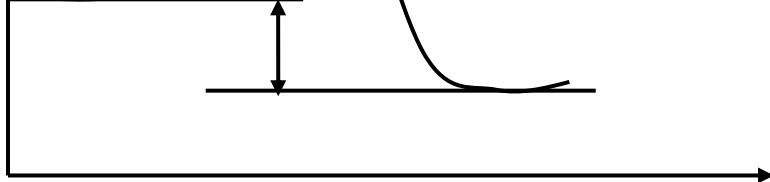
Energy



$\Delta H$



Reaction coordinate

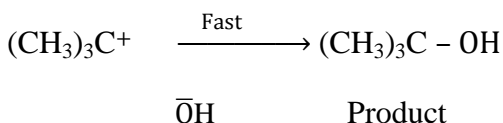


**NB:**

Activated complex is an unstable intermediate in which bonds of the reactant molecules are partially breaking while the new bonds of the product molecules are partially being formed.

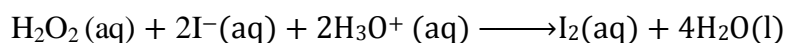
v. **Hydrolysis of tertially alkyl halides (2 - Bromo - 2 - methyl propane)**

**Equation:**

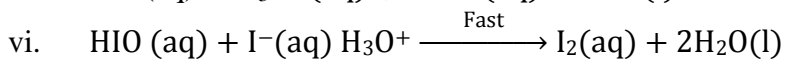
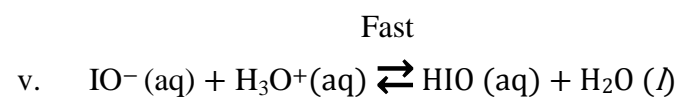
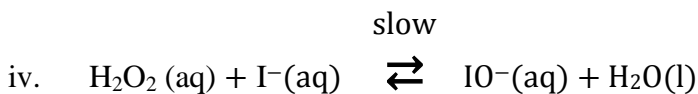


**Reaction profile of substitution Nucleophilic Unimolecular (SN)**

vi. **Oxidation of Iodine to Iodide by H<sub>2</sub>O<sub>2</sub>**



**Mechanism**



Rate = K [H<sub>2</sub>O<sub>2</sub>][I]

Overall order = 2

**Questions (UNEB 1999 QN 14)**

3. 2 - Bromo - 2- methyl propane reacts with aqueous NaOH to form 2 - methyl - propan - 2 - ol

- d) Write the rate equation for the reaction.
  - e) Draw an energy diagram for the reaction
  - f) Write the mechanism for the reaction
  - g) State the;
    - iii. Rate determining step of the reaction
    - iv. Technique which was used to study the reaction
4. Bromo - methane reacts with aqueous NaOH according to the following equations
- $$\text{CH}_3\text{Br} + \text{OH}^- (\text{aq}) \longrightarrow \text{CH}_3\text{OH} (\text{aq}) + \text{Br}^- (\text{aq}) \quad \Delta H = -\text{VE.}$$
- The overall order is 2
- c) Draw a fully labeled diagram of energy versus reaction pathway for the reaction.
  - d) Explain what is meant by the term activated complex.
    - iii. Write the rate equation for the reaction
    - iv. Outline a mechanism for the reaction.

**NOTE:**

- Transition state is a state of maximum potential energy during a chemical reaction in which the substance present at that state can now form the products of the reaction or can give back the reactants.
- Activation energy is an energy barrier that must first be overcome for any chemical reaction to occur.

## PHYSICAL EQUILIBRIA

Some common terms;

### Solution

- ✓ Is the mixture of two or more non chemically reactive substance whose composition/ relative amounts vary within a certain limits
- ✓ can be gaseous, liquid or solid of variable composition

### Binary solution

- ✓ is a solution which consists of only two components e.g.
  - Solution of volatile component such as **carbon dioxide in water**
  - Solution of non volatile component such as **bromine in water**

For each of the above cases, the major component is the solvent and the minor is the solute

### SOLUTION OF A VOLATILE COMPONENT

- ✓ when a binary solution contains a volatile solute, the vapour from the solution would contain both molecules of the solution and the solvent
- ✓ Vapour pressure of each component above the liquid mixture will be lowered at particular temperature

**NB.** Presence of non-volatile solute at the surface of the solution; reduces the escaping tendencies of the solvent molecules ; lowering its vapour pressure resulting in the boiling point of the solution to be raised.

### THE IDEAL SOLUTION AND RAOULT'S LAW

- ✓ An ideal solution is one in which the inter molecular force A-A, A-B and B-B are all equal; and obeys Raoult's law exactly.

### PROPERTIES OF IDEAL SOLUTION

- No heat change on mixing.
- No volume change in mixing; total volume of the solution is equal to the sum of the individual volumes.

**Example of the mixtures that form ideal solution include;**

- Water and methanol
- Chlorobenzene and bromobenzene
- Heptane and octane
- Benzene and methylbenzene.
- Aminopentane and amino hexane

## RAOULT'S LAW

States that:

*"For an ideal solution, partial pressure of a given component, above the liquid mixture; is directly proportional to its mole fraction in the liquid mixture"*

i.e.

$$P_i = P_i^0 X_i$$

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$$P_i \propto X_i$$

Where  $P_i$  = Partial pressure of component,  $i$

$X_i$  = Mole fraction of the component,  $i$

$P_i^\circ$  = saturated water vapour of the component,  $i$

OR:

**For a dilute ideal solution, partial pressure of a given component above the liquid mixture; is equal to its saturated vapour pressure multiplied by its mole fraction.**

Consider a liquid mixture of two components A and B which obeys Raoult's law

$$P_A = P_A^\circ \cdot X_A$$

$$P_B = P_B^\circ \cdot X_B$$

where  $n_A$  = number of moles of compound A

$$X_A = \frac{n_A}{(n_A + n_B)}$$

$$X_B = \frac{n_B}{(n_A + n_B)}$$

$n_B$  = number of moles of component B

$$P_A^\circ X_A + P_B^\circ X_B = P_{\text{total}}$$

But  $P_A + P_B = P_{\text{total}}$

**Limitations of Raoult's law/conditions under which Raoult's law hold**

- ✓ Ideal solution should be sufficiently dilute
- ✓ Temperature must be constant
- ✓ Solute should be non-volatile

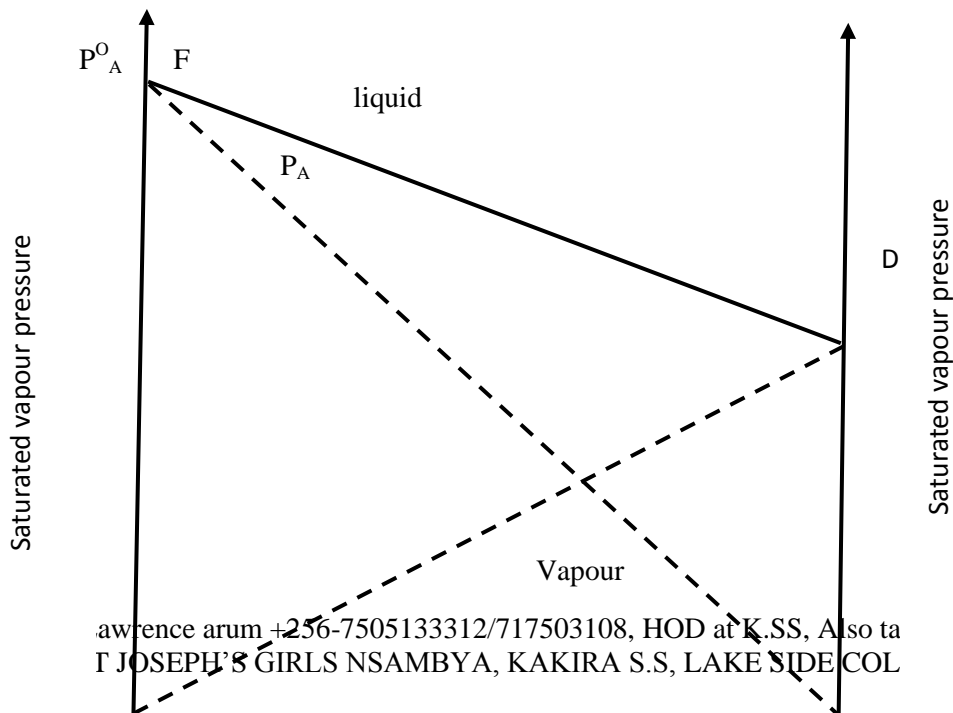
**VAPOUR PRESSURE COMPOSITION DIAGRAM FOR A BINARY SOLUTION THAT OBEYS RAOULT'SLAW**

Consider a binary solution containing components A and B

❖ From  $P_A = P_A^\circ X_A$  When  $X_A = 1, X_B = 0$  for  $X_A + X_B = 1, P_A = P_A^\circ$

❖ Similarly  $P_B = P_B^\circ X_B$

Where  $X_B = 1$  and  $X_A = 0; P_B = P_B^\circ$ .



C	composition/mole fraction	E
$X_A = 1, X_B = 0$		$X_A = 0, X_B = 1$
100% A		100% B

### CURVES:

CD;- Shows the variation of vapour pressure of component B with its composition

EF; - Shows the variation of vapour pressure of component A with its composition

FD; -Variation in total vapour pressure of the solution with composition

- The more volatile component has a higher saturated vapour pressure at a given temperature if the composition is the same.
- If the solution is ideal, the composition of the liquid boiling at a particular temperature is given

$$P_{\text{total}} = P_A + P_B$$

$$P_{\text{total}} = P_A^{\circ} X_A + P_B^{\circ} X_B$$

The vapour composition in terms of the mole fraction of components A and B is given by;

$$y_A = P_A / P_{\text{total}} = (P_A^{\circ} X_A) / P_{\text{total}}$$

$$y_B = P_B / P_{\text{total}} = (P_B^{\circ} X_B) / P_{\text{total}}$$

### Examples

1(a). Calculate the composition benzene- toluene mixture which at 760mmHg boil at 88°C if the saturated vapour pressure of benzene and Toluene at this temperature are 957 and 378mmHg respectively.

(b). Calculate the composition of the vapour obtained when the liquid mixture in A boils.

(c) Which of the two liquids is more volatile? Give a reason for your answer.

### **SOLUTION**

a)  $P_{\text{total}} = 760 \text{ mmHg}$

$$P_{\text{Benzene}}^{\circ} = 957 \text{ mmHg}$$

$$P_{\text{Toluene}}^{\circ} = 378 \text{ mmHg}$$

$$P_{\text{total}} = P_{\text{toluene}} + P_{\text{Benzene}}$$

$$= (P_{\text{toluene}}^{\circ} X_{\text{toluene}}) + (P_{\text{Benzene}}^{\circ} X_{\text{Benzene}}) \quad \text{But } X_T + X_B = 1$$

$$\rightarrow X_B = (1 - X_T)$$

$$P_{\text{total}} = P_T^{\circ} X_T + P_B^{\circ} (1 - X_T)$$

$$P_{\text{total}} = P_T^{\circ} X_T + P_B^{\circ} - P_B^{\circ} X_T$$

$$760 = 378 X_T + 957 - (957 X_T)$$

$$760 - 957 = 378 X_T - 957 X_T$$

$$-197 = -579 X_T$$

$$X_T = \mathbf{0.34}$$

$$X_B = 1 - 0.34 = \mathbf{0.66}$$

b)  $Y_T = P_T^{\circ} X_T / P_{\text{total}}$   
 $= 378 X_{0.34} / 760$   
 $= 0.169 \approx \mathbf{0.17}$

$$Y_B = P_B^{\circ} X_B / P_{\text{total}}$$

$$= 957 X_{0.66} / 760$$

=0.83

- c) Benzene is more volatile  
➤ Because it has the highest vapour composition

2. Calculate the composition of a liquid mixture of A and B which at 760mmHg boils at 98<sup>o</sup>c if the vapour composition of A and B are equal given that the saturated vapour pressure of A and B are 950mmHg and 320mmHg respectively.

### SOLUTION

Vapour composition of A ;  $y_A = P_A/P_{total}$

Vapour composition of B;  $y_B = P_B/P_{total}$

$y_A = y_B$

$P_B/P_{total} = P_A/P_{total}$

$P_A = P_B$

$P_A^0 X_A = P_B^0 X_B$  ,  $X_A + X_B = 1$  ,  $X_B = 1 - X_A$

→  $P_A^0 X_A = P_B^0 (1 - X_A)$  ,  $950X_A = 320(1 - X_A)$  ,  $950X_A = 320 - 320X_A$

$1270X_A = 320$

$X_A = 0.25$

$X_B = 1 - 0.25$

$X_B = 0.75$

### ASSIGNMENT

1. (a). The vapour pressure of ethanol at 20<sup>o</sup>c is 43.6mmHg while that of benzene at the same temperature is 75.2mmHg. the mole fraction of Benzene is 0.09 for a mixture of benzene and ethanol at 20<sup>o</sup>c. Calculate the total vapour pressure of the mixture .  
(b) Calculate the mole fraction of benzene at the vapour phase

### BOILING POINT CURVES

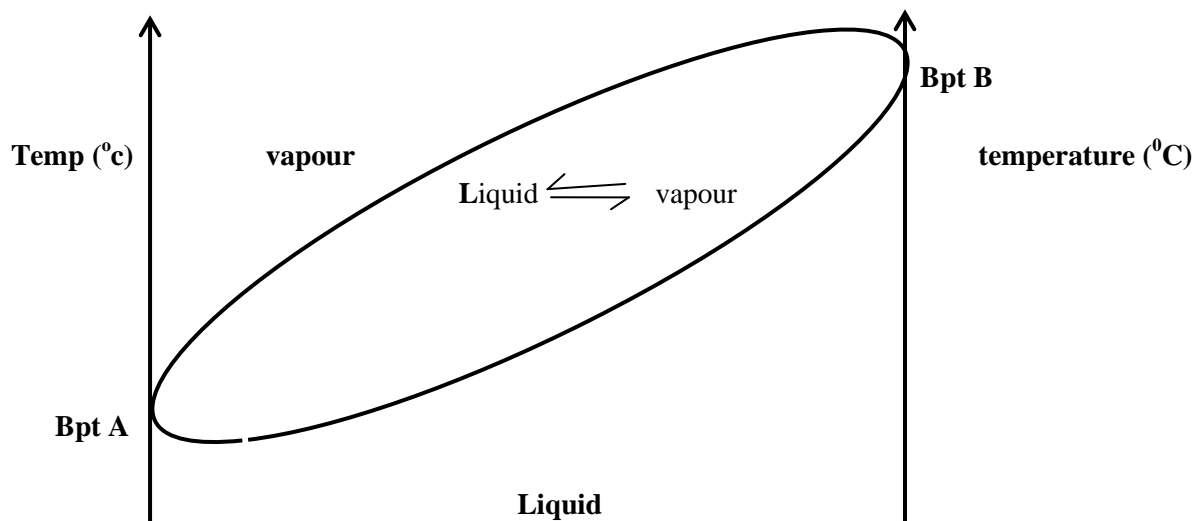
Boiling point curve;

❖ a graph of temperature at which the mixture boils when plotted against composition.

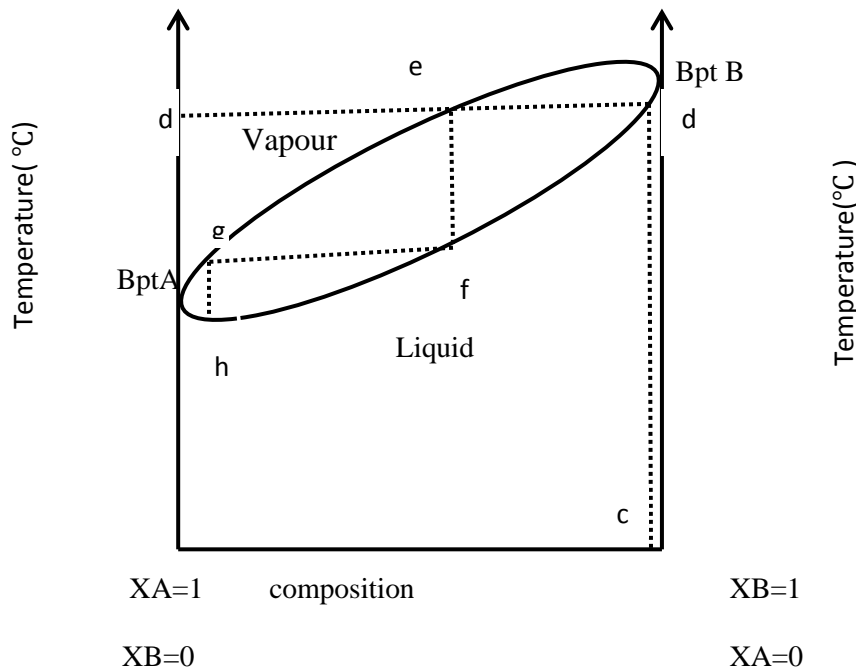
⇒ Increasing temperature increases the vapour pressure of both liquids in the mixture, but the vapour pressure of a more volatile component increases more rapidly, such that the vapour above the liquid mixture boiling is richer in the more volatile component,

⇒ so the composition of the vapour lies on the other side of straight line joining boiling point

### BOILING POINT COMPOSITION DIAGRAM OF AN IDEAL SOLUTION



$X_A=1$  composition  $X_B=1$   
 $X_B=0$   $X_A=0$   
 A binary mixture can be separated into its components by fractional distillation



- Heating a liquid of composition C richer in B, It boils at a temperature d; giving off a vapour of composition e, at the same temperature
- Condensing the vapour, the liquid of the same composition, f is formed
- The liquid when boiled gives a vapour of composition g, at boiling point P which when condensed gives a liquid, h of the same composition as the vapour at g.
- A series of successive boiling and condensation finally produces the pure vapour of the more volatile component A while the residue in the flask becomes richer in the less volatile component
- Pure vapour when condensed gives pure liquid A  
***This is the principle of fractional distillation; a process of separation of two miscible liquids with different boiling points***

Question. Compound A, Boiling point  $380^{\circ}\text{C}$  and compound B boiling point  $410^{\circ}\text{C}$  forms an ideal solution  
 (a). Sketch a labeled boiling point composition diagram for the mixture.  
 (b). Using the diagram, describe and explain how pure B can be obtained from a mixture containing 50% A and 50% B

Solution

a) Boiling point composition diagram for compound A and B

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- b) - A liquid mixture containing 50% B is heated ; boiling at temperature  $t$ ; to give vapour of composition  $r$ , richer in more volatile component A than the less volatile component B  
 -Condensing the vapour, liquid mixture of composition  $s$ , and so on until pure A is obtained as distillate and the residue will be pure B.

**Assignment**

1. The normal boiling point of liquids A and B are  $80^{\circ}\text{C}$  and  $110^{\circ}\text{C}$  respectively. The mixture of A and B can be assumed to obey Raoult's law. Show how the two substances can be separated by fractional distillation and explain the principle involved in the process.

**NON IDEAL/REAL/IMPERFECT SOLUTION.**

- ✓ A real solution is the one which shows deviation from ideal behavior i.e. Raoult's law,
- ✓ Thus, *a real solution is one which deviates from Raoult's law.*
- ✓ These deviations arise from the differences in the intermolecular forces of attraction between the molecules of pure components and the molecules of different components.
- ✓ Vapour pressure of such solution is either higher or less than those predicted from Raoult's law and therefore, the deviation are either positive or negative.

a) **NEGATIVE DEVIATION**

- ✓ Occurs when the vapour pressure of the system is lower than that expected by Raoult's law.
- ✓ This is because of the greater bond of attraction between molecules of different kind, A.....B than those of molecules of the same kind, A....A or B...B.
- ✓ this attraction leads to a reduction in the rate of escape of the molecules to the vapour phase, decreasing volume and evolving heat.

Examples of solution which show negative deviations from Raoult's law

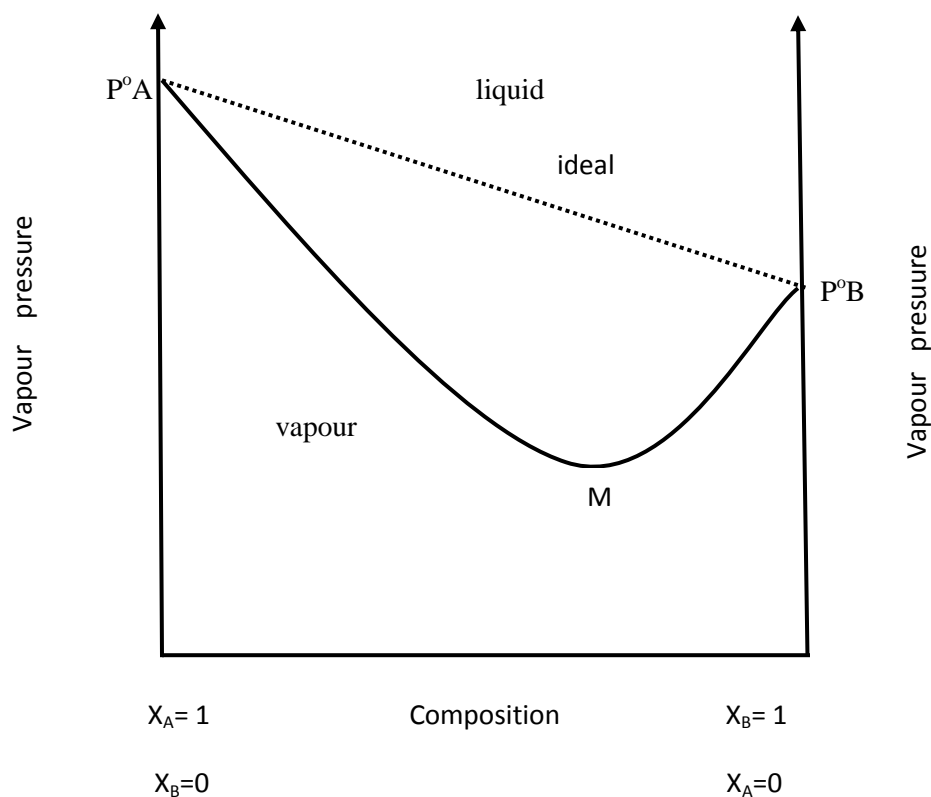
Liquid mixture / solution	Reasons for deviation
a) HCl/HNO <sub>3</sub> and water	- Acid ionizes in water producing ions , and as ions are hydrated, strong ion – dipole attraction are formed compared to Van der-Waals forces in acid and hydrogen bonds in water. - This reduces the escaping tendency of molecules into vapour state
B) Trichloromethane/ Chloroform and propanone	- Intermolecular hydrogen bonding between the chloroform and acetone formed, evolves a lot of heat and reduces the volume of the mixture which reduces the escaping tendency of the molecules into vapour state.
C) Phenol-Phenyl amine mixture	- Intermolecular hydrogen bond formed by the phenol and phenyl amine due to the differences in their polarities outweighs cohesive force in phenol and phenyl amine . - heat is evolved and the volume decreases on mixing, reducing the escaping tendency of the molecules into vapour state.

**PROPERTIES OF MIXTURE WHICH DEVIATE NEGATIVELY FROM RAOULT'S LAW.**

- ❖ Total volume decrease when the liquids are mixed
- ❖ Heat energy is evolved
- ❖ Adhesive forces between components are stronger than the cohesive forces in the individual component

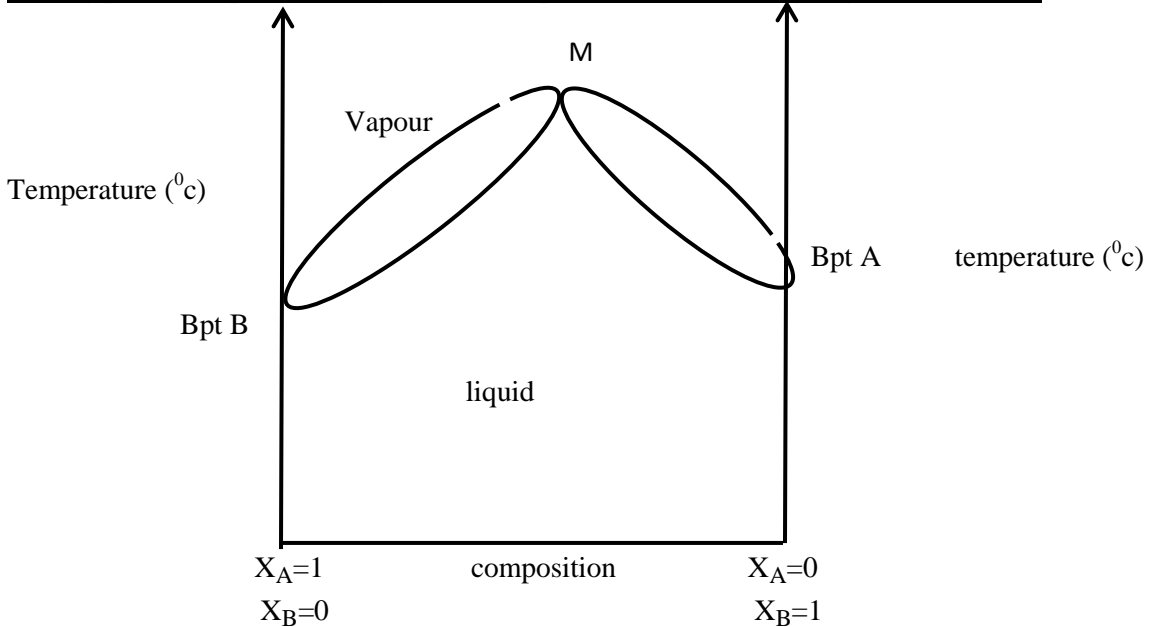
**Vapour pressure composition diagram of a liquid mixture showing negative deviation from**

**Raoult's law**



- ✓ Minimum, M in the diagram above implies that the solution will have to be heated more in order for its vapour pressure to reach atmospheric pressure hence a maximum boiling point .

**Boiling point composition diagram for a liquid mixture showing negative deviation**

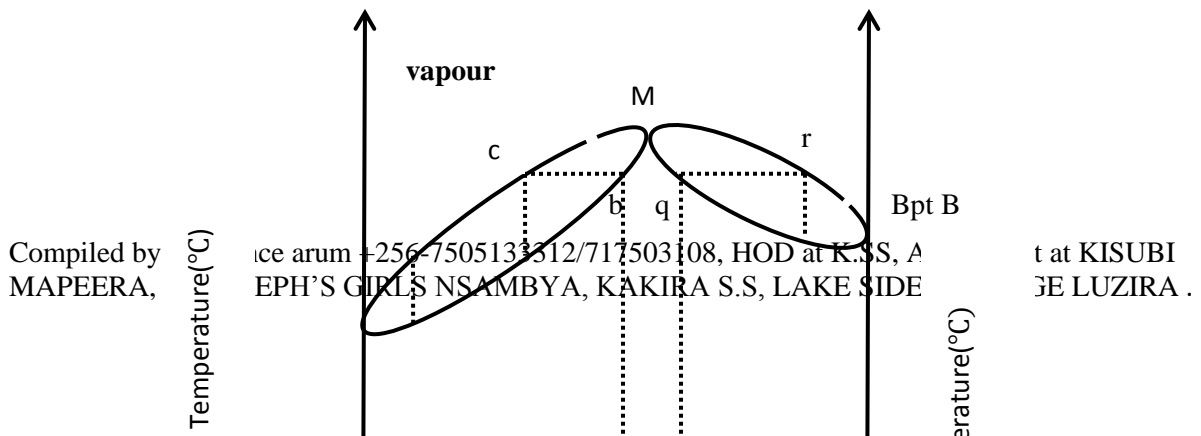


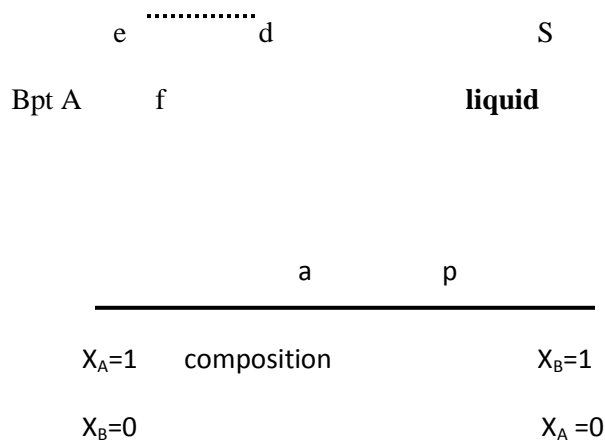
At M, vapour and liquids are indistinguishable i.e.the liquid mixture giving off vapour of the same composition behaving as a pure liquid mixture is called **maximum boiling azeotrope or constant boiling mixture.**

**Definition.**

**An azeotrope**

Is the liquid mixture that boils at a constant temperature ; yielding vapour of the same composition as that of liquid at a constant pressure.





- ✓ Successive boiling and condensation of a liquid mixture of composition **a**, a long **a,b,c, d e**, and **f** gives off pure A in the vapour phase while the residue in the flask tends towards a mixture of composition M(mixture of A and B).
- ✓ At M, any further boiling and condensation produces no change in composition
- ✓ Similarly for original mixture of composition **P**, boiling and condensation proceeds a long **p,q,r,s**.
- ✓ Component B will be distilled off in the vapour phase while the residue in the flask tends towards M.
- ✓ Frictional distillation therefore cannot completely separate the two components.

**Reasons**

- ❖ Separation by friction distillation is possible for mixture with components that differ in their boiling point.
- ❖ However azeotropic mixture boils at a fixed constant temperature; with no change in composition; hence volatile vapour of any component can be obtained from azeotropic mixture thus cannot be separated by friction distillation

**Assignment**

- 1) At a constant temperature, a mixture of 11.95g of Trichloromethane and 14.5g propanone deviates from Raoult's law and has a total vapour pressure of 300mmHg. If the saturated vapour pressure of propanone and Trichloromethane are 380mmHg and 300mmHg respectively
  - (a).State the type of deviation from Raoult's law and briefly explain them.
  - (b).How does the mixture of Trichloromethane and propanone deviate from Raoult's law? Show your working (C=12, O=16, H=1, Cl=35.5)
  - (c).(i) State what is observed when propanone is mixed with trichloromethane .
  - ii) Explain your answer in c (i)

2. a) Nitric acid (boiling point 86<sup>0</sup>c) and water (boiling point 100<sup>0</sup>c) are completely miscible and yet their mixture cannot be completely separated by a single frictional distillation .

(i). Explain why a mixture of nitric acid and water which is miscible even with a marked difference in boiling point of 14°C cannot be completely separated by fractional distillation.

(b). The table below shows the composition of nitric acid in the liquid mixture and vapour above in various temperatures.

Temp( <sup>0</sup> c)	86	100	120	111	103	100
-----------------------	----	-----	-----	-----	-----	-----

%age of HNO <sub>3</sub> in liquid	100	81	68	50	20	0
%age of HNO <sub>3</sub> in water	100	87	68	30	06	0

- (i) Plot a graph of temperature against vapour and liquid composition. Label the axes.  
(ii) Write the coordinates of the azeotropic point and mark it on the graph as S  
(iii) How many distillations are needed to obtain a distillate from a mixture of 50% nitric acid by mass? Identify the distillate  
(iv) Calculate the volume of the residue of fractional distillation of any mixture that would completely react with marble chips to produce 448cm<sup>3</sup> of carbon dioxide at s.t.p (density of solution = 1.866gcm<sup>-3</sup>)

### **(b). POSITIVE DEVIATION**

- ❖ Total vapour pressure of the system is higher than that expected from Raoult's law.
- ❖ This is because of the less attraction (greater repulsion) between the molecules of different components than that of the pure component.
- ❖ Bonding of A-A and B-B are broken on mixing two components.
- ❖ This causes the molecules of A and B have great tendency to escape from a liquid phase giving higher vapour pressure

### **Properties of mixtures which deviate positively from Raoult's law**

- ❖ Increase in volume of the resultant solution
- ❖ Heat energy is absorbed
- ❖ Adhesive force between different components are weaker than cohesive force of the pure component.

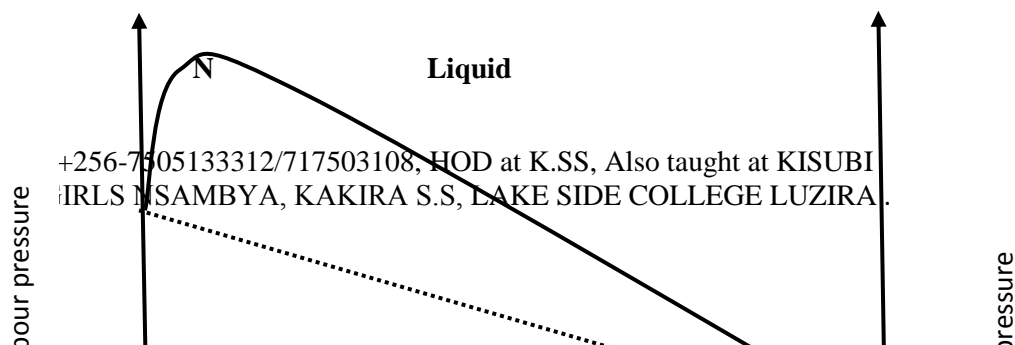
### **Examples of mixtures which deviate positively from Raoult's law**

Liquid mixture /solution	Reason for deviation
Benzene-ethanol mixture	<ul style="list-style-type: none"> <li>- Benzene has no polar molecules with only van der waal forces of attraction present.</li> <li>- Ethanol has polar molecules which can associate through hydrogen bonding .</li> <li>- Those two forces are different in nature and when the components are put together, there will be great repulsion between the molecules of benzene and ethanol.</li> <li>- This increase escaping tendencies of the molecules in the mixture to vapour state.</li> </ul>
Water-ethanol mixture	<ul style="list-style-type: none"> <li>- Water and ethanol associate through a strong intermolecular hydrogen bonding.</li> <li>- Mixing the two, hydrogen bonds are broken down; causing less attraction between the molecules of ethanol and water mixture than the average attraction between the molecules of the pure component of ethanol –ethanol and water-water molecules hence increasing the escaping tendency in vapour phase.</li> </ul>

Other examples include;

- ✓ Cyclohexane and methanol mixture
- ✓ Carbon disulphide and ethanol mixture
- ✓ carbontetrachloride and methanol mixture
- ✓ Acetone and Carbon disulphide
- ✓ Benzene and cyclohexane
- ✓ Chloroform and ethyl alcohol.

### **Vapour pressure composition diagram of a liquid mixture showing positive deviation from Raoult's law**



$P^0_A$

ideal

vapour

$P^0_B$

$X_A=1$

composition

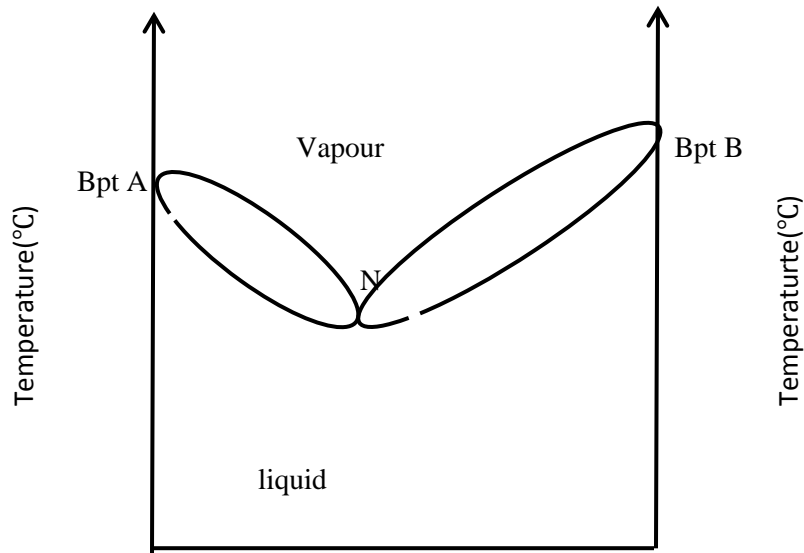
$X_B=1$

$X_B=0$

$X_A=0$

Maximum  $N$ , in the vapour phase for its vapour pressure to reach atmospheric pressure and hence *minimum boiling point*.

**Boiling point composition diagram for a liquid mixture showing a positive deviation**



$X_A=1$

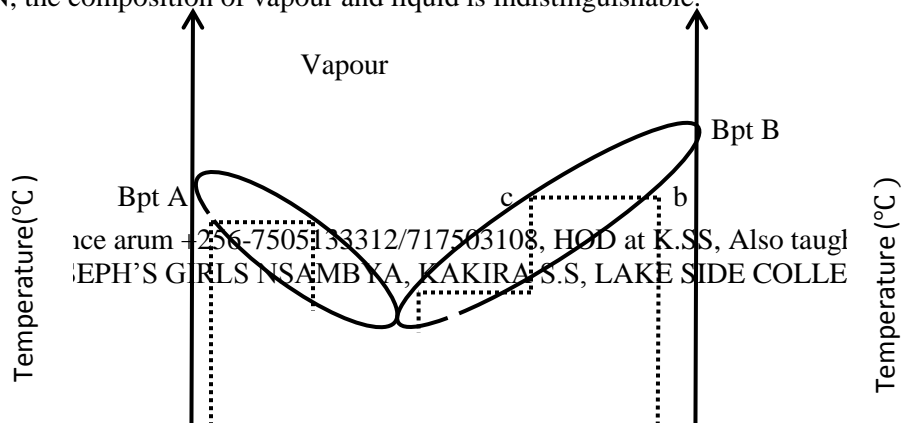
composition

$X_B=1$

$X_B=0$

$X_A=0$

At minimum  $N$ , the composition of vapour and liquid is indistinguishable.



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SUBI  
ZIRA .

q r e  
s N d  
f  
liquid

P		a
$X_A=1$	composition	$X_B=1$
$x_o=0$		$x_o=0$

- ⇒ When a liquid of composition is **a**, is heated, successive boiling and condensation along **a, b, c, d, e, f** gives off a vapour richer in azeotropic mixture while the residual liquid mixture in the flask becomes richer in B.
- ⇒ Also if a liquid mixture of composition **p** is heated, successive boiling and condensation proceeds along **p,q,r,s** giving off vapour richer in the azeotropic mixture whereas the residue liquid in the flask becomes richer in A
- ⇒ It's also not possible to completely separate components by fractional distillation

### Assignment

Two liquids are usually classified according to whether they obey Raoult's law.

(a). State Raoult's law and draw a diagram to show how the vapour pressure of an ideal binary mixture vary with composition.

(b). (i) Give an example of a binary mixture which shows positive deviation from Raoult's law and draw a labeled diagram of temperature against composition.

(ii) Explain in terms of molecular interaction the reasons for the deviation

(c) Explain why the mixture in (i) above cannot be separated by fractional distillation.

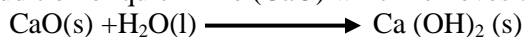
### Properties of an azeotropic mixture

- Constant boiling point of the liquid mixture.
- Liquid and vapour have fixed compositions.

### Separation of azeotropic mixtures

#### i. Chemical methods

-Involves addition of quick lime (CaO) which removes the water e.g. azeotropic mixture of water and ethanol.



#### ii. Distillation by use of third component

-E.g. an azeotropic mixture of ethanol and water can be separated by the addition of benzene and then distilling mixture of the 3 components.

-First distillation yields an azeotropic mixture of the three components.

-The second distillation produces the mixture of ethanol and benzene and on distilling the mixture, pure ethanol is obtained.

#### iii. solvent extraction

-One component can be extracted using a solvent in which it dissolves.

#### iv. adsorption

-Always effective by addition of silica gel which absorbs one of the components.

### IMMISCIBLE LIQUID

- Are liquids which do not mix at all conditions. E.g Benzene and water, Trichloromethane and water, Tetrachloromethane and water, Chlorobenzene and water etc.

In a mixture of two immiscible liquids;

- Each liquid exerts its own vapour pressure corresponding to its pure state at a particular temperature independent of the other.
- vapour pressure above the liquid mixture will be the sum of vapour pressure of the two pure components at that temperature.
- A mixture of two immiscible liquids will boil at a temperature lower than the normal boiling point of the two liquids. This is because the total vapour pressure of the liquid reaches the given external pressure at a lower temperature than either liquid alone.
- This is the principle of steam distillation.

Example:

(a). mixture of Chlorobenzene(bpt 131) and water (bpt 100) boils at 91°C

(b). mixture of amino benzene (bpt 180) and water (bpt 100) boils at 96.5°C

### STEAM DISTILLATION

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- ✓ is a technique of separating immiscible with water at a temperature below its boiling point by bubbling steam through the mixture.

Experimental set up.

### Procedure

- Flask containing immiscible mixture is gently heated and steam is passed through the container having an impure mixture to be purified.
- Distillate is collected in the receiver and it contains two purified immiscible liquid e.g. water and organic compound.
- Organic compound is then isolated using a separating funnel, dried using a drying agent.

NB: steam is preferred to liquid water because:-

- ✓ It keeps the mixture agitating
- ✓ Equilibrium between the vapors and the two liquids is rapidly attained.

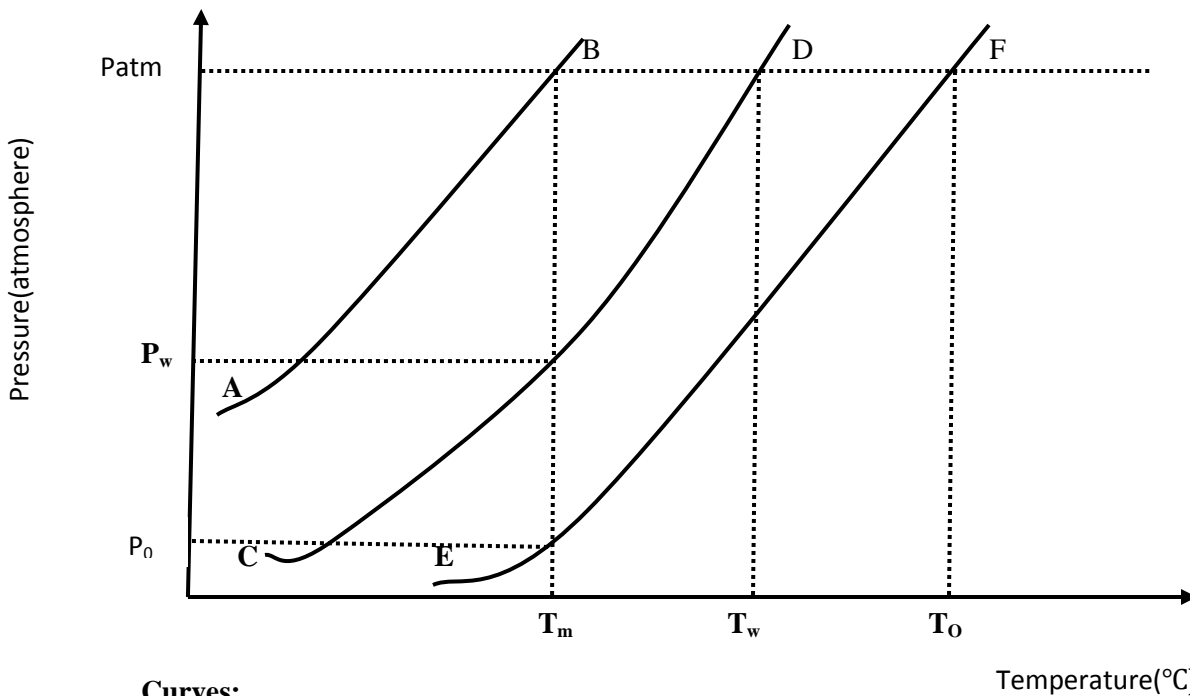
### **CONDITIONS FOR STEAM DISTILLATION**

- ✓ Components should have high RMM
- ✓ One of the components should be immiscible with water.
- ✓ Impurities in the mixture should be nonvolatile, so that they do not appear in the distillate.
- ✓ Components being separated should have a considerable saturated vapour pressure at temperature near the boiling point of water.

### **Advantages of steam distillation.**

- ✓ Used for purification of organic compounds which decompose near their boiling points.
- ✓ Thermal decomposition of compounds which occurs at high temperature doesn't take place.

**Graphical determination of composition of distillate.**



**Curves:**

AB-variation of total vapour pressure of water and organic compound with temperature

CD-variation of vapour pressure of water with temperature

EF- variation of vapour pressure of pure organic compound with temperature.

From Dalton's law; **Partial vapour pressure of a gas is directly proportional to its mole fraction**

Partial pressure = mole fraction  $\times$  P total ;  $P_w = X_w \times P$  total

But  $X_w = \frac{n_w}{n_w + n_o}$

$P_w = \frac{n_w}{n_w + n_o} P$  total -----(i)

Similarly  $P_o = \frac{n_o}{n_w + n_o} P$  total ----- (ii)

Dividing (i) by (ii)

$\frac{P_w}{P_o} = \frac{n_w}{n_o}$

But  $n_w = \frac{m_w}{M_w}$  where  $m_w$  = mass of water  
 $M_w$  =Relative molecular mass of water

$n_o = \frac{m_o}{M_o}$  where  $M_o$  = RMM of organic compound  
 $m_o$  =mass of organic compound

$\frac{p_w}{p_o} = \frac{m_w/M_w}{m_o/M_o}$ ,  $\frac{p_w}{p_o} = \frac{m_w \cdot M_o}{m_o \cdot M_w}$

$\frac{m_w}{m_o} = \frac{P_w \cdot M_w}{P_o \cdot M_o}$

<b>Example</b>	<b>Mass of water</b>	<b>=</b>	<b>partial pressure of water X</b>	<b>RMM of water</b>
	<b>Mass of organic compound</b>		<b>partial pressure of organic compound X</b>	<b>RMM of organic compound</b>

1. When an organic compound P is steam distilled at normal atmospheric pressure of 760mmHg. The distillate was found to contain 80% by composition of P. At this temperature, Vapour pressure of water is 640mmHg. Calculate the RMM of P.

**Solution**

$$\text{From; } \frac{\text{mass of water}}{\text{Mass of organic compound}} = \frac{\text{partial pressure of water} \times \text{RMM of water}}{\text{partial pressure of organic compound} \times \text{RMM of organic compound}}$$

Total pressure = 760mmHg

% mass of P = 80%

Partial pressure of water = 640mmHg

$$\begin{aligned} \text{Partial pressure of organic compound} &= \text{total pressure} - \text{partial pressure of water} \\ &= (760 - 640) \text{ mmHg} \\ &= 120\text{mmHg} \end{aligned}$$

RMM of water = 18

Let the mass of water be Xg

Let the mass of p be Yg

$$\left( \frac{Y}{X+Y} \right) \times 100 = 80$$

$$\frac{100Y}{X+Y} = \frac{80}{1}; 100y = 80(X+Y)$$

$$20Y = 80X$$

$$\frac{X}{Y} = \frac{1}{4}$$

$$\Rightarrow \frac{1}{4} = \frac{\text{partial pressure of water}}{\text{partial pressure of P}} \times \frac{\text{RMM of water}}{\text{RMM of P}}$$

$$\frac{1}{4} = \frac{640 \times 18}{120 \times \text{RMM of P}}$$

$$\text{RMM of P} = \frac{640 \times 18 \times 4}{120}$$

$$= 384$$

2. When Bromo benzene is steam distilled at normal atmospheric pressure of 760. The temperature of distillation was found to be 95.7°C. At this temperature, the vapour pressure of water is 640mmHg. Calculate the percentage composition of Bromo benzene in the distillate.

**Solution**

$$\begin{aligned} \text{Partial pressure of bromo benzene} &= \text{Total pressure} - \text{partial pressure of water} \\ &= (760 - 640) \text{ mmHg} \\ &= 120\text{mmHg} \end{aligned}$$

RMM of water = 18g

RMM of C<sub>6</sub>H<sub>5</sub>Br = 72 + 5 + 80 = 157

Let the mass of water be Xg; mass of Bromo benzene be Yg

$$\text{From; } \frac{\text{mass of water}}{\text{Mass of Bromobenzene}} = \frac{\text{partial pressure of water} \times \text{RMM of water}}{\text{partial pressure of bromobenzene} \times \text{RMM of bromobenzene}}$$

$$\frac{X}{Y} = \frac{640 \times 18}{120 \times 157}$$

$$\frac{X}{Y} = \frac{11520}{18840}$$

Mass of water = 1152, mass of C<sub>6</sub>H<sub>5</sub>Br = 1884

Total mass of distillate = X + Y

% age mass of C<sub>6</sub>H<sub>5</sub>Br =  $\left( \frac{\text{mass of C}_6\text{H}_5\text{Br}}{\text{Total mass}} \times 100 \right)$

Total mass

$$\frac{1884 \times 100}{30.36} = 62.06\%$$

### ACTIVITY

1. A mixture of naphthalene (C<sub>10</sub>H<sub>18</sub>) and water distilled at 98.3 °C and 753mmHg. Calculate the composition of distillate as percentage by mass given that the vapour pressure of water at 98 °C is 715mmHg.
2. At 744mmHg, the steam distillation of a certain liquid takes place at 90 °C. The vapour pressure of water at this temperature is 634mmHg, and the distillate contains 50% by mass of liquid T. Calculate the RMM of T.
3. (a) What is steam distillation?  
(b) Explain the principle behind isolation of substance by steam distillation.  
(c) Describe briefly how you would perform steam distillation in a laboratory.

## **DISTRIBUTION OF SOLUTE BETWEEN TWO NON MISCIBLE SOLVENTS**

### **Distribution law \ distribution coefficient (K<sub>D</sub>)**

#### Statement

*“A non-volatile solute dissolved in two immiscible liquids in contact; distributes itself in such a way that at equilibrium; the ratio of concentration of the solute in a mixture of two liquids is constant at a fixed constant temperature”*

i.e. consider a non volatile solute X in a mixture of two immiscible A and B.

$\frac{[X]}{[A]}$  = constant = K<sub>D</sub> of X between A and B.

$\frac{[X]}{[B]}$

OR  $\frac{[X]}{[B]}$  = constant = K<sub>D</sub> of X between B and A.

$\frac{[X]}{[A]}$

### **Limitation of the law**

Partition coefficient will remain constant if:

- Temperature must be constant i.e. Change in temperature alters the solubility of the solute between the two solvents.
- Solvent must be immiscible
- Solution in contact must be dilute.
- Solute in each solvent should be of the same molecular state i.e. No dissociation and association

### **EXPT: TO DETERMINE PARTITION COEFFICIENT, K<sub>D</sub>**

- a) **For iodine between water and Tetrachloromethane at a given temperature.**

#### **Procedure**

- A known volume of an aqueous solution of Iodine is shaken with Tetrachloromethane in a separating funnel; at a given temperature.
- The mixture is then left to settle for about ten minutes as to attain equilibrium.
- Known volumes of aqueous layer and organic layer are separately pipetted in different conical flasks; titrated with standard sodium thiosulphate solution; using starch indicator.



Knowing the volume of sodium thiosulphate needed in a reaction, concentration of iodine in both layers can be calculated from  $\frac{[I_2]}{[I_2]_{CCl_4}} = K_D$

$[I_2]_{CCl_4}$

Example.

- 1) 20cm<sup>3</sup> 0.1M iodine solution in KI was shaken vigorously in a separating funnel with 20cm<sup>3</sup> of CCl<sub>4</sub>. The color of CCl<sub>4</sub> gradually turned purple and finally dark purple. Explain the;  
(a). (i). the role of KI in the experiment.  
(ii). Observed colour change in the CCl<sub>4</sub> layer.  
(b) 10cm<sup>3</sup> of CCl<sub>4</sub> layer reacted completely with 18cm<sup>3</sup> of 0.02M thiosulphate solution.  
(i) Write an equation for the reaction.

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(ii) Determine the  $K_D$  of iodine between two solvents.

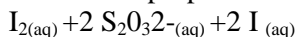
**solution**

(a). (i). KI provide  $I^-$  which reacts with iodine to form a soluble complex.

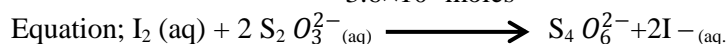


(ii). Iodine distributes its self initially between  $CCl_4$  and KI solution causing a colour change of  $CCl_4$  to be purple

Because of more solubility of iodine in  $CCl_4$  than in aqueous KI, more  $I^-$  move to  $CCl_4$  layer making it dark purple.



(b).  $100\text{cm}^3$  of solution contain 0.02 moles of  $S_2O_3^{2-}$   
 $18\text{cm}^3$  of the solution contain  $\left(\frac{0.02 \times 18}{100}\right)$  moles of  $S_2O_3^{2-}$   
 $= 3.6 \times 10^{-4}$  moles



Moles of iodine  $\frac{3.6 \times 10^{-4}}{2}$  moles = 0.00018 moles

$10\text{cm}^3$  of  $CCl_4$  layers contain 0.00018 of  $I_2$

$1000\text{cm}^3$  of  $CCl_4$  layers contains  $\left(\frac{1000 \times 0.00018}{10}\right) = 0.018\text{M}$

$[I_2]$  in  $CCl_4$  layers; 0.018M

Original concentration of  $I_2 = 0.1\text{M}$

$[I_2]_{H_2O} = 0.1 - 0.018$

= 0.082M

$$K_D = \frac{[I_2]_{H_2O}}{[I_2]_{CCl_4}} = \frac{0.082}{0.018} = 4.556$$

$K_D = 4.56$

**b) Ethanol acid between water and Butanol**

**Procedure**

- A known volume of water is mixed with known volume of Butanol in a separating funnel.
- A known mass of ethanoic acid is then added to the mixture, separating funnel is stoppered.
- The mixture is shaken for about 5min. left to settle so as to attain the equilibrium
- After the mixture has clearly separated into 2 layers, known volumes of each layer are pipette and titrated with standard solution of NaOH using methyl orange indicator.



- knowing the concentration of NaOH,, concentration of ethanoic acid in both layers can be determined , hence

$$K_D = \frac{[CH_3COOH]_{Butanol}}{[CH_3COOH]_{water}}$$

**C) Butan -1, 4- dioc acid (succinic acid ) between water and ethoxyethane**

**Procedure**

- A known volume of water is mixed with a known volume of ethoxyethane in a glass flask.
- A known mass of succinic acid is then added to the flask, and shaken vigorously.
- The mixture is then left to settle so as to attain equilibrium.
- known volumes of organic and aqueous layers are pipetted into conical flask, titrated with standard solution of NaOH using methyl orange as indicator.
- knowing the volume of NaOH required for complex reaction, the concentration of succinic acid in both layers can be determined ; hence

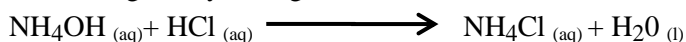
Compiled by Lawrence arum +256-7505133312/717503108, HOD at K.SS, Also taught at KISUBI MAPEERA, ST JOSEPH'S GIRLS NSAMBYA, KAKIRA S.S, LAKE SIDE COLLEGE LUZIRA .

$$K_D = \frac{[\text{Butan -1, 4- diol acid}]_{\text{water}}}{[\text{Butan -1, 4-dioic acid}]_{\text{ethoxyethane}}}$$

D) **Ammonia between water and Trichloromethane.**

**Procedure.**

- A known volume of aqueous solution of ammonia is shaken with trichloromethane for about 5 minutes; in a separating funnel at a fixed temperature.
- after equilibrium has been established, known volumes of aqueous layer and trichloromethane layer are separately pipetted into different conical flasks; titrated with a standard solution of Hydrochloric acid using methyl orange indicator.



- knowing the volume of HCl, the concentration of NH<sub>3</sub> in the two layers can be determined; and hence

$$K_D = \frac{[\text{ammonia}]_{\text{H}_2\text{O}}}{[\text{Ammonia}]_{\text{CHCl}_3}}$$

**Examples**

1. An aqueous solution of ammonia was shaken with 120cm<sup>3</sup> of trichloromethane at 298K. When equilibrium was attained, 25cm<sup>3</sup> sample of each layer were titrated against 0.1M Hydrochloric acid. If 25cm<sup>3</sup> of aqueous layer required 27.5cm<sup>3</sup> of 0.1M of HCl while 25cm<sup>3</sup> of trichloromethane layer required 5cm<sup>3</sup> of 0.1M Hydrochloric acid. Calculate coefficient of ammonia between trichloromethane and water.

**Solution**

**Concentration of ammonia in CHCl<sub>3</sub> layer**

1000cm<sup>3</sup> of solution contain 0.1M of HCl

$$5\text{cm}^3 \text{ of solution contain } \left( \frac{5 \times 0.1}{1000} \right) \text{ moles of HCl.} = 0.0005 \text{ moles.}$$



1mole of NH<sub>4</sub>OH reacts with 1 mole of HCl

→ Moles of NH<sub>4</sub>OH in CHCl<sub>3</sub> layer = 0.0005 moles

25cm<sup>3</sup> of solution contains 0.0005 moles of NH<sub>3</sub>

$$1000\text{cm}^3 \text{ of solution contains } \left( \frac{1000 \times 0.0005}{25} \right) = 0.02\text{M}$$

**Concentration of ammonia in aqueous layers**

1000cm<sup>3</sup> of solution contains 0.1 moles of HCl

$$27.5\text{cm}^3 \text{ of solution contain } \left( \frac{0.1 \times 27.5}{1000} \right) \text{ moles of HCl} = 2.75 \times 10^{-3} \text{ moles}$$

→ moles of NH<sub>4</sub>OH in aqueous solution layer = 0.000275 moles (from the reaction equation)

25cm<sup>3</sup> of aqueous layer contains 0.000275 moles

$$1000\text{cm}^3 \text{ of aqueous layer contains } \left( \frac{0.000275 \times 1000}{25} \right) = 0.11\text{M}$$

$$K_D = \frac{[\text{NH}_3]_{\text{CHCl}_3}}{[\text{NH}_3]_{\text{H}_2\text{O}}} = \frac{0.02}{0.11} = 0.182$$

**KD= 0.18**

2. 50cm<sup>3</sup> of 1.5M ammonia solution was shaken with 50cm<sup>3</sup> of Trichloromethane in a separating funnel. After equilibrium had been reached 20cm<sup>3</sup> of Trichloromethane layer was pipetted and titrated with 0.05M Hydrochloric acid. If 23cm<sup>3</sup> of the acid was required for neutralization. Calculate the K<sub>D</sub> of NH<sub>3</sub> b/w H<sub>2</sub>O and CHCl<sub>3</sub> at this temperature.

**Solution**

Eqn

**Concentration of ammonia in CHCl<sub>3</sub> layer**

1000cm<sup>3</sup> of solution contains 0.05moles of HCl  
23cm<sup>3</sup> of solution contains  $\left( \frac{23 \times 0.05}{1000} \right)$  moles of HCl. == 0.00115moles



1mole of NH<sub>4</sub>OH reacts with 1mole of HCl

→ Moles of NH<sub>4</sub>OH in CHCl<sub>3</sub> layers = 0.00115moles .

20cm<sup>3</sup> of solution contains 0.00115moles

1000cm<sup>3</sup> of CCl<sub>4</sub> layers contain  $\left( \frac{0.00115 \times 1000}{20} \right)$  [NH<sub>3</sub>] CHCl<sub>3</sub> = 0.0575M

But original concentration of ammonia = 1.5M

[NH<sub>3</sub>] in aqueous layer = 1.5 - 0.1575

= 1.4425M

$$K_D = \left( \frac{[\text{NH}_3]_{\text{H}_2\text{O}}}{[\text{NH}_3]_{\text{CHCl}_3}} \right) = \left( \frac{1.4425}{0.0575} \right) = 25.087 \sim 25.1$$

**ACTIVITY**

1. 50cm<sup>3</sup> of 0.1M ammonia solution was shaken to equilibrium with 50cm<sup>3</sup> of CHCl<sub>3</sub> in a stoppered bottle at 25°C. 25cm<sup>3</sup> of aqueous layer reacted completely with 24cm<sup>3</sup> of 0.1M HCl solution. calculate the concentration of NH<sub>3</sub> in;

- (a) CHCl<sub>3</sub> layer
- (b) Aqueous layer at equilibrium
- (c) K<sub>D</sub> for NH<sub>3</sub> between H<sub>2</sub>O and CHCl<sub>3</sub> at 25°C

2 In an experiment to determine the K<sub>D</sub> of NH<sub>3</sub> between water and CHCl<sub>3</sub>, 50cm<sup>3</sup> of NH<sub>4</sub>OH was shaken with 250cm<sup>3</sup> of CHCl<sub>3</sub> until equilibrium was established; and the number of moles of NH<sub>3</sub> in each layer was determined. The experiment was repeated several times using aqueous ammonia of different concentration and the results are given below

Amount of NH <sub>3</sub> in 50cm <sup>3</sup> of water (moles)	0.0065	0.0070	0.0095	0.014	0.019	0.025	0.028
Amount of NH <sub>3</sub> in 250cm <sup>3</sup> of CHCl <sub>3</sub>	0.0005	0.001	0.002	0.003	0.004	0.005	0.006

- a) Plot a graph of concentration of NH<sub>3</sub> in water against concentration of NH<sub>3</sub> in trichloromethane.
- b) Use your graph to determine K<sub>D</sub> of ammonia between water and trichloromethane.

**APPLICATION OF K<sub>D</sub>**

**(a). SOLVENT EXTRACTION**

- ✓ Is a technique of extracting a solvent from one solvent system to another solvent system; both solvents being immiscible, solute maintaining its molecular state and temperature remaining constant.

**OR**

- ✓ Is the isolation of organic compounds from aqueous solution in which the organic compound is immiscible by extracting it using another solvent in which the extracted compound is more soluble.

**NOTE:** Its more efficient to use smaller portions of the organic solvent.

#### Conditions of solvent extraction

- ✓ Solvents must be immiscible
- ✓ Temperature must be constant
- ✓ Solute must be more soluble in the extracting organic solvent
- ✓ Solute must not react in solvent

Example.

1. a)  $60\text{cm}^3$  of an aqueous solution containing  $0.3\text{g}$  of compound Y was shaken with  $30\text{cm}^3$  of ethoxyethane and the mixture allowed to stand. Calculate the mass of Y which was extracted into the ethoxyethane layer. ( $K_D$  of Y between ethoxyethane and water is 4.7)

b) The aqueous solution in (a) was extracted with two successive  $15\text{cm}^3$  of ether, calculate the mass of Y that was extracted by ether and comment on your answer.

#### Solution

(a). Volume of aqueous solution =  $60\text{cm}^3$ , Mass of compound Y =  $0.3\text{g}$ , Volume of ethoxyethane =  $30\text{cm}^3$ , ( $K_D$  between **ethoxyethane and water** is 4.7)

Let the mass of Y extracted by ethoxyethane be Xg

Mass of Y remaining in aqueous layer =  $(0.3 - x)\text{g}$

$$K_D = \frac{[\text{Y}]_{\text{ethoxyethane}}}{[\text{Y}]_{\text{aqueous layer}}}$$

$$K_D = \left( \frac{x/30}{\frac{0.3-x}{60}} \right) = 4.7$$

$$X = 0.210447 \sim 0.21045\text{g}$$

Mass of Y extracted into  $\text{CH}_3\text{CH}_2\text{OC}_2\text{CH}_3$  layer is  $0.21045\text{g}$ .

b) Let the mass of Y extracted by first  $15\text{cm}^3$  of  $\text{CH}_3\text{CH}_2\text{OC}_2\text{CH}_3$  be Mg

Mass of Y remaining in aqueous layer =  $(0.3 - M)\text{g}$

$$K_D = \frac{[\text{Y}]_{\text{CH}_3\text{CH}_2\text{OC}_2\text{CH}_3}}{(\text{Y})_{\text{Aqueous layer}}}$$

$$= \left( \frac{M/15}{\frac{0.3-M}{60}} \right) \text{ hence } M = 0.1621\text{g}$$

Mass of Y remaining in aqueous layer =  $0.3 - 0.1621$   
= **0.1379g**

Let the mass of Y extracted by 2<sup>nd</sup>  $15\text{cm}^3$  of  $\text{CH}_3\text{CH}_2\text{OC}_2\text{CH}_3$  be Pg.

Mass of Y remaining in aqueous layer =  $(0.1379 - P)$

$$\rightarrow 4.7 = \left( \frac{P/15}{\frac{0.1379-P}{60}} \right) = P = 0.0745\text{g}$$

**Comment; single extraction is less effective than successive extraction**

#### ACTIVITY

1. An aqueous solution contains  $0.2\text{g}$  of aspirin ( $\text{C}_9\text{H}_8\text{O}_4$ ) in  $50\text{cm}^3$  of solution. To this solution was added  $20\text{cm}^3$  of Diethyl ether. The mixture was shaken and allowed to reach equilibrium at  $25^\circ\text{C}$ . At this temperature, the  $K_D$  of  $\text{C}_9\text{H}_8\text{O}_4$  between diethylether and water is 4.7

(a). Calculate the mass of  $\text{C}_9\text{H}_8\text{O}_4$  that remains in the aqueous layer

- (b). If the extraction is carried out using two successive 10cm<sup>3</sup> portion of ethoxyethane, determine the mass of C<sub>9</sub>H<sub>8</sub>O<sub>4</sub> that remain unextracted.
- 2 a) (i) Explain what is meant by the term solvent extraction  
 ii) State two conditions for solvent extractions
- b) (i) calculate the mass of aniline [C<sub>6</sub>H<sub>5</sub>NH<sub>2</sub>] that can be extracted from 100cm<sup>3</sup> of water containing 3g of C<sub>6</sub>H<sub>5</sub>NH<sub>2</sub> by using 20cm<sup>3</sup> of Benzene [K<sub>D</sub> of C<sub>6</sub>H<sub>5</sub>NH<sub>2</sub> between Benzene and water is 10]  
 ii) Determine the mass of C<sub>6</sub>H<sub>5</sub>NH<sub>2</sub> that can remain in the aqueous layer if two extractions are carried out using two successive portions of 10cm<sup>3</sup> of Benzene.

**(b) ANALYSIS OF COMPLEX ION**

**Determination of formula of the complex formed btm excess ammonia and copper (ii) ion i.e. [Cu(NH<sub>3</sub>)<sub>n</sub>]<sup>2+</sup>**

**Procedure**

- ✓ A known volume of excess ammonia solution is added to a glass flask containing an equal volume of solution of Cu<sup>2+</sup> with known concentration of, X moldm<sup>-3</sup>.
- ✓ Resultant deep blue solution (complex, [Cu (NH<sub>3</sub>)<sub>n</sub>]<sup>2+</sup>) formed is shaken with trichloromethane and the mixture is allowed to settle so as to reach equilibrium.
- ✓ A known volume of the organic layer is pipetted into a conical flask, titrated with a standard solution of Hydrochloric acid using methyl orange.
- ✓ The volume of Hydrochloric acid required for complex neutralization is noted, concentration of ammonia in the trichloromethane layer is then calculated, Y moldm<sup>-3</sup>
- ✓ Procedure is repeated with aqueous layer and the total concentration of ammonia in the aqueous layer determined, Z moldm<sup>-3</sup>

**Results**

- ✓ Partition coefficient of ammonia between water and chloroform = K<sub>D</sub>
- ✓ Concentration of Cu<sup>2+</sup> = X moldm<sup>-3</sup>
- ✓ Concentration of NH<sub>3</sub> in the organic layer = Y moldm<sup>-3</sup>
- ✓ Original concentration of ammonia in the aqueous layer = Z moldm<sup>-3</sup>

**Treatment of result**

$$K_D = \frac{[\text{NH}_3]_{\text{free}}}{[\text{NH}_3]_{\text{organic layer (CHCl}_3\text{)}}$$

$$K_D = \frac{[\text{NH}_3]_{\text{free}}}{Y}$$

$$[\text{NH}_3]_{\text{free}} = (K_D \cdot Y) = W \text{ moldm}^{-3}$$

But total [NH<sub>3</sub>] aqueous layer = Z

$$\Rightarrow [\text{NH}_3]_{\text{complexed}} = \text{total } [\text{NH}_3]_{\text{aqueous layer}} - [\text{NH}_3]_{\text{free}}$$

$$[\text{NH}_3]_{\text{complexed}} = (Z - W) \text{ moldm}^{-3}$$

$$\text{Number of ligands, } n = \frac{[\text{NH}_3]_{\text{complexed}}}{[\text{Cu}^{2+}]}$$

$$n = \frac{(Z - W)}{\frac{1}{2} X}$$

**Examples:**

1. When 0.05M of an aqueous solution of copper (ii) ion was allowed to reach equilibrium with excess ammonia and trichloromethane, the aqueous layer was found to contain 0.725M while the organic layer was found to contain 0.021M of ammonia (K<sub>D</sub> of aqueous ammonia between aqueous layer and organic layer = 25)

- a) Calculate the concentration of free NH<sub>3</sub> in the aqueous layer  
 b) Determine the value of n in copper

**Solution**

a)  $K_D = 25$ ,  $[NH_3]_{CHCl_3} = 0.021 \text{ mol dm}^{-3}$

From  $K_D = \frac{[NH_3]_{\text{free}}}{[NH_3]_{\text{organic layer}}}$

$[NH_3]_{\text{organic layer}}$

$\Rightarrow 25 = \frac{[NH_3]_{\text{free}}}{0.021}$

$\Rightarrow [NH_3]_{\text{free}} = 0.525 \text{ mol dm}^{-3}$

b)  $[NH_3]_{\text{complexed}} = \text{total } [NH_3]_{\text{aqueous layer}} - [NH_3]_{\text{free}}$   
 $= 0.725 - 0.525$

$[NH_3]_{\text{complexed}} = 0.2 \text{ mol dm}^{-3}$

$n = \frac{[NH_3]_{\text{complexed}}}{[Cu^{2+}]} = \frac{0.2}{0.05}$

$n = 4$

Number of ligands = 4

**Equation of formation of complex**



2.  $25 \text{ cm}^3$  of excess ammonia solution was added to  $25 \text{ cm}^3$  to  $0.1 \text{ M } CuSO_4$  solution. The resulting deep blue solution was shaken with  $50 \text{ cm}^3$  of  $CHCl_3$  and the mixture allowed to settle.  $50 \text{ cm}^3$  of the  $CHCl_3$  layer required  $25.5 \text{ cm}^3$  of  $0.05 \text{ M}$  of  $HCl$  for neutralisation.  $20 \text{ cm}^3$  of the aqueous layer was neutralized by  $33.3 \text{ cm}^3$  of  $0.5 \text{ M } HCl$ . ( $K_D$  between water and trichloromethane = 25). Find the formula of the complex formed

**Solution**

**Concentration of ammonia in organic layer**

$1000 \text{ cm}^3$  of solution contain  $0.05$  moles of  $HCl$

$25.5 \text{ cm}^3$  of solution contain  $\left( \frac{25.5 \times 0.05}{1000} \right)$  moles of  $HCl$

$= 0.001275$  moles of  $HCl$



From the equation above, 1 mole of  $NH_4OH$  reacted with 1 mole of  $HCl$

Moles of aqueous ammonia =  $0.001275$  moles

$50 \text{ cm}^3$  of organic layer containing  $0.001275$  moles of  $NH_{3(aq)}$

$1000 \text{ cm}^3$  of organic layer contain  $\left( \frac{0.001275 \times 1000}{50} \right)$

$= 0.0255 \text{ M}$

$[NH_3]_{\text{organic layer}} = 0.0255 \text{ M}$

**Concentration of ammonia in aqueous layer**

$1000 \text{ cm}^3$  of organic layer contain  $0.5$  moles of  $HCl$

$33.3 \text{ cm}^3$  of solution contain  $\left( \frac{33.3 \times 0.5}{1000} \right)$  moles of  $HCl$

Moles of  $HCl$  reacts with ammonia in the aqueous layer =  $0.01665$  moles

Moles of  $NH_{3(aq)}$  in the aqueous layer that reacted in  $HCl = 0.01665$  (from mole ratio as per the eqn)

$20 \text{ cm}^3$  of aqueous layer contain  $0.01665$  moles of  $NH_{3(aq)}$

$1000 \text{ cm}^3$  of aqueous layer contain  $\left( \frac{1000 \times 0.01665}{20} \right)$  moles of  $NH_3$

$= 0.8325 \text{ M}$

Total [NH<sub>3</sub>] aqueous layer = 0.8325

$$K_D = \frac{[\text{NH}_3]_{\text{free}}}{[\text{NH}_3]_{\text{CHCl}_3}}$$

$$[\text{NH}_3]_{\text{free}} = K_D \times [\text{NH}_3]_{\text{CHCl}_3} = 25 \times 0.0255$$

$$[\text{NH}_3]_{\text{free}} = 0.6375 \text{ mol dm}^{-3}$$

$$[\text{NH}_3]_{\text{complexed}} = \text{total } [\text{NH}_3]_{\text{aqueous layer}} - [\text{NH}_3]_{\text{free}}$$

$$= 0.8325 - 0.6375$$

$$[\text{NH}_3]_{\text{complexed}} = 0.195 \text{ M}$$

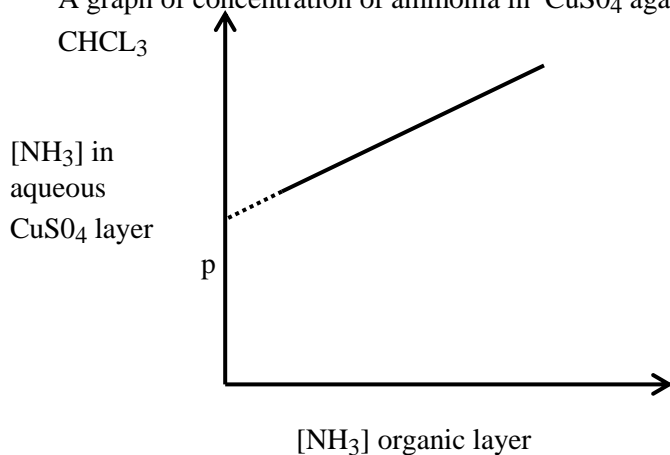
$$n = \frac{[\text{NH}_3]_{\text{complexed}}}{[\text{Cu}^{2+}]}$$

$$n = \frac{0.195}{(1/2 \times 0.1)}$$

$$n = 3.9 \sim n = 4$$

**GRAPHICAL DETERMINATION OF THE FORMULA OF COMPLEX FORMATION BETWEEN EXCESS NH<sub>3</sub> AND Cu<sup>2+</sup>**

A graph of concentration of ammonia in CuSO<sub>4</sub> against concentration of ammonia in organic layer CHCl<sub>3</sub>



From the graph

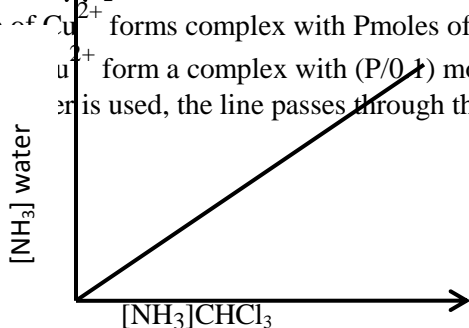
Y- Intercept → P (gives the minimum amount of ammonia required to form complex)

**Number of complexed ammonia**

0.1 mol of Cu<sup>2+</sup> forms complex with P moles of NH<sub>3</sub>

1 mol Cu<sup>2+</sup> form a complex with (P/0.1) moles of NH<sub>3</sub>

**Note:** If P is used, the line passes through the origin showing no complex is formation



**Question**

The table below shows the partition of ammonia between 0.1M CuSO<sub>4</sub> and CHCl<sub>3</sub>

[NH <sub>3</sub> ] (0.1M CuSO <sub>4</sub> )	0.86	1.10	1.57	1.80	2.40
----------------------------------------------	------	------	------	------	------

[ NH <sub>3</sub> ](CHCl <sub>3</sub> )	0.02	0.03	0.05	0.06	0.08
-----------------------------------------	------	------	------	------	------

- Plot a graph of concentration of ammonia in 0.1 CuSO<sub>4</sub> against [NH<sub>3</sub>] in CHCl<sub>3</sub>
- Determine the intercept on Y- axis
- What is the signification of the intercept? (show your working)
- What happens when the above experiment is repeated using water instead of 0.1M Cu<sup>2+</sup>. Give a reason for your answer

### C) ION EXCHANGE:

- ✓ is the type of partition of ionic compounds
- ✓ *Ion exchange resin is a polymer which removes undesirable cations or anions and replaces them with other cations or anions.*
- ✓ Cation exchangers contain reactive hydrogen ions which may exchange with other cations like Na<sup>+</sup>, Ca<sup>2+</sup>, or Mg<sup>2+</sup> in a reversible reaction. E.g R(CH<sub>2</sub>)<sub>n</sub> C-00H, -SO<sub>3</sub>H and R(CH<sub>2</sub>)<sub>n</sub> OH.
- ✓ Anion exchangers contain basic OH which are exchanged for other anions like chloride or sulphate e.g. secondary, tertiary and quaternary amino gps.
- ✓ Ion exchange can be used in purification of water in the following ways;
  - Water may be softened by ion exchange by removing the Ca<sup>2+</sup> or Mg<sup>2+</sup>

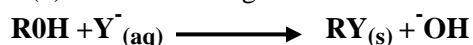
$$\text{NaR(s)} + \text{Ca}^{2+} \longrightarrow \text{CaR}_2(\text{s}) + \text{Na}^+(\text{aq}) \quad \text{where R- resin}$$
  - Water is then further purified by using both cations and anion exchange to form de-ionized water.

This is a two state process;

(a) A cation exchanger removes cations replaces them with H<sup>+</sup>



(b). Anion exchanger removes cations and replaces them with OH anion



### (D) DETERMINATION OF SOLUBILITY AND EQUILIBRIUM CONSTANTS

- ✓ Knowing the solubility of iodine in CS<sub>2</sub> and the partition coefficient, solubility of iodine in water can be determined from;

$$K_D = \frac{\text{solubility of iodine in pure H}_2\text{O}}{\text{Solubility of iodine in CS}_2}$$

**Example.** Some iodine was dissolved in 0.3M KI solution and solution was shaken with CS<sub>2</sub> until equilibrium was established. The concentration of iodine in both layers was then determined by titration. The solubility of iodine in pure H<sub>2</sub>O and CS<sub>2</sub> are given in the table below

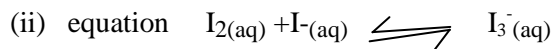
Concentration (M)	Aqueous layers	Organic layer
	0.044	0.13
Concentration (M)	Pure H <sub>2</sub> O 4X10 <sup>-4</sup>	CS <sub>2</sub> 0.234

- Determine the K<sub>D</sub> of iodine between water and CS<sub>2</sub>
- Calculate the equilibrium for the reaction

### Solution

i)  $K_D = \frac{\text{solubility of } I_2 \text{ in pure water}}{\text{Solubility of } I_2 \text{ in } CS_2}$   
 $= \frac{4 \times 10^{-4}}{0.234}$

$$K_D = 1.71 \times 10^{-3}$$



$$K_D = \frac{[I_2]_{\text{free}}}{[I_2]_{CS_2}}$$

$$[I_2]_{\text{free}} = K_D \times [I_2]_{CS_2}$$

$$= 1.71 \times 10^{-3} \times 0.13$$

$$[I_2]_{\text{free}} = 2.2 \times 10^{-4} \text{ mol dm}^{-3}$$

$$[I_2]_{\text{complexed}} = \text{total } [I_2]_{\text{aqueous layer}} - [I_2]_{\text{free}}$$

$$= 0.044 - 2.2 \times 10^{-4}$$

$$[I_2]_{\text{complexed}} = 0.04378 \text{ mol dm}^{-3}$$

$$K_{\text{equilibrium}} = \frac{[\text{Product}]}{[\text{Reactants}]}$$

$$= \frac{[I_3^{-}]}{[I_2] [I^{-}]}$$

$$[I^{-}] = 0.3 - 0.04378 (\text{iodine complexed})$$

$$= 0.25622 \text{ mol dm}^{-3}$$

$$K_{\text{equilibrium}} = \frac{0.04378}{2.2 \times 10^{-4} \times 0.25622}$$

$$= 776.68 \text{ mol}^{-1} \text{ dm}^{-3}$$